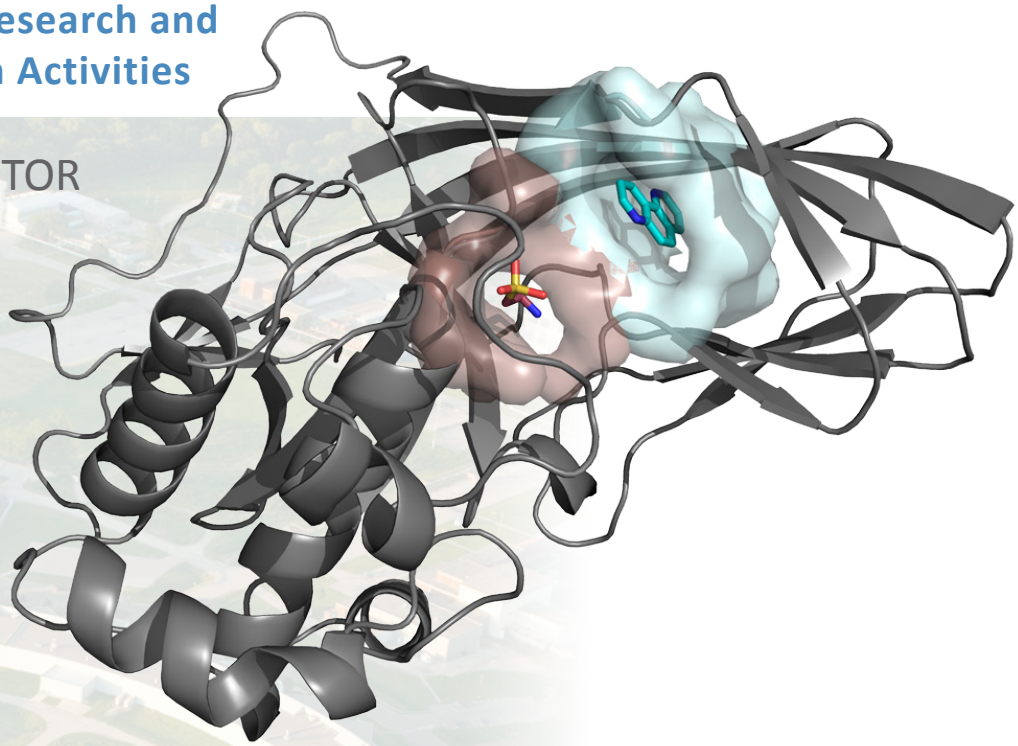
LDRD

Laboratory Directed Research and Development Program Activities

OFFICE OF THE DIRECTOR

March 2011



FY2010 Annual Report

ANL-11/10

Argonne NATIONAL LABORATORY

ON THE COVER

Transglutamase (shown in a gray cartoon representation) is an important protein recently linked to neurodegenerative diseases. The APPLIED (Analysis Pipeline for Protein Ligand Interactions and Experimental Determination) pipeline, a high-performance computational and high-throughput experimental pipeline for performing protein-ligand interaction analysis, was used to screen small molecule compounds as potential inhibitors to combat this protein's deleterious effects. The virtual screening of millions of compounds against the protein's active sites (represented by brown and light cyan surfaces) identified suitable candidate molecules for experimental studies. X-Ray crystallographic data validated the computational predictions for two small molecules (shown as a small yellow stick figure and dark cyan rings). For details, see the project report of T. Andrew Binkowski, Ian Foster, Andrzej Joachimiak, Michael Kubal, Benoit Roux, Rick Stevens, and Michael Wilde (2008-166-R2) on page 165

ABOUT ARGONNE NATIONAL LABORATORY

Argonne is a U.S. Department of Energy Laboratory managed by UChicago Argonne, LLC under contract DE-AC02-06CH11357. The Laboratory's main facility is outside Chicago at 9700 South Cass Avenue, Argonne, Illinois 60439. For information about Argonne and its pioneering science and technology programs, see www.anl.gov.

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I am pleased to submit Argonne National Laboratory's Annual Report on its Laboratory Directed Research and Development (LDRD) activities for FY 2010. Our laboratory has seen much progress over the last year. We are continuing apace with the design of an upgraded Advanced Photon Source that will offer much improved characterization power to the user community. Our continued leadership in the photon sciences was also evident in our contributions to the success of the Linac Coherent Light Source (LCLS), the free-electron laser at SLAC National Accelerator Laboratory: Argonne built the LCLS undulators to more rigorous specifications than any other undulators in the world. In other arenas, we have licensed a unique Argonne-developed cathode material for lithium-ion batteries to private industry as part of our continuing strategic pursuit of better energy-storage technologies. We have also substantially strengthened our capacity in computational science, a strategic advance that parallels our hosting of the IBM Blue-Gene/P supercomputer as we prepare for Blue Gene/Q. That computational power has been a major contributor to our world-class leadership in metagenomics, with Argonne's MG-RAST tool accessed via the World Wide Web by the world's biogeochemical community. Past investments in Argonne's LDRD program have made crucial contributions to the realization of these and other enhancements to our laboratory's accomplishments and capabilities.

LDRD is an invaluable resource for positioning the Laboratory to anticipate, and thus be prepared to contribute to, the future science and technology needs of the U.S. Department of Energy (DOE) and the nation. During times of change, LDRD becomes all the more vital for facilitating the necessary adjustments while maintaining and enhancing the capabilities of our staff and facilities.

In FY 2010, we placed added emphasis on acquiring leaders — as new members of staff — in computational science, an area becoming ever more important to all aspects of DOE missions. We also inaugurated a Director's Grand Challenge component within the LDRD program and funded our first such project in the area of energy storage.

I can attest that Argonne's program adhered closely to the requirements of DOE Order 413.2b and associated guidelines governing LDRD. Our LDRD program management continually strives to be more efficient. In addition to meeting all reporting requirements during FY 2010, our LDRD Office continues to enhance its electronic systems to streamline the LDRD management process.

You will see from the following individual project reports that Argonne's researchers have once again done a superb job of pursuing projects at the forefront of their respective fields and have contributed significantly to the advancement of Argonne's strategic thrusts. This work has not only attracted follow-on sponsorship in many cases but is also proving to be a valuable basis upon which to continue realignment of our strategic portfolio to better match the Laboratory's Strategic Plan.

Eric D. Isaacs
Laboratory Director

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** Some projects topically associated with a strategic initiative area, as well as other innovative projects, were reviewed and selected by the Laboratory Director outside the normal annual LDRD call for proposals and review cycle.*

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Special appreciation is, of course, due to the many expert researchers who perform the research and provide their project reports; the technical and administrative management of Argonne's programmatic divisions within which the R&D is pursued; and the leaders of the Laboratory's strategic initiative areas, whose vision and understanding of the nation's technological needs help guide and refine the content of Argonne's LDRD portfolio.

Those of us in the Program's management are grateful for the critical support we receive throughout the year, and particularly while preparing this Annual Report, from the individuals listed below.

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LABORATORY OVERVIEW

Argonne National Laboratory, as a U.S. Department of Energy (DOE) National Laboratory, is dedicated to advancing the energy frontier through science and technology. Argonne works to accelerate innovation in science and technology for its primary sponsor, the DOE Office of Science (SC), as well as the Office of Energy Efficiency and Renewable Energy (EERE) and the National Nuclear Security Administration (NNSA), and a variety of other federal agencies. Argonne designs, builds, and operates one-of-a-kind national scientific user facilities that enhance the Laboratory's research capabilities and serve a broad community of researchers from academia, industry, and government laboratories.

As a national laboratory, Argonne concentrates on scientific and technological challenges that can only be addressed through a sustained, interdisciplinary focus at a national scale. Argonne's eight major initiatives, as enumerated in its strategic plan, are Hard X-ray Sciences, Leadership Computing, Materials and Molecular Design and Discovery, Energy Storage, Alternative Energy and Efficiency, Nuclear Energy, Biological and Environmental Systems, and National Security. They are organized around the following core capabilities:

Fundamental Sciences

- Nuclear Physics
- Particle Physics
- Accelerator Science and Technology
- Condensed Matter Physics and Materials Science
- Chemical and Molecular Science
- Advanced Computer Science, Visualization, and Data Handling
- Computational Science
- Applied Mathematics
- Biosciences

Applied Sciences and Engineering

- Applied Materials Science and Engineering
- Chemical Engineering
- Applied Nuclear Science and Technology
- Systems Engineering and Integration
- Climate Change Science

User Facilities

- The Advanced Photon Source (APS) provides a high-brightness, high-energy electron beam, a unique source of high-energy x-rays for scattering, spectroscopy, and imaging studies with a timing structure enabling time-resolved research from picoseconds to seconds. The planned APS upgrade project will result in an improved world-class source of high-energy, high-brightness, tunable x-rays for scientific research.
- The Center for Nanoscale Materials (CNM) combines advanced scanning probes (including an x-ray nanoprobe; organic, inorganic, and digital synthesis; and nanofabrication) that are all coupled with theory and modeling.
- The Electron Microscopy Center (EMC) provides state-of-the-art, aberration-corrected electron microscopy (e.g., TEAM) with applications to three-dimensional elemental imaging and in-situ environmental studies of catalysts and other nanoscale materials.
- The Argonne Tandem-Linac Accelerator System (ATLAS) is a scientific user facility based on a superconducting linear accelerator that provides heavy ions in the energy domain best suited to study the properties of the nucleus, the core of matter, and the fuel of stars.
- The Argonne Leadership Computing Facility (ALCF) offers user access to petascale computing for research in energy systems, catalysis, life sciences, and environmental and basic sciences.
- The Transportation Research Analysis and Computing Center (TRACC) operates the largest high-performance computing cluster available to U.S. transportation researchers and performs targeted research to foster technology transfer from the national laboratory's energy research complex to the transportation research community.
- The DOE Atmospheric Radiation Measurement (ARM) Climate Research Facility provides the world's most comprehensive, continuous observational capabilities specifically for observing atmospheric data for the conduct of climate change research.

In addition to these facilities, Argonne hosts its Transportation Technology Research and Development Center, Theory and Computing Sciences (TCS) Building, and the University of Chicago's Howard T. Ricketts Laboratory.

Program Assessment

Program Overview

The purposes of Argonne's Laboratory Directed Research and Development (LDRD) Program are to encourage the development of novel technical concepts, enhance the Laboratory's research and development (R&D) capabilities, and pursue its strategic goals. Projects are selected from proposals for creative and innovative R&D studies that require advance exploration before they are considered to be sufficiently developed to obtain support through normal programmatic channels. Among the aims of the projects supported by the LDRD Program are the following: establishment of engineering proof of principle, assessment of design feasibility for prospective facilities, development of instrumentation or computational methods or systems, and discoveries in fundamental science and exploratory development.

The projects supported by LDRD are distributed across the major mission areas at Argonne, as indicated in the Laboratory's LDRD Plan for FY 2010. All LDRD projects have demonstrable ties to one or more of the science, energy, environment, and national security missions of the U.S. Department of Energy (DOE), and many are also relevant to the missions of other federal agencies that sponsor work at Argonne. A natural consequence of the more applied projects is their simultaneous relevance to industry.

In addition to their relevance to strategic and programmatic activities, LDRD projects also naturally fall under one or more areas of science and technology corresponding to the disciplines and fields in which Argonne's technical staff are trained and excel in supporting existing programs. In fact, perusal of the project reports in this document will demonstrate that, more often than not, expertise is drawn from several technical areas to pursue the goals of any given project. Quite often, theory and computational work are integrated with experiment in these projects. This multidisciplinary approach is a hallmark of Argonne as a multi-program national laboratory and reflects the synergistic manner in which both our LDRD and our programmatic work are pursued.

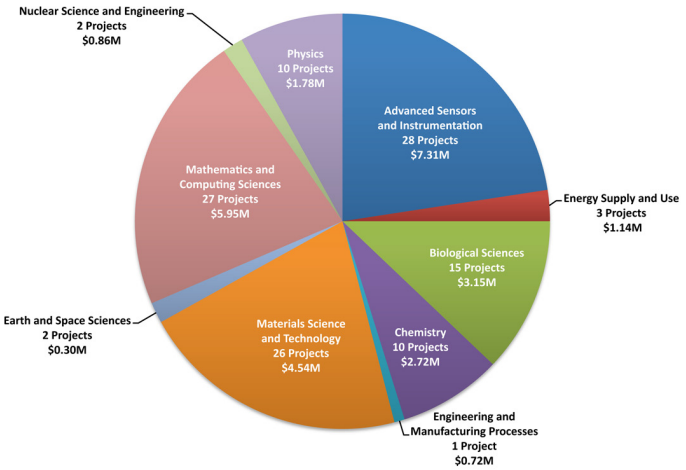


Figure 1. Number and Dollar Value of LDRD Projects across the DOE-Defined "Categories of Work"

The distribution of LDRD projects across the DOE-defined categories of work, as shown in the chart below, reflects the types of actual "hands-on" work performed by our LDRD-supported investigators. However, a better indication of the ultimate purpose(s) of the work and therefore of the potential future benefit to specific programs — for example, using high-performance computation to simulate biological or catalytic processes — is found in the description of the research itself in the body of this report.

The FY 2010 DOE-approved funding cap for LDRD was $30.0 million, or about 4.5% of Argonne's estimated FY 2010 operating plus capital budgets. Actual expenditures amounted to $28.5 million, which includes an overhead levy of approximately 23%. A table of planned or actual funding profiles for each project active in FY 2010 is provided at the end of this section. Individual brief project reports for FY 2010 comprise the bulk of this document. A list, by title, of new projects begun to date in FY 2011 is provided in the appendix.

LDRD Management Process

Argonne's R&D activities are organized under four associate laboratory directors (ALDs), who oversee the research conducted in some 14 programmatic divisions. At the top of the organization is the Laboratory Director, who is assisted by the Deputy Laboratory Director for Programs. This senior management group makes final recommendations concerning the LDRD program.

Argonne's LDRD Program consists of four components: the Strategic Initiatives, the Director's Grand Challenge, the Director's Competitive Grants (DCG), and a director's strategic reserve (a portion of the total allowed expenditure temporarily reserved to handle mid-year opportunities, strategic hires for LDRD projects, and LDRD collaborative arrangements). The Strategic Initiatives, Director's Grand Challenge, and director's strategic reserve components fund R&D projects that are aligned with the Laboratory

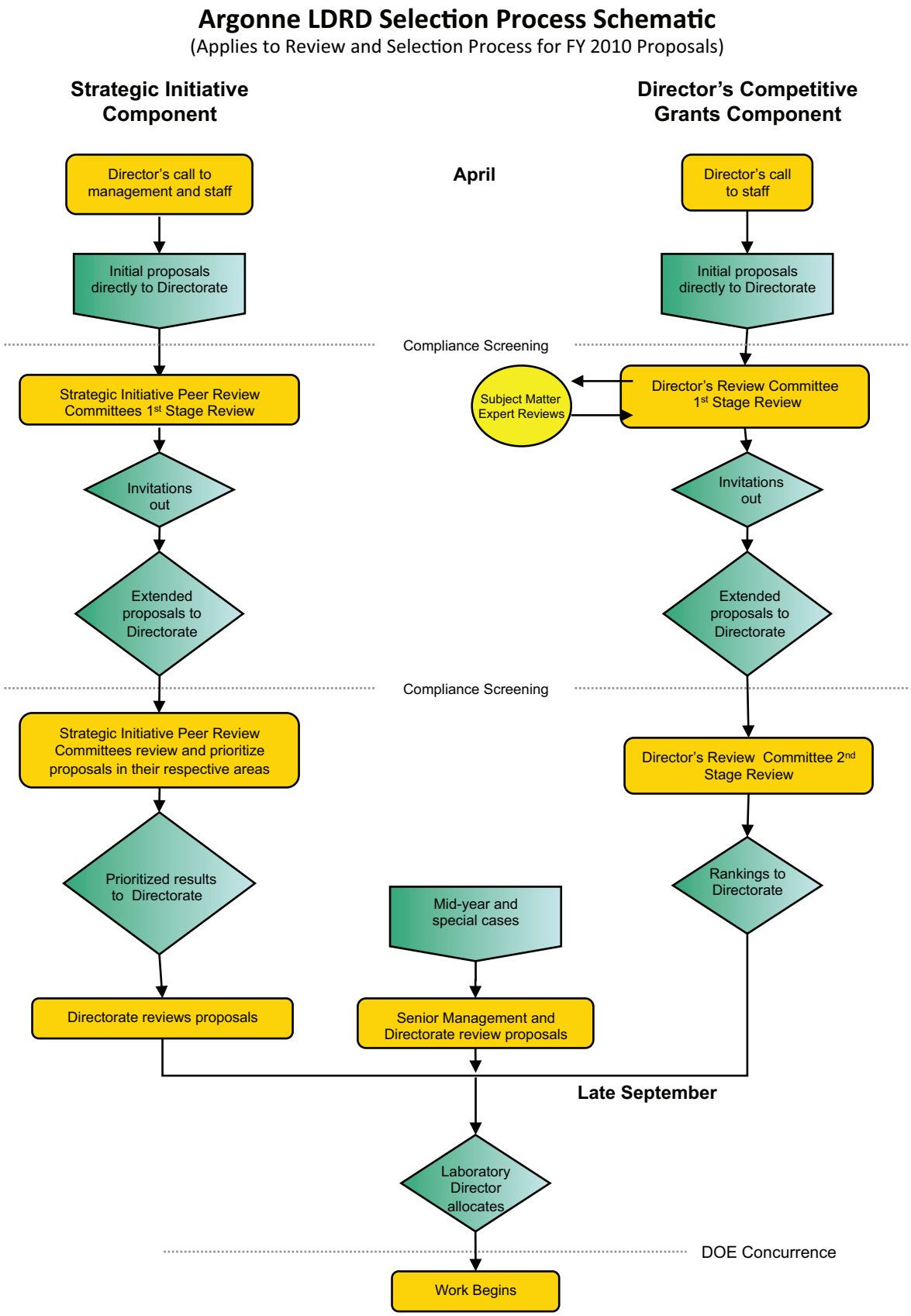


Figure 2. Argonne LDRD Selection Process Schematic

initiatives consistent with Argonne's Strategic Plan, while the DCG component supports exploratory research aligned with DOE mission areas and core competencies of the Laboratory. The Laboratory Director determines the appropriate balance of funding between the four components on an annual basis. All final decisions concerning Argonne's LDRD program reside with the Laboratory Director. Certain responsibilities regarding funding, oversight, proposal evaluation, and project direction are delegated.

The LDRD Program Office reviews all proposals to ensure their adherence to DOE Order 413.2b and associated guidelines, as well as to Laboratory administrative procedures. The flow chart in Figure 2 illustrates the relationships of the management and review processes for two of the components of the FY 2010 program.

The LDRD program is funded lab-wide through the Laboratory's indirect budget, which derives from a levy against all program operating budgets. Although many researchers propose projects with durations of two or three years, funding levels and project selection are determined annually on the basis of technical progress and the Laboratory's strategic goals and resources.

LDRD funds may be used in collaborative arrangements with third parties to enhance the application or scope of the research, with attendant beneficial interactions. To effect these arrangements, the Laboratory has in place DOE-approved procedures and instruments, such as Cooperative Research and Development Agreements (CRADAs), subcontracts, and Guest Agreements (regarding site access). These instruments and procedures enable the application of LDRD funds to these endeavors while ensuring that appropriate terms and conditions are applied thereto, including those related to intellectual property rights.

Line managers in Argonne's programmatic divisions are responsible for monitoring the progress and performance of LDRD research during execution. Strategic Initiative leaders and line managers confirm that mid-year progress reviews have occurred and indicate whether any remedial action or advice is needed. Responsibility for the actual conduct of all Laboratory Directed R&D, including associated environmental safety and health requirements, resides with the ALDs and their line managers.

During FY 2010, all program management requirements were satisfied. Reports required by DOE, including the Annual Report for FY 2009, the LDRD Program Plan for FY 2011, and project data uploaded to the DOE Office of the Chief Financial Officer's database, were submitted in a complete and timely fashion.

Concurrence request forms (also referred to as "data sheets" in relevant guidance documents) were submitted electronically to the DOE Argonne Site Office (ASO) to obtain the DOE site manager's concurrence on a project-by-project basis before proceeding with the FY 2010 LDRD projects.

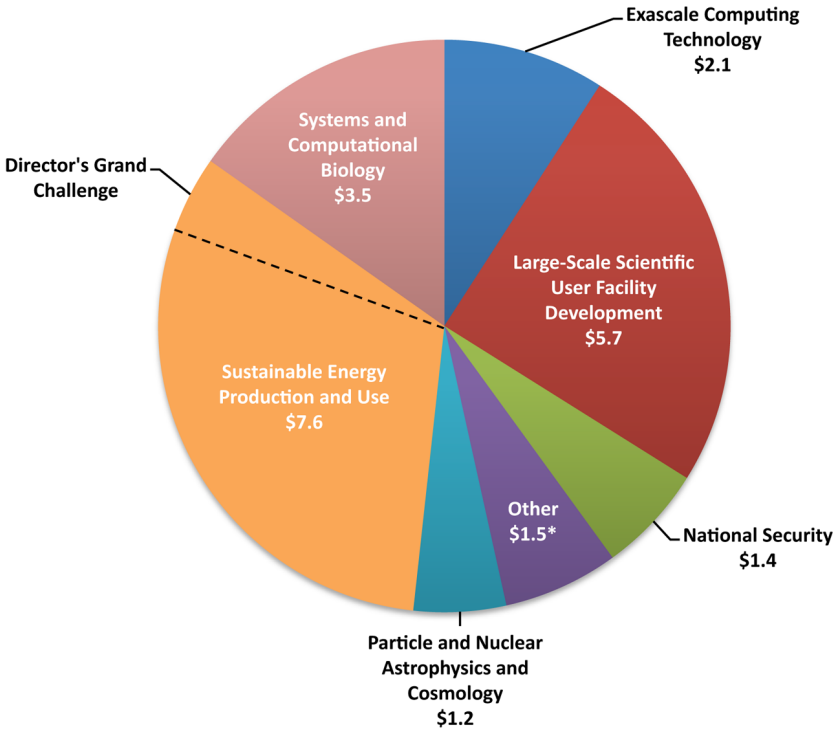
FY 2010 LDRD Components

Strategic Initiatives

This larger component of LDRD emphasizes R&D explicitly aligned with Laboratory and Department missions as reflected in strategic initiatives proposed by senior management and consistent with Argonne's Strategic Plan. Strategic goals are revised periodically and reevaluated as necessary. The choice of initiative areas reflects an evaluation of the state of development of the relevant technical fields, the potential value to the Department and the nation of advancing those fields, and, of course, the compatibility and synergy these fields have with existing facilities, capabilities, and staff expertise at Argonne.

Six strategic initiative areas implemented for FY 2010 cover (in part) similar topical areas as in FY 2009, with some changes in terminology and organization, while initiating some new directions as well. The FY 2010 review procedures continued to insure that all individual proposals identified as fitting under a strategic initiative are reviewed for scientific quality, innovativeness, and value to each respective mission-related initiative.

Review of proposals to this component relies on a combination of peer and management review within initiative areas. The Laboratory Director appoints a Strategic Initiative leader for each of the respective Strategic Initiatives to evaluate and recommend projects for funding. The Strategic Initiative leader selects internal and external subject matter experts to serve on review panels to assist in reviewing proposals submitted. Results are reported to the Laboratory Director, who makes final selections and approves content and aggregate budget. In FY 2010, 32 new and 48 continuing projects in the six Strategic Initiative areas listed below were funded at an aggregate level of $21.5 million. Some additional mid-year and strategic-hire projects, selected by the



* Special and Mid-Year Start Projects

Figure 3. Distribution of Funding among Strategic Initiative Areas ($ in millions)

Laboratory Director, are included in these figures. Also in FY 2010, four new and six continuing strategic projects totaling $1.5 million, whose topics fall in other novel technical areas, were selected by the Laboratory Director. The overall FY 2010 funding level for the Strategic Initiative component equaled $23.0 million (Figure 3).

The FY 2010 Strategic Initiative areas are as follows:

Exascale Computing Technology

The key elements of this initiative fall under the following general areas: programming models, performance tools, and debugging; operating systems, resiliency, and system management; new system architectures; new I/O architectures and software; and, extremely scalable algorithms and novel computing methodologies.

Large-Scale Scientific User Facility Development

This initiative focuses on developing new or enhanced science capabilities by developing and expanding existing large-scale scientific user facilities in technical areas, such as forefront accelerator research (including modeling and simulations), and science enablers that leverage those programs that will use new or significantly expanded Argonne user facilities (such as an imaging, ultrafast science and other facility-based science).

National Security

LDRD projects under the national security initiative focus on current and emerging scientific and technological challenges in both homeland security and national defense. Key research areas include: nonproliferation and forensics of weapons of mass destruction; sensor research; advanced computational data management and analysis; the application of complex modeling to infrastructure assurance; and social science problems, such as terrorism, behavioral and decision analysis, and cyber security.

Particle and Nuclear Astrophysics and Cosmology

Projects focus on the following key areas to address some of the basic questions about the universe: fundamental science addressing the nature and understanding of dark matter and dark energy; fundamental science of nucleosynthesis in stellar explosions and the origin of the heavy elements in nature, using petascale computing capabilities to address key questions in particle astrophysics and cosmology and nuclear astrophysics; and development of novel detector technologies for future experiments aimed at addressing key questions in particle astrophysics and cosmology and nuclear astrophysics.

Sustainable Energy Production and Use

Key focus areas of projects under this initiative include: climate change and impact of advanced energy technologies, science-based engineering for nuclear energy supply, advanced materials for energy conversion and storage, and transportation science and technology.

Systems and Computational Biology

Projects address high-throughput methods for the development and use of massively parallel approaches for genome sequencing; the formulation of computational techniques related to genome analysis and sequencing; protein science and engineering; biofuels and bioenergy research and development; and microbial ecology and ecosystem analysis. Key focus areas of projects under this initiative include: method development for metagenomics in-vitro data generation and primary in-silico data analysis, and development of novel tools for the secondary analysis of metagenomic data sets (e.g., visualization, modeling, statistical analysis).

Director's Grand Challenge

A new component of the LDRD portfolio is the Director's Grand Challenge, which may be included in the LDRD program of any given fiscal year by the Laboratory Director. Also at the discretion of the Laboratory Director, the schedule of call-for-proposals, review, and selection for this component need not match that of the Strategic Initiatives or Director's Competitive Grants components. A Grand Challenge project will devote sufficient talent and resources to a specific technical topic within an area of substantial strategic value to the Laboratory and to DOE to allow major strides toward its research and development goals. Emphasis will be placed on cross-cutting initiatives that draw synergistically upon the core competencies of Argonne.

As a precursor to formal LDRD proposal submission, brief "white papers" are solicited. The white papers are evaluated by a Grand Challenge Review and Oversight Panel, which is comprised of four to six internal and external subject matter experts. The panel members recommend which white paper authors should be invited to submit more extensive formal proposals. The latter are reviewed and ranked based on expected impact, creativity, degree of cross-cutting utilization of core Argonne capabilities and staff, and potential for success. The successful Grand Challenge LDRD project is expected to target a specific outcome enabled by a specific innovative approach with a well-coordinated team. The awarded project is formally reviewed by the Grand Challenge Review and Oversight Panel semi-annually to evaluate progress.

The topic addressed by the Director's Grand Challenge in FY 2010 was energy storage with a focus on long-term solutions that will make dramatic improvements to, or take us beyond, current lithium-ion technologies to provide higher energy and power densities with safe operating characteristics.

The project chosen for this Grand Challenge topic was awarded $1.0 million in FY 2010, with expected funding to increase to $3.0 million by FY 2012, depending upon the project team's progress toward its research goals.

Director's Competitive Grants

The DCG component invests in a full spectrum of investigator-initiated proposals across Laboratory and DOE mission-related science and engineering areas. This component provides an avenue for R&D staff to propose highly innovative projects directly to the laboratory director. Proposals are submitted for peer review to the Director's Review Committee to assess their scientific and technical quality. The Review Committee is comprised of non-managerial scientists and engineers selected by the Laboratory Director. The committee currently comprises 22 members who have substantial expertise in their technical fields, are familiar with the peer review process, and represent a broad cross section of the Laboratory. The Director's Review Committee conducts an initial peer review that results in invitation of a smaller number of proposals for further review by the Committee. The products of the review procedure are a rank-ordered list of proposals given to the Laboratory Director and brief critiques of proposals sent to the proposing investigators.

The DCG review process was augmented this year by the recruitment of members of the laboratory research community who served as volunteer subject matter experts to assist the Director's Review Committee in reviewing proposals. More than 200 researchers volunteered and, with their assistance, made it possible for the Director's Review Committee to recommend the highest-quality proposals for funding in FY 2010. These projects comprise about 18% of the Laboratory's LDRD budget. In FY 2010, 15 new and 18 continuing projects were funded at $5.4 million.

FY 2011 Update

DOE approved Argonne's FY 2011 LDRD Plan and program expenditure not to exceed $32 million. A list, by title, of projects begun so far in FY 2011 is provided in an appendix to this report.

For the 2011 fiscal year, we are continuing to refine our use of electronic tools to communicate with investigators and reviewers, and to collect and document performance information on LDRD projects. We are improving existing Web-based applications and developing a new electronic proposal submission process. A new proposal submission Web site was available for the FY 2011 cycle.

New Web-based tools are under development now for use in the FY 2012 LDRD cycle that will provide authors of LDRD proposals with real-time status information about their submissions during the review and selection process and that will also provide reviewer feedback in a timelier manner.

Peer Review Experience in FY 2010

The pursuit of LDRD research is managed and its performance is reviewed as an integral part of the activities of the respective technical divisions in which the work resides. Periodic peer reviews of each division's programs and research are conducted by committees empanelled by Argonne's M&O contractor, UChicago Argonne, LLC. The Laboratory believes that the quality of the science and technology performed under LDRD funding by a division cannot be distinguished from that reflected in the division's performance of programmatic R&D. By and large, the same research personnel and the same facilities are applied to both, and no discernible qualitative differences have been observed. LDRD is therefore not reviewed separately; however, results and plans relevant to LDRD projects are routinely exposed to review committee scrutiny. A tabulation of such reviews for FY 2010 is provided below, along with an aggregate accounting of the number of LDRD projects exposed to committee review and their total dollar value. The LDRD Program Office also requires principal investigators to report all other relevant external reviews of their work. LDRD projects from the Accelerator Systems (ASD), High Energy Physics (HEP), Materials Science (MSD), X-ray Sciences (XSD), Physics (PHY) divisions, the Center for Nanoscale Materials (CNM), the Leadership Computing Facility (LCF), and the Photon Sciences (PSC) ALD area were reviewed as part of an overall contractor-chartered review.

Organization	Date of Review	Nunber of LDRD Projects	Dollar Value of Projects ($ in thousands)
ASD	8/29/2010	2	$708.4
CNM	9/26/2010	1	$597.8
HEP	11/1/2009	6	$2,045.8
LCF	9/26/2010	1	$139.1
MSD	9/26/2010	5	$1,532.8
PHY	11/1/2009	24	$7,862.8
PSC	8/29/2010	1	$50.5
XSD	8/29/2010	5	$2,830.2
Totals		**45**	**$15,767.4**

Table 1. Summary of Peer Review History by Organization

Performance Metrics

The LDRD Program Office collects statistical data on current and completed LDRD projects. Such data relate, for example, to publications, inventions, follow-on sponsorship, and staff enhancement through post-doctoral appointees and new hires. Although these data are of little value on a project-by-project basis, in the aggregate, they provide a picture of overall program productivity. The management processes employed to collect these data include surveys of current and former investigators, analysis of project annual reports, and validation against records of the Office of Technology, Development, and Commercialization (TDC), the Legal Department (LEG), and the Publications and Record Services section of the Technical Services Division (TSD). A summary of the most recently collected data is provided in the two tables below. Table 2 displays project outcomes realized only during FY 2010 but derived from projects active in any year or years from FY 2007 forward. For the same prior and currently active projects, Table 3 displays those metrics for which cumulative results are monitored, with no restriction as to when the accomplishments occurred. Table 4 presents a summary of the LDRD Program's five-year funding levels, by project.

Table 2. Aggregate FY 2010 Outcomes for Recently Completed and Current Projects

Most Recent Project Year	LDRD Component	Number of Refereed Publications	Number of Students/ Postdocs Supported	Number of New Staff Hires	Number of Non-Publi-cation Copyrights	Number of Invention Disclosures	Number of Patents Issued/ Pending
2007							
	Competitive Grants	4	0	0	0	1	2
	Strategic Initiative	3	0	0	0	1	0
2008							
	Competitive Grants	11	0	0	0	0	1
	Strategic Initiative	21	0	2	0	3	5
2009							
	Competitive Grants	3	0	0	1	0	7
	Strategic Initiative	16	0	3	0	1	0
2010							
	Competitive Grants	26	41	2	0	4	5
	Strategic Initiative	98	125	20	2	5	2
Grand Totals: 311 Projects		**182**	**166**	**27**	**3**	**15**	**22**

Table 3. Aggregate Outcomes for All Years of Recently Completed and Current Projects (2007 – 2010)

Most Recent Project Year	Number of Projects Receiving Follow-on Funds	Number of Proposals Submitted To Sponsors	Number of External Reviews
2007	26	144	22 DOE 5 Other 10 UofC
			37 Total
2008	30	217	34 DOE 17 Other 10 UoC
			61 Total
2009	22	133	11 DOE 12 Other 3 UoC
			26 Total
2010	25	193	18 DOE 25 Other 4 UoC
			47 Total
Totals: 311 Projects	103	687	85 DOE 59 Other 27 UoC
			171 Total

LDRD Five-Year Funding Summary ($ in thousands)*

Proposal No.	2008	2009	2010	2011 (a)	2012 (b)	Total
2008-003-R2	99.2	116.3	116.0			331.5
2008-008-R2	123.5	139.2	162.0			424.7
2008-020-R2	136.0	155.0	157.6			448.6
2008-026-R2	153.5	152.8	161.5			467.8
2008-035-R2	173.1	190.1	228.4			591.6
2008-036-R2	185.2	225.1	233.0			643.3
2008-070-R2	143.0	103.0	69.0			315.0
2008-090-R2	129.7	125.4	154.0			409.1
2008-118-R2	296.4	504.4	560.0			1,360.8
2008-119-R2	39.4	80.5	81.5			201.4
2008-121-R2	651.4	699.8	458.3			1,809.5
2008-122-R2	124.6	250.4	64.4			439.4
2008-124-R2	449.0	243.7	222.3			915.0
2008-128-R2	183.0	271.9	88.1			543.0
2008-130-R2	191.6	109.6	105.5			406.7
2008-135-R2	60.9	66.6	79.2			206.7
2008-138-R2	201.7	149.4	88.9			440.0
2008-140-R2	749.8	524.1	264.6			1,538.5
2008-141-R2	248.0	200.0	197.1			645.1
2008-142-R2	219.0	219.7	197.5			636.2
2008-147-R2	199.1	259.9	229.1			688.1
2008-150-R2	273.9	376.5	303.3			953.7
2008-152-R2	80.4	91.9	88.2			260.5
2008-154-R2	600.6	601.2	552.6			1,754.4
2008-156-R2	348.2	410.5	348.6			1,107.3
2008-157-R2	99.8	99.3	98.5			297.6
2008-159-R2	311.6	319.5	405.0			1,036.1
2008-160-R2	724.6	751.4	568.1			2,044.1
2008-161-R2	371.2	474.2	288.7			1,134.1
2008-166-R2	199.1	98.5	89.3			386.9
2008-171-R2	493.4	479.9	442.7			1,416.0
2008-177-R2	168.1	151.0	174.3			493.4
2008-179-R2	483.7	551.7	576.8			1,612.2
2008-188-R2	159.1	204.9	182.6			546.6
2008-190-R2	42.0	180.0	1,037.3	817.0		2,076.3
2008-191-R2	114.7	498.6	152.0			765.3
2008-192-R2	40.7	154.3	122.6			317.6
2008-193-R2	483.3	853.4	381.0			1,717.7
2008-195-R2	163.0	192.2	191.9	201.0		748.1
2009-017-R1		99.3	69.8			169.1
2009-028-R1		150.2	163.3			313.5
2009-035-R1		251.8	267.0	95.0		613.8
2009-037-R1		112.2	128.4			240.6
2009-047-R1		194.2	196.7	225.0		615.9

LDRD Five-Year Funding Summary ($ in thousands)*

Proposal No.	2008	2009	2010	2011 (a)	2012 (b)	Total
2009-050-R1		407.8	349.8	55.0		812.6
2009-059-R1		70.7	178.6			249.3
2009-068-R1		154.9	152.1	159.0		466.0
2009-070-R1		199.0	204.0	181.0		584.0
2009-071-R1		180.0	146.9	50.0		376.9
2009-076-R1		173.9	165.3	150.0		489.2
2009-080-R1		99.2	177.6			276.8
2009-083-R1		112.2	164.7	163.0		439.9
2009-085-R1		220.4	355.9			576.3
2009-097-R1		598.5	618.4	800.0		2,016.9
2009-111-R1		100.5	127.9	126.0		354.4
2009-115-R1		234.1	296.8	350.0		880.9
2009-117-R1		245.1	102.9			348.0
2009-138-R1		153.7	181.1	188.0		522.8
2009-146-R1		119.7	113.7	80.0		313.4
2009-155-R1		221.4	198.8	200.0		620.2
2009-156-R1		173.6	151.0	180.0		504.6
2009-158-R1		243.4	261.8	250.0		755.2
2009-171-R1		132.1	222.5	200.0		554.6
2009-177-R1		99.6	106.9			206.5
2009-180-R1		320.4	277.4	300.0		897.8
2009-186-R1		165.8	287.0	200.0		652.8
2009-190-R1		144.4	169.3	171.0		484.7
2009-204-R1		125.6	136.4	123.0		385.0
2009-209-R1		205.4	247.5	205.0		657.9
2009-212-R1		141.4	167.5			308.9
2009-214-R1		109.7	109.4	110.0		329.1
2009-226-R1		323.9	252.2			576.1
2010-003-N0			148.0	151.0	165.0	464.0
2010-010-N0			180.8	168.0	185.5	534.3
2010-029-N0			160.9	183.0	215.0	558.9
2010-042-N0			169.2	174.0	204.0	547.2
2010-043-N0			200.1	196.0	239.0	635.1
2010-044-N0			299.3	300.0	500.0	1,099.3
2010-047-N0			522.5	330.0	641.0	1,493.5
2010-049-N0			155.9	139.0	174.0	468.9
2010-050-N0			173.5	165.0	185.0	523.5
2010-063-N0			132.5	118.0		250.5
2010-073-N0			159.8	166.0	215.0	540.8
2010-074-N0			177.1	300.0	260.0	737.1
2010-093-N0			160.0	90.0	210.0	460.0
2010-108-N0			98.5			98.5
2010-110-N0			344.6			344.6
2010-114-N0			69.6			69.6

LDRD Five-Year Funding Summary ($ in thousands)*

Proposal No.	2008	2009	2010	2011 (a)	2012 (b)	Total
2010-117-N0			170.3	360.0	490.0	1,020.3
2010-119-N0			133.5	150.0	150.0	433.5
2010-129-N0			129.5	138.0	156.0	423.5
2010-131-N0			702.1	400.0	500.0	1,602.1
2010-137-N0			157.8	186.0	210.0	553.8
2010-138-N0			142.3	126.0	130.0	398.3
2010-139-N0			222.1	200.0	250.0	672.1
2010-150-N0			452.6			452.6
2010-151-N0			450.8			450.8
2010-156-N0			140.2	186.0	260.0	586.2
2010-158-N0			179.1	186.0	225.0	590.1
2010-161-N0			207.4	190.0	223.0	620.4
2010-167-N0			199.5	250.0	350.0	799.5
2010-175-N0			292.2	185.0	250.0	727.2
2010-181-N0			89.0	40.0	240.0	369.0
2010-183-N0			269.8	300.0	150.0	719.8
2010-184-N0			207.9	200.0		407.9
2010-185-N0			1,047.5	2,000.0	3,000.0	6,047.5
2010-187-N0			139.1			139.1
2010-188-N0			506.5	500.0	1,000.0	2,006.5
2010-189-N0			248.3			248.3
2010-190-N0			118.4	325.0	335.0	778.4
2010-191-N0			715.1	350.0		1,065.1
2010-192-N0			107.0	113.0	116.0	336.0
2010-193-N0			542.5	220.0	220.0	982.5
2010-194-N0			32.7	215.0	230.0	477.7
2010-195-N0			83.4	565.6	600.0	1,249.0
2010-196-N0			128.9	475.0		603.9
2010-197-N0			126.4	559.0	607.0	1,292.4
2010-198-N0			169.9	347.0	353.0	869.9
2010-199-N0			99.4	462.0	600.0	1,161.4
2010-200-N0			106.0			106.0
2010-201-N0			193.8	400.0	400.0	993.8
2010-202-N0			26.0	100.0	100.0	226.0
2010-203-N0			62.0			62.0
2010-204-N0			50.5	422.0	441.0	913.5
Totals	**9,914.5**	**17,560.0**	**28,471.9**	**18,209.6**	**14,779.5**	**88,935.5**

* For projects active in FY 2010
(a) FY 2011 figures represent allocations and not actual expenditures.
(b) FY 2012 figures represent projections assuming the project continues into FY 2012.

RESEARCH REPORTS

DIRECTOR'S COMPETITIVE GRANTS

Hybrid Block Copolymer-Nanocrystal Material for Efficient Photovoltaics

2008-003-R2

Seth B. Darling

Project Description

The opportunities for and the potential benefits of using organic materials for photovoltaics (OPVs) are considerable and could lead to flexible, large-area solar cells that are low-cost, lightweight, easy to process, and with ultrafast optoelectronic response. The principal reason the use of OPV and hybrid devices has not yet been widely adopted is that they have low efficiency levels. This project aims to tackle some of the fundamental obstacles to enhanced efficiency that have limited OPV and hybrid devices to date.

In OPVs, unlike in conventional inorganic solar cells, absorbed photons create tightly bound pairs of charges called excitons. To be useful, the excitons must diffuse to the donor/acceptor (D/A) interface where charge separation can occur. The active region of a device is roughly the D/A interface plus the sum of the exciton diffusion length within the donor and acceptor regions — on the order of 10 nm. A diblock copolymer naturally self-assembles two dissimilar polymeric blocks into a morphology with alternating domains on the length scale of the molecule — again on the order of 10 nm. Therefore, diblock copolymers permit the entire volume of the material to be within the active region, so the device can be made sufficiently thick to absorb most of the incident photons — a few hundred nanometers. In this project, the diblock copolymer Poly(3-hexylthiophene)-*block*-polylactide (P3HT-*b*-PLLA) is designed with molecular weights of the two blocks that encourage lamellar morphology — a structure consisting of alternating nanoscale layers (Figure 1). The PLLA block is removed after it facilitates the self-assembly of the nanoscale phase-separated structure. Once the PLLA block is selectively removed, the resulting nanostructured P3HT is used as a scaffold for the self-organization of electron acceptors.

Mission Relevance

This project is tied to DOE's missions in energy and environment. The commitment to developing novel approaches to sustainable, renewable energy sources — such as solar energy — represents a cornerstone of the DOE missions in energy and the environment. Additional benefits from advances in this area include energy independence, which is intimately tied to national security, and new fundamental insights into the structure-property relationships in nanostructured optoelectronics.

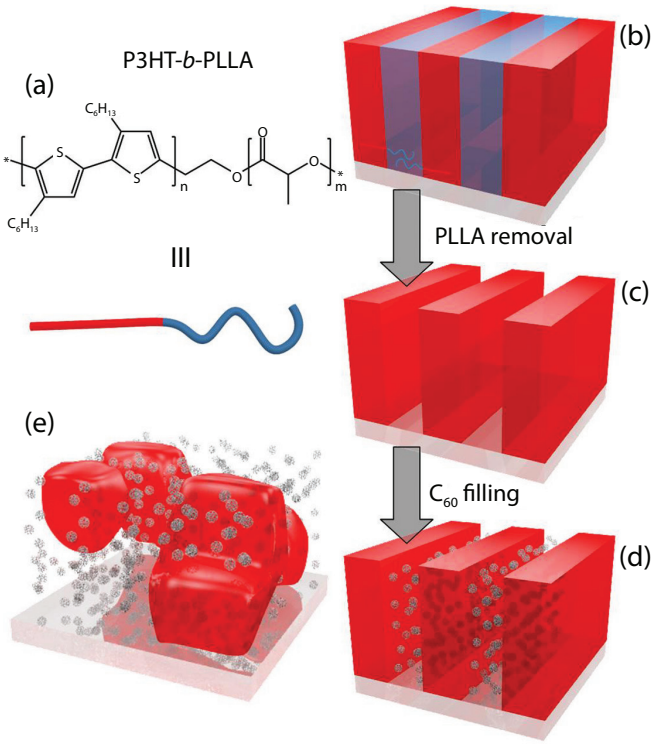


Figure 1. Schematic of block copolymer approach to create nanostructured organic photovoltaic devices. (a) Chemical structure of P3HT-b-PLLA polymer. (b) Schematic of lamellar phase domains formed by self-assembly of the block copolymer. (c) Structure following selective removal of the PLLA blocks. (d) Domains previously occupied by PLLA are infiltrated with electron-accepting materials, such as C_{60}, to form an idealized morphology. (e) Schematic of disordered bulk heterojunction obtained by depositing a blend of P3HT and C_{60}.

FY 2010 Results and Accomplishments

Thin films of P3HT-*b*-PLLA have been prepared on various substrates, and the self-assembled lamellar domains have precisely the orientation and spacing desired for PV applications. PLLA has been selectively removed from these films by using chemical degradation, and C_{60}-hydroxide electron acceptors have been incorporated into the patterned P3HT film. Photoluminescence spectroscopy provides a useful tool for quantifying the degree of charge transfer from the P3HT to the C_{60}. These data indicate that by nanostructuring the films through the use of the block copolymer methodology, we have doubled the degree of exciton separation (electron transfer) relative to a simple bilayer structure.

Another issue we have explored relates to the structural integrity of the P3HT domains following PLLA removal. We have shown that the remaining nanostructured thiophene domains tend to collapse laterally, compromising the idealized morphology. By controlling the surface-tension forces associated with the drying process, we find that domain collapse can be minimized, and desirable photophysical properties can be preserved as a result. Photoluminescence quenching, which is correlated with exciton separation, is found to be closely tied to the quality of the nanoscale morphology (Figure 2).

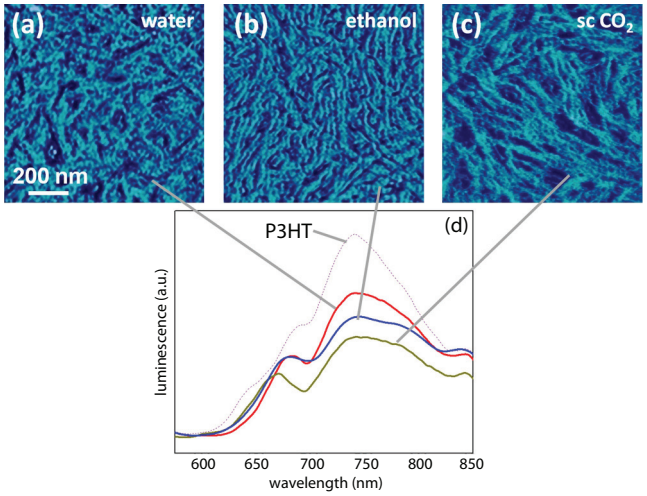


Figure 2. Atomic force micrographs and corresponding photoluminescence spectra of thin films of P3HT-b-PLLA following processing to control surface-tension forces and hence morphology. (a) Simple aqueous-etched P3HT-b-PLLA film, (b) P3HT-b-PLLA film processed with ethanol, (c) P3HT-b-PLLA film processed with supercritical carbon dioxide, and (d) Photoluminescence spectra showing increased quenching with improvements in morphology.

Refereed Publications

Botiz, I., and S.B. Darling, "Optoelectronics Using Block Copolymers," *Materials Today* **13** (2010), 42–51.

Botiz, I., and S.B. Darling, "Self-Assembly of Poly(3-hexylthiophene)-*block*-Polylactide Block Copolymer and Subsequent Incorporation of Electron Acceptor Material," *Macromolecules* **42** (2009), 8211–8217.

Botiz, I., and S.B. Darling, "Rational Design of Nanostructured Hybrid Materials for Photovoltaics," in *Active Polymers*, edited by A. Lendlein, V. Prasad Shastri, and K. Gall, Mater. Res. Soc. Symp. Proc. Volume **1190** (2009), 1190-NN03-20, Warrendale, PA.

Botiz, I., A.B.F. Martinson, and S.B. Darling, "Minimizing Lateral Domain Collapse in Etched Poly(3-hexylthiophene)-*block*-polylactide Thin Films for Improved Optoelectronic Performance," *Langmuir* **26** (2010), 8756–8761.

Darling, S.B., "Block Copolymers for Photovoltaics," *Energy and Environmental Science* **2** (2009), 1266–1273.

Non-Refereed Publications and Presentations

Darling, S.B., "Rational Design of Nanostructured Hybrid Materials for Photovoltaics," presented at Michigan State University, East Lansing, MI, June 14, 2010.

Darling, S.B., "Block Copolymers for Photovoltaics," presented at Purdue University, Lafayette, IN, May 5, 2010.

Darling, S.B., "Rational Design of Nanostructured Hybrid Materials for Photovoltaics," presented at Brookhaven National Laboratory, Upton, NY, May 18, 2009.

Darling, S.B., "Coaxing Nanomaterials to Build Themselves," presented at South Dakota State University, Brookings, SD, April 25, 2008.

Automated Theoretical Chemical Kinetics

2008-008-R2

Stephen J. Klippenstein and Lawrence B. Harding

Project Description

The field of gas-phase theoretical chemical kinetics has recently undergone an important paradigm shift. Until about 10 years ago, theory in this area was primarily used as an empirical tool for correlating sets of data and representing the temperature and pressure dependence of experimental observations. Numerous advances in quantum-chemical methodologies and software, coupled with ever-increasing computational power, have now made it feasible to obtain "chemically accurate" electronic energies for "interesting" systems. At the same time, the procedures for converting the electronic energies into rate estimates have also been undergoing major improvements in both their accuracy and their efficiency. As a result, it is now feasible to make reliable *a priori* rate predictions for many important reactions.

This paradigm shift for theoretical chemical kinetics — from an empirical to a predictive science — presents tremendous opportunities that have not yet been realized. Currently, the limiting step in application studies is simply the human time involved in gathering, correlating, preparing, and analyzing the input and output from various programs employed in the theoretical analysis. The focus of this project is the automation of the theoretical analysis in a variety of ways, with the goal of reducing the need for human intervention and data manipulation as much as possible.

Mission Relevance

This project contributes to the Grand Challenge arising from DOE-BES's Basic Research Needs Workshop on Clean and Efficient Combustion of 21st Century Transportation Fuels (October 30–November 1, 2006), which is to develop "a validated, predictive, multi-scale, combustion modeling capability to optimize the design and operation of evolving fuels in advanced engines for transportation applications." Such a predictive modeling capability will necessarily involve several aspects, with the generation of accurate chemical

mechanisms being one of the central components. The automated chemical-kinetics approach will provide a means for obtaining quantitative predictions of the rate constants comprising the chemical mechanism. An automated chemical-kinetics approach is also relevant to many other areas of gas-phase kinetics. As such, the project is also of relevance to such agencies as NASA (National Aeronautics and Space Administration — Planetary Atmospheres, Laboratory Astrophysics, and Interstellar Chemistry), the Department of Defense (DOD) (Air Force Office of Scientific Research [AFOSR], Office of Naval Research [ONR], Army Research Office [ARO] for atmospheric chemistry and signatures, kinetics of energetic materials, and novel fuels, among others), the U.S. Environmental Protection Agency (EPA), and the National Science Foundation (NSF).

FY 2010 Results and Accomplishments

Our major progress in FY 2010 involved two further software developments. First, we made improvements in our approach to solving the master equation. Our prior approach encountered difficulties and inaccuracies at high temperatures as the chemical rates became equivalent to or greater than the energy-transfer rates. We implemented improved procedures that allow us to accurately and automatically predict the rate constant regardless of temperature. This approach involves the reduction of the number of chemical species by one each time a chemical eigenvalue enters the continuum of energy-transfer eigenvalues.

The second development involved a new code for treating the association kinetics in the high-pressure regime. This code implemented a generalization of the transition-state dividing surfaces. It also implemented trajectory procedures for propagating from statistical distributions initiated on these dividing surfaces. As a result, we are able to automatically predict the high-pressure rate constants for a more complete set of reaction classes, including the roaming radical reactions that have been extensively explored here at Argonne during the last two years.

Work at meshing these various programs together into one automated kinetics scheme continues. Currently, we are working with Judit Zador at Sandia in this endeavor through our DOE-BES funded Argonne-Sandia consortium for High Pressure Combustion Chemistry.

A Cell-Free Approach toward Membrane Protein Production

2008-020-R2

Philip D. Laible and Deborah K. Hanson

Project Description

Membrane proteins represent an extremely important class of hydrophobic biomolecules, the functions of which are vital to normal cells. As such, membrane proteins represent the majority of drug targets being pursued at present. In contrast to soluble proteins, we know little about them, primarily because the production of sizable quantities of them in natively folded, functional, and pure form is an arduous task. Researchers are seeking paradigm-shifting technologies so that these molecules can be approached and studied with greater efficiency and, thus, with improved success at reduced cost. Paramount among these is a means for overexpression of membrane proteins to increase their abundance as source material for biochemical studies. In this project, we are developing a cell-free membrane protein expression system to fill this need.

Mission Relevance

This project is relevant to DOE's mission in science. The inability to produce membrane proteins is a bottleneck that frustrates any program that is attempting to understand their functions. The restructured Genomic Science Program in the DOE's Office of Biological and Environmental Research has vested future interests in such functional studies.

FY 2010 Results and Accomplishments

Building upon results from previous years with controls and candidate proteins derived from bacterial genomes, target membrane proteins of increasing complexity were expressed in the cell-free system. These proteins included G-protein-coupled receptors (e.g., mouse olfactory receptors and human chemokine receptors). These proteins were localized to the membrane fraction of the cell-free reaction mixture and could be solubilized with the use of detergents, thus suggesting structural integrity. Our most significant effort in FY 2010 was on the development and testing of hybrid reaction mixtures that favored the synthesis and folding of target membrane proteins. One goal this year was the demonstration of the value that could be added to commercially available cell-free synthesis systems by the addition of *Rhodobacter* membranes for sequestration of newly synthesized membrane proteins and membrane protein complexes (Figure 1). Our test hybrid system used transcription/translation-competent extracts derived from *E. coli* to which *Rhodobacter* intracytoplasmic membranes had been added. Several types of membrane fractions were produced from *Rhodobacter* and tested in the

cell-free synthesis reactions for their ability to sequester newly synthesized membrane proteins. A notable difference between these subpopulations is their "sidedness," and this feature can be exploited in the design of functional assays. We perfected protocols for separation of these membrane subpopulations from *Rhodobacter* host strains that vary in the complement of membrane proteins that are present in their intracytoplasmic membranes and evaluated their use in *Rhodobacter*-based, *E. coli*-based, and commercial extracts. Inside-out vesicles were prepared by mechanical lysis of whole cells. Membrane vesicles oriented with the cytoplasmic face outward were prepared by using a procedure that generates spheroplasts as a first step. Detergent lysis or mechanical, detergent-free disruption of the spheroplasts then leads to vesicle formation. For the majority of our samples, Brij-58 was used to lyse the spheroplasts. Each type of membrane preparation was pelleted by ultracentrifugation before resuspension for addition to the cell-free synthesis reactions. The added membranes were not inhibitory to the synthesis reaction, and newly synthesized proteins were localized to them.

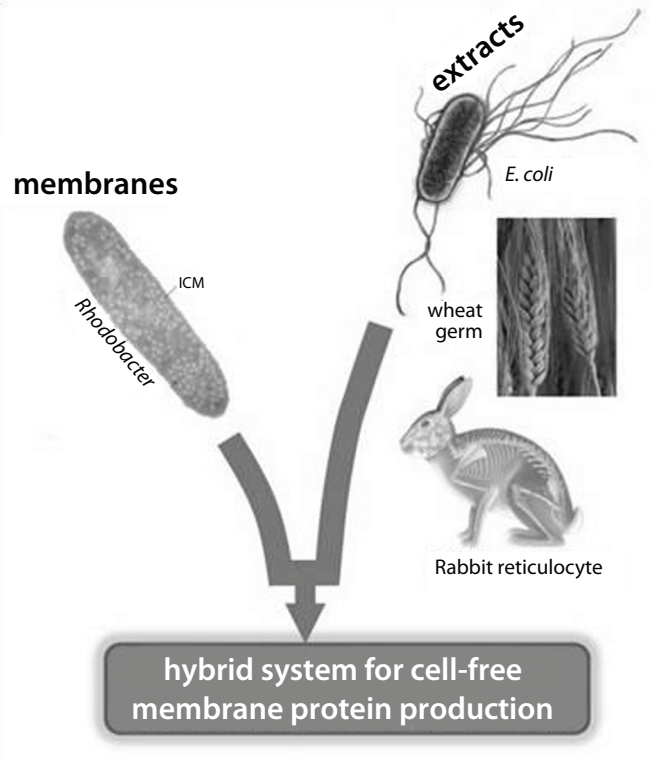


Figure 1. Recent experiments examine the utility for membrane protein production of adding Rhodobacter *membranes to commercially available systems for* in vitro *protein synthesis (e.g., those based on* E. coli*, wheat germ, or rabbit reticulocyte extracts).*

We also succeeded in using short DNA fragments from restriction enzyme digestion or polymerase chain reaction experiments as templates in the synthesis reactions in lieu of providing the gene of interest in the form of a cloned gene carried by a plasmid. This result represents a breakthrough in efficiency, since it eliminates the need to clone a target gene as a prerequisite. These short linear templates were much longer-lived if their ends were protected from exonuclease degradation, and we demonstrated that the amount of protein product obtained scaled with the amount of template added to the reaction. These protected templates are now the templates of choice for larger-scale reactions of longer duration.

This work forms part of a National Institutes of Health proposal that will be revised and resubmitted when reviewers' concerns can be addressed.

Refereed Publications

Hanson, D.K., D.L. Mielke, and P.D. Laible, "Harnessing Photosynthetic Bacteria for Membrane Protein Production," in *Current Topics in Membranes*, edited by L. DeLucas, Burlington: Academic Press, Vol. **63** (2009), 51–82.

The Use of the Hedvall Effect to Control Catalytic Properties of Subnanometer-Size Magnetic Clusters

2008-026-R2

Seth B. Darling , Jeffrey P. Greeley, Mark B. Knickelbein, and Stefan Vajda

Project Description

The main goal of the project is to understand and exploit the Hedvall Effect (HE), a phenomenon wherein changes in the magnetic state of a nanoparticle lead to measurable changes in the particle's catalytic activity on size-selected subnanometer clusters. These clusters are known to possess both very high catalytic activities for certain reactions and much higher per-atom magnetic moments than larger nanoparticles; both of these characteristics suggest that these materials would be ideal for HE studies. We are pursuing this initiative on two fronts, both by developing detailed electronic structure-based catalytic models of the clusters and by synthesizing/testing the clusters with our unique, size-selected cluster-deposition apparatus. By developing a comprehensive understanding of the HE on subnanometer metal particles, we will ultimately be able to use magnetic effects to manipulate the catalytic activity of these particles and thereby introduce a new "tuning parameter" for catalytic processes.

Mission Relevance

This project will benefit the science and energy missions of the DOE Office of Basic Energy Sciences. Catalysis is an extremely important component of many energy and chemical production processes in the United States, and the need to develop improved catalysts for systems ranging from fuel cells to petrochemical refineries is great. DOE recognizes this national need and has focused on it in several recent DOE reports. By developing a new "tuning knob" for the catalytic properties of subnanometer metal clusters, our project will provide an important contribution to the development of future catalysts, with subsequent direct impacts on these national priorities.

FY 2010 Results and Accomplishments

We have studied the HE on subnanometer Ni (nickel), Co (cobalt), and Fe (iron) clusters (these magnetic materials are particularly susceptible to the HE), focusing on the catalytic properties of these clusters for the methanation reaction, wherein CO (carbon monoxide) and hydrogen are converted to methane and water. Most of the theoretical and experimental components of this work have now been completed and reports are being prepared for publication.

Theoretical modeling. We have completed computational (Density Functional Theory) modeling of the methanation reaction on gas-phase Ni_4 and Co_4 clusters. In addition to finalizing our analysis of the reaction kinetics, we determined the electronic orbital interactions that lie behind the predicted change in catalytic activity during the transition from magnetic to non-magnetic clusters. Briefly, we find that the CO $2\pi^*$ orbitals interact more strongly with the *d*-orbitals of non-magnetized clusters, leading to stronger binding; in general, stronger binding is expected to produce higher catalytic activity. These electronic effects are very general, suggesting that there may be scope to tune the catalytic properties of other metal clusters for the methanation reaction with similar manipulations of the magnetic structure.

We also determined the likely oxidation state of the clusters as a function of the ambient temperature and oxygen pressure, and we calculated the magnetic state of the clusters resulting from the change in oxidation state. Gas-phase Ni_4 and Co_4 clusters are predicted to be almost completely oxidized at ambient conditions. This oxidation, in turn, leads to a quenching of the clusters' spin magnetic moments, implying that the magnetocatalytic effect may be attenuated in highly oxidizing environments; we determined similar results for the clusters when they are immersed in CO-rich environments. Additionally, we found that the adsorption energy of CO, an important parameter in determining the catalytic activity of the clusters for methanation, is significantly perturbed by the presence of adsorbed oxygen (Figure 1); as the clusters are successively oxidized, the binding energy is weakened by 1.3 and 2.0 eV for Co_4 and Ni_4, respectively. Calculations to further probe these effects on supported clusters are now being completed [for this purpose, we are modeling Ni_4 adsorption on the (010) surface of theta-alumina].

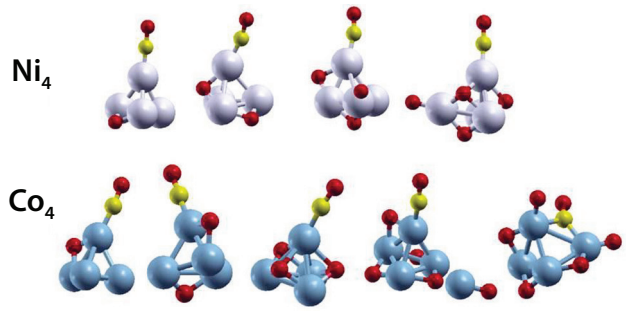


Figure 1. Most favorable geometries for carbon monoxide adsorption on Ni_4 and Co_4 clusters at different oxidation states, as determined by explicit Density Functional Theory calculations (a test calculation for a Co_5 cluster, second from right, is also included). Gray atoms represent nickel, blue is cobalt, yellow is carbon, and red is oxygen.

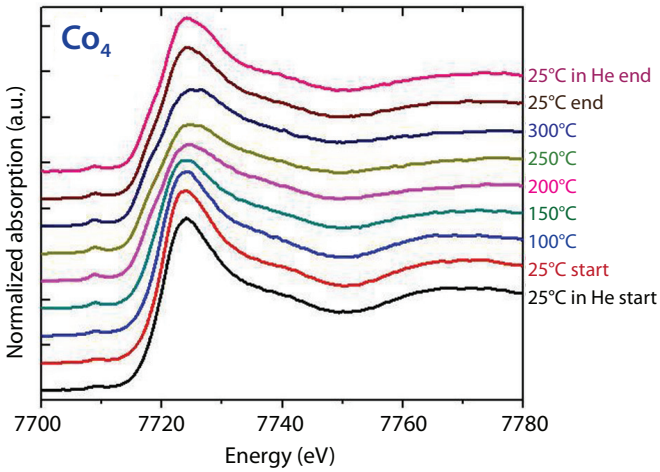


Figure 2. X-ray absorption spectra (XANES) of supported Co_4 clusters recorded at various temperatures in a reducing atmosphere. The spectra reveal partially oxidized cobalt clusters. No significant change in the oxidation state is observed under the given reaction conditions.

Determination of the oxidation state of alumina-supported Ni_4 and Co_4 clusters and related analyses. This year marked the successful determination of the oxidation state of alumina-supported Ni4 and Co4 clusters that have been exposed to air. By using a combination of grazing incidence small-angle x-ray scattering (GISAXS) to monitor the cluster shapes under reaction conditions and x-ray absorption (GIXANES) to probe their oxidation states, we obtained detailed information about the clusters' stability and oxidation state. The supported Co_4 clusters are found to be in a partially oxidized state that does not change noticeably with increasing temperature, even in the presence of reaction gases (Figure 2). This finding implies

that the support partially impedes cluster oxidation, a result that we are currently trying to understand in more detail from the computational perspective (see above). In addition to the work on alumina, we analyzed, experimentally and computationally, the structure of these partially oxidized clusters on ultra-nanocrystalline diamond surfaces and found that this support, too, appears to be associated with a lower oxidation state (as in the case of the alumina-supported clusters described above) than what would be predicted for gas-phase clusters exposed to air.

Magneto-tunnel junction (MTJ) sensor installation and testing. Our combined experimental and computational work established that the oxidation state of metal clusters can have a significant impact on their catalytic properties. To provide further experimental information about the properties of truly metallic subnanometer clusters (no oxygen present), we recently installed a new ultra-high vacuum (UHV) chamber that will house the magneto-tunnel junction (MTJ) sensor. Our installation is the first ever to make use of an MTJ sensor to study magnetic nanoclusters, and it will provide the only method available to obtain magnetic information on such systems. We are currently working to eliminate a drift in the output voltage of the MTJ sensor, after which we will complete combined magnetic and catalytic measurements on Ni_4 and Co_4 clusters for the methanation reaction.

We are finishing simultaneous measurements of the magnetic and catalytic properties of the subnanometer Ni_4 and Co_4 clusters; this work is currently continuing through a user project at the Center for Nanoscale Materials. These results will form an important complement to our theoretical results, reports on which are now being prepared for publication.

Refereed Publications

Mehmood, F., J. Greeley, and L. Curtiss. "Density Functional Studies of Methanol Decomposition on Subnanometer Pd Clusters," *J. Phys. Chem. B* **113** (2009), 21789.

Torres-Rangel, D., and J. Greeley, "Coverage Effects in Carbon Monoxide Adsorption on Gas Phase and Supported Ni Clusters," in preparation.

Torres-Rangel, D., J. Greeley, S. Lee, and S. Vajda, "Impact of the Oxidation State of Metallic Base Metal Clusters on Methanation Kinetics," in preparation.

Non-Refereed Publications and Presentations

Greeley, J., and D. Torres-Rangel, "Electronic and Structural Effects on Subnanometer Metal Clusters," presented at the ACS (American Chemical Society) Annual Meeting, San Francisco, CA, March 21–25, 2010.

D. Torres-Rangel, "Magnetocatalysis on Subnanometer Metal Clusters." presented at the APS (American Physical Society) Annual Meeting, Boston, MA, March 15–19, 2010.

Rapid XRF Elemental Imaging for High-Throughput Identification of Metal-Binding Proteins Critical to Life, Disease, and Bioremediation

2008-035-R2

Lydia A. Finney and Stefan Vogt

Project Description

An estimated one-third of all proteins bind metal ions (such as calcium, manganese, iron, zinc, and copper), and many of these proteins have regulatory or catalytic functions. However, no practical resources exist to identify and measure the levels of metals bound to proteins in complex mixtures. We seek to enable routine scanning and analysis of an entire two-dimensional (2-D) gel by micro x-ray fluorescence (XRF) and develop methods to preserve intact metalloproteins during electrophoresis. This capability will enable the high-throughput, systematic identification of metal-binding proteins that act as switches for numerous physiological functions, as well as provide a new way to track the biological fates of metallic environmental contaminants.

Mission Relevance

This project is tied to DOE's missions in science and environment, particularly to the missions of the Office of Science's Environmental Remediation Science Program. Metalloproteins are key to the electron transport mechanisms of bacteria that are endogenous to numerous DOE waste sites. The methods developed and preliminary data produced by the project thus will provide a unique avenue of investigation pertinent to DOE's environmental remediation mission. At the same time, both the development of new tools for visualizing post-translational regulation of cellular activity and the study of metals in biology are areas of active interest at the National Institutes of Health.

FY 2010 Results and Accomplishments

We relocated a test XRF system installed at beamline 2-ID-E of the Advanced Photon Source (APS) at Argonne to a permanent home at beamline 8-BM-B, which has been redeveloped and dedicated to high-throughput x-ray fluorescence techniques for life sciences. We improved many factors affecting sensitivity, including the installation of a helium sample chamber and the commissioning of a 4-element Vortex fluorescence detector.

In the past year, we have continued to functionally verify our ability to identify metalloproteins in complex mixtures. We published our study of chromium's binding to human proteins, establishing our methods and demonstrating our capabilities for 1-D separations. Also in FY10, we demonstrated that we can analyze 2D separations of natural samples, imaging proteins isolated from *Shewanella Oneidensis*. This work is in preparation for publication.

Refereed Publications

Finney, L., Y. Chishti, T. Khare, C. Giometti, A. Levina, P.A. Lay, and S. Vogt, "Imaging Metals in Proteins by Combining Electrophoresis with Rapid X-ray Fluorescence Mapping," *ACS Chemical Biology* **5** (6) (2010), 577–587, DOI: 10.1021/cb1000263.

Non-Refereed Publications and Presentations

Finney, L., "Enhancing the Context of X-ray Fluorescence Imaging: Update on the Redevelopment of Beamline 8-BM," invited presentation at the Biological Applications of X-ray Fluorescence Microscopy Satellite Workshop of the 10th International Conference on X-ray Microscopy, Chicago, IL, August 13–14, 2010.

Finney, L., E. Maxey, C. Roehrig, and S. Vogt, "Enhancing the Context of X-ray Fluorescence Imaging: Highlights from the Redevelopment of Beamline 8-BM," poster presentation at the APS User Meeting, Argonne, IL, May 3–5, 2010.

Systematic Analysis of the Role of Zinc in Stem Cell Plasticity and Pluripotency

2008-036-R2

Lydia A. Finney, Liaohai Chen, and Qiaoling Jin

Project Description

Human embryonic stem cells (hESCs) are capable of unlimited self-renewal and retain pluripotency (i.e., the ability to differentiate into all cell lineages in the body). However, stem cells only retain their pluripotency when they grow slowly in monolayer colonies. We have found evidence that a direct correlation exists between the differentiation of hESCs and their levels of endogenous zinc. As a result of this finding, we characterized the way in which this highly detectable aspect can serve as both a biomarker and an intervention point for the entire cellular system. This project resulted in a better understanding of the role of zinc in the balance between stem cell proliferation and differentiation.

Mission Relevance

This project will benefit DOE's mission in science by improving the quality of life through innovations in bioscience and biotechnology. Achieving research goals at the forefront of stem-cell pluripotency will establish new lines of hypothesis-driven research.

FY 2010 Results and Accomplishments

We interrogated the relationship that we discovered earlier between pluripotency of hESCs and their zinc content. This work used x-ray fluorescence microscopy to determine the zinc content in stem-cell colonies induced to differentiate and those that are as pluripotent as can be maintained. In FY 2010, we expanded our studies to show that nearly twice as much zinc is present in differentiated cells as compared to pluripotent cells. We found this to be the case whether we differentiated the cells with retinoic acid or with Activin A. Thus, we clearly showed that zinc accumulation is specific to differentiation itself, not an artifact of the particular agent used to cause differentiation.

We also began to use antibodies for known zinc-binding proteins to identify which zinc proteins are affected during differentiation. Through this approach, we hoped to identify specific proteins we could target to control the process. We found that metallothionein, a zinc-binding protein known to play a role in cell-fate determination, is present in the nucleus of stem cells. Since metallothionein is not typically found in the nucleus of other types of cells, we hypothesize it may be involved in the zinc accumulation we have seen.

We earlier set out to identify the macromolecular partners of this metal specific to stem-cell differentiation. In FY 2008, we established our ability to identify zinc-binding proteins by using our proteomics approach. In FY 2009, by comparing differentiated and undifferentiated cell lysates, we found that the difference in cellular zinc does not appear to correspond to the presence of additional zinc-binding proteins. In FY 2010, we found, by using x-ray fluorescence microscopy to look at dividing stem cells, that the zinc in the nucleus does not appear to be associated with nuclear DNA.

Refereed Publications

Wolford, J. L., Y. Chishti, Q. Jin, J. Ward, L. Chen, S. Vogt, and L. Finney, "Loss of Pluripotency in Human Embryonic Stem Cells Directly Correlates with an Increase in Nuclear Zinc," *PLoS One* **5**(8) (2010), e12308.

Wolford, J., Y. Chishti, J. Ward, S. Vogt, and L. Finney, "Zinc's Role in Stem Cell Biology: Preserving the Picture," in Proceedings for the 10th International Conference on X-ray Microscopy, Chicago, IL, August 15–20, 2010.

Non-Refereed Publications and Presentations

Finney, L., "Visualizing a Role for Zinc in Stem Cell Differentiation," presented at the 10th International Conference on X-ray Microscopy, Chicago, IL, August 15–20, 2010.

Finney, L., "Zinc and Pluripotency in Human Embryonic Stem Cells: 'Mapping' a Relationship," invited presentation at FASEB (Federation of American Societies for Experimental Biology) Summer Conference: Trace Element Metabolism in Biology and Medicine, Snowmass Village, CO, June 13–18, 2010.

Selective, Efficient C-H Bond Activation of Alkanes by High-Surface-Area, Size-Selected Noble-Metal Clusters

2008-090-R2

Michael J. Pellin, Larry A. Curtiss, Jeffrey W. Elam, Jeffrey P. Greeley, Stefan Vajda, and Randall E. Winans

Project Description

The key to selective transformation of short-chain, relatively unreactive alkanes to olefins, alkynes, and longer-chain alkanes is the efficient, selective activation of the terminal C-H bond (without activation of the C-C bond). The experimental work described below builds on theoretical work which argues that subnanometer noble-metal clusters can activate these bonds because of their intrinsic structure. In this project, we aim to find a reliable, inexpensive synthesis path to the production of such clusters on standard catalytic supports. The project builds on a demonstration that 10-nm-sized clusters can be produced by using Atomic Layer Deposition (ALD). It will use unique analytical capabilities at the APS (beamline 12-ID) — specifically, grazing-incidence small-angle x-ray scattering (GISAXS) — to accurately measure subnanometer cluster size distributions on flat substrates, allowing synthesis conditions to be optimized now for the later production of subnanometer-cluster catalysts on silica powder supports.

Mission Relevance

Among the missions of Basic Energy Sciences within the Office of Science is to conduct world-class research in areas relevant to energy efficiency in the United States. The selective transformation of ubiquitous but inert C–H bonds to other functional groups has far-reaching practical implications, ranging from more efficient strategies for fine-chemical synthesis to the replacement of current petrochemical feedstocks by less-expensive and more readily available alkanes. At present, a significant fraction of the energy used for chemical transformations is used in converting alkanes. The purpose of this project is to provide a demonstration of a practical synthesis method for catalysts that have recently been demonstrated to be by far the most active and selective catalysts for a variety of reactions, including the epoxidation of propene and the oxidative dehydrogenation of propane and cyclohexane. Such a practical synthesis method for useful C–H bond activation will ultimately allow us to exploit the Earth's alkane resources (of which the United States has major reserves) more efficiently and cleanly.

FY 2010 Results and Accomplishments

The usefulness of subnanometer metal clusters for the selective, specific, and active conversion of alkane products to important industrial products has been demonstrated this year with studies of direct propylene epoxidation by molecular oxygen using three-atom metal clusters (i.e., Ag_3) on ALD-prepared alumina substrates. Propylene oxide is an important chemical, the current industrial production of which is energy-intensive and environmentally unfriendly. Attempts to solve this problem by using catalysts based on bulk silver surfaces with direct propylene epoxidation by molecular oxygen have been hampered by either low conversion or poor selectivity toward propylene oxide (with the accompanying loss of product to significant amounts of CO_2), and the detailed mechanism of the epoxidation process is unclear for the bulk process.

In Figure 1, we demonstrate that Ag_3 is stable over a wide temperature range on ALD-prepared alumina surfaces and that under these conditions of stability, Ag_3 is the most active, specific catalyst ever discovered for the direct conversion of propylene to its epoxide. A common problem encountered with the use of small metal particles on oxide supports is that their catalytic performance is often diminished by sintering, the agglomeration of particles caused by heating during reactions. Figure 1 demonstrates that agglomeration does not occur below 110°C. Below this temperature, the two possible epoxide products dominate the reaction products. Beginning at room temperature, the rate of both propylene oxide and acrolein formation increased sharply with temperature. At 60°C, we observed the onset of combustion. The formation of CO_2 coincided with the decrease of acrolein production, which indicates that these two channels are competitive.

GISAXS revealed that the sintering of Ag_3 clusters begins at around 110°C, leading to the formation of silver particles with an average size of 3.5 nm at 200°C (Figure 1A). The analysis of the two-dimensional GISAXS data revealed particle height and diameter of 2 nm and 4 nm, respectively. These nanoparticles did not sinter further. Remarkably, the sintered particles had dramatically better catalytic properties than silver nanoparticles formed by more conventional chemical methods. At 100°C, for instance (following aggregation at 110°C), nearly pure propylene oxide was formed (Figure 2).

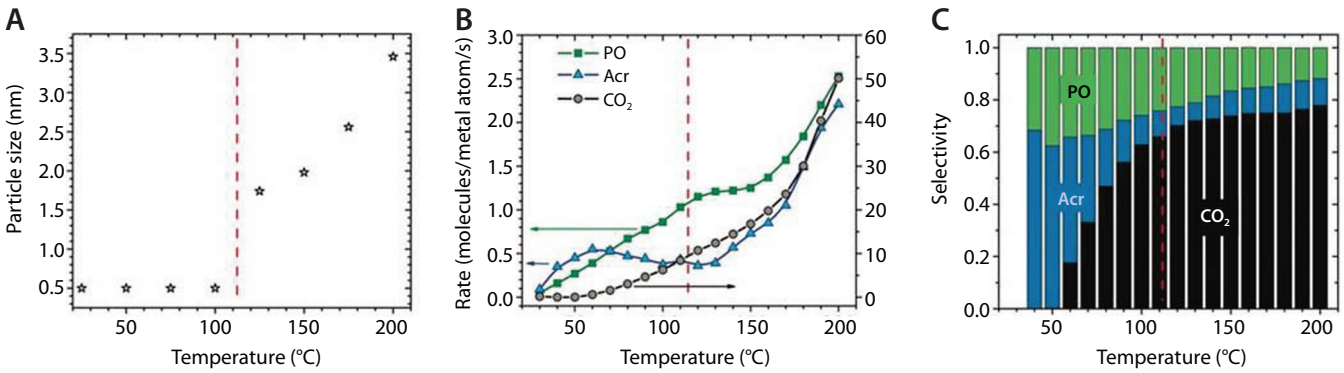


Figure 1. (A) Temperature-dependent average cluster size determined by GISAXS. (B) Rate of propylene oxidation toward propylene oxide (PO), acrolein (Acr), and CO_2 per surface silver atom. (C) Selectivity of propylene oxide, acrolein, and CO2 versus temperature. The vertical dashed lines indicate the temperature at which the sintering of the silver trimers begins. During an additional hour of reaction at 200°C, no change in the size of the aggregates was observed and the turnover rate for propylene oxide decreased to 1.55 s^{-1}; this finding likely indicates annealing of the newly formed nanostructure. The data shown are results from one run. The estimated uncertainty is ~ ±0.2 nm for GISAXS and ~5% for the turnover rates.

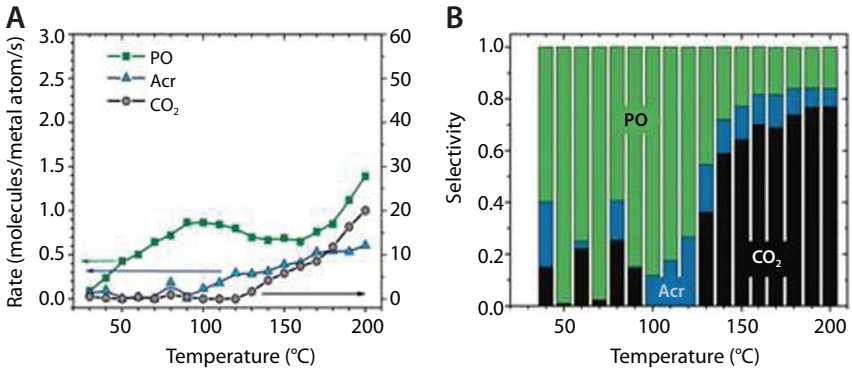


Figure 2. (A) Rate of propylene oxidation toward propylene oxide, acrolein, and CO_2 per surface silver atom and (B) selectivity on the nanometer-sized, sintering-resistant silver aggregates that formed from Ag_3 clusters during the first reaction cycle.

Theoretical studies of this system demonstrate that the angular nature of these small metal clusters gives rise to their remarkable activity and specificity. Further, the system stabilizes a high-spin pathway for catalytic conversion that is simply not present in larger Ag systems. The remarkable stability of the aggregated samples indicates that in these constructs the high spin is still active, likely as a result of a very rough structure that maintains the angular bonding of the three-atom cluster. This work is attracting significant industrial interest.

We expect that the project will continue with funding from DOE/BES-DMSE.

Refereed Publications

Lee, S., B. Lee, F. Mehmood, S. Seifert, J.A. Libera, J.W. Elam, J. Greeley, P. Zapol, L.A. Curtiss, M.J. Pellin, P.C. Stair, R.E. Winans, and S. Vajda, "Oxidative Decomposition of Methanol on Subnanometer Palladium Clusters: The Effect of Catalyst Size and Support Composition," *J. Phys. Chem.* C **114** (2010), 10342.

Lei, Y., F. Mehmood, S. Lee, J. Greeley, B. Lee, S. Seifert, R.E. Winans, J.W. Elam, R.J. Meyer, P.C. Redfern, D. Teschner, R. Schlogl, M.J. Pellin, L.A. Curtiss, and S. Vajda, "Increased Silver Activity for Direct Propylene Epoxidation via Subnanometer Size Effects," *Science* **328** (2010), 224.

Vajda, S., S. Lee, K. Sell, I. Barke, A. Kleibert, V. von Oeynhausen, K.-H. Meiwes-Broer, A.F. Rodriguez, J.W. Elam, M.J. Pellin, B. Lee, S. Seifert, and R.E. Winans, "Combined Temperature-Programmed Reaction and in situ X-Ray Scattering Studies of Size-Selected Silver Clusters under Realistic Reaction Conditions in the Epoxidation of Propene," *J. Chem. Phys.* **131** (2009), 121104.

Vajda, S., M.J. Pellin, J.P. Greeley, C.L. Marshall, L.A. Curtiss, G.A. Ballentine, J.W. Elam, S. Catillon-Mucherie, P.C. Redfern, F. Mehmood, and P. Zapol, "Subnanometre Platinum Clusters as Highly Active and Selective Catalysts for the Oxidative Dehydrogenation of Propane," *Nat. Mater.* **8** (2009), 213.

The Development of Neutron Skins

2009-037-R1

Christopher J. Lister, Elizabeth T. Ricard-McCutchan, and Robert B. Wiringa

Project Description

We are making a combined theoretical and experimental investigation of excited states and their decays in light neutron-rich nuclei. These are nuclei, such as the beryllium isotopes ^{9}Be, ^{10}Be, and ^{11}Be, which are now amenable to accurate theoretical calculation by using quantum Monte Carlo (QMC) methods and the sophisticated two-nucleon (NN) and three-nucleon (3N) potentials that the Argonne theory group has developed over the past decade. Experimental properties, such as lifetimes, of many of the excited states in these nuclei are poorly known, but they are also amenable to newly improved experimental techniques like the Doppler shift attenuation method, which the Argonne low-energy nuclear physics group is developing to ever-greater precision. The new experimental results that are being obtained are presenting new challenges to the theoretical models, which in turn are suggesting possible new experiments. The outcome will be a greatly improved understanding of the structure of light neutron-rich nuclei, particularly in the weakly bound regime where extended neutron skins develop.

Mission Relevance

The project is relevant to DOE's basic science mission. Argonne has played a leading role in the development of ab initio theory for light nuclei, and this work has been prominently featured in the last two DOE Nuclear Science Advisory Committee (NSA C) Long-Range Plans. The combination of the Argonne Tandem Linac Accelerator System, the Fragment Mass Analyzer, and Gammasphere allow for the most precise experimental techniques to be applied to the problems under study.

FY 2010 Results and Accomplishments

The theory group continued calculations of the beryllium isotopes and extended these to the mirror nuclei, in particular ^{10}C, which provides an interesting contrast to ^{10}Be, having two protons outside the ^{8}Be (two-alpha-particle) core instead of two neutrons. The electromagnetic transition rates depend sensitively upon how those last two nucleons orbit the core. The theoretical calculations suggest that the electric quadrupole transition probability *B(E2)* between the 0^{+} ground state and the first 2^{+} excited state should increase slightly for ^{10}C relative to ^{10}Be, and that there is considerable dependence on the choice of 3N potential in the Hamiltonian. We are also developing code to look at one- and two-nucleon overlaps, which measure how much a given A-body nucleus looks like a combination of subclusters. For example, the overlap $<^{8}\mathrm{Be} + n + n \mid ^{10}\mathrm{Be}>$ quantifies how much the ^{10}Be nucleus looks like a ^{8}Be core and two uncorrelated neutrons. Such calculations will help determine the distribution of the last two nucleons.

The experimental group carried out precision experiments on the only bound-state decay in ^{10}C. A result of similar precision to that of ^{10}Be was achieved. Reconciling this result with theory is in progress. Experiments were started at the A.W. Wright Nuclear Structure Laboratory (WNSL) accelerator at Yale University to explore the possibility of measuring the intermediate isobaric analogs in ^{10}B. A test run, using inelastic proton scattering on ^{10}B, was very successful and a publishable result was obtained. Analysis is under way.

Robert Wiringa and Argonne colleague Steven C. Pieper shared the 2010 Tom W. Bonner Prize of the American Physical Society for their work in the development of the nuclear QMC calculations being used in this project.

Although the LDRD project is now ending, the theoretical and experimental groups plan to continue their collaboration. Additional experiments in this region of the chart of the nuclides can be used to test the microscopic theory, particularly in the realm of large neutron (or proton) excess. Plans include calculations for ^{11}Be and continuing work on the A=10 nuclei.

Refereed Publications

McCutchan, E.A., C.J. Lister, R.B. Wiringa, S.C. Pieper, D. Seweryniak, J.P. Greene, M.P. Carpenter, C. J. Chiara, R. V.F. Janssens, T.L. Khoo, T. Lauritsen, I. Stefanescu, and S. Zhu, "Precise Electromagnetic Tests of *Ab Initio* Calculations of Light Nuclei: States in ^{10}Be," *Phys. Rev. Lett.* **103** (2009), 192501.

Non-Refereed Publications and Presentations

Lister, C.J., "Precision Test of Ab-Initio Calculations," presented at the Tata Institute of Fundamental Research, Mumbai, India, March 5, 2010.

Lister, C.J., "Precision Determination of ^{10}C Excited State Lifetime," presented at the Annual Fall Meeting of the Division of Nuclear Physics, American Physical Society, Santa Fe, New Mexico, November 6, 2010.

McCutchan, E.A., "Precision Lifetime in the Mirror Pair of ^{10}C and ^{10}Be," presented at Nuclear Structure 2010, University of California, Berkeley, California, August 11, 2010.

Wiringa, R.B., "Quantum Monte Carlo Calculations of Light Nuclei," presented at the National Nuclear Security Administration/Advanced Scientific Computing Research (NNSA/ASCR) Conference on Scientific Grand Challenges in National Security: the Role of Computing at the Extreme Scale, Gaithersburg, MD, October 6, 2009.

Wiringa, R.B., "Nuclear Forces and the Universe," Bonner Prize Talk, presented at the April Meeting of the American Physical Society, Washington, D.C., February 14, 2010.

Wiringa, R.B., "Nuclear Forces and Ab Initio Calculations of Nuclei," presented at the Exotic Beam Summer School 2010 Lectures, Oak Ridge National Laboratory, Oak Ridge, TN, August 3–4, 2010.

Wiringa, R.B., "Nuclear Quantum Monte Carlo," Peter Axel Lecture, presented at the University of Illinois, Urbana, Illinois, September 30, 2010.

Coherent Diffraction Imaging of Complex Polymeric Networks

2009-068-R1

Jyotsana Lal and Lee Makowski

Project Description

The development of coherent diffraction imaging (CDI) for use at today's synchrotron light sources and the next-generation sources that will come on line in the next few years will provide an extraordinary opportunity for studying complex polymeric matrices that constitute a very important but poorly characterized class of biomaterials. This project aims to capitalize on CDI's unique suitability for studying these structures to develop a robust approach to mapping the distributions of a variety of chemical constituents within complex polymeric networks.

Mission Relevance

The project is relevant to DOE's missions in energy and basic science. The development of CDI for use at synchrotrons and next-generation light sources that will come on line in the next few years will provide an extraordinary opportunity for the study of complex polymeric matrices that make up a large fraction of the volume of multicellular organisms and constitute a very important but poorly characterized class of biomaterials. This project stems from the insight that CDI is uniquely suited to the study of these structures. In particular, the structure of plant cell walls is of great importance for developing strategies for optimal generation of biofuels and is thereby of particular interest to DOE.

FY 2010 Results and Accomplishments

In the first year of the project, CDI data were collected from dried maize vascular bundles. Initial CDI characterizations indicate that many of the largest cellulose crystallites (those most likely to be recalcitrant to processing) are formed through the convergence of multiple fibrous domains. Different allomorphs of cellulose appear to be associated with crystallites exhibiting different crystalline habits.

We have demonstrated the use of CDI to image cellulose nanocrystals embedded within maize vascular bundles (opaque fibers from cornstalks). We know of no other technique capable of providing detailed information on the structure of these crystals *in situ*. During the second year of this project, we focused exclusively on samples maintained at cryogenic temperatures and expanded our studies to include immature plants fresh-frozen immediately on harvest. These studies have identified systematic changes in the organization of cellulose crystals due to harvesting and drying and demonstrate the power of the approach for elucidating molecular changes that occur in response to materials processing.

Fresh-frozen material. In the second year, we collected CDI data from approximately a dozen cellulose crystals within material that was flash-frozen immediately on harvesting. Comparing the form of speckle around the Bragg peaks from these crystals with those from dried material indicated that the shapes of cellulose crystals in the fresh-frozen material differed substantially from those in the dried material. Preliminary reconstructions of these particles suggest well-defined smaller crystallites compared to mature dried corn. Later in the maturation cycle, they seem to arrange themselves in the helical arrangement of compact domains observed in dried material, although additional work will be required to understand the basis for this similarity.

Algorithms for reconstruction. We successfully used several distinct algorithms for reconstruction of images from the Bragg reflection speckle. All are based on the limited support intrinsic to the size of the small cellulose crystallites. The speckle intensity is the square of the Fourier transform of the shape of the crystal. If phases can be obtained for these intensities, then a simple Fourier transform will provide the crystal shape. There are a number of existing algorithms for choosing initial phase sets and limits of support. We recently implemented the "shrink-wrap" algorithm (in which the real space support shrinks as the phases are refined) to compute the images shown in Figures 1 and 2.

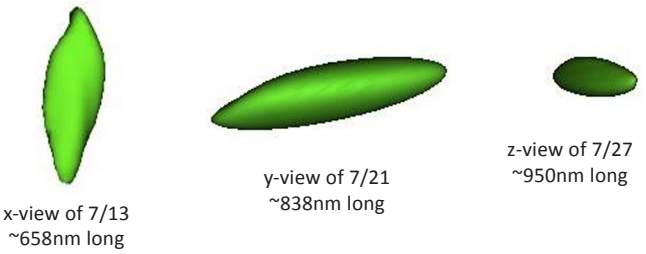


Figure 1. Preliminary 3D reconstruction, using the shrink-wrap algorithm, of flash-frozen crystals from the rind (outer stem layer) measured at different ages in the maturation cycle, approximately one week apart (7/13, 7/21, and 7/27/09, respectively).

Figure 2. Previous-year data on cellulose crystallites from the vascular bundles of dried maize stover, reconstructed by using the shrink-wrap algorithm. We hypothesize that these larger cellulose crystallites (~2135 nm long) may be detected in older internodes.

Proposed Work for FY 2011

During the third year of the project, we will work to optimize data collection and processing protocols in order to enable collection of data from smaller crystals and at a rate sufficient to make a substantive impact on our understanding of these complex polymeric matrices.

Non-Refereed Publications and Presentations

Makowski, L., J. Lal, I. Robinson, and R. Harder, "*In situ* Imaging of Cellulose Crystals Using Coherent Diffraction Imaging," Invited Talk presented at the Cellulose Research Institute, College of Environmental Science and Forestry, Syracuse University, Syracuse, NY, February 7, 2010.

Makowski, L., J. Lal, I. Robinson, and R. Harder, "*In situ* Imaging of Cellulose Crystals," Invited Talk presented at the Workshop on Coherent X-ray Imaging for Biological Applications, Brookhaven National Laboratory, May 17, 2010.

Makowski, L., J. Lal, I. Robinson, and R. Harder, "*In situ* Imaging of Cellulose Crystals Using Coherent Diffraction Imaging," poster presented at XRM2010 (10th International Conference on X-ray Microscopy), Chicago, IL, August 15, 2010.

Characterization of Proteins from *Anaeromyxobacter dehalogenans*, a Newly Identified Bacterium of Metabolic and Respiratory Versatility Important for Bioremediation

2009-070-R1

Marianne Schiffer, Phani R. Pokkuluri, and Rosemarie Wilton

Project Description

Anaeromyxobacter dehalogenans can perform reduction of uranium, technetium, and other metal ions in addition to respiration utilizing halogenated compounds. It is found in contaminated subsurface environments, such as the U.S. DOE-NABIR (Natural and Accelerated Bioremediation Research) Field Research Center at Oak Ridge, where *Anaeromyxobacter* species are thought to be key players in metal reduction at the site. Because of the favorable characteristics of *A. dehalogenans* for bioremediation, the DNA sequence of its genome was determined at the DOE Joint Genome Institute. Very few details are known regarding the proteins and the molecular processes of *A. dehalogenans*. In this project, we have chosen to study two protein families that are important in the respiration of *A. dehalogenans*: (1) multiheme *c*-type cytochromes and (2) sensor domains of signal-transduction/chemotaxis proteins.

Multiheme c-type cytochromes have been implicated in the respiratory versatility of metal-reducing bacteria. Cytochromes are proteins containing heme cofactors that are part of the electron-transfer chains used by the organism to reduce metals. *Sensor domains of signal transduction proteins* are used by the bacterium to sense the outside environment and initiate the necessary regulation processes required for the cell's survival.

Mission Relevance

The project is relevant to DOE's missions in basic science and the environment. Microbial research is especially important to DOE's Office of Biological and Environmental Research (BER) because it can promote understanding for the development of innovative biotechnological applications that result in better and less-expensive ways to clean up contaminated sites. *A. dehalogenans* is a well-suited bacterium for this purpose because of its metabolic and respiratory versatility. It can grow under a variety of redox and pH conditions. It can clean up metal and radionuclide contaminations (such as uranium and technetium) and contamination by chlorinated

compounds. The structure-function understanding of proteins from *A. dehalogenans* will enable ways to stimulate the bioremediation properties of this bacterium as suited to the needs of a given contaminated site.

FY 2010 Results and Accomplishments

In FY 10, we have continued to focus on three protein families from *A. dehalogenans* strain 2CP-C for expression and characterization: (1) cytochromes c_7, (2) large multiheme cytochromes, and (3) sensor domains. These are briefly described below.

Cytochromes c_7. The cytochromes c_7 encoded by the genes Adeh_1696 and Adeh_1697 from *A. dehalogenans* 2CP-C were successfully expressed in *E. coli*. The purification of these cytochromes has presented unexpected challenges. However, following extensive work, both proteins were purified to the required purity for crystallization experiments. The Adeh_1696 cytochrome c_7 was purified by using the polyhistidine tag and metal-affinity chromatography. The other cytochrome c_7 (Adeh_1697), which did not include the polyhistidine tag, was purified by using hydrophobic interaction chromatography followed by ion-exchange chromatography. The Adeh_1697 protein was confirmed by mass spectrometry to contain three heme cofactors attached to the polypeptide. Experiments to identify crystallization conditions for both proteins are in progress.

Large multiheme cytochrome Adeh_3077. Sequence analysis of the 40-heme cytochrome Adeh_3077 from *A. dehalogenans* revealed that it has novel penta-heme domains not previously seen in other organisms. Cloning of two of the penta-heme domains in *E. coli* had proved difficult because of the high Guanine and Cytosine content in these genes. However, we have now obtained synthetic DNA constructs optimized for their expression in *E. coli*. Initial experiments using UV-VIS (ultraviolet-visible) spectroscopy demonstrated expression of cytochromes. Optimization of expression conditions to isolate these protein fragments is under way.

Sensor domains. A. dehalogenans contains 18 methyl-accepting chemotaxis proteins and 76 histidine kinase (HisKa) proteins with a periplasmic sensor domain. A total of 31 periplasmic sensor domains were cloned by using the high-throughput ligation-independent cloning system. In solubility measurements, among the total of 31 sensor domains expressed, seven sensor domains from HisKa and four sensor domains from the chemotaxis proteins were found to be soluble. Eight of these sensor domains were purified (see Figure 1 for an SDS-PAGE gel image), and trials to identify their crystallization conditions are in progress.

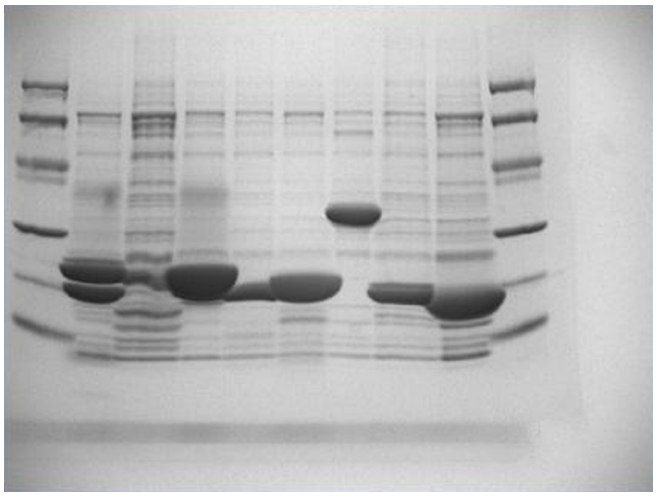


Figure 1. An SDS-PAGE (sodium dodecyl sulfate polyacrylamide) gel electrophoresis results of sensor domains at an intermediate stage of purification. Proteins by lanes from left to right: Molecular weight markers; Adeh_1071; Adeh_2011; Adeh_1380; Adeh_3718; Adeh_3897; Adeh_2090; Adeh_2210; Adeh_2942.

Proposed Work for FY 2011

Cytochromes c_7. We will continue our efforts to identify crystallization conditions for both cytochromes c_7 (Adeh_1696 and Adeh_1697). When diffraction-quality crystals are obtained, they will be used for structure determination. In addition, these samples will be supplied to our colleague, Prof. Carlos Salgueiro (UNL, Portugal), for reduction-potential measurements.

Pentaheme domains from large multiheme cytochrome Adeh_3077. The Adeh_3077 penta-heme domains will be expressed by using synthetic DNA constructs optimized for expression in *E. coli*. The purified proteins will be characterized by mass spectrometry and UV-VIS and CD (circular dichroism) spectroscopy. Dynamic light scattering will be used to assess the monodispersity of the protein samples. Pure protein samples will be used for crystallization trials. Diffraction-quality crystals, when available, will be used for structure determination.

Sensor domains. All purified sensor domains will be characterized in solution with dynamic light scattering and CD spectroscopy and will be subjected to crystallization trials. The sensor domains that produce diffraction-quality crystals will be used for structure determination. Purified sensor domains will be sent to Olga Egorova (Structural Genomics Consortium, University of Toronto) for ligand screening to determine the binding properties of the sensor domains.

Local Probe of Novel Electronic States at Complex Oxide Interfaces

2009-083-R1

John W. Freeland and Nathan P. Guisinger

Project Description

The transistor, which has shaped so much of our modern technology and economics, grew out of scientists' desire to gain a greater understanding of the interfaces between different materials. In the same way, today's materials scientists seek to expand our understanding of complex oxides by creating new states at the interface of two materials. To understand the spatial variations of these interface states, this project is focused on developing the use of cross-section scanning tunneling microscopy (STM), which has worked well in the case of semiconductor interfaces but to date has never been applied to the case of oxide heterostructures.

Mission Relevance

This project is tied to DOE's mission in basic science. This work seeks to provide new, high-spatial-resolution routes to electronic structure mapping across interfaces, which to our knowledge has never been applied to complex oxide interfaces. The knowledge to be gained in this project will be of interest to scientists studying new states at the oxide interface in a wide variety of oxide systems. Understanding these systems is the first step toward the development of novel low-power electronics, which is key to reducing the massive power loss in the current generation of electronics. The Center for Nanoscale Materials houses not only scanning probe capabilities but also premiere tools for studying complex oxide growth, which are accessible to a wide community of interested users.

FY 2010 Results and Accomplishments

In the first year of this project (FY 2009), we laid the important groundwork for high-resolution imaging of fractured surfaces. This lead directly to the two major milestones we achieved during FY 2010. First, we directly imaged a complex oxide interface for the first time. The second success was a direct imaging of a multilayered superlattice sample consisting of a ferromagnetic ($LaCaMnO_3$) and a superconducting ($YBa_2Cu_3O_7$) oxide. To answer key questions about these interfaces, we needed the unique information that we are in fact able to extract by using this imaging approach.

One of the main challenges of interfaces is understanding the correspondence of the electronic states on one side to those on the other side of the boundary. For example, the physics behind the junction made by dissimilar semiconductors is the essential element that underpins all of today's electronics. For complex oxides, no such framework exists or has been validated. However to test any such framework, the states across the interface must be tracked directly. Figure 1 shows our first results for direct imaging of an interface. It turns out that we were able not only to directly identify the film-substrate interface due to the change in density of states (dI/dV), but by tracking the dI/dV across the interface, we could also determine how the states evolve across the boundary. This method is the only means by which we can directly monitor the interface bands to give insight into how to develop a proper theory of interfacial electronic states in strongly correlated oxide systems.

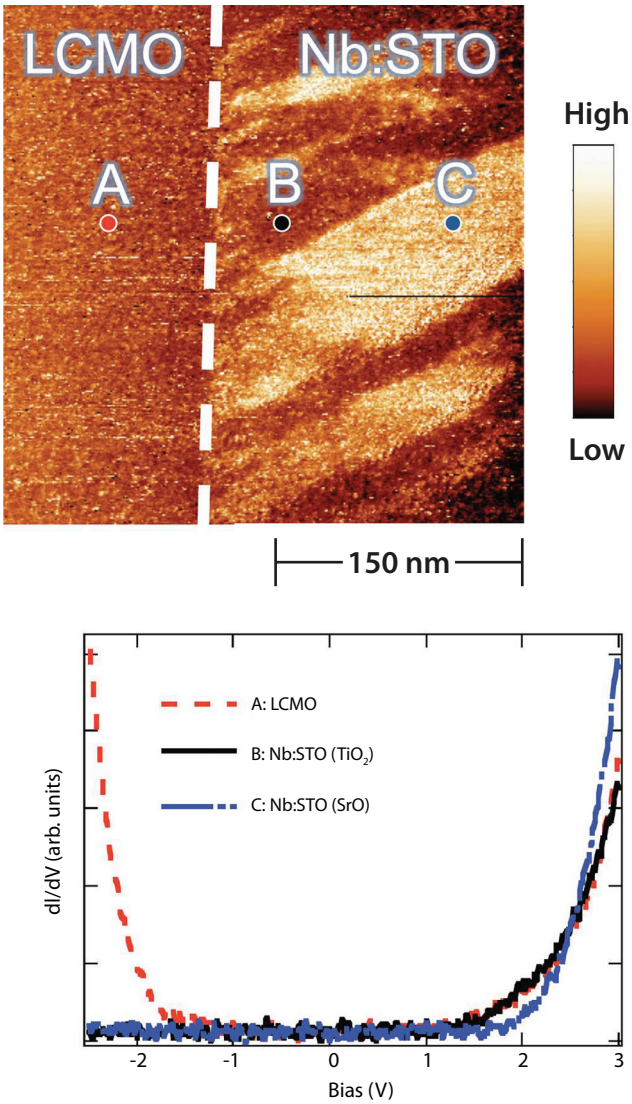


Figure 1. Conductance map (top) of in-situ *cleaved $LaCaMnO_3$ (LCMO)/$SrTiO_3$ (STO) interface. Note the clear contrast between the layers, which is enhanced (bottom) with point-by-point spectroscopy.*

The other major accomplishment of FY 2010 was the direct imaging of a superlattice sample, as shown in Figure 2. The ability to image this system, which consists of a ferromagnetic ($LaCaMnO_3$) and a superconducting ($YBa_2Cu_3O_7$) oxide, was one of the main motivations of the project. With STM, we can watch the electronic properties evolve from one layer to the next. As Figure 2 shows, where the two types of order compete (ferromagnetism versus superconductivity), we can directly monitor how the system evolves spatially across the interface.

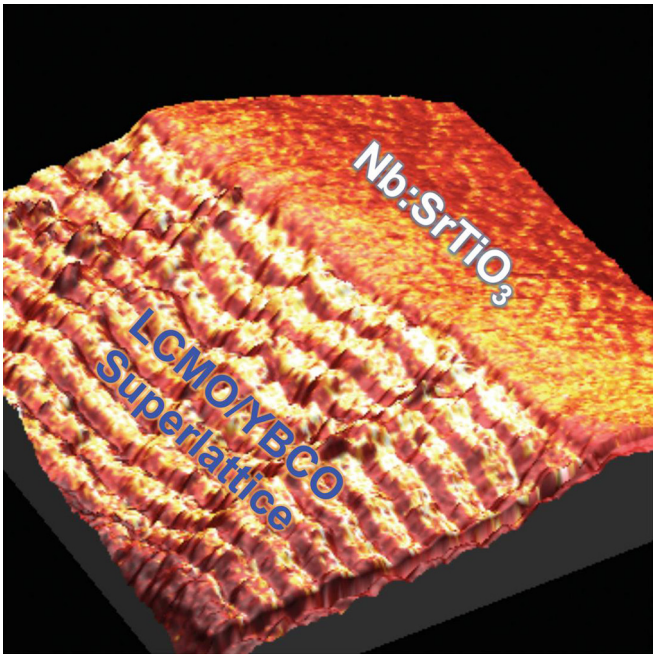


Figure 2. Topography and conductance map of a ferromagnetic/superconducting ($LaCaMnO_3/YBa_2Cu_3O_7$) superlattice on an $SrTiO_3$ substrate. The image size is 300 × 300 nm^2.

Proposed Work for FY 2011

During FY 2011, we will refine our initial interface and superlattice results to explore the details of electronic properties in the interface region. Now that we have successfully imaged several oxide systems in the cross-section view, we will focus on improving the quality of the imaged surface with the hope of resolving atoms across the interface.

Refereed Publications

Chien, T.-Y., T.S. Santos, M. Bode, N.P. Guisinger, J.W. Freeland, "Controllable Local Modification of Fractured Nb-doped $SrTiO_3$ Surfaces," *Applied Physics Letters* **95** (163107) (2009).

Chien, T.-Y., J. Liu, J. Chakhalian, N. Guisinger, and J.W. Freeland, "Visualizing Nanoscale Electronic Band Alignment at the $La_{2/3}Ca_{1/3}MnO_3$/Nb:$SrTiO_3$ Interface," *Physical Review B* **82** (41101) (2010)

Chien, T.-Y., N.P. Guisinger, and J.W. Freeland, "A Survey of Fractured SrTiO3 Surfaces: From the Micro-Meter to Nano-Meter Scale," *Journal of Vacuum Science & Technology B* **28** (C5A11) (2010).

Guisinger, N.P., T.S. Santos, J.R. Guest, T.-Y. Chien, A. Bhattacharya, J.W. Freeland, and M. Bode, "Nanometer-Scale Striped Surface Terminations on Fractured $SrTiO_3$ Surfaces, *ACS Nano* **3** (4132) (2009).

Non-Refereed Publications and Presentations

Chien, T.-Y., "Controllable Local Modification of Fractured Nb-doped $SrTiO_3$ Surfaces," presented at the 2010 American Physical Society March Meeting, Portland, OR, March 15–19, 2010.

Chien, T.-Y., "Controllable Local Modification of Fractured Nb-doped $SrTiO_3$ Surfaces," poster presented at the Center for Nanoscale Materials User Meeting 2009, Argonne, IL, October 2009.

Chien, T.-Y., "Probing Complex Oxide Interfaces by Cross-Sectional Scanning Tunneling Microscopy," presented at the 2010 American Physical Society March Meeting, Portland, OR, March 15–19, 2010.

Chien, T.-Y., "Probing Complex Oxide Interfaces Scanning Probe Microscopy for Energy Applications," poster presented at Oak Ridge National Laboratory, September 2010.

Chien, T.-Y., "Probing Complex Oxide Surfaces and Interfaces by Cross-Sectional Scanning Tunneling Microscopy," presented at the 37th Conference on the Physics and Chemistry of Surfaces and Interfaces, Santa Fe, NM, January 10–14, 2010

Freeland, J.W., Seminar: "1+1=3: Using Interfaces and Strain to Design New Materials," seminar presented at Pennsylvania State University, Department of Physics, December 2009.

Freeland, J.W., "Orbital Control in Heterostructures: Myth vs. Reality," seminar presented at the University of Virginia, Department of Physics, August 2010.

Guisinger, N.P., "Current Trends in Scanning Probe Microscopy at Argonne National Laboratory: From Complex Oxides to Graphene On Demand," seminar presented at the University of Alabama, MINT (Materials for Information Technology) Center, April 2010.

Guisinger, N.P., "Epitaxial Graphene: Synthesis, Characterization, and Modification," seminar presented at the University of Wisconsin, Department of Materials Science, May 2010.

Three-Dimensional Metamaterials with Negative Refractive Index

2009-111-R1

Matthew A. Pelton, Stephen K. Gray, and Xiao-Min Lin

Project Description

In the past several years, new materials based on nanometer-scale metallic elements have been developed that display a negative refractive index for light. To date, these materials have been produced by top-down fabrication techniques, which are capable of producing arbitrary nanoscale patterns but are inherently limited to producing planar structures. Our goal is to use bottom-up colloidal synthesis to produce metal nanoparticles and then chemically functionalize these particles so that they assemble into configurations that result in a negative refractive index at optical frequencies.

Mission Relevance

The goals of this project will help fulfill DOE's mission in basic energy sciences to perform cutting-edge research in materials design. The materials we are developing will enable unprecedented control over the flow of optical energy, which has the potential to enable a range of technologies that are relevant to DOE's missions in energy and national security.

FY 2010 Results and Accomplishments

A material made up of pairs of gold nanorods arranged side by side has the potential to exhibit a negative refractive index at optical frequencies. In FY 2009, we began development of the necessary techniques to synthesize, assemble, purify, and model these nanorod pairs. In FY 2010, we continued to investigate and optimize these processes.

As synthesized, the gold nanorods are stabilized in water by charged surfactant molecules. The sides of the rods are better protected by the surfactants than are the ends, so that, when additional ligand molecules are added to the solution, they preferentially attach to the ends of the rods. In our first attempt at assembly, we used this selectivity to bind polystyrene molecules to the ends of the rods and then transferred the rods into mixed organic-inorganic solvents. This method has been reported to result in the arrangement of rods into different configurations, but we found that it was difficult to reproduce.

We therefore attempted a new assembly method, which was based on selectively binding reactive molecules to the sides of the rods so that these molecules would bind to one another and thereby arrange the rods side by side. To carry out this procedure, we first needed to protect the ends of the rods with inert molecules. We found, unexpectedly, that when we attach nonfunctional alkanethiol molecules to the ends of the nanorods, the particles spontaneously organize into end-to-end chains (see Figure 1). We performed detailed kinetic studies and found that the assembly is driven by interactions between the capping molecules and the surrounding solvent.

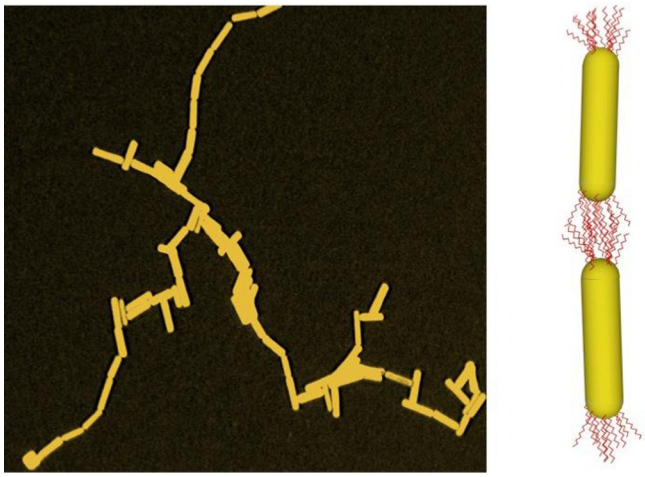


Figure 1. Left: Transmission-electron-microscope image of gold nanorods assembled end to end by using a solvent-mediated method. The rods are approximately 70 nm long and 15 nm in diameter. Right: Schematic of the assembled gold nanorods, which have been functionalized at their ends with alkanethiol molecules.

We then investigated a third method that involved using charged disodium chromoglycate molecules that bind electrostatically with the charged surfactant on the sides of the rods, resulting in the successful side-by-side assembly of the rods. However, when this reaction is allowed to proceed to completion, it produces large side-by-side nanorod bundles rather than pairs. We therefore interrupted the reaction by introducing polystyrene sulfonate (PSS), a negatively charged polymer, to the solution. The PSS wraps around the nanorods, forming a protective shell that also allows for subsequent purification of the sample.

In order for the ensemble of nanorod pairs to act as a negative-index material, it will be crucial to adjust their dimensions and the spacing between them correctly. To determine the optimal geometry, we began to simulate the response of candidate materials by using rigorous computational methods. When performing these simulations, we found that it can be challenging to infer whether a given configuration of metal nanoparticles will produce a negative index because of multiple branches in the possible solutions to the problem. To deal with this issue, which has sometimes led to the reporting of incorrect results in the literature, we developed a new procedure for extracting the effective refractive index from simulations.

Proposed Work for FY 2011

In FY 2011, we will optimize the assembly and purification of gold-nanorod pairs so that we arrive at a sample that consists of nearly 100% pairs with controlled size and separation. We will use the newly developed numerical techniques to determine the optimal nanorod size and separation to pursue realization of a material with a negative refractive index. We will verify that the material we make has a negative refractive index by performing optical measurements, including direct measurements of beam displacement, interferometric measurements, and measurements of scattering patterns.

Refereed Publications

Wang, Y., A.E. DePrince III, S.K. Gray, X.-M. Lin, and M. Pelton, "Solvent-Mediated End-to-End Assembly of Gold Nanorods," *J. Phys. Chem. Lett.* **1** (2010), 2692.

Ultra-Sensitive Protein Biomarker Screening Assay for Early Stage Disease Diagnosis

2009-138-R1

John T. Bahns, Liaohai Chen, Ralu S. Divan, and Jiufeng Fan

Project Description

Early stage disease diagnosis requires the detection and characterization of very small quantities of proteins. Ideally, we would like to take a drop of blood (or other bodily fluid) and analyze it for the presence of a particular protein, an array of proteins, or a pattern of the proteins, each of which is produced only when a patient has cancer. However, such a task is extremely difficult, because in an early stage of tumor growth, only one of every 10 billion (or more) proteins in blood plasma may be the one we want to detect. Given this fact, the challenges become (1) how to design a test that will reliably identify and detect that single protein and (2) how to make certain that this test produces no false positives (leading to a false initial diagnosis of the presence of cancer). The way to accomplish these objectives is to develop *a protein sorting assay* that is capable of detecting and characterizing extremely low levels (to a single protein molecule) from a bulk specimen sample.

The goal of this project is to build a detection platform via the combination of molecular biology, advanced spectroscopy, and micro/nano fabrication technologies.

Mission Relevance

This project is related to DOE's missions in science and national security. The proposed assay has strong potential for use in ultimate screening and discrimination against a wide range of biological agents at a high level of confidence and is expected to find immediate use in three major areas: early stage diagnosis of lethal diseases (e.g., cancers, AIDS, Alzheimer's), national security and public safety (in the countering of bioterrorism threats and mounting of response efforts to epidemics), and biomedical research (development of new drugs and treatments).

The success of the project will be of strong interest to a wide range of agencies, including the National Institutes of Health, U.S. Department of Homeland Security, U.S. Department of Defense, U.S. Department of Energy, National Aeronautics and Space Administration, and industrial organizations. In particular, the National Cancer Institute (NCI) is committed to supporting nanotechnology for cancer research. Molecular imaging and early detection are identified as key areas in the NCI's Cancer Nanotechnology Plan.

FY 2010 Results and Accomplishments

Accomplishments in FY 2010 included (1) achieving an improved design and integration of metal nanoslits on nanofluidic channels and (2) establishing near-field illumination and fluorescence correlation spectroscopy (FCS) measurements in nanofluidics (see Figure 1). Improving the basic channel design (Figure 1a) means it is more practical and easier to fabricate as compared to the previous version. A new photomask was designed by using L-edit and was built by using Laser Writer. Photoresist exposure dosages and photomask channel widths were optimized and characterized with surface profile analysis and microscopic imaging to evaluate channel surfaces. In the current design, nanoslit integration has become the last (and fastest) of channel components to fabricate (i.e., nanoslits are simply "written" in the gold film channel bottoms by using a focused electron beam).

Under near-field illumination (Figure 1b), FCS measurements were recorded of a single near-field slit while dye-labeled nanobeads flowed through the channel. Autocorrelation curves of the flowing nanobeads (not shown) provided flow rates and established that less than one bead (on average) occupied a given near-field slit.

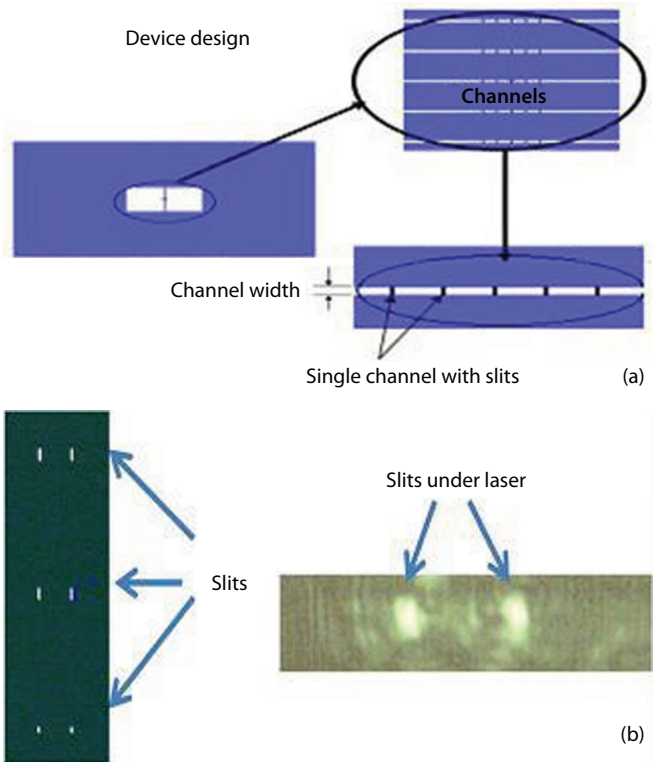


Figure 1. Images showing (a) improved channel/near-field slit design, and (b) images of illuminated near-field slits (top) using white light and laser light (bottom).

Proposed Work for FY 2011

Our efforts in FY 2011 will concentrate on device performance in terms of throughput and specificity. Device throughput will be improved by reengineering channel structure to enable greater flow rates. Specificity will be evaluated by analyzing a carefully prepared series of reference solutions containing a sparse concentration of (target) two-color-labeled nanoparticles (or viruses) dispersed within a larger background concentration of single-color-labeled nanoparticles. Using two color fluorescence cross-correlation analysis, we will evaluate the ability of the device to discriminate the two-color-labeled (target) particles from the single-color background particles (i.e., we will evaluate the false-positive rejection figure of merit for the device). Following completion of this analysis, experiments with biological fluids can begin.

Laboratory Simulations of Plasma Conditions near Active Galactic Nuclei and Black Holes

2009-146-R1

Elliot P. Kanter, Robert W. Dunford, and Linda Young

Project Description

The objective of this project is to use the Advanced Photon Source (APS) to obtain some of the first measurements of a low-density photoionizing plasma. In this project, we and our collaborators at the Smithsonian Astrophysical Observatory (SAO) are creating and characterizing exotic photoionized plasma conditions that are representative of the gas located near active galactic nuclei (AGN) and black holes. SAO provides two uniquely portable, state-of-the art spectroscopy instruments, including (1) a new Electron Beam Ion Trap (EBIT) that is designed to produce well-controlled plasmas and (2) a cryogenically cooled microcalorimeter capable of measuring broad-band x-ray spectra with high spectral resolution.

Mission Relevance

The project is relevant to DOE's mission in science. These instruments create two unique opportunities in support of DOE missions: the first is to study the interactions of hard x-rays with highly ionized plasmas, a major field of research planned for the Linac Coherent Light Source and other X-ray Free Electron Laser (XFEL) sources. The second is to take advantage of the availability of a high-resolution x-ray calorimeter by using it in other precision atomic spectroscopy measurements at the APS, such as in studies of multi-electronic atomic transitions, which have been shown to be an important signature of hollow atoms created by XFEL sources.

FY 2010 Results and Accomplishments

On the basis of our 2009 results, we had planned to conduct a follow-up experiment in FY 2010. However, we found it necessary to move our experimental set up from the 12ID-C hutch in Sector 12 at the APS to beamline 7ID-B. This beamline provides both pink and white undulator radiation in a hutch, which can accommodate the large EBIT support table, as well as the ancillary equipment. We have devoted our efforts this year to developing a vertical focusing optic to match the size of the 70-μ EBIT electron beam with the full and complete pink beam flux and to procuring a Be-compound refractive lens for this purpose. Our SAO collaborators have rebuilt the EBIT electron gun such that it now can achieve the promised performance of both electron current and acceleration voltage. A focusing optic has also been designed and built to increase the detector solid angle. With these improvements, we anticipate being able to utilize two planned beam times

at 7ID-B: We will commission the lens next April, and then in June, we will carry out a complete experiment with the EBIT and calorimeter.

Proposed Work for FY 2011

Our principal objective is to observe the Fe Kα lines that result from photoionization of various charge states of Fe. The major technical hurdle will be interfacing the microcalorimeter with the EBIT and APS beam. We will make a conventional, collisionally ionized plasma of Fe by using the 100-ma electron beam that is internal to the EBIT. We conservatively expect an Fe K photon rate of approximately 0.2 counts/second. In a 10-hour run, for example, we would obtain more than 7,000 counts in the Fe K line alone. We could substantially increase the count rate by cooling the ion cloud and more tightly focusing the photon beam or by boosting the electron current. The high resolution and broad bandwidth of the microcalorimeter will make it possible to observe the Fe K and the Fe L emissions simultaneously. In actuality, the data will be time tagged and analyzed as a function of the EBIT trapping period, which can be as long as 2 seconds. The resulting spectrum will be extremely rich with new information.

Non-Refereed Publications and Presentations

Kanter, E.P., N. Brickhouse, R. Brissenden, R.W. Dunford, J. Gillaspy, K. Kirby, J. McDonald, D. Schneider, E. Silver, and L. Young, "Laboratory Simulations of Astrophysical Plasmas," presented at 2009 Advanced Photon Source Users Week, Argonne, IL, May 4–6, 2009.

Gillaspy, J.D., E. Silver, E.P. Kanter, N.S. Brickhouse, R.W. Dunford, K. Kirby, T. Lin, J. McDonald, D. Schneider, S. Seifert, and L. Young, "First Deployment of an Electron Beam Ion Trap at an Advanced Source of Hard X-rays," *Bulletin of the American Physical Society*, **55**(1) (2010), C1.00045.

Single Photon Receiver Using Abrikosov Vortices

2009-190-R1

Goran T. Karapetrov, Maria Iavarone, Valentyn Novosad, and Volodymyr G. Yefremenko

Project Description

In the last decade, the rapid development and application of thermal superconducting detectors (SDs), or bolometers, have provided breakthroughs in many areas of science and industry where the detection of single photons is essential. The SDs have been developed for measurements across the electromagnetic spectrum, including millimeter, near and far infrared (IR), x-ray, and gamma ray spectroscopies. They have been an instrumental aid for advancements in the studies of dark matter and supersymmetry and quantum information processing.

Although improvements in the design of SD arrays have enabled their widespread use, the major limitation remains the same — the direct proportionality of SD sensitivity to its intrinsic response time makes it difficult to construct fast and highly sensitive receivers. This limitation occurs because the sensitivity of the SD is determined by the thermal isolation of the active area from the environment, and good thermal isolation leads to the long recovery times of the detector. Fast and sensitive detectors are required for many applications, such as observation of far-away pulsars or standoff detection of explosives.

We are developing a sensor element that employs the effect of Abrikosov vortex creep in type-II superconductors — in particular, very abrupt non-linear dependence of the vortex creep near the lower critical field H_{c1} in thin films. This type of detection avoids some of the pitfalls of superconducting bolometers and offers high sensitivity without sacrificing speed. Another remarkable property is that, in the ideal case, the sensitivity of this detection scheme is not dependent on the intensity of the radiation hitting the superconductor.

Mission Relevance

This project is relevant to DOE's missions in basic science and national security. High-sensitivity, scalable, and high-speed image-forming arrays of direct detectors are required for materials science research (x-rays), security screening (THz), remote sensing, medical imaging, and surveillance (IR, THz, and millimeter waves). They also are essential for ground- and space-based applications, such as astronomy-related tasks (x-rays and sub-millimeter and millimeter waves).

In the October 2009 report to the DOE High Energy Physics Division, the Independent Committee on the Future Funding of Particle Astrophysics strongly recommended a substantial increase in investments for novel detectors for cosmic-ray experiments (*Nature* 461 [2009], 1181). Our work is directed toward the design and implementation of novel, superior-performance detectors for these applications.

FY 2010 Results and Accomplishments

In FY 2009, proof of concept was confirmed. We established that we could use the superconducting vortices as a detecting mechanism for photons and also could effectively manipulate the superconducting vortices.

During FY 2010, we optimized the material and design of the detector element. By using state-of-the-art sputtering tools and fabrication resources at Argonne, we evaluated several superconducting materials and selected thin film niobium

(Nb) as a preferred material for the detector. High-quality Nb thin films were prepared by magnetron sputtering. The films exhibit very low pinning strength due to the extremely clean conditions for thin film growth provided by our dedicated Nb growth system, as well as thickness uniformity and few defects. The Nb superconducting penetration depth is an order of magnitude smaller than that of molybdenum-germanium, thus the magnetic field modulation by the vortices is significantly stronger. The latter leads to stronger vortex-vortex interaction and, in case of a weak pinning landscape, a much better controlled vortex manipulation over longer distances. Effectively, the vortex lattice in this material is more rigid, thereby enabling forces to be transmitted over longer distances.

The 100-nm-thick Nb films were sputtered by using a DC magnetron on a silicon wafer covered with 500 nm of silicon nitride. The critical temperature of the Nb film was 9.1 K. The other relevant parameters extracted from the measurements were the coherence length of $\xi(0) = 13.5$ nm and the penetration depth of $\lambda(0) = 145$ nm. We used e-beam lithography and reactive ion etching (a combination of CF_4 and SF_6 plasma) to define structures similar to those shown in the inset of Figure 1. The low-temperature vortex transport properties of the structures indicate detectable non-local voltage in the flux flow regime due to vortex movement as far as several microns away from the point where the vortices experience Lorentz force because of the applied current (Figure 1). The very well-defined peaks that occur in the non-local voltage correspond to commensurate vortex phases in the narrow vortex channel, which is 250 nm wide. With a penetration depth on the order of the width of the structure, most of the magnetic field from the vortex is thus concentrated within the superconducting stripe and correlated vortex motion can be seen over large distances.

We also designed and fabricated a fiber-optic-based tool with a moving stage for testing the coupling efficiency of incoming radiation to the detector (Figure 2a). The low-temperature tool consists of an optical fiber coupled on one side with a laser diode at room temperature and coupled on the other end (liquid helium temperature) to the alignment stage. A space for the photon detector chip holder is located under the stage. The chip is placed under the detector, and the alignment procedure can be done at room temperature. The device is designed to minimize the thermal drift between the stage and the waveguide when cooling down in the cryostat.

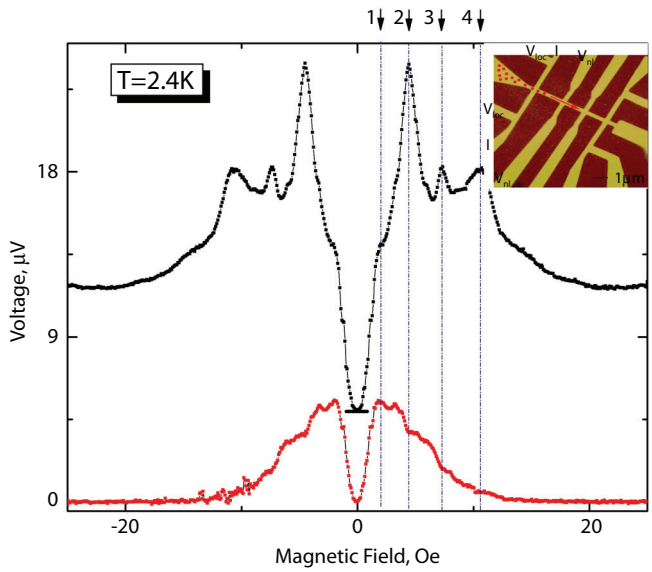


Figure 1. Non-local voltage signal due to long-range correlated vortex motion in the Abrikosov photon detector. The inset displays a schematic image of the detector element structure. The diagram shows non-local voltage taken at two different positions: closer to (at 2 µm, in black) and further from (at 4 µm, in red) the driving current in the structure outlined in the inset. The peaks correspond to the commensurate vortex ordering in the submicron Nb bridge. The smaller kinks correspond to the fractional vortex filling.

Proposed Work for FY 2011

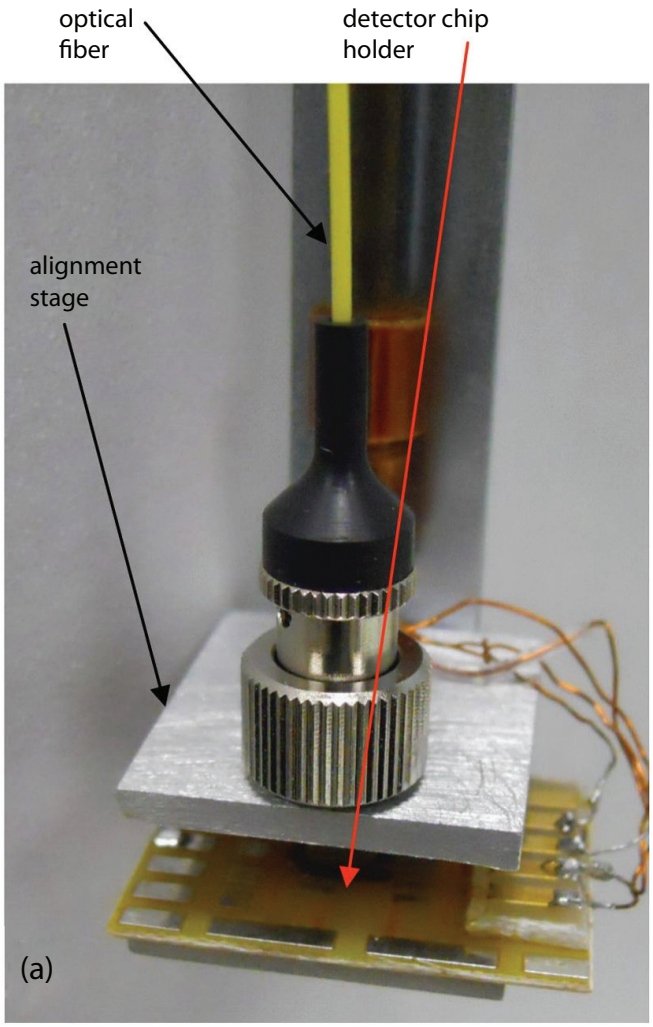
We plan to interface the sensor with the SQUID multiplexer and optimize the performance characteristics, such as coupling the incident photons with the sensitivity and speed of operation. We plan to move from a single sensor element with one active area to multiple active area sensors that are multiplexed to a SQUID amplifier (Figure 2b). The fiber-optic setup will be our primary tool to test and compare the detector elements. We will continue the development of a 2D sensor array and finalize the details of the cryogenic readout electronics that can be applied to address matrix elements of the 2D sensor array. This development will enable imaging applications in the THz, x-ray, and millimeter wave regimes. In addition, arrays of single photon receiver sensors will be examined and tested.

Non-Refereed Publications and Presentations

Karapetrov, G., V.G. Yefremenko, G. Mihajlovic, A.M. Datesman, S.D. Bader, and V. Novosad, "Single Photon Receiver Based on Abrikosov Vortices," presented at Applied Superconductivity Conference, ASC-2010, Washington, D.C., August 1–6, 2010.

Karapetrov, G., "Nonlocal Vortex Transport in Superconducting Nb Nanostrips," presented at Katholeieke University, Leuven, Belgium, July 14, 2010.

Karapetrov, G., "Vortex Dynamics in Submicron Superconductors," presented at the Institute of Electrical Engineering, Slovak Academy of Sciences, Bratislava, Slovakia, April 8, 2010.



8-pixel array with a parallel readout for all channels

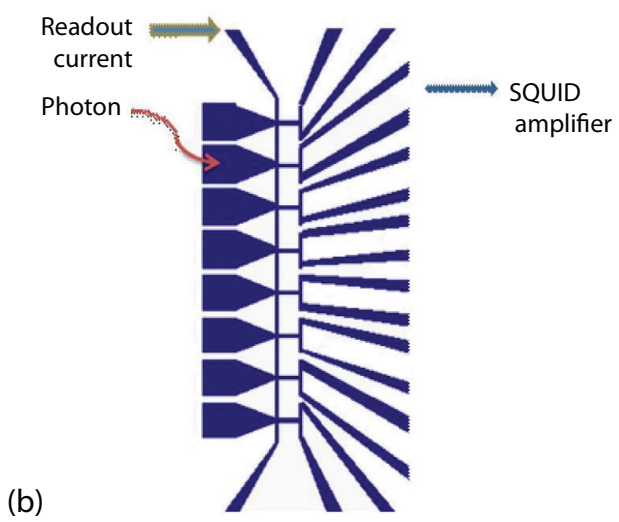


Figure 2. (a) Low-temperature fiber-optic tool for testing the optical coupling and effectiveness of the photon detector; and (b) layout schematic of the multiple active area array to be coupled with the low-temperature SQUID amplifier.

Engineering Nanostructures Atom by Atom for Optical Activity and Quantum Coherence

2009-204-R1

Jeffrey R. Guest and Nathan P. Guisinger

Project Description

Bottom-up assembly of nanostructures tailored for function is one of the most intriguing aspects of nanoscience and nanotechnology because of its potential to produce novel materials and capabilities. Scanning tunneling microscopy (STM) in an ultra-high vacuum (UHV) environment ($<10^{-10}$ torr) has led the way not only in characterizing systems at sub-nanometer length scales, but also in assembling novel nanostructures atom-by-atom, such as the "quantum corral" and atomic scale magnets, or by controlling molecular adsorption on engineered surfaces. These types of systems could provide chemical and environmental sensing capabilities, ultra-high-density data storage, or platforms for quantum information processing. The goal of our project is to develop new methodologies to bring the power of high-resolution laser spectroscopy and coherent optical control — previously achieved with great success on subsurface quantum dots and laser-cooled atoms — to bear on nano- and molecular systems on surfaces that have been characterized or fabricated by the UHV STM.

Mission Relevance

This project is relevant to DOE's missions in energy and basic science. Combining lasers with scanning probe microscopy provides significant potential for scientific applications to many other measurements, including the investigation of ultra-fast and ultra-small phenomena at the core of many fundamental and energy-related research fields. For example, understanding the photophysics of molecular heterojunctions at the molecular scale would provide important guidance for optimizing interfaces between organic photovoltaic materials and device structures.

FY 2010 Results and Accomplishments

In FY 2010, we made significant strides toward understanding and fabricating nanoscale materials for optical activity. Having fabricated the UHV STM with integrated high-numerical-aperture optical access in FY 2009, we successfully commissioned the microscope and brought all of the *in situ* sample preparation equipment online in FY 2010. Figure 1a shows an atomic resolution image of the 7×7 reconstruction of Si(111), at 36 Kelvin in the UHV, acquired with this STM.

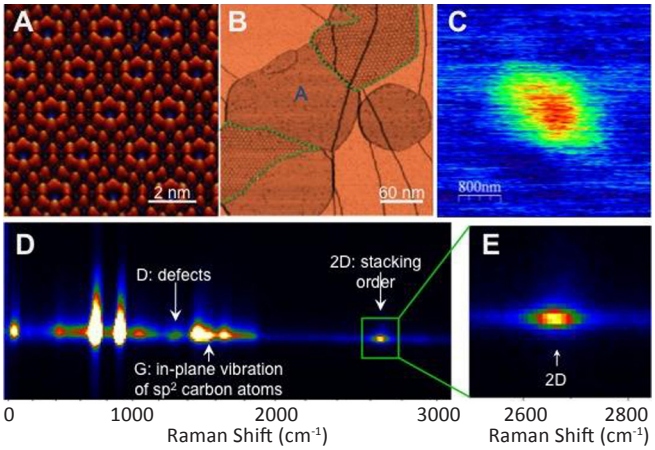


Figure 1. (a) STM image of Si(111) 7×7 reconstruction, (b) STM map of the electronic response of graphene on Cu(111), (c) image of the laser spot under the STM tip in UHV, (d) Raman spectrum from a micron-size spot of graphene on SiC, and (e) detail of the 2D Raman peak of graphene.

In FY 2009, we developed procedures for producing high-quality graphene as a transparent conductor through hydrogen cleaning of the silicon carbide (SiC) substrates and high-temperature processing in the UHV. In FY 2010, we produced graphene on single crystal Cu(111) via thermal decomposition of ethylene in a UHV chamber and investigated the structural and electronic properties with the UHV STM (Figure 1b). In addition, we observed the nucleation of monolayer islands and two predominant domain orientations. This work carries important implications for understanding the electronic and structural properties of this revolutionary new material (graphene was recognized with the Nobel Prize in physics in 2010). We also developed an alternate plasmonically enhanced transparent conductor by using a thin gold film on mica substrate.

In FY 2010, we demonstrated that we can achieve extremely small laser spots (~1 micrometer) for spectroscopy aligned with the STM tip with our integrated optics (Figure 1c). Thermal expansion of the STM tip due to laser irradiation — often a major complication in laser-STM experiments because it swamps the interesting photophysical signals — was investigated in our system and determined to be manageable (~40 picometers/milliWatt) under our focused laser beam. Figures 1d and 1e show the measured optical Raman spectrum for graphene on SiC. These peaks represent various vibrational modes of the graphene sheet that can be correlated with the local structural and electronic properties measured by the STM (Figure 1b).

Proposed Work for FY 2011

In FY 2011, we plan to correlate optical spectroscopy and UHV STM to understand and manipulate the nanoscale systems. In addition to molecular studies, we will use our recently developed technique to nanostructure graphene with hydrogen adsorption and desorption in the UHV STM to fabricate optically active systems. Additionally, we will also take advantage of the optical field enhancement associated with a sharp metal tip in order to achieve an extremely intense and small (~10-nm) laser spot to perform tip-enhanced Raman, absorption, and nonlinear spectroscopies on nanostructured systems.

Refereed Publications

Gao, L., J.R. Guest, and N.P. Guisinger, "Epitaxial Graphene on Cu(111)," *Nano Letters* **10** (2010), 3512.

Sessi, P., J.R. Guest, M. Bode, and N.P. Guisinger, "Patterning Graphene at the Nanometer Scale via Hydrogen Desorption," *Nano Letters* **9** (2009), 4343.

Non-Refereed Publications and Presentations

Gao, L., M. Bode, N.P. Guisinger, and J.R. Guest, "Laser-Coupled Ultrahigh Vacuum Scanning Tunneling Microscope: Towards Optical Probing and Manipulation of Nanostructures on Surfaces," poster for the Center for Nanoscale Materials User Meeting, Argonne National Laboratory, Argonne, IL, October 5–7, 2009.

Gao, L., J.R. Guest, and N.P. Guisinger, "Epitaxial Graphene on Cu(111)," presented at the 2010 APS March Meeting, Portland, OR, March 15–19.

Physics of the Superinsulating State

2009-209-R1

Valerii Vinokour and Andreas Glatz

Project Description

The goal of our project is to investigate and explore the physical properties of a new state of matter: the superinsulator. Since the superinsulating state is a low-temperature Berezinsky-Kosterlitz-Thouless (BKT) state in a charged system, we plan to thoroughly and theoretically investigate BKT transport, taking into account the quantum fluctuations and the effects of disorder and geometry in the film. We will explore different realizations of the superinsulating system (superconductor/normal conductor/superconductor [SNS] structures and artificial Josephson arrays) and examine non-linear transport in these systems, focusing on the effects of conductivity

and current jumps at the voltage depinning threshold. Our results will assist in determining novel ways to design artificial superinsulating materials that will work successfully over a wide range of temperatures and magnetic fields.

Mission Relevance

The superinsulating state is a novel macroscopic dynamic quantum state, which forms as a result of the subtle interplay of quantum, correlation, and disorder effects. The understanding and description of the underlying microscopic mechanisms of the formation of the new phase and its peculiar transport properties will bring further conceptual breakthroughs in our understanding of macroscopic quantum states and will drive the search for superinsulating states in other systems and in artificially manufactured structures. The expected impact of our fundamental knowledge can be compared to that of studying superconductivity in the first decades after its discovery. On the applied side, the ability of a superinsulator to change its resistivity by 3–6 orders of magnitude upon crossing the superinsulating transition with a few millikelvin of temperature resolution characterizes superinsulators as materials of unprecedented technological promise (e.g., supersensitive radiation sensors, filters).

The proposed research and achieved accomplishments fit within the DOE mission to support world-class research in the area of energy efficiency and relate to at least two of the "Five Challenges for Science and the Imagination" (see: http://www.science.doe.gov/bes/reports/files/GC_rpt.pdf), namely:

1. The Superinsulator is excellent example of an "emergent collective phenomenon in strongly correlated multi-particle system" and
2. Is also a system "far beyond equilibrium."

Furthermore — since it is an almost perfect insulator — it could become important for information technologies on the nanoscale (at cryogenic temperatures) in the future, which is another grand challenge.

FY 2010 Results and Accomplishments

The two major accomplishments during FY 010 are highlighted below.

1. On the basis of our results from the static situation of the Ginzburg-Landau (GL) theory for a thin film coupled to a substrate — which under certain conditions leads to a regular "island" state — we extended our efforts to include the additional effects of magnetic and electric fields. This problem is computationally much more demanding and requires an adaptation for massive parallel computations. Therefore, we decided to implement the time-dependent GL equation on modern general-purpose graphics processing units (GPUs), which allowed us to run the simulations up to two orders of magnitude faster than on traditional GPU systems. The initial results for the influence of an external magnetic field (Figure 1) indicate that the island structure is additionally stabilized by vortices formed between the maxima of the order parameter.

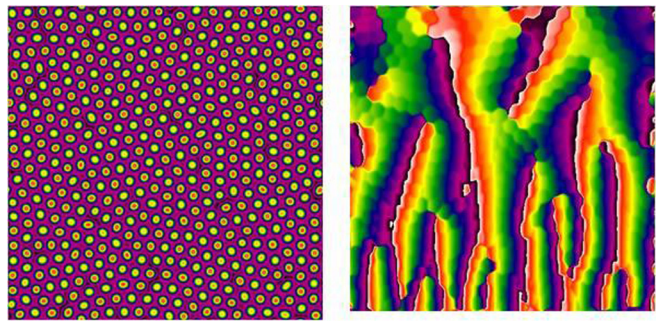


Figure 1. Preliminary results for superconducting islands in a magnetic field. Left: *Amplitude of the order parameter: In the bright round islands, the amplitude of the order parameter is maximum (on the order of one in dimensionless units), while in between (pink and dark network), superconductivity is suppressed (the amplitude here can be as small as 10^{-6}).* Right: *Phase distribution: Vortices are visible as jumps in the phase from white to black (white corresponds to a phase of 2π and black to 0).*

2. Another important facet of the superconductor-superinsulator transition involves the effects of superconducting fluctuations. As such, we revisited the enduring problem of the fluctuation conductivity (FC) of a disordered 2D superconductor placed in a perpendicular magnetic field. The derived complete solution for the FC allows one to both perform numerical calculation of the FC surface in the whole phase diagram of temperature and magnetic field (Figure 2) and obtain the asymptotic expressions in all its qualitatively different domains. In particular, at low temperatures, this surface becomes non-trivial: the FC is negative and it is trough-shaped. Close to the quantum phase transition point located at zero temperature and the magnetic field equal to the upper critical field, the lines of constant FC are non-monotonic. The obtained behavior is in perfect agreement with the experimental findings. On the basis of the obtained results, we predict a new quantum state that forms near $H=H_{c2}(0)$ and $T = 0$. This state consists of the fluctuation Cooper pairs, which rotate with the cyclotron frequency and Larmor radius.

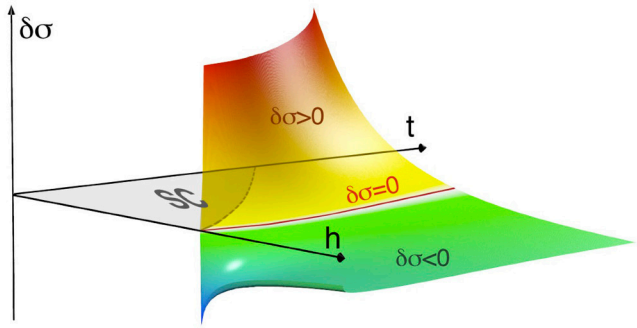


Figure 2. Fluctuation corrections to the conductivity (δς) near the superconductor transition in thin disordered films in the reduced dimensionless temperature (t) – the dimensionless magnetic field (h) plane. The fluctuation corrections to conductivity is the unique and, in many cases, the only tool allowing the extraction of material parameters — such as T_c , $B_{c2}(0)$, scattering time, and quantum dephasing time — from the experimental data. Positive δς values are color coded from yellow to red for high values and negative from green to blue for lower values. The line at the δς (t,h) surface marks the δς =0 value.

Our accomplishments during FY 2010 can be summarized as follows:

- Simulation of the charge transport in systems, which exhibits regular structures of superconducting islands in electric and magnetic fields (ac and dc); (refer to highlight 1, above).
- Investigation of the out-of-the-equilibrium properties of an electron liquid in a two-dimensional disordered superconductor subject to an electric bias and temperature gradient. After calculating the kinetic coefficients and Nyquist noise, we found that they are characterized by distinct effective temperatures: T_e, characterizing the single-particle excitations; T_{Cp}, describing the Cooper pairs; and T_{eh}, corresponding to the electron-hole or dipole excitations.
- Examination of the synchronized Andreev reflections in one-dimensional SNSNS arrays.
- Study of the heating effects in thin films and arrays.
- Derivation of the fluctuation corrections to conductivity near the superconductor-superinsulator transition (refer to highlight 2, above).

Proposed Work for FY 2011

During FY 2011, we will focus on the following research:

- Examination of hysteretic effects near the depinning threshold.
- Detailed investigation of synchronization in hybrid superconducting systems: SNS proximity arrays and Josephson junction arrays.
- Large-scale simulations of quantum transport and synchronization processes in thin films and SNS arrays.
- Collaboration with experiment aimed at the design of model cryogenic diode and radiation detectors.

Refereed Publications

Chtchelkatchev, N.M., T. Baturina, A. Glatz, and V.M Vinokur, “Synchronized Andreev Transmission in SNS Junction Arrays,” *Phys. Rev. B*. **82** (2010), 024526.

Glatz, A., I. Aranson, V.M. Vinokur, N.M. Chtchelkatchev, and T.I. Baturina, “Heating Effects in a Chain of Quantum Dots,” *Phys. Rev. B*. **82** (2010), 075314.

Glatz, A., and I.S. Beloborodov, “Thermoelectric Performance of Granular Semiconductors,” *Phys. Rev. B*. **80** (2009), 245440.

Glatz, A., A.A. Varlamov, and V.M. Vinokur, “Quantum Fluctuations and Dynamic Clustering of Fluctuating Cooper Pairs,” under review at *Phys. Rev. Lett*. (2010), arXiv:1006.4124.

Petkovic, A., N.M. Chtchelkatchev, T.I. Baturina, and V.M. Vinokur, “Out-of-Equilibrium Heating of Electron Liquid: Fermionic and Bosonic Temperatures,” *Phys. Rev. Lett*. **105** (2010), 187003.

Non-Refereed Publications and Presentations

Glatz, A., “Superconducting Nanotextures in Thin Superconducting Films,” presented at the MRSEC Workshop: Transport in Nanoengineered Materials, University of Chicago, Chicago, Illinois, September 13–17, 2010.

Glatz, A., “Quantum Fluctuations and Dynamic Clustering of Fluctuating Cooper Pairs,” presented at the 6th International Workshop on Nanomagnetism and Superconductivity, Coma-Ruga, Spain, June 30–July 4, 2010.

Vinokour, V., “Superinsulators and Cascade Relaxation,” presented at the 6th International Conference on Nanomagnetism and Superconductivity, Coma-Ruga, Spain, June 30–July 4, 2010.

Vinokour, V., “Charge BKT Transition and Superinsulating State in Two-Dimensional Superconducting Systems: Experiment and Theory,” presented at the Lebedev Institute, Moscow, Russia, May 12, 2010.

Vinokour, V., “Cascade Relaxation and Superinsulating State in Two-Dimensional Superconducting Systems: Experiment and Theory,” presented at the University of Cologne, Germany, May 6, 2010.

Vinokour, V., “Superinsulators: Reverse of a Superconductivity,” presented at the Departamento Física de Materiales, Facultad CC. Físicas, Universidad Complutense, Madrid, Spain, February 17, 2010.

Development of a Novel Instrument for Argon-39 Analysis

2009-212-R1

Peter Mueller, Wei Jiang, Zheng-Tian Lu, and William D. Williams

Project Description

We explore the use of Atom Trap Trace Analysis (ATTA) for ultrasensitive detection of the argon radioisotope ^{39}Ar. This isotope has a radioactive half-life of 270 years and occurs naturally in the atmosphere with an isotopic abundance at the parts-per-quadrillion (10^{-15}) level. ATTA is an atom-counting method based on laser cooling and trapping that was developed by our group at Argonne. The method has so far been capable of analyzing trace isotopes at the parts-per-trillion (10^{-12}) level and used to measure the abundance of the krypton radioisotopes ^{81}Kr and ^{85}Kr in environmental samples. Recent progress in developing our ATTA setup suggests that its sensitivity level can be further improved by three orders of magnitude. This project aims to establish these sensitivity levels for atom trapping of argon and to enable new applications of ^{39}Ar analysis.

Mission Relevance

In nature, ^{39}Ar is produced mainly by cosmic-ray-induced nuclear reactions of ^{40}Ar in the atmosphere. It has an isotopic abundance of ^{39}Ar/Ar = 8×10^{-16}. Being a noble gas, ^{39}Ar is not involved in chemical processes and its distribution in terrestrial reservoirs is relatively simple. These favorable properties make ^{39}Ar the ideal isotope for dating underground and ocean water samples that range in age from 100 to 1,000 years. A new instrument for practical ^{39}Ar analysis of water samples would have a large impact in hydrologic, oceanographic, and climate studies. This project is therefore relevant to DOE's environmental mission.

Our project is also relevant to DOE's science mission. A technique for analyzing ^{39}Ar is a key component needed to develop the next generation of dark matter detectors based on cryogenic liquid argon. The direct observation of dark matter particles on earth would constitute a major breakthrough in modern physics and represents a high-priority goal in high-energy and nuclear physics. It was recently demonstrated that liquid argon could be an ideal choice for a detector material. However, the presence of atmospheric ^{39}Ar is a major source of background radioactivity. An ^{39}Ar analyzer would therefore be extremely beneficial in searching for and identifying an underground source of argon depleted in ^{39}Ar (^{39}Ar/Ar ~ 10^{-18}).

FY 2010 Results and Accomplishments

In FY 2009, we measured the required atomic properties of ^{39}Ar through laser spectroscopy and demonstrated atom trapping of stable isotopes. In FY 2010, we accomplished laser cooling and trapping of ^{39}Ar and successfully performed ^{39}Ar analysis of an atmospheric sample and a sample originating from old groundwater. By detecting ^{39}Ar in these samples, we established that ATTA can indeed perform rare isotope analysis at and below the parts-per-quadrillion level.

Two of the major technical accomplishments were (1) increasing both the capture efficiency and counting rate of the ATTA instrument by a factor of 200 over previous results and (2) detecting single ^{39}Ar atoms with a high signal-to-noise

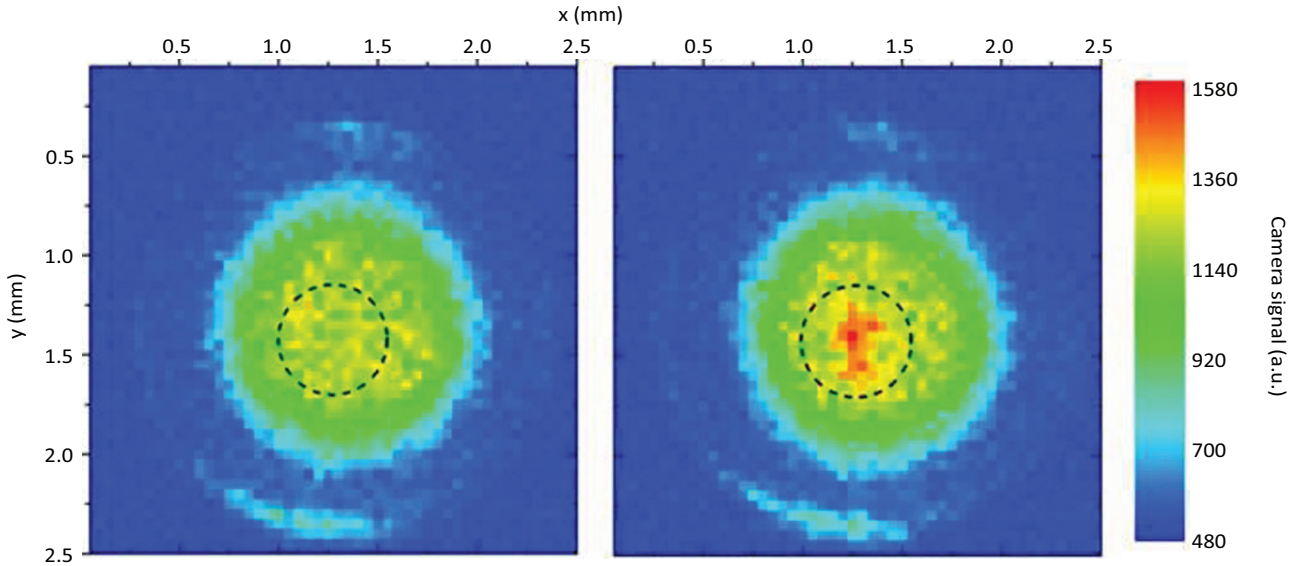


Figure 1. False-color CCD images of the laser trap center at ^{39}Ar settings. On the left, no atom is present; the background is dominated by scattered laser light imaged through a 1-mm-diameter aperture. On the right, the fluorescence emitted by a single ^{39}Ar atom can be clearly distinguished above background. The dashed circle indicates a 0.5-mm-diameter region of interest for signal size analysis.

ratio by using a sensitive charge-coupled device (CCD) camera to record the laser-induced fluorescence emitted by a trapped atom (Figure 1).

While the counting rate for ^{39}Ar at the atmospheric level of about one event every three hours is still too low by a factor of about three for routine measurements, all envisioned milestones for this project in terms of isotopic selectivity, background level, and sample size required have been achieved. As a result of this new analytical capability, exciting applications (e.g., in oceanography and dark matter detector development) are within reach. Further improvements of the counting rate will be addressed in the framework of a direct follow-on project that has received funding from the DOE Office of Science.

Refereed Publications

Jiang, W., W.D. Williams, K. Bailey, A.M. Davis, S.-M. Hu, Z.-T. Lu, T.P. O'Connor, R. Purtschert, N.C. Sturchio, Y.R. Sun, and P. Mueller "Ar-39 Detection at the 10^{-16} Isotopic Abundance Level with Atom Trap Trace Analysis," *Physical Review Letters*, In press.

Williams, W., Z.-T. Lu, K. Rudinger, C.-Y. Xu, R. Yokochi, and P. Mueller, "Spectroscopic Study of the Cycling Transition $4s[3/2]_2$–$4p[5/2]_3$ at 811.8 nm in ^{39}Ar: Hyperfine Structure and Isotope Shift," *Physical Review A* **83**, 012512 (2011).

Non-Refereed Publications and Presentations

Mueller, P., "Isotope Detection at the Part-per-Quadrillion Level with Atom Trap Trace Analysis," invited talk presented at the Fifth International Conference on Laser Probing, Vancouver, Canada, September 27–October 1, 2010.

Williams, W., Z.-T. Lu, K. Rudinger, C.-Y. Xu, R. Yokochi, and P. Mueller, "Towards Laser Trapping of Argon-39 – A Spectroscopic Study of the Metastable Cycling Transition at 811.8 nm," presented at the 2010 Annual Meeting of the Division of Atomic, Molecular, and Optical Physics of the American Physical Society, Houston, TX, May 25–29, 2010.

Magneto-Vibrational Energy Conversion at the Nanoscale

2010-003-N0

Axel F. Hoffmann and Omar D. Lopez

Project Description

In 1915, the seminal works by Einstein and de Haas (magnetization change results in mechanical rotation) and Barnett (mechanical rotation results in magnetization change) proved that magnetic moments possess corresponding mechanical angular momentum. This fact elicited renewed interest recently, when several experiments showed that magnetism-related mechanical torques are sufficient to significantly modify the dynamics of micrometer-sized mechanical objects (usually known as microelectromechanical systems or MEMS) with kHz resonance frequencies.

It was also recently demonstrated that patterned magnetic nanostructures have well-controlled magnetization dynamics at frequencies of a few hundred MHz, which is well below their ferromagnetic resonance (typically a few GHz and above). Moreover, the magnetization dynamics of these nanostructures can be excited by applying local alternating electric currents through them. These recent developments open up the possibility of having hybrid magnetomechanical nanostructures with commensurable resonance frequencies. The integration of magnetic nanostructures on top of submicrometer-sized mechanical objects (nanoelectromechanical systems or NEMS) will allow very precise control of their mechanical motion and increase the efficiency of the magnetomechanical coupling by orders of magnitude.

Our goal is to integrate magnetic domain wall oscillators with high-frequency torsional NEMS oscillators and investigate the magnetomechanical coupling between them. When a submicrometer ferromagnetic material with small magnetocrystalline anisotropy (such as permalloy) is patterned into a wire, a domain wall can be stabilized in a notch structure. This geometrically defined notch gives rise to a harmonic or anharmonic pinning potential defined by the shape and slope of the notch sidewalls. This geometry, in turns, allows the selection of specific domain wall resonance frequencies, which can be excited and detected via radiofrequency electric transport measurements. In particular, although it had been demonstrated that these frequencies can be as low as 10 MHz, the lower frequency limit has not been sufficiently explored. Such domain wall dynamics result in an oscillating net magnetic moment around the notch position. If one of these domain wall oscillators is integrated on top of a nanomechanical system, the change in magnetization will induce an oscillating mechanical torque along the rotational axis of the NEMS oscillator.

The resonance frequencies of either oscillator can be controlled individually by geometry and thus can be varied independently from each other. Furthermore, the resonance frequency of the magnetic domain wall oscillator may be tuned via applied external magnetic fields, thereby enabling us to directly test the role of commensurability of the two resonance frequencies for the magnetomechanical coupling.

Mission Relevance

This project is relevant to DOE's energy and science missions. The demonstration of frequency-matched magnetomechanical coupling has direct basic and applied impacts. From a fundamental point of view, measurements of such coupled systems allow researchers to determine the micromechanical ratio *g'* in ferromagnetic thin films and nanostructures and to observe magnetomechanical polaritons. An efficient conversion between magnetic and mechanical kinetic energy will provide a novel transduction mechanism to actuate mechanical structures with dimensions below 100 nm. This can excite high-frequency nanomechanical devices (using magnetization dynamics to actuate mechanical motion) or enable unique energy-harvesting structures to collect power from continuously renewable energy sources, such as vibrations or thermal energy (converting mechanical motion in magnetization dynamics and ultimately electricity).

FY 2010 Results and Accomplishments

As a result of discussions with researchers from the United States and Canada who performed a wide variety of experiments and analyzed nanomagnetomechanical phenomena, we revised our original ideas for using magnetic vortex oscillators for investigating magnetomechanical coupling. We decided that domain wall resonators are better suited for achieving the goals of this project for several reasons: (1) magnetic domain wall resonators have lower demonstrated resonance frequencies (down to 10 MHz), and these reduce the challenge of developing a frequency-matched torsional MEMS oscillator; (2) the linear structure is readily compatible with placing the resonator on top of the torsional axis of a mechanical oscillator; and (3) varying the notch geometry from parabolic to linear sidewalls makes it possible to introduce anharmonicity into the pinning potential, which allows the resonance frequency to be tuned via the excitation amplitude. With these reasons in mind, we began fabricating domain wall resonators with a permalloy wire having a width of 1 µm and a notch having a central width of 100 nm and a length of 4 µm along the wire. Work by Lepadatu et al. on domain wall resonators indicates that this effort should result in a domain wall resonance frequency of about 20 MHz.

We used magnetic force microscopy (MFM) to confirm that a domain wall is pinned within the pinning potential. We then performed micromagnetic simulations to gain further insight into the internal magnetic structure of the domain wall and theoretical guidance for designing the notch structure for the desired resonance frequencies. One surprising result of these simulations was that the equilibrium position of the domain wall was not centered on the notch, which may result in more complicated dynamics. Unfortunately, the numerical simulations have not yet revealed any information about the dynamics, since the low frequencies of the dynamics require longer simulation times than we currently have available. We plan to circumvent this problem with new types of micromagnetic simulations that directly solve for the dynamic eigenmodes of the magnetic structure.

Concurrently, we began the magnetotransport characterization of these devices, but the preliminary data are inconclusive. The main problem is that the frequency dependency of the device impedance is currently dominated by capacitive effects. We are now redesigning the sample structure to alleviate this problem.

In parallel with the magnetic domain wall resonator development, we began the development and fabrication of torsional MEMS/NEMS with sufficiently high resonance frequencies up to 20 MHz. We are thus independently fabricating MEMS torsional oscillators and magnetic domain wall resonators, which are designed for identical resonance frequencies. Furthermore, the magnetic domain wall resonators are compatible with the MEMS designs, since the width of the central torsional rod is 500 nm to 1 µm.

A big challenge was to characterize the actual resonance frequencies of the MEMS/NEMS oscillators. To this end, we used an optical interferometric technique developed at Argonne for dynamical MEMS characterization. An incoming laser beam is split into two beams that focus on different parts of the device. The interfering reflected signals are then detected, and the frequency noise spectrum is analyzed. This work allows us to directly detect the dynamic eigenmodes from the thermal noise, without the need to externally drive the system. By using this approach, the eigenmode of test MEMS structure at about 3 MHz is clearly resolved, even though the displacement amplitudes are only 5 pm. Furthermore, the spot size of the laser focus is about 1 µm, which makes this system well suited for investigating the dynamic properties of the MEMS structures intended for this project. In addition, we plan to adapt a similar interferometric system to our microwave probe station, so that we can detect MEMS displacement at the same time we measure radiofrequency transport.

Proposed Work for FY 2011

We plan to (1) integrate NEMS structures with magnetic vortex structures, (2) characterize the mechanical response to electrically driven magnetization dynamics (Einstein-de Haas effect), and (3) vary the ratio between mechanical and magnetic resonance frequencies via geometries and/or the magnetic field.

Laser Manipulation of Nuclear Spin Embedded in Noble-Gas Ice

2010-010-N0

Zheng-Tian Lu and Ulrich Welp

Project Description

Optical pumping is usually performed in the gas phase where atomic structure is well defined. In the condensed phase (liquid or solid), atomic structure is so severely perturbed that resonant excitation and optical pumping cease to be effective. In this project, we are performing optical pumping on atoms embedded in a solid noble-gas matrix. Frozen noble gas at cryogenic temperature may be an ideal medium that confines atoms (or molecules) indefinitely while, at the same time, only weakly perturbing the atom's internal structure, so optical pumping remains effective. If successful, this novel approach would add to our tools for controlling spins. In particular, we plan to investigate using this technique for testing time-reversal symmetry, measuring the nuclear moments of exotic isotopes, and possibly quantum computation.

Mission Relevance

The proposed method of spin manipulation is a general technique that, if successfully developed, will benefit many applications across disciplines, including fundamental symmetries in physical laws, nuclear structure, and quantum simulation and computation. As such, the project aligns with missions of DOE's Basic Energy Sciences, which supports fundamental research to understand, predict, and ultimately control matter and energy at the electronic, atomic, and molecular levels, as well as with DOE's Nuclear Physics program, which supports fundamental research to discover, explore, and understand all forms of nuclear matter.

FY 2010 Results and Accomplishments

We met both FY 2010 milestones: (1) investigating the growth of neon, argon, and para-hydrogen matrices on a substrate and (2) performing laser spectroscopy of ytterbium atoms embedded in a solid matrix. With regard to the first milestone, we studied the growth of neon and argon matrices under a variety of conditions. Neon consistently outperformed argon in matrix growth. A neon matrix can be grown quickly (up to 10 µm in an hour) to a large thickness (30 µm) while maintaining good transparency. In contrast, argon matrices became opaque at a thickness of more than 15 µm, even at slow growth rates. Because neon is lighter and its inter-atom van der Waals force is weaker, we hypothesize that neon atoms are more likely to tunnel between atomic sites and repair any defects in the crystal. Although a high-quality argon or para-hydrogen matrix can be grown, we are satisfied, at present, with the quality of the neon matrix and chose neon for the next stages of research. With regard to the second milestone, we performed laser spectroscopy of ytterbium atoms embedded in a neon solid matrix and observed a clear absorption signal. The solid gases, if grown rapidly, become opaque due to the development of defects. We found that by annealing the solids (i.e., raising the temperature of the solids to near and below the melting point), the defects can be repaired and the solids becomes more transparent.

Proposed Work for FY 2011

In FY 2011, we propose to polarize the embedded ytterbium and measure its polarization using a SQUID (superconducting quantum interference device) and to investigate the spin coherence time under various conditions. Laser spectroscopy and optical pumping can be performed on the strong electric dipole (E1) transition $6s^2\ {}^1S_0$, F=½ – $6s6p\ {}^1P_1$, F=½. This transition can be resonantly induced by a laser of wavelength of 399 nm (blue/ultraviolet). Angular momentum is transferred from circularly polarized photons to the atoms via resonant excitation, then to the nuclei via hyperfine interaction in the excited state. The end result is an ensemble of polarized nuclear spins in atoms embedded in the matrix.

The buildup of nuclear spin/magnetic-moment is detected with a sensitive SQUID magnetometer, which is also installed inside the cryostat. We propose to investigate a new technique that has never been demonstrated. If we can show that nuclear spin embedded in noble-gas ice can be polarized via optical pumping, that in itself would be very interesting. Quantitatively, the polarization needs to reach a level that can be detected; we estimate this level to be about 1%. Once we observe a polarization, we could investigate both the optical pumping rate and various de-polarization rates and study their causes. For example, we plan to investigate whether annealing the noble-gas crystal would reduce de-polarization rates. Such understanding would lead to improved results. A polarization of 10% would signify a definitive demonstration of this novel technique.

Single Quantum Flux Magnetometer

2010-029-N0

Wai-Kwong Kwok, Dario Antonio, Omar D. Lopez, and Valerii Vinokour

Project Description

Our goal is to develop a novel nano-mechanical magnetometer (n-MM) by using state-of-the-art nanofabrication techniques. The proposed tool will be able to sense the bulk behavior of a single quantum flux in a superconductor under a variety of experimental configurations. This preliminary magnetometer will be a unique tool for tackling some of the most fundamental basic science problems in condensed matter physics.

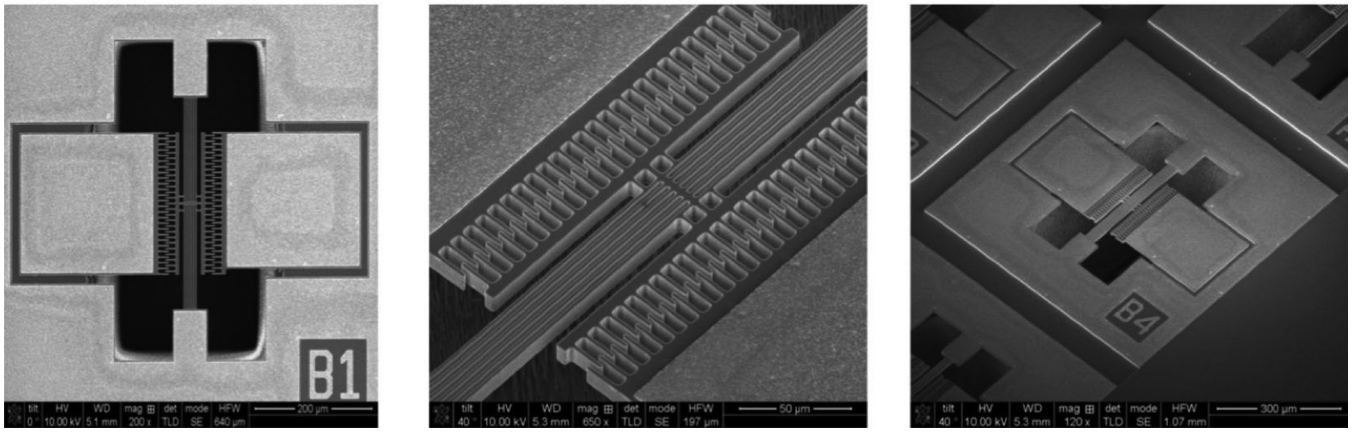


Figure 1. Various designs of the clamped-clamped nonlinear magnetometer. Electrostatic actuation and capacitive detection are implemented with comb drive electrodes. The moving structure can be composed by one or several parallel beams anchored at both ends.

Mission Relevance

This project is relevant to DOE's missions in energy and science. DOE's Office of Basic Energy Sciences recently published a report outlining the high-risk/high-payoff research needed to develop the next generation of superconducting materials for energy delivery, which could revolutionize the U.S. electric grid in the 21st century. High-temperature superconducting (HTS) cables based on a complex multilayer structure are currently being tested for application in the power grid. Although the cooling-related issues associated with these cables have been largely solved, the cost to manufacture them remains prohibitively high, and their ability to be used in rotating machinery (e.g., electric motors) where high magnetic fields are present is far from ideal. Any increase in the current-carrying ability of these materials would proportionately reduce their cost and could improve their performance at high temperatures and high fields.

The main factor limiting the current-carrying ability of HTS cables is the motion of magnetic vortices. Vortices are nanometer-sized magnetic flux tubes, each carrying a single quantum of magnetic flux, which appear in the superconductor when the applied magnetic field is high enough. The dynamic behavior of vortices controls all the electromagnetic behavior of a superconductor. A fundamental understanding of the vortex "pinning" phase – derived from a microscopic perspective of a single pinned vortex – could pave the way for a rational design approach for enhancing the critical current of high-temperature superconductors.

FY 2010 Results and Accomplishments

In FY 2010, our team achieved a major portion of the first-year milestones, including:

1. *Design, fabrication, and characterization of magnetometers based on clamped-clamped resonators working in the nonlinear regime (Figure 1).* We developed a new type of magnetic field sensor. This first-of-its-kind sensor takes advantage of the geometrically induced nonlinearities in a clamped-clamped beam, it does not incorporate magnetic materials, and its fabrication is fully compatible with standard semiconductor processes. The oscillation of a double-clamped beam in a magnetic field B induces electrical currents that dissipate energy through ohmic losses. Because of the nonlinear response of the oscillator, the resulting mechanical damping creates shifts in its resonance frequency that can be used to detect magnetic fields. Thanks to the high Q of the oscillator, very small variations in the peak frequency can be detected, which results in sensitivities of better than 1 μT when measuring fields of 0.1 T (the quality factor, Q, of an oscillator is defined as its resonance frequency f divided by its resonance width Δf. Generally, the higher the Q, the more stable the oscillator).

2. *Resonators for post FIB (focused ion beam) processing.* We implemented new micromechanical resonator designs for measuring torque and dissipative effects. They included (1) resonators designed specifically for post-processing with an FIB tool to increase sensitivity and (2) a torsional resonator with a low elastic constant and low moment of inertia to obtain maximum sensitivity. The fabrication process used for the former resonators allowed for a minimum feature size and a minimum limit of 2-μm (micrometer) separation between features. These structures were designed at Argonne's Center for Nanoscale Materials and were sent to a MEMS foundry for fabrication. Following MEMS fabrication, we will mill the structure with a FIB, reducing the limit to less than 0.5 μm. Thinner springs will reduce the elastic constants, thus increasing sensitivity to torque variations. Furthermore, narrower gaps between the detection electrode and rotating plate will increase the electrical capacitance and improve the sensitivity of the rotation angle measurement.

3. *Minimization of clamping losses.* We developed a modified "tuning fork" for an in-plane resonator and a triple plate torsional resonator to minimize clamping losses (Figure 2). These losses originate in the vibration energy that leaks into the material that supports the moving structures. In these components, we mitigate these losses by minimizing the stress in the anchors for the relevant modes of vibration.

4. *Coupled micromechanical resonators and self-sustained oscillators.* We began the development and fabrication of (1) coupled micromechanical resonators to study the effect of coupling in their nonlinear dynamics and (2) coupled self-sustained oscillators to investigate synchronization in MEMSs and nanoelectomechanical systems (NEMSs). A self-sustained oscillator is a dissipative system with an internal energy source that allows nondecaying stable oscillations. In these systems, the phase of the oscillations is free, and a very weak coupling between different oscillators is enough to synchronize their phases. This phenomenon – called synchronization or frequency entrainment – is encountered in many dynamical systems and is a consequence of their nonlinear dynamics. In the second year of this project, we will study this phenomenon in the context of micromechanical and nanomechanical systems to increase our understanding of this type of dynamics and open the door to designing new sensors based on their use.

5. *Mesoscopic $Ba_2Sr_2CaCu_2O$ (BSCCO) and $YBa_2Cu_3O_x$ (YBCO) single crystals.* We developed new methods for growing ultra-high-purity YBCO single crystals from BaZrO crucibles. These crystals have shown remarkable purity even in their underdoped state, with very sharp superconducting transitions ranging in T_c from 17 to 92 K. We are currently developing techniques to thin these 100-µm-thick crystals down to a few micrometers via polishing. The lateral dimensions of the thinned crystals will be reduced via FIB to form mesoscopic crystals with various geometric shapes. These crystals will constitute the first trial test samples for the MEMS magnetometers.

6. *Low-temperature electronics.* We developed and designed the setup of the characterization electronics for capacitive motion sensing of micromechanical resonators (Figure 3). We paid special attention to minimize the effect of parasitic capacitances and to use a preamplifier stage that can be placed close to the sensor in low-temperature measurements in order to avoid radiofrequency interference and parasitic capacitance introduced by long cables. To measure a capacitance Cx, we use the trans-impedance amplifier setup shown in Figure 3. Here, the cryogenic transistor J1 provides high input impedance and low output impedance, and the feedback maintains the voltage at Vi as fixed, thus minimizing the effect of the parasitic capacitances Cp introduced by the cables.

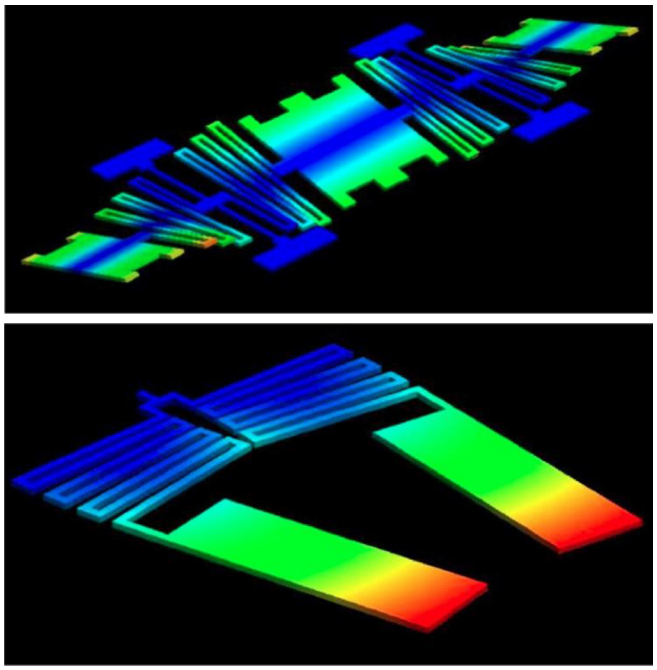


Figure 2. Two different oscillators designed for minimizing stress at the anchors. Top: Torsional oscillator where the central and end plates oscillate in counter-phase. Nodes are then located where the structure connects to the anchor beams. Botom: In-plane tuning-fork resonator. The two plates oscillate in counter-phase, minimizing stress at the anchor.

7. *Probe.* We ordered a new probe from American Magnetics Inc. to mount the MEMS magnetometer described above into the triple-axis vector magnet at Argonne's Materials Science Division. Next year, we will test the low-temperature characteristics of these novel MEMS magnetometers and optimize their responses at low temperatures and high magnetic fields. We will test the system with pristine and underdoped mesoscopic HTS single crystal samples.

Proposed Work for FY 2011

In FY 2011, we will experiment with FIB-processed designs with MEMSs fabricated by the foundry at which our designs were implemented. These devices will be tested at low temperatures and high magnetic fields in our triple-axis vector magnet. We expect that the sensitivity and response of these magnetometers will allow us to detect the real-time dynamic response of an isolated vortex line moving through a superconductor.

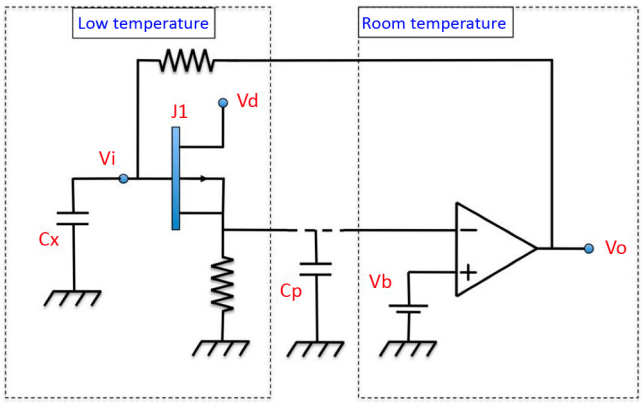


Figure 3. Trans-impedance amplifier with a cryogenic preamplifying stage. The cryogenic transistor J1 provides a high input impedance and a low output impedance for effectively driving the long cables that go from the cryostat to the room-temperature electronics. In addition, the feedback maintains the voltage at Vi fixed, thus minimizing the effect of the parasitic capacitances Cp introduced by these cables.

To optimize the system, we will continue to design and fabricate newer magnetometers by relying on state-of-the-art micromachining processes and the latest nanofabrication technique using a focused ion beam to further modify the critical micro-machined components. The design and optimization of the magnetometer will be guided by using finite element simulations of the magnetometer response.

The ability to detect the bulk property of a single flux quantum opens new horizons for addressing basic science problems that have not been understood despite several experimental attempts. One of the first tests of the n-MM will be its efficacy in addressing a critical fundamental problem related to the science of glassy dynamics.

The vortex system, subject to randomly distributed defects, forms a new fundamental and unique glassy state with controllable and tunable parameters that allow for a reliable theoretical description of a true glass state from using realistic quantitative models with predictive power. The nonlinear response of the pinned vortex configuration in the vortex glass state is due to the so-called extreme order statistics that govern the distribution of the energies of pinned vortices. A new vortex phase – a marginal or critical glass with peculiar dynamics – has been predicted. Our quantum flux magnetometer offers, for the first time, a direct window to the microscopic dynamic behavior of a single vortex and direct measurements of the distribution of vortex energies, thus providing an experimental base for resolving one of the most fundamental problems in contemporary condensed matter physics. A firm understanding of the vortex glassy state in high-temperature superconductors will promote new rational strategies for enhancing the critical current of these materials. In FY 2011, we will use our n-MM to measure a mesoscopic $NbSe_2$ single crystal to check whether single vortex pinning can be observed with our system.

Another hotly debated issue with regard to high-temperature superconductors is whether compound disorder in the glassy state could enhance the critical current of these materials. Columnar defects induced by high-energy heavy ions constitute one of the strongest pinning centers for vortices at high temperatures in superconductors. On the other hand, weak random point defects are effective at pinning vortices at high fields and low temperatures. There are arguments on whether compound disorder (consisting of columnar and point defects) is additive or competitive with regard to raising the critical current and affecting the pinning anisotropy of HTS. Our n-MM with quantum flux sensitivity could provide a definitive answer to this debate by probing the interaction of a single vortex with a single columnar defect and point disorder. In FY 2011, we will measure the magnetization response of mesoscopic single crystals of the high-temperature superconductor $YBa_2Cu_3O_{7-d}$, which has been irradiated with high-energy heavy ions and protons.

Finally, the n-MM can also be used to study the dynamic behavior of a single vortex depinning from a defect site. Once the above experiments are successful and we have tested the critical parameters of the n-MM, we will proceed to check whether our n-MM can be used to conduct a cause-and-effect experiment, where electrical contacts will be attached to the sample residing on top of the magnetometer, and the response of a single vortex to a Lorentz force (J × B) will be monitored. The flexibility of patterning electrical contacts directly onto the n-MM provides a unique way to explore both dynamic (transport) and thermodynamic (magnetization) response simultaneously.

Emerging Technologies for Scientific Databases

2010-042-N0

David M. Malon, Jack Mark Cranshaw, Robert B. Ross, and Peter Van Gemmeren

Project Description

While relational databases are widely employed throughout the sciences, such databases are often not used to store the scientific data themselves at any significant scale. There are many reasons for this: (1) no native support for necessary data types, including arrays; (2) no scientific query or transform operators (not even relatively standard spatial and temporal query operators); (3) transaction models limit scalability and potential for parallel and distributed processing, even though many data are, in practice, read-only (with updates handled by additional data versions rather than by changes to existing data); (4) insufficient versioning, provenance tracking, and

infrastructure to ensure reproducibility; and (5) others. For many scientific applications and for commercial data mining applications as well, the row-oriented storage of a conventional relational database leads to performance issues, even for certain analysis operations that are, in principle, feasible. In this project, we seek to address some of the obstacles to scalable scientific databases, both by taking advantage of emerging technologies and initiatives, such as the relatively recent open-source SciDB project, and by contributing to the development of such technologies.

Mission Relevance

This project is related to DOE's basic science mission. The basic and applied sciences that are integral to DOE's mission increasingly generate vast amounts of data, both from scientific instruments and from simulations. Technologies that support more than data storage and retrieval – those that support the efficient, scientific analysis of data in which DOE has invested and for which it has custodial responsibility – are vital to its mission. DOE is a key contributor to international particle physics projects underway at the Large Hadron Collider (LHC) in Geneva, Switzerland. The technologies that support efficient particle physics data analysis are directly relevant to the effectiveness of those contributions. Moreover, their relevance is much broader: The tens of millions of gigabytes of data generated by the LHC experiments are just one example of the need throughout DOE's science enterprise for scalable technologies to manage scientific data.

FY 2010 Results and Accomplishments

The focus of the first year of this effort was to develop a data testbed for evaluating emerging database technologies and to evaluate available and emerging technologies. We developed a testbed on the basis of event-level metadata records of the earliest proton collisions at the LHC. We imported these data into the earliest releases of SciDB software; this work was possibly the first use of SciDB for real (not simulated) scientific data. We evaluated the early features available in this nascent technology; results will appear in conference proceedings in FY 2011. An important consideration in applying any technology to bulk scientific data is its ability to support in situ data without transformation to a special format, thereby allowing the costs of importation to be avoided and existing tools to continue to work. One of the more widely used storage technologies for scientific data is the Hierarchical Data Format (HDF5). Although LHC data do not employ this format, we built HDF5 representations of the LHC data and tools to populate such representations so our testbed may deliver results of interest to a broader range of scientific data enterprises.

Proposed Work for FY 2011

In the next phase of this project, we will investigate importing bulk particle physics data, which have substantially more complicated data structures than those in event-level metadata records, and explore whether SciDB and related technologies can be made to support such structures and the complex selections and operations that are required to analyze particle physics data. We will test the ability to support *in situ* data in the ROOT format ubiquitous in high-energy physics. We will explore support for user-defined functions that may be discipline-specific for provenance tracking and for ensuring reproducibility, adopting or adapting technologies as appropriate.

Non-Refereed Publications and Presentations

Malon, D., "I/O and Persistence Infrastructure: Emerging Technologies and Software Upgrade R&D," presented at ATLAS Software and Computing Workshop, Geneva, Switzerland, July 15, 2010.

Malon, D., J. Cranshaw, P. van Gemmeren, and Q. Zhang, "Emerging Database Technologies and Their Applicability to High Energy Physics: A First Look at SciDB," presented at Computing in High Energy and Nuclear Physics 2010, Taipei, Taiwan, October 18–22, 2010.

Vaniachine, A., "Emerging Database Technologies and What ATLAS Might/Should Do in This Arena," presented at the Second ATLAS Future Computing and Upgrade Workshop, Berkeley, CA, September 17, 2010.

Low Mass Optical Readout for High-Data-Bandwidth Systems

2010-043-N0

David G. Underwood, Patrick M. De Lurgio,
Waruna S. Fernando, Omar D. Lopez,
Maria B. Salvachua-Ferrando, and Robert W. Stanek

Project Description

In this project, we are using micro-electro-mechanical system (MEMS) technology to build free-space, all-optical, high-bandwidth transmission channels that can be used to get data from large-scale physics experiments. A MEMS is a silicon micro-machine built in the same way as are electronic integrated circuits. One main project goal is to move the lasers out of tracking detectors for reasons of mass, power, and reliability. Another is to establish the technology of data beams in air as it relates to the high-energy physics (HEP) environment for data transmission, on-board triggering, and trigger-clock distribution. We are solving technical issues, such as closed-loop control loops to steer the beams by means of the MEMS mirrors. We are investigating many lens systems to find the best ones for transmitting and capturing beams on this distance scale (a few meters at most) and for modifying

the MEMS steering to capture beams more easily. We are also investigating the detectors that are needed to steer the laser beams and extract data from the beams.

Mission Relevance

Detectors at large particle colliders, such as ATLAS and the Compact Muon Solenoid (CMS) at the Large Hadron Collider (LHC) at CERN and STAR at the Relativistic Heavy Ion Collider (RHIC) at Brookhaven National Laboratory, have limits as a result of (1) mass in the tracking system, (2) limited bandwidth in the readout, (3) failures of data-transmitting lasers called VCSELs (vertical-cavity surface-emitting lasers), and (4) delays in transmitting data for fast triggering. Also, tracking detectors need internal triggering electronics, and a data path between tracking layers is needed to provide data for calculations. The technology we are investigating and developing (beams in air steered by MEMS mirrors combined with small, low-powered light modulators) could play a big part in dealing with these issues. This project is therefore relevant to DOE's mission in scientific discovery and innovation which underlies several DOE national user facilities other such facilities where DOE-sponsored researchers pursue studies.

FY 2010 Results and Accomplishments

We achieved most of the goals for the first year and conducted a radiation hardness study. We became familiar with aspects of MEMS mirrors, lenses, and control loops needed for our project. We established a data beam in air over a 1 m distance using a wavelength of 1,550 nm, with an error rate of less than 10^{-13}. We did this with a continuous wave (CW) laser and external modulator – the geometry proposed for a real system. We steered beams in air using a MEMS mirror, novel feedback loop, and detector geometry. Most important, we implemented our idea of using the reflection from the receiving lens as part of the feedback loop in order to eliminate the need for detectors, electronics, and wiring for steering at the receiving end of the laser beam (Figure 1). We tested our idea with a moving lens driven over 1 mm in transverse distance at various frequencies up to 200 Hz (Figure 2). Our control loop controls the beam motion within 5 µm (micrometers) (Figure 3). At present, the beam steering is for visible light beams, but we have most of the hardware needed to use 1,550-nm infrared light. We tried many analog and digital control loops to deal with the resonances found in all MEMS mirrors. We worked with the Massachusetts Institute of Technology (MIT) Microphotonics Center on a study of the radiation hardness of the special SiGe alloy used in an MIT test-model light modulator. We exposed the material to very large electron fluxes (3×10^{16} and 3×10^{17}) at the Argonne Chemistry Division Van de Graaf generator. It appears that the material would still work as a modulator but with increased dark current after such exposure.

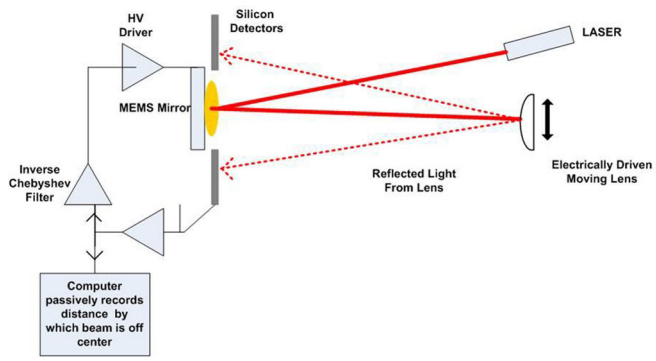


Figure 1. Setup used to test an analog control loop for guiding a MEMS mirror for steering a laser beam.

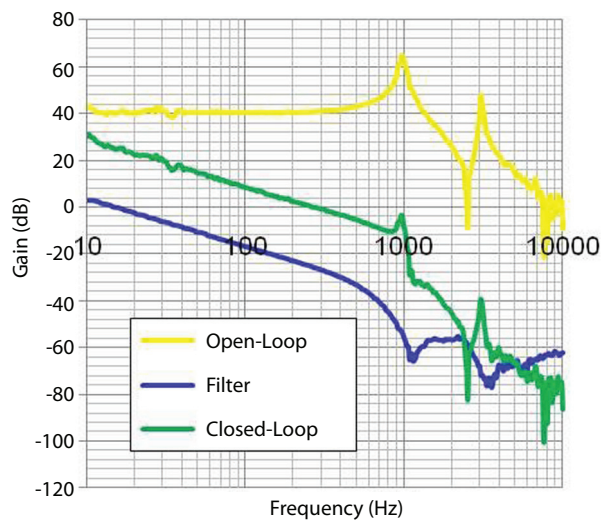


Figure 2. Gain for the MEMS control loop. As the MEMS mirror is "tickled" at various frequencies, the resulting amplitude of the MEMS displacement is measured in the gain of the system. Notice that the open-loop (no feedback) gain has a sharp mechanical resonance at 1 and 3 kHz. The two stage filter has notches corresponding to the open-loop 1 and 3 kHz resonances of the MEMS mirror. The closed-loop response has a unity gain frequency of 260 Hz and 54 degrees of phase margin.

We designed two new MEMS mirrors, one for polycrystalline silicon and one for single crystal silicon, and submitted the designs to a foundry. An invention report (IN-10-066), "Created-in-Place Fiber Optic Coupler," was filed.

Proposed Work for FY 2011

The main goal for the next year is to combine all our developments into a system that will steer the 1,550-nm data beam. This work will involve making and steering the infrared (IR) beam onto the MEMS mirror and commissioning a detector system made of multiple GaAs instead of silicon detectors. We need to develop a lens system that is balanced between capture and reflection and that captures very efficiently. We will work to understand optical power losses in lenses, modulators, and fiber connections. Finally, the MEMS mirrors should be available for testing; we will test them and try to use them in the system.

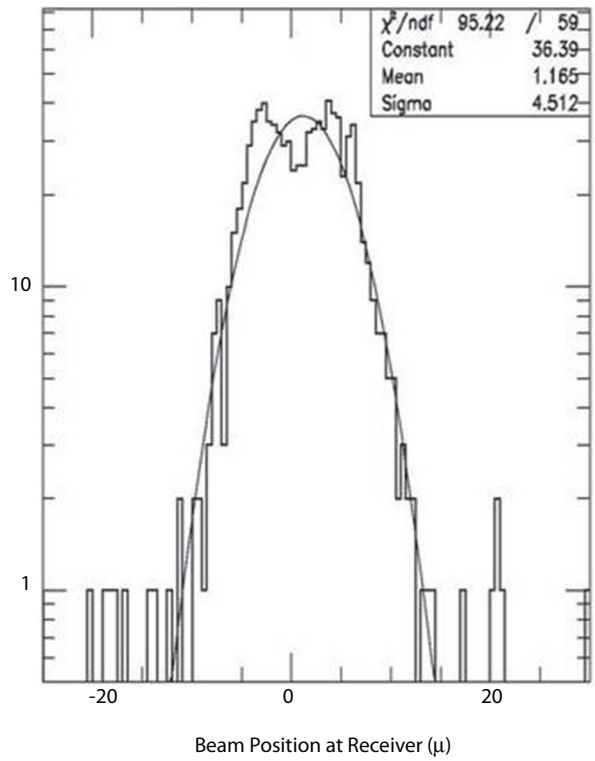


Figure 3. Results of our beam steering using a MEMS mirror, showing control of the beam position within 5-μm root mean square (rms) variation at a distance of more than 1 m.

Refereed Publications

Underwood, D., M.B. Salvachua-Ferrando, R. Stanek, D. Lopez, J. Liu, J. Michel, and L.C. Kimmerling, "New Optical Technology for Low Mass Intelligent Trigger and Readout," *JINST* **5** (2010), C0711.

Non-Refereed Publications and Presentations

Underwood, D., M.B. Salvachua-Ferrando, R. Stanek, D. Lopez, J. Liu, J. Michel, and L.C. Kimmerling, "New Optical Technology for Low Mass Intelligent Trigger and Readout," presented at WIT2010, workshop on intelligent trackers, Lawrence Berkeley National Laboratory, Berkeley, CA, February 4, 2010.

Underwood, D., P. De Lurgio, G. Drake, W. Fernando, D. Lopez, M.B. Salvachua-Ferrando, and R. Stanek, "Development of Low Mass Optical Readout for High Data Bandwidth Systems," presented at Institute of Electrical and Electronics Engineers Nuclear Science Symposium (IEEE-NSS), Knoxville, TN, November 2, 2010.

Underwood, D., D. Lopez, P. De Lurgio, B. Fernando, R. Stanek, "New Optical Technology for Low Mass Intelligent Trigger and Readout," Meeting of U.S. high-energy physics groups doing optical technology, Fermilab, August 19, 2010.

Compact Solid-State Sources of Coherent THz Radiation

2010-049-N0

Ulrich Welp, Nachappa Gopalsami, Kenneth E. Gray, and Alexei E. Koshelev

Project Description

The interest in terahertz (THz) radiation is based on two unique properties – its spectral specificity to the vibrational and rotational modes of a wide variety of important chemical and biomolecular species and its penetrating properties through packaging materials, clothes, plastics, and other materials. Furthermore, the wavelength range of 30 μm to 1 mm (corresponding to 300 GHz to 10 THz) allows for imaging with good spatial resolution.

Compact, high-power, solid-state sources of THz radiation are highly desirable for these applications, and a variety of technologies for THz-wave generation have been developed. Nevertheless, the important frequency range of 0.5 to 2 THz has been difficult to fill with compact solid-state sources, resulting in the so-called THz gap. Sources with enough power will (1) enable real-time imaging by reducing the integration time (currently, image acquisition may take minutes), (2) minimize the number of false positives by enabling subtle spectroscopic features to be reliably recognized, (3) increase the distance in the standoff detection, and (4) enable concealed threats to be detected through absorbing screens. A characteristic power level that is considered necessary lies in the milliwatt (mW) range.

We recently demonstrated that the unique properties of the highly anisotropic high-temperature superconductors enable the development of a new class of THz sources that can bridge the THz gap. We obtained emission frequencies of up to 0.85 THz and emission powers of up to 0.5 μW from a very compact device that is 300 × 60 × 1 μm^3 in size. Even more recently, we reached 5 μW at 0.62 THz with harmonics extending up to 2.5 THz. The goal of this integrated experimental and theoretical project is to demonstrate that the output power of our devices can be increased to a level of about 1 mW. Recent modeling of our device structures indicates that such power levels are possible with an optimized excitation of the internal high-frequency oscillations and improved extraction of the radiation power.

Mission Relevance

This project is relevant to DOE's missions in national security and science. The rapidly emerging field of THz science and technology holds immense promise in fields as diverse as medical diagnostics, space science, environmental monitoring, security, manufacturing, and pharmaceuticals. Directly related to DOE's missions are the atmospheric monitoring of ozone and greenhouse gases, detection of drugs and explosives through packaging, and standoff screening of personnel with nonionizing radiation.

FY 2010 Results and Accomplishments

Our theoretical considerations suggest that THz emissions arise from anisotropic high-temperature superconductors, such as BSCCO (bismuth strontium calcium copper oxide), when the sample is shaped as a resonator for electromagnetic waves. High emission power and conversion efficiency are expected when superconducting properties (e.g., critical current density or T_c) are deliberately modulated across the width of the resonator. Irradiating of a section of the resonator with energetic particles (ions, protons, or electrons) is a convenient and well-established way to introduce a controlled modulated critical and to locally tune the superconducting critical temperature or T_c. In this project, we chose employ proton irradiation at the facilities at Western Michigan University in Kalamazoo.

We performed a first test of the irradiation procedure for inducing a modulated critical current at Michigan. The facility allows for irradiation with protons with energies up to 9 MeV. We covered half of an existing 100-µm-wide resonator with 80-µm-thick aluminum foil and irradiated the sample with 1.75-MeV protons to a fluence of 4×10^{16} p/cm^2. To block the beam and thus create an irradiation pattern, 80 µm of aluminum was sufficient. Post-irradiation measurements revealed that irradiation damaged the sample. Before irradiation, weak emission was observed. After irradiation damage, the current-voltage characteristics changed in such a way that the emission did not occur anymore. This damage was most likely caused by over-heating of the sample in the proton beam.

We have also irradiated one side-face of a 40-µm-wide resonator with 10-keV Ga-ions in a Focused Ione Beam machine. This irradiation causes ablation of the surface and implantation of Ga-ions. In contrast to the proton irradiation, Ga-ion irradiation did not damage the sample, as is revealed by the before and after temperature dependences of the device resistance. Whereas before irradiation this resonator did not emit, after irradiation, clear emission at a frequency of 0.85 THz is observed (see Figure 1). These findings demonstrate that partial particle irradiation is a viable approach to generate THz-emitting states in BSCCO resonators.

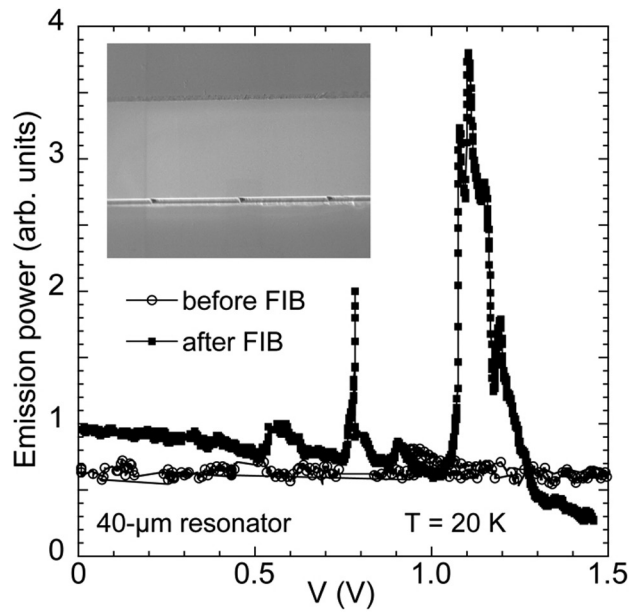


Figure 1. THz-emission obtained from a 40-µm-wide resonator before and after irradiating one side face with Ga-ions measured on decreasing bias voltage. After irradiation, a clear emission line emerges at a bias voltage of 1.1 V. The inset shows the central section of the resonator in top view as seen in SEM. The bottom face has been irradiated.

On the theoretical side, we performed a comprehensive stability analysis of the dynamic coherent states with respect to small perturbations. One can distinguish short-scale and long-scale instabilities, which have different physical origins and lead to very different stability criteria.

Proposed Work for FY 2011

To alleviate the heating problem, we will fabricate a new generation of BSCCO resonators mounted on copper substrates. Copper has good thermal conductivity throughout the entire temperature range. We will achieve electrical insulation by inserting a 10-µm mylar sheet between the copper substrate and the cold stage of the cryostat.

We will fabricate BSCCO mesas of various widths on the new mounts and establish modulations of the T_c across the width of the mesas by using partial irradiation. In addition to proton irradiation, we will pursue Ga-ion irradiation to create modulated and emitting BSCCO resonators. We will evaluate the performance of the devices by measuring the current-voltage characteristics and emission power on our existing test setups and optimize the sample layout and irradiation guided by theoretical modeling of the device structure.

Non-Refereed Publications and Presentations

Koshelev, A.E., L. Bulaevskii, L. Ozyuzer, U. Welp, C. Kurter, K.E. Gray, W.-K. Kwok, H. Yamaguchi, T. Yamamoto, H. Minami, and K. Kadowaki, "Structure and Stability of Dynamic Coherent States in Intrinsic Josephson-Junction Stack," presented at Dubna-Nano2010, Dubna, Russia, July 5–10, 2010.

Welp, U., A.E. Koshelev, T. Benseman, K.E. Gray, W.-K. Kwok, L. Ozyuzer, H. Yamaguchi, T. Yamamoto, H. Minami, K. Kadowaki, and M. Tachiki, "THz-Emission from IJJ in the Low Bias and High Bias Regimes," presented at Plasma 2010: 7th International Symposium on Intrinsic Josephson Junction Effects and Plasma Oscillations in High-Tc Superconductors, Hirosaki, Japan, April 29–May 2, 2010.

Welp, U., A.E. Koshelev, C. Kurter, K.E. Gray, W.-K. Kwok, L. Ozyuzer, K. Kadowaki, T. Yamamoto, H. Minami, H. Yamaguchi, and M. Tachiki, "Terahertz Radiation from Intrinsic Josephson Junctions," presented at Fifth Forum on New Materials, CIMTECH Conferences, Montecatini Terme, Italy, June 13–18, 2010.

Highly Efficient SERS-Active Substrate with Designer Hot-Spots and Multiple-Stage Light Amplification

2010-050-N0

Vitalii Vlasko-Vlasov, Stephen K. Gray, Alexandra Imre, and Elena Shevchenko

Project Description

Surface-enhanced Raman spectroscopy (SERS) is a fast-developing optical technique for the detection and analysis of nanoscale amounts of chemical analytes. Its unique sensitivity, with the capability for single-molecule detection, makes it an attractive tool for a wide range of applications including national security, environmental protection, and medical research and diagnostics. The main challenge in the development of SERS-based detectors is the creation of SERS-active substrates that will provide substantial enhancement of the light intensity in an efficient and reproducible way.

We propose to develop and prove experimentally a new approach to the creation of such substrates, based on resonance interactions in hierarchical regular patterns combining different periodic substructures tuned to the same frequency. The resulting enhancement factor will be the product of the enhancement factors of these substructures. Accounting for the regular "hot-spots" (maximum light-enhancement points) in the gaps between metal nanoparticles forming lattices in grating pitches, we expect a high efficacy and fidelity of the reproducible high-gain SERS signal in our substrates. In addition, the proposed substrates will allow a direct excitation of propagating and localized plasmon modes responsible for the light amplification and thus will simplify the optical detection scheme.

In this project, we will realize a collaborative integrated experimental and theoretical effort aimed at the fabrication and characterization of precisely controlled model substrates, enabling a multistage amplification of the light fields for high-fidelity SERS spectroscopy.

Mission Relevance

This project will result in the creation of new SERS substrates with enhanced sensitivity and extended analytical capability for the detection and recognition of extremely small numbers of biomolecules, potentially at the single-molecule level. These substrates will find multiple applications in basic sciences and applied research, including medical and biological studies. Also, the strong light amplification in our substrates will be applicable to enhancing the efficiency of solid-state lighting devices and solar cells. The results of this project will be of high interest for manufacturers of bio/chemical sensors and for homeland security programs. Thus, the project is relevant to DOE's science and national security missions.

FY 2010 Results and Accomplishments

During FY 2010, we established the process for manufacturing large ordered hexagonal arrays of 80-nm gold nanoparticles on glass, transparent indium tin oxide, and silicon (Figure 1) for applications in Raman spectroscopy. Their sensing efficiency was tested by recording SERS spectra of organic rhodamine 6G (R6G) molecules and inorganic 5-nm CdSe quantum dots (Figure 2). In addition, we demonstrated a considerable enhancement of the photoluminescence from R6G and CdSe (Figure 3), which shows the potential of our structures for applications in light-emitting devices and solar cells. Using electron-beam lithography, we fabricated grating templates and successfully self-assembled periodic stripes of Au nanoparticles (Figure 4).

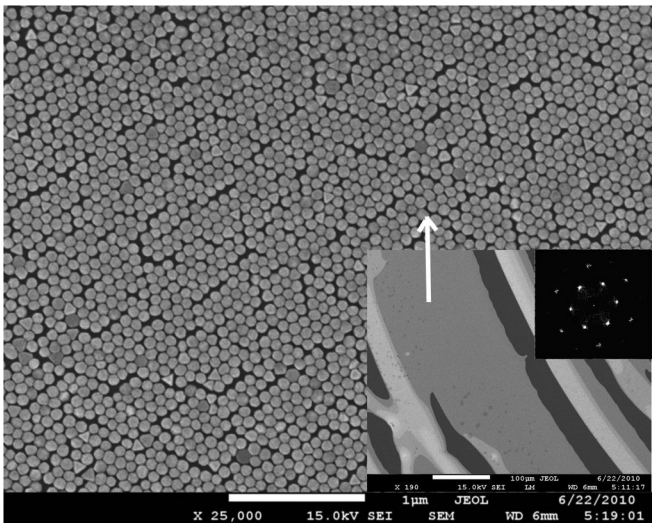


Figure 1. Monolayer of well-ordered 80-nm Au nanoparticles assembled over more than 200-µm areas. Fourier transform of the SEM image in the insert confirms the robust hexagonal order.

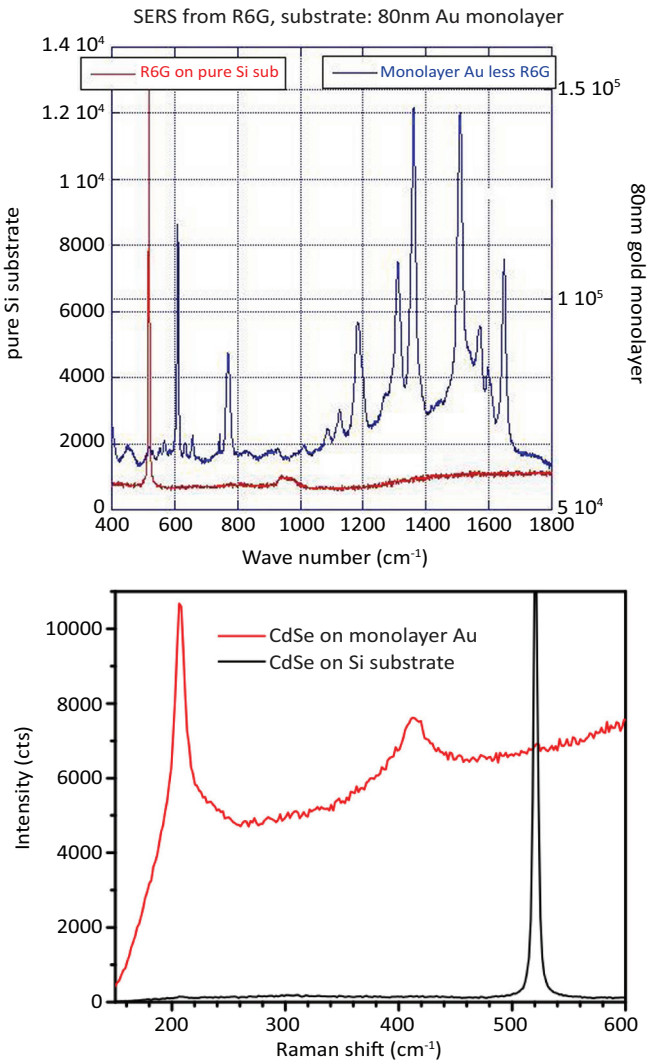


Figure 2. Raman spectra of Rhodamine 6G (top) and CdSe quantum dots (bottom) on the self-assembled Au arrays are strongly enhanced compared to the same spectra measured in neighboring Si substrate areas.

Proposed Work for FY 2011

We will investigate mechanisms of capillary self-assembly allowing controlled growth of large plasmonic arrays of 50–100-nm particles and will grow large-scale ordered arrays of gold and silver nanoparticles on silver films, supporting propagating plasmon waves. We will fabricate nanoparticle arrays in periodic grating templates on top of the silver films and study effects of the resonant light enhancement by coupled propagating and localized plasmons in such distributed mirror structures. The SERS performance and photoluminescence enhancement in our substrates will be evaluated by using R6G and semiconducting quantum dots as reporters. Optimization of the structures will be performed by using finite difference time domain modeling.

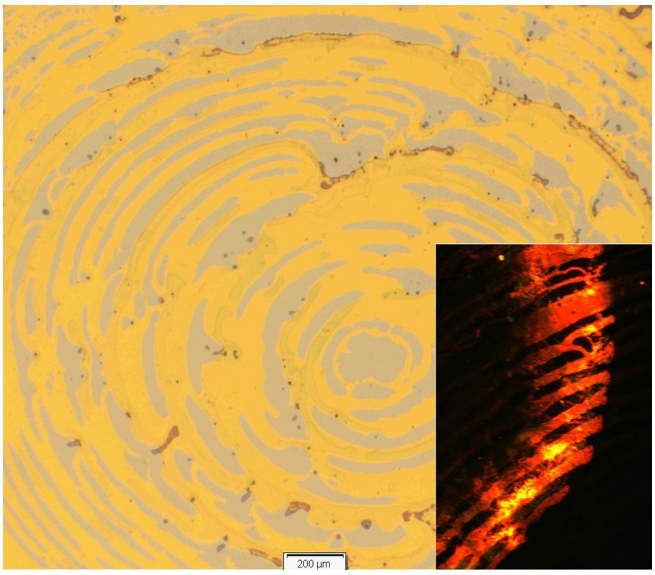


Figure 3. Bands of ordered Au nanoparticle arrays (yellow) formed during the capillary self assembly from a colloid in a Teflon ferrule. The gray areas are the clean Si substrate. The luminescence of CdSe quantum dots drop-deposited on this substrate is enhanced by an order of magnitude in the bands with Au nanoparticles (inset).

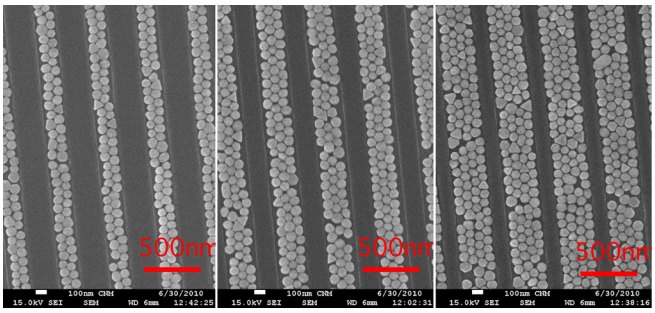


Figure 4. With our grating templates fabricated using electron-beam lithography, we successfully self-assembled regular stripes of Au nanoparticles of different width and periodicity.

Refereed Publications

Vlasko-Vlasov, V., A. Joshi-Imre, J.T. Bahns, L. Chen, L. Ocola, and U. Welp, "Liquid Cell with Plasmon Lenses for Surface Enhanced Raman Spectroscopy," *Applied Physics Letters* **96** (2010), 203103.

Non-Refereed Publications and Presentations

Chen, A., A. Joshi-Imre, E. Shevchenko, L. Ocola, A. Demortiere, A.E. DePrince, S.K. Gray, U. Welp, and V.K. Vlasko-Vlasov, "Self-Assembly of Colloidal Gold Nanoparticles for SERS-Active Substrates," poster presented at the MRSEC (Materials Research Science and Engineering Center) Workshop on Electronic Transport in Nanoengineered Materials, Chicago, IL, September 16–18, 2010.

Tactile MEMS-Based Sensor

2010-063-N0

Young Soo Park, Nachappa Gopalsami, and Omar D. Lopez

Project Description

While artificial sensing has been a grand challenge in the field of artificial intelligence and human-machine interface, mimicking a sense of touch has been the most difficult aspect of this challenge. The objective of this project is to develop a high-fidelity, tactile microsensor that is capable of replicating and excelling in the sensation of fingertip touch. Successful development of such a microsensor will have significant impacts, not only in the field of robotics, but also in improving the usefulness of haptics technology (i.e., technology that interfaces with the user through the sense of touch). Haptics technology has recently emerged in numerous applications that we use in our daily lives. While most innovations in haptics have focused on haptic display (rendering cutaneous stimulus), relatively few efforts have focused on the development of haptic sensors. Based on micro-electromechanical systems (MEMS) technology, the micro-sensor that we propose will have an order-of-magnitude higher spatial resolution and equivalent sensitivity compared with existing state-of-the-art sensors.

Mission Relevance

This project is relevant to DOE's missions in science and national security. Since telerobotics were first developed at Argonne for nuclear applications, such systems have been used to safely fulfill DOE missions in nuclear materials handling, decontamination and decommissioning (D&D), and — recently — national security. The poor sensory feedback of the robotics systems, however, limits their potential applications. Development of a high-fidelity tactile sensor will resolve a long-standing technical challenge to enable dexterous robotic manipulation. In addition, because haptics is an emerging technology with broad potential application to our everyday lives, development of the tactile sensor will offer a unique opportunity for DOE to establish a technical basis for haptics technologies that will benefit both DOE's own mission areas and society as a whole.

FY 2010 Results and Accomplishments

In the first year of the project (FY 2010), we completed design and fabrication of a developmental microsensor element using MEMS technology. The design was based on assumed improvements to the sensory feedback capabilities of a surgical robot system. We conducted a series of interviews with surgeons to identify their needs for tactile feedback in dexterous robotic surgery. After evaluating various tactile and force sensors materials, we designed a sensor that is capable of measuring the stiffness (or softness) of human tissues (e.g., kidney, prostate, bladder, and intestine). The sensor element consists of a diaphragm and piezoresistive transducers.

We developed a MEMS process for fabricating the tactile sensor element from SU-8 with negative-tone; gold was used as a piezoresistive material. The SU-8 is an epoxy-based photoresistive material that is stably cured when exposed to ultraviolet light. The fabrication process we developed is a first-of-its-kind process that offers many unique advantages, such as increased robustness due to the polymer substrate material, decreased fabrication cost and complexity, low temperature, and highly flexible structure. Sensor elements of various sizes were made to match a range of material elasticities. Figure 1 shows a sensor node consisting of an array of transducer elements. As shown in Figure 2, the gold piezoresistive element was successfully fabricated with uniform thickness of 5 micrometers (µm). Sensor nodes of various sizes were fabricated with inter-node distances as small as 200 µm.

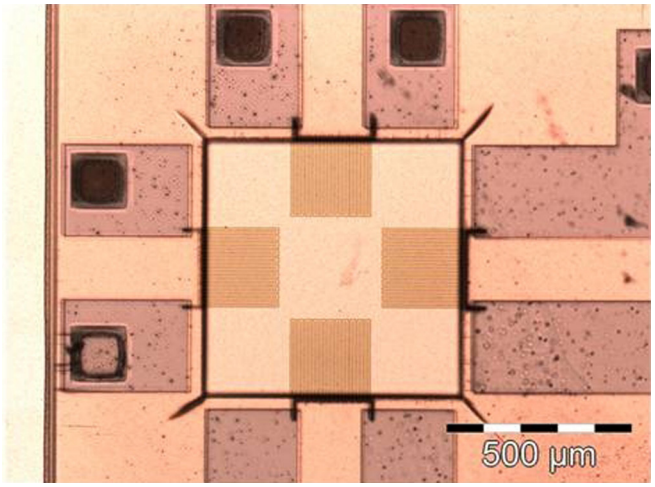


Figure 1. Tactile microsensor.

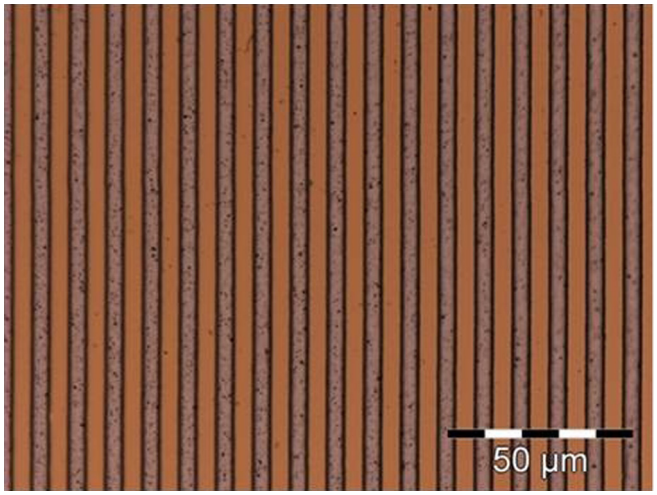


Figure 2. Piezoresistive transducer element.

Proposed Work for FY 2011

The project effort during FY 2011 will be focused on testing and improvement of the tactile microsensor developed during the first year. The tests, conducted in three stages, will include *in vitro* testing of the sensor and robotic operation tests. First, the fabricated sensor element will be tested in the laboratory environment to verify proper functionality. The sensor will then be tested, in partnership with The University of Chicago Medical Center staff, to evaluate its capability in characterizing biological tissues. After each of the first two stages, the sensor will be redesigned and re-fabricated to incorporate improvements. Finally, the sensor will be retrofit onto a DaVinci surgical robot system and tested for effectiveness in providing tactile feedback.

Polymerized Ionic Liquid Nanostructures for Biocatalytic Fuel Production

2010-073-N0

Millicent A. Firestone, Lei Cheng, Larry A. Curtiss, Jeffery P. Greeley, and Rees B. Rankin

Project Description

The objective of the proposed research is to develop a nanostructured heterogeneous biocatalyst that can be used in the biotransformations needed to produce biofuels. The work involves (1) development of a synthetic platform that will allow stable incorporation of aqueous enzymes and (2) evaluation of the platform to determine its suitability for use in heterogeneous biocatalysis.

Mission Relevance

This project is relevant to DOE's science and energy missions. Currently, the world's energy is overwhelmingly supplied by fossil fuels. The depletion of global petroleum reserves and the growing concern over the environment (e.g., generation of greenhouse gases) has led to an increasing interest and need for alternative, renewable energy sources. Production of biofuels, which are made by converting plant or animal byproducts (e.g., triglycerides) to an alkyl fatty acid methyl ester (biodiesel) with methanol, is one approach to providing an alternative fuel source. The results of this project will provide insights into (1) methods that can be used to design and synthesize materials to advance the emerging field of heterogeneous biocatalysis and (1) low-cost means for producing bio-derived fuels as a renewable energy source.

FY 2010 Results and Accomplishments

We prepared a new, interpenetrating polymer by using photopolymerization of a self-assembled binary mixture of 1-(10-(acryloyloxy)decyl)-3-methylimidazolium chloride [C_{10}mim$^+$acr][Cl$^-$] monomer in water (Figure 1A). We then exchanged the chloride counter-anion of the polymer for a polymerizable acrylate group via a metathesis reaction with silver acrylate to yield poly(1-(10-(acryloyloxy)decyl)-3-methylimidazolium) acrylate, poly[C_{10}mim$^+$Acr][Acr$^-$]. In the second polymerization step, we linked the acrylate anion by photo-initiation with 365-nm ultraviolet (UV)light to produce poly(1-(10-(acryloyloxy)decyl)-3-methylimidazolium)-*inter*-poly(acrylate), poly[C_{10}mim$^+$acr]-*inter*-poly[acr]. The successful polymerization through both the ionic liquid (IL) cation and anion was determined by means of vibrational spectroscopy. By using small-angle x-ray scattering (SAXS) at the Advanced Photon Source, we determined that the structure was lamellar (Figure 1B).

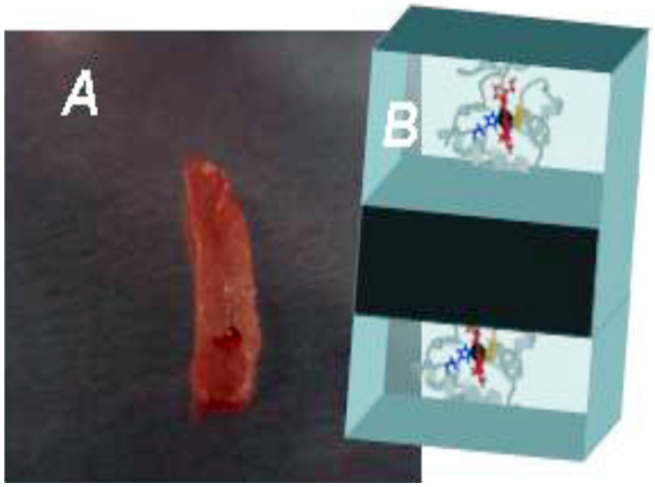


Figure 1. (A) Digital photograph of interpenetrating polymer network gel containing encapsulated cytochrome c; (B) Schematic of cytochrome c encapsulated within lamellar architecture of the polymer gel.

Initial studies to evaluate approaches for successfully encapsulating a model enzyme, horse heart cytochrome *c*, were carried out during FY 2010. Cytochrome *c* was selected because it is a relatively small globular protein (12.4 kDa; R_g of 12.6 Å; molecular dimensions of 26 × 32 × 33 Å) and contains no free sulfhydryl groups or disulfide bonds. The small size of the protein, the absence of disulfide bonds, and the ease with which scientists can monitor its integrity by using optical spectroscopy (i.e., the heme Soret and Q bands are well known to be sensitive to changes in ligand binding, oxidation state of iron, and conformation of the polypeptide in the vicinity of the porphyrin group) made it ideal for this study.

We also determined that cytochrome *c* was best introduced after the first polymerization step and exchange of the anion. Specifically, the solid poly(1-(10-(acryloyloxy)decyl)-3-methylimidazolium) acrylate, poly[C_{10}mim$^+$acr][acr$^-$] was swollen in an aqueous buffered solution that contained cytochrome *c* for 20 minutes. Our previous work demonstrated that this was sufficient time to allow diffusion of the protein

throughout the polymer matrix. The protein-"loaded" polymer was then subjected to short UV (365 nm) exposure (5 minutes) to initiate the second polymerization step: covalently linking the acrylate anions. This procedure produced a solid red polymer (Figure 1A). The integrity of the encapsulated protein was examined by means of UV-Vis spectroscopy. The UV-Vis spectrum recorded on the polymer encapsulated cytochrome *c* compared well with that of ferricytochrome *c* in aqueous buffered (pH 7.4) solution. The close correspondence of the spectra for the solution state and encapsulated protein suggests that no profound changes occur for protein encapsulated within the poly(IL) (i.e., cytochrome *c* remains in its native form). Our work resulted in the preparation of a new poly(ionic liquid) and the successful demonstration of the stable encapsulation of a model enzyme, horse heart cytochrome *c*. This work was important, yielding an optimized polymer and development of a synthetic approach for protein encapsulation.

Proposed Work for FY 2011

The information gathered from our cytochrome *c* studies during FY 2010 will serve as a starting point for the encapsulation of lipase, a transesterification biocatalyst. We will use a commercially available bacterial lipase from *Pseudomonas cepacia*. Lipase will be reconstituted into the new, interpenetrating polymer network, and enzyme activity will be determined by monitoring the transesterification reactions employing the encapsulated enzyme compared with (1) those conducted in free solution and (2) those supported on diatomaceous earth (a commercially available product). The assay will be completed by using a discontinuous approach with periodic sampling and gas chromatography/mass spectroscopy (GC-MS) analysis to determine the amount of product and/or substrate. At this phase, we will examine the lipase-mediated conversion of 1-phenethyl alcohol with vinyl acetate to form *R*-1-phenethyl acetate and *S*-1-phenethyl alcohol.

Theoretical studies employing density functional methods will be used to advance our understanding of the mechanism of transesterification reactions catalyzed by lipase and the effect of structure and environment (such as solvent effect) on the catalytic activity. These studies will augment our experimental studies, providing information for further optimization of the polymer for use in biocatalysis.

Layered Oxides for Thermoelectric Energy Conversion

2010-129-N0

Kenneth E. Gray, Qing'an Li, John Mitchell, and Hong Zheng

Project Description

Thermoelectric (TE) materials can directly convert heat into electrical energy. A search for better materials is merited because TE conversion is a technology with inherent reliability. Reduced dimensionality (e.g., layered materials) has been predicted to lead to improvements in the conversion efficiency, and the opportunity exists to identify commercially viable materials. This project provides vital characterization data and novel sample syntheses and addresses economic viability.

Mission Relevance

Improved materials with high TE conversion efficiency are needed in the DOE context of energy and environment missions. An effort to find breakthrough materials is a reachable challenge. A particularly important energy-saving application is to use the waste heat from automobile engines for cooling in summer.

FY 2010 Results and Accomplishments

We began with two oxides that show some encouraging TE properties: tetragonal $YBa_2Cu_3O_x$ and single crystals of $RBaCo_2O_{5+x}$. In the former case, polycrystals were reported to show a linearly increasing figure of merit *ZT* ($ZT = TS^2s/k$, where *S* is the Seebeck coefficient, σ = electrical conductivity, and k = thermal conductivity) that is ~0.35 at 0°C and extrapolates to ~1 at ~800°C.

We have extensively studied the Seebeck coefficient, *S* (Figure 1), and electrical conductivity, s, of melt-textured $YBa_2Cu_3O_x$ with various oxygen doping levels x and cation substitutions, and discovered an opportunity for both n-type and p-type TE materials. Unfortunately, as x approaches 6, there is a significant decrease in s that reduces $ZT = TS^2s/k$. Apart from this, we developed a mechanism for reducing the thermal conductivity, k, in $YBa_2Cu_3O_x$. Since Au substitutes only on the chain Cu sites, it has little effect on electron transport in the Cu-O planes, but its much larger mass should act as a very effective phonon "rattler" to lower k. Oxygen stability in O-deficient $YBa_2Cu_3O_x$ is poor for T > 250°C. To overcome this problem, underdoping was achieved by cation doping. Both Fe and Co were tried and Co, which substitutes on the chain Cu site, gave a considerable *S* (Figure 2), but the power factor, S^2s, remained very small. Interestingly, when O was removed from the Co-doped sample (y = 0.7), the value of *S* rose to >600 μV/K at 300 K

(see Figure 2). This result allows for the possibility of operating over a wider T range with large *S*. This approach may overcome the O instability, but it must be tested for long time periods, and higher s must be achieved.

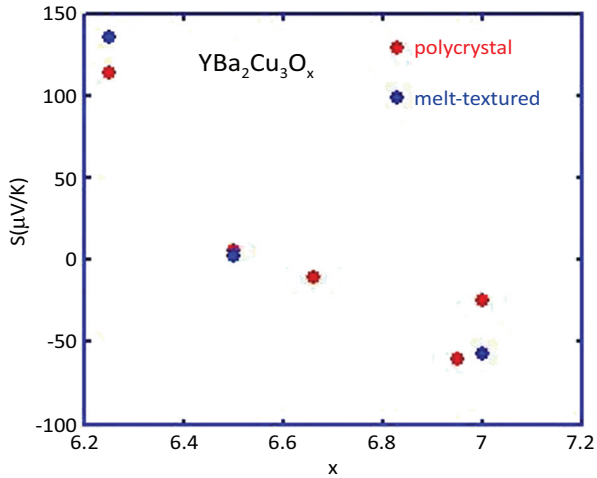


Figure 1. Seebeck coefficient in O-deficient YBCO for both melt-textured and random polycrystal.

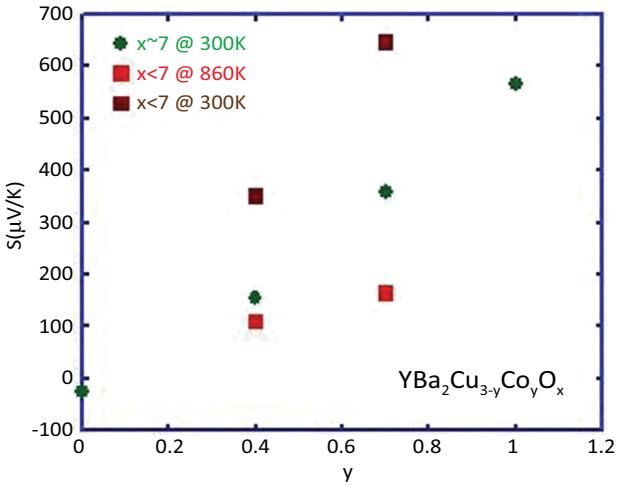


Figure 2. Seebeck coefficient for Co-doped YBCO before (circles) and after vacuum annealing.

Proposed Work for FY 2011

The large *S* for O-deficient $YBa_2Cu_3O_x$ is undermined by the poor σ, giving $S^2\sigma < 1$ μW/K²cm. At the other extreme, $LaNiO_3$ has metallic-like σ but a very low *S*, so that $S^2\sigma \sim 0.25$ μW/K²cm. This observation exposes a potential challenge for oxides, as the high values of *S* seem to be always associated with a small σ, due possibly to a large band-gap. We thus seek to avoid either limit in oxides like $YBa_2Cu_{3-y}Co_yO_x$ — to do so, we need to better understand our material. One may need to emulate properties of typical thermoelectrics that are narrow-gap semiconductors with intermediate charge-carrier concentrations. Theory would suggest that an optimum band-gap is likely about six times the operating temperature (i.e., ~150 meV). Therefore, we will conduct an optical determination of the energy gap in these oxides and Hall-effect measurements for carrier concentration.

On the basis of the year-1 results, we will also expand the objectives and milestones of this project beyond the oxides by exploiting our encouraging result for a heavy Fermion. For this new scope, our second-year (FY 2011) milestone will be to synthesize new and, if possible, larger crystals and to measure the thermopower *S* and, importantly, the thermal conductivity k in order to evaluate the vital parameter, S^2s/k. We also intend to make these measurements at higher temperatures. If these materials still look promising, we will address real-life applications by identifying other, possibly related, compounds to obtain p-type materials and to find replacements for the expensive elements in the existing compound.

Novel Bifunctional Low-Temperature Catalysts at the Sub-Nanometer Scale

2010-137-N0

Larry A. Curtiss, Jeffrey W. Elam, Jeffrey P. Greeley, Michael J. Pellin, Stefan Vajda, and Randall E. Winans

Project Description

This highly interdisciplinary project, based on a unique combination of theoretical and experimental approaches, addresses a roadblock to developing the next generation of catalytic materials for energy applications by pursuing atomic-precision design of entirely new classes of materials based on size- and composition-tuned bifunctional bimetallic clusters. A prototypical reaction, which is to be tuned, is the dehydrogenation of propane to propene followed by the partial oxidation of propene to preferentially form either propylene oxide or acrolein.

Mission Relevance

This project is relevant to DOE's missions in science and energy. New catalyst compositions, based on optimization of heterogeneous catalysts at the sub-nanometer scale toward environmentally more friendly and efficient catalysts for chemical and fuel production, represent a new approach to solving energy-related problems. The Basic Energy Sciences Workshop Report entitled *Opportunities for Catalysis in the 21st Century* stated that "…the Grand Challenge for catalysis science in the twenty-first century is to understand how to design catalyst structures to control catalytic activity and selectivity." Catalysis has clearly reemerged as a centerpiece of DOE-supported research, and it is anticipated that the need for the production of classical fuels from today's available but not yet used resources, and for the development of future alternative fuels, will further increase the importance of catalysis research within DOE.

FY 2010 Results and Accomplishments

During the past year, the focus of our experimental/theoretical work was on silver clusters for propylene epoxidation (EO) and mono-metallic clusters for their oxidative dehydrogenation (ODH) capabilities (i.e., activity for C-H bond breaking in alkanes). The results from these studies serve to build a database for bimetallic catalysts and lead to strategies for the design of bifunctional metal alloy clusters for ODH-EO catalysis.

A combined experimental/theoretical analysis of the propylene EO catalysis data was completed on silver trimers. This work provided us with key information needed to develop EO-ODH bifunctional catalysts.

Experimental/theoretical studies provided important data for determining which mono-metallic clusters are optimal for ODH. They also revealed a possible reason for the higher temperature required for ODH on Pt clusters — a potential roadblock — and how to tailor metal alloy clusters to overcome this obstacle. These results were incorporated into our strategy for the development of ODH-EO bifunctional catalysts. The catalytic activity of Co_4 clusters for ODH of cyclohexane is shown in Figure 1.

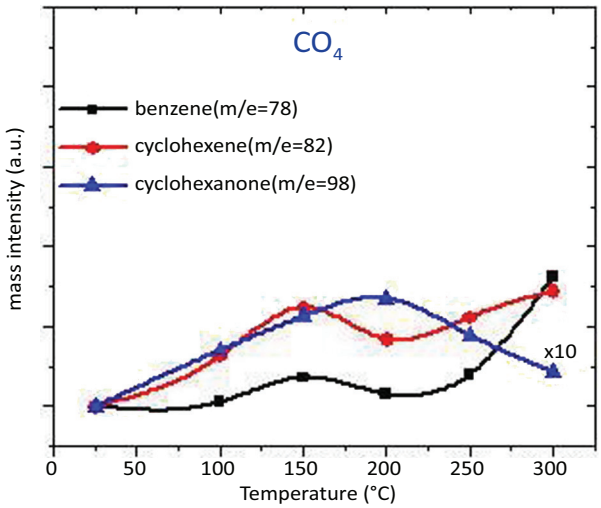


Figure 1. Temperature-programmed reaction (TPRx) data on alumina-supported partially oxidized Co_4 clusters in the ODH of cyclohexane. The intensities in the data represent the amounts of different species formed in the ODH process. They reveal that cyclohexene starts forming at temperatures as low as 100°C and is the major product at the lower temperatures. They also indicate that the cyclohexanone is a minor product (it has been scaled by a factor of 10 so it can be seen). Benzene is formed at the the upper end of the temperature range.

Theoretical calculations were performed on Ag/Pt alloy clusters, and they show that Pt retains its high activity for C-H bond breaking in the bimetallic cluster. This is one of the keys to our strategy for making a successful ODH-EO bifunctional catalyst. We also initiated studies of oxygen-molecule dissociation from alloy clusters on an alumina support, another key to our strategy. The structure of a Ag_2Pt_2 cluster on alumina before and after O_2 dissociation is shown in Figure 2.

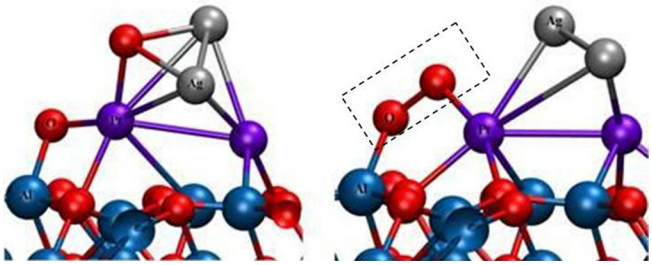


Figure 2. Structure of Ag_2Pt_2 cluster on alumina with O_2 adsorbed (right) and dissociated (left). The O_2 is shown in the rectangular box on the right.

Proposed Work for FY 2011

Bimetallic, bifunctional clusters of various compositions will be studied experimentally; the initial size and composition of the clusters will be based on the size of the best-performing monofunctional catalyst. Structural information from theoretical modeling will be central to predicting surface compositions that would mimic the optimal active sites identified for the dehydrogenation and for the subsequent selective-oxidation step. Computational studies will be focused on predicting likely candidates for experimental examination of the monofunctional catalysts and their combination into bifunctional catalysts. To attain the goals, many possible combinations of alloy clusters and supports must be considered. We will use density-functional calculations to screen bimetallic clusters to find possible candidates that will provide for better activity and selectivity. We will also investigate different support materials such as Al_2O_3, MgO, ZnO, and carbon nanotubes to determine if any of them will improve the performance of the catalyst by raising or lowering activation barriers. Plans for FY 2011 include the following:

- Finish theoretical/experimental assessment of mono-metallic clusters for propane ODH with the goal of finding optimal candidates for the low-temperature performance needed for bifunctional catalysis and resistance to sintering.
- Investigate size dependence of propylene EO of Ag_n clusters to determine optimal size for bimetallic clusters.
- Initiate experimental studies to assess bifunctional catalysis on Ag_nPt_m alloy clusters.
- Complete theoretical studies of propane ODH on supported Ag_nPt_m clusters and initiate studies of configurations optimal for both dehydrogenation and EO.

Trapped-Field Magnets: A Paradigm Shift for Applications of High-Field Magnets at a Synchrotron

2010-138-N0

Zahirul Islam and Jonathan C. Lang

Project Description

The primary objective of this project is to develop a practical continuous-field magnet based on high-temperature superconductors (SCs) to mitigate two long-standing problems in x-ray and neutron scattering studies in applied magnetic fields: (1) limited optical access and (2) the practical impossibility of applying magnetic fields parallel to the x-ray (neutron) momentum transfer. It is quite common for researchers to face the need to measure order parameters (OP) with the primary ordering vector parallel to the applied magnetic fields (**B**) and determine OP anisotropy by measuring the dependence of scattering intensity on azimuth (i.e., rotation of the sample around the momentum transfer). By using conventional split-pair and solenoid geometries, these measurements are in general impossible to carry out. To overcome these deficiencies, we are developing an application of superconducting magnets. In this approach, a single-crystal sample, of dimensions smaller than a human-hair cross-section, is mounted on the surface of a melt-textured bulk SC the size of a dime. Once magnetized by trapping flux below the superconducting transition temperature T_c, such a SC acts as a permanent magnet (known as a trapped-field magnet, TFM) with **B** normal to the TFM surface. As a result, the sample is in an ideal geometry for photon-in (k_i) and photon-out (k_f) scattering experiments with unrestricted optical access to the entire hemisphere.

Mission Relevance

This project is relevant to DOE's mission in science. The study of materials under extreme conditions (such as very high magnetic fields) has been identified as one of the long-term missions of DOE-BES. The DOE funds a large number of programs to explore the properties of energy-related functional materials, superconductors, frustrated magnets, spin-gap compounds, and oxides, among others. The proposed TFM application has the potential to generate DC fields in excess of 15 Tesla. As a result, it will open up new opportunities for studying field-induced properties in these materials.

FY 2010 Results and Accomplishments

This past year, we have worked out the physical specifications for initial square- and cylinder-shaped disks of YBCO (yttrium-barium-copper-oxide) melt-textured bulk superconductors to be used as TFMs. Disks of smaller dimension were determined to be sufficient, since the initial scope of this project involved trapping fields only up to ~4–5 Tesla. We focused on the homogeneity of chemically induced pinning centers, which can be optimized for smaller disks. Furthermore, the maximum field these disks can trap before becoming mechanically unstable was considered. The dimensions chosen for these disks are 8–12 mm in diameter and 4–6 mm in thickness. They can easily trap 10 Tesla and fit into the compact closed-cycle cryostat discussed below. The sizes are small enough to be within the high field-homogeneity volume inside the ~5-Tesla activation magnet. Figure 1 shows the characterization of a typical magnetic-field profile at liquid-nitrogen temperature, measured at a fixed distance (~0.8 mm) away from the surface

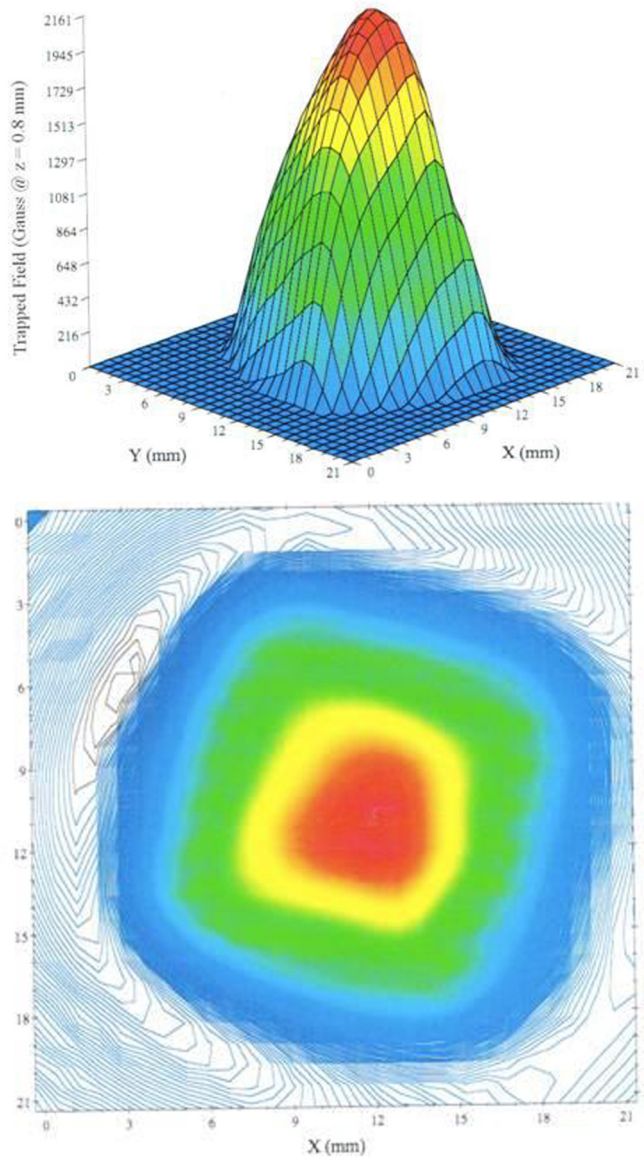


Figure 1. Top: Magnetization profile of a small YBCO magnet. Bottom: Contour plot showing practically uniform magnetic fields over millimeters around the center parallel to the surface at a given height.

of a TFM disk. The SC was field cooled through T_c and then the external field was reduced to zero to trap magnetic flux. At these temperatures, the maximum trapped field, $B_{trapped}$, is of the order of ~2 Tesla on the surface. Note that there is a single peak near the center of the magnet. The peak has the shape of a steep dome, indicating that $B_{trapped}$ is close to its maximum value for this temperature. It is important to note that even though $B_{trapped}$ is close to the maximum, the field at a given distance from the surface is practically uniform over a length scale of millimeters around the center.

We procured a cryostat that is compact for portability while cold, low in weight, and capable of reaching ~3 K. We have built a multi-port feedthrough instrumentation skirt, vacuum shroud with Be hat, radiation shield, and TFM chamber in order to couple this cryostat to our existing superconducting magnet and diffractometer. We have implemented an array of micro-Hall probes with its special PC-based control system and software. We have also installed an AC resistance bridge to monitor resistance of the TFM as needed. A cryostat support with translation stage to insert the TFM into the magnet has been assembled. Figure 2 shows the ~5-Tesla magnet and the new cryostat, illustrating how the activation process will be implemented. First, the TFM magnet will be cooled down to ~120 K, above T_c (~93 K), and translated to position the TFM at the magnet center. Then the magnet will be ramped slowly to the desired activation field, and the TFM will be field cooled to 60–70 K. The activation field will be reduced slowly to zero, and the heater for the TFM will be turned off immediately in order to continue cooling to operating (measurement) temperatures, which are typically well below 40–50 K. The process of magnetizing at higher temperature than the operating temperature practically eliminates thermal fluctuations of the trapped field.

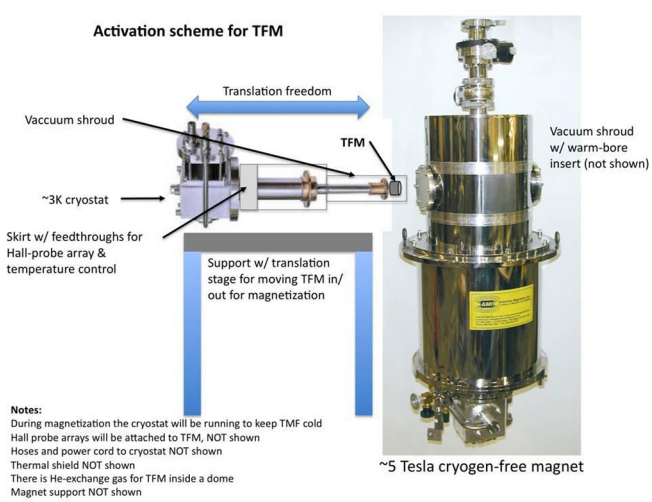


Figure 2. Illustration of activation process by using the ~5 Tesla magnet and cryostat.

Proposed Work for FY 2011

We will carry out the activation process by using the existing cryogen-free magnet, determine field profile across the TFM surface by using a Hall-probe array, identify thermal instabilities (if any), and determine appropriate operational parameters (e.g., temperature and field ranges) for applications. We will perform on-line tests to develop the instrumentation, including tests of the effects of local radiation heating with controlled exposure using fast shutters. Preliminary scientific studies will include measurements of longitudinal magnetostriction and resonant-scattering determination of meta-magnetic phases in rare-earth intermetallic compounds.

Study of Superconducting Films Made by Atomic Layer Deposition

2010-156-N0

Jeffrey W. Elam, Andreas Glatz, Michael J. Pellin, Thomas Prolier, and Valerii Vinokour

Project Description

The overall goals of this project are to reduce the operating and capital cost of superconductor-based devices by increasing their performance and reducing the amount of bulk materials needed.

In particular, the superconducting properties of materials in a magnetic-field environment are limited by magnetic flux, or vortices, penetrating into the bulk material in fields greater than the critical field H_{c1}. An idea developed by Alex Gurevich (APL, 88, 012511 [2008]) suggests that a multilayer structure of tens of nanometers of alternating superconductor/insulator films on top of a bulk superconductor screens the external magnetic fields and prevents the entry of vortices — which would degrade the device's performance — into the bulk. This new technology can be applied to superconducting wires for magnets and electrical networks to increase their performance. Also, the major costs associated with any high-quality bulk superconductor come from the material itself, its processing, and cryogens. A few micrometers of superconducting film on an inexpensive substrate should preserve the performance of the bulk thickness (centimeters) currently used in superconducting devices. Processing the surface *in situ* by deposition of the multilayer structure, all in one step, will deliver a less-expensive product with better performance.

This approach relies on the ability to coat conformally arbitrary substrates/devices of complex shape with atomic-scale control. To our knowledge, only one technique is able to meet these challenges: atomic layer deposition (ALD). ALD is

also an inexpensive synthesis method that has already been scaled to industrial applications. Therefore, the scope of this work is to study the growth and optimize the properties of superconducting compounds synthesized by ALD, such as NbN, NbTiN, TiN, MoN, MoNbN, and NbSi.

Mission Relevance

Office of Basic Energy Sciences. A recent report, "Basic Research Needs for Superconductivity," discusses the coming needs for new superconducting-based technologies to address the increasing demand for electricity and the efficiency of energy delivery through wires (i.e., the power-grid problem: "Superconductivity offers powerful new opportunities for restoring the reliability of the power grid and increasing its capacity and efficiency."). We understand that The Office of Electricity Delivery and Energy Reliability plans to issue a call for research proposals to address these problems.

Office of High Energy Physics (HEP). The Fundamental Research in Superconducting RF Cavities program and the corresponding recent call for proposals indicate a serious interest by HEP in boosting the performance of accelerator devices using new superconducting technologies.

Several defense-related agencies have also shown interest in technologies that rely on high-performance superconductors.

FY 2010 Results and Accomplishments

During the past year, we conducted an extensive synthesis effort using thermal ALD. For the first time, several alloys made by ALD, such as TiN, NbSi, NbCN, NbN, MoN and NbTiN, were found to be superconducting with homogeneous properties all along the reactor length of ~30 in. Homogeneity is particularly crucial for radio frequency applications, as a local lower-superconducting phase will create a hot spot and significantly degrade the cavity performance (as has been shown for Nb). We increased the superconducting transition temperature, T_c, of our NbTiN films by a factor of 4, from 3 K to 12.5 K, the highest ever reported, for a film thickness of 30 nm (Figure 1, top). This improvement was only possible through a careful investigation of the optimal growth parameters; as an example (Figure 1, bottom), the T_c of our films can be increased by varying the amount of TiN with respect to NbN during film growth and by increasing the deposition temperature.

We also investigated different chemistries; for instance, adding a fourth component, Zn, was found to greatly improve the film's superconducting properties (blue curve in Figure 1, bottom). Elemental and structural analysis (done by x-ray photoemission Spectroscopy, Rutherford Back scattering, and x-ray diffraction) show that the best films are stoichiometric with the (Nb+Ti)/N ratio of 0.98 — they are very pure with concentrations of impurities of 0.05% and crystalline in the (200) cubic δ-NbN phase, even on an amorphous substrate. The size of the crystallites is found to be on the order of the film thickness (up to 80 nm). These results are very encouraging, as ultimately the multilayer will have to be grown on amorphous oxides, and among all the phases that NbN can have, cubic is the one with the highest T_c (16 K). Similar improvements and results were obtained for MoN grown by ALD (not shown).

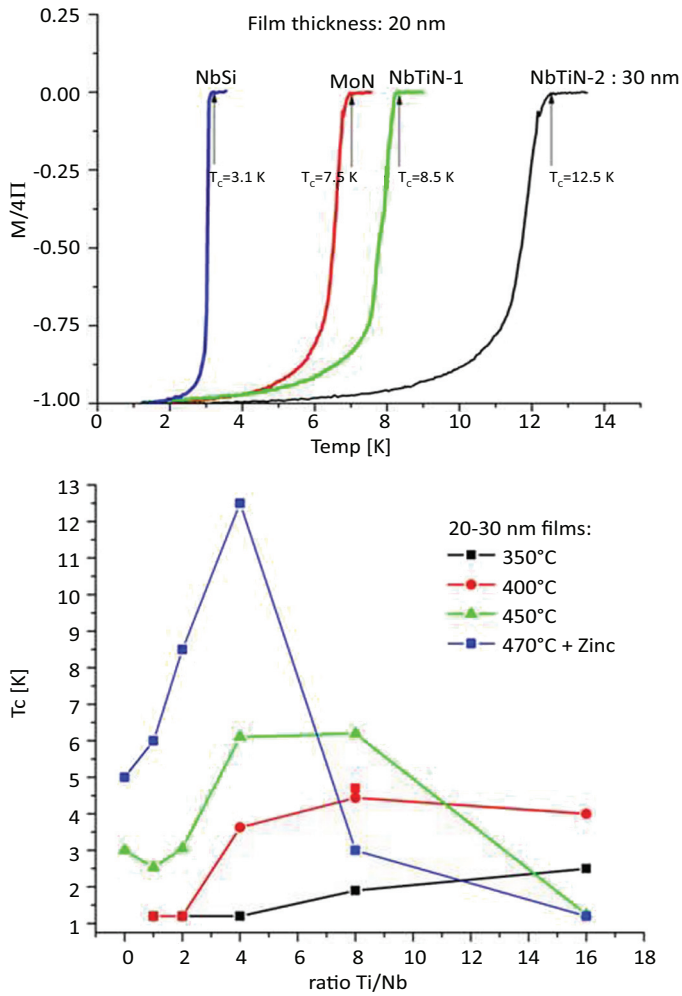


Figure 1. (Top) T_c of various alloys made by ALD, measured by SQUID. (Bottom) an example of the optimization of T_c as a function of selected growth conditions, here the Ti/Nb ratio (as programmed during ALD growth) and the synthesis temperature.

Motivated by the good superconducting properties obtained for NbTiN, we invested our effort in growing a multilayer structure. We grew 10-nm AlN films by ALD with material properties identical to the bulk. The multilayer structure (40 nm NbTiN/10 nm AlN) was also found to grow successfully on a variety of substrates — for example, Nb single and poly-crystals, sputtered Nb film on sapphire, quartz, and silicon (100); each material preserved its individual properties when grown together.

An invention report has been filed on NbSi superconducting films made by ALD. Another invention report is in preparation for the multilayer structure AlN/NbTiN and its superconducting properties.

Proposed Work for FY 2011

We will optimize the superconducting properties of NbTiN and will study, in parallel, the growth of MgB_2 and FeSeTe pnictide superconductors. Milestones for FY 2011 include:

- Demonstrate the screening properties of a NbTiN/Al multilayer and to coat it on a high-aspect-ratio superconducting structure and
- Show that MgB_2 and FeSeTe can be synthesized by ALD.

Refereed Publications

Prolier, T., Y. Ha, J. Zasadzinski, G. Ciovati, P. Kneisel, C. Reece, R. Rimmer, A. Gurevich, L. Cooley, G. Wu, M. Pellin, J. Norem, J. Elam, and C. Antoine, "Atomic Layer Deposition for SRF Cavities," in *Proceedings of PAC09,* Vancouver*, BC, Canada (2009)*, pp. 1–3**.**

Prolier, T., J. Klug, N. Becker, J. Elam, and M. Pellin, "Optimization of the Superconducting Properties of NbTiN Made by Atomic Layer Deposition," accepted for publication in *IEEE (Institute of Electrical and Electronics Engineers) Transactions on Applied Superconductivity* (Applied Superconductivity Conference 2010, Washington, D.C., August 1–6).

Non-Refereed Publications and Presentations

Klug, J., T. Prolier, N. Becker, J. Elam, and M. Pellin, "Growth of Thin Transition Metal-Based Superconducting Films by Atomic Layer Deposition," presented at the MRS (Materials Research Society) Fall Conference, Boston, MA, symposium : "Atomic layer deposition", November 28, 2010.

Prolier, T., J. Klug, N. Becker, J. Elam, and M. Pellin, "Optimization of Superconducting NbTiN Made by Atomic Layer Deposition," presented at ASC (Applied Superconductivity Conference) 2010, Washington, D.C., August 1–6, 2010.

Prolier, T., J. Klug, N. Becker, M. Kharitonov, H. Claus, and M. Pellin, "Summary of SRF Project at Argonne National Laboratory," presented at the SCRF ILC-CLIC (Superconducting Radio Frequency International Linear Collider-Compact Linear Collider) meeting, Geneva, Switzerland, October 20, 2010.

Prolier, T., J. Klug, J. Elam, and M. Pellin, "Superconductors Made by Atomic Layer Deposition," presented at the 6th SRF Materials Workshop, Tallahassee, Florida, February 18, 2010.

Converting CO_2 to Fuel through Functionalized MOFs

2010-158-N0

Di-Jia Liu, Liaohai Chen, and Shengqian Ma

Project Description

The concern over global climate change has drawn unprecedented public attention to CO_2 emissions. At present, the only viable technology for carbon dioxide capture and storage is to concentrate CO_2 into a nearly pure form before pumping it underground or to the ocean bottom. Such a process consumes additional fuel and adds to the electricity cost paid by consumers. The objective of this project is to develop a new class of dual-property materials, functionalized metal-organic frameworks (MOFs), that can effectively trap CO_2 and photocatalytically or enzymatically convert it to methanol or other chemical fuels. The goal is to provide economical and environmental benefits by not only capturing CO_2 but also converting it to value-added products. MOFs can be synthesized through solvothermal reactions between organic linkers and secondary building units (SBUs) of transition metals, as shown in Figure 1. Our approach is to incorporate photocatalytic activity or enzyme size selectivity in MOFs through rational design and synthesis while retaining a high CO_2 storage capacity. Such designs could create high concentrations of CO_2 localized inside the confined spaces proximate to the reaction center, thus enhancing the conversion rate and equilibrium towards final products that are otherwise difficult to achieve.

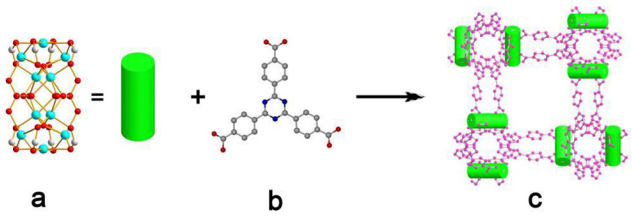


Figure 1. An example of preparing a functionalized MOF: (a) multinuclear metal oxide SBU, (b) aromatic carboxylate ligand, (c) porous MOF with regularly arranged catalytic active sites.

Mission Relevance

This project is relevant to DOE's missions in science and energy. Mitigating the environmental impact of CO_2 emissions from fossil fuel consumption represents a key DOE mission. Converting solar energy for a variety of applications represents a key initiative at DOE. Next-generation adsorbent and photocatalyst materials represent key components in the future energy-efficiency and renewable-energy-technology portfolio.

FY 2010 Results and Accomplishments

We designed and synthesized a wide range of MOFs by using transition metal M (M = Zn, Mg, Cu, Ti,...) as the metal center, coordinated by various organic ligands. Over 200 solvothermal reactions were carried out, and about 40% of the preparations yielded MOF crystals. We synthesized several series of MOFs using rational design by systematically varying either the SBU cluster size or the organic-ligand dimension. For material characterization, we carried out x-ray diffraction experiments at the Advanced Photon Source to study the single-crystal structure. One or more new MOF crystals were detected. Meanwhile, we completed the modification of a Sievert-type apparatus in our laboratory for measuring the CO_2 adsorption isotherm for prepared MOFs.

One example of our approach involved systematically adjusting the photo-absorption band-gap of the MOF as the first step toward improving photocatalytic conversion efficiency. The inorganic metal clusters used as the SBUs in an MOF can be considered as discrete quantum dots, which are stabilized and interconnected by the conjugated organic linkers acting as the photon antenna. By improving the level of electronic conjugation in the ligand, one would expect a lowering of the band gap ("red shift") of the entire MOF. To demonstrate this effect, we prepared MOFs by using fumaric acid, benzenedicarboxylic acid and 2,6-naphthalene dicarboxylic acid as ligands in combination with Zn_4O as the SBU. The resulting MOFs, prepared via solvothermal reactions, have α-Po-type framework structures. We observed a red shift of the band-gap energy from 4.13 to 3.80 to 3.27 eV when the functional group connected to the dicarboxylic group changed from ethylene to benzene to naphthalene.

Proposed Work for FY 2011

We plan to continue developing various MOFs and other porous-oxide-based materials for CO_2-to-fuel conversion. We will explore Zn, Ti, and other metal-based SBUs with different cluster sizes and structural compositions. We also plan to explore the photocatalytic activity of CO_2-to-fuel conversion by using porous organic polymers (POPs) as bifunctional materials on the basis of the discoveries and the recently developed expertise of our project team. Such an approach adds the flexibility of incorporating a catalytic activity center without the limitations of SBU/ligand compatibility or hydrothermal stability.

Refereed Publications

Ma, S., C.-K. Lin, D. Zhao, S. Yuan, T. Xu, and D.-J. Liu, "Tuning Band Gaps of Metal-Organic Frameworks via Ligand Functionalization," *Chemical Communication*, submitted, 2010.

The Biochemistry of Plant-Fungal Symbiotic Relationships

2010-161-N0

Deborah K. Hanson, Frank R. Collart, and Philip D. Laible

Project Description

Trees develop complex symbiotic associations with soil fungi such that the interactions provide nutritional benefits to both partners. The scientific goal of this project is to study the proteins, such as transporters and two-component sensory systems, which participate in important symbiotic and nutrient exchange interactions between plant and fungal species. Its focus is on the fungal transporters that are extremely important in the utilization and regulation of carbohydrates, phosphorous, and nitrogen. To date, the biochemical and structural characterization of many of these enzymes is hampered because they are integral membrane proteins that require a hydrophobic environment to maintain their stability and functional integrity. This project seeks to develop systems to support the production of workable quantities of membrane-bound transporters for functional characterization.

Mission Relevance

This project is relevant to DOE's missions in science and the environment. Because approximately 25–30% of every genome encodes membrane proteins, the study of these proteins is essential to meeting the goals of multiple research areas in DOE's Office of Biological and Environmental Research (BER). In its Genomes-to-Life, Carbon Sequestration, Climate Change, and Environmental Science programs, BER's goals include using emerging genomic sequence data for "studying the proteins encoded by microbial and plant genomes to explore their amazingly diverse natural capabilities."

FY 2010 Results and Accomplishments

This project focuses on proteins derived from the fungus *Laccaria (L.) bicolor* and poplar, which serve as a laboratory model for fungal-plant symbiosis. Previously, we had analyzed transcripts obtained from genes expressed when symbiosis between *Laccaria* and poplar is established in culture, revealing the activity of eight transmembrane carbohydrate transporters. Seven of these genes were cloned from *Laccaria bicolor* by G. Podila's group at the University of Alabama – Huntsville and were provided to our team members for cloning into expression vectors. The target set will expand as more transporters are identified from the *Laccaria*-poplar co-culture experiments, and we have initiated contact with the laboratory of F. Martin (INRA, France) to facilitate future cloning of additional genes for expression.

The initial set of transporter genes was cloned for expression in the prokaryotic organisms *E. coli* and *Rhodobacter (R.) sphaeroides* and in the eukaryotic yeast *Pichia (P.) pastoris* (Figure 1). Cloning of the genes into different vectors for expression of affinity-tagged versions of the target proteins in *R. sphaeroides* and *E. coli* was completed, and the generation of *P. pastoris* expression plasmids is in progress.

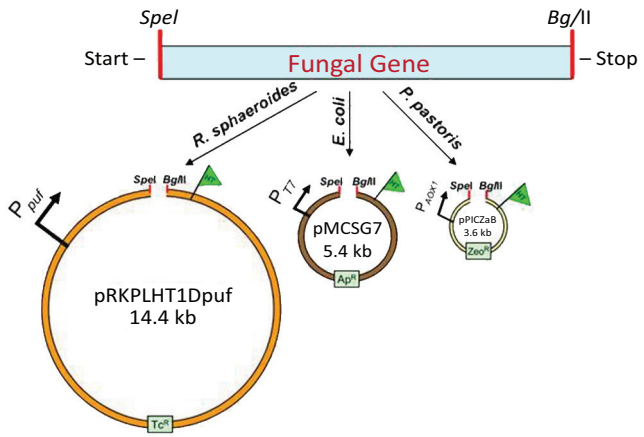


Figure 1. Cloning strategies allow for straightforward incorporation of the genes via SpeI *and* BglII *restriction sites into three different host organisms with minimal manipulation. Each engineered expression vector carries a promoter (P) that is specific to the desired host (P_{puf}, P_{T7}, or P_{AOX1}, as indicated for each host) and encodes an affinity tag (HT) for detection and purification of the expressed protein. Antibiotic resistance markers for selection of each expression plasmid are also indicated (tetracycline, Tc^R; ampicillin, Ap^R; zeocin, Zeo^R).*

Initial results were obtained for polyhistidine-tagged target proteins expressed in the *R. sphaeroides* system. Membrane proteins expressed in this organism are localized to its intracytoplasmic membranes. Expression of several target proteins appears to be promising, especially of transporter 300971. Purification of polyhistidine-tagged transporter 300971 from large-scale cultures of *Rhodobacter* is in progress, employing the tag in affinity chromatography strategies. Initial purification experiments made use of the detergent Deriphat 160. Future purification attempts will implement other detergents and solubilization conditions to identify the conditions that extract the transporter from the membrane quantitatively while maintaining its functional integrity.

In preparation for functional assays of the transporters that are planned for FY 2011 and FY 2012, we succeeded in producing several types of membrane fractions from *Rhodobacter* by using different conditions for cell lysis followed by differential centrifugation and sucrose density gradient fractionation. These procedures yielded discrete membrane populations that are enriched in the target protein and will be the initial subjects for functional assays to determine the activities of membrane-bound transporters produced by *Rhodobacter* expression strains. A notable difference between these subpopulations is their "sidedness," and this feature will be exploited in the development of assays of substrate binding and activity.

Proposed Work for FY 2011

We will complete the construction of expression strains for the target transporter proteins and develop assays for functional analysis of transporter specificity. The challenge for this experimental component is the development of ligand libraries that reflect the diversity of carbohydrate polymers and their degradation products. We will use heterogeneous libraries derived from partial degradation of complex carbohydrates (e.g., xylans, glucans, mannans, chitin) for initial screens followed by secondary screens to refine transport specificity. This approach can link the activity and regulation of particular types of transporters to the characteristics and components of biomass derived from field samples.

DIRECTOR'S GRAND CHALLENGE

Beyond Lithium-Ion Battery Technology for Energy Storage

2010-185-N0

Khalil Amine, Mahalingham Balasubramanian, Zonghai Chen, Larry A. Curtiss, Jeffrey P. Greeley, Christopher Johnson, Di-Jia Liu, Nenad M. Markovic, Yang Ren, Yugang Sun, Michael M. Thackeray, Lynn Trahey, and Zhengcheng Zhang

Project Description

The inherent energy potential of lithium metal approaches that of gasoline; however, unlocking that potential has eluded today's battery manufacturers. While today's lithium-ion batteries may provide acceptable amounts of energy to power hybrid electric vehicles (HEVs) and all-electric vehicles (EVs), they do not provide sufficient amounts of energy over an acceptable driving distance. This range limitation and the absence of a battery-charging infrastructure have limited public interest in EVs, particularly for long-distance travel. A breakthrough in Lithium-air (Li-air) battery technology would significantly increase the possibility of extending the electric range of these vehicles, with the added advantages of reducing battery cost and weight. Severe materials and technological problems have limited electrochemical performance for these reasons: (1) the nonaqueous electrolytes are unstable at high potentials and are easily oxidized by the oxygen released during charge, thereby seriously limiting cycle life; (2) during discharge, the solid and insoluble Li_2O_2 (lithium peroxide) and/or Li_2O products are deposited on the surface or within the pores of the carbon cathode, thereby clogging the pores and restricting oxygen flow; (3) the poisoning of the lithium electrode resulting from oxygen crossover destroys the integrity and functioning of the cell; and (4) commonly used cathode catalysts, such as MnO_2 or Mn metal, do not access the full capacity of the oxygen electrode or enable sufficiently high rates.

In this project, a multidisciplinary team is focused on finding solutions to the severe limitations of the electrolytes and electrode catalysts in present-day Li-air cells. By using new approaches that combine innovation in advanced electrode, electrolyte, and catalytic materials research (and assisted by extensive computer modeling and use of advanced characterization techniques), the team seeks to enable development of a Li-air battery system with exceptionally high energy density and reversibility.

Mission Relevance

This project is relevant to DOE's missions in energy and science. The major benefit will be the development of a reversible Li-air battery that provides many times the energy density of the state-of-the-art lithium ion battery for powering electric vehicles. The discovery and development of new materials needed to support the lithium-air technology is relevant to DOE's mission to promote development of new energy technologies that can enhance U.S. energy security. The technology can also benefit many U.S. Department of Defense military applications that require very high energy density, such as satellites, EV tanks, and military vehicles for "silent watch" and operation. It will be of interest to the automotive and satellite industries and the military. In addition, if the technology is applied successfully to large batteries, it can be easily scaled down for consumer electronic applications, as well.

FY 2010 Results and Accomplishments

Electrolyte Research and Development (R&D)

Siloxane-Based Electrolytes. Our main focus in the first year was to investigate the siloxane-based electrolyte with the formula 2SM3. The 2SM3 solvent has many advantages over its carbonate-based electrolyte counterpart: it is nonvolatile and highly resistive to oxidation and reduction, has good wetting characteristics and good conductivity, and is nonflammable (or has self-extinguishing properties, i.e., thermal stability). The preliminary test of the 2SM3 electrolyte showed that the siloxane electrolyte can deliver high charge and discharge capacity and cycling performance. Screening work on low-molecular-weight silane, such as 1NM3, showed some promise. Compared with 2SM3, 1NM3 has higher conductivity, a higher dielectric constant, and lower viscosity. Initial first charge and discharge profiles are shown in Figure 1. Compared to a carbonate-based propylene electrolyte, 1NM3 can deliver higher charge and discharge capacity and shows similar voltage polarization because of its high conductivity and good compatibility with the air cathode.

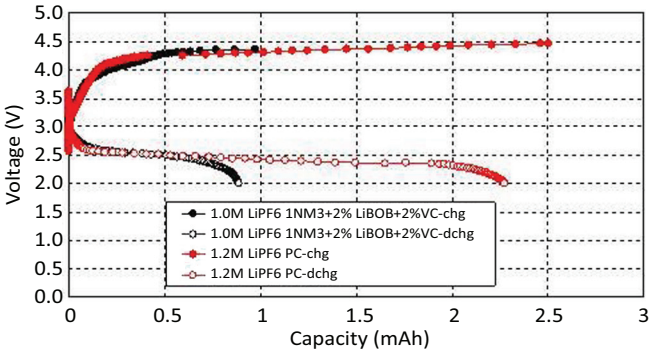


Figure 1. Charge and discharge profiles of a lithium-air cell using the 1NM3 electrolyte.

Additives. We also investigated the electrolyte additive effect on the performance of the Li-air cell. Our main focus was on the boron-based anion receptors to dissolve Li_2O_2 and prevent clogging of the porous structure of the air cathode. The anion receptors we selected are tri(pentafluorophenyl)benzene (TPFPB), 2-(pentafluorophenyl)-tetrafluoro-1,3,2-benzodioxa borole (PFPTFBB), and 1,1,1,3,3,3-hexafluoroisopropyl borate (HFPB).

Membranes. Accomplishments in the first year included (1) development of methods for fabricating test cells; (2) evaluation of lithium-ion conductivity in the single crystalline silicon membranes with varying thicknesses; and (3) *in situ* characterization of the structural variation of the silicon membranes with lithium present under electrical fields by using time-resolved, high-energy x-ray diffraction (HEXRD). A series of XRD patterns obtained at different times indicates that there is essentially no change. As a result, the single crystalline Si membrane may be promising for use as a membrane in the Li-air batteries to protect the Li anodes because of its high conductivity of Li ions and the extremely low diffusion coefficient of air.

Theory and modeling of electrolytes. Density functional calculations were used to help understand the properties of the new siloxane-based electrolyte systems that can resist oxidation at high voltage. In particular, we studied the thermochemistry of siloxane electrolyte decomposition, siloxane oxidation potentials, and siloxane complex formation with lithium ions. For example, the thermodynamic stability of the siloxane-based electrolytes with various ligands and spacers was investigated by calculating the thermochemistry of defragmentation patterns. The results suggest that the strength of the Si-O bond is the key to the stability of the siloxanes.

Catalyst R&D

Lithium metal oxides. Several potentially relevant electrocatalysts were designed and synthesized for evaluation at the University of St. Andrews (Scotland). These catalysts included sol-gel synthesized Li_2MnO_3 and Li_2MnO_3•$LiFeO_2$, their acid-treated analogues, and Li_5FeO_4. The materials were chosen on the basis of group experience studying transition metal oxides with high surface area. Cycling data indicate that the acid-treated forms of Li_2MnO_3 and the Fe-containing composite were the superior electrocatalysts in terms of cell capacities, cycle life, and (lowest) charging voltages. We are currently investigating the structural properties of the acid-treated electrocatalysts to elucidate the reasons for their superior performance. The reasons most likely include reduction in particle size, roughening of particle edges, and changes in the transition metal's local environments.

Ex situ *Advanced Photon Source (APS) experiments.* At the APS, we studied two sets of electrocatalyst materials, namely Li_2MnO_3 and Li_2MnO_3•$LiFeO_2$, along with their acid-treated analogues. The structural characterizations of these compounds were carried out by using HEXRD and x-ray absorption spectroscopic (XAS) measurements. We found that the acid-treated Li_2MnO_3, which shows very promising electrocatalytic activity, is a mixture of two types of MnO_2 structures: one with a 2-x-2 tunnel hollandite-like structure and the other with a ramsdellite-like structure with 1-x-2 tunnels. Rietveld refinements are shown in Figure 2. Analysis of extended x-ray absorption fine structure (EXAFS) data of acid-treated Li_2MnO_3 showed that the edge sharing and corner sharing Mn-Mn correlations are present in a 1:1 ratio. This result is consistent with the Rietveld refinement of the HEXRD data of the acid-treated Li_2MnO_3, as both the ramsdellite- and hollandite-type structures contain edge and corner sharing Mn-Mn correlations in a 1:1 ratio. We believe that this topological approach in understanding the structure could provide significant insight into the possible structural changes accompanying the electrocatalytic activity of the material in a Li-O_2 electrochemical cell.

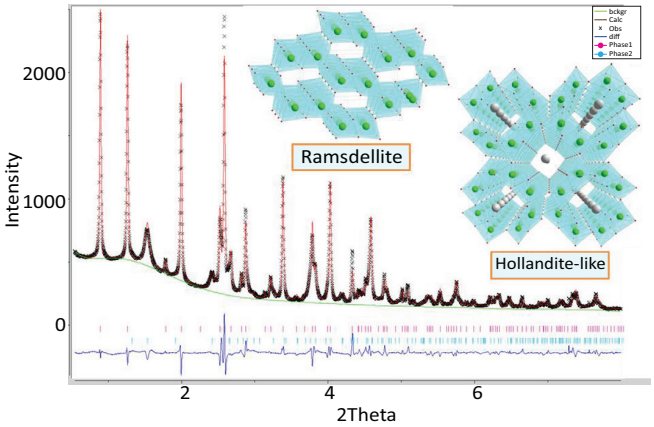


Figure 2. Rietveld-refined XRD pattern of the acid-treated Li_2MnO_3 using a mixture of ramsdellite- and hollandite-type structures along with the experimental pattern.

Reactivity and stability of interfaces. We are seeking to obtain a rational predictive understanding of three important factors that determine reactivity and stability of interfaces in Li-air systems: (1) formation of lithium oxide clusters on well-defined metal surfaces; (2) reactivity of the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER) on *3d* group metal oxide catalysts (M_xO_y; M = Ni, Co, Fe, Cr, Mn); and (3) stability of M_xO_y catalysts and Li_yO_x oxides, as well as nonaqueous electrolytes, at high voltages. To address these challenges, we have been developing *in situ* and *ex situ* experimental methods such as Differential Electrochemical Mass Spectroscopy (DEMS) and Scanning Tunneling Microscopy (STM) in our labs that will help define the landscape for the development of improved M_xO_y nanostructured catalysts.

Metal organic cathode materials. The research activity in this area was focused on developing a new composite cathode catalyst using metal doped organic frameworks as the precursor materials. The design target is to develop one or more dual functional catalysts with (1) minimum overpotential for oxygen reduction and lithium oxides reoxidation, (2) high catalytic active site density that is uniformly distributed throughout the conductive matrix, and (3) improved electrode architecture balancing between oxygen and solvent mass transfer. We used two parallel approaches using metal doped porous organic polymer (MPOP) and metal-organic framework (MOF) designs. Both classes of materials contain a highly porous organic matrix decorated by the uniformly and periodically distributed transition metal ions. Upon activation (such as by thermal treatment), the organic matrix is be pyrolyzed into an electron-conducting substrate, whereas metals are converted into zero-valence or oxidized states serving as the catalytic center to promote the oxygen reduction and reoxidation reactions. At the same time, significant fractions of porosity and surface area are maintained, which are critical for a catalyst. The results of testing of some of these new materials for Li-air cells have been promising in terms of high capacities on discharge and are being analyzed to understand what is causing the high overpotential.

Theory and modeling of interfaces. The theory and modeling component of this project is similarly focused on finding solutions to the severe limitations of the electrode catalysts in present-day Li-air cells.

- *Small lithium oxide clusters:* We calculated free energies for the charge and discharge of lithium oxide clusters with stoichiometries up to Li_6O_6, including Li_2O, Li_2O_2, and LiO_2 monomers, dimers, and trimers, and all reaction pathways involving the addition of Li and O_2 between them. This work provided free energies for Li_xO_y discharging and charging, together with the associated overpotentials. These calculations on small clusters are immediately relevant to the nucleation thermodynamics of Li_xO_y and, in future work, they will form the basis for studies of the catalytic effects of small metal and metal oxide clusters on Li-O bond breaking/formation reaction energies; these results, in turn, will be used to predict potential catalyst materials.

- *Lithium oxide nanoparticles:* We carried out molecular dynamics (MD) simulations of a series of $(Li_2O)_n$ and $(Li_2O_2)_m$ nanoparticles having up to 5,000 atoms. As part of this work, we carried out density functional calculations on bulk Li_2O, LiO_2, and Li_2O_2 to obtain potentials for use in the MD simulations. Figure 3 shows the structure of a $(Li_2O)_{500}$ nanoparticle with a total of 1,500 atoms as obtained from the MD simulations. By using these structures, we are also employing GPAW, a highly parallelizable electronic structure code on Argonne's Blue Gene/P machine, to carry out density functional calculations of the structure and energies of these nanoparticles.

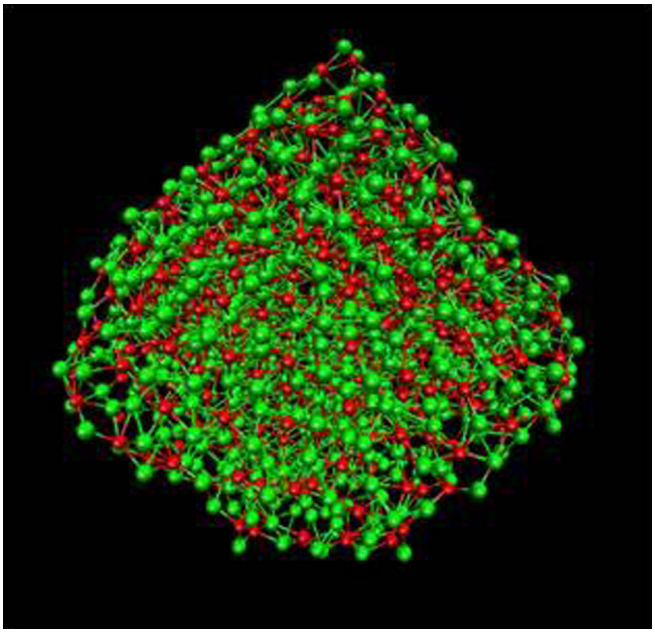
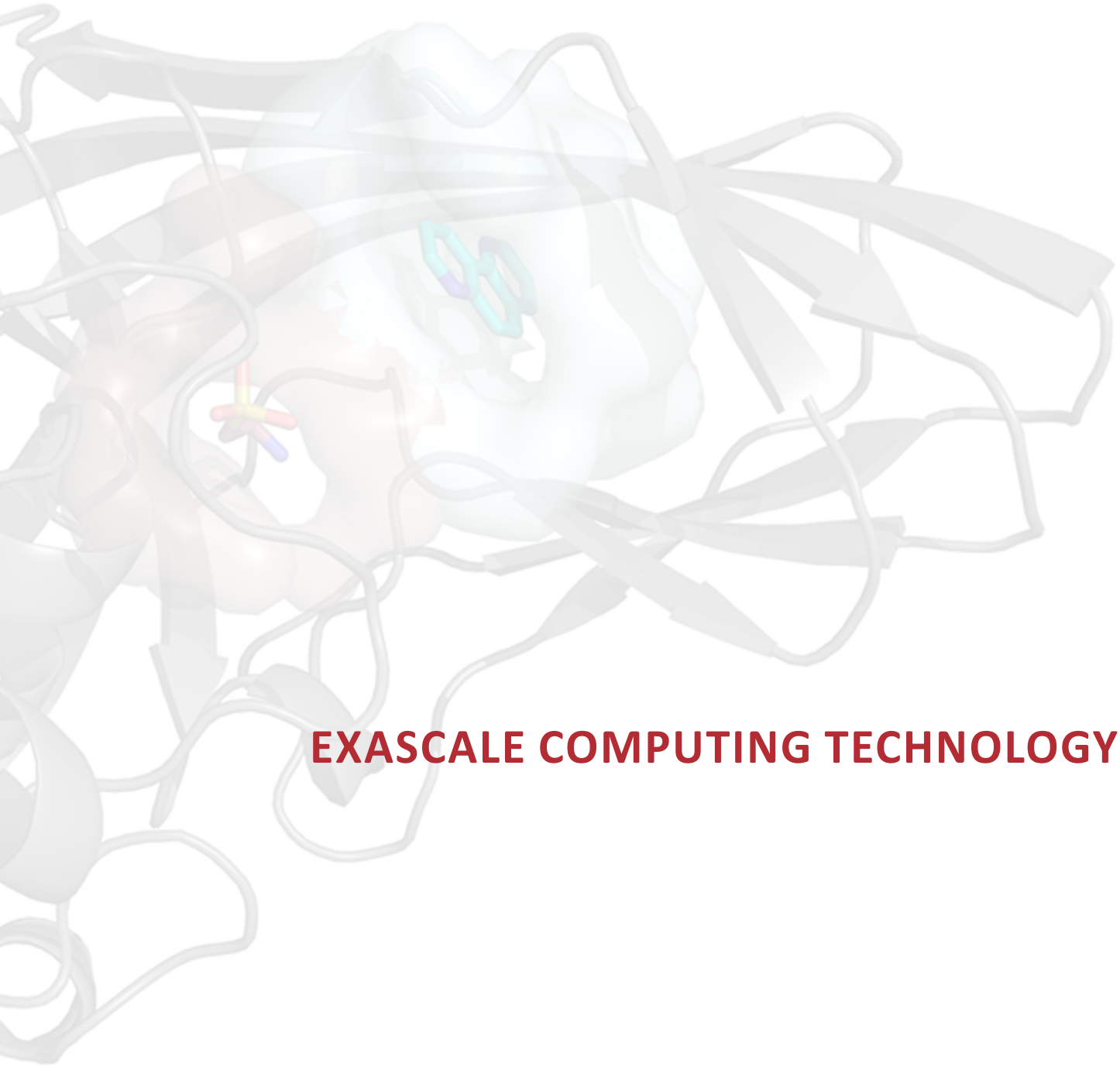


Figure 3. A $(Li_2O)_{500}$ nanoparticle computed on BlueGene/P using GPAW. These calculations are used to compute charge and discharge potentials.

- *Design of catalysts:* We are also applying the approach to generating free energies of the Li_yO_x cluster charging and discharging processes described above to metal-catalyzed charge/discharge processes. In this preliminary work, periodic density functional theory (DFT) calculations using standard generalized gradient approximation (GGA) functionals were employed to determine the energetics of Li_yO_x moieties of varying stoichiometries on close-packed transition metal surfaces. These energetics are then used to determine the metal-catalyzed charge/discharge potentials for the close-packed surfaces of each of eight transition metals (i.e., Au, Ag, Cu, Pt, Pd, Rh, Ru, and Ni).

Proposed Work for FY 2011

We will continue R&D on a siloxane-based electrolyte, additives, and membranes, as well as on the theory and modeling of electrolytes. We will build on our catalyst R&D work to continue exploring lithium metal oxides with respect to (1) synthesis of new catalysts, (2) X-ray studies, and (3) electrochemistry of oxidation/reduction of oxygen. The catalyst work will encompass reactivity and stability of interfaces, metal organic cathode materials, and the theory and modeling of interfaces.



EXASCALE COMPUTING TECHNOLOGY

Exascale Agent-Based Modeling System

2008-142-R2

Michael North, Charles M. Macal, Michael Papka, David L. Sallach, and Rick L. Stevens

Project Description

Agent-based modeling is an emerging computational simulation approach that allows system-level consequences to be derived from knowledge of individual-level choices. The successful application of this technology to a wide variety of domains demonstrates its potential to advance science, engineering, and policy analysis. However, realizing the full potential of agent-based modeling to find breakthrough results in research areas relevant to DOE missions requires far greater computing capability than is available through current agent-based modeling tools. This project is developing a next-generation agent-based modeling system explicitly focusing on exascale computing platforms. The system is leveraging Argonne's existing world-class capabilities, such as the Repast Simphony agent-based modeling toolkit, and distributed computing expertise to target multi-core chips; the aim is to scale to 10^6 to 10^7 threads. The design and implementation path of the exascale agent-based modeling system is being determined by a focused series of stepwise experiments. Each experiment is, in turn, driven by the chosen pilot application areas (i.e., microbial biodiversity and cybersecurity) and the requirements that were input for modeling the social aspects of climate science.

Mission Relevance

This project supports DOE's energy security, national security, environmental, and scientific discovery and innovation missions. It supports the energy security mission by developing a platform for testing the performance, feasibility, and utility of potential new energy technologies; studying the possible benefits and impacts of energy policies; and investigating the strengths and weaknesses of existing and proposed energy supply chains. It supports the national security mission by developing a platform for studying national security issues and policies, such as those embodied in the planned cybersecurity prototype model of the DOE laboratory computing infrastructure. It supports the environmental mission by developing a platform for testing environmental technologies and policies. The input on user requirements from experts on the social aspects of climate science helps to ensure the success of this thrust. Finally, the project supports DOE's scientific discovery and innovation mission by developing a platform for scientific investigation in many areas of basic science, as exemplified by the microbial biodiversity modeling effort.

FY 2010 Results and Accomplishments

During FY 2008, the first year of the project, we focused on user requirements analysis; implementation platform testing and selection; and initial system design and implementation. User requirements analysis meetings were held with representatives of each of the application areas, namely cybersecurity, social aspects of climate science, and microbial biodiversity. Design requirements spanning all three areas were derived. For implementation platform testing and selection, four viable candidate platforms were identified and initially investigated: pure message passing interface (MPI); MPI for inter-node exchanges, and either OpenMP or Pthreads for intra-node exchanges; Unified Parallel C (UPC); and Titanium. The top three alternative implementation platforms, namely UPC, Titanium, and pure MPI, were selected for further investigation, and initial experiments were performed. Two reports were prepared to document the results, namely, *Repast Simphony UPC Testing Report and Repast Simphony Titanium Testing Report*. As part of system design, the key algorithms that ultimately needed to be parallelized and strategies for successfully implementing them were identified and documented in a report titled, *How the Key Repast Simphony Algorithms Might Be Parallelized*. These areas include time scheduling, space management, spatial querying, agent watching, scenario storage, scenario initialization and restoration, and log storage. As part of system implementation, the top two runtime platforms, namely pure MPI and UPC, were used to implement selected functions identified in the initial project plan. The results of further testing eliminated UPC as a candidate. The pure MPI implementation was then tested for initial scalability on Argonne's Blue Gene/P. The testing was successful for the project's primary goal of achieving "weak scaling." Weak scaling is maintaining constant program execution time as the number of agents and the number of computing nodes simultaneously increase.

During FY 2009, we completed the initial version of the core exascale agent-based modeling platform; we completed a supporting Eclipse integrated development environment configuration; and we initiated design planning for the applications areas of cybersecurity and microbial biodiversity. The application area, social aspects of climate science, was rescoped to serving as a source of advising requirements to accommodate funding limitations. The core exascale agent-based modeling platform features included fundamental data structures for simulation, such as dynamic lists, linked lists, hash maps, priority queues, and graphs; an agent identification structure to uniquely track agents; a distributed discrete event priority queue scheduler; distributed discrete grid spaces; distributed network spaces; and aggregate and non-aggregate (i.e., per process) data collection and logging. During FY 2009, the platform implementation was also upgraded from C to C++. A fundamental ecological test simulation was implemented using the system components. The system was tested on Argonne's

Blue Gene/P, and benchmarked data were generated and documented in a report titled, *Exascale Repast Simphony Benchmark Results Report*. Excellent weak scalability was observed. The software components were subsequently documented, a tutorial was written, and the overall implementation was documented in a working report titled, *Exascale Repast Simphony C Implementation Report*. The Eclipse integrated development environment (IDE) configuration was also documented in a working report titled, *Exascale Repast Simphony Development with Eclipse*.

During FY 2010, we completed the exascale agent-based modeling system's feature set (the system was renamed Repast High Performance Computing, or Repast HPC); developed preliminary demonstration models for cybersecurity and social networking; prepared the platform for public release (which included extensive verification and validation work); and completed documents detailing the research progress, including a *Repast HPC Manual*. The resulting system is the first fully functional agent-based modeling platform for TOP500 supercomputers. It implements the core Repast Simphony concepts (e.g., contexts and projections), modifying them to work in a highly parallel environment. As mentioned above, we successfully tested the system for scalability on Argonne's Blue Gene/P. This achievement solves a long-standing problem identified in the research literature — and partly addresses a second such problem. Specifically, Repast HPC is the first complete agent-based modeling platform developed for and successfully tested on TOP500 computing systems. As such, it meets the discipline's need for a general purpose, agent-based model platform that is usable on TOP500 supercomputers. As a further example of the project's innovations, portable agent models can be written in either standard or Logo-style C++. The Logo-style C++ dramatically lowers the skill level required to develop computationally efficient models on TOP500 supercomputers. This innovation partly addresses another need: that scientists have increased accessibility to TOP500 systems. These technical innovations have been recognized in (1) an invited chapter for a Wiley book on high performance computing and agent-based modeling that is currently in press, and (2) an invitation from CRC Press to publish a book in its high performance computing series. Repast HPC is available online as a free and open source tool (http://repast.sourceforge.net/) and has been downloaded by nearly 300 users in more than 35 countries.

Refereed Publications

Collier, N.T., and M.J. North, "Repast HPC: A Platform for Large-scale Agent-based Modeling," in W. Dubitzky, K. Kurowski, and B. Schott, eds., *Large-Scale Computing Techniques for Complex System Simulations*, Wiley (In Press 2011).

Exascale Hardware Designs

2008-154-R2

Peter H. Beckman, Raymond A. Bair, Narayan Desai, Ewing L. Lusk, Robert B. Ross, Rick L. Stevens, and Rajeev Thakur

Project Description

Exascale systems will likely require between 10 and 100 million processing elements and will pose challenges in several key areas: processor architecture, power, and fault tolerance. This project explores hardware changes in the context of system software, algorithms, and application performance. Exascale computer architectures will be a radical departure from existing systems: slower processors with large core counts, very large numbers of processors, and a much greater imbalance between processing capabilities and memory and storage subsystems. Designing an exascale system will require the use of exotic power-efficient components in order to be practical in current facilities, even state-of-the-art ones, such as the SSF (Scalable Simulation Framework).

Mission Relevance

This project will benefit DOE's mission in science. The DOE is embarking on an initiative to develop exascale computing resources within the next 10 years. Exascale computing will fundamentally change our understanding of the world around us, unlocking secrets not only in fields that have been traditional users of high-end computing resources, such as climate modeling, astrophysics, combustion, and materials science, but also in areas only beginning to leverage the power of computation, such as economics and the biological sciences.

FY 2010 Results and Accomplishments

During the past year, we continued to use the SiCortex system as an exemplar of predicted future architectures. Using Mathematics and Computer Science (MCS) research projects in parallel programming models, parallel I/O (input/output), and scalable applications., we evalutated hardware design tradeoffs caused by low-power-processor designs, as exemplified by the SiCortex system. We will describe each effort in detail.

Several groups conducted work in models. By far, the most work was conducted with the Message Passing Interface (MPI); however, work with Unified Parallel C (UPC) and other programming models was also done. Most of the MPI work was done by the MPICH team in MCS. They developed new collective operation algorithms and implementations that are well suited to large-scale parallel systems. They also developed a new set of collective operations that are topology aware; these will be critical on upcoming large-scale systems where hierarchy is growing increasingly prominent. Finally, the Hydra

process manager was developed, which provides a scalable start-up mechanism for parallel processes on large machines.

Compiler development on the Pathscale compiler was performed on the SiCortex system. The SiCortex system uses a power efficient architecture comprised of low-power slow cores in large numbers. These compiler developments refined our understanding of the performance implications for applications on systems designed in this way.

Finally, work into alternative programming models has been conducted on the SiCortex system. The Active Directory Load Balancing (ADLB) system is a dynamic load-balancing library that is used to build scalable applications. Its initial target was the Quantum Monte Carlo (QMC) code built as a part of the Universal Nuclear Energy Density Functional (UNEDF) project. ADLB has primarily been developed on the SiCortex system; however, the QMC application was successfully scaled to 131,072 cores on the Intrepid system in the Argonne Leadership Computing Facility (ALCF).

Other work was done in scalable I/O. A port of the Parallel Virtual File System (PVFS) to the SiCortex architecture was performed. Also, some work on I/O forwarding was done on the system as well. This provided insight into the adaptations needed for system software on systems with many relatively slow cores.

Several application groups used the SiCortex system to analyze and tune application performance. The UNEDF project made extensive use of the system in preparation for use of the Intrepid system. The Nek5000 group also made similar use of the system. Finally, the machine enabled the development of scalable parallel compositing algorithms for data visualization.

Finally, our collaboration with SiCortex continued. This joint work resulted in direct support for the SiCortex fabric in the Argonne parallel I/O stack, which includes PVFS and I/O forwarding software. Also, SiCortex recently shifted to providing customers with the latest MPICH2 version from Argonne.

Collaboration with IBM on the development effort for Blue Gene/Q continued. This system has many characteristics in common with the SiCortex machine. The development process has been informed by our experiences using and operating the SiCortex 5832.

Exploratory work was performed on the Graphics Processing Unit (GPU) testbed to determine the feasibility of GPU use in the solution of partial differential equations.

Software Infrastructure to Enable Exascale Computational Science

2008-179-R2

Robert B. Ross, Peter H. Beckman, Mark Hereld, Ewing L. Lusk, Boyana R. Norris, Michael Papka, Rick L. Stevens, Rajeev Thakur, and Albert F. Wagner

Project Description

Our goal is to understand three crucial software areas for exascale computing: tools for understanding and debugging applications at the exascale; system software for managing millions of processors, complex networks, and exascale storage systems; and frameworks and algorithms for extracting and representing knowledge contained in exascale data sets.

Mission Relevance

This project is related to DOE's mission in basic science. DOE is embarking on an initiative to develop exascale computing resources in the next ten years. Our project is highly relevant to this initiative. Exascale computing will fundamentally change our understanding of the world, unlocking secrets not only in fields that have traditionally used high-end computing (HEC) resources (e.g., climate modeling) but also in areas just beginning to leverage the power of computation (e.g., economics). Exascale computer architectures will be a radical departure from existing systems; there will be a large number of processors that are slower with large core counts and a much greater imbalance between processing capabilities and the memory and storage subsystems. Advances in software infrastructure will be critical to overcoming these challenges so the new resources can be used to make scientific discoveries.

FY 2010 Results and Accomplishments

In previous years, we began the implementation of tools for collective behavior analysis. We further worked with the ScalaTrace team to port their tools to the IBM Blue Gene/P. This work highlighted the potential overhead of such approaches and uncovered new research directions. We also developed a matrix-based representation for communication patterns and used this to research MPI task mapping. We participated in the IBM Blue Gene/Q architecture development and gathered data on device counts and storage organization. On the basis of these data, in part, we developed a simulator to help us understand the impact of data placement on reliability and rebuild. We investigated peer-to-peer approaches for resiliency in storage systems, and we explored distributed key/value stores. We prototyped *in situ* processing for simulations running on ALCF (Argonne Leadership Computing Facility) computer resources. We also performed a study of visualization codes on the Intrepid and Eureka systems at ALCF, and we quantified time spent in various phases of the code

(e.g., data loading, rendering, communication, and compositing). We researched applying general interpolative methods to condensing data. We then developed a suite of 17 data sets, and by using a multigrid approach, we obtained an interpolation function that reproduce all data sets with a high degree of accuracy.

In FY 2010, we enhanced software developed under this project and produced new additional software to investigate storage issues on exascale systems. Our Message Passing Interface (MPI) -based distributed hash table implementation (Content-MPI [C-MPI]) was refined, released on SourceForge, and supported for users at Northwestern University. Our storage reliability simulator (General OBject Space [GOBS]) was employed to investigate disk and file server failure scenarios for exabyte capacity systems under multiple configurations. We developed the collective data management (CDM) module, a set of data access optimizations for the Swift workflow system. The system boosts performance for many-task applications used by the National Center for Atmospheric Research (NCAR), the Computation Institute (CI), and others on high-performance computing (HPC) systems and is currently being analyzed for publication regarding the Argonne Leadership Computing Facility (ALCF) BG/P Intrepid system and the National Energy Research Scientific Computing Center (NERSC) XT4 Franklin. Additionally, new file system libraries have been developed to maintain server clusters containing thousands of nodes in next-generation file systems.

We articulated a model of the ALCF for studying *in situ*, in-flight, and co-analysis opportunities. We characterized the performance of I/O forwarding and optimized it to get near maximal throughput in support of co-analysis. We analyzed this improved forwarding kernel and estimated that most of the memory and computational capacity of I/O nodes remain unused and are therefore available for in flight analysis — which we demonstrated. Scaling tests of M to N data streaming from Intrepid to Eureka were carried out to understand and then optimize performance in support of improved I/O performance and co-analysis by using Eureka. We tested these methods on two Innovative and Novel Computational Impact on Theory and Experiment (INCITE) Program applications to demonstrate that applications could be transparently augmented to enable co-analysis. We produced a detailed performance model of our visualization framework, vl3, and used this model to optimize the performance of the code on several platforms. We continued work on multi-streaming of high-resolution visualization produced on a parallel renderer (vl3) and viewed on a tiled display over the Wide Area Network (WAN), and we are beginning to include interactive capabilities.

We continued developing the ROSE-based PBound tool for collecting computational metrics based on source code analysis (e.g., integer and floating-point operations and memory accesses) and the generation of different derived metrics (e.g., performance models) based on these base quantities. In addition to significantly extending single-node behavior analysis capabilities, we began development of parallel analysis capabilities that rely on a hybrid static/runtime approach. The goal is to capture communication latencies and volume and use this information in conjunction with the computational characteristics (operations, memory accesses) model to create a complete model of MPI-based applications. Our current implementation is able to generate a sliced version of the application, which excludes all computations that do not directly influence control flow and include new directives for evaluating metrics of interest (e.g., communication volume, floating point operations). Given a high-level architecture description as input, this reduced version of the application can be executed on any architecture to produce estimates for execution time or other performance metrics of interest without requiring execution of multiple instances of the full application. The initial tool has been applied on a benchmark code based on the VORPAL electromagnetics code, which is part of the ComPASS project.

Our three proposals were accepted by DOE. As a result, three new projects — CODES, NoLoSS, and Damsel — will begin in FY 2011.

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Hereld, M., R. Hudson, J. Norris, M.E. Papka, and T.D. Uram, "Enabling Scientific Teamwork," *Journal of Physics: Conf. Series* **180** (2009), 012085.

Narayan, S., J. Chandy, S. Lang, P. Carns, and R. Ross, "Uncovering Errors: The Cost of Detecting Silent Data Corruption," *Proceedings of the 4th Petascale Data Storage Workshop*, Portland, OR, November 15, 2009 (published in ACM Digital Library).

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Wozniak, J., S.W. Son, and R. Ross, "Distributed Object Storage Rebuild Analysis via Simulation with GOBS," presented at the Workshop on Fault-Tolerance for HPC at Extreme Scale, Chicago, IL, June 28, 2010 (http://institute.lanl.gov/resilience/workshops/ftxs2010/).

Wu, W., T.D. Uram, M. Wilde, M. Hereld, and M.E. Papka, "A Web 2.0-Based Scientific Application Framework," *Proceedings of the 2010 IEEE International Conference on Web Services*, July 5–10, 2010, 642–643.

Non-Refereed Publications and Presentations

Gropp, W., E. Lusk, R. Ross, and R. Thakur, "Advanced MPI," presented at SC2009, Portland, OR, November 2009.

Latham, R., R. Ross, M. Unangst, and B. Welch, "Parallel I/O in Practice," presented at SC2009, Portland, OR, November 2009.

Ross, R., "Extreme Scale I/O Systems," presented at the IEEE Nuclear Science Symposium Data-Intensive Workshop, Orlando, FL, October 2009.

Ross, R., "Input/Output (I/O) in Computational Science," presented at the Computation Institute at the University of Chicago, Chicago, IL, February 2010.

Ross, R., "Storage in an Exascale World," presented at the IEEE International Workshop on Storage Network Architecture and Parallel I/Os (SNAPI), Incline Village, NV, May 2010.

Ross, R., "Data Models and Data Analysis at Exascale," presented at the High-End Computing File Systems and I/O Conference, Arlington, VA, August 2010.

Ross, R., P. Carns, and D. Metheney, "Parallel File Systems," book chapter in *Data Engineering: Mining, Information and Intelligence*, edited by Y. Chan, J. Talburt, and T. Talley, Springer, October 2009.

Ross, R., A. Choudhary, G. Gibson, and W.-K. Liao, "Parallel Data Storage and Access," book chapter in *Scientific Data Management: Challenges, Technology, and Deployment*, edited by A. Shoshani and D. Rotem, Chapman & Hall/CRC Computational Science, 2010.

Novel Computing Methodologies for the Simulation of Complex Molecular Systems

2009-047-R1

Benoît Roux, Millicent A. Firestone, and Jorge J. Moré

Project Description

Classical simulations based on atomic models play an increasingly important role in a wide range of applications in physics, biology, and chemistry. They are particularly valuable for the study of soft-matter systems involving liquids, polymers, membranes, microemulsions, and surfactants, as well as complex biomolecules like proteins and nucleic acids. A central issue in classical simulations concerns the accuracy and predictive value of the force fields used. The latter are mathematical objects constructed from analytical functions, which are parameterized to approximate the Born-Oppenheimer potential energy surface and reproduce known experimental results. In practice, the neglect of induced polarization has severely limited the usefulness of molecular dynamics (MD) simulations. This project addresses an urgent need in the community for new and extremely scalable algorithms for accurate simulation of complex systems incorporating induced polarization. An objective method for optimizing atomic force fields used in the simulations is also necessary for a wide variety of applications. This project will provide novel computational approaches for simulating large-scale self-assembled systems with induced polarization.

Mission Relevance

The project is relevant to DOE's mission in basic science. The impact of reliable and physically accurate large-scale simulations of complex molecular systems will be directly beneficial to a number of DOE researchers with respect to the design and refinement of soft materials for engineering applications in the energy sciences using theory, modeling, and simulations (TMS). With the significant increase in computational power made available by the Argonne Leadership Computing Facility (ALCF), the impact of TMS based on accurate atomic models for these various projects is expected to continue to grow in the near future. This research also advances DOE's long-term mission goals through the development of the relevant mathematical methodologies, as well as through contributions to the understanding of specific material systems with great potential for engineering applications in the energy sciences.

FY 2010 Accomplishments and Results

We developed rapid and systematic protocols for computing free energy of solvation. We also developed a novel replica-exchange, free-energy simulation (FEP/REMD) protocol for Blue Gene. The method was also extended and combined with an accelerated MD simulation method based on Hamiltonian replica-exchange MD (H-REMD) to overcome the additional problems arising from the existence of kinetically trapped conformations within the protein receptor. In the combined strategy, each system with a given thermodynamic coupling factor, lambda, in the extended ensemble is further coupled with a set of replicas evolving on a biased energy surface with boosting potentials that are used to accelerate the inter-conversion among different rotameric states of the side chains in the neighborhood of the binding site. Tests executed on Blue Gene demonstrate the high scalability of the method to several thousand processors. Finally, we implemented the basic ingredients of the polarizable force field into NAMD, a highly parallelized code from the Schulten Laboratory at the University of Illinois at Urbana-Champaign [UIUC], which runs efficiently on Blue Gene/L. An extended Lagrangian dynamics with a dual-Langevin thermostat scheme applied to the Drude-nucleus pairs is employed to generate classical dynamic propagation efficiently near the self-consistent field limit. Large-scale MD

simulations based on the Drude polarizable force field scale very well on massively distributed supercomputing platforms, the computational demand being only about 50–100% higher than what is used for nonpolarizable models. As an illustration, a large-scale 150 mM NaCl aqueous salt solution is simulated, and the calculated ionic conductivity is shown to be in excellent agreement with experiment.

Proposed Work for FY 2011

We plan to continue the NAMD development that supports our polarizable force field. In addition, we will continue our development of replica-exchange methods in free-energy computations for Blue Gene/P. The new extensions comprise a replica-exchange method for the umbrella sampling potential of mean force simulations. Early tests indicate that this method will have a very high scalability on Blue Gene. We will continue to refine the polarizable force field for lipid membranes, primarily focusing on the statistical properties of the phospholipids called dipalmitoyl phosphatidylcholine (DPPC), an important constituent of biological membranes. Lastly, we are developing an engine to fit the parameters of the force field from quantum chemistry data. We will develop a global, derivative-free optimization method for rapidly determining the best set of parameters of the force field that accurately models an arbitrary molecule for MD simulations according to a set of target data (e.g., quantum mechanical, experimental). We expect to have a general tool for automatically optimizing the force field according to well-defined standards of quality. The classical potential function is expected to require minimal effort to be implemented into all of the current major MD simulation drivers, such as Sandia National Laboratory's LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator).

Refereed Publications

Shivakumar, D., Y.Q. Deng, and B. Roux, "Computations of Absolute Solvation Free Energies of Small Molecules Using Explicit and Implicit Solvent Model," *J. Chem. Theo. Comp.* **5**(2009), 919–930.

Harder, E., A.D. Mackerell, and B. Roux, "Many-Body Polarization Effects and the Membrane Dipole Potential," *J. Am. Chem. Soc.* **131**(2009), 2760–2761.

Jiang, W., M. Hodoscek, and B. Roux, "Computation of Absolute Hydration and Binding Free Energy with Free Energy Perturbation Distributed Replica-Exchange Molecular Dynamics," *J. Chem. Theo. Comp.* **5**(2009), 2583–2588.

Jiang, W., and B. Roux, "Free Energy Perturbation Hamiltonian Replica-Exchange Molecular Dynamics (FEP/H-REMD) for Absolute Ligand Binding Free Energy Calculations," *J. Chem. Theo. Comp.* **9**(2010), 2559–2565.

Jiang, W., D.J. Hardy, J.C. Phillips, A.D. MacKerell, Jr., K. Schulten, and B. Roux, "High-Performance Scalable Molecular Dynamics Simulations of a Polarizable Force Field Based on Classical Drude Oscillators in NAMD, *J. Phys. Chem. Lett.* **2**(2011), 87–92.

New Framework for Electromagnetic Simulations on Exascale Supercomputers

2009-155-R1

Paul F. Fischer, Mi Sun Min, Timothy J. Tautges, and Jin Xu

Project Description

This project focuses on the development of highly scalable, efficient, and accurate numerical algorithms and software that will enable us to perform simulation-based investigations on exascale machines for exploring beam dynamics with accelerator devices. Efficient computations will enable us to predict better designs for future-generation accelerator devices at a lower cost.

Our recent research, based on the development of the time-domain electromagnetic solver, NekCEM, has shown significant progress in scalable electromagnetic modeling at the terascale and petascale. The aim of this project is to add a new framework that will increase both the computational capability and the efficiency of our high-order code. Specifically, the following key capabilities will be designed and implemented: (1) the enhancement of geometric flexibility with simplicial elements, (2) the development of efficient eigenvalue and frequency-domain solvers, and (3) the extension of scalable parallel algorithms to exascale simulations.

Mission Relevance

This project is relevant to the DOE future science mission in advanced scientific computing and nuclear physics. After successful completion of this project, the framework can be used as a platform to perform further research involving electromagnetic simulations at Argonne and elsewhere. Extensions can be added in different disciplines to greatly improve their quality and efficiency. For accelerator devices, it can provide highly accurate predictive modeling, which will greatly improve the technical design and next engineering phases and lead to substantial savings in building and operating costs. More importantly, successful completion of this project will further strengthen support of DOE in accelerator simulation.

FY 2010 Results and Accomplishments

During FY 2010, our main focus was to develop a new eigenvalue solver based on high-order Nedelec edge elements. Both 2D and 3D eigensolvers have been developed on triangle and tetrahedron elements. We also implemented scalable algorithms in the production code, NekCEM, and demonstrated their effectiveness on significant applications. Our results and algorithm developments include the following:

- Development of the Nedelec basis for 2D and 3D simplicial elements.
- Development of parallel algorithms for an eigenvalue solver using the Nedelec basis.
- Development and testing of scalable algorithms up to 131K cores on IBM BG/P for NekCEM with 75% efficiency using up to 1.1 billion grid points (Figure 1).
- Development and testing of scalable parallel I/O algorithms up to 65K cores on IBM BG/P for NekCEM with a best write-performance of 14 GB/s.
- Development of a high-order time integrator based on the Krylov approximation for cost-reduction by allowing a larger timestep size as the approximation order increases in time (Figure 2).

Proposed Work for FY 2011

In FY 2011, we will continue development of the framework and will apply it to physical problems in accelerator design and optimization. Our efforts will focus on developing the eigenvalue solvers, systemizing all the solvers in the framework, and applying them to real simulations. The systemization will include complete benchmarks that use up to >100K cores, as well as a high-quality user interface. The key aspects of these efforts are summarized below:

- Enhancement of the mesh capability for more than 100 millions of elements using Cubit and ANSYS.
- Development of a user-friendly interface aimed at a broad range of physical applications.
- Expansion of algorithmic methods for checkpointing and data visualization at the petascale and exascale.
- Development of a new parallel eigenvalue solver based on the Lanczos algorithm.
- Implementation of petascale and exascale simulations for ultra-short beams on various superconducting cavities.
- Preparation of full documentation and a detailed manual.

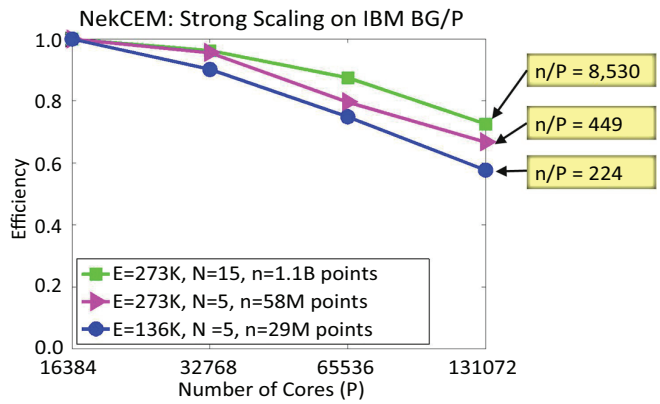

Figure 1. NekCEM Performance, demonstrating 75% efficiency on 131,072 cores for n/P=8,530 grid points per core compared to a base case on 16,384 cores for n/P=68,250 grid points per core. This figure shows that, even with an unrealistically small number of grid points per core n/P=224, NekCEM achieves 58% efficiency on 131,072 cores compared to a base case on 16,384 cores for n/P=1,793 grid points per core.

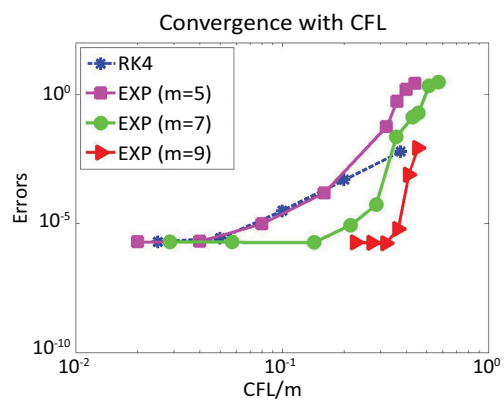

Figure 2. Error convergence in time depending on the maximum allowable timestep sizes (CFL [Courant–Friedrichs–Lewy] number) for the fourth-order five-stage Runge-Kutta (RK4) and the m*th order exponential time-stepping, EXP(*m*), schemes. This figure demonstrates that a high-order exponential time integration scheme allows larger time-step sizes, compared to the RK4, with larger CFL numbers as the Krylov subspace dimension* m*=5,7,9 increases.*

Refereed Publications

Xu, J., "Developing Peta-Scalable Algorithms for Beam Dynamic Simulations," in *Proceedings of IPAC'10* (International Particle Accelerator Conference 2010), TUYM03 (2010), 1256–1261.

Xu, J., and P.N. Ostroumov, "Solving 2D2V Vlasov Equation with High-Order Spectral-Element Method," *Communication in Computational Physics* **8** (2010), 159–184.

Xu, J., P.N. Ostroumov, B. Mustapha, M. Min, and J. Nolen, "Advanced Software Packages for Beam Dynamics Simulation," in *Proceedings of SciDAC (*Scientific Discovery through Advanced Computing*) 2010*, Chattanooga, TN (2010).

Xu, J., P.N. Ostroumov, B. Mustapha, and J. Nolen, "Scalable Direct Vlasov Solver with Discontinuous Galerkin Method on Unstructured Mesh," *SIAM (Society for Industrial and Applied Mathematics) Journal on Scientific Computing* **32** (6), (2010), 3476–3494.

Non-Refereed Publications and Presentations

Min, M., "Scalable High-Order Algorithms for Applications in Plasmonics, Particle Accelerator Physics, and Fluids," invited talk, presented at the Computational and Applied Mathematics Seminar, Purdue University, West Lafayette, IN, April 23, 2010.

Min, M., "Large-Scale Simulations Based on Spectral-Element Discontinuous Galerkin Methods: Nanoscience and Accelerator Applications," invited talk, presented at the First Joint Meeting of KMS (Korean Mathematical Society) and AMS (American Mathematical Society), CSE (Computer Science and Engineering) Session, Seoul, Korea, December 16–20, 2009.

Min, M., "High-Order Methods in Space and Time for Time-Dependent Electromagnetic Problems," invited talk, presented at the CSE Mini-Workshop, Yonsei University, Seoul, Korea, December 18, 2009.

Min, M., and P. Fischer, "An Efficient High-Order Time Integration Method Based on Krylov Approximations for Electromagnetic Modeling," invited talk, presented at the AMS Fall Central Section Meeting, University of Notre Dame, South Bend, IN, November 5–7, 2010.

Min, M., and P. Fischer, "Scalable High-Order Algorithms for Wakefield Simulations," in *Proceedings of IPAC'10*, TUPEC061 (2010) 1865–1867.

Min, M., and P. Fischer, "Scalable High-Order Algorithms for Wakefield Simulations," poster at IPAC'10, Kyoto, Japan, May 23–29, 2010.

Xu, J., "High-Performance Software Packages Developed in the Accelerator Development Group at ANL Physics Division," invited talk, presented to the Computational Accelerator Physics Group, Fermi National Accelerator Laboratory, Batavia, IL, October 13, 2010.

Xu, J., "Developing Peta-Scalable Algorithms for Beam Dynamic Simulations," invited talk, presented at IPAC'10, Kyoto, Japan, May 24–28, 2010.

Xu, J., "Scalable Solvers for Beam Dynamic Simulations," presented at the SIAM Conference on Parallel Processing for Scientific Computing (PP10), Seattle, WA, February 24–26, 2010.

Xu, J., "Scientific Computing with High-Order Numerical Methods," invited talk, presented to the Applied Mathematics Division, Illinois Institute of Technology, Chicago, IL, December 2, 2009.

Xu, J., B. Mustapha, and M. Min, "Efficient Numerical and Parallel Methods for Beam Dynamics Simulations," submitted to the special edition of PRST-Accelerator and Beam, (2011), (under revision review).

Xu, J., P. Ostroumov, P. Fischer, B. Mustapha, M. Min, and J. Nolen "Advanced Software Packages for Beam Dynamic Simulations," poster at the SciDAC 2010, Chattanooga, TN, July 11–15, 2010.

Xu, J., P. Ostroumov, B. Mustapha, J. Nolen, and K-J Kim, "Highly Scalable 2P2V Vlasov Solver with Discontinuous Galerkin Method on Unstructured Mesh," poster at the SC09 Conference, Portland, OR, November 14–20, 2009.

Correlated Electronic-Structure Simulations of Materials: Advanced Algorithms for Blue Gene/P and Q

2010-187-N0

Nichols A. Romero and Jeffrey R. Hammond

Project Description

Quantum-mechanical simulations of materials at the electronic-structure level of theory are an essential computational tool in materials design and discovery. Electronic-structure methods are computationally demanding and can make excellent use of petascale computational resources, such as the Blue Gene/P supercomputer at the Argonne Leadership Computing Facility (ALCF). The scalability and performance of these codes cross-cut a number of distinct software components. Electronic-structure applications sit on top of a software stack that includes parallel-programming paradigms (e.g., MPI and OpenMP), math libraries (e.g., ScaLAPACK), and other run-time environments. The goal of our efforts is to bring this software stack into the petascale era and pave the way for the deca-petascale Blue Gene/Q supercomputer targeted to arrive in the 2012 time frame. NWChem, a DOE-funded code, was chosen as the target application to benefit from our software innovations; however, we anticipate that the software developed will be beneficial to the electronic-structure community at large.

Mission Relevance

The software developed from this research will support DOE's science mission as funded through the Basic Energy Sciences (BES) and Advanced Scientific Computing Research (ASCR) division of the Office of Science. These electronic-structure codes are of broad applicability to the discovery and design of new materials relevant to energy security. The codes that we have enhanced as part of this work are utilized in a number of BES-funded scientific efforts in the areas of electrical energy storage, catalyst, and nuclear-fuel reprocessing, just to name a few. They will provide capabilities for high-accuracy simulation on petascale leadership-class computing facilities funded by ASCR.

FY 2010 Results and Accomplishments

Our accomplishments in FY 2010 span a number of components of the aforementioned software stack, as well as performance improvements to key electronic-structure codes that will be utilized on the ALCF's Blue Gene/P and the next-generation supercomputer, Blue Gene/Q. Our efforts necessitated strong collaborations with a number of software developers from universities, as well as other national laboratories.

ARMCI is the communication sub-layer of Global Arrays, a key component of NWChem. We re-implemented ARMCI for Blue Gene/P as a version called A1 (Argonne 1-sided), which will be contributed back into the main distribution of Global Arrays. As a follow-up to this work, a new one-sided communication run-time system for leadership-class supercomputers, known as OSPRI (One-Sided PRImitives), was created. The OSPRI runtime environment targets state-of-the-art supercomputers like the Blue Gene series, IBM PERCS, and Cray XE. We ported Elemental, a dense linear-algebra library, to Blue Gene/P by exploiting optimized collective algorithms and by adding OpenMP threading. Elemental was demonstrated to achieve peak performance exceeding that of ScaLAPACK.

We also worked with researchers from Pacific Northwest National Laboratory and the University of Oregon to extend the capabilities of the Tuning and Analysis Utilities (TAU) Performance System® to allow profiling of ARMCI. This functionality was invaluable in analyzing the performance of NWChem on a variety of supercomputers, not only Blue Gene/P but also the Laboratory Computing Resource Center (LCRC) Linux cluster. We added OpenMP threading and Blue Gene/P "double hummer" vectorization to the key compute kernels in the triples part of the NWChem CCSD(T) code. This work allowed us to achieve > 50% per node utilization for CCSD(T) calculations.

Finally, we worked with Sandia National Laboratories to port MPQC (Massively Parallel Quantum Chemistry) to the Blue Gene/P platform. Performance analysis revealed critical scaling bottlenecks, which were subsequently fixed. The MPQC implementation of MP2 achieved >60% strong-scaling efficiency from 512 to 40,960 nodes. Further improvements in strong-scaling efficiency will require dynamic load-balancing and a more scalable dense eigensolver. Both tasks will be undertaken as part of the ALCF Blue Gene/Q Early Science Program. Also under the sponsorship of the ALCF Blue Gene/Q Early Science program, we will also continue our work to integrate the Elemental library into MPQC.

Refereed Publications

Poulson, J., B. Marker, J.R. Hammond, N.A. Romero, and R.A. Van De Geijn, "Elemental: A New Framework for Distributed Memory Dense Matrix Computations," submitted to *Transactions on Mathematical Software.*

Non-Refereed Publications and Presentations

Hammond, J.R., W.A. Scullin, and R. Bair, "The Software of the Future on the Hardware of the Future," presented at SciDAC (Scientific Discovery through Advanced Computing) 2010, Chattanooga, TN, July 15, 2010 .

Hammond, J.R., "Scalability of Quantum Chemistry Codes on Blue Gene/P and Challenges for Sustained Petascale Performance," poster presented at Supercomputing 2009, Portland, OR, November 17, 2009.

Open GATS: An Open Unified Framework for Global Address and Task Space Computing in the Exascale Era

2010-199-N0

Pavan Balaji, Jeffrey R. Hammond, Ewing L. Lusk, Nichols A. Romero, and Rajeev Thakur

Project Description

Exascale systems will bring many challenges to scientific applications and their associated software libraries or "stacks." Challenges with respect to managing the programming and runtime infrastructure for these systems, including communication models, I/O and storage subsystem, and operating-system issues, are increasingly becoming the key aspects that need to be addressed for us to take true advantage of the performance provided by exascale systems.

The previous decade, which marked the increase of compute power from terascale (ASCI Red in 1996) to petascale (Roadrunner and Cray XT5 in 2008), passed without a significant need for any paradigm shift in parallelization techniques; a three-orders-of-magnitude increase in performance did not require a three-orders-of-magnitude increase in concurrency. Unfortunately, the arrival of petaflop supercomputers coincided with processors "hitting the power wall." Since the clock

speeds and hence compute-power-per-compute-core are not expected to increase substantially, we can anticipate that another three-orders-of-magnitude increase in performance implies *at least* a three-orders-of-magnitude increase in necessary concurrency. Expressing and managing such amounts of concurrency demand a shift in parallelization and programming techniques and asynchrony in every aspect of computation. A possible exascale hardware architecture is illustrated in Figure 1, which shows a large amount of hardware concurrency possible within each node as well as across nodes. The concurrency can come from CPU architectures with many cores, from threads within a CPU core, or from accelerator units (such as graphics processing units) attached to each node.

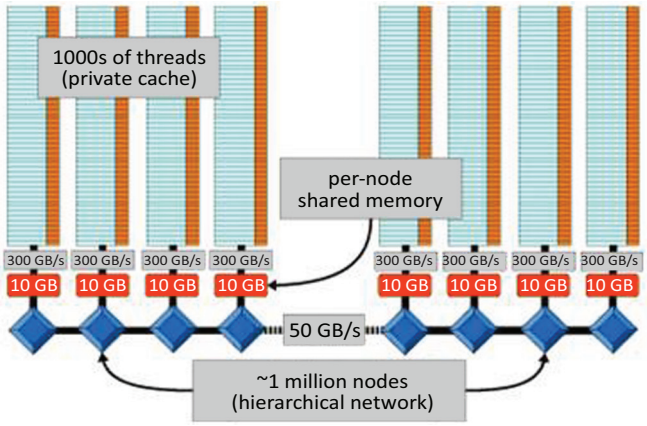

Figure 1. Possible architecture for exascale hardware.

Most contemporary programming models strive to maximize concurrency and asynchronicity of computation and communication. Message-passing models, such as MPI (message passing interface), have traditionally handled this challenge by providing a portable mechanism to exchange data between pairs or groups of processes. Global address space (GAS) models (such as global arrays [GA], global trees and other partitioned global address space [PGAS] models) and global task space (GTS) models (such as MADNESS Runtime, Asynchronous Dynamic Load-Balancing [ADLB], and Charm++) are emerging as popular alternatives to MPI by making asynchronous data and task management more natural to application developers.

As we build exascale-capable software stacks, several problems need to be tackled. First, handling concurrency in just one form at a time is no longer sufficient. Given the enormous amount of hardware concurrency that exascale systems are expected to provide, we need a framework that will allow applications to specify their overall computation as a combination of asynchronous data, as well as asynchronous task management, allowing the runtime system to optimize the overall computation in multiple dimensions simultaneously. Second, the underlying operating system infrastructure that allows different runtime systems to interact with the computational hardware has to be scalable and flexible enough for future architectures. Third, I/O and storage systems that form the backbone of data-intensive applications must take advantage of upcoming architectures and handle the challenges that they bring along.

The goals of this project are threefold: (1) design and investigate an integrated model that provides the capabilities of message passing, as well as global address and task sharing in an environment where all three models can be used concurrently; (2) formulate a model that will allow applications to take full advantage of exascale hardware by using scalable and flexible operating-system capabilities; and (3) investigate how data-intensive applications can take advantage of advanced I/O and storage capabilities built for exascale systems.

Mission Relevance

This project directly falls under the DOE science-related mission of exascale computing and ties well into Argonne's efforts with the Exascale Software Center and the Exascale application co-design centers.

FY2010 Results and Accomplishments

During FY 2010, we worked on a unified framework for global address and task space models. The project involved two major aspects: (1) integration with existing external DOE-funded projects, and (2) initial research to put together such a unified stack.

Integration with existing external DOE-funded projects. A part of the work completed during FY 2010 was formation of a unified infrastructure for programming models and runtime systems. This infrastructure unifies the efforts of high-end computing users in a number of DOE-funded areas, including low-level runtime systems (such as MPI [message passing interface], ARMCI [Aggregate Remote Copy Interface], GASNET [Global Address Space Networking], and OSPRI [One-Sided Primitives]), GAS models (such as GAs, global trees, and data spaces), GTS models (such as ADLB, Scioto, and MADNESS runtime) and high-level compilers (such as UPC [Unified Parallel C], Chapel, and CAF [Coarray Fortran]).

Research and development of the unified framework. Toward the research in the unified stack effort, we worked with collaborators at Oak Ridge National Laboratory on efforts related to improving the performance of GAS models, such as GA, as well as interoperating GA with MPI. In this regard, we worked on two topics:

- The one-sided primitives runtime infrastructure (OSPRI) layer provides a one-sided communication model that represents an alternative to GA's native communication layer (ARMCI). OSPRI provides a richer set of functionality

that better matches the architectural features of leadership-class machines, such as Blue Gene and Cray, and allows GA to scale on these systems.
- As part of our effort to unify ARMCI with MPI, we worked on implementing ARMCI on top of MPI-2.2 to understand which features of MPI can be directly utilized by ARMCI and which need to be implemented natively on the internals of MPICH2.

Proposed Work for FY2011

The work is being continued into FY 2011, and particular enhancements for GAS models and topology-aware enhancements are planned.

Milestones and success metrics include:

- A working implementation of MPI-3 RMA draft functionality (the MPI-3 RMA standard is not expected to be out in FY 2011, but the PIs are heavily involved in the MPI-3 RMA standardization and will use the internal draft standard as a guiding model). The implementation of MPI-3 RMA will cover at least BG/P and one other network that provides true hardware RDMA capabilities, such as IB.
- A working implementation of a GAS model such as GA on top of MPI-3 RMA.
- A working implementation of selected tensor contraction operations by using new GAS functionality.
- Design of evaluation criteria suitable for co-design to evaluate node-local storage that is capable of comparing alternatives, like memrister and phase-change-memory technologies.
- Design of the needed intra-node and inter-node messaging support within an exascale operating system on architectures with large numbers of cores with predictable scheduling and possibly partitioned functional domains.

Refereed Publications

Hammond, J., S. Potluri, J. Dinan, D.K. Panda, V. Tipparaju and P. Balaji, "OSPRI: an Optimized One-Sided Communication Runtime for Leadership-Class Machines," submitted to the International Conference on Parallel Processing (ICPP).

Non-Refereed Publications and Presentations

Balaji, P., "A Unified Runtime Infrastructure for Exascale Programming Models," presented at the Advanced Scientific Computing Advisory Committee Meeting, Argonne, IL, November 9, 2010.

Studying Oil Plumes with the Nek5000 Code

2010-200-N0

Paul F. Fischer and Aleksandr Obabko

Project Description

We are modifying the Argonne-developed fluid simulation code, Nek5000, to support a study of buoyant plumes released from a point source at the bottom of a stratified and rotating environment, as a step toward resolved modeling of oil and gas plumes. This project aims to provide scalable simulation tailored to this class of problems. The proposed capabilities will allow simulations needed for insight into the underlying dynamics of these plumes. The models are based mainly on a Boussinesq approximation to Newtonian fluid flow. We are, however, exploring two modifications to the equation set: (1) the addition of evaporation to represent loss of volume over the first two days after surfacing and (2) the inclusion of non-Boussinesq effects in order to include density differences of some 20% between the source plume and the background flow. In addition, we are equipping Nek5000 with requisite tracer capabilities that will allow quantification of plume dispersion and developing computational grids that will efficiently concentrate resolution near the source while simultaneously avoiding sources of spurious gravity-wave reflections.

With these modifications in place, we will work closely with collaborators at the University of Miami to address the following issues: (1) What are the flow patterns of a buoyant plume in the presence of a sub-mesoscale (spatial range of 100 m to 10 km, temporal range of a few days to a few weeks) oceanic environment? Does it show subsurface intrusions detraining from the main plume? How does the buoyant plume interact with mixed-layer density fronts? What are the parameters controlling its ability to reach the surface? (2) What is the relative dispersion of the plume? How do surface and subsurface relative dispersion differ? and (3) What is the nature of dispersion of a 3D buoyant plume after its source is shut down? How long does it take to dissipate? Where does it modify the surrounding water characteristics?

Mission Relevance

This work is in support of DOE's science and environmental missions. Steadily increasing oil exploration in locations deeper than 300 meters is found in many regions in the world. The number of exploratory wells in the Gulf of Mexico increased by 70% from 1996 to 1998, and it was estimated that the production from installations deeper than 800 meters was more than half of the total production by 2007. With larger numbers of wells and more production, the potential for

spills increases. This study seeks to understand the dynamics of buoyant plumes released from a point source in stratified and rotating oceanic environments. Such basic information as dominant time scales and preferred depth for advection, spreading, evaporation, and dilution will allow construction and evaluation of improved transport models in the event of future leaks.

FY 2010 Results and Accomplishments

During FY 2010, we developed computational meshes that efficiently concentrate resolution near the plume source without introducing sudden jumps in resolution, which can trigger spurious gravity waves in the presence of density stratification. An example of such a mesh is illustrated in Figure 1, which shows a 3-to-1 linear resolution gain at the center of the domain, resulting in an order-of-magnitude savings over the use of a uniform mesh at comparable resolution. This mesh was used for initial studies, and we are working with collaborators at the University of Miami to analyze the results. A typical simulation result is displayed in Figure 2, which shows a rising buoyant plume (red and yellow velocity contours) viewed from below the surface. (The aspect ratio for the image is stretched vertically 20:1.) Following the predictions of the Taylor-Proudman theorem for rotational flows, the plume tends to disperse in a columnar fashion, with the dispersion driven in this case by density gradients at the surface, which are manifest as green bumps in an isopycnal layer near the surface.

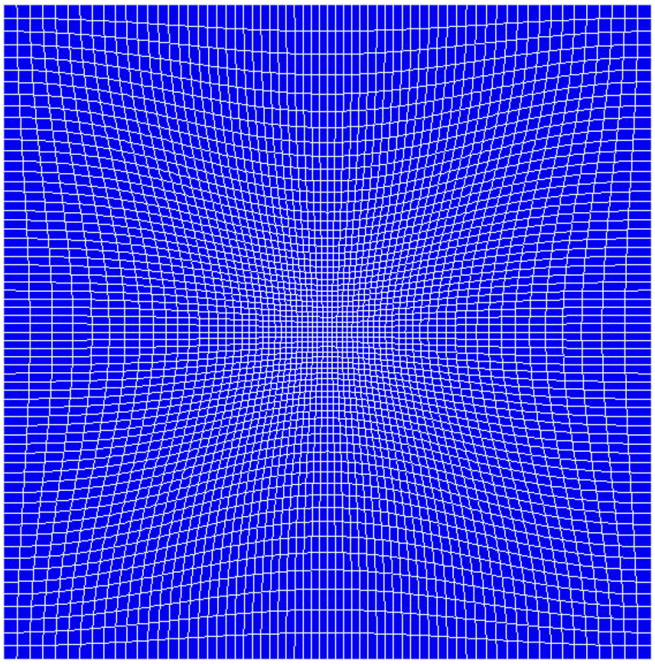

Figure 1. Computational mesh showing a 32 × 32-graded array of spectral elements in the horizontal plane (8 elements in the vertical). Each element comprises N^3 basis coefficients, with N = 7 – 11 being typical expansion orders.

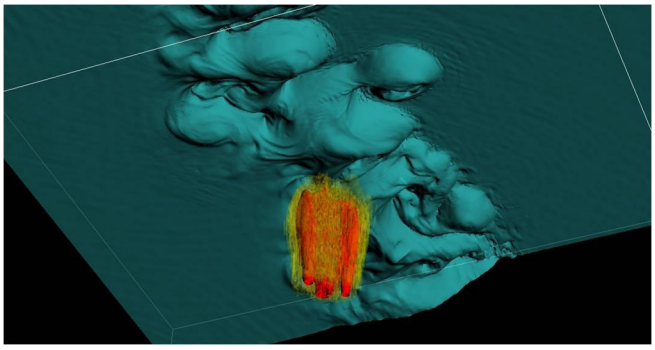

Figure 2. Simulation of a buoyant plume red and yellow velocity contours) interacting with currents driven by density variations near the surface, which are manifest as bumps in an isopycnal layer near the surface. The plume disperses in columns tied to the surface currents, as predicted by the Taylor-Proudman theorem.

LARGE-SCALE SCIENTIFIC USER FACILITY DEVELOPMENT

Complex Dynamic Behavior Investigated with Real-time X-Ray Photon Correlation Spectroscopy

2008-070-R2

Alec R. Sandy, Pete R. Jemian, Brian J. Tieman, and John Weizeorick

Project Description

The project focus provides a revolutionary improvement in x-ray photon correlation spectroscopy (XPCS) data collection and reduction procedures. XPCS data, gathered in parallel over many length scales, are compressed on the fly and time auto-correlated on a pixel-by-pixel basis, and results are periodically updated on control screens — all in real time. Thresholding and compression are performed in firmware; in addition, a high-performance computing (HPC) PC cluster that executes appropriate parallelized analysis code efficiently calculates time autocorrelations across a wide range of time scales. These developments will allow multi-speckle XPCS to seamlessly probe fluctuations persisting from a few milliseconds to more than thousands of seconds — more than six orders of magnitude in time. Our technical developments will be applied to the study of multi-timescale dynamics in glassy systems.

Mission Relevance

This project is tied to the U.S. Department of Energy's mission in science. The primary benefit of this project is the ability to probe multi-timescale dynamics in complex glassy and soft materials (such as gels) with dynamics on a variety of length- and timescales. The understanding of the glass transition remains a challenge in condensed-matter physics. While our primary interest is in addressing fundamental scientific problems, XPCS also has important potential applications within the food, cosmetics, and paint industries (among others); these developments will facilitate access to the XPCS technique by researchers with more expertise in technologically important materials than in synchrotron x-ray science. Also, with the successful development and deployment of such a system, we will be able to offer user-scientists visiting beamline 8-ID at the Advanced Photon Source (APS) the ability to seamlessly probe equilibrium and non-equilibrium sample fluctuations ranging from milliseconds to thousands of seconds. We expect that many new sample systems will be studied with XPCS, because the need to match "predicted" sample dynamics beforehand into the available length scale and frequency window will be greatly reduced. This functionality will revolutionize the breadth of XPCS and its applicability to a wide range of scientific problems.

FY 2010 Results and Accomplishments

During the past fiscal year, firmware-based lower-level discrimination and compression was placed into production at beamline 8-ID. The firmware and software to control the firmware was successfully applied to rapidly streaming data from two fast XPCS detectors: the Argonne National Laboratory-Lawrence Berkeley Laboratory Fast CCD (charge-coupled device) and our home-built SMD (surface-mount device) camera. The compression algorithm functioned perfectly for both detectors and reduced the data rate by up to nearly a factor of 20.

We also significantly improved the robustness and the user interface to the HPC cluster that reduces the data provided by the firmware compression described above. We developed scripts that automatically transport the acquired compressed data to the HPC cluster. The scripts then initiate data processing on the cluster, making the entire process operationally friendly. This was an important goal of our project.

In addition to this effort, we also significantly enhanced the user interface to the data produced by the cluster. The improved interface allows real-time visualization and updates of the data while they are being processed on the cluster. It also provides a friendly user interface for retrieving and displaying batch-processed results.

As a concrete example of the power and utility of our development effort, all of these tools were applied to support a thesis project under the supervision of Dr. David Green of the University of Virginia. The goal was to connect the microscopic dynamics of nanoparticles grafted with polymers, observed via XPCS, with macroscopic rheological measurements on the same system. One week of beam time at beamline 8-ID produced 10 terabytes (TB) of compressed data, that were then analyzed in 10 days by using HPC. Without our developments, the uncompressed data, if it were even possible to acquire, would have totaled 150 TB and the analysis time on a powerful multicore workstation would have taken an unrealistic 120 days.

We are now receiving follow-on support from DOE's Office of Science, Basic Energy Sciences program and through the Software Solutions Group within the APS Engineering Support Division to maintain and enhance the delivered analysis system.

Non-Refereed Publications and Presentations

Madden, T., X. Jiao, S. Narayanan, A.R. Sandy, M. Sikorski, and J. Weizeorick, "Real-Time Lower-Level Discrimination and Compression Applied to Streaming Data from a Fast, Direct-Detection Area Detector," presented at the SRI 2010 Meeting, Argonne, IL, September 21–24, 2010.

Sikorski, M., S. Narayanan, A.R. Sandy, and B. Tieman, "A User Interface for Real-Time Analysis of XPCS using HPC," presented at the SRI 2010 Meeting, Argonne, IL, September 21–24, 2010.

Tieman, B., S. Narayanan, A.R. Sandy, M. Sikorski, "MPICorrelator: A Parallel Code for Performing Time Correlations," presented at the SRI 2010 Meeting, Argonne, IL, September 21–24, 2010.

Development of the Emittance Exchange Technique for Improved Accelerator Facility Performance

2008-141-R2

John Power, Wei Gai, and Kwang-Je Kim

Project Description

The objective of this research is to develop a novel accelerator scheme for generating beams capable of meeting the most demanding accelerator requirements for the next generation of particle accelerators. The goal of this proof-of-principle Emittance Exchange Experiment (EEX) is to exchange the initial (low) longitudinal emittance (ε_{z0}) with the initial (high) transverse horizontal emittance (ε_{x0}) and to incorporate room for possible parametric studies (e.g., using an incoming flat beam with tunable horizontal emittance).

Mission Relevance

This project is relevant to DOE's science mission. Next-generation accelerator applications will require charged particle beams with an optimized phase space partition. For example, high-gain free-electron lasers (FELs) will potentially benefit from high transverse quality at the expense of reduced longitudinal quality. Proper phase space partitioning of electrons may eliminate the need for an electron damping ring for the International Linear Collider (ILC). A megawatt-scale average-power FEL based on an energy recovery linac (ERL) would benefit from an emittance exchange to significantly reduce the energy spread before the beam dump.

FY 2010 Results and Accomplishments

The EEX and longitudinal phase space simulations are mature and await only the final installation of the hardware in the Argonne Wakefield Accelerator (AWA) facility. All components of the half-EEX beamline (two magnetic dipoles, one deflecting cavity, a table, two vacuum chambers, three quadrupole magnets, and three yttrium aluminum garnet [YAG] screens) are being installed on the table, and the beamline is nearly ready for operation. The strip line was fabricated, as has its (preliminary) associated radio frequency (RF) receiver board. In FY 2010, a new branch of simulation was initiated to explore the possibility of generating electron profiles that are ramped in the longitudinal direction for the purposes of generating high transformer ratios in collinear wakefield experiments. A paper on this work was submitted. The half-EEX beamline will be used to measure the longitudinal phase space, bunch length, and half EEX characterization.

FY 2010 was the final year of this project. In the future, using AWA programmatic funding, we will prepare for the full beamline extension, which will include the second "half-dogleg," when the AWA tunnel is expanded as part of the AWA upgrade. We will perform simulations to include an EEX-based beamline into the tunnel expansion for high-transformer-ratio studies.

Refereed Publications

Jiang, B., C. Jing, J.G. Power, and W. Gai, "High Transformer Ratio of the Ramped Bunch," submitted to *Physical Review Special Topics – Accelerators and Beams* (2010).

Piot, P., Y.-E Sun, J.G. Power, and M. Rihaoui, "Generation of Relativistic Electron Bunches with Arbitrary Current Distribution via Transverse-to-Longitudinal Phase Space Exchange," *Phys. Rev. ST Accel. Beams* **14** (2011), 022801.

Rihaoui, M., P. Piot, J.G. Power, Z. Yusof, and W. Gai, "Observation and Simulation of Space-Charge Effects in a Radio-Frequency Photoinjector Using a Transverse Multibeamlet Distribution," *Physical Review Special Topics – Accelerators and Beams* **12** (2009), 124201.

Non-Refereed Publications

Rihaoui, M., D. Mihalcea, W. Gai, P. Piot, and J.G. Power, "Design and Analysis of a Single-Shot Longitudinal Phase Space Measurement Diagnostics at the Argonne Wakefield Accelerator," in *Proceedings of the Advanced Acceleration Concept (AAC10) Workshop*, Annapolis, MD, July 16–19, 2010.

Rihaoui, M.M., P. Piot, J.G. Power, D. Mihalcea, and W. Gai, "Verification of the AWA Photoinjector Beam Parameters Required for a Transverse-to-Longitudinal Emittance Exchange Experiment," in *Proceedings of the 2009 Particle Accelerator Conference (PAC09)*, Vancouver, British Columbia, Canada, May 4–8, 2009.

Design and Fabrication of a Model HOM-Suppressed High-Beam-Power CW Superconducting RF Structure and a High-Performance Cryomodule for Light Source Energy Recovery Linacs

2008-152-R2

Alireza Nassiri, Joel D. Fuerst, Michael P. Kelly, and Geoff Waldschmidt

Project Description

The next-generation high-performance light sources, including Energy Recovery Linacs (ERLs) and X-ray Free Electron Lasers (XFELs), will most likely be superconducting. Our goal is to develop a highly efficient high-current multi-cell superconducting radio frequency (SRF) structure and cryomodule that will meet the performance requirements of future superconducting accelerators. The SRF structures envisioned for the Advanced Photon Source upgrade will be required to operate in the continuous wave (CW) mode (100% duty factor) with a moderate field gradient and high cavity quality factor. High-quality SRF cavities are needed to reduce total RF power and surface residual resistance to decrease the overall power requirements of cryogenic plant operation. The specific objectives of this project are (1) develop and fabricate a suitable multi-cell SRF structure, (2) investigate and apply a suitable surface treatment process that will enhance the accelerating gradient and improve the cavity quality factor, and (3) develop and fabricate a multi-cell cryomodule.

Ampere class (high average beam current) multi-cell SRF cavities require strong higher-order-mode (HOM) damping because of the large HOM power and multi-bunch effects that limit the maximum-achievable current. As the number of cells per cavity increases, a larger number of excited HOMs are trapped in the interior cells. It is imperative to channel and extract the unwanted HOMs power away from the cavity interior by an appropriately designed damping system, as proposed here.

Mission Relevance

This project supports DOE's mission in basic science, as it will address some of the key developmental SRF technology issues for future light sources. Future accelerator facilities including light sources will greatly benefit from recent advances in SRF technology, as future accelerators will need to attain higher energies and future light sources will be required to operate in a wide range of modes to meet the requirements of x-ray science experiments. SRF technology will best meet stringent machine technical requirements; however, large SRF facilities tend to be very expensive. Design optimizations and the application of novel niobium surface treatments could make such large machines more affordable.

FY 2010 Results and Accomplishments

We successfully designed a novel SRF structure operating at 1.4 GHz (see Figure 1) that is extremely efficient in damping the higher-order modes of SRF structures for ampere-class CW SRF linacs. This cavity is made up of three equal parts, each of which can be deep-drawn from a single niobium sheet. This slotted cavity design has several advantages over a conventional design. It provides the necessary damping of the dipole and quadrupole modes without adversely damping the accelerating mode and makes the damping easier and more effective (see Figure 2). With this design, we demonstrated that the trapped modes inside the cavity are eliminated, thus allowing a larger number of cells per structure for a better accelerator packing factor.

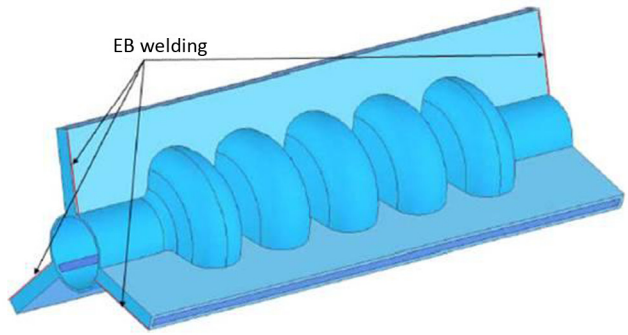

Figure 1. Slotted cavity structure.

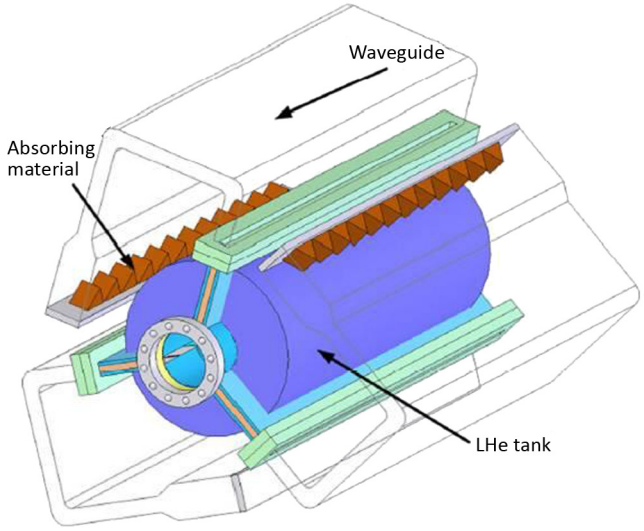

Figure 2. Slotted cavity with waveguide attachments and absorbing material for higher order modes of damping.

In addition to the design and simulation work on the slotted cavity, we and Jefferson Accelerator Laboratory scientists completed a preliminary 5-cell elliptical cavity, which awaits test and measurement.

Refereed Publications

Liu, Z., and A. Nassiri, "Novel Superconducting RF Structure for Ampere-Class Beam Current for Multi-GeV Energy Recovery Linacs," *Phys. Rev. ST AB* **13**, 012001 (2010).

Liu, Z., A. Nassiri, and G. Waldschmidt, "Design and Study of a High-Current 5-Cell Superconducting RF Cavity," *Chinese Physics C* **34**(5) (2010).

An X-Ray Free-Electron Laser Oscillator in an Energy Recovery Linac

2008-156-R2

Kwang-Je Kim, Deming Shu, and Yuri Shvyd'ko

Project Description

Laboratories around the world are pursuing development of next-generation x-ray sources that will provide higher performance than current third-generation sources, such as Argonne's Advanced Photon Source (APS). The x-ray free-electron laser (FEL) oscillator (XFELO) is one of three major approaches, which distinguishes itself by being a fully coherent source of x-rays having an extremely narrow spectral bandwidth (about 10^{-7}). This project aims to demonstrate the feasibility of the x-ray optics necessary for an XFELO.

Mission Relevance

Developing an XFELO is directly relevant to DOE's mission in basic science and the related stewardship of accelerator-based user facilities. It offers hard x-ray capabilities that can dramatically improve the techniques developed at the APS and provide for new applications as well.

FY 2010 Results and Accomplishments

FEL simulation. Additional simulation tools that address the novel optics required for the FEL x-ray cavity, particularly the Bragg crystal mirrors, continued to be developed. We implemented an algorithm into the GINGER code that includes a realistic spectral bandpass of the Bragg mirrors and used this code to more accurately simulate the two-crystal FEL cavity. Additionally, we are in the final stages of including the angular acceptance of the Bragg crystals, which will permit more complete simulations of the four-crystal, tunable x-ray oscillator.

Bragg reflectivity of diamond crystals. A four-bounce silicon x-ray monochromator (C-mono) with an energy resolution of 1 meV has been built. First reflectivity measurements from diamond crystals by using the C-mono strongly indicate a reflectivity close to 99%. To evaluate the influence of instantaneous absorption of the radiation pulses on the crystal lattice, we studied time-dependent Bragg reflectivity of diamond crystals in backscattering by using highly monochromatic x-rays with meV-narrow bandwidth from the C-mono. A characteristic response time of the crystal lattice to the ultrashort laser pulse was found to be a few nanoseconds.

Thermal expansion issues. Systematic ultra-precise studies of the thermal expansion coefficient of diamond were conducted using Bragg diffraction in backscattering from diamond crystals by using highly monochromatic 23.7 keV x-rays. Neither negative thermal expansion nor any substantial difference in the thermal expansion coefficient in crystals of different types was observed.

Stabilization of multi-axes high-resolution optics. The null-detection feedback method we developed last year has become a standard tool in APS user operations. The solution is very reliable and requires very little or no maintenance. During feedback operation, angular positions of two beamline optical components are now adaptively controlled simultaneously. A detailed understanding of nanoradian angular stabilization of x-ray optical components has been developed.

Nanoradian stages and low vibrational cooling. A preliminary design was completed in FY 2010 for a novel two-axis precision flexure tip-tilting stage system for XFELO with a 2-kg load capacity and nanoradian-scale positioning sensitivity and stability. As shown in Figure 1, the two-dimensional tip-tilting weak-link stage system consists of two high-stiffness weak-link stages: (1) a vertical-axis rotary weak-link stage at the top and (2) a new horizontal-axis tip-tilting stage at the bottom. Effort has also been dedicated to creating a compact cryo-cooling system with ultra-low vibrational disturbance for the XFELO cryo-cooled diamond crystal optics.

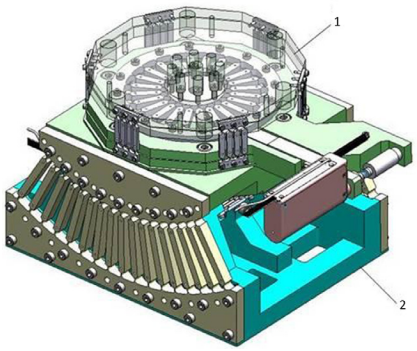

Figure 1. Two-stage tip-tilting weak-link stage system having (1) a vertical-axis rotary weak-link top stage and (2) a horizontal-axis tip-tilting weak-link base stage.

Refereed Publications

Shu, D., W.-K. Lee, W. Liu, G.E. Ice, Y. Shvyd'ko, and K.-J. Kim, "Development and Applications of a Two Dimensional Tip-tilting Stage System with Nanoradian-level Positioning Resolution," *Nucl. Instr. Meth., A*. In press.

Lindberg, R.R., K.-J. Kim, Y.V. Shvyd'ko, and W.M. Fawley, "Performance of the X-ray Free-Electron Laser Oscillator with Crystal Cavity," *Phys. Rev. ST-AB*, **14**, 010701 (2011).

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Stoupin, S., F. Lenkszus, R. Laird, K. Goetze, K.-J. Kim, and Y.V. Shvyd'ko, "Nanoradian Angular Stabilization of X-ray Optical Components," *Rev. Sci. Instrum*. **81** (2010), 055108.

Non-Refereed Publications and Presentations

Kim, K.-J., "An X-ray FEL Oscillator: Promises and Challenges," presented at the Workshop on Physics and Applications of High Brightness Electron Beams, Maui, Hawaii, November 16–19, 2009.

Kim, K.-J., "An X-ray FEL Oscillator: Promises and Challenges," presented at the 2nd RIKEN Workshop on FEL Science: Emerging X-ray Applications in Biological Systems, Kenting, Taiwan, December 6–9, 2009.

Kim, K.-J., "X-ray Free Electron Lasers: Current Status and Challenges," presented at the 5th Future Light Source Workshop 2010: Science and Technology, POSCO (Pohang Iron and Steel Company) International Center, Pohang, Korea, February 9–10, 2010.

Kim, K.-J., "Recent Advances and Future Trends in X-ray Free Electron Lasers," presented at the 12th International Conference on X-ray Lasers, Gwangju, Korea, May 30–June 4, 2010.

Kim, K.-J., "Towards the Next Generation X-ray Free-Electron Lasers: Promises and Challenges," presented at the 5th Asia-Oceania Forum on Synchrotron Radiation Research and the 22nd PAL (Pohang Accelerator Laboratory) User's Joint Workshop, POSCO International Center, Pohang, Korea, July 5–9, 2010.

Lindberg, R.R., Y.Y.V. Shvyd'ko, K.-J. Kim, and W.M. Fawley, "Beam Dynamics and Performance of the X-ray Free-Electron Laser Oscillator with Crystal Cavity," presented at FEL (Free Electron Laser Conference) 2010, Lund, Sweden, August 23–27, 2010.

Lindberg, R.R., G.-T. Park, and K.-J. Kim, "The Effects of Grazing Incidence Mirror Roughness on Coherent Radiation Propagation for the X-ray FEL Oscillator," presented at FEL 2010, Lund, Sweden, August 23–27, 2010.

Lindberg, R.R., and K.-J. Kim, "Noise and Coherence Propagation in Multi-Stage FELs: Application to Echo-Enhanced Harmonic Generation," presented at FEL 2010, Lund, Sweden, August 23–27, 2010.

Shu, D., W-K. Lee, W. Liu, G.E. Ice, Y. Shvyd'ko, and K-J. Kim, "Development and Applications of a Two-dimensional Tip-Tilting Stage System with Nanoradian-Level Positioning Resolution," *Proceedings of SRI-2010, Nucl. Instrum. and Methods A*, Chicago, Illinois, September 21–24.

Shvyd'ko, Y., "Feasibility of Diamond X-ray Cavities for Hard X-ray FEL Oscillators," presented at the 10th International Conference on Synchrotron Radiation Instrumentation, Melbourne, Australia, September 27–October 2, 2009.

Shvyd'ko, Y., "Advanced Angular Dispersive Monochromators and Analyzers for Inelastic X-ray Scattering," presented at the 10th International Conference on Synchrotron Radiation Instrumentation, Melbourne, Australia, September 27–October 2, 2009.

Shvyd'ko, Y., "XFELO X-ray Cavity: Feasibility Studies," presented at the 48th ICFA Advanced Beam Dynamics Workshop on Future Light Sources, SLAC National Accelerator Laboratory, Menlo Park, California, March 1–5, 2010.

Shvyd'ko, Y., "XFELO: X-ray Cavity Feasibility Studies," presented at the EuroFEL Workshop on Photon Beamlines & Diagnostics, DESY (Deutsches Elektronen Synchrotron), Hamburg, Germany, June 28–30, 2010.

Shvyd'ko, Y., "Nuclear Resonance: from Radioactive Source to XFELO," presented at Festkolloquium – 25 Years of NRS-SR and the 75th birthday of Erich Gerdau, DESY, Hamburg, Germany, July 2, 2010.

Shvyd'ko, Y., "X-ray Cavities for XFELO," presented at the 32nd International Free Electron Laser Conference FEL 2010, Malmö, Sweden, August 23–27, 2010.

Shvyd'ko, Y., "X-ray Free-Electron Laser Oscillator and Challenges for X-ray Optics," presented at the 16th Pan-American Synchrotron Radiation Instrumentation Conference, Workshop on Coherence Preserving Optics for High Brightness Light Sources, Argonne National Laboratory, September 21, 2010.

Shvyd'ko, Y., "Development of Optical Cavities for Hard X-ray FEL Oscillators," presented at the 16th Pan-American Synchrotron Radiation Instrumentation Conference, Argonne National Laboratory, September 22–24, 2010.

Stoupin, S., "Instruments and Methods for High-Energy-Resolution X-ray Diffraction Characterization of Diamond Crystals," presented at the NSLS-II Seminar, Brookhaven National Laboratory, July 2010.

Stoupin, S., "R&D on X-ray Optical Cavity for Hard X-ray Free-Electron Laser Oscillator," presented at the Physics Colloquium, Illinois Institute of Technology, September 2010.

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Stoupin, S., F. Lenkszus, R. Laird, K. Goetze, K.-J. Kim, and Y.V Shvyd'ko, "Nanoradian Angular Stabilization of X-ray Optical Components," *Vir. J. Nan. Sci. & Tech*. **21**(23) (2010).

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Ultrafast X-Ray Tracking of Laser-Controlled Molecular Motions

2008-161-R2

Linda Young, Anne M. March, Andrew B. Stickrath, Bernhard W. Adams, Dohn A. Arms, Klaus Attenkofer, Lin X. Chen, Eric Dufresne, Elliot P. Kanter, Bertold M. Kraessig, Yuelin Li, Stephen H. Southworth, Donald A. Walko, and Jin Wang

Project Description

A fundamental and enduring challenge in science has been the quest to understand the relationship between structure and function in complex systems. Ultrafast x-ray science provides the ability to observe motion on atomic time and length scales. Advances in optical laser technology permit photonic control of atomic and electron motion. In this project, we marry these two frontiers to tackle a 21st-century challenge: observation of laser-controlled electron and atomic motion using ultrafast x-rays.

Mission Relevance

This project is relevant to DOE's mission in science. As the steward of advanced photon sources in the United States, the Office of Basic Energy Sciences (BES) is interested in advancing the capabilities of these tools. Historically, x-rays have been used primarily for structural studies. This project will expand capabilities for time-domain x-ray studies by providing high-repetition-rate laser excitation sources that allow efficient use of the x-ray flux, enhancing statistical precision 6500-fold to enable an array of applications.

FY 2010 Results and Accomplishments

During FY 2008, we procured a high-repetition-rate laser system (DUETTO), operating at 1.06 μm (micrometers) with 10-Watt average power, variable pulse width (10 and 130 picoseconds), and variable repetition rate (50 kHz–6.5 MHz). We devised plans for an amplification scheme based on a resonant passive-enhancement cavity, where successive laser pulses are coherently added to boost the laser pulse energy by a factor of ~100. We also devised plans for high-repetition-rate x-ray absorption experiments probing ultrafast structural changes of molecules in solution. During FY 2009, we implemented the customized electronics that enable synchronization between the master oscillator of the DUETTO (78 MHz) and the 352-MHz storage-ring radio frequency (rf). We demonstrated laser stabilization to a precision of 250 fs over the entire range of repetition rates in an offline laser laboratory. In collaboration with colleagues at JILA, a joint institute of the University of Colorado at Boulder and the National Institute of Standards and Technology, we designed, fabricated, and tested the resonant passive-enhancement cavity by using a continuous-wave laser having excellent phase stability. In addition, a fast-flowing liquid-jet target and a fast fluorescence-detection assembly were developed.

During FY 2010, there were two major accomplishments: we moved the high-repetition-rate DUETTO laser system from the offline laser test laboratory to the Advanced Photon Source (APS) and successfully conducted a first demonstration experiment by using the previously developed liquid-jet target. Installation of the DUETTO at the APS required integration of the synchronization system, previously tested with an rf synthesizer, with the actual rf transmitted from the APS control room to the experimental area some 300 m away in Sector 7 (Figure 1). The output of the DUETTO at 10 ps pulse duration was frequency-doubled (532 nm) with 70% efficiency and focused to 30 micrometer spot size, demonstrating the ability to achieve standard photoexcitation fluences of ~1 mJ/mm^2 (as used in previous work at 1 kHz, L.X. Chen et al., JACS 129 9616-9618 [2007]), at the full 6.5-MHz repetition rate of the APS. For a demonstration experiment, we chose the well-studied, radiation-stable NiTMP molecule. Because of the flow velocity of the liquid jet, we limited the repetition rate of the demonstration to 135 kHz. In this demonstration, we collected high statistics near-edge spectra of photoexcited and ground-state NiTMP in two hours, compared to the 12 day acquisition at 1-kHz. This demonstration constitutes a first realization of the potential gain of the high-repetition rate approaches for pump-probe time-domain studies at the APS utilizing 100% of the x-rays rather than the 0.015% used with

1-kHz lasers. High-repetition rate methods play an important role in the future Short-Pulse X-ray (SPX) facility planned for the APS Upgrade.

As a direct outgrowth of the work carried out through this project, we and our colleagues were awarded a Single-Investigator and Small-Group Research grant, which will allow for the continuation of this work. The liquid-jet apparatus will be used to study the transient laser-excited states of other molecules in solution, explore the range of useful repetition rates for solution-phase experiments, and quantify laser- and x-ray-induced damage. Also, development of the resonant enhancement cavity will continue, including plans for implementation of the cavity in x-ray absorption experiments to understand and control the behavior of laser-aligned gas-phase molecules.

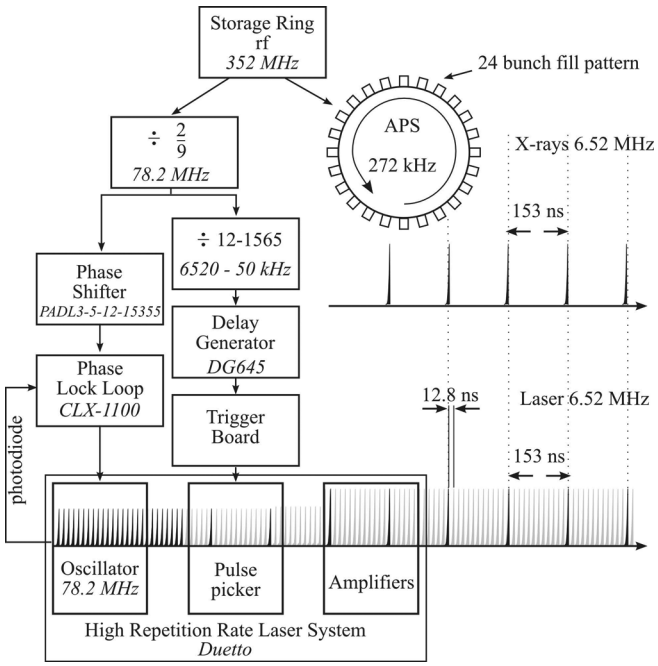


Figure 1. Schematic of the synchronization electronics of the DUETTO laser system with the APS radiofrequency system. The oscillator of the DUETTO runs at 78.2 MHz and must be multiplied by 2/9 to synchronize with the 352 MHz of the APS. A phase lock loop locks the DUETTO oscillator with the APS rf to an rms precision of 250 fs and a delay generator selects the appropriate oscillator pulse to amplify. Repetition rates between 50 kHz and 6.5 MHz are achievable. The high average power of the DUETTO, 10 W, combined with microfocus techniques allows the typical excitation fluences of 1 mJ/mm^2 to be achieved at repetition rates of 6.5 MHz, thus allowing the potential use of 100% of APS x-rays for pump-probe studies of ultrafast dynamics.

Non-Refereed Publications and Presentations

March, A.M., A.B. Stickrath, S.H. Southworth, E.P. Kanter, B. Krässig, G. Doumy, D. Ray, L.X. Chen, and L. Young, "High-Repetition-Rate Pump-Probe Experiments with X-rays and Intense Lasers," presented at the Pan-American Synchrotron Radiation Instrumentation Conference, Argonne, IL, September 21–24, 2010.

Coherent Diffraction Imaging of Nonperiodic Materials

2008-171-R2

Ian McNulty, Paul H. Fuoss, Jörg M. Maser, Stephen K. Streiffer, and Linda Young

Project Description

Coherent x-ray diffraction imaging (CDI) is a rapidly advancing method for determining the structures of objects by numerically inverting their coherent diffraction patterns. The small-angle CDI geometry is suited to imaging non-crystalline and highly disordered systems. Bragg CDI is sensitive to strain as well as structure in crystalline samples and is highly specific to particular crystal lattices in complex materials. Both approaches offer imaging at diffraction-limited resolution without the limitations of x-ray optics. In this project, we have combined CDI theory and experiment to address high-impact questions in materials science and nanoscience.

Mission Relevance

This project is relevant to DOE's mission in science. Hard x-ray, materials, and energy sciences all need high-resolution x-ray imaging tools for nanoscale characterization. Establishing and strengthening CDI approaches will provide a fundamentally new leading-edge characterization capability that leverages the Laboratory's instrumentation and computing strengths and supports DOE missions.

FY 2010 Results and Accomplishments

We developed new small-angle and Bragg CDI methodology, including plane-wave, Fresnel (focused beam), and scanning (ptychographic) techniques. We tested them in both resonant and non-resonant modes in experiments at APS sectors 2, 26, and 34. We developed codes for reconstructing data from small-angle Fresnel and scanning CDI experiments and a theoretical approach to understanding Bragg coherent diffraction with highly focused illumination that qualitatively agrees with experimental data. Our recent experimental efforts were on materials and material systems of scientific interest and technological relevance, including nanoporous Au, ferrimagnetically ordered GdFe, orbital ordering in $LaMnO_3$, and lattice-mismatched growth in Bi_2O_3.

Soft x-ray Fresnel CDI was used to quantify the pore size distributions and density profiles in dealloyed nanoporous Au samples (Figures 1 and 2) to ~25 nm resolution. Hard x-ray Bragg CDI was used to study dealloying of Ag/Au nanocrystals (Figure 3). In particular, we showed that the crystalline structure of the original alloy is maintained after dissolution of the silver. Transmission x-ray microscopy experiments were carried out at APS sector 32 to clarify the behavior of

dealloying and coarsening processes in nanoporous Au at lower (~50 nm) resolution. We developed a new method for imaging magnetic domain structure in extended samples by resonant scanning small-angle CDI with linearly polarized x-rays. The method was used to visualize the evolution of out-of-plane ferromagnetic domains in a multilayer GdFe film in an applied magnetic field (Figure 4). The ptychographic reconstruction code that we developed to reconstruct the data, based on the "steepest descent" approach, is of general utility and is available to APS users. Current work includes exploring magnetic instabilities as a function of temperature in the GdFe system, and improving the handling of data with poor signal/noise ratio by using conjugate gradient methods in the reconstruction code. We also explored the use of linearly polarized x-rays in the Bragg regime to probe orbital ordering in undoped crystalline at the Mn^{3+} resonance (~6.555 keV), near the Mn K-edge. We found that the 300–800-nm Mn^{3+} orbital domains remain static above as well as below the Néel temperature of 140 K for this progenitor manganite. We continued to study the use of scanning CDI with highly focused x-rays, with the goal of ultimately obtaining 3D strain maps of individual nanoscale structures (Figure 5). Using this approach, we studied epitaxially stabilized, isolated Bi_2O_3 nanoislands on strontium titanate substrates to understand better the role of strain in phase stabilization. We developed algorithmic approaches to (i) simulate interaction of the convergent beam with an arbitrarily shaped compact nanocrystal and (ii) integrate this approach into an iterative phasing algorithm by using a Fienup-derived approach.

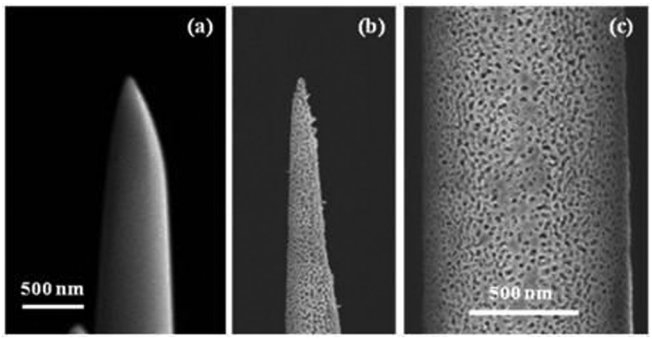


Figure 1. Scanning electron micrographs of (a) a nanoporous Au specimen before dealloying, (b) another nanoporous Au specimen after dealloying, and (c) the latter at higher magnification, showing ~30 nm pores at the surface.

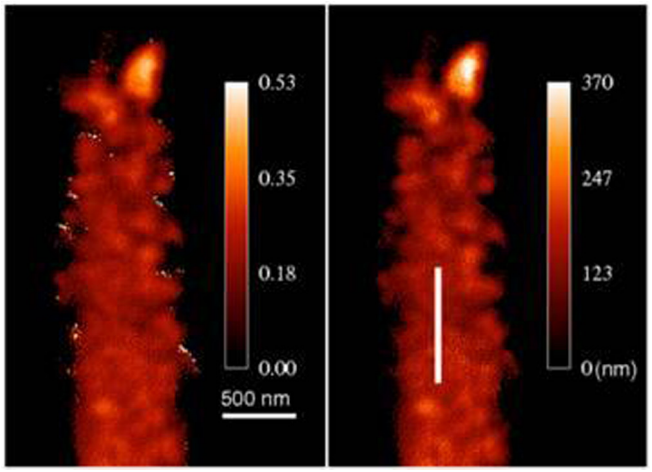


Figure 2. (left) Reconstructed absorption coefficient of the nanoporous Au sample in Figure 1 from Fresnel CDI data. (right) Projected thickness map obtained from the reconstructed phase of the sample exit surface wave.

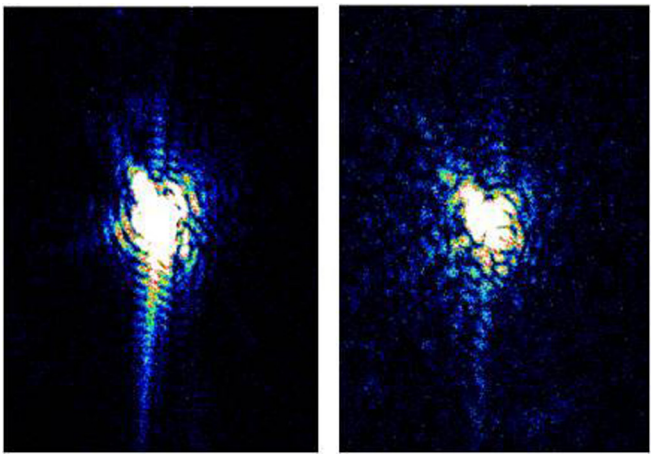


Figure 3. X-ray Bragg coherent diffraction patterns taken from the same Ag/Au nanocrystal (left) before dealloying and (right) after 20-s dealloying. Speckle appearing in the right-hand pattern shows the formation of nanoporosity.

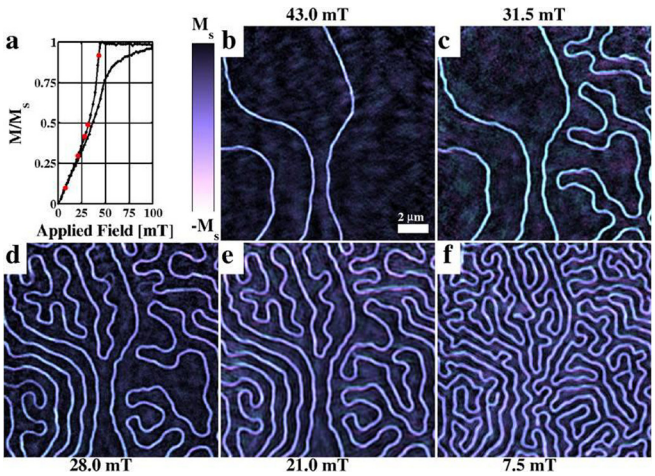


Figure 4. Study of domain evolution in a GdFe multilayer film as a function of applied magnetic field using scanning resonant CDI. (a) Hysteresis loop of sample magnetization as a function of magnetic field applied normal to the film surface. (b-f) Reconstructions from a series of diffraction patterns taken at indicated points in the hysteresis curve, from near-saturation towards zero. Bright domains are anti-parallel to the applied magnetic field. The use of linearly polarized x-rays tuned to the Gd M5 absorption edge (1189 eV) made this method uniquely sensitive to the magnetic structure of the sample.

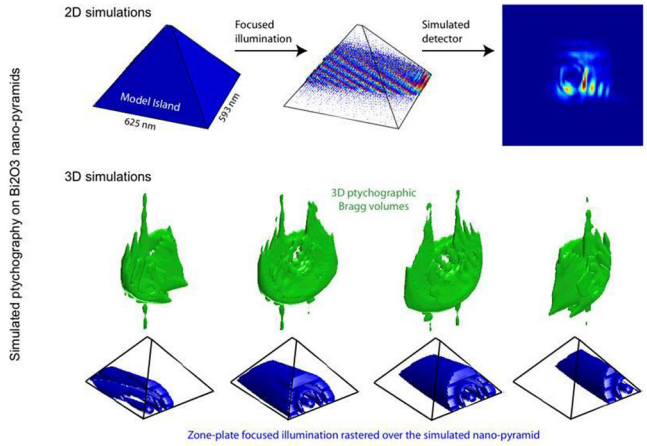


Figure 5. Simulation of Bragg CDI with a nano-focused beam. The 2D simulations show the interaction of the incident wavefront with a nanostructure. The 3D simulations show combinations of scanned acquired data taken at different positions across the rocking curve.

Refereed Publications

Abbey, B., K.A. Nugent, G.J. Williams, J.N. Clark, A.G. Peele, M.A. Pfeifer, M. de Jonge, and I. McNulty, "Keyhole Coherent Diffractive Imaging," *Nature Phys.* **4** (2008), 394–398.

Abbey, B., G.J. Williams, M.A. Pfeifer, J.N. Clark, C.T. Putkunz, A. Torrance, I. McNulty, T.M. Levin, A.G. Peele, and K.A. Nugent, "Quantitative Coherent Diffractive Imaging of an Integrated Circuit at a Spatial Resolution of 20 nm," *Appl. Phys. Lett.* **93** (2008), 214101.

Chen, Y.-C., Y. Chu, J. Yi, I. McNulty, Q. Shen, P. Voorhees, and D.C. Dunand, "Morphological and Topological Analysis of Coarsened Nanoporous Gold by X-ray Nanotomography," *Appl. Phys. Lett.* **96** (2010), 043122.

Clark, J.N., C.T. Putkunz, M.A. Pfeifer, A.G. Peele, G.J. Williams, B. Chen, K.A. Nugent, C. Hall, W. Fullagar, S. Kim, and I. McNulty, "Use of a Complex Constraint in Coherent Diffractive Imaging," *Opt. Express* **18**(3) (2010), 1981–1993.

Dilanian, R.A., G.J. Williams, L.W. Whitehead, D.J. Vine, A.G. Peele, E. Balaur, I. McNulty, H.M. Quiney, and K.A. Nugent, "Coherent Diffractive Imaging: A Statistically Regularized Amplitude Constraint," *New J. Phys. Rev.* **12** (2010), 093042.

Miao, J., T. Ishikawa, Q. Shen, and T. Earnest, "X-ray Crystallography without Crystals," *Ann. Rev. Phys. Chem.* **59** (2007), 387-409.

Putkunz, C.T., J.N. Clark, D.J. Vine, G.J. Williams, M.A. Pfeifer, E. Balaur, I. McNulty, K.A. Nugent, and A.G. Peele, "Phase-Diverse Coherent Diffractive Imaging: High Sensitivity with Low Dose," *Phys. Rev. Lett.* **106** (2011), 013903.

Putkunz, C.T., M.A. Pfeifer, A.G. Peele, G.J. Williams, H.M. Quiney, B. Abbey, K.A. Nugent, and I. McNulty, "Fresnel Coherent Diffraction Tomography," *Opt. Express* **18**(11) (2010), 11746–11753.

Vine, D.J., G.J. Williams, B. Abbey, M.A. Pfeifer, J.N. Clark, M.D. de Jonge, I. McNulty, A.G. Peele, and K.A. Nugent, "Ptychographic Fresnel Coherent Diffractive Imaging," *Phys. Rev. A* **80** (2009), 063823.

Whitehead, L.W., G.J. Williams, H.M. Quiney, K.A. Nugent, A.G. Peele, D. Paterson, M.D. de Jonge, and I. McNulty, "Fresnel Diffractive Imaging: Experimental Study of Coherence and Curvature," *Phys. Rev. B* **77** (2008), 104112.

Whitehead, L.W., G.J. Williams, H.M. Quiney, D.J. Vine, R.A. Dilanian, S. Flewett, K.A. Nugent, A.G. Peele, E. Balaur, and I. McNulty, "Diffractive Imaging Using Partially Coherent X Rays," *Phys. Rev. Lett.* **103**(24) (2009), 243902-1 to 243902-4.

Non-Refereed Publications and Presentations

Chen, Y.-C., "Coarsening in Nanoporous Au by 3D X-ray Nanotomography," presented at the Denver X-ray Conference, Denver, CO, August 2008.

Chen, Y.-C., "X-ray Imaging of Nanoporous Gold," presented at the APS User Seminar, Argonne National Laboratory, Argonne, IL, April 2009.

Chen, Y.-C., "3D X-ray Imaging of Nanoporous Metal: Evolution of Morphology and Internal Strain during Dealloying and Coarsening," PhD Candidacy presentation, Northwestern University, Evanston, IL, September 2009.

Chen, Y.-C., "Dealloying and Coarsening Behavior of Nanoporous Gold by X-ray Nanotomography," presented at the TMS 2010 Conference, Seattle, WA, February 2010.

Chen, Y.-C., "X-ray Imaging and Tomography of Nanoporous Gold - Dealloying and Coarsening," invited talk presented at the X-ray Imaging Group Seminar, ESRF, Grenoble, France, February 2010.

Clark, J., "Improving Solutions in Fresnel Coherent Diffractive Imaging," presented at the CDI Working Group Seminar, Argonne National Laboratory, Argonne, IL, December 2009.

Guizar-Sicairos, M., "Advances in Phase Retrieval with Transverse Translations and Holography with an Extended Reference for X-Ray Imaging and Wavefront Measurement," presented at the CDI Working Group Seminar, Argonne National Laboratory, Argonne, IL, December 2009.

Harder, R., and L. Beitra, "*In-situ* Confocal Microscopy for Nanoscale Strain Mapping with Coherent X-Rays Diffraction Imaging at 34-ID-C," presented at the APS User Seminar, Argonne National Laboratory, Argonne, IL, August 2009.

Harder, R., "Imaging Strain on the Nanoscale with Coherent X-ray Diffraction," invited talk presented at the Physics Department Colloquium, University of Wisconsin—Milwaukee, February 2010.

Hruszkewycz, S., "Preliminary Coherent Diffraction Experiments at the Sector 26 Nanoprobe," presented at the CDI Working Group Seminar, Argonne National Laboratory, Argonne, IL, May 2009.

Hruszkewycz, S., "Effects of Beryllium Windows on Accuracy of CDI Data Reconstruction," presented at the CDI Working Group Seminar, Argonne National Laboratory, Argonne, IL, August 2009.

Hruszkewycz, S., "Simulation of Bragg Coherent Diffraction from Epitaxial Bi_2O_3 Nanoislands," presented at the CDI Working Group Seminar, Argonne National Laboratory, Argonne, IL, November 2009.

Hruszkewycz, S., "Bragg Coherent Diffraction Imaging Using <100 nm Focused Hard X-rays," invited talk presented at the 10th International Conference on X-ray Microscopy, Chicago, IL, August 15–20, 2010.

Hruszkewycz, S.O., M.V. Holt, D.L. Proffita, M.J. Highland, A. Imreb, J. Maser, J.A. Eastman, G.R. Bai, and P.H. Fuoss, "Bragg Coherent Diffraction Imaging of Epitaxial Nanostructures Using Focused Hard X-ray Ptychography," *Proc. XRM 2010 Conference*, in press.

Kim, S., "Phase Retrieval Method Using Predetermined Phase Information," presented at the CDI Working Group Seminar, Argonne National Laboratory, Argonne, IL, September 2008.

Kim, S., "3D Phase Recovery from Fresnel Coherent Diffraction Data," presented at the CDI Working Group Seminar, Argonne National Laboratory, Argonne, IL, March 2009.

Kim, S., "Fresnel Coherent Diffractive Imaging of Gold Nanofoams," presented at the APS User Seminar, Argonne National Laboratory, Argonne, IL, September 2009.

Kim, S., "Determination of Porosity Distribution in Nanoporous Au by Fresnel Coherent Diffractive Imaging," presented at the American Physical Society March Meeting 2010, Portland, OR, March 2010.

Kim, S., Y.K. Chen, C.T. Putkunz, D.C. Dunand, and I. McNulty, "Use of Justified Constraints in Coherent Diffractive Imaging," *Proc. XRM 2010 Conference*, in press.

Klug, J., "Nanoscale Coherent Diffraction Investigation of Epitaxial Bifeo3 Thin Film Nanostructures," presented at the CDI Working Group Seminar, Argonne National Laboratory, Argonne, IL, July 2009.

Maser, J., "Nanoscience Using Advanced X-Ray Microscopy," invited talk presented at the Symposium on Frontiers in Optics/ Laser Science, 93rd Annual Meeting of the Optical Society of America, San Jose, CA, October 15, 2009.

Maser, J., "Nanoscience using Advanced X-ray Microscopy," presented at the Workshop on Science with Nanobeams, ESRF, Grenoble, France, February 2010.

Maser, J., "The Hard X-Ray Nanoprobe Beamline at Argonne National Laboratory," invited talk presented at the ESRF User's Meeting, Grenoble, France, February 11, 2010.

Maser, J., "Materials Characterization Using the Hard X-Ray Nanoprobe at Argonne National Laboratory," invited talk presented at the TMS Annual Meeting, Seattle, WA, Feb. 15, 2010.

McNulty, I., "Applications of Coherent Imaging in Condensed Matter Science," invited talk presented at the Wisconsin Free Electron Laser Symposium, University of Wisconsin—Madison, October 2007.

McNulty, I., "Soft X-ray Imaging at the APS," invited talk presented at the Workshop on New Opportunities in X-ray Microscopy, Stanford University, Palo Alto, CA, October 2007.

McNulty, I., "Imaging: Overview and Recent Applications," invited talk presented at the Research Course on New Materials in New Light, DESY, Hamburg, Germany, March 2008.

McNulty, I., "Phase Singularities and Orbital Angular Momentum in X-ray Microscopy," invited talk presented at the Ninth International Conference on X-ray Microscopy, Zürich, Switzerland, August 2008.

McNulty, I., "Coherent Diffraction at APS," invited talk presented at the I13L Beamline Design Review Meeting, Diamond Light Source, Didcot, UK, August 2008.

McNulty, I., "A Perfect Storm: Lensless X-Ray Imaging at the Nanometer Scale," invited talk presented at the Physics Department Colloquium, University of Colorado at Boulder, August 2008.

McNulty, I., "No Pain, No Gain: Noise and Background in X-ray CDI Experiments," presented at the CDI Working Group Seminar, Argonne National Laboratory, Argonne, IL, September 2008.

McNulty, I., "Soft and Hard X-ray Microscopy," invited talk presented at the AOFSRR Cheiron Summer School 2008, SPring-8, Hyogo, Japan, October 2008.

McNulty, I., "Coherent Imaging in Condensed Matter and Biology," NSF Reverse Site Visit for the Wisconsin FEL Project, Arlington, VA, November 2008.

McNulty, I., "Coherent Diffractive X-Ray Imaging of Biomaterials," invited talk presented at the Workshop on Imaging Structural Hierarchy in Biological Systems," presented at the Advanced Photon Source Annual Users Meeting, Argonne, IL, May 2009.

McNulty, I., "Opportunities for Nanoscale Imaging at High Pressure by Coherent X-Ray Diffraction," invited talk presented at the Workshop on High Pressure Synchrotron Science, Advanced Photon Source Annual Users Meeting, Argonne, IL, May 2009.

McNulty, I., "Coherent X-ray Applications for ERLs," invited talk presented at the 2009 International Conference on Energy Recovery Linacs, Cornell University, Ithaca, NY, June 2009.

McNulty, I., "Coherent Diffractive Imaging: APS Activity and Experiments for DLS," invited talk presented at the I13L Working Group Meeting, Diamond Light Source, Didcot, UK, September 2009.

McNulty, I., "Probing Magnetic Structure by Coherent X-Ray Diffraction," invited talk presented at the Workshop on Developments in Coherent X-ray Methods, 2009 International Synchrotron Radiation Instrumentation Conference, University of Melbourne, Australia, October 2009.

McNulty, I,. "Coherent X-ray Diffraction into the Next Decade," invited talk presented at the NSLS-II Workshop on Coherent Diffractive Imaging, Upton, NY, May 2010.

McNulty, I., "Imaging Magnetic Structure by Coherent X-ray Diffraction," invited talk presented at the Coherence 2010 Conference, Warnemünde, Germany, June 2010.

McNulty, I.,"Dichroic Coherent Diffractive Imaging," invited talk presented at the Third International Workshop on FEL Science, Hokkaido, Japan, October 2010.

McNulty, I., and Q. Shen, "Coherent X-ray Microscopy Workshop," *Synchrotron Rad. News* **21** (2008), 12–13.

Mohanty, J., "Magnetic Domain Dynamics in Fe/Gd Magnetic Multilayers," presented at the American Physical Society March Meeting 2010, Portland, OR, March 2010.

Nugent, K., "Partial Coherence in X-Ray Diffractive Imaging," presented at the CDI Working Group Seminar, Argonne National Laboratory, Argonne, IL, August 2009.

Ourmazd, A., "Single Particle Imaging with Coherent Diffraction," presented at the CDI Working Group Seminar, Argonne National Laboratory, Argonne, IL, December 2007.

Ourmazd, A., "Virus Simulations and Xiao Data Analysis: New Results with GTM," presented at the CDI Working Group Seminar, Argonne National Laboratory, Argonne, IL, September 2008.

Ourmazd, A., "Update on XFEL projects in Europe and Nanofoam Diffraction Pattern Orientation," presented at the CDI Working Group Seminar, Argonne National Laboratory, Argonne, IL, December 2008.

Pfeifer, M., "Progress with the New FCDI Instrument at 2-ID-B," presented at the CDI Working Group Seminar, Argonne National Laboratory, Argonne, IL, December 2008.

Shen, Q., "Imaging Materials Structures and Processes by X-ray Microscopy: Current Status and Future Prospects," invited talk presented at the Materials Science and Engineering Colloquium, Northwestern University, Evanston, IL, October 2007.

Shen, Q., "Overview and Future Plans of X-ray Microscopy and Imaging at APS," presented at the DOE Triennial Review of the Advanced Photon Source, Argonne National Laboratory, Argonne, IL, December 2007.

Shen, Q., "Coherent X-ray Diffraction Imaging at the Advanced Photon Source," invited talk presented at the Three-Way Meeting, Nanoscience Workshop, Argonne National Laboratory, Argonne, IL, March 2008.

Shen, Q., "Can Coherent X-ray Diffraction Imaging Reach Atomic Resolution?," invited talk presented at the International Workshop on Coherent X-ray Diffraction, Brookhaven National Laboratory, Upton, NY, March 2008.

Shen, Q., "Studies of Material Structure and Process with Coherent Diffraction & Time Resolved X-ray Imaging," invited talk presented at the XXI Congress of the International Union of Crystallography, Osaka, Japan, August 2008.

Shen, Q., "Applications of Coherent X-ray Diffraction Imaging in Material Science," invited talk presented at the IUCr Satellite Meeting on X-ray & Neutron Applications in Nanostructure Research, SPring-8, Hyogo, Japan, August 2008.

Shen, Q., "Advanced X-Ray Imaging at Modern Synchrotron Facilities," invited talk presented at the 9th Biennial Conference on High Resolution X-Ray Diffraction and Imaging (XTOP), Linz, Austria, September 2008.

Shen, Q., "Coherent X-ray Optics and Microscopy," Chapter 27 in *Optical Society of America Handbook of X-ray Optics, Volume V*, edited by M. Bass, C. DeCusatis, J. Enoch, V. Lakshminarayanan, G. Li, C. Macdonald, V. Mahajan, and E. Van Stryland, McGraw-Hill, New York, in press.

Song, C., "Nano-scale Imaging with the Coherent Diffraction Microscope," presented at the CDI Working Group Seminar, Argonne National Laboratory, Argonne, IL, February 2008.

Treacy, M.M.J., D. Kumar, A. Rougée, G. Zhao, P.R. Buseck, I. McNulty, L. Fan, C. Rau, and J.M. Gibson, "Glimpsing Order within the Disarray," *J. Phys.: Conf. Ser.* **126** (2008), 012001.

Tripathi, A., "Outstanding Questions in Manganite Physics," presented at the CDI Working Group Seminar, Argonne National Laboratory, Argonne, IL, November 2008.

Tripathi, A., "Beating the Missing Data Problem with Ptychography," presented at the CDI Working Group Seminar, Argonne National Laboratory, Argonne, IL, April 2009.

Tripathi, A., "Ptychographic Imaging of Magnetically Ordered Systems," PhD Candidacy presentation, University of California—San Diego, La Jolla, CA, June 2009.

Tripathi, A., "Ptychography Measurements on Ferrimagnetic Multilayer Gdfe Films," presented at the CDI Working Group Seminar, Argonne National Laboratory, Argonne, IL, November 2009.

Tripathi, A., "Scanning Coherent X-ray Diffraction Imaging of GdFe Magnetic Multilayers," presented at the American Physical Society March Meeting 2010, Portland, OR, March 2010.

Tripathi, A., O. Shpyrko, and I. McNulty, "Influence of Noise and Missing Data on Reconstruction Quality in Coherent X-ray Diffractive Imaging," *Proc. XRM 2010 Conference*, in press.

Xiao, X., "Recent CDI Results with Dealloyed Nanofoams," presented at the CDI Working Group Seminar, Argonne National Laboratory, Argonne, IL, May 2008.

Xiao, X., "Phasing Results of Coherent Diffraction Imaging of Au Foam: an Introduction to a Hard X-Ray Coherent Diffraction Imaging Instrument at APS," presented at the CDI Working Group Seminar, Argonne National Laboratory, Argonne, IL, October 2008.

High Brightness CW Injector Technology and Design Studies for the Energy Recovery Linac

2008-177-R2

Katherine C. Harkay, Vijayalakshmi Kalyanaraman, Yuelin Li, and Marion M. White

Project Description

Future energy-recovery linacs and free-electron lasers can provide greatly enhanced x-ray brightness and coherence, but a key requirement is improved electron injector performance, which in turn depends on photocathode emission properties. The goal of this project is to develop photocathodes that meet the requirements of next-generation light sources.

Mission Relevance

This project supports DOE's mission in basic science, which includes planning, constructing, and operating premier national scientific user facilities. Synchrotron light sources — such as the Advanced Photon Source (APS) — are excellent

tools for advancing many scientific frontiers. DOE recognizes the importance of such tools and supports the development of next-generation light sources, including a major accelerator upgrade for the APS.

FY 2010 Results and Accomplishments

Over the past two years, activity has ramped up significantly in the area of photocathode R&D, not only for future light sources but also for accelerators and detectors for high energy physics. The main U.S. laboratories pursuing photocathode R&D are Brookhaven National Laboratory (BNL), Jefferson Lab (JLab), Lawrence Berkeley National Laboratory (LBNL), SLAC National Accelerator Laboratory, and CLASSE (Cornell Laboratory for Accelerator-based Sciences and Education). Most of the non-Argonne efforts are focused on understanding and optimizing the growth recipes for photocathodes based on III-V (e.g., GaAs) or multi-alkali (e.g., CsKSb) semiconductors for longer-lived, high-QE performance. The effort under this project is complementary and unique: the goals were to develop approaches for tailoring the properties of photocathodes to yield electron sources having ultrahigh brightness and to develop an experimental capability to characterize these properties. Our focus evolved from studying ordinary metal cathodes, to developing novel cathode concepts (with ideas borrowed from systems used for surface catalysis), and to thinking of ways to tailor the properties of existing cathodes (such as cesium telluride [Cs_2Te]).

A key and novel feature of our photocathode design is based on band structure engineering, whereby the work function, band structure, and potentially the photon absorption and electron-electron scattering properties can be manipulated to result in ultralow intrinsic emittance emission with sufficient charge density. We successfully demonstrated this approach with a system based on magnesium oxide monolayers on a silver substrate. Our numerical computations showed a lowering of the intrinsic emittance and the work function. Preliminary theoretical work was begun on tailoring the properties of cesium telluride (Cs_2Te). This cathode was chosen to leverage expertise developed under a different project, 2009-076-R1, "Photocathodes Development for Accelerator Research and Development," for which the investigators have developed the capability of growing Cs_2Te cathodes with QE consistently above 10%.

To measure the energy and emission angle of the photoelectrons produced by tailored cathodes, the component parts of an angle-resolved photoemission spectroscopy (ARPES) system, including a time-of-flight (TOF) electron detector, were acquired, assembled, and partially commissioned. This new system and an existing x-ray photoemission spectroscopy system enable the determination of the emittance and the surface chemistry, which are important in evaluating cathode lifetimes under exposure to ambient gases. Added this year was a Kelvin probe that enables measurement of the work function with sub-meV resolution and a spatial resolution on the order of a few millimeters. Linda Spentzouris (Illinois Institute of Technology [IIT]) and her students assisted in commissioning the ARPES system. Discussions were initiated with IIT on the fabrication of candidate cathode systems for study.

Characterizing cathodes in the ARPES chamber requires a loadlock device that allows the cathodes to be removed from a growth chamber, transported under vacuum, and then transferred onto the sample holder in the ARPES chamber. A loadlock system that is compatible with different apparatuses (i.e., is "universal") is recognized in the cathode R&D community as being both needed and challenging. Preliminary work was begun on a loadlock system design that is compatible with the Cs_2Te growth chamber and the APRES system, in cooperation with Zikri Yusof and Igor Veryovkin (Argonne), who, under a separate project (2009-076-R1) and with our group, are leading the field in this activity.

Refereed Publications

Dowell, D.H., I. Bazarov, B. Dunham, K. Harkay, C. Hernandez-Garcia, R. Legg, H. Padmore, T. Rao, J. Smedley, and W. Wan, "Cathode R&D for Future Light Sources," *Nucl. Instrum. Meth. A* **622** (2010), 685–697.

Németh, K., K.C. Harkay, M. van Veenendaal, L. Spentzouris, M. White, K. Attenkofer, and G. Srajer, "High-Brightness Photocathodes through Ultrathin Surface Layers on Metals," *Phys. Rev. Lett.* **104** (4) (2010), 046801.

Non-Refereed Publications and Presentations

Harkay, K., "Photocathode R&D at Argonne," presented at Future Light Sources Workshop (FLS2010), SLAC (Stanford Linear Accelerator), Menlo Park, CA, March 2010.

Németh, K., K.C. Harkay, M. van Veenendaal, L. Spentzouris, M. White, K. Attenkofer, and G. Srajer, "Theoretical Design of High-Brightness Photocathodes Based on Ultrathin Surface Layers on Metals and on Nanostructures," *Proceedings of the 14th Advanced Accelerator Concepts Workshop* **1299** (2010), 522–527, November 4, 2010.

Feasibility Studies and Pre-Conceptual Design of Continuous Wave (CW) Superconducting RF Deflecting Cavities for the Generation of Short X-Ray Pulses at the Advanced Photon Source

2008-190-R2

Alireza Nassiri, Michael D. Borland, Katherine C. Harkay, and Patric Den Hartog

Project Description

This project focuses on the design and development of transverse superconducting radio frequency (SRF) structures ("crab cavities") for the production of short x-ray pulses at the Advanced Photon Source (APS). In this concept, known as the Zholents' Scheme (see Figure 1), transverse-deflecting SRF cavities are used to impose a correlation ("chirp") between the longitudinal position of an electron within the electron population density, known as the "electron bunch," and its vertical momentum. The x-rays emitted by each electron tend to travel along the same path as the electron. Hence, by placing an undulator just downstream of the crab cavity, for example, we can produce a chirped x-ray beam. At a sufficient distance (e.g., 30 m) from the undulator, this angular chirp will evolve into a spatial chirp, so that a strong correlation appears in the x-ray pulse between its arrival time and vertical coordinate. Use of vertical slits then permits filtering the pulse in the time dimension, allowing production of an x-ray pulse that is shorter than the electron bunch length.

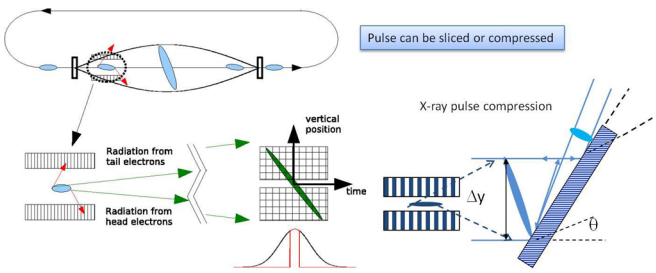


Figure 1. Zholents' Scheme using RF deflection cavities for production of short x-ray pulses.

Mission Relevance

This project is tied to DOE's mission in basic science through the Department's support of x-ray-based national user facilities. The immediate beneficiaries of this work will be members of the short-pulse, time-resolved x-ray science community, because this scheme will make it possible to deliver picosecond-type x-ray pulses at very high repetition rates.

FY 2010 Results and Accomplishments

The development, fabrication, and testing of two single-cell structures were completed with help from researchers at Jefferson National Accelerator Laboratory (JLab), and a single-cell (type 1) cavity equipped with a lower-order-modes and higher-order-modes (LOM/HOM) damping waveguide and input power coupler was successfully fabricated and processed. This structure (Figure 2) is now being prepared for vertical cold tests. A potential second cavity (type 2), employing an "on-cell" waveguide damper (see Figure 3), was also developed. The latter cavity provides improved damping of unwanted frequencies within it and will be shorter in overall length. The multipacting (breakdown) issue for the on-cell damping structure has been extensively modeled and simulated by using a 3D code (Omega3P/Track3P) developed at SLAC. Recent measurements at JLab confirmed the simulation results predicted by Omega3P/Track3P that the on-cell damper structure is free of multipacting within the cavity operating deflecting voltage. Multipacting simulation results are shown in Figure 4.

Lorentz force detuning (LFD) was investigated to validate the experimental data, as well as to consider its effect on the tight phase tolerance required to assure that the short-pulse x-ray system is transparent to the remainder of the APS storage ring. The non-uniform niobium shell thickness of the cavity was shown to cause a large LFD, but the addition of waveguide groups attached to the cell irises is expected to reduce this effect.

An LFD value of 7.9–10.5 kHz/MV^2 or 22.4–29.8 Hz/(MV/m)^2, depending on structural constraints, was obtained in an ANSYS simulation for the baseline design. At 0.5-MV deflecting voltage on each cavity, the folded resonance peak, with a loaded Q of 1.2E6, is tilted over its −3-dB bandwidth (−1.17 kHz, in Figure 5). A fast digital self-excited loop control can be used to quickly recover from an RF trip without requiring cavity stiffeners.

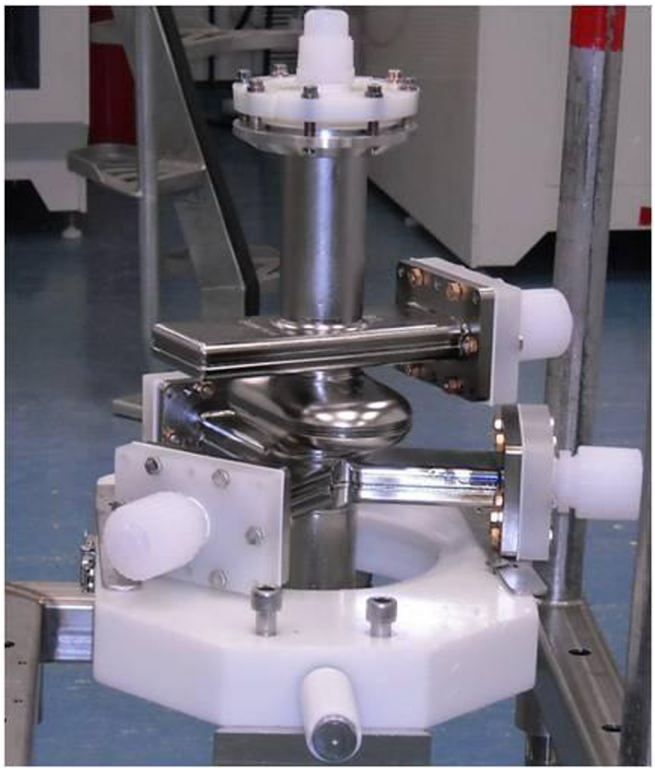


Figure 2. A single-cell deflecting prototype cavity with waveguide input coupler and LOM/HOM dampers.

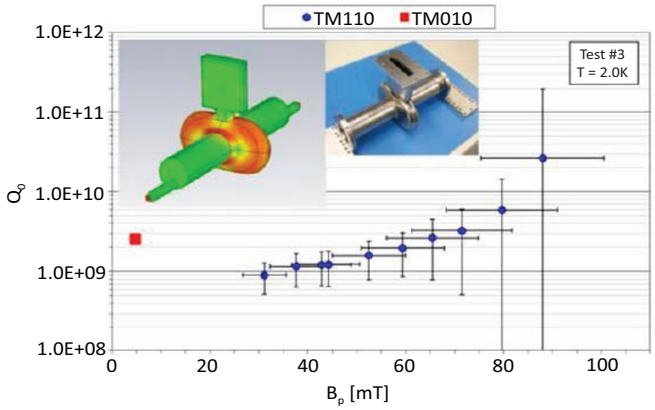


Figure 3. A maximum surface magnetic field of 90 mT in the TM110 mode has been achieved. An unphysical Q slope seen as the field is increased is due to a large error caused by a weak RF coupling at the input coupler.

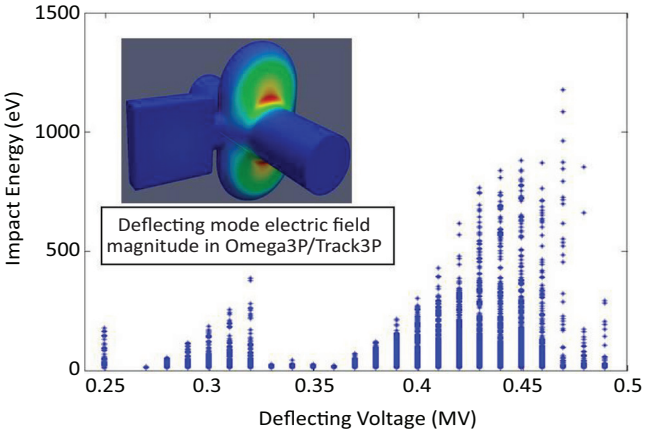


Figure 4. Multipacting results of the on-cell damper deflecting cavity.

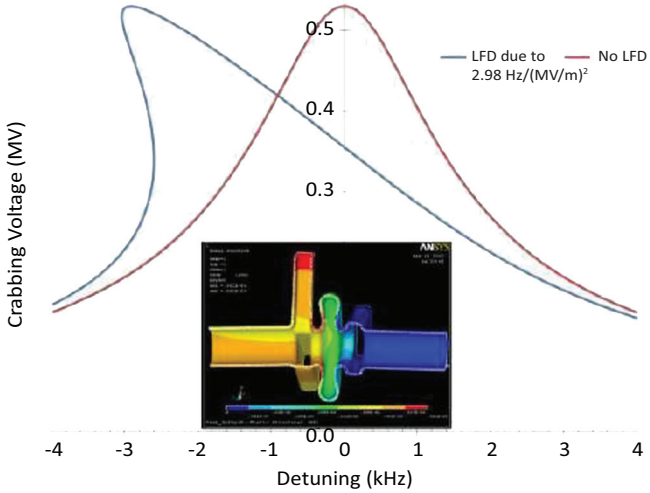


Figure 5. Structural deformation of the type 1 deflecting cavity due to Lorentz force and the resultant detuning of the cavity resonance (blue curve).

Non-Refereed Publications and Presentations

Nassiri, A., "Short Pulse X-ray (SPX) Project at the APS," invited talk at 2nd ICFA (International Committee for Future Accelerators) Beam Dynamics Mini-Workshop on Deflecting/Crabbing Cavity Applications in Accelerators, Cockcroft Institute, Daresbury, UK, September 1–3, 2010.

Wang, H., "ANL Crab Cavity Development," invited talk at 2nd ICFA Beam Dynamics Mini-Workshop on Deflecting/Crabbing Cavity Applications in Accelerators, Cockcroft Institute, Daresbury, UK, September 1–3, 2010.

Wang, H., G. Cheng, C. Ciovati, J. Henry, P. Kneisel, R.A. Rimmer, G. Slack, L. Turling, A. Nassiri, and G. Waldchmidt, "Design and Prototyping Progress Toward a Superconducting Crab Cavity Cryomodule for the APS," presented at 2010 International Particle Accelerator Conference, IPAC10, Kyoto, Japan, May 23–28, 2010.

Catalyst Station at Advanced Photon Source Beamline 9-BM

2009-050-R1

Trudy B. Bolin, Steve M. Heald, Jeffrey T. Miller, Peter C. Stair, and Randall E. Winans

Project Description

This project will enhance catalyst research opportunities at beamline 9-BM and at the Advanced Photon Source (APS) in general. Synchrotron radiation methods have important applications in catalyst research, and the completion of this capability-enhancement project will allow us to make concurrent extended x-ray absorption fine structure (XAFS) and powder-diffraction measurements on catalysts in operando conditions.

Mission Relevance

Catalysis is an essential technology for economic prosperity, energy security, and environmental preservation in the twenty-first century and is therefore supportive of DOE missions in both energy and environment. The use of synchrotron radiation to study catalysts has a long history, and most synchrotron facilities have beamlines with equipment for catalyst research. This project will bring the APS up to the state of the art for catalyst research at synchrotron facilities. It will provide the capability for concurrent operando XAFS and powder diffraction measurements, a capability found at only a few beamlines worldwide. It will also be the first step in facilitating catalyst research at other beamlines around the APS.

FY 2010 Results and Accomplishments

In FY 2009, the basic instrumentation for the 9-BM-C station was installed and the first XAFS experiments were carried out. At the same time, laboratory enhancements began with the installation of a high-quality glove box. This glove box has been in high demand for supporting experiments at 9-BM and other sectors involved in catalyst work. During FY 2010, instrumentation upgrades of the 9-BM-C endstation continued, mainly aimed toward integrating and characterizing the systems installed in FY 2009. A new and expanded workstation area was established, and the beamline controls were upgraded to support the popular Sector-20 EXAFS software. Working with neighboring beamlines, we installed a high-purity N_2 gas system, which will help support a second glove box that has been established for handling samples containing sulphur or other volatile materials that could contaminate the high-quality glove box. An upgrade of the endstation ventilation system serving sectors 8 and 9 was completed, allowing independent operation of experiments involving hazardous gases at 9-BM. The 9-BM-C endstation is fully capable of operations and has begun to be used for experiments.

We have added *in-situ* infrared (IR) spectroscopy to 9-BM-C. A basic spectrometer and sample cell for diffuse reflectance Fourier transform infrared spectroscopy (FTIR) (DRIFT) were delivered, and work has begun on modifying them for simultaneous XAFS and IR spectroscopy.

The associated laboratories continue to be upgraded to support catalyst research. We began the conversion of the 432-A020 laboratory into a chemical laboratory capable of supporting catalyst sample preparation. The biggest component was the purchase of a fully capable fume hood.

Proposed Work for FY 2011

In preparation for accepting general users from the catalyst community, we will complete the characterization and documentation of the new 9-BM-C endstation. In partnership with catalyst researchers in the Chemical Sciences and Engineering Division, we will also be carrying out the initial simultaneous XAFS and IR measurements using the new spectrometer. The planned catalyst system is a catalytic-converter catalyst that has been previously characterized by these techniques separately. The simultaneous measurement will allow direct correlation of the two results and serves as an excellent test case for our new instrumentation.

Refereed Publications

Trovitch, R.J., G. Neng, M.T. Janicke, L. Hongbo, C.L. Marshall, J.T. Miller, A.P. Sattelberger, K.D. John, and R.T. Baker, “Spectroscopic Characterization of Alumina-Supported Bis(allyl)iridium Complexes: Site-Isolation, Reactivity, and Decomposition Studies,” *Inorg. Chem*. **49** (2010), 2247–2258.

Non-Refereed Publications and Presentations

Heald, S., T. Bolin, R. Winans, J. Miller, and P. Stair, “Catalyst Center at the Advanced Photon Source Beamline 9-BM,” poster presented at the American Chemical Society Fall National Meeting, Division of Fuel Chemistry, Advances in Fuel Science and Technology, August 22–26 2010.

Heald, S., T. Bolin, R. Winans, J. Miller, and P. Stair, “An Update on the XOR Sector 9-BM Beamline Catalyst Center Effort,” poster presented at the Chicago Catalysis Club Spring Meeting, May 10, 2010.

Large-Scale Beam Dynamics Optimization for More Efficient Operation of Large User Facilities

2009-071-R1

Peter N. Ostroumov, Brahim Mustapha, Jerry A. Nolen, Jr., Richard C. Pardo, and Jin Xu

Project Description

Our goal is to develop a realistic computer model that could be relied upon to operate an accelerator-based user facility. This effort requires developing both a realistic three-dimensional (3D) model for every element on the beamline and a good understanding of the initial beam parameters at the source by combining source models and beam measurements. It also requires that we develop specific interfaces between the beam diagnostic devices and the beam dynamics code, in addition to developing all possible optimization tools.

Mission Relevance

This project is relevant to DOE's basic science mission. The successful application of the model to operations at the Argonne Tandem Linear Accelerator System (ATLAS) and the Californium Rare Isotope Breeder Upgrade (CARIBU) will improve the beam transmission, which is critical for radioactive beams and should also reduce downtime. The techniques and methods developed here could be used to improve the performance of other DOE user facilities, such as the planned Facility for Rare Isotope Beams and other high-power, linac-based facilities.

FY 2010 Results and Accomplishments

Detailed Design and Simulation of a Radio Frequency Quadrupole (RFQ) for the ATLAS Upgrade:

For the design of the 60.625-MHz radio frequency quadrupole (RFQ) that is part of the upgrade to ATLAS's efficiency and intensity, we established a new and fully 3D approach to performing the electromagnetic and beam dynamics simulations of an RFQ. A detailed, fully 3D (four-meter-long) model that includes vane modulation was built and simulated by using the CST Microwave Studio tool (and made possible by ever-advancing computing capabilities). The approach was validated by using experimental measurements on a 57.5 MHz RFQ model. The effects of the radial matchers, vane modulation, and tuners on the resonant frequency and field flatness were carefully studied. The full-3D field distribution was used for performing beam dynamics simulations by using both the CST Particle Studio tool and the beam dynamics code, TRACK. In the final design, we used trapezoidal modulation instead of the standard sinusoidal in the accelerating section of the RFQ to achieve greater energy gains for the same total length. In our case, the output energy increased from 260 keV/u to 295 keV/u, with minimal change occurring in the rest of the beam dynamics. Figure 1 shows the fully 3D model of the RFQ, with the calculated longitudinal field component along the axis.

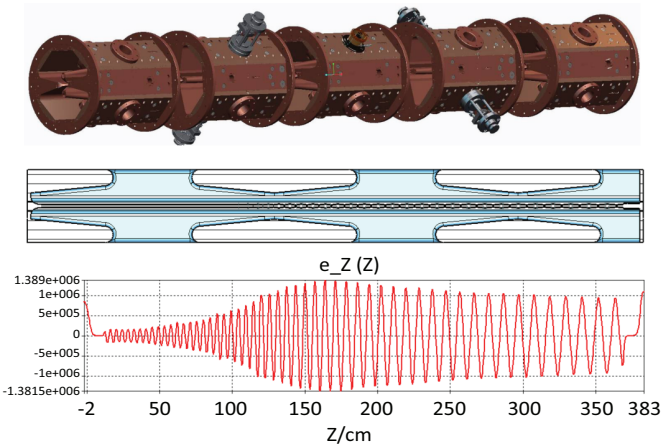


Figure 1. 3D engineering model of the ATLAS upgrade RFQ (top), 3D model with vane modulation built for electromagnetic simulations (middle), and the longitudinal field component along the beam axis calculated by using CST Microwave Studio (bottom).

Highly Optimized Design of a Quarter Wave Resonator (QWR) for the ATLAS Upgrade:

A new cryomodule is being designed for the ongoing efficiency and intensity upgrade to ATLAS. The cryomodule consists of seven quarter-wave resonators (QWRs) with a geometric relative velocity $ß_G$=0.075 and four superconducting (SC) solenoids to replace the existing split-ring cavities. To reduce the resonator frequency jitter caused by microphonics, we chose a frequency of 72.75 MHz instead of 60.625 MHz. At 72.75 MHz, the cavity is shorter by about 20 cm. The choice of the design ß was based on the beam dynamics and the actual performance of ATLAS cavities. To reach a record-high accelerating voltage of 2.5 MV per cavity or higher, the electromagnetic design was carefully optimized. The main goal of the optimization was to minimize the peak magnetic and electric fields while still keeping good values for the stored energy, the shunt impedance (R/Q), and the geometric factor (Rs/Q). The cavity height was also another important parameter. Our optimization attempts led to a final shape that is cylindrical in the bottom and conic on the top to keep a high real-estate gradient. The optimization also included the internal drift tube face angle required for performing beam-steering correction. Figure 2 shows the final QWR geometry and the corresponding electric and magnetic field distributions.

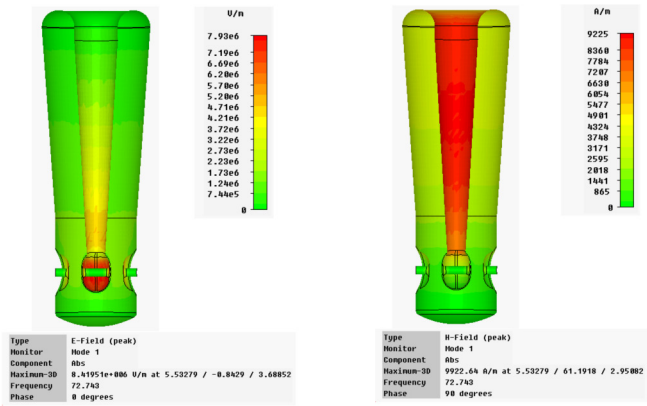


Figure 2. Final cavity geometry after detailed optimization accompanied by the electric and magnetic field distributions calculated by using CST Microwave Studio.

Proposed Work for FY 2011

In FY 2011, we will be focused on the following activities:

- Developing a good understanding of the initial beam conditions at the electron cyclotron resonance (ECR) ion sources.
- Performing appropriate measurements for general characterization of the beam line.
- Developing specific optimization tools to help reproduce the measured data.

Refereed Publications

Xu, J., B. Mustapha, P.N. Ostroumov, and J.A. Nolen, "Direct Vlasov Solvers with High Order Spectral Element Method," *Comm. Comp. Phys.* **8** (2010), 159–184.

Non-Refereed Publications and Presentations

Mustapha, B., A.A. Kolomiets, and P.N. Ostroumov, "Full 3D Modeling of a Radio-Frequency Quadrupole," *Proceedings of LINAC-2010*, Tsukuba, Japan, September 12–17, 2010.

Mustapha, B., and P.N. Ostroumov, "Electro-Magnetic Optimization of a Quarter-Wave Resonator," *Proceedings of LINAC-2010*, Tsukuba, Japan, September 12–17, 2010.

Ostroumov, P.N., R.V.F. Janssens, M.P. Kelly, S.A. Kondrashev, B. Mustapha, R.C. Pardo, and G. Savard, "Efficiency and Intensity Upgrade of the ATLAS Facility," *Proceedings of LINAC-2010*, Tsukuba, Japan, September 12–17, 2010.

Photocathodes Development for Accelerator Research and Development

2009-076-R1

Zikri M. Yusof, Katherine C. Harkay, John Noonan, Matthew J. Virgo, and Alexander V. Zinovev

Project Description

This project proposes to develop the next generation of photocathodes by using new materials based on semiconductors. This broad-based effort seeks to understand the material properties of photocathodes and how such properties translate to their performance in an accelerator. In particular, we will be seeking photocathodes that can produce a high-brightness electron beam, have high quantum efficiencies (QEs), and the potential to produce very low beam emittance.

This effort can be categorized into two broad areas: (1) development and deployment of a large (~1.2-inch-diameter) cesium telluride (Cs_2Te) photocathode for accelerator photoinjectors and (2) development and use of a system for the study of photocathodes' response time.

The first task involves the fabrication of a Cs_2Te photocathode with high QE and a QE variation over the surface of the photocathode of less than 10%. It should also be designed such that it can be transferred in ultra-high vacuum (UHV) into the Argonne Wakefield Accelerator (AWA) photoinjector.

Knowledge of the response time of a photocathode is very important, especially for more demanding applications, such as in a free-electron laser where the electron beam must satisfy very stringent parameters of bunch length and emittance. The response time indicates how fast all electrons are emitted by the photocathode after a light pulse impinges on its surface. In general, photocathodes with the shortest response times are more desirable.

Mission Relevance

Accelerator-based user facilities are a cornerstone of modern science and technology. Many high-priority aspects of the DOE Office of Science portfolio find that accelerator technology forms the primary limitation on the pace at which discoveries can be made. Increasingly, photocathodes are being used as the sources of the beams for accelerators because they yield excellent brightness. However, existing photocathode materials do not provide an optimal combination of lifetime and brightness and are currently limiting progress in accelerator development and use.

The impact of this project would be broad, as it would benefit a large number of diverse facilities requiring high brightness or more efficient light sources. The AWA requires robust photocathodes with a high QE that can deliver 50–80 nC per bunch. This work will directly address this need as part of the AWA expansion plan that has been approved by DOE. It will produce a suitable photocathode that is required for the high current demand of the new AWA beamline. Also, free-electron laser facilities, possible energy recovery linacs, and future linear colliders, such as the International Linear Collider, may all require photocathodes that meet parameters as demanding as these (or even more).

An additional beneficiary has now come to the fore through the detector development effort at Argonne. Fast, picoseconds-level detectors require high-QE photocathodes inside the photodetectors, and many of these photocathodes, such as the GaAs family and bialkalis, are the same type of photocathodes that are being investigated and surveyed in accelerator research and development. Our efforts in measuring the response time of photocathodes would be highly relevant to this research effort. Because of the knowledge and expertise gained as a result of this project, members of this project's team are also involved in the DOE-funded Large Area Photodetector effort.

FY 2010 Results and Accomplishments

Significant progress has been made in understanding the fabrication "recipe" and in consistently achieving high QE. The QE obtained has increased from being consistently above 1% to being consistently above 5%, even reaching as high as nearly 18%. This value of QE is more than sufficient to address the needs concerning the AWA expansion plan, which requires a photocathode with a minimum QE of 1%. At this stage, we consider that the refinement of the fabrication process was completed successfully. A more extensive study of the photocathode lifetime and the non-uniformity of QE over the cathode's surface was carried out. Although the non-uniformity of the QE over the photocathode's surface was reduced slightly, it is still larger than what would be preferred. We are implementing new procedures to reduce the QE non-uniformity further, if possible.

The lifetime of the QE appears to be very stable when examined in the UHV chamber. In fact, the QE tends to rise by a few percent (~10%) within one day after the end of deposition, reaching a high of 18% for this particular photocathode. This QE is the highest level achieved here so far. In fact, the QE for the majority of the surface area remained above 10% for the duration of this study.

We also investigated possible QE rejuvenation. The photocathode was intentionally exposed to a poor vacuum condition (10^{-3} Torr). The QE dropped to around 0.3%. Two different techniques were used to rejuvenate the photocathode. The first technique involved reheating the photocathode at 120°C — the same temperature used during the initial deposition. It was discovered that the QE can be recovered to about 1.5%.

Upon heating and the small recovery of the QE, the second technique was then performed. This involves the re-cesiation of the photocathode surface (i.e., the photocathode was subjected to cesium deposition once again). The QE recovered up to 6%.

Final refinements are being made to the design of the load-lock streak camera for photocathode response-time measurements. The design of the response-time measurement chamber was challenging because of the conflicting requirements for injecting the laser pulse and extracting the electron beam. The system is to be assembled and tested in the next fiscal year.

Proposed Work for FY 2011

Our five objectives for FY 2011 are to:

1. Develop and test a vacuum sample transfer system for the Cs_2Te photocathode.
2. Reduce non-uniformity of the QE on the Cs_2Te photocathode surface.
3. Refine and produce a fabrication recipe to achieve a more consistent fabrication of the Cs_2Te photocathode.
4. Install the Cs_2Te photocathode into the AWA photoinjector.
5. Assemble and install the time-response measurement system.

Improving Charged Particle Optical Device Designs: From Realistic 3D Field Maps to Transfer Maps

2009-080-R1

Bela Erdelyi, Shashikant L. Manikonda, and Jerry A. Nolen, Jr.

Project Description

Although accelerators and other particle optical devices have been ubiquitous in science for more than a century, to date there is no seamless way to bridge the gap between measurements of electromagnetic fields and realistic modeling of the devices based on these fields, including their design optimization. The latter has been elegantly solved over the last three decades by making use of transfer maps. The aim of this project is to

develop methods and software that would solve the "from-field-maps-to-transfer-maps" problem, as well as other design optimization challenges by using extracted transfer maps.

Mission Relevance

This project is tied to DOE's mission in science. The methods applied and the software developed as a part of this project are in the general area of accelerator science and have a variety of on-site uses, such as on the Advanced Photon Source and Argonne Tandem Linear Accelerator System (ATLAS)/Californium Rare Isotope Breeder Upgrade (CARIBU) isobar separator upgrades and on spectrometers, electron microscopes, and other instruments.

FY 2010 Results and Accomplishments

Continuing the work completed in FY 2009, the map extraction tool was optimized further for speed and accuracy. A framework was developed in which the extracted Taylor transfer maps can be used for full beam-optics design and optimization. With this new framework, it is now possible to start from a magnet model or measured field maps and design and optimize accelerator lattices via the transfer map approach. For some cases, such as the air-core magnet models, it is possible to perform combined optimization of both the beam-optic parameters, as well as magnet design parameters. This capability is a unique feature made possible by this new framework. Because extraction of the Taylor transfer maps is computationally intensive, tools were developed and enabled for saving and reusing the transfer maps to expedite design and optimization by using realistic fields. Intermediate steps for computing both the multipole expansion of the electric or magnetic fields and the Taylor transfer map are now tightly integrated within the new framework. The COSY Infinity code was used to implement this new framework and associated tools. The code can be used on high-performance computing clusters and multi-core processor computers, on which some of the computationally intensive tasks, such as evaluating multipole expansion and pushing particles though maps, are parallelized.

This framework enabled study of the Super Separator Spectrograph (S^3) device to be built as a part of the SPIRAL2 upgrade project at Grand Accélérateur National d'Ions Lourds (GANIL), France. Preliminary simulation studies were carried out for the S^3 lattice by using realistic transfer maps for the multipole magnets and electrostatic sector magnet. An air-core magnet model implemented within COSY Infinity was applied for study of multipole magnets, and electromagnetic design software, Opera-3d, enabled us to model the electrostatic sector magnet. A schematic view of the electrostatic sector magnet is shown in Figure 1.

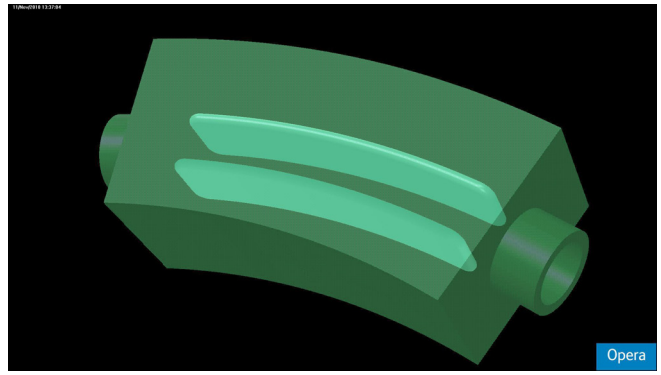


Figure 1. Plates, shielding, and reference trajectory for the electrostatic sector magnet.

Refereed Publication

Drouart, A., A.M. Amthor, D. Boutin, O. Delferrière, M. Duval, S. Manikonda, J.A. Nolen, J. Payet, H. Savajols, M.-H. Stodel, D. Uriot, "The Super Separator Spectrometer (S3) for SPIRAL2 stable beams," *Nuclear Physics A* **834** (Issues 1–4) (March 1, 2010), 747c–750c.

Non-Refereed Publications and Presentations

Boutin, D., M. Authier, F. Dechery, O. Delferrière, A. Drouart, J. Payet, D. Uriot, M. Amthor, H. Savajols, M.-H. Stodel, S. Manikonda, J. Nolen, "Optical studies for the super separator spectrometer S3," *Proceedings of IPAC'10 (International Particle Accelerator Conference),* Kyoto, Japan (2010), 4464–4466.

Manikonda, S., and J. Nolen, "Application of Maps-to-Maps Technique for Super Separator Spectrograph (S^3)," presented at the SPIRAL2 (Système de production d'Ions Radioactifs en Ligne de 2ème génération) Week 2010, Mémorial, Caen, France, January 25–28, 2010.

Nolen, J., "S^3 Status report," presented at the SPIRAL2 Week 2010, Mémorial, Caen, France, January 25–28, 2010.

Concept of Ultra-Low Emittance Injector for Future X-Ray Free Electron Laser Oscillator

2009-085-R1

Kwang-Je Kim, Alireza Nassiri, John Power, and Nicholas S. Sereno

Project Description

Electron injectors with the ability to produce ultra-low emittance bunches with a high, constant repetition rate will have important applications for the advancement of x-ray free-electron lasers (XFELs). Such injectors are needed in

XFEL oscillators (XFELOs), which are predicted to produce record high spectral purity and brightness. Injectors based on a laser-driven photocathode have been successful and widely employed for pulsed, high-gain FEL facilities for short wavelengths. When the lifetime and stability are at a premium, such as in an XFELO, another approach starting from a *thermionic* cathode may be advantageous. A pulsed, low-repetition-rate thermionic injector was demonstrated to be capable of producing low-emittance beams suitable for short wavelength FELs at the Spring-8 FEL in Japan. The aim of this project is to develop an ultra-low-emittance injector at a MHz repetition rate that satisfies the requirements of an XFELO. The injector consists of a thermionic cathode with a 1-MHz gate electrode, a 100-MHz gun cavity, and an energy-filtering section, together with two stages of acceleration and bunch compression. This project has sought to address the following critical research and development (R&D) items: the performance of the thermionic cathode with a gate electrode; the performance of the gun cavity, a 1-MHz, high-voltage (HV) pulsing circuit; and emittance diagnostics.

Mission Relevance

This project is tied to DOE's mission in science. High-brightness, coherent x-rays have become a major tool for probing atomic and molecular structures and dynamics, the understanding of which is essential to developing advanced materials. The XFELOs will very significantly increase the analytic power of the x-rays. The injector R&D of this project paves the way for future x-ray capabilities incorporating XFELOs.

FY 2010 Results and Accomplishments

Beam dynamics. In the 100-MHz gun cavity, the back bombardment was a serious issue. ASTRA (a well-known simulation code) simulation showed that by embedding three-pole wiggler magnets around the beam's exit tube, the back bombardment power into the cathode was significantly reduced, from 200 W to 8 W. We investigated a scheme of using a pulsed gate electrode to produce a 1-MHz bunch repetition rate and then eliminating the heat load issue on the momentum filter. The gate electrode placed 1 mm away from the cathode has a single on-axis, 1-mm-diameter circular opening that allows the electron beam to flow through on the flat top of a waveform generated by a fast pulser.

Design of 100-MHz radio frequency (RF) gun cavity. We investigated the designs of several 100-MHz RF structures, including a capacitively loaded structure and a folded coaxial structure with a short circuited end-plate. By optimizing the folded coaxial design, a geometry resulted that is similar to Lawrence Berkeley National Laboratory's 187-MHz gun structure with the addition of a reentrant gap. The XFELO injector linear accelerator RF gun, with its reentrant design increased the shut impedance (thereby enhancing efficiency) and reduced the wall losses. Thermal and structural simulations were also performed by using ANSYS (a commercial simulation code).

Design of the 300-kV direct current (DC) gun. The first-generation 300-kV DC gun with a 3-cm gap was designed for emittance testing of various cathodes. The design was modified by introducing a gate electrode in front of the cathode to test the triode gun design for mitigation of back bombardment. The design of the gun is similar to the successful SPring-8's 500-kV DC gun with 5-cm gap but with a constant-radius ceramic tube and gate electrode. The maximum E-field for our design is approximately 60% of that of the SPring-8 design.

Pulsed DC gun test bench. To gain experience and confirm the performance of the CeB_6 cathode, testing of a low-duty-factor, 300-kV, 6-µs pulsed gun (a pulsed DC gun) and its test stand was planned (the schematic is shown in Figure 1). The cathode assembly unit consists of the cathode, the heater, and the current leads for heater power. This assembly is followed by a beamline outfitted with the appropriate diagnostics to provide emittance measurements by using a thermionic cathode and an aperture. Beam dynamics simulations show that 300 kV is sufficient to suppress beam space charge and preserve the thermal emittance in a short beam transport system where the emittance measurements will be performed. The test bench will also investigate the operation of the gate electrode. One of the major challenges for the triode gun design was to modify the existing DC gun design to apply the fast pulse. This goal was accomplished by adding a 50-ohm load at the end of a broadband-matched transmission line to minimize reflections. Our simulations show that a triode gun-based injector could meet the requirements for an XFELO.

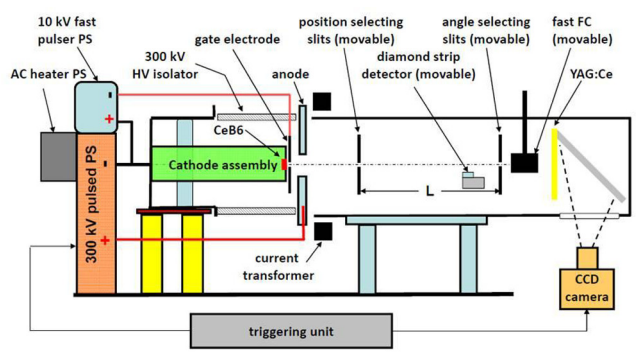


Figure 1. A schematic layout of a 300-kV cathode assembly test stand with emittance diagnostics. (Note: PS=power supply; FC=Faraday Cup; CCD=charge-coupled device.)

Development of a 300-kV solid state pulsed voltage for DC test gun. The team possesses all of the components, and most of them have been tested. Eight out of 350 gate drivers were found to be malfunctioning and were then fixed. High-voltage printed circuit (PC) boards are being tested with associated ferrite and gate driver boards. So far, four high-voltage boards

were tested satisfactorily. Each board produces a 12-kV pulse; pulse width is adjustable. The span of the rise and fall time is about 250 ns. Next, we will remove the voltage droop at the pulse end.

High-voltage switching circuit for gate electrode. We have analyzed the requirements for a pulse generator capable of driving the gun assembly as described. We assume a peak voltage of 10 kV, a peak current of approximately 180 A, a pulse width of approximately 1 ns, a 1-MHz repetition rate, and a 50-ohm load at the end of a broadband-matched transmission line to minimize reflections. Because of the high repetition rate and resulting high average power output, no commercially available, off-the-shelf pulse generators capable of this performance were found. We decided to pursue in-house development of the pulse generator.

Developing the pulse generator in-house has centered on the use of several possible technologies, including vacuum tube high-voltage switches, RF power transistors, avalanche transistors, and step-recovery diodes. Whereas vacuum tubes are natural devices for high-voltage applications, there are few RF amplifier vacuum tubes presently available that can deliver 180 A peak current and provide a broadband match at 1 GHz. It appears, based on our research into past work, that avalanche transistors or step-recovery diodes are the devices of choice for this application. Either way, the design of such a pulse generator will be very elaborate and will require significant investment to develop and perfect.

We have submitted a proposal to the National Science Foundation under the Instrumentation for Materials Research-Major Instrumentation Projects program.

Non-Refereed Publications and Presentations

Borland, M., B. Brajuskovic, R. Lindberg, and N. Sereno, “Pulsed Laser Heating of Thermionic Cathodes in RF Guns,” in *Proceedings of the LINAC 2010 Conference*, Tsukuba, Japan, September 12–17, 2010, In press.

Dong, X., M. Borland, J. Power, G. Decker, K.-J. Kim, and N. Sereno, “Potential for an Ultra-Low Emittance Thermionic Triode Gun,” in *Proceedings of the LINAC 2010 Conference*, Tsukuba, Japan, September 12–17, 2010, In press.

Lindberg, R., “Thermionic-Based Injector R&D at Argonne National Laboratory,” at the Compact X-Ray FELs Using High-Brightness Beams Workshop, Lawrence Berkeley Laboratory, August 5, 2010.

Advances in 2 Kelvin Superconducting Cavities for Future Accelerators

2009-158-R1

Michael P. Kelly, Joel D. Fuerst, Scott M. Gerbick, Mark J. Kedzie, and Alireza Nassiri

Project Description

The goal of this project is to establish a 2 K (Kelvin) superconducting radio-frequency (SRF) test cryostat for International Linear Collider (ILC) -type elliptical cell and transverse electromagnetic superconducting cavities in order to develop advanced cavity designs for new electron and ion accelerators. The project will include the design and commissioning by Argonne’s Physics Division of a new cryogenic vessel suitable for housing single-cell 1.3-GHz elliptical cavities. The vessel fabrication will be performed by U.S. industry. RF measurements will be performed with these cavities by using a new rf system, including control electronics for a phased-lock loop and high-level rf power. The rf system will (1) allow conditioning of the cavities up to the maximum possible fields for a given cavity surface and (2) work in conjunction with the 2 K second sound quench detection system to locate cavity defects. Commissioning of the system is planned using one of several dozen single-cell elliptical cavities purchased by Fermi National Accelerator Laboratory (Fermilab) and available for this investigation through the joint Argonne/Fermilab work on the ILC. Follow-on work will test the effect of high-Tc superconducting layers deposited on 1.3-GHz superconducting cavities by using atomic layer deposition. Finally, this 2 K system will permit detailed studies of the quench location in all cavities tested at Argonne. This research will be of particular value to ILC cavities as well as to new superconducting cavities for ion linacs, for which the capability to perform detailed quench location has not been adequately developed

Mission Relevance

The future of two premier user facilities at Argonne, the Advanced Photon Source and the Argonne Tandem LINAC Accelerator System (ATLAS), is likely to depend on next-generation particle accelerators for the delivery of intense, high-power and/or very low-emittance beams. These and similar facilities have been and continue to be a strongly supported component of DOE’s science mission. In addition, there is interest in building ion accelerators for applications that are of interest nationally, including the in areas of accelerator-driven systems, medical isotope production, and ion interrogation for national security applications. For the next decade, SRF cavities will remain the only viable technology capable of meeting these demands. Building and maintaining a 2 K SRF cavity test capability and continuing to advance the

state of the art for SRF cavity performance also would also be relevant to Project-X at Fermilab, the Soreq Applied Research Accelerator Facility at Soreq Nuclear Research Center, and the Facility for Rare Isotope Beams at Michigan State University. The expanded cavity test capabilities will enable testing of SRF cavities fabricated by using new thin-film technologies, including SRF cavities coated by using the atomic layer deposition techniques.

FY 2010 Results and Accomplishments

In FY 2009, a new 2 K test cryostat was installed in the SRF test area. During FY 2010, all major goals were accomplished, including:

- Acquisition of a 1.3-GHz single-cell cavity for testing purposes as a result of our combined efforts with FNAL on the ILC.
- Installation of the 1.3-GHz cavity into a new helium cryogenic vessel, shown in Figure 1, specifically designed for 1.3-GHz cavities.

Figure 1. A 1.3-GHz single-cell elliptical cavity (center of photograph) instrumented for second sound quench detection and a new, ASME code-stamped, liquid helium vessel (lower left) assembled below the lid of the new, large 2 K test cryostat.

- Cooldown of the cavity with liquid helium and operation of the cavity at 2 K.
- Testing of the second-sound technique in the test cryostat by using a moveable germanium resistance thermometer.
- Procurement, assembly, and installation of a 1.3-GHz radio-frequency (RF) system, including high-level RF power (40 W) and a 1.3-GHz phase-lock control system. A 2-kW RF power source planned for delivery in FY 2010 will now be supplied in the second quarter of FY 2011 due to manufacturer delays.
- Installation of a new high-power, 4-kW nominal, continuous-wave variable power coupler suitable for the ATLAS and completion of successful testing on a half-wave cavity in the new cryostat as shown in Figure 2. This coupler will be used for the ongoing ATLAS Intensity Upgrade Project; however, it also is suitable for the wide variety of ion LINAC applications discussed above.

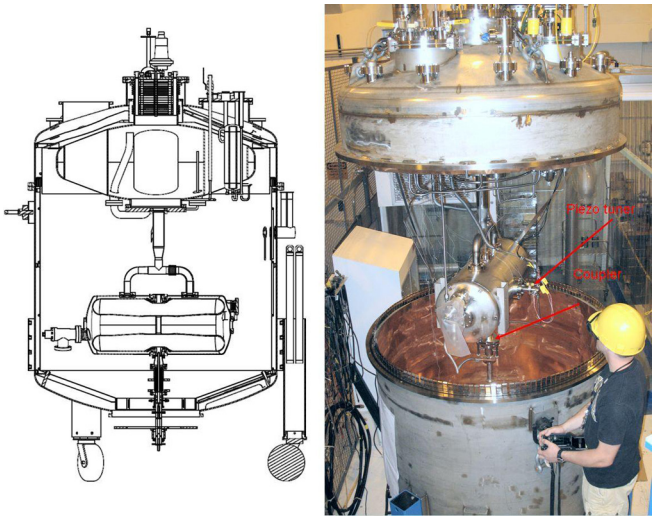


Figure 2. Test apparatus for coupler and piezoelectric tuner development, including a new, large (2-m-diameter), 2–4.5 K test cryostat and a 170-MHz half-wave cavity.

Proposed Work for FY 2011

Several fundamental questions about the ultimate performance of niobium cavities will be considered. These question all focus on the root cause of thermal-magnetic quench at the superconducting surface, the limiting factor in almost all of today's cavities. These questions include:

- Is the cavity quench located in the high magnetic field regions of the cavity?
- Is the cavity quench localized at a single defect, or does the quench location migrate?
- Is the cavity quench associated with fabrication techniques such as electron beam welds or strongly cold worked surfaces?
- Do the quench location(s) correlate with identifiable features on the cavity RF surface?

To effectively and practically answer these questions, we will complete the following work in FY 2011:

- Fabricate an array of germanium second-sound thermometers by using both germanium crystals and the recently acquired oscillation superleak transducers to perform 2 K second-sound detection with an SRF cavity.
- Design and procure an optical inspection tool to be used with SRF cavities with relatively small access ports. Obtain the charge-coupled-device (CCD) camera/lens required for the tool and incorporate it into the inspection tool.
- Perform cold testing of elliptical and drift-tube structures at 2 K and conduct a detailed optical inspection of the quench location in order to correlate some physical parameter with the cavity quench.

Non-Refereed Publications and Presentations

Kelly, M., S. Gerbick, M. Kedzie, P. Ostroumov, and S.I. Sharamentov, "A New Fast Tuning System for ATLAS Intensity Upgrade Cryomodule, THP057," in the Proceedings of the 25th Linear Accelerator Conference, Tsukuba, Japan, September 12–17, 2010.

A High-Performance Computational Framework for Structure Determination at Large-Scale Facilities

2009-226-R1

Raymond Osborn, Jorge J. Moré, and Brian H. Toby

Project Description

We are developing a computational framework to advance the joint analysis of x-ray and neutron measurements for the structural refinement of crystalline and disordered materials. Although sophisticated tools for such refinements were developed in the past, they are not optimized for high-performance computing, not well-adapted to the latest advances in instrumentation, and not flexible enough to cope with simultaneous refinements of a variety of experimental techniques. In this project, we are developing advanced numerical algorithms, high-performance tools for scientific data management, and powerful frameworks for modular programming.

Mission Relevance

This project is relevant to DOE's science mission. DOE operates major x-ray and neutron user facilities that enable more than 10,000 researchers to perform world-class science each year. The current focus on individual measurement techniques significantly limits the use of these facilities. It is often advantageous to combine the results from x-ray and neutron experiments, with each probe providing a different experimental constraint on the theoretical interpretation. This computational framework is designed to enable such analyses in a high-performance computing environment.

FY 2010 Results and Accomplishments

A new Python-based tree interface to NeXus files was completed. This comprehensive application program interface (API) allows the interactive inspection, modification, and export of all data and metadata in a user-friendly syntax for use on the command line or within a scripting framework. The new API was presented at a number of neutron and x-ray scattering conferences, and after a vote by the NeXus International Advisory Committee, it was accepted into the core distribution of NeXus. The graphical user interface (GUI) was integrated into the new API, so that modifications to the NeXus files can be made by actions on the GUI tree or from the command-line shell. A range of data transformations was incorporated in the new GUI interface. The GUI was installed at the Spallation Neutron Source (SNS) for testing by the instrument scientists and used on two Advanced Photon Source (APS) beamlines. The aim is to install it on several other beamlines in conjunction with the APS Beamline Controls and Data Acquisition group.

We developed code to read streamed data from the event-mode data acquisition system at SNS. This involves reading event files, correlating them with sample environment log files in order to determine the metadata associated with each event, and then producing a NeXus data structure containing the data in histogram form. The histogram coordinates are either in units of the raw instrumental parameters (scattering angles and times-of-flight) or transformed directly into reciprocal-space and energy units by using a predefined orientation matrix. The preliminary version was very inefficient, so we have been developing methods to accelerate the processing of data streams by parallelization, involving either multiple cores or graphics processing units (GPUs).

In FY 2010, on-line access to GSAS-II began as a development project, allowing it to be used by outside researchers. An example is that some of the initial capabilities are already being used to develop x-ray standards at the National Institute of Standards and Technology (NIST).

The major FY 2010 development task focused on a powder diffraction data reduction code for area-detector experiments. Although this technique is used very commonly at the APS, the exact corrections for detector alignment had never been derived heretofore. GSAS-II now has these corrections implemented and tested; it can fit the calibration constants from diffraction by using a standard sample. Once the calibration is done, the powder diffraction intensity can be displayed or tabulated as a function of a two-theta and

azimuthal angle. It is expected that this capability will become an integral data reduction step for the high-energy small- and wide-angle x-ray scattering (HE-SAXS/WAXS) program at beamline 1-ID in FY 2011.

Other tasks in FY 2010 included starting work on a crystal structure viewer and developing documentation and self-tests for core sections of GSAS-II that involve lattice computations, symmetry, and reflection generation.

Combined Approaches toward a Hierarchical Understanding of Battery Materials

2010-074-N0

Karena W. Chapman, Jonathan D. Almer,
Mahalingam Balasubramanian, and Karoly Nemeth

Project Description

An integrated program of state-of-the-art materials characterization and sophisticated data modeling is needed to understand the mechanisms within the different cell components that limit lithium ion battery (LIB) performance. This project involves the integrated application of a suite of emerging hard x-ray capabilities to the fundamental understanding of the factors that limit the performance of LIBs. Our unique approach involves application of unified experimental protocols to obtain directly comparable, complementary data covering multiple length and time scales. We are developing new *in-situ* capabilities to directly probe material behavior within the operating electrochemical cell. Such simultaneous analysis of all available data through multi-scale modeling will yield fundamental new insights into battery materials and lead to enhanced performance in next-generation LIBs.

We have identified key x-ray methodologies, each capable of providing unique structural information and insights into battery materials. While the individual analyses are primarily focused on particular aspects of the structure, by combining the complementary insights from the different methodologies, we can build a complete understanding of the material structure – from the atomic scale (e.g., x-ray absorption fine structure [XAFS], atomic pair distribution function [PDF]) to particle size and shape (e.g., small-angle x-ray scattering [SAXS] imaging). Our unique approach brings together complementary information that can be obtained by using multi-scale modeling of the separate data sets based largely on reverse Monte Carlo (RMC) methods.

Mission Relevance

This project is relevant to DOE's missions in energy and science. Battery research is a high priority within DOE. The facilities and capabilities developed as part of this project will be valuable to DOE battery programs, including those at a number of new Energy Frontier Research Centers; programs at other DOE laboratories; universities; and industries. The APS (Advanced Photon Source)-based electrochemical preparatory laboratory assembled as part of our project will be of pivotal importance to the APS user community and to programs seeking to undertake synchrotron studies that are currently limited by strict Li transport regulations.

FY 2010 Results and Accomplishments

- Designed *in situ* cell suitable for PDF and SAXS experiments;
- Identified materials test system (α–Fe_2O_3) for optimizing our approach;
- Performed preliminary *ex situ* and some *in situ* XAFS and PDF experiments for initial test system;
- Completed preliminary application of RMC to develop global structural models consistent with XAFS and PDF data;
- Assembled materials to equip the local electrochemistry laboratory; and
- Evaluated the concept of probing longer micro-length scales using imaging methods.

We selected hematite (α–Fe_2O_3) as the model electrode system to initially study lithium insertion ($Fe_2O_3 \rightarrow Li_xFe_2O_3$, x = 0-6) and as a suitable focus for development of our integrated approach. The selection was based on the suitability of the material for PDF and XAFS studies and the recent documentation of exemplary Li uptake by α–Fe_2O_3 nanoparticles. We prepared nano-Fe_2O_3 and verified the product using SAXS, diffraction line broadening (particle size distribution), and electrochemical cycling. We also collected *ex-situ* PDF and XAFS data for a bulk Fe_2O_3 sample to assist in the development and assessment of the multi-scale RMC modeling. Simultaneous fitting of both data sets within newly developed RMC programs yielded excellent unconstrained fits compared with single-data-set fits.

We designed an *in-situ* sample environment suitable for *in-situ* XAS, PDF, SAXS, and imaging measurements during electrochemical cycling. We also designed and fabricated a testing cell that accommodates different window materials that are easily changed to allow optimization of the cell for different techniques; the cell also includes the wide scattering apertures needed for PDF analysis and imaging. We collected *in-situ* XAS data using an XAS-specific cell during the electrochemical cycling of the nano-Fe_2O_3 to gain preliminary insight into the structural and chemical changes that occur in that system during Li^+ insertion.

We began to assemble equipment for an electrochemical laboratory and completed nanoparticle synthesis and size verification.

Following established literature procedures, we verified the electrochemistry of the synthesized nano-Fe_2O_3 in both conventional coin cell and pouch cell designs. The results were encouraging for extending electrochemistry studies to an *in situ* cell compatible with PDF, SAXS, and imaging.

Total scattering data suitable for PDF analysis were collected for bulk (Sigma-Aldrich) and nano-scale Fe_2O_3 at beamline 11-ID-B at the APS. High-energy x-rays were used, in combination with a large amorphous-silicon-based area detector, to collect data to high values of momentum transfer (Q_{max} ~ 20-30 $Å^{-1}$).

We conducted combined RMC simulations of the PDF data for the bulk Fe_2O_3 using a 9,000-atom model. The combined simulations provided exemplary unconstrained fits to the individual data sets. Most notably, the features in the structure were revealed with greater precision than fits to a single data set. This technique represents the state of the art for constraint-free RMC modeling of polycrystalline systems.

Finally, we successfully completed *in situ* XAFS using the pouch cell design. The chemical and local structural information obtained will be used as input in subsequent RMC simulations. The information on three-body correlations (intrinsic to the multiple scattering contributions in XAFS) within the RMC framework is expected to provide insights about key constraints on models to elucidate the structural evolution on the varied length scales in operating battery systems.

Preliminary x-ray tomography of the Fe_2O_3-Al laminate (cross-sectional area ~1 × 0.085 mm^2, using an energy of 65 keV and 1 × 1 mm^2 beam) yielded 1,000 full-field images. Three partial slices of the reconstructed volume are shown in Figure 1, where image brightness is proportional to electron density. While the slice within the Al layer illustrates a relatively homogenous microstructure, those within the Fe_2O_3 indicate significant density modulations on the scale of tens of microns. This finding is attributed to inhomogeneous distributions of the three phases (Fe_2O_3, polymer binder and carbon) used to form the laminate. Our ability to distinguish this structure highlights the sensitivity of the reconstructions, which we will use in fiscal years 2011 and 2012 to follow microstructural evolution across the electrode/electrolyte interfaces during battery cycling.

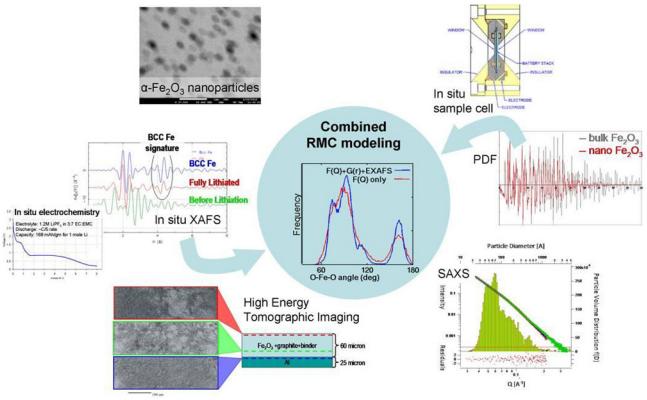


Figure 1. Illustration of the results obtained for the project to date. The combined RMC analysis provides greater insight into the structure than analysis of individual data sets.

Proposed Work for FY 2011

During FY 2011, the project will be extended to include the following:

- Collection of *in-situ* PDF, XAFS, SAXS, and imaging data for an initial test system using the custom-designed cells;
- Application of our multi-scale tools, combining ex situ PDF/EXAFS with RMC, to a screen library of battery materials; and
- Development of more efficient RMC algorithms to permit faster convergence and the additional combination of SAXS to the modeling

Can We Raise the Q of Superconducting RF Accelerating Structures?

2010-114-N0

Michael J. Pellin, Jeffrey W. Elam, Michael P. Kelly, Alireza Nassiri, James H. Norem, and Thomas Prolier

Project Description

A worldwide initiative is under way to develop a next-generation light-source technology based on superconducting Energy Recovery Linacs (ERLs) or higher-energy superconducting Free Electron Lasers (FELs). A significant constraint on this technology is the efficiency of the superconducting rf (SRF) system. Since a majority of the operational power (electrical, cooling) is involved in the refrigeration system, we expect that this power cost should be inversely proportional to the superconducting quality factor Q (defined as ~ rf $loss^{-1}$). A higher Q implies that less rf input power is needed for a given acceleration voltage and therefore less heat is generated and less cooling power is needed to maintain the constant 2 K operation temperature. A significant increase in Q would result in significant savings in both rf and cooling cost.

The objectives of this project are summarized below.

1. The first objective of our project is to understand how the losses in SRF systems depend on magnetic oxides. Recent results from point-contact tunneling (PCT) seem to correlate the presence of magnetic impurities with the highly dissipative part of the cavity that triggers the failure of the superconducting regime (called quench) above a threshold accelerating gradient. The dissipation of magnetic impurities in an external rf magnetic field could be a heating mechanism responsible for the highly dissipative spots (hot spots) found on the cavity and could explain the variation of Q as a function of the accelerating voltage (called medium- and high-field Q-slope).
2. The second objective of our project is to experimentally study how SRF losses depend on contamination, microstructure, and thermal and vacuum history of cavities and coupons.

Mission Relevance

This project is relevant to DOE's missions in science and energy. In the past few years, the emphasis in DOE on large facilities, such as the ILC (International Linear Collider), FRIB (Facility for Rare Isotope Beams), ERLs, and high-energy FELs, has altered the direction of superconducting R&D toward establishing the capability for commercial production of SRF structures, with the primary goal of laboratory programs like those at Fermi National Accelerator Laboratory (Fermilab) (as well as Cornell University), both here and abroad, ultimately aimed more at quality control of commercial modules. The result of this change is a general impression that basic R&D is not being pursued at a level justified by the problems and the promise of better performance.

This work would benefit all users of SRF systems, including ERLs, high-energy FELs, and high-energy physics facilities, as well as Fermilab's Project X and future nuclear physics facilities, by lowering the refrigeration power required. We expect that the cost savings produced by using optimized materials could be a significant fraction of the operating cost.

FY 2010 Results and Accomplishments

During FY 2010, using Tunneling spectroscopy and x-ray photoelectron spectroscopy, we demonstrated that cavity-grade, electro-polished Nb surfaces possess a wide range of oxides, the properties of which include magnetism. These oxides have, for the first time, been demonstrated to cause dissipation for electron transport in the underlying superconducting metal, creating an undesirable loss mechanism and possible acceleration-gradient limitation during SRF acceleration. Recent data show that "hot spots" cut from cavities that perform poorly seem to contain increased concentrations of these magnetic oxides.

We demonstrated a path toward repair of the extremely reactive Nb surface that can be applied even to the complex SRF cavity shapes necessary for optimum acceleration. This repair mechanism begins with the precision synthesis on the Nb oxide surface (inevitably present even in UHV environments) of an alumina film (3–10 nm thick) by using atomic layer deposition (ALD). As aluminum is one of the few metals more reactive than Nb, this alumina layer provides a diffusion barrier protecting the underlying Nb metal surface from further reaction. Subsequent annealing allows dissolution of the remaining oxygen into the bulk Nb, producing an abrupt dielectric (alumina)/metal (Nb) interface. Coupon and cavity studies demonstrate that this process substantially reduces the dissipation induced by magnetic oxides. Cavity tests show increased Q, which we attribute to this mechanism.

We demonstrated that the ALD-based surface improvement mechanism is both cavity-"friendly" and capable of improving cavity performance. The results of the first cavity acceleration tests are shown in Figure 1. The first cavity showed improved gradient and Q, the second was baked at high temperature and showed a factor-of-two increase in Q.

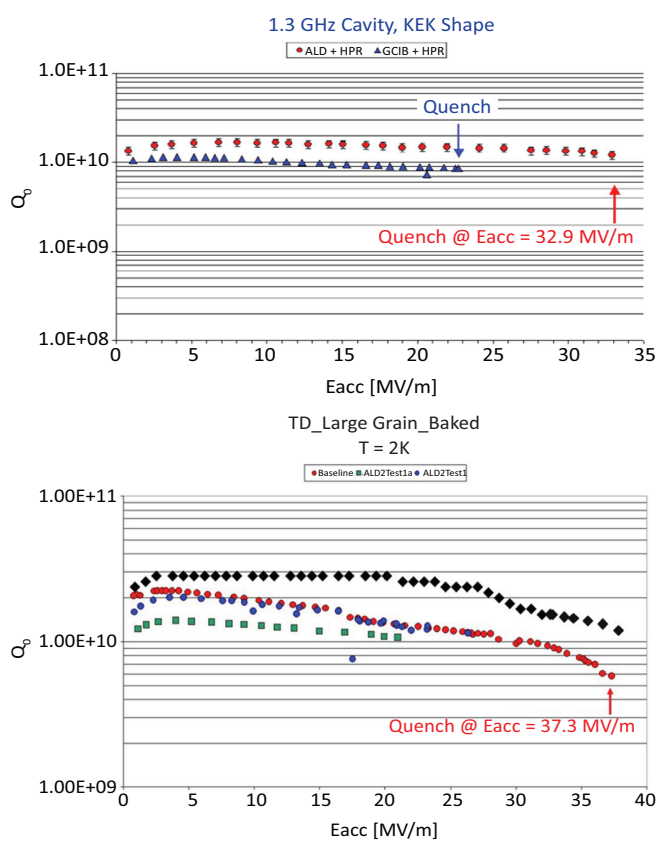


Figure 1. Increase in Q for two ALD-coated cavities. On the top: In blue the cavity baseline, in red after a dielectric ALD coating. On the bottom: In the red the cavity baseline, in black after an ALD coating followed by a post annealing at 450°C in Ultra High Vacuum.

We are testing very thin (approximately nanometer) coatings of Al_2O_3 and Nb_2O_5 with high-pressure water rinsing. We found that while the thin Nb oxide seems impervious to water rinsing, alumina, which is soluble (and would not be used as a top surface because of electron yield), has shown some damage at the monolayer level. We are studying the effects of much longer rinsing periods on Nb.

Refereed Publications

Prolier, T., J. Klug, N. Becker, J. Elam, and M. Pellin, "Optimization of the Superconducting Properties of NbTiN Made By Atomic Layer Deposition," accepted for publication in *IEEE (Institute of Electrical and Electronics Engineers) Transactions on Applied Superconductivity* (ASC 2010 Conference).

Non-Refereed Publications and Presentations

Klug, J.A., T. Prolier, N. Becker, J. Elam, and M. Pellin, "Growth of Thin Transition Metal-Based Superconducting Films by Atomic Layer Deposition," presented at the MRS (Materials Research Society) Fall Conference, Boston, MA, symposium: "Atomic layer deposition", November 28, 2010.

Prolier, T., J. Klug, N. Becker, J. Elam, and M. Pellin, "Optimization of Superconducting NbTiN Made by Atomic Layer Deposition," presented at ASC (Applied Superconductivity) 2010, Washington, D.C., August 1–6, 2010.

Prolier, T., J. Klug, N. Becker, M. Kharitonov, H. Claus, and M. Pellin, "Summary of SRF Project at Argonne National Laboratory," presented at the SCRF ILC-CLIC meeting, CERN, Geneva, Switzerland, the 20th of October 2010.

Prolier, T., J. Klug, J. Elam, and M. Pellin, "Superconductors Made by Atomic Layer Deposition," presented at the 6th SRF Workshop, Tallahassee, FL, the 18th of February 2010.

Development of Picosecond X-Ray Pulses at the APS Using MEMS-Based X-Ray Optics

2010-117-N0

Jin Wang, Yuelin Li, Omar D. Lopez, Gopal K. Shenoy, Deming Shu, and Donald A. Walko

Project Description

Rapid progress in micro- and nanoelectromechanical systems (MEMS and NEMS) provides a unique technical opportunity to design and fabricate x-ray modulating optics that can spatially disperse the current synchrotron-based x-ray pulses (of 100-ps width) so that experimentalists can achieve picosecond temporal resolution for both scattering and spectroscopy experiments with close to 100% optical efficiency. The ultimate objective of this project is to develop MEMS-based x-ray optics that can lead to demonstration of the feasibility of producing x-ray pulses with a picosecond temporal resolution, with broad energy tunability and a high pulse-repetition rate, from the Advanced Photon Source (APS). The major short-term goal of this development work is the ability to tailor and manipulate x-ray pulse trains delivered to each experiment using MEMS-based optics, largely independently of the electron fill pattern of the storage ring, which can have an immediate scientific impact.

Mission Relevance

This project is relevant to DOE's mission in science. The importance of developing fundamental understanding of far-from-equilibrium systems and processes has been epitomized by the DOE's "Five Grand Challenges" study. Ultrafast x-rays have been identified worldwide as the critical tool to investigate the temporal development of far-from-equilibrium processes responsible for the control of complex materials and chemical processes, as well as real-time evolution of chemical reactions and dynamics of spins in the microsecond to femtosecond domains.

FY 2010 Results and Accomplishments

We have achieved the first-year deliverables, as described below:

1. Designed and fabricated a simple MEMS to prove the concept. The single-mirror MEMS consists of a 500-µm × 500-µm mirror of 10-µm-thick crystalline silicon. The layout of the device is shown in Figure 1. The resonance frequency is designed to be 12 kHz and the maximum deflection angle is 0.3° at a driving voltage of 25 V. By using MEMS design tools (such as ANSYS, COMSOL, and CoventorWare-ANALYZER), we confirmed that the MEMS mirror can meet the surface flatness criteria (better than 0.02°, or about 1/10 of the mirror critical angle).

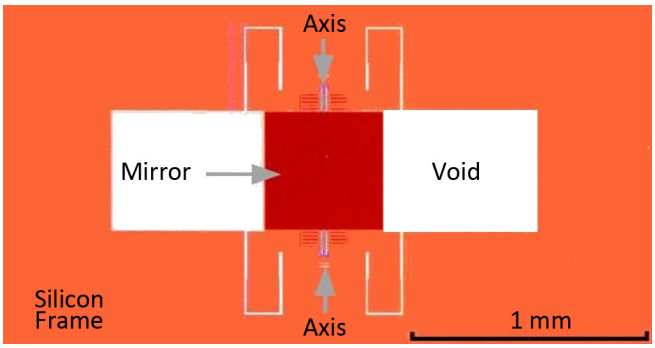


Figure 1. Layout of the single-mirror MEMS showing the crystalline-Si-based MEMS torsional oscillator mirror (500 µm × 500 µm × 10 µm thick).

2. Measured the x-ray reflectivity of the mirror. The MEMS-based mirror can be used as an x-ray-beam-deflecting device only if the mirror surface is atomically smooth so that it can reflect x-rays efficiently at grazing-incidence angles and the mirror is flat enough so that the reflection does not distort the x-ray wave front. X-ray reflectivity of the mirror was measured at APS Sector 7. Both position-sensitive and single-element detectors were used to measure the reflected x-rays from the mirror. At this stage, the mirror was not energized, so we measured the static x-ray reflection from the mirror. To simulate a rotating mirror, we used a goniometer to position and rotate the sample with micrometer-level translational precision and 0.001° angular resolution. First, we used a charge-coupled device camera to record the reflected beam, which is observed to be high-quality, as shown in Figure 2a. As the mirror is rotated to higher angles (below the critical angle of the mirror, 0.18°), the x-ray beam was reflected to high angles while the beam was shown to be a tight spot on the area detector. This finding is confirmed quantitatively by a point detector, which can record the reflected beam intensity. The reflectivity curve is shown in Figure 2b, which demonstrates close-to-theory reflection efficiency.

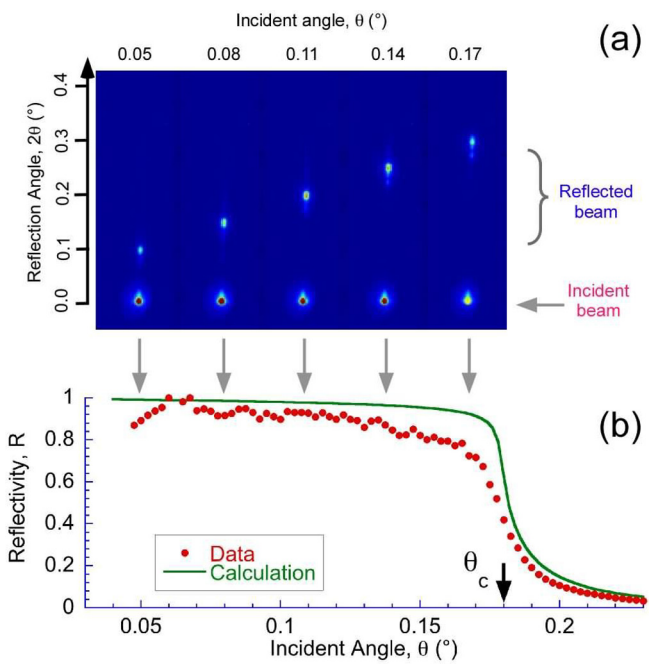


Figure 2. X-ray reflectivity measurement of the mirror with an area detector (a) and a point detector (b). The critical angle, ϑc, of the mirror is measured to be at 0.18°.

3. Made progress in using optical profilometry to measure the mirror flatness. We will continue to make measurements on the single-mirror sample and to compare them with the x-ray results. The optical measurement made on a different mirror indicated that gold coating on both the top and bottom surfaces of the mirror can be used effectively to correct the mirror curvature to an even smaller value than what has been achieved thus far.

Proposed Work for FY 2011

1. Design and develop packaging methods for MEMS arrays for x-ray reflectivity and frequency response measurements with available MEMS and perform initial studies.
2. Design MEMS arrays with 10–300-kHz frequency response (for damping of spurious modes, harmonics, etc.).
3. Evaluate MEMS temperature stability in x-ray applications and develop compensation methods if needed.
4. Test the single-element x-ray response of the MEMS by using the SOM1 mode at the APS with a full-synchronization scheme.
5. Explore the double-sided coating theme with a goal of preparing perfect x-ray mirror surfaces with the MEMS technology.

Development of High-Power Targets for Isotope Production with Low-Energy Beams

2010-181-N0

Jerry A. Nolen, Jr., and Bradley J. Micklich

Project Description

Our project aims to develop a target for low-energy alpha particle beams that will operate with beam power levels never previously used for medical isotope production: ~50-kW beams of 30-MeV alpha particles. Typical targets used in the industry today are for proton beams with power levels of up to ~10 kW. The present development is challenging because of both the higher beam power and the shorter range (higher linear energy transfer) of the alpha particle beams versus the proton beams.

As a specific case study for the present project, we proposed to develop a high-power target design to solve the problem of the shortage of an important isotope, ^{211}At, which has been listed in Ekaterina Dadachova, "Cancer Therapy with Alpha-Emitters Labelled Peptides," Seminars in Nuclear Medicine, **40** (2010) 204, as an important radionuclide for clinical trials of a therapeutic cancer treatment via targeted radio-immunotherapy. It is in short supply, however, even for the

clinical trial stage, because there are very few accelerators worldwide with the necessary high-current, 30-MeV beam of alpha particles. Several other studies have also come to similar conclusions on the potentially important applications and the shortage of this isotope for clinical trials now, with an even greater need developing in the future following the trials. The proposed target development is generic in the sense that the same engineering concepts can be applied with small variations for the effective production of a wide variety of isotopes that are required for use in the fields of nuclear medicine, as well as in basic nuclear physics.

The main challenge of the present application is to limit the temperature increase of the bismuth target material to less than ~100°C because of its low melting point and the relative volatility of the astatine product. The excitation function for the reaction $^{209}Bi(\alpha,2n)^{211}At$ peaks at 900 mb at a beam energy of 30 MeV. Higher energies cannot be used because the threshold for the production of ^{210}Po as a serious contaminate is exceeded beyond this beam energy. With a thin bismuth target layer that utilizes the beam energy from 30 MeV down to 25 MeV, the measured yield is >1 Ci/mA for an irradiation of one half-life (7 hours). Production yields at this level are certainly high enough to supply the larger amounts that will be needed beyond the clinical trials stage.

Mission Relevance

This project is relevant to DOE's science mission. The DOE Office of Nuclear Physics now oversees the program for research isotopes that are needed for clinical trials but are not available commercially. Because ^{211}At falls into this category, it is therefore a candidate for support from this Office. The Argonne Tandem Linear Accelerator System (ATLAS) has the alpha and lithium beams necessary to produce research quantities of this isotope so they are available for clinical trials in the United States. The ATLAS intensity upgrade that is currently in progress will enable the larger production rates of this isotope that will possibly be required following the present generation of clinical trials.

FY 2010 Results and Accomplishments

We developed a preliminary design that would limit the temperature increase of the bismuth layer to less than 20°C, as follows: a thin titanium foil, 25 × 10 cm^2, would be brazed to a stainless-steel frame with a ~1-mm-thick region behind the foil to serve as a channel for liquid metal cooling. Next, a bismuth layer 11 micrometers (µm) thick would be plated onto the titanium foil. Tilted at a glancing angle of 11.5 degrees from the beam direction, the effective target thickness is five times the layer thickness, or 55 µm for the bismuth in this geometry – the thickness required for the beam energy to cover the production range of 30 MeV down to 25 MeV. The titanium foil would be 20 µm thick, with an effective thickness in the beam direction of 100 µm, which drops the beam energy further, from 25 MeV to 16 MeV. Finally, the 16-MeV beam would be stopped in the flowing liquid metal behind the titanium foil. The liquid metal could be either NaK (with a melting point of –11°C) or a Ga-In-Sn eutectic (with a melting point of 16°C). A liquid metal coolant is required because it has a surface heat transfer coefficient several times that of water, and it is the temperature increase at the Ti-coolant surface that dominates the design. With this size target and the 11.5-degree glancing angle from the beam direction, the beam spot would cover 250 cm^2, giving a heat load of 200 W/cm^2 from a 50-kW beam power. As viewed from the beam direction, a beam spot that is uniform over an area 10 cm wide by 5 cm tall is required. Considering the energy loss in each layer, the thermal conductivities of bismuth (8 W/m•K) and titanium (22 W/m•K), and the surface heat transfer coefficient for the liquid metal (~5 W/cm^2•K), the temperature increases in the bismuth, titanium, and coolant surface layers are <1°C, <1°C, and 20°C, respectively. With NaK as the coolant, the target assembly could be operated at 0°C, so that the temperature increase of the bismuth layer would be ~20°C. By using Ga-In-Sn, the system could be operated at ~20°C, giving a bismuth layer temperature of ~40°C.

By the end of the first year of this project, we had completed the thermal analysis that validated this approach for the target design.

Non-Refereed Publications and Presentations

Nolen, J., "Current and Possible New Methods for Accelerator-Based Production of Medical Isotopes," presented at the XXV International Linac Conference, Tsukuba, Japan, September 12–17, 2010.

X-Ray Nanoimaging for Life Sciences

2010-183-N0

Barry Lai, Lydia A. Finney, Mark P. Jensen, Kenneth M. Kemner, Jörg M. Maser, Lynda Soderholm, and Stefan Vogt

Project Description

In recent years, it has become increasingly clear that metals bound to proteins and enzymes play vital roles in the control and signaling of many cellular or pathologic processes. It is estimated that one-third of all known proteins contain metal cofactors, often with important regulatory or enzymatic functions. At the same time, metals may also act as environmental contaminants (Hg, Pb) or carcinogens (As, Cr), which may present significant health hazards. This project aims to develop a high-resolution, x-ray nanoimaging method that will allow elements of interest to be studied naturally without any chemical labeling. In particular, it will enable for the first

time not only the visualization and analysis of trace elemental content at the 30-nm level — an order of magnitude better than current x-ray fluorescence microscopes (XFM) — but also of frozen-hydrated samples, which are as close as possible to the native state.

Mission Relevance

X-ray nanoimaging will impact many areas crucial to DOE missions, including basic science, environmental stewardship, and national security. For instance, bacteria can drastically influence the fate of environmental contaminants, and a better understanding of the local chemistry and metal reduction process near a bacterium may lead to a more effective bioremediation scheme. Among all actinides, plutonium is the most poisonous and has a long residence time in the body, although its cellular uptake and retention pathway are almost unknown. x-ray nanoimaging will reveal the subcellular location and oxidation state of intracellular plutonium, possibly providing targets for interruption. x-ray nanoimaging will also provide insights on the growth of diatoms, which play a major role in carbon fixation in vast regions of the global ocean. The growth of diatoms, however, is often limited by the availability of the micronutrient iron. In general, the fundamental capability to study metalloproteins, metalloenzymes, and nanoparticles at the level of the individual organelle within cells and tissues preserved in a native state will enable novel research in diverse areas of interest to DOE and other federal agencies, such as the National Science Foundation, National Institutes of Health, and U.S. Environmental Protection Agency.

FY 2010 Results and Accomplishments

To preserve the sample in its native frozen-hydrated state and to reduce radiation damage, the sample needs to be maintained at a cryogenic temperature both before and during the measurement within the nanoprobe. To this end, we investigated two sample cooling schemes: by conduction and by convection. We concluded that the conductive approach would offer higher resolution, whereas the convective approach would offer greater flexibility in sample environment and temperature range. Together with an external vendor, we completed the development of an in-vacuum, conductively cooled bionanoprobe. We also identified a beamline that will host the bionanoprobe. In preparation, we measured the stability of the beamline to ensure that it would not degrade the performance of the bionanoprobe, and we designed a white-beam slit that would deliver a symmetrical beam to the bionanoprobe. At the same time, we also completed the conceptual design of a convectively cooled cryostream nanoprobe, which uses laser interferometers for real-time position feedback and novel piezo-driven, weak-link stages with large travel range and nanometer repeatability.

Proposed Work for FY 2011

We will proceed with the installation and testing of the two nanoprobes. First, nanoimaging experiments of biological specimens will be performed with these two instruments, initially at room temperature and then later at a cryogenic temperature. In particular, we will study whether radiation damage is indeed reduced at the cryogenic temperature and will then quantify the effect in the fluorescence mode and in the spectroscopy mode.

Non-Refereed Publications and Presentations

Lai, B., "Status and Plans for XRF Nanoprobes at the Advanced Photon Source," presented at the Biological Applications of X-ray Fluorescence Microscopy Workshop, Chicago, IL, August 14, 2010.

Real-Life Imaging: Before and after the Microscope

2010-193-N0

Chris J. Jacobsen

Project Description

This project is aimed toward the development of new capabilities for x-ray microscopy and imaging. One activity is to develop equipment and experimental protocols for the preparation of frozen hydrated specimens for biological and materials science research. A second activity is to develop methods for multivariate statistical analysis of spectrum image data acquired by using x-ray microscopes and imaging systems at the Advanced Photon Source (APS) and to apply those methods to electron microscope studies.

Mission Relevance

This project is relevant to the DOE mission, as supported in the Office of Biological and Environmental Research (BER), in several ways. Cryo-specimen preparations provide the best means for excellent preservation of structure and biochemistry in cells, tissues, and bacteria. This is relevant to the DOE BER mission in providing new means to understand the interaction of soil bacteria with metals and radionuclides in soils and for seeing how metals and radionuclides can be incorporated in cells and tissues (both in connection with environmental contamination and in connection with biomaterials interactions, such as titanium dioxide nanoparticles). The spectrum image analysis component of the project is also relevant to BER since biological and environmental specimens exhibit considerable heterogeneity and chemical variation; multivariate statistical analysis methods offer a good way to see the patterns in such rich and complex data. The project is also expected to be of benefit to interests of the Office of Basic Energy Sciences, since cryo-sample preparations will be

of use for studies of organic photovoltaics (as one example), and the data analysis methods can be applied to studies of metal contamination in silicon-based photovoltaics.

FY 2010 Results and Accomplishments

In the area of cryo-sample preparation, in FY 2010 we selected and procured the necessary cryo-sample preparation equipment. This equipment has been installed in a newly established cryo-sample preparation laboratory. In the laboratory, we began to use the equipment for demonstration preparations in a hands-on session led by representatives of the manufacturer of the equipment. Our use of this equipment (beyond basic demonstrations) is on hold until the Bio Nanoprobe instrument is delivered to Argonne in June 2011; with this instrument, we will, for the first time, be able to examine specimens in a frozen hydrated state.

In the area of multivariate statistical analysis, a team of collaborators from the Software Services group and the Beamline Control and Data Acquisition group at the APS (Advanced Photon Source) have been working to specify a common data file format for spectromicroscopy analysis. A draft format has been developed, and read/write subroutines were delivered.

We also selected, received, and installed two graphical processing unit (GPU) -based servers for computational analysis, and we are beginning to write code to make use of these servers.

The main activity in data analysis was the ongoing development of methods for non-negative matrix factorization of spectromicroscopy data. Collaborating with the Mathematics and Computer Science Division we are developing ways to recover "pure" absorption spectra from samples with mixed oxidation states. In extended absorption fine structure (EXAFS) analysis, different oxidation states lead to different relationships between incident photon energy and ejected electron wavelength that can, in turn, cause inaccuracies in standard measurements of atomic distances. We have been developing non-negative matrix factorization approaches to recover the "pure" signature spectra, by introducing cost functions based on spectral smoothness and sparsity into the iterative solutions.

Finally, calculations on the performance of circular versus crossed cylindrical optics for nanofocusing applications were done at Northwestern by a visiting graduate student. This is of relevance to comparing conventional circular Fresnel zone plates with Multilayer Laue Lenses (MLLs) as pioneered at Argonne. The fraction of energy in the central focus versus optic central stop size for both the circular and crossed cylindrical cases calculated and thus showed that MLLs should provide good performance for elemental analysis.

Proposed Work for FY 2011

In the area of cryo-sample preparation, we will assemble and characterize our cryo-light microscope and begin to carry out preparations of frozen hydrated samples in support of the first experiments of the Bio Nanoprobe that is being installed at beamline 21-ID at the APS. We will use high-pressure freezing and plunge freezing to prepare frozen hydrated preparations of yeast for our first experiments and then move on to selected specimen types as our first commissioning users are scheduled.

In the area of multivariate statistical analysis, we will use our new Python-based analysis code to do pattern recognition and non-negative matrix factorization analysis of spectromicroscopy data. We will apply this to EXAFS data of arsenic contaminants in the environment and x-ray fluorescence microprobe data produced by the Bio Nanoprobe. We will also begin to convert our previous code based on IDL (programming language developed by ITT Visual Information Systems, Inc.) to Python to produce a unified analysis package.

Non-Refereed Publications and Presentations

Jacobsen, C., "Pushing against Damage Limits in X-Ray Microscopy," presented at the Sixth International Workshop on X-Ray Radiation Damage to Biological Crystalline Samples, Stanford Synchrotron Light Source, Palo Alto, CA, March 11, 2010.

Jacobsen, C., "Cryo: Samples, Damage, and Instruments," presented at the Workshop on Biomedical Applications of X-ray Microprobes, Northwestern University, Evanston, IL, August 14, 2010.

Jacobsen, C., "X-ray Microscopy: Freezing Complex Biological Processes, " presented at the Workshop on Evolution and Control of Complexity: Key Experiments Using Sources of Hard X-Rays, Argonne National Laboratory, Argonne, IL, October 11, 2010.

Jacobsen, C., S. Vogt, and R. Mak, "Using X rays to Probe the Nanoscale in All of Its Complexity," presented at the NanoImaging Workshop of the National Synchrotron Radiation Research Center, Hefei, Taiwan, October 21, 2010.

Jacobsen, C., S. Vogt, and R. Mak, "Soft and Hard X-Ray Microscopy of Soft Materials," presented at the NU*ANCE* (Northwestern University Atomic and Nanoscale-Characterization Experimental) Center Workshop on Microscopy of Soft and Hybrid Materials, Northwestern University, Evanston, IL, October 25, 2010.

Jacobsen, C., and R. Mak, "X-Ray Imaging for Environmental Science," Colloquium at the Environmental Molecular Science Lab (EMSL) at Pacific Northwest National Laboratory, February 7, 2011.

NATIONAL SECURITY

Risk-Based Decision System toward Risk Excellence

2008-119-R2

Shih-Yew Chen, Bruce M. Biwer, and David J. LePoire

Project Description

A "risk-based approach" has become part of the general guidance in U.S. efforts to ensure national security. The approach addresses a wide range of risk concerns, including human (nuclear, biological, and chemical) risks, critical infrastructure risks, cyber security risks, and a host of others that present important considerations for national security. The objective of our project is to develop a basic framework and methods for a risk-based decision system that will serve as an overarching approach. The primary focus of this work is the development of a national "risk-based approach" for decision makers responsible for homeland security that addresses the consequences of a radiological attack. The focus of this work is on the topic on long-term recovery, specifically on decontamination technologies relevant to site cleanup issues.

Ensuring the long-term recovery of an area after the widespread dispersal of radioactive material is a complex problem that requires coordination among many local, state, and federal agencies. The early phase following a radiological event, such as one involving a radiological dispersal device (RDD), is characterized by the immediate protection of the public through such actions as sheltering or evacuation. Once the immediate danger is past, an assessment of the current conditions must be made as a prelude to remediation of the affected area as part of a community's long-term recovery effort. While guidance has been issued on emergency planning for such events at various levels, similar guidance for long-term recovery planning is sparse.

Mission Relevance

This project will benefit the DOE's mission in national security. Other federal agencies, including the U.S. Department of Homeland Security, the U.S. Department of Defense, the U.S. Environmental Protection Agency, and the Nuclear Regulatory Commission, will likely be interested in the results of this project.

FY 2010 Results and Accomplishments

We have developed a framework that can be used both for systematic training and as a planning tool for RDD long-term recovery. This decision framework can be used to optimize recovery efforts in the context of interim guidance from the Department of Homeland Security.

A review of existing strategies performed as part of the prior years' work determined that existing frameworks were hampered by a lack of reliable data, primarily in application of relevant technology. Through the use of technology, risk can be minimized by threat reduction (event avoidance), lowering of vulnerability (enhanced protection), and mitigation of consequences (management of the aftermath). Threat reduction can be achieved through intelligence and surveillance/detection. Enhancement of protection relies on technology robustness and defense in depth. Consequence management involves assessing the impacts and removing hazards to restore normality — activities that rely on the accessibility of effective, relevant technologies.

With our simple decision framework in the area of consequence management, the strategy for cleanup can be accelerated by breaking the long-term recovery effort into its component parts. The process is begun by setting clear cleanup goals for specific areas affected by contamination. For each cleanup area, the common types of contaminated surfaces are identified, and then a particular cleanup technology is assigned to each surface type. Once the overall strategy has been approved and cleanup initiated, the entire decision process or portions of the process related to a particular surface type or technology may need to be revised on the basis of feedback as the actual work progresses.

Determining the cleanup areas and setting cleanup goals and priorities may be contested issues involving large uncertainties. Components of the decision framework with less uncertainty, such as determining the types and extent of contaminated surfaces and the relevant potential decontamination technologies, provide an objective means to optimize the long-term cleanup effort.

The categorization of surface types allows for a systematic approach to the cleanup process on the basis of the underlying assumption that a single cleanup technology or the same series of technologies can be applied to those surfaces grouped in the same category. Knowledge of the surface types (and their extent) requiring cleanup within a specific area is becoming more readily available to planners and managers, especially with the establishment of municipal Geographic Information System (GIS) departments and access to past studies on such issues as the urban heat-island effect and stormwater runoff, where surface types (such as pavement and rooftops) play an important role.

Once the surface type categories are assigned, each is paired with potential cleanup technologies. Applicable radionuclide decontamination technologies have been developed over the past few decades for the maintenance and decontamination of existing nuclear facilities, as well as the remediation of contaminated sites. A database has been compiled for more

than 60 technologies, from vacuuming or hosing with water to the application of specialty foams and gels. Given a particular surface type for decontamination, an objective and systematic review of viable options is then possible, and the potential results can be optimized through selection of the technologies most likely to minimize human exposure, costs, waste, and cleanup times while maximizing effectiveness.

Plasmonics-Based Methods for Fast, Selective Chemical, Biological, and Explosives Detection

2008-122-R2

Hsien-Hau Wang, Hual-Te Chien, Nachappa Gopalsami, Stephen K. Gray, Alexander Heifetz, and Ulrich Welp

Project Description

New field-deployable chemical, biological, and explosive (CBE) detection methods are urgently needed to provide early warning against terrorist attacks. The detection of improvised explosive devices (IEDs) also poses a particular challenge in view of their easy deployment and concealment and potential for mass casualties. We address this broad spectrum of threats with a two-pronged approach in which we develop plasmonics-based methods in the terahertz and optical spectral regions. Central to the work is using the properties of surface plasmon excitations in metals. We develop a new terahertz spectrometer based on surface plasmon resonance with the goal of achieving ultra-sensitive, selective detection. We also work to develop novel nanostructured interferometric chemical sensors that turn into colors in the visible region upon exposure to IED molecules.

Mission Relevance

This project addresses the national security mission of DOE by developing early warning sensing techniques and devices to thwart terrorist activities involving CBE threat agents. The plasmonics-based sensing is useful to other DOE programs involving the characterization of nanoscale materials, energy process instrumentation/diagnostics, and environmental sensing/emission control. This project will also directly benefit the U.S. Department of Homeland Security (DHS) and U.S. Department of Defense (DOD) by developing a simple, thin-film-based sensor that changes color upon exposure to explosive molecules.

FY 2010 Results and Accomplishments

In previous years, we identified organic molecules with guest-host functioning that would selectively bind IED molecules, such as TNT (trinitrotoluene) and DNT (dinitrotoluene). We found that anthracene is about one order of magnitude more sensitive toward DNT in terms of fluorescence quenching than is aminoanthracene. However, aminofluorescein is 20 times more sensitive toward DNT than a very similar fluorescein dye. These highly sensitive fluorescence-quenching molecules will help us develop new IED sensors.

We developed anodized aluminum oxide (AAO) nanoporous membranes with a high surface area. When AAO is functionalized with reagents with basic functional groups, the AAO membranes turn from white to orange upon exposure to TNT solution. The color change can serve as the basis for colorimetric IED detection.

When AAO is made very thin (less than 500 nm), light reflection from the surface, together with the reflection from the aluminum (Al) substrate, causes interference colors. We found that an additional ultra-thin (less than 10 nm) coating of silver (Ag) or gold (Au) significantly enhances the interference colors that made the membranes visible (Figure 1) and allows for better analysis with the thin-film interference formula. When thin AAO is modified to attract IED molecules, a small but noticeable red shift (on the order of 1–4 nm) can be observed (Figure 2). The shift in the reflectance spectra is consistent with surface layer thickening and the detection of IED molecules.

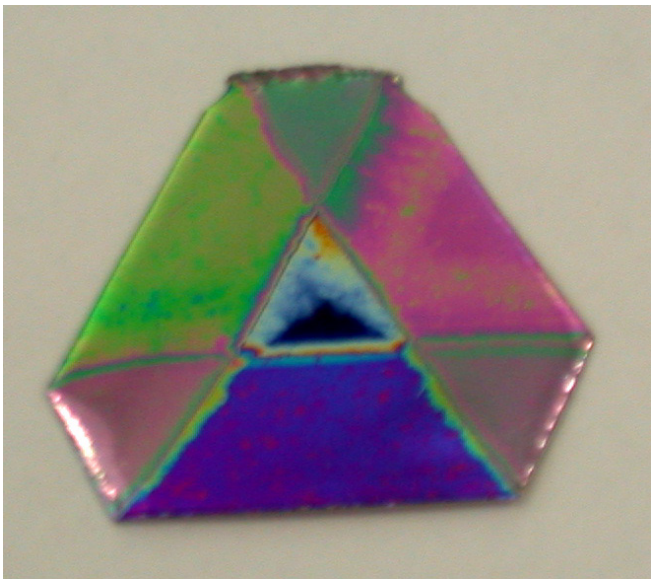


Figure 1. AAO/Al color patterns made from two-step anodization with a final anodization of 4, 8, and 10 min and Ag thin coating to generate each of the three different colors.

The guiding principles for making IED sensors were developed. More work is needed to optimize their sensitivity and detection limit and build a field-deployable IED sensor. We are actively seeking additional funding from DHS and DOD's Defense Advanced Research Projects Agency (DARPA).

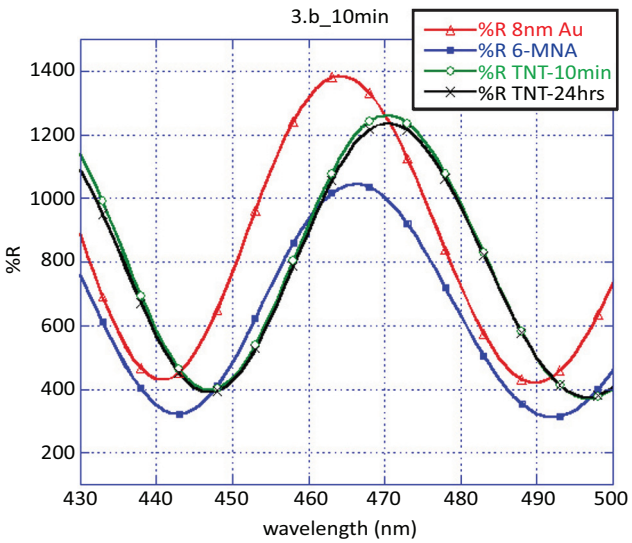


Figure 2. Ultraviolet-visible reflectance spectra of AAO/Al. Red = 10-minute anodization with 8-nm Au coating, blue = after treatment with 6-mercaptopyridine-3-carboxylic acid, green = upon 10-minute exposure to TNT solution, and black = upon 24-h exposure to TNT.

Refereed Publications

Wang, H.H., "Flexible Chemical Sensors," chapter in *Semiconductor Nanomaterials for Flexible Technologies: From Photovoltaics and Electronics to Sensors and Energy Storage*, edited by J. Rogers and Y. Sun, William Andrew Inc., April 15, 2010.

Non-Refereed Publications and Presentations

Gopalsami, N., A. Heifetz, H.-T. Chien, and A.C. Raptis, "Terahertz Subwavelength Structures for Sensing and NDE," *AIP Conference Proceedings,* Vol. 1211, edited by D.O. Thompson and D.E. Chimenti, 2010.

Gopalsami, N., H.-T. Chien, T. Elmer, S. Bakhtiari, and A.C. Raptis, "Surface Plasmon THz Resonators for Security Applications," in *Review of Quantitative Nondestructive Evaluation,* AIP Conference Proceedings, Vol. 1096, edited by D.O. Thompson and D.E. Chimenti, 2009.

Liu, Y., H.H. Wang, J.E. Indacochea, and M.L. Wang, "Interference Color of Anodized Aluminum Oxide (AAO) Films for Sensor Application," in SPIE Proceedings*, Sensors and Smart Structures Technologies for Civil, Mechanical, and Aerospace Systems 2009,* Vol. 7292, edited by Masayoshi Tomizuka.

Zientek, B., H.H. Wang, J.E. Indacochea, Y. Liu, and M.L. Wang, "Development of Nanowell Based Sensors for the Detection of Improvised Explosive Devices," in SPIE Proceedings, *Sensors and Smart Structures Technologies for Civil, Mechanical, and Aerospace Systems 2010,* Vol. 7647, edited by Masayoshi Tomizuka.

Global Modeling Initiative for National Security Event Dynamics

2008-138-R2

Charles M. Macal, Jonathan Ozik, and David L. Sallach

Project Description

The goal of the Global Modeling Initiative (GMI) is to conduct research on computational tools that could be used to identify and better understand emerging worldwide threats to U.S. national security. As part of the GMI, the Global Modeling Simulation (GMS) models the dynamic social and cultural processes that germinate threats to national security. The technical approach is multi-layered, consisting of the macro, meso, and micro layers. At the macro level, a selected set of worldwide databases is linked into a graphical user interface that makes relevant information accessible on a geo-spatial basis. At the meso-scale level, social and organizational networks are the primary relational medium for data presentation and indexing; such networks could include terrorist networks and proliferation networks. At the micro scale, social processes that embody social mechanisms (including incentives) allow for the dynamic interactions of individuals and groups that result in emergent social structure, such as terrorist networks.

Mission Relevance

Modeling the domain of social dynamics and behavior presents scientific problems that are challenging and that have some of the most important policy consequences. The focus has been on developing models of heterogeneous agents that use simple but plausible behavioral rules and exploring the consequences that emerge from such models. One of the strengths of computational social science is its ability to develop models that integrate existing knowledge in the social sciences reflecting a variety of fields. Such formal and theoretical integration of current social science knowledge will be one of the significant scientific contributions of this project. The comprehensive, global scope of the GMI and the multi-scale nature of the threat generation problem are great challenges in applying large-scale computational modeling and high-performance computing to national security and energy issues. Therefore, this project is relevant to DOE's national security and energy missions.

FY 2010 Results and Accomplishments

In FY 2010, substantial progress was made in analyzing unstructured data. Figure 1 shows the updated visual network representation of the AQ Khan nuclear proliferation network, based on publicly available and open-source, unstructured data sources. An ontology for weapons of mass destruction (WMDs) was implemented to supply contextual (network)

information (Figure 2). We developed automated techniques for developing the ontology from unstructured data sources, superseding the manual process that was used in year two of the project. These techniques are potentially applicable to a wide range of analyses of WMD data, including real-time analyses.

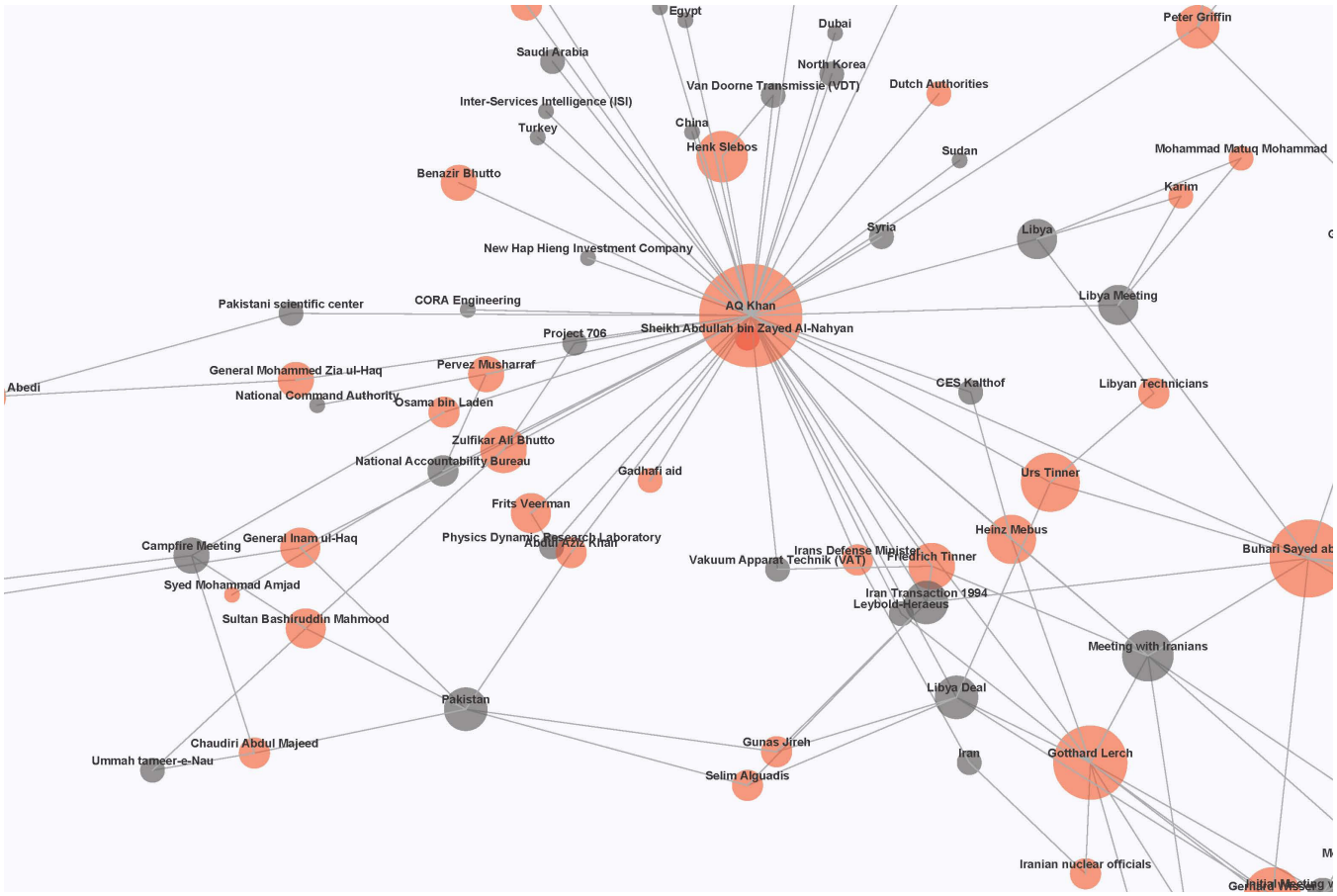


Figure 1. Visual representation of the A.Q. Khan nuclear proliferation network.

FY 2010 accomplishments were based on the first two years of work. In year one of the project, we developed the software architecture for representing a multilevel, social-cultural model using the *Repast* agent-based modeling toolkit. The multilevel capability allowed the representation of social-cultural systems at three scales: macro-, meso-, and micro-. Each scale was differentiated by the granularity of the representation of social and cultural objects included in the model. At the macro level, global and regional processes are represented to include, for example, country-to-country interactions. At the meso-scale level, individuals and organizations are represented at the subnational level. At the micro-level, agent-to-agent interactions can be modeled at the finest level of granularity. In year two of the project, we developed a meso-scale application within the software architecture that allowed us to model the A.Q. Khan nuclear proliferation network and supply chain for illicit nuclear materials as a example of the application. To support this application, all of the available literature, stories, and documents on the A.Q. Khan network were manually encoded into the application, and objects were manually categorized. This application demonstrated the application and benefits of network analysis techniques to modeling proliferation networks.

Non-Refereed Publications and Presentations

Macal, C.M., *Network Analysis of the A.Q. Khan Network*, presented at National Security Community Meeting, Argonne National Laboratory, Argonne, IL, May 27, 2009.

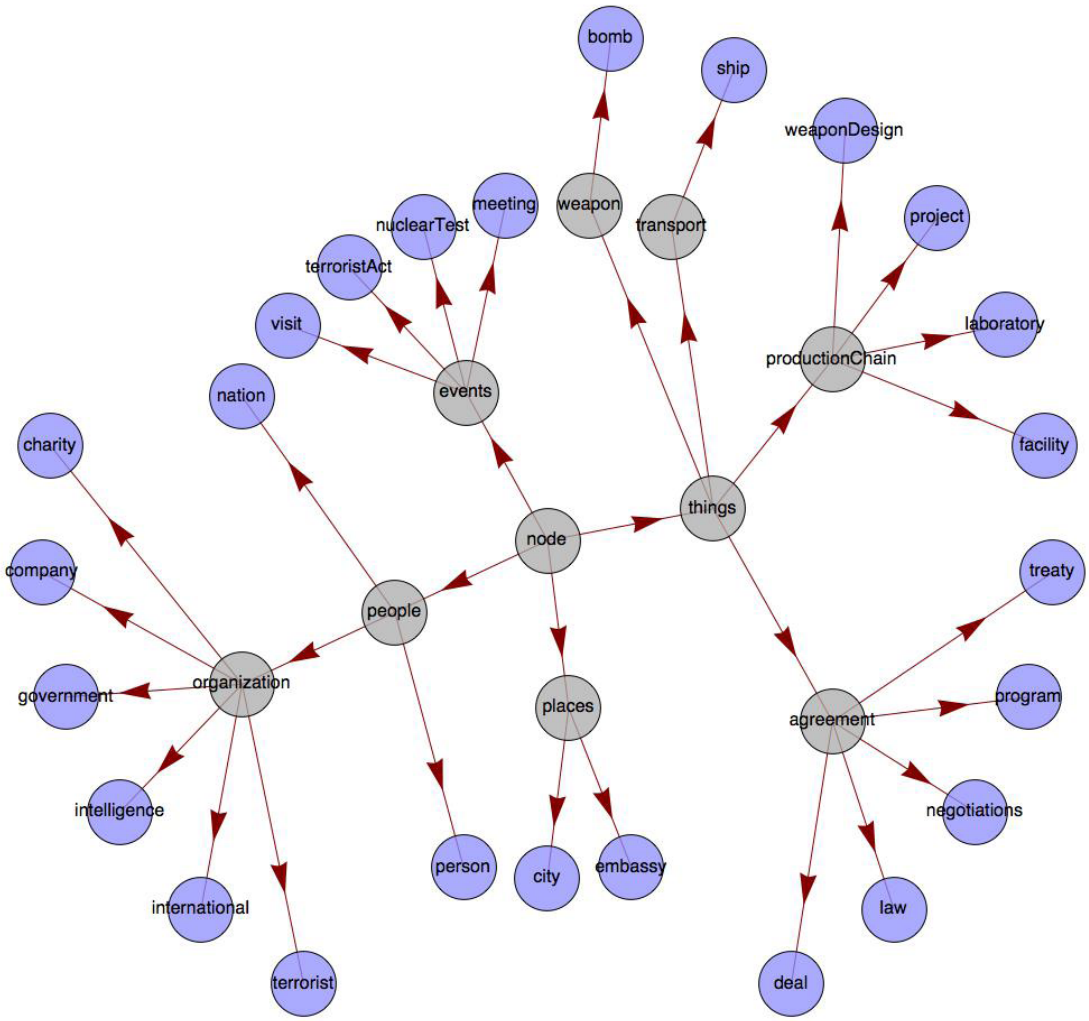


Figure 2. Visual representation of the ontology for the nuclear proliferation network.

Science and Technology for Development of High-Sensitivity Biosensors

2008-157-R2

Orlando H. Auciello, Derrick C. Mancini,
Muruganathan Ramanathan, and Anirudha V. Sumant

Project Description

The project focuses on developing a portable, high-sensitivity, real-time nanoscale biosensor. The science focuses on acquiring the knowledge for demonstrating an anthrax detector. However, it is expected that the knowledge acquired will also be applicable to the detection of other dangerous bioagents that could be used in a terrorist attack or on the battlefield. Initial work focused on studying the detection of biomolecules simulating anthrax protective antigen (PA), using antibodies that directly recognize the critical factor (Anaspec CAT#54312). Antibodies against PA can be conjugated to functionalized ultrananocrystalline diamond (UNCD) -based nanocantilevers or to the surface of UNCD nanowires, which can be used to perform essentially as a transistor-type device, where transport of an electronic current from a source to a drain is modified by the adsorption of biomolecules. Purified PA proteins are being investigated at a range of concentrations to establish the appropriate sensitivity and dynamic range for a sensor.

The proposed biosensor technology is based on the UNCD film technology developed at Argonne. UNCD thin films were synthesized by using microwave plasma-enhanced chemical vapor deposition (MPCVD) with argon-rich Ar/CH_4 plasmas and shown to consist of 3–5-nm grains of pure sp^3-bonded carbons and sp^3/sp^2 mixtures at grain boundaries. These films show low friction coefficients, extreme chemical and

biological inertness, and electrochemical performance over a wide voltage range. At present, the program focuses mainly on investigating the MEMS/NEMS-based resonant-cantilever approach, where selective attachment of biomolecules produces resonant frequency changes (Figure 1), enabling detection of biomolecules in the second-to-microsecond time frame and in the nanosecond range if nanodevices can be fabricated.

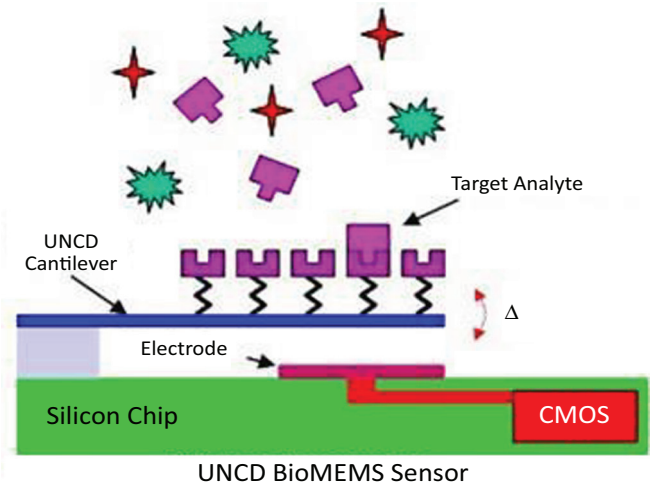


Figure 1. Schematic of UNCD resonator-based biosensor under development in this project.

A critical step in the fabrication of a UNCD-based biosensor is surface functionalization via tailoring of the surface chemistry. Functionalization of the UNCD surface has been investigated in prior work by researchers involved in this project, and surfaces have been engineered for specific applications. Oxygen or ammonia plasma treatment enables the introduction of oxygen- or nitrogen-containing functional groups onto H-terminated UNCD surfaces. Electrochemical reduction of diazonium salts can also be used to introduce different aryl derivatives onto the UNCD surface, enabling control of UNCD surface charges and surface hydrophobicity. The surface hydrophobicity prevents the stabilization of many biomolecules directly at the surface, and the lack of chemically reactive groups precludes the attachment of biomolecules to the surface. Thus, surface modification of UNCD is required to provide chemical functional groups amenable to the covalent coupling of biomolecules, while preserving its otherwise favorable biomaterials properties (e.g., bioinertness).

Mission Relevance

This project is relevant to DOE's national security mission. The development of high-sensitivity biosensors is critical to the present and future outlooks for national security. Hazards to the general population's health are posed by airborne diseases, such as anthrax. Marine toxins, brucellosis, encephalomyelitis, hemorrhagic fever, cholera, mycotoxins, plague, chimeras and homologues, Q fever, shigellosis, smallpox virus, tularemia, bioregulators, and typhus are also potential threats, as they can be employed for attacks on large segments of the population. A key problem with current detection methods is slow response in identifying a biological attack by terrorists or an outbreak of a contagious disease, owing mainly to the long time it takes to do analysis in laboratories far removed from the location of the attack or outbreak. Therefore, the development of high-sensitivity portable personal biosensors, which could detect a biological threat immediately upon exposure, could save lives.

FY 2010 Results and Accomplishments

We successfully identified functional groups that worked for functionalizing the UNCD surface (Figure 2).

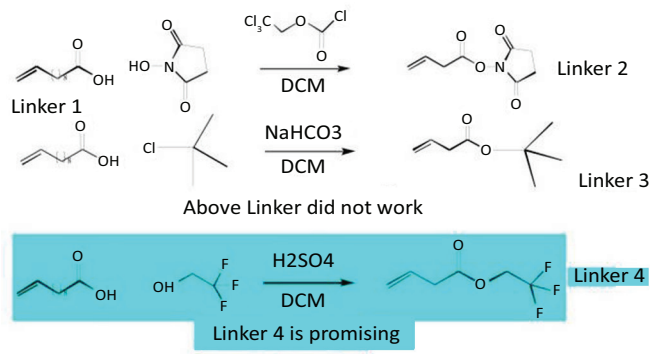


Figure 2. Functional groups investigated for functionalization of the surface of UNCD.

In addition, studies using atomic force microscopy (AFM) showed the successful linkage of the T7 phage to the surface of UNCD layers (Figure 3).

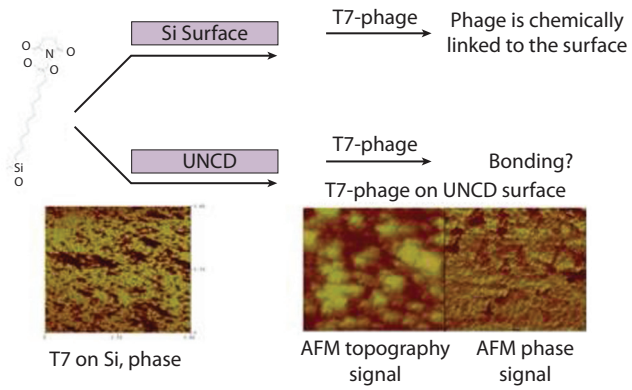


Figure 3. Linkage of T7 phage to Si and UNCD surfaces.

Initial analyses of functionalized UNCD surfaces, using IR (infrared) absorption spectroscopy, showed the potential to identify functional groups on the surface of UNCD films (Figure 4).

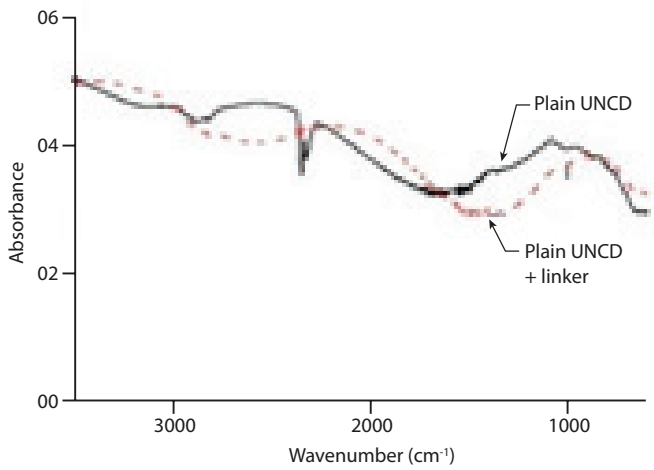


Figure 4. IR absorption spectroscopic analysis of the surface of a plain UNCD layer and one functionalized with linker 4 (shown in Figure 2).

The work on functionalization of UNCD surfaces described above was very preliminary, and the current work shows promise as the basis for identifying a good anthrax species simulator to investigate the performance of the biosensor. In addition, we procured an ATR (attenuated total internal reflection) accessory for use in making Fourier transform infrared spectroscopy (FTIR) measurements of functionalization of the UNCD by coating the ATR crystals with UNCD and observing chemical modifications to the functionalized surface.

The reasons for choosing anthrax for demonstrating the performance of the biosensor being developed included the following: (a) anthrax is one of six category-A biological weapons, (b) it has a high potential for casualties, and (c) it might cause public panic and it therefore requires special public health preparedness. Anthrax exhibits activity that is dangerous but non-contagious, owing to its ability to easily spread as a microorganism or toxin. While in the ground or on a surface, anthrax spores are relatively harmless, but once they come into contact with the right environment, they begin to germinate. In addition, they are rich in amino acids, nucleosides and glucose, and they can reproduce in blood and tissues in humans and animals. Anthrax bacteria secrete three major virulent factors — PA, edema factor, and lethal factor — which are the main factors to be identified by a biosensor. However, our original plan to demonstrate a UNCD-based biosensor to sense these factors (anthrax simulants) was hampered by new Argonne-initiated safety regulations, which made working with these factors much more expensive and required much longer timeframes for obtaining approvals than what the project budget would allow. Hence, we had to change the direction of this research to develop high-sensitivity sensors for plasmid DNAs, to at least demonstrate the feasibility of a UNCD-based MEMS biosensor.

Bio-conjugation of diamond surfaces with double-stranded DNA is not a straightforward process, as there are no inherent functional sites to selectively adsorb on or link to the sensor substrate. We tackled this issue by using photochemical electron transfer to anchor the DNA onto a planar UNCD surface. This route involves three steps:

1. Hydrogen termination on the UNCD substrate;
2. Developing a photoactive linker molecule; and
3. Conjugation of fluorescent-labeled plasmid DNA.

Using a Lambda MPCVD tool connected to a commercial high-purity hydrogen cylinder, we grew UNCD films with a hydrogen-terminated surface. The XPS (x-ray photoelectron spectroscopy) high-resolution spectra of UNCD taken at the C 1s edge after H-termination is shown in Figure 5; it shows a Gaussian curve corresponding to C-C bonding at 284.7 eV and a very low C-O peak, indicating good H-termination. The C-C peak is shifted by about 0.6 eV towards higher energy owing to the charging caused by H-termination, which is well known in the literature.

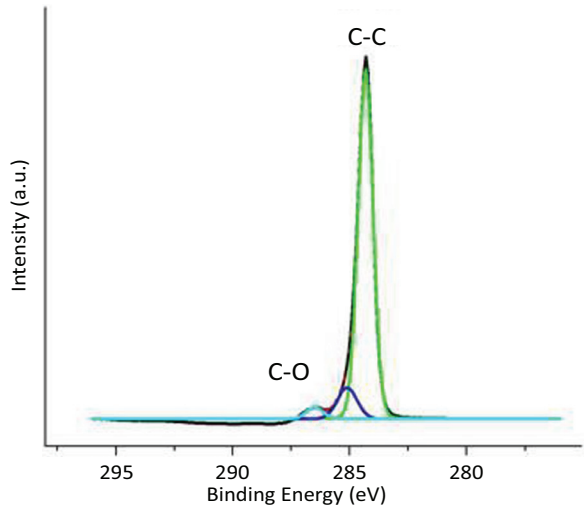


Figure 5. XPS spectrum obtained on the surface of a UNCD film after H-termination using high-purity hydrogen. The spectrum shows a big C-C peak with a very small C-O peak, indicative of good hydrogen termination.

For photo-assisted bio-conjugation, we used UV light from a low-pressure mercury vapor quartz grid lamp (254 nm) under dry nitrogen. For safe operation, we custom-made a UV-safe box with a built-in ozone removal capability. We used the Hamers' process to custom-synthesize the photochemical linker molecule (i.e., trifluoroacetic acid [TFA] -protected 10-amino-dec-1-ene, shown in Figure 6).

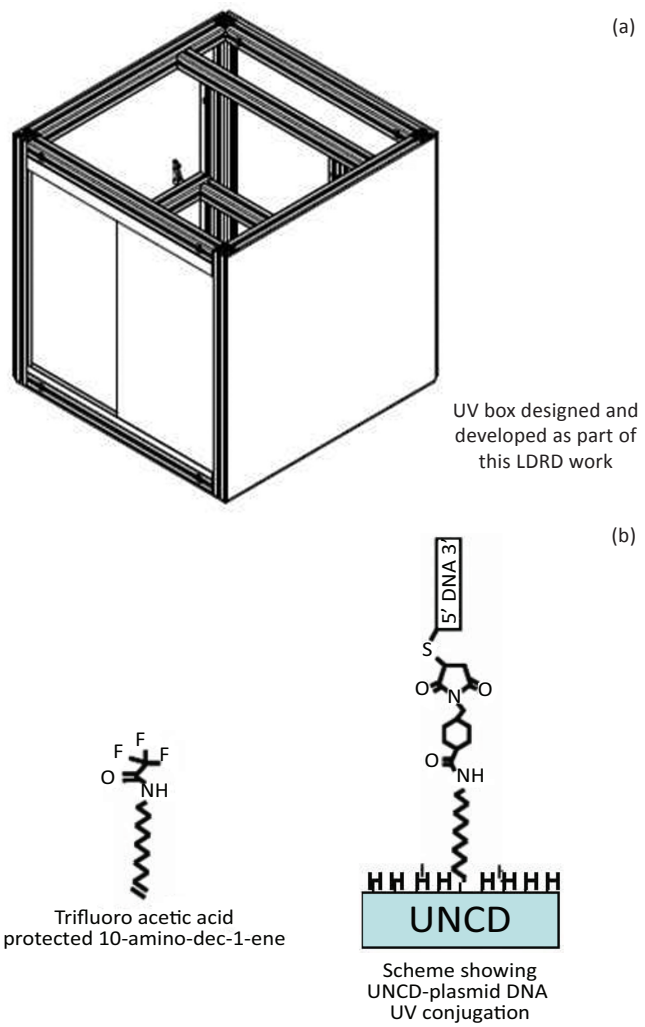


Figure 6. Schematic showing (a) UV-assisted plasmid-DNA functionalization of the (b) UNCD film surface.

We made significant progress in demonstrating the feasibility of UNCD-MEMS based biosensors. We are now exploring external collaboration and other funding that would allow to progress further in the development of UNCD-MEMS biosensors.

Refereed Publications

Ramanathan, M., S.B. Darling, A.V. Sumant, and O. Auciello, "Nanopatterning of Ultrananocrystalline Diamond (UNCD) Thin Films via Block Copolymer Lithography," *J. Vac. Sci. Tech. A* **28** (2010), 979–983.

Ramanathan, M., S.B. Darling, A.V. Sumant, and O. Auciello, "Self-assembly of Cylinder-Forming Block Copolymers on Ultrananocrystalline Diamond (UNCD) Thin Films for Lithographic Applications," *Mater. Res. Soc. Symp. Proc.* **1203** (2010), 1203-J17-15.

Non-Refereed Publications and Presentations

Auciello, O., "Science and Technology of Multifunctional Ultrananocrystalline Diamond (UNCD) for Implantable Biomedical Devices and as Platform for Developmental Biology," University Colloquium, University of Colorado-Colorado Springs, August 24, 2010.

Auciello, O., A.V. Sumant, S. Balachandran, C. Goldsmith, S. O'Brien, S. Sampath, A. Datta, C. Gudeman, J.A. Carlisle, D.C. Mancini, J. Swonger, D. Czaplewski, S. Balachandran, J.M. Hiller, B. Kabius, W. Li, B. Shi, Q. Jin, and L. Chen, "Science and Technology of Ultrananocrystalline Diamond Films for Application to Multifunctional Micro and Nanodevices," keynote talk presented at the 4th International Conference on New Diamond and Nano Carbons, Suzhou, China, May 16–20, 2010.

Ramanathan, M., "Power of Soft Materials Self-Assembly," invited presentation at the Center for Nanophase Materials, Oak Ridge National Laboratory, September 20, 2010.

Ramanathan, M., "Power of Soft Materials Self-Assembly and Its Applications," invited presentation at the Center for Nanoarchitectonics, National Institute of Materials Science, Boston, MA, USA, November 31, 2010.

Ramanathan, M., S.B. Darling, A.V. Sumant, O. Auciello, and D.C. Mancini, "Nanostructuring of Carbon Based Thin Films," presented at EIPBN 2010, Anchorage, Alaska, June 1–4, 2010.

Sumant, A.V., X. Wang, L.E. Ocola, D. Lopez, B. Kabius, O. Auciello, and D.C. Mancini, "Fabrication and Characterization of Ultrananocrystalline Diamond Nanowires for Developing Next Generation of Nanoelectronic and NEMS Devices," presented at the SPIE 2010 Conference on Micro- and Nanotechnology Sensors, Systems, and Applications, Orlando, FL, April 5–9, 2010.

Rapid Elemental and Isotopic Analysis of Trace Actinides and Fission Products in Fused Materials Using Advanced Extraction Methods and Resonant Ionization Mass Spectrometry

2009-017-R1

Ilya A. Shkrob and Michael R. Savina

Project Description

This project focuses on rapid isotope analysis of trace radionuclide elements in the environment for nuclear

forensics applications. Nuclear forensics aims to trace fissile and radioactive materials back to their source in order to thwart terrorist activities and guide the emergency response. Current procedures require more than 24 hours for precise determinations of the isotope ratios for the elements of interest. These long analysis times result from lengthy chemical separations of *f*-shell ions (lanthanides and actinides), many isotopes of which have the same mass (isobaric interferences). These elements are not distinguishable when conventional low-resolution mass spectroscopic techniques are applied to trace amounts of radionuclides. Our approach bypasses these difficulties by using resonance ionization mass spectrometry (RIMS), which is both extremely sensitive and element-specific. With this method, the isotopic composition is determined by using multiphoton excitation that is tuned to a particular element, so that only atoms of that element are ionized. The laborious analytical separations become redundant; the "separations" occur by tuning the laser frequency to particular transitions in an atom rather than by chemical means. This method accelerates and simplifies the preparations, since the chemical processes are used only for preconcentration of the radionuclides in a form suited for RIMS analyses. The scope of this work is to develop and demonstrate this method in a realistic system. The deliverable of this project is a method suitable for rapid (less than 6 hours) and accurate analyses.

Mission Relevance

This project is tied to DOE's mission in national security. The need for rapid analytical capabilities has been articulated by the Office of Nonproliferation Research and Development and the Office of Defense Nuclear Nonproliferation in DOE's National Nuclear Security Administration and by the Science and Technology Innovation Office of the Defense Threat Reduction Agency, which seek nuclear forensics technologies that provide rapid field and/or fixed laboratory analysis for chemical separation and isotopic measurement. The objective is complete analysis in less than 24 hours.

FY 2010 Results and Accomplishments

In FY 2009, we modified polystyrene magnetic microspheres by decorating them with ion-binding ligands. We used these microspheres to demonstrate rapid sequestration of lanthanides from liquid samples. The microspheres with the sequestered ions were magnetically separated and analyzed by using RIMS. We also demonstrated sequestration by using nanoporous, impregnated resins. In the latter case, the resin microparticles were separated by centrifugation. Both the resin and magnetic microparticles yielded promising results in the test trials. The measured isotope ratios were stable and reproducible. Each individual particle analysis exhibited a precision of better than 0.4% in the $^{151}Eu/^{153}Eu$ ratio in 1 hour of analysis time. This type of high precision in such a short period demonstrated the feasibility of the approach.

In FY 2010, we adapted the chemistry to highly acidic, oxidizing nitric acid solutions that are common in the analysis of environmental samples. For that we used an ion-exchange resin with covalently attached diphosphate groups that bind ions of *f*-elements. The distribution ratios of $(2–20) \times 10^3$ mL/g for 1 M nitric acid solutions were achieved after 2 hours of equilibration. The extent of sequestration depended on hydrodynamic separation of resin particles by rapid stirring and good flow around the individual particles. We readily collected more than 90% of the metal ions from the representative liquid samples on 100 microparticles. (In RIMS, the sample is analyzed one particle at a time.) The sequestration–preconcentration step can be carried out *en route* to the analysis site, so this step does not add to the overall time of the analysis. Since the ion binding for diphosphate resin (unlike the impregnated acrylic ester resin that we used in our 2009 studies) is 10–100 times stronger at lower acidity, it is possible to neutralize the acidic solutions in order to prepare the sample for RIMS analysis without the loss of the sequestered ions. The laser resonance ionization scheme that we used was also improved, and we achieved 0.12% precision for the $^{151}Eu/^{153}Eu$ ratio in 45 minutes on a single 50-micrometer resin particle. This precision compares favorably with the established methods, such as thermal ionization or inductively coupled plasma mass spectrometry, but with much less sample preparation and at much higher sensitivity.

Another milestone was the detection of lanthanides simultaneously by precise tuning of the resonance lasers. Figure 1 depicts the lanthanum (La), europium (Eu), and erbium (Er) detected in a single microparticle. In this experiment, the ionization laser beam was the same for all three elements, while the other two laser beams were tuned to atomic transitions in La and Eu. The Er was resonantly excited and ionized by the same (third) laser beam. As shown in the figure, Spectrum A displays the full three-laser scheme with all three lanthanides excited and detected simultaneously. Spectrum B, taken with the La resonance laser blocked, shows the absence of the La signal. Spectrum C, taken with the Eu resonance laser blocked, shows the absence of the Eu signal. Finally, in Spectrum D, taken with the Er resonance laser blocked, *all* atom signals have disappeared because the Er resonance laser was also the ionization laser for La and Eu. This experiment demonstrates the feasibility of elemental and isotope analyses that avoid isobaric interferences for a microscopic sample containing concentrated fission products. With these advances, we have laid all of the necessary groundwork for practical applications of this method in nuclear forensics.

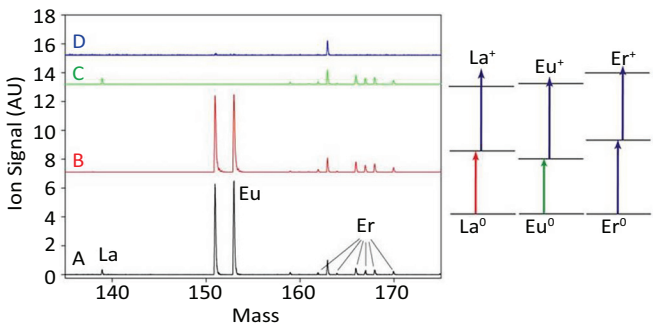


Figure 1. Simultaneous three-element (La, Eu, and Er) detection by RIMS using three lasers (given the false colors of red, green, and blue in the diagram on the right) overlapped on a single lanthanide-loaded polymer ion-exchange resin microparticle. The two-photon excitation scheme is shown in the diagram. In A, all three lasers are on; in B, the La resonance laser (red) is blocked; in C, the Eu resonance laser (green) is blocked; and in D, the Er laser (blue) is blocked. The residual peak in trace D (also seen in other traces) is from the organic matrix. The color of the traces in the plot corresponds to the color of the laser beam blocked in the diagram.

This project is continuing under the sponsorship of the U.S. Department of Homeland Security.

Refereed Publications

Shkrob, I.A., M.D. Kaminski, C.J. Mertz, P. Rickert, M.S. Derzon, and K. Rahimian, "Sequestration, Fluorometric Detection, and Mass Spectroscopy Analysis of Lanthanide Ions Using Surface Modified Magnetic Microspheres," *J. Am. Chem. Soc.* **131** (2009), 15705–15710.

Shkrob, I.A., M.D. Kaminski, K. Rahimian, and M.S. Derzon, "Magnetic Extraction, Detection, and Isotope Analysis of Metal Ions Using Surface Modified Microspheres for Lab-on-a-Chip Applications," *Sep. Sci. Technol.* **45** (2010), 186–197.

Non-Refereed Publications and Presentations

Savina, M.R., and I.A. Shkrob, "Rapid Isotopic Analysis of Lanthanides and Actinides by Resonance Ionization Mass Spectrometry," presented at the 5th International Conference on Laser Probing, Vancouver, BC, September 27–October 1, 2010.

Savina, M.R., and I.A. Shkrob, "Sequestration and Analysis Methods for Lanthanides and Actinides Using Resonance Ionization Mass Spectrometry," presented at the Asia-Pacific Symposium on Radiochemistry, Napa, CA, November 29–December 4, 2009.

Savina, M.R., and I.A. Shkrob, "Development of Rapid Sequestration and Isotopic Analysis Methods for Lanthanides and Actinides Using Resonance Ionization Mass Spectrometry," poster presentation at the 18th International Mass Spectrometry Conference, Bremen, Germany, August 31–September 4, 2009.

Tagging and Monitoring Sealed Radiological Sources

2009-028-R1

Roger G. Johnston and Jon S. Warner

Project Description

There is a significant need to tag and monitor tens of thousands of sealed radiological sources, because these are a credible threat for use in terrorist Radiological Dispersal Devices (RDDs). Most or all of the tags, seals, locks, and monitoring schemes that have been informally proposed are impractically expensive, are too large and heavy, interfere with the authorized use of the sources, and are easy (based on the extensive experience of the Argonne Vulnerability Assessment Team and others) for amateurs to bypass or spoof, including those based on the use of radio frequency identification devices (RFIDs).

This project involved developing and demonstrating a novel concept that avoids these problems. The intent was to design a low-cost but high-security tag/seal/monitoring technology that can detect theft, misplacement, or tampering with a sealed radiological source in real time. This approach has the potential for providing a practical way of addressing sealed-source security.

The approach used was a novel "anti-evidence" method of tagging and monitoring. It is potentially simpler, less expensive, and more secure than other approaches. Anti-evidence is based on the idea that we do not want the asset being monitored to sound an alarm if it is being moved, stolen, or tampered with (nor store an alarm condition in or on a seal until inspection time) because the alarm is too easy for an adversary to block or hide. The problem of alarm blocking is typically addressed by using two-way (often encrypted) communication and/or periodic polling of the security hardware and sensors. This approach, however, has great complexity, which substantially increases the cost. Moreover, it is not very practical for assets that are in motion, and it introduces a host of reliability problems and easy-to-exploit security vulnerabilities.

With anti-evidence, instead of having an alarm, we send out an occasional "All-OK" signal, typically a single byte. Only authorized individuals know the exact value of this byte at any given time. If tampering is detected or the item being monitored is missing, the All-OK signals cease. It is the absence of the signal that is the evidence of theft or tampering. This one-way, very low-bandwidth communication (we simply listen to the asset, we do not try to talk to it) permits simple, low-cost

monitoring with very high levels of security. The assumption with real-time monitoring is that there are security guards, technical personnel, or police who can respond quickly in the event of theft of the asset. Otherwise, real-time monitoring has little merit and tamper detection is a less-expensive approach.

To make things even simpler and less expensive, it is not necessary to send a full byte or have any information (or serial number or modulation) in the All-OK signal. As long as everything is fine, the microprocessor-based monitoring circuit on or adjacent to the sealed radiological source of interest will "chirp" at random, unpredictable times known only to authorized individuals. The chirp can be an ultrashort flash from an infrared LED, or a radio frequency pulse, but for the lowest cost and greatest practicality, we believe an ultra-short chirping acoustical pulse is ideal.

The use of a chirping sound to signal that the sealed radiological source is still present and has not been tampered with has the additional advantages that sound goes around corners, requires little battery power, and unlike RFIDs does not suffer interference from metals and liquids, nor is it trivial to block or spoof. The sound chirps are so short (23 milliseconds [ms]) that many different sealed radiological sources in the same general area can all be randomly chirping, each one emitting a chirp once each minute or so on average, with the random chirps overlapping very infrequently. (If the chirp sounds become annoying to people, ultrasonic chirps can be used, but this option significantly decreases the 200-plus-foot range we initially felt was possible for audible chirps.)

The implementation of this chirping tag, seal, and security monitor would then look something like this: Instead of attaching a security device directly to the sealed radiological source (which presents a number of practical problems), we would instead design a thin, lightweight plastic case to hold each source. For many authorized radiological applications, the sealed radiological source could be used without having to even remove it from the case. Built into the plastic case is a coin battery and a small, inexpensive microprocessor-based electronic circuit with built-in redundancy to deal with slightly elevated failure rates due to an increased radiation environment near the source. This circuit does the random audible chirping and checks whether the case was opened, using a photosensor and other low-cost, small commercial solid-state sensors that have not been much exploited for security applications. If any evidence of opening is detected, the case stops chirping.

In summary, the potential advantages of acoustical chirp tagging and monitoring that this project attempted to demonstrate include the following:

- Simplicity
- Low-cost
- Good range
- Works around corners
- Works inside packages
- Low power requirements
- Good for safety awareness
- Humans can tell if the asset is still present
- Works near metals or liquids (unlike RFIDs)
- Harder to suppress than radio frequency or infrared signals
- Works under any illumination or electromagnetic noise background

Mission Relevance

This project is relevant to DOE's national security mission. Better tagging and monitoring of sealed radiological sources has important implications for homeland security (protecting against radiological dispersal devices); nuclear environment, safety, and health (ES&H); nuclear security/safeguards; nonproliferation; and treaty monitoring. There are other potential security applications as well, not involving sealed radiological sources.

FY 2010 Results and Accomplishments

In FY 2010, we fabricated additional chirping circuits, bringing the total to five (see Figure 1). These circuits emit a 23-ms acoustic chirp centered at approximately 3.9 kHz. The acoustical background noise in most industrial settings, medical treatment centers, or nuclear facilities is typically minimal at 3.9 kHz, with most human speech occurring below 2.0 kHz. We also added a tamper-detection sensor to three of the circuits to demonstrate how removal of the tag/seal from the asset of interest could be immediately detected.

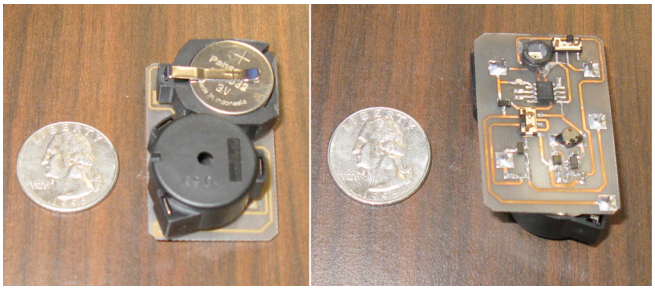


Figure 1. Top and bottom views of the early prototype acoustic chirping tag/seal and real-time monitor. It has not been fully miniaturized.

We identified, procured, and tested a new commercial parabolic microphone and demonstrated that it can be used to reliably detect the chirps at a distance exceeding 260 meters outdoors in a relatively windy and noisy environment (see Figure 2). This is a much greater distance than the original *indoors* distance of 60–90 meters that was originally envisioned. In fact, 260 meters is a much greater detection distance than any passive RFID has achieved, and it is better than almost all semi-active and even many active RFIDs (while avoiding the cost and numerous other disadvantages of RFIDs discussed above). While we did not originally expect this device to be relevant for outdoor use, that view should probably be reexamined. We also demonstrated good sound performance around corners — and even through doors.

Figure 2. Detecting the chirps outdoors at a distance of 875 ft (~260 m) with 5–8 mph winds and noisy construction taking place 400 yd away (microphone is located away form the chirp source). The chirping tag/seal is located next to the distant automobile. The inset figure in the lower left-hand corner shows a Fast Fourier Transform (FFT) of the acoustical spectrum, clearly demonstrating detection of the 3.9-kHz chirp even at this distance.

We identified and programmed a chirp-detection algorithm and tested its performance on a notebook computer.

In FY 2010, we also presented the concept of the Chirping Tag/Seal and some preliminary performance data in seven invited talks, three contributed talks, and one proceedings paper. There was considerable interest in this concept.

Non-Refereed Publications and Presentations

Johnston, R.G., "Securing Against Theft, Tampering, and Counterfeiting," Invited Talk presented at the APEX Security Seminar, Deerfield, IL, March 18, 2010.

Johnston, R.G., "Tamper Detection and Cargo Security," Invited Talk presented at the Takeda Pharmaceuticals Seminar, Deerfield, IL, July 27, 2010.

Johnston, R.G., "Proving Voltaire Right: Security Blunders Dumber than Dog Snot," Invited Keynote Address presented at the 19th USENIX Electronic Security Conference, Washington, D.C., August 11–13, 2010.

Johnston, R.G., "Vulnerability Assessment of Tags and Seals," Invited Talk presented at the Product Authentication and Brand Security Conference, Rosemont, IL, October 4–5, 2010.

Johnston, R.G., "Security Against Theft, Tampering, and Counterfeiting," Invited Talk presented at the Pharmaceutical Security Institute General Assembly, McLean, VA, October 28, 2009.

Johnston, R.G., and J.S. Warner, "Better Approaches to Physical Tamper Detection," Invited Plenary Talk presented at the ShmooCon 2010, Washington, D.C., January 5–6, 2010.

Johnston, R.G., and J.S. Warner, "Town Crier Monitoring and the Chirping Tag/Seal," presented at the 9th Security Seals Symposium, Houston, TX, August 31–September 2, 2010.

Warner, J.S., "The Argonne Vulnerability Assessment Team," Invited Talk presented at the Technology Surprise Seminar, Sandia National Laboratory, Albuquerque, NM, May 10, 2010.

Warner, J.S., and R.G. Johnston, "Chirping Tag and Seal," presented at the 51st INMM (Institute of Nuclear Materials Management) Annual Meeting, Baltimore, MD, July 11–15, 2010.

Warner, J.S., and R.G. Johnston, "Why RFIDs Offer Poor Security," presented at the 51st INMM Annual Meeting, Baltimore, MD, July 11–15, 2010.

Warner, J.S., and R.G. Johnston, "Chirping Tag and Seal," Proceedings of the 51st INMM Annual Meeting, Baltimore, MD, July 11–15, 2010.

Photoacoustic Technique for Remote Detection of Special Nuclear Materials

2009-059-R1

Hual-Te Chien and Shuh-Haw Sheen

Project Description

The goal of this project is to develop and evaluate a nonconventional technique for detecting shielded special nuclear materials (SNM). Instead of directly detecting nuclear radiation, the photoacoustic spectroscopy (PAS) technique focuses on detecting radiation-induced gases, such as ozone and nitrogen oxides, in the ambient air surrounding the shielded SNM.

Mission Relevance

The project is relevant to DOE's national security mission. Because nuclear materials can cause mass destruction, their proliferation and unauthorized movement are great threats to our national security. The success of this project will lead to further development of a portable or standoff remote sensing instrument for search and surveillance of SNM in broad areas. This technique may also be used for remote detection of explosives, chemicals, and biological agents.

FY 2010 Results and Accomplishments

The PAS technique has been used for detection of chemicals, explosives, emissions, and bio agents in a laboratory environment. The PAS technique uses a pulsed tunable laser to excite target molecules that are in either gas or condensed phase. Then, an acoustic sensor is used to detect the acoustic waves (i.e., pressure waves) generated from the thermal relaxation process of the excited molecules. In FY 2009, we studied the sensitivity of ozone detection. We also demonstrated that the PAS technique could remotely detect ozone, one of the radiation-induced gases, in the ambient air surrounding the shielded SNM. Our PAS system for remote ozone detection consists of a carbon dioxide (CO_2) laser, a mechanical chopper, acoustic resonators, an ozone generator, and a data acquisition and analysis system. On the basis of the change in the energy state, the lasing transitions are grouped into two branches: *P*-branch and *R*-branch transitions. Within each branch, there are various dominant transitions. Distinct ozone absorption lines are in the region of the 9P branch (wavelength 9.44 to ~9.78 µm) of the CO_2 laser.

For a single radioactive source, the ozone concentration is proportional to the electrons produced by the source in the volume of the containing space. We evaluated the capability of the PAS system for remote detection of ozone by using a non-radioactive HG-1500 gas generator with variable ozone output of up to 750 mg/h in dry air or up to 1,500 mg/h in dry nitrogen and an ozone detector, Model OS-4, with a remote sensor head, which has a detection range between 0.03 and 20.00 ppm, detection resolution of 0.01 ppm, and accuracy of 10–15%.

The detection sensitivity and detection distance for the PAS system were evaluated. Figure 1 shows the PAS intensity of line 9*P*(18) - 9.54 µm for detection distances from 1 to 6 ft with the ozone output level set at 60% (≈ 0.25 ppm). Figure 2 shows the PAS intensity of line 9*P*(18) - 9.54 µm for various ozone output levels from 0 to 50% (0.15 to 0.3 ppm) with an acoustic resonator set at a distance of 12 in. from the ozone generator. The result confirms that PAS intensity is proportional to ozone concentration. According to the model of ozone production due to radioactive sources, ^{85}Kr emits 500-keV electrons and can induce ozone at levels of 3.45 ppm/Ci. Therefore, the maximum distance for detecting ^{85}Kr may be extended to about 80 ft per Ci, or we can detect 0.07 Ci of ^{85}Kr at a distance of 6 ft. By employing an Argonne acoustic resonator, we have demonstrated that the detection distance and sensitivity are both enhanced greatly.

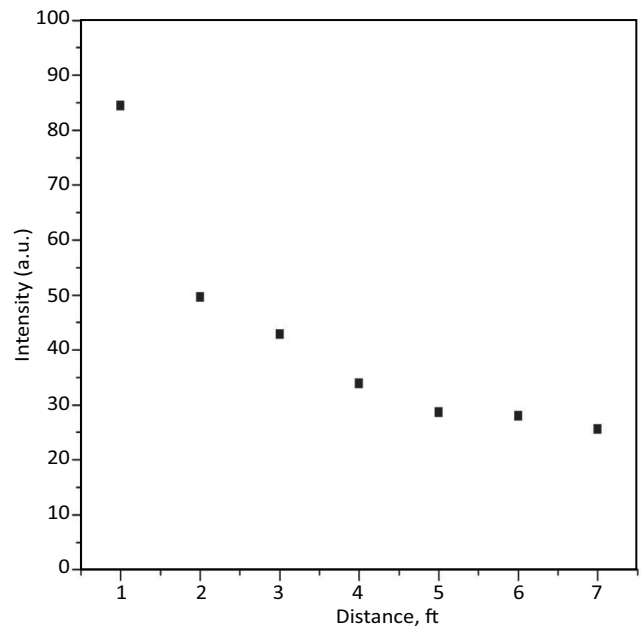


Figure 1. PAS intensity vs. detection distance for O_3 output level set at 60% (≈ 0.25 ppm) of line 9P(18) - 9.54 µm.

We used the high-resolution transmission molecular absorption database (HITRAN) to study the spectra of nitrogen oxides, which lie in the range of mid-IR lasers. For example, nitrous oxide (N_2O) has strong absorption spectra between 4.4 and 4.6 µm, nitric oxide (NO) between 5.1 and 5.6 µm, and nitrogen dioxide (NO_2) between 6 and 6.5 µm. A carbon monoxide (CO) laser is best suited for remote detection of nitrogen oxides. Unfortunately, none of the commercially available CO lasers are able to cover the entire spectra of the targeted nitrogen oxides. After considering chemical stability, safety, and funding constraints, we chose to evaluate nitric oxide first. A CO laser, Infrared Instruments model IRCO-4-W-GT-VP, with wavelengths between 5.2 and 5.9 µm and maximum power of 1.5 watts, was selected and ordered.

After further study and validation as a result of this project, a patent application was submitted and granted. (S.-H. Sheen, A.C. Raptis, and H.-T. Chien, "Photoacoustic Spectroscopy System and Technique for Remote Sensing of Explosives and Toxic Chemicals," U.S. Patent No. 7,644,606, January 12, 2010.)

Another patent, an extension of the previous one, was also granted recently. (S.-H. Sheen, H.-T. Chien, and A. C. Raptis, "Photoacoustic Spectroscopy (PAS) and Technique for Remote Sensing of Explosives and Toxic Chemicals," U.S. Patent No. 7,861,574 B2, January 4, 2011.)

A joint proposal with the University of Chicago to use the same PAS technique to study the skin penetration rate of chemicals was approved for 2010 funding by the Defense Threat Reduction Agency, but funding has been delayed. Seven other proposals based on the results of this project have been submitted to various agencies.

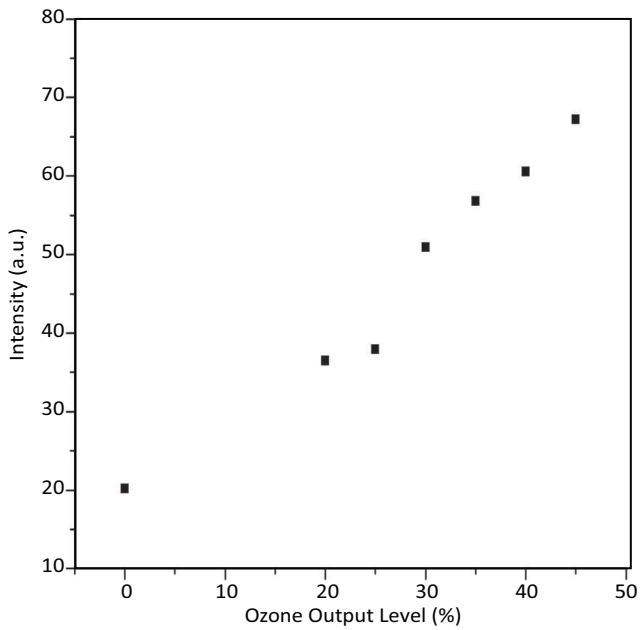


Figure 2. PAS intensity vs. O_3 output level at a distance of 12 in. from O_3 source of line 9P(18) - 9.54 µm.

Non-Refereed Publications and Presentations

Chien, H.-T., and D. Muh, "Photoacoustic and Millimeter-wave Techniques for Detection of Explosives and Explosive Components," presented at the National Consortium for MASINT Research (NCMR), Spring Technical Review, Maui, HI, March 30–April 2, 2010.

Fusion Cell Nucleus

2009-117-R1

James P. Peerenboom, David K. Brannegan, Ronald E. Fisher, and Daniel J. Miller

Project Description

The establishment of a network of "fusion centers" to facilitate nationwide information sharing is a top priority of federal, state, and local partners. Fusion centers were created by the Department of Homeland Security (DHS) to serve as focal points for the collection, analysis, and dissemination of homeland security, terrorism, law enforcement, and intelligence information. Fusion centers securely integrate federal data with state and local data and officials. To date, fusion-center data collection efforts have been extremely successful; however, subsequent analysis of collected resources has not met requirements. This dual-track project seeks to enhance fusion-center analytic capabilities by (1) addressing the processing limitations of fusion centers in "crossing" large sets of unrelated data and (2) reducing the subjectivity of fusion-center tools by adding strong analytic capabilities to existing geographic information system (GIS) platforms. The purpose of this project is to create a process and hardware/software toolset, called a Fusion Center Nucleus, that supports this complex integration requirement. Enabling fusion centers to overcome processing limitations while maximizing the analytic potential of existing GIS tools will ensure that the national network of fusion centers meets baseline analytic requirements in support of the U.S. Intelligence Community and the first preventers and first responders that it serves.

Mission Relevance

Effective fusion-center analytic capabilities are critical to U.S. Intelligence Community efforts to detect, prevent, disrupt, preempt, and mitigate the effects of terrorism against the territory, people, and interests of the United States. As a core departmental component of the U.S. Intelligence Community, this project supports the DOE national security mission and is directly relevant to the activities of the DOE Office of Intelligence and Counterintelligence. Fusion centers are consumers of and contributors to DOE intelligence analyses and associated technical, research, and operational efforts. This project will enable rapid development of new, cutting-edge capabilities that will support the integrated activities of all levels and sectors of government and the private sector involved in the national information-sharing environment. Finally, all 72 state and local fusion centers will benefit from the results of this effort and potential follow-on activities.

FY 2010 Results and Accomplishments

At a technical level, this project has been focused on two primary goals: (1) investigating and expanding the use of general purpose graphical processing units (GPGPUs) and (2) supporting the critical national security goals of the nation's fusion-cell program. GPGPUs are arrays of CPU cores typically used in graphics controllers that have been modified (sometimes only in software) to support additional general-purpose functionality. This project developed an initial analytical methodology and system (algorithms, hardware, and software) to enhance fusion centers' capabilities to "cross" large sets of otherwise unrelated data and transform them into actionable information. The project will result in the development of a stand-alone tool/technology that will materially improve two key fusion-center capabilities: (1) real-time analyses and (2) information sharing.

The mission of fusion centers is to provide federal-state-local data sharing and data leveraging. Fusion cells have, by their nature, fewer computational resources than national data centers. Their mission is to focus on content analysis rather than computational efficiency. This project provides a methodology and tool set that allows fusion centers to do analytic integration of local data streams and data sets. Many of the most common and critical steps involved in integrating data sets is pattern matching. A commonly used metric for ranking the correlation of objects such as documents is the Levenshtein Edit Distance (LED). Algorithms to determine LED were implemented in GPGPUs as a part of this project. By determining the LED between documents and fragments of documents, a fusion center will be able to determine correlations and extract similarities.

Previous phases of this work included the following:

- Research existing data streams that feed current fusion-center analytics.
- Conduct gap and effectiveness analyses of existing analytic tools/technologies deployed to fusion centers by the Federal government and private sector, as well as those developed by fusion-center personnel.
- Develop a phased project plan that articulates steps for finalizing the analytic methodology, integrating the methodology with existing analytic tools, and developing the associated software package.
- Review existing technologies to determine lessons learned and identify logical connecting points to conceptual analytical design.
- Initiate methodology development through review of existing dependency/interdependency data.
- Coordinate with internal and external Subject Matter Experts regarding assigning weights to existing dependency/interdependency data.
- Develop an initial scoping of requirements of the Fusion Center Program appropriately targeted by this work.

LED Design for Basic Text

We designed and implemented two versions of a Levenshtein distance calculator. One version was written using OpenCL to run on GPUs and to perform the calculations simultaneously. The other version was written in C++ and was used to serve as a baseline for speed comparisons. In each version, a target word was compared to a list of candidate words for potential matches. Because each comparison in the dynamic programming algorithm depends on the results of previous comparisons, parallelizing the computation of one Levenshtein distance calculation is useless at best. The comparisons required for one distance must be performed in sequence. For this reason, we parallelize the task over the candidate words. This means that each thread of execution computes the distance between the target word and one of the candidate words, so there will be as many threads as there are candidate words. We hand these threads off to OpenCL, and OpenCL executes as many threads as it can at one time, with any queued threads starting when the running ones finish.

The other significant difference between the two implementations, besides the parallelization, is in their memory footprint. The algorithm usually requires M × N bytes of memory for use as a workspace for calculating one distance, where M and N are the lengths of the target and candidate words. For the serial implementation in C++, we recycled the allocated workspace for each new word; this approach prevented us from encountering any memory limitations. However, in the OpenCL implementation, workspace needs to be allocated for all running threads. GPU memory is limited, so space became a serious constraint as the number of candidate words increased past a few hundred thousand. We were able to work around this constraint after changing the algorithm slightly: by performing the comparisons in a particular order, we could discard used values and effectively recycle M × 2 bytes over and over during the comparisons. The required workspace is still much larger than what is required for the C++ version, but that change allowed us to process many more candidate words (several million) on the GPU memory.

Results

In the time trials, our test platform was a 3.1-GHz AMD Phenom II X4 945 with 8 GB of RAM. The GPU was an ATI Radeon HD 5750 with nine 700-MHz compute units and 256 MB of GPU RAM. We used the AMD OpenCL SDK v2.1 and MSVC compiler. Our target word was “target,” and the list of candidate words came from English spell-check dictionaries. We were able to calculate up to three million distances before the GPU ran out of memory. In a production application, workloads greater than three million would be split into jobs that would be sent to the GPU for processing, but that kind of bookkeeping was beyond the scope of this project.

As we would expect, the rate of calculation on the CPU is roughly the same for different numbers of candidate words. Twice as many distance calculations will take twice as long. The GPU, on the other hand, increases in performance up to about a million candidate words, after which it levels off to around six times the speed of the CPU implementation. This initial ramp-up in performance is due to an under-utilization of the GPU on smaller workloads. Without enough work to do, some threads of execution will sit idle (e.g., stalled on memory access), thus decreasing total throughput. Although the performance improvement often attributed to GPUs is usually due to faster floating-point operations, we can see from the above that the speedup applies to other domains as well.

LED Design for Documents

A full text search, as opposed to a keyword search, looks through a set of documents and examines all words before returning those documents that it determines to be the most relevant to the search terms. For a smaller corpus, it is possible to make a new scan through the documents for each query. When the document set becomes too large to scan quickly, however, an index of potential search terms is built to facilitate new queries. Indices commonly rank the relevance of documents in a corpus to search terms on the basis of their "term frequency-inverse document frequency" (TFIDF), which is a method by which a term's importance is increased proportionally to the number of times it appears in a document, but decreased proportionally to its frequency in the corpus. In other words, a term's importance to a particular document is offset by its importance to all documents.

The bulk of the work for calculating TFIDFs in a full-text index lies in counting the occurrence of all terms in a corpus. Parsing characters into words and matching words with existing word counts is a conceptually simple but computationally demanding task, especially as document sizes grow to several megabytes. Developing a method for creating word counts and parallelizing this method for faster execution on GPUs is the focus of this project.

The time trials were run on the same hardware platform that was used for the Levenshtein distance calculations. For software, however, we used the updated AMD OpenCL SDK v2.2 and the GCC compiler. We used documents of sizes up to 10 MB, and both versions produced identical counts for the same words.

The results show that after some initial variability, the serial C++ implementation levels off at processing about 16 MB/second. The OpenCL implementation seems to reach its full potential starting around 4 MB, and thereafter hovers around 35 MB/second. This means that in larger texts, terms are counted a little more than twice as fast on GPUs as on CPUs.

While this speedup is significant, given the similarity of the two implementations, it is a little less than we may have expected after seeing the results from the Levenshtein distance calculations. Because the Levenshtein distances were calculated on the same hardware, the change in speed improvement is almost certainly due to the different nature of the two problems, and in particular to the different ways in which GPU memory is used. When calculating Levenshtein distances, each thread performed most of its work in its own section of the workspace. This allows for a better use of cache and is what AMD calls coalescing global memory access. When counting document terms, on the other hand, all threads will spend some time looking for the correct row in the global hash table, especially when the documents are large and the hash table becomes more populated with term counts.

In FY 2011, under sponsorship from DHS, we plan to mature and apply the capability we have developed, with a focus on state and local fusion-center applications.

Non-Refereed Publications and Presentations

Brannegan, D., "Argonne's Infrastructure Assurance Center: Overview and Partnership Opportunities," presented at the 2009 Research and Industrial Collaboration Conference, Boston, MA, October 28, 2009.

Molecular Characterization of Spore Coat Proteins

2010-093-N0

Daniel S. Schabacker and Apostolos C. Raptis

Project Description

There is a critical need for methodologies that generate a detailed signature of a biothreat agent (BTA). Genetic analysis alone cannot provide a full description of a BTA, including how the material was prepared, by whom, and the resources available to the operator. Obtaining useful information will require novel methods that provide a signature of the BTA that is highly sensitive and detailed enough for attribution. In some scenarios, the signature must be sufficiently reliable to withstand legal challenges in court. The proteome — which is the set of expressed proteins in a given type of cell or an organism — is the most appropriate source of molecular signatures. The goal of this project is to develop a novel forensic methodology specific to BTA attribution through proteomic signatures. Such signatures will provide detailed information regarding the methods used to culture, purify, and store the BTA. This methodology can help identify not only the specific organism used, but also the facilities used in its preparation and the technical sophistication of the operator. *Bacillus anthracis* spores, which cause anthrax, are the model organism for this research.

Mission Relevance

This project supports the national security mission of DOE to reduce the global danger from weapons of mass destruction by enhancing the capability to attribute a BTA to individuals or organizations. This approach is an innovative improvement on previous spore analytic methods because of its molecular separation and protein chip fabrication technologies and the manner in which they are integrated into a single system. The methodology is particularly well suited for security missions

because it combines sensitivity with a highly robust, semi-automated platform that does not require a specialized laboratory or expensive mass spectral analysis.

FY 2010 Results and Accomplishments

The initial year of this research focused on developing the methods required for generating robust proteomic signatures. The signatures must be reproducible because they will be the basis of a signature library used for competitive analyses. To this end, we are working with Dr. Adam Driks, an expert in *B. anthracis* at Loyola University Medical Center, in developing a standard operating procedure (SOP) for spore purification and protein extraction. During the initial work, we discovered that our system is able to discern even slight variations in sample preparation. Initial signatures of *B. anthracis* cultured in liquid or solid media, provided ample evidence that our methods are sound. As shown in Figure 1, liquid (a) versus solid (b) growth conditions result in grossly different proteomic signatures. To further elucidate differences in the proteins expressed — beyond protein expression — we used biochips to characterize the expressed proteins. For example, sugar-binding lectins were used to generate interactive signatures identifying variations in glycosylation of the proteins, thereby providing additional signatures supporting attribution.

Proposed Work for FY 2011

In FY 2011, the project will focus on generating *B. anthracis* spore proteome signatures to confirm that the sample preparation methodology is robust. We will also begin the task of populating the signature library for comparative analysis. Total protein signatures will be combined with interactive signatures, resulting in the most informative proteomic signature available. In addition, we will initiate the process of optimizing software and algorithms for automated comparative analysis.

Non-Refereed Publications and Presentations

Pravecek, T., D. Schabacker, and A. Driks, "Microbial Forensics and Signatures," presented at Air Mobility Command – Scott Air Force Base, IL, February 4, 2010.

Sagoff, J., "Tracking Down Terrorists with a Biochip," *Innovation, America's Journal of Technology Commercialization – The Best and the Brightest Innovators in the Energy Labs*, **8** (2) (2010).

Schabacker, D., "An Ultrahigh Resolution Method for Identification and Attribution in Microbial Forensics," presented at FBI Laboratory, Quantico, VA, Oct. 15, 2009.

Schabacker, D., "Method for Characterizing Protein Signatures in Food Technology," presented at National Center for Food Safety and Technology, Summit-Argo, IL, Nov. 6, 2009.

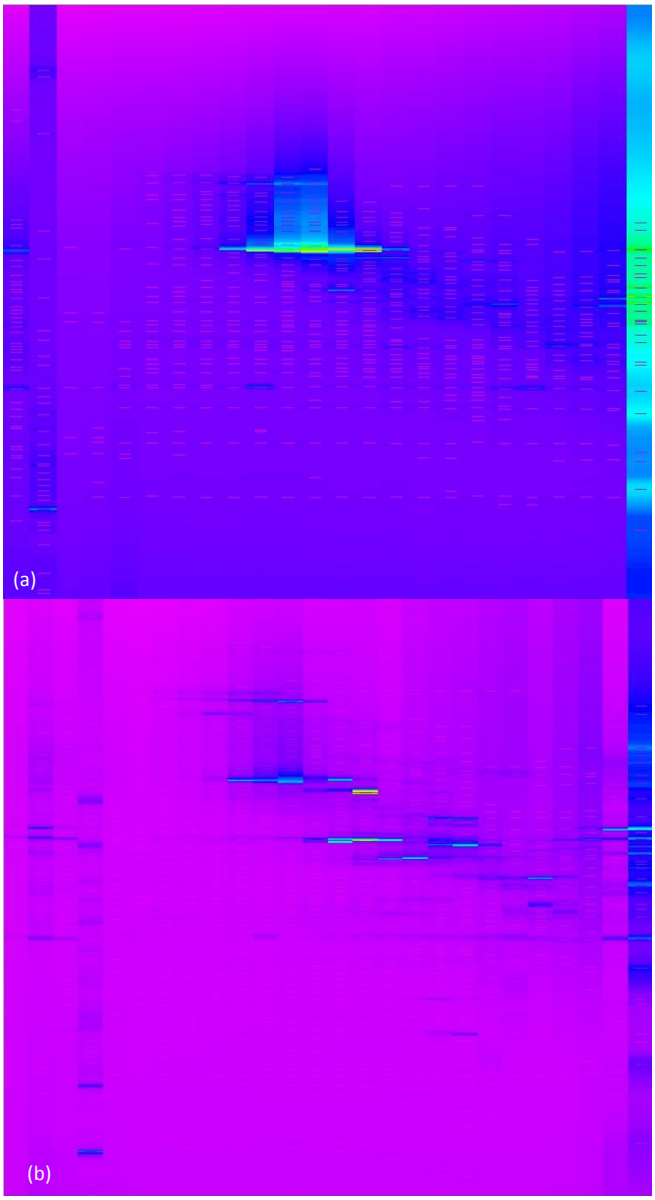


Figure 1. A protein expression heat map displaying all proteins expressed by an organism. A single strain of B. anthracis *was grown in (a) liquid culture medium or (b) solid culture medium. The heat map clearly indicates significant differences in protein expression when grown in liquid vs. solid media. This differentiation of growth conditions is not possible through standard strain identification using genetic analysis.*

Schabacker, D., and T. Pravecek, "Characterizing Biological Matrices through Proteomic Signatures," presented at Air Force Research Laboratory Command – Wright Patterson Air Force Base, Dayton, OH, May 13, 2010.

Multi-User Virtual Reality Environments for Emergency Response Planning and Training

2010-108-N0

David J. LePoire, Joseph J. Adduci, John J. Arnish, Thomas E. Baldwin, Bruce M. Biwer, David B. Chamberlain, Frederick A. Monette, Frank Moore, and Cory C. Weber

Project Description

Current tabletop and field-based exercises that address the ramifications of an improvised nuclear device (IND), radiological dispersion device (RDD), or accidental release event are inadequate in terms of simulated detector readings, radiation physics modeling, scenario planning, mobile team communications and actions, situational awareness, and temporal realism. Our project addresses this issue through the development of an online, multi-user, interactive virtual reality training simulator for weapons of mass destruction (WMD) scenarios. The simulator initially focused on IND and RDD scenarios by integrating current first-person video game technology and current radiological and nuclear models, equipment simulators, and incident management procedures. The final product will be an online virtual reality environment that enables controllers to develop scenarios and first responders to act out their roles in a virtual environment. For example, the controller could create a search environment in which a cesium 137 (Cs-137) source is hidden in a virtual cityscape. The scenario would begin when the first responders (e.g., DOE Radiological Assistance Program [RAP] team members) are deployed. The search team will have a view on the screen of all available RAP detection instruments and communication devices. Search team members will be able to communicate with the command staff as they would in real life. The command staff will direct the search teams based on the simulated radio communications and run the operation from anywhere in the world.

Mission Relevance

This system is relevant to DOE's national security mission. Current emergency preparedness training, based on periodic hands-on equipment training and exercises, leaves gaps because (1) cost prohibits routine training scenarios; (2) current technology limits field scenarios for instruments; and (3) the realism of team interaction, communications, and command participation is inadequate. Full-scale exercises attempt to address the last two issues but are expensive and limited to participation by only a small set of the potential responders. Tabletop exercises allow greater access at a lower cost but suffer from reduced realistic decision and logistical reality. A virtual-reality-based exercise area would allow for inexpensive, frequent opportunities to test the integration of instruments in a dynamic team environment, preparing emergency response personnel to respond more effectively in an actual IND, RDD, or accidental release event.

FY 2010 Results and Accomplishments

We identified a platform and development environment, the Unreal Engine, which is a widely used (including by the U.S. Army), easily accessible (free software development kit), community-supported (a library of objects and textures is easily imported), and well-documented (including video-based learning modules) environment.

In FY 2010, we developed and refined the simulation environment. The first demonstration included an artificial environment with a simple detector. Based on feedback from and the real-world experience of the project team, we refined the simulation environment to increase the realism of the following: setting (urban parking lot and garage), detector (spatially dependent background), responses, radiation behavior (explored many possible alternatives to effectively model shielding), and interaction (explored multiple players and roles). We also developed a simplified virtual laboratory setting to support initial training for the interaction of source, detector, and shielding.

We extended the demonstration capabilities of the simulation environment, acquiring a laptop to support quick and portable demonstrations and exploring the capability of audio integration through existing tools for the gaming community.

We followed the commercial development context for the Unreal Engine, which was freely released this year – allowing easier use for the project team and encouraging use in academic communities as a teaching platform. We also considered integrating objects from Google Earth and Virtual Philadelphia; a common framework, Collada, is being implemented to allow sharing of objects but full-city development like Virtual Philadelphia is still commercial.

We pursued contacts with the U.S. Department of Homeland Security (DHS) Domestic Nuclear Detection Office and Science and Technology Directorate (S&T) and the U.S. Department of Defense (DOD) Homeland Response Force (HRF), which expressed interest in the simulation system. We provided a hands-on demonstration to the Federal Air Marshals' Visual Intermodal Prevention and Response (VIPR) team that (1) showed the training capability of the tool for the end user; (2) demonstrated its potential use as refresher training to the VIPR team manager; and (2) described the potential cost savings associated with using the tool for training to the DHS session organizer. A fact sheet published on an Argonne Web site was quickly republished in a DHS newsletter, leading to requests for more information from DOD/HRF and DHS/S&T.

Proposed Work for FY 2011

In FY 2011, we will extend the multi-user team aspects of the simulation tool to include different roles and communication options. We will also extend the detector features to include neutron detection and interfaces similar to those of real detectors and communication devices and further develop the building shielding effects. At this stage, the tool will be ready for use in a set of demonstration exercises. The feedback from the exercises will help focus the project priorities for the third year, when advanced features – such as mobile search vehicles, plume dispersion of contamination, and options for conversion and incorporation of customized, three-dimensional environments – will be considered. These features would allow the tool to be used in a larger range of exercises. Each year, the deliverables will include the software and documents concerning its use, design, and example applications.

Detection of Low Copy Number of Pathogenic Microbes by Litmus Strip

2010-175-N0

Qiaoling Jin, Liaohai Chen, and Daniel S. Schabacker

Project Description

The development of a rapid and portable bioassay — one that can be deployed with the minimum engagement of sophisticated instruments and reagents, yet is sensitive enough for early detection of pathogenic microbes — presents a grand challenge, as such a device would assist in countering terrorism and preventing the spread of epidemic diseases. Although many of the commonly used approaches — including enzyme-linked immunosorbant assays (ELISAs) and polymerase chain reactions (PCRs) — have very high sensitivity and specificity, they require advanced instruments or multiple reagents, and thus these approaches are not suitable for field use or first responders. This project aims to develop a colorimetric assay with high sensitively for detecting pathogenic microbes by using simple visualization. The assay is based on an autocatalytic chemical system that yields a color change upon exposure to a low copy number of pathogenic microbes. Our goal is to develop a bioassay that is simple, highly sensitive, potentially highly selective, and suitable for incorporation into economical, portable sensors for on-site decision-making.

Mission Relevance

The proposed technology will enable detection of the presence of a wide range of biological agents in the field by use of simple visualization; thus, it is directly relevant to DOE's missions in national security and public safety (i.e., countering bioterrorism threats and responding to epidemics). We expect the technology will also have great impact in early stage disease diagnosis, as well as in basic biology and biomedical research.

FY 2010 Results and Accomplishments

In FY 2010, we focused on five main areas.

1. *Generating polymeric micelles with uniform size and higher loading capacity.* We were able to modify the protocols and optimize the conditions to synthesize stable polymeric micelles with uniform diameters of 23 nm for native polymeric micelles and 37 nm for loaded polymeric micelles. The dimension and morphology of the polymeric micelles were confirmed by light scattering, atomic force microscope, and transmission electron microscopy. The loading capacity of the polymeric micelles was proved by the releasing assays.

2. *Synthesizing target-specific polymeric micelles.* The synthesis of target-specific polymeric micelles was achieved by conjugating affinity reagents (we tested oligos, peptides, and antibodies) to the block copolymer with a carboxylic group attached to the polyethylene glycol terminal. The target specificity of the affinity reagent conjugated micelles was confirmed by ELISAs.

3. *Synthesizing the reactant of the autocatalytic acid-generation reaction — tert-butyl 2-methyl-2-(p-toluenesulfonyloxymethyl) acetoacetate.* The reactant was synthesized in three step reactions: (1) the mono-methylation of tert-butyl acetoacetate to form tert-butyl 2-methyl-3-ketobutanoate, (2) the hydroxymethylation step to generate tert-butyl 2-methyl-2-(hydroxymethyl)-3-ketobutanoate, and (3) the tosylation step with p-tuluenesulfonyl chloride to yield the final product. The overall yield is 22%, and the structure of the product was confirmed by nuclear magnetic resonance (NMR) spectroscopy.

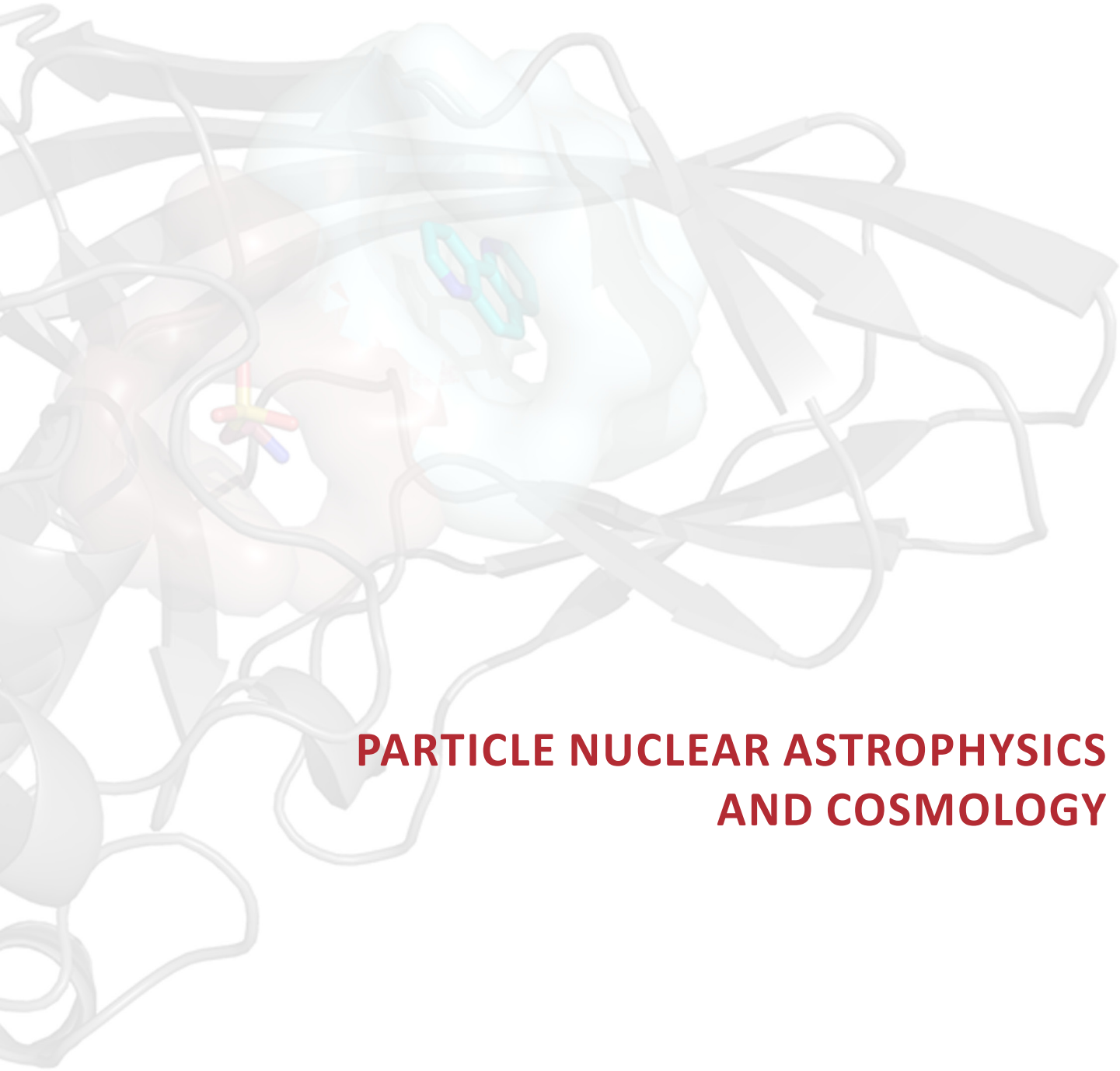
4. *Selecting initiators for autocatalytic acid-generation reactions.* In considering the feasibility of various candidate materials to be encapsulated within the polymeric micelles and to initiate autocatalytic acid-generation reactions, we evaluated five potential initiator candidates and identified dodecyl-p-toluenesulfonate, which is stable enough for the encapsulation reaction and can initiate the autocatalytic acid-generation reaction most efficiently.

5. *Encapsulating initiator molecules by polymeric micelles and characterizing the corresponding autocatalytic acid-generation reactions.* We demonstrated that tert-butyl 2-methyl-2-(p-toluene-sulfonyloxymethyl) acetoacetate underwent deprotection of the tert-butyl ester in the presence of dodecyl-p-toluenesulfonate, which was unloaded from the polymeric micelles. Followed by decarboxylation and the subsequent liberation of another sulfonic acid from the reaction, we observed an exponential increase in the concentration of sulfonic acid in solution. This acid amplification reaction was followed by use of NMR and monitoring the reduction in the proton signals of tert-butyl and β-methyl (δ = 1.28 ppm) and the increase of the proton signals from the vinyl group of unsaturated ketone (δ = 5.50 ppm). The formation of sulfonic acid is confirmed by proton concentration changes, which are measured by pH meter and visualized by pH indicators.

Proposed Work for FY 2011

In FY 2011, we will focus on the following activities:

- Optimizing conditions to enhance the efficiency of autocatalytic reactions, which will be initiated by the catalyst within the micelles.
- Developing and establishing a polymeric, micelle-based colorimetric assay to detect viral/phage particles and deoxyribonucleic acid/ribonucleic acid (DNA/RNA) molecules via visualization.
- Benchmarking the sensitivity and specificity against the Nucleic Acid Sequence-Based Amplification (NASBA) assay (the current state of the art).



PARTICLE NUCLEAR ASTROPHYSICS AND COSMOLOGY

Study of the Fundamental Properties of Buoyancy-Driven Turbulent Nuclear Burning in the Context of Type Ia Supernovae

2008-130-R2

Raymond A. Bair, Robert J. Latham, Ewing L. Lusk, Michael Papka, Katherine M. Riley, and James W. Truran

Project Description

This project optimized the FLASH astrophysics code to run efficiently on the Intrepid IBM Blue Gene/P computer and refined the parallel processing tools needed to analyze datasets from Blue Gene/P simulations, many of which are expected to exceed 100 terabytes. The capabilities produced by this project have the potential to produce a major paradigm shift in the understanding of SN Ia. It has already enabled astrophysics computations carried out as part of a series of groundbreaking simulations of the fundamental properties of buoyancy-driven turbulent nuclear burning in Type Ia supernovae (SN Ia).

Mission Relevance

The project is relevant to DOE's science mission. Observations using SN Ia as "standard candles" led to the discovery of "dark energy." Understanding dark energy is widely regarded as one of the most important challenges in the science of physics. The project is also relevant to the goals of DOE's Innovative and Novel Computational Impact on Theory and Experiment (INCITE) program.

FY 2010 Results and Accomplishments

SN Ia are powerful stellar explosions that are usually considered to be homogeneous. A proposed detonation mechanism is the gravitationally confined detonation (GCD) model, in which ash created during subsonic nuclear combustion ejects from a star, flows around the surface, and collides with itself at the opposite point of breakout, sparking a detonation (Figure 1). In FY 2009, our collaborators at the University of Chicago's FLASH Center used computer time allocations from the INCITE program to run more than 25 additional GCD models on Intrepid at Argonne. The models pushed the GCD model into regimes of extreme stellar pre-expansion and demonstrated that the model can produce a detonation in those regimes. This set of simulations revealed correlations within the GCD model that suggest the nature of the homogeneity of SN Ia.

High-resolution studies of how buoyancy instabilities enhance the surface and burning rate of thermonuclear flames were extended to a new regime in which the buoyancy-generated turbulence interacts strongly with the flame surface. The studies associated with this project have gone a long way to quantify the scale dependence of flame surface structure induced by buoyancy-generated turbulence.

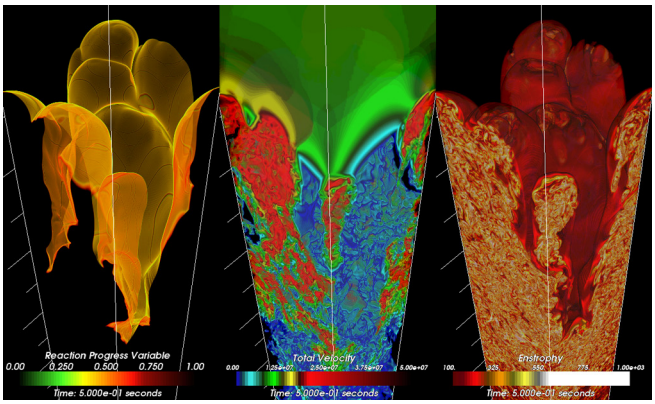


Figure 1. Buoyancy-driven turbulent nuclear combustion. The three frames show three ways to visualize the same snapshot of a simulation of a buoyancy-driven turbulent reactive flow; each is complementary to the rest yet distinctive. The left frame shows the flame surface, the middle shows the velocity field generated by the burning, and the right shows the enstrophy (or kinetic energy) generated by it. In this three-dimensional simulation, an initially planar flame surface perturbed with a multimode sinusoidal perturbation burns its way upward through a stratified medium under conditions characteristic of the degenerate material at the center of a near-Chandrasekhar mass C/O white dwarf star. Gravity is directed downward.

Some of the simulations had to be extended further than expected because the stochastic nature of the combustion is greater than suggested by the previous limited simulations carried out by other researchers. This situation was particularly true for slow flame speeds (which are the most interesting because the combustion is more turbulent). These simulations demonstrated that for the conditions investigated, the properties of buoyancy-driven turbulent combustion (including the burning rate) do not depend on whether the Gibson scale and somewhat larger scales are resolved; thus, it is not necessary to resolve the Gibson scale in order to calculate the burning rate. These results have profound implications for whole-star simulations of Type Ia supernova models, since they mean that accurate simulations of the deflagration phase in these models can be carried out at coarser resolutions than would otherwise be necessary.

Computations at unprecedented scales (like those in this project) often stress computer software and hardware in ways that reveal scaling issues. In FY 2010, we continued to eliminate input/output (I/O) bottlenecks and optimized several aspects of the FLASH code that were limiting scalability, as described below.

Input/Output performance optimizations. The I/O performance limitation was exposed when frequent outputs of small amounts of Lagrangian data became necessary. Using the previous I/O scheme, the amount of time taken increased

steadily as the number of processors increased, even though the volume of data did not change significantly. A detailed analysis of the I/O patterns identified the bottlenecks. In addition there was a metadata corruption issue related to the Message Passing Interface I/O (MPI-IO) library, which was revised to permit the use of collective operations in with the HDF5 file toolset. Another optimization was the identification and removal of a spurious restrict operation within FLASH's own I/O. All of these problems were resolved, and I/O was successfully scaled up to 64K cores. Figure 2 shows the results of the two major optimizations described above on the I/O performance.

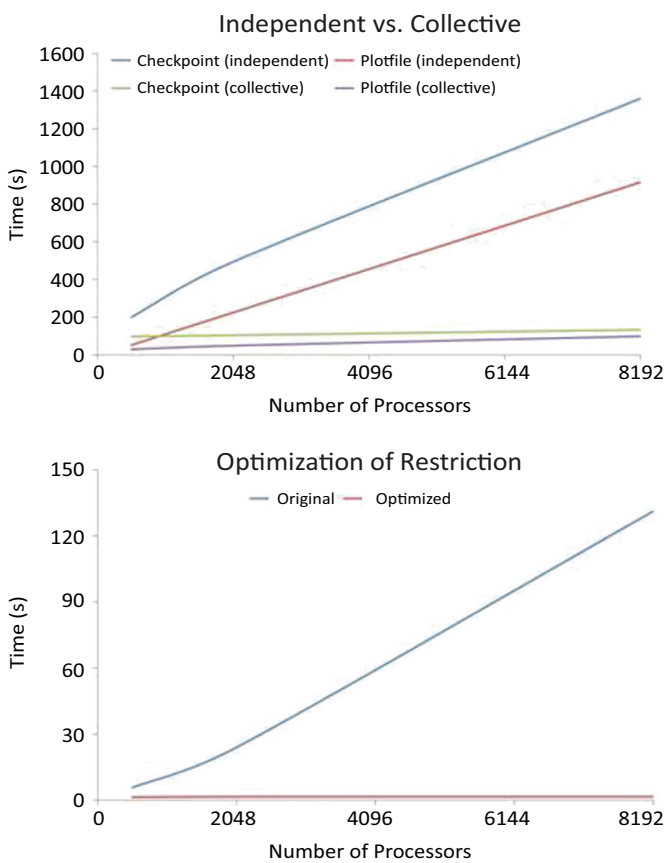


Figure 2. Results of I/O optimization. The top panel shows the effect of enabling collective operations, and the bottom shows the results of eliminating extra restriction operations.

Regridding optimization. Similar to I/O, with the increase in the size of the simulation required by the problems mentioned above (and therefore the number of processors), the scaling limitation in the PARAMESH regridding algorithm became visible. A clever modification to the method of accumulating metadata eliminated this scaling limitation, as shown in Figure 3, which has performance data collected from a science production run. It has two curves; both show the average time it takes to compute on one block per time step, which was obtained by dividing the evolution time by the number of steps computed and the average number of blocks per processor. The metric therefore includes all costs of computation, except initialization. The dotted curve shows weak scaling characteristics without optimizations, which demonstrated a clear upward trend. The optimized version resulted in the much flatter weak scaling, as shown by the solid line. Both curves used optimized I/O.

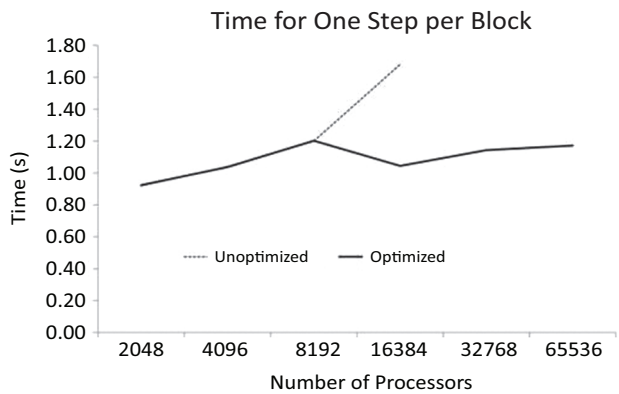


Figure 3. Per-block computation cost in a production run on the BG/P. The dotted line shows the cost before optimization, and the solid line shows the cost after.

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Dubey, A.C. Daley, G.C. Jordan, P. Rich, D.Q. Lamb, R. Latham, K.M. Riley, D. Townsley, and K. Weide, "Challenges of Computing with FLASH, a Highly Capable Multiphysics Multiscale AMR Code, on Leadership Class Machines," presented at ScicomP, San Francisco, CA, May 2010.

Dubey, A. C. Daley, K. Weide, and R. Latham, "FLASH's Answers to the Challenges of Computing on Largest HPC Platforms," presented at ICNAAM (International Conference of Numerical Analysis and Applied Mathematics), Rhodes, Greece, September 2010.

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Nuclear Astrophysics

2008-147-R2

James W. Truran, Roy J. Holt, Kenneth Nollett, Karl E. Rehm, Craig D. Roberts, and Guy Savard

Project Description

In this project, we pursue (1) the development of experimental techniques essential for determining a significantly more accurate rate for the critical $^{12}C(\alpha,\gamma)^{16}O$ reaction rate for astrophysical studies and (2) theoretical studies we believe essential to answer critical questions about stellar and supernova nucleosynthesis. Both a more accurate determination of the $^{12}C(\alpha,\gamma)^{16}O$ reaction rate and the identification of the nuclear processes in stellar and supernova environments that are responsible for the synthesis of the elements from iron to uranium are DOE nuclear physics milestones.

Mission Relevance

This project is relevant to DOE's missions in basic science. A more accurate determination of the rate of the $^{12}C(\alpha,\gamma)^{16}O$ reaction will represent a milestone in our investigations of the origin of the elements in extreme astrophysical environments. This reaction is one of the most important in nuclear astrophysics. It not only determines the relative abundance of carbon and oxygen (two elements crucial for life on earth), but it also determines the fate of a star at the end of its life (whether it becomes a neutron star or a black hole). Improving the accuracy of this reaction rate is also a DOE Nuclear Physics milestone. Our focus on the nucleosynthesis of nuclei through the actinide region is consistent with the stated goals of a recent National Research Council report that identified the question, "How were the heavy elements from iron to uranium made?" in astrophysical environments as one of the most important unanswered questions in physics. The development of a resource for exotic beam experiments is the U.S. nuclear physics community's highest priority for new construction related to basic science. The resource will enable the terrestrial measurement of reaction rates, masses, and lifetimes that are expected to play an important role in studies of the nuclear processes that provide the energetics of supernova and the associated synthesis of heavy elements. We will test and develop aspects of that theory and expand our expertise in techniques associated with large-scale numerical computation.

Results and Accomplishments

In 2010, we achieved substantial progress in our nuclear astrophysics efforts, going in new directions in experimental nuclear astrophysics and conducting significant studies in theoretical nuclear astrophysics. Our theoretical research focused on understanding the r-process mechanism of neutron capture synthesis of heavy elements, and our experimental research focused on the $^{12}C(\alpha,\gamma)^{16}O$ reaction.

Investigation of the $^{12}C(\alpha,\gamma)^{16}O$ reaction. As noted above, this reaction is one of the most important in nuclear astrophysics. It not only determines the relative abundance of carbon and oxygen (two elements crucial for life on earth), but it also determines the fate of a star at the end of its life (whether it becomes a neutron star or a black hole). Improving the accuracy of this reaction is also a DOE Nuclear Physics milestone. Because of the very small cross sections at astrophysical energies, all direct and surrogate measurements have reached the limits of their sensitivities, and new techniques need to be developed. After 40 years of laboratory experiments, the current uncertainty of this reaction is approximately 30%. The main reason is the small cross section of the $^{12}C(\alpha,\gamma)^{16}O$ reaction and the need to use very thin targets in terrestrial experiments, which result in typical count rates of 0.5 count/day. We developed a new technique that increases the count rate by a factor of at least 4,000. With detectors that use superheated liquids (i.e., bubble chambers), which are presently being developed at various laboratories for dark matter searches, we can study the time-inverse $^{16}O(\gamma,\alpha)^{12}C$ reaction. In the first year of the work, the theoretical backgrounds for operating a bubble chamber were developed, and the thermodynamic properties of possible liquids were evaluated. In the second year, a test chamber that operates with a refrigerant liquid was designed and fabricated, and the software needed to operate this chamber for nuclear astrophysics experiments was developed. After extensive tests with cosmic rays and neutron sources, the test chamber was shipped and installed at the world's most intense free electron laser, which operates at Duke University: High-Intensity Gamma-Ray Source (HIGS).

The first experiment was a proof-of-principle experiment to demonstrate the increased detection efficiency. As expected, the intensity of the incoming gamma-ray beam had to be reduced by a factor of 5,000. In the second step of the experiment, a well-known resonance in the $^{19}F(\gamma,\alpha)^{15}N$ reaction was measured. The measurements, which were carried out over two days, demonstrated the stability of the chamber (see Figures 1 and 2).

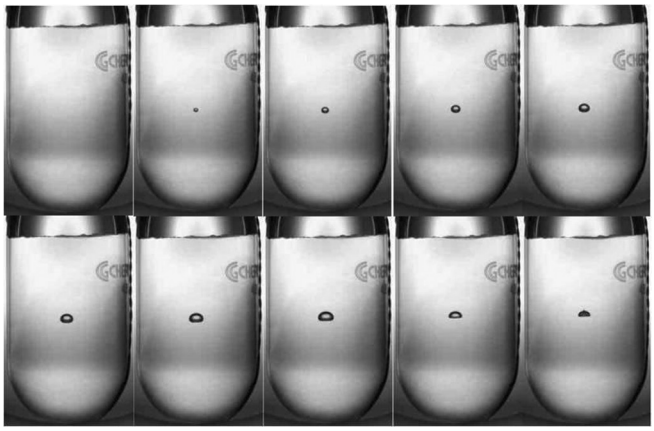

Figure 1. Series of pictures taken in 10-ms intervals showing the development of a bubble induced by the $^{19}F(\gamma,\alpha)^{15}N$ reaction (top pictures 1–5) and the subsequent quenching of the bubble through a fast increase in pressure (bottom pictures 6–10).

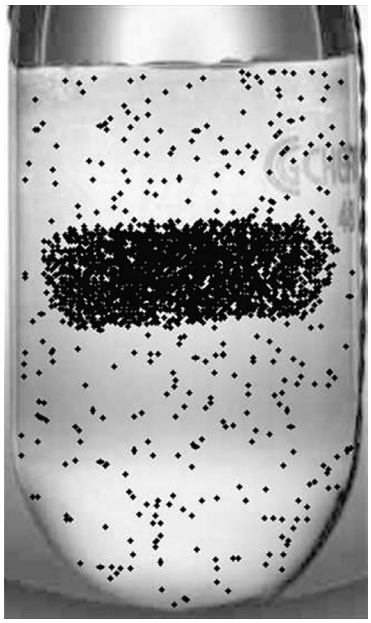

Figure 2. Events produced in the fiducial volume generated by the intersection of the gamma beam (diameter of about 12 mm) and the superheated liquid (contained in a glass cylinder with a 27-mm diameter) that had accumulated during one day of running at HIGS. The events outside the fiducial volume were generated by cosmic rays.

On the basis of these results, we designed and fabricated a new bubble chamber using enriched ^{16}O water. The chamber will be used in a first test of the $^{16}O(\gamma,\alpha)^{12}C$ reaction in the spring of 2011. The continuation of the $^{16}O(\gamma,\alpha)^{12}C$ work is supported by the DOE Office of Science, Nuclear Physics program. Another interesting effect discovered during the tests of the bubble chamber with cosmic rays was the high detection efficiency for neutrons. In some cases, we were able to detect neutrons generated at the ATLAS accelerator, which is more than 30 meters away. A position-sensitive neutron detector might find applications in several fields both inside and outside physics.

Nucleosynthesis of heavy elements. We also addressed a range of other challenging problems in nuclear astrophysics, including the (1) synthesis of the heaviest nuclei by neutron capture processes (the r-process) in explosive (e.g., Type II supernova) environments, with particular attention to the role of fission; (2) nature of the outbursts of classical novae and the composition of their ejecta; (3) production of iron peak nuclei (with nuclei of mass A = 56 being formed as ^{56}Ni) in supernovae and the powering of supernova light curves; and (4) evolution of the composition of our galaxy (and the universe itself) as revealed in studies of the oldest stars and the compositions of gas clouds at high redshifts. Emphasis was on the r-process, with interest in the site and character of this process. Theoretical calculations of the operation of the r-process of neutron capture synthesis in the "high entropy winds" of SNe II identified and constrained conditions that are required to reproduce the extraordinary robustness of the observed r-process abundance patterns in the most metal-deficient stars in our galaxy's halo. We and collaborators at the University of Chicago also investigated the "neutrino-p" process, in which outgoing neutrinos interacting with proton-rich nuclei have been shown to produce abundance levels of nuclei through the strontium-yttrium-zirconium regime that are comparable to those observed in metal-deficient galactic halo stars. One of us (Truran) is also collaborating with Chicago Flash Center researchers in the nucleosynthesis "post-processing" of temperature/density trajectories recovered from hydrodynamic models of SNe Ia in order to provide more accurate determinations of the composition of the ejecta and to identify the expected range of peak SNe Ia brightness resulting from our models.

Aspects of this research will continue under the NSF Physics Frontiers Grant "Joint Institute for Nuclear Astrophysics" (JINA) at the University of Chicago.

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Very High Energy Gamma-Rays: Present and Future

2008-159-R2

Karen Byrum, John T. Anderson, Gary R. Drake, Victor Guarino, Andrew S. Kreps, Andrew W. Smith, and Robert G. Wagner

Project Description

This project is focused on two goals. The first is to search for the dark matter particle via possible decay modes involving very high energy (VHE) gamma rays. Gamma rays produced in the decays of galactic halo concentrations of weakly interacting massive dark matter particles (WIMPs) can possibly be detected by observations of Imaging Atmospheric Cherenkov Telescope arrays (IACTs, e.g., the Very Energetic Radiation Imaging Telescope Array System [VERITAS]). The second goal is research and development (R&D) aimed at a next-generation gamma-ray telescope array that achieves sensitivity levels that are an order of magnitude better than current instruments, while also operating at an energy threshold in the 20–50-GeV range, compared to the current typical value of 100 GeV. Telescope R&D has been pursued through the design and fabrication of a very fast pattern-recognition trigger and through the mechanical design of a conventional Davies-Cotton (DC) and a novel Schwarzschild-Couder (SC) telescope structure.

Mission Relevance

This project supports DOE's science mission through its High Energy Physics Program in non-accelerator-based physics at the cosmic frontier. Specifically, the project uses the detection of VHE gamma rays from astrophysical sources to explore particle and astroparticle physics in searching for the mysterious component of matter that constitutes nearly 25% of the energy density of our universe (i.e., dark matter). This project is also developing cutting-edge technology to advance the sensitivity of the telescope arrays used to perform gamma-ray astrophysics. In addition, the project fosters the development of scientific and technical expertise in applying the technology to both gamma-ray astrophysics and, in the case of the pattern-recognition trigger, to accelerator-based particle physics.

FY 2010 Results and Accomplishments

Part 1: Analysis of VHE Gamma-Rays. VERITAS data were analyzed for four low-surface brightness dwarf spheroidal galaxies: Ursa Minor, Draco, Boötes 1, and Willman. VERITAS was able to set the best limits on WIMP dark matter from indirect searches with these data.

Part 2: Fast Pattern-Recognition Trigger. We continued development of our preliminary trigger system, implementing firmware changes to the Xilinx Vertex 5 field-programmable gate array to achieve better than 3-nanosecond pixel-to-pixel timing alignment in our test stand. Our trigger scheme was selected for a VERITAS Level 2 trigger upgrade, and we received funding in June 2010 to build and implement a new Level 2 trigger at VERITAS on the basis of the enabling work from this project. Upon successful implementation of our new Level 2 trigger, we plan to propose to DOE that we implement the Level 4 topological implementation defined in this work.

Part 3: Future Telescope Design. During the past two years, our role in mechanical telescope design has been substantially expanded in two projects under consideration for a next-generation, ground-based gamma-ray experiment: (1) the Atmospheric Gamma-Ray Imaging System (AGIS) and (2) the Cherenkov Telescope Array (CTA). Figure 1 shows a 12-m telescope, the mechanical design of which is being developed by three national laboratories in three countries: Argonne in the United States, DESY in Germany, and Saclay in France. The group plans to fabricate a telescope based on this design by using DESY funds starting early in the calendar year of 2011. We designed the dish and counterweight structure and are responsible for the overall structural analysis of the complete system.

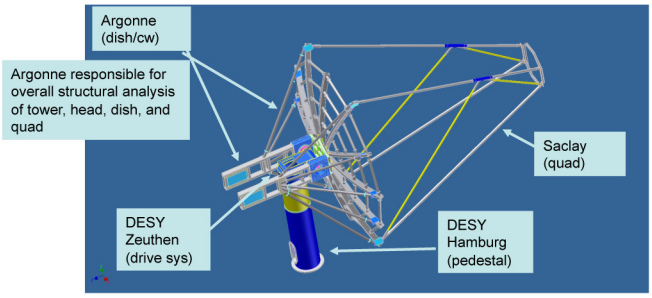

Figure 1. The current design of a 12-meter Davies Cotton Telescope. This design is a joint effort between three national laboratories in three countries. Argonne in the United States designed the dish and counterweight structure; Sacaly in France designed the quadruped structure; DESY in Zeuthen designed the drive system; and DESY in Hamburg designed the tower/pedestal. Argonne is also responsible for the overall structural analysis of the complete system. This design is currently the baseline for the future Cherenkov Telescope Array (CTA) experiment.

Non-Refereed Publications and Presentations

Acciari, V.A., T. Arlen, T. Aune, M. Beilicke, W. Benbow, D. Boltuch, S.M. Bradbury, J.H. Buckley, V. Bugaev, K. Byrum, A. Cannon, A. Cesarini, J.L. Christiansen, L. Ciupik, W. Cui, R. Dickherber, C. Duke, J.P. Finley, G. Finnegan, A. Furniss, N. Galante, S. Godambe, J. Grube, R. Guenette, G. Gyuk, D. Hanna, J. Holder, C.M. Hui, T.B. Humensky, A. Imran, P. Kaaret, N. Karlsson, M. Kertzman, D. Kieda, A. Konopelko, H. Krawczynski, F. Krennrich, G. Maier, S. McArthur, A. McCann, M. McCutcheon, P. Moriarty, R.A. Ong, A.N. Otte, D. Pandel, J.S. Perkins, M. Pohl, J. Quinn, K. Ragan, L.C. Reyes, P.T. Reynolds, E. Roache, H.J. Rose, M. Schroedter, G.H. Sembroski, G. Demet Senturk, A.W. Smith, D. Steele, S.P. Swordy, G. Tešić, M. Theiling, S. Thibadeau, A. Varlotta, V.V. Vassiliev, S. Vincent, R.G. Wagner, S.P. Wakely, J.E. Ward, T.C. Weekes, A. Weinstein, T. Weisgarber, D.A. Williams, S. Wissel, and B. Zitzer, "VERITAS Search for VHE Gamma-ray Emission from Dwarf Spheroidal Galaxies," *Astrophysical Journal* **720**(2) (2010), 1174–1180.

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Solar and Astrophysical MHD

2008-188-R2

Paul F. Fischer, Fausto Cattaneo, and Aleksandr Obabko

Project Description

The purpose of this project is to investigate some basic properties of astrophysical and solar magnetohydrodynamics (MHD) by using petascale platforms. The work involves both theoretical and computational components, with the former providing guidance in identifying problems that will elucidate the essential mechanisms of observable MHD phenomena, such as the solar dynamo.

Mission Relevance

The project is tied to the DOE's mission in basic science. The solar dynamo is still poorly understood. It is, however, a central driver for many observable phenomena that affect life on earth, including the sun spot cycle and the formation of coronal ejections. In addition to solar/stellar dynamos, MHD is believed to play a critical role in the generation of some of the most energetic phenomena in the universe, such as the energy releases from the in-fall of matter onto compact objects such as black holes. Current theories for the phenomenal rate of energy release center on the magneto-rotational instability (MRI) providing the trigger to destabilize what would otherwise be a stable orbit of matter around these objects. In addition to these astrophysical phenomena, MHD is also of relevance to terrestrial physics. Liquid metal film cooling has been proposed for targets in high-energy accelerators and as the first wall for tokamaks (a device using a magnetic field to confine a plasma in the shape of a torus [donut]).

FY 2010 Results and Accomplishments

In the past year, we identified some of the outstanding challenges in shearing-box computations, which are commonly used to investigate the small-scale turbulence central to MRIs and self-sustained dynamos. In particular, we showed that the aspect ratio of the computational domain can have a profound effect on the degree of intermittency in angular momentum transport. For unit-aspect ratio domains, our computations showed strong intermittency, as found in previous studies. However, in boxes with larger aspect ratios, the intermittent behavior disappears and angular momentum transport is inhibited. The results of this study call into question the viability of the shearing box as a surrogate for a global model of magneto-rotational turbulence simulations in astrophysical settings.

In addition to the question of intermittency, we used our large-scale simulation results to investigate fundamental scaling laws in MHD turbulence. The exact analytic relations of Politano and Pouquet are often invoked to suggest that the spectrum of MHD turbulence follows the −5/3 Kolmogorov scaling. Recent observations and high-resolution numerical simulations, however, indicated a −3/2 spectrum. These observations can be reconciled with the Politano-Pouqet relationship if one accounts for scale-dependent dynamic alignment between the velocity and magnetic fields. Using our large-scale MHD turbulence data (computed on the Argonne Leadership Computing Facility [ALCF]), we were able to qualitatively demonstrate the correctness of this interpretation, which lends further insight into the properties of MHD turbulence, including the case of imbalanced MHD turbulence.

We also continued our development of our macro-scale MHD code (in the context of the Argonne hydrodynamics code, Nek5000), which will allow us to simulate global instabilities in spherical shells. We identified a roadmap for development of a new MHD formulation for Nek5000 that will accommodate general boundary conditions for the magnetic field. Specifically, this new formulation allows imposition of "far-field" boundary conditions that are more realistic than the standard Neumann or Dirichlet types that were supported in the past. As the first step in this roadmap, we are on track to finish the implementation of a decoupled version of standard magnetic boundary conditions in which the type of boundary conditions on the magnetic field is independent of the type of velocity boundary condition. The new MHD formulation will be validated and tested at scale on the ALCF BG/P system by using time provided under the Nek5000 project.

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Mignone, A, A. Ferrari, G. Bodo, P. Rossi, and F. Cattaneo, "Aspect Ratio Dependence in Magnetorotational Instability Shearing Box Simulations" in *Protostellar Jets in Context*, Berlin, 2009, pp. 77–82

Non-Refereed Publications and Presentations

Fischer, P., "Scaling the Spectral Element Method to One Million Processors," presented at, ICOSAHOM 09 (International Conference on Spectral and High Order Methods 09), Trondheim, Norway, June 22–26, 2009.

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Explosive Nucleosynthesis of Heavy Elements

2009-035-R1

James W. Truran and Craig D. Roberts

Project Description

The focus of this research in theoretical nuclear astrophysics concerns (1) the mechanisms of heavy-element synthesis in the iron-to-uranium range (iron-peak nuclei and r-process heavies), (2) the natures of the explosive stellar environments (supernovae and novae) in which nucleosynthesis occurs, (3) the impact of the nuclear energetics on the explosive events (classical novae and Type Ia supernovae [SNe Ia]), and (4) the resulting histories of the compositions of galaxies (chemical evolution). Spectroscopic analyses are placing increasingly stringent constraints upon the possible sites of production of heavy nuclei, from the iron-peak region synthesized in supernovae of both Type Ia and Type II to the heaviest nuclei formed by neutron-capture processes both in red-giant stars and in supernovae of Type II (SNe II) (the r-process). We have performed nucleosynthesis calculations appropriate to diverse astrophysical environments and thereby tested stellar and supernova model predictions and significantly constrained the nature of the earliest stellar populations in the Universe. We have used the best-available nuclear-physics input to constrain the equation of state for dense matter and explore its consequences. The project has yielded both nuclear-theory inputs for specific astrophysical problems and refined theoretical methods that will be of use far into the future.

Mission Relevance

This project is relevant to DOE's mission in science. We have tested and will develop and test aspects of theory and expand expertise in techniques of large-scale numerical computation. Strong motivation for an expanded level of activity in nuclear astrophysics and nucleosynthesis is provided by the NAS (National Academy of Sciences) report "Connecting Quarks to the Cosmos," which identified *How were the heavy elements from iron to uranium made?* as one of the outstanding physics challenges for the new century [DOE Nuclear Astrophysics Milestone NA7]. We also note that our studies of SNe Ia can be expected to impact the reliability of their use as distance indicators and probes of dark energy [DOE Nuclear Astrophysics Milestone NA3]. These efforts can have a major impact on national and international programs.

FY 2010 Results and Accomplishments

The project has achieved significant progress in several areas: thermonuclear (Type Ia) supernovae, core collapse (Type II) supernovae, classical novae, and equations of state.

Thermonuclear supernovae. The early emphasis of research was on modeling the outbursts of SNe Ia. The significance of these events arises from their brightness at maximum enabling their use as distance indicators, tied to the powering of their light curves by the production and subsequent decay of ^{56}Ni and the concomitant production of iron-peak elements. The currently favored interpretation of SNe Ia is the disruption of a near-Chandrasekhar-mass carbon/oxygen white dwarf by a thermonuclear runaway. We and researchers at the University of Chicago Center for Astrophysical Thermonuclear Flashes have realized significant progress in our understanding of flame propagation in the deflagration phase of SNe Ia . While there continue to be significant uncertainties with respect to the nature of the progenitor systems and the explosion mechanism itself, the 3D whole-star simulations performed thus far have taught us much about these "thermonuclear supernova" events. In the context of the gravitationally confined detonation (GCD) model discovered by Flash Center scientists, a slightly off-center ignition point burns, expands, rises rapidly due to buoyancy; breaks through and spreads around the stellar surface; and collides with itself. The inward-directed jet-like flow may effect a detonation. The generally spherical structure of the observed shells of SNe Ia strongly suggests that detonation by some mechanism is demanded, and we are encouraged by the fact that such detonation is a forced consequence of the GCD model.

We are continuing to study this problem in an attempt to identify the physics of the constrained range of ignition conditions that can naturally explain the distribution of peak luminosities of observed SNe Ia events. We are also working with Flash Center researchers in the nucleosynthesis "post-processing" of the temperature/density trajectories recovered from hydrodynamic models of SNe Ia in order to provide more accurate determinations of the composition of the ejecta and to identify the expected range of peak SNe Ia brightness

resulting from our models. (We note here that the peak SNe Ia brightness is directly proportional to the mass of ^{56}Ni ejected.)

Type-Ia simulations by groups worldwide will benefit from the in-depth study of energetics made possible by our involvement. We collaborated with the supernova group at The Hebrew University, Jerusalem, in studies of possible signatures of helium detonations in systems in which helium accretion onto C/O white dwarfs may provide progenitors of Type Ia supernova-like systems. We addressed the issue of how outward mixing (dredge-up) of carbon from the underlying C/O degenerate core can impact the nuclear evolution of the accreted shell, the mass of ^{56}Ni produced, and the brightness of the supernova at maximum.

Heavy-element nucleosynthesis in SNe II. Our research also addressed questions associated with the production of the heaviest elements (through the actinides) via neutron-capture reactions, of explosive nucleosynthesis of elements in nova explosions, and of explosive nucleosynthesis of iron-peak nuclei in supernovae. We undertook a detailed investigation of the nucleosynthesis processes that are understood to be responsible for the origin of the heavy elements. Since the synthesis of elements from iron to uranium occurs under explosive conditions in supernova events, and predictions of the composition of matter ejected in supernovae provide important clues to and constraints upon supernova models, our studies were closely tied to progress in research concerning SNe Ia and SNe II. Theoretical calculations of the operation of the r-process of neutron capture synthesis in the "high-entropy winds" of SNe II identified and constrained conditions that are required to reproduce the extraordinary robustness of the observed r-process abundance patterns in the most metal-deficient stars in our galaxy's halo. We and colleagues at the University of Chicago also investigated the "neutrino-p process," in which outgoing neutrinos interacting with proton-rich nuclei were shown to produce abundant levels of nuclei through the strontium-yttrium-zirconium regime that are comparable to those observed in metal-deficient galactic-halo stars.

Classical novae. Classical nova explosions are a consequence of thermonuclear runaways in accreted hydrogen shells on white dwarfs in binary systems, while the significantly more violent behaviors characteristic of x-ray bursts result from accretion onto neutron stars. We explored the behaviors of nova runaways resulting from matter accretion at low rates onto massive white dwarfs of low central temperatures. The high temperatures (greater than ~400 million K) achieved under these conditions can drive "breakout" from the conventional carbon-nitrogen-oxygen (CNO) hydrogen-burning cycles and result in the production of nuclear species through iron. Spectroscopic studies of nova ejecta can then in principle be used to impose constraints on numerical simulations of nova events. We conducted sensitivity tests that confirm a strong dependence on the rate of the ^{15}O(α,γ)^{19}Ne reaction. This motivated us to consider whether a significantly improved experimental determination of this rate is feasible by using the CARIBU facility at Argonne. This effort can contribute to our progress in improving experimentally our knowledge of critical reaction rates and to better simulating the history of the composition of the crusts of accreting neutron stars. We also continued our multidimensional studies of the final stages of evolution of classical novae to thermonuclear runaway. The composition of nova ejecta (nebular shells) predicted by these hydrodynamic studies, when compared with observations, impose important constraints on nova models.

Proposed Work for FY 2011

We will continue to seek a comprehensive picture of the history of nucleosynthesis in supernovae and of nuclear energetics and the associated nucleosynthesis history of matter in galaxies, dominated by input from supernovae of both Type Ia and Type II. This knowledge will be used to address broader questions, such as the observed trends in galactic enrichment in heavy elements as reflected in the abundance histories of galaxies. Our immediate emphasis will be on constraining models for SNe Ia and understanding their luminosity histories and on identifying the site of r-process neutron-capture synthesis in the early Galaxy. These results will also serve both to identify critical nuclear parameters to be determined with future nuclear experiments and to better constrain stellar evolution and supernova models. We will continue working toward an equation of state appropriate for compact astrophysical objects and the identification of unambiguous signatures of quark matter in their cores.

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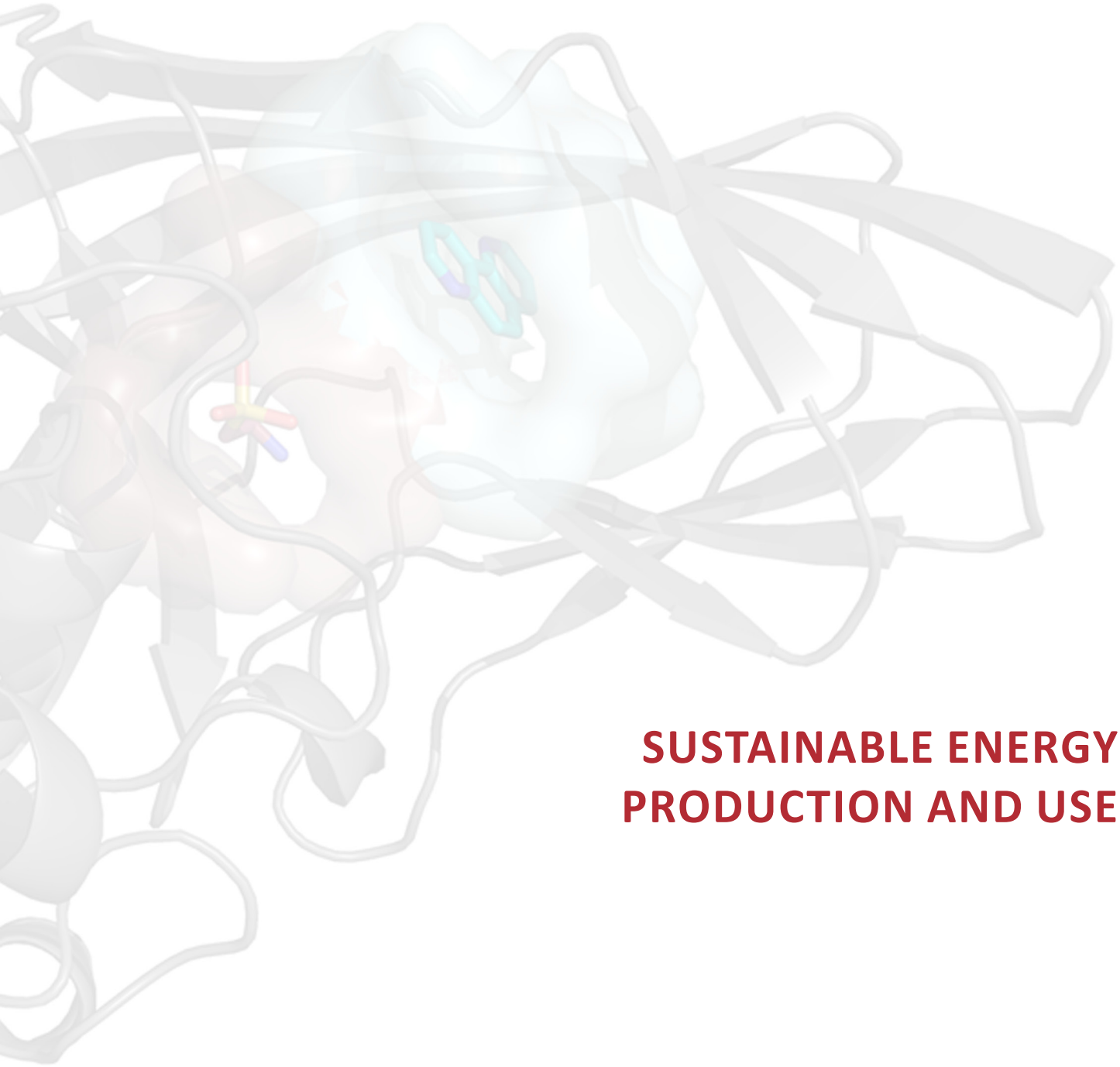

SUSTAINABLE ENERGY PRODUCTION AND USE

Innovations in Advanced Simulation and Experimental Code Validation for Nuclear Energy Applications

2008-118-R2

William D. Pointer, Paul F. Fischer, Stephen W. Lomperski, Elia Merzari, and Aleksandr Obabko

Project Description

In response to goals outlined by the U.S. Department of Energy's Generation IV Nuclear Energy Systems program, an effort is under way to develop an integrated multi-physics, multi-resolution thermal-hydraulic simulation-tool package for the evaluation of nuclear power plant design and safety. As part of this effort, initial guidance has been proposed for the development of experiments to supply validation data sets for the computational fluid dynamics (CFD) -based thermo-fluid simulation capability. Validation is viewed as necessary if the simulation tools are to gain widespread acceptance in both licensing and design activities. The data required for such validation differ, however, from the data used to benchmark traditional systems codes. It remains to be seen whether fluid-dynamics instrumentation and measurement techniques have progressed sufficiently to provide the types of data sets needed for acceptable validation of the envisioned CFD tools. With this in mind, a fluid-dynamics experiment has been developed to demonstrate that contemporary measurement methods are indeed able to validate these new tools and to provide a number of data sets to contribute to the ongoing task of developing CFD simulations. The experiment focuses on a class of turbulent mixing phenomena that occur in the outlet plenums of both sodium- and gas-cooled reactors. The analysis work accompanying the experiment includes refining data reduction and comparison methods suitable for very large data sets.

Mission Relevance

Argonne's recognized expertise in thermo-fluids science (both experimental and computational) and in reactor design are key elements in enabling the development of a high-resolution integrated multi-physics reactor-simulation tool set for the prediction of reactor performance and safety. High-fidelity science-based tools will enable renewed efforts to develop more efficient and economical reactor designs without compromising safety or reliability and thus will strongly contribute to DOE's energy mission.

FY 2010 Results and Accomplishments

In FY 2008, we selected parallel jet mixing in the reactor outlet plenum as the initial focus, designed an air-based parallel jet-mixing apparatus, and initiated procurement of the critical state-of-the-art velocity- and temperature-measurement instrumentation. Also in the first year, two CFD codes, STAR-CD and NEK5000 (an in-house Argonne code), were configured to simulate the mixing phenomena and used to perform pre-experiment simulations that helped guide the development of the apparatus. Argonne received a DOE competitive Innovative and Novel Computational Impact on Theory and Experiment (INCITE) grant to use Argonne's BlueGene/P computer for these studies.

In FY 2009, a parallel jet-mixing experiment was constructed and experiment checkout and tune-up were initiated. Also, a series of simulations with STAR-CD and NEK5000 were performed to explore the influence of various parameters on jet behavior and to compare features of both codes.

In FY 2010, instrumentation applicability was confirmed, with particular focus on the demonstration of the ability to acquire relevant time-resolved velocity fields using intensified particle-image velocimetry and temperature fields using infrared thermography. Initial time-averaged velocity fields (Figure 1) and time-averaged temperature fields (Figure 2), as well as RMS data describing local fluctuations in the measurements, were measured in the test section under selected flow conditions. Comparisons of these data with predictions from the RANS- (Reynolds-averaged Navier–Stokes) and LES- (large-eddy simulation) based simulations show that fluid-dynamics characteristics are generally captured by the simulation tools for the nominal configuration but that more complex representations of the conjugate heat transfer through the solids in the system may be needed to enable useful comparisons to measured temperature data.

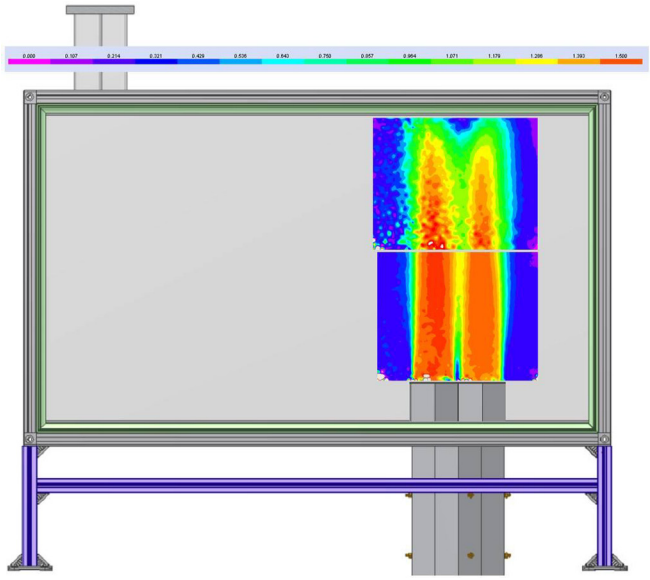

Figure 1. Vertical velocity contours measured via intensified time-resolved particle-image velocimetry at the center-plane of the MAX thermal-mixing experiment for isothermal flow at room temperature and 893 liters/minute per channel. Image shows position of measurement within test section.

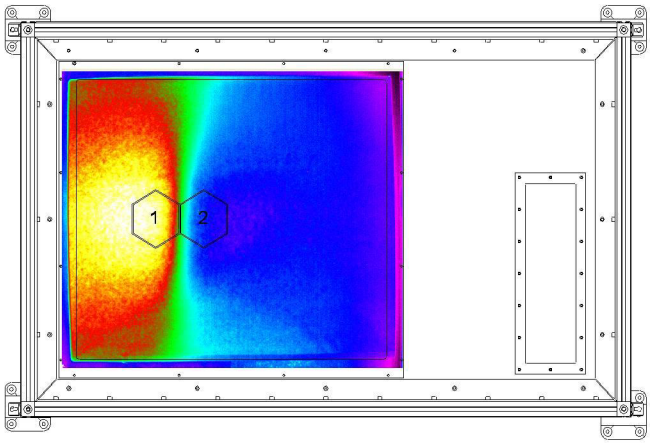

Figure 2. Temperature contours measured via time-resolved infrared thermography across the MAX thermal-mixing experiment's thermal window for 893 liters/minute per channel and with the bulk temperature of jet 1 raised to 10°C above the bulk temperature of jet 2. Image shows position of thermal screen on upper surface of test section.

In FY 2011, work will continue under support from the Nuclear Energy Advanced Modeling and Simulation program of the U.S. Department of Energy, Office of Nuclear Energy, Advanced Modeling and Simulation Office. We will begin to collect initial data sets under high-priority conditions in the test matrix and begin the task of quantifying uncertainty in system measurements and simulation predictions under those conditions.

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Characterization of Ignition, Combustion, and Emissions for Advanced Engines and Fuels

2008-121-R2

Stephen T. Pratt and R. Raj Sekar

Project Description

The ultimate goal of this project is to develop a fundamental understanding of, and predictive models for, the combustion of petroleum-based and alternative fuels. To address this grand challenge, we are drawing upon Argonne's acknowledged expertise in the Energy Systems (ES) and Chemical Sciences and Engineering (CSE) Divisions to assemble a vertically integrated team of researchers spanning disciplines from fundamental combustion chemistry to applied engines and emissions research. In this project, we develop mechanisms and models for novel ignition schemes in several advanced engine/fuel combinations, as well as investigate some aspects of particulate formation in the combustion of these fuels. Fundamental knowledge of chemical ignition mechanisms is vital for optimizing the efficiency and pollutant emissions in these systems. The approach combines experimental studies of the kinetics of fundamental reactions, theoretical studies of these reactions, the development of chemical mechanisms and models for the ignition processes, and direct experimental testing of the models by using the ES Division's Rapid Compression Machine (RCM) and test engines.

Mission Relevance

This research program is providing solutions to specific issues related to the performance of advanced engines and alternative fuels. Improvements in both engine efficiency and emissions are expected. As a result, this project has direct relevance to DOE missions of providing energy security while minimizing environmental impacts. This research is also expected to be of substantial benefit to both stationary and transportation engine manufacturers, such as Caterpillar, Cummins, and Waukesha, as well as potential producers of biofuels, such as Archer Daniels Midland and Cargill.

FY 2010 Results and Accomplishments

A number of new shock-tube studies were performed to characterize reactions relevant to ignition processes in advanced engines. First, the study of the reactions of OH and selected alkanes was completed. This work identified differences in OH reactivity for various types of primary, secondary, and tertiary CH bonds in alkanes. This information allowed the development of expressions, based on experimental measurements that can be used to estimate rate constants for any linear alkane up to C_{16}. These new rate constants have already been incorporated in chemical kinetic models being developed at the University of Galway and Lawrence Livermore National Laboratory. Second, the new roaming-radical mechanism that was first identified in photo-initiated experiments was observed in a thermal decomposition process for the first time. This work involved the decomposition of acetaldehyde, but it has now been extended to a number of other combustion intermediates and fuels. This new mechanism may have important implications in the high-temperature oxidation of fuels.

Shock-tube studies have also been performed on a number of oxygenated species relevant to the combustion of alternative fuels. Shock-tube studies of the pyrolysis of 1,4-dioxane have yielded information about the dissociation of cyclic ethers.

This work shows that, at least for some ethers, large quantities of OH and H are generated early in the reaction. The rapid production of these radicals could reduce ignition delay times by promoting chain reaction. Pyrolysis studies of ethylene glycol vinyl ether (EGVE) were also performed. EGVE is a major primary product of the decomposition of 1,4-dioxane, and its decomposition is the major source of OH radicals. This work will be extended to the study of the CH_2CH_2OH and vinoxy radicals.

A significant effort was made in upgrading the RCM and addressing several issues with the apparatus, including leaky seals, corrosion of the pistons, and the difficulty of introducing liquid fuels. The RCM is now operational, and a number of studies of gaseous fuels were performed. Adaptations for liquid fuels are currently being developed. The rapid-sampling valve, which will be used to extract stable species from the reaction vessel, is nearly complete and will likely be incorporated into the RCM in the near future. This work will continue with new funding from the Energy Efficiency and Renewable Energy (EERE) Vehicle Technologies Program.

In addition, one of the goals of this project was to develop combustion modeling capabilities, and we are well on our way toward achieving that goal with the new program support. Thus, even though FY 2010 was the final year of this project, two sources of ongoing funding have been secured, either completely or in part, as a result of this work. First, a new program has been established, supported by DOE's Basic Energy Sciences (BES) Chemical Sciences Division, for the study of high-pressure combustion chemistry. This project is a joint effort with the Combustion Research Facility at the Sandia National Laboratories. Second (as mentioned above), a new program has been established under the DOE EERE Vehicle Technologies Program for the continued improvement of the RCM.

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Integrating Radiatively Important Aerosols into a New Argonne Socioeconomic/Global Change Modeling Framework

2008-135-R2

David G. Streets, Ian T. Foster, Robert L. Jacob, Veerabhadra R. Kotamarthi, and Fang Yan

Project Description

The objective of this project is to develop and implement aerosol analytical capability and integrate it into the Argonne Socio-Economic-Environmental (SEE) model being developed under a related project, 2008-160-R2, "End-to-End Biofuels Analysis: Building Capability in HPC Socio-Economic-Environmental Modeling." Tasks include assembling the capability to forecast future aerosol emissions, integrating radiative forcing estimates of aerosols, and assessing mitigation opportunities (such as modern biofuels). This task will be performed in connection with project 2008-160-R2 related to ultra-high resolution integration of the Community Climate System Model on the BlueGene/P computer platform. We acknowledge the contribution of Professor Tami Bond of the University of Illinois.

Mission Relevance

Modeling, quantifying, and evaluating fundamental aerosol-related processes have been identified to be of the highest priority by the U.S. Climate Change Program. This objective has been taken up by DOE's Office of Biological and Environmental Research. As Argonne develops a world-class capability to model the interactions between human activities and the global climate, it is essential that aerosols be integrated in an effective way. This project will also provide data to verify observations from a new generation of National Aeronautics and Space Administration (NASA) satellites.

FY 2010 Results and Accomplishments

In the last year of the project, we finished developing the aerosol model for on-road vehicles, work that included an assessment of the model sensitivities and a Monte Carlo uncertainty analysis. We used the Speciated Pollutant Emissions Wizard (SPEW) model to project aerosol emissions in future years. SPEW provides flexibility and transparency in producing global inventories. It tabulates values of emission characteristics from the literature (including particulate matter [PM] emission factors and black carbon [BC] and organic carbon [OC] fractions) keyed to a fuel/technology combination. Forecasts to the year 2050 were developed for four future pathways of human development (the so-called marker scenarios of the Intergovernmental Panel on Climate Change), and these results were used as a test-bed for developing the generic aerosol predictive module, which can accept any socioeconomic driver data. The model contains details about the technology stock, including vehicle vintages, and uses exogenous data from economic scenarios to choose new technologies and retire old ones. Choices for model parameters (such as growth, retirement, emission standards, emission factor and degradation rates, and the fraction of vehicles with extremely high emission factors [termed "superemitters"]) are included.

Because some of the relationships represented in the model (such as vehicle retirement age, superemitter generation fraction, and lag years between different emission standards) are only loosely constrained by observations, we focused on quantifying the uncertainty inherent in the emission projections. Results show that there is forecasting power in portraying the sensitivity of future aerosol emissions to the vehicle retirement rate, scrappage rate, superemitter generation, and new vehicle emission standard. Global model results were prepared, including projections of emissions of total vehicle-exhaust primary PM to the year 2050 and regional contributions. The global and regional emission projections show diverse trends in all scenarios over the period 2005–2050. The trade-off between decreasing emission intensity and increasing fuel consumption results in relatively lower rates of increase for PM emissions than for fuel consumption. Superemitters, which contribute more than 50% after around 2020, drive the PM emission trend. If superemitters are eliminated, the global emissions decline at an average rate of 1.3% to 2.0% per year.

Because the role of vehicle replacement has been extensively explored, we generated important data on the role of scrapping old, polluting vehicles. This information is relevant to policy issues like the "Cash for Clunkers" program. We have already linked this module to SEE so that dynamic aerosol emission forecasts result. Work was also completed on off-road vehicles, which are major sources of aerosol emissions. We explored many kinds of inter-module linkages, such as using the land-use component of SEE and its forecasts of agricultural cropland to drive estimates of emissions from agricultural vehicles (e.g., tractors). Thus we completed our analysis and model building for mobile sources. The final step — developing a similar module for industrial sources — will continue at the University of Illinois.

Refereed Publications

Yan, F., E. Winijkul, S. Jung, T.C. Bond, and D.G. Streets, "Global Emission Projections of Particulate Matter: I. Exhaust Emissions from On-Road Vehicles," *Atmospheric Environment*, in review.

Non-Refereed Publications and Presentations

Yan, F., and T.C. Bond, "Future Emissions from Vehicle Fleets," presented at Air and Waste Management and Association (AWMA) 101st Annual Conference and Exhibition, Portland, OR, June 24–27, 2008.

Yan, F., E. Winijkul, T. Bond, D. Streets, and Z. Klimont, "Isolating Critical Uncertainties: Emission Projections Built on Drivers," presented at Global Emission Inventory Activity (GEIA) Open Conference, Oslo, Norway, November 26–28, 2009.

Yan, F., E. Winijkul, T. Bond, and D. Streets, "Emission Projection and Uncertainty Analysis of Exhaust Emissions from Global and Asian On-Road Vehicles," presented at American Geophysical Union (AGU) Fall Meeting, San Francisco, CA, December 14–18, 2009.

Yan, F., E. Winijkul, T.C. Bond, and D.G. Streets, "Global Emission Projection from Transportation Sector and Its Uncertainty Analysis," presented at 19th Annual International Emissions Inventory Conference, San Antonio, TX, September 27–30, 2010.

Yan, F., E. Winijkul, T.C. Bond, and D.G. Streets, "A Probabilistic Approach to Emissions from Transportation Sector in the Coming Decades," presented at American Geophysical Union (AGU) Fall Meeting, San Francisco, CA, December 13–17, 2010.

Advanced Simulation of Separations

2008-150-R2

David A. Nowak, Mihai Anitescu, Candido Pereira, Monica C. Regalbuto, Branko Ruscic, Andrew Siegel, and Kent E. Wardle

Project Description

The initial goal of this effort is to provide a firmer foundation for applying advanced simulation techniques to nuclear separations. The work is focused on three areas where significant advances are needed to take full advantage of modern computational capabilities. First, limited thermodynamic data exist for many radionuclides. ATcTs (Active Thermochemical Tables) can be expanded to include actinides and fission products, thus broadening the thermochemistry parameter space and intrinsically boosting reliability. ATcTs derive accurate, reliable, and internally consistent thermochemical values for stable, reactive, and transient chemical species. Second, safeguards are needed to prevent the diversion of nuclear material. Our approach sets up an algorithm to model the propagation of small-scale perturbations for a simple chemical process and evaluates diversion strategies through a stochastic optimization with constraints. Third, dynamic process simulations of the process equipment and operations are needed. Time-varying systems must be understood at the unit operations level through better models of fluid flows and interfacial chemistries and through integration of multiple operations.

Mission Relevance

This project is tied to DOE's missions in science, energy, and national security. Our mix of projects is expected to address fundamental basic-science problems of interest to the Office of Science and more applied problems that are of interest to the Office of Nuclear Energy or the National Nuclear Security Administration. DOE-NE's Fuel Cycle Research and Development (FCRD) program is developing campaigns in aqueous-separations safeguards and simulations as part of the Nuclear Energy Advanced Modeling and Simulations (NEAMS) project. The approach, models, and software developed here should be directly relevant to development of advanced treatment technologies for spent fuels and their safeguarding.

FY 2010 Results and Accomplishments

The ability of ATcTs to correctly handle condensed phases relevant to actinide thermochemistry was successfully tested by using representative solid/liquid/aqueous species intertwined with gas-phase species in the current Core Thermochemical Network (TN). As part of this effort, a seed Actinide Thermochemical Network (AxTN) that describes key species pertinent to actinide systems was developed. Several hundred original papers and reports were accumulated and critically examined (and, when necessary, reinterpreted), and the relevant information was distilled into a series of condensed summaries. The summaries were then used to define the elements of the seed AxTN. The resulting seed AxTN is fully superimposable on the current Core TN, thus obviating the need to re-describe non-actinide chemical species that are already defined in the Core TN. The condensed summaries that form the base for the seed AxTN contain the analysis of all relevant measurements that adequately define no less than two dozen "key" species. With this seed AxTN, it was possible to successfully demonstrate that ATcT is an approach that is significantly superior to and more efficient than traditional sequential thermochemistry, which is currently used to obtain the thermodynamic parameters of chemical species relevant in actinide chemistry. It is clear that the ATcT approach has a number of inherent advantages, such as more complete use of the available thermodynamically relevant measurements, the ability to uncover and successfully resolve inconsistencies in the available information, and the ability to conveniently update the results by simply inserting new knowledge when it becomes available and propagating its consequences through all the affected species in the AxTN.

After developing an initial model-based product diversion assessment for a steam-methane reforming model, with input taken from ATcTs, we applied the approach to the separation of rare-earth elements by solvent extraction, a class of process models more relevant to fuel-cycle research and development. The work was centered on formulating and testing the "maximum likelihood" approach for the recovery of the best information from all sources available for a chemical process. The goal was to obtain the best estimate of the diverted output after incorporation of information from multiple inputs. Overall, this portion of the project is at a stage where an assessment can be conducted for a moderate number of scenarios for reactions of the type that describe separations chemistry. Reduced models of the solvent extraction process were developed from the continuity, momentum, and mass transfer equations. From a set of initial conditions, mass transfer ratios and elemental concentrations were determined for a ten-stage simulation. The equilibrium reactions were computed in a portable extensible toolkit for scientific computing (PETSC) to serve as the function/gradient interface. The posterior density-function solution to determine the probability of detecting a diversion or loss of material for this system was then developed by using Monte Carlo methods and Importance Sampling to address the high dimensionality of the problem.

In separations modeling, the focus was on the full-scale testing of the open-source computational fluid dynamics (CFD) code OpenFOAM on a number of different computational platforms to demonstrate modeling capability for turbulent, multiphase fluid dynamics in an annular centrifugal contactor. As an initial step, simulations of the contactor mixing zone using free surface volume of fluid (VOF) and turbulence large eddy simulation (LES) methods were completed and compared to existing experimental velocity measurements for this configuration. The results were in good agreement with data and previous simulations done by using a commercial code. In addition, as a specific demonstration of the utility of such modeling for providing insight into existing flow issues, we conducted various targeted simulations to explore design modifications to the heavy-phase underflow and weir cap region of the contactor to mitigate unstable flow patterns that have previously been identified. These simulations of the heavy-phase underflow section of the rotor, combining free-surface modeling with a moving reference frame (MRF), provided insight into flow phenomena previously predicted using a commercial CFD code. To lay the foundation for further work with multiple liquid phases, explorations of parallel scaling of the code and modifications to enable coupled mixing-zone and separation-zone simulations were also conducted. A three-phase, liquid-liquid-air mixing simulation was conducted for a highly refined mesh by using 2000 processors of the SiCortex machine. The general results demonstrate the limits of the current modeling methodology — interface capturing by using VOF — and the need for the development of advanced mixing models. In addition, a first-of-a-kind coupled mixing-zone/separation-zone model of the contactor was run by using both VOF and MRF, which showed the start-up and filling of the contactor with a single liquid phase and air.

The goal of the first leg of this project was to demonstrate the capabilities of ATcT when applied to actinide thermochemistry. This goal was successfully met. The logical follow-up is to embark on a massive full-scale project that will apply the ATcT approach to a broad range of chemical species of interest in actinide chemistry. Such an ambitious project would require substantial long-term funding. The feasibility of initiating and funding such a large-scale project will be explored.

The second leg of this project will continue to be supported under the DOE-NE Fuel Cycle R&D program through the Material Protection, Accountability and Control Technology project. The approach will use a hidden Markov model (HMM) coupled with the high-fidelity model of rare-earth separations processes to describe the uncertainty in chemical separations. As a material accountancy assessment, an estimate of the uncertainty of the accountancy target will be calculated by a high-dimensional integration conditioned on a measured quantity. The assessment will be conducted by using a high-performance library. The viability of the Monte Carlo-based solution approach to the assessment of the uncertainty in the complex chemical processing will be evaluated. The project will continue to focus on the rare-earth system with eventual extension to spent-fuel reprocessing.

The third leg of this project will continue to build a basis for a dynamic process simulation with an emphasis on using OpenFOAM to develop codes to examine the fluid dynamics of centrifugal contactors. This project will continue under the DOE Nuclear Energy Advanced Modeling and Simulation initiative under the Safeguards and Separations team. Efforts are under way to build upon the insights generated from this work to develop advanced, coupled multiphase simulation methods based on OpenFOAM that are capable of capturing three-phase (liquid-liquid-air) flows in the annular centrifugal contactor.

Refereed Publications

Wardle, K.E., "Open-Source CFD Simulations of Liquid–Liquid Extraction in the Annular Centrifugal Contactor," *Computers & Chemical Engineering,* submitted, 2010.

Non-Refereed Publications and Presentations

Wardle, K.E., "Ongoing Studies of the Flow in Annular Centrifugal Contactors," presented at Mixing XXII, Victoria, BC, Canada, June 20–25, 2010.

Wardle, K.E., "Computational Fluid Dynamics (CFD) Simulation of the Flow in Annular Centrifugal Contactors," poster presented at the 34th Actinide Separations Conference, Argonne National Laboratory, May 17–20, 2010.

Wardle, K.E., "Application of Open-Source CFD to Simulation of the Flow in Solvent Extraction Equipment," presented at the 16th Symposium on Separation Science and Technology for Energy Applications, Gatlinburg, TN, October 18–22, 2009.

End-to-End Biofuels Analysis: Building Capability in HPC Socio-Economic-Environmental Modeling

2008-160-R2

Ian T. Foster, Richard D. Doctor, Stephen M. Goldberg, Donald A. Hanson, Robert L. Jacob, Veerabhadra R. Kotamarthi, Sven Leyffer, Charles M. Macal, Todd S. Munson, Michael Q. Wang, and Michael J. Wilde

Project Description

General equilibrium models have been used for decades to obtain insights into the economic implications of policies and decisions. Despite successes, however, these economic models have substantive limitations, many of which are due to computational and methodological constraints that can be overcome by leveraging recent advances in computer architecture, numerical methods, and economics research. Motivated by these considerations, we are developing a new modeling framework: the Community Integrated Model of Economic and Resource Trajectories for Humankind (CIM-EARTH).

An integrated assessment model contains several submodels, such as economic activity, agriculture production, and climate models, that interact and complement each other, with the goal of obtaining a more complete model that accurately represents the activities and variables involved. The result of this work will be an extensible framework that can accommodate a large set of components and the means to solve the resulting problems. In particular, we are developing a portfolio of models to assess and quantify the socio-economic impact of climate change, undertaking computations for the economic management of limited biomass resources, formulating computational problems that explicitly include distributions for key unknown parameters, and applying them to study the impact of biofuels on the climate.

Mission Relevance

The DOE Office of Biological and Environmental Research supports research on models and tools for integrated analysis of both the drivers and consequences of climate change. The work performed in this project is directly relevant to this program, developing methods that can be used to (1) study the economic impacts of both climate change and policies intended to respond to climate change and (2) characterize uncertainties associated with these issues. Moreover, the DOE Biomass Program and Vehicle Technologies Program are interest in the economic impacts of biofuels. Our models are being applied to biofuel problems.

Results and Accomplishments

We have made substantial progress in developing the framework and several implementations of the model.

We enhanced our static and recursive-dynamic computable general equilibrium model by incorporating biofuel and alternative energy sectors; endogenous taxes for cap-and-trade policies where the rate is set by the model to achieve revenue or emissions targets; and improved dynamic models of energy efficiency, labor productivity, and natural resource depletion. We used this model to conduct studies on carbon leakage in the context of unilateral carbon mitigation policy. A wide range of policy options for mitigating carbon leakage were studied, including carbon border tax adjustments, subsidies to ease the competitiveness burden experienced by local producers, and carbon uptake limitations on developing economies through international treaty and/or bilateral trade relationships.

We used a statistical approach to address uncertainty in the models and the propagation of uncertainty. For the uncertainty work, we needed to solve a massive number of problems on parallel machines. To perform these studies, we further developed the Swift/Falkon infrastructure that enables the parallel execution of such massive parameter studies on the large-scale resources available at Argonne and the Computation Institute. This work focused on supporting the computational needs of the modeling efforts ready for large parallel runs, making the parallel scripting technology user-friendly and well documented and supported with hands-on tutorials, scaling the parallel scripting technology to the needs of the these models, and working to facilitate the execution of coupled models.

Emissions. Economic and climate models can be linked through carbon emissions from the production of goods and services. Economic mitigation policies, such as cap-and-trade programs, require the computation of these emissions. We took a value-added approach to accounting for emissions embedded in the products produced around the world that works off the concept of conservation of emissions. We also correctly account for industries that sequester oil rather than burn it, such as the plastics industry. The resulting embedded emissions are then used for border tax adjustments. These computations can be coupled directly with the model.

Land use. We began producing models to downscale the land-use results of our economic model to scales relevant to the high-resolution climate models in use today and to help inform local and regional-scale decision makers about local economic and climate impacts. In particular, we developed a model for distributing increases in demand for land, to meet an increased demand for agriculture and biofuel feedstocks by using an optimization-based approach.

Crops and roots. We completed the integration of three crop species, corn, soybean, and spring wheat into the coupled carbon-nitrogen Community Land Model (CLM-Crop). CLM-Crop was used to simulate crop fluxes from current agriculture practices, and results were validated against observations from two AmeriFlux sites growing corn and soybean. CLM-Crop-simulated gross primary productivity, net ecosystem exchange, and leaf area index compared well with observations. Crop yields also agreed with U.S. Department of Agriculture statistics for the U.S. for soybean and wheat, but crop yields were underestimated by the model for corn, mainly the result of technology advances and management practices not simulated by the model (such as irrigation). CLM-Crop was also used to investigate the effects on soil organic carbon (SOC) from land-use changes, different residue management practices, and varied fertilizer application for four alternative scenarios.

The National Center for Atmospheric Research (NCAR) has shown interest in incorporating this crop model, or several components of CLM-Crop, in a future release of the CLM model. Some of this work will continue under NSF funding at the University of Chicago. We have already begun porting the agriculture model into CLM4, the latest release of CLM. We have also begun working on expanding the capacity of the model to run with transient land-use data, a requirement if future agriculture land-use scenarios are to be simulated. Collaboration with NCAR and the CLM community continues under LDRD project 2011-129-N0. , as several other groups are interested in this capability for use with glaciers, wetlands, and urban land uses. The work is also included in the multi-lab Climate Science for a Sustainable Energy Future proposal.

Refereed Publications

Elliott, J., I. Foster, K. Judd, E. Moyer, and T. Munson, "CIM-EARTH: Framework and Case Study," *B. E. Journal of Economic Analysis and Policy* **10**(2) (2010).

Elliott, J., M. Franklin, I. Foster, M. Loudermilk, and T. Munson, "Propagation of Data Error and Parametric Sensitivity in Computable General Equilibrium Models," *Computational Economics*, to appear (2011).

Hanson, D., Y. Kyrukov, S. Leyffer, and T. Munson, "Optimal Control Model of Technology Transition," *International Journal of Global Energy Issues* **33**(3/4) (2010).

Non-Refereed Publications and Presentations

Drewniak, B., Song, J., Prell, J., and Kotamarthi, V. R., "Estimating Changes in Soil Organic Carbon under Selected Agriculture Residue and Fertilizer Management Practices with the Community Land Model," *2010 American Geophysical Union Fall Meeting*, San Francisco, CA, December 13–17, 2010. (Abstract and Oral Presentation)

Drewniak, B., V. Kotamarthi, R. Jacob, J. Prell, and J. Song, "Modeling Soil Organic Carbon for Agriculture Land Use Under Various Management Practices," *2009 American Geophysical Union Fall Meeting*, San Francisco, CA, December 14–18, 2009. (Abstract and Poster)

X-Ray Studies of Catalysts

2008-193-R2

Jeffrey T. Miller

Project Description

The goal of this project is to develop new capabilities for investigating heterogeneous catalysts by using x-ray absorption techniques. With the high brilliance of the APS (Advanced Photon Source), such techniques have the capability to interrogate catalysts under realistic reaction conditions, thereby leading to an unprecedented level of understanding about the active site and its role in the control of the rate and product quality.

Mission Relevance

Catalytic technology is essential for economic prosperity, energy security, and environmental preservation in the twenty-first century. The world demand for energy is expected to increase by 50% in the next 25 years. Therefore, to develop clean, safe alternative energy materials and processes while protecting our environment, it will be necessary to develop high performance catalysts by control the synthesis with a level of precision that has never before been possible. To meet this need, it is necessary to determine the structure and electronic properties of the active site under realistic reaction conditions for a variety of catalytic problems. In addition, determination of surface reaction intermediates will make it possible to elucidate reaction mechanisms leading to the development of new, high-performance catalytic materials for new energy processes.

FY 2010 Results and Accomplishments

A series of reaction cells were developed, which allowed for the study of most catalytic materials and reactions under realistic process conditions. These cells include a plug-flow, fixed-bed automated catalyst testing unit capable of high-quality kinetics and detailed product analysis that can simultaneously measure x-ray absorption near edge spectroscopy (XANES) and extended x-ray absorption fine structure (EXAFS). Additional cell designs include an environmental cell for low-energy catalytic materials and a grazing incidence cell for single-crystal model catalysts, and a controlled atmosphere for homogeneous catalysts.

The high-pressure, liquid-phase, kinetic-reactor was used to study the reaction mechanism of biomass reforming (i.e., turning biomolecules into H_2), which is needed for the production of renewable transportation fuels from bio-oils. Along with the development of new reaction cells, a new analysis technique of the L-edge XANES spectrum also allows for identification of key reaction intermediates and their surface coverage. Figure 1 shows the XANES spectrum of a Pt/C reforming catalyst reduced and under reforming conditions (25 atm, 225°C in liquid H_2O and glycerol). The change in the shape of the XANES, or ΔXANES, is shown in Figure 2. Comparison of these changes with those due to adsorbed CO suggest that about 40% of the Pt surface is covered with CO during the biomass reforming. Although CO is not an observed product, these results indicate that the decomposition of biomolecules to H_2 goes through a CO surface intermediate. Furthermore, H_2 is likely formed by the water-gas shift reaction mechanism. These findings also suggest potential catalyst compositions likely to give improved performance.

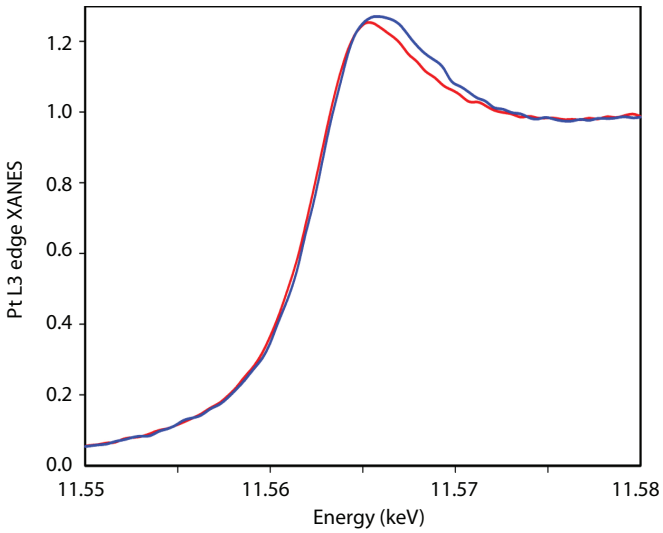

Figure 1. Pt L_3 XANES spectra of reduced Pt/C (Red, in He, and Blue, liquid phase glycerol reforming at 225°C, 25 atm)

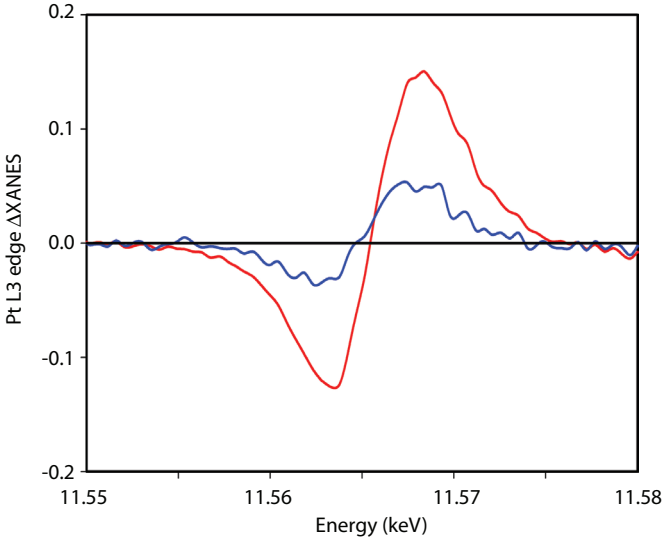

Figure 2. Pt L_3 ΔXANES of reduced Pt/C (Red, with adsorbed CO at RT, and Blue, under glycerol reforming conditions)

Experimental studies on the effect of adsorbates on XANES spectrum of metallic Pt nano-particles indicate that these changes result from the formation of chemical bonds. By using density functional theory, we successfully modeled the changes in the XANES spectra. At the absorption edge, a decrease in intensity occurs because of the chemical bond formation and the transfer of metal electron density to the surface reactant. Slightly above the edge, the intensity increases as a result of the transfer of the photoelectron to the newly formed, empty anti-bonding adsorbate orbital. The ability to measure and model the L-edge XANES spectra has also been applied to better understand the chemical interaction of two metals in alloy catalysts and to elucidate the reaction mechanism of the water-gas shift reaction — a large-scale industrial process for the production of H_2.

Finally, while XANES and EXAFS spectroscopies are widely used for the study of heterogeneous catalysts, they are seldom utilized for the characterization of homogeneous catalysts. The development of a high-pressure flow cell suitable for the analysis of air- and water-sensitive homogeneous catalysts also enabled efforts to determine the structural and electronic properties of these important catalysts. With this homogenous catalyst cell, it also will be possible to determine the structure of reaction intermediates, the changes in the oxidation state, and the kinetics of key reaction steps in the homogeneous catalytic cycle. The study of homogenous catalysts presents a new opportunity to make important contributions to this field.

Refereed Publications

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Integrated Biofuel/Engine Design

2009-097-R1

Douglas E. Longman, Philip D. Laible, YuPo Lin,
Stephen T. Pratt, Seth W. Snyder, and Michael Q. Wang

Project Description

The need exists to integrate the efficient production of biofuels with the design of internal combustion engines that have high efficiency and ultra-low emissions. Historically, combustion regimes and thus overall engine designs have been dictated by a given set of fuel properties. By designing the fuel properties in coordination with engine research following a multidisciplinary team approach, we are seeking to realize the full potential of the energy source (fuel) and conversion device (engine). Fuel design during engine development may hold the key to unlocking promising new combustion regimes, such as low-temperature combustion in diesel engines.

Mission Relevance

This project is relevant to DOE's missions in energy and the environment. It directly responds to the advanced biofuel mandates defined in the Energy Independence and Security Act of 2007. The primary benefit to DOE is the potential for replacing foreign petroleum with renewable fuel while increasing fuel conversion efficiency and reducing engine emissions. The associated increase in efficiency and lowering of emissions would have a global impact by providing sustainable energy. Success in this project will lay the groundwork for developing integrated pathways to design fuels and engines that reach their maximum potential. Beneficiaries include fuel manufacturers and other renewable energy companies.

FY 2010 Results and Accomplishments

In the first two years of interdisciplinary effort, biofuels databases were built and interactive discussions and experimentation resulted in the identification of target biofuels molecules that potentially could (1) be produced efficiently in engineered organisms, (2) be delivered by using existing fuels infrastructures, (3) produce sufficient power with low emissions, and (4) function in present-day combustion regimes. Building on this progress, in the past year, we have made tangible progress in the design, construction, and evaluation of new strains of photosynthetic bacteria employed in strategies to produce biodiesel surrogate molecules. Our metabolic engineering efforts initially focused on the design of strains that produce phytol (a C20 alcohol) – a molecule that is produced in large quantities by photosynthetic bacteria – and it serves as the first top-down test case for the global research strategy. Because the branched carbon chain of phytol, through testing (*vide infra*), may prove to be too long, we have shifted efforts toward the production of reduced forms of farnesol, geraniol, and prenol (C15, C10, and C5 alcohols, respectively). And because phytol is made up of repeating 5-carbon units of a branched isoprenyl moiety, the change to focusing on these shorter molecules – preserving the same branched, reduced chemical composition – was straightforward.

In anticipation of the needs for separation processes to aid in extracting biodiesel surrogates from bacterial extracts and cell suspensions, the separations group developed a process to use a separative bioreactor to produce biodiesel from soybean oil. This work renovated a manufacturing process that significantly lowers production costs and energy consumption. One U.S. Provisional Patent has been filed, titled "*Integrated System for the Production and Separation of Biodiesel and Method Thereof,*" and one new invention was filed, titled "*Engineered Photosynthetic Bacteria and Methods of Manufacture of Advanced Biofuels.*"

Our team discussions have indicated that the C5 alcohol, $(CH_3)_2C{=}CHCH_2OH$, is a possible alternative target to phytol. This smaller alcohol is more readily studied theoretically and may also have improved fuel properties (e.g., viscosity). Thus, the decomposition channels for this species have been examined. The lowest-energy pathway corresponds to the loss of a water molecule with the formation of a second double bond in the fragment molecule; this process has an activation energy of 69 kcal/mol. Simple fission of the CO bond to produce an OH radical and a radical hydrocarbon $(CH_3)_2C{\bullet}CH{=}CH_2$ has a somewhat higher activation energy of 83 kcal/mol. At higher temperature, this process should begin to compete with the H_2O loss channel.

The physical properties of C5, C10, C15, and C20 as fuel components that could be blended together and/or with diesel fuel were determined by using laboratory-grade samples. The results indicated that the most desirable fuel blend may come from using predominately C10 and C15 components. The distillation curves shown in Figure 1 indicate that these components are in the range of those found with petroleum-based No. 2 diesel fuel and a typical type of methyl ester type biodiesel fuels, which are commonly referred to as FAME (Fatty Acid Methyl Ester) fuels and are made from soy or rapeseed feedstocks.

The physical properties were further investigated through computational fluid dynamics modeling of the fuel flow through an engine's fuel injector and then of the subsequent fuel spray atomization. The properties of viscosity, density, and vapor pressure were found to have significant effects and will be used to guide the formulation of the fuel blends for future modeling and experimental engine tests.

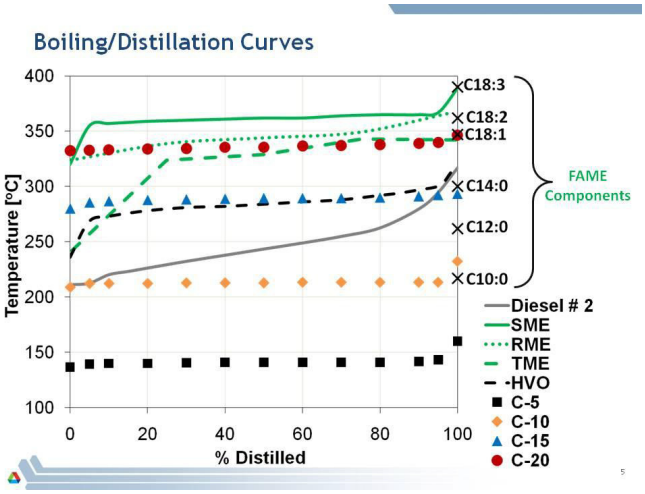

Figure 1. The boiling/distillation curves of the possible biofuels under study as compared with Diesel #2 and FAME fuels. (Note: SME=soy methyl ester; RME=rape methyl ester; TME=tallow methyl ester; HVO=hydrogenated vegetable oil.)

Proposed Work for FY 2011

The bioscience and separations efforts will focus on developing new strategies to produce the biofuel components in 5-carbon chain units. Concurrently, the chemistry effort will focus on creating a reaction mechanism for a C5 molecule based on the recent C4 (butanol) mechanisms. In our effort related to engines, we will prepare blends of the fuel components, characterize the physical and combustion properties, conduct engine simulations, and run experimental engine validation tests for those models. In addition, a full life cycle analysis will be performed for this newly created biofuel based on an algae type feedstock.

Refereed Publications

Klippenstein, S.J., L.B. Harding, M.J. Davis, A.S. Tomlin, and R.T. Skodje, "Uncertainty-Driven Theoretical Kinetics Studies for CH_3OH Ignition: HO_2 + CH_3OH and O_2 + CH_3OH," in *Proceedings of the Combustion Institute 33*, Issue 1, pp. 351–357, 2011.

Luo, Z., T. Lu, S. Som, and D.E. Longman, "Numerical Study on Combustion Characteristics of Biodiesel Using a New Reduced Mechanism for Methyl Decanoate as Surrogate," *Proceedings of the 2010 ASME Internal Combustion Engines Division Fall Technical Conference*, San Antonio, TX, ICEF2010-paper no. 35198, September 12–15, 2010.

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Non-Refereed Publications and Presentations

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Klippenstein, S.J., L.B. Harding, M.J. Davis, A.S. Tomlin, and R.T. Skodje, "Uncertainty-Driven Theoretical Kinetics Studies for CH_3OH Ignition: HO_2 + CH_3OH and O_2 + CH_3OH," presented at the 33rd International Combustion Symposium, Beijing, China, August 2010.

Snyder. S.W., "Advanced Biofuels Workshop," drop-in biofuels panel at the 2010 International Fuel Energy Workshop & Expo, St. Louis, MO, June 2010.

Snyder, S.W., "Sustainability, Compatibility, and Economics: The Critical Barriers to Bioenergy," International Bioenergy Days (IBED) 2010, Rockford, IL, September 2010.

Snyder, S.W., "Sustainability, Compatibility, and Economics: The Critical Barriers to Bioenergy," Future Fuels, Chicago Council on Science and Technology, Chicago, IL, September 2010.

Advanced Cathode Materials for High-Performance Lithium-Ion Batteries

2009-115-R1

Jie Li, Khalil Amine, Zonghai Chen, Russell E. Cook, Jeffrey W. Elam, Yung Y. Liu, Anil U. Mane, Michael J. Pellin, Yan Qin, Lee K. Walker, and Huiming Wu

Project Description

A lithium, manganese, and oxygen (Li-Mn-O) composite has the potential to serve as the best cathode material for future plug-in hybrid electric vehicles because of its higher working voltages and lower cost as compared to other materials. However, the composite suffers from electrochemical instability: the Mn^{3+} ions dissolve into the electrolyte, and the reduced metallic Mn blocks the channels of the graphite anode, leading to rapid battery degradation. Exploiting the capability of applying a film coating to increase the electrical stability of cathode particles may enable processing of the Li-Mn-O composite on a larger scale. Until recently, technological progress has been prevented by the unfavorable trade-off between enhanced surface protection and the

increased electrical impedance for the coated layers grown by using current technologies.

With its unique feature of two-step and self-terminated reactions, the atomic layer deposition (ALD) method is particularly well suited to synthesizing ultra-thin, highly conformal protective coatings with the film thickness that can be controlled at the atom scale. ALD can provide an ideal solution to satisfy the demands of both surface protection and charge transport. The goals of this project are to (1) demonstrate that significant improvements in battery performance can be achieved by applying ultra-thin ALD nano-films to the granular cathode materials and (2) develop an advanced material processing technology on a large scale.

Mission Relevance

This project supports DOE's mission in energy security. We anticipate that, because it will result in the development of advanced ALD-coating technology in a fluidized bed reactor (ALD is one of five key areas identified), this project will contribute to DOE's Industrial Technology Program in the area of nano-manufacturing. Because it involves manufacturing advanced nanostructured cathode materials on a large scale, the project will also contribute to DOE's Synthesis and Processing Science Program (within Basic Energy Sciences) and Energy Storage Technologies (under the Vehicle Technology Program of DOE EERE).

FY 2010 Accomplishments and Results

In previous years, a series of samples was prepared in a fixed-bed ALD reactor. The series consisted of Al_2O_3, ZrO_2, V_2O_5, and HfO_2, which were deposited via ALD on either $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$-constructed cathodes or granular materials. Battery performance tests using the ALD Al_2O_3 surface-coated cathodes indicated improvements in both capacitance retention and impedance. With a cathode made of the (Al_2O_3) ALD-coated powders, the battery's performance has been further enhanced: a more than 30% increase in capacitance retention was recorded after 200 cycles under a high-temperature condition (55°C). Performance tests in which other coating materials were used, including ZrO_2 and V_2O_5, also exhibited various degrees of improvement in cell performance.

In FY 2010, we continually demonstrated that the ALD Al_2O_3 and ZrO_2 coatings have positive impacts on cycling performance (see Figure 1) for another promising Li-ion battery made of the $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) cathode material that has the highest voltage (5 V vs. 3.7 V for the current Li-Co-O battery). The ALD Al_2O_3, or ZrO_2, thickness on the LNMO powders was varied from 0.25 nm to 3 nm (see Figure 2) by controlling the number of ALD cycles of 2, 5, and 10.

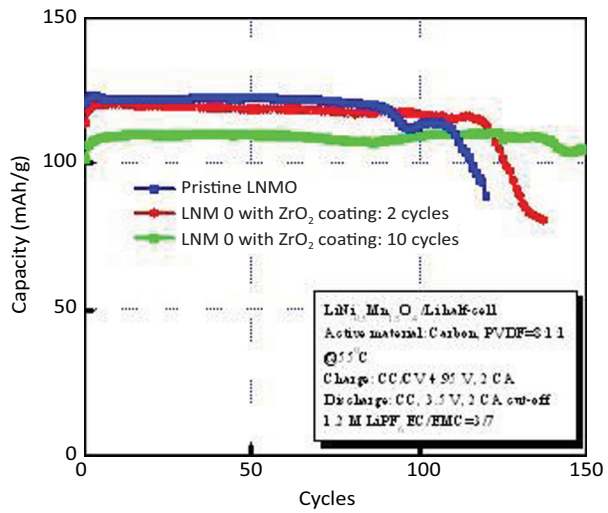


Figure 1. ALD coating of ZrO_2 on the cathode of LNMO, demonstrating better cycling performance than a non-coated electrode. The film growth rate is about 0.3 nm per cycle.

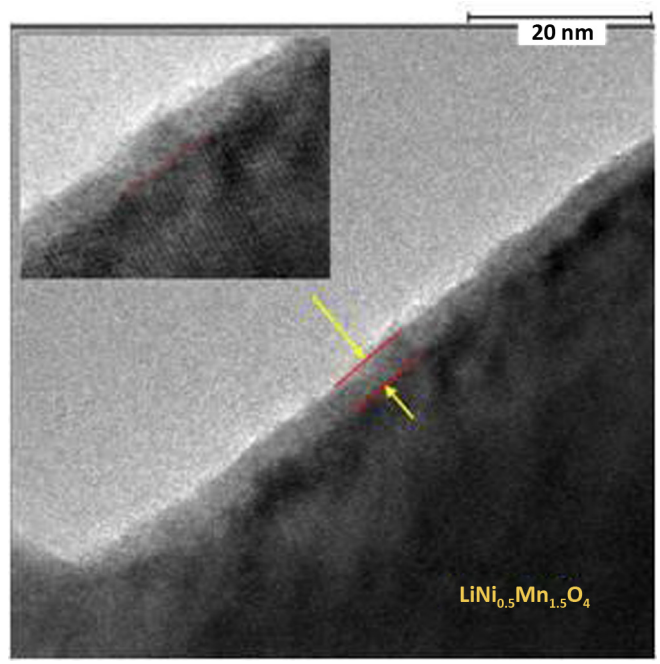
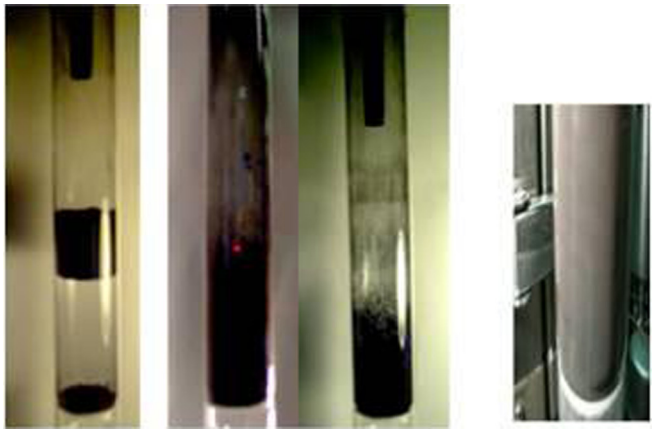


Figure 2. The transmission electron microscopy (TEM) images of ALD-coated ZrO_2 thin film, which is about 3 nm in thickness per 10 ALD cycles, on an LNMO powder. Images show a highly uniform film (insert), clear lattice fringes of the particle, and the particle/film interface.

In addition, the research team observed that, with an increase in film thickness, the cycling curve is flattened out (i.e., a longer lifetime). However, the initial battery capacitance is meanwhile reduced. The Al_2O_3-coated cell battery is much more sensitive than the ZrO_2-coated battery, especially when the film is thicker than 5 nm. Because Al_2O_3 is an insulating material, whereas ZrO_2 is an ion-conducting material, the result suggests that a relatively thicker but still conductive ALD-coating layer may provide an optimal solution.

The team also completed the fabrication of a coherently controlled gas-fluidized bed (CCGFB) reactor that can be operated under a vacuum of 1 to about 10 Torr. The reactor will be used for massive ALD powder coatings. In contrast to a conventional fluidized-bed reactor, the new reactor incorporates a nonlinear controlling technology. The technology was implemented by adaptively superimposing a standing fluid wave on suspended particles to suppress flow instabilities, such as plug, clustering, and channeling fluidizations. We successfully demonstrated, for the first time, that 5~10-μm cathode powders, $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ and LNMO, can be uniformly fluidized in our CCGFB without using energy-intensive mechanical vibration/rotary approaches. Such a gas-particle system otherwise displays as either plug or channeling fluidization in a conventional gas-solid reactor (see Figure 3). Dispersing the primary cathode particles uniformly in a gas flow, which is a historic challenge, creates the necessary conditions that enable application of a conformal ALD coating on each of the primary cathode particles at a large (i.e., production) scale. Our innovation will have significant economic impacts on the manufacturing of advanced cathode powders specifically and on granular materials in general.



(a) (b) (c)

Figure 3. Comparison of fluidization quality of the ultrafine LNMO powders in the conventional gas-fluidized bed reactors, namely, (a) plug flow, (b) channeling flow, and (c) highly homogeneous flow in our standing-wave assisted, gas-fluidized bed reactor.

Proposed Work for FY 2011

In FY 2011, we will use the ALD technique to deposit various ultra-thin film coatings on the surfaces of Li-Mn-O cathode powders in our newly fabricated CCGFB reactor, with both the small (4-cm ID) and the large (10-cm ID) beds, and will characterize them both structurally and electronically. We expect to achieve further performance improvements by using the ALD-coated cathode particles in our CCGFB reactor through which each particle can come into intimate contact with the gas flow and thus be fully coated. In addition, we will investigate the influence of film properties, mainly material conductivity, on cell performance. The goal of this investigation will be to optimize the material design for cathode powders. Moreover, the team will study the size, grain boundary, and porosity effect of primary cathode particles on cell performance by using existing resources. Through this research, we expect to further enhance cell performance as a result of a dramatically enlarged interface area and a superionic effect in which the building block shrinks to a small dimension (i.e., on the nanometer scale).

Advancing the Frontiers of Computational Design of Materials

2009-180-R1

Larry A. Curtiss, Ian T. Foster, Jeffrey P. Greeley, Kalyanasundaram Kumaran, Nichols A. Romero and Peter Zapol

Project Description

The objective of the work is to create a powerful, new capability to design materials with preferred properties. The focus of this project is to develop the machinery required to create a successful materials by design program. The developmental work is targeted toward the design of new catalytic materials — a forefront research area for energy applications.

Mission Relevance

Computational materials design can greatly improve the efficiency of the search process for new materials. Accordingly, it has a major impact on science and engineering. The design and discovery of new materials are essential to many energy-related technologies and to the DOE mission of energy security. In the proposed work, the development of a materials design workbench for catalytic materials provides a first step toward a more general, theory-based design of materials with sought-after functional properties that would revolutionize the materials discovery process.

FY 2010 Results and Accomplishments

Hydrogen peroxide synthesis was selected as an initial reaction to be studied in our materials by design program, since it presents an ideal compromise between industrial relevance (significant interest in the development of improved, low-cost catalysts that can produce hydrogen peroxide directly from H_2 and O_2) and computational tractability (relatively simple chemical reaction intermediates are involved). To develop a comprehensive description of the reactivity of transition metal catalysts for this reaction, we first identified a set of elementary reaction steps (17 in all) that describe the primary chemistry. We then determined the binding energies of the intermediates associated with these reactions, together with selected elementary activation barriers, on standard transition metal surfaces, such as Au, Pt, Pd, Ni, and Cu, among others.

Methanol Decomposition: Data Generation and Screening
We developed scaling relationships and activity correlations for subnanometer cluster catalysts. This was accomplished by developing models and identifying properties that can be calculated relatively simply for a large number of systems of interest. Our density functional calculations for methanol decomposition on subnanometer copper, cobalt, and palladium clusters identified several important differences for these three clusters. The calculation of the complete thermodynamics and kinetics of each subnanometer cluster to predict a new catalyst with low activation barriers for methanol decomposition and weak carbon monoxide binding to the catalyst would take a significant amount of time. The predicted volcano plot is shown in Figure 1.

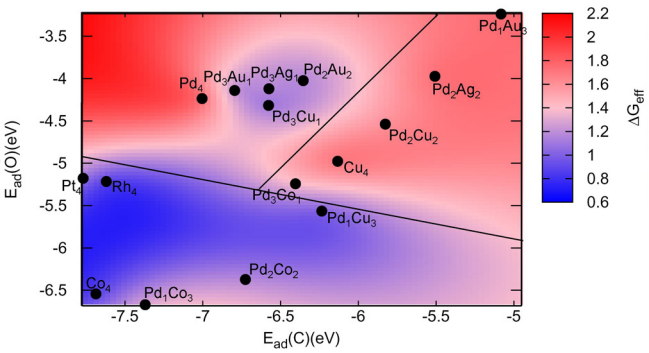


Figure 1. Volcano plot of the activity for methanol decomposition of four atom metal alloy clusters. Predicted potential energy curves were obtained by screening four atom catalysts for methanol decomposition.

Development of Materials Design Workbench Software
We designed and implemented a flexible and extensible platform for storing data produced by electronic calculations, such as GPAW, Dacapo VASP, and Gaussian, that can be searched and analyzed efficiently. The data are stored in a relational database with a hybrid schema that represents the names of properties common among all calculations, while calculation-specific property names are part of the data. Thus, adding new properties to data from an existing experiment can be done without schema modification (an expensive operation for beta testing of relational databases).

Proposed Work for FY 2011

We will continue to develop a powerful computational materials design program. During FY 2011, the focus of our research will be as follows:

- Employ screening to predict new catalysts for H_2O_2 formation and methanol decomposition based on the descriptors derived in FY 2010.
- Derive descriptors for carbon dioxide reduction and oxygen addition catalysis for use in large-scale screening.
- Obtain feedback from experimental studies to achieve validation and improvement in the descriptors.
- Complete the third phase of the materials design and database software, including incorporation of materials design algorithms.
- Establish database access for outside users in the catalysts design network and conduct a corresponding seminar.

Refereed Publications

Lei, Y., F. Mehmood, S. Lee, J.P. Greeley, B. Lee, S. Seifert, R.E. Winans, J.W. Elam, R.J. Meyer, P.C. Redfern, D. Teschner, R. Schlögl, M.J. Pellin, L.A. Curtiss, and S. Vajda, "Increased Silver Activity for Direct Propylene Epoxidation via Subnanometer Size Effects," *Science* **328** (2010), 224–228.

Mehmood, F., J. Greeley, and L.A. Curtiss, "Comparative Density Functional Study of Methanol Decomposition on Cu4 and Co4 Clusters," *J. Phys. Chem*. C **113** (2009), 21789.

Vajda, S., M.J. Pellin, J.P. Greeley, C.L. Marshall, L.A. Curtiss, G.A. Ballentine, J.W. Elam, S. Catillon-Mucherie, P.C. Redfern, F. Mehmood, and P. Zapol, "Subnanometer Platinum Clusters: Highly Active and Selective Catalysts for Oxidative Dehydrogenation of Propane," *Nature Materials* **8** (2009), 213–216.

Novel Power System Operations Methods for Wind-Powered Plug-In Hybrid Electric Vehicles

2010-044-N0

Jianhui Wang, Mihai Anitescu, Audun Botterud, Emil M. Constantinescu, Anantray D. Vyas, and Victor M. Zavala Tejeda

Project Description

The objective of this project is to address how power systems can incorporate large amounts of wind power and a high penetration of plug-in hybrid electric vehicles (PHEVs) into their operation, as they plan a few days ahead and during real-time operations. We propose developing a novel, improved, stochastic security-constrained unit commitment and dispatch algorithm for power system operations, as opposed to the traditional deterministic method, which does not consider the uncertainty in wind power generation and PHEV charging/discharging.

Mission Relevance

This project is relevant to DOE's energy mission. The project supports DOE's strategic goal of promoting a low-carbon environment by enhancing transmission reliability through advanced power system operations and large-scale stochastic optimization. It also supports the DOE Office of Electricity

Delivery and Energy Efficiency's strategic goal of improving the protection and restorative capability of national and international critical energy infrastructure assets and key resources. The proposed approach may significantly improve the bulk power system's operations and planning by lowering system costs, reducing blackouts, increasing social welfare, and advancing research on power system and large-scale computing. By using the method, the benefits of new energy sources and applications could be realized without compromising the reliability and security of power system operations.

FY 2010 Results and Accomplishments

We focused on the impacts of PHEV charging patterns on power system operation and scheduling. We developed a stochastic unit commitment model. It includes PHEV loads and the penetration of large-scale wind power. To evaluate possible scenarios in which PHEVs will be connected to the electric grid, we analyzed data from the 2009 National Household Travel Surveys (NHTS) with respect to the ending time of the last trip of each vehicle. We ran the model to simulate power system scheduling with different PHEV charging scenarios. The results showed that a smart charging pattern can reduce the operating costs of a power system and help accomodate fluctuations in wind power.

We also developed a large-scale computational framework to integrate stochastic optimization and uncertainty quantification in unit commitment and economic dispatch operations. The framework uses the state-of-the-art numerical weather prediction model that is now running on Argonne's high-performance computers. We used this framework to analyze the economic impacts of advanced weather forecasting systems on grid operations. We evaluated the predictability, resolution, and computational limitations of the system. A main conclusion is that a dedicated, grid-oriented weather forecasting system is required for next-generation operations.

Proposed Work for FY 2011

We will continue our work in quantifying uncertainty and developing advanced optimization methods to solve large-scale unit commitment problems. We will analyze the contingency of power system components because it is critical for solving the large-scale power system simulation problem. We will also develop a new family of dynamic market models that can capture strong volatile markets with high wind supply and elastic demands. Our models will pave the way to more integrated analyses and simulations of power grid operations.

Refereed Publications

Constantinescu, E.M., V.M. Zavala, M. Rocklin, S. Lee, and M. Anitescu, "A Computational Framework for Uncertainty Quantification and Stochastic Optimization in Unit Commitment with Wind Power Generation," *IEEE (Institute of Electrical and Electronic Engineers) Transactions on Power Systems* **26**(1) (2011), 431–441, 2011.

Kannan, A., and V.M. Zavala, "A Game-Theoretical Dynamic Model for Electricity Markets," *IEEE Transactions on Power Systems*, submitted, 2010.

Liu, C., J. Wang, A. Botterud, and Y. Zhou, "Assessment of Impacts of PHEV Charging Patterns on Power System Operations by Stochastic Unit Commitment," IEEE Innovative Smart Grid Conference, submitted, 2010.

Valenzuela, J., and J. Wang, "A Probabilistic Model for Assessing the Long-term Economics of Wind Energy," Electric Power Systems Research, in press, 2011.

Wang, J., L. Cong, D. Ton, Y. Zhou, and A. Vyas, "Impact of Plug-in Hybrid Electric Vehicles on Power Systems with Demand Response and Wind Power," *Energy Policy*, in press, 2011.

Wang, J., Z. Zhou, A. Botterud, "An Evolutionary Game Approach to Analyzing Bidding Strategies in Electricity Markets with Elastic Demand," *Energy – The International Journal*, submitted, 2011.

Zavala, V.M., A. Botterud, E.M. Constantinescu, and J. Wang, "Computational and Economic Limitations of Dispatch Operations in the Next-Generation Power Grid," presented at the IEEE Conference on Innovative Technologies for an Efficient and Reliable Power Supply, Waltham, MA, September 27–29, 2010.

Zavala, V.M., and M. Anitescu, "On the Dynamic Stability of Electricity Markets," *Mathematical Programming*, submitted, 2011.

Optimization of Luminescent Solar Concentrators

2010-047-N0

Seth B. Darling, George W. Crabtree, Jeffrey R. Guest, Roy J. Holt, Matthew A. Pelton, David H, Potterveld, Tijana Rajh, Elena Shevchenko, and Gary Wiederrecht

Project Description

We are developing an approach to address the challenges associated with large-scale solar energy harvesting that uses a multilayer solar concentrator based on luminescent quantum dots (QDs). Solar concentrators are a promising means for reducing the cost of photovoltaic (PV) power, because concentrating solar radiation allows less active material to be used. Luminescent concentrators are stationary and operate efficiently under diffuse light.

We are pursuing QDs because they are solar stable, can have high luminescence efficiencies, can operate throughout the solar spectrum (including infrared, where organic dyes fail) because of tunable band gaps, and can have significant Stokes shifts that reduce energy losses associated with light reabsorption. Significant advantages are associated with the multilayer concentrator as well (Figure 1). A multilayer QD concentrator will open major opportunities to develop flexible, economic, and efficient PV cells by accommodating for the mismatch between the incident energy of the solar spectrum and the band gap of semiconductors used in PV devices.

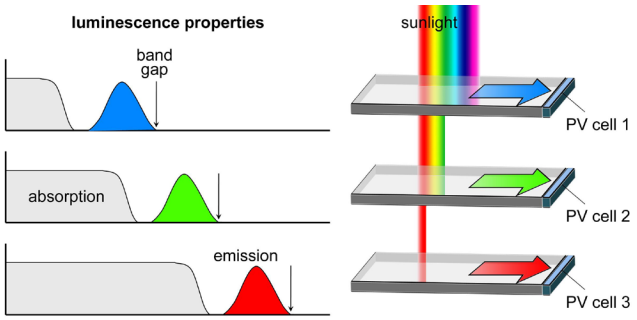


Figure 1. Illustration of a three-layer luminescent solar concentrator. Each layer is optimized for a specific part of the solar spectrum. The figure on the left illustrates the absorption and emission spectra of three different nanocrystalline materials with three different band gaps, each of which is embedded in one of the slabs.

Mission Relevance

This project is relevant to DOE's missions in energy and the environment. DOE aims to provide energy security for the nation, and lowering the cost of solar energy is a very promising pathway to do this. Moreover, investigations of the luminescent solar concentrator will result in new scientific insights in the areas of self-assembly, materials synthesis, and the photophysics of organic/inorganic materials. The potential value of these results in the applications arena is significant.

FY 2010 Results and Accomplishments

To direct synthetic efforts, we developed a simulation code based on Monte Carlo ray tracing techniques. We can use this code to track the fate of every photon entering a simulated device in order to isolate loss mechanisms and optimize parameters. To obtain a benchmark of performance, we simulated single-layer concentrators with CdSe/CdS quantum nanorods by using published absorption and emission data and variable Stokes shift and quantum yield (QY). The global optimization computations will be carried out on a supercomputer.

Nanoparticles (NPs) of CdSe ranging from 2 to 6 nm were synthesized by a high-temperature solution-based process. Small-angle x-ray scattering and transmission electron microscope (TEM) imaging were used to characterize the size distribution, which was found to be less than 5%. These monodisperse CdSe NPs were used as seed materials to further grow an anisotropic CdS shell (Figure 2) with a variable length and variable core size. Figure 2 shows absorption and emission spectra of the CdSe/CdS core/shell NPs with different sizes of emitting cores. Such systems demonstrate Stokes shifts up to 175 nm, thereby reducing self-absorption. Longer rods mean more relative absorption by CdS than by CdSe, thereby minimizing reabsorption.

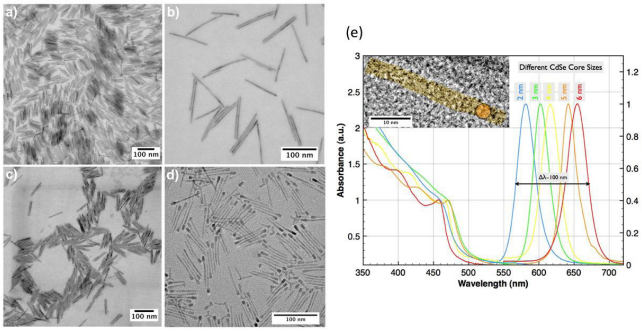


Figure 2. Transmission electron micrographs of CdSe/CdS core-shell NPs obtained with CdSe seeds of different sizes: (a) 3 nm, (b) 4 nm, (c) 5 nm, and (d) 6 nm. (e) Absorption and emission spectra of CdSe/CdS NPs with CdSe seeds of different sizes. Inset is a high-resolution TEM image.

Changing the CdS rod length has a dramatic effect on the QY. The reason for limited QY is likely related to the trapping of electrons and/or holes by defects on the surface of the CdS rods. To determine how this trapping competes with the desired transfer of the hole to the CdSe core, we measured transient absorption on a series of samples. We are currently trying to understand the complex charge-transfer dynamics and its relationship to the nanoparticle structure. The understanding we gain from studying these measurements will ultimately allow us to design nanostructures that can

efficiently transfer excitation energy from the shell to the core and then emit that energy as light to power solar cells.

Proposed Work for FY 2011

In FY 2011, we will continue the optical characterization of the nanostructures in order to understand the charge transfer and trapping mechanisms. We will use this information to design and synthesize nanocrystal heterostructures with greater QY and yet maintain minimal reabsorption. In addition, we will extend the synthesis and characterization to different material systems, which will allow the absorption and emission of light at longer wavelengths. Finally, we will incorporate the nanoparticles into a slab of material with a high refractive index, thereby constructing a single-layer concentrator. We will characterize the properties of the nanocrystals in this material, determine whether they are modified, and then characterize the overall performance of the single-layer concentrator.

Probing Catalytic Transient Intermediate in Ultrafast Time Domain

2010-167-N0

Di-Jia Liu and Lin X. Chen

Project Description

Catalyst development has traditionally been tedious and time-consuming. For practitioners in the field, catalyst synthesis is often regarded as "black magic" that can only be practiced after toiling for years to gain experience and know-how. To design a catalyst rationally, it is vital to gain the insight of the catalytic intermediate at the excited state so that the improved active site will have a lower potential barrier. In spite of various sophisticated characterization tools available at present, there is still an amazing lack of fundamental knowledge about the catalytic reaction pathway at the molecular level. To catch the catalyst "in the act," a characterization method must be in a time domain relevant to the molecular processes. The objective of this project is to explore and develop time-resolved spectroscopic techniques, such as transient spectroscopy, laser-initiated, time-resolved x-ray absorption spectroscopy (LITR-XAS), and terahertz spectroscopy. These techniques will be used to evaluate the time-dependent behavior of model catalytic systems and catalysts relevant to energy and environmental applications. The goal is to introduce the new ultrafast techniques that break the current time barrier for catalyst characterization and to open up a new frontier in structural and dynamic studies in catalysis.

Mission Relevance

This project is relevant to DOE's missions in energy and the environment. Catalytic processes account for nearly 20% of the U. S. Gross Domestic Product and impact more than 20% of all industrial products. Catalyst technology is widely applied not only in clean and affordable energy production, but also in environmental control and mitigation. All of these areas are directly linked to DOE missions. This project aims to develop innovative tools to promote better understanding, design, and discovery of catalyst materials.

FY 2010 Results and Accomplishments

The first LITR-XAS experiment was carried out at beamline 11-IDD of the Advanced Photon Source (APS). We focused on the homogenous catalytic system and investigated three organometallic catalyst systems, including triruthenium dodecacarbonyl [$Ru_3(CO)_{12}$], acetylacetonatobis(ethylene) rhodium [$C_9H_{15}O_2Rh$], and cyclopetadienyl molybdenum(II) tricarbonyl dimer [$C_5H_5Mo(CO)_3]_2$, respectively. These organometallic compounds are known mononuclear or multinuclear molecular catalysts, mainly for organic synthesis in the liquid phase and triggered by heat or light.

Photo-dissociation of $Ru_3(CO)_{12}$ is particularly interesting because it represents a molecular analog of a ruthenium metal cluster saturated with carbon monoxide during a catalytic reaction. We investigated the CO dissociation mechanism through x-ray absorption spectra (XAS) after ultraviolet (UV) laser excitation at different time delays. Shown in Figure 1(a) is the difference in absorption spectra against the background (ground state) at the delay of 100 ps and 300 ns. The largest difference in XAS was observed at the shortest time delay, suggesting that a significant change in the ruthenium coordination structure already occurred. During the photo-excitation, one or two CO ligands among the 12 available were dissociated from the triruthenium cluster. Furthermore, one Ru-Ru bond was cleaved. Such structural changes were partially recovered through the recombination of the Ru-CO and Ru-Ru bonds after excitation energy was dissipated through the interaction of the ruthenium-carbonyl cluster with the solvent, as is indicated in Figure 1(b).

Proposed Work for FY 2011

For FY 2011, we will fabricate and test a terahertz pump-probe system in the laboratory as a new way to excite the reaction through nuclear-electronic vibrational coupling. Once fabrication of the system is completed, we will investigate the transient spectroscopy by using a THz pump-optical probe on model catalytic systems, such as metal complexes and metal nanoparticles. We will also continue the LITR-XAS study by using the synchrotron at the APS.

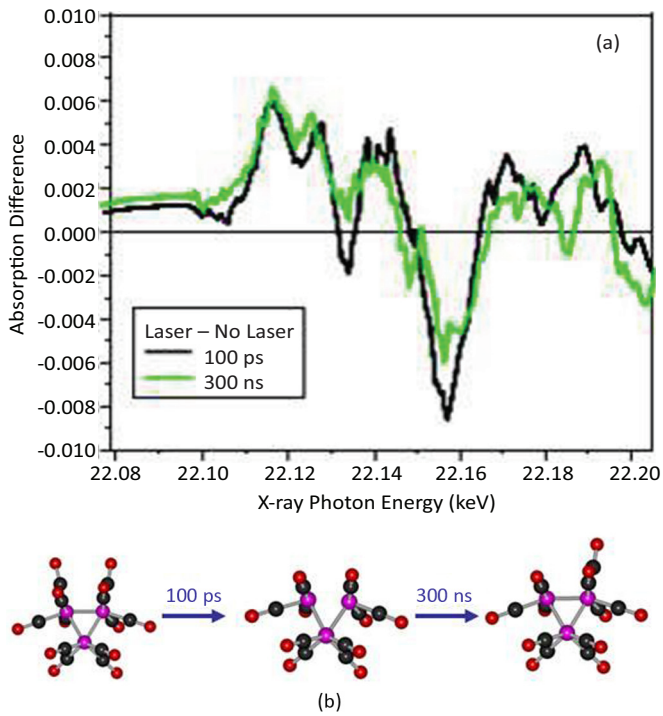


Figure 1. (a) Difference in x-ray absorption spectra with laser excitation at 100 ps and 300 ns delay and (b) the extrapolated structure of triruthenium carbonyl at ground state, 100 ps after excitation and 300 nm after excitation.

Refereed Publications

Chen, L., X. Zhang, J. Lockard, A. Stickrath, K. Attenkofer, G. Jennings, and D.-J. Liu, "Excited State Molecular Structures Captured by X-ray Transient Absorption Spectroscopy: A Decade and Beyond," *Acta Crystallographica* **A66** (2010), 240–251.

Homogeneous Catalysis of Water Oxidation for Photochemical Energy Storage

2010-184-N0

Marc J.A. Johnson and SonBinh T. Nguyen

Project Description

This project aims to design catalysts that can convert water into O_2 and H^+ in the so-called water oxidation reaction (Figure 1, left), a critical half-reaction in the production of H_2, a clean energy source, from water by using renewable energy sources, such as sunlight. The generated H^+ ion can then be reduced to hydrogen by an electron in a separate second half-reaction that is often called proton-coupled electron transfer (PCET).

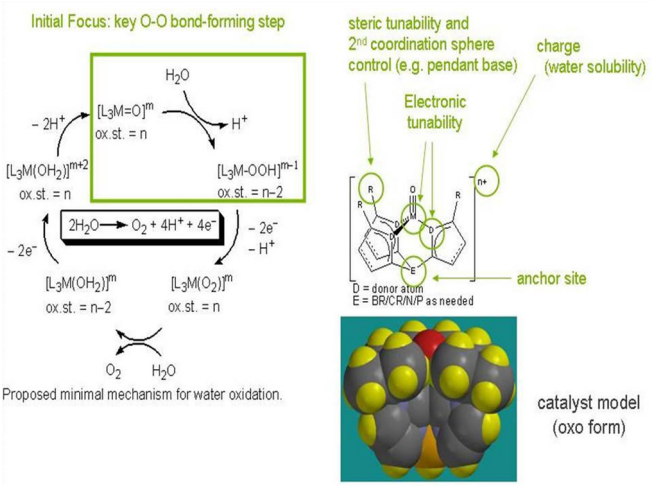


Figure 1. Left, the proposed mechanism for the oxidation of water into O_2. Right, a proposed intermediate for a tripodal metal-oxo catalytic intermediate that is capable of oxidizing water.

Mission Relevance

This project is relevant to DOE's missions in energy and science. The demand for H_2 in the United States is expected to increase significantly in the coming decades as we begin to refine more unconventional crude oil reserves, such as oil sand and oil shale. Although approximately 95% of the H_2 is currently produced by steam methane (natural gas) reforming (SMR), the United States does not have sufficient natural gas reserves to meet both the projected new demands for H_2, as well as current demands for natural gas to provide heat and generate power. Because SMR contributes to global climate change by producing 7.3 tons of CO_2 per ton of H_2 produced, it is one of the largest sources of greenhouse gas emissions (GHGs) in the chemical industry. To meet the future demands for H_2, new sustainable catalyst technologies that make use of feedstocks such as water and renewable energy sources (such as wind or solar) must be developed.

FY 2010 Results and Accomplishments

Work began in the laboratory to synthesize several tridentate ligands for our proposed catalysts. Catalyst precursors of the form $[M(L_3)L']^{n+}$, where (M = V – Cu; L' = H_2O, CO, Cl, Br, I, OH, O; n ≥ 0; see Figure 2), are being synthesized, beginning with known compounds, such as $Co(Tp^{t\text{-}Bu,Me})(I)$. In addition, computational modeling of the proposed metal-oxo catalytic intermediate (Figure 1, right side) was carried out, which shows the expected trend that these species prefer the singlet state and means it is favorable that these species will form O_2.

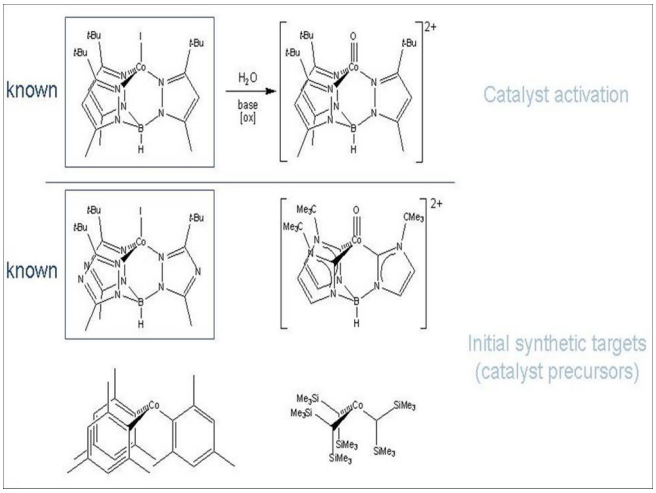


Figure 2. Representative catalyst precursors and how they can be activated to a metal-oxo intermediate.

Proposed Work for FY 2011

In FY 2011, we will survey the complexes we made this past year for activity in water oxidation in a number of solvents, including in the ideal solvent, water. The electrochemical behavior of all complexes will be measured by cyclic voltammetry (CV) to elucidate the factors that lead to high turnover number (TON) and turnover frequency (TOF). Catalyst decomposition products will be fully characterized and the mechanisms of their formation probed to learn how to prevent decomposition. New ligands and metal-ligand combinations will be prepared to test hypotheses that arise concerning the electronic and structural properties that govern longevity and TOF so that progressively more active and more robust catalysts can be prepared.

We will also begin to synthesize stronger-field bulky ligands in an attempt to identify what will cause the singlet state of our proposed metal-oxo catalytic intermediates to be more stable than the triplet. We plan to prepare and oxidize $Co(Mes)_3$ (Mes = 2,4,6-$Me_3C_6H_2$) or prepare and arylate $Co(O)X_3$. We will also prepare a ligand family that will provide only 5 L to nucleate an $M_4O_4L_6$ (L = bidentate ligand) cluster, such as $Mn_4O_4(O_2PPh_2)_6$, which, upon losing L, releases O_2 and can be re-oxidized. Finally, we will attempt to prepare LM_4O_4 for M = V to Ni. M_4O_4 clusters and larger clusters based on this subunit are showing up in heterogeneous catalysts for water oxidation that are analogous to the Co clusters discovered at the Massachusetts Institute of Technology.

Non-Refereed Publications and Presentations

Johnson, M.J.A., "Adventures with Fluorinated Ligands in Multiple-Bond Metathesis Reactions," presented at the Spring 2010 ACS (American Chemical Society) National Meeting, San Francisco, CA, March 22, 2010.

Johnson, M.J.A., "Homogeneous Catalysis at Argonne National Laboratory," presented at the Bar Ilan University – Argonne Workshop, Argonne, IL, October 12, 2010.

Johnson, M.J.A., "Synthesis, Reactivity, and Deactivation of Catalysts for Triple-bond Metathesis," presented at the 2010 Catalysis: Advances and Perspectives Workshop, Heidelberg, Germany, September 3–4, 2010.

Johnson, M.J.A., "Tuning the Reactivity of Metal-Element Multiple Bonds for Applications in Metathesis," presented at University of Edinburgh, Scotland, September 6, 2010.

Johnson, M.J.A., "Tuning the Reactivity of Metal-Nitrogen and Metal-Carbon Multiple Bonds: Applications to Metathesis," presented at University of Ottawa, Canada, October 6, 2010.

Johnson, M.J.A., "Tuning the Reactivity of Metal-Nitrogen and Metal-Carbon Multiple Bonds: Applications to Metathesis," presented at University of Chicago, IL, November 6, 2009.

Johnson, M.J.A., "Tuning the Reactivity of Metal-Nitrogen and Metal-Carbon Multiple Bonds: Applications to Metathesis," presented at Technical University of Munich, Germany, January 26, 2010.

Nguyen, S.T., "From Functional Supramolecular Chemistry to Metal-Organic Frameworks: Biomimetic Catalysts and Sensors," presented at Technical University of Munich, Germany, January 25, 2010.

Nguyen, S.T., "Metal-Organic Frameworks (MOFs) and Porous Organic Polymers (POPs) as Versatile Platforms for the Deployment of Homogeneous Catalysts," presented at the 2010 Catalysis: Advances and Perspectives Workshop, Heidelberg, Germany, September 3–4, 2010.

Nanoscale Architectures for Energy Storage

2010-188-N0

Tijana Rajh, Klaus Attenkofer,
Mahalingam Balasubramanian, Ralu S. Divan,
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Nenad M. Markovic, Elena Shevchenko,
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Project Description

The goal of our project is to develop novel nanoscale electrode materials for rechargeable Li-ion batteries to maximize power and energy density. Nanotechnology enables the surface of the electrode in a secondary battery to be coated with

nanoparticles, nanotubes and nanowires that are engineered at the molecular level. Electrodes made this way have the advantages of high surface area, short electronic and ionic transport length, and extraordinary mechanical strength. The high surface area of nanoscale electrodes leads to fast charge/discharge rates to enhance power density. The short transport length in these electrodes facilitates operation at high power because of the enhanced diffusion at the nanoscale. Moreover, nanoscale properties promote new reaction pathways that are not possible in bulk materials. We will focus on synthesis and characterization of nanomaterials with various morphologies (e.g., nanotubes, core/shell nanoparticles, and nanowires) for both positive and negative electrodes. In-depth understanding of the structure-performance relationship will be achieved for a variety of materials (e.g., TiO_2, FeO_x, MnO_x).

Mission Relevance

This project is in support of DOE's energy mission of fundamental research on electrical energy storage with a link to new energy technologies or technology roadblocks. This research is relevant to the planned DOE initiative "The Batteries and Energy Storage Hub" planned for 2011. This project focuses on solving the problems of energy storage and provides an interdisciplinary environment in which both basic and applied research will be simultaneously directed at the research challenges facing energy storage.

FY 2010 Results and Accomplishments

In this project, we have developed nanoscale electrodes in the forms of nanotubes (TiO_2, V_2O_5, FeO_x, o.d. 50–60 nm), nanowires (Mn_2O_3, diam 8–12 nm), and core/shell nanoparticles (Co/CoO, Fe/Fe_2O_3, diam 10 nm) for Li batteries. We fabricated the electrodes by using electrochemical approaches that result in molecular-level connectivity of all battery components. Because of this molecular connectivity, high electrical conductivity of the battery components was achieved. Also, as the electrodes and inter-gap regions are on the nanoscale, we achieved high ionic conductance and complete intercalation owing to their small diffusion path. Synthesis of hollow nanoscale structures enabled improved elasticity and accommodated electrode expansion. We found that all nanostructured electrodes investigated have reversible capacities close to theoretical values, with much better performance than conventional electrodes (Figure 1). Interestingly, when amorphous TiO_2 nanotubes were used as electrodes, we observed capacity increase with cycles during rapid cycling. The samples were characterized by synchrotron x-ray diffraction, x-ray fine-structure spectroscopy, and transmission electron microscopy (TEM). All cells investigated show fast charging/discharging with near-theoretical capacities and high coulombic efficiency. The electrode demonstrates a long cycle life (over 500 cycles). A study of Liion diffusion in TiO_2 structures was carried out by using molecular dynamics and density functional theory calculations with a classical interaction potential, to obtain insights into the dynamical properties of Li-ion transport in anatase and amorphous titania.

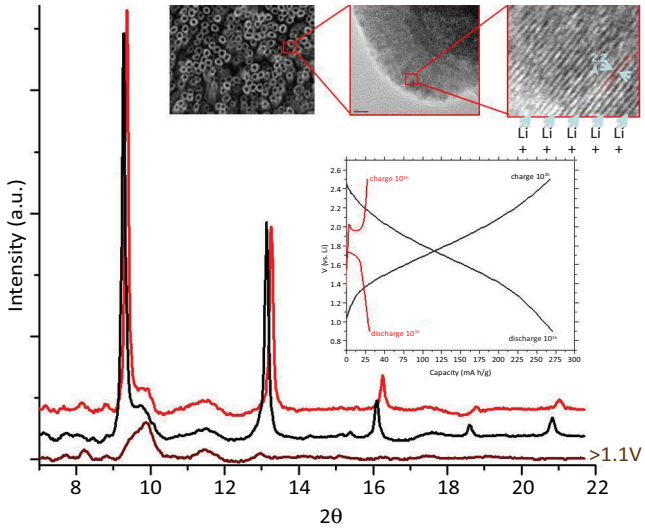

Figure 1. Charge-discharge curves of new TiO_2 nanotube electrode (black) compared to TiO_2 conventional electrode (red) after 10 cycles, in conjunction with morphology (SEM) and structure (HRTEM) of high-performance, electrochemically active nanotubes after 100 cycles. Ex situ *synchrotron XRD measurements at the discharged (red) and charged (black) stages after 100 cycles show formation of crystalline structure upon cycling.*

Proposed Work for FY 2011

During FY 2011, we will integrate nanoscale anodes (TiO_2, Fe_2O_3) and cathodes (V_2O_5 and MnO_2) into all of our nanoscale batteries and investigate the solid-state electrolytes that can accommodate small inter-gap regions. We will also focus on alternative battery concepts beyond the existing Li-ion battery, such as Be- and Mg-ion-based cells. We have already shown that all nanoscale anodes and cathodes investigated can operate with Na transporting ions — with even larger capacities, in some cases. We expect that our electrochemical methods for preparation of nanoscale electrodes will allow for electrodes that can operate with divalent transporting ions (such as Mg and Be). We will try to apply x-ray nanoprobe techniques to monitor the fate of Na and Mg transporting ions during cycling.

Non-Refereed Publications and Presentations

Xiong, H., C. Johnson, and T. Rajh, "Three Dimensional Architectures of Metal Oxide for Li-ion Batteries," presented at the 218th ECS (Electrochemical Society) Fall Meeting, Las Vegas, NV, October 10–15, 2010.

Process Engineering Research for Scalable Energy Storage Materials

2010-191-N0

Gregory K. Krumdick, Ilias Belharouak, and Zhengcheng Zhang

Project Description

The specific objective of this project is to conduct process engineering research to demonstrate scalable process development for energy-storage materials. Process engineering research is needed to identify and resolve process and material constraints on the development of scalable processes for advanced battery chemistries. As the complexity of advanced-battery chemistries increases to achieve multiple performance goals for both mobile and stationary applications, concurrent process engineering research is required to ensure that these materials can be consistently and cost-effectively manufactured for applications that would need a high volume of materials. We have initiated process R&D to identify and resolve scale constraints and propose to demonstrate the process scalability of two battery materials: lithium-ion battery electrolyte materials (which includes electrolytes and electrolyte additives) and high-capacity cathode materials.

Mission Relevance

This project is relevant to DOE's energy mission. This project is relevant to the Vehicle Technologies Program of the Energy Efficiency & Renewable Energy Program in the development of more energy efficient and environmentally friendly highway transportation technologies that will enable America to use less petroleum. The need for systematic process engineering research to support the scale-up of advanced battery chemistries and materials has been clearly recognized by stakeholders

FY 2010 Results and Accomplishments

Development of electrolyte materials process scale-up and system design. While the initial project was to scale up 1NM3 electrolyte, shortly after we started work on this project, interest shifted to an electrolyte additive, ANL-RS2. This additive is seen as having greater initial impact on prototype-battery manufacturing. We assessed the initial process for production of ANL-RS2 and concluded that certain steps developed at the bench scale were not scalable because of the high volumes of hazardous chemicals used. Furthermore, we determined that running the process at scale using these chemicals would not be economical. Several possible alternative processes were designed and are being tested at the bench scale.

Mini-pilot-scale assembly for electrolyte-materials development. An electrolyte materials scale-up laboratory was established. Process equipment for 1–10-L (liter) batches, as well as the necessary analytical equipment, was ordered. Argonne's fire-protection subject-matter experts were consulted and guidance was provided to allow for the use of the volumes of flammable solvents needed for scaling up batch processes to the 1–10-L range.

Development of cathode materials process scale-up and system design. A system was designed for the production of 1- to 10-kg (kilogram) batches of cathode materials and equipment was specified for this target batch size. Upon completion of this task, it became evident that the bench-scale process required additional unit operations for generating more than 1 kg of material. The required unit process operations included water-content control during the calcination step and material processing methods that would not alter the particle morphology. These advances were incorporated into the system design.

Order and receive materials for cathode materials system. After the design of the cathode materials processing system was completed and equipment quotes were received, DOE reviewed the status of the work and indicated that continuation of this work would be funded under a DOE project.

Proposed Work for FY 2011

In FY 2011 we will conduct process engineering research for scale-up of a new electrolyte-additive material, ANL-RS2. Up to this point, ANL-RS2 has only been synthesized in small batches by using 1–5-L vessels, which produce approximately 200 mL of material. The current process is labor-intensive and time-consuming, requiring approximately 1–2 weeks of a skilled chemist's effort to produce 200 mL of material. Scaling up the process involves (1) modification of the bench-scale process chemistry to allow for the continuous production of ANL-RS2, (2) development of a process engineering flow diagram, (3) development of a mini-scale system layout, (4) fabrication of the experimental system, and (5) experimental validation of the optimized process. The mini-pilot-scale system will use an existing synthesis reactor system. Electrolyte materials produced will be analyzed to confirm material properties.

FY 2011 milestones include the following:

- Development of electrolyte materials process scale-up and system design.
- Development of a mini-pilot-scale system for electrolyte materials development.
- Process optimization for development of the electrolyte-materials batch process.

Microscopic Building Blocks of a Better Lithium-Ion Battery

2010-192-N0

John Mitchell and Qiyin Lin

Project Description

The microscopic mechanisms underpinning the operation of lithium-ion batteries are largely a mystery. The objective of this project is to shed light on these fundamental mechanisms with an eye toward improving materials design for next-generation systems. To achieve this goal, we will create model systems based on bulk crystals, with highly controlled structure, stoichiometry, and surfaces. We will then exploit the spatio-temporal capabilities of x-ray, electron, and neutron probes to microscopically visualize electrochemical phenomena in these model systems. Rigorous evaluation of these results will validate models and provide insights into effective ways to modify these systems to improve Li-ion transport.

Mission Relevance

This project is relevant to DOE's missions in science and energy because it directly addresses fundamental aspects of the electrical energy storage (Li-ion battery) programs at Argonne and sister national laboratories. Liquid fuels use chemical bonds to efficiently *store* energy (energy density) and to *deliver* it rapidly (power density), presenting two significant barriers for competing approaches. Despite the inherent advantages of chemical bonds, the past two decades have shown that innovative electrochemistry and the use of nanomaterials can bring the energy density of Li-ion batteries to within an order of magnitude of liquid fuels. Parallel increases in the power density that battery technologies can deliver remain a high priority for research on novel storage materials. This challenge must be addressed to realize the vision of electric vehicles, plug-in hybrids, and other new vehicle technologies, which require rapid charge/discharge cycling to be a competitive element of a future U.S. energy portfolio free from reliance on fossil fuels.

FY 2010 Results and Accomplishments

We focused exclusively on crystal-growth activities in preparation for characterization work that we will phase in during the remainder of the project. Specifically, we grew crystals and performed structural and electrochemical characterization of two model systems: $LiFePO_4$ (LFPO) and $LiCoO_2$ (LCO), both of which are established battery compounds. LFPO is an olivine, whose structure is characterized by one-dimensional tunnels parallel to the b-axis (Figure 1). Li ions have been shown to preferentially migrate through these tunnels during electrochemical charge/discharge processes. We used two approaches for the growth of LFPO: floating-zone and self-flux growth methods. Using the former technique, we succeeded in growing ~1-cm-long pieces that were verified by x-ray diffraction to be monodomain; that is, a single crystal. The latter technique yielded crystals that are smaller (a few millimeters), but whose surfaces look extremely smooth; these crystals will be used for x-ray scattering studies of the lithium surface configuration *in situ* during charging/discharging. Large (~1 mm), black crystals of LCO that are tens of micrometers thick were grown with lattice structure consistent with literature reports. We began preliminary electrical characterization of the LCO crystals in standard electrochemical coin cells. The charging curve is shown in Figure 2; it compares extremely well to standard curves from the literature measured on polycrystalline samples. Important features of the LCO system are the phase changes upon delithiation in Li_xCoO_2, which were correlated with the literature as follows: trigonal I in $0.94<x<1$; trigonal I + trigonal II in $0.94>x>0.75$; trigonal II in $0.75>x>0.5$; monoclinic in $x=0.5$, which is attributed to a lithium/vacancy ordering; and trigonal II in $x<0.5$. These results are extremely encouraging and provide the baseline data needed to move to the next step in the project.

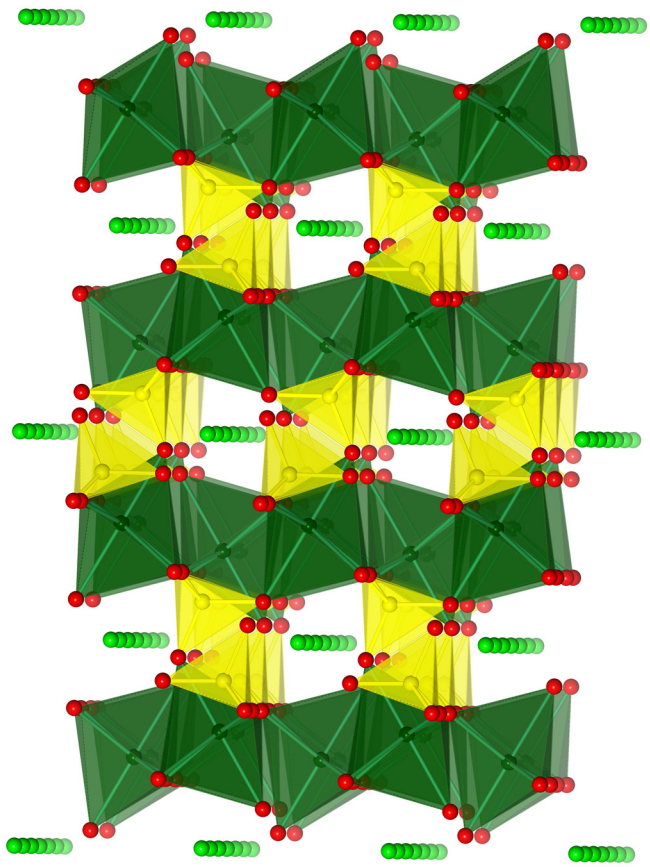

Figure 1. Olivine $LiFePO_4$ crystal structure.

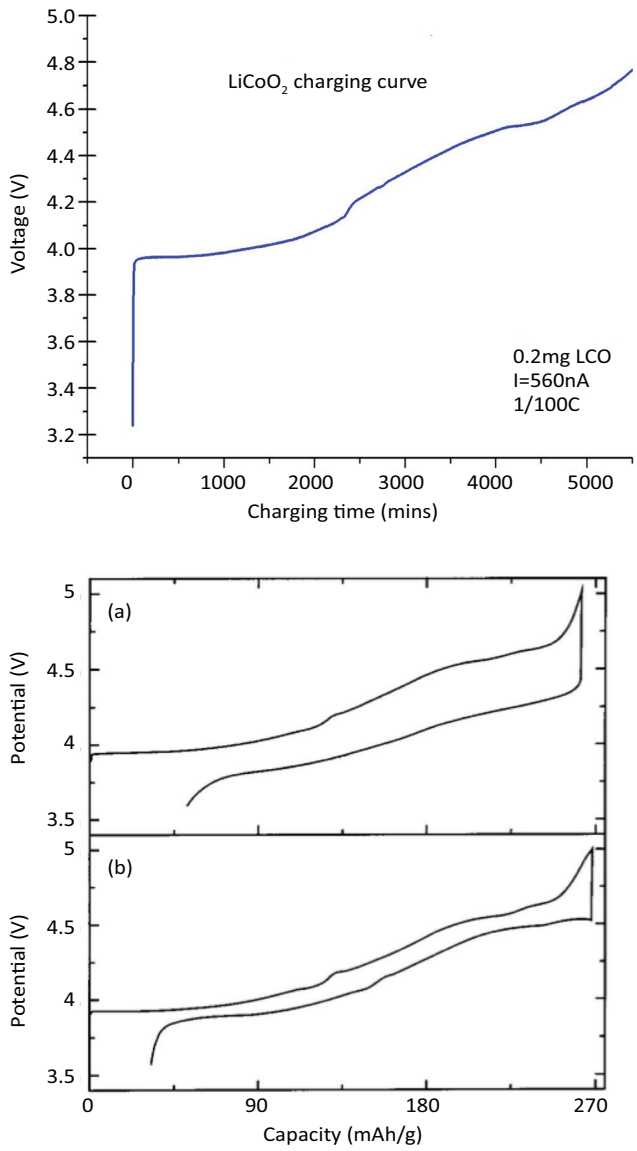

Figure 2. (Top) Electrochemical cycling of $LiCoO_2$ crystals in a coin cell. (Bottom) Data measured on powders. Adapted from Figure 1 of Z. Chen et al., J. Electrochem. Soc. ***149**, A1604 (2002).*

Proposed Work for FY 2011

We will use our crystals in electrochemical cells designed for single-crystal battery studies to undertake *in situ* studies using x-ray probes through peer-reviewed proposals at the Advanced Photon Source. We will specifically target microscopic structural and electronic changes at the transition metal (Fe or Co) site during the charge/discharge process. We will also work with Oak Ridge National Laboratory scientists to explore real-space probes, such as scanning probe and atomic force microscopy, of lithium motion in and out of the crystals.

Atomistically Informed Mesoscale Simulation of Gradient Nuclear-Fuel Microstructure

2010-196-N0

Dieter Wolf

Project Description

Building on mesoscale modeling work on irradiation effects in nuclear materials, in this project we will incorporate the effects of the *temperature and stress gradients* present across all nuclear fuel into a computational framework based on the phase-field model. Gradients in temperature and stress across a fuel pin provide the driving forces, for example, for thermo-migration of voids and gas bubbles, directional grain growth, and alloy-species migration (the so-called Soret effect). These processes in turn give rise, for example, to changes in phase behavior, gas bubble-induced grain refinement near the fuel surface (the so-called rim effect) and enhanced grain growth under irradiation near the center of the pin. All of these affect the thermo-mechanical behavior in a negative way. Incorporation of gradient effects into a mesoscale model requires knowledge of the underlying atomic, void, and gas-bubble mobilities. These mobilities will be determined by molecular dynamics (MD) simulations on molybdenum (Mo) as a model metal fuel and uranium dioxide (UO_2) as a model oxide fuel material. Together with other material properties, they provide the input to the mesoscale phase-field code to be developed.

Mission Relevance

This project is relevant to DOE's mission in energy — more specifically, nuclear energy. Because traditional nuclear-fuel performance simulations are based on incorporated empiricism, they have little predictive capability in regimes for which no test data exist (e.g., under transient conditions in the reactor). The same holds for simulations of materials degradation under irradiation and in corrosive environments. The first step toward making these simulations more predictive is to incorporate materials microstructure into engineering performance codes. Based on a materials science-nuclear engineering scale-linkage approach, next-generation fuel-performance codes will ultimately provide higher-fidelity predictions of overall system performance. In addition, they will begin to enable predictions of fuel and safety performance under transient conditions and thus provide a valuable modeling tool for the development of more reliable and safer nuclear materials.

FY 2010 Results and Accomplishments

This project was active for the final two months of the fiscal year. Computer time on Argonne's Fusion cluster was secured and initial MD test runs were performed on UO_2. These simulations aim to elucidate point-defect evolution in single crystals under different radiation conditions. Initial results revealed the formation of large defect clusters involving radiation-induced interstitials and vacancies on both the uranium and oxygen sublattices.

Proposed Work for FY 2011

We will incorporate stress- and temperature-gradient terms as driving forces into our phase-field code; this objective will require simultaneous solution of the phase-field equations and stress calculation on an evolving, adaptively refined mesh. This effort will subsequently enable us to determine the microstructural gradients (e.g., in the grain- and void-size distributions) that develop after the application of a temperature gradient across a two-dimensional model fuel pin.

We will perform MD simulations of irradiation-induced defects and defect clustering in body-centered cubic Mo and UO_2 as model metallic and oxide fuel materials; these simulations will provide the necessary input parameters to the mesoscale simulations that are being developed in parallel.

Controlled Heterogeneity of Materials for Energy Applications

2010-197-N0

Marius Stan

Project Description

Materials for energy applications, such as nuclear fuels and electrical batteries, are multi-component ceramics or alloys that are subjected to extreme radiation, temperature, and chemical environments during their manufacturing, use, and storage. Changes in composition and micro (nano)-structure cause the properties to evolve with time and can severely impact performance. However, the heterogeneous character of the materials (that is, the presence of multiple phases with distinct properties) makes it difficult to understand and control their properties.

In this work, we will develop theoretical models of heterogeneity and perform advanced transport simulations to understand and control materials properties during synthesis and operation. Moreover, we hypothesize that in some instances, controlling heterogeneity can lead to improved materials properties, creating the framework for developing materials that are "heterogeneous by design." For this purpose, we will develop a state-of-the-art theoretical and computational tool kit for the analysis of heterogeneity at the micro- and nano-scale levels in nuclear fuels and solid electrolytes for batteries. Then, by performing simulations of heat, chemical and electrical transport in selected meso (nano)-structures (grains, interfaces) for a variety of heterogeneous features (point-defect clusters, pores, gas bubbles, cracks), we will identify the optimal structure and assist the design and synthesis of the materials.

The scientific objectives of this project are: (1) to understand the effect of heterogeneity at the micro(nano)-scale on the thermal, chemical, and electrical transport properties of materials and (2) for a given material, to determine the micro(nano)-scale heterogeneous features that correspond to the optimal thermal, chemical, and electrical transport properties.

Achieving these objectives will assist the design and synthesis of nuclear fuels capable of maintaining high thermal conductivity at high temperatures and burnup levels and the design and synthesis of materials capable of storing more energy while maintaining stable electrode-electrolyte interfaces.

Mission Relevance

The project opens a new area of research centered on materials that are "heterogeneous by design." It has the potential to accelerate the development of new materials for a variety of applications, such as nuclear energy and energy storage. The project fosters theoretical and computational work resulting in new models, methods, and algorithms. It will also propose innovative design experiments that can transform the understanding of materials, thus moving materials science from observation and analysis to prediction and control. All these elements benefit both basic and applied energy-related scientific research and are well aligned with the missions and strategies of the DOE Offices of Science and Nuclear Energy. The project will serve as seed for a multi-scale (atomistic, meso-scale, and continuum) high performance materials simulation program at Argonne.

FY 2010 Results and Accomplishments

During FY 2010, a simulation domain consisting of a cylindrical uranium oxide (UO_2) fuel pellet and steel cladding separated by a helium gap was set up using the software COMSOL Multiphysics, which provides an ideal tool for studying coupled phenomena and allows for mesh refinement in 3-D configurations. In this fuel element, we solved for the coupled equations describing thermal expansion of the fuel pellet and steel cladding, heat transport, and oxygen diffusion. The fuel pellet and steel cladding were allowed to expand freely in the radial direction. A moving-mesh application in the Lagrangian–Eulerian formulation was used to account

for the changing gap size with thermal expansion of the fuel and the cladding. The heat transport in the gap was approximated using an effective thermal conductivity model. Dirichlet (fixed-value) boundary conditions were imposed on the temperature at the cladding outer surface, while Dirichlet or Neumann (zero-flux) boundary conditions were used for oxygen diffusivity at the fuel pellet outer surface. In this work, the models of the materials properties were obtained from published correlations or from analysis of published data. The initial simulations of heat transport in UO_2 showed that a meso-scale void can change the local temperature by more than 100 K.

Proposed Work for FY 2011

We will further study the effect of the size distribution, position, shape, and orientation of meso-scale heterogeneous features — such as grain boundaries and interfaces — on the heat, chemical, and electronic transport phenomena in UO_2.

Near-Term Spent-Nuclear-Fuel Disposal Using an Accelerator-Driven System

2010-201-N0

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Project Description

The first objective of this project is to characterize and develop an innovative approach for disposing of the spent nuclear fuel (SNF) inventory of the United States. The U.S. commercial SNF inventory, currently at ~60,000 MT, is growing by ~2,000 MT per year. It is estimated that the inventory will reach 70,000 MT by 2015 and a total of 120,000 MT over the lifetimes of the currently operating commercial nuclear power plants. The SNF contains ~1% transuranics (~700 MT), including ~40 MT of minor actinides (MA). The proposed accelerator-driven system (ADS) is intended to transmute/fission the MA, thus eliminating the long-term radiotoxicity of the SNF. A fraction of the SNF plutonium will be used with the SNF MA to reduce the elimination cost and to accelerate the elimination time. The other fraction of the SNF plutonium will be used as MOX (mixed oxide) fuel in current/future light-water power reactors or as a starting fuel for future fast power reactors. The uranium from the SNF will be recycled for use in future nuclear power plants. The short-term fission products will be stored for ~ 300 years to reduce their radiotoxicity by decay to that of the natural uranium ore. The proposed disposition scenario for the SNF uses the elimination approach, which is the option recommended by the U.S. National Academy of Sciences for disposition of excess weapons-grade plutonium. The proposed ADS makes use of existing, proven technology as much as possible with minimum extrapolation, so it will be possible to deploy such a system in the near term.

Mission Relevance

In support of DOE's energy mission, our proposed system provides a disposal solution for SNF, a potential path for breeding fissile material from uranium-238 or thorium, and another approach for a sustainable non-carbon-based energy source in the future. This system significantly reduces the required geological repository capacity for nuclear waste and eliminates the need for a large storage facility, such as Yucca Mountain.

FY 2010 Results and Accomplishments

During FY 2010, we started to define the main system parameters to dispose of U.S. SNF accumulated up to 2015 from nuclear power plants. The system utilizes a few accelerator-driven subcritical systems driven by spallation neutron sources. The subcritical core used a mobile fuel without uranium for utilizing the transuranics and transmuting some long-lived fission products. The definition of the design concept, including the assessment of the required validating R&D, is under way.

We developed a concept for the 1-GeV/10-MW proton linac. The high-energy section of the high-power proton linac, above ~500 MeV, can be based on elliptical superconducting cavities like those at CEBAF (Continuous Electron Beam Accelerator Facility, Thomas Jefferson Lab) and SNS (Spallation Neutron Source). The front end of a 10-mA CW proton linac, up to 500 MeV, can be based on TEM (transverse electromagnetic)-class superconducting accelerating structures developed primarily at Argonne in the past decade.

Proposed Work for FY 2011

The plan for FY 2011 is to characterize and develop this innovative system, determine its performance, define the required R&D, and propose a work plan to address the R&D. System studies, neutronics, thermal hydraulics, mechanical design, material selection, chemical engineering design and analyses, and accelerator assessment and design will be carried out to perform the system development and the analyses. Argonne computer clusters and the new energy simulators for nuclear-systems design and analyses will be utilized for performing these activities.

Front-end processing activities will center on developing technologies that (1) recover the MA and a fraction of the plutonium from SNF for transmutation in the ADS and (2) produce a uranium-plutonium product that can be used in nuclear power reactors.

Regarding the accelerator, we will develop a layout for a CW superconducting linac with a proton-beam energy of 1 GeV

and beam power of 10–20 MW (10–20 milliamperes) and identify any remaining R&D required to be completed before finalizing the design of this driver. This effort will include studies of system reliability and control issues.

In addition, demonstration experiments on the main components will be defined and analyzed. The goal of this activity is to prepare for the development of a device to obtain the necessary experience for developing and building such systems in the near term.

Non-Refereed Publications and Presentations

Ostroumov, P., "Concept for 1 GeV/10 MW Superconducting Proton Linac for ADS," invited talk presented at the 1st International Workshop on Accelerator-Driven Sub-Critical Systems and Thorium Utilization, Blacksburg, VA, September 27–29, 2010.

The Rational Synthesis of Kinetically Stabilized, Higher-Order Inorganic Materials for Catalysis

2010-202-N0

Adam S. Hock and Theodore R. Krause

Project Description

The objective of this project is to synthesize ternary chalcogenides for photon-harvesting applications by atomic layer deposition (ALD) and to evaluate the effects of chalcogenide substitution upon the physical (e.g., grain size, lattice structure, morphology), photoelectronic (e.g., photon absorption energy efficiency, carrier concentration, and mobility), and catalytic properties. The goal is to develop new materials for harvesting solar photons and generating electricity that are more efficient than the current generation of commercial materials, which are 10–20% efficient, thus reducing the cost of solar-produced electricity.

Mission Relevance

This project supports DOE's missions in energy and science. It is well understood that major challenges exist to the large-scale adoption of solar energy as a significant contributor to our energy sources, whether it is used to directly generate electricity (photovoltaic devices) or whether the photon energy is used to drive chemical reactivity (photoelectrochemical devices). New technologies in photon harvesting, such as dye-sensitized, nanocrystalline, and organic solar cells, all suffer from problems related to low efficiency, sintering, and bleaching. By comparison, inorganic materials, such as ternary chalcogenides, are far more robust physically and photochemically than their organic counterparts.

FY 2010 Results and Accomplishments

This project was active for the final two months of the fiscal year. Thus, the major activity focused on establishing laboratory facilities to conduct the experimental work and specifying and ordering an atomic layer deposition (ALD) apparatus.

Proposed Work for FY 2011

Thin films of Group 4 or 5 mixed chalcogenides, MA_xB_y (M = Ti, Zr, Hf; A ≠ B = O, S, Se), will be prepared by low-temperature ALD synthesis techniques that make use of known precursors of ML_x [L = $N(CH_3)_2$, NMeEt; x = 4] coupled with varying pulse cycles of H_2A and H_2B. The primary objectives will be to understand the effect of the composition (i.e., the O/S/Se ratio as a function of film thickness) and process conditions (i.e., deposition temperature during the ALD synthesis and post-deposition treatment) on the photoelectrical properties (conductivity and photoconductivity, Hall effect, photoluminescence, photocatalysis) of these materials. The O/S/Se ratio of these thin films will be systematically varied as a function of film thickness by varying the pulse sequence of H_2O, H_2S, and H_2Se. The films will be prepared at various deposition temperatures during ALD synthesis and subjected to a range of different post-deposition treatments. The thin films will be characterized compositionally, structurally, and photoelectrically.

The bulk composition of thin films (especially the impact of deposition conditions on the ratio of A to B) will be determined by Rutherford backscattering spectrometry and the structure of the film by x-ray and/or electron diffraction. Scanning electron microscopy and ellipsometry will be used to characterize film thickness and morphology. Optical band gaps will be determined as a function of film composition.

Non-Aqueous Flow Battery for Stationary Energy Storage

2010-203-N0

Andrew Jansen, Zonghai Chen, Christopher Johnson, and John T. Vaughey

Project Description

The current state-of-the-art battery systems for stationary energy storage have round-trip energy efficiencies of ~75%, which means that 25% of the diverted "excess energy" is wasted. Minimizing this large energy loss would greatly enhance the dispatchable energy rating of renewable-energy systems, like wind and solar. A non-aqueous flow battery system, we believe, could become the next revolutionary step in large-scale energy storage on the basis of its similarity to

present-day lithium-ion batteries, which have proven energy efficiencies near 95%. The main goal of this novel high-risk/high-reward task is to create a new stationary storage-battery system based on a non-aqueous electrochemical flow system that has a high round-trip energy efficiency (>90%), remains liquid, and operates near ambient conditions. The unique feature of this flow-battery idea is its non-aqueous character, which enables the use of novel cell couples that have voltages of 2–5 V. Also, a higher-voltage cell is a major improvement over a lower-voltage cell; less current or fewer cells are needed for the same power. This feature has a strong impact on the hardware cost and reliability of the complete flow-battery system.

Mission Relevance

This project is relevant to DOE's energy mission. Electrical energy storage for grid stability and wide-scale integration of renewable energy desperately needs a new generation of high-performance flow batteries. This battery effort will support the DOE-Office of Electricity's mission to modernize the electric grid, enhance security and reliability of the energy infrastructure, and facilitate recovery from disruptions to the energy supply. It will also help enable the DOE-EERE's mission of 20% wind energy by 2030.

FY 2010 Results and Accomplishments

This year's effort was spent in the search for candidate species for the positive and negative electrodes that are electrochemically active. The selection of these species is based on their electrochemical potential, reversibility, safety, physical properties, and cost. In an ideal system, both species are liquids and are immiscible. Most of the species explored in this project were solids that were then dissolved in organic solvents (such as propylene carbonate, ethylene carbonate, and gamma butyrolactone). This work used Li^+ as the cation, but other simple alkali metal ions, such as Na^+ and K^+, could most likely be used. An initial preference was given to lithium ions because of their widespread use in lithium-ion batteries, with the expectation of later transitioning to sodium or potassium-based systems, since these elements are extremely abundant.

For the negative electrode, numerous species were investigated that fall into the following general chemical groups: metal alkoxides, naphthalene-based compounds (including their derivatives and azeotropes), carboxylate-derivatized conjugated organic systems, and tri-substituted boron-based Lewis acids. Some redox activity was seen for methylcoumarin, methylquinoline, and dimethyl-pyrroline-*N*-oxide. Redox activity was also seen with bipyridyl and phenanthroline complexed with iron and nickel cations. A few of these species had redox peaks between 1 and 2 V versus the lithium potential, which is the target potential window for the negative electrode. Below 1 V versus lithium is not expected to be practical, because of the irreversible chemical reduction of the solvent molecules.

The choice of electrochemically active species that could be considered for development as the positive electrode includes derivatized metal organic ring systems, heteroatom-substituted ring systems, NO-based radicals, and lithium-boron-containing clusters. Many of these ring-based species have already been explored for overcharge protection in lithium-ion batteries. In this project, we investigated a few more that contain fluoride on the rings. An example of a candidate cell couple for a non-aqueous flow battery that resulted from this effort is shown in Figure 1, where the negative electrode is iron (II+) complexed with phenanthroline and the positive electrode is a fluorinated biphenyl borate. As can be seen from this figure, a cell voltage of 2.5 V can be obtained, which is twice that of typical aqueous flow batteries.

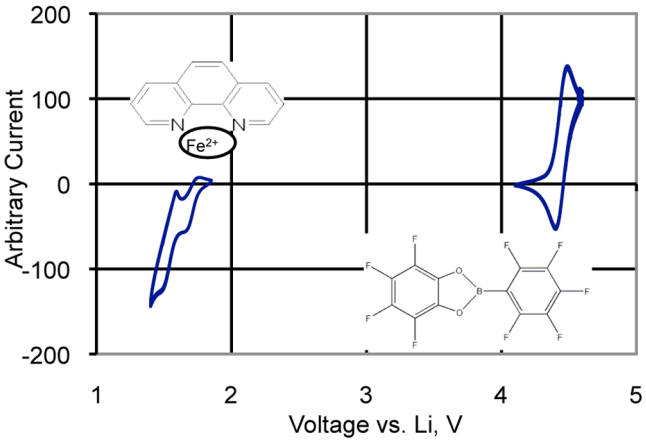
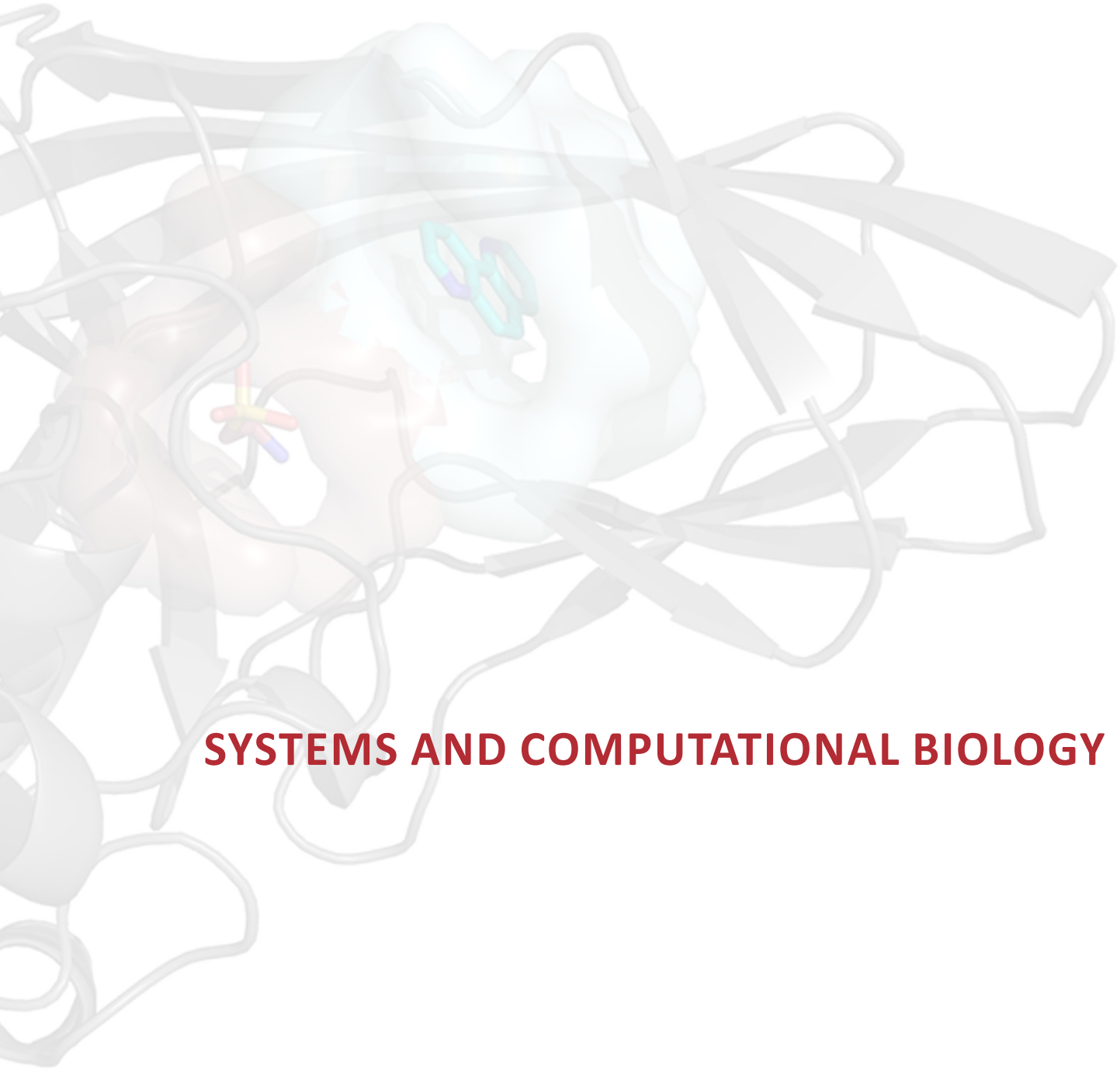


Figure 1. Candidate couple for a non-aqueous flow battery with a total cell voltage of 2.5 V.

Non-Refereed Publications and Presentations

Jansen, A., J. Vaughey, Z. Chen, and C. Johnson, "Exploratory Research of Non-Aqueous Flow Batteries," presented at ANL/PNNL Workshop on Energy Storage, Argonne, IL, November 18–19, 2010.



SYSTEMS AND COMPUTATIONAL BIOLOGY

Stabilization of Subsurface Contaminants through Augmentation of Natural Biological and Geochemical Processes

2008-124-R2

Kenneth M. Kemner, Dionysios A. Antonopoulos, Folker Meyer, and Edward J. O'Loughlin

Project Description

Often projections about the performance of subsurface remediation techniques and long-term stewardship strategies are based on knowledge about the mechanisms of natural chemical transformation and about the transport behavior of subsurface contaminants that is insufficient. The activity of subsurface microbial communities, in addition to having geochemical effects on transport, can have a profound effect on the mobility of subsurface contaminants. Argonne's unique capabilities in high-performance computing, synchrotron-based measurements, and high-throughput methods for analyzing biomolecules, together with the expertise of its scientific staff, offer a unique opportunity to use high-performance computing in metagenomic studies — together with synchrotron-based experimental approaches — to study biogeochemical cycling, particularly as it relates to physical and chemical transformations of contaminants in both laboratory- and field-based systems.

In this project, we have been conducting batch experiments to demonstrate the feasibility of integrating metagenomic studies of subsurface microbial communities. The goal is to elucidate natural biogeochemical processes that can be augmented to help stabilize subsurface contaminants. To achieve that goal, we have used two of Argonne's unique resources: high-performance computing, which enables rapid data analysis to identify active microbial processes, and the Advanced Photon Source (APS) to make geochemical measurements of subsurface processes. The work includes studies of the (1) evolution of a natural microbial community, (2) speciation of iron (Fe) and sulfur (S), and (3) transformations of uranium (U) within sediment collected from a contaminated DOE site, as the sediment is biostimulated with the addition of an electron donor and augmented with an electron shuttle.

Mission Relevance

This project is relevant to DOE's environmental mission. DOE oversees some of the largest environmental cleanup operations in the world. The processing of uranium for nuclear power and weapons during the Cold War era left an enduring legacy of contaminated soils, groundwater, and other environmental media. Innovative solutions are needed to clean up, manage, and monitor contamination at DOE sites. The knowledge and capabilities that result from this work will directly apply to issues related to remediating contaminated subsurface environments. These issues and ways to address them are the focus of several DOE programs, including the Subsurface Biogeochemical Cycling Program called "Genomic Systems Science Program", and a future Knowledgebase/Exascale Computing Initiative.

FY 2010 Results and Accomplishments

Progress included the continued development of a molecular microbiology laboratory with many capabilities required to extract, concentrate, and initially characterize deoxyribonucleic acid (DNA) from natural subsurface materials before they are provided to the University of Chicago's Institute for Genomics and Systems Biology (IGSB) for analysis of the microbial community. We performed test runs on the operation of a gas chromatograph used to analyze hydrogen in these systems. We initiated a new series of biostimulation experiments in batch reactors on Fe-rich materials in the presence and absence of an electron shuttling compound (Figure 1). The materials were inoculated with sediment from a DOE field site (Old Rifle UMTRA-IFC [Uranium Mill Tailings Remedial Action Project at an integrated field challenge site in Rifle, Colorado]). Sediment suspensions were extracted from these experimental systems about every 24 hours for two months. We extracted DNA from and ran terminal restriction fragment-length polymorphism (TRFLP) analyses on all of the samples to gain insight on the evolution of the microbial community. Wet chemical analysis approaches were used to determine Fe(II) production and acetate consumption in the samples; results indicated that the onset of Fe reduction was coincident with acetate consumption. Additional characterization of the sulfate consumption in these systems was also performed. We also characterized the speciation of U that was added to each of the batch reactors with x-ray absorption spectroscopy. Results identified the partial reduction of U. Additional characterization of Fe and S solid-phase speciation with synchrotron radiation at the APS was also performed.

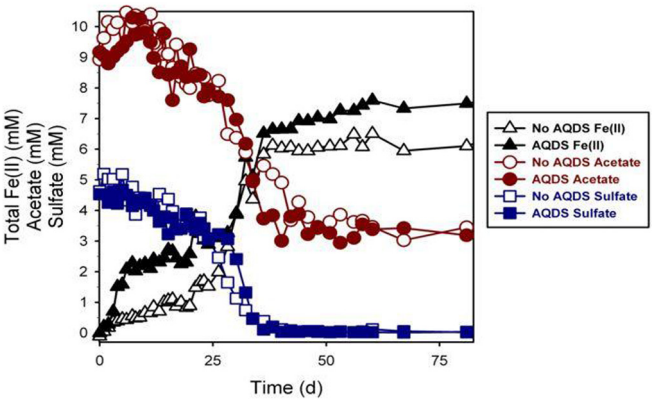


Figure 1. Results of wet chemical measurements to identify the loss of sulfate and the production of Fe(II), indicative of microbial sulfate and iron reduction. The presence of anthraquinone-2,6-disulfonate (AQDS) seems to increase the rate of Fe(II) production.

Non-Refereed Publications and Presentations

Antonopoulos, D.A., A. Ammar, M.I. Boyanov, M.H. Domanus, P. Long, F. Meyer, E.J. O'Loughlin, D. Sholto-Douglas, K. Skinner -Nemec, K.H. Williams, and K.M. Kemner, "Microbial Community Analyses of Iron-Rich Mineral Suspensions Inoculated with Sediments from a Uranium Mill Tailings Site," presented at American Society of Microbiology Annual Meeting, Philadelphia, PA, May 2009.

Glass, E., D. Bartels, M. d'Souza, J.M. Brulc, K. Keegan, T. Paczian, A. Wilke, J. Wilkening, M.I. Boyanov, M. Kwon, E.J. O'Loughlin, K.A. Skinner, M. Domanus, P. Long, K.H. Williams, D.A. Antonopoulos, K.M. Kemner, and F. Meyer, "Metagenome Analysis and Microbial Genome Reconstructions from an UMTRA Site Sediment," presented at International Society of Microbial Ecology Symposium, Seattle, WA, August 22–27, 2010.

Kemner, K.M., "The Advanced Photon Source and the ANL-SFA: Synergies with the PNNL-SFA Abound," presented at Scientific Focus Area (SFA) Collaborator Meeting, Pacific Northwest National Laboratory, February 25, 2009.

Kwon, M.J., D. Antonopoulos, D. Bartels, B.S. Bates, M. Boyanov, J. Brulc, M. Egholm, A. Garoutte, C. Giometti, T. Harkins, P. Long, T. Marsh, M. McCormick, F. Meyer, J. Osterberger, R. Sanford, K. Skinner, J. Wilkening, K.H. Williams, K.M. Kemner, and E. O'Loughlin, "Microbial Community and Biogeochemical Dynamics under Sulfate- and Iron-Reducing Conditions," presented at Subsurface Biogeochemistry Research Program (PI) Meeting, Washington, D.C., March 29–31, 2010.

Kwon, M., D. Antonopoulos, M. Boyanov, J. Brulc, P. Long, B. Mishra, K. Skinner, K. Williams, K.M. Kemner, and E.J. O'Loughlin, "Electron Donor Dependent Iron and Sulfate Reduction and Microbial Community Development," presented at International Society of Microbial Ecology Symposium, Seattle, WA, August 22–27, 2010.

Wide-Angle X-Ray Scattering as a Probe of Protein Structure, Dynamics, and Function

2008-128-R2

Lee Makowski

Project Description

The microbial world includes thousands of proteins with functions useful for advancing DOE missions, including the production of biofuels and environmental remediation. A bottleneck in using these proteins is identifying their function. Wide-angle x-ray scattering (WAXS) is a novel approach that has significant potential for characterizing the structure, dynamics, and function of proteins of any size without the need for crystallization. It can be applied to membrane proteins or large molecular complexes. Its impact is greatly enhanced when experimental efforts are coordinated with computational studies of protein structure and dynamics. The goal of this project is to develop the capabilities of WAXS used in coordination with molecular dynamics (MD) to study the structure, dynamics, and function of proteins in solution. It involves (1) methods for using WAXS to determine the secondary, tertiary, and quaternary structure of a protein; (2) methods for analyzing WAXS data; and (3) the combination of WAXS and MD as a tool for studying protein dynamics.

Mission Relevance

This project relates to DOE's basic science mission. Both DOE and the National Institutes of Health (NIH) recognize the importance of macromolecular complexes and the challenges in characterizing their structure and dynamics. Crystallography and nuclear magnetic resonance (NMR) have well-defined limitations when used to study these systems, and solution scattering is rapidly becoming an important accessory tool. We are rapidly advancing the capabilities of WAXS for use in these studies. An indication of the importance of these studies is the fact that one of the topics listed in the NIH "Challenge Grants" request for proposals was "Enabling Structural Studies of Macromolecular Complexes." A proposal was submitted in response. The area is a high priority for NIH and relevant to the DOE Office of Biological and Environmental Research/ Genomic Science programs.

FY 2010 Results and Accomplishments

In recent years, small-angle x-ray solution scattering (SAXS) has become an increasingly important tool for analyzing the structures of macromolecules and macromolecular complexes. A key reason for the increasing impact of SAXS is ability to predict, from atomic coordinates, the intensity profile of the expected scattering. As experimental techniques are improving, solution scattering data are being collected to increasingly wide angles (through WAXS), thereby greatly enhancing the potential value of the approach. However, the software currently used to calculate SAXS data from atomic coordinates includes approximations that are invalid at wide angles. In particular, the software uses a continuum model for solvent and excluded volume. The approximations intrinsic to these representations break down when they are beyond the small-angle regime. We demonstrated that an explicit atom approach to the representation of water can be used to accurately calculate x-ray solution scattering to at least 2.0 Å spacing. With this finding, we have a substantial competitive advantage over comparable research under way elsewhere. In the previous funding period, we demonstrated the ability to calculate — to within experimental errors — the WAXS pattern

of a protein from a set of atomic coordinates without needing to adjust free parameters. This achievement will greatly accelerate the use of WAXS for analyzing macromolecular structure and dynamics.

Progress during FY 10 was made in three areas, as follows:

1. *Calculation of WAXS data from atomic coordinates*. As shown previously, the WAXS pattern of a protein can be calculated from its atomic coordinates. This process is laborious and computationally intense. In FY 2010, we explored two approaches. One involved a coarse-grained representation of the amino acid chain. We calculated the spherically symmetric scattering factor from the 20 amino acids making up most proteins and added them with phase factors that are encoded to the locations of the amino acids. This very rapid approach can be used to calculate the scattering patterns from ensembles of structures by adding the scattering from each member of the ensemble. A computation of that magnitude is currently beyond the capabilities of the explicit atom approach to water of hydration that we pioneered. The second approach was to calculate the pair correlation function between the atoms of a protein and the atoms of water molecules in the hydration layer of the protein. With Dr. Tobin Sosnick, we developed a strategy to calculate a continuum model for the water of hydration that can be calculated for any protein on the basis of the atomic coordinates. Initial results suggest that this continuum model will be as accurate as the explicit atom representation for calculating WAXS patterns. The completion of a Web site for these types of calculations should provide a substantial test of the strategy.

2. *Study of hemoglobin structure in solution*. Our initial WAXS experiments involved studies of hemoglobin because it was inexpensive and easy to obtain and everything about its structure was well understood. It represented the perfect sample on which to develop a new technique. However, we were surprised to learn that not everything is known about hemoglobin structure. Our calculation of WAXS patterns from atomic coordinate sets of hemoglobin routinely fall far outside expected error levels. Whereas calculations of scattering from myoglobin and lysozyme and many other proteins reproduce the observed scattering very accurately, hemoglobin calculations are inconsistent with observations. The reasons remain unclear. Hemoglobin clearly exhibits substantial quaternary fluctuations in aqueous solution. The discrepancies we have uncovered, however, cannot be explained by these levels of fluctuations. Comparisons of a number of hemoglobin variants and mutants, plus comparisons of the scattering from hemoglobins under different oxygenation conditions, have provided some clues, but we must continue working to understand the basis for the discrepancies.

3. *Study of the reaction intermediates of catalyzing systems*. Perhaps the most exciting result of the past year relates to our work with Dr. George Phillips (University of Wisconsin). We began to collect WAXS data from adenylate kinase (ADK). ADK catalyzes the transfer of a phosphate group from ATP to AMP to form a pair of ADP molecules. It is possible to create conditions in which ADK carries out this catalysis in steady state for hours at a time. We collected WAXS data from apoADK, inhibited ADK, and ADK undergoing steady-state catalysis. The apo and inhibited forms are essentially the end points of the catalytic process. We showed that the scattering from the catalyzing enzyme cannot be reconstructed from a linear combination of the scattering patterns from the end points. This finding strongly demonstrates that at least one intermediate state is present in sufficient abundance during catalysis that we can detect scattering from it. We collected data from ADK at a large number of solution conditions (more than 70) and carried out a principal components analysis of the corresponding WAXS patterns. At least four different states of the protein are present in sufficient abundance that significant scattering data about it can be collected. Two states are the end points; the other two represent intermediate states that had not been characterized.

Refereed Publications

Bardhan, J.P., S. Park, and L. Makowski, "SoftWAXS: A Computational Tool for Modeling Wide-Angle X-ray Solution Scattering from Biomolecules," *J. Appl. Cryst.* **42** (2009), 932–943.

Makowski, L., "Characterization of Proteins with Wide-Angle X-ray Solution Scattering (WAXS)," *J. Struct. Funct. Genomics* **11** (2010), 9–19.

Makowski, L., D.J. Rodi, S. Mandava, D. Minh, D. Gore, and R.F. Fischetti, "Molecular Crowding Inhibits Intramolecular Breathing Motions in Proteins," *Journal of Molecular Biology* **375** (2008), 529–546.

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Virtanen, J.J., L. Makowski, T.R. Sosnick, and K.F. Freed, "Modeling the Hydration Layer around Proteins: HyPred," *Biop. J.* **99** (2010), 1611–1619.

Yang, S., S. Park, L. Makowski, and B. Roux, "A Rapid Coarse Residue-Based Computational Method for X-ray Solution Scattering Characterization of Protein Folds and Multiple Conformational States of Large Protein Complexes," *Biop. J.* **96** (2009), 4449–4463.

Yang, S., L. Blachowicz, L. Makowski, and B. Roux, "Multidomain Assembled States of Hck Tyrosine Kinase in Solution," *Proc. Natl. Acad. Sci.* **107** (2010), 15757–15762.

Non-Refereed Publications and Presentations

Makowski, L., "MADMAX: Multiwavelength Anomalous Diffraction Using Medium Angle X-ray Solution Scattering," presented at American Crystallographic Association Annual Meeting, Chicago, IL, July 24–29, 2010.

Makowski, L., "Probing Protein Ensembles and Functional Intermediates with X-ray Solution Scattering," presented at Workshop on Evolution and Control of Complexity, Argonne/DESY/SLAC Symposium, Argonne, IL, October 11–13, 2010.

Makowski, L., "WAXS – Going beyond SAXS," presented at EMBO Practical School of X-ray Scattering, Hamburg, Germany, October 2010.

Microbial Basis for Soil-Inorganic Carbon Sequestration

2008-140-R2

Robert A. Edwards and Folker Meyer

Project Description

The purpose of this project is to explore the role of soil in carbon sequestration and to create a database linking traditional soil biogeochemistry and other data with genomic data.

Soil microbial communities are critical to terrestrial ecosystem stability and the global carbon cycle. The complexity of these communities poses significant challenges with regard to describing the explicit mechanistic roles of individual soil microorganisms *in vivo*. Here, we use shotgun metagenomics via second-generation sequencing technology (454) and high-throughput annotation (Metagenome Rapid Annotation using Subsystems Technology [MG-RAST]) — a novel, culture-independent tool for harnessing information about the potential function of intact soil microbial communities — to explore drivers of microbial community function across ecosystems in the newly established National Ecological Observatory Network (NEON). This unprecedented characterization of soil microbial communities and their local environments seeks to explore the relative importance of local parameters (physical/chemical conditions) and geographic location (latitude/longitude) on microbial community functional potential.

Mission Relevance

This project is relevant to DOE's environmental mission. The DOE mission of global carbon management requires that we gain a comprehensive understanding of terrestrial and marine microbial communities so we can learn the role that they play in carbon sequestration. This understanding should start at the single protein level and go up to whole organisms, communities, and ecosystems. Establishing a map of U.S soil types linked to metagenomic data will provide key information to researchers interested in understanding the role of soil in carbon sequestration.

FY 2010 Results and Accomplishments

The cumulative data sets comprise about 888.6 Mb of DNA (about 3.8 million metagenomic fragments), allowing identification of distinct metagenomic profiles conserved within an ecosystem type (grassland or forest) across geographic locations. This represents a major advance in the coarse resolution previously available from using such techniques. To further explore the external mechanistic controls of microbial function, we measured a wide range of soil physical and chemical parameters. We found that pH was the critical driver of the microbial functional gene pool across ecosystems, a finding that improves the understanding of pH-driven patterns in microbial community structure observed in 16S rRNA inventories. A suite of correlated pathways appears to drive this relationship; 24 subsystems differed significantly in an ANOVA (ANalysis Of Variance) comparison among pH ranges.

Shotgun metagenomics using second-generation DNA sequencing demonstrated the distinct functional composition of soil microbial communities across North America and clearly partitioned these communities between forest and grassland sites. These results represent a major advance in the power of the metagenomics approach to resolve problems in environmental systems and show that the ecosystem type (potentially land use) can affect metabolic cycling associated with terrestrial ecosystem function.

Refereed Publications

Glass, E.M., J. Wilkening, A. Wilke, D. Antonopoulos, and F. Meyer, "Using the Metagenomics RAST Server (MG-RAST) for Analyzing Shotgun Metagenomes," *Cold Spring Harbor Protocols* (2010) **2010**(1), doi:10.1101/pdb.prot5368.

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Nonrefereed Publications and Presentations

Antonopoulos, D.A., "Microbial Communities and Ecosystem Function: Challenges of Making White Boxes Out of Black Boxes," presented at Challenges in Environmental Microbiology Workshop, Argonne, IL, April 26–27, 2010.

Antonopoulos, D.A., "Soil Microbial Metagenomes Track with Ecosystem Type: Uncovering Soil Metabolic Clusters," presented at First Annual Argonne Soils Workshop, Argonne, IL, October 25–26, 2009.

Mapping Protein Binding Domain and Small Molecule Interactions

2008-166-R2

T. Andrew Binkowski, Ian T. Foster, Andrzej Joachimiak, Michael D. Kubal, Benoît Roux, Rick L. Stevens, and Michael J. Wilde

Project Description

Although a well-defined paradigm exists for predicting the interactions of small molecules with protein surfaces, current computational methods have both theoretical and computational limitations. While advancements in algorithms continue to reduce computational complexity and optimize the scoring of molecules of interest, studies have shown that different methods produce accurate results only for a small set of problems (i.e., there are no protein-ligand docking methodologies or scoring functions that can be universally applied to molecular systems). To address this challenge, we are developing a computational pipeline that combines evolutionary analysis of protein binding sites with cheminformatics obtained from large-scale computational docking experiments to create a high-quality library of protein-ligand interaction data. This library provides a global-scale analysis of protein domain-small molecule interactions that can be used to derive novel scoring functions and compute more accurate small molecule binding predictions.

Mission Relevance

The project serves DOE's science, as well as its national security, missions. Exascale computing advances provide opportunities to further understand bimolecular phenomenon and complex systems. Algorithmic improvements in modeling protein-ligand interactions have been dogged by their complexity, making them computationally prohibitive. Reimplementation of these algorithms on a scalable architecture makes the superior technology accessible to a broader class of researchers. Development of our discovery pipeline serves as a model for allowing scientific applications to benefit from high-throughput computing. Use of our pipeline to improve modeling and simulations of protein-ligand interactions has tremendous value in terms of furthering the understanding of biological systems and in national security drug discovery efforts. As our advanced scoring functions bridge the gap between theoretical and experimentally obtained small compound binding affinities, we improve our ability and efficiency in identifying drugs, which will be important in combating bio-terror agents.

FY 2010 Results and Accomplishments

We have developed the combined high-performance computational and high-throughput experimental APPLIED (Analysis Pipeline for Protein Ligand Interactions and Experimental Determination) pipeline for protein-ligand interaction analysis (Figure 1). The pipeline uses state-of-the-art physics-based biomolecular simulation methodologies (e.g., molecular mechanics generalized Born surface area approximation, free energy perturbation molecular dynamics) to predict ligand-binding affinities that are experimentally validated by using biochemical and high-throughput x-ray crystallography approaches. The computational component is implemented on the BlueGene/P at Argonne National Laboratory, and the principal investigator (TAB) has received a DOE Innovative and Novel Computational Impact on Theory and Experiment (INCITE) program award to operate it.

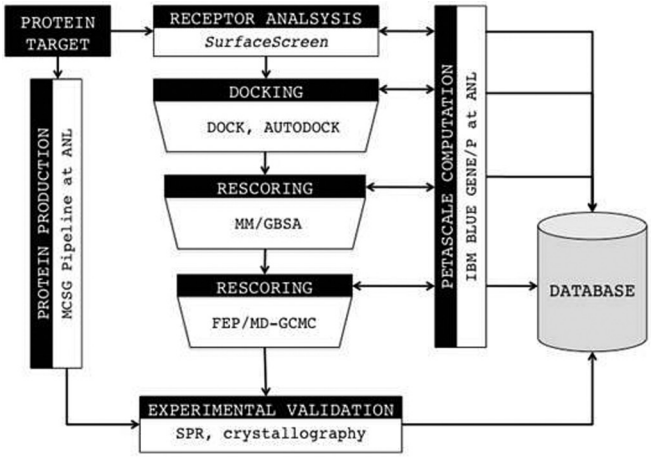

Figure 1. Workflow of the APPLIED computational and experimental pipeline for ligand-binding analysis.

During the past year, we have used the APPLIED pipeline to study important proteins in biofuel production, metagenomics, and human health. For example, our methods have been used to identify small molecule inhibitors against transglutamase proteins, which have been implicated in neurodegenerative diseases and autoimmune conditions (Figure 2). Virtually screening millions of compounds in our pipeline allowed us to identify a handful predicted to bind to our transglutamase target. X-ray crystallographic studies at Argonne's Structural Biology Center experimentally validated the computational predictions. Two compounds are shown bound in Figure 2.

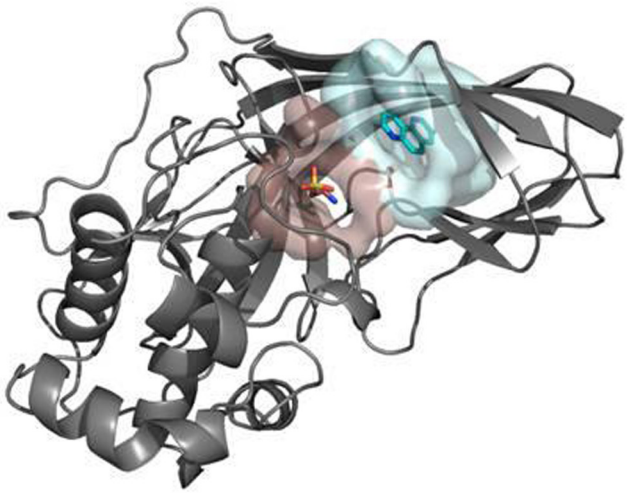

Figure 2. The APPLIED pipeline was used to identify transglutamase, small molecule inhibitors of an important protein in neurodegenerative diseases. Of the millions of compounds screened virtually, the pipeline was able to identify a best set of candidates for experimental studies. Crystallographic data validates the predictions for two small molecules.

Refereed Publications

Binkowski, T.A., and A. Joachimiak, "Protein Functional Surfaces: Global Shape Matching and Local Spatial Alignments of Ligand Binding Sites," *BMC Structural Biology* **8** (2008), 45.

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Deng, Y., and B. Roux, "Computations of Standard Binding Free Energies with Molecular Dynamics Simulations," *J. Phys. Chem. B* **113**(8) (2009), 2234–2246.

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Raicu, R., Z. Zhang, M. Wilde, I. Foster, P. Beckman, K. Iskra, and B. Clifford, "Toward Loosely Coupled Programming on Petascale Systems," *Proceedings of the 2008 ACM/IEEE Conference on Supercomputing*, 22:1–22:12.

Shivakumar, D., Y. Deng, and B. Roux, Computations of Absolute Solvation Free Energies of Small Molecules Using Explicit and Implicit Solvent Model," *J. Chem. Theory Comput.* **5**(4) (2009), 919–930.

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Binkowski, T.A., "High-Throughput Computational and Experimental Ligand-Binding Pipeline for Human Pathogen Targets," OpenEye CUP XI, Santa Fe, NM, March 2010.

Binkowski, T.A., and A. Joachimiak, "Comparison and Analysis of Protein Functional Surfaces," Keystone Symposium, Structural Genomics and Its Applications to Chemistry, Biology and Medicine, Steamboat Springs, CO, January 6–11, 2008.

Binkowski, T.A., D. Shivakumar, M. Kubal, M. Wilde, I. Foster, B. Roux, R. Stevens, and A. Joachimiak, "Mapping Protein Binding Domain and Small Molecule Interactions," American Chemical Society Annual Meeting, Philadelphia, PA, August 17–28, 2008.

Roux, B., "Using Simulations to Estimate Free Binding Energies," Keystone Symposium, Computer-Aided Drug Design, Steamboat Springs, CO, March 29–April 3, 2008.

Zhang, Z., A. Espinosa, K. Iskra, I. Raicu, I. Foster, and M. Wilde, "Design and Evaluation of a Collective IO Model for Loosely Coupled Petascale Programming," MTAGS08 (Workshop on Many-Task Computing on Grids and Supercomputers, co-located with ACM/IEEE SC08 (International Conference for High Performance, Networking, Storage and Analysis), Austin, TX, November 17, 2008.

Metagenomics-Enabled Discovery of Protein Function

2009-156-R1

Elizabeth M. Marland Glass, Christopher S. Henry, Folker Meyer, and Rick L. Stevens

Project Description

New technology for DNA sequencing (the 454 Pyrosequencer) enables discovery of the "DNA world" that surrounds us and significantly contributes to our environment. Previously, mostly large teams of researchers sequenced individual genomes. However, because of the decreasing cost, small groups have

recently embarked on the same endeavor. This trend allows considerably more researchers to study complex communities of microbes in diverse environments, such as marine sediment, soil, and human mucosal tissue. These studies aim to dramatically expand our understanding of the microbial biosphere. More importantly, this research offers the potential to resolve the ambiguities surrounding the complex symbiotic relationship in various environments. An important prerequisite for such discoveries is the accessibility of computational tools that can rapidly and accurately compare the large datasets generated from complex bacterial communities to identify their distinguishing features.

Hundreds of metagenomes have already been sequenced, and we are striving to lead in the analysis of metagenomic data sets. Argonne staff have developed a version of the NIH/NMPDR (National Institutes of Health/National Microbial Pathogen Database Resource) -funded RAST server. It was created by a joint Argonne/UChicago team for metagenome analysis and is called MG-RAST. To meet the growing demand for analysis and the broadening scope and types of comparative analyses that are needed, we are:

- Extending metabolic reconstruction for metagenomes,
- Developing tools for metagenome analysis,
- Coupling the high-performance computing (HPC) resources to the existing metagenomics analysis front-end, and
- Implementing improvements in the user front-end.

Mission Relevance

Identifying and defining the characteristics of microbial communities in the biosphere is vital to understanding their contributions to various ecological systems. Little is known about microbial communities; therefore, the potential for discovery is significant in any habitat chosen for study. Areas relevant to DOE missions include:

- *Climate Change*: The development of microbial ecosystem models to describe and predict global environmental processes, change, and sustainability.
- *Energy*: The development of microbial systems and processes for new bioenergy resources that would be more economical, environmentally sustainable, and resilient in the face of disruption by world events.
- *Bioremediation*: The development of tools for monitoring environmental damage at various levels and methods for restoring the health of an ecosystem.

Other federal agencies also would benefit from the proposed work. For example, the NIH Human Microbiome Project is sponsoring projects that explore and analyze microbial communities of human mucosal tissue for advancing research on human health and disease. In addition to DOE and NIH, both the Department of Homeland Security and the Department of Defense would be likely users of technology that helps to unveil microbial community dynamics.

FY 2010 Results and Accomplishments

During FY 2010, our research efforts focused on four key areas.

1. *Detailed comparison of metabolic reconstructions.* Determining the metabolic processes performed by a microorganism in a community is important both for understanding and for manipulating ecosystems (for example, environmental conservation). In FY 2010, we integrated metabolic models into the framework of the MG-RAST system. Built upon the reconstructions produced from the functional annotation via the MG-RAST analysis pipeline, the resultant models are now available through the MG-RAST v3 system.

2. *Extensions of the user interface and comparative analysis tools.* Analysis tools for single metagenomes and those for comparative analysis were extended to enable users to alter tool parameters for interactive analysis. To generate meaningful comparisons between data sets, researchers need information about the samples. Therefore, we built a metadata editor and integrated it into the system to provide a mechanism to enter relevant information regarding the sequencing and environment from which a metagenomic sample was derived. This editor is Genomic Standards Consortium MIMS-compliant (Minimum Information about a Metagenome-compliant). New search and browsing capabilities were developed. The new web modules allow users to browse by biome, project, or location (via an interactive Google Earth map). This feature utilizes the data gathered from the metadata editor that was developed during the course of this project.

3. *New assembly pipeline and visualization tools.* The sequence fragments produced from next-generation sequencers are increasing in length as the technologies improve. However, assembly of those fragments is still required to increase fragment length for analysis, which can then provide insights into population composition and evolution. A de novo assembly pipeline was developed that uses a combination of Velvet, CAP3, and MAQ assembly software.

   Assembly permits the examination of conserved clusters (organization) of the genes on the scaffolds and their comparison to genome sequences from microbial organisms. To examine the assemblies in the context of these clusters, we built a mapping and visualization tool that plots the assembled contigs to conserved chromosomal gene clusters in complete microbial

genomes. Focusing on these assemblies can reveal variability in genome content among closely related strains of microbes. Variation in gene content has been hypothesized to be the primary mode of adaptive evolution in microorganisms; however, very little is known about the spatial and temporal distribution of variable genes. By building this framework, researchers will be able to delve into the analysis of pan-genomes to gain an understanding of microbial genome evolution.

4. *Interface with high-performance computing.* As high-throughput sequencing becomes more prevalent, the bottleneck in metagenomics has moved from generating data to data analysis. As of March 2010, users from 50 countries or territories had submitted 5,798 metagenomes (~160 Giga base-pairs) to the MG-RAST annotation server. To deal with the deluge of sequence data being produced, the connection to scalable computing resources became vital. We have incorporated a new software layer into the analysis pipeline that allows the system to connect to the high-performance computing engine developed at Argonne — the Argonne Work Engine (AWE).

Proposed Work for FY 2011

As we continue to explore a diverse set of environments through metagenomics, mining these data sets for novel proteins is emerging as an increasingly important project. These proteins will help to "fill the gaps" in our understanding of cellular and community functions. Novel proteins also will be of interest in scientific and industrial processes, such as carbon management, biofuel production, or remediation.

We propose to provide an analysis pipeline for large-scale comparisons of multiple metagenomic data sets to perform systematic mining for novel proteins. A comparative framework will be established to allow for large-scale sequence comparisons to identify sequences that are unique to a given sample or community, as well as those that are shared. Our approach also will include supporting the building of "cross-contigs" — the systematic comparison of unassigned fragment abundance across a large number of metagenomes to identify DNA fragments that can be linked to specific environments or biological processes. The identified sequences will then be functionally characterized. For those with no similarity to the sequence space, we will incorporate a tool to develop primers for researchers to investigate these unknown proteins experimentally.

We will leverage the cloud-based high-performance computing resources and workflow engine developed at Argonne (AWE). These applications will enable the large-scale metagenomic comparisons for identifying novel proteins or signature proteins for a given biome. Additionally, we will integrate software into the existing framework to increase the capabilities of the metabolic modeling effort.

Refereed Publications

Angly, F.E., D. Willner, A. Prieto-Davó, R.A. Edwards, R. Schmieder, R. Vega-Thurber, D.A. Antonopoulos, K. Barott, M.T. Cottrell, C. Desnues, E.A. Dinsdale, M. Furlan, M. Haynes, M.R. Henn, Y. Hu, D.L. Kirchman, T. McDole, J.D. McPherson, F. Meyer, R.M. Miller, E. Mundt, R.K. Naviaux, B. Rodriguez-Mueller, R. Stevens, L. Wegley, L. Zhang, B. Zhu, and F. Rohwer, "The GAAS Metagenomic Tool and Its Estimations of Viral and Microbial Average Genome Size in Four Major Biomes," *PLoS Comput Biol.* (2009), Dec;5(12):e1000593.

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Meyer, F., "Standards for Democratized Sequencing World," presented at the Genome Informatics Alliance Meeting, Seattle, WA, May 7, 2010.

Meyer, F., "Analysis of Metagenomic Sequences, from Megabases to Terabases," presented at the Max-Planck-Institue for Informatics, Saarbrücken, Germany, August 8, 2010.

Meyer, F., "Analysis of Metagenomic Sequences, from Megabases to Terabases," keynote address at the 5th Annual Sequencing, Finishing, and Analysis in the Future Meeting, Santa Fe, NM, June 2–4, 2010.

Combinatorial Deletions to Produce a Minimal Strain of *Bacillus subtilis*

2009-171-R1

Elizabeth M. Marland Glass, Christopher S. Henry, Folker Meyer, and Rick L. Stevens

Project Description

Essentiality studies suggest that the number of genes required to synthesize the proteins necessary for an organism to be viable under controlled laboratory conditions is on the order of 300 to 800 genes — far fewer than the number of genes typically encoded within microbial genomes (e.g., *Bacillus subtilis*, with 4,105 open reading frames). While some naturally occurring microbial genomes do encode less than 800 genes, these organisms exist in host-dependent environments and are non-culturable outside their hosts (e.g., *Mycoplasma genitalium*, with 482 genes). However, the existence

of these organisms with reduced gene sets suggests that many proteins used within larger genomes exist purely to confer adaptability and flexibility upon the organism, and these proteins may be deleted without impacting viability in controlled laboratory conditions. In fact, deletion of nonessential proteins may enhance the organism by reducing metabolic burden and removing regulatory controls on growth rates.

In this project, our objective is to explore gene dispensability by fabricating a minimal strain of the microorganism *B. subtilis*. We are fabricating our minimal *B. subtilis* by iteratively combining 140 existing gene interval deletions to produce progressively smaller strains. Throughout the deletion combination process, we are also producing a genome-scale model of *B. subtilis*, which is used to predict the outcome of combinations that are performed experimentally. Successful model predictions help to explain why certain deletion combinations result in unviable strains. Unsuccessful model predictions help to elucidate portions of the cellular machinery in *B. subtilis* that are not well understood. This work will produce a minimal strain of *B. subtilis*, as well as an accurate computational model of the organism.

Mission Relevance

This project supports DOE's mission through innovations in science and technology. The simplified strains of *B. subtilis* that we are actively producing in this research will help to accelerate the validation and curation of whole-cell models. This capability will provide a means of generating quantitative predictions of cellular behavior, which are invaluable for efforts to engineer an organism to secrete a product or degrade a toxin. Ultimately, we will produce a viable minimal strain of *B. subtilis*, thereby providing an ideal system for testing metabolic engineering theoretical tools and for developing systems biology methodologies.

FY 2010 Results and Accomplishments

In the first year of this project, 256 knockout combinations were attempted, involving the 26 largest single-interval knockout strains. Seventy-eight combinations were successful, producing four strains with cumulative knockouts of more than 900 KB (23% of the wild-type genome). Additionally, the first version of our genome-scale metabolic model of *B. subtilis*, the *i*Bsu1103, was published.

In FY 2010, our experimental efforts focused entirely on the combination of interval deletions to continue the reduction of our reduced *B. subtilis* strains. By building upon the 256 combinations attempted during 2009, an additional 94 combinations were attempted, 80 of which were successful (Figure 1). Because our combinations began with the largest intervals first, we experienced diminishing returns in the reduction of the *B. subtilis* genome with each additional combination. To overcome this problem, we began to split the large intervals that previously could not be combined into our reduced strain, and the split sub-interval knockouts were subsequently combined into the reduced strains. This strategy was successfully applied with two interval deletions that could not be combined. In total, we produced four reduced strains of *B. subtilis*: (i) 1.381 MB KO (32% reduction), (ii) 1.379 MB KO (32% reduction), (iii) 1.436 MB KO (33% reduction), and (iv) 1.379 MB KO (32% reduction).

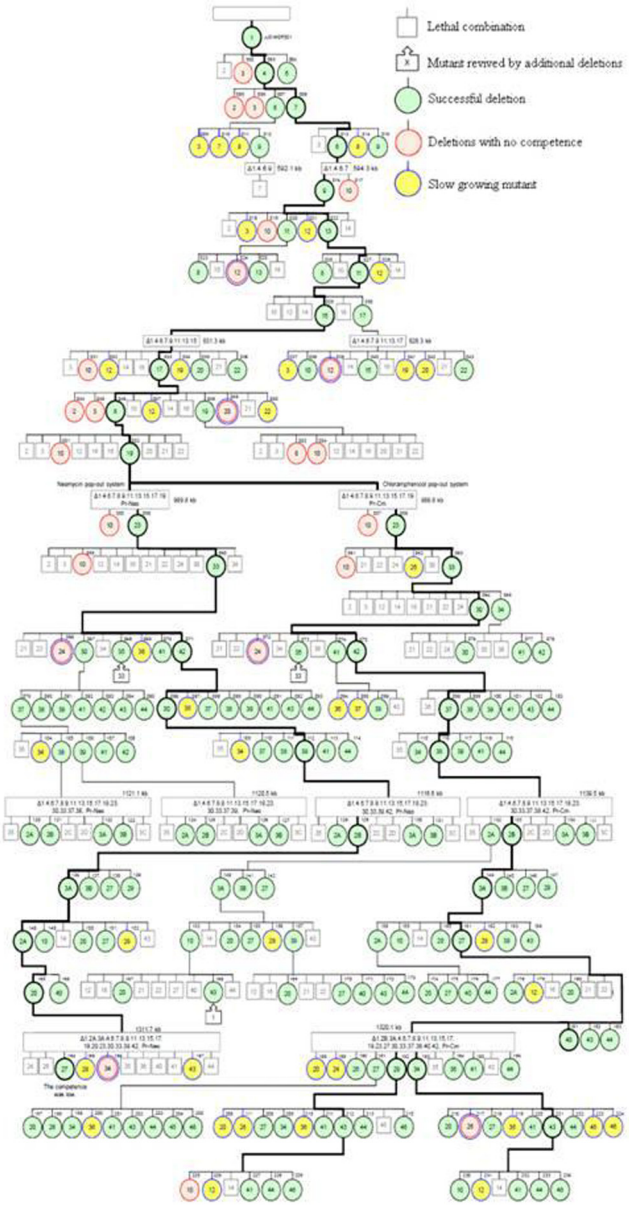

Figure 1. Tree of knockout combinations attempted during research. Each node represents a strain. Node color indicates viability.

Also during FY 2010, work continued on our *i*Bsu1103 genome-scale metabolic model of *B. subtilis 168*. This work focused on correcting problems in the model that prevented the correct prediction of knockout strain phenotypes. Before model corrections, the model was 85% accurate in predicting strain phenotypes. After the model corrections, accuracy improved to 90%. These model corrections revealed insights into the nature of the genes knocked out during the experimental efforts, into the experiments themselves, and into the essentiality of cofactor biosynthesis and metabolic pathways within *B. subtilis*.

Proposed Work for FY 2011

In FY 2011, the most healthy and naturally competent reduced strains of *B. subtilis* will be further combined with other interval knockout strains, progressing toward our goal of producing a minimal strain. However, at this stage, knockouts will be specifically directed at gene targets identified by our industrial collaborators. These more selective knockouts will enable us to progress more rapidly toward an industrially useful strain. Additionally, we will explore the feasibility of restoring specific functionality to reduced strains via the addition of tailor made modules of metabolic activity. This will further test the predictive ability of the metabolic model, which will be used to design the metabolic modules that are inserted. This will also test the feasibility of the reduced strains as platforms for engineered biosynthetic functionality.

Refereed Publications and Presentations

Henry, C.S., R. Overbeek, and R. Stevens, "Building the Blueprint of Life," *Biotechnology Journal* **5**(7) (2010), 695–70.

Recovery of Full-Length Genes for Expression of Proteins from Metagenomic Sequence Data

2009-177-R1

Deborah K. Hanson and Philip D. Laible

Project Description

Current estimates of the world's genetic diversity are increasing dramatically following analysis of new data that are accumulating exponentially from genomic sequencing efforts. In particular, the sequencing of genomic DNA derived from environmental samples that contain microbial communities — so-called *metagenomics* — has revealed a tremendous new level of genetic diversity that had not been appreciated previously. The overwhelming majority of the genes that are identified is derived from unknown or unculturable organisms. Therefore, the only way to approach such genes is by using the DNA sequence data that are in hand. The aim of this project is to develop methods to exploit these data to recover enzymes that perform novel reactions. Methods are required to take us in a stepwise fashion from short DNA sequence fragments to complete genes to expressed, purified proteins.

Mission Relevance

This project is relevant to DOE's energy and environment missions. The Genomic Science Program of the DOE Office of Biological and Environmental Research (BER) was established to explore and exploit the diverse functions of proteins encoded by plants and microbes. Even though the number of completely sequenced genomes is increasing rapidly, the overwhelming majority of new sequence data is derived from environmental samples. This project describes developments in the capability to mine these metagenomic sequence data for the expression of novel proteins.

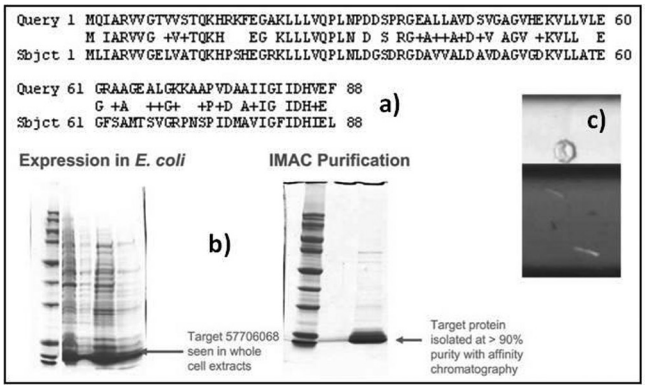

Figure 1. (a) BLASTp alignment of translated ORF 57706068 (query) with EutN/Ccm1 protein from Solibacter usitatis *(subject; E value = 6e-20), (b) the protein was expressed in* E. coli *and purified, and (c) some initial crystals were obtained.*

FY 2010 Results and Accomplishments

In FY 2009, we developed strategies to identify and recover sequences that flank protein-coding regions (open reading frames [ORFs]) that were identified from the prairie metagenome sequencing project. Inverse-affinity-nested polymerase chain reaction (PCR) was employed to amplify genomic regions both upstream and downstream of the fragment of known sequence. The resulting amplified DNA fragments were sequenced to reveal the beginnings and ends of the target ORF. The complete gene was then amplified from the prairie soil DNA sample and cloned into an expression vector for the production of protein from induced cultures of *E. coli*. Figure 1 shows the results of this "pipeline" for metagenome fragment 57706068, which encodes a carboxysome shell protein from an unknown organism.

In FY 2010, it was necessary to revise many steps of this strategy in order to obtain better results for the remainder of the target sequences. The supply of the prairie soil DNA sample was, by far, the reagent that was most limited, thus protocols were changed to minimize the amount that was used in each experiment. This strategy also minimized the requirements for the costly thermostable polymerases. It also became necessary to define more stringent conditions for the two-round PCR experiments in order to prevent the amplification of nonspecific "nonsense" sequences and to obtain PCR amplification products that were specific for the target ORFs. Only then could we derive sequences that extended the target ORFs, thereby leading to the identification and recovery of the full-length gene. These measures were an absolute requirement for scale-up to high-throughput, inverse-affinity-nested PCR experiments. Pertinent to scale-up goals, we adapted all protocols that require liquid handling to a 96-well format for implementation on the Biosciences Division's robots.

During our research, it became apparent that the inverse-affinity-nested PCR strategy for the recovery of full-length genes from metagenomics sequence data has an inherent high failure rate. Success is hampered by the extremely limited amounts of DNA that are available from environmental samples, the short lengths of the target sequences, and the high costs associated with affinity-tagged primers and polymerases. However, new technology has recently increased the lengths of sequences that can be derived from environmental samples. Consequently, a more efficient strategy will soon be enabled, whereby an entire ORF of interest can be recovered from overlapping sequence fragments. The ORF of interest could then be amplified directly from the environmental DNA sample, or a synthetic version of the gene could be purchased from a commercial entity. Alternatively, the proteins of interest in the environmental sample could be studied by the cloning and expression of sequence and/or functional homologs from organisms that are amenable to laboratory culture.

Non-Refereed Publications and Presentations

Hanson, D.K., H.N. Scott, M.B. Culpepper, L.L. Kressel, J.R. Ramalie, F. Meyer, and P.D. Laible, "Recovery of Full-Length Genes for Expression of Proteins from Metagenomic Sequence Data," presented at the Challenges in Environmental Molecular Microbiology meeting, Chicago, IL, April 26–27, 2010.

Characterization of Microbial Community Dynamics

2009-186-R1

Dionysios A. Antonopoulos, Carol S. Giometti, Kenneth M. Kemner, and Folker Meyer

Project Description

In this project, we are focusing on the dynamic consortia of microbial populations involved in the biogeochemical cycling of elements in natural subsurface and terrestrial environments. Following microbial population dynamics across spatial and/or temporal scales traditionally has been conducted by inventorying the variation and relative abundance of a single, highly conserved gene marker as a proxy for the microbial populations and metabolisms that are present (for example, the gene encoding the 16S rRNA molecule, which is a crucial component of protein translation in all microorganisms). However, the decreased cost of DNA sequencing technology relative to data acquisition has enabled direct access to the functional gene sequences that occur in an environmental sample by the adoption of shotgun metagenomics. The metagenome of a sample represents the totality of all genes that are present — essentially its metabolic potential. Current efforts are focused on reducing the sequence "search space" for functional genes that bestow unique properties to one microbial community versus another by sequencing its metatranscriptome — the genes actively expressed by the microbial community in total. We seek to identify the genetic and metabolic potential of microbial communities and to establish how functions are partitioned in and between microbial populations.

Mission Relevance

This project is relevant to DOE's missions in the environment and basic science. The current sequencing effort builds on previous work that evaluated the kinetics of chloroethene transformation, the enzymes and genes involved, and the microbial community composition and activities within these bioaugmented flow column systems. The work described in this project complements these efforts through the study of microbial processes that contribute to the degradation of organic contaminants and the transformations of metal and radionuclide contaminants in the context of natural biogeochemical processes. A robust set of chemical and physical metadata for the system will allow the mining of metagenome- and metatranscriptome-derived datasets for the functional genes involved, as well as for novel gene discovery.

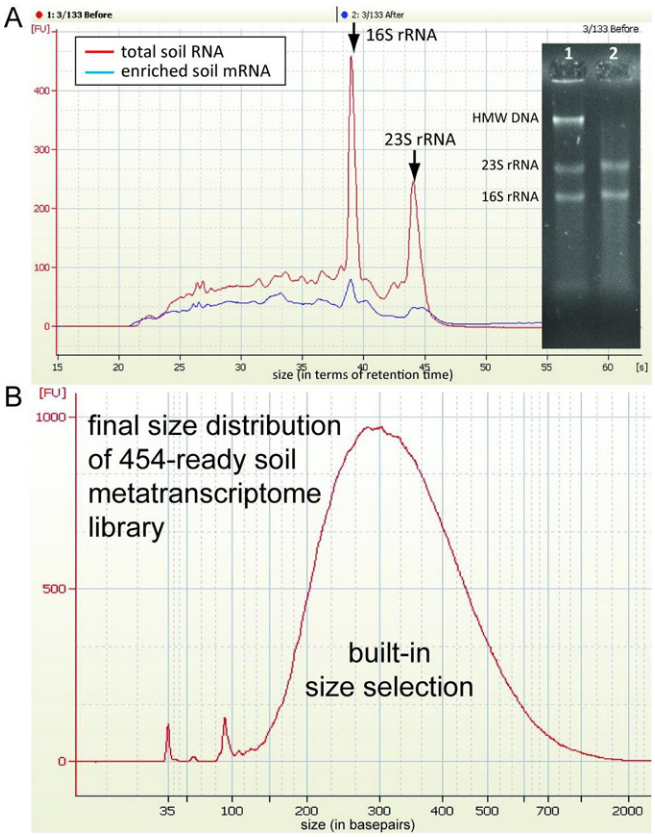

Figure 1. Demonstration of mRNA extraction from topsoil and preparation of size-selected DNA sequencing libraries for next-generation DNA sequencing platforms. (A: inset) Extracted nucleic acids from a topsoil sample are size fractionated by using gel electrophoresis to demonstrate (1) the integrity of whole RNA (inferred from the integrity of ribosomal RNA [rRNA]) and (2) the removal of DNA. (A: main graphic) Effective removal (subtraction) of rRNA and enrichment of mRNA from topsoil (blue trace) relative to whole RNA (red trace). (B) Final preparation of the size-selected DNA sequencing library.

FY 2010 Results and Accomplishments

A protocol previously had been established (FY 2009) for whole nucleic acid extraction from environmental samples, removal of DNA, and effective subtraction of ribosomal RNA (rRNA), thereby enriching the mRNA from these microbial communities. The current work (FY 2010) has improved the yields and enrichment of mRNA and has shifted to refining a metatranscriptome library construction workflow for second-generation DNA sequencing platforms. These workflows not only allow for conversion of mRNA to DNA, but they also provide a built-in size selection strategy that is optimal for the DNA sequencing platform (see Figure 1). In addition, bench-top topsoil incubation experiments have been initiated to test the effects of global environmental parameters (moisture and temperature) on microbial community response.

Proposed Work for FY 2011

During FY 2011, metatranscriptome datasets will be analyzed in the context of previously generated metagenomes from environmental samples, including topsoil and laboratory-scale batch reactors seeded from subsurface environmental materials. We will use these results to (1) inform metabolic models of the microbial community and (2) establish bench-scale experiments to verify microbial community requirements for the degradation and transformation of environmental contaminants.

Development of a High-Throughput Approach to Soil Physical and Chemical Characterization in Tandem with Soil Metagenome Analysis

2010-119-N0

Raymond M. Miller, Julie D. Jastrow, Roser Matamala Paradesa, and Folker Meyer

Project Description

The overall aims of this study are to develop a soil diffuse-reflectance spectral library, derive soil spectral calibrations for the prediction of soil properties with uncertainty, and assess the accuracy of the predictions and populate the legacy soil samples with good-quality information. A secondary goal is the application of mid-infrared (IR) spectroscopy for identification of soil biomarkers. Currently, the advantage of biomarker approaches is that specific organic compounds with known origins can be used to indicate the source, fate, and transformation of related molecules. Analysis generally involves sample hydrolysis, derivatization, and usually gas chromatography. Although somewhat tedious, techniques are reasonably well established for routine use of bulk amino sugar concentrations as a quantitative indicator of microbial residues in soils, and the ratios of glucosamine, muramic acid, galactosamine, and mannosamine can be used as indicators of fungal vs. bacterial residues. Amino sugars are relatively stable over time and thus have been used to evaluate long-term dynamics. However, they have also been shown to vary over much shorter periods, suggesting the existence of both stable pools and more rapid-turnover pools. Similarly, neutral sugar hexose/pentose ratios have been used to distinguish microbial from plant residues in soil. For example, one of the subsystem clusters from the National Ecological Observatory Network (NEON) soil metagenomes is driven by amino sugars. One of the first goals will be to determine if we can incorporate amino-sugar biomarkers into a mid-IR library. If so, this approach would allow for a very tedious group of analyses to become routine.

Mission Relevance

Our research is relevant to DOE's missions in science and the environment (U.S. DOE, 2009; 2010). A significant unknown is in our understanding of the vulnerability of soil carbon to the activities of the soil microbial community. Soils can be either a source or sink for carbon with the interplay of vegetation, soil type, climate, and the soil microbial community being major determinants of sink strength. Major challenges face the integration of soil characteristics, especially those soil traits associated with the quality and quantity of soil carbon, with the rapidly advancing high-throughput datasets used to characterize microbial communities. Significant analytical challenges and overall complexity of soil environments hamper efforts to fully understand those factors influencing a soil's metagenome. In support of DOE missions in environmental genomics and climate change (U.S. DOE, 2009; 2010), and to overcome this constraint, we identified a need for developing analytical and library capabilities that may enhance our understanding of soil metagenomics databases by using biomarker analysis of plant/microbial residues and mid-IR spectroscopy. Recent research in soil metagenomics has demonstrated that taking a subsystem approach to soil metagenomics may help further the understanding of soil metabolic processes at both local and continental scales. For example, by using Argonne's MG-RAST web site, we have been able to identify distinct subsystem metabolic clusters that appear to be associated with biome type. These metabolic subsystem clusters appear to be influenced by climate, vegetation, and soil characteristics. The subsystem pathways for the respective clusters indicate that the quality of soil organic residues and such factors as soil texture, pH and base cations appear to be major drivers. These clusters also suggest that a more refined measure of soil organic-substrate composition is needed to better identify those drivers influencing these metabolic subsystems. This project will meet this need.

FY 2010 Results and Accomplishments

A requirement for using Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy to assess soil is the creation of soil spectral databases or libraries, and there is widespread interest in their development. However, only a few that are geographically diverse and specific to soil properties have been described. Three important requirements for the development of a soil spectral library are: (1) it should contain as many samples as are needed to adequately describe the soil variability in the region in which the library is to be used; (2) the samples should be carefully subsampled, handled, prepared, stored, and scanned (everything that has happened to the sample up to the time of scanning will be embodied in the sample and recorded in the spectra); and (3) the reference soil analytical data used in the calibrations should be acquired using reliable and accredited analytical procedures. With relation to (1) above, if the library is being developed for a particular region from scratch, then the soil sampling strategy used will be critical. If the library is being developed from a legacy soil sample, then the recommendation is to scan all of the samples, then correlate the spectra with the relevant soil properties and use these to assess the quality of the legacy soil data.

We have several thousand archived soils obtained from the Fermi (Fermi National Accelerator Laboratory) National Environmental Research Park (NERP) site that have undergone extensive physical, chemical, and biological characterization. We used these soils to develop libraries for the mid-IR. We also have soils collected from each of the NEON sites that cover a range of soil physical and chemical characteristics. These soils can be used for developing the library, but they can also be used as a test case for integrating soil results with those of the soil metagenomic data sets created by using these soils.

To date, we have accomplished the following:

1. *Sample preparation*. Preparing the soils for analysis is a crucial step. Because soils by definition are heterogeneous, replicate samples will give slightly different results. We are measuring small changes in concentration over a period of time, so a reproducible sample is critical for accurate analysis. We found that first tamping down the sample and then running a spatula (flat side) over it minimizes sample variation.

2. *Sample dilution vs. pure sample*. Pure-sample analysis was selected. Sample dilution with KBr does improve sample reproducibility; however, it also changes the relative peak intensity by diluting out the carbon residues and enhancing the mineral structure. There may be uses for the mineral structure obtained by dilution, but at this time we will proceed by analyzing pure samples. On the other hand, organic soils will require mixing with KBr.

3. *Identifying outliers*. Because of the heterogeneous nature of soils, it is important to determine if the soil subsample being evaluated is a fair representative of the soil being characterized. Several methods were tested to determine the method that would most accurately identify sample outliers. Methods tested over multiple samples were peak area, peak height, first-derivative peak area and height, and a partial-least-square (PLS) method. The PLS method was shown to work best.

4. *Particle-size studies*. Sample reproducibility improves until particle size reaches approximately 100 micrometers (µm). Beyond 100 µm, there is no real improvement. Larger particles tend to be minerals that do not easily grind. Because mineral content in the soil is important for characterization, we must retain mineral information.

Hence, we are working on a statistical method to minimize sample reproducibility issues. We studied the effect of sieving samples and analyzing different fractions. The sieving did not improve reproducibility, but it did provide information on relative abundances of different soil components at each sieve size.

5. *Grinding before analysis*. Use of a mortar and pestle improves reproducibility. Soil samples will settle over time. To obtain as homogeneous a sample as possible, samples were placed on a vortex mixer before analysis. Reproducibility was still poor. These samples were then poured into a mortar and ground to determine if this final grinding would improve reproducibility. Grinding provided an improvement over simple vortex mixing. The improvement varied from none to 30% for the original 20 replicates. Outliers were identified by calculating the average and standard deviation. Samples that were either one standard deviation above or below the average were eliminated. Both ground and non-ground samples with mirror backgrounds were compared after the outliers were removed, using as criteria the percent of the standard deviation over the average. With the outliers removed, we found the reproducibility of ground samples improved by a factor of two over non-ground samples.

6. *Resolution of the sample reproducibility issue*. Resolving the variance in sample reproducibility is critical for the success of the study. As described above, 20 replicates were run for each standard, and outliers were identified. After the outliers were removed, the remaining samples were again analyzed to identify those samples within the range of average plus one standard deviation through average minus one standard deviation. Those meeting the criteria were selected and again analyzed, and the average spectrum was obtained for each selected set. It was found that when the percent of standard deviation/average was less than 5%, further removal of outliers was not necessary because the average spectra were essentially identical. The average of the first 10 replicates compared to the average of the second set of ten replicates showed a spectral variation of less than 2%. Hence, 10 samples will be used for sample analysis, but a full 20 samples will be used for developing the calibration and training sets.

7. *Muffle-furnace treatment of samples to remove carbon*. A sample is placed in a muffle furnace at 350°C for 24 hours to remove organic carbon without changing the mineral structure. In theory, subtracting the muffle-furnace spectrum from the original spectrum should result in a carbon-residue spectrum. We are currently investigating the value of this approach. The subtracted spectrum enhances the C-H, C-OH, and C=O regions of the spectrum.

8. *Dilution of the organic fraction*. A 20X dilution of the sample with KBr was tested to see if the carbon fraction could be diluted out without thermally changing the mineral structure. A KBr background had to be used. The lower response using KBr as background hampered this approach for soils containing low organic matter, but greatly improved response in soils containing high organic matter.

Proposed Work for FY 2011

We are in the data-collection phase of creating a training set. As previously mentioned, our first focus will be on Fermi NERP soil samples. These mineral soil samples have high organic carbon contents and are well characterized. The calibration set will be built by running 20 replicates for each sample. The outliers will be removed using the methods described above. The remaining spectra will be averaged and the average used as the training set spectrum. The training set then will be used to develop a PLS method that will be used for sample analysis. A validation set will be generated by using the same methodology used to collect the training set. The validation set will be analyzed with the PLS method to determine experimental error. Improvements will be made to the method as required. Once the method is validated, samples will be run. Ten replicates will be run for each sample and outliers will be removed. We will then determine if it is best to take the average of all spectra, take the average of the outliers, or analyze each spectrum and determine the average result. A database of results will be developed, and sample results will be entered into it.

Non-Refereed Publications and Presentations

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Accelerating the MG-RAST Metagenomics Pipeline

2010-131-N0

Narayan Desai, Ewing L. Lusk, and Folker Meyer

Project Description

MG-RAST is the leading pipeline for the analysis of metagenomics data worldwide. Because of the rapid growth of sequence-data production on next-generation sequencing platforms, at a rate approaching tenfold annual growth, better analytical techniques and algorithms are needed to analyze these new data sets in a timely and cost-effective manner. Our

goal for this project is to improve the throughput of MG-RAST to keep pace with the growth in sequence data-set sizes by approximately tenfold annually.

Mission Relevance

This project is relevant to DOE's missions in science and the environment. Traditionally, gene-sequencing technologies have only been applicable to organisms that could be isolated and cultured. This restriction limited the use of these technologies to a very small percentage of the natural biosphere. Metagenomics is an approach to analyze the microbial communities present in samples of genetic materials gathered from the environment, often from soil. Metagenomic analysis provides insights into the ecology of these communities, as well as metabolic effects of communities, and allows direct comparison of disparate communities.

Large-scale metagenomics provides insight into the abundances of organisms, functions, and proteins in the natural environment, leading to applications in bio-energy and remediation and enabling bio-prospecting. High-quality, high-performance metagenomics analysis tools are critical to fully understanding the carbon cycle and links between microbial communities and climate effects.

FY 2010 Results and Accomplishments

Our primary technical priority was to improve the aggregate throughput of the MG-RAST pipeline to keep pace with the explosive growth in sequence data. We were quite successful in this regard: MG-RAST had analyzed 60 gigabase-pairs (GBP) of data in the two years before the start of the project. During FY 2010, MG-RAST analyzed over 360 GBP of data, accomplishing the same each month as in each of the two prior years.

We developed metrics to assess our progress. Because bioinformatics is quickly growing to be a data-analysis-limited science, understanding the properties of our analysis is critically important. Our initial work in this area consisted of benchmarking key bioinformatics analysis applications on platforms offered by commercial cloud providers. This work is notable because it quantifies the exact costs of metagenomics data analysis, on the basis of commercial cloud pricing. A cost-estimation regimen enables reasoned discussion about the costs of various data-analysis operations, along with the statistical properties of these approaches. We are convinced that the addition of these data to research discussions of algorithms and techniques will help to begin the transformation of genomics into a mature computational science.

Performing this exercise verified two of our hypotheses about genomics in the near future. First, the cost of data analysis consumes an increasing portion of the overall costs of data sequencing. This cost breakdown is quite different from that seen historically in genomics. Previously, computing costs had been so low as to not be considered in cost breakdowns; computing was effectively free. With the rapidly growing fidelity in sequencing instruments, this is no longer the case, and we can now quantify the growth in these costs. Second, well-established analysis techniques often have dramatically different costs. These insights have shaped our strategy for the DOE-KBASE initiative.

As a result of the exploratory work done on clouds, as well as the expertise developed in parallel load balancing in the ADLB (Asynchronous Dynamic Load-Balancing Library) project, we implemented the AWE system as infrastructure for MG-RAST. AWE is a wide-area work-coordination system. It distributes a bioinformatics workload across a set of distributed, unreliable computational resources. AWE uses domain-specific representation of work, representing data in terms of bioinformatics constructs. It is able to scale the sizes of work units on the basis of the capacity and speed of available compute resources, as well as tools available on client platforms. Reliability becomes a more visible problem on distributed systems, so AWE implements a lease-based reliability mechanism to ensure that work is not lost.

Increased pipeline throughput provided by AWE was used to great effect in the NIH Human Microbiome Project, in the context of our work in the UH2 phase of the project. These capabilities were used to analyze a large volume of data we would have been unable to analyze previously. These efforts were recognized by the HMP project management and have resulted in a funded project in the UH3 phase.

Proposed Work for FY 2011

While we have dramatically increased the throughput for MG-RAST, much more work remains to be done. We expect growths in sequence data in FY 2011 that are similar to FY 2010, so more performance improvements are needed. In FY 2011, we are targeting algorithmic improvements to increase the performance of data analysis. Currently, the major computational cost in metagenomics analysis is in the sequence-similarity comparison. MG-RAST currently uses BLAST from NCBI. We plan to investigate alternatives to the BLAST algorithm for sequence similarity, performing a thorough comparison of the tradeoffs of different techniques in terms of fidelity and performance, as well as scaling up the analytical routines to support modern multi-core architectures effectively.

Another new bottleneck we have experienced after scaling up MG-RAST throughput lies in the database layer. As more information is known about the breadth of microbial diversity, the size and complexity of metagenomics data products has increased. New data approaches are needed to enable comparison of metagenomics data sets and an overall view of the communities being analyzed. We plan to develop new mechanisms for storing data and building comparison tools to build more powerful metagenomics analysis capabilities.

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Wilkening, J., A. Wilke, N. Desai, and F. Meyer, "Using Clouds for Metagenomics: A Case Study," in Proceedings of IEEE International Conference on Cluster Computing (Cluster09), New Orleans, LA, Pages 1–6, August 31–September 4, 2009.

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High-Throughput Reconstruction of Metabolic Models for Organisms with Applications in Energy, Bioremediation, and Carbon Sequestration

2010-139-N0

Rick L. Stevens, Christopher S. Henry, and Folker Meyer

Project Description

Since the first prokaryotic genome was sequenced in 1995, extensive effort has been applied toward the construction of genome-scale models of bacterial metabolism in order to better understand how the cell converts simple sugars into DNA, RNA, proteins, and complex lipids. These models are useful for a variety of important applications: predicting the media conditions that will enable an organism to be cultured in the lab; predicting and controlling the interactions between different organisms in a microbial community to improve carbon sequestration in the environment; designing metabolic engineering strategies to reshape the metabolism of a cell to produce biofuels, commodity chemicals, and pharmaceuticals; and improving crop yield by identifying organisms that best contribute to soil fertility. Unfortunately, because of the extensive amount of manual curation and computation that is required to build a new genome-scale metabolic model, the pace of new model reconstruction is dwarfed by the pace at which new complete genome sequences are emerging.

In the past 10 years, 40 genome-scale metabolic models have been published, while 1,000+ genomes have been sequenced. Fortunately, new methods have emerged that enable automation of various steps in the model-reconstruction process, which we have implemented and integrated into an automated model-reconstruction pipeline. Now that this pipeline exists, we have the opportunity to put it to work building genome-scale models for organisms that are important for applications of interest to the DOE, including: cellulose degradation, metal reduction, bioremediation, biosolar energy, climate change, energy production, carbon sequestration, and soil sustainability. We are also exploring options for migrating the most computationally intensive steps of our pipeline to large-scale computing environments (clouds and clusters).

Mission Relevance

This project is relevant to DOE's missions in science and energy. The genome-scale metabolic models produced as the main product of this research drive forward numerous DOE research areas: cellulose degradation, metal reduction, bioremediation, biosolar energy, climate change, energy production, carbon sequestration, and soil sustainability. Experimental biologists will benefit from these models as they provide a means of analyzing existing experiment results and optimizing the design of future experiments to maximize learning. The proposed scale-up of the model pipeline will enable reconstruction of models for all sequenced prokaryotes, including many pathogens. This work will benefit NIH (National Institutes of Health) researchers studying methods to fight these pathogens. Because we will be establishing the technology and infrastructure required to maintain these models with the most up-to-date information, these models will be an enduring resource for the entire research community.

FY 2010 Results and Accomplishments

In FY 2010, we released a website for the automated reconstruction, optimization, and analysis of genome-scale meta-

bolic models: *http://seed-viewer.theseed.org/models/*. In total, we built models for over 1,000 distinct organisms. This effort effectively increases the number of available genome-scale metabolic models by a factor of 25 in a single year and clearly demonstrates the success of our efforts to develop infrastructure needed to generate models in high-throughput mode. We also transitioned portions of our Model and Biochemistry database to SQL, making it possible to rapidly expand this database to accommodate significant growth in the number of models available for analysis, and we constructed a web API (Application Programming Interface) for our model data, facilitating the distribution of model computations over the cloud, as well as enabling users to access model data programmatically.

To improve the coverage and quality of our models, we performed curation and literature data mining on biofuel biosynthesis pathways (namely, isoprene and short-chained alcohol biosynthesis) and carbon fixation pathways (namely, archaeal and prokaryotic non-photosynthetic pathways). We built detailed models of these pathways and are using these models to identify organisms most suitable for carbon sequestration, biofuel production, and linking carbon sequestration to biofuel production.

Proposed Work for FY 2011

In FY 2011, we will continue to construct new genome-scale metabolic models by using the Model SEED, including models for the over 3000 currently sequenced prokaryotes. We will also continue to develop new subsystems and biochemical pathways to represent biological pathways that are important for DOE missions. These include metal reduction pathways and fuel biosynthesis pathways. We will gather experimental data on the DOE target organisms to validate and improve the models of these organisms. We will continue to build on our network of researchers engaged in enhancing the Model SEED and the models, subsystems, and biochemical pathways found within the Model SEED. Finally, we will be applying metabolic models to simulate interactions and activities within a microbial community.

Refereed Publications and Presentations

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Next-Generation Sequencing Core: Expanding the Number of Environments Reachable with Metagenome-Directed DNA Sequencing

2010-150-N0

Next-Generation Sequencing Core: Increased-Resolution Metagenomics

2010-151-N0

Kevin White, Dionysios A. Antonopoulos, and Folker Meyer

Project Description

Biological systems play a key role in such processes as environmental remediation or the control of carbon uptake by terrestrial ecosystems, thereby playing a crucial role in larger climate-scale phenomenon. In these two projects, our aim is to apply second-generation DNA sequencing technology to study problems like these relevant to DOE missions. These genome-driven capabilities are used to conduct metagenomic sequencing of complex microbial communities from environmental samples in order to obtain information about the types of genes and their relative abundances.

The project 2010-151-N0 is focused on developing approaches for increasing yields of high-quality DNA from sub-gram amounts of environmental samples and the generation of high-quality libraries for next-generation DNA sequencing platforms from ever smaller amounts of input of DNA (sub-microgram amounts).

Advances in high-throughput DNA sequencing technologies are allowing systems-oriented approaches to characterize microbial community structure and function. By taking advantage of second-generation DNA sequencing technologies and integrating it with powerful informatics analysis capability, we can generate the scale of sequence data that parallels the number of genes underlying these processes. However, the present sequencing technologies need inputs of DNA that, in many cases, require biomass surpassing the carrying capacity of the environments from which they are sampled. The amount of DNA obtained per sampled system drives the quality of the *in silico* reconstructions derived from the data. Sampling an increased number of DNA fragments will allow higher-quality metabolic and phylogenetic reconstructions. Some environments are therefore not tractable with current (next-generation) DNA sequencing technology.

The project 2010-150-N0 serves to develop approaches for accessing the genetic information associated with lower-abundance members of environmentally derived microbial communities. These approaches include the development of internal standards to gauge sequencing coverage, subtraction approaches to enrich rare occurring sequences, and RNA-oriented approaches to focus on expressed genes.

Another limitation regarding systems-oriented approaches is the loss of resolution, or "granularity," of the system; essentially, the effect and impact of lower-abundance microorganisms are lost as noise in the milieu of the community as a whole. Ever-increasing output of next-generation DNA sequencing platforms is a brute-force approach that we are using to obtain information about low-abundance organisms; it has previously been leveraged successfully in mapping rarely occurring microbial community composition via deep sequencing of specific gene markers (i.e., 16S rRNA-based approaches).

Mission Relevance

Accessing the gene content of environmental microbial communities has been the basis for inferring *en masse* the function of the uncultivable fraction. Metagenome sequencing has been ongoing for several years; however, the combination of next-generation DNA sequencing with shotgun metagenomics is unique to Argonne National Laboratory. Nevertheless, only by increasing the throughput of samples analyzed will a systems-based analysis be possible.

This type of analysis is necessary to make the linkages to environmental-scale processes underlying climate change, which is directly relevant to DOE's energy and environment missions. Indeed, in a call for proposals in 2010, the DOE Office of Biological and Environmental Research (BER) stated that it "supported basic research aimed at achieving a systems-level understanding of plants, microbes, and microbial communities relevant to DOE missions." The work in these two projects is clearly related to this BER program. Moreover, the work in these two projects adds value to the approaches used for soil and subsurface metagenomics conducted in other allied LDRD projects.

FY 2010 Results and Accomplishments

Both projects were designed to address facets of a fundamental problem facing the study of natural environmental communities — increasing the frequency of data capture of a dynamic microbial community over spatial and temporal scales. The challenge is compounded by the fact that for many microbial communities being studied, their sheer biological diversity begets rare occurring species that, under the appropriate environmental condition, play a significant role in a system's function. The advent of next-generation DNA sequencing technologies provides the appropriate depth of sequencing (i.e., over-sampling) necessary to retrieve information about these rare microorganisms. However, increasing the number of sampling events to create dynamic models of how these communities form and respond is predicated on minimizing the amount of biomass needed for shotgun sequencing. The minimization of biomass needed for shotgun metagenomics was required for the following three experimental scenarios: (1) low-biomass environments, (2) smaller-volume samples, and (3) intensive spatial-distribution sampling. (These examples can be extended to bench-top experimental systems that would be limited in the scale needed for intensive temporal sampling). Two major laboratory approaches to solving these problems concerning low-yield systems were selected in FY 2010: (1) modifying the upstream processing of the samples (e.g., whole-genome amplification-based approaches) and (2) modifying the DNA sequencing processes (e.g., library generation).

Whole-genome amplification via multiple displacement amplification (MDA) has been increasingly used for generating sufficient template DNA for library constructions. With the adoption of 454-based DNA sequencing at Argonne (the initial widely used next-generation DNA sequencing platform available), template requirements were on the order of 5 micrograms of high-quality DNA. As the platform and workflows matured, this requirement decreased over time (including adoption of the Illumina series of DNA sequencing platforms for shotgun metagenomics). However, issues of accurate representation of gene abundance within the samples have been an ongoing concern. To offset this, we focused on quality control efforts to temper the amount of amplification necessary to construct high-quality DNA sequencing libraries. This work led to modifications of library construction methodologies in order to maximize the yield of appropriately sized fragments of template DNA (i.e., focusing the size distribution of fragments). Adoption of sonication-based technologies into this part of the workflow allowed a further decrease in the template requirements to sub-microgram amounts. These combined efforts overall have decreased the input requirements by an order of magnitude. The technologies currently are being used to explore temporal developments of environmentally derived microbial communities.

Additionally, increasing the throughput of sampling for experiments produced a corresponding increase in data production that required the development of new bioinformatics approaches. In relation to data handing and analysis, we had previously added single-gene-based community reconstruction to further the resolution of microbial community composition from environmental sample sets via inventories of conserved gene markers (i.e., the gene encoding for the small subunit of ribosomal RNA). Although the identification of low-abundance populations within these communities was possible, the real advantage was the increased throughput

of sample analysis. Further collaboration with the group of Dr. R. Knight (University of Colorado) demonstrated the correlations between these types of data (SSU rRNA-based) with the functional gene data sets produced from shotgun metagenomics (multigene-based). This led to augmentation of the MG-RAST analysis pipeline to be able to integrate these data types from the in-house prototype that had initially been developed.

Associated strategies developed for an increased throughput of data analysis included adoption of physical and chemical parameters associated with samples ("metadata") into the MG-RAST framework, thereby enabling cross-sample comparisons between experiments. This was implemented in relation to a high-intensity sampling of microbial communities from a prairieland ecosystem (e.g., Fermilab National Environmental Research Park [NERP] site). The ability to sample, process, and analyze the approximately 750 samples associated with this study would not have been possible without the developments made during the course of the projects described here (developments in both the wetlab and bioinformatics components).

Further efforts on developing automated workflows in MG-RAST for analyzing assembled genomes from metagenomic data were carried out following the implementation of the Illumina GAIIx DNA sequencing platform. The first set of Illumina data used to inform these workflows was associated with research on contaminant stabilization in a subsurface environment (e.g., the reduction of uranium at the DOE's Uranium Mill Tailings Remedial Action [UMTRA] site). From the relatively simple microbial community found in this environment, the workflows developed are geared toward exploring fine-scale variation in microbial communities.

Simultaneous Ecological Assessment and Characterization of Novel Proteins from a Soil Microbial Community

2010-195-N0

Jack A. Gilbert and Folker Meyer

Project Description

Communities of microbial organisms play a major role in earth's biogeochemical cycles. However, until recently, studying those microbial communities presented major technical challenges, leading to a very sketchy understanding of microbial systems. With the advent of second-generation DNA sequencing technology, we can now study microbial systems *in situ* by sequencing their genomes (metagenomics) and also study the gene expression in those communities (metatranscriptomics). However, while we can generate large quantities of data, interpreting the data relies on existing biological knowledge captured in a variety of databases. A major source of uncertainty is the fact that we cannot identify proteins of identical function from metagenomic data alone. Identifying those *isofunctional* proteins (and studying the overall diversity of proteins) has become much more relevant with the advent of metagenomics.

Currently, metagenomic and metatranscriptomic approaches suffer from a significant knowledge gap about the function of many of the putative proteins identified. The problem is that there are hundreds of thousands to millions of unknown sequences—and only three ways of assigning function to these proteins. The first and most reliable way is to clone the gene, express it in another cell, and see what function it may impart; this is a very slow process, and fundamentally, the function of interest needs to be known. To circumvent this problem, researchers compare the protein to already characterized proteins, by either sequence or structure. Sequence is the currently accepted method, but many proteins having different sequences perform the same function. Hence structure is currently the easiest route to market: If an unknown protein has the same structure as a known one, it is very likely going to have the same function.

To identify which proteins to focus on from the millions of targets, the researcher must determine which ones are important in the ecosystem of choice. It is therefore necessary to apply next-generation sequencing to produce an ecologically relevant, statistically designed experiment, for example, to examine a soil ecosystem. From this study, one can determine the top 1,000 relevant targets.

Moreover, promising targets from this analysis can be further analyzed and protein structures confirmed by using the high-throughput protein crystallization facility at Argonne. Once we have such protein structures, a protein-folding homology search can be run to determine the putative function of that protein. The data can then be fed back into the ecologically relevant data to determine what impact this information has on the interpretability of metagenomic and metatranscriptomic analyses.

Mission Relevance

The genetic and protein information acquired during this study is of direct relevance to the DOE missions in renewable energy, environmental analysis and remediation, and basic science. In energy production, we have already seen the use of synthetic organisms that could have major ramifications for renewable energy from photo bioreactors. Identifying key genes in the process and using metagenomics to determine genes that produce more efficient proteins for these processes is a potential objective of this research. Environmental analysis

and remediation will be informed by metagenomic and metatranscriptomic analysis to explore environments for genes and proteins of interest. The targets could be used for remediation purposes, and characterization of different environments will have dramatic impacts on how we view, for example, uranium cycling at contaminated sites. In the context of fundamental science, this research will produce a paradigm shift in microbial ecology and ecological theory by exploring microbial life from the microbes' perspective. We want to help define how microbes exist in communities and how they interact with plant life. In soil ecosystems, this knowledge has direct relevance to rhizosphere and leaf-based community interaction and plant productivity, which are especially relevant for agriculture.

FY 2010 Results and Accomplishments

This project was active for the final three months of the fiscal year. Thus, in FY 2010, we began to furnish and set up the laboratory required for analytical techniques. We anticipate processing our first samples in early FY 2011. We acquired more than 4000 environmental samples for analysis, and we began processing the metadata associated with these to determine which groups they fall into.

Proposed Work for FY 2011

We will start by analyzing existing metagenomic information and exploring patterns in the unknown fraction of the DNA and/or RNA that codes for novel but unidentifiable proteins. From this information, we will produce a list of targets for protein exploration using alternative facilities at Argonne. In addition, we hope to generate one of the largest contiguous metagenomic datasets on Earth through the use of Illumina sequencing and communication with various institutes. Using this method, we hope to produce a first global map of proteins versus environmental parameters.

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OTHER NOVEL R&D

Inducement of Targeted-Organ Protective Cooling by Using Ice-Slurry Coolants

2008-191-R2

Kenneth E. Kasza, Paul F. Fischer, Adrian M. Tentner, and Yue Wu

Project Description

This project focuses on the development of exploratory versions of ice-slurry medical cooling equipment and use protocols for inducing targeted organ/cell protective cooling for protection against ischemia, reperfusion, and neurological damage. The experiments involve a combined effort between Argonne researchers and University of Chicago physicians. As surgical procedures push the limits in less-invasive excision, and to protect ischemic organs, there is an unmet need to provide rapid cooling protection. We are developing ice-slurry coolants that possess large cooling capacities generated from the melting of transported, tiny ice particles that can be topically applied or selectively injected into organs to induce protective cooling. We have devised ice-slurry production and delivery equipment to induce protective cooling during minimally invasive laparoscopic kidney, cardiac/cardiovascular, and neurological impacting surgeries, as well as to preserve transplant organs in deceased donors.

Mission Relevance

This project is tied to DOE's mission in science, with potential interest from DOE-OBER. The research represents an important step in utilizing and extending the results of previous breakthrough DOE energy research by developing and applying slurry protective cooling to help improve surgical outcomes and save lives. Patients and the medical community are the direct beneficiaries. The research being conducted is also of relevance to the missions of the National Institutes of Health (NIH) and U.S. Department of Defense (DOD.) This work is an excellent example of how DOE-developed technological capabilities may also be applied to larger and different needs of the nation.

FY 2010 Results and Accomplishments

In FY 2010, we established the ability to reliably make and deliver slurry of 50% ice (our previous best was 25%) through various medical delivery ports — for example, 85-cm-long, 1.5-mm-diameter catheters used for heart and other organs (Figure 1).

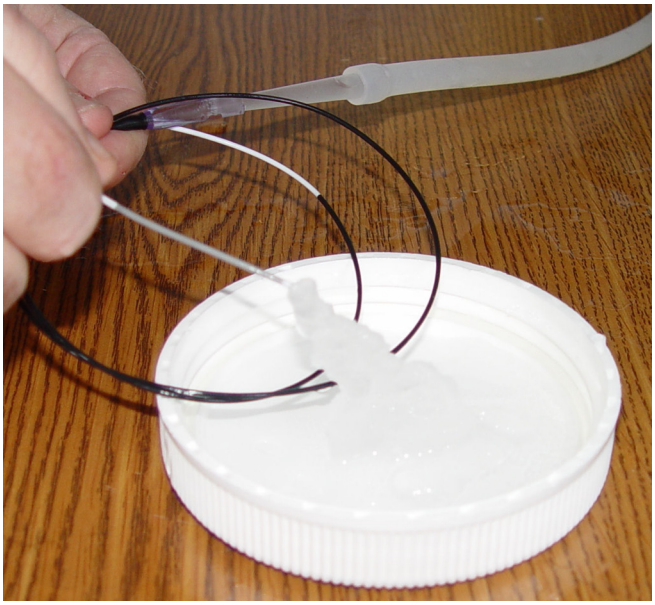

Figure 1. Cardiac catheter delivering ice-slurry for use in cooling the heart and other organs deep within the body.

We also designed the first portable-computer automated ice-slurry production and delivery system for use in the operating room (Figure 2).

Figure 2. Portable-computer automated ice-slurry production and delivery system.

A sterilization protocol for producing sterile ice-slurry was developed and validated in animal renal surgery. The sterilization protocol is compatible with the sterile requirements for human surgery to facilitate the human clinical trial.

An air bubble removal device was designed to remove potentially deadly air bubbles that could occur in the ice-slurry if it is infused with blood. This air bubble removal device worked well in the animal experiments related to heart cooling. In addition, the ice-slurry recipe has been improved from hypertonic ice-slurry (1.36% salinity) to isotonic ice-slurry (salinity 0.9%) to avoid the side effects of hypertonic solution to the body.

In a combined effort with University of Chicago urologists, 28 animal experiments (11 ice-slurry cooling, 11 cold-saline cooling, 6 no cooling) were conducted in swine laparoscopic renal surgery. These experiments show that ice-slurry cools kidneys faster, uses less volume of coolant, maneuvers easily during the surgery, and provides equivalent protection to the renal function as cold saline. The results of the experiments will be used to support the application to U.S. Food and Drug Administration for a clinical trial on human renal surgery.

In a combined effort with University of Chicago cardiologists, three animal experiments were conducted to assess the use of ice-slurry for heart cooling/protection during a heart attack. The ice-slurry was delivered into the coronary artery of the heart, and rapid cooling was achieved. These experiments indicate promising results for the use of ice-slurry in heart disease treatment.

Patent Application

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Smart Polymers as Molecular Therapeutics and Sensing Agents

2008-192-R2

Millicent A. Firestone and Simonida Grubjesic

Project Description

The objective of this research is to design optimal polymeric materials that can facilitate directed interactions with cell membranes, thus allowing control (i.e., polymeric therapeutic agents) and/or monitoring (i.e., sensing agents) of cell membrane function. More specifically, our goal is to determine how to appropriately functionalize biocompatible tri-block polymers in order to retain biological activity, while building the robustness of synthesized materials.

Mission Relevance

The research for this project focuses on addressing one of the DOE-identified grand challenges in soft materials, "design principles for the synthesis of self-assembled materials." In this multidisciplinary research project, the basic physical sciences effort in the synthesis and characterization of bioactive polymers at Argonne is coupled with the life sciences effort of testing these materials in a biologically relevant environment at the University of Chicago. This effort offers a unique opportunity to further biomolecular materials applications in solving energy-related challenges. In addition, this research project lays valuable groundwork for a significantly larger effort to examine basic research on the physical principles of polymer architecture and its relationship to the association and function of cell membranes. In support of DOE's mission, this effort will be applied toward building platforms for the development of biomolecular soft materials and devices with potential energy significance.

FY 2010 Results and Accomplishments

Prior work evaluated the insertion of a family of amphiphilic block copolymers within the artificial membranes developed here at Argonne. Small-angle x-ray scattering (SAXS) studies were used to image the nanoscopic association of a bisphenol A linked poly(ethylene glycol) (PEG) diblock with artificial membranes. These studies showed that the polymer architecture results in the hydrophobic bisphenol A linkage inserting (shallow) into the alkyl bilayer region of the membrane, thus causing the two symmetric PEG blocks to be laterally directed

across the membrane surface. The conformational state results in the polymer forming a steric coating, or chemical barrier, on the membrane surface. *In vitro* studies were conducted to test the polymer's ability to function as a steric barrier against a common gut-derived pathogen, *P. aeruginosa*, and invasion on IEC-18 cells (a cell line derived from the ileum of rat intestines). Fluorescence microscopy monitored the temporal association of the dye-labeled bacteria against unperturbed, radiation exposed (13 gray), and radiation exposed and polymer-treated cells. These studies ascertained that the polymer architecture, as predicated by X-ray scattering, was effective at repelling the bacteria off the cell surfaces, thereby inhibiting bacterial translocation. Therefore, it was determined that the polymer can function as an artificial mucin. This research demonstrates the successful linkage between the fundamental physicochemical studies and biochemical functioning.

Refereed Publications

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NEMS-Based Nanosensors for Basic Science Research

2008-195-R2

Omar D. Lopez and Derrick C. Mancini

Project Description

This project involves the integration of metallic nanostructures with nanomechanical devices to control the short-range optical forces that act among nanostructures. The plasmon resonance frequencies of these nanostructures can be controlled by mechanically tuning the interparticle separation. This effect can be experimentally demonstrated by depositing metal nanoparticles on top of micron-size probes, the relative position of which can be controlled by electrostatic forces. The probes are nanomechanical actuators capable of sub-nanometer (nm) control of the relative position between the particles. This research project will demonstrate the integration of plasmonic structures with nanomechanical devices to allow real-time control of their optical properties by tuning the short-range interaction between the nanoparticles.

Mission Relevance

This project focuses on the development of new nanomechanical sensors and device architectures, which would thereby result in novel detectors with ultra-high sensitivity. The ultimate goal of the project is to understand the fundamental forces that occur in the nanoscale world in order to manipulate and control them in engineered nanostructures. This project is therefore relevant to DOE missions to promote scientific and technological innovation. Further, the findings are expected to have an impact on DOE programs that require precise measurements of small forces.

FY 2010 Results and Accomplishments

The main activities developed during FY 2010 focused on the optimization of the mechanical actuator design and on the calibration of the fabricated devices *after* we incorporated nanostructures onto them. All of these activities have been completed, and the optical characterization of these devices is under way.

As stated above, we designed, simulated, and fabricated a variety of micro-electro-mechanical-systems (MEMS) probes capable of controlling the spacing between metallic nanoparticles with sub-nanometer precision control. After fabricating the mechanical probes, we studied a variety of nanofabrication processes, which allowed us to fabricate nanostructures at the tip of the probes. The simplest approach employed focused ion beam (FIB) technology to etch (Figure 1a) and/or deposit (Figure 1b) the desired pattern onto the tips. This nanofabrication process is very flexible, and it allows one to pattern a large variety of nanostructures on any substrate. After the first fabrication, we performed optical measurements of the scattered light from these nanostructures. To our surprise, we discovered that the reflected light from the substrate that supports the nanoparticles (in this case, Si) generates a large illumination background, which makes it very difficult to identify the radiation coming from the nanoparticles.

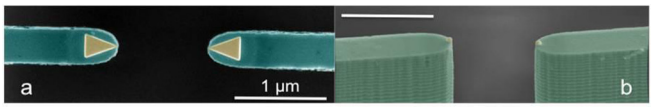

Figure 1. Scanning electron microscope (SEM) images of metallic nanostructures integrated onto MEMS actuators (the scale bar represents 1 µm in both pictures). The images show details of two characteristic silicon tips with two different types of gold nanostructures: (a) depicts a gold (Au) "bow-tie" nano-antenna (~200 nm in size), and (b) displays Au nanospheres of ~80-nm diameter. As the distance between tips is reduced (almost forming the bow tie), the distance between the nanostructures is diminished and thus the interaction between nanoparticles can be controlled.

To reduce this unwanted background, we decided that the optimum device should have the nanoparticles located as far as possible from the substrate. As a consequence, we developed a unique fabrication process that allowed us to fabricate nanostructures, such as those shown in Figure 2, where the metallic structures are suspended on the space between the tips. This novel process uses FIB to deposit high-aspect-ratio, needle-like structures made with SiO_2. This is not a trivial task in nanofabrication, since the process requires *simultaneous*

high-precision control of the position and the length of the sharp needles. By using this process, we could fabricate structures with a minimum feature on the order of 5 nm (the tip of the needle) and an alignment accuracy of better than 1 nm. Once the needles were fabricated, we coated them with evaporated Au in order to achieve a metallic nanostructure capable of supporting plasmons. When the SiO_2 needles were coated with Au, the SiO_2 material could be etched away with vapor fluorhydric acid without attacking the gold. The nanoneedles shown in Figure 2, as well as similar structures, were fabricated in this manner.

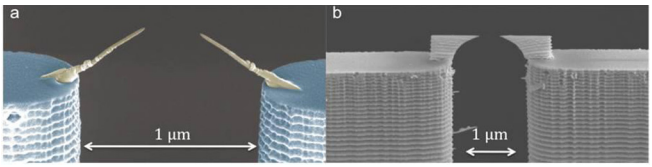

Figure 2. SEM pictures of out-of-plane nanostructures fabricated by FIB. The fabrication of these metallic nanostructures requires simultaneous sub-nm precision control of the location and the height of the structures.

After fabrication of the metallic nanostructures, we performed extensive characterization of the mechanical properties of the devices to experimentally determine the degree of control achievable with these structures. Figure 3 depicts a typical response of the devices. This figure presents experimental data for the gap between the metallic nanoneedles, as shown in Figure 2a, as a function of the applied voltage. The data clearly demonstrate that nanometer-size gaps are achievable with this technology. To our knowledge, this device represents the state of the art for a MEMS device used for position control.

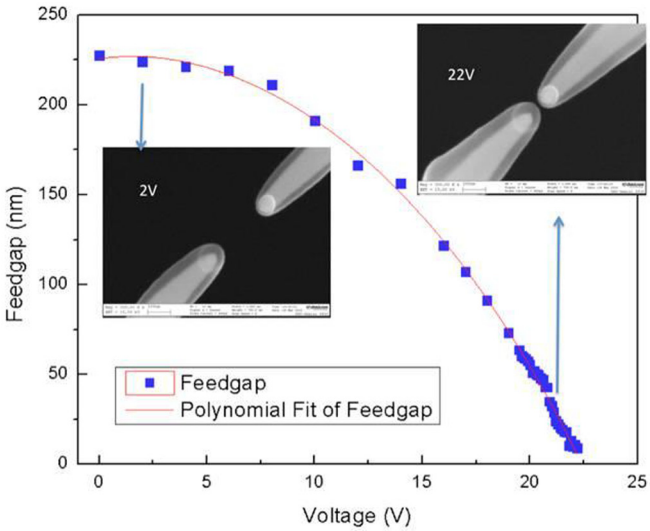

Figure 3. Displacement-voltage characteristic of a MEMS-based nanopositioning device with 50-nm particles incorporated. The device is capable of controlling the gap between particles down to nanometer size.

Currently, we are using devices similar to those described above to control the optical interaction between nanoparticles located at the end of the tips. These designs do not present any significant background generated from the material around the nanoparticles. In addition, we have been able to obtain the optical spectrum of each nanostructure with an acceptable signal-to-noise ratio.

The results achieved in FY 2010 are summarized below:

- We designed and fabricated MEMS-based actuators capable of nanometer position control of nanostructures.
- We developed and demonstrated a novel nanofabrication process capable of incorporating nanometer-size structures onto MEMS devices. This process allows simultaneous control of the position and height of the patterns to be created.
- We characterized the mechanical performance of the devices and demonstrated the ability to control the distance between nanoparticles with a resolution of a nanometer or better.

Proposed Work for FY 2011

During FY 2011, we will finalize the optical measurements of these structures. We expect to demonstrate real-time manipulation of the optical interaction between metallic nanostructures.

Materials Theory

2009-214-R1

Alexei Abrikosov, Konstantin Matveev, and Michael R. Norman

Project Description

This project consists of research on (1) the transport properties of quantum wires, (2) local order in transition metal oxides and layered dichalcogenides, and (3) fluctuation effects in high-temperature superconductors.

Mission Relevance

This project supports the DOE science mission, particularly Office of Basic Energy Sciences (BES) goals in materials research, as outlined in the BES Grand Challenges report ("Directing Matter and Energy: Five Challenges for Sciences and the Imagination," December 2007). The work on quantum wires has direct implications on future device technologies. The work on local order supports experimental programs for developing diffuse scattering capabilities at Argonne's Advanced Photon Source (APS) and Oak Ridge National Laboratory's Spallation Neutron Source (SNS). The work on superconductors will affect the next-generation energy grid.

FY 2010 Results and Accomplishments

We explored the effect of electron equilibration on the transport properties of quantum wires. In the regime of weak interactions, we calculated conductance, thermopower, and thermal conductance in partially equilibrated wires. We showed that in the presence of a long-range disorder potential, full equilibration of the electron system may never be achieved, and, as a result, the resistance of the wire will increase dramatically.

In the local order project, we determined that in the relevant part of the phase diagram where charge ordering could be present, high-temperature superconducting cuprates should exhibit a unidirectional (stripe) order as opposed to a bidirectional (checkerboard) order. Below the charge ordering temperature, nonlinear effects in the Ginzburg-Landau equations that describe the charge order parameter can lead to another instability to checkerboard order. We find that this instability can occur only in a narrow region of parameter space near where the charge ordering effect itself becomes unstable.

In the fluctuation project, we calculated the electronic contribution to the longitudinal and Hall conductivities by using model Green's functions, which have an energy gap due to pair formation. The latter functions were developed to describe angle-resolved photoemission data (taken at Argonne) on the cuprates above the superconducting transition temperature in the so-called pseudogap phase. We found that the planar conductivity as a function of temperature is metallic-like, whereas both the interplanar conductivity and Hall conductivity are insulating-like, in qualitative agreement with the experiment.

Proposed Work for FY 2011

Transport properties of quantum wires. We will study electron lifetimes in one dimension caused by three-electron collisions and by coupling to lattice vibrations (phonons). This project will enable us to address the various properties of quantum wires in the regime where the system is very far from full equilibration. In particular, we will develop a theory on thermal transport in quantum wires where no backscattering of the electrons is present. We expect to find temperature-dependent corrections to the thermal conductance of the wire, despite the fact that the electrical conductance remains quantized.

We will also work on equilibrating strongly interacting electrons, taking into account their spins. In this case, apart from the phonons, there are low-energy spin excitations in the system. They will likely provide the most effective channel for equilibrating the system. This project will enable us to apply our recent studies of equilibration in quantum wires to the long-standing experimental puzzle of the "0.7 structure," where the conductance of the wires plateaus at a value of about half the fundamental quantum unit of conductance – a situation that is thought to be related to the spin polarization of the wire.

Local order in transition metal oxides and layered dichalcogenides. We will consider our Ginzburg-Landau theory in the context of superconducting dichalcogenides such as Cu-doped $TiSe_2$ by comparing theory with the extensive data on these materials from angle-resolved photoemission spectroscopy (ARPES), scanning tunneling microscopy (STM), and x-ray diffuse scattering at Argonne. These materials show unusual behavior where the superconductivity is a function of doping peaks when charge ordering is suppressed. Diffuse scattering demonstrates that there is an entire region in momentum space where the charge susceptibility is soft. Our goal is to understand the origin of the momentum dependencies seen in these measurements, as revealed by autocorrelations of the APRES spectra (which measures the joint density of states) and by Fourier transform of the local density of states from STM (which measures a similar quantity). We will then calculate the charge susceptibility itself in order to comprehend the novel soft mode region mentioned above. We will relate this result to the nature of the charge order in these systems and its relation to superconductivity.

Fluctuation effects in high-temperature superconductors. We will try to understand the qualitative change of the Nernst effect (transverse current response to a magnetic field in the presence of a temperature gradient) in the cuprates when entering the pseudogap phase where an energy gap exists above the superconducting transition temperature. In particular, we want to know if the giant enhancement of the Nernst signal in this phase is due to fluctuating vortices or to the strong temperature dependence of the number of gapless electronic states caused by the formation of the pseudogap. We will determine this by generalizing the Gaussian theory for the fluctuational Nernst signal to account both for the reduced electronic density of states due to the pseudogap and for the short wavelength fluctuations due to vortex-like excitations. We will do this by considering a model in which the amplitude of the pairs is fixed in magnitude but the pairs have a finite relaxation time. This can be achieved by using a pair propagator that is factorized in terms of its spatial and time dependencies. The Nernst signal will then be calculated by using a many-body diagrammatic scheme involving pair fluctuations.

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Dual-Polarization Bolometric Focal Plane Detector for Inflation-Era High Energy Physics

2010-110-N0

Valentyn Novosad, Aaron M. Datesman, Gensheng Wang, and Volodymyr G. Yefremenko

Project Description

Cosmic microwave background (CMB) radiation is an effective probe of the cosmic Big-Bang model of the Universe. The CMB uniform temperature distribution, one-part-in-100,000 temperature anisotropy, and the much smaller E-mode and B-mode polarization anisotropies carry information about the fundamental properties of the early Universe after the Big Bang. High-sensitivity detectors are the key enabling component in observations of CMB anisotropies. Superconducting transition-edge sensor (TES) bolometric detectors have attained photon-background-limited performance. By increasing the number of detectors and using a high-throughput telescope such as the 10-m (meter) South Pole Telescope (SPT), one can achieve the sensitivity required to detect and characterize the faint polarization of the CMB B-mode signal, which is less than 0.1 μK RMS (root mean square). The goal of this project is to improve TES characteristics and to develop a state-of-the-art detector array technology for precision measurements of the polarization anisotropy of the CMB B-modes using the SPT.

Mission Relevance

This project supports DOE's mission in basic science. The project is relevant to several areas of DOE interest, such as dark energy, materials science, and multi-user instrumentation development. The detector under development enables technology for pushing measurements to higher precision, which will lead to new, innovative experiments. The accurate measurement of the CMB B-mode polarization is a critical step in extending our knowledge of both the early universe and fundamental physics at the highest energies. The same type of detector technology (but with a different radiation absorber) can also be applied to soft- and hard-x-ray detectors, where it provides excellent energy resolution and fast array readout.

FY 2010 Results and Accomplishments

1. Polarimeter Design

Design advancements from a basic predecessor project have been made in several areas at multiple scales, from the overall level of the SPT focal plane down to the design of individual absorber-coupled TES detector dies. At the highest level, technological guidance driven by scientific goals and observational strategies has now been firmly established. This guidance allowed us to finalize detector design targets. A waveguide mounting scheme for our dual-polarization configuration has been developed and assessed for functionality and suitability. Methods for integrating this mounting scheme with feedhorns, readout circuitry, and the dual-frequency focal plane array were developed, interrogated, and refined.

We implemented new detector designs that meet project targets for thermal conductance, TES resistance, and operational temperature, along with an effective scheme for face-to-face mounting of individual detectors at a required spacing of ~50 μm or less. Plans to fabricate an entire production run of ~200 detector dies that meet design targets were developed, interrogated, and found to be robust. The polarimeter and TES structure are illustrated in Figure 1.

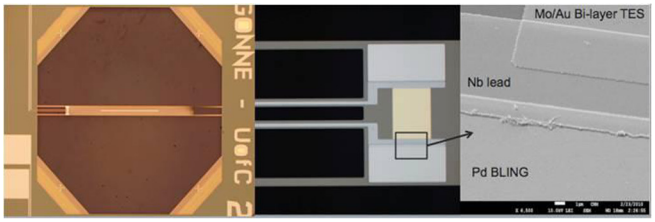


Figure 1. Absorber coupled TES polarimeter. (Left) A 1340-μm × 8-μm PdAu absorber in the middle of 2200-μm × 200-μm silicon nitride rectangle for millimeter wave coupling, a TES at the left end of the rectangle for a thermal power readout, and silicon nitride support beams for thermal isolation. (Center) TES, Pd BLING (i.e., extra metal with a significant amount of heat capacitance to slow down the TES) at both sides of the TES, and Nb leads. (Right) A magnified view of the joint part of TES, BLING, and leads.

2. TES Theory

Theoretical efforts to understand the TES thermal performance were yielded excellent results. Owing to continuing refinements, thermal-modeling results for the absorber-coupled TES detector accord well with experiment and were employed to refine the detector design without the burden of expensive testing. In addition, application of a boundary-limited phonon-scattering model to cryogenic results measured for our suspended silicon nitride structures led to the first empirical determination of the phonon mean free path in this technologically important material.

The TES superconducting transition width and heat capacitance define the detector's response time. The detector's speed is limited by the readout electronics, a frequency-domain SQUID multiplexing system with a 50-kHz bandwidth. To enable stable operation of the detector, we need to slow it down to achieve a 1–2-ms time constant. By tuning the TES superconducting transition width with tailored TES structures and by adding Pd with 2-pJ heat capacitance directly connected to the TES, we are able to control the time constant as desired.

3. Facilities

During FY 2010, we optimized the operational parameters of a 6-in. wafer DC magnetron sputtering deposition system which is dedicated to superconducting thin films. The new system has demonstrated better than 1% thickness uniformity over a 4-in. wafer, along with the ability to deposit superconducting thin films in a confocal geometry, which are simultaneously highly uniform and of excellent quality. Using this system, we demonstrated the ability to produce 25 or more detector dies per week for several consecutive weeks.

Currently, Mo/Au bi-layer superconducting TES performance is well controlled. The bi-layer superconducting sensor's transition temperature is tuned by controlling the thicknesses of the molybdenum layer (~23 nm) and gold layer (~30 nm) and by adjusting the argon pressure in a DC magnetron deposition chamber. The superconducting transition temperature Tc is 480±5 mK; the transition width is 3±0.5 mK.

We are nearing completion of the multiplexed optical cryostat necessary to test detectors with high throughput. The time-domain SQUID multiplexing cryostat and He-3 refrigerator were tested. The cryostat has a liquid helium consumption of 1.2 L/h. The refrigerator has a base temperature of 285 mK, with a holding time of over 30 hours. All the parts for the SQUID multiplexing, including electronics, mechanical parts, and purchased cables and connectors, are complete. Design of the detector focal plane PCB board and on-chip inductor is under way. The SQUID multiplexing system will be used for absorber coupled TES polarimeter testing with a high throughput. The polarimeters will be deployed with SPT for CMB polarization B-modes detection in 2012. The following-up program is called SPTpol, which is jointly funded by DOE and NSF

4. Experimental Characterization

Significant advances were made in FY 2010 in optical, thermal, and electrical testing of preliminary detectors. The project is at a transition from the early demonstration stage to detector mass production mode. Testing included measurements of the optical time constant and optical response, the cross-polarization, beam maps with co- and cross-polar response, and thermal readout efficiency. In every case, test results are promising and are quickly converging to design goals. The dual-polarization polarimeter's optical performance was measured. It has a 30% bandwidth centered at 95 GHz and an optical efficiency of 80%; its cross-polarization absorption is less than 1%. The polarimeter's time constant is ~5 ms for optical powers.

Refereed Publications

Wang, G., L. Bleem, J.E. Carlstrom, C.L. Chang, A.T. Crites, A. Datesman, R. Divan, J. McMahon, J. Mehl, S.S. Meyer, T. Natoli, V. Novosad, J. Pearson, J. Ruhl, J. Sayre, and V. Yefremenko, "Thermal Properties of Silicon Nitride Beams below One Kelvin", IEEE (Institute of Electrical and Electronics Engineers) Trans. on Applied Superconductivity (ASC 2010 proceedings), in press.

Non-Refereed Publications and Presentations

Crites, A.T., L. Bleem, J. E. Carlstrom, C.L. Chang, A. Datesman, R. Divan, W. Everett, J. McMahon, J. Mehl, S.S. Meyer, T. Montroy, T. Natoli, V. Novosad, J. Pearson, J. Ruhl, J. Sayre, G. Wang, and V. Yefremenko, "Progress on ANL/KICP Bolometers for SPTPOL," IEEE Trans. on Applied Superconductivity (ASC 2010 proceedings), in press.

Chang, C.L., J.E. Carlstrom, A. Datesman, V. Novosad, J. Pearson, G. Wang, and V. Yefremenko, "SPTpol," presented at SnowPAC, Salt Lake, UT, March 23–28, 2010.

Datesman, A., L. Bleem, J.E. Carlstrom, C.L. Chang, A.T. Crites, A.R. Divan, J. McMahon, J. Mehl, S.S. Meyer, T. Natoli, V. Novosad, J. Pearson, G. Wang, and V. Yefremenko, "Analytical Solutions for the Design and Evaluation of Absorber-Coupled Waveguide Bolometer Detectors," accepted for presentation at IEEE, IMS2011, Baltimore, Maryland, June 5–10, 2011.

Materials with Square Nets at the Metal/Semiconductor Boundary for Exploring Superconductivity and Other Correlated Electron Phenomena

2010-189-N0

Mercouri G. Kanatzidis

Project Description

This project includes control and manipulation of material phases with square nets to search for new superconductors and other quantum critical phenomena. Materials that provide especially clear or compelling examples of building-block-dependent energy gaps, charge density wave behavior, strongly correlated electrons, superconductivity, and/or unusual magnetism are of particular interest. A fine example

of these materials, pnictide compounds, have generated enormous interest recently because this new class of superconductor behaves very differently from the previously known cuprate superconductors. While the pairing mechanism in iron arsenides might be different from that of the cuprates, the two types of materials also have similarities: they share key magnetic properties, layered structures, variable-valence constituents, and competing states. This new class of solid-state materials presents an exciting opportunity to explore the interrelationship of structure evolution and superconductivity.

Mission Relevance

This project is relevant to DOE's missions in science and energy. Understanding superconductivity and discovering new superconductor materials contributes to our ultimate goal of achieving an "energy superhighway" by replacing copper wires with a superconducting alternative that has higher capacity while eliminating the enormous resistive losses of energy. The properties of modern novel materials, such as high-temperature superconductivity, semiconductivity, phase-change, magnetism, and charge density wave instabilities, are all sensitively controlled by correlations and competition between the lattice, electrons, and magnetism. A complete understanding of the interrelations among these different entities, and the necessary conditions for producing materials with these properties enhanced or tailored, has been identified as a Grand Challenge to the scientific community. Particularly in layered iron pnictide superconductors, only a few groups in North America have undertaken this challenge. The present project goes beyond the existing efforts by targeting a new class of superconductors with a different strategy from those pursued by other groups. The success of the project hinges on our ability to discover target materials and solve aperiodic crystal structures with square nets using superspace crystallography. Use of this technique is, to our knowledge, extremely rare in the United States, and it needs to be strengthened.

FY 2010 Results and Accomplishments

Single-phase $Ba_{1-x}K_xFe_2As_2$ has been the most challenging iron pnictide superconductor to synthesize, because of the extreme difficulty in controlling the Ba/K ratio. We discovered the optimal synthetic conditions for large-scale homogeneous single-phase samples of large single crystals and polycrystalline powders for the entire range of x. The materials obtained showed the best quality among all those reported, on the basis of x-ray diffraction and magnetic susceptibility. An entire series of compositions was studied to elucidate the electronic and magnetic properties related to their superconductivity.

NaFeAs, reported to be a superconductor, turned out to be non-superconducting in a stoichiometric composition, which we synthesized and analyzed. Also, an exciting phenomenon that has not previously been reported for iron pnictides was found. The NaFeAs reacts with water in the presence of air and converts to a new compound, $NaFe_2As_2$, via an intermediate phase $(NaFeAs)_{1-x}(NaFe_2As_2)_x$. The $NaFe_2As_2$ compound is superconducting.

Another approach to exploring new superconductors was attempted and a new class of superconductor, $CsBi_4Te_6$, was discovered. This intrinsic narrow-gap semiconductor, previously identified by us as the best thermoelectric material below 225 K, turned out to be superconducting at 4 K when subjected to p- or n-type doping. Investigations of homologous series, as well as further studies on $CsBi_4Te_6$ are in progress. This project is continuing under the sponsorship of DOE-BES.

Refereed Publications

Manuel, P., L.C. Chapon, I.S. Todorov, D.Y. Chung, J.-P. Castellan, S. Rosenkranz, R. Osborn, P. Toledano, and M.G. Kanatzidis, "Incommensurate Spin-Density Wave and Magnetic Lock-In Transition in $CaFe_4As_3$," *Phys. Rev. B* **81** (2010), 184402.

Todorov, I., D.Y. Chung, H. Claus, K. Gray, Q. Li, J. Schlueter, T. Bakas, A. Douvalis, M. Gutmann, and M. Kanatzidis, "Selective Substitution of Cr in CaFe4As3 and its Effect on the Spin Density Wave," *Chem. Mater.* **22** (2010), 4996–5002.

Todorov, I., D.Y. Chung, H. Claus, C. Malliakas, A. Douvalis, T. Bakas, J. He, V. Dravid, and M. Kanatzidis, "Topotactic Redox Chemistry of NaFeAs in Water and Air and Superconducting Behavior with Stoichiometry Change," *Chem. Mater.* **22** (2010), 3916–3925.

Non-Refereed Publications and Presentations

Osborn, R., S. Rosenkranz, J.P. Castellan, F. Weber, E.A. Goremychkin, D.Y. Chung, I.S. Todorov, H. Claus, M.G. Kanatzidis, and T. Guidi, "Doping Dependence of Resonant Spin Excitations in $Ba_{1-x}K_xFe_2As_2$," presented at the 2010 APS (American Physical Society) March Meeting, Portland, OR, March 15–19, 2010.

Castellan, J.P., S. Rosenkranz, R. Osborn, F. Weber, E.A. Goremychkin, I.S. Todorov, H. Claus, D.Y. Chung, M.G. Kanatzidis, and T. Guidi, "Single Crystal Inelastic Neutron Scattering Measurements of the Unconventional Superconductor $Ba_{0.6}K_{0.4}Fe_2As_2$," presented at the 2010 APS March Meeting, Portland, OR, March 15–19, 2010.

Investigation of Novel Relativistic Quantum States in Iridates

2010-190-N0

John Mitchell and Bum Joon Kim

Project Description

This project takes as its central task the creation of new 5*d* transition metal oxide (TMO) materials, which are the next frontier in TMO science. TMOs figure prominently in condensed-matter science because of their rich spectrum of electronic and magnetic phenomena; their ready ability to be tuned chemically and structurally to expose these phenomena; and their potential for harnessing these phenomena in such functional materials as superconductors, magnets, battery electrodes, and thermoelectric platforms. Considerable effort has been focused on studying and understanding first-row (3*d*) TMOs, under the assumption that it is these early TMOs that have the greatest range of competing phases because of the relatively localized nature of the atomic orbitals (leading to strong electron-electron interactions called correlation). 5*d* TMOs are thought to be wide-band metals because of their spatially extended orbitals. In contrast to this conventional wisdom, we have found that 5*d* systems based on iridium (Ir) defy description in terms of conventional theories and classification as weakly correlated systems, owing to the interplay of strong spin-orbit coupling and weak electron correlation. Spin-orbit coupling, in which the electron's intrinsic angular momentum and its motion around the nucleus are intertwined, provides a mechanism for electric control of spin and forms a basis for spintronics, while correlation effects in oxides lead to emergent phenomena that have characteristics of the collection and not the constituent elements. The objective of this project is to create and understand these emergent phenomena.

Mission Relevance

This project is relevant to DOE's science mission. Our work product is squarely in the area of discovery science, addressing the Grand Challenge of fundamental understanding and ultimately control of electron correlation and novel states of matter through manipulation of materials structure, composition, and architecture. We will deliver science based on insight into systems where spin-orbit coupling is more than a perturbation. Such systems are considered as candidates for spintronics and other low-energy electronics platforms, as well as potential platforms for quantum computing.

FY 2010 Results and Accomplishments

In FY 2010, we focused on single-crystal growth of several classes of iridates with the objective of doing angle-resolved photoemission, transport, and x-ray scattering experiments to investigate novel physical properties that arise from the spin-orbit coupling effects. We successfully grew single crystals of Sr_2IrO_4 of sufficient quality and size for measurements using synchrotron x-rays to acquire its magnetic excitation spectra. Our measurement marks the first successful case of observing the spin-wave dispersion by x-ray in a bulk TMO material. Figure 1 shows the magnetic excitation spectrum of Sr_2IrO_4. At low energies below ~0.5 eV, we observed spin-wave dispersion similar to that observed in the high-temperature superconductor La_2CuO_4, demonstrating that iridates can also be used to study the longstanding problem of the mechanism of superconductivity in the high-T_C cuprates. At energies above ~0.5 eV, we observed new high-energy dispersive modes. On the basis of energetics arguments, we tentatively assigned them as orbital waves — that is, excitations of the spin-orbital ordered structure. A theoretical study is under way.

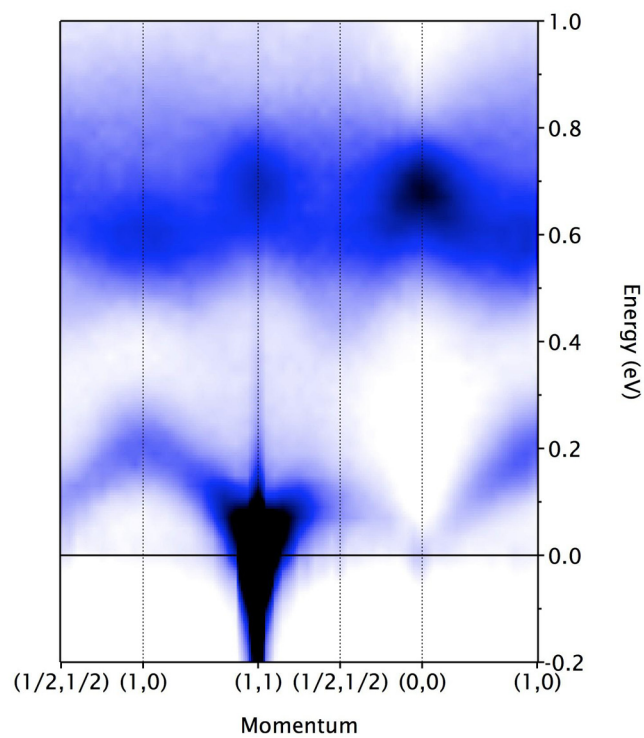


Figure 1. Resonant inelastic X-ray scattering spectra along high symmetry lines in the Brillouin zone showing two branches of magnetic modes. The low-energy (E<0.2 eV) branch corresponds to magnons, while the high-energy branch (0.4~0.8 eV) is attributed to spin-orbit excitons. The notations for momentum follow the convention for the Brillouin zone of a tetragonal cell with unit dimensions and are normalized by p. Color table used is such that darker color maps to higher intensity. The magnon shows vanishing and diverging intensity at the (0,0) and (1,1), respectively.

Proposed Work for FY 2011

Going forward, we will explore novel competing phases where correlation and spin-orbit (relativistic) effects compete markedly. So far, Sr_2IrO_4 is the only established correlated electron insulator in 5*d* TMO; it is, however, very stable against chemical doping. Thus, investigations of materials with different cation elements and different crystal structures in which

solid solutions are possible must be done. We are particularly interested in pyrochlore and low-dimensional systems, such as $R_2Ir_2O_7$ (R = rare earth) and A_2IrO_3 (A=alkali metal), respectively. Metal-insulator transition and superconductivity are expected at the quantum critical point between two phases. We will also perform scattering investigations on samples that will be prepared in this project, exploiting the state-of-the-art synchrotron resources available at the Advanced Photon Source. Spin-orbit coupling is strong in such 5*d* TMO systems, meaning that new states that include both orbital and spin contributions, such as the J_{eff}=1/2 state found in Sr_2IrO_4, are the rule. These spin and orbital entangled states are expected to display unconventional magnetism, which can be best studied by resonant x-ray scattering.

Non-Refereed Publications and Presentations

Kim, B.J., "Kondo-like Quasiparticle Formation in Electron-doped Sr_2IrO_4," presented at the International Conference on Strongly Correlated Electron Systems, Santa Fe, NM, June 27–July 2, 2010.

Kim, B.J., "Zooming into the Electronic Fine Structure Using Resonant X-Ray Scattering," presented at Seoul National University, Seoul, Korea, March 5, 2010.

Kim, B.J., "Kondo-like Quasiparticle Formation in Electron-doped Sr_2IrO_4," presented at the Korea-Japan-Taiwan Symposium on Strongly Correlated Electron Systems, Himeji, Japan, March 11–13, 2010.

Kim, B.J., "Emergence of Kondo-like Quasiparticle at the Mott Transition in 2D Square Lattice,", presented at POSTECH, Pohang, Korea, March 10, 2010.

Kim, B.J., "Emergence of Kondo-like Quasiparticle at the Mott Transition in 2D Square Lattice," presented at Seoul National University, Seoul, Korea, March 5, 2010.

Acceleration of Cloud Microphysical Retrievals for Climate Models

2010-194-N0

Edwin F. Campos Ortega and Douglas L. Sisterson

Project Description

The project is driven by the assumption that significantly improved climate models are needed to address important scientific and policy questions, and that the development of analytical and visualization tools and software are essential for understanding environmental and climate changes. The general objectives are to (1) adapt and enhance existing computing codes in order to develop new software for data analysis and display, (2) create advanced visualizations of multi-sensor observations of clouds and precipitation, and (3) validate and refine multi-sensor cloud-microphysical retrievals.

Mission Relevance

This research activity is relevant to DOE's mission in the environment. It also aligns with the DOE/SC discovery mission for understanding relationships between climate change and Earth's ecosystems, driving predictive understanding of the Earth system and potential impacts of climate change.

FY 2010 Results and Accomplishments

During FY 2010, the following accomplishments were made:

- This project was active for the final two months of the fiscal year. Thus the major activity focused on the organizational aspects of the project.
- We customized our previous weather-research software to use it in climate research. For that, we adapted original computer codes for analysis and display of non-DOE remote-sensing observations. The adapted software can now run on Argonne laptop and desktop systems. We are now modifying these codes to ingest instrument datasets available at the Atmospheric Radiation Measurement (ARM) Climate Research Facility.

Proposed Work for FY 2011

1. Continue modifying original codes for analysis and display of remote-sensing observations, which were originally built for weather research. For that, we will make these codes able to ingest ACRF instrument datasets, particularly those from microwave profiling radiometer, wind profiler radar, and scanning radar. We will test these codes on ARM observations to be taken during the STORMVEX and MC3E field experiments.
2. Use microwave radiometer observations to improve the understanding of cloud processes and its impacts on climate dynamics in cold regions.
3. Use radar meteorology observations to improve the understanding of cloud and precipitation impacts on climate dynamics.

Non-Refereed Publications and Presentations

Campos, E., "Cloud Processes over the 2010 Winter Olympic Venues as Analyzed from Combined Remote-Sensing Observations," presented at the Environmental Science Department, Brookhaven National Laboratory, Upton, NY, September 29–30, 2010.

Molecular and Fluidic Transport in Nanostructured Soft Materials and Composites

2010-198-N0

Derrick C. Mancini

Project Description

The study of nanostructured soft materials (which includes polymer science, colloid science, mesoscale phenomena, soft-matter physics, and complex fluids) is a burgeoning field of research with a wide variety of applications. Many soft-material systems consist of polymers, macromolecules, clusters, and/or nanoparticles that are in fluid or aqueous environments or that are permeated with solvents. Their particular properties often depend upon their interaction with the fluid or with chemical species or moieties whose transport within or through the nanoscale fluidic environments and complexes governs the behavior, properties, and functions of the materials. Also, many of the systems self-assemble or organize, driven thermodynamically but still controlled by the same nanoscale transport phenomena.

Soft-material systems and composites will be synthesized or procured, including hydrogels, hydrogel-nanoparticle composites, membranes of organic-chain self-assembled monolayers, nanoparticles with organic-chain functionalization, colloidal suspensions based on any of these, and composites of any of these materials to form more complex systems. Other molecules, macromolecules, ions, and clusters will either be incorporated into these systems or made to interact with them in the aqueous phase.

The soft-material systems and composites will be (1) characterized structurally by using optical microscopy, transmission electron microscopy (TEM), scanning electron microscopy (SEM), x-ray diffraction (XRD), small-angle x-ray scattering (SAXS), and ultra small-angle x-ray scattering (USAXS) and (2) characterized chemically with FTIR, Raman, and UV-vis spectroscopy. Moreover, real-time modification of these materials and transport phenomena will be measured by using some of the same techniques in real time and *in situ*, as well as with dynamics-sensitive techniques, like x-ray photon correlation spectroscopy (XPCS).

We will use a multiscale approach to simulation, in which the continuous range of length and time scales that occur within dynamic soft-material systems is divided into a number of discrete scale ranges for which the relevant physics and chemistry can be effectively modeled. The global system behavior will then be predicted by the union of the simulations at the different scales. These results will be compared to the experimentally observed behavior and related to the physical and chemical structure of the soft-material systems.

Mission Relevance

This project is relevant to DOE's mission in science. The enhanced capabilities and modeling tools will build upon and advance the development of modeling and simulations of nanoscale transport of fluids and ions in nanostructured polymeric and membrane systems. These systems are ubiquitous and have applications in many areas, including energy storage and conversion, environmental systems and mitigation, and sensor technology, as well as drug delivery.

Results and Accomplishments

In FY 2010, we executed the initial setup of the synthesis and modeling tasks. We initiated the extension of the molecular dynamics modeling approach to the prediction of nanostructured soft-material morphology for hydrogel oligomers. We identified the *ab initio* modeling needs and defined an approach by using available codes. We identified hydrogel systems to synthesize that would be suitable for modeling and characterization. We started synthesis of some of the newly identified systems, including PNIPAM [poly(N-isopropylacrylamide)], PEG (polyethylene glycol), PAAm [poly(acrylamide)], and the alginates. We also set up a dedicated computer workstation for calculations using COMSOL for finite-element analysis and DL-Poly for molecular dynamics. We identified approaches to executing molecular dynamics on the Center for Nanoscale Materials (CNM) computer cluster using either DL-Poly or LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) for hydrogel modeling. Small equipment items and supplies are now in place to support the synthesis tasks, and laboratory facilities were set up for this project.

Proposed Work for FY 2011

We will extend the molecular-dynamics modeling approach to the simulation of interfacial interactions between liquid and solid phases. Linear Boltzmann methods will be defined for multi-species flow-modeling capabilities. We plan to demonstrate the integration of finite-element methods and molecular-dynamics multi-species simulations by using a coupling scheme between the atomistic and mesoscopic scales. The initial soft-material systems (polymers, hydrogels, membranes) and composites (nanoparticles) will be synthesized and then characterized for their material structure and properties and compared to initial predictions of early models.

Spin and Charge Dynamics in Oxide Heterostructures

2010-204-N0

Olle G. Heinonen

Project Description

This project increases our fundamental understanding of spin and charge dynamics in oxide heterostructures, as well as our ability to design complex nanostructured materials systems with specific properties. The scope of the work is twofold. First, we are studying, through modeling and theory and in conjunction with experiments, spin torques and their effects on magnetization dynamics in nanoscale magnetic tunnel junctions. The main part of the work has been directed at understanding ferromagnetic resonances in nanoscale magnetic tunnel junctions and how the resonances are affected by spin torque and charge transport. Second, a model is being constructed to study the effects of defect motion on charge transport in metal/oxide/metal nanostructures, with a goal of understanding how resistive switching is influenced by defects and how the switching can be controlled.

Mission Relevance

The project supports the DOE-BES mission to support research in areas relevant to energy efficiency through use-inspired R&D on new materials for information storage.

FY 2010 Results and Accomplishments

The main accomplishments are (1) elucidating the influence and behavior of spin torque on magnetization resonances in nanoscale magnetic tunnel junctions and (2) constructing a transport model for metal/oxide/metal nanostructures capable of producing hysteretic resistive behavior.

Magnetization dynamics in 150-nm × 300-nm and 250-nm × 250-nm elliptical magnetic tunnel junctions were studied in conjunction with experimental work at Goteborg University, Sweden. Micromagnetic modeling and calculations of the magnetic resonances in such structures revealed that spin-polarized currents give rise to a torque, so-called spin torque, which causes a linear decrease of the observed resonance frequency with increasing bias voltage at low to moderate applied external fields. In particular, this component of the spin torque has a linear dependence on bias voltage. At large external fields (~1,000 Oe) applied along the long axis, the observed quadratic decrease of the resonance frequency with bias voltage is due to Joule heating, not to spin torque. Furthermore, several of the branches of resonances were identified. In particular, one observed branch appears to be an edge mode, in which the magnetization motion is confined near an edge of the structure.

A model for electronic conduction based on electronic hopping between localized states in metal/oxide/metal heterostructures was constructed. The metal electrodes are at fixed electrostatic potentials, and the Coulomb potential is solved self-consistently and simultaneously with the charge motion. Charged defects, for example oxygen vacancies or charged oxygen ions, were added to the model. The defects have an activated motion with specified activation energy. The main result obtained was that the model does show hysteretic I-V curves with bipolar resistive switching, in agreement with experimental observations of some metal/oxide/metal heterostructures. This model then provides a platform through which characteristics of the defects (e.g., charge, activation energy) — as well as the forces acting upon them (e.g., electrostatic forces, diffusion forces, strain fields) — affect the resistive switching behavior.

Proposed Work for FY 2011

Micromagnetic models for spin dynamics in magnetic tunnel junctions will be expanded to include defect structures in the junction barrier and in the magnetic layers. Defects are anticipated to alter the magnetization dynamics and magnetic switching behavior. The transport model for metal/oxide/metal heterostructures will be expanded to include strain fields and grain boundaries to study the competing interactions between the electrostatic forces and the forces due to strain fields on the defect motions and, subsequently, on the resistive behavior of the heterostructures.

Refereed Publications

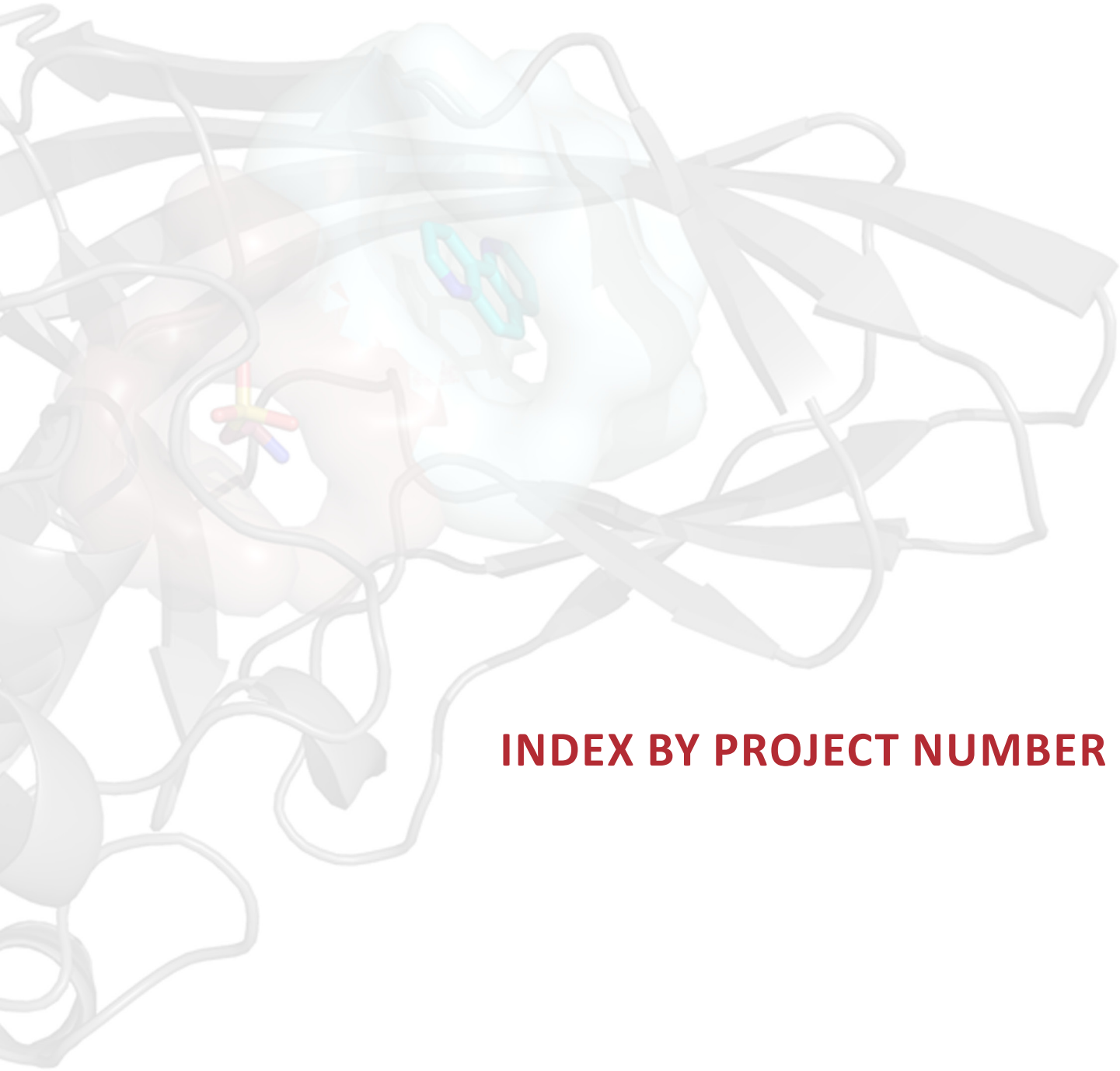
Liu, Y., A.N. Chiaramonti, D.K. Schreiber, H. Yang, S.S.P. Parkin, O.G. Heinonen, and A.K. Petford-Long, "Effect of Annealing and Applied Bias on Barrier Shape in CoFe/MgO/CoFe Tunnel Junctions," accepted, *Physical Review B*.

Non-Refereed Publications and Presentations

Heinonen, O., "Perpendicular Spin Torque in Magnetic Tunnel Junctions," presented at the NordForsk Workshop on Spintronics, Norrköping, Sweden, September 22–24, 2010.

Heinonen, O. "Spin Torque in Magnetic Tunnel Junctions," presented at the Department of Physics, Case Western Reserve University, Cleveland, OH, September 9, 2010.

APPENDIX



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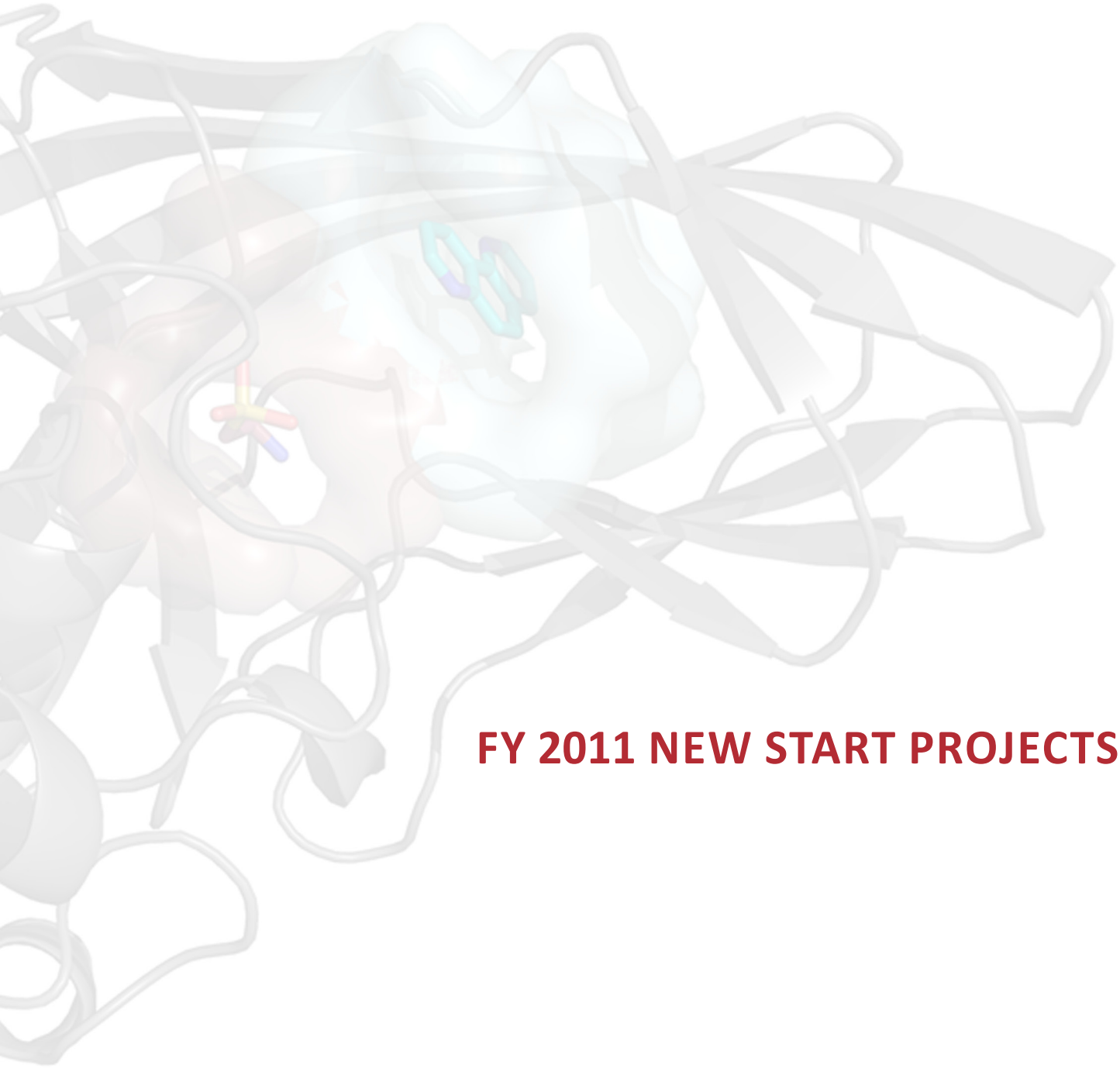

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FY 2011 New Start Projects

LDRD #	Project Title	Lead Investigator
2011-005-N0	Tunnel-Diode Oscillator Detection Technique for Ultrasensitive Magnetometery and Resistivity Measurements of Microscopic Samples	Oleksiy Snezhko, MSD
2011-012-N0	Synthesis, Characterization and Properties of Fast Acting Amorphous Drugs	Chris Benmore, XSD
2011-022-N0	From Plastic Bags to High-performance Lubrication Additives: A Green Chemistry Solution to Energy Efficiency and Environmental Challenges in Transportation	Kuldeep Mistry, ES
2011-023-N0	Tuning Electronic Structure at High Pressures: Towards Novel Materials Discovery from X-ray Science Under Extreme Conditions	Daniel Haskel, XSD
2011-027-N0	Data Encryption and Compression for Cybersecurity Applications	Alexander Heifetz, NE
2011-038-N0	Runtime Support for Integrating MPI and Accelerator Programming Models for Exascale Systems	Rajeev Thakur, MCS
2011-052-N0	Toward Understanding Cloud Processes and Uncertainty Modeling in Next-Generation High-Resolution Climate Models	Yan Feng, EVS
2011-060-N0	Soft Catalysts for Green Chemistry and Energy Applications	Marc Johnson, CSE
2011-063-N0	Development of In Situ Radioactive Materials Probes using High-energy X-rays	Meimei Li, NE
2011-067-N0	Fast X-Ray Detectors Based on Multichannel Plates	Bernhard Adams, XSD
2011-071-N0	Achieving Efficient Thermal Energy Transport with One-dimensional Polymer Nanofibres	Zhang Jiang, XSD
2011-079-N0	Performance of the Nested Regional Climate Model over the U.S. Midwest	Jay Larson, MCS
2011-083-N0	Guided Discovery of Crystalline Molecular Materials for Advanced Energy, Information and Communication Technologies	John Schlueter, MSD
2011-093-N0	New Technologies for Label-free Antibody-based Multiplexed Biosensors	Rosemarie Wilton, BIO
2011-097-N0	Dynamics of Spin-polarized Carriers in New Spin Electronic Materials and Devices	David Keavney, XSD
2011-101-N0	Reactive Synthesis of Metastable Materials	Peter Zapol, MSD
2011-104-N0	High-performance X-ray Optics Fabrication Using Self-assembled Nanostructures	Yuxin Wang, XSD
2011-106-N0	Exascale Data Analysis for Multiphysics Computational Science	Michael Papka, CELS
2011-109-N0	Architectures and Algorithms for Protecting Sensitive Information in Mobile Wireless and Sensing Environments	Charlie Catlett, MCS

FY 2011 New Start Projects (continued)

LDRD #	Project Title	Lead Investigator
2011-110-N0	Development of a Design Concept for a Ring Imaging Cherenkov Detector	Kawtar Hafidi, PHY
2011-116-N0	Synthesis of New Sodium Layered Oxide Cathode Materials for Ambient Temperature Sodium Batteries	Christopher Johnson, CSE
2011-121-N0	Multilevel Optimization Tools for the Simulation, Detection, and Mitigation of Cyber Attacks	Sven Leyffer, MCS
2011-123-N0	Next Generation Multicomponent Nanocatalysts: in situ Study of the Growth and Function	Elena Shevchenko, CNM
2011-126-N0	Development of Software Infrastructure for the Simulation of Microbial Communities on HPC Architectures	Christopher Henry, MCS
2011-129-N0	Evaluation of Microtopography Effects on the Terrestrial Biosphere and Hydrosphere Under Regional Climate Change	Beth Drewniak, EVS
2011-134-N0	Inorganic Synthons: Toward Scalable Materials Design, Discovery, and Creation	Lynda Soderholm, CSE
2011-140-N0	Detailed and Reduced Chemical Kinetics of Green Fuels for Compression Ignition Engine Modeling	Raghu Sivaramakrishnan, CSE
2011-147-N0	Magnetomechanical Actuation of Membrane Channels and Cellular Signaling via Direct Energy Transfer	Valentyn Novosad, MSD
2011-149-N0	Next Generation Data Exploration: Intelligence in Data Analysis, Visualization and Mining	Stefan Vogt, XSD
2011-153-N0	Development of Wireless Data and Power Techniques for Large Instrumentation Systems	Zelimir Djurcic, HEP
2011-169-N0	Enhancing Smart Grid Cyber Security with Near Real-time Message Passing Techniques	Jianhui Wang, DIS
2011-170-N0	Development of Grating Interferometers for Quantitative High-energy X-ray Imaging and for Real-time Wavefront Monitoring	Lahsen Assoufid, XSD
2011-188-N0	Synthesis Science of Functional Layered Complex Oxides	John Freeland, XSD
2011-193-N0	Ultra-small Nanoparticles: A New Opportunity for Discovery of Catalytic Materials for Energy	Stefan Vajda, MSD
2011-196-N0	Will Linking Ultra-large-scale Metagenomics with Models Representing Biogeochemical Cycling Improve Existing Carbon Flux Models?	Folker Meyer, MCS
2011-197-N0	Multiscale Computational Molecular Science	Gregory Voth, CELS
2011-198-N0	Fundamental Developments in Theory and Modeling of Nanoscale Systems and Phenomena	Julius Jellinek, CSE
2011-199-N0	Oxide Surfaces: Nanoparticles to Single Crystals	Kenneth Poeppelmeier, CSE

FY 2011 New Start Projects (continued)

LDRD #	Project Title	Lead Investigator
2011-200-N0	Novel materials for active nanostructures	Omar Lopez, CNM
2011-202-N0	Multifunctional Polymers for Regulating Membrane Function	Millicent Firestone, MSD
2011-203-N0	Enzyme Processes in Energy Production.	Jyotsana Lal, BIO
2011-204-N0	Development of Revolver Undulator for APS	Elizabeth Moog, ASD
2011-205-N0	High-Power, Ultra-Stable Radio-Frequency Test Apparatus for Superconducting Radio-Frequency (SRF) Deflecting Cavity Testing and Development	Alireza Nassiri, ASD
2011-206-N0	High-Power RF Dampers for Superconducting RF Deflecting Cavities	Alireza Nassiri, ASD
2011-207-N0	Device Engineering for High-Performance Photocathodes	Klaus Attenkofer, XSD
2011-208-N0	Chemical Reactions in Li-Air Batteries; Insight from Multiconfiguration Molecular Dynamics	Jessica Swanson, CSE
2011-209-N0	Rare Earth Elements	John Hryn, ES
2011-210-N0	Improved Catalytic Performance by Applying Electrochemical Control	Stefan Vajda, MSD
2011-211-N0	Beyond-petascale Monte Carlo Methods for Practical Nuclear Reactor Analyses	Andrew Siegel, MCS

GLOSSARY OF DIVISIONS

Glossary of Divisions

ASD..... Accelerator Systems

BIO ..... Biosciences

CELS..... Computer, Environment, and Life Sciences

CNM ..... Center for Nanoscale Materials

CSE ..... Chemical Sciences and Engineering

DIS..... Decision and Information Sciences

ES ..... Energy Systems

EVS ..... Environmental Sciences

HEP..... High Energy Physics

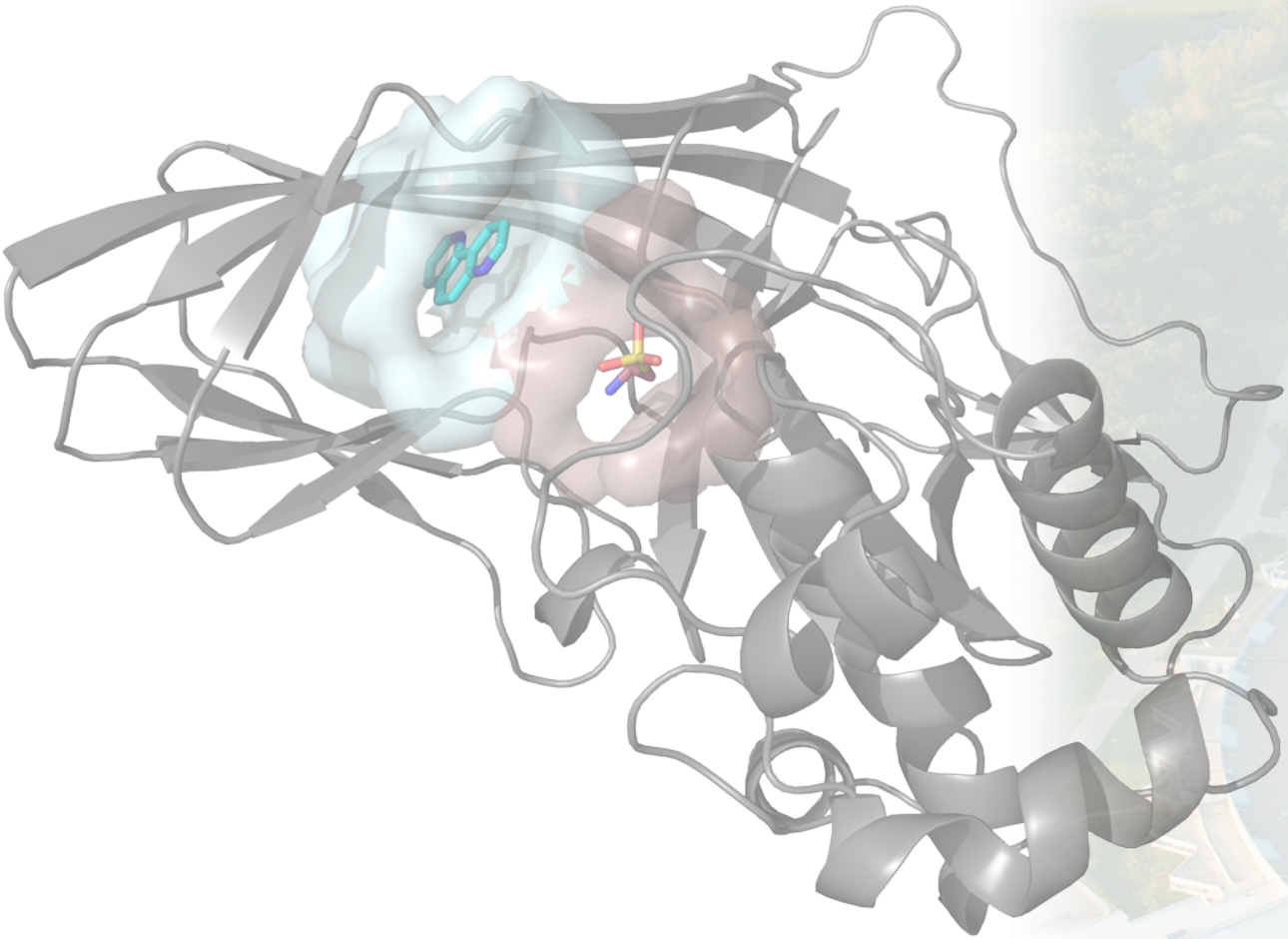
MCS..... Mathematics and Computer Science

MSD ..... Materials Science

NE..... Nuclear Engineering

PHY..... Physics

XSD..... X-ray Sciences



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