

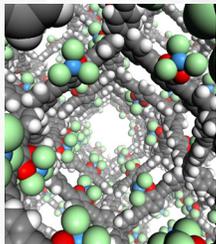
LDRD

LABORATORY DIRECTED
RESEARCH AND DEVELOPMENT
PROGRAM ACTIVITIES

Office of the Director
March 2012

FY2011 ANNUAL
REPORT

ON THE COVER



The image on the cover is based on the illustration of a calculated minimum-energy structure described in the project report “Soft Catalysts for Green Chemistry and Energy Applications (2011-060-N0).” It pictures a wide channel in an idealized porous organic polymer network with designed-in catalytic metal-binding sites (blue) and associated ligands (green and red). The tetrahedra formed by the metal atoms and ligands are attached to linear strut molecules (gray) to complete the structure. Such a structure is expected to support a more efficient catalytic transformation of alternative raw materials (such as carbon dioxide) into fuels and chemical feedstocks.

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 fiscal year 2011. Our laboratory has seen much progress over the last year. The design phase for an upgraded Advanced Photon Source received Critical Decision 1 approval from the Department in FY 2011. Thus we are well on our way to providing users with the ability to image real materials under real conditions in real time, with spatial, energy, and temporal resolution far better than the APS can deliver today. In other arenas, our preparations for hosting of the IBM Blue Gene/Q supercomputer are on schedule. That computational power will be a major contributor to our continued leadership in metagenomics, and in simulations of systems ranging from catalysts to energy storage systems to nuclear power reactors. In a joint program with the University of Chicago, we are opening new interdisciplinary

frontiers through the newly chartered Institute for Molecular Engineering. By bringing together several distinct disciplines of the physical and biological sciences, the IME will develop novel engineering approaches at the molecular scale and bring a new perspective to fundamental problems of great importance to society. Finally, I am pleased to report that construction of the state-of-the-art Energy Sciences Building is well underway on our site. When complete, it will enable synergies among five energy-related technical themes that are central both to implementing Argonne's energy strategy and to strengthening our basic science infrastructure. Investments in Argonne's LDRD program have, over time, made crucial contributions to the realization of these and other advances at our laboratory.

In FY 2011, we continued to place added emphasis on acquiring leaders in computational science as new members of staff who will make good use of Blue Gene/Q when it arrives. We also continued support for the "Beyond Lithium-Ion" Director's Grand Challenge LDRD project. That project, now in its third year, has already achieved significant new understanding and performance improvements that can lead to new high-energy-density lithium-air batteries.

LDRD is an invaluable resource that allows us to anticipate, and thus be prepared to contribute to the future science and technology needs of DOE and the nation. It primarily satisfies two vital needs. First, it enables our exploration of potential new directions for Department programs with the built in flexibility to adjust to a changing environment and new opportunities. Second, and of equal importance, it serves to maintain and enhance the capabilities of both our staff and our R&D facilities.

I can attest that in managing Argonne's LDRD program, we have adhered without exception to the requirements of DOE Order 413.2b and associated guidelines. Our program management continually strives to be more efficient. In addition to meeting all reporting requirements during FY 2011, our LDRD Program Office continues to implement intranet-based process enhancements that better serve all LDRD stakeholders, from our researchers and managers to our DOE Site Office colleagues.

The individual project reports that follow demonstrate that Argonne's researchers have pursued projects at the forefront of their respective fields and have contributed significantly to the advancement of Argonne's major initiatives. Evidence of the continuing strength of this program is not only found in the follow on sponsorship garnered in many cases but is also clear from its contribution to significant aspects of the laboratory's Strategic Plan.

A handwritten signature in black ink that reads "Eric D. Isaacs". The signature is fluid and cursive, with the first letters of the first and last names being capitalized and prominent.

Eric D. Isaacs
Laboratory Director



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Acknowledgments

Argonne's LDRD Program Office comprises the Associate Chief Scientist for LDRD, Dr. Elton N. Kaufmann; LDRD Program Office Manager, Rebecca R. Rank; and Administrative Specialist, Marianne I. Lohr-Dietz. The program as a whole reports to the Laboratory Director, Dr. Eric D. Isaacs, through the Deputy Laboratory Director for Programs, Dr. Mark T. Peters. Those of us in the program's management are grateful for the critical support received throughout the year, particularly while preparing this Annual Report, from the individuals listed below. Special appreciation, of course, is due to the many experts who perform the research and provide their project reports; to the technical and administrative management of Argonne's programmatic divisions, within which the research and development are pursued; to the many members of the several peer-review panels that evaluate the LDRD proposals; and to 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.

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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 DOE's Office of Energy Efficiency and Renewable Energy (EERE) and its National Nuclear Security Administration (NNSA), and for 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 be addressed only 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 for Energy, 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, which is 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-brightness, high-energy, tunable x-rays for scientific research.
- ▶ The Center for Nanoscale Materials (CNM), one of five DOE Nanoscale Science Research Centers, combines advanced scanning probes (including an x-ray nanoprobe; organic, inorganic, and digital synthesis; and nanofabrication), all of which are coupled with theory and modeling.
- ▶ The Electron Microscopy Center (EMC) provides state-of-the-art aberration-corrected electron microscopy (e.g., TEAM, the Transmission Electron Aberration-Corrected Microscope) 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. It provides heavy ions in the energy domain that is 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 users access to petascale computing for research on energy systems and catalysis and in the life, 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. It 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 for observing atmospheric data specifically for 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. From proposals, projects that require advanced exploration before being sufficiently developed for support through normal programmatic channels are selected for creative and innovative R&D studies. Among the aims of the projects supported by the LDRD program are the establishment of engineering proofs 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 the LDRD program are distributed across the major mission areas at Argonne, as indicated in the Laboratory's LDRD Plan for fiscal year (FY) 2011. 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"-type projects is their concurrent 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 experiments in these projects. This multidisciplinary approach is a hallmark of Argonne as a multiprogram national laboratory, and it reflects the synergistic manner in which both our LDRD and our programmatic work are pursued.

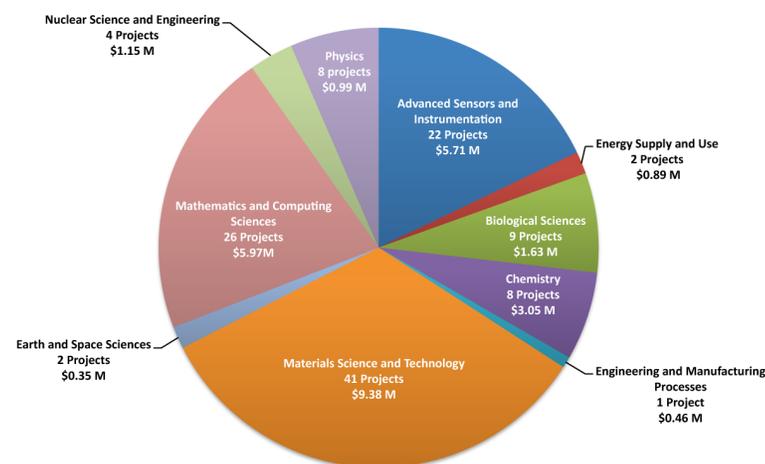


Figure 1. Number and Dollar Values of LDRD Projects across the DOE-Defined "Categories of Work"

The distribution of LDRD projects across the DOE-defined categories of work, as shown in Figure 1, 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 benefits 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 2011 DOE-approved funding cap for LDRD was \$32.0 million, or about 4.5% of Argonne's estimated FY 2011 operating plus capital budgets. Actual expenditures amounted to \$29.6 million, which includes an overhead levy of approximately 23%. A table of planned or actual funding profiles for each project active in FY 2011 is provided at the end of this section. Individual brief project reports for FY 2011 comprise the bulk of this document. A list, by title, of new projects begun to date in FY 2012 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 LDRD Selection Process Schematic

(Applies to Review and Selection Process for FY 2012 Proposals)

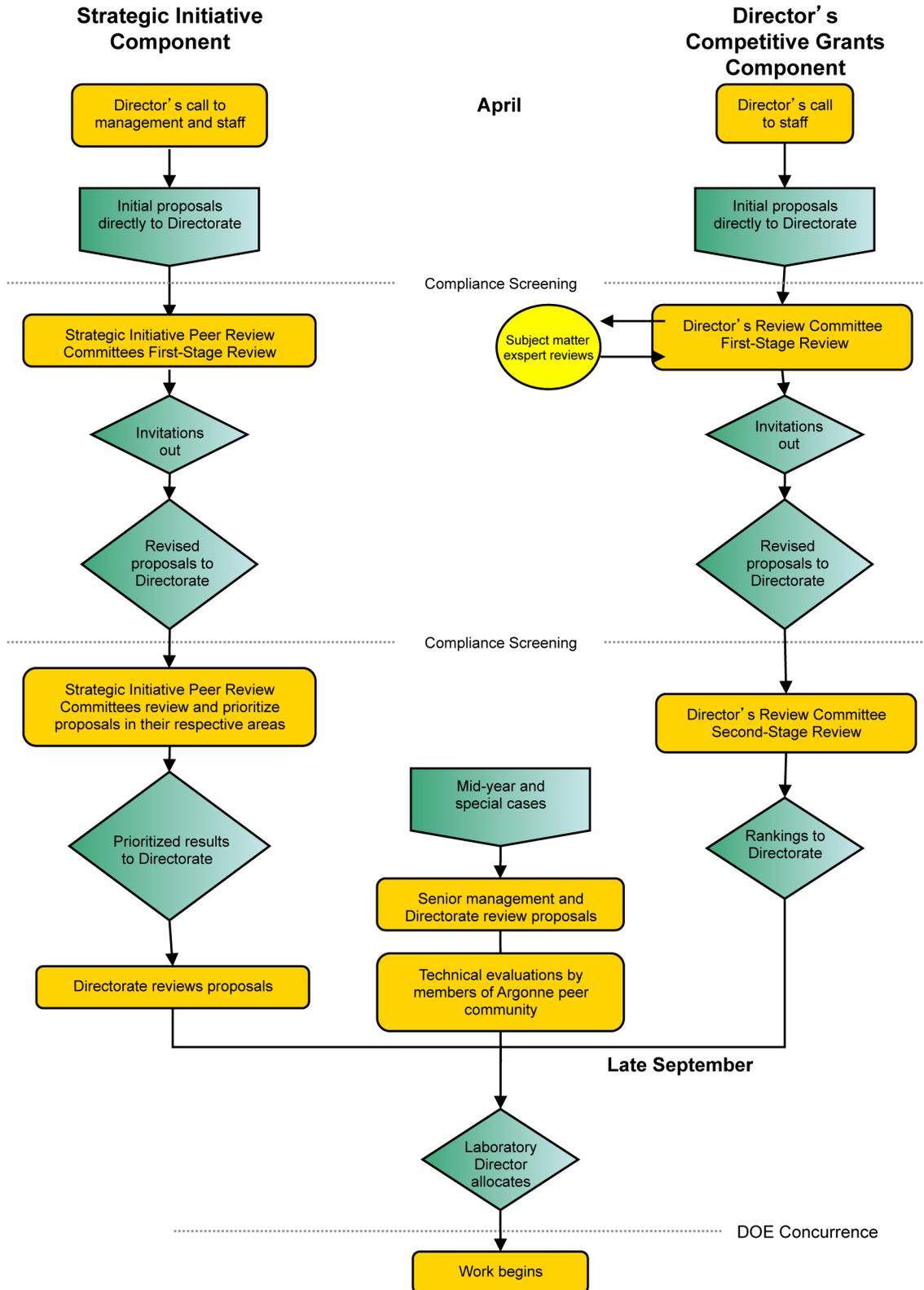


Figure 2. Argonne LDRD Selection Process Schematic

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 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. Annually, the Laboratory Director determines the appropriate balance of funding among the four components. 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 2011 program.

The LDRD program is funded lab-wide through the Laboratory's indirect budget, which derives from a levy against all program operating and equipment budgets. Although two- or three-year durations are proposed for many projects, funding levels and project selection are determined annually and based on 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 site access Guest Agreements. These instruments and procedures enable the application of LDRD funds 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. The responsibility for the actual conduct of all LDRD projects, including associated environmental safety and health requirements, resides with the ALDs and their line managers.

During FY 2011, all program management requirements were satisfied. Reports required by DOE, including the Annual Report for FY 2010, the LDRD Program Plan for FY 2012, and project data uploaded to the DOE/CFO (Office of the Chief Financial Officer) database, were submitted completely in a timely fashion.

Concurrence request forms (also referred to as "data sheets" in relevant guidance documents) were submitted electronically, on a project-by-project basis, to the DOE Argonne Site Office (ASO) to obtain the DOE Site Manager's concurrence before work on the FY 2011 LDRD projects proceeded.

FY 2011 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 that these fields have with existing facilities, capabilities, and staff expertise at Argonne.

In FY 2011, there were six strategic initiative areas in which proposals could be submitted. The FY 2011 review procedures continued to ensure that all individual proposals identified as fitting under a strategic initiative were reviewed for their scientific quality, innovativeness, and value to each respective mission-related initiative.

The review of proposals with regard to the strategic initiatives component relies on a combination of peer and management reviews 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 the proposals that have been submitted. Results are reported to the Laboratory Director, who makes final selections and approves the content and aggregate budget. In FY 2011, 42 new projects and 41 continuing projects in the six Strategic Initiative areas listed here were funded at an aggregate level of \$24.0 M. Some additional mid-year and strategic-hire projects, selected by the Laboratory Director, are included in these figures. Also in FY 2011, one new and three continuing strategic projects totaling \$0.5 M, whose topics fall in other novel technical areas, were selected by the Laboratory Director. The overall FY 2011 funding level for the Strategic Initiative component equaled \$24.5 M (Figure 3).

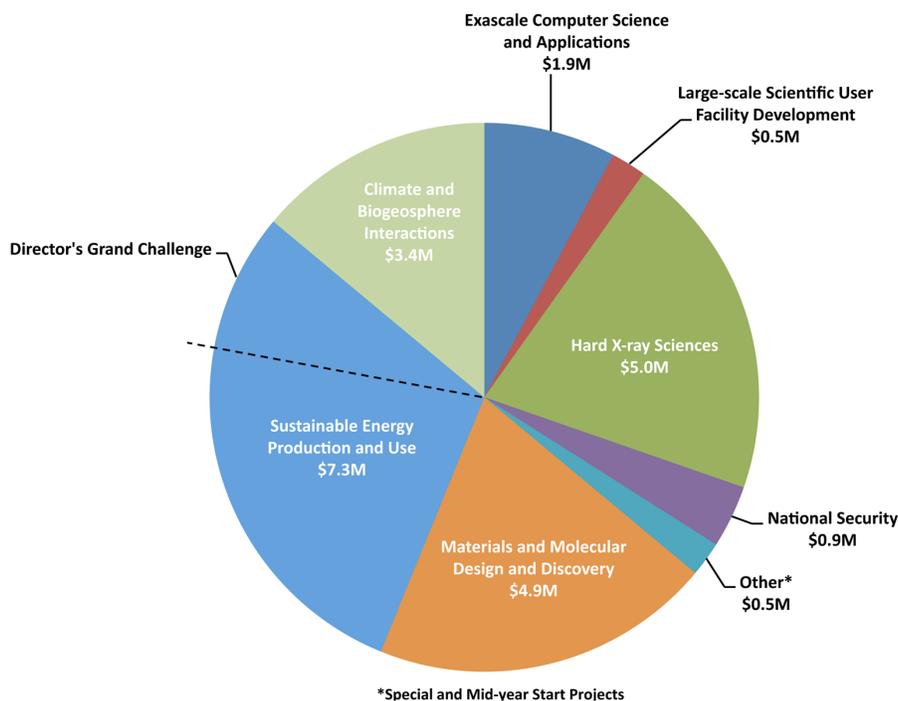


Figure 3. Distribution of Funding among Strategic Initiative Areas

The six FY 2011 Strategic Initiative areas are as follows:

Climate and Biogeosphere Interactions

The key elements of this initiative fall under the following general areas: leveraging ultra-high-resolution regional and global climate simulations by using the Geophysical Fluid Dynamics Laboratory (GFLD) global climate model and the National Center for Atmospheric Research (NCAR) Nested Regional Climate Model (NRCM) regional-scale model on Argonne high-performance computing systems; conducting metagenomics-enabled analyses of terrestrial microbial communities to demonstrate connections to the global carbon cycle; enriching metagenomics-enabled approaches for understanding key biotic regulators in carbon cycling; and developing instrumentation for greenhouse gas monitoring.

Exascale Computer Science and Applications

The key elements of this initiative fall under the following general areas: novel system architectures, strategic application development, extreme-scale system software, and extremely scalable algorithms and computing methodologies.

Hard X-ray Sciences

Key focus areas for projects under this initiative area are as follows: R&D for the Advanced Photon Source upgrade, hard x-ray sciences, and next generation photon source development.

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. The work involves modeling and simulations and science enablers that leverage those programs that will use new or significantly expanded Argonne user facilities (such as imaging, ultrafast science, and other facility-based science).

Materials and Molecular Design and Discovery (M2D2)

Two initial research focus themes were selected for this initiative on the basis of how much they represent core areas of expertise and provide an opportunity for future scientific growth: “Complex Oxides and Beyond” and “Innovative Catalysts.” The M2D2 initiative focuses on fundamental advances in the understanding of materials design, growth, and functions in these areas, with credible translation to the use-inspired space.

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. The key research area in FY 2011 was cyber security.

Sustainable Energy Production and Use

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

Director’s Grand Challenge

The Director’s Grand Challenge component of the LDRD portfolio may be included in the LDRD program of any given fiscal year by the Laboratory Director. Also at the discretion of the Laboratory Director is the schedule for the call for proposals and for the review and selection of projects for this component, which does not need to match the schedules for the Strategic Initiatives or Director’s Competitive Grants components. For a Grand Challenge project, sufficient talent and resources are devoted to a specific technical topic within an area that is of substantial strategic value to the Laboratory and to DOE, in order to allow major strides to be made toward achieving its R&D goals. The emphasis is on cross-cutting initiatives that synergistically draw on Argonne’s core competencies.

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 that is composed 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 on the basis of their expected impact, creativity, degree of cross-cutting utilization of Argonne core 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 semiannually to evaluate progress.

In FY 2011, there were no new Grand Challenge topics addressed as part of the LDRD portfolio. However, the energy-storage-related topic addressed in FY 2010 was continued. The project was awarded \$1.87 M in FY 2011, with funding expected to be at the same level in FY 2012.

Director’s Competitive Grants (DCG)

The DCG component invests in a full spectrum of investigator-initiated proposals across the Laboratory in 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 subjected to peer review by the Director’s Review Committee to assess their scientific and technical quality. The Committee is composed of nonmanagerial scientists and engineers selected by the Laboratory Director. The Committee currently comprises 21 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 a smaller number of proposals being retained 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 is augmented by the recruitment of members of the Laboratory's 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 their assistance made it possible for the Director's Review Committee to recommend the highest-quality proposals for funding in FY 2011. These projects make up about 17% of the Laboratory's LDRD budget. In FY 2011, 12 new projects and 24 continuing projects were funded at a total level of \$5.1 M.

FY 2012 Update

DOE approved Argonne's FY 2012 LDRD Plan and program expenditures not to exceed \$30 M. A list of projects begun so far in FY 2012, by title, is provided in an appendix to this report.

For the 2012 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 new electronic tools as necessary.

Two new web-based tools were available for use during the 2012 fiscal year cycle. The first was an enhancement to the proposal submission website that provides authors of LDRD proposals with real-time status information about their submissions during the review and selection process. The second was a new proposal feedback website that allows review committee members to input their feedback about a submission and that then, in turn, provides this feedback to the author of the proposal in a timely manner.

It is likely that FY 2013 will see a phasing out of those strategic initiative areas that are reaching maturity, having achieved significant successes and having prospects for continuing under programmatic support. We anticipate that the strategic portfolio will be refreshed and have new thrusts that are well-aligned with the technological needs and opportunities of current and future DOE programs.

Peer Review Experience in FY 2011

The pursuit of LDRD 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 management and operations (M&O) contractor, UChicago Argonne, LLC. The quality of the science and technology performed under LDRD funding within 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 2011 is provided here in Table 1, along with an aggregate accounting of the number of LDRD projects exposed to committee review and their total dollar values. The LDRD Program Office also requires principal investigators to report all other relevant external reviews of their work. LDRD projects from the APS Engineering Support (AES), Accelerator Systems (ASD), Biosciences (BIO), Chemical Sciences and Engineering (CSE), Decision and Information Sciences (DIS), Energy Systems (ES), High-Energy Physics (HEP), Mathematics and Computer Sciences (MCS), Materials Science (MSD), Nuclear Engineering (NE), Physics (PHY), and X-ray Sciences (XSD) divisions; the Center for Nanoscale Materials (CNM); and the Computer, Environment, and Life Sciences (CELS) ALD area were reviewed as part of an overall contractor-chartered review.

Table 1. Summary of Peer Review History by Organization

Organization	Date of Review	Number of LDRD Presentations	Number of LDRD Projects	Dollar Value of Projects (\$ in thousands)
AES	7/26/11	2	2	557.3
ASD	7/26/11	3	4	4,321.9
BIO	9/19/11	7	7	3,383.1
CELS	9/19/11	5	4	2,081.6
CNM	9/7/11	2	2	3,978.3
CSE	9/7/11	1	1	145.4
DIS	11/17/10	4	6	2,152.8
ES	11/17/10	5	5	3,179.6
HEP	9/7/11	1	1	200.9
MCS	9/19/11	4	3	2,256.4
MSD	9/7/11	1	3	1,553.9
NE	11/17/10	4	6	4,607.7
PHY	9/7/11	4	6	2,329.2
XSD	7/26/11	6	9	6,461.8
Totals		49	59	37,209.9

Performance Metrics

The LDRD Program Office collects statistical data on current and completed LDRD projects. Such data cover various items; examples include publications (see citations in the appendix to this report), inventions, follow-on sponsorship, and the enhancement of staff by post-doctoral appointees and new hires. Although these data are of little value on a project-by-project basis, in aggregate, they do provide a picture of overall program productivity. The management processes employed to collect these data include surveys of current and former investigators, analyses 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 Computing and Information Systems (CIS) division. A summary of the most recently collected data is provided here in Tables 2 and 3. The first table displays project outcomes realized only during FY 2011 but derived from projects active in any year or years from FY 2008 forward. For the same prior and currently active projects, the second table displays those metrics for which cumulative results are monitored, with no restriction as to when the accomplishments occurred.

Table 2. Aggregate FY 2011 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-Publication Copyrights	Number of Invention Disclosures	Number of Patents Issued/ Pending
2008							
	Competitive Grants	4	0	0	0	0	0
	Strategic Initiative	22	0	4	0	2	5
2009							
	Competitive Grants	2	0	0	0	0	0
	Strategic Initiative	16	0	3	0	0	0
2010							
	Competitive Grants	4	0	2	0	0	0
	Strategic Initiative	42	0	12	0	1	1
2011							
	Competitive Grants	26	44	1	0	4	3
	Strategic Initiative	68	132	16	0	11	4
Grand Totals: 290 Projects		184	176	38	0	18	13

Table 3. Aggregate Outcomes for All Years of Recently Completed and Current Projects (2008–2011)

Most Recent Project Year	Number of Projects Receiving Follow-on Funds	Number of Proposals Submitted To Sponsors	Number of External Reviews
2008	37	240	28 DOE 49 Other 4 UoC
			81 Total
2009	24	156	13 DOE 23 Other 11 UoC
			47 Total
2010	31	181	21 DOE 25 Other 25 UoC
			71 Total
2011	9	106	17 DOE 20 Other 46 UoC
			83 Total
Totals: 290 Projects	101	683	79 DOE 117 Other 86 UoC
			282 Total

LDRD Five-Year Funding Summary (\$ in thousands) for Projects Active in FY 2011

Proposal No.	2009	2010	2011	2012 (a)	2013 (b)	Total (c)
2008-190-R3	180.0	1,037.3	775.6			2,034.9
2008-195-R3	192.2	191.9	203.6			750.7
2009-035-R2	251.8	267.0	78.0			596.8
2009-047-R2	194.2	196.7	201.7			592.6
2009-050-R2	407.8	349.8	48.8			806.4
2009-068-R2	154.9	152.1	136.0			443.0
2009-070-R2	199.0	204.0	162.1			565.1
2009-071-R2	180.0	146.9	69.4			396.3
2009-076-R2	173.9	165.3	148.9			488.1
2009-083-R2	112.2	164.7	168.1			445.0
2009-097-R2	598.5	618.4	739.7			1,956.6
2009-111-R2	100.5	127.9	124.9			353.3
2009-115-R2	234.1	296.8	326.5			857.4
2009-138-R2	153.7	181.1	168.2			503.0
2009-146-R2	119.7	113.7	67.5			300.9
2009-155-R2	221.4	198.8	181.6			601.8
2009-156-R2	173.6	151.0	152.0			476.6
2009-158-R2	243.4	261.8	256.6			761.8
2009-171-R2	132.1	222.5	170.8			525.4
2009-180-R2	320.4	277.4	287.6			885.4
2009-186-R2	165.8	287.0	180.2			633.0
2009-190-R2	144.4	169.3	96.3			410.0
2009-204-R2	125.6	136.4	117.4			379.4
2009-209-R2	205.4	247.5	193.7			646.6
2009-214-R2	109.7	109.4	94.6			313.7
2010-003-R1		148.0	140.1	135.0		423.1
2010-010-R1		180.8	170.6	150.0		501.4
2010-029-R1		160.9	171.1	155.0		487.0
2010-042-R1		169.2	156.9	150.0		476.1
2010-043-R1		200.1	200.3	180.0		580.4
2010-044-R1		299.3	241.0	500.0		1,040.3
2010-047-R1		522.5	319.5			842.0
2010-049-R1		155.9	131.8	135.0		422.7
2010-050-R1		173.5	137.9	150.0		461.4
2010-063-R1		132.5	106.4	75.0		313.9
2010-073-R1		159.8	154.9	135.0		449.7
2010-074-R1		177.1	267.6	250.0		694.7
2010-093-R1		160.0	77.1	125.0		362.1
2010-117-R1		170.3	320.5	340.0		830.8
2010-119-R1		133.5	133.9	150.0		417.4
2010-129-R1		129.5	130.0	110.0		369.5
2010-131-R1		702.1	793.0	400.0		1,895.1
2010-137-R1		157.8	176.3	160.0		494.1
2010-138-R1		142.3	112.9	115.0		370.2

LDRD Five-Year Funding Summary (\$ in thousands) for Projects Active in FY 2011

Proposal No.	2009	2010	2011	2012 (a)	2013 (b)	Total (c)
2010-139-R1		222.1	215.0	200.0		637.1
2010-156-R1		140.2	171.3			311.5
2010-158-R1		179.1	189.0	185.0		553.1
2010-161-R1		207.4	169.1	175.0		551.5
2010-167-R1		199.5	225.8	350.0		775.3
2010-175-R1		292.2	165.6			457.8
2010-181-R1		89.0	39.1			128.1
2010-183-R1		269.8	273.1	152.0		694.9
2010-184-R1		207.9	200.4			408.3
2010-185-R1		1,047.5	1,918.0	2,000.0		4,965.5
2010-188-R1		506.5	506.3	500.0		1,512.8
2010-190-R1		118.4	324.6	330.0	340.0	1,113.0
2010-191-R1		715.1	455.3	200.0		1,370.4
2010-192-R1		107.0	111.8	129.0		347.8
2010-193-R1		542.5	219.2	220.0		981.7
2010-194-R1		32.7	220.8	235.0	30.0	518.5
2010-195-R1		83.4	571.9	550.0	275.0	1,480.3
2010-196-R1		128.9	466.7	500.0		1,095.6
2010-197-R1		126.4	536.3	627.0	449.0	1,738.7
2010-198-R1		169.9	340.7	353.0	190.0	1,053.6
2010-199-R1		99.4	422.4	300.0	150.0	971.8
2010-201-R1		193.8	392.7	400.0		986.5
2010-202-R1		26.0	94.6	100.0	100.0	320.6
2010-204-R1		50.5	415.0	465.0	432.0	1,362.5
2011-005-N0			67.2	125.0	135.0	327.2
2011-012-N0			102.6	120.0	140.0	362.6
2011-022-N0			150.0	185.0	230.0	565.0
2011-023-N0			106.8	260.0	252.0	618.8
2011-027-N0			44.6	125.0	225.0	394.6
2011-038-N0			179.4	200.0	200.0	579.4
2011-052-N0			220.7	250.0	250.0	720.7
2011-060-N0			599.1	670.0	670.0	1,939.1
2011-063-N0			296.6	320.0	250.0	866.6
2011-067-N0			254.3	156.0	200.0	610.3
2011-071-N0			147.1	135.0	180.0	462.1
2011-079-N0			124.4			124.4
2011-083-N0			238.0	350.0	350.0	938.0
2011-093-N0			105.9	95.0	127.9	328.8
2011-097-N0			80.2	120.0	153.5	353.7
2011-101-N0			430.5	520.0	520.0	1,470.5
2011-104-N0			161.4	166.0	169.0	496.4
2011-106-N0			206.3	220.0	220.0	646.3
2011-109-N0			176.1	125.0	365.0	666.1
2011-110-N0			73.1	115.0	123.0	311.1

LDRD Five-Year Funding Summary (\$ in thousands) for Projects Active in FY 2011

Proposal No.	2009	2010	2011	2012 (a)	2013 (b)	Total (c)
2011-116-NO			110.9	105.0	135.0	350.9
2011-121-NO			183.4	125.0	280.0	588.4
2011-123-NO			194.5	275.0	275.0	744.5
2011-126-NO			221.9	250.0	250.0	721.9
2011-129-NO			81.0	90.0	90.0	261.0
2011-134-NO			548.5	570.0	570.0	1,688.5
2011-140-NO			163.9	220.0	275.0	658.9
2011-147-NO			171.9	230.0	252.0	653.9
2011-149-NO			137.6	264.0	325.0	726.6
2011-153-NO			177.9	180.0		357.9
2011-169-NO			111.1			111.1
2011-170-NO			264.7	217.0	224.1	705.8
2011-188-NO			676.4	597.0	565.0	1,838.4
2011-193-NO			185.1	185.0	242.0	612.1
2011-196-NO			474.4	190.0	190.0	854.4
2011-197-NO			236.8	250.0	250.0	736.8
2011-198-NO			145.4	173.0	181.0	499.4
2011-199-NO			150.3	150.0	150.0	450.3
2011-200-NO			286.2	298.4		584.6
2011-202-NO			148.2	150.0		298.2
2011-203-NO			200.6			200.6
2011-204-NO			290.5	760.0	203.0	1,253.5
2011-205-NO			919.2			919.2
2011-206-NO			266.8	330.0		596.8
2011-207-NO			200.9	153.0	125.0	478.9
2011-208-NO			77.6			77.6
2011-209-NO			251.5	400.0		651.5
2011-210-NO*			59.1	136.0	136.0	331.1
2011-211-NO*			149.1	200.0	200.0	549.1
2011-212-NO			130.3	397.5		527.8
2011-213-NO*			354.7	1,013.6	1,019.2	2,387.5
2011-214-NO			138.5	490.0	209.4	837.9
2011-215-NO			234.9	325.0		559.9
2011-216-NO			67.6	85.0	60.0	212.6
2011-217-NO*			51.7	337.8	348.0	737.5
Totals	5,094.3	16,105.0	29,563.7	24,790.3	13,281.1	89,039.4

(a) FY 2012 figures represent allocations and not actual expenditures.

(b) FY 2013 figures represent projections assuming the project continues into FY 2013.

(c) Totals for FY 2008 projects include funding from 2008 not shown in the table.

* FY 2011 late-start projects may have costs in FY 2014 that are not shown in the table.



RESEARCH REPORTS



DIRECTOR'S COMPETITIVE GRANTS

Coherent Diffraction Imaging of Complex Polymeric Networks

2009-068-R2

Jyotsana Lal

Project Description

Coherent diffraction imaging (CDI) makes use of transverse coherence — obtained at third-generation synchrotron sources by spatial filtering — to realize a spatial resolution beyond that available from focusing optics. This technique enables “lens-less imaging” — the images are directly constructed from the angular distribution of the x-ray waves scattered by the object. Of particular interest in nanoscale CDI imaging are complex polymer matrices, such as those formed by cellulose. At the next-generation sources that will come on-line in the next few years (e.g., linac coherent light source [LCLS]; x-ray free-electron lasers [XFELs]), the spatial resolution will come down to the level of the atomic structure of single macromolecules. This project is based on the insight that CDI is uniquely suited to the study of these structures. Here, CDI is used to image crystalline cellulose *in situ* in maize stover at the nanometer-scale resolution.

Mission Relevance

The project is relevant to DOE missions related to energy and basic science. In particular, the structure of plant-cell walls holds great importance for developing strategies for optimal generation of biofuels, and is, therefore, of particular interest to DOE.

FY 2011 Results and Accomplishments

During the first two years of the project, CDI data were collected from dried and young maize vascular bundles, and preliminary reconstruction of images from the data set was achieved by using hybrid input-output and shrink-wrap algorithms. On the basis of research by Chen et al. (“Application of Optimization Technique to Noncrystalline X-ray Diffraction Microscopy: Guided Hybrid Input-Output Method,” *Phys. Rev. B* 76, 064113 [2007]), we developed a guided hybrid input-output (GHIO) algorithm for *ab initio* phase retrieval. The GHIO started with 10 independent reconstructions on each 3-D x-ray diffraction pattern, in which different random phase sets were used as the initial inputs. Each reconstruction iterated back and forth between real and reciprocal space. In real space, the electron density ρ outside the support and the negative density inside the support were slowly pushed close to zero, where the support is a boundary somewhat larger than the sample envelope. In reciprocal space, the experimental Fourier magnitude remained unchanged, and only the phases were updated. After 200 iterations, we obtained 10 images

(defined as the 0th generation). An error factor R for each image can be expressed as:

$$R = \frac{\sum_{k_x, k_y, k_z} |F_{\text{exp}}(k_x, k_y, k_z)| - \alpha |F_{\text{cal}}(k_x, k_y, k_z)|}{\sum_{k_x, k_y, k_z} |F_{\text{exp}}(k_x, k_y, k_z)|}$$

where $|F_{\text{exp}}(k_x, k_y, k_z)|$ and $|F_{\text{cal}}(k_x, k_y, k_z)|$ represent the experimental and calculated Fourier magnitude; α is a scaling factor; and k_x, k_y, k_z are the coordinates in reciprocal space. A seed image was selected that corresponded to the smallest R factor. After aligning the 10 images (ρ_{old}^i) to the seed (ρ_{seed}), a new set of 10 images was obtained:

$$\rho_{\text{new}}^i = \sqrt{\rho_{\text{seed}} \rho_{\text{old}}^i}, \quad i=1, 2, 10$$

These new images were used as the initial inputs for the next generation. The purpose of this step was to merge the best image in the current generation with each of the 10 images, so that a smaller R factor would be passed to the succeeding generations. Furthermore, after the multiplication of the two independent images, the density fluctuation in the new image was reduced significantly. We repeated the procedure for each generation and, usually after 6 generations, the 10 reconstructed images became more closely identical. The reconstructed image is an average of these 10 images (see Figures 1 and 2). Although it requires more computational power, GHIO is precise and reliable in *ab initio* phase retrieval of coherent x-ray diffraction patterns.

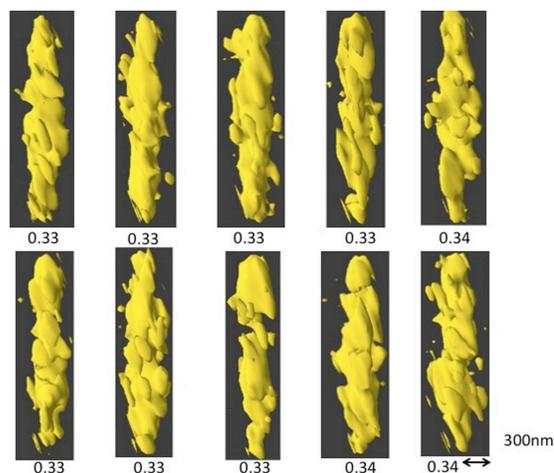


Figure 1. Ten reconstructed images of a cellulose crystallite in the 6th generation.

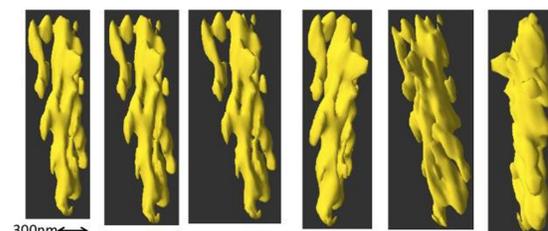


Figure 2. Different 3-D views of an averaged reconstructed image of a cellulose crystallite from the 10 images shown in Figure 1 in the 6th generation.

We have therefore identified differences in cellulose crystals in young and mature plants. The results obtained from this study have increased our understanding of the complex structure of cellulose by providing three-dimensional *in situ* images. During the third year of this project, we focused exclusively on the development of a guided hybrid input-output algorithm (GHIO) for *ab initio* phase retrieval for the final reconstruction of the image in real space. As a result, we realized vast improvements in the reconstruction of images from the data set compared with the hybrid input-output and shrink-wrap algorithms used during the first two years of the project.

Seminars

Lal, J., L. Makowski, I. Robinson and R. Harder (2011). "In-situ Coherent Diffraction Imaging of Cellulose Crystals." Gordon Research Conf., Waterville, ME, Aug. 7–12, 2011.

Lal, J., L. Makowski, I. Robinson and R. Harder (2011). "In-situ Coherent Diffraction Imaging of Cellulose Crystals." Gordon-Kenan Res. Seminar, Waterville, ME, Aug. 6–7, 2011.

Makowski, L., J. Lal, R. Harder and I. Robinson (2010). "In-situ Coherent Diffraction Imaging of Cellulose Crystals." Cellulose Research Institute, College of Environmental Science and Forestry, Syracuse University, NY, Feb. 7, 2010.

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

2009-070-R2

P. Raj Pokkuluri, Marianne Schiffer, and Rosemarie Wilton

Project Description

Anaeromyxobacter dehalogenans can reduce uranium, technetium, other metal ions, and it uses halogenated compounds in respiration. It is found to thrive in contaminated sub-surface environments. Because of the importance of *A. dehalogenans* in biogeochemical cycling, its genome sequence has been determined at the DOE Joint Genome Institute. At present, several years after the determination of the genome sequence, very few details are known about the proteins and 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 that have been implicated in the respiratory versatility of metal-reducing bacteria and (2) sensor domains of signal transduction/chemotaxis proteins that are used by the bacterium to sense the outside environment and initiate the necessary regulation processes required for the cell's survival.

Mission Relevance

This project is relevant to DOE's missions in basic science and the environment. Microbial research is pursued under DOE's Office of Biological and Environmental Research. This type of research can provide insights for the development of innovative biotechnological applications and result in better and less costly 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. *A. dehalogenans* can clean up metal and radionuclide contaminations, such as uranium and technetium, and contamination by chlorinated compounds. An understanding of the structure-function 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 2011 Results and Accomplishments

Cytochromes *c*₇: The cytochromes *c*₇, Adeh_1696 and Adeh_1697 from *A. dehalogenans* 2CP-C were successfully cloned and expressed in *E. coli*. Following unexpected challenges in their purification, both proteins were purified to the required purity for crystallization experiments. Extensive crystallization trials in FY 2011 produced crystals of Adeh_1696 cytochrome *c*₇ that carry a histidine (His)-tag, but not in the case of Adeh_1697, which did not carry a purification tag. Although the crystals of Adeh_1696 were of decent size (approximately 0.15 mm³), they diffracted x-rays poorly. A diffraction data set was collected to 4 Å resolution at the Advanced Photon Source 19BM beamline.

Large multiheme cytochrome Adeh_3077: Sequence analysis of the 40-heme cytochrome Adeh_3077 from *A. dehalogenans* revealed novel penta-heme domains. Following failed cloning attempts from the genomic DNA, we purchased synthetic DNA constructs for two penta-heme domains optimized for expression in *E. coli*. The initial experiments demonstrated the expression of cytochromes by ultraviolet-visible spectroscopy. However, large-scale expression experiments in FY 2011 to isolate these proteins were not successful because of the very low expression yields of the cytochrome fragments.

Sensor domains: A search of the *A. dehalogenans* genome revealed that it contains 18 methyl-accepting chemotaxis proteins and 76 histidine kinase (HisKa) proteins. A total of 31 such proteins contain a periplasmic sensor domain. All 31 sensor

domains were cloned and expressed in *E. coli*. Eight of these sensor domains were purified in sufficient quantities required for crystallization trials. Crystallization conditions were identified for three of the sensor domains. In FY 2011, optimization of the initial “hit” conditions led to diffraction-quality crystals of two sensors: Adeh_3718 and Adeh_2942. These two proteins are described in the following sections.

Adeh_3718 sensor domain: Adeh_3718 is a chemotaxis protein with a periplasmic sensor domain. The sensor domain (153 amino acids) was crystallized, and its structure was determined at 2.0 Å resolution (R-factor = 19.5%) in FY 2011. The structure of the Adeh_3718 sensor was similar to a pre-autophagosomal structure (PAS), as we predicted from the sequence (Figure 1). Interestingly, an acetate ion moiety was found at the ligand binding site of the protein. This observation raises the possibility that this sensor may be involved in acetate “sensing” by *A. dehalogenans*. Acetate is commonly used by this organism as an electron donor for its respiration. To date, there have not been any acetate sensing proteins described in the literature, thereby making the Adeh_3718 sensor the first of its kind.

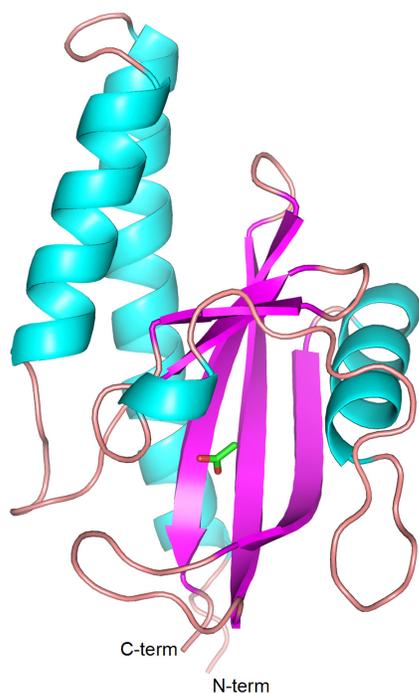


Figure 1. The PAS-like fold structure of the Adeh_3718 sensor domain. The acetate ion in the binding site is shown as a stick drawing.

Adeh_2942 sensor domain: Adeh_2942 is a HisKa protein involved in signal transduction. The periplasmic sensor domain (152 amino acids) was isolated and crystallized. The structure was determined at 2.0 Å resolution (R-factor = 19.8%) in FY 2011. The Adeh_2942 sensor formed a helical bundle, as we predicted (Figure 2). Surprisingly, the crystal structure

revealed a head-to-tail dimer in the crystal, which was not the case for other helical sensors reported in the literature.

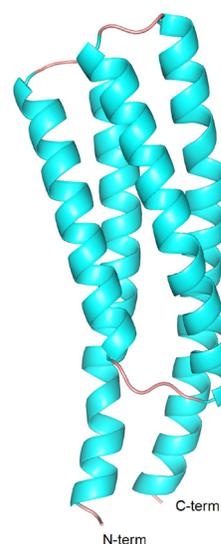


Figure 2. The helical bundle structure of the Adeh_2942 sensor domain.

Local Probe of Novel Electronic States at Complex Oxide Interfaces

2009-083-R2

John Freeland and Nathan Guisinger

Project Description

The development of the transistor — which has shaped so much of our modern technology and economics — stemmed from scientists’ efforts to acquire a greater understanding about the interfaces between different materials. In the same way, today’s materials scientists seek to expand their understanding of complex oxides by creating new states at the interface of two materials. To understand the spatial variation of these interface states, this project focuses on developing the use of cross-section scanning tunneling microscopy (STM). Although cross-section STM has worked well in the case of semiconductor interfaces, it has never been applied to oxide heterostructures.

Mission Relevance

This project is tied to DOE’s mission in basic science. This work will 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 information gained from this project is of interest to scientists who aspire to study new states at the interface in a wide variety of oxide systems. Understanding these systems is the first step toward the development of novel low-power elec-

tronics, which is key to reducing the massive power loss in the current generation of electronics. The Center for Nanoscale Materials (CNM) is an excellent location for this project. The CNM houses a scanning probe user site, as well as a premiere user site for complex oxide growth, which are accessible to a wide community of interested users.

FY 2011 Results and Accomplishments

In the first two years of this project, we not only were the first to demonstrate the ability to image a single interface in cross section but we developed the methodology to reliably image samples in this geometry.

During the third year of the project, we achieved our final major milestone, which was the direct imaging of a multilayered superlattice sample consisting of ferromagnetic (LaCaMnO_3 [LCMO]) and superconducting ($\text{YBa}_2\text{Cu}_3\text{O}_7$ [YBCO]) oxides. The unique information that we were able to extract by using this approach provides answers to key questions about these interfaces. This is the first time that a complex oxide superlattice has been imaged in cross-section by STM. In Figure 1, the layered structure of the LCMO (10-nm)/YBCO (10-nm) superlattice is clearly evident in both the topographic and electronic contrast. This image was taken at a temperature of 56 K, which is below the transition of the high-temperature superconducting YBCO layer. To study the interface in more detail, we completed a one-dimensional mapping of the density of states (see Figure 2). The abrupt transition highlights the sharp interface between the two disparate constituents. The conduction bands at the positive bias show close alignment across the interface, while a large mismatch occurs between the valence bands at the negative bias. The ability to map the electronic states across the interface enables us to provide input to theory in order to understand how to predict the interfacial electronic structure in systems with strongly correlated electrons. This capability will be an important step in harnessing these novel materials for next-generation electronic devices.

Seminars

Chien, T.Y. (2010). "Controllable Local Modification of Fractured Nb-doped SrTiO_3 Surfaces." Center for Nanoscale Materials User Meeting, Argonne National Laboratory, Oct. 2009.

Chien, T.Y. (2011). "Low Dimensional Electronic Properties Studied in Real and in Reciprocal Space." Colloquium, Department of Physics, University of Arkansas, Fayetteville, AR., Oct. 2009.

Chien, T.Y. (2011). "Probing Electronic Properties Across $\text{La}_2/3\text{Ca}_{1/3}\text{MnO}_3/\text{Nb:SrTiO}_3$ Interface with Cross-Sectional Scanning Tunneling Microscope." Colloquium, Department of Physics, National Sun Yat-Sen University, Kaohsiung, Taiwan, Jan. 2011.

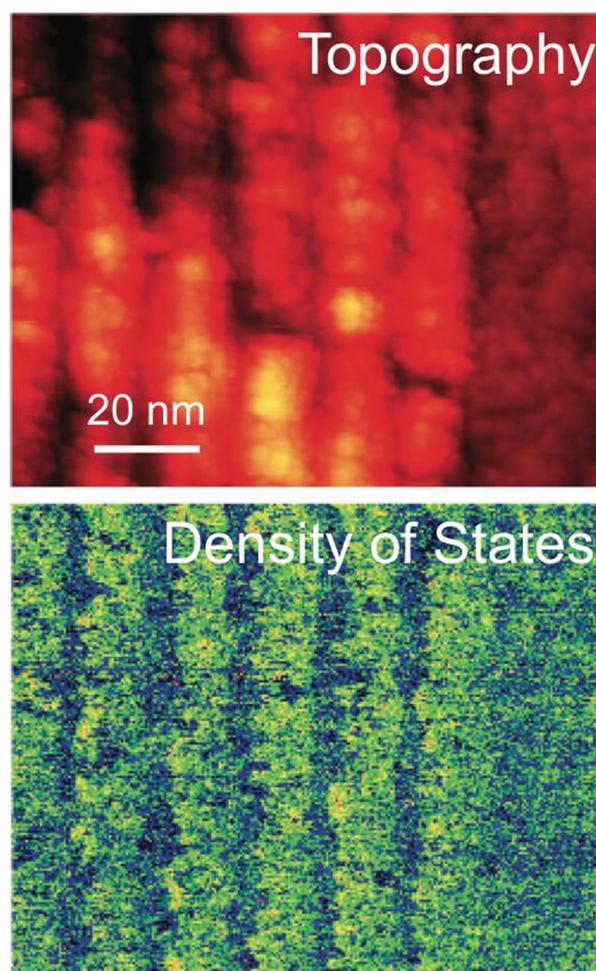


Figure 1. Cross-sectional imaging of an in-situ cleaved LaCaMnO_3 (LCMO)/ $\text{YBa}_2\text{Cu}_3\text{O}_7$ (YBCO) superlattice (top). The top panel shows the topography of a superlattice showing illustrating the layered structure. In the bottom panel, the figure shows the (top) together with a simultaneous map of the electronic density of states at a bias of +3V (bottom).

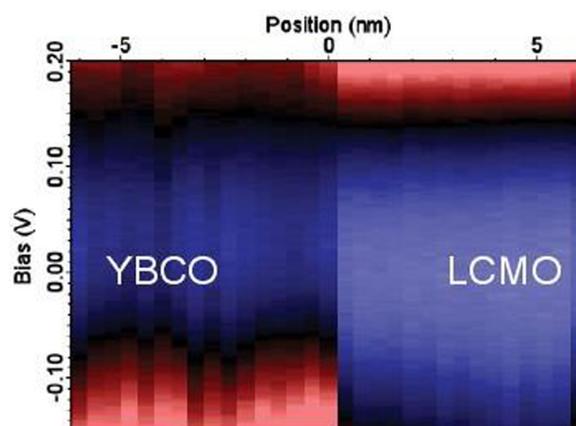


Figure 2. One-dimensional electronic structure image across the YBCO/LCMO interface showing an abrupt change with crossing the boundary.

Chien, T.Y. (2011). "Probing Electronic Properties at Complex Oxide Interfaces with Cross-Sectional Scanning Tunneling Microscope." Colloquium, Department of Physics, National Taiwan University, Taipei, Taiwan, Dec. 2010.

Freeland, J. (2010). "1+1=3: Using Interfaces and Strain to Design New Materials." Department of Physics, Pennsylvania State University, Dec. 2009.

Freeland, J. (2011). "Emergent Correlated Electron States at Surface and Interfaces." Max Planck Institute for Solid State Research, Stuttgart Germany, Dec. 2010.

Freeland, J. (2010). "Orbital Control in Heterostructures." Department of Physics, University of Virginia, Aug. 2010.

Freeland, J. (2011). "Understanding and Controlling Phases of Complex Oxides." Leibniz Institute for Solid State and Materials Research, Dresden, Germany, Dec. 2010.

Freeland, J. (2011). "Understanding and Controlling Phases of Complex Oxides." Max Planck Research Department for Structural Dynamics, Hamburg, Germany, Nov. 2010.

Guisinger, N. (2010). "Current Trends in Scanning Probe Microscopy at Argonne National Laboratory: From Complex Oxides to Graphene on Demand." MINT Center, University of Alabama, Apr. 2010.

Guisinger, N. (2009). "Current Trends in Scanning Probe Microscopy at Argonne National Laboratory: from Complex Oxides to Graphene on Demand." Purdue University. West Lafayette, Indiana, Oct. 2009.

Guisinger, N. (2010). "Epitaxial Graphene: Synthesis, Characterization and Modification." Department of Materials Science, University of Wisconsin, May, 2010.

Three-Dimensional Metamaterials with Negative Refractive Index

2009-111-R2

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

Project Description

New materials that display a negative refractive index for light, based on the presence of nanometer-scale metallic elements, have been developed over the past several years. To date, these materials have been produced by top-down fabrication techniques, which are capable of generating 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 they assemble into configurations that result in a negative refractive index at optical frequencies.

Mission Relevance

The goals of this project supports DOE's mission in fundamental science as it relates to the design of new materials for basic energy sciences. 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 2011 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. We have been developing the necessary techniques to synthesize, assemble, purify, and model these nanorod pairs. As synthesized, the gold nanorods were stabilized in water by charged surfactant molecules. Successful side-by-side assembly was accomplished by using charged disodium chromoglycate molecules that bind electrostatically with the charged surfactant on the sides of the rods. The reaction was interrupted by introducing polystyrene sulfonate, a negatively charged polymer, into the solution. The polymer wrapped around the nanorods to form a protective shell that stabilized the sample, thereby allowing for further processing.

Further processing was necessary because the assembly process leads to a random distribution of single nanorods, side-by-side pairs of nanorods (or "dimers"), and other aggregates. Optimization of the assembly process resulted in a product in which nearly 30% of the particles were in side-by-side dimers, but a higher yield is required to provide a robust negative refractive index. We therefore developed a protocol to purify the product through rate-zonal centrifugation. A centrifuge tube was filled with viscous sucrose solution, with the sucrose concentration increasing from the top of the tube to the bottom, and a concentrated layer of the assembled-nanorod solution was laid on top. High-speed centrifugation of this solution separated the product into different bands, as shown in Figure 1. Isolation of the second band resulted in a solution in which 80% of the nanorods were in side-by-side dimers. This degree of purification was limited by the quality of the sucrose gradients that could be formed manually and the precision with which the band could be removed from the centrifuge tube. We therefore acquired an automated gradient former and fractionator, which we expect to allow nearly 100% purification of side-by-side dimers. This purified solution should exhibit the exotic optical effects that are the goal of this project.

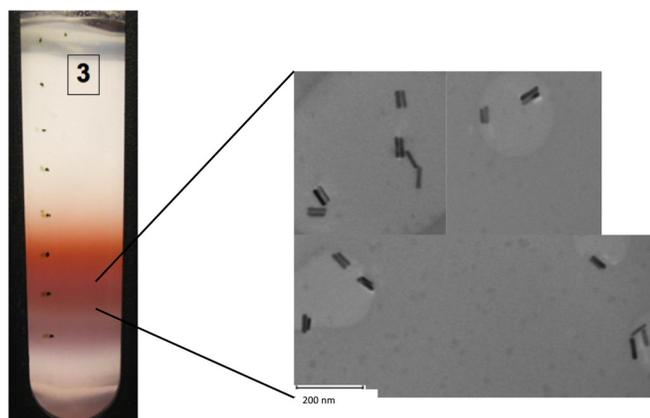


Figure 1. Purification of nanorod dimers by rate-zonal centrifugation. The left panel is a photograph of a solution of assembled nanorods after centrifugation, showing a separation into bands that consist of single nanorods, side-by-side dimers, and larger aggregates. The right panel depicts transmission-electron microscope images of the particles in the central band.

Obtaining a negative refractive index, in particular, requires optimizing the dimensions and separations of the nanorods in the dimers. We began large-scale, finite-difference, time-domain simulations of light transmission by arrays of nanorod pairs and applied the procedure developed in the previous period to infer effective refractive indices from the calculated transmission values. The optimization used a novel procedure based on Gaussian process modeling, which seeks to maximize the figure of merit, $f = -n/k$, where n and k are the real and imaginary parts of the refractive index, respectively. We were able to find a configuration that yields a negative index at a wavelength of 700 nm within the visible region of the spectrum. Unfortunately, the relatively small magnitude of the real index ($n = -0.07$) and the relatively large magnitude of the imaginary index ($k = 6$) indicate that this particular design will not have practical value as a negative-index material.

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

2009-138-R2

John Bahns, Liaohai Chen, and Ralu Divan

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 proteins that would be produced only when a patient has cancer. Such an endeavor is extremely difficult, since in an early stage tumor only one of every 10 billion

(or more) proteins in the blood plasma may be the one that we want to detect. To address this issue, it is essential that we design a test to reliably identify and detect these specific proteins. Further, we must ensure that this test does not produce false positives, which could lead to a false initial diagnosis of the presence of cancer. Achieving this level of accuracy requires the development of a protein sorting assay that can detect and characterize extremely low levels (to a single protein molecule) from a bulk specimen sample. Therefore, the goal of this project is to build a detection platform through a 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 a high potential for ultimate screening and discrimination against a wide range of biological agents at a high level of confidence. The assay is expected to find immediate use in three major areas: early stage diagnosis of lethal diseases, such as cancer, AIDS, and Alzheimer's disease; matters of national security and public safety, such as countering bioterrorism threats and responding to epidemics; and biomedical research and 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, the Department of Homeland Security, the Department of Defense, the Department of Energy, and the National Aeronautics and Space Administration, as well as 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 Cancer Nanotechnology Plan.

FY 2011 Results and Accomplishments

In the past year, we implemented a new design to fabricate and integrate nanoslits into the nanofluidic device. The nanoslits are simply "written" in the gold film channel bottoms by using focused ion or electron beams. Figure 1 shows the experimental setup (top) and the schematic side view of the device (bottom). The device is made by an e-beam and lift-off process and includes five layers: glass substrate, gold (slits), SU8, cover glass with two holes, and polydimethylsiloxane (PDMS). The 5- μm -thick SU8 coating on the slits is accomplished by controlled exposure and alignment to make the channels. In the test experiments, a laser light was adjusted to a spot size that included all six nanoslits. To simplify interpretation of the fluorescence time-trace, however, only a small region ($\sim 0.6\text{-}\mu\text{m}$ diameter) of a single slit was imaged by the confocal optics of the detection system. Thus, the fluorescence from beads passing through only one nanoslit was imaged by the microscope/detector and processed by the computer.

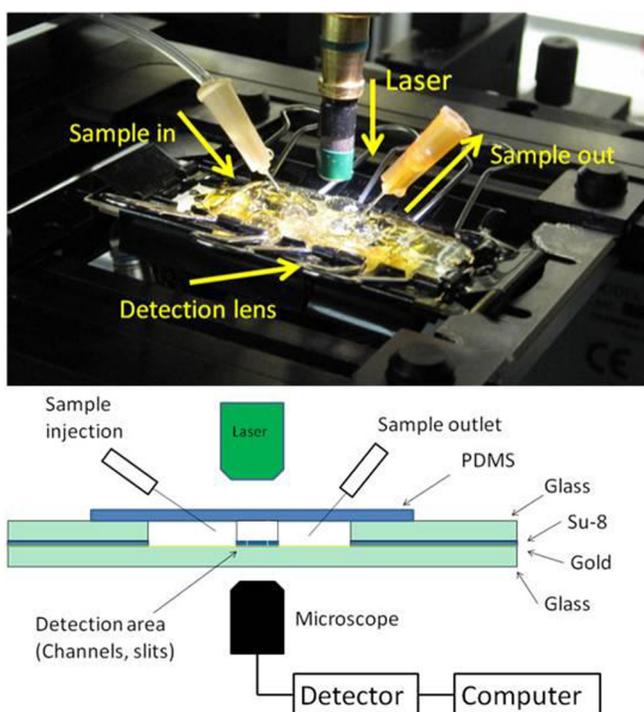


Figure 1. Photo of instrument setup (top) and schematic side view of the device with nanoslits and instrument setup (bottom). The device includes five layers: glass substrate, gold film (5 nm Cr plus 100 nm gold) with slits, SU-8, cover glass with two holes (reservoirs), and PDMS (polydimethylsiloxane).

In FY 2011, we also established near-field illumination and fluorescence correlation spectroscopy (FCS) measurements in nanofluidics and provided a new fluorescence correlation algorithm suitable for nanofluidics. Figure 2 (left) shows the six nanoslits that occupy the three parallel channels when illuminated with unpolarized white light. The nanoslits are 3 μm in length and 100 nm in width. The bottom two nanoslits are smaller than the other four because of overdevelopment in the lift-off process. Optimization of the lift-off process will eliminate this flaw, since it is important to span the entire channel width (3 μm in this case). However, this artifact does not affect the nanoslit function. Figure 2 (right) depicts the nanoslits under laser (multimode and unpolarized) illumination. The larger apparent image size of the nanoslits is the result of overexposure. In this case, the charge-coupled-device camera was adjusted to high ISO status under the weak light.

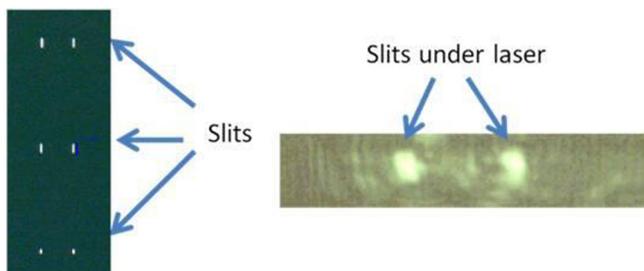


Figure 2. The image of slits under white light (left) and under laser (right).

The device was successfully tested by using fluorescent nano-beads. The test was conducted by flowing 200-nm (dragon green) polystyrene nanobeads in ultrapure water through the channels, while the fluorescence from a small region ($\sim 0.6 \mu\text{m}$) of a single slit was monitored with confocal optics. The collected fluorescence was sent to a detector (avalanche photodiode) and analyzed with a real-time autocorrelator. With a nominal laser power of $\sim 3 \text{ mW}$ (at a wavelength of 488 nm), the fluorescence bursts were very bright (Figure 3, top), typically peaking at $\sim 80 \text{ kHz}$ above a very low, stable background count of $\sim 5 \text{ kHz}$. The background could be made smaller by increasing the gold film thickness. The largest spikes occurred from beads that crossed the nanoslit in the immediate vicinity of the detection region ($\sim 0.6\text{-}\mu\text{m}$ diameter). The smaller peaks resulted from beads that crossed the slit further from this region (under optimum excitation and detection overlap conditions, all bursts would be nearly equal in intensity). The applied pressure ($\sim 0.1\text{--}0.3 \text{ atm}$) produced a nominal channel flow rate of $\sim 10 \mu\text{m/s}$. As shown in Figure 3, the autocorrelation curves (bottom) indicate that less than one bead ($1/3$ and $2/3$ for blue and black, respectively) crossed the slit at any given time, and the flow rate for the blue data was roughly twice that of the black. We are extremely encouraged by the outcome of the testing, which clearly demonstrates a device of superior analytic potential compared with conventional FCS.

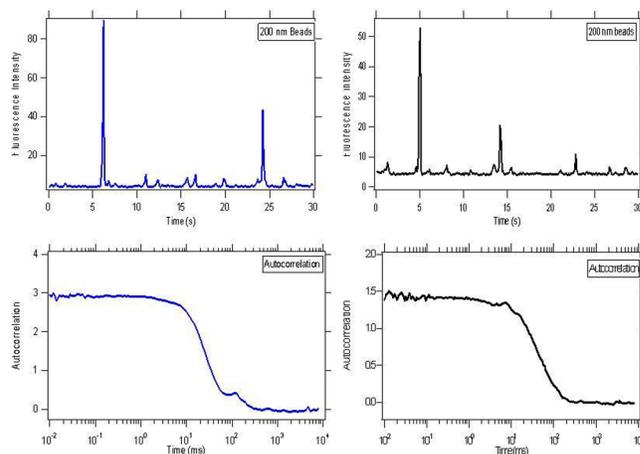


Figure 3. Fluorescence traces (30 s) (top) from a single laser illuminated slit when green 200-nm polystyrene beads ($\sim 10^9/\text{mL}$) flow in a single channel. Note the low, stable background light level. Fluorescence intensity is in counts per second $\times 1000$.

The major technical hurdle for using the above-mentioned device was the leak of channels at the interface between the glass and SU-8 when the device was under pressure to drive through the solution. Our search for an easy, yet robust way to fabricate the desired nanofluidic devices led to the invention of the optical directed assembly (ODA) process. This process is a new way of making continuous solid mesostructures from nanomaterials. When a low-power laser — similar in intensity to those used in office laser pointers — is focused to a spot within a suspension of gold (or other metal) and

carbon nanoparticles (NPs), the carbon NPs entering the spot deform into a type of “glue” that enables the creation of long gold and carbon chains or surface traces wherever the laser spot is pointed (Figure 4a). Localized heating at the focused spot causes a “convective flow” that rapidly conveys the nanoparticles to the hot spot where the material is deposited. The resulting structures are biocompatible, permanent, and capable of surviving multiple wash/dry cycles. A few milliwatts can materialize millions of nanoparticles per second. “Handcrafted” traces of up to a centimeter (at widths typically 10–60 times that of the original nanoparticles) can be formed with arbitrary shape and design. Figures 4b and 4c show an example of direct one-step writing and patterning of high conductivity micro-circuitry in two-dimensions. “Written” traces on glass with gold and carbon NPs produce Ohmic circuitry with high conductivities of ~ 250 S/cm. The ODA offers control, simplicity, and possible cost advantages for nanomaterial assembly and fabrication into functionally attractive flexible nanodevices.

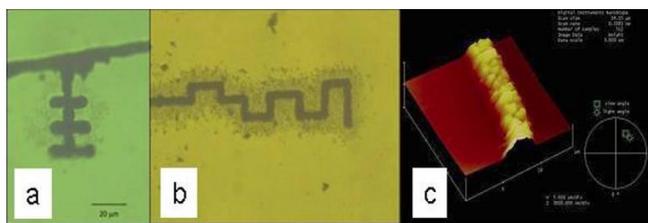


Figure 4. ODA images. (a) Handcrafted microscopic glyph made by using ODA of 50 nm carbon and gold nanoparticles with a 1-mW laser — the Chinese character for “king.” (b–c) Optical and AFM images of gold/carbon traces “written” on a glass substrate.

This work resulted in the following inventions/patents:

Chen, L., S. Gray, and S. Sankaranarayanan., “Method for Patterning Nanoparticles,” invention report submitted February 2011. [ANL-IN-11-009]; Patent application filed September 2011. [Patent Application No.: 13/249,865]

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

2009-146-R2

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

Project Description

The objective of this project is to use the Advanced Photon Source (APS) light source to obtain some of the first measurements ever made 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 near active galactic nuclei (AGN) and black holes. SAO is providing two uniquely portable, state-of-the-art spectroscopy instruments: a new electron beam ion trap (EBIT) designed to produce well-controlled plasmas and a cryogenically cooled microcalorimeter to measure broad band x-ray spectra with high spectral resolution.

Mission Relevance

This 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 (LCLS) and other x-ray free-electron laser (XFEL) sources. The second, the high-resolution x-ray calorimeter can be used for other precision atomic spectroscopy measurements at the APS; for example, for the study of multielectronic atomic transitions, which are an important signature of hollow atoms created by XFEL sources.

FY 2011 Results and Accomplishments

Because of the 12ID beamline upgrade, we could not follow up on our successful 2009 measurements and thus sought an alternative venue. We identified beamline 7ID-B as the most practical alternative because it provides both pink and white undulator radiation in a hutch that can accommodate the large EBIT support table and the ancillary equipment. The only component missing was a vertical focusing optic to match the size of the 70- μ m EBIT electron beam with the full complete pink beam flux. In FY 2010, we procured a Be compound refractive lens (CRL) to vertically focus the white beam. In FY 2011, we installed and commissioned the CRL system to prepare for next year’s experiment. The successful commissioning measurements showed that we can now vertically focus a 10-keV monochromatic beam to 8.6 μ m. When averaged over an energy corresponding to the pink beam undulator spectrum, this increases to 16.1 μ m — well below the ~ 70 - μ m limit of the EBIT electron beam focus. The beamline can now carry out such experiments in the future.

Seminars

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

Single Photon Receiver Using Abrikosov Vortices

2009-190-R2

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

Project Description

In the last decade, the rapid development and application of thermal superconducting detectors (SDs) or bolometers opened the door for breakthroughs in many scientific and industrial areas that require the detection of single photons. SDs were developed to take measurements across the electromagnetic spectra, starting from millimeter, to infra-red (IR), near-IR, and far-IR, and extending to x-ray and gamma ray spectroscopy. They are used to study dark-matter and supersymmetry and quantum information processing. However, although SDs, with their improved array designs, are widely used, they have a major limitation: the direct proportionality of a SD's sensitivity to its intrinsic response time makes it difficult to fabricate fast, highly sensitive receivers. The reason is that the SD's sensitivity is determined by the thermal isolation of the active area from the environment, and good thermal isolation leads to long SD recovery times. Yet many applications (e.g., observing distant pulsars or detecting stand-off explosives) require fast, sensitive SDs.

We are developing a sensor element that employs the effect of Abrikosov vortex creep in Type II superconductors; in particular, it employs the very abrupt nonlinear dependence of the vortex creep near lower critical field H_{c1} in thin films. This type of detection avoids some pitfalls of superconducting bolometers and offers high sensitivity and speed. Moreover, in an ideal case, the sensitivity of this detection scheme does not depend on the intensity of the radiation hitting the superconductor.

Mission Relevance

This project is relevant to DOE's mission in basic science and national security. High sensitivity, scalable, and high-speed image-forming direct detector arrays are required for materials science research (x-rays), security screening (THz), remote sensing, medical imaging and surveillance (infrared, terahertz, and millimeter waves), and both ground- and space-based applications, such as astronomy tasks (x-rays, sub-millimeter and millimeter waves). A 2009 report by an independent committee on funding particle astrophysics strongly recommended to DOE's Office of High Energy Physics that investments in novel detectors for cosmic-ray experiments be substantially increased (*Nature* 461, p. 1181). Our objective is therefore to develop and implement novel, superior-performance detectors for these applications.

FY 2011 Results and Accomplishments

In FY 2009, we established that we can use the superconducting vortices as a detecting mechanism for photons and effectively manipulate those vortices. In FY 2010, we optimized the material and design of the detector element. We used the latest sputtering tools and fabrication facilities at the Center for Nanoscale Materials to select thin film Nb as the material for the detector and prepare it. The material had very low pinning strength (because of the extremely clean conditions for growing thin film), uniform thickness, and few defects. Because Nb's superconducting penetration depth is an order of magnitude smaller than that of MoGe, magnetic field modulation by vortices is significantly stronger. This leads to stronger vortex-vortex interaction, and, in the case of a weak pinning landscape, much better control when the vortex is manipulated over long distances. The vortex lattice in this material is more rigid, so forces can be transmitted over longer distances. Also in FY 2010, we fabricated a fiber-optic-based tool with a moving stage for testing the coupling efficiency of incoming radiation to the detector. The tool has an optical fiber that is coupled on one side with a laser diode at room temperature and on the other end with the alignment stage at liquid helium temperature.

In FY 2011, we conducted experiments on the vortex mobility in very specific constrained geometries that could strongly affect the performance of single vortex counters and multiplexers and have far-ranging consequences on engineered nanoscale superconductors in superconducting wires and microwave electronics. In the first set of experiments, we demonstrated the vortex jamming effect through long-range manipulation of Abrikosov vortices in mesoscopic superconducting wires (Figure 1). Voltage asymmetry (rectifying effect) with respect to the direction of vortex flow in funnel-like constrictions is evidence that vortex jamming can significantly moderate vortex dynamics in mesoscopic geometries. This finding could be applied to devices exploiting vortex dynamics and vortex manipulation (e.g., photon receivers).

In the second set of experiments on tailored ferromagnet-superconductor-ferromagnet (F/S/F) structures, we explored the vortex mobility in the superconductor that is modified by the proximity of magnetic domain structures in the adjacent ferromagnetic layers. Ordered magnetic stripe-domain structure defines perfect channels along which the vortices slide. By changing the direction of the magnetic stripe domains (using a small magnetic field), one can change the vortex's mobility or stop its motion altogether. The results (Figure 2) show that at the same vortex density (applied perpendicular magnetic field), the current voltage characteristics depend strongly on the mutual orientation of the magnetic stripe domains and the direction of vortex motion. The possibility of changing the current-voltage characteristics of the device by switching the magnetic domain structures renders this nonvolatile element

as an important gate-like control element when manipulating vortices in more complicated vortex circuits.

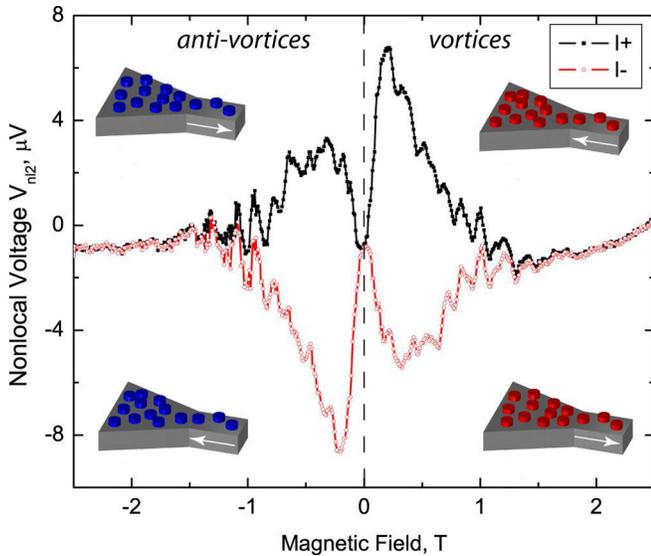


Figure 1. Nonlocal voltage $V_{nl2}(I,H)$ as a function of the applied magnetic field for two opposite directions of the driving current ($T = 2.4$ K). Vortices of opposite polarities exhibit the same rectification behavior when moving in the same direction.

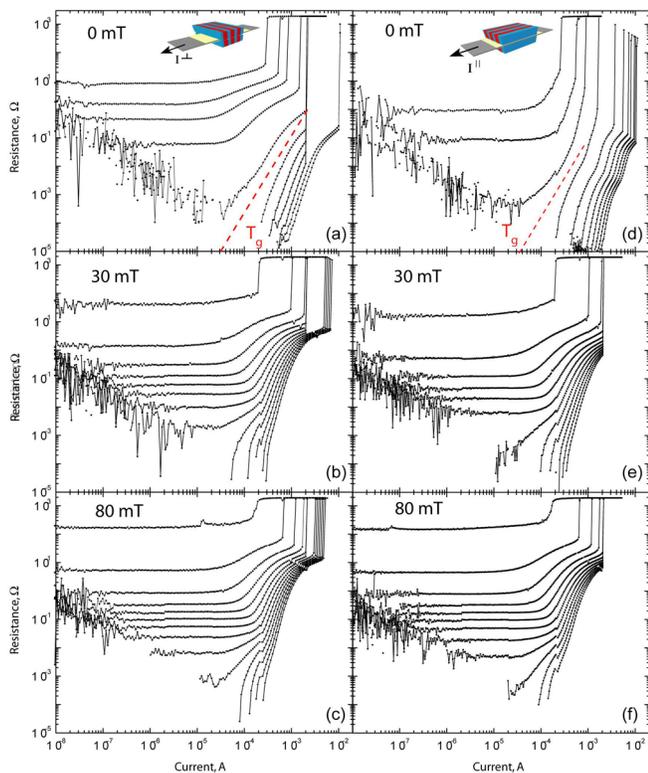


Figure 2. Resistance-current isotherms of a 20-nm thin superconducting film magnetically coupled with two Permalloy layers, in cases where magnetic stripe domains are oriented perpendicular to the applied current (a-c) and parallel to the current (d-f). The external magnetic field applied perpendicular

to the surface of the film is 0 mT (a, d), 30 mT (b, e), and 80 mT (c, f). The isotherms are recorded at 4.0, 4.2, 4.4, 4.6, 4.8, 5.0, 5.2, 5.4, 5.5, 5.55, and 5.6 K (a, d); between 3.2 and 5.6 K (b); between 3.0 and 5.6 K (c); and between 3.4 and 5.6 K (e, f) with a 0.2 K interval. Note the shift between frames (a) and (d) of T_g , the vortex glass transition temperature at which the I-V isotherm changes its curvature.

FY 2011 was the final year of the project. Potential future sponsors of this work include DOE's Office of High Energy Physics and the National Aeronautics and Space Administration.

Engineering Nanostructures Atom by Atom for Optical Activity and Quantum Coherence

2009-204-R2

Jeffrey R. Guest and Nathan P. Guisinger

Project Description

Bottom-up assembly of nanostructures tailored for function is an intriguing aspect 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 (e.g., "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, platforms for quantum information processing, or valuable insight into photophysical functioning. 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 UHV STM.

Mission Relevance

This project is relevant to DOE's missions in energy and basic science. Combining lasers with scanning probe microscopy has significant potential for scientific application to many other measurements, including the investigation of the ultra-fast, 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 2011 Results and Accomplishments

Previously, we fabricated the UHV scanning tunneling microscope (also STM) with integrated high-numerical-aperture optical access (FY 2009), commissioned it, and demonstrated that we could perform laser spectroscopy and laser excitation with micron-scale laser spots under the STM tip in UHV with minimal thermal expansion of our tip-sample junction (FY 2010). For our transparent and atomically controllable substrates, we developed epitaxial graphene on silicon carbide (FY 2009) and performed STM studies of the morphology of chemical vapor deposited graphene on copper (FY 2010).

In FY 2011, we developed a process to transfer graphene grown on copper onto an annealed sapphire substrate (Figure 1A). This effort was critical because it provides an atomically controlled and resolved surface that is isolated electronically and optically. (Figure 1B shows an atomic-resolution STM image of the carbon honeycomb lattice.) Local STM measurements and transport measurements now provide a clean measure of the electronic properties of the graphene, and optical measurements are largely background-free. Raman spectroscopy of the graphene on sapphire shows the sharp Raman peaks of pristine graphene (Figure 1C).

We developed two physical nanoscale systems to correlate atomic-scale characterization and control over atoms and molecules at surfaces with their optical properties. Expanding on previous studies of hydrogen adsorption and desorption on graphene, we demonstrated that the mechanism for desorption of hydrogen from graphene is electronic excitation at high voltage and local electric field effects at low voltage (Figure 2A). Also, we explored the morphology and electronic properties of C_{60} molecules and showed that not only do they form a close-packed two-dimensional (2D) lattice (Figure 2B), they also show electronic properties of molecules independent of the substrate, which should improve their optical properties.

In FY 2012, we expect to continue exploring the nanophotonic properties of nanostructured hydrogen on graphene and through DOE single investigator and small group research (SISGR) funding, we will continue exploring photophysical systems by assembling molecular acceptor-donor systems and studying their photovoltaic properties with the laser-STM approach. The C_{60} molecules on graphene will be an ideal platform for depositing donor molecules and exploring these processes.

Seminars

Gao, L., M. Bode, N.P. Guisinger and J.R. Guest (2010). "Laser-coupled Ultra-high Vacuum Scanning Tunneling Microscope: Towards Optical Probing and Manipulation of Nanostructures on Surfaces." Center for Nanoscale Materials User Meeting, Argonne, IL, October 5–7, 2009.

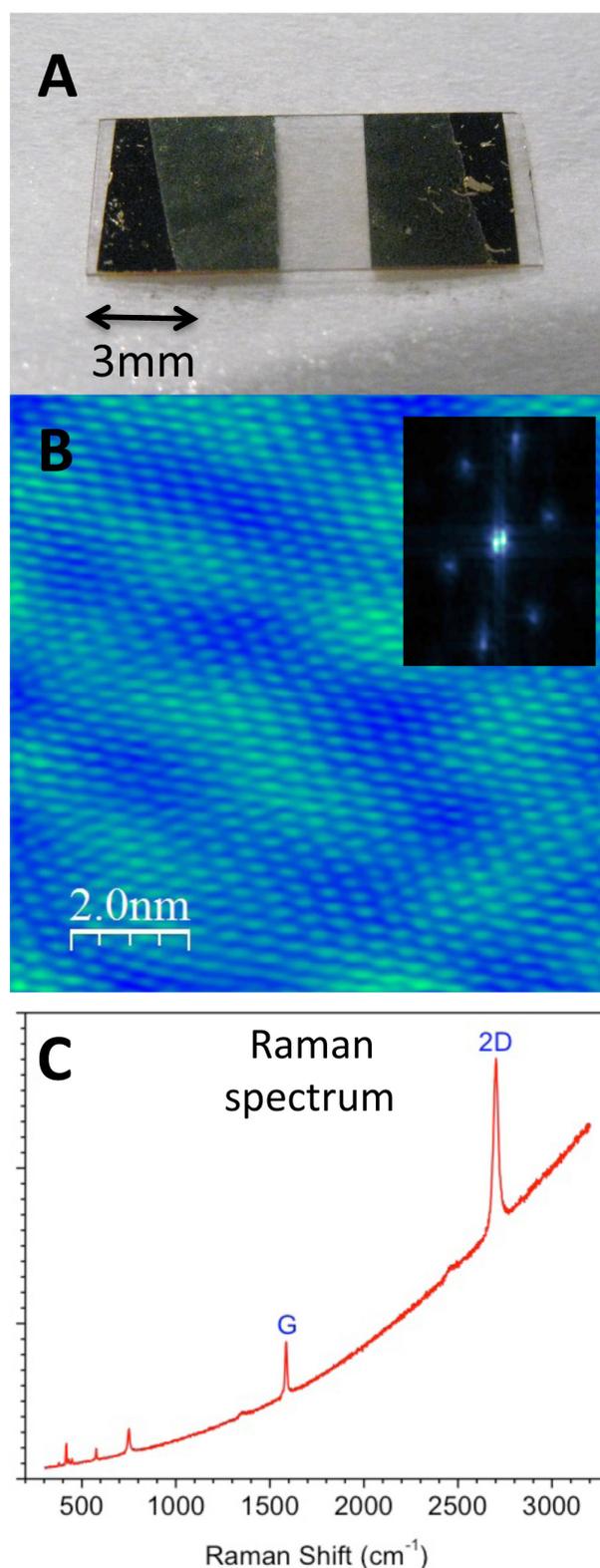


Figure 1. Graphene isolated on a sapphire substrate as a platform for optical STM studies: (A) graphene on sapphire sample, (B) STM topographic image (color range corresponds to surface height spanning 280 nm, dark being low and light being high), (C) optical micro-Raman spectroscopy result.

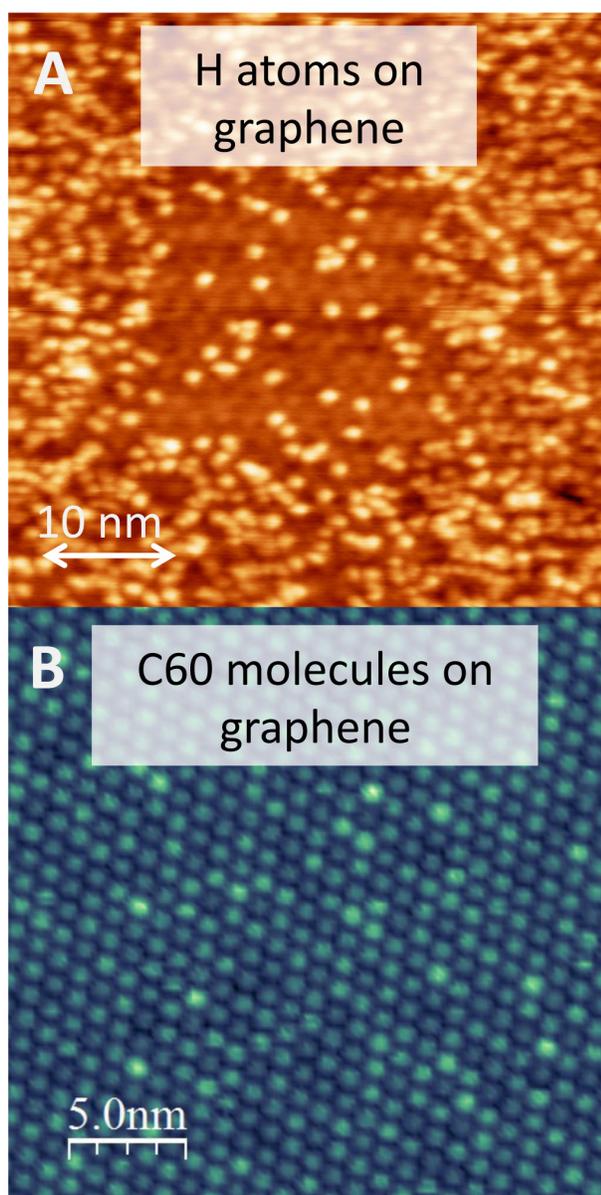


Figure 2. Atoms and molecules on graphene: (A) Light patches are hydrogen clusters on graphene, selectively removed by the tip near the center; (B) Ordered 2D lattice of C_{60} on graphene.

Physics of the Superinsulating State

2009-209-R2

Valerii Vinokur and Andreas Glatz

Project Description

The superinsulating state is a novel macroscopic dynamic quantum state that forms as a result of the subtle interplay of quantum, correlation, and disorder effects. The project goal is to investigate the physical properties of this new state of matter, the superinsulator, and related aspects of the super-

conductor-superinsulator quantum phase transition. Since the superinsulating state is a low-temperature Berezinsky-Kosterlitz-Thouless (BKT) state in a charged system dual to the vortex-BKT transition in the superconducting film, we plan to thoroughly investigate BKT transport at either side of the transition, accounting for the quantum fluctuations and the effects of the film's disorder and geometry. We will explore different realizations of the superinsulating system (superconductor/normal conductor/superconductor [SNS] structures and artificial Josephson arrays) and nonlinear transport in these systems. Our results will help researchers find novel ways to design artificial superinsulating materials that will work over a wide range of temperatures and magnetic fields.

Mission Relevance

This project and its expected results fit within DOE's mission to support world-class research on energy efficiency and relate to at least two of the DOE Office of Basic Energy Sciences "Five Challenges for Science and the Imagination" (<http://science.energy.gov>); namely, this work demonstrates that (1) superinsulation is an example of an "emergent collective phenomenon in a strongly correlated multiparticle system" and (2) the superinsulator is a system "far beyond equilibrium." On the applied side, superinsulators have high potential as a technological base for a new generation of sensors, bolometers, and radiation detectors that will have unprecedented sensitivity and exceptionally high and useful signal-to-noise ratios.

Understanding and describing the underlying microscopic mechanisms of the formation of this new phase and its peculiar transport properties will foster breakthroughs in our knowledge of macroscopic quantum states and drive a search for superinsulating states in other systems and in artificially manufactured structures. On the applied side, the ability of superinsulators to change their resistivity by three to six orders of magnitude upon crossing the superinsulating transition with a few millikelvin of temperature resolution characterizes them as materials of unprecedented technological promise (e.g., supersensitive radiation sensors, filters).

FY 2011 Results and Accomplishments

In the previous years we constructed the underlying qualitative theory of the superinsulating state, built the basis for the full theory of superconducting fluctuations in thin films and superconducting fluctuations in far from the equilibrium state, and developed a quantitative theory of the novel superconducting state: the superconducting textures in the films attached to an elastic substrate. These achievements constituted the foundation for our FY 2011 studies.

In FY 2011, there were four major accomplishments. First, we conducted a comparative study of the transport properties of continuous and nanoporated TiN films. We separated the effects of disorder from the geometry of the film.

Nanopatterning transformed a thin TiN film into an array of superconducting weak links and, on its own, stimulated the disorder-driven and magnetic-field-driven superconductor-to-insulator transitions, shifting both transitions to a lower degree of microscopic disorder. The results obtained open the route to manufacturing systems that exhibit tunable superconductor-superinsulator transitions and to the technological use of this phenomenon. We observed magnetoresistance oscillations, reflecting the collective phase-frustration behavior of the multiconnected superconducting weak link network in a wide range of temperatures. We found that nanopatterning enhances the role of the two-dimensional (2D) Coulomb interaction and changes the characteristic energies of the film on length scales significantly larger than the mean free path or the superconducting coherence length.

Second, we revised the long-studied problem of fluctuation conductivity (FC) in disordered 2D superconductors and obtained a complete description of the temperature-magnetic field phase diagram for a superconducting film above the transition temperature. On the basis of our results, we established a novel tool, fluctuoscropy, that allows researchers to infer, with unprecedented accuracy, the material parameters of superconducting films from the measurements of transport properties in the fluctuation-dominated domain of the phase diagram.

Third, we generalized the Ginzburg-Landau description of superconducting fluctuations in a 2D disordered superconductor under far-from-equilibrium conditions in a fluctuational regime. We applied that approach to a technologically important hybrid system (a thin superconducting film sandwiched between two normal electrodes) and demonstrated that by tuning the temperatures and electrochemical potentials of the electrodes, one can independently control the temperatures of different electron subsystems in a superconducting film.

Finally, by building on a complete account of quantum contributions to conductivity, we demonstrated that the resistance of thin superconducting films exhibits non-monotonic temperature behavior as a result of the competition between weak localization, electron-electron interaction, and superconducting fluctuations. We showed that superconducting fluctuations give rise to an appreciable decrease in resistance, even at temperatures much higher than the superconducting transition temperature, with this decrease being dominated by the so-called Maki-Thompson process. We developed a method for very precisely determining the superconducting transition temperature and, for the first time, directly observing the BKT transition, which we detected both by the power-law behavior of current-voltage characteristics and by flux flow transport in the magnetic field.

Seminars

Baturina, T.I., A.Y. Mironov, D.A. Nasimov, A.V. Latyshev, N.M. Chtchelkatchev and V.M. Vinokur (2011). "Nanopattern-stimulated Superconductor-insulator Transition in Thin TiN Films." Seminar - Bar-Ilan University, Bar-Ilan, Israel, Sep. 15, 2011.

Baturina, T.I., A.Y. Mironov, C. Strunk, D. Kalok, A. Bilusic, M.R. Baklanov, A. Satta, V.M. Vinokur and N. Chtchelkatchev (2011). "Superinsulation: Reverse of the Superconductivity. Experiment and Theory." Autonoma University, Madrid, Spain, Feb. 20, 2011.

Glatz, A., V. Vinokur, I. Aranson, T. Baturina and N. Chtchelkatchev (2011). "Self-organized Regular Superconducting Patterns in Thin Films." Superconductor-Insulator Transition Workshop, Argonne, IL, Nov. 16–19, 2010.

Glatz, A. (2012). "Superconducting Island in Two Dimensions." Invited Lecture, NIU, Dekalb, IL, Nov. 30, 2011.

Vinokur, V. (2010). "Superinsulators: Reverse of a Superconductivity." Departamento Fisica de Materiales, Facultad CC., Fisicas, Universidad Complutense, Madrid, Spain, Feb. 17, 2010.

Vinokur, V. (2010). "Cascade Relaxation and Superinsulating State in Two-dimensional Superconducting Systems: Experiment and Theory." University of Cologne, Cologne, Germany, May 6, 2010.

Vinokur, V. (2010). "Charge BKT Transition and Superinsulating State in Two-dimensional Superconducting Systems: Experiment and Theory." Lebedev Institute, Moscow, Russia, May 12, 2010.

Vinokur, V., N. Chtchelkatchev, A. Glatz, A. Petkovic and T. Baturina (2011). "Localization of Disordered Bosons." Seminar - Institute High Pressures, Russian Acad. Sci., Troitsk, Russian Federation, Jul. 16, 2011.

Vinokur, V., N. Chtchelkatchev, A. Glatz, A. Petkovic and T. Baturina (2012). "Transport and Localization of Disordered Bosons in a Cooper Pair Insulator." Colloquium - University of Illinois at Chicago, Chicago, IL, Oct. 17, 2011.

Magneto-Vibrational Energy Conversion at the Nanoscale

2010-003-R1

Axel Hoffmann and Daniel 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 unambiguously that magnetic moments possess corresponding mechanical angular momentum. Interest in this phenomenon has been renewed since several recent experiments have shown that magnetism-related mechanical torques are sufficient to significantly modify the dynamics of micron-sized mechanical objects (usually known as a microelectromechanical system [MEMS]) with kHz resonance frequencies.

Furthermore, it has also been recently demonstrated that patterned magnetic nanostructures have well-controlled magnetization dynamics at frequencies of a few hundred MHz, well below their ferromagnetic resonance (typically a few GHz and above). Moreover, the magnetization dynamics of these nanostructures can be excited by passing local alternating electric currents through them. These recent developments open up the possibility of having hybrid magnetomechanical nanostructures with commensurable resonance frequencies. Integration of magnetic nanostructures on top of submicron-sized mechanical objects (or nanoelectromechanical system [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 submicron ferromagnetic material with small magnetocrystalline anisotropy (e.g., 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 side-walls. This potential, in turn, allows the selection of specific domain wall resonance frequencies, which can be excited and detected via radiofrequency electric transport measurements. Although these frequencies have been demonstrated to be as low as 10 MHz, the low frequency limit has not been sufficiently explored. The domain wall resonance results 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 varied independently from one another. Furthermore, the resonance frequency of the magnetic domain wall oscillator may be tuned via applied external magnetic fields. This enables 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 both direct basic and applied impacts. From a fundamental point of view, measurements of such coupled systems allow for researchers to determine the magnetomechanical 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 actuation can excite high-frequency nanomechanical devices (using magnetization dynamics to actuate mechanic motion) or enable unique energy harvesting structures to collect power from continuously renewable energy sources, such as vibrations or thermal energy (converting mechanical motion into magnetization dynamics and, ultimately, electricity).

FY 2011 Results and Accomplishments

We prepared structures for magnetic domain wall oscillators. They consist of extended wires with a notch for domain wall pinning in the center and a nucleation pad for controlled domain wall injection at one end of the wire. We used magnetic force microscopy to confirm the presence of a domain wall at the notch. Then we used anisotropic magnetoresistance to detect a resistive signature of the domain wall in the wire, which manifested itself as a 0.01% change of the overall resistance. This allowed us to use magnetotransport measurements to identify depinning fields and also any current-driven dynamics. At this point, the depinning fields in our structures are still significantly higher than the ones reported in the literature, which suggests that extrinsic pinning (from, for example, side-wall roughness, defects, or impurities) is dominating the dynamic behavior. We are now working on changing the fabrication of the wires to reduce any extrinsic pinning. While optimizing the magnetic domain wall oscillators, we also started to tackle the integration process with the torsional MEMS oscillators. The latest linear design adapts well to the MEMS structures, which we are optimizing for their mechanical resonance frequencies.

We continued FY 2010 efforts to design and fabricate torsional MEMS/NEMS with sufficiently high resonant frequencies. We successfully addressed MEMS fabrication problems caused by

large paddle structures that resulted in incomplete release. We did so by adding through-holes to each large paddle, resulting in completely released MEMS torsional oscillators.

To characterize the actual resonance frequencies of the MEMS/ NEMS oscillators, we used an interferometric technique. In short, an incoming laser beam is split into two, each focused on different parts of each device. The interfering reflected signals are then detected, and the frequency noise spectrum is analyzed. This procedure allows the direct detection of the dynamic eigenmodes from the thermal noise, with no need to externally drive the system. For our torsional MEMS oscillators, we typically observed several eigenmodes starting at about 1 MHz and ranging close to 7 MHz. The various modes can be identified through numerical finite-element simulations. The mode with the lowest frequency is the in-phase torsional motion of all paddles; the next two modes are flexure modes of the beam. The mode with the highest frequency observed can be assigned to an out-of-phase torsional mode, with the largest rotation amplitude at the central paddle.

The flexural and torsional modes can be distinguished by placing the probing laser beam on different locations of the MEMS torsional oscillator. If the beam is placed on the end of the central paddle, both torsional and flexural modes can be detected; if it is placed on the torsional bar, only flexural modes can be detected because of the negligible small displacement along the torsional axis. The frequencies of the calculated modes and of the experimentally observed ones differ slightly, probably because of minor differences between the dimensions of the various features of the actual device and those of the simulated structure. Also, the overall frequencies of the mechanical resonances are reduced from the targeted 20 MHz as a result of the reduced mass of the paddles, which is caused by the holes needed for the release. Nevertheless, the highest frequency is within a factor of two with respect to the previously demonstrated magnetic domain wall resonance; thus, minor modifications to the geometry should allow us to establish good frequency matching. Furthermore, since the maximum torsional rotation amplitude of the high-frequency mode is at the precise location of the magnetic domain wall oscillator, magnetomechanical coupling is enhanced for the out-of-phase torsional mode.

Proposed Work for FY 2012

The immediate next steps will be to investigate how the thermal noise spectrum changes as a result of the presence or absence of a magnetic domain wall, since magnetomechanical coupling could already result in a frequency shift that should be readily observable due to the high Q-factor [1030 for the highest mode] of the mechanical resonance.

We also plan to:

- ▶ Integrate NEMS structures with magnetic vortex structures,
- ▶ Characterize mechanical response to electrically driven magnetization dynamics (Einstein-de Haas effect),
- ▶ Vary the ratio between mechanical and magnetic resonance frequencies via geometries and/or magnetic fields,
- ▶ Characterize magnetic response to electrostatically driven mechanical motion (Barnett effect),
- ▶ Determine if mechanically driven magnetization dynamics generate voltages as a result of spin motive forces, and
- ▶ Optimize devices with respect to actuation efficiency and electric voltage generation.

Laser Manipulation of Nuclear Spin Embedded in Noble-Gas Ice

2010-010-R1

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 disturbed 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, since it confines atoms (or molecules) indefinitely while only weakly disturbing the internal structure of the atom, so optical pumping remains effective. If successful, this novel approach would be an additional tool for controlling spins. In particular, we are using this technique for the testing of time-reversal symmetry, measurement of 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 2011 Results and Accomplishments

In FY 2010, we investigated the growth of neon, argon, and hydrogen matrices on a substrate cooled to 4 K in a cryostat, and performed laser spectroscopy of the embedded ytterbium (Yb) atom. Based on this experience, we chose to focus our effort on solid neon because of its favorable properties in crystal growth and its relatively weak perturbation on ytterbium.

In FY 2011, we carried out a detailed study of laser interaction with atoms embedded in solid neon and demonstrated the controlled transfer of the atomic population. We discovered that the $6s6p\ ^3P_0$ level of Yb atoms remains metastable with surprisingly long lifetimes, in a range of ten to hundreds of seconds. We demonstrated controlled transfer of the atomic population between the ground level and metastable level via optical excitation and spontaneous decay. An examination of the dynamics of this population transfer process revealed explicitly that the broadening of Yb transitions in solid neon is due to homogeneous mechanisms. In other words, a narrow bandwidth laser can simultaneously interact with all Yb atoms embedded in the solid neon matrix. This is a very promising finding with regard to the planned upcoming work of manipulating the spin population.

Proposed Work for FY 2012

In FY 2012, we will upgrade the apparatus for spin polarization and detection. Critical parts, including the polarization laser and SQUID (superconducting quantum interference device) detector, were acquired and are being characterized. The Yb polarization will be generated via transverse optical pumping and detected via a SQUID magnetometer. With suitably chosen excitation laser pulse parameters (intensity, duty cycle, frequency), a precessing Yb magnetization is expected, and it will result in an oscillating magnetic flux in an adjacent set of pickup coils. A “gradiometer” geometry is being used for the pickup coils in order to suppress the common-mode magnetic field noise present within the cryostat. In addition, we may also enclose the cryostat within MuMetal® shielding to further suppress magnetic noise external to the cryostat. The magnetic flux measured in the pickup coils will be insensitive to our bias field, since the bias field is oriented parallel to the surface of the loops. Transverse optical pumping allows us to take advantage of the lock-in detection technique, which further improves our sensitivity to the signal. At the Larmor frequency (1 kHz under a 1.3 Gauss field) at which we plan to operate, we expect a signal-to-noise ratio (S/N) of 20 for 10% polarization. Once polarization has been demonstrated, we will perform a series of systematic nuclear magnetic resonance (NMR) studies of Yb embedded in a solid matrix.

After the ensemble polarization has been demonstrated, we plan to investigate the possibility of addressing and detecting a single polarized ^{171}Yb atom in a solid matrix. Optical pumping will be performed by a focused and polarized laser beam

through the microscope lens. Spin will be manipulated via standard radiofrequency-based NMR techniques. The laser detection of an individual spin state is possible if the environmental coupling of the spin with the matrix is sufficiently weak.

Single Flux Quantum Magnetometer

2010-029-R1

Wai-Kwong Kwok, Dario Antonio, Daniel Lopez, and Valerii Vinokur

Project Description

The goal of this project is to use state-of-the-art nanofabrication techniques to develop a novel nanomechanical magnetometer (n-MM). 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. It will provide a unique tool to tackle some of the most fundamental basic science problems in condensed matter physics, in general areas such as glassy dynamics and in particular areas like the dynamics of single vortex pinning.

Mission Relevance

This revolutionary tool will be applied in the field of basic sciences to extract the physical behavior of a single vortex in a superconductor. The research is highly relevant to the DOE Office of Basic Energy Science’s (BES’s) grand challenge to predict and control both the superconductors’ electromagnetic behavior from their microscopic vortex and their pinning behavior in order to achieve significantly higher critical currents.

FY 2011 Results and Accomplishments

In FY 2010 we designed and fabricated a variety of unique proto-type nano-mechanical magnetometers pursuing state-of-the-art sensitivity and time response by incorporating novel approaches based on non-linear dynamics and implementing ‘tuning fork’ designs to mitigate clamping losses. For example, we designed a new type of magnetic field sensor, a first of its kind, that takes advantage of the geometrically induced nonlinearities in a clamped-clamped beam, does not incorporate magnetic materials, and whose fabrication is fully compatible with standard semiconductor processes. We further designed a workable low temperature electronics scheme for electrical drive and signal recovery.

In FY 2011, the design options for the n-MM were narrowed down to one: a torsional paddle. Figure 1(a) shows such a device. It consists of a central paddle to which the mesoscopic superconducting sample will be attached, two serpentine springs, and an external rectangular frame that is included

to minimize clamping losses. Figure 1(b) shows details of the central paddle where the driving and detection electrodes can be observed. We included these electrodes in order to drive the oscillator electrostatically and detect its motion capacitively. Because of the paddle's small area and the pads' parasitic capacitances, however, we also considered an alternative detection method involving an optical interferometric setup. In this setup, a laser beam is split in two and focused on two spots on the sample platform. The reflected beams are then joined again, and the fringes resulting from their interference are sensed with a photodetector. The laser beam spots can be focused on, for example, opposite sides of the paddle, or perhaps on the paddle and the substrate, giving a signal proportional to the height variations between the two points. The setup has other features (e.g., a low-frequency drift-compensating mechanism and automated stage control) that will ultimately allow us to detect the thermal motion of nano-MEMS (microelectromechanical system) torsional resonators with amplitudes of a few picometers. We used both capacitive and optical detection to characterize the torsional resonators, demonstrating their operability and obtaining information about the required driving signal levels and resonance frequencies. Figure 2 shows one of the resonance curves.

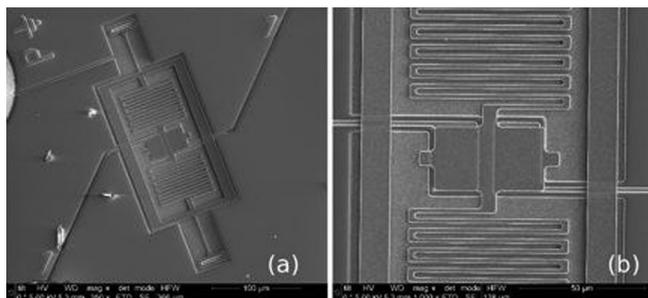


Figure 1. Scanning electron micrographs of the torsional oscillator.

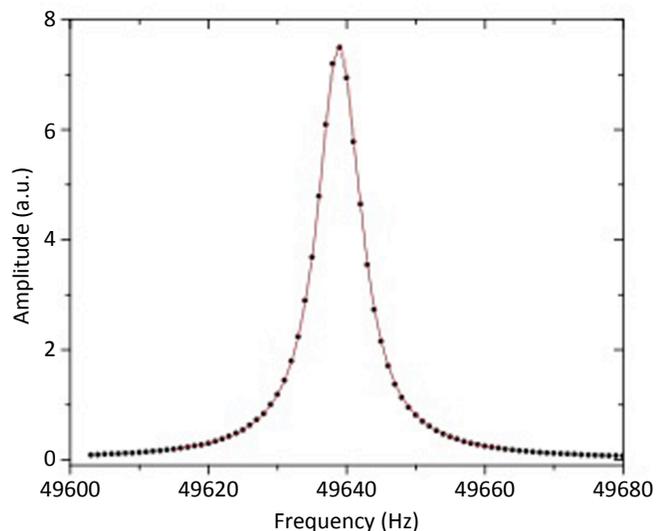


Figure 2. Resonance curve of the torsional micromechanical oscillator.

Proposed Work for FY 2012

We will test the low-temperature characteristics of this magnetometer by inserting it into a superconducting triple-axis vector magnet, measuring its response at various magnetic field angles, and measuring the magnetic response of a single flux quantum and an array of carefully arranged flux quanta in a high-temperature superconductor. If time allows, we will also test the nonlinear response of pinned vortices in the glassy state. The key focus, however, will be on detecting a single flux quantum with this magnetometer. We will test mesoscopic single crystals of the high-temperature superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-d}$ (YBCO), which will be prepared by using a focused ion beam. The first crystal will be an optimal doped ($T_c = 90$ K) crystal containing a series of carefully patterned holes, with the expectation that each hole will contribute a single flux quantum for the magnetometer to measure. The second sample will be an underdoped YBCO crystal shaped into a ring (single hole) to detect the variation of the flux quantum from $hc/2e$ to hc/e . The latter test, if successful, will answer a longstanding problem related to the pseudogap phase in high-temperature superconductors and could shed light on the mechanism of high-temperature superconductivity.

Emerging Technologies for Scientific Databases

2010-042-R1

David Malon, Jack Cranshaw, Peter van Gemmeren, and Robert B. Ross

Project Description

Although relational databases are used widely throughout the sciences, they are not often used to store the scientific data at any significant scale. There are many reasons: (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 the potential for parallel and distributed processing (even though many data are, in practice, read-only, with updates handled by additional data versions, not by changes to existing data); (4) insufficient versioning, inadequate provenance tracking, lack of infrastructure to ensure reproducibility; and (5) others. For many scientific applications and commercial data mining applications, the row-oriented storage of a conventional relational database leads to performance issues, even for analysis operations that are, in principle, feasible. In this project, we seek to address some of the obstacles to scalable scientific databases by contributing to the development of emerging technologies and initiatives (e.g., open-source SciDB project). So far, the focus has been on evaluating technologies that might contribute toward building

scalable scientific databases and, more recently, on extending them to support types of scientific data. Proton collision data from the Large Hadron Collider (LHC) in Geneva have served as the principal testbed for developing and evaluating scalable scientific database technologies.

Mission Relevance

This project is relevant to DOE's basic science mission. The basic and applied sciences integral to DOE's mission generate vast amounts of data from scientific instruments and simulations. Technologies that do more than support data storage and retrieval (i.e., that support the scientific analysis of the data in which DOE has invested and for which it has custody) are vital to its mission. DOE is a key contributor to international work on particle physics at the LHC, and technologies to support the analysis of these particle physics data are relevant to the effectiveness of its contribution. This project's importance is even broader; the tens of millions of gigabytes of data generated by LHC experiments are just an example of the need throughout DOE's science enterprise for scalable technologies to manage scientific data.

FY 2011 Results and Accomplishments

In FY 2010, our efforts focused on evaluating available and emerging technologies and creating a testbed of scientific data for such evaluations and prototyping. We then built a testbed at Argonne based on event-level metadata records of the earliest proton collisions at the LHC. We imported these data into the earliest releases of SciDB (arguably the first use of SciDB for real, not simulated, scientific data). We evaluated the early features of this nascent technology in fragile alpha releases and, more recently, in the first genuine SciDB release in June 2011.

In FY 2011, we grew the evaluation testbed at larger scales on the basis of current LHC data, and we augmented and diversified our basis for evaluation and exploration by adding very different data from large-scale cosmological simulations run at DOE supercomputing facilities. We delivered extensions to SciDB by using its fledgling support for user-defined types and operators in order to support scientific data types, including support for three- and four-dimensional vectors and geometric vector operations, as well as Lorentz vectors and related operators. These efforts were a foundation for outreach, the goal of which was to address scientific data challenges in other areas.

Proposed Work for FY 2012

In the next phase of this project, we will investigate support for *in situ* data (e.g., support for data in a manner that does not require they first be transformed or imported from a "native" format into a SciDB-specific one). We propose to evolve our Argonne Tandem Linac Accelerator System (ATLAS) data testbed into a service for physicists, not just developers,

and, as part of that effort, to implement a mechanism to routinely and automatically import current ATLAS data. We will seek support for an Argonne role in upgrades to the LHC data management infrastructure and in handling astrophysics and cosmology data.

Seminars

Malon, D. (2011). "I/O, Persistence, and Database Infrastructure: Emerging Technologies, Software Upgrade R&D, and Planning." ATLAS Upgrade Week, Oxford, UK, Mar. 28–Apr. 1, 2011.

Malon, D.M. (2010). "I/O and Persistence Infrastructure: Emerging Technologies and Software Upgrade R&D." ATLAS Software and Computing Workshop, Geneva, Switzerland, Jul. 15, 2010.

Vaniachine, A. (2010). "Emerging Database Technologies and What ATLAS Might/Should Do in this Arena." 2nd ATLAS Future Computing and Upgrade Workshop, Berkeley, CA, Sep. 17, 2010.

Low Mass Optical Readout for High-Data-Bandwidth Systems

2010-043-R1

David G. Underwood, Waruna S. Fernando, Daniel Lopez, and Robert W. Stanek

Project Description

In this project, we are using microelectromechanical 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 that electronic integrated circuits are built. One 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, onboard triggering, and trigger-clock distribution. We are solving technical issues, such as closed-loop control loops to steer the beams by means of multiple MEMS mirrors. We investigated 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 needed to steer the laser beams and the high-speed devices needed to extract data from the beams. Our focus now is more on optical modulators.

Mission Relevance

This project is relevant to DOE's scientific discovery and innovation mission being pursued at several DOE national user facilities and other locations that carry out DOE-sponsored research. Detectors at large particle colliders have limits as a result of (1) mass in the tracking system, (2) limited bandwidth in the readout, (3) failures of the vertical-cavity surface-emitting lasers (VCSELs) that transmit data, and (4) delays in transmitting data for fast triggering. Moreover, tracking detectors need internal triggering electronics, and a path between tracking layers is needed to provide data for calculations. The technology for steering beams in air by MEMS mirrors could play a big part in dealing with these issues, as could the development of radiation-hard, low-mass light modulators. Of particular relevance now is the upgrade of the Large Hadron Collider to high luminosity; for this, we need mechanisms for much-higher data transfer rates and to reduce the amount data transferred to higher-level triggers.

FY 2011 Results and Accomplishments

In FY 2010, we fabricated a lens system to transmit data with a 1,550-nm laser beam over about 1 m with no MEMS steering. We also fabricated a system to steer a red laser beam with no data to a moving target to an accuracy of a few microns by using analog feedback and a MEMS mirror. This had a limited range of motion. In addition, we fabricated a system of lenses and mirrors that was used to transmit data in a bi-directional way over 80 m.

In FY 2011, we fabricated a new device to test the lens system, MEMS mirrors, and feedback together (Figure 1). A pseudo random digital electrical signal was generated from a field-programmable gate array (FPGA) board at 1.25 Gb/s. That signal was used to modulate a 1,550-nm continuous-wave (CW) laser beam with an electro-optic modulator (EOM). The modulated light was then launched in air by using an aspheric lens. The beam was reflected from a MEMS mirror in the direction of the gradient index (GRIN) lens in the receiving setup, which had millimeter movement at up to 1 kHz to simulate vibration. The light captured by the lens was then fed to a 1,550-nm, small form-factor pluggable (SFP) transceiver to convert the optical signal back to an electrical one, which fed back to the FPGA board to be compared with the original signal to check the bit error ratio (BER). The motion of a moving target simulated both the mechanical vibration in an experiment and initial survey errors, which must be corrected by steering with feedback. We captured the beam to a target that was moved by +6 mm and -6 mm in both x and y directions with good optical power and a very low bit error rate. The low error rate over a large area demonstrated success. The target's speed of motion, measured as frequency, was also very important. We established a data beam in air over a distance of 1 m by using

a wavelength of 1,550 nm with an error rate of less than 10^{-15} (Figure 2).

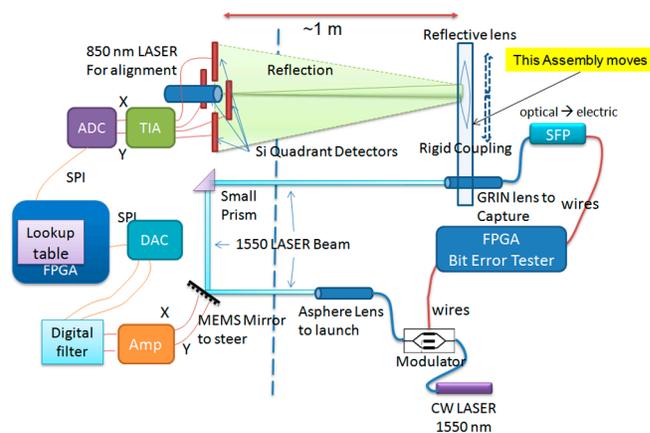


Figure 1. Setup used to test an analog control loop used to guide a MEMS mirror for steering a laser beam.

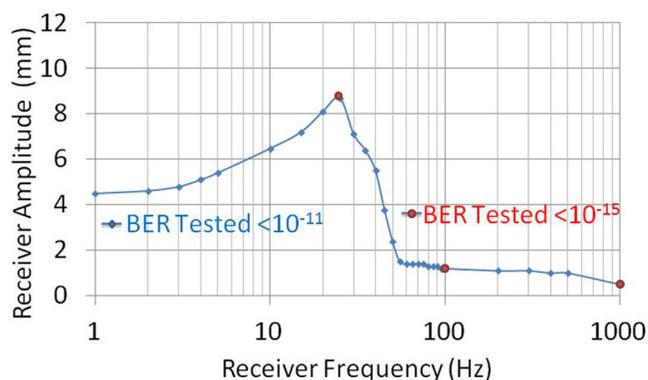


Figure 2. Tested working range of the moving receiver. In this plot, the BER was only tested for the points below the blue line; limitations in the setup restricted the movement of the receiver below the blue line. The receiver is moving in order to simulate both vibration and initial alignment errors.

A new crystalline silicon MEMS mirror designed at Argonne's Center for Nanoscale Materials (CNM) was received from a foundry and is being studied. The degrees of freedom are shown in Figure 3.

Proposed Work for FY 2012

We will emphasize studies of optical modulators, while continuing our beam steering and capture work. Rad-hard, low-mass modulators are essential for this project, and the HEP community needs a replacement for modulated lasers. We will combine our developments into a system that will steer the 1,550-nm data beam with multiple MEMS mirrors and incorporate the CNM-produced MEMS mirrors rather than the commercial devices now used. We will further develop the moving receiver for higher data rates, approaching 10 Gb/s. We will use commercial telescopes and micro-motor positioning devices to further develop the long-range data link.

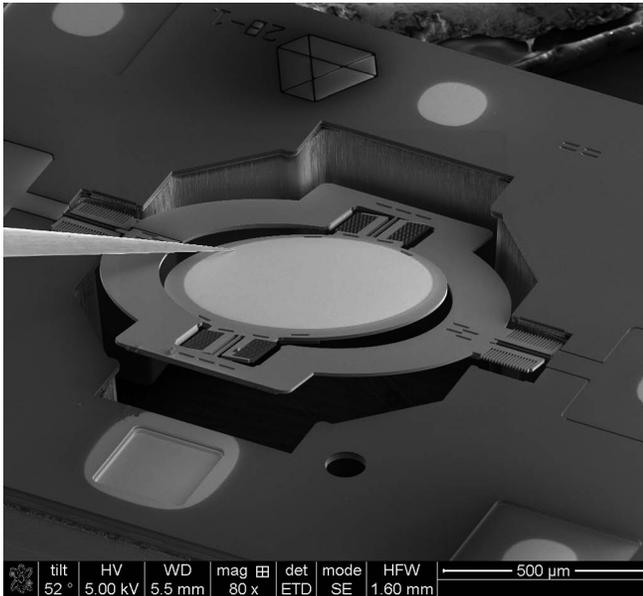


Figure 3. Scanning electron microscope (SEM) picture of a MEMS mirror designed at CNM, showing mechanical degrees of freedom.

Compact Solid-State Sources of Coherent THz Radiation

2010-049-R1

Ulrich Welp, Nachappa Gopalsami, Kenneth Gray, and Alexei 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, 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. A variety of technologies for generating THz waves have been developed, but 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 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 had previously demonstrated that the unique properties of highly anisotropic high-temperature superconductors, such as BSCCO (bismuth strontium calcium copper oxide), 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 $300 \times 60 \times 1 \mu\text{m}^3$. 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 properly designed BSCCO resonators can be increased to a level of about 1 mW. Recent modeling of our device structures indicates that such power levels are possible with 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, environmental quality and science. The rapidly emerging field of THz science and technology holds immense promise for diverse areas, including 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 2011 Results and Accomplishments

In previous work on single resonators, we discovered that heat dissipation inside the resonators seriously impedes the emission of strong THz-radiation. We minimized these effects by introducing high-thermal-conductivity mounting procedures. In FY 2011, we demonstrated that phased arrays of several BSCCO resonators allow for a significant increase of THz emission power. We obtained a BSCCO chip with an array of eight parallel resonators patterned on top (Figure 1a). The resonators are 300- μm -long, 60- μm -wide with a distance of 60 μm between them. They were contacted by using silver epoxy paint strips that led from the Au top contact (visible in Figure 1a) of the resonators to the wiring points and by using a common contact on the underlying BSCCO crystal (right side of Figure 1a). We can adjust the current bias of the individual resonators to synchronize several mesas.

Figure 1b shows the voltage dependence of the emission power of one, two, and three mesas when tuned to the same emission frequency. The increase of the output power with increasing mesa number is stronger than linear. We measured a radiation mesa power of $\sim 300 \mu\text{W}$ for three mesas versus $\sim 32 \mu\text{W}$ for one. This increase in power is close to the square of the number of emitting mesas (the behavior expected for coher-

ent phase-synchronized emitters). In contrast, for incoherent emitters, the power increases linearly with the number of emitters. Currently, the largest number of mesas that we were able to synchronize is three. It turns out that at further increase of the number of active mesas the heat dissipation in the present device becomes so large that emission ceases (see 2012 Proposed Work).

Figure 1c shows the corresponding THz spectra; one strong emission line near 0.51 THz originates from the three synchronized mesas.

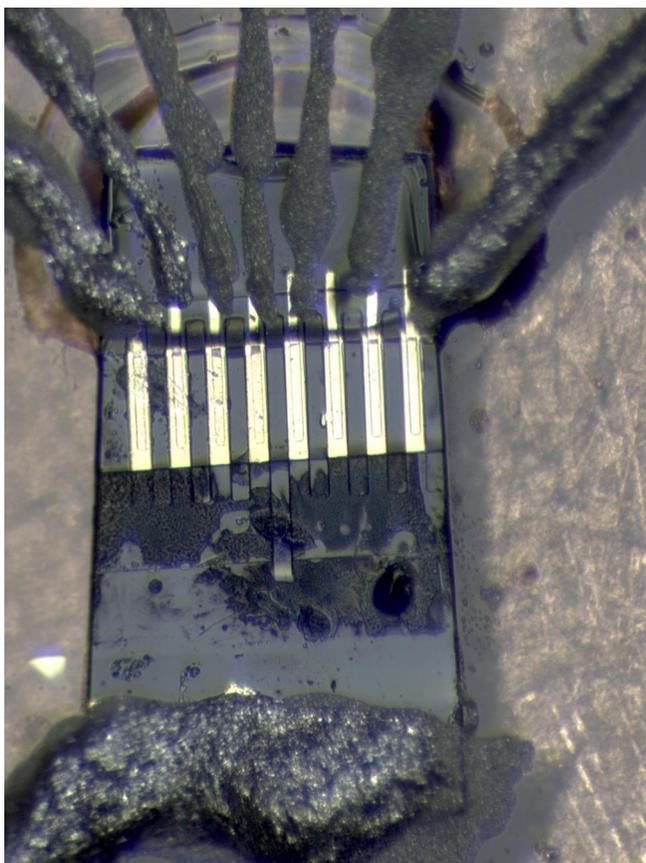


Figure 1a. BSCCO crystal (black) with an array of eight parallel mesas (the golden contacts). (Painted silver epoxy contacts lead to the wiring points. From the top down, the mesas are considered “a” through “h”; see Figures 1b and 1c).

Results so far demonstrate that the approach of increasing the emission power by synchronizing arrays of mesas is viable. The $\sim 300 \mu\text{W}$ emission power from junction stacks that we obtained is the highest that has yet been reported and is close to the goal of 1 mW.

Proposed Work for FY 2012

We will advance our fabrication procedures for producing phased arrays of BSCCO resonators. An important design feature will enable heat to be removed from the resonators efficiently. Self-heating in the BSCCO resonators limits the

number of synchronized resonators and thus the achievable emission power. Since the thermal conductivity of BSCCO in the direction perpendicular to the chip plane is very low, we will develop procedures for chips 3–5- μm thick (not the 30- μm thickness used now). Furthermore, current chips are glued with silver epoxy onto sapphire substrates and thus incur large thermal interface resistances. In improved devices we will use the same high-thermal-conductivity solder mounts developed before for single resonators.

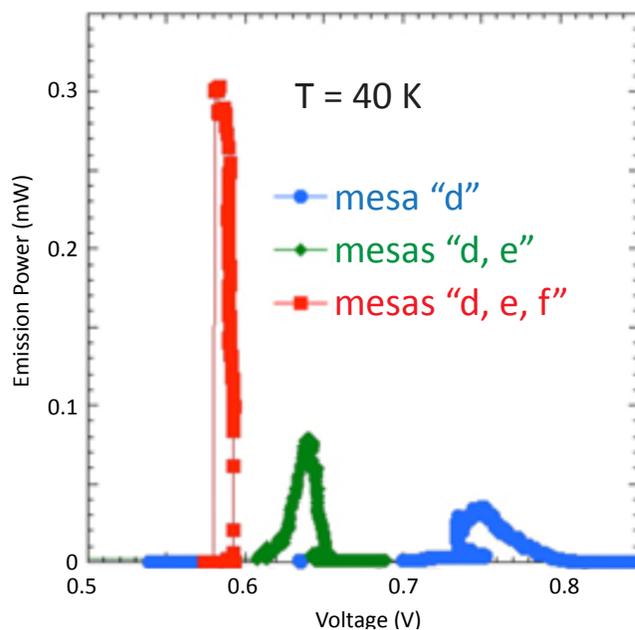


Figure 1b. Emission power of the BSCCO sample with one, two, and three active mesas plotted as a function of the voltage across mesa “d”.

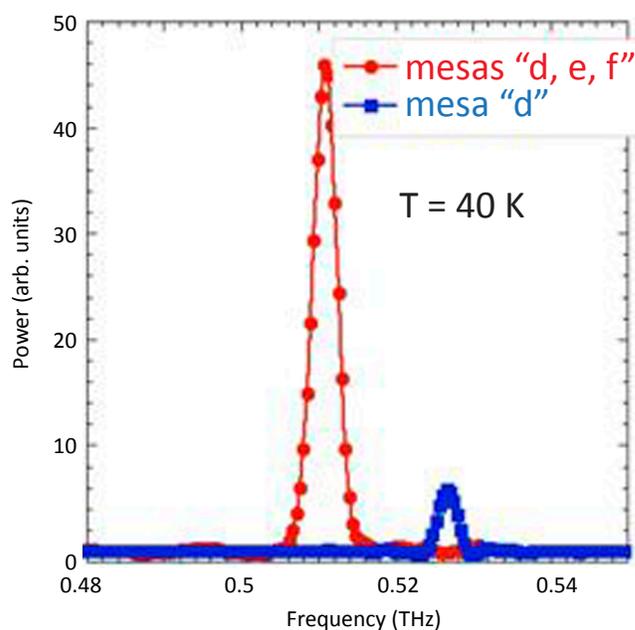


Figure 1c. THz spectra at 40 K of three synchronized mesas and an individual mesa.

Our estimates of emitted THz power have large uncertainties that result from using electronic rather than optical calibrations of the bolometer and uncertainties in estimates of the collection efficiency and of losses in the wave guiding. We will establish the metrology to accurately determine THz emission power.

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

2010-050-R1

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

Project Description

The project addresses the development of highly efficient and reproducible sensors for Raman spectroscopy of nanovolumes of biochemical analytes. This integrated experimental and theoretical project aims to fabricate and characterize precisely controlled model substrates, thus enabling a multistage amplification of the light fields for high-fidelity surface-enhanced Raman spectroscopy (SERS). The first stage of amplification results from controlled hot spots in self-assembled regular arrays of monodisperse spherical metal or metal/dielectric core/shell nanoparticles. A unique aspect of this project, designed to further increase the SERS enhancement, is a second stage of light amplification in which the particles are coupled to surface plasmon polaritons (SPPs) on a metal film substrate. By introducing periodic modulation of the metal film, intense standing waves will be formed through Bragg reflection, leading to an additional increase in the surface field and SERS enhancement. The grating effect due to the periodic structure will also enable the efficient directional emission of the Raman light at the Bragg angle.

Mission Relevance

This project will enhance the role of DOE in the competitive field of biosensor technologies as well as its ongoing biological and chemical research programs. In addition, the development of highly efficient light-enhancing substrates is relevant to catalytic and fuel cell projects. The plasmonic structures proposed in this project can be used to increase the efficiency of solid lighting devices and solar cells. The project results will also be of interest with regard to applications in diverse areas such as homeland security, analytical chemistry, medical diagnostics, forensic science, pharmaceuticals, and photonic microcircuitry technologies to name a few. Thus, the project is relevant to DOE's science and national security missions.

FY 2011 Results and Accomplishments

In the previous years we established protocols for the capillary self-assembly of extended regular arrays of large gold (Au) nanoparticles on dielectric and silver (Ag) covered substrates and experimentally and theoretically studied their optical properties.

In FY 2011, we manufactured multiscale SERS substrates composed of gold nanoparticles in grating templates on a silver mirror covered with thin dielectric spacer. We confirmed sizable light amplification resulting from the tuned optical resonances of separate components of the structure by measuring the Raman signal of benzenethiol (BT) and rhodamine 6G molecules. We experimentally measured the electromagnetic SERS enhancement factor of $\sim 3 \times 10^{10}$ of the structure when compared to the signal on the neat BT sample (Figure 1). We demonstrated the high efficiency and high fidelity of the structure by monitoring two-dimensional Raman raster scans over ordered nanoparticle arrays.

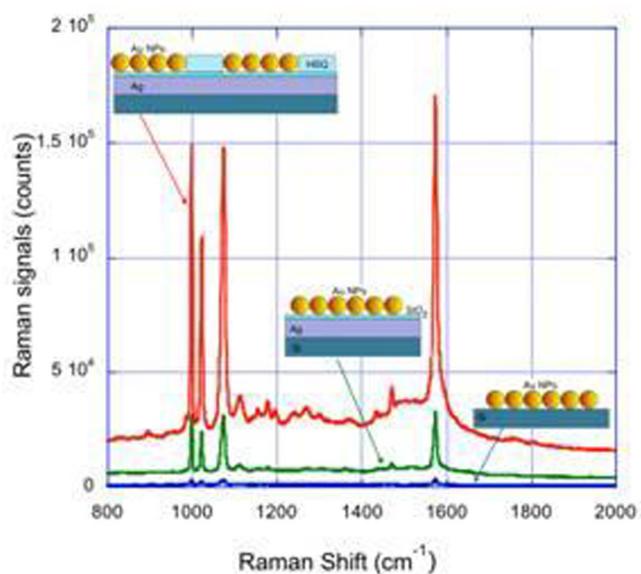


Figure 1. Raman signals of BT molecules on 80-nm Au NP arrays on Si (blue line), on a metal Ag mirror with 20-nm SiO_2 spacer (green line), and on NPs assembled in gratings on Ag film. A comparison with neat BT yields an enhancement factor of 2.2×10^8 for NPs on Si and of 1.5×10^{10} for NPs in gratings. When one accounts for the fact that there are two times fewer NPs in gratings than in continuous NP arrays, the enhancement factor is $\sim 3 \times 10^{10}$.

Proposed Work for FY 2012

We plan to improve the process of the templated self-assembly of Au nanoparticles in dielectric gratings. We will demonstrate the directional response of the design for angular collection of the Raman signal. Finally, we will test the applications of the structure for solid-state lighting and photovoltaic applications.

Tactile MEMS-Based Sensor

2010-063-R1

Young Soo Park, Nachappa Gopalsami, and Daniel Lopez

Project Description

The objective of this project is to develop a high-fidelity, tactile microsensor that is capable of replicating the sensitivity of a human finger tip. Such a microsensor will have significant impact 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), which has recently emerged in numerous everyday life applications. Most innovations in haptics have focused on the display (rendering cutaneous stimulus), and relatively few have focused on the sensors. The human sense of touch is a complex, multimodal perception, and this sensor will focus on the most delicate tactile sensing, which requires a highly sensitive, microscale sensor array. Based on microelectromechanical systems (MEMS) technology, this microsensor will have a spatial resolution that is an order-of-magnitude higher than and a sensitivity that is equivalent to those of existing, state-of-the-art sensors.

Mission Relevance

This project is relevant to DOE's missions associated with the nuclear industry, environmental management, and national security, all of which could benefit from telerobotic manipulations that incorporate a higher level of dexterity. This work also represents a significant innovation in emerging haptics technology, which has ubiquitous applications in our everyday lives and thus will have a significant impact on industry in the future.

FY 2011 Results and Accomplishments

We developed a novel tactile microsensor element based on MEMS technology by using gold as the piezoresistive element and a photoresistive epoxy, SU-8, as a stretchable substrate material. The developed sensor element exhibits unique characteristics that enable the microsensor to replicate and exceed the sense of touch of the human fingertip. Being a microscale device, it is suitable for high-resolution spatial array sensing. Also, its unique multi-element design allows it to sense a wide stiffness range. In addition, because of its flexible substrate structure, it can be retrofitted onto irregularly shaped devices as a skin sensor. This research started in FY 2010 where the focus was devoted to conceptual design proof-of-concept fabrication of prototype sensors. Subsequently in FY 2011, efforts were devoted to its testing and improvement. We now have an optimized fabrication process that results in a stable structure with a uniform resistive line thickness of 5 μm . Sensor nodes with internode distances as small as 200 μm were fabricated. In a silicon substrate wafer, more than 100 tactile

sensors of various piezoresistor configurations and diaphragm sizes were batch produced. Tests were performed to evaluate the sensor's properties (Figure 1) where the sensor membrane is pushed with a force sensing probe. Strain is measured by the change in resistance, $\Delta R/R$, as a function of membrane deflection. Figure 2 summarizes the test results for various membrane widths shown as different colors. The results showed highly accurate (linearity and sensitivity) measurements.

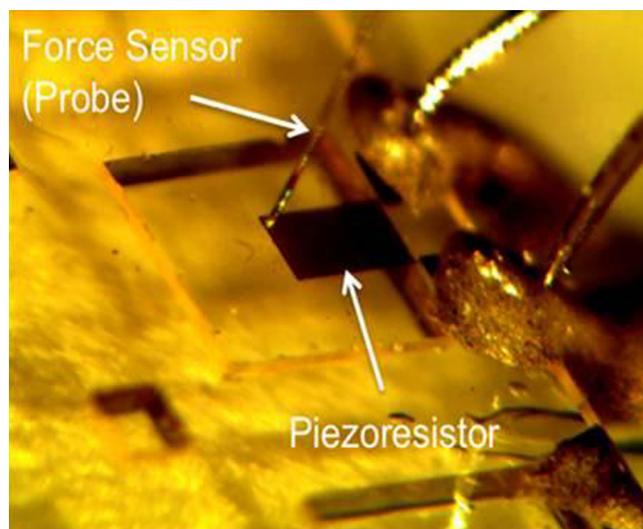


Figure 1. Tactile microsensor in characteristic test.

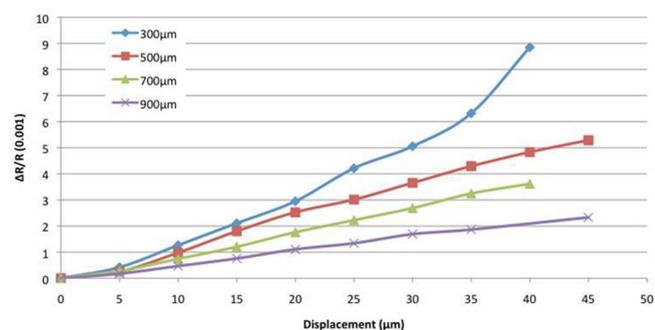


Figure 2. Measurement of change in resistance as a function of diaphragm deflection for various membrane widths.

Proposed Work for FY 2012

The project will focus on further improvements to the sensor so it can be demonstrated in dexterous teleoperation-robotic surgery. The first task will be to take *in vitro* measurements of the softness of various biological tissues. We will then modify the sensor to match the tissue stiffnesses. A subsequent task will involve packaging an array of microtactile detectors that can discern a multidimensional distribution of forces with high spatial resolution and sensitivity. Finally, the sensor will be retrofitted onto a DaVinci surgical robot system and tested for its effectiveness in providing tactile feedback.

Polymerized Ionic Liquid Nanostructures for Biocatalytic Fuel Production

2010-073-R1

Millicent A. Firestone, Lei Cheng, and Larry Curtiss

Project Description

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

Mission Relevance

This project is relevant to DOE's science and energy missions. The world's energy is now overwhelmingly supplied by fossil fuels. The depletion of global petroleum reserves and the growing concern over the environment (e.g., generation of greenhouse gases) have led to an increased interest in and need for alternative renewable energy sources. The production of biofuels, which are made by converting plant or animal by-products (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 (2) low-cost means for producing bioderived fuels as a renewable energy source.

FY 2011 Results and Accomplishments

Using the synthetic chemistry that we developed in our first project year, we prepared an interpenetrating polymer network (IPN) in FY 2011, which we evaluated as a solid support for heterogeneous biocatalysis. First we examined a model enzyme, horse heart cytochrome *c*, since it is a well-characterized soluble protein that contains an optical reporter group (heme) that facilitates the assessment of structural and functional integrity by spectroscopy. Global protein secondary structure was monitored by vibrational spectroscopy after polymer entrapment (Figure 1). We observed amide I (C=O stretching) and amide II (N-H and C-N stretching) modes for polymer-encapsulated protein at 1,653 and 1548 cm^{-1} , respectively. The modes were shifted relative to those determined for native cytochrome *c* in aqueous buffered solutions. The minor positional shifting of the amide I mode ($\Delta 3 \text{ cm}^{-1}$ to higher wave numbers) suggests that only a small perturbation on protein α -helical structure (i.e., a slight expansion in the globin) occurred during encapsulation. A more significant shift ($\Delta 6 \text{ cm}^{-1}$ to higher wave numbers) was observed for the amide II mode; this shift in position indicated a loss of hydrogen-bonded amide nitrogen. The disruption in protein intra-

molecular hydrogen bonding arose from competition with the (stronger) hydrogen bonding with the IPN. Enhanced protein-polymer hydrogen bonding promotes tight integration of the enzyme within the polymer. Most importantly, however, the tight integration did not significantly alter the protein secondary structure.

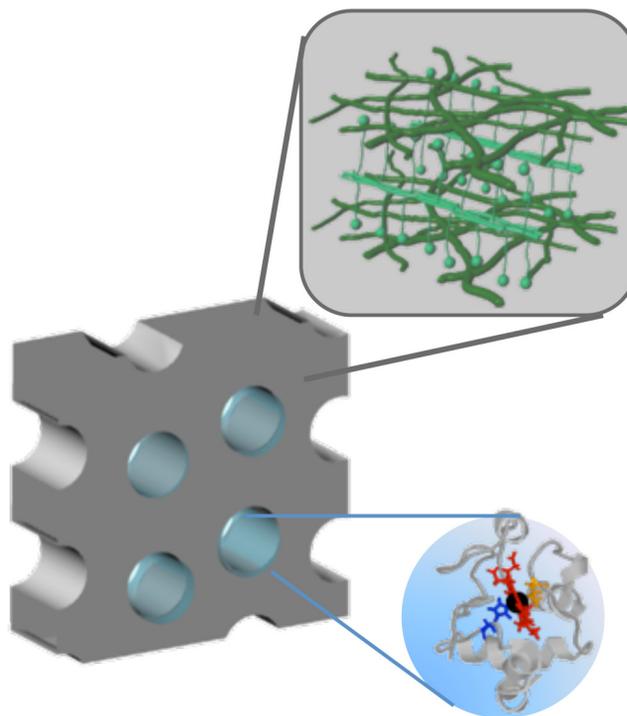


Figure 1. Schematic of cytochrome *c* encapsulated within the water-rich regions of a perforated lamellar-structured interpenetrating polymer network.

Optical spectroscopy provided complementary information on cytochrome *c* integrity, by selectively probing the heme prosthetic group after its incorporation in the IPN. Monitoring both the Soret band's and Q band's position and intensity yielded information on ligand binding, the oxidation state of iron, and the conformation of the polypeptide in the vicinity of the porphyrin group. The visible spectrum recorded on the IPN-encapsulated cytochrome *c* displayed a redshifted Soret band (409 nm) and a split Q band, possessing two distinct spectral features positioned at 525 and 548 nm. The charge transfer band at 695 nm was lost, and a weak band at 653 nm emerged. Those spectral changes suggest that there was partial conversion of the protein from the ferric to ferrous (reduced) state. The partial formation of the ferrous state is attributed to the photoreduction of the protein during the second polymerization step required to form the IPN; that is, the brief (less than 10-minute) photoirradiation with 350 nm ultraviolet light caused detectable changes in the protein's oxidation state. This result motivated the need to further refine the synthetic procedure used to prepare the supporting polymer matrix.

We also examined cytochrome *c*'s integrity after storage under various solvent conditions, including storage in an aqueous buffered solution (10 mM potassium phosphate, 7.4 pH), ethanol, and air (dehydrated state), all at 4°C. Storage (for 48 hours) in ethanol unexpectedly resulted in no further detectable changes in protein integrity and was thus deemed the best storage medium. (Cytochrome *c* unprotected by the polymer undergoes complete denaturation in ethanol within hours.) Ethanol is an important solvent for conducting bio/organotransformations with sufficient rate and yield. Conversely, storage in air resulted in protein denaturation (loss of the native heme-pocket structure), as evidenced by a blue-shifted Soret band. Theoretical studies on the heme-coordination environment were performed to gain more insight into the observed spectral changes. Specifically, minor perturbations in axial bond length, Met80 (S-Fe) and His18 (N-Fe) were found to generate changes in the Soret band position. The results of these studies showed that bond elongation (+0.4 Å) of either axial ligand can lead to a (Δ 3–5-nm) blue shift in the Soret band position. Axial ligand bond elongation would be expected to occur with globin (polypeptide chain) expansion. Loss of secondary structure, such as globin expansion, might occur under conditions in which there are strong protein surface-polymer interactions. The environment created in the contracted (non-solvent-swollen) polymer matrix would likely favor strong interactions with the protein that cause loss of structure. These studies have yielded insights on how to engineer the polymer matrix so as to improve and control protein structure and function.

Proposed Work for FY 2012

In FY 2012, we will focus on introducing a more benign visible initiator for the second polymerization step. This will be important for preventing the partial reduction of the enzyme during encapsulation and for forming the heterogeneous biocatalyst. Successful refinement of the synthetic procedure for forming the IPN will result in a supporting matrix applicable for encapsulating a wide variety of enzymes. We will finish the integration and evaluation of lipase, a transesterification biocatalyst. Results from these studies will lay the groundwork for future research exploring cascade reactions and membrane-soluble catalysts.

Layered Oxides for Thermoelectric Energy Conversion

2010-129-R1

Kenneth Gray, Qing'An Li, John F. Mitchell, Boyd Veal, and Hong Zheng

Project Description

A search for improved thermoelectric (TE) materials is merited because this all-solid-state technology is inherently reliable. Predicted ways to improve the thermopower (voltage output per degree of temperature difference) include sharp features in the density of electrons versus their energy and low-dimensionality (e.g., layered materials). We choose materials that exhibit these features and optimize their conversion efficiency through directed synthesis, using feedback from measurements that reflect the desire for a small ratio of thermal to electrical conductivity.

Mission Relevance

This project is relevant to DOE's missions in science, energy, and the environment. The benefits of finding economically viable materials that exhibit high thermoelectric conversion efficiency include utilization of waste heat from vehicle exhaust emission and as a mechanically reliable alternative to steam engines for the conversion of heat from solar concentrators. Success in either application could positively affect our energy security and environmental quality. Other relevant DOE programs include the Vehicle Technologies Programs in EERE and various EFRCs (Energy Frontier Research Centers) in the DOE Office of Science, such as (1) the Center on Materials for Energy Efficiency Applications, U.C. Santa Barbara; (2) the Center for Inverse Design, NREL; (3) the Center for Excitonics, MIT; and (4) the Solid-State Solar-Thermal Energy Conversion Center, MIT.

FY 2011 Results and Accomplishments

Prior to FY 2011, we found many layered oxides that exhibit excellent thermopower ($\text{YBa}_2\text{Cu}_3\text{O}_x$ and $\text{RBaCo}_2\text{O}_{5+x}$, for R=Gd or Nd at various oxygen doping levels, x). However, their figures of merit were invariably limited by very low electrical conductivity, likely due to the formation of a gap in available electron states. In FY 2011, we searched for alternatives, and Figure 1 shows $\text{Ce}_2\text{PdGa}_{12}$, a layered intermetallic that we discovered, which exhibits a sharp feature in its electron density, thus displaying both features that were predicted to improve the thermopower. Our data showed a very promising figure of merit of 0.44 at room temperature. To obtain this value, we measured the electrical conductivity, thermopower and thermal conductivity, in the latter case using phase-pure polycrystalline $\text{Ce}_2\text{PdGa}_{12}$ from room temperature up to 400°C. We identified numerous second-phase impurities in $\text{Ce}_2\text{PdGa}_{12}$,

which may affect the thermal conductivity, when it is grown from a Ga-rich flux. This materials discovery of $\text{Ce}_2\text{PdGa}_{12}$ opens a whole new class of potential TE compounds.

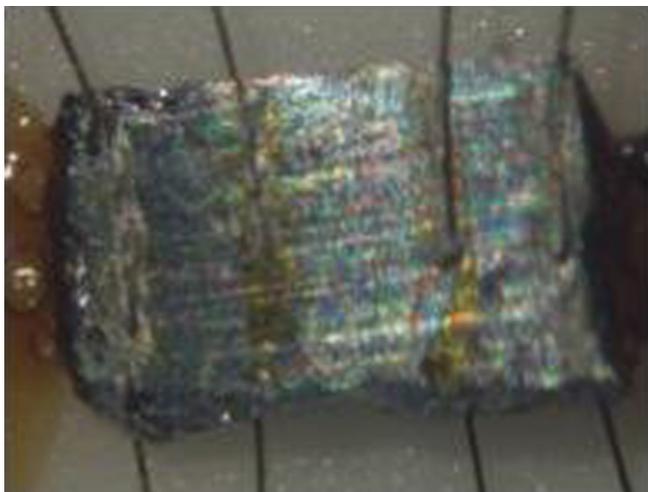


Figure 1. This crystal of $\text{Ce}_2\text{PdGa}_{12}$, grown from a Ga-rich flux, has second-phase inclusions that may beneficially reduce the thermal conductivity, compared to the pure phase, without adversely affecting the thermopower.

Proposed Work for FY 2012

Our first milestone will be the identification of substitutions in the $\text{Ce}_2\text{PdGa}_{12}$ structure type, to eliminate the expensive palladium (Pd). This synthesis will benefit from rapid feedback of the measured TE properties. Substituting nickel (Ni) for Pd will keep us in the same column of the periodic table, but it will be interesting to explore whether cobalt (Co) or copper (Cu) substitutions could optimize the power factor by better aligning the sharp feature in the electron density with the Fermi level. Our second milestone will be reduction of the relatively high thermal conductivity we found in phase-pure $\text{Ce}_2\text{PdGa}_{12}$. It has been well demonstrated that nano-scale impurity phases can disrupt the thermal conductivity while having much less effect on the power factor. The Ce-Pd-Ga system exhibits numerous phases neighboring the $\text{Ce}_2\text{PdGa}_{12}$ phase, including a pseudo-cubic CePd_3Ga_8 . Our Ga-flux growth procedure led to fine-scale Ga inclusions and other second phases within the “single crystal,” and these could dramatically reduce the thermal conductivity compared to our phase-pure samples. We will exploit the optimization of these second phases through modified synthesis conditions.

Novel Bifunctional Low-Temperature Catalysts at the Subnanometer Scale

2010-137-R1

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

Project Description

This highly interdisciplinary project addresses a roadblock to the next generation of catalytic materials for energy applications through atomic-precision design of entirely new classes of materials at the subnanometer scale and fundamental understanding of how these materials work. The research is aimed at the discovery of new catalysts that can perform more than one catalytic reaction on one site and thus save considerable energy. It involves closely coupled theoretical predictions/catalyst screening and experimental catalytic testing and understanding.

Mission Relevance

This project is relevant to DOE’s missions in science and energy. Optimization of heterogeneous catalysts at the subnanometer scale toward more environmentally friendly and efficient catalysts for chemical and fuel production represents 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 21st century is to understand how to design catalyst structures to control catalytic activity and selectivity.” This challenge is a central topic of this work. 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 resources that are available today but not yet used, as well as the development of future alternative fuels, will further increase the importance of catalysis research within DOE.

FY 2011 Results and Accomplishments

One of the challenges that must be overcome for the development of bifunctional catalysts is the temperature difference required for oxidative dehydrogenation (ODH) on Pt clusters (~400°C) compared to ethylene oxidation (EO) on Ag clusters (~100°C). During the past year, the focus of our experimental/theoretical work has been the properties of cobalt clusters, which we have found are capable of reducing the temperature requirement. In FY 2010, we found that cobalt clusters were active for C-H bond activation as predicted by theory, and that they had a much lower temperature for ODH than platinum clusters. The lower-temperature C-H activation is a key requirement for a bifunctional catalyst for ODH-EO catalysis, so during FY 2011 we focused on understanding this unique low-temperature ODH property of cobalt clusters and how to

incorporate it into a catalyst that adds oxygen to an alkene as well. The experimental and theoretical studies were largely done on cyclohexane. These studies showed that the low-temperature performance of the clusters is due to their suboxide nature (i.e., the Co:O ratio is greater than 1). This is a very significant discovery and will be used in our third year to develop the bifunctional catalysts.

During the past year, we performed *in situ* x-ray studies of the stability, composition, and reactivity of oxidized sub-nm cobalt clusters of various sizes supported on alumina and ultra nanocrystalline diamond (UNCD) supports. The results reveal partly oxidized clusters. To understand the catalytic mechanism of the partial oxidation of cyclohexane by alumina-supported cobalt subnanometer clusters, we carried out a detailed density functional study. We modeled the system by using an alumina surface with a Co₄ catalyst, as shown in Figure 1. Calculations reveal that molecular oxygen will dissociate on the cluster without a barrier, creating a Co₄O₂ cobalt suboxide on the surface. The calculations show that there are three key steps in the reaction profile of cyclohexane dehydrogenation. The first is the carbon-hydrogen bond activations that form cyclohexene. The second is cyclohexene desorption. The final step is the formation of water. After water is formed, the catalyst is then regenerated by molecular oxygen dissociation.

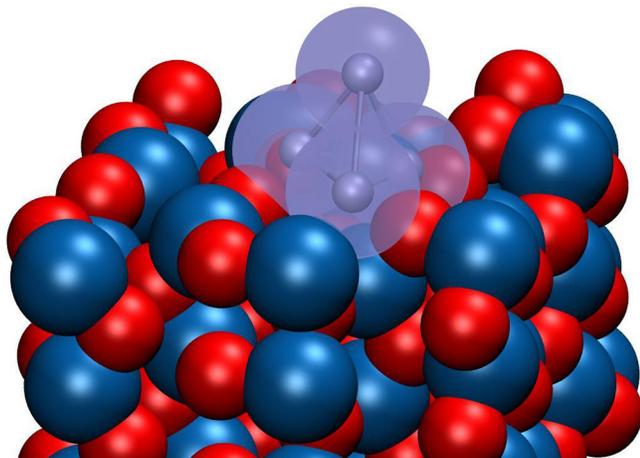
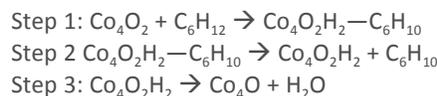


Figure 1. A schematic of Co₄ catalyst on an alumina surface prior to reaction with atmospheric oxygen.

Proposed Work for FY 2012

We will focus on bimetallic suboxide clusters and specifically Co₄O_y, Ag_y clusters, as we believe that the addition of Ag will enhance the oxygen addition capabilities found for the Co₄O_y clusters, and the Co₄O_y will provide the low temperature needed. We will use theory to predict the optimal bimetallic

ratios in these clusters. In addition, we are currently carrying out experimental studies of propane on the CoO clusters for comparison with the cyclohexane results, as we are interested in bifunctional catalysts for a range of alkanes. An important finding of the experimental studies is that the subnanometer cobalt oxide catalysts were observed to have some bifunctional catalytic activity in our experiments, where cyclohexanone is present as a minor product. The mechanism for the reaction is presently unknown but will be studied in detail during the next phase of the project. We will explore the complete catalytic pathway that produces cyclohexanone.

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

2010-138-R1

Zahirul Islam, Ritesh K. Das, and Jonathan C. Lang

Project Description

The primary objective of this project is to develop a practical continuous-field magnet based on type-II superconductors (SCs) to mitigate two long-standing problems in scattering studies in applied magnetic fields: (1) limited optical access and (2) the impossibility of applying magnetic fields parallel to the x-ray (neutron) momentum transfer. Researchers often need to measure order parameters (OPs) 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). With conventional split-pair and solenoid magnet geometries, these measurements are in general impossible to carry out. To overcome these deficiencies, a tiny single-crystal sample is placed close to the surface of a melt-textured bulk SC. 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 diffraction experiments, such as x-ray resonant exchange scattering (XRES) with unrestricted optical access.

Mission Relevance

This project is relevant to DOE's mission in science. The study of materials under extreme conditions (e.g., very high magnetic fields) has been identified as one of the long-term missions of DOE-BES. The DOE funds many programs to explore the properties of energy-related functional materials, SCs, 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 would usher in new opportunities for studying field-induced properties in these materials.

FY 2011 Results and Accomplishments

In FY 2010, we developed the specifications for YBCO-based TFMs and designed a portable magnetization scheme utilizing a cryogen-free SC magnet. We characterized the TFMs to determine the degree of uniformity of their magnetization at liquid nitrogen temperature. Primary accomplishments in FY 2011 include (1) the implementation of a large TFM to reach fields above 3 T and (2) a detailed XRES study of meta-magnetic phases (MPs) in a rare-earth compound.

We installed a 20-mm-diameter, 8-mm-thick TFM. Unlike our initial smaller (8 mm × 8 mm × 4 mm) TFM, it can trap fields above 3 T at a much higher temperature than 4.5 K. Figure 1 shows magnetization data for the TFM at ~32 K as a function of time. Fields above 3 T (30 K) can be used for measurements after magnetizing the TFM, which can be cooled on the first stage of our cryostat without interfering with the sample temperature. Note that the field of the top plateau (~4.6 T) in Figure 1 is the maximum applied field; with external field ramped down to zero, the initial trapped field in TFM is ~4 T, which decays quickly to a more stable field of 3.2–3.4 T.

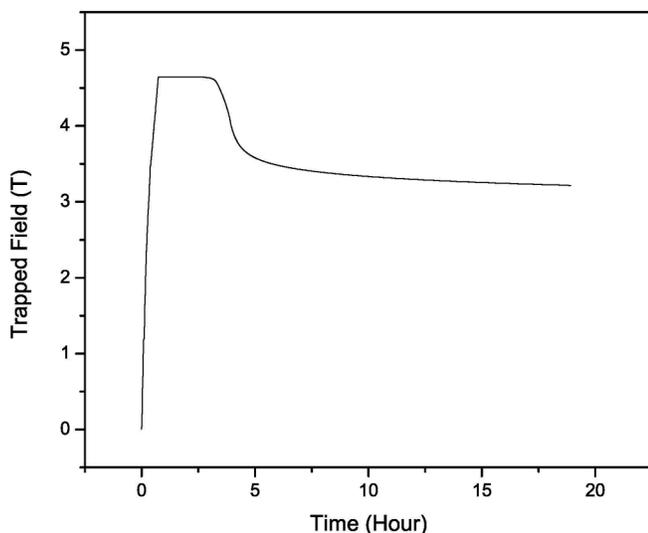


Figure 1. A TFM was magnetized by using an external magnetic field of ~4.6 T. After the field was removed ~3.5 hours later, a field of ~3.6 T was initially trapped and remained practically unchanged during the course of the measurements.

To demonstrate the potential of the instrument, we performed detailed XRES studies on TbNi₂Ge₂ (Tb122). It is a tetragonal system with a strong uniaxial (c axis) anisotropy, which undergoes two antiferromagnetic (AFM) transitions at low temperatures with Tb moments locked along the c axis [S.L. Bud'ko *et al.*, *J. Magn. Magn. Mater.* **205**, 53 (1999)]. The low-temperature ordered phase is a stack of ferromagnetic (FM, denoted by +/- for moments along +/- c axis) and AFM (denoted by 0)

planes. The stacking is determined by $\tau_1=(0, 0, 3/4)$, while the AFM planes are described by $\tau_2=(\frac{1}{2}, \frac{1}{2}, 0)$ wave vectors, with an ordered sequence of “+-+0-+” for the magnetic unit cell [Z. Islam *et al.*, *Phys. Rev. B* **58**, 8522 (1998)]. With a magnetic field (<5 T) applied along the c axis, a series of MP transitions are observed [Bud'ko *et al.*, *J. Magn. Magn. Mater.* **205**, 53 (1999)]. By placing the Tb122 sample at a known distance from the TFM, these MPs have been investigated with B parallel to the c axis. Figure 2 shows the behavior of the magnetic peaks at various fields up to 1.85 T. The peak at 7.0 (τ_2) arises from AFM planes, while that at 7.5 ($2\tau_1+\tau_2$) originates from an interference between FM and AFM planes of the magnetic unit cell. On entering the first MP at 1.625 T, the former satellite starts to decrease in intensity while the latter splits. The splitting occurs as τ_1 becomes incommensurate (not shown) in this phase, highlighting the delicate interplay between FM and AFM planes. Structural models of these phases are currently being worked out.

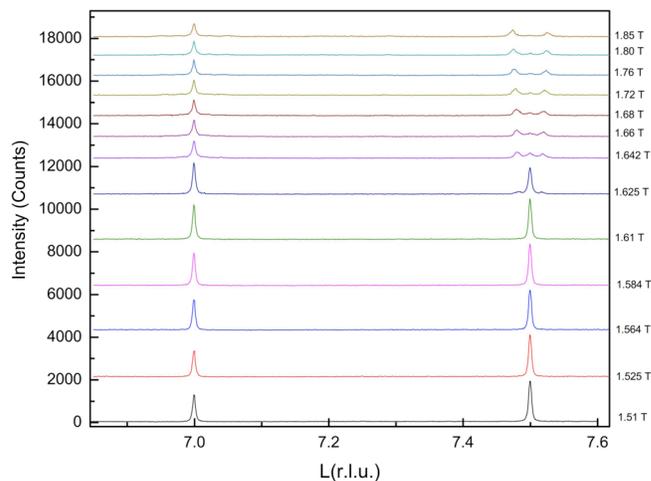


Figure 2. Magnetic scattering intensity along $[\frac{1}{2}, \frac{1}{2}, L]$ line in the reciprocal space (in r.l.u.) showing the behavior of magnetic peaks as a function of magnetic field. Data for different fields are shown in different colors and are offset vertically for clarity.

Proposed Work for FY 2012

In FY 2012, we will work to (1) install a TFM with stronger flux-pinning centers so that fields at or above 5 T can be trapped, (2) increase the range of *in-situ* sample translation so that the full range of the magnetic fields can be accessed, (3) improve thermal links to reach sample temperatures below 4.5 K, and (4) perform XRES studies to further develop the methodology of using TFM.

Study of Superconducting Films by Atomic Layer Deposition

2010-156-R1

Thomas Proslie, Jeffrey W. Elam, Andreas Glatz, Jeffrey Klug, Michael Pellin, and Valerii Vinokur

Project Description

The ability to grow and synthesize thin, superconducting films on complex surfaces is a major challenge, but offers benefits in many applications, including the following:

- ▶ *Superconducting radio frequency (SRF) cavities.* It is believed that a multilayer-structure superconductor/insulator deposited on the inside wall of the cavity will increase performance by a factor of two.
- ▶ *Superconducting wires for magnet applications.* Depositing a superconducting film or multilayers onto an inexpensive copper (Cu) “frame” of pre-bent wires incorporated into the final magnet shape would significantly reduce production costs and increase the critical current in a high-magnetic-field environment.
- ▶ *Superconducting bolometers for particle detectors.* We have shown that the critical temperature (T_c) of films on complex surfaces can be tuned by controlling (down to the atomic level) both the chemical composition and thickness of the film. Such tuning can pave the way for new three-dimensional bolometer structures in which more than one T_c is present (i.e., different alloys in a multilayer structure) and therefore more than one type of detection threshold can be designed.
- ▶ *Fundamental studies of coulomb interactions in quasi-two-dimensional (2D) superconducting films.* New phenomena, such as super insulating transition at ultra-low temperatures, have emerged in ultra-thin superconducting films.

In this project, we are investigating the limits of the superconducting properties of various alloys in ultra-thin films. The goal is to demonstrate that phase transition is a general property that always emerges in the thin-film limit.

Mission Relevance

This project addresses one element of DOE’s mission in basic energy science: deterministic design and discovery of new materials and chemical assemblies with novel structures, functions, and properties. The SRF cavities multilayer technique that we will develop addresses a key component of the high-energy physics accelerator mission of expanding the intensity and energy frontier.

FY 2011 Accomplishments and Results

By using atomic layer deposition (ALD), we successfully grew, for the first time, a series of alloy nitrides (NbN, NbTiN, MoN, MoNbN), silicides (NbSi), and, recently, selenides and tellurides (FeSeTe, K(FeSe)₂). NbTi_{0.2}N was found to have a T_c of 14 K, the highest ever obtained by ALD. We also investigated and successfully grew a multilayer structure composed of alternating stack of insulator (AlN: 15-nm thick) and superconductor (NbTiN: 100-nm thick) on any desired substrates: from niobium films to copper wires. We are now in the process of synthesizing this multilayer on superconducting niobium cavities and copper coils. Niobium silicide: NbSi was never grown before by any deposition technique and has a T_c of 3.1 K; we are building bolometers made of NbSi by ALD. The transport properties of NbSi films with various thicknesses from 45 nm to 5 nm were measured down to 0.3 K under an external magnetic field of up to 5 T; results to date show a metal-to-insulator transition upon reducing the film thickness, resulting from quantum corrections appearing in quasi two-dimensional films. Pnictides superconducting alloys are of interest because of their extremely high H_{c2}; we successfully grew FeSe and FeTe films by using a new ALD chemistry. Work on these compounds is ongoing. The record T_c obtained for these thin films grown by means of ALD provides a strong case for pursuing the original synthesis approach with more complex alloys such as high-T_c superconductors: BaKBiO (Barium Potassium Bismuth oxide), BiSrCaCuO (Bismuth Strontium Calcium Copper Oxide), YBaCuO. (Yttrium Barium Copper Oxide).

Future work will be supported under the early career award Dr. Proslie obtained in 2011 for a period of 5 years. In FY 2012, we expect to demonstrate a significant improvement in SRF cavity performance, as well as an enhanced critical current in superconducting magnets. On the basis of the result of our work thus far, other organizations such as DOE-HEP, Fermilab, Jefferson Lab, and Lawrence Berkeley National Laboratory have expressed interest in the project.

We will also pursue the fundamental investigation of the thin superconducting films in the quasi 2-D regime and seek new superconducting alloys and geometries that could present significant improvement over existing devices. In particular, the superconducting alloy MgB₂ offers potential in a wide range of applications.

This research resulted in the following invention/patent:

Thomas Proslie, Jeffrey Elam, Jeffrey Klug, Michael J. Pellin “Atomic Layer Deposition of Superconducting Niobium Silicide” invention report submitted April 2010. [ANL-IN-09-049] Application # 051583-0478, submitted Feb. 25, 2011.

Converting CO₂ to Fuel through Functionalized MOFs

2010-158-R1

Di-Jia Liu, Liaohai Chen, Shengqian Ma, and Dan Zhao

Project Description

Concern about global climate change has drawn unprecedented public attention to CO₂ emissions. At present, the only viable technology for CO₂ capture and storage is to concentrate CO₂ into a nearly pure form before pumping it underground or to the ocean floor. Such processes consume additional fuel and add to consumers' energy costs. The objective of this project is to develop a new class of dual-property materials, functionalized metal-organic frameworks (MOFs), that can effectively trap CO₂ and photocatalytically convert it to methanol or other chemical fuels. The goal is to provide economic and environmental benefits by not only capturing CO₂ but also converting it to value-added products. MOFs can be synthesized through solvothermal reactions between the organic linkers and the secondary building units (SBUs) of transition metals. Our approach is to incorporate photocatalytic activity in MOFs through rational design while retaining their high CO₂ storage capacity. Such designs could create highly concentrated CO₂ localized inside the microporous spaces proximate to the photocatalytic reaction center, thus enhancing the conversion rate and equilibrium towards final products that are otherwise difficult to achieve.

Mission Relevance

This project is relevant to DOE's missions in environment and energy. Mitigating the environmental impact of CO₂ emissions from fossil fuel represents a key DOE mission. Converting solar energy for a variety of applications represents a key initiative at DOE. Next-generation adsorbent and photocatalytic materials represent key components in the future energy efficiency and renewable energy technology portfolio.

FY 2011 Results and Accomplishments

In FY 2011, we continued our investigation of systematic reduction of the MOF band-gap as the first step toward improving photocatalytic conversion efficiency. The metal oxide cluster SBUs in MOFs can be considered as discrete quantum dots, which are connected into a framework by the conjugated organic linkers acting as the photon antenna, as shown in Figure 1A. By changing the molecular dimension of either the SBU or the ligand, one would expect to change the electronic delocalization and therefore the overall MOF photo-absorption band-gap. In FY 2010, we initially attempted to lower the MOF band-gap by improving the ligand electronic conjugation. We synthesized three MOFs with similar α -Po type structure by using different dicarboxylate acids with increasing π -orbital

conjugation and found that the overall band-gap can be reduced through greater electronic delocalization, as shown in Figure 1B. In FY 2011, we shifted our focus to tuning the band-gap energy via SBU cluster size by preparing three MOFs of similar crystal structure with increasing zinc oxide cluster dimensions. Figure 1C shows the change in cluster size and the associated band-gap reduction, with benzenedicarboxylate as the ligand in all three cases. Indeed, a red-shift of the photo-absorption energy was observed. However, the energy shift is relatively small compared with the effect on ligand adjustment. This observation suggests that (1) the band-gap in MOF is dominated by ligand electronic transition and (2) the electronic coupling between the ligand and SBU is limited, primarily as a result of the relatively high electronic transfer barrier between the carboxylic and the ZnO bonds.

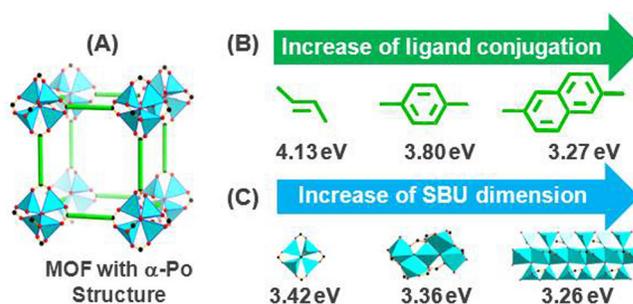


Figure 1. (A) The unit cell of a MOF with α -Po structure, (B) reducing the band-gap through ligand design with increasing π -conjugation, (C) reducing the band-gap through increased SBU cluster dimension.

To evaluate CO₂ conversion activity, we modified an existing photocatalytic apparatus in our laboratory with a new reactor design. The new design can harvest more photo radiation with quantified exposure and batch sampling capability. We tested several reference photocatalysts and validated the design. The new reactor will be used for CO₂ conversion studies of the new materials prepared in the coming year.

Proposed Work for FY 2012

We plan to continue developing various MOFs and other porous oxide-based materials for CO₂-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 new methods of preparing microporous photocatalysts using MOF as the porous template. We will also solicit support from theoretical modeling and simulation to guide our CO₂ conversion catalyst design and synthesis effort.

The Biochemistry of Plant-Fungal Symbiotic Relationships

2010-161-R1

Deborah K. Hanson, Frank 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 goal of this project is the study of proteins, such as transporters, and two-component sensory systems that participate in important symbiotic and nutrient exchange interactions between plant and fungal species. Its focus is fungal transporters that are extremely important in utilization and regulation of carbohydrates, phosphorous, and nitrogen. To date, biochemical and structural characterization of many of these enzymes has been hampered because they are integral membrane proteins that require a hydrophobic environment for stability and functional integrity. This project seeks to develop an integrated suite of systems for 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. Since approximately 25–30% of every genome encodes membrane proteins, their study is essential to meet the goals of multiple research areas in DOE's Office of Biological and Environmental Research (BER). In its Genomic Science and Environmental System 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 2011 Results and Accomplishments

This project focuses on proteins derived from the fungus *Laccaria 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* by the collaborating group of G. Podila, University of Alabama–Huntsville, and were provided to our team members for cloning into expression vectors.

The initial set of transporter genes was amplified with the polymerase chain reaction (PCR) from the cDNA clones for expression in the prokaryotic organisms *E. coli* and *Rhodobacter* (*R.*) *sphaeroides* and in the eukaryotic yeast *Pichia* (*P.*) *pastoris*. Cloning of the same PCR product into expression vectors for the three organisms required specific, extensive engi-

neering of the vectors. Insertion of all of the genes into the different vectors for expression in *R. sphaeroides* and *E. coli* was completed, and a subset is being cloned and expressed by using the newly engineered variant of the *P. pastoris* expression plasmid that we designed for this project.

The *Rhodobacter* expression strategy excelled for transporter 300971; Figure 1A shows that it is localized to the membrane fraction of *Rhodobacter*. Other transporters were expressed at lower levels in this organism and were sensitive to the induction conditions and density of the culture. Figure 1B shows that target 305352 is expressed maximally of the culture in early stages of the culture. Affinity tags facilitated purification of transporter 300971 from large-scale cultures of *Rhodobacter* employing the mild detergent Deriphath 160.

Additional results showed that *E. coli* was capable of expressing a different set of proteins, complementing the set that was expressed in *Rhodobacter* (e.g., target 191542, Figure 1C). By combining the use of both of these prokaryotic expression systems, we were able to broaden the set of fungal transporters that can move into the most important phase of this research project: functional characterization. We expect to be able to produce the full complement of fungal transporter targets once the yeast expression strategies are fully implemented.

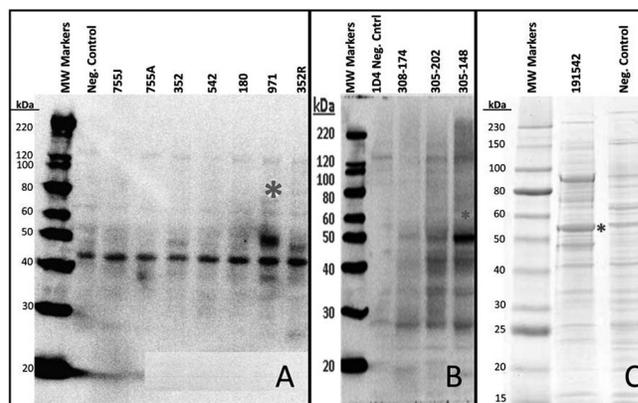


Figure 1. Two different prokaryotic expression systems complement each other for success in expression of multiple fungal transporters. Panels A and B represent proteins expressed in *Rhodobacter* membranes; Panel C depicts results from *E. coli* expression. (A) Immunoblot probed with anti-polyhistidine antibody; (B) Immunoblot probed with anti-1D4 antibody; and (C) SDS-PAGE gel stained with Coomassie Brilliant Blue. Asterisks denote target proteins at their predicted molecular weights.

Proposed Work for FY 2012

Assays for sugar specificity are being adapted for use with *Rhodobacter* membrane preparations and will then be applied to transporters expressed in *E. coli* and yeast membranes, and to purified, detergent-solubilized transporters. Although previous experiments in the literature have utilized radiolabeled sugars, the procedures will be modified to enable the use of sugars labeled with the fluorophores 2 anthranilic acid or 2-aminobenzoic acid. Competition experiments that address

the specificity of transporters for a particular sugar will be performed by using unlabeled sugars in the same reaction as fluorescently labeled sugars.

Additional target transporter genes from *Laccaria bicolor* have been identified and will be cloned. In particular, proteins that transport nitrogen, primarily in the form of ammonium and amino acids, will be targeted. A large repertoire of these genes has been annotated in the *Laccaria* genome, and a variety of transmembrane topologies are predicted for these transporters. Phosphorus transporters are another targeted class; they are members of the ABC transporter superfamily and are also characterized by various topologies. These genes will be cloned from cDNA libraries that have been provided by the collaborating group of F. Martin (INRA, France).

Tunnel-Diode Oscillator Detection Technique for Ultrasensitive Magnetometry and Resistivity Measurements of Microscopic Samples

2011-005-NO

Oleksiy Snezhko and Daniel Lopez

Project Description

Novel high-temperature superconducting cables based on a complex multilayer structure are currently being tested for applications on the U.S. electrical power grid. The high manufacturing costs of the cables, their poor performance in electric motors (where high magnetic fields are present), and costs related to cooling them remain prohibitively high, thus inhibiting the widespread use of these cables. Therefore, any increase in the current-carrying ability of these materials or the discovery of novel superconducting systems with higher critical currents would improve the performance of the cables and may help justify their widespread use. One of the main factors limiting the current-carrying ability of high-temperature superconductors (HTSs) — apart from the material itself — is the motion of magnetic vortices, nanometer-sized magnetic flux tubes appearing in the superconductor in magnetic fields above the first critical field. The vortices have normal cores and therefore dissipate energy when driven by the applied current. The dynamic behavior of vortices controls the electromagnetic response of a superconductor.

Existing measurement tools, such as DC (direct current) and AC (alternating current) magnetometers, point contact transport measurements, etc., require rather large samples before they can produce reasonable (i.e., above noise) results; however, large samples are not always available, especially with

new sensitized systems. The goal of our project is to develop a novel micromechanical tunnel-diode oscillator (mm-TDO) platform that is capable of performing ultrasensitive measurements of AC susceptibility, resistivity and magnetic field penetration depth of small (micro-scale) samples. This tool is intended to provide unique capabilities that researchers can use to tackle some of the most fundamental and basic science problems in condensed matter physics, such as a pairing symmetry of the Cooper pairs facilitating superconducting properties of the material (pairing symmetry is recovered through ultrasensitive magnetic field penetration depth measurements) and understanding the electro-transport properties of novel superconductors.

Mission Relevance

This project is relevant to DOE's energy mission. One of the primary missions of the U.S. Department of Energy is to develop next-generation superconducting materials that could revolutionize energy delivery for the United States electrical grid for the 21st century. This proposal is enabling development of new instrumentation that will provide "materials characterization-on-chip" with superior sensitivity (i.e., sub-angstrom resolution when measuring a magnetic field penetration depth in superconductors). This novel tool will dramatically enhance our ability to address the fundamental questions of electron transport in superconductors, thereby helping to improve the design of next-generation HTS cables and materials for the U.S. electrical grid.

FY 2011 Results and Accomplishments

The resonator circuit was developed and assembled with a 1-mm-diameter coil. The resonator was designed and fabricated to be capable of working in an ultra-low-temperature environment. Low-noise supporting circuitry was developed to allow a stable oscillation frequency for the resonator. The circuit is driven, in turn, by a stable 10-V DC source. The tunnel diode resonator was tuned to be resonating at 92 MHz. The resonator is also stable and can be used for conducting ultrasensitive measurements of samples ranging from 0.5 mm to 0.9 mm in diameter.

To accept much smaller samples, microcoils for the resonator were fabricated by using microfabrication techniques. Figure 1 shows a sketch of the fabricated structures.

The metallic coils are made from gold and are isolated from the Si layer by a layer of SiN. This SiN/silicon membrane supports the coils on one side and the sample on the other side. Access to the center conductor of the sample coil is obtained through the back of the chip (see Figure 1, right), where a cavity is etched away to provide a well-controlled space to insert samples.

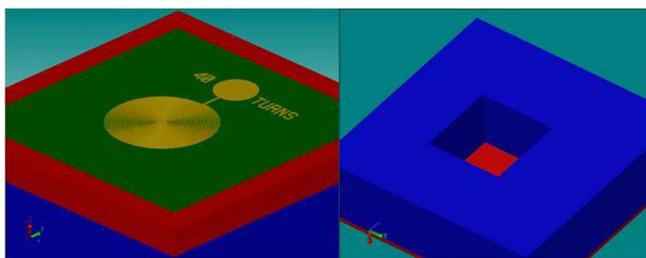


Figure 1. Layout of fabricated coils: (left) top view of the flat coil, (right) the back side of the chip. Access to the center contact point of the flat coil is provided through a rectangular-shaped opening in the wafer. Size of the flat coil is 250 μm .

Microcoils will replace the 1-mm coil in the resonator circuitry to provide a better sensitivity for measurements of microscopic samples.

Proposed Work for FY 2012

Sets of coils with diameters from 100 to 200 μm will be fabricated to increase sensitivity of the system even further. The resonator will be adapted for the ultra-low-temperature system (down to 250 mK). Newly fabricated coils will be tested in experiments in order to obtain a complete characterization of their performance at low temperatures. In order to add the *in-situ* and real-time tunability of the resonator, we will integrate actuators based on microelectromechanical systems (MEMS) at the side of the coils. The MEMS actuators will allow us to deform the coils by applying controlled forces to one end of the coil while the other end remains anchored to the substrate. In this way, the microcoil can be deformed continuously, which will significantly improve the filling factor of micro-scale samples and, therefore, the performance of the proposed tunnel-diode oscillator.

Synthesis, Characterization, and Properties of Fast-Acting Amorphous Drugs

2011-012-N0

Chris J. Benmore and Johann K.R. Weber

Project Description

Today, a limited range of amorphous pharmaceutical compounds — which provide greatly increased solubility, faster dissolution, and higher bioavailability to researchers than do their crystalline counterparts — are commercially available. Given the significant advantages of working with these types of materials, this project has the following principal objectives: to (1) establish the scientific basis for a next-generation drug delivery technology and (2) advance the capabilities for generating these and other amorphous pharmaceutical com-

pounds. These experiments demonstrated a new, proprietary method for processing these materials. We have employed an acoustic levitation technique that uses the pressure from intense sound waves to suspend pharmaceutical materials. The technique provides a way to solidify the atoms or molecules in a liquid without risking interaction with the potentially contaminating effects of a container, either by solvent evaporation or laser quenching. The focus of the project is to characterize pharmaceutical materials before and after “containerless” processing by using hard x-rays and nuclear magnetic resonance (NMR) spectroscopy to find the optimum levitation conditions. A wide range of well-known drugs and pharmaceutical compounds have been processed by using different solvents and stabilizers, and their stability has been monitored using hard x-ray diffraction. Colleagues who have contributed to this effort include pharmacists Professors Stephen Byrn and Lynne Taylor (both of Purdue University) and NMR expert Professor Jeffery Yarger (Arizona State University).

Mission Relevance

The results of this work have the potential to improve the quality of life through an innovation in science and technology and increase U.S. economic competitiveness through the synthesis of new amorphous pharmaceuticals. This project is relevant to DOE’s basic science mission, as it utilizes and demonstrates the utility of DOE science-based facilities in support of national needs. Other agencies that may benefit from this research include the National Institutes of Health, research divisions of pharmaceutical companies, and universities. Synthesizing the amorphous forms of a drug is not always possible by using conventional pharmaceutical processes — and it is becoming increasingly important to develop the amorphous forms because of the emergence of new drugs that are virtually insoluble in their crystalline forms. The benefits of our containerless processing technique are wide ranging, as this technique is likely to lead to the generation of many faster-acting drugs for patients. Over the long term, the introduction of new drug compounds will improve patient treatment outcomes, reduce drug delivery costs, and reduce the percentage of drug dosages that patients are unable to absorb. These innovations may also lead to cheaper and higher-yielding drug-processing routes.

FY 2011 Results and Accomplishments

In FY 2011, we characterized a wide range of well-known pharmaceutical materials before and after containerless processing by using hard x-rays and NMR spectroscopy. We took steps to optimize the acoustic levitator (Figure 1) for pharmaceuticals production by minimizing dust contamination and by finding the best levitation conditions for different solvents. We demonstrated the process for amorphizing six “reluctant” (i.e., difficult to amorphize) glass-forming drugs from levitated solution droplets by using acoustic levitation. We also demon-

strated the melt quenching technique by using laser heating for six different drugs in the levitator.

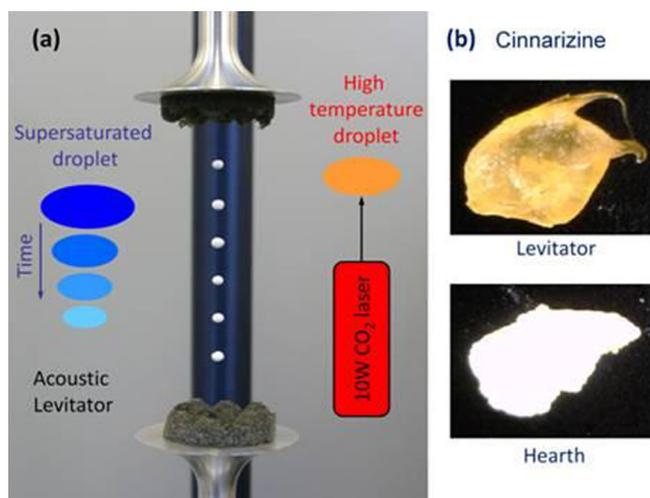


Figure 1. (a) A photograph of the acoustic levitator as it levitates several samples simultaneously (white spheres) with 7-mm spacing. (b) A photograph of the pure antihistamine drug Cinnarizine, which was melted in the levitator to form a yellow amorphous product, as compared to the same starting material that, when melted in the laser hearth, formed a white crystalline product. The color difference is due to a few broken hydrogen bonds in less than 1% of the molecules present, whereas the main effect of processing is a change in texture and viscosity.

A provisional patent was filed on January 31, 2011, by C.J. Benmore and J.K.R. Weber entitled "Containerless processing of amorphous and nanophase organic materials." In addition, the results of our work were featured in two scientific highlights:

(i) "Drugs take flight" in *Materials Today* magazine: Tools and techniques, a Research news article by Laurie Donaldson, Oct. 2011, Vol. 14(10), p. 45.

(ii) "A floating apothecary," an American Physical Society physics highlight by Jessica Thomas (Physics editor) on our *Phys. Rev. X* paper, Aug. 2011.

Proposed Work for FY 2012

We aim to perform high-energy x-ray measurements on a selection of pharmaceuticals to characterize the time-resolved structure, *in situ*, during the containerless melt-quenching process. This effort will involve the installation and setup of a laser-controlled area for a low-power 10-W CO₂ laser system for melting drugs. We also intend to test a series of new drugs that will present amorphization challenges, including some specific HIV (human immunodeficiency virus) drugs. We will also investigate the effect of the containerless processing technique on liquid crystals and drugs mixed with polymer binders. Throughout the year, we will monitor the processed drug products to develop a detailed understanding of how amorphous drugs crystallize over time.

From Plastic Bags to High-Performance Lubrication Additives: A Green Chemistry Solution to Energy Efficiency and Environmental Challenges in Transportation

2011-022-N0

Kuldeep Mistry, Ali Erdemir, Vilas Pol, and Michael Thackeray

Project Description

We are developing a revolutionary technique to convert waste plastic into micro-/nanoscale carbon spheres and carbon tubes and to use them as nano/micro-colloidal additives in lubricating oils that, under the severe operating conditions of combustion engines, are able to achieve superior performance. Indeed, the main objectives of the project are to develop novel carbon particles (as presented in Figure 1) with superior physical, chemical, and tribological properties and to demonstrate their usefulness when operating in the engine and drivetrain components of advanced automotive systems. Moreover, the project also focuses on (1) gaining an understanding of the science behind the lubrication mechanisms and (2) optimizing the lubricants to achieve even greater performance in terms of friction and wear.

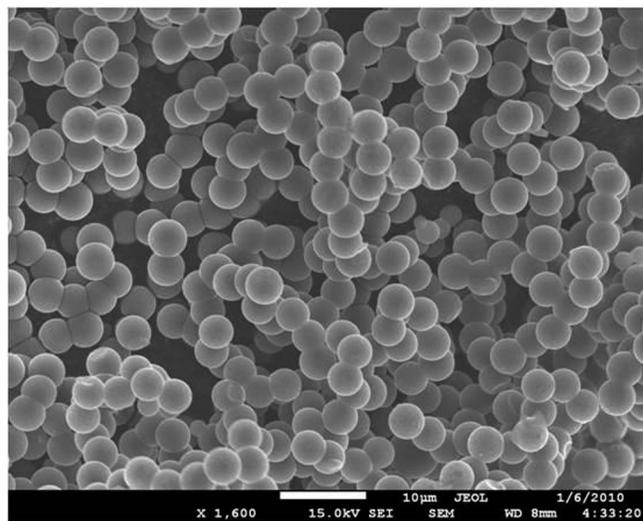


Figure 1. Carbon spheres fabricated by using an autogenic reaction process and tested as lubricant additives. These novel carbon particles with superior physical, chemical, and tribological properties demonstrated their usefulness under simulated very harsh operating conditions similar to that of engine and drive-train components of advanced automotive systems.

Mission Relevance

This project supports DOE's missions in science and energy. Every day, we consume about 13 million barrels of petroleum for transportation. However, engine and drivetrain friction accounts for 10–15% of total fuel use in current vehicles. This rate of use translates to about 1.3–2 million barrels of petroleum per day lost to friction alone. Furthermore, a significant amount of energy is spent to remanufacture and/or replace worn parts in these systems. In short, the energy efficiency, durability, and environmental compatibility of all transportation vehicles are very closely related to the effectiveness of the lubricants being used on their rolling, rotating, and sliding contact surfaces.

In this project, we are developing a low-cost solution that addresses the efficiency, durability, and environmental compatibility problems in advanced transportation systems. Specifically, we are developing a revolutionary technique to convert waste plastic into micro/nanoscale carbon spheres and carbon tubes and to use them as nano/micro-colloidal additives in lubricating oils.

FY 2011 Results and Accomplishments

Results and accomplishments during the past fiscal year have included the following:

- ▶ The tribological performance of the initial batch of carbon particles was evaluated and their lubrication mechanism was explored.
- ▶ Carbon-based lubricant demonstrated excellent tribological performance under severe sliding conditions and at high temperature (more tests under different conditions are underway).
- ▶ Carbon-based lubricants formed a very thick (i.e., more than 200 nm thick) carbon-rich protective boundary film on sliding surfaces and we believe that this was the main reason for superior tribological performance. Further analytical studies are underway to elucidate lubrication mechanisms.

Proposed Work for FY 2012

On the basis of the results we have obtained so far, we will further optimize the carbon particles (especially in terms of their size and structural nature) by pursuing better surface functionalization. Moreover, more effective surfactants will be tested as we pursue making further improvements to surface reactivity/compatibility and, hence, to realizing much superior tribological performance. Initial studies also showed that particles produced at highly elevated temperatures (i.e., at more than 2,000°C) offered better lubrication characteristics. That aspect of the material will be investigated further, as well.

Achieving Efficient Thermal Energy Transport with One-Dimensional Polymer Nanofibres

2011-071-N0

Zhang Jiang, Joseph W. Strzalka, Tao Sun, Hsien-Hau Wang, Jin Wang, and Zhenxin Zhong

Project Description

Polymers (e.g., polyethylene) that are usually good thermal insulators in bulk forms were found to be very good thermal conductors: the polymers are on a par with commonly used metallic heat transfer materials when they are drawn into one-dimensional fibers with high draw ratios and nanoscale diameters. The internal structures (such as the crystalline domains), chain entanglements, and defects morphologies are believed to affect the phonon propagation that is directly related to the thermal energy transport properties of a polymer. However, no systematic and quantitative understanding of this structure and function relationship exists to date. Understanding the correlation between the structure and properties under real conditions during the growth of the polymer nanofibers is crucial to designing and fabricating polymer nanofibers that meet the need for an efficient thermal energy transfer that requires high thermal conductivity as well as electrical insulation, high chemical stability, lightweight, high mechanical performance, and can be mass-produced at low cost. We propose to use the x-ray-based techniques (small- and wide-angle x-ray scattering [SAXS/WAXS], x-ray nanotomography, and coherent x-ray imaging), in combination with the *in situ* drawing process and thermal conductivity measurement, to address these challenges.

Mission Relevance

This project supports DOE's science and energy missions. Its success will have a great impact on both the technical applications of a new type of energy-efficient material and the fundamental understanding of low-dimensional, nanoscale thermal transfer physics. This project aims to unveil the correlation between material structure and the functional properties of polymer nanofibers. The knowledge we build throughout the project will apply directly to the design, optimization, and production of nanostructured polymer nanofibers with enhanced thermal transfer capabilities and other properties that are desirable in energy-efficient devices.

FY 2011 Results and Accomplishments

In the past year, we selected several semi-crystalline linear polymers, including polyethylene, nylon, and polyvinylidene fluoride, as candidate materials. An electrospinning device with parallel collectors was fabricated and commissioned

for preparing a series of polymer nanofibers with controlled fiber diameters ranging from several microns to a few nanometers. We designed, fabricated, and optimized an *in situ*, hot-stretching apparatus for a time-resolved x-ray scattering study of polymer nanofibers. The microstructure development in polymer nanofiber was investigated on highly aligned fiber bundles, for the first time, by WAXS at the Advanced Photon Source. We examined the effect of fiber diameters, annealing temperature, and the stretching ratio on the interior structure of polymer nanofibers. WAXS patterns indicate a dramatic improvement in crystallinity, crystal size, and crystal orientation in polymer nanofibers after a hot-stretching treatment of as-spun polymer nanofibers. It is these highly oriented crystalline regions that are believed to cause the enhanced thermal conductivity and mechanical properties of polymer nanofibers. We also conducted preliminary experiments at Argonne's Center for Nanoscale Materials to study the thermal transport properties of individual polymer nanofibers by using a noncontact Raman spectra shift method.

Proposed Work for FY 2012

We will further investigate the thermal transport properties on polymer nanofibers of various sizes and degrees of crystallinity, as well as other functions (such as the mechanical strength and electric conductivity) of individual polymer nanofibers. In addition to wide angle scattering, we also plan to use x-ray microbeam diffraction to study the interior structure of individual fibers and to correlate the structural information with their thermal properties. Facilities across the laboratory — including those with capabilities in atomic force microscopy for mechanical properties, scanning electron microscopy for fiber dimension and surface characterization, transmission electron microscopy for *ex situ* internal structures, and thermal analysis instruments for heat transfer properties — will be used for studying the morphology and nanostructure of polymer nanofibers as we seek to build a preliminary diagram of the correlation between the polymer fiber nanostructure and its functions, in particular the thermal transport capability.

New Technologies for Label-Free, Antibody-Based Multiplexed Biosensors

2011-093-NO

Rosemarie Wilton and Ani Sumant

Project Description

The development of robust, antibody-based reagents for biosensors, as well as integration of these reagents into sensitive detectors, represents an essential step toward the development of field-deployable, multiplexed biosensors. Such biosensors, intended to be capable of sustained exposure to harsh

environmental conditions, will find application in the detection of multiple threats related to bioterrorism and biowarfare, in medical diagnostics, and in environmental monitoring. The goals of this project include development of stabilized, redox-active binding proteins; development of ultrananocrystalline diamond (UNCD) -based sensors; incorporation of the engineered proteins into these devices; and demonstration of changes in electrical signal as a function of binding events.

Mission Relevance

The project is applicable to DOE missions in science, environment and national security. In particular, the project integrates materials development, engineering of novel biological sensing components, and new methods for signal detection in support of the 2011 Strategic Plan for Materials in Energy and Security-Related Systems. Other federal agencies that could benefit from our research in sensitive antibody-based detectors include the U.S. Department of Homeland Security and the Defense Advanced Research Projects Agency (e.g., its Antibody Technology Program).

FY 2011 Results and Accomplishments

A. Cuprebody Design and Synthesis

Protein engineering was carried out in the laboratory and proceeded along two lines: (1) introduction of a redox-active copper binding site into a stabilized antibody domain and (2) development of binding reagents from redox-active proteins.

Antibody-Based Redox Site Engineering

A highly stabilized antibody variable domain, developed in our laboratory, served as the framework for redox site engineering. Using sequence alignment and structure analysis, we identified amino acid modifications that could potentially produce a copper binding site. To date, we have produced antibody domains containing two of the three proposed Cu-binding ligands: Cys-88 and His-33. Production of a domain containing the second histidine residue to complete the Cu site was unsuccessful to date because of the instability of the structure upon addition of the second histidine; thus, additional stabilizing mutations are planned. If we are unsuccessful in engineering the trio of copper-binding residues into the current framework, we are poised to conduct rapid tests of several other highly stabilized immunoglobulin constructs that we developed in our laboratory.

Redox Protein Expression, Purification, and Mutagenesis

We developed expression vectors for several redox proteins to identify a suitable scaffold for development of redox-active binding reagents. Excellent soluble protein expression was obtained with three of the four candidates, and two of the proteins were expressed and purified on a large scale. Thermal stability of the candidate proteins was measured by a fluores-

cence-based thermal stability assay and by circular dichroism. Candidate A has high thermal stability, which makes it an excellent candidate for protein engineering, as well as for incorporation into UNCD materials. To verify that the protein structure and redox function are maintained in the presence of amino acid modifications — a requirement for the eventual development of novel binding reagents — we produced and characterized a number of redox protein mutants. We replaced loop residues with serines and tyrosines and inserted additional serine, tyrosine, and glycine residues to extend loop lengths. In general, mutation of the loop regions reduces the thermal stability of the protein; however, because of the inherently high stability of the starting scaffold, the mutant proteins are still expressed well. We are in the process of characterizing changes in reduction potentials by cyclic voltammetry.

Cuprebody Phage Display

We obtained an expression vector for production of a combinatorial phage display library. The vector encodes the M13 phage pIII protein for expression of cuprebody-pIII fusion proteins. We started to modify the vector to accommodate our planned cloning strategy.

B. Fabrication of Carbon-Based Nanomaterials

We were successful in designing and executing a complete fabrication process that reproducibly fabricates UNCD nanowires in a field-effect transistor (FET) type of configuration, which are going to be used as a sensor platform for detecting proteins and biomolecules. It is important to note that this is one of the possible ways of developing biosensors, and we are also exploring a biosensor based on an electrochemical approach. We will assay the performance of both of these approaches and then down-select one approach to take forward into the next phase.

Fabrication of the UNCD Nanowire with a FET-Type Structure

In this case, either nitrogen-incorporated or boron-doped UNCD thin films were first deposited by using a chemical vapor deposition process grown on an oxidized silicon (Si) wafer coated with 10 nm of tungsten (W), which enhances nucleation for void-free growth of the ultra-thin UNCD films. The detailed fabrication sequence is shown in Figure 1. Critical point drying in isopropyl alcohol (IPA)/CO₂ is used to avoid structure collapse due to stiction. The whole fabrication process is complicated as it involves a number of fabrication steps, including e-beam exposure, development, reactive ion-etching (RIE), metal pad deposition and lift-off, and, again, RIE. However, after a number of fabrication trials, it was possible to fabricate the UNCD nanowire FET-type of structure. The next step in this process will be to functionalize these nanowires for attachment of the target biomolecules/proteins. The change in the electrical response of the FET as a function of attachment/detachment of these biomolecules will be recorded, and all electrical data will be further analyzed to find out whether we

can see (and reproduce) consistent and characteristic electrical responses to these events.

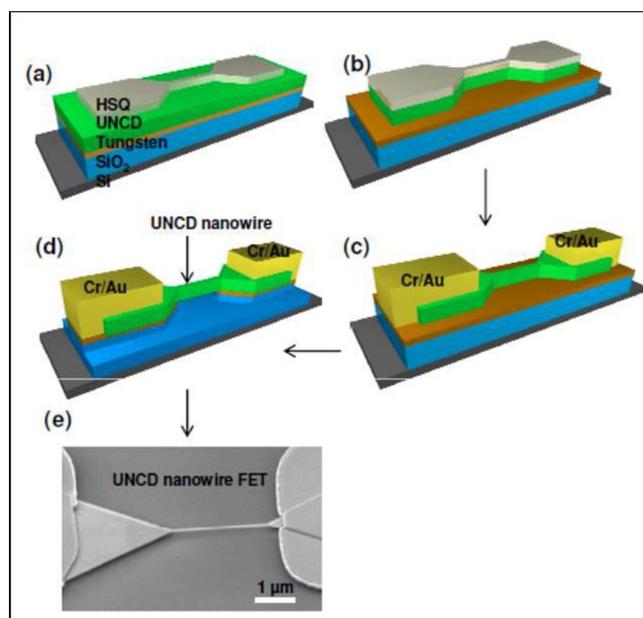


Figure 1. The top-down process to fabricate a UNCD, nanowire-based FET structure for the biosensor. The steps in the fabrication process are as follows: (a) spin coating of electron beam photoresist (HSQ); (b) pattern transfer into a UNCD via the reactive ion-etch (RIE) system with an O₂ plasma; (c) use of optical lithography for Cr/Au deposition and lift-off; (d) the RIE process using a Fluorine-based chemistry to etch W/SiO₂ and undercut the nanowire, followed by a timed HF dip to release it fully; (e) the resulting scanning electron microscopy image of a fabricated UNCD nanowire with an FET type of structure.

Proposed Work for FY 2012

A. Cuprebody Design and Synthesis

- ▶ We will complete initial work to determine the suitability of the azurin scaffold for use in a combinatorial phage display library. Elemental analysis and measurement of the redox potential of selected mutants are planned. We will produce an ultra-stable azurin framework by using homologous sequence analysis.
- ▶ We will produce an M13 phage display library for selection of binding reagents based on the azurin framework or stabilized antibody-based copper-binding protein, as appropriate.

B. Fabrication of Carbon-Based Nanomaterials

- ▶ We had planned to functionalize nanowires for attachment of the target biomolecules/proteins and to measure changes in the electrical response of the FET as a function of attachment/detachment of these biomolecules. However, budget considerations mandate that our goal is to make substantial progress on the protein engineering component of the project in 2012, and to return to device testing in 2013, the anticipated final year of the project.

Dynamics of Spin-Polarized Carriers in New Spin Electronic Materials and Devices

2011-097-NO

David J. Keavney and Philip Ryan

Project Description

This project seeks to enhance our understanding of spin dynamics in semiconductors through direct imaging of spin-polarized carrier populations in real device environments. We use x-ray photoemission electron microscopy and x-ray excited luminescence microscopy to obtain magnetic images. The major objective of the work is to obtain element-specific images of spin injected into a semiconductor device, ultimately with a time resolution of 100 ps, in order to study how device geometries and structure influence the spin currents. These spin currents are small, producing an expected signal of 1 part in 10^6 in our x-ray experiments. Therefore, development of low-noise techniques has played a role in the initial stages of the project.

Mission Relevance

The data obtained through this project will help in the synthesis and discovery of new electronic materials for low-power electronics and information storage, which are of relevance to DOE missions of energy technology and basic science. These materials, by enabling spin instead of charge to process information, are expected to enable a new generation of non-volatile electronic devices, including non-volatile memory technologies and field programmable gate arrays. Such devices would enhance functionality and operate at lower power, thereby enhancing energy security on the consumption side of the equation. In addition, a basic understanding of spin dynamics in semiconductor materials is relevant to four of the five Grand Science Challenges in the DOE-BESAC Report "Directing Matter and Energy: Five Challenges for Science and the Imagination:" control of materials at the electronic level, emergent properties, information at the nanoscale, and physics far from equilibrium.

FY 2011 Results and Accomplishments

Toward the experimental goals for FY 2011, we performed x-ray magnetic circular dichroism spectroscopy measurements. Because of the long spin diffusion lengths, on the order of tens of microns, even nonspatially resolved spectroscopy experiments are well matched to our beam size ($100 \times 300 \mu\text{m}$). Therefore, these experiments are an important beginning step that will provide guidance on where the spin-polarized states exist with respect to the absorption edges and the expected size of the effect. These experiments

were performed on a $200 \times 1,600$ -micron n:ZnSe spin injection device with three ferromagnetic Fe contacts, one at each end and one in the center. The sample was saturated in a 500-G field along the long edge of the center contact, and a 1-mA current was passed from the center contact out toward the end contacts. We, therefore, expected spin accumulation to be generated within the spin diffusion length (~ 30 microns in ZnSe) of the center contact. The x-ray beam was focused on a 100×300 -micron spot at the center contact, and dichroism spectra were taken in fluorescence at the ZnL_3 edge at 50 K to search for induced spins on the cations. No measurable dichroic signal was detected above the noise level of 0.8% of the absorption edge jump.

A second experiment was performed on a similarly designed n:GaAs channel, in this case using x-ray excited luminescence microscopy as the detection mode. This approach provides higher counting statistics and allows full-field imaging of the device at a spatial resolution of 1–2 microns, thus removing uncertainties about beam alignment with the small spin accumulation region. In Figure 1, we show (a) an optical micrograph and (b) an x-ray excited optical luminescence image taken at the GaL_3 edge of this device. In these experiments, we established a noise floor of 1 part in 10^5 , while seeing no dichroic signal. This result suggests further improvements in count rate and signal-to-noise ratio are needed for this imaging project.

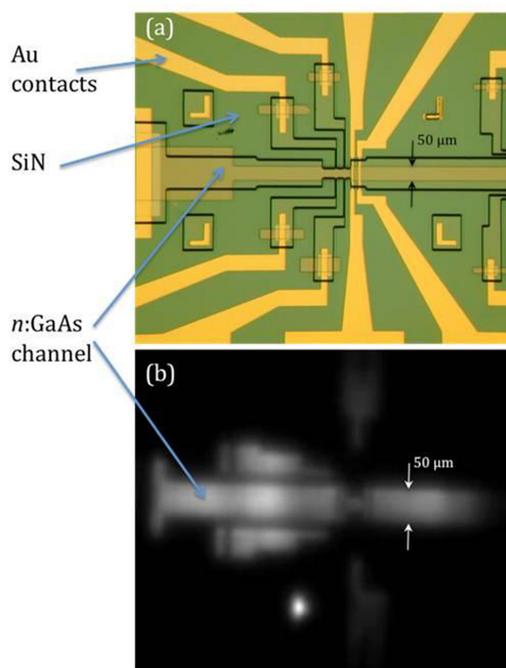


Figure 1. (a) Optical micrograph of an n:GaAs spin transport device used in x-ray excited optical luminescence microscopy experiments and (b) luminescence image taken at the GaL_3 edge. Ferromagnetic Fe contacts were deposited on the ends of the channel and at the center contacts, followed by deposition of Au contact pads. A 1-mA current is applied from the Au contacts at the left edge of the image and at the center contacts; thus, a spin accumulation is expected within the spin diffusion length of the contacts (10–50 microns). The channel width of this device is 50 microns.

Proposed Work for FY 2012

In FY 2012, we plan to build on the spectroscopy and imaging work we began in FY 2011. The first half of FY 2012 will be dedicated to continuing the static imaging of spin injection structures and on improving the signal-to-noise ratio to 1 part in 10^6 . This objective can be accomplished with higher flux densities achieved by using a focused x-ray beam. We expect to be able to demonstrate a measurable x-ray magnetic circular dichroism (XMCD) signal at the semiconductor cation sites. Building on the expectation of achieving this milestone, we will proceed with static imaging studies, with the goal of demonstrating an XMCD image in the second half of the year. Once static imaging is achieved, it will be relatively straightforward to apply a pump-probe setup for our time-resolved studies. We will also continue to work with colleagues who are providing growth samples suitable for imaging with photoemission electron microscopy.

Development of a Design Concept for a Ring Imaging Cherenkov Detector

2011-110-NO

Kawtar Hafidi

Project Description

The goal of this project is to develop a design concept for a Ring Imaging Cherenkov Detector (RICH). A RICH detector will greatly enhance the particle identification capabilities of the CLAS12 spectrometer located in Hall B of Thomas Jefferson National Accelerator Facility (Jefferson Lab). By providing clean separation between pions, kaons, and protons over a momentum range from 2.5 to 8 GeV/c, the RICH detector will have a strong impact not only on the CLAS12 physics program, but also on Jefferson Lab's 12 GeV mission as a whole. These feasibility studies will allow Argonne to play a leadership role in the design and later the construction of the RICH detector. Several design concepts are being studied. The goal of these studies is to explore all available options, including radiators, optical systems, and light detection methods, in an attempt to maximize particle identification and minimize the cost.

Mission Relevance

This project is relevant to DOE's basic science mission. The successful completion of this project is imperative before the detector construction. A RICH detector for CLAS12 will enable the following: (1) to know whether the anti-up and anti-down quarks contribute symmetrically to the polarization of the proton; (2) to precisely measure the contribution of the strange quark to the polarization of the proton; (3) to study whether the quark energy loss in the nucleus is different for up, down, and strange quarks; and (4) to test whether the formation

time of the hadron depends on its quark flavor content. These are but a few of the very important accomplishments we can expect with the addition of a RICH detector to CLAS12. These research topics are all very well aligned with the mission of the DOE Office of Science in advancing our understanding of the structure of the nucleon and nuclei from their most fundamental degrees of freedom, quarks and gluons.

FY 2011 Results and Accomplishments

In the past year, we developed a simulation based on a C++ code by using the GEANT4 toolkit. We used the existing simulation of a well-understood RICH detector in Hall A to benchmark the code. We also learned that the proximity RICH technology based on the ultraviolet wavelengths of the Cherenkov photons is not a viable option for our particle momentum range. Because one has to detect the visible band, the photon detector should consist of photomultipliers (PMTs). Our simulation showed that an aerogel-type radiator would be the best solution to achieve better particle identification, especially for particle momenta above 4 GeV/c. Extensive simulations were performed to optimize the radiator and gap thicknesses in addition to the pad size of the light detectors. The configuration providing the best performance corresponds to a radiator thickness of 3 cm, an index of refraction of 1.06, and pad size below 1 cm. The use of the aerogel produced with the new "pinhole-drying" method will result in increased transparency and index of refraction. The RICH detector will consist of six radial sectors to match CLAS12 geometry. One RICH sector must span over 6 m² to achieve the desired acceptance. For the proximity RICH detector, where the PMTs have to cover the whole area, the cost of PMTs alone would be at least \$5M for one sector. Aside from monetary returns, reducing the number and area of PMTs will also minimize the effect on the downstream time-of-flight detector. A dual mirror system was simulated with inward and outward reflections relative to the beam line. The inward option had several advantages and, therefore, was adopted. A tracking reconstruction algorithm based on a likelihood approach was also developed. This code is crucial for the reconstruction of the Cherenkov rings, and indispensable for particle identification.

Proposed Work for FY 2012

The plan for FY 2012 is to complete the simulation for the RICH detector by including a realistic background in the reconstruction of the Cherenkov rings. We will also study the impact of the RICH detector on the performance of the CLAS12 spectrometer. We will explore the possibility of using micro channel plates for light detection. We will also test three multi-anode PMTs from Hamamatsu Photonics, in addition to the aerogel, and later check their performance in the beamline environment. We will also investigate the mirror technologies and the front-end and readout electronics.

Synthesis of New Sodium Layered Oxide Cathode Materials for Ambient Temperature Sodium Batteries

2011-116-N0

Christopher S. Johnson and Mahalingam Balasubramanian

Project Description

In this project, we are undertaking a research and development effort in Na-based batteries. Because the cathode limits the performance in Na-ion cells, our effort is devoted to producing new materials and optimizing known materials that will be incorporated as cathodes. Major tasks include the synthesis, characterization, and testing of these cathode materials in Na-ion cells. Materials that are produced are optimized for electrochemical Na insertion and extraction. Not only is synthesis involved, but also physiochemical characterization using x-ray diffraction and neutron scattering. In addition, *in situ* battery x-ray absorption spectroscopy is being used to understand the structure evolution during cycling and to determine the mechanism of charge compensation.

Our FY 2011 milestone was to achieve a cathode capacity of 120 mAh/g. High-capacity cathodes were then paired with a 220-mAh/g carbon anode to produce a full high-energy Na-ion cell.

Mission Relevance

This project is relevant to DOE's mission of transforming the nation's energy system and securing U.S. leadership in clean energy technologies. Accordingly, we are acquiring battery performance data that will be used to convey the message to the research community and DOE that Na-ion batteries are a viable option as an energy storage technology. To date, there have been no reports in the literature of Na-ion batteries that provide an energy density that matches Li-ion batteries. However, our calculations show that a cathode with specific capacity of 200 mAh/g and an anode with specific capacity of 500 mAh/g can be coupled to produce a high energy 3-V cell that is 15% greater in energy density than the Li-ion cell. It is also important to establish a backup battery technology in order to provide an option if the extensive effort to develop Li-ion battery were to fail due to unforeseen circumstances.

We believe that promising results for a low-cost, long-life Na-ion battery using either a non-aqueous or aqueous electrolyte might be interesting to the DOE Office of Electricity Delivery and Energy Reliability, which oversees energy storage for grid applications.

FY 2011 Results and Accomplishments

We discovered that cathode materials of Fe-based layered transition metal oxide, $\text{Na}(\text{Ni}_{1/3}\text{Fe}_{1/3}\text{Mn}_{1/3})\text{O}_2$, possess initial high capacities of 120 mAh/g (meeting the above FY11 milestone) and excellent capacity retention over 150 cycles in a full Na-ion cell (see Figure 1). The layered structure is maintained over many charge-discharge cycles, indicating exceptional structural stability. *In situ* x-ray absorption spectroscopy indicated that Ni changes its redox state from Ni(II) to Ni(IV), and the Fe(III) cycles modestly between Fe(III) and Fe(IV). This behavior suggests an interesting charge compensation mechanism as the Fe(IV) state has not been previously documented in a Na-ion cell and does not occur reversibly in a Li-ion cell. This finding promises the chance for developing even higher capacity Fe-containing materials.

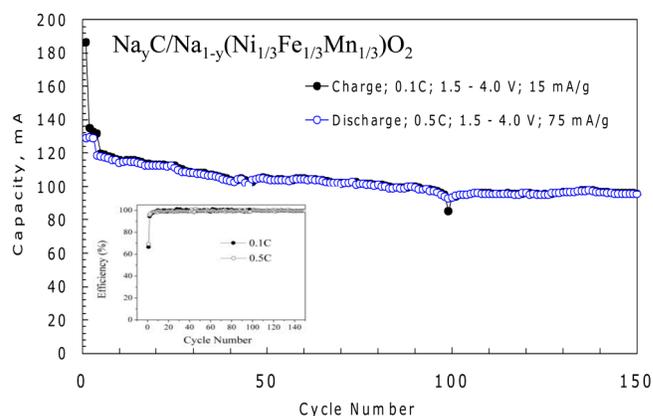


Figure 1. Capacity versus cycle number for $\text{Na}_y\text{C}/\text{Na}_{1-y}(\text{Ni}_{1/3}\text{Fe}_{1/3}\text{Mn}_{1/3})\text{O}_2$ cell.

This work generated Invention Report No. ANL-IN-10-056, and the U.S. Provisional Patent Application, No. 13/006,512, filed January 14, 2011, "Electrode Materials for Sodium Battery," C. S. Johnson, S.-H. Kang, D. Kim, and M. Balasubramanian.

Proposed Work for FY 2012

For FY 2012, we will develop new cathode materials with the milestone of increasing the usable specific capacity to 150 mAh/g and will work on new Na-alloy anodes that possess higher capacities than hard carbon. We will perform physiochemical characterization of these new materials. In addition, we will start an effort on improving the Nabased electrolytes.

Detailed and Reduced Chemical Kinetics of Green Fuels for Compression Ignition Engine Modeling

2011-140-NO

Raghu Sivaramakrishnan, Michael J. Davis,
Douglas E. Longman, and Sibendu Som

Project Description

The need for an energy scenario dominated by alternative fuels derived from domestic sources — coupled with stringent emissions compliance legislation affecting future transportation systems — has led to a substantial redirection of efforts over the past few years within the combustion research community to focus simultaneously on both clean-burning fuels and more efficient engines. Biodiesel is one among several alternative fuels that, when used either as such or in blends with conventional petro-derived fuels, offer substantial emissions advantages in compression ignition (CI) engines. Biodiesel is technically defined as a fuel comprised of mono-alkyl esters of long-chain fatty acids (C_{16} - C_{18} saturated and unsaturated) derived from vegetable oils (soybean oil is a primary source in the United States) or animal fats. Despite their significance for alternative-fuel scenarios, fundamental and applied combustion studies on these alkyl esters have been very limited. Consequently, the focus of this project is the development of a high-fidelity CI engine model for the combustion of biodiesel fuel. This modeling project represents a multi-dimensional computational study incorporating three main facets:

1. The development of detailed chemical kinetic models for biodiesel surrogates,
2. Reduction in the size (number of species and reactions) of these detailed chemistry models, and
3. Application of these reduced chemistry models for predictive 3-D engine simulations.

Mission Relevance

This project is relevant to the challenges addressed in a recent workshop convened jointly by the Office of Basic Energy Sciences, the Office of Science, and the Vehicle Technologies Program, Office of Energy Efficiency and Renewable Energy at DOE to identify basic and applied research needs and impacts in **Predictive Simulations for Internal Combustion Engines – PreSICE** (available at http://science.energy.gov/~media/bes/pdf/reports/files/PreSICE_rpt.pdf). This project is also relevant to the Grand Challenge addressed in DOE's Basic Energy Sciences Workshop on Basic Research Needs for Clean and Efficient Combustion of 21st Century Transportation Fuels (report available at http://science.energy.gov/~media/bes/pdf/reports/files/ctf_rpt.pdf), which envisions the develop-

ment of a validated, predictive combustion-modeling capability that has the potential for significant long-term impact on efficiency and emissions from the utilization of evolving transportation fuels in advanced engines. This combustion modeling project is also of relevance to the Combustion and Diagnostics program at the Air Force Office of Scientific Research (AFOSR), the Strategic Environmental Research and Development Program at DoD, and the Combustion and Propulsion programs at NASA.

FY 2011 Results and Accomplishments

In FY 2011, we targeted (a) the development and validation of detailed and reduced chemical kinetic models for our choice of a first-generation biodiesel surrogate, a blend of n-heptane and methylbutanoate (MB, a C_4 methyl ester) that closely matches the Cetane Number of soybean-oil-derived biodiesel, and (b) the application of these reduced models to 3-D engine simulations. Our accomplishments over the past year include the following:

1. Applied global sensitivity analyses to existing n-heptane and MB models over a wide range of parametric conditions (T , P , Φ) to identify important reactions and reaction classes.
2. Performed *ab initio* electronic structure theory-based transition state theory calculations of rate constants for $H + MB$. Updated rate rules for key reaction classes ($Fuel + H$, OH , HO_2 , CH_3O_2) on the basis of theory, fundamental experimental assessments, and analogies included in a detailed model for MB/n-heptane.
3. Systematically reduced the detailed model (~700 species, 3,000 reactions) for MB/n-heptane to a 150-species model, by using graph techniques.
4. Determined that the reduced models used in CONVERGE for 3-D engine simulations of realistic biodiesel are in reasonable agreement with experimental data for ignition delays and flame lift-off lengths.

Proposed Work for FY 2012

For FY 2012, we will continue our testing of the reduced model for MB and n-heptane against engine data and a variety of other 0-D ignition and 1-D flame and speciation targets. We also will perform brute-force sensitivity analyses of key elementary reaction rate constants in the engine simulations. Of course, the biggest challenge in FY 2012 is to extend our model development capabilities to more realistic biodiesel surrogates, C_{10} saturated and unsaturated methylesters. Advanced turbulence models will be implemented, along with detailed chemical kinetic models for 3D spray-combustion and engine simulations.

Magnetomechanical Actuation of Membrane Channels and Cellular Signaling via Direct Energy Transfer

2011-147-NO

Valentyn Novosad and Elena A. Rozhkova

Project Description

Application of nanoscale magnetic materials allows integration of inorganic material with biological molecules and therapeutics to achieve a combination of multivalent properties in one designer material. While most experimental results have been reported on applications of superparamagnetic materials, including their bio-conjugates, interfacing of ferromagnetic nanomaterials with biomaterials is a novel approach. In contrast to hyperthermia treatment modalities, we will explore a completely different and new pathway to achieve tumor regression (cytotoxicity effect) with magnetic nanomaterials.

In this project, we investigate a new phenomenon discovered by our group by using lithographically defined magnetic particles as mediators of cellular mechanotransduction for cancer therapy. Our data show that with the proper choice of magnetic particles, a magnetic field of extremely low frequency (a few tens of Hertz) applied for 10 min is sufficient to achieve ~90% cancer cell destruction *in vitro*. For comparison, in the case of commonly studied hyperthermia effects, magnetic fields with frequencies of hundreds kHz are needed to achieve cell thermal ablation. In other words, the external power supplied to the cell cultures in our experiments is ~100,000 times smaller than the most efficient use of magnetic nanoparticles to fight cancer known to date. Direct energy transfer and low operating field strength may create unprecedented treatment opportunities with low cost, large working volume, and minimal invasiveness.

Although the use of micron-size particles (~1 μm in preliminary experiments) has great fundamental impact and can be applied for diagnostic identification of mechanical properties of cancerous cells, we seek to scale down the magnetic disk size to improve possible applicability *in vivo* and clarify the intracellular mechanism of the novel phenomenon of magnetomechanical cancer cell destruction.

Mission Relevance

This project focuses on the understanding of mechanisms of intra- and intercellular energy transfer, in support of the DOE's mission in basic science and innovation. Furthermore, the design of novel nano-bio hybrid materials is a cutting-edge research area that is expected to contribute greatly to

emergent challenges connected with exponentially growing societal demands for clean energy and upgraded medical and health technologies to combat disease.

Understanding and controlling the way cells communicate with each other is crucial for advancing therapy options that may not only improve the quality of life for an individual patient but also have a tremendous socioeconomic impact on our nation, as even small, incremental advances in reducing cancer mortality and disability will inevitably lead to a large health care benefit. Specifically, we anticipate that with the completion of our research, we will have obtained the critical data needed to support the rational design and fabrication of novel biocompatible nanomagnetic materials.

FY 2011 Results and Accomplishments

Optimization of magnetic-disk fabrication process

We investigated two different methods for fabrication of magnetic disks in order to optimize their shape. In the first approach, Permalloy (Fe-Ni alloy) disks were deposited on a photolithographically defined photoresist template by using magnetron sputtering. This process allows for time-efficient deposition of metal films at room temperature, which makes it advantageous because of its low impact on the photoresist pattern. However, as seen in Figure 1(a), sputtering results in metal deposition not only on the target surface of the photoresist structure but also on the sides, thus yielding particles which have noticeable side walls, as shown in Figure 1(b). Electron beam-assisted metal film formation provides the benefit of highly directional metal deposition, as illustrated in Figure 1(c, d). As a result, we were able to fabricate magnetic disks with virtually ideal as-designed shapes.

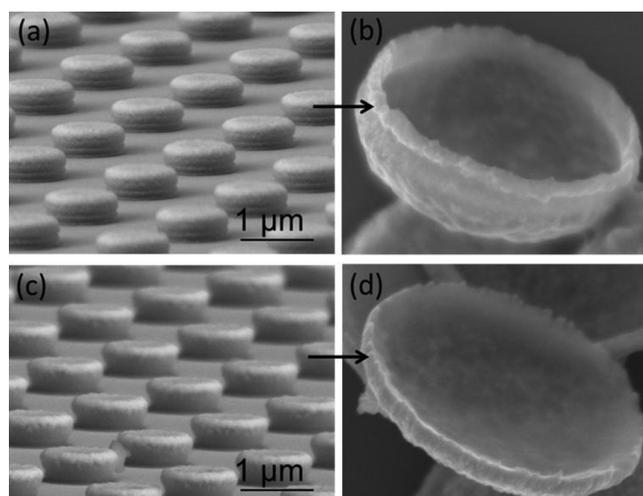


Figure 1. Scanning electron microscopy (SEM) micrographs of 1- μm -diameter magnetic disks on the patterned photoresist after deposition by (a) magnetron sputtering and (c) electron beam deposition. Panels (b) and (d) show the corresponding single disks after lift-off. E-beam deposition eliminates the formation of side walls and yields disks with the as-designed aspect ratio.

Scaling down the diameter of magnetic disks from $\sim 1 \mu\text{m}$ to $\sim 300 \text{ nm}$

We successfully reduced the size of the magnetic disks to 300 nm by using advanced extreme UV interference lithography. Figure 2 (top) shows the image of the disks on the substrate and after lift-off when the photoresist was dissolved (inset). Note that scaling down the diameter of the disks requires the reduction of their thickness to preserve the spin-vortex ground state. Here, the thickness of the disks was 20 nm. Furthermore, we also optimized the lift-off process, which could otherwise lead to disk deformation. The magnetic hysteresis loops measured with a superconducting quantum interference device (SQUID) confirmed the magnetization reversal via nucleation and annihilation of magnetic vortices (Figure 2, bottom). Thus, we demonstrated scalability of the magnetic vortex disk concept down to nanosize dimensions.

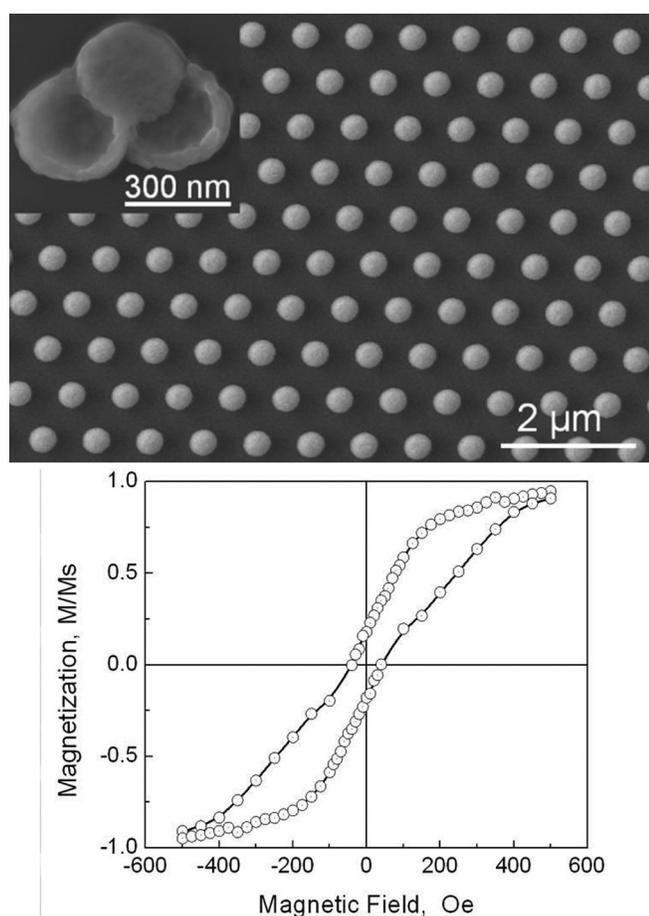


Figure 2. (top) SEM micrograph of 300-nm-diameter magnetic disks before lift-off. The inset shows disks after release from the substrate. (bottom) SQUID hysteresis loop measured for 300-nm-diameter 20-nm-thick Permalloy disk array.

Increasing accessible modulation frequency of magnetic field

To improve the efficacy of magnetomechanical cancer cell destruction, it is necessary to gain better control over the dynamic behavior of the magnetic disks. As a further step beyond the initial studies, in which a single magnetic field

was applied to induce the oscillation of the magnetic disks, we implemented a dual-field approach wherein the disks were controlled by two orthogonal magnetic fields. Modulation of transmitted light intensity was utilized as a measure of the orientation of the disks relative to the illuminating light beam. Figure 3 shows the frequency response curves obtained. For the single-field-driven modulation, the cutoff frequency was about 60 Hz, which is limited by thermal relaxation of the magnetic disks [Figure 3, curve (a)]. Employing the second field, which aligns the disks perpendicular to the light beam, leads to tremendous broadening of the modulation frequency range, up to 1 kHz [Figure 3, curve (b)]. This result is of great importance for further improvement of the magnetomechanical cell actuation efficacy at higher frequencies.

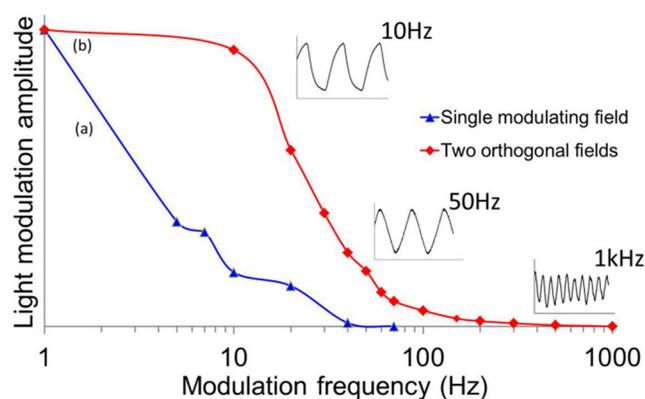


Figure 3. Normalized frequency-dependent light modulation amplitude for (a) single modulating magnetic field and (b) two orthogonal magnetic fields. Addition of the second magnetic field results in significant broadening of the frequency modulation range. The inset graphs demonstrate the shape of the light intensity signal at different modulation frequencies for this configuration of the magnetic fields.

Proposed Work for FY 2012

During FY 2012, we will focus on mechanistic studies of magnetomechanically induced cellular apoptosis. First, the role of mitochondria (the cellular “power plants”), as one of the key intracellular organelles involved in apoptosis, will be assessed. Second, we will analyze the nuclear DNA (chromatin) structure in cells subjected to magneto-mechanical stimulation by using acridine orange and ethidium bromide staining, which allows for detailed time-dependent assessment of apoptosis progression.

To elucidate the mechanism of magnetomechanically induced signal transduction, we will investigate the major pathways of calcium-mediated signaling. By selectively inhibiting the calcium ion channels and mechanosensitive receptors, we will evaluate their role in magnetomechanical stimulation of the cell membrane. At the same time, we are planning to broaden this study by looking at the adenosine triphosphate-dependent purinergic receptors, which are known to be responsible for transduction of calcium signals in glial cells.

Furthermore, we will apply additional advanced methods allowing simultaneous assessment of multiple cellular responses: for example, using surface-enhanced Raman spectroscopy, we will study the modulations of Raman signals from the cell membrane by placing cells on a glass substrate with gold nanoparticles attached to it.

Seminars

Ulasov, I., B. Lai, V. Rose, N. Dimitrijevic, D.H. Kim, J. Maser, M.S. Lesniak, S. Bader, V. Novosad and T. Rajh (2011). "Nano-bio Hybrid Materials as Tools for Intramolecular Signal Transduction." Pacifichem 2010, Honolulu, HI, Dec. 15–20, 2010.

Development of Wireless Data and Power Transfer Techniques for Large Instrumentation Systems

2011-153-NO

Zelimir Djurcic, Michelangelo D'Agostino, Patrick De Lurgio, Gary Drake, Maury Goodman, and Jonathan Paley

Project Description

The objective of this project is to develop new wireless techniques and technologies for use in large detector and instrumentation systems. The motivation comes primarily from particle physics research, where the size and complexity of the detectors have become very large. For these experiments, there is generally a premium placed on the front-end electronics in terms of power and mass. Thus, the data acquisition system and power supplies are usually off-detector. This means that there is infrastructure associated with running data cables and power cables from remote locations to the detector. In high energy physics, detectors often have thousands or millions of channels, and this infrastructure has become substantial. With the advent of commercial low-power mobile devices, integrated wireless technologies, and local area networks, the use of wireless techniques is now viable for large instrumentation systems. Wireless data transmission combined with wireless power transmission would be revolutionary for particle physics experiments and other large instrumentation systems as well. The purpose of this R&D is to develop new techniques for wireless data transmission and wireless power transmission.

Mission Relevance

This project will contribute directly to DOE's basic science mission through the development of enabling technology specifically applicable to measurements in high energy physics. The objective of this project is to develop wireless techniques to read out detector systems with large numbers of channels. The goal is to design a practical, relatively low-cost, and reli-

able system that reduces the complexity of such systems. The simplification of the infrastructure by the use of wireless techniques would also benefit detectors requiring increased mobility or decreased mass.

The development effort here is focused on phototube-based detectors, although the techniques developed here should be applicable to other large readout systems.

FY 2011 Results and Accomplishments

In FY 2011, we actively worked on the wireless system design, which included mobile/cellular technologies (GPRS, UMTS, CDMA/EVDO Rev.A, WiMAX, LTE, etc.) and wireless local area network (WLAN) technologies (802.11x, Bluetooth, Zigbee, etc.). Of the various WLAN technologies, 802.11x, and specifically 802.11n, offered the highest data throughput and sufficient range for this application.

The ubiquity of wireless hardware components makes this technology an optimal option. The greater data throughput of 802.11n will be sufficient to achieve the total data throughput of a small detector. However, to achieve the total data throughput of a very large detector requires a modification to the standard implementation. Our approach was to use a custom but compliant implementation of 802.11n wireless technology that will facilitate achieving the data rate necessary for larger detectors. The core of the current scheme is an ultra-low-power dual-band 802.11n module built by connectBlue. The connectBlue module uses a custom chipset from Redpine Signals, the RS9110-N-11-03. The development effort planned thus far will utilize these technologies.

The design consists of a charge-sensitive amplifier, shaping amplifier, and constant fraction discriminator for timing and triggering. The field programmable gate array (FPGA) is used to interface to an ADC (analog-to-digital converter), a DAC (digital-to-analog converter), two RAM chips for alternating read/write operations, and the 802.11n wireless radio. For a number of technical reasons, an FPGA is the preferred interface chip. The initial design used a Xilinx FPGA, although the technology is being migrated to an Actel Igloo FPGA, which uses very little power dynamically and allows for advanced "sleep" modes called "Flash Freeze" to significantly reduce power.

The module and firmware are currently under development, with the initial design cycle to be completed by the end of calendar year 2011. Subsequent to the initial development phase, several test modules will be produced. With multiple modules and multiple access points, the data throughput parameter space of large instrumentation systems will be explored.

Proposed Work for FY 2012

The initial goal is to complete the wireless data transfer module described above. Then the focus will be on implementing wireless power transmission. There will be no cables connected to the photomultiplier tubes (PMTs). There are two significant challenges in this implementation: power transmission and local energy storage, the latter of which has implications for low-power electronics. Through careful design and device selection in the first two stages, we hope to incorporate low-power electronics at the outset. Advances in FPGAs and low-voltage CMOS (Complementary Metal-Oxide Semiconductor) components over the past decade offer opportunities to develop a highly integrated system with a large dynamic range and low power consumption at the front end. Also, the front-end electronics must now incorporate a low-voltage-to-high-voltage energy conversion device, such as a Cockcroft-Walton voltage multiplier, to replace the high-voltage cable for biasing the PMTs.

We will test two options for wireless power transfer. The first is to transmit power wirelessly over a distance by using an infrared laser that is received by a high-efficiency diode for electrical conversion. The second technique is to transmit high-power radio frequency in free space or, ideally, inside a waveguide.

Ultra-Small Nanoparticles: A New Opportunity for Discovery of Catalytic Materials for Energy

2011-193-NO

Stefan Vajda, Larry Curtiss, Jeffrey Greeley, Michael Pellin, Subramanian Sankaranarayanan, and Randall Winans

Project Description

The goal of this project is to identify new catalytic materials in the intriguing, but not yet explored, 1–3-nm size regime by identifying controlled assembly strategies that inherently combine the advantages of the high activity and selectivity of sub-nanometer-size building blocks. The primary challenges that must be overcome to meet this goal include the following: (1) develop a full understanding, through theory and experiment, of the novel catalytic properties of ultra-small nanoparticles (USNPs) of the form $(A_n)_m$, created from small clusters A_n ; (2) find treatment conditions to control the assembly process toward the formation of desired two- and three-dimensional ultra-small architectures; and (3) design and test USNPs with powerful new catalytic properties.

Mission Relevance

This project is relevant to DOE's basic science mission as it is related to DOE's energy mission. Catalysis has clearly reemerged as a centerpiece in 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, as well as the development of future alternative fuels and new materials for energy storage, will increase the importance of catalyst discovery. Some of the reactions studied are also relevant for the Air Force Office of Scientific Research, namely, the low-temperature activation of jet fuels.

FY 2011 Results and Accomplishments

1. Experimental Results

Assembly and characterization of nanometer-size silver USNPs made of size-selected sub-nanometer clusters.

The formation of nanosized silver aggregates made of Ag_3 and Ag_{15-19} clusters on UNCD (ultrananocrystalline diamond) and alumina supports, respectively, was studied. Ag_3 clusters were deposited on UNCD film with the goal of investigating the role of support in the aggregation process. *In situ* grazing incidence small angle scattering technique (GISAXS) at 12-ID-B&C of the Advanced Photon Source was used to monitor the change in particle size and shape in the course of the aggregation/assembly process. During the heat treatment, the formation of targeted ~ 3.5 -nm-size $(Ag_3)_m$ aggregates was achieved and the resulting USNPs were found to be sintering resistant at temperatures as high as 500°C. The data demonstrate the effect of the chemical composition and morphology of the support material (oxide vs. carbon-based) on the final shape of the particles formed from identical Ag_3 precursors: ~ 3.5 -nm-size hemispheres on alumina and ~ 3.6 -nm spheres on UNCD. Deposition of Ag_{15-19} on alumina also yielded ~ 3.5 -nm hemispheres. Preliminary analysis of part of the reactivity data does indicate that the oxide support may play a central role in activating oxygen molecules at the cluster/support interface.

Assembly and characterization of cobalt-based USNPs made of size-selected sub-nanometer clusters.

While supported cobalt clusters were found to be very stable on most of the surfaces used, reversible structural changes of highly reactive $Co_{27}O_x$ -based aggregates were observed in magnesia (MgO)-supported 27-atom cobalt clusters during the dehydrogenation of cyclohexene (see Figure 1). At the highest point of reactivity, the sub-nanometer 27-atom clusters form a ~ 2.5 -nm-size USNP. When the reaction is over, this USNP disintegrates. To the best of our knowledge, this is the first study that reveals such assembly/disintegration of a functioning nanostructure made of uniform building blocks.

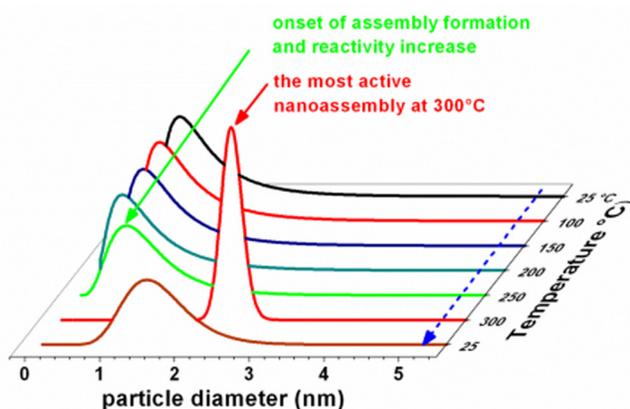


Figure 1. Dynamic formation and disintegration of a USNP nanostructure upon turning the reaction on and off, respectively, shown as the evolution of USNP particle/nanoassembly size distribution of the magnesia-supported clusters during the reaction with cyclohexene (0.39 %) and oxygen (3.90 %) in helium at total pressure of 800 torr. The vertical axis shows, in arbitrary units, the relative fraction of the particles at given particle diameter.

2. Results from Theory and Modeling

Size-dependent catalytic propensities of silver cluster building blocks and USNPs assembled from them.

We carried out density functional theory calculations of oxygen molecule dissociation on Ag_{19} and Ag_{20} clusters as models for USNPs and found them both to be about 1 eV exothermic. The magnetic moment of Ag_{19} clusters significantly reduces the activation energy barrier of oxygen dissociation by more than 1 eV compared to Ag_{20} ; this finding underlines the variation in cluster activity when the size of the cluster is changed by a single (!) atom.

This result is further substantiated by calculations on a 377-atom silver cluster, which is the size of the silver aggregates studied experimentally. Results support the previously made argument that a higher spin state structure in Ag_{377} contributes to higher activity of these clusters. These theoretically obtained results on cluster reactivities are consistent with the propylene epoxidation reaction being favorable on silver USNPs, as found experimentally.

Studies of supported Co_xO_y USNP aggregates.

To perform detailed studies of the reactivity of cobalt USNP aggregates, it is necessary to determine the geometry of the cluster precursors first. We investigated a Co_{27} cluster and optimized several geometries to determine if there is a strong preference for either crystalline-type geometry or one that maximizes the number of cobalt-cobalt bonds. The complex catalytic process can be controlled by the local geometries, electronic states, the magnetic moment, or other properties of the system. It is therefore necessary to develop accurate quantum chemical models to understand and optimize reac-

tivity. For the alumina-supported Co_{27} cluster (Figure 2), this is a challenging endeavor, now in progress.

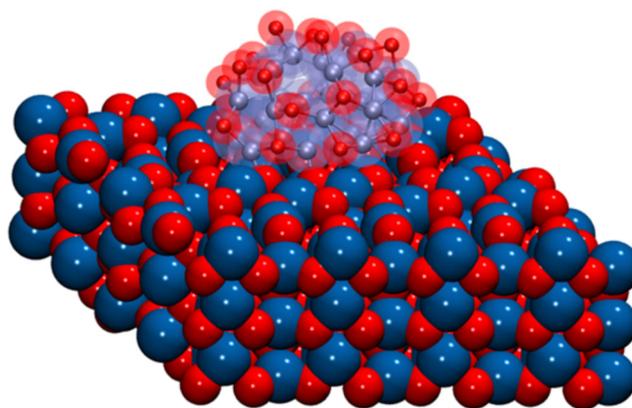


Figure 2. Model of a $\text{Co}_{27}\text{O}_{20}$ nanoparticle on an $\text{Al}_{192}\text{O}_{288}$ alumina surface. Oxygen and aluminum atoms of the alumina surface are shown as large red and large blue spheres, respectively. Oxygen and cobalt atoms in the $\text{Co}_{27}\text{O}_{20}$ nanoparticle shown as small red and small blue spheres, respectively.

Proposed Work for FY 2012

- ▶ Complete studies of catalytic properties of silver USNPs for oxygen addition.
- ▶ Perform experimental studies of gold and cobalt USNPs, including dependence on the size of the sub-nanometer-cluster building blocks.
- ▶ Perform theoretical studies of the growth and structure of gold and cobalt USNPs and initiate studies of potential catalytic properties.

Seminars

Vajda, S. (2011). "Catalysis by Small Clusters and Nanoparticles." INEOS, Naperville, IL, Feb. 15, 2011.

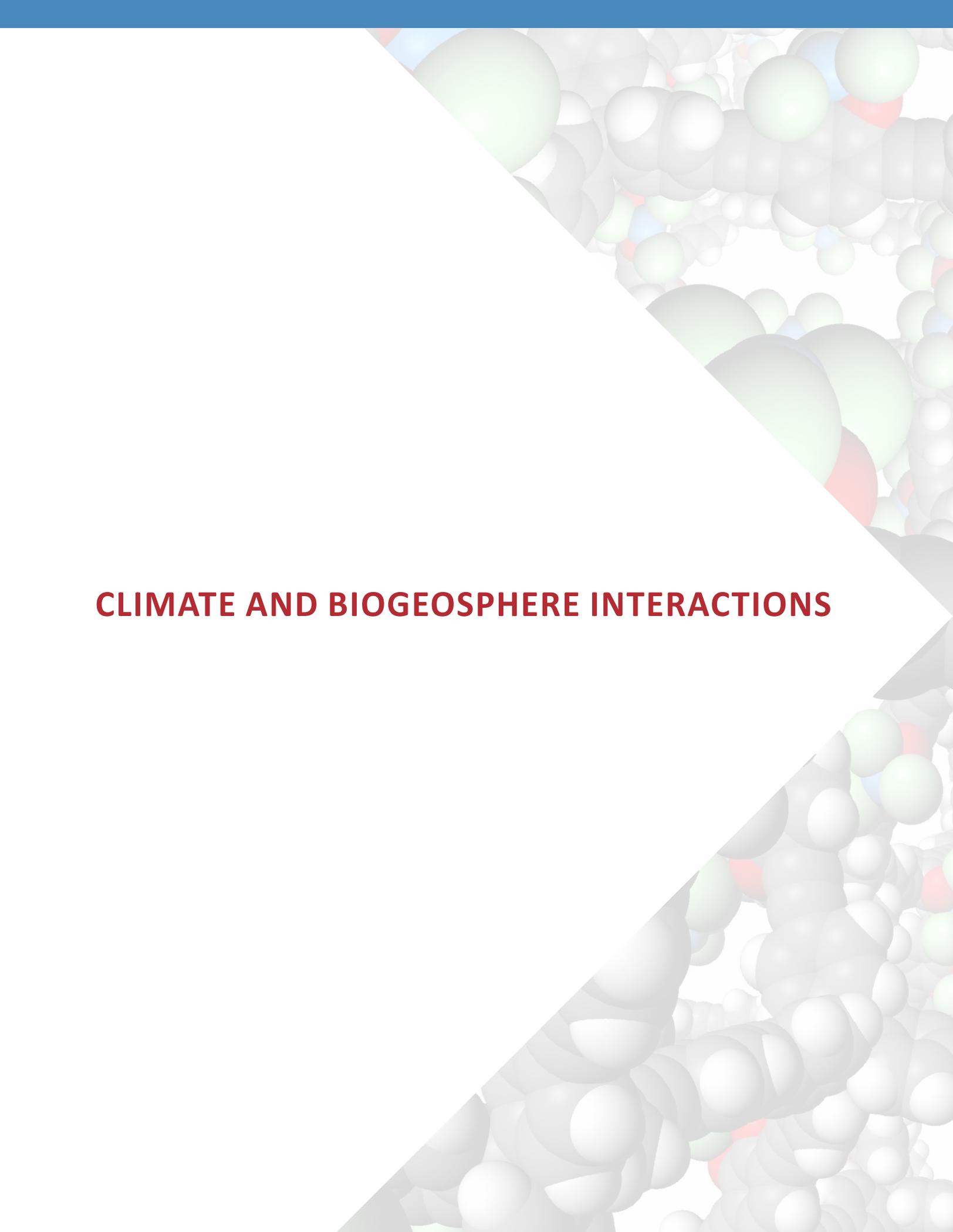
Vajda, S. (2011). "Catalysis by Small Clusters and Nanoparticles." Colloquium - Penn State Univ., State College, PA, Jan. 20, 2011.

Vajda, S. (2011). "Catalysis by Small Clusters and Nanoparticles Under Realistic Reaction Conditions: I. Bridging the Subnanometer to Nanometer Size Range and II. Coupling the Studies of Model and Practical Catalysts." Department of Chemical Engineering Colloquium, Universitat Rostock, Germany, Dec. 15, 2010.

Vajda, S. (2011). "Catalysis by Small Clusters and Nanoparticles." Colloquium - Technische Universitat, Munchen, Germany, Dec. 13, 2010.

Vajda, S. (2011). "Catalysts Designed at the Subnanometer to the Nanometer Scale for Bond-selective Reactions: Bridging the Size Gap and Coupling Studies of Model, and Practical Catalysts." Colloquium - Karlsruhe Inst. Tech. and Universitat Karlsruhe, Karlsruhe, Germany, Dec. 3, 2010.

Winans, R.E., S. Lee, B. Lee, S. Seifert, S. Vajda, L. Curtiss, J. Elam and M.J. Pellin (2011). "Insitu Studies of Nano Catalytic Reactions Using X-ray Techniques." CNM/APS Workshop: Chemically Synthesized Nanoparticles for Catalysis, Argonne National Laboratory, IL, May 2-5, 2011.



CLIMATE AND BIOGEOSPHERE INTERACTIONS

Metagenomics-Enabled Discovery of Protein Function

2009-156-R2

Elizabeth Glass, Christopher Henry, Folker Meyer, and Rick Stevens

Project Description

New technology for DNA sequencing (454 Pyrosequencer) has enabled the discovery of the “DNA world” surrounding us and contributed significantly to our understanding of the environment we live in. Previously, individual genomes were sequenced by large teams of researchers, but recently, because the cost of sequencing has been decreasing, small groups have been doing it. This situation has allowed more researchers to study complex communities of microbes in environments as diverse as marine sediment, soil, and human mucosal tissue. The aim of these studies is to dramatically expand our understanding of the microbial biosphere and, more importantly, to reveal the secrets of the complex symbiotic relationships found in various environments. A prerequisite for such discoveries is computational tools that can rapidly and accurately compare large data sets generated from complex bacterial communities; researchers need them to identify the features that distinguish those communities.

Hundreds of metagenomes have already been sequenced. To play a leading role in analyzing these metagenomic data sets, a joint Argonne/UChicago team for metagenome analysis created a version of the National Institutes of Health (NIH) National Microbial Pathogen Database Resource-funded RAST server (called MG-RAST). Designed to meet the growing demand for comparative analyses, the goals are to:

- ▶ Extend metabolic reconstruction for metagenomes,
- ▶ Develop tools for metagenome analysis,
- ▶ Couple high-performance computing (HPC) resources to the front end of existing metagenomic analysis, and
- ▶ Improve the user front end.

Mission Relevance

Researchers must identify and define the characteristics of microbial communities in the biosphere in order to understand their contributions to various ecological systems. Since not much is known about microbial communities, the potential for discovery is great for any habitat that is chosen for study. Areas relevant to DOE missions include the following:

- ▶ *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 will be more

economical, environmentally sustainable, and resilient in the face of disruption by world events.

- ▶ *Bioremediation.* The development of tools to monitor environmental damage at various levels and methods to restore the health of an ecosystem.

Other federal agencies would also benefit from the proposed work. For example, NIH’s Human Microbiome Project is sponsoring work that explores and analyzes microbial communities of human mucosal tissue in order to advance research on human health and disease. The U.S. Department of Homeland Security and U.S. Department of Defense would probably use technology that would help unveil microbial community dynamics.

FY 2011 Results and Accomplishments

Results and accomplishments from previous years are summarized below.

- ▶ We developed a new visualization tool that allows MG-RAST users to compare metagenomes on a tree. Users can then analyze the variations of relative abundance of specific genes or metabolic pathways in various organisms.
- ▶ MG-RAST contains metabolic “heat maps” that enable users to compare the results of metagenome analysis (metabolic and phylogeny) with those of other metagenomes. Users are therefore able to compare the prevalence (relative abundance) of different subsystems or taxonomies in different samples. The functionality of this tool was also expanded to allow users to compare various levels of metabolism and virulence subsystems. This provides the user with various comparative views in which to compare metagenomic samples. In addition, the heat maps allow more flexibility in inclusion/exclusion of genes based on similarity scores.
- ▶ The recruitment plot, which compares the functional roles of the genome to a given microbial genome, was expanded to include BLAST hits and alignments. Users are therefore able to evaluate overall similarities between the community and an organism, as well as on the gene level.

Extended user interface and comparative analysis tools. We added new statistical tools for single and multiple metagenome comparisons and metabolic map comparisons. We established this framework to enable comparisons of large-scale sequences (i.e., to identify sequences that are unique to a given sample or community and those that are shared). For example, by comparing metagenomes of hot springs microbial mats, users can view differences in the abundance of protein functional classes and then find the differences between two similar data sets. By using exported tables with functional annotations and taxonomic mapping, they can also analyze the distribution of organisms that play a given functional role

and plot the abundance per species. We extended analysis tools for single metagenomes and for comparative analysis so users could alter their parameters for interactive analysis. We developed new search and browsing capabilities, and created web modules that allow users to browse by metadata and project information.

Interfaced with HPC. As high-throughput sequencing has become more prevalent, the bottleneck in metagenomics has moved from generating data to analyzing data. We leveraged the cloud-based HPC resource and workflow engine AWE (Argonne Work Engine) to enable large-scale metagenomic comparisons and thus the identification of novel proteins or signature proteins for a given biome. By September 2011, more than 25,000 metagenomes (~5 TB) were submitted to the MG-RAST annotation server by users from 50 countries or territories. To deal with the deluge of sequence data being produced, such a connection to scalable computing resources was vital.

If future funding is acquired, we propose to provide an analysis pipeline for large-scale comparisons of multiple metagenomic data sets to perform systematic mining for novel proteins. Our approach will also include supporting the building of “cross-contigs” (i.e., the systematic comparison of unassembled fragment abundance across a large number of metagenomes) in order to identify DNA fragments that can be linked to specific environments or biological processes. The identified sequences will then be functionally characterized. For fragments with no similarity to the sequence space, we will incorporate a tool to develop primers that researchers can use to investigate these unknown proteins experimentally.

Combinatorial Deletions to Produce a Minimal Strain of *Bacillus subtilis*

2009-171-R2

Rick Stevens, Christopher Henry, Liz Marland, and Folker Meyer

Project Description

Essentiality studies suggest that the number of genes required to synthesize the proteins needed for an organism to be viable under controlled laboratory conditions is around 300–800, which is far fewer than the number typically encoded in microbial genomes (e.g., *B. subtilis* with 4,105 open reading frames). Although some naturally occurring microbial genomes do encode less than 800 genes, they exist in host-dependent environments and are not 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 are there only to make the organism adaptable and flexible and could be deleted without affecting their viability under controlled laboratory conditions. In fact, deletion of nonessential proteins might enhance the organism by reducing metabolic burden and removing regulatory controls on growth rates.

This project’s objective is to explore gene dispensability by constructing a minimal strain of *B. subtilis*. We are constructing it 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 we are using to predict the outcome of combinations being performed experimentally. Successful model predictions help explain why certain deletion combinations result in unviable strains; unsuccessful model predictions help elucidate portions of the cellular machinery in *B. subtilis* that are not well understood. This work will produce both a minimal strain of *B. subtilis* and an accurate computational model of it.

Mission Relevance

This project supports DOE’s mission through innovations in science and technology. The simplified strains of *B. subtilis* we produce will help 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 in efforts to engineer an organism so it secretes a product or degrades a toxin. Ultimately, we will produce a viable minimal strain of *B. subtilis*, providing an ideal system for testing metabolic engineering theoretical tools and developing methodologies for systems biology. We now know how to reliably design knockouts (i.e., interval deletions), what combinations of knockouts to avoid, and how to accurately predict the outcome of knockouts. These insights are directly applicable to enhancing our ability to engineer microbes to produce biofuels, cleanse the environment, and fix CO₂.

FY 2011 Results and Accomplishments

FY 2010 experimental efforts focused entirely on combining interval deletions to continue the reduction of our reduced *B. subtilis* strains. We built on the 256 combinations attempted in FY 2009 with an additional 94, 80 of which were successful. Because our combinations began with the largest intervals first, we experienced diminishing returns in reducing the *B. subtilis* genome with each combination. To overcome this problem, we began splitting the large intervals that could not previously be combined into our reduced strain, and we then combined split subinterval knockouts into the reduced strains. We successfully applied this strategy with two previously uncombinable interval deletions. In total, we produced four reduced strains of *B. subtilis*.

In FY 2011, we continued applying phenotype data observed from our mutant strains to correct and improve our *iBsu1103* genome-scale metabolic model of *B. subtilis* 168. Initially, our model was successful when predicting conditions under which strains would be viable (96% accurate) but often failed when predicting conditions under which viability was lost (36% accurate). We systematically analyzed the model to identify what caused the prediction errors and corrected them to produce the new *iBsu1103V2* model. It predicted deletion mutant viability with an accuracy of 99% for conditions under which strains were viable, 71% for conditions where strains were not viable, and 95% overall. False positive predictions remain for 14 deletion strains, 9 (64%) of which we can attribute to non-metabolic phenomena that cannot be simply captured within a steady-state metabolic model.

When a false positive prediction error was corrected in the model, or when the model properly predicted unviable strains in the first place, these corrections and predictions came bundled with a model-generated hypothesis about why the deletion mutant is not viable (e.g., the strain is not viable in nitrate mineral salts (NMS) because the strain lacks heme biosynthesis pathways, and NMS does not contain heme). In these cases, we applied the model to identify compounds that could restore strain viability if added to the growth media (e.g., add heme to NMS to restore viability when heme biosynthesis is lacking). We then verified the viability hypotheses experimentally by supplementing the media with the proposed metabolites (when commercially available) and testing for the growth of deletion mutants. When the model was adjusted to correct false positive predictions, this experimental validation was useful for confirming that these changes were correct. When we applied this approach to the 42 mutants found to be unviable on at least one of our tested media conditions, our refined model correctly identified rescue metabolites for 32 mutants, confirming our understanding of the metabolic pathways responsible for the loss of viability of these strains. Most vitally, these results serve to validate changes made to the metabolic model to improve accuracy.

Finally, we constructed a strain database and strain management system. The system became invaluable for tracking all strains created and for managing all phenotype data and predictions from multiple versions of our model.

Characterization of Microbial Community Dynamics

2009-186-R2

Dionysios A. Antonopoulos, Carol S. Giometti, Ken Kemner, and Folker Meyer

Project Description

In this project, we focus on the dynamic consortia of microbial populations that are involved in the biogeochemical cycling of elements in natural subsurface and terrestrial environments. The dynamics of microbial populations have traditionally been followed across space and time by inventorying the variation and relative abundance of a single, highly conserved gene marker, which acts as a proxy for the populations and metabolisms that are present. (An example is the gene that encodes the 16S ribosomal RNA [rRNA] molecule, a crucial component of protein translation in all microorganisms.) Now, 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 through the adoption of “shotgun” metagenomics. The metagenome of a sample represents the totality of all the genes that are present (and thus, essentially, its metabolic potential).

Current efforts focus on reducing the sequence “search space” for functional genes that bestow unique properties on one microbial community versus another by sequencing the community’s metatranscriptome — the genes actively expressed by the microbial community in total. We seek to identify the genetic and metabolic potential of microbial communities and establish how functions are partitioned in and between microbial populations. Some questions we aim to answer are:

- ▶ What genes are expressed by microbial communities after a step change in temperature?
- ▶ How does gene expression change after acclimation to a change in temperature?
- ▶ Does a shift in community composition lead to changes in community gene expression under constant conditions?

Mission Relevance

This project is relevant to DOE’s missions in environmental quality and basic science. The current sequencing effort builds on 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. This project complements these efforts by studying 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 data sets for the functional genes involved, as well as for novel gene discovery.

FY 2011 Results and Accomplishments

By coupling next-generation DNA sequencing technologies with messenger RNA (mRNA) enrichment from soils, we are measuring the gene expression of soil microbial communities in response to environmental change. This work has involved a multistage process, including the development of novel procedures and an experimental protocol. In FY 2009, a procedure was established to extract whole nucleic acid from environmental samples, remove DNA, and effectively subtract rRNA, thereby enriching the mRNA from these microbial communities. In FY 2010, this work was supplemented by improving the yields and enrichment of mRNA and refining work flows for constructing a metatranscriptome library for next-generation DNA sequencing platforms (including both 454 and Illumina). In FY 2011, benchtop topsoil incubation experiments tested the effects of global environmental parameters (moisture and temperature) on microbial community response.

The experimental setup was designed to acquire samples, conduct replicate sampling, and monitor CO₂ emissions. The microbial community in the soil will emit CO₂ and other gases as a by-product of their metabolism that can be measured with an infrared gas analyzer (IRGA). In our laboratory incubation, warmer conditions (25°C) induced a three- to fivefold increase in soil respiration compared to cool, baseline conditions (4°C), indicating that there is a substantial increase in microbial activity with a shift to a higher temperature. Monitoring these functions over time allows us to map the genes being expressed to these functions. By comparing the responses of these microbial communities in different environmental conditions, we can identify the organisms and, specifically, the genes that respond to these conditions (including ones previously not described).

Development of a High-Throughput Approach to Soil Physical and Chemical Characterization in Tandem with Soil Metagenome Analysis

2010-119-R1

R. Michael Miller, Julie Jastrow, Roser Matamala, and Folker Meyer

Project Description

Recently, we demonstrated that using a subsystem approach to soil metagenomics offers possibilities for understanding soil

metabolic processes at a continental scale. We used the subsystem classification of MG-RAST [metagenomic RAST Server (<http://metagenomics.nmpdr.org>)] to identify distinct metabolic clusters in soils on the basis of 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 the soil's organic residues and other factors (e.g., soil texture, pH, and base cations) are major drivers. They also suggest that a more refined measure of the soil's organic substrate composition is needed to better identify the drivers that influence the soil metagenome subsystem. Therefore, a characterization of the chemistry of soil fractions could provide critical information about the quality of SOM (soil organic matter) pools with various turnover times, which could, in turn, help elucidate the mechanisms controlling SOM cycling. We have recently found that much more information can be gained by using mid-infrared (mid-IR) spectroscopy, since it can characterize the quality of soil (i.e., mineral and organic matter composition, as well as its decomposability) with regard to its potential for high throughput.

What differentiates this study from the few studies that have been conducted on soils using mid-IR is our intent to identify the appropriate scale that a soil trait integrates with the MG-RAST soil metagenome metabolic subsystems. Although mid-IR spectroscopy has the potential as a means for high throughput soil analysis, its true potential is with the information contained within the spectra on soil organic matter and mineral content quality. Incorporation of such spectral information with soil metagenomic data should allow for a greater understanding of those factors that drive microbial community composition.

Even though mineral content and soil organic matter are the known primary soil components that drive the spectral quality within the mid-IR region, the science is still in a phase where structural assignments based on organic matter quality is in an annotation phase. Ideally, by using mid-IR spectroscopy it should be possible to characterize soil organic matter in a manner that has potential for identifying those organic matter compounds that influence microbial composition and especially the metabolic profiles that they represent.

The overall aims of this study are therefore to develop a soil diffuse reflectance spectral library by using Fermilab legacy and National Ecological Observatory Network (NEON) soil samples, derive soil spectral calibrations for predicting soil properties with their uncertainties, and assess the accuracy of the predictions and populate the legacy soil samples with good-quality information. A secondary goal is to integrate the spectral information with that from the metagenomic analysis of soils, focusing on the NEON soil samples.

Mission Relevance

This project is relevant to DOE's missions in science and the environment. One of DOE's primary missions is to anticipate the environmental consequences of energy use. In the area of climate change research, a major goal is to understand carbon cycling. Because soils are the largest reservoir of carbon (due to the vast amount of carbon sequestered in soil organic matter), there is a need to better quantify carbon stocks, including their vulnerability to such factors as climate change and land-use. Similarly, there is a need to determine what form the carbon is in and its subsequent vulnerability to microbial activity.

FY 2011 Results and Accomplishments

In FY 2010 we developed a series of protocols that allowed us to evaluate various sample preparation approaches with a goal of improving mid-IR spectral quality at both the local and landscape scales. The difficulty encountered in achieving good mid-IR spectra for soils was brought about by soil carbon contents that ranged from less than 1.0% to over 45% soil carbon content of the soil. Also, the rather large spatial gradient encompassing the location of the NEON sites, these soils represented a range of biomes having differences in parent material, topography, and climate.

In FY 2011, a total of 119 soil samples were characterized by mid-IR spectroscopy for their mineral and organic matter quality; each soil sample was run 20 times by diluting soil with KBr (transparent to the IR spectrum) versus 20 times with a mirror background, for a total of 4,760 runs. The samples were primarily from two sources: NEON (National Ecological Observatory Network) and the Fermi National Environmental Research Park located at Fermilab. The NEON soils were placed in a partial least square (PLS) training set to determine the percent of carbon in the samples. Several parameters were varied to determine the best prediction model. The mid-IR spectral regions that hold most promise are the regions between 3,800–950 cm^{-1} . We also found that during analyses of the absorbance data that mean centering and baseline correction allowed for delineating those spectral regions that enabled separation of soils based on soil organic matter quality.

The mid-IR spectrum for individual NEON soils appeared to delineate the soils in a manner that correspond to their respective biomes of origin. A graph representing the absorption spectra for three characteristic soils demonstrates potential differences among these soils (Figure 1). The forest soil (TF-1) is characterized by a peak located around 1400 cm^{-1} , a region characteristic of aliphatic carbon compounds. The soils from the grassland (WF-2) and prairie (KP-1) sites also show a peak in this region. The three soils also show a peak in the 1626 cm^{-1} region, characteristic of aromatic-C (C=C bonds). What is interesting is the difference in peak heights for the three soils and may be an indicator of soil organic matter quality.

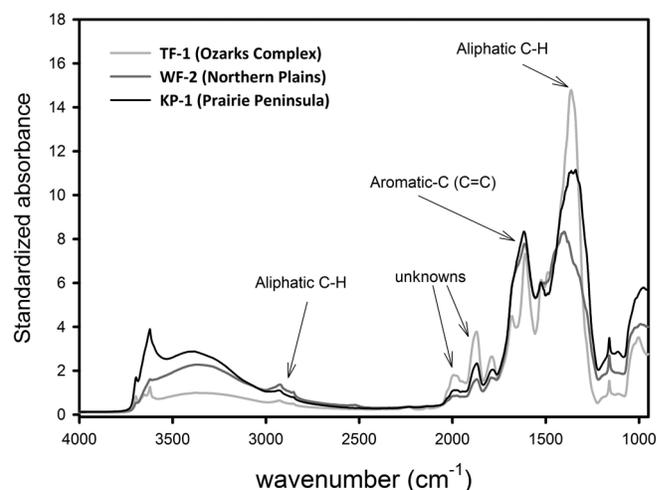


Figure 1. An example of soil absorbance differences using mid-IR. The three spectra graphed above are representative of forest (TF-1), grasslands of the Northern Plains (WF-2), and tallgrass prairie (KP-1). Primary differences among these soils are demonstrated by their relative peak heights in the Aliphatic-C peak regions at $\approx 1400 \text{ cm}^{-1}$ and the Aromatic-C peak regions at $\approx 1626 \text{ cm}^{-1}$.

We initiated a cooperative study with the U.S. Department of Agriculture's Agricultural Research Service (ARS) to take advantage of its expertise on developing spectral libraries for agro-nomic systems. Our goal is to understand soil organic matter dynamics in undisturbed soil profiles and, more specifically, to find ways that soil spectra can interact with soil metagenomic data sets. With researchers from ARS, we are now comparing and interpreting mid-IR spectra for soils obtained from permafrost areas. Thus far, it appears that a mid-IR approach could be a high-throughput approach for these soils. We are exploring various ways to conduct analyses, including using multivariate approaches for spectral analysis and for integrating such spectral information with data obtained from soil metagenomes by using the subsystems identified in MG-RAST.

Proposed Work for FY 2012

A primary goal is to determine if the question of whether calibrations beyond a field level can be useful is directly related to the basis on which soils can be selected for or included in a single calibration and determine whether finding the answer requires a great deal of further research (e.g., on analyte levels, textures, soil types, or combinations thereof). At the local scale, calibration appears to be achievable. Preliminary runs using the NEON samples and soils from Fermilab and elsewhere suggest larger calibrations are possible, provided soil carbon levels are not too low or high. Questions remain on the ability to calibrate at continental or global scales. However, preliminary analysis of spectra obtained from permafrost soils collected throughout Alaska suggest that a large continental gradient approach using mid-IR is achievable.

Accelerating the MG-RAST Metagenomics Pipeline

2010-131-R1

Narayan Desai, Ewing Lusk, and Folker Meyer

Project Description

MG-RAST is currently one of the premier metagenomics analysis platforms in the world, serving over 2500 users from organizations worldwide. On a daily basis, over 200 people use MG-RAST and spend a significant amount of time using its analysis tools. MG-RAST has analyzed over 6500 metagenomes, accounting for over 280 gigabase-pairs (Gbp) of data. A majority of the datasets range in size from 40 to 200 megabase-pairs (Mbp) each, though we have begun to see a large number of 2-Gbp jobs. Processing for these jobs takes 700 to 3000 CPU hours from start to completion. Current-generation high-throughput sequencer datasets were increasing in size to 200 Gbp as of the beginning of 2010. This explosive growth in data volume is rapidly creating a crisis in data analysis; sequencing technology is outpacing even Moore's law.

These datasets provide a key opportunity to understand the impact of bacterial communities on life, medicine, and the environment at unprecedented depth. Understanding the interactions, capabilities and structure of these communities are the strengths that have made MG-RAST a critical asset to microbial ecologists. Unfortunately, without infrastructure improvement, the current MG-RAST pipeline is unable to accept these new datasets. To support the continuing efforts of the metagenomics community in the United States and worldwide, the MG-RAST pipeline needs to be redesigned to handle large datasets, interface with exotic hardware, and have the necessary flexibility to adapt to the changing requirements of the research community. This project is directly targeted at these issues, improving the analysis performance of MG-RAST and offering new analytical tools.

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 insight into microbial communities highly relevant to issues of climate and bioenergy.

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 2011 Results and Accomplishments

Our highest initial technical priority in previous years was to increase the overall analysis throughput of MG-RAST. We quickly realized that our limiting factor was our accessibility to computational resources. MG-RAST was designed to run on a purpose-built computational infrastructure, where configuration could be tightly controlled. While this approach allowed a comfortable development experience, we were unable to grow this infrastructure to the scale necessary to satisfy the needs of MG-RAST users. This problem is frequently cited as a key motivating factor for the adoption of cloud computing technologies, so we began to investigate cloud computing, specifically as it pertains to bioinformatics.

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 metagenomic data analysis, based on 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.

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 the historical picture in genomics. Previously, computing costs were 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) project, we implemented the AWE (Argonne Workflow Engine) 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.

After the initial AWE was developed, a production-grade version of AWE was implemented. It now forms the primary infrastructure for the MG-RAST computational process. This improvement has greatly improved the scalability and throughput of MG-RAST. At the start of the project last year, MG-RAST had analyzed 60 GBP of data over the previous two years of operation. In the last year, MG-RAST has processed over 220 GBP of data. This rate is still increasing: recently, MG-RAST analyzed 30 GBP of data; this throughput is equivalent to a full year's analysis prior to the start of this work.

AWE also provided a portable infrastructure that enables rapid adoption of new platforms. This capability allowed MG-RAST to provide the first scientific results computed on Magellan, the DOW midrange cloud testbed, less than a day after the machine was first opened to friendly users.

In contrast to the initial dedicated system, MG-RAST can now efficiently utilize resources on the Fusion cluster, Argonne Leadership Computing Facility machines, and the PADS (Petascale Active Data Store) system in the ANL/UOC Computation Institute, as well as Magellan. AWE provides all of the infrastructure to run at large scale; we have run in production with upwards of 3200 commodity cores with excellent results.

Increased pipeline throughput provided by AWE was used to great effect in the NIH Human Microbiome Project (HMP), in the context of our efforts in the UH2 phase of the project. These capabilities were used to analyze a large volume of data that we would have been unable to analyze previously. These efforts were recognized by the HMP project management, and may result in a funded project as a part of the UH3 phase.

Proposed Work for FY 2012

In FY 2012, we will build highly scalable mechanisms for data access in support of large-scale computation. This system builds on the previous efforts in high-throughput metagenomics workflows. We will also begin to explore the use of data-mining techniques to extract high-abundance features from the large volume of uncharacterized sequence data contained in MG-RAST.

High-throughput Reconstruction of Metabolic Models for Organisms with Applications in Energy, Bioremediation, and Carbon Sequestration

2010-139-R1

Rick Stevens, Christopher 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 1000+ 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 comprising the main product of this research drive forward numerous DOE

objectives: 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 experimental 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 National Institutes of Health (NIH) 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, they will not be a one-time advancement but an enduring resource for the entire research community.

FY 2011 Results and Accomplishments

In FY 2010, we released a website for the automated reconstruction, optimization, and analysis of genome-scale metabolic models: <http://seed-viewer.theseed.org/models/>. Since the initial release of this site, it has been applied to construct over 7500 genome-scale metabolic models for over 1000 unique users. This resource has rapidly become the source of draft metabolic models for the scientific community worldwide. In total in FY 2010, we built models for over 1000 distinct organisms, including organisms of interest to the DOE (listed above). 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 for our model data, facilitating the distribution of model computations over the cloud as well as enabling users to access model data programmatically.

In FY 2011, we demonstrated the improved scalability of our Model SEED pipeline by applying it to construct 3500 new genome-scale metabolic models, effectively producing a model for every complete prokaryotic genome sequence available in 2011. This effort brought the total number of models available in the Model SEED to 11,000. To build our 3500 models, we developed infrastructure to run the Model SEED on the new Beagle supercomputer, now available at the Argonne/University of Chicago Computation Institute. To facilitate the process of validating these models, we gathered experimental data for numerous organisms. These include gene expression data for 29 genomes, including many genomes of interest to bioenergy. These data were integrated into our SQL database and made available for use over our web API. We analyzed these data to identify portions of the metabolic network that are universally active or inactive. We also gathered additional gene essentiality and biologic phenotype data for four genomes: *E. coli*, *B. subtilis*, *S. oneidensis*, and *C. difficile*. We applied our models to the analysis of these phenotypes and

used the results to correct model errors. We also constructed a database for these phenotype data, and we are working with experimental groups to enable them to contribute data directly to this database. We continued to improve our web-API tools, including a tool for applying the models to the simulation of gene expression experiments. We also improved our web interface, including pages to support the online curation of models and enabling the download of all model data in Excel format.

Proposed Work for FY 2012

In FY 2012, we will continue our efforts to construct new subsystems in the SEED (the annotation backend for our pipeline) that are specifically targeted at modeling the unique metabolic capabilities of our target organisms. This effort has been ongoing, focusing initially on catabolic pathways, CO₂ fixation, isoprene biosynthesis, and methanogenesis. We will also continue to mine literature for gene expression data and growth phenotype data relevant to our 144 target organisms. These data will be integrated into our database and used to validate and correct our models. In particular, we plan to integrate the extensive phenotype data being produced for five DOE organisms by the Arkin group at JBEI (Joint BioEnergy Institute).

We also plan to expand our modeling framework beyond single organisms to construct multi-organism community metabolic models. In these small community models, individual organisms are treated as compartments existing in a shared environment where these organisms may exchange nutrients with one another. Such models are essential for teasing out the possible interactions that can exist between various species present in a microbial community. We will apply these models to analyzing systems of interest for various DOE applications: cellulose degradation, metal reduction, bioremediation, biosolar energy, climate change, energy production, carbon sequestration, and soil sustainability.

Finally, we will develop new model optimization techniques aimed at identifying the reactions that must be added to enable any reaction associated with an annotated gene to function. This provides a mechanism to build truly complete models, identify missing functions in the annotation, and identify functions that are incorrectly annotated and have little support for their presence in the organism. This methodology can also be extended to improve our prediction of biomass compositions for models, an essential component involved in the prediction of the conditions when growth will and will not occur.

Acceleration of Cloud Microphysical Retrievals for Climate Models

2010-194-R1

Edwin Campos and Douglas Sisterson

Project Description

This 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.

New science, uncertainty quantification, and computational tools are needed to promote understanding of the central issues of climate change science. With a better understanding of the atmospheric processes that are relevant to climate, it is then possible to increase the fidelity and applicability of regional climate and biogeospheric simulations to levels that enable informed policy.

Toward a better understanding of the atmospheric processes that are relevant to climate, the general objectives are to: (1) adapt and enhance existing codes, developing new software for 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

The main deliverables of this research are multi-instrument data products representing key cloud processes. These products have the potential for reducing the time required for developing the sophisticated cloud modeling parameterizations needed to significantly improve climate models. Therefore, this research activity is relevant to key DOE missions related to the environment. It also aligns with the U.S. DOE Office of Science 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 2011 Results and Accomplishments

The computer codes that were developed analyze and retrieve geophysical variables needed for climate modeling and were previously used in the weather domain. In spite of differences in space and time scales, the commonality between climate and weather domains is that of atmospheric microphysical processes, which require further understanding before attempting a complete atmospheric numerical simulation. A microphysical process of particular importance corresponds to the role of air vertical velocity on the growth (or depletion) of cloud particles in ice and liquid phases.

To understand that process, original codes (previously used in Canada for the 2010 Winter Olympics) were adapted and modified for analysis and display of remote-sensing observations (weather radar, wind profiler, ceilometer, and radiometer) at Argonne, and new codes to ingest and analyze the corresponding instrument datasets from the Atmospheric Radiation Measurement (ARM) Program's Climate Research Facility (ACRF) continued to be implemented. Examples of these activities include the following:

- ▶ The G-band Vapor Radiometer at the ARM site in Barrow, Alaska: With the assistance of the instrument mentor (Dr. Maria Cadetdu), we were able to analyze the main statistical parameters and the retrieval representativeness of cloud liquid-water paths occurring during 2010 over the site.
- ▶ The STORMVEX experiment (where the ARM Mobile Facility 2 operated at Steamboat Springs, Colorado, this past winter): We were able to test our computer codes for the analysis of wind profiler radar observations.
- ▶ The MC3E experiment (this past spring at the ARM Southern Great Plains site, Oklahoma): Working with instrument mentors (R. Newsom and R. Coulter), we are integrating vertical air velocities estimated by scanning Doppler lidar and wind profiler radar.

In addition, theoretical work to understand how weather radar pulses propagate in the atmosphere is continuing. This is a fundamental issue for determining the optimal location of a new weather radar site (e.g., new deployments of the ARM mobile facilities) or for mapping radar observations in a regular model-like grid (data analysis of ARM weather radars at fixed sites). Over almost a decade, a numerical model to simulate radar beam propagation over mountain terrains has been built. This model is now able to run on Argonne's desktops and laptops, at two horizontal resolutions (~1 km and ~90 m), and is ready to be implemented on a faster computer (e.g., the Argonne LCRC [Laboratory Computing Resource Center] Fusion cluster).

Proposed Work for FY 2012

ARM datasets will be used to continue the development and analyses of multisensor cloud-microphysical retrievals for storm-scale models, and these will be transitioned toward climate models. We will employ microwave radiometer observations (in Alaska) to analyze the role of cloud processes in the climate dynamics of cold regions. Radar meteorology observations, particularly those by wind profiler radar (in Alaska, Oklahoma, Colorado, and Illinois), will be used to analyze cloud and precipitation impacts on climate dynamics. We will experiment on advanced visualizations of clouds and precipitation processes by using ACRF multi-sensor datasets.

Seminars

Campos, E. (2011). "Multi-scale Remote Sensing of the Atmosphere: Profiling." Invited Seminar, Department of Atmospheric Sciences, University of Illinois at Urbana-Champaign, IL, Jul. 13, 2011.

Campos, E. (2010). "Cloud Processes Over the 2010 Winter Olympic Venues as Analyzed from Combined Remote-Sensing Observations." Environmental Science Department, Brookhaven National Laboratory, Upton, NY, Sep. 29–30, 2010.

Simultaneous Ecological Assessment and Characterization of Novel Proteins from a Soil Microbial Community

2010-195-R1

Jack Gilbert

Project Description

Communities of microbial organisms play a major role in Earth's biogeochemical cycles. Until recently, however, studying those microbial communities presented major technical challenges, leaving us with a poor understanding of microbial systems. But with the advent of second-generation DNA sequencing technology, we can now study microbial systems *in situ* by sequencing their genomes (metagenomics) and by studying the gene expression in those communities (metatranscriptomics). Although 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 stems from our inability to identify proteins of identical function from metagenomic data alone. The need to identify those *isofunctional* proteins (and to study the overall diversity of proteins) has become much more acute — and yet more possible with advances in metagenomics.

To identify which proteins to focus on from the millions of targets, we must determine which are important in the ecosystem of choice. Therefore, next-generation sequencing needs to be applied to produce an ecologically relevant, statistically designed experiment — for example, the examination of a soil ecosystem. From such a study, the top 1,000 most relevant targets can be determined. 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. These data can then be fed back into the ecological data to determine the impact of

this information on our ability to interpret metagenomic and metatranscriptomic analyses.

Therefore, a key objective of this project is to determine what genes can produce more efficient proteins for these desired processes. We also want to help define how microbes exist in communities and how they interact with plant life. In soil ecosystems, these questions have direct relevance to rhizosphere and leaf-based community interactions and plant productivity, all of which are highly relevant for agriculture.

Mission Relevance

The genetic and protein information acquired during this study is of direct relevance to the DOE missions in renewable energy, environmental analysis, remediation, and basic science. This year, in the area of energy production, we have already seen the use of synthetic organisms that could have major ramifications for renewable energy from photo bioreactors. Environmental analysis and remediation will be improved by metagenomic and metatranscriptomic analyses, permitting exploration of environments for genes and proteins of interest. Identified targets could be used for remediation purposes, and characterization of different environments will have dramatic impacts on how we view, for example, uranium cycling in contaminated sites. Fundamentally, this research will produce a paradigm shift in microbial ecology and ecological theory by exploring microbial life from the microbes' perspective.

FY 2011 Results and Accomplishments

A major effort was implemented, with sample acquisition and sequencing analysis being conducted on samples from around the globe. The initiation of the first phase of the Earth Microbiome Project has already generated 16S rRNA and shotgun metagenomic data from more than 3,000 samples processed during FY 2011. We instigated collaborations to have an environmental, physical, chemical, and biological metadata acquisition pipeline for all these samples. Hence, we built a database of sequencing data and metadata against which we can start to screen for proteins of interest. An Illumina HiSeq2000 (SY-401-1001) and MiSeq (<http://www.illumina.com/systems/miseq.ilmn>) sequencing platform for appropriate sequence data generation are now in use in support of this project. Finally, we generated an analytical approach, predictive relative metabolic turnover (PRMT), to help interpret the protein function information in environmental contexts (Figure 1).

Proposed Work for FY 2012

Now that datasets are available that allow comparable and interpretable analysis of sequence data from thousands of environmental samples, the task for FY 2012 and FY 2013 is to explore the proteins found in these datasets that track with environmental gradients. This work will target 1,000 feasible protein structures for analysis.

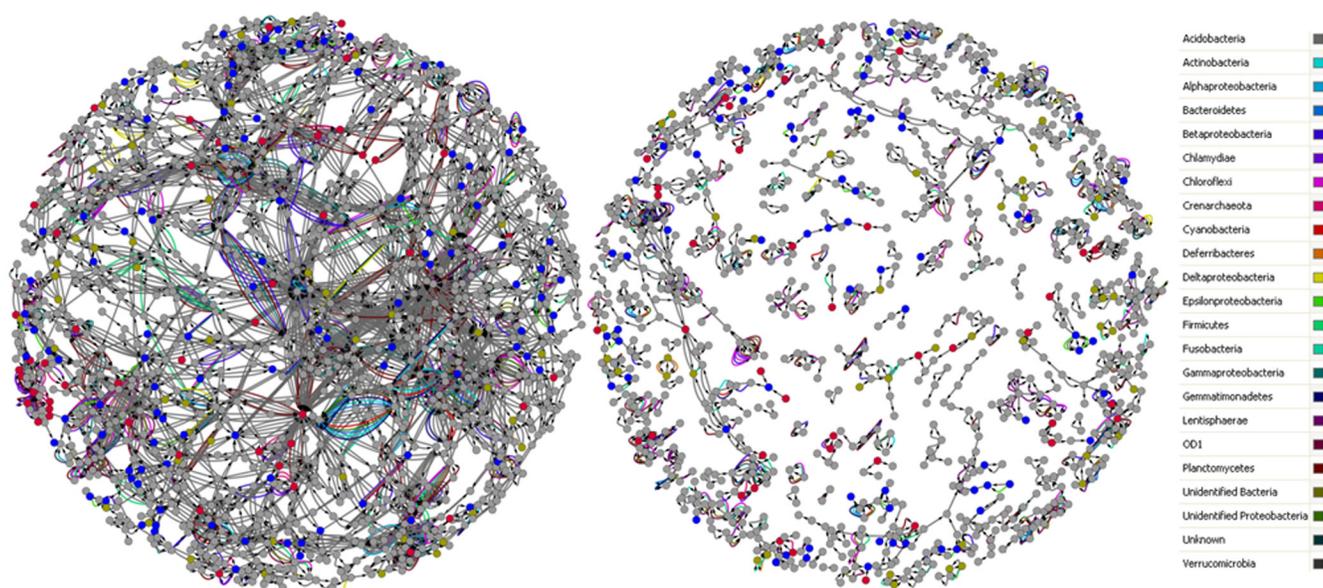


Figure 1. In both images, edges represent enzyme functions identified in annotated metagenomes. Nodes are predicted metabolites, inferred from the reactions catalyzed by detected enzyme functions. Nodes are highlighted if calculated PRMT scores of seasonal metagenomes correlate strongly (i.e., in the top or bottom 5th percentile of randomized resamples) with relative abundance of measured environmental parameters (red for total organic carbon, blue for total organic nitrogen, and gold for soluble reactive phosphorus). Edges are highlighted in one of 23 colors if they connect nodes that correlate with relative abundance of a bacterial phylum.

Seminars

Gilbert, J. (2011). "Lecture Notes: Beyond the Genome: Creating Predictive Models of Microbial Communities." Oregon State University Expert Series, Corvallis, OR, Apr. 21, 2011.

Gilbert, J. (2011). "Lecture Notes: The Earth Microbiome Project." Special Session, Waterloo University, Canada, Apr. 15, 2011.

Gilbert, J. (2011). "Lecture Notes: Marine Microbial Metagenomics: Lessons Learned from a Coastal Observatory." CAMERA Inspirational Lecture Series-UCSD, San Diego, CA, Jan. 2, 2011.

Toward Understanding Cloud Processes and Uncertainty Modeling in Next-Generation, High-Resolution Climate Models

2011-052-NO

Yan Feng, Mihai Anitescu, Emil Constantinescu, and Robert L. Jacob

Project Description

Cloud processes in global climate models (GCMs) are highly parameterized and often tuned to obtain the Earth's radia-

tive balance and global mean temperature. As a result, clouds constitute the single-largest uncertainty in terms of radiative forcings and climate feedbacks. Improving cloud processes in models — and especially the interactions of clouds with aerosols in high-resolution climate models — is definitely a priority for the coming decade. In addition to the uncertainties associated with physical processes, the climate system has an inherent stochasticity, and errors associated with predictions cannot be faithfully simulated in a deterministic modeling framework. The dynamic nature of uncertainty itself needs to be taken into consideration.

In this project, we are evaluating and quantifying the uncertainties associated with cloud processes in a high-resolution climate model (CESM) by using observations, as well as developing and testing new parameterizations in cloud microphysics and dynamics suitable for the high-resolution models. We are also developing an error model that is based on Gaussian processes (GPs) to capture both the characteristic parametric and nondeterministic errors in cloud process models. The proposed new treatment of cloud physics and the error modeling will focus on improving the climate model's predictive capability regarding precipitation on a regional scale. Such an interdisciplinary approach poses novel and critical challenges for the climate modeling, mathematics, and high-performance computing communities.

Mission Relevance

This project is relevant to DOE's environmental mission. In the next decade, DOE, the National Science Foundation, and the U.S. Department of Agriculture are projecting that this emerging field of developing next-generation climate models and quantifying uncertainty in GCMs will be major areas of climate science research. The outcome of this research will provide interdisciplinary engineers and scientists with the sophisticated tools they need to help in generating reliable decadal and regional climate projections with reduced uncertainty and that are useful for policy and decision making.

FY 2011 Results and Accomplishments

We generated multiple-year climate data for analysis by running the latest 0.9-degree and 1.9-degree Community Earth System Model (CESM) and the Community Atmospheric Model (CAM). To evaluate cloud parameters simulated by the CAM, we analyzed multi-platform aerosol and cloud microphysics data sets, such as the DOE Atmospheric Radiation Monitoring (ARM) long-term surface measurements and the National Aeronautics and Space Administration's real-time satellite products.

The key findings include that the global climate model significantly underestimates the elevation of and absorption of sunlight by aerosols in the atmosphere. Because aerosols could act as cloud condensation nuclei, their presence leads to more but smaller cloud droplets and the suppression of rainfall. Therefore, these underestimations of aerosols and their efficiency of absorption would result in large uncertainties in the global model representations of clouds, such as clouds' liquid water content, which controls the onset and intensity of rainfall. We developed a new parameterization to account for solar radiation absorption due to organic carbons, which will be implemented in the CAM model. Moreover, we implemented a heuristic cloud model based on the liquid-phase cloud microphysics of the CAM model. This model allows us to examine the sensitivities of surface precipitation with respect to each of the model parameters that have large uncertainty, such as the mixing ratio of clouds' liquid water mass, number concentration, and sub-grid liquid water variability. These findings will reveal parameters in the CAM model, to which the precipitation is most sensitive, and further help us to rank the uncertainty associated with those parameters.

Proposed Work for FY 2012

To demonstrate the effect of elevated aerosols on the climate, we will derive and use the observed aerosol vertical profiles to drive the GCM cloud microphysics. Sensitivity studies will thus indicate the uncertainty in precipitation associated with the current convection scheme, which is responsible for aerosols' vertical transport. We will then examine/improve aerosol transport in strong convection and constrained by satellite and in situ data. In addition, we will investigate and improve the

cloud microphysics parameterization in the CAM model, focusing on subgrid variabilities of in-cloud liquid water content. We will also verify the heuristic cloud model against CAM's output and compute derivatives of the precipitation rate with respect to model parameters. Finally, we will use observations and the surrogate model outputs to develop inferences for GCMs both to correct model parameters and to obtain uncertainty estimates.

Performance of the Nested Regional Climate Model (NRCM) over the U.S. Midwest

2011-079-N0

Jay W. Larson and Robert L. Jacob

Project Description

Understanding climate change impacts at the regional scale requires developing global climate models with higher spatial resolution, as well as an ability to resolve regional-scale phenomena. Early versions of these models, such as the 4-km global model from the National Oceanic and Atmospheric Administration's Geophysical Fluid Dynamics Laboratory, are too expensive to run for more than a few simulated months — long enough to test the representation of basic physical properties but not to determine the simulated climate. Another way to achieve higher resolution is through the use of "dynamical downscaling." In this approach, a high-resolution model covering only the region of interest is forced on the boundaries by results from a more coarsely resolved global climate model. The dynamics of the regional model are used to refine the output from the large-scale global climate model.

A new generation of regional climate model, the Nested Regional Climate Model (NRCM; <http://www.nrcm.ucar.edu>), is a platform that promises dramatic improvement in our ability to model current and future climates and to provide the resolutions necessary for adaptation and mitigation planning. The NRCM combines the National Center for Atmospheric Research's Advanced Research Weather research and forecasting model with the Community Climate System Model (CCSM) bringing together two widely used community modeling systems that have considerable experience in global climate simulation and detailed weather prediction. This project aims to build capability by using the NRCM and develop techniques for analyzing regional climate model performance.

Mission Relevance

This project is relevant to DOE's environmental mission. Approximately one-third of the U.S. economy is sensitive to the climate and/or the weather. Climate change will likely

have profound economic and national security impacts on the United States and other nations. Climate impacts occur at a regional scale, and modeling these effects demands high-resolution, high-quality climate scenario output. The project’s aims of developing cutting-edge modeling capacity and novel techniques for model output evaluation serve DOE goals and those of other major government agencies to develop high-resolution regional climate models capable of producing climate scenarios amenable to driving climate impacts models for environment, energy, and economics.

FY 2011 Results and Accomplishments

Work was initiated on building local capacity in using the NRCM system, and test runs were performed on Argonne’s BlueGene/P system. Benchmark reanalysis data sets (i.e., NCEP-1, NCEP/DOE AMIP-2, ECMWF ERA-40, and NARR) were gathered for comparison purposes.

A novel information-theoretic/symbolic dynamic method was developed for apportioning predictability versus randomness in meteorological time-series data. The method leverages block entropy — the Shannon entropy computed for successively longer “blocks” of L observations (Figure 1) — and entropy rates of convergence to arrive at an upper-bound estimate of the entropy rate h (a measure of a system’s inherent randomness) and a lower-bound estimate of the excess entropy E (a measure of the “memory” present in a system). These techniques require coarse graining of data to convert a real-valued time series into a symbol stream. A simple example is precipitation occurrence, whereby precipitation amounts are coarse-grained as “0” or “1” for periods of time during observations and indicate no rainfall or a nonzero amount, respectively. Application of this technique to a long (121-year) time series of Australian rainfall data demonstrated its ability to classify climatic regimes on the basis of values of h and E (Figure 2). Comparisons of station data (patched point dataset [PPD]) with assimilated data (Australian Water Availability Project [AWAP] analyses) show that model influence in the assimilation process weakens the classification power of (h,E) through the broadening and convergence of climatic regime clusters. These results demonstrate the classification power of block entropy and may potentially offer the ability to quantify structural versus random biases in model output.

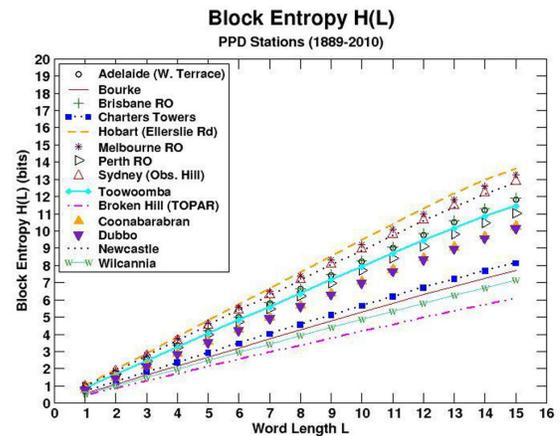


Figure 1. Block entropy growth curve for coarse-grained precipitation station data.

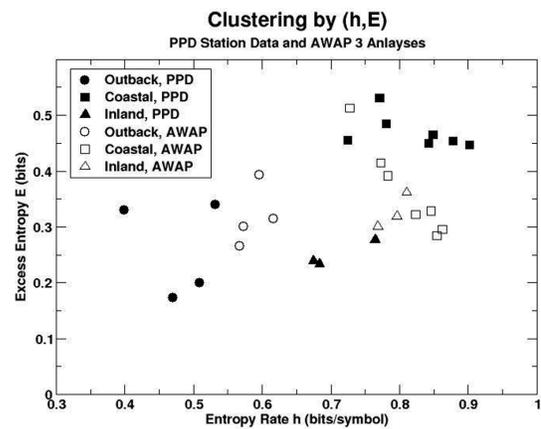


Figure 2. Clustering by (h,E) of data from desert, inland, and coastal locations in the Patched Point Dataset (observations) and the AWAP analyses.

The definition of climate depends on the choice of a sampling period — which, by convention, is 30 years. Information-theoretic techniques can be used to assess the sufficiency of a sample to construct climate distribution functions. Climate variability can be viewed either as the evolution of the two principal moments — mean and variance — or in the evolution of the distribution function itself. Work was undertaken to explore the time evolution of climate distribution functions, with the long-term goal of deriving governing equations — *master equations* — for their dynamics and then using master equations derived from observational or model output data as a means of comparison. A simple example is the Central England Temperature Record, for which daily observations are available for the period from 1772 to the near-present (2006), making it the longest daily meteorological observation record. The time evolution for the climate cumulative distribution function (CDF) for the period 1772–2006 (Figure 3) shows (1) how the CDF’s quantiles evolve in time and (2) the twentieth-century warming trend. These results form a dataset from which candidate master equations can be fit.

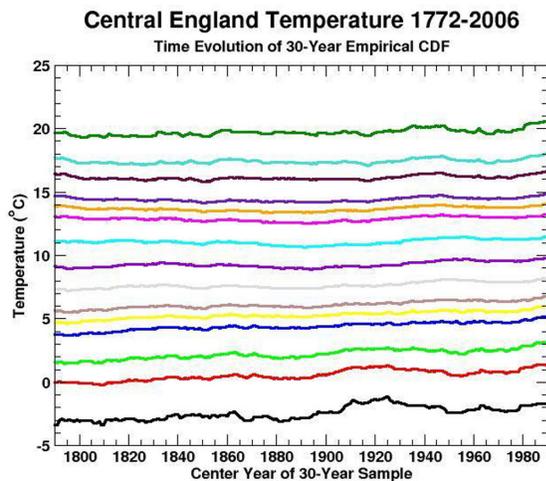


Figure 3. Central England Temperature dataset CDF 1772–2006. Quantiles are computed from daily data by using a sliding 30-year window. The bottom and top two contours indicate (1st, 5th) and (95th, 99th) percentiles, respectively. Other curves mark 10-percentile increments.

Evaluation of Microtopography Effects on the Terrestrial Biosphere and Hydrosphere under Regional Climate Change

2011-129-NO

Beth Drewniak, Satish Balay, Todd Munson, Barry Smith, and Y. Eugene Yan

Project Description

Soils in current land surface models do not allow for changes in microtopography, which can impact the soil drainage and moisture, below-ground soil biogeochemical cycles, carbon storage, plant productivity, species richness, and decomposition through the creation of anaerobic and aerobic zones. To quantify the effects of microtopography, our main objectives are to (1) identify and construct a microtopographic surface; (2) modify a land surface model to incorporate mechanisms of soil infiltration, surface water storage, surface runoff, and evapotranspiration under the microtopographic environment; (3) understand interactions among hydrologic processes, plant growth processes, and climate changes in the presence of microtopography; and (4) evaluate impacts of microtopography on flow generation, soil moisture, plant productivity, and carbon storage. The approach and tools developed in this proposed work will be applicable across multiple land surface models.

We will develop software that is capable of constructing ensembles of microtopography surfaces for sand dunes, agriculture tillage, and vegetation mounding in wetland ecosys-

tems. The tool will include three components: (1) a series of algorithms to identify soil types based on soil texture, types of crops and tillage practices, type of wetlands, and type of sand dunes by scanning the U.S. Department of Agriculture (USDA) soil database; (2) discretization of a land surface model grid to subgrids as representative microtopography units (RMTU) based on soil texture, plant types, and tillage; and (3) construction of microtopography for each RMTU by employing a fractal method, multifractal analysis, or mathematical formulation for sinusoidal or power-law microtopographic features. The microtopography surface will be constructed for each RMTU by adding the generated fractal surface, sinusoidal surface, or power-law surface to the topographic surface from the digital elevation model (DEM).

We propose to integrate variations in surface elevation in the Community Land Model (CLM) through the hydrological interactions of three processes: (1) early stage of infiltration prior to ponding, (2) surface storage during ponding on micro-depressions, and (3) sheet flow over the microtopographic surface. We will perform simulations by using the improved CLM at the RMTU level, with high-resolution North American Regional Climate Change Assessment Program (NARCCAP) data as model inputs for climate forcing. The simulation will include a baseline run without microtopography and runs with several variations of microtopography to analyze surface runoff, plant productivity, evapotranspiration, and soil moisture distribution, with 2- and 3-D visualizations. The uncertainty of parameters used as model inputs will be evaluated to construct microtopography.

Mission Relevance

This work is relevant to DOE's environmental mission. It will provide tools and methodologies to evaluate the effects of microtopography at a regional scale. The improvements for the land surface model will help to develop the next-generation high-resolution regional models, with an approach that will bridge the scale gap of four orders of magnitude and improve the representation of subgrid soil biogeochemistry and hydrologic properties.

FY 2011 Results and Accomplishments

Efforts for FY 2011 focused on CLM development. The agriculture model CLM-Crop, written for use in CLM3.5, was transferred into CLM4. The National Center for Atmospheric Research (NCAR) is integrating several modifications from CLM-Crop into CLM4.5, including fertilization, soybean nitrogen fixation, dynamic roots, carbon:nitrogen ratios, nitrogen retranslocation, harvest scheme, and separating organ components into a new grain pool.

We also began adding transient land-unit capability to CLM4, which will allow model users to expand or contract land types. We modified the CLM4 subgrid hierarchy so that each of the

six land units on a grid cell (ice, lake, wetland, urban, vegetated, and crop) is allocated memory as a placeholder, regardless of the current weight on the grid cell. A function to calculate changes in weight for each land unit, column, and plant functional type (PFT) for every time step is currently being tested. We will ensure that this new capability is applicable for all land-unit types and processes.

Proposed Work for FY 2012

We plan to begin establishing microtopography databases by building tools to identify soil texture, plant/crop types and tillage, wetlands, and sand dunes. We will also discretize CLM grids to subgrids as representative RMTUs to construct microtopography for every RMTU across each land-surface grid. We will also initiate CLM modifications to include the hydrologic processes that occur on the microtopographic surface.

Will Linking Ultra-Large-Scale Metagenomics with Models Representing Biogeochemical Cycling Improve Existing Carbon Flux Models?

2011-196-NO

Folker Meyer

Project Description

Microbial organisms are the key players dominating the major biogeochemical cycles. Nevertheless, existing carbon flux models exhibit considerable uncertainty because of a lack of parameterization of the microbial contribution to these processes. The time has come to systematically attack this problem, with the objective of reducing the uncertainty in current models for carbon cycling and carbon flux in terrestrial systems. Specifically, we believe that 35% of the uncertainty due to the mean value of the net carbon flux in simulation can be reduced by including data about the microbial community metabolism. While the high degree of microbial diversity prevents many direct molecular assays that would be based on pre-existing databases of *known* (i.e., cultivable) microorganisms, we will leverage metagenomic data to design a set of directed molecular probes that will inform and ultimately reduce the uncertainty in the existing models for carbon cycling. Similar approaches of identifying additional parameters have been shown to be successful in reducing model uncertainty. Because of large-scale environmental sequence datasets produced at Argonne via second-generation DNA sequencing, we are positioned to use this approach as a framework to shift from a static model of microbial community metabolism to a dynamic one.

This study is enabled specifically by recent advances in genomic and metagenomic technology at the intersection of biology, bioinformatics, and computer science. In particular, ultra-high-throughput direct environmental shotgun sequencing enables us to study the genomic content of complex microbial communities from environmental systems. By sequencing (meta)genomic data directly from the environment, we will gain an inventory of not only the microbial species present but also the metabolic functions present. The detected metabolic functions inferred from the metagenomic data will then be used to inform a dynamic systems-based model in order to screen and identify key enzymes that we can use as proxies for measuring microbial metabolisms in response to environmental parameters. Observing the abundance of those key enzymes will allow quantification of specific metabolic processes to infer the microbial community function and inform environmental system processes. These data will significantly improve the current state of the art of estimating soil carbon flux as a function of soil temperature.

Mission Relevance

This project has direct relevance to the DOE BER mission for understanding the relationships between climate change and Earth's ecosystems, and assessing options for carbon sequestration, by exploring carbon/nitrogen cycling and carbon sequestration processes in soils. We believe that this research is in a unique position to start bridging the gap between molecular and field scale. If we are able to do so successfully, we can positively impact the efforts to devise regional climate models by providing a set of cost-effective "field site" molecular probes that will provide deep insights into the carbon-flux state of soils. The project has great potential for improving numerous project designs across the DOE national laboratory system, and hence will be exceptionally relevant to DOE's environmental mission.

FY 2011 Results and Accomplishments

Most soil processes, including microbial diversity and CO₂ efflux, are extremely variable across spatial scales. The destructive and labor-intensive nature of traditional soil sampling and processing methods has hampered broad investigation of spatial heterogeneity in soil function. In order to provide context for any temporal measurement of microbial community dynamics, an assessment of the spatial heterogeneity needs to be performed first.

In FY 2011, we collected a total of 750 soil cores to characterize the drivers of spatial structure in microbial diversity and an additional 480 cores to quantify soil moisture at the scale of the microbial populations. This is an unprecedented number of samples to describe microbial communities at a landscape scale. Specifically, we capitalized on an ongoing biofuels experiment at the Sustainable Bioenergy Crop Production Research Facility at Fermi National Accelerator Laboratory (Fermilab).

We focused on one of the seven vegetation treatments, using relative monocultures of the Kanlow switchgrass cultivar to minimize the confounding effects of plant diversity. Twenty-five soil samples were collected from a 10 × 10-cm grid at five points along a 36-m transect in each of six 36 × 20-m plots representing a low-diversity perennial grassland dominated by *Panicum virgatum* (fertilized and unfertilized treatments; Figures 1 and 2).



Figure 1. Sampling design. Plots are 36 m x 20 m. Red lines indicate fertilized treatments, blue lines indicate unfertilized plots. Sampling stations in each plot (each with 25 soil micro-cores) are denoted by yellow thumbtacks.

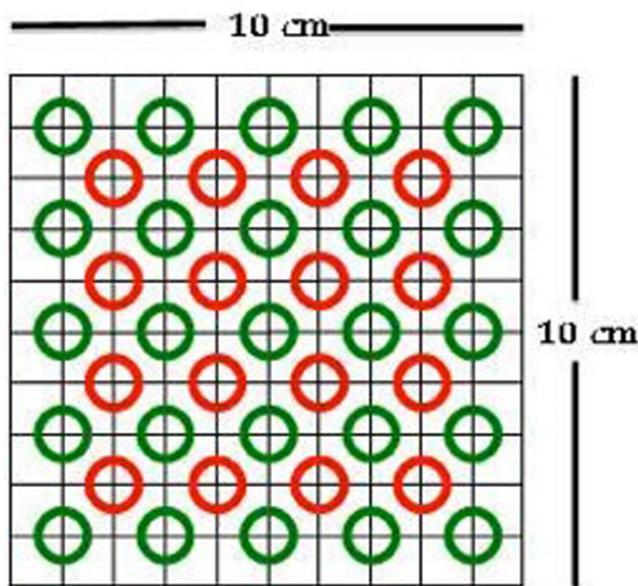


Figure 2. Sampling grid. Green circles represent the twenty-five samples collected to characterize spatial structure of microbial diversity. Red circles indicate where cores were collected for moisture quantification.

We used an innovative “micro-core” approach that allowed us to characterize the soil at a much higher resolution (Figure 3). These “microsamples” of soil (<1 g each) provided enough material for DNA extraction to characterize the microbial community while reducing sample processing time (which can result in DNA degradation) and dramatically enhancing the spatial resolution of the diversity metrics.



Figure 3. Example of a soil “micro-core.”

On the basis of the 750 samples that were collected as part of this study, we made several field observations that established the degree of resource patchiness at the site. For instance, soil moisture for all samples obtained ranged from 18 to 37% when we sampled, but most of the variability was restricted to only one of the three blocks (Figure 4). Soil bulk density was also quite heterogeneous (Figure 5); however, this metric is notoriously problematic, particularly given the compaction risk inherent in small-diameter samples. Regardless of measurement issues, variability appears to be more tightly linked to position in the field than to fertilization treatment.

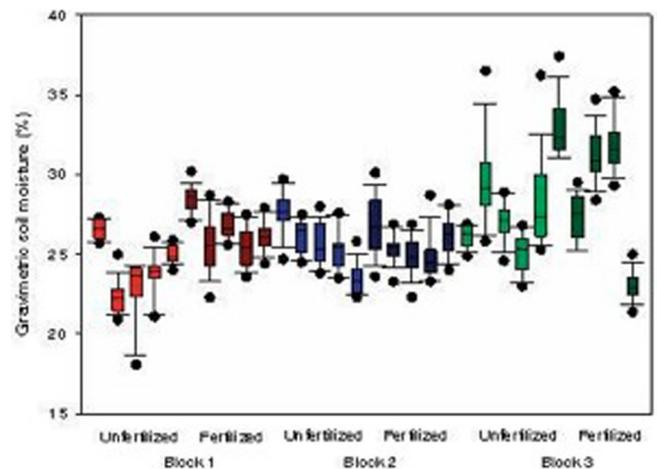


Figure 4. Variability in gravimetric soil moisture in the thirty sampling grids (n=15-16 in each grid). Boxes show the median, 25th, and 75th percentiles. Error bars indicate 90th and 10th percentiles. Circles indicate outliers.

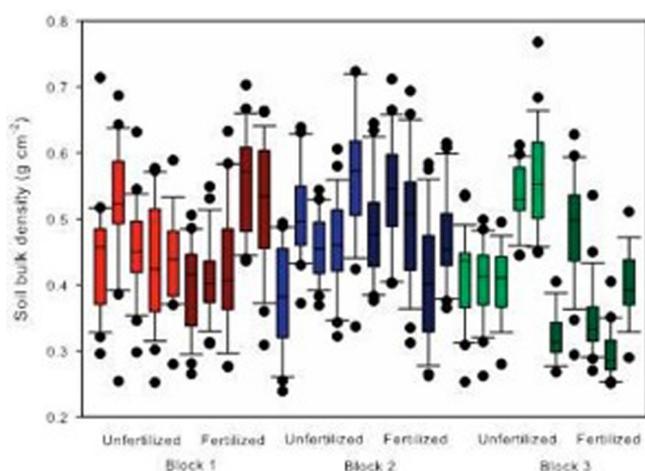


Figure 5. Variability in soil bulk density in the thirty sampling grids ($n=16-25$ in each grid; values <0.25 were discarded, as they indicate insufficient material was collected.). Boxes show the median, 25th, and 75th percentiles. Error bars indicate 90th and 10th percentiles. Circles indicate outliers.

Soil CO_2 efflux from the sampling sites also varied. Many studies have shown strong correlations between CO_2 flux and moisture. Interestingly, there was only a marginally significant relationship between flux and soil moisture during our field campaign (Figure 6), suggesting that other factors, such as microbial community structure, may be important predictors of flux.

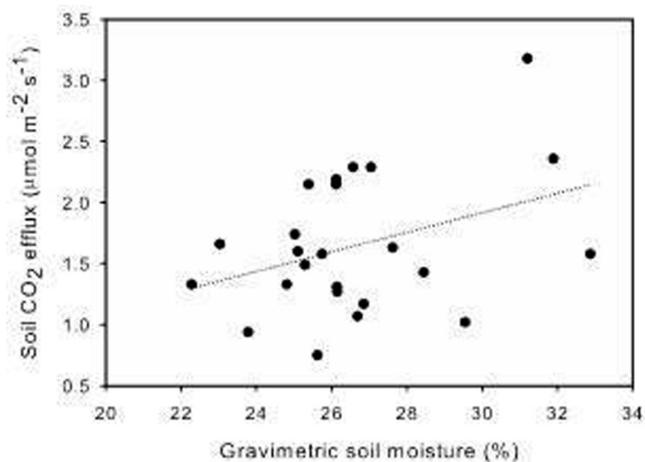


Figure 6. Relationship between soil respiration and soil moisture. Each point represents one sampling grid where CO_2 efflux was measured just prior to sampling. Dotted line is a marginally significant linear regression ($r^2=0.04$, $p=0.08$).

Proposed Work for FY 2012

Processing soil samples in preparation for laboratory analyses is extremely labor intensive. We have processed the 480 samples intended for moisture quantification and the 750 samples intended for microbial diversity analysis. We are preparing to extract DNA from the latter in preparation for sequencing the 16S rRNA-encoding gene that allows determination of microbial taxonomy. After subsampling the soil for this extraction,

there will be enough material remaining for pH measurement as well as soil carbon and nitrogen quantification.

The study site at Fermilab is a controlled fertilization experiment for exploring the differential impacts of fertilization on plant and microbial biomass production in prairie soils. Although there is a thorough understanding of belowground dynamics at this site, there is less information detailing microbial enzymatic mechanics that mediate carbon and nitrogen cycling in this system and very little information regarding the specific metabolic fate of carbon after it enters the soil. Together with soil moisture and CO_2 flux measurements, the aim is to correlate microbial community structure with abiotic factors, which will help build a mechanistic understanding of feedbacks between soil microbes and ecosystem carbon fluxes. By comparison to environmental parameters co-collected at this site, such information will enable extrapolative prediction over time and space, especially when focused on the long-term monitored environmental parameters. In this way, we could generate a microbial weather map for the spatial and temporal fluctuation in assemblage structure and function-derived metabolite turnover in this system.

High-Performance Computation: Developing and Testing a 3-D Regional-Scale Climate Model in the Ganges Valley, India

2011-216-N0

John Krummel, Yan Feng, and Veerabhadra Rao Kotamarthi

Project Description

The Ganges Valley Aerosol eXperiment (GVAX) began a one-year observation period using the DOE Atmospheric Radiation Monitoring (ARM) mobile facility at Nainital, India, in July 2011. Measurements of radiative flux; cloud properties; convection; and aerosol physical, chemical, and optical properties are being made to develop core data sets for scientific analysis. The observational data range from surface measurements that yield point and profile data sets to a few selected aircraft-platform-based measurements. These measurements must be placed in a larger regional context in order to relate the observations to a particular dynamic state of the atmosphere and to develop hypotheses that explain observed phenomena.

This project on developing and testing the 3-D regional-scale climate model generates the conditions required to develop such a regional context, which will facilitate the GVAX field experiment in climate research. Baseline simulations of a 3-D

regional-scale model will provide the necessary analytical support for scientific studies done under GVAX. The 3-D model will be a test bed for high-performance computing data storage and visualization.

Mission Relevance

This project is relevant to DOE's missions in basic science and the environment. The modeling results for air pollution and meteorological fields will become one of the central "data" products archived at the DOE ARM websites. The large volumes of model outputs generated can also be used to test or assess the feasibility of using cloud computing systems, such as Magellan. It demonstrates to the DOE ARM program that the capability exists to operate a 3-D regional climate model and managing a large volume of forecast data sets, thus making the regional model forecast a regular part of the mobile ARM facility support. In addition, the DOE Climate Change Prediction Program has recently requested proposals on developing regional-scale resolving models and modeling activities designed for Integrated Assessment Modeling.

FY 2011 Results and Accomplishments

We set up the latest version of the 3-D regional-scale climate model, WRF-Chem 3.3, on the Argonne Fusion clusters. The regional model was scaled up to run on 200 processors. The WRFChem model embedded with the new MOZCART chemistry module was used to study air pollution and regional climate over the South Asia region. Operational daily forecasts for GVAX were performed. On a daily basis, about 180 GB of forecast data products were archived on the Fusion climate disk. This data set consists of three-day hourly meteorological data (temperature, winds, planetary boundary height, water vapor, rain, and clouds) and air pollution distributions (e.g., ozone, black carbon, PM2.5, dust particles) over a domain ranging from 55°E to 95°E and 0° to 35°N. We built a new online data and visualization server by using the National Oceanic and Atmospheric Administration (NOAA) Live Access Server in order to display the daily generated forecast products. This tool was introduced and made available to the GVAX scientists in early September (<http://atmos.anl.gov:8080/las>). It allowed them to visualize and/or download the forecast data at first hand.

Proposed Work for FY 2012

We will continue the daily forecasts and evaluate the model performance with the in situ data and satellite observations. During the three-month intensive operational period from February to April 2012, we will archive the forecast products at 10-min intervals to accommodate the GVAX principal investigators' requests. We are working on the evaluation and improvement of the aerosol and radiative transfer calculations in the MOZCART or SORGAM chemistry module of the WRF-Chem.

This work will be done in collaboration with NOAA and the University of Colorado. We are working with Argonne's Laboratory Computing Resource Center staff to scale the model up to run on more than 200 processors on Fusion. We will also test the model on the Blue Gene/P. Following the GVAX experiment, we are planning on running the WRF-Chem model in the diagnostic mode (driven by the re-analysis fields instead of forecast fields) to study air pollution and regional climate in comparison with the GVAX observations.



DIRECTOR'S GRAND CHALLENGE

Beyond Li-ion Battery Technology for Energy Storage

2010-185-R1

Khalil Amine, Mahalingam Balasubramanian, Anthony Burrell, Zonghai Chen, Larry Curtiss, Jeffrey Greeley, Brian Ingram, Di-Jia Liu, Nenad M. Markovic, Yang Ren, Yugang Sun, Lynn Trahey, Michael Thackeray, and Zhengcheng Zhang

Project Description

While the inherent energy potential of lithium (Li) metal approaches that of gasoline, today's battery manufacturers have not yet been able to unlock this potential. Today's Li-ion batteries may provide acceptable power for hybrid electric vehicles (HEVs) and all-electric vehicles (EVs), but they do not provide sufficient range. This limitation and the absence of a battery-charging infrastructure have limited public interest in EVs, particularly for long-distance travel. A breakthrough in 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. Successful implementation of non-aqueous Li-air cells has been hampered by the following severe materials and technological problems that have limited electrochemical performance: (1) the non-aqueous 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 lithium peroxide (Li_2O_2) and/or lithium oxide (Li_2O) products are deposited on the surface or within the pores of the carbon cathode, clogging the pores and restricting oxygen flow; (3) poisoning of the lithium electrode due to oxygen crossover destroys the integrity and functioning of the cell; and (4) commonly used cathode catalysts, such as manganese dioxide (MnO_2) or Mn metal, do not access the full capacity of the oxygen electrode or enable sufficiently high rates.

For this project, we have established a multidisciplinary team of basic and applied scientists to tackle these challenges, with particular emphasis on resolving the severe limitations of the electrolytes and electrode catalysts in present-day Li-air cells. We are working to enable a Li-air battery system with exceptionally high energy density and reversibility. We are using new approaches that combine innovation in advanced electrode-, electrolyte-, and catalytic materials research with extensive computer modeling and use of advanced characterization techniques.

Mission Relevance

The major benefit of this research will be the development of a reversible Li-air battery that provides many times the energy density of state-of-the-art Li-ion batteries for powering EVs. The design and discovery of new materials needed for the Li-air technology is relevant to the DOE mission of developing new energy technologies to contribute to U.S. energy security. The technology can also benefit many Department of Defense military applications that require very high energy density such as satellite, EV tanks, and military vehicles for silent watch and operation. Customers will be the automotive industry, satellite industry, and the military. Also, if the technology is successful for large batteries, it can be easily scaled down for consumer electronics applications.

FY 2011 Results and Accomplishments

Electrolyte

Siloxane-based electrolytes compared to propylene carbonate (PC). On the basis of our experimental/theoretical study of PC and tri(ethylene glycol)-substituted trimethylsilane (1NM3) under similar conditions, we obtained a more complete picture of the role of electrolyte stability in Li-air batteries. During the first discharge, oxygen reduction products contribute to decomposition of carbonate-based electrolytes. Density functional theory (DFT) calculations reveal a favorable reaction assuming that the PC electrolyte reacts with the solvated oxygen reduction species. The other solvated reduction species also result in similar decomposition products assuming two electron transfer reactions. During the charging process, the decomposition of Li_2CO_3 results in a large overpotential of the cell.

DFT calculations reveal that 1NM3 is more stable when introduced to the highly active oxygen reduction species than PC, resulting in a significantly lower overpotential for the Li-air cell (Figure 1). X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and Fourier transform infrared spectroscopy (FTIR) data provide evidence that only Li_2O_2 is formed on discharge. Further exploration of how both solvents and salts in electrolytes control the discharge and charge processes is needed to improve the charging capacity and cycling performance in Li-air cells. The results obtained thus far reveal that electrolyte solvent stability plays a key role in the performance of Li-air batteries and will be a key factor in reducing overpotential and improving efficiency. Theoretical modeling of the stability of electrolytes, such as that shown in Figure 2, is being used to find more stable electrolytes.

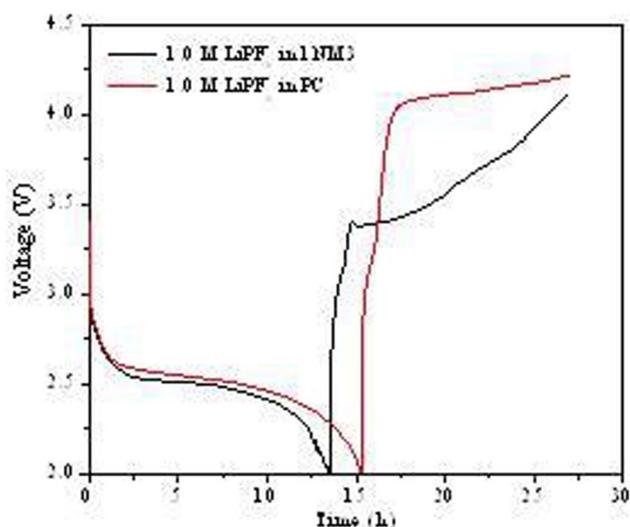


Figure 1. First charge and discharge cycles of a Li-air cell with PC and 1NM3 showing the reduced charge overpotential due to the stability of 1NM3 to oxygen reduction products.

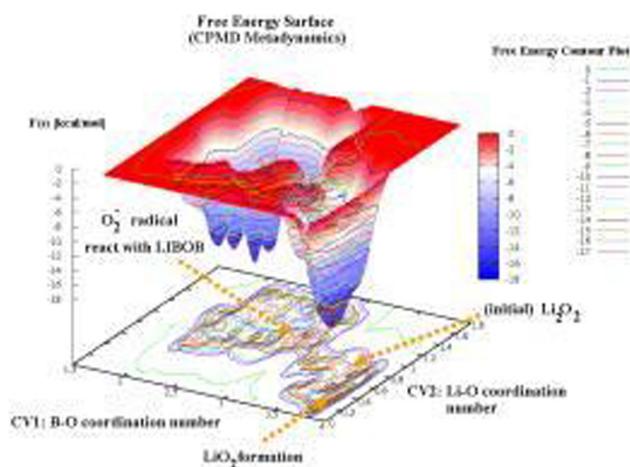


Figure 2. Ab initio molecular dynamics potential energy surface used to investigate the decomposition of lithium bis(oxalato)borate (LiBOB) by oxygen reduction species in 1NM3.

Membranes. We fabricated single-crystal silicon membranes with varying thicknesses (1–20 μm) and systematically measured their conductivities for Li ions. The results reveal that the resistance of the membranes exhibits a V-shaped dependence on their thickness. The single-crystalline silicon membranes exhibit exceptional lithium conductivity, and their single crystallinity remains, even with current density of $1 \text{ mA}\cdot\text{cm}^{-2}$. We evaluated single-crystal membranes in Li-air batteries by sandwiching the membranes between the Li anodes and air cathodes. A typical cell can be operated for two normal discharge/charge cycles followed by a failure caused by a significant increase in resistance. The resistance increase is attributable to the formation of additional solid electrolyte interface/interphase (SEI) layers on the surface facing the air cathode; the formation of these layers is caused by the accelerated

decomposition of electrolyte. The collection of decomposition materials on the membrane clearly shows the instability of the electrolyte in the Li-air system and indicates that a more stable electrolyte must be used in future development.

Catalyst

MnO_2 alpha forms. We studied two main types of MnO_2 : (1) an alpha/ramsdellite mixture (70/30) made via the acid treatment of sol-gel-synthesized lithium manganese oxide (Li_2MnO_3) and (2) pure alpha MnO_2 made by the conversion of electrolytic manganese dioxide through a manganese oxide (Mn_2O_3) intermediate. The capacities were in the 5,000–6,000-mAh/g range. XPS measurements indicated that our catalyst promotes the desired cell chemistry. High-energy x-ray diffraction (HE-XRD) measurements showed that the crystal structure of the alpha- MnO_2 undergoes significant changes during the discharge and charge processes. We proposed a possible mechanism for the role of the Li_2MnO_3 electrocatalyst, as illustrated in Figure 3. We used density functional studies to investigate the effect of oxide lattice reduction on the concentration of Li in the tunnels and electron transfer to O_2 to help understand the role of the tunnels in catalyst performance.

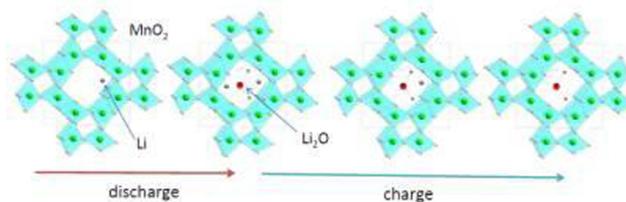


Figure 3. A possible mechanism for the role of VAT- Li_2MnO_3 electrocatalyst during the discharge/charge processes in the Li-air battery.

MnO_2 nanospheres. We also investigated materials with uniformly dispersed MnO_2 nanospheres on the carbon support that preserve the original porous structure of carbon during the synthetic process. The surface area and porous structure of the carbon cathode should play important roles in the performance of Li-air batteries during electrochemical reactions. Typically, a large surface area allows more uniform dispersion of catalytic particles and more active sites to facilitate electrochemical reactions. With this catalyst, the initial charge voltage can be reduced to 3.7 V and cycling performance can sustain more than 10 cycles with good capacity retention. This is one of the two catalysts (with alpha MnO_2) chosen for more detailed investigation with more stable electrolytes.

Metal organic cathode materials. We examined three new classes of cathode catalyst, all significantly different from any described in available literature. Although the metal loadings were extremely low, the active sites were atomically dispersed over the catalyst surface. Consequently, the charging/discharging capacities were significantly improved. The voltages for discharge and charge are at 2.8 V and 3.8 V, respectively,

with excellent coulombic efficiency. The catalysts we tested demonstrated high charge/discharge capacities and unique properties, such as high active site density, uniform distribution, and novel nanostructure with improved mass-transfer.

Model catalytic systems. We completed work to understand the role of the catalyst in the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) in the presence of Li-ions in a non-aqueous electrolyte. PC was used as the baseline solvent to allow us to unambiguously identify the role of the catalyst. Our results showed that the measured activity at a given voltage is indeed dependent on the catalyst material. Such experiments on well-defined systems provide insights into the reaction mechanism. Estimating the charge under the reduction curve provides a likely estimate of the charge, and therefore the nature, of the species formed during the reduction process. Our observations were also consistent with computational studies.

Proposed Work for FY 2012

Figure 4 illustrates the integrated strategy for electrolyte and catalyst development. The illustration is based on both full cell studies that can be used for screening potential candidates, as well as model systems for more thorough investigation and understanding. The electrolyte part of the strategy will continue with its effective use of characterization and theory to find salts and electrolytes that are stable to oxygen reduction products, as well as to promote reversibility. Recent results demonstrated the promise of solvent mixtures and variation of salts. The electrolyte work will utilize characterization and theory to develop an understanding of the charge and discharge chemistry. New characterization techniques will be used to build a fundamental knowledge base, which will be used, along with theory, to help design electrolytes with the desired properties. The catalyst part of the strategy will be more closely aligned with the electrolyte effort in the third year and will utilize the novel and stable electrolytes that evolve from that part of the project, including the polyether siloxanes. In addition, the catalyst work will more fully utilize the characterization and modeling capabilities to improve our understanding of the role of the catalysts and how new catalytic materials can be optimized for reversibility in the Li-air cells. The most promising candidates will be chosen for more thorough studies on model systems.

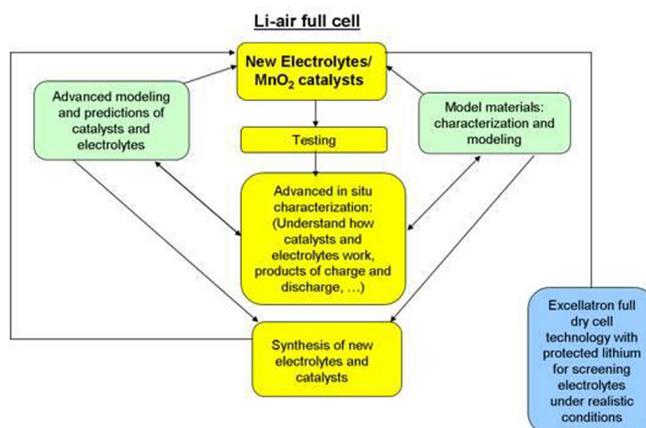
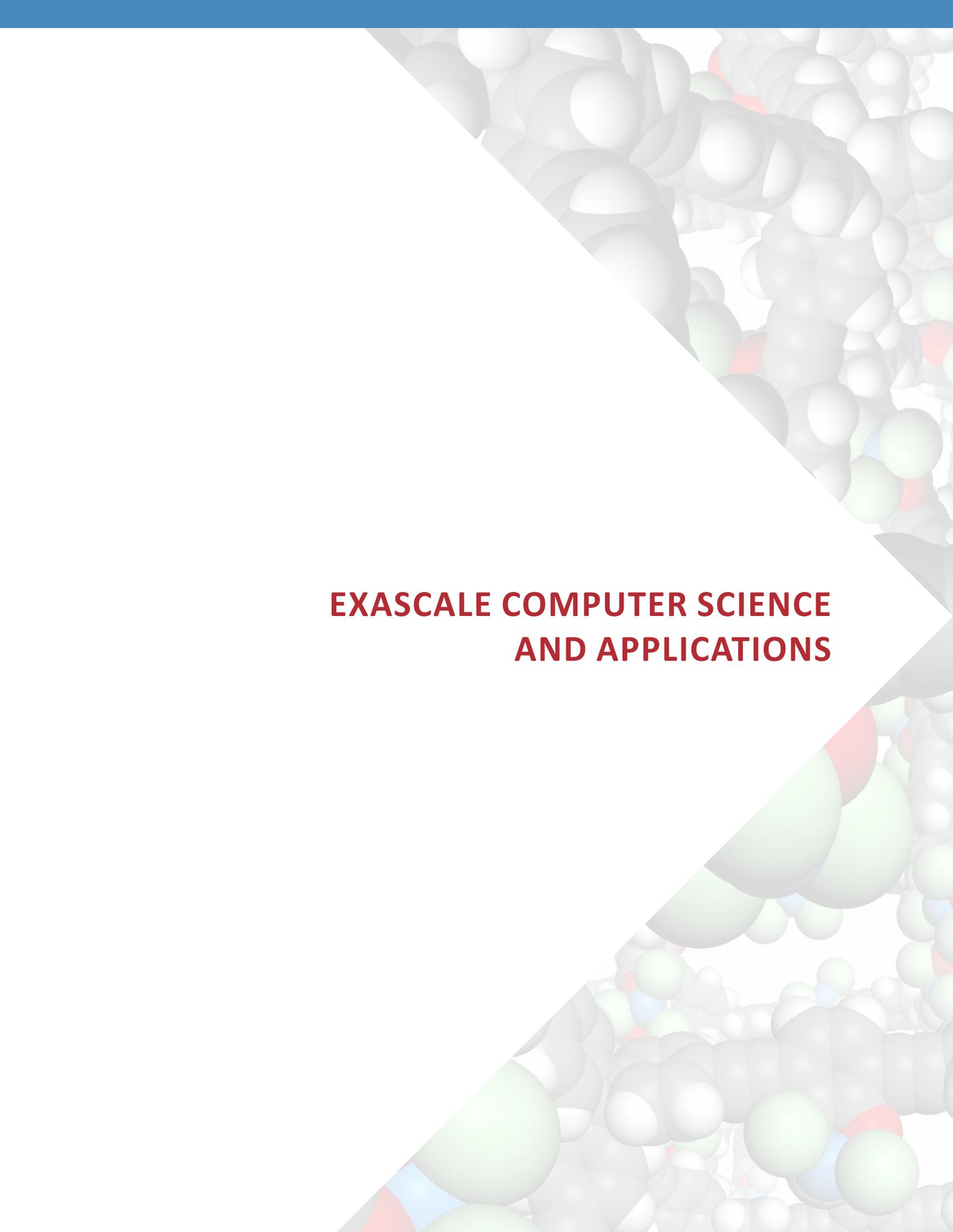


Figure 4. Integrated electrolyte and catalyst development studies for the third year.

Seminars

Amine, K. and L. Curtiss. (2011). "Lithium-Air Battery Research Activities at Argonne." U.S. China Workshop, Argonne, IL, Aug. 3–4, 2011.



**EXASCALE COMPUTER SCIENCE
AND APPLICATIONS**

Novel Computing Methodologies for the Simulation of Complex Molecular Systems

2009-047-R2

Benoît Roux, Millicent A. Firestone, and Jorge More

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 studying 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 the urgent need for new and extremely scalable algorithms to accurately simulate complex systems that incorporate induced polarization. Also needed for a wide variety of applications is an objective method for optimizing atomic force fields used in the simulations. 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. Reliable and physically accurate large-scale simulations of complex molecular systems will directly benefit a number of DOE energy science researchers who are using theory, modeling, and simulations (TMS) to design and refine soft materials for engineering applications. With the significant increase in computational power made available by the Argonne Leadership Computing Facility (ALCF), it is expected that in the near future, the impact of TMS based on accurate atomic models on these various projects will continue to grow. This project also advances DOE's long-term basic science goals by developing relevant mathematical methodologies and by helping researchers understand material systems that have a lot of potential for engineering applications in energy science.

FY 2011 Results and Accomplishments

In FY 2010, we developed (1) rapid and systematic protocols for computing free energy of solvation, and (2) a novel replica-exchange free-energy simulation (FEP/REMD) protocol for the Blue Gene/P computer. This method was extended and

combined with an accelerated MD simulation method based on Hamiltonian replica-exchange MD (H-REMD) to overcome additional problems that arise from the existence of kinetically trapped conformations within the protein receptor. In the combined strategy, each system with a given thermodynamic coupling factor λ in the extended ensemble was further coupled with a set of replicas evolving on a biased energy surface; boosting potentials were used to accelerate the interconversions among different rotameric states of the side chains in the neighborhood of the binding site. Tests executed on Blue Gene demonstrated the high scalability of the method — to several thousand processors. Finally in FY 2010, we had implemented the basic ingredients of the polarizable force field into NAMD (Not (just) Another Molecular Dynamics program). NAMD is a highly parallelized code from the Schulten Lab at the University of Illinois at Urbana-Champaign (UIUC) that runs efficiently on Blue Gene/L. Extended Lagrangian dynamics with a dual-Langevin thermostat scheme applied to the Drude-nucleus pairs were employed to efficiently generate classical dynamic propagation near the self-consistent field limit. Large-scale MD simulations based on the Drude polarizable force field scale ran very well on massively distributed supercomputing platforms, because the computational demand was only about 50–100% higher than it is for nonpolarizable models. As an illustration, a large-scale, 150-M NaCl aqueous salt solution was simulated, and the calculated ionic conductivity was shown to be in excellent agreement with experiment.

In FY 2011, we continued the NAMD development that supports our polarizable force field. In addition, we continued to develop replica-exchange methods in free-energy computations for Blue Gene/P. The new extensions comprise a replica-exchange method for enhancing the umbrella sampling potential of mean force simulations. Tests indicated that this method has a very high scalability on Blue Gene. We continued refining the polarizable force field for lipid membranes, focusing on the statistical properties of the phospholipids called dipalmitoyl phosphatidylcholine (DPPC), an important constituent of biological membranes. Lastly, we developed an engine to fit the parameters of the force field from quantum chemistry data. We developed a global derivative-free optimization method for rapidly determining the best set of force field parameters for accurately modeling an arbitrary molecule for MD simulations according to a set of target data (quantum mechanical, experimental). We now have a general tool for automatically optimizing the force field according to well-defined standards of quality, installed as a web server on Argonne's Laboratory Computing Resource Center (LCRC) Fusion cluster. We expect that only minimal effort will be needed to implement the classical potential function in all the current major MD simulation drivers, such as Sandia's Large-Scale Atomic/Molecular Massively Parallel Simulator (LAMMPS).

New Framework for Electromagnetic Simulations on Exascale Supercomputers

2009-155-R2

Paul Fischer, Misun Min, Tim Tautges, and Jin Xu

Project Description

This project focuses on developing advanced numerical algorithms and software to leverage petascale and exascale computing for diverse applications in accelerator modeling. Predictive modeling will be critical in the design and upcoming engineering phases for next-generation accelerator devices, to help engineers improve technical designs and develop possible upgrade paths.

Mission Relevance

This project is relevant to DOE's future science mission with regard to advanced scientific computing, energy materials, 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. The framework can be extended in different disciplines to greatly improve their quality and efficiency, thereby further strengthening support for DOE in diverse areas with scientific applications.

FY 2011 Results and Accomplishments

In prior years, we developed an eigenvalue solver based on high-order Nédelec edge elements for triangle and tetrahedron meshes in 2D and 3D, respectively. We also implemented a high-order time integrator based on the Krylov approximation and demonstrated its cost-reduction.

During FY 2011, our main focus was to develop scalable algorithms in NekCEM, the production code. We demonstrated their effectiveness on the Argonne Leadership Computing Facility (ALCF) Blue Gene/P up to 131K cores. We are extending tests on the Oak Ridge Leadership Computing Facility (OLCF) Cray XK6 and developing scalable algorithms to improve their performance on the upcoming machines with 200–800K cores and multicore nodes. Our results and the algorithms developed include the following:

1. Developing restart routines for long-time simulations:
 - a. Developing message swap routines using Crystal-Router (CR) algorithms for communication
 - b. Checkpointing for restart outputs in single and double precision formats
2. Upgrading an initial field calculation for wakefields using CR-based algorithms

3. Developing and conducting tests for NekCEM:
 - a. Improving peak performance with intensive use of double-hammer intrinsic
 - b. Implementing hybrid message passing interface for MPI plus multi-threading framework for computation and I/O.
 - c. Conducting performance tests on the OLCF Cray XK6.

The framework can be extended to applications in solar energy materials, multiphase flows, and fuel cells. In FY 2012–2014, further development will occur under DOE's Applied Math Research Program. There may be other opportunities in upcoming years as part of DOE's Scientific Discovery through Advanced Computing (SciDAC) work, through its Office of Basic Energy Sciences (BES) and Office of High Energy Physics (HEP) Advanced Scientific Computing Research Partnership Programs, if our proposals are successful.

Seminars

Min, M. (2011). "High-performance High-order Simulations for Scientific Applications in Accelerator Physics, Plasmonic Nanodevices, and Fluids." Seminar at the Department of Mechanical Engineering, The City College of New York, NY, Mar. 31, 2011.

Min, M. (2011). "NekCEM: Performance and Scalability for Electromagnetic Modeling." First Nek5000 Users' Meeting, Argonne National Laboratory, Argonne, IL, Dec. 10, 2010.

Min, M. (2009). "NekCEM: High Performance Electromagnetic Simulations." Mathematics and its Applications Seminar, University of Illinois, Chicago, IL, Feb. 25, 2009.

Min, M. (2010). "Scalable High-order Algorithms for Applications in Plasmonics, Particle Accelerator Physics and Fluids." Computational and Applied Mathematics Seminar, Purdue University, Apr. 23, 2010.

Min, M. (2009). "High-performance Electromagnetic Modeling." Applied and Computation Seminar, University of North Carolina, Jan. 28, 2009.

Xu, J. (2011). "High-performance Software Packages Developed in Physics Accelerator Group at ANL." Seminar at Fermi National Accelerator Laboratory, Batavia, IL, Oct. 13, 2010.

Xu, J. and M. Min (2010). "Scientific Computing with High-order Numerical Methods." Applied Mathematics Division, Illinois Institute of Technology, Chicago, IL, Dec. 2, 2009.

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

2010-199-R1

Pavan Balaji, Jeffrey Hammond, Ewing Lusk, Nick Romero, and Rajeev Thakur

Project Description

Computing research has produced a rich variety of mature parallel programming models and runtime systems, each with its individual set of capabilities and advantages demonstrated on DOE applications. For applications to take full advantage of the massive parallelism of emerging multi-petascale and exascale systems, it is becoming increasingly clear that they need to use the capabilities of multiples of these models together. A well-known example is an MPI (message passing interface) application that needs to use a threading model within a node to better exploit the shared memory and many cores on the node. However, emerging applications and extreme-scale machines require a richer and more complex interleaving of programming models. For example, how can multimodule applications primarily based on Unified Parallel C (UPC) or Coarray Fortran (CAF) utilize math libraries written in MPI, such as PETSc, that have had hundreds of programmer-years of development invested in them? Similarly, how can an application written in global arrays (GA) utilize load-balancing tools written in Charm++? Can the threading infrastructures of Charm++ and OpenMP coexist within the same application, over the limited resources available on the node? For promoting software reuse, especially for expensive high-performance computing (HPC) software, it is also important that one be able to reuse an existing module or library in a new application, irrespective of the programming model in which it is written.

The overall goals of the project are to:

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 using scalable and flexible operating system capabilities.
3. Investigate how data-intensive applications can take advantage of advanced I/O and storage capabilities built for exascale systems.

Mission Relevance

DOE's missions, i.e., energy, environment, national security, and science supporting these, all require advanced computer-based modeling and simulation on the fastest supercomput-

ing systems. A goal of the Advanced Scientific Computing Research (ASCR) program in DOE's Office of Science is to reach a computing capability of 1 exaflop/sec by the end of this decade, which is also known as exascale computing. This project is directly related to the goal of exascale computing, which includes new exotic architectures and requirements for new methods for programming on these architectures. This project is aimed at initial research that would allow us to propose relevant topics in this area in response to upcoming DOE calls.

FY 2011 Accomplishments and Results

Over the past year, substantial progress has been made toward a unified runtime system for exascale computers, in terms of both building the necessary programming interface requirements to sustain this effort and meeting the immediate technical challenge of integrating new functionality into a common infrastructure. These improvements include improvements to the One-Sided PRimitives (OSPRI) framework, which allows us to study basic interoperability requirements of one-sided communication models with message-passing models, and the design of a new Aggregate Remote Memory Copy Interface (ARMCI)/GA implementation that is fully interoperable with the standard message passing interface (MPI). This work has allowed such computational chemistry applications as NWChem to utilize — for the first time — the entire capability of MPI and scale on the Argonne Intrepid Blue Gene/P system and the University of Chicago Beagle Cray XE6 system.

OSPRI Enhancements: OSPRI provides the necessary communication functionality to implement GA, which is an important instantiation of the partitioned global address space (PGAS) programming model with significant buy-in from the computational chemistry community. The software design of OSPRI was modeled after MPICH2 because (1) MPICH2 is extremely robust software that has been vetted by all major HPC vendors and (2) this approach will streamline the process of formally integrating OSPRI into MPICH2 as Argonne implements the unified software stack.

In FY 2011, we made further progress with OSPRI to understand its various performance characteristics as compared to the ARMCI model and the MPI RMA (remote-memory access) model. OSPRI consistently achieved the best performance compared to all other one-sided models. The basis for the improved performance is the OSPRI device-design, which is more tailored to leadership-class architectures, such as Blue Gene/P, and makes better use of hardware resources. OSPRI also optimizes for noncontiguous operations using the low-level active-message capability provided by DCMF, the low-level communication API (application programming interface). That OSPRI is more optimized for Blue Gene/P than ARMCI does not mean that it is less optimized for other architectures, but rather that OSPRI can always be better optimized for the hardware because of the MPICH2-derived device design,

which allows for maximum code reuse with targeted replacement when a specialized implementation is warranted.

ARMCI/GA-MPI Interoperability: As a first step toward native interoperability between GA and MPI, we designed an infrastructure to allow ARMCI, which is GA's runtime system, to operate natively on top of MPI. By harnessing the portability of MPI, we created a highly portable, high-performance runtime layer for GA that extends the usability of GA and the NWChem computational chemistry suite to a wide variety of systems, including systems where a native ARMCI implementation is not available or has not yet been fully tuned. Currently, although GA and MPI are commonly used together, they have separate runtime systems, leading to duplication of effort and consumption of extra resources (e.g., duplicated pinned buffer management and asynchronous progress engines). By enabling GA to share MPI's runtime system, we achieved a greater degree of interoperability that increases the resources available to the application. We also demonstrated that, in spite of the measurable performance gap between moderately tuned MPI one-sided operations and aggressively tuned ARMCI one-sided operations, ARMCI-MPI provides the level of support needed to achieve competitive and portable application-level performance for the NWChem computational chemistry suite.

Proposed Work for FY 2012

Our proposed activities in FY 2012 include the following:

1. A working implementation of active messages and topology awareness extensions to the MPICH2 implementation of MPI.
2. A working implementation of a global task-space model using the active message and topology awareness functionalities in MPICH2.
3. A working implementation of quantum Monte Carlo integration by using global task-space capability.

Seminars

Balaji, P. (2011). "Trends in One-sided Communication Models." Institute of Software, Chinese Academy of Science (CAS), Beijing, China, Jan, 10, 2011.

Balaji, P. (2011). "Will Existing Programming Models Evolve for Exascale Systems or Die." Center for Development of Advanced Computing (CDAC), Pune, India, Dec. 23, 2010.

Balaji, P. (2011). "Is Hybrid Programming the Next Step in the Evolution of HPC." Institute of Computing Technology, Chinese Academy of Sciences (CAS), Beijing, China, Dec. 2, 2010.

Balaji, P. (2011). "Is MPI Relevant at Exascale." Institute of Software, Chinese Academy of Science (CAS), Beijing, China, Nov. 29, 2010.

Runtime Support for Integrating MPI and Accelerator Programming Models for Exascale Systems

2011-038-N0

Rajeev Thakur, Pavan Balaji, and Ewing Lusk

Project Description

The overall challenge that we address in this project is how we can design a mechanism that will allow new as well as existing applications to be programmed for upcoming heterogeneous architectures. More specifically, we need a mechanism that is not only efficient and easy to program but also provides a natural transition path so that existing applications can use future systems, which may have large numbers of cores per node, including accelerator cores. The main goal of this project is to develop a library and an associated runtime system that provides the ability to manage data movement both for general-purpose central processing unit (CPU) cores and accelerator cores in an integrated and unified manner. The primary idea is to allow different message passing interface (MPI) processes to express data movement ability for shared accelerator cores as well as general purpose CPU cores, allowing the runtime system to manage the sharing and taking advantage of the architecture-specific flexibility in data movement and other aspects of resource management.

We have divided the proposed work into deliverables resulting from five tasks and related subtasks, as described below:

Task 1: A programming interface to provide a collective view of the shared resources to applications.

Task 2: Runtime support to allow for processes to access shared resources in a coordinated manner. This task includes several subtasks: (1) allowing multiple MPI processes to view and utilize accelerator resources either transparently or with minor modifications to the applications; (2) dynamically migrating tasks on the available accelerators, which will allow for improved resource utilization and performance; (3) creating a high-level task management library that would utilize this runtime support and provide an easier-to-use interface.

Task 3: Runtime performance improvements for data movement. This task includes several subtasks: (1) the ability to pipeline data movement between the accelerator and host-accessible memory and between hosts; (2) utilization of accelerator-specific, memory-mapping techniques and coordinated direct memory access (DMA) techniques (such as those provided by NVIDIA accelerators and Mellanox InfiniBand adapters) to perform zero-copy communication; and (3) efficient movement of noncontiguous data chunks for accelerators.

Task 4: Improvements to accommodate future architectures, including Intel's Knights Ferry and AMD Fusion.

Task 5: Integration and evaluation with applications.

Mission Relevance

DOE's missions (i.e., energy, environment, national security, and science) all require advanced computer-based modeling and simulation on the fastest supercomputing systems. A goal of the Advanced Scientific Computing Research (ASCR) program in DOE's Office of Science is to reach a computing capability of 1 exaflop/second by the end of this decade, which is also known as exascale computing. This project is directly related to the goal of exascale computing, as accelerator-based architectures are one of the paths to exascale computing.

FY 2011 Accomplishments and Results

Parts of tasks 1 and 2 (described previously) were completed in FY 2011. The work mainly addressed shared access to the accelerator units from multiple MPI processes. Specifically, we designed a framework called VOCL (Virtual OpenCL) to allow MPI processes to access all accelerators available in the system (such as graphics processing units [GPUs]) transparently. Our goal is to understand the feasibility of "virtualizing" accelerators in such environments, allowing for computer nodes that can transparently view remote accelerators as local virtual accelerators. The VOCL framework provides the OpenCL-1.1 application programming interface (API) but with the primary difference that it allows an application to view all accelerators available in the system (including remote accelerators) as local virtual accelerators. VOCL uses MPI internally to perform the data management associated with remote accelerators and, thus, is fully compatible with MPI. However, it does not yet utilize the internal knowledge of MPICH2 (a widely used MPI implementation developed at Argonne) to optimize such data management. VOCL uses several techniques, including argument caching and data pipelining, to improve performance.

We also started investigating approaches to integrate data movement between accelerators and MPI. Specifically, in the context of GPU-based accelerator devices, the lack of efficient and transparent movement of GPU data in hybrid MPI+GPU environments challenges GPU acceleration of large-scale scientific and engineering MPI simulations. As long as GPUs continue using discrete memory separate from the CPU's main memory, direct network and input/output access will likely remain disabled, and, arguably, CPU-driven execution flow and GPU data management into the main memory for MPI communication will continue as the prevailing model. This model, however, introduces numerous challenges to allowing efficient communication between the different memory spaces.

To close this gap, we investigated end-to-end data movement frameworks that can work with GPU memory together with main memory. For internode communication, we examined

whether to use parallelism with the GPU DMA engines, pipelining, and other techniques for achieving high performance. For intranode communication, we investigated context sharing for multiple processes to enable simultaneous access of multiple GPU devices from each process. We also studied the requirements for communicating large, irregular, and non-contiguous data representations by exposing a fine-grained, element-by-element level of parallelism run as a GPU kernel, along with an efficient and serialized datatype representation based on an in-order traversal of the datatype specification. Our techniques demonstrated up to 100-fold improvement for such communication.

Proposed Work for FY 2012

We plan to continue progress in tasks 1 and 2. Most of the remaining work in these areas relates to utilizing these raw capabilities in higher-level libraries and even end applications, if possible (although realistically, end application evaluation for these parts might be performed in year 3).

Apart from these two tasks, we have started working on initial pieces for the remaining three tasks, as well. Specifically, we have started investigating unified data movement capabilities and Intel Knights Ferry architectures. Application testing is also planned for FY 2012.

Seminars

Balaji, P. (2011). "Transparent Virtualization of Graphics Processing Units." Institute of Software, Chinese Academy of Sciences (ISCAS), Beijing, China, Aug. 22, 2011.

Balaji, P. (2011). "Are Graphics Processing Units Viable as Cloud Services?," Tsinghua University, Beijing, China, Aug. 23, 2011.

Balaji, P. (2011). "Towards Virtualized Environments for Using Graphics Processing Units as a Cloud System Service." Shenzhen Institute of Advanced Technology (SIAT), Shenzhen, China, Sep. 8, 2011.

Exascale Data Analysis for Multiphysics Computational Science

2011-106-N0

Michael Papka, Mark Hereld, Thomas Peterka, Robert B. Ross, and Venkatram Vishwanath

Project Description

In this project, we are developing and implementing our acceleration techniques for data analysis to provide scientists with new capability and better performance. We are working in four technical areas to address challenges that are not being exploited, even for petascale computation: (1) the relatively

inexpensive cycles on the simulation platform that could be applied to analysis; (2) the computational cycles and memory available on I/O processors (e.g., Blue Gene I/O nodes (IONS), file system server nodes); (3) the computational cycles and memory available on local analysis engines (i.e., fast network attached graphics clusters); and (4) the network bandwidth between simulation and analysis engines. The outcome will be robust solutions to problems that scientists in many disciplines are struggling with now and will enable powerful new capability and levels of performance for their future research.

Mission Relevance

This project is relevant to DOE's basic science mission, in supporting transformative science in the areas of climate sciences, biosciences, astrophysics, computational chemistry, high-energy physics, materials science, and nuclear physics. Today's largest computational systems are providing unprecedented opportunities to advance science in these areas. Current DOE leadership-class machines, such as the IBM Blue Gene/P (BG/P) supercomputer at Argonne National Laboratory and the Cray XT system at Oak Ridge National Laboratory, consist of a few hundred thousand processing elements. In the case of FLASH, a multiphysics, multiscale simulation code with a wide international user base, the Intrepid BG/P supercomputer at the Argonne Leadership Computing Facility (ALCF) is enabling scientists to better model, validate, and verify phenomena in various fields, such as the study of thermonuclear-powered supernovae and high-energy density physics.

FY2011 Accomplishments and Results

In FY 2011, we integrated efficient "data passing" with the I/O layer to enable full use of the network bandwidth out of IONS. We accomplished this task by modifying common I/O abstraction layers such as HDF5 and pnetCDF, allowing users to apply new efficient approaches without changing their code. This enhancement was tested with FLASH. Related to this effort we designed a portable file layout within netCDF and HDF5 for augmenting original raw data with derived fields and data structures for accelerating access for analysis. We began to implement this layout within the netCDF parallel I/O layer, as transparently as possible to the application. We tested this file layout with FLASH, PHASTA (Parallel Hierarchic Adaptive Stabilized Transient Analysis), and several benchmark I/O codes that mimic I/O behavior. We designed and implemented an abstraction layer and application programming interface (GLEAN) for run-time analysis on I/O nodes, and tested it with both FLASH and PHASTA codes on the Intrepid system at Argonne.

In partnership with the FLASH code team, we initiated run-time analyses tests, calculating derived values of surface area and regions of maximum curvature. We are comparing the placement of analysis operations on compute, I/O, and Eureka nodes against predicted performance models. We are both

storing derived data alongside simulation data for later post-processing and using it only at runtime, deleting it before writing to disk.

Research and development continued on the Do It Yourself (DIY) library. DIY was tested in three analysis applications: parallel particle tracing, parallel information theory, and parallel topological analysis. Science domains included fluid dynamics, astrophysics, and combustion. The results indicated a 2X performance improvement in particle tracing, a 59% strong scaling efficiency in information theory, and a 35% end-to-end strong scaling efficiency in topological analysis.

In addition, to better identify applications we need to target, we developed methods to study combined data from several system logging sources to help better understand resource usage patterns on supercomputing resources. We are using the ALCF computing, storage, and network resources as a test bed for these studies. From the data, we are able to detect and verify I/O patterns, anomalous performance patterns, and opportunities for significant improvement in application performance.

Proposed Work for FY2012

In FY 2012, we plan to work more closely with Argonne computational teams in materials and cosmology in order to anticipate the arrival of the BG/Q supercomputer, Mira. We will also continue to work with key strategic computational teams such as the Flash Center and PHASTA. In particular, we will attempt to generalize the tools to work on not only the Blue Gene series of computing resources, both P and Q, but also Cray supercomputers. We will be working to generalize GLEAN, DIY, and the interface infrastructure so that working with other application teams is straightforward.

We plan to update our topology-aware mechanisms and reduce synchronization requirements of GLEAN so it can be used to optimize the performance of MPI-IO implementations on various platforms. This update will greatly benefit the higher-level I/O libraries (including HDF5, pnetCDF, and ADIOS) built on top of the high-level file interface MPI-IO. We also plan to continue to promote GLEAN as a new infrastructure for supporting co-processing. We will be adapting it to running on OSX and Linux, Linux-based clusters, and BG/P systems.

We are working on transferring GLEAN to Cray Systems and making our topology-aware mechanisms more generic to extend the systems it can support. Additionally, we plan to incorporate the topology-aware data movement optimizations to the MPI-IO layer on BG/P to allow the broader community of applications to benefit from our efforts (including HDF5 and pnetCDF). We believe this is a significant step toward scaling the performance of applications on current large-scale systems and will provide insight for the design of I/O architectures for exascale systems.

Development of Software Infrastructure for the Simulation of Microbial Communities on HPC Architectures

2011-126-NO

Christopher Henry, Narayan Desai, Folker Meyer, and Rick Stevens

Project Description

Biological systems have tremendous potential for application to biofuel production, carbon biosequestration, and waste cleanup, and this realization has led to significant investment in the development of high-throughput experimental techniques directed at rapidly advancing our knowledge in how these systems respond to environmental and genetic perturbations. In recent years, this investment has resulted in significant dividends: protein profiles from mass-spectrometry (MS) data; gene expression profiles from microarrays and sequencing; gene profiles from metagenomics sequencing; metabolite profiles from MS, nuclear magnetic resonance, and chromatography data; phenotype profiles from Biolog arrays; and transcription factor and binding site profiles from chromatin immune precipitation with microarray technology (chIP-chip). At the same time, investment in the design and construction of high-performance-computing (HPC) platforms has led to the development of massively parallel architectures containing over 100,000 interlinked processors with petaflops of computing power. These HPC platforms are capable of simulating systems at a scale and complexity that has never previously been possible. Unfortunately, the conceptual paradigms and software infrastructures needed to apply these HPC platforms for the simulation and analysis of biological systems are still not available.

We are proposing to build an integrative and extensible computational framework that will provide biological researchers with the capability to assemble multi-cell models of complex biological communities and to scalably simulate these communities on modern HPC architectures to gain new insights into community dynamics, emergent community behaviors, cell-to-cell interactions, and cell interactions with the environment. This framework will provide a generalized platform to predict how individual cell behavior affects the organization of a microbial community in its natural environment. The new platform will facilitate the incremental building of biological models, as it will enable the combination of coarse-grained representations with more detailed biological modules. The modular architecture of this system will provide the flexibility needed to utilize the framework to pursue a wide variety of scientific questions relating to cellular communities. Most importantly, the framework will be parallel ready, capable of

efficiently utilizing 100K+ processors and memory spaces on a wide variety of architectures to simulate biological communities at a massive scale.

At the conclusion of the project, we will be able to create large-scale simulations of the communities being observed and analyzed by the metagenomics community. This capability is essential to translating catalogues of biological functions and microbial cell types into functioning and predictive models of microbial community behavior. The ultimate goal is to use metagenomic data to improve our understanding of how microbes influence their environment and how that influence may be controlled by human intervention.

Mission Relevance

This project is relevant to DOE's mission in science as through that, to its energy and environment missions as well. The proposed framework will enable researchers in biology and computational biology to apply HPC infrastructure to the analysis of any biological phenomena that involves interactions within a complex community of cells. This includes simulations of microbes in the human gut, cells organized into tissues, microbial communities in the soil and oceans, and microbe competition and evolution. Large-scale simulations of microbial communities are essential for gaining a complete understanding of the principal driving forces that control these communities. They will enable us to better predict how microbial communities will respond to a change in the environment, such as global warming or an oil spill. They will also enable us to control these communities and direct them toward a useful application such as degradation of biomass, sequestration of CO₂, synthesis of biofuel, or storage of energy in chemical form. These simulations will be invaluable to research efforts in human health, including improving our understanding of how microbes interact with each other and with human tissue when living inside the human body. We will be able to simulate infection and microbial symbiosis with human tissue at a level of detail never previously possible.

FY 2011 Results and Accomplishments

In FY 2011, significant progress was made in developing the core of the proposed simulation framework. The framework now includes software infrastructure for creating new simulations, printing simulation results, coordinating intra-processor and inter-processor communication between simulation modules, and assembling hybrid models into a single integrated simulation environment. Additionally, an XML parser was integrated into the software, enabling users to specify complex models in terms of XML, negating the need to write code to formulate new models. A module was added for printing simulation output in HDF5 (high dimensional file) format, which will be essential for holding the output of the large multi-scale models simulated by our framework.

We also made progress in the development of new simulators for our framework. Specifically, we created a simple finite difference method (FDM) simulator to capture the flow of nutrients through a 3D environment over time. We created an agent-based modeling (ABM) chemotaxis simulator to capture the movement of cells within the environment. A flux balance analysis (FBA) simulator was created to capture the flow of nutrients through the metabolic networks of each individual cell in the environment. A stochastic simulator was implemented to capture stochastic processes in the environment, such as gene expression or protein biosynthesis. Finally, a script-based simulator was implemented, enabling users to write their own simulators and models of cell behavior in the programming language Perl, with the resultant model being automatically integrated into the core framework. This capability makes the system more extensible, and it dramatically reduces the expertise required for a new user to begin writing new models that function within the community simulator environment. With all of these simulators integrated into our simulation framework, we now have all components needed to generate powerful multi-scale hybrid models of microbial communities in the environment.

The simulation framework was tested for scalability while running in parallel on the Blue Gene/P (BG/P) system. Specifically, using 1,000 CPUs, we applied our framework to simulate approximately 1 million cells independently foraging for nutrients. Scalability tests conducted using 256, 512, and 1024 processors indicated a near-linear scaling for our test simulation. We applied this simulation to explore the trade-off between various metabolic strategies and foraging strategies in different environmental conditions. Simulation results indicated that the ideal behavior depended substantially on the stress level and nutrient abundance available in the environment.

To apply our simulation system to predict and understand the behavior of microbial communities, we need to create models of the metabolism of the individual that make up these communities. To this end, our Model SEED system was applied to construct models of 3,000 complete genome sequences available for prokaryotic organisms. These models will be used to construct simulations of a microbial community metabolism based on metagenomic data.

Proposed Work for FY 2012

In FY 2012, we will continue to build on our core simulation framework by integrating algorithms for dynamic load balancing. As cells move through the 3D environment, they will often aggregate into concentrated groups, causing the simulation, which is distributed spatially across our available processors, to become unbalanced. Load balancing algorithms adjust the distribution of the spatial environment among processors to produce a more balanced load and improve the efficiency of parallel computations. We will be creating a test system that

produces load imbalance, and we will apply this model to evaluate our implementations of load balancing algorithms. We will use this system to test the ability of our software to scale to the 160,000 processors currently available in BG/P.

We also plan to develop elements of the interface employed by users to create models and view results. We will produce modules for visualizing simulation output, and we will develop XML files for specifying the hybrid models that will run in our simulation framework.

Next, we will create the template models that will apply our now implemented simulation methods to replicate various biological activities. Specifically, we will create ABM models of cell growth, cell division, and cell death; FBA models of metabolism; finite element models of various environments; and an ordinary differential equation (ODE) model of nutrient utilization.

Finally, we will apply our simulation software to study the behavior of a real microbial community present in a soil environment. To this end, we will be developing methods to produce metabolic models of community microbes based on metagenomic data. Then, we will create a simulation of this community, including the activity of approximately 1 billion cells. One important goal is to study the potential impact that species of low abundance can have on the global community, emphasizing the need for simulations at scale. In this study, we will also explore the speed and level of detail possible in a simulation that includes 1 billion cells. On the basis of this work, we plan to submit at least one publication on our simulation framework itself, and at least one publication on our soil community model.

Beyond-Petascale Monte Carlo Methods for Practical Nuclear Reactor Analyses

2011-211-N0

Andrew Siegel

Project Description

The goal of this work is to build a flagship, state-of-the-art, highly scalable Monte Carlo (MC) neutron transport code. To demonstrate the code's capabilities, we aim to use it to be first to solve the so-called *Kord Smith Challenge* community benchmark problem. To build such a code is both a major research and a development project, requiring considerable underlying algorithmic and fundamental analytical insight; thus, as a first step we are working on much of the theory and many of the basic properties of such an algorithm, refining these approaches on reduced applications kernels.

Mission Relevance

This project is relevant to both DOE's energy and science missions. This work is highly relevant to the Nuclear Energy Enabling Technologies division of DOE-NE, where next-generation methods in neutron transport will be necessary for the design and analysis of innovative reactor concepts, especially those further from existing design points, such as the Small Modular Reactors currently gaining popularity. Advanced safety modeling (e.g., for accident-resistant fuels) and the study of reactor physics in other non-ideal scenarios all require fundamental algorithmic advances in accuracy and time to solution. This research is also relevant to the DOE ASCR (Advanced Scientific Computing Research) office. Innovative, extremely scalable (million+ way concurrency) algorithms for next-generation exascale machines need to be explored well ahead of the deployment of those machines. ASCR, as evidenced by the Co-Design Centers, has great interest in ensuring that key application areas are "ready" when exascale machines with non-traditional characteristics are deployed. This research fills this need perfectly, especially given that neutron transport is, in many ways, a broad and canonical area of computational physics. It is probably also the case that a general, robust, highly scalable MC code could also be used, in principle, to pursue work in a broad range of applied areas supported by such agencies as the National Science Foundation (NSF), National Institutes of Health (NIH), National Nuclear Security Administration (NNSA), and DOE-BES, where large particle simulations are necessary to explore a variety of issues in, for example, medical dosimetry and particle material interactions, among others.

FY 2011 Results and Accomplishments

In FY 2011, we completed the Monte Carlo Communication Kernel (MCCK) mini-application for exploring scalable MC algorithms on Blue Gene/P. MCCK was used to study fundamental performance issues related to the need for and feasibility of carrying out domain decomposition for reactor analysis. Using MCCK together with theoretical analysis, we were able to identify the parameter regime over which domain-decomposed MC codes should attain good scalability and performance. This is a critical step in assessing the path forward for algorithmic strategies in next-generation MC production codes. The MCCK mini-app was carefully developed and packaged for external use. We currently plan to use MCCK as one of the mini-apps in the Argonne-led Center for Exascale Simulation of Advanced Reactors (CESAR) project.

In a second critical performance analysis, the goal was to quantify the computational cost of load imbalances when employing domain decomposition for MC. We derived formulas predicting the performance "penalty" of load imbalances

for reactor applications and calibrated these with results from the OpenMC code. This work proved that for reasonably large levels of concurrency, the performance penalty of imbalance is modest in light of the cost of cycles predicted for next-generation architectures. This result also was critical for determining the best path forward for next-generation MC codes.

Finally, we began the transition from fundamental algorithmic studies to real-world, full-physics scalable MC code development and application. Further details are discussed in the "Proposed Work" section below, but our principal strategy has been to work with engineers at MIT (Kord Smith, Ben Forget, and Paul Romano) to use their OpenMC code as a starting point for our own development of incorporating OpenMC into this project and merging it with MCCK has begun and should be finished by the end of FY 2012.

We also began exploring implementations of MC on Argonne's Tesla GPGPU (general-purpose computing on graphics processing units) machine.

Proposed Work for FY 2012

In FY 2012, we will focus our efforts in several new directions:

- ▶ Incorporating the full-physics, parallel OpenMC code from our collaborators at MIT into the project. OpenMC will form the foundation for the next steps of this project (i.e., to test the ideas developed in the first year on real reactor physics benchmarks with a full-physics code). Porting OpenMC to Argonne will take place during the first quarter of FY 2012. This code will also form the foundation of a highly scalable MC flagship code.
- ▶ Exploring MC algorithmic issues on more exotic architectures via abstract architectural descriptions. This work is intended to flow into the CESAR project and provide a potential future source of redirected or new funds for MC work.
- ▶ Building an MC implementation on the Tesla GPGPU architecture via CUDA (compute unified device architecture) addressing fundamental issues in doing random number generation and fast branching on SIMD (single instruction, multiple data) architectures. This implementation will provide a real-world case study of interesting aspects of next-generation MC methods.

Towards the Exascale Sky

2011-213-NO

Salman Habib, Sanghamitra Deb, Katrin Heitmann, Juliana Kwan, and Hendrik Weerts

Project Description

The unveiling of the large-scale universe by sky surveys has transformed cosmology, fundamental physics, and astrophysics. An intense global effort is under way to fathom the deep mysteries posed by the existence of dark energy and dark matter. Near-future observations — the “Great Surveys” — promise new discoveries and an unprecedented increase in our knowledge of the universe. The project team has developed the first petascale cosmology code suite designed to exploit a variety of current and future high-performance computing architectures. Combined with the arrival of the Mira supercomputer at Argonne, this capability puts us in a unique position to create breakthroughs in fundamental aspects of cosmology and to produce the best predictions for structure formation probes of the “Dark Universe.”

Specifically, under this project, we are building the first exascale computational cosmology capability for next-generation sky surveys suited for next-generation computational architectures (see Figure 1). The HACC (hardware/hybrid-accelerated cosmology code) framework being developed under this project is designed to encompass different high-performance computing (HPC) architectures, including multi-core as well as hardware-accelerated systems. HACC is being developed in conjunction with contemporary hardware and software advances. In addition, we are developing the Cosmic Calibration Framework (CCF), an advanced statistical framework that melds HPC simulations with observational data to provide rigorous error-controlled estimation of cosmological and modeling parameters.

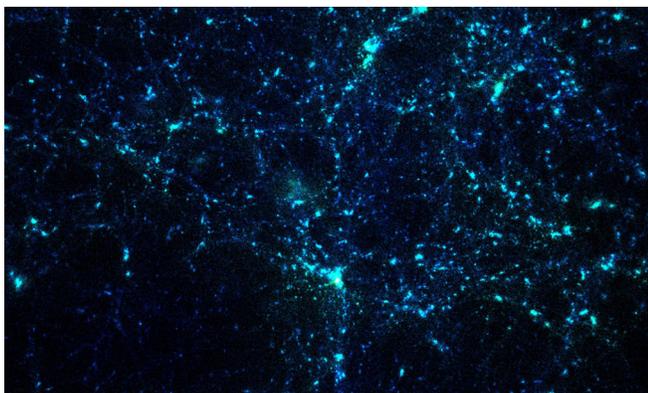


Figure 1. The dark matter distribution in the Universe, as obtained from a large test simulation run with HACC. The distribution is characterized by large, relatively empty “void” regions and by filamentary and clumpy concentrations of dark matter. Galaxies form within the localized clumpy regions. HACC has been used to carry out several large state of the art simulations to characterize the distribution and shape of dark matter clumps or “halos.”

Mission Relevance

This project is relevant to DOE’s basic science mission. The HPC advances that underlie this project will have a broad impact on several fields, including accelerator and plasma physics, computational co-design, particle transport simulations, and management and analysis of very large datasets. The advent of the “Great Surveys” presents a significant and timely opportunity for Argonne to play crucial frontline roles in DOE missions, covering both the discovery (cosmology, particle physics) and capability spheres (HPC, large datasets).

FY 2011 Results and Accomplishments

We made significant progress in the major focus areas. In FY 2011, the medium-resolution version of the HACC framework was ported to the Argonne-IBM Blue Gene (BG)/P supercomputer, Intrepid. This work included the development of a new parallel Fast Fourier Transform that scales to a very large number of processors (tested across the full BG/P array), allowing the code to scale to the largest supercomputers available over the next decade. A new high-resolution, tree-based solver was developed for the BG architecture. Additionally, the HACC framework was ported to graphics processing unit (GPU) accelerated systems with a code written in OpenCL. Initial runs were carried out on the Argonne Eureka system.

To extend the CCF for the next round of cosmological predictions, we mapped out our simulation campaign by using simplified surrogate models. We found that a mix of medium- and high-resolution simulations will be optimal to achieve the required accuracy. We also developed a powerful set of analysis tools for HACC and began testing the incorporation of the galaxy formation code Galacticus within our simulation framework.

Proposed Work for FY 2012

In FY 2012, we will complete the porting of the full high-resolution version of the code to the BG/P and to the new BG/Q, Mira, when it arrives. Once this is achieved, we will carry out a set of large simulation runs on the BG/Q system. On this time frame, we will also run our GPU-enhanced code on the Oak Ridge National Laboratory hybrid system, Titan.

To model small scales of interest in cosmology at the accuracy level required by next-generation surveys, it will be essential to include hydrodynamics effects in our simulations. The HACC framework provides an ideal platform to use particle-in-cell (PIC) methods for this purpose. Currently, two methods are most commonly used for cosmological hydro-simulations: adaptive mesh refinement (AMR) methods, which are grid-based, and smooth-particle hydro (SPH) simulations, which are particle-based. Both methods have shortcomings: AMR codes currently do not perform well in cosmological settings,

while SPH methods have problems with resolving shocks. Our aim is to develop a PIC method that combines the virtues of AMR and SPH in order to develop an optimal pathway for cosmological hydro-simulations. In FY 2012, we aim to have the PIC method operational on three-dimensional test problems.



HARD X-RAY SCIENCES

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-R3

Alireza Nassiri, Joel Fuerst, and Geoff Waldschmidt

Project Description

Storage-ring-based synchrotron radiation sources produce light in pulses with a typical duration of several tens to hundreds of picoseconds; defined by the equilibrium electron bunch length. This pulse length is adequate for many applications. However, for a broad class of dynamics phenomena that occur in the shorter time scales, sub-100-ps x-ray pulses are preferred to probe very fast structural changes. To provide this unique capability, we are exploring the development and implementation of a novel scheme to use continuous-wave superconducting radio-frequency (SRF) deflecting cavities in two sectors of the APS storage ring to generate 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 development of a high-repetition-rate picoseconds short-pulse x-ray (SPX) source will enable an understanding of the relationship between structure and function in complex systems at the molecular level. The picoseconds timescale has unique importance, since it is an excellent match for the structural dynamics of nanoscale systems and for conformational changes in supramolecular systems, which have technological relevance and generate fundamental interest. The high-repetition-rate SPX source can be uniquely and efficiently developed at the APS because of the large storage ring architecture and advantageous timing structure. At completion, the SPX will be unique and complementary to x-ray free-electron lasers, provide approximately 100x improvement in time resolution for hard x-ray synchrotron science, and serve as an integral component of the photon research-site strategy for the United States.

FY 2011 Results and Accomplishments

In FY 2008, we completed beam dynamics studies of a single-cell deflecting cavity, single-cell geometry optimization, surface field analysis, fabrication and testing of the first single-cell niobium cavity, and extensive modeling and analysis of eigenmodes distribution in single- and multi-cell superconducting RF deflecting cavities.

In FY 2009, we completed the design and fabrication of a niobium single-cell structure with an on-cell waveguide damping and a niobium 2-cell structure. These structures were fabricated and tested in association with the Jefferson National Accelerator Laboratory. Initial test results in achieving the required deflecting field gradient and the cavity quality factor (Q) were encouraging. These measurements also revealed multipacting (breakdown) activities in the vicinity of the on-cell damping waveguide. The multipacting issues are being analyzed by using a three-dimensional simulation code in association with Stanford Linear Accelerator Laboratory. On the basis of this analysis, the cavity's shape and fabrication process will be modified to mitigate this problem. In FY 2009, we also designed and fabricated a novel 2.5-cell deflecting structure made of copper as part of our cavities modeling effort. This cavity is now being tested.

In FY 2010, two single-cell structures were designed, fabricated, and tested. Researchers from the Thomas Jefferson National Accelerator Laboratory (JLab) participated in this effort. Together, we successfully fabricated and processed a single-cell cavity (Mark I) equipped with a lower- and higher-order-mode (LOM/HOM) damping waveguide and an input power coupler. A second cavity design concept (Mark II), employing an "on-cell" waveguide damper, was also developed in parallel. The latter design provides improved damping of the unwanted frequencies within the cavity and will be shorter in overall length. Multipacting (breakdown) issues for the on-cell damping structure have been extensively modeled and simulated by using a 3D code (Omega3P/Track3P) developed at Stanford Linear Accelerator Center (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 limit (required voltage to vertically deflect charged particles inside the RF deflecting cavity).

In FY 2011, we focused on the development and testing of several SRF deflecting cavities in a joint effort with JLab. We successfully fabricated and tested two RF deflecting structures that meet the performance requirements of the APS-U SPX project. Both cavities produced the required deflecting field of 500 kV (see Figure 1). In cooperation with SLAC researchers, we conducted a simulation and analysis of the surface magnetic field and multipacting phenomena in the cavity to study these effects on the deflecting voltage limit and potential breakdown within the structure. The simulation and analysis findings from using SLAC's parallel suite of 3D codes, ACE3P, resulted in modification of the cavity geometry before the start of the modeling phase. In addition, the Argonne/JLab alliance developed a slow and fast tuner (to adjust cavity frequency due to environmental changes) to keep the cavity on resonance. This tuner system is now ready for modeling.

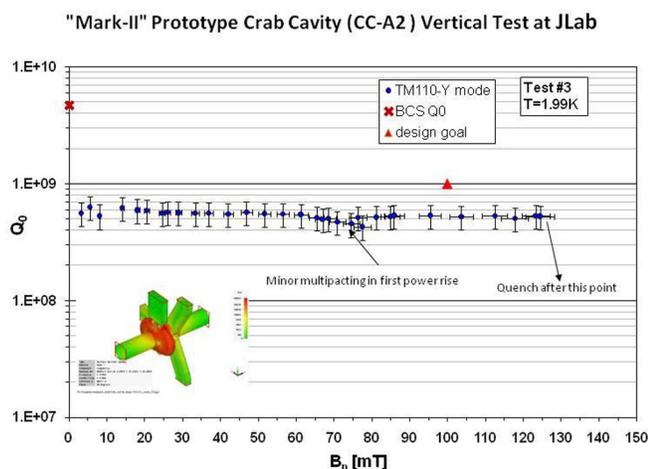


Figure 1. Results of "Mark-II" Crab Cavity (CC-A2) Vertical Test at JLab. The figure shows the variation of the cavity quality factor, Q_0 (frequency \times stored energy/dissipated power), with magnetic field at the surface at a temperature of 1.99 K. The test was done in the vertical magnetic deflecting mode (Y-direction). The theoretically predicted Q -factor based on the BCS theory of superconductivity is indicated by the X symbol and the triangle symbol shows the design goal for our cavity.

Catalyst Station at Advanced Photon Source Beamline 9-BM

2009-050-R2

Steve Heald, Trudy Bolin, Jeffrey Miller, Peter Stair, and Randall Winans

Project Description

This project involves an experimental capability upgrade for beamline 9-BM and the associated laboratory to enhance catalyst research opportunities at 9-BM and the Advanced Photon Source (APS) in general. Synchrotron radiation methods have important applications in catalyst research. The completion of this project will enable us to support DOE missions by making automated concurrent x-ray absorption fine-structure (XAFS) and Fourier transform infrared (FTIR) 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 — all relevant to DOE mission areas. 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 enhances our local capabilities to the state-of-the-art level for catalyst research at synchrotron facilities, thereby supporting those DOE missions. Further, it will provide the capability for automated concurrent operando XAFS and FTIR — a capability found at only a few beamlines worldwide. In addition, this project is the first

step toward facilitating catalyst research at other beamlines around the APS.

FY 2011 Results and Accomplishments

In the first two years of the project, the 9-ID-C hut was fully instrumented for operando XAFS studies of catalysts, including a full range of detector options, catalyst sample cells, and hazardous gas handling facilities. We also expanded the capabilities of the supporting laboratories with a full range of options for catalyst sample preparation, including bringing into operation a high-quality glove box.

Efforts during this final (third) year of the project began to wind down. The primary goal this year was to bring the infrared (IR) spectrometer into full operation for simultaneous collection of IR and XAFS data. Last year, we purchased an IR spectrometer from Bruker Optics, including a customizable sample chamber. We also acquired a diffuse reflectance IR cell, capable of heating the sample and flowing gases through it, from Harrick Scientific. This year, we modified both the spectrometer and the cell to allow the x-rays to pass through the sample contained inside the IR cell simultaneously as IR spectra are collected. We designed a mounting platform to allow mounting of the entire spectrometer to our standard optical table and to permit independent alignment of the spectrometer with the x-ray beam. In February 2011, we collected combined IR and x-ray absorption spectroscopy spectra characterizing a zeolite-supported copper catalyst, similar to those used for nitrogen oxide reduction. During the experiment, IR spectra were obtained in as little as 15 seconds, and x-ray absorption near-edge structure spectra were collected in just over 2 minutes.

The second major accomplishment was the automation of the gas handling systems that were previously installed. Computer-controlled valves, flow controllers, temperature controllers, and custom Labview software now allow programmed sequences of operando catalyst treatments, as well as FTIR and XAFS measurements.

The associated laboratories continued to be upgraded to support catalyst research. We started to convert the 432-A020 laboratory into a chemical laboratory capable of supporting catalyst sample preparation. Also, we installed at the beamline a previously purchased glove box for "dirty" samples, which consist of samples that are not compatible with the formerly installed high-quality glove box in the sample preparation laboratory.

FY 2011 was the last year for this project. We are planning to add another beamline scientist at 9-BM to increase the user support and beam time available for the new capabilities.

Combined Approaches toward a Hierarchical Understanding of Battery Materials

2010-074-R1

Karena W. Chapman, Jonathan D. Almer, Mahalingam Balasubramanian, and Karoly Nemeth

Project Description

This project addresses integrating the application of a suite of emerging hard x-ray capabilities to help us understand the factors that currently limit battery performance. Our unique approach applies 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 the behavior of materials in an operating electrochemical cell. The simultaneous analysis of all the available data through multiscale modeling will yield fundamental insights into battery materials.

To understand the cell component mechanisms that limit the performance of current-generation lithium-ion batteries (LIBs) and enhance the performance of next-generation LIBs, state-of-the-art materials characterization and sophisticated data modeling must be integrated. We have identified key x-ray methodologies, each able to provide structural information on battery materials. Although analyses focus on particular aspects of the material's structure, we can combine insights from the methodologies to gain a complete understanding of it — from the atomic scale (x-ray absorption fine structure [XAFS], pair distribution function [PDF]) to particle size and shape (small-angle x-ray scattering [SAXS], imaging, etc). Our approach brings together complementary information by using multiscale modeling of the data sets, based mostly on reverse Monte Carlo (RMC) methods.

In situ studies are a cornerstone of the project, since battery materials must be studied at other-than-ambient conditions (those at which batteries operate) in order to explore the often-complex structure-function relationships (including structural changes that occur during cycling). The electrochemical sample cells are being optimized to allow high-quality, comparable data to be collected *in situ* by different methodologies.

An electrochemical laboratory was equipped to prepare electrode materials and assemble and test electrochemical cells. This effort is pivotal to battery research at the Advanced Photon Source (APS), since such studies require the cycling of electrode materials (positive and negative) against metallic Li^0 , with strict transport constraints for metallic Li^0 .

Mission Relevance

This project is relevant to DOE's missions in energy and science. Battery research is a high priority in DOE. This project provides a strategic path by which DOE can pursue hard x-ray studies of energy storage materials. It will have a significant impact on work being done by users at the APS. The integrated approach being developed will resolve complex structural problems relevant to batteries and can be readily extended to challenges associated with other materials. The capabilities developed will be valuable for DOE battery programs being conducted at DOE laboratories, universities, and industries. The APS-based electrochemical preparatory laboratory being assembled will be very important to this user community for synchrotron studies now limited by strict Li transport regulations.

FY 2011 Results and Accomplishments

In FY 2010, our accomplishments included the following:

- ▶ A test *in situ* electrochemical cell was designed.
- ▶ Equipment and supplies to equip a local electrochemistry laboratory were sourced.
- ▶ An initial test material ($\alpha\text{-Fe}_2\text{O}_3$) was identified, prepared, and used to optimize experimental approach.
- ▶ *Ex situ* (and some preliminary *in situ*) XAFS and PDF experiments were conducted for $\alpha\text{-Fe}_2\text{O}_3$.
- ▶ A preliminary application of RMC was undertaken to develop structural models consistent with both *ex situ* XAFS and PDF data.

Our accomplishments of FY 2011 are discussed in more detail here:

1. Optimized and performance benchmarked *in situ* cell (electrochemical and x-ray data)
2. Completed analysis of initial material ($\alpha\text{Fe}_2\text{O}_3$) (*ex situ* PDF)
3. Completed *in situ* PDF, x-ray absorption spectroscopy (XAS), and SAXS measurements of initial test material ($\alpha\text{Fe}_2\text{O}_3$).
4. Conducted preliminary studies of related conversion systems
5. Optimized the RMC code written and evaluated for simultaneous fitting of PDF and XAS data on model Fe systems ($\alpha\text{Fe}_2\text{O}_3$, αFe)
6. Equipped the electrochemistry laboratory at APS Sector 11 so it is now fully operational and is being used for Li battery experiments
7. Completed initial tomography/diffraction imaging studies

We optimized an *in situ* sample environment for taking PDF, XAS, SAXS, and imaging measurements during electrochemical cycling; more than 20 cells were fabricated. We benchmarked electrochemical performance against standard 2032 coin cells.

We established measurement protocols to allow accurate normalization of data. A six-cell holder, combined with the multi-channel Maccor cycler, allows parallel, *in situ* measurements of systems. The timing is well matched to the timescale of the x-ray scattering measurements (1–10 minutes per dataset) and electrochemistry (probe every 1–2 hours) and allows for efficient use of the x-ray instruments.

We studied the electrochemical conversion reaction of our initial test material by using *ex situ* PDF measurements as a prelude to the broader *in situ* study that combines methodologies. The PDF study of the electrochemical reaction of nanoscale α -Fe₂O₃ with lithium gave us detailed insight into the atomic structures of the redox-active Fe phases. We showed that the metallic Fe produced by this reaction is not simply nano-sized α -Fe but instead forms as highly defective nanoparticles that restructure continuously with lithiation. The reaction proceeds via a rock-salt-type intermediate, with reduced oxygen stoichiometry and local distortions matching those of wüstite. On the basis of this analysis, we revised the mechanism for the conversion reaction, and we propose a basis for its high capacity for reversibility and cyclability.

We took *in situ* PDF, x-ray diffraction (XRD), XAFS, and SAXS measurements for α -Fe₂O₃. The analysis of these data by using traditional methods is ongoing. A combined analysis by using RMC methods is planned. Initial assessments suggest a high degree of disorder and particle size uniformity in the Fe nanoparticles formed upon discharge.

We conducted initial studies (PDF) on a broad range of materials on the basis of related Fe and other conversion systems (FeF₃, FeF₂, FeOF, FeO, CuF₂). PDF analysis is well-suited for screening new materials for further analysis, since it offers the opportunity for insights from the immediate coordination environment extending to several nanometers (toward the length scale of nanoparticles). The method allows for the reliable identification of phases and evaluation of changes in particle dimensions throughout the electrochemical reaction. Initial assessments indicate the electrochemical reaction of oxo-containing Fe systems proceeds via a highly disordered rock-salt intermediate that transforms into disordered nanoparticles with frustrated particle growth. This appears to enhance cyclability.

We implemented simultaneous RMC modeling of PDF and extended XAFS (EXAFS) spectra. The implementation connects x-ray PDF with EXAFS involving explicit multiple scattering contributions. The extension allows for EXAFS updates following atom-swaps and, thus, for the study of Li migration in crystalline electrode materials. EXAFS computation was significantly accelerated via the discretization of effective path lengths and subsequent reduction of operation counts. The validity and accuracy of the approach were illustrated for small atomic

clusters and on 5,500–9,000-atom models of bcc-Fe and α -Fe₂O₃. The increased accuracies of combined EXAFS and PDF fits were compared to PDF-only and EXAFS-only RMC fits. This modeling approach may be widely used in PDF- and EXAFS-based investigations of disordered crystalline materials.

In addition, the electrochemical laboratory at APS Sector 11 is fully operational. We delineated and approved standard operating procedures for protecting equipment and safely handling Li metal.

Proposed Work for FY 2012

The project will be extended to:

- ▶ Use the custom-designed *in situ* cells to conduct PDF, XAFS, SAXS, and imaging studies
- ▶ Explore new opportunities for time-resolved studies using *in situ* cells to isolate reaction kinetics
- ▶ Apply our multiscale tools (combining *in situ* PDF/EXAFS with RMC) to understand the electrochemical reaction mechanism in selected Fe conversion systems, identify the factors that contribute to improved cyclability, and target higher-performance systems
- ▶ Develop more efficient RMC algorithms, with suitable constraints, to permit faster convergence and the addition of SAXS to PDF and EXAFS modeling
- ▶ Package the RMC codes for broader use by the project team

Development of Picosecond X-ray Pulses at the APS using MEMS-Based X-ray Optics

2010-117-R1

Jin Wang, Il Woong Jung, Yuelin Li, Daniel Lopez, Deep Mukhopadhyay, Gopal Shenoy, Deming Shu, and Don 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 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 demonstrate the feasibility of producing x-ray pulses with picosecond temporal resolution, broad energy tunability, and a high pulse-repetition rate using the Advanced Photon Source (APS). The major short-term goal of this development work,

which can have an immediate scientific impact, 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.

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 for investigating 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 2011 Results and Accomplishments

In FY 2010, a number of single-mirror MEMS devices were designed and fabricated to prove the concept. Static x-ray reflectivity of the mirrors was performed to demonstrate the feasibility of using the mirrors as x-ray optics.

Building on last year's success, we have made the following progress to fulfill the FY 2011 deliverables:

1. Several MEMS-based x-ray micro-mirror optics were designed, fabricated, and tested for x-ray modulation with resonant frequencies ranging from 2 to 75 kHz.
2. Design improvements were implemented to yield devices with resonant frequencies reaching 300 kHz. A MEMS-specific finite-element analysis (FEA) was performed to optimize their geometry while improving both speed and quality of these MEMS optics.
3. Extensive dynamic characterizations of these devices were performed with optical profilometry. The frequency response of the mirror deflection angle and dynamic deformation were measured by using a stroboscopic method with an LED pulse and an optical profilometer.
4. Dynamic x-ray reflectivity measurements at the APS showed great promise for using the current MEMS devices as x-ray choppers. Through a general user program at Sector 7 of the APS, we measured a number of MEMS-based mirrors with resonant frequencies ranging from 2 to 75 kHz. For the 75-kHz mirror, time-dependent x-ray reflection in grazing-incidence geometry (shown in Figure 1a) was clearly observed when the mirror deflected the incident x-rays into the detector during the mirror's fast rotation, as shown in Figure 1b. The optimum oscillation frequency was observed to be 75.62 kHz for this mirror, indicating that it is actively modulating the reflected x-ray beam intensity. With this scattering geometry, we were able to produce x-ray pulses with a

width of $\sim 2 \mu\text{s}$, capable of separating the singlet pulses from the rest of the pulse trains in the APS Special Operation Mode 1.

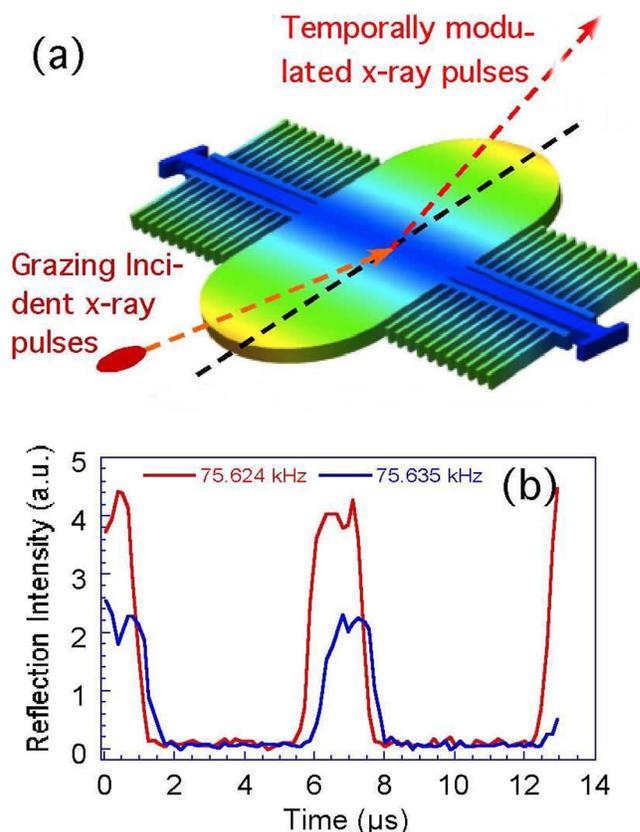


Figure 1. X-ray pulse modulation using a 75-kHz single-mirror MEMS: a) schematic of grazing-incidence geometry in total external reflection condition, b) measured x-ray reflection modulated by the fast-rotating mirror with reflection peak width of about $2 \mu\text{s}$ at the optimal driving frequency of 75.624 kHz.

5. To capture a significant footprint of the incoming x-ray beam at low incidence angles, arrays of micromirrors were designed and fabricated. A scanning electron microscope image of a fabricated mirror array with 270-kHz resonance frequency is shown in Figure 2. The individual elements in the arrays will be made to oscillate in unison by use of synchronization techniques.

As a result of our research, an invention report (IN-11-021), "Method for Spatially Modulating X-ray Pulses using MEMS-based X-ray Optics," was filed.

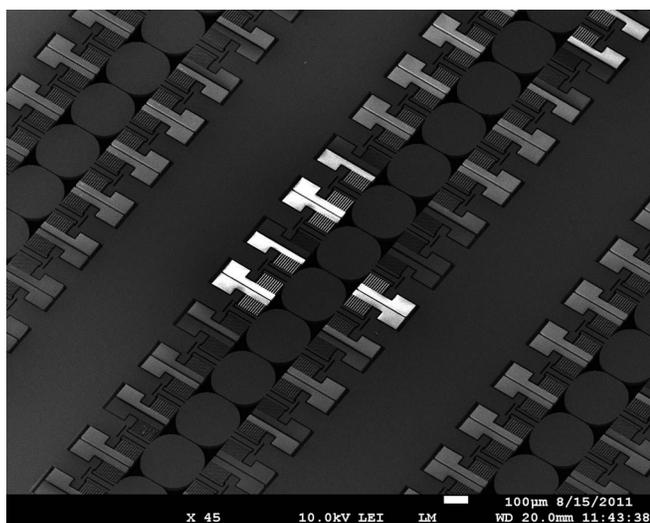


Figure 2. Scanning electron microscope image of fabricated mirror array with 270-kHz resonance frequency. The size of each mirror is designed to be 250 μm by 250 μm .

Proposed Work for FY 2012

1. Perform optical and x-ray metrology of 1D MEMS arrays at 300 kHz and extract x-ray pulses with nanosecond temporal resolution by using single and 1D-array MEMS devices by spatially dispersing a 0.5- μs pulse to demonstrate the concept for the future picosecond-pulse capability.
2. Package the 1D MEMS array for x-ray measurements; analyze the measured x-ray reflectivity and frequency response.
3. Compare experimental results with those from simulations using optical data.
4. Develop and test picosecond metrology and synchronization methodologies.

X-ray Nanoimaging for Life Sciences

2010-183-R1

Barry Lai, Lydia Finney, Chris Jacobsen, Mark Jensen, Ken Kemner, Jörg 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 (e.g., Hg, Pb) or carcinogens (e.g., As, Cr), which may present significant health hazards. This project aims to develop high-resolution x-ray nanoimaging methods that will allow elements of interest to be studied in their natural form

without any chemical labeling. In particular, it will enable for the first time not only the visualization and analysis of trace elemental content at a spatial resolution of 30-nm — an order of magnitude better resolution than current x-ray fluorescence microscopes — but also visualization of frozen-hydrated samples, which are as close as possible to the native state.

Mission Relevance

X-ray nanoimaging will impact 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 more effective bioremediation schemes. 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 into the growth of diatoms, which play a major role in carbon fixation in vast regions of the global ocean but the growth of which 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 2011 Results and Accomplishments

To reduce radiation damage and to preserve the sample in its native frozen-hydrated state, the sample needs to be maintained at a cryogenic temperature both before and during the measurement within the x-ray nanoprobe. To this end, we investigated two sample cooling schemes: conduction and 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 had designed in FY 2010 and completed the development in FY 2011 of an in-vacuum, conductively cooled bionanoprobe, which was installed at Beamline 2-ID-D. All major components, including the control system and cryogenic sample transfer, were thoroughly tested off-line and deemed ready for x-ray commissioning in FY 2011. In preparation, a white-beam slit that would deliver a symmetrical beam was also designed (FY 2010) and installed (FY 2011) at the beamline while the experimental station was modified accordingly for proper operation of the bionanoprobe. At the same time, we also conducted testing of a convectively cooled cryojet with an

existing x-ray microprobe at Beamline 2-ID-D and confirmed that the cryojet did not adversely affect the spatial resolution down to 200 nm. An initial experiment using the cryojet on plunge-frozen desmid green algae was performed, and the result indicated that there were visible differences in the manganese absorption spectra (micro-XANES) taken at room and cryogenic temperature, indicating protective effects of the cryogenic sample environment.

Proposed Work for FY 2012

We will continue with the development of and experimentation with the two micro/nanoprobes in FY 2012. The bionanoprobe will be commissioned with x-rays for the first time, initially at room temperature to demonstrate the high spatial resolution and the proper operation of the control system. Next it will be cooled down to cryogenic temperature to verify the robotic sample transfer. Nanoimaging of frozen-hydrated specimens will be performed for the first time. In particular, we will study whether radiation damage is indeed reduced at cryogenic temperatures and will then quantify the effect in the fluorescence mode and in the spectroscopy mode. At the same time, we will complete the modification of the 2-ID-D microprobe for cryojet operation, including using laser interferometers for real-time position feedback and novel weak-link stages for high-resolution specimen scanning. When completed, this effort will significantly enhance the scientific capability of Beamline 2-ID, not only in life sciences but also in soft materials (e.g., new applications involving organic photovoltaics, polymer batteries and fuel cells).

Seminars

Lai, B., S. Vogt, L. Finney, J. Maser and C. Jacobsen (2010). "Status and Plans for XRF Nanoprobes at the Advanced Photon Source." Biological Applications of X-ray Fluorescence Microscopy Workshop, Chicago, IL, August 14, 2010.

Vogt, S. (2011). "X-ray Fluorescence Microscopy: Imaging Trace Metals." Xradia, Inc., Pleasanton, CA, May 27, 2011.

Vogt, S. (2011). "X-ray Fluorescence Microscopy Capabilities at ANL." QBICANL Collaborative Meeting, Northwestern University, Evanston, IL, April 12, 2011.

Real-Life Imaging: Before and After the Microscope

2010-193-R1

Chris Jacobsen, Lydia Finney, Qiaoling Jin, Rachel Mak, and Stefan Vogt

Project Description

This project is aimed toward the development of new capabilities for x-ray microscopy and imaging. One activity is to develop capabilities 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. Electron microscopes are able to acquire spectrum image data with different physical mechanisms and over smaller length scales, yet mathematically the treatment of the data can be identical; this allows one to find image regions with common compositional characteristics automatically.

Mission Relevance

This project is relevant to DOE missions in Basic Energy Science (BES) and in Biological and Environmental Research (BER). The BES mission includes the development of high-end instrumentation for synchrotron radiation research of materials, while the BER mission includes improved methods to elucidate the structure of biological materials. This project supports the BES mission by developing ways to make better use of the data acquired in x-ray microscopes at the Advanced Photon Source. A workshop on Data and Communications in Basic Energy Sciences held in October 2011 highlighted the need to add sophisticated analysis approaches, such as we are developing (non-negative matrix factorization), to process the flood of data emerging from DOE's light source facilities. The cryo sample handling capabilities we are developing are relevant both to BES studies of soft materials and to BER studies of biological materials, since cryogenic sample conditions provide a way to study organic films, cells, plant tissues, and the like with a thousandfold reduction in radiation damage.

FY 2011 Results and Accomplishments

In the area of cryo sample preparation, we entered FY 2011 having selected and procured the basic instrumentation for the cryo lab: a high-pressure freezer and a cryo ultramicrotome. These instruments allow for the high-quality freezing of millimeter-thick hydrated samples and their sectioning to the micrometer-range thickness needed for x-ray microscopy studies. First tasks were to develop written procedures for the safe operation of the cryo lab equipment, including equipment purchased under this LDRD (the high-pressure freezer and

cryo ultramicrotome noted above) and equipment brought by the lead PI (Jacobsen) from his former position at Stony Brook University (a FEI Vitrobot plunge-freezer, a Nikon/Instec cryo light microscope, an Olympus inverted light microscope, and a cryogenic sample storage dewar). Additional equipment needed for cell growth and processing was procured, including an incubator, -20°C freezer, and refrigerated microcentrifuge. We then began to develop protocols for cryo preparation of samples, both on thin substrates (electron microscope grids and silicon nitride windows) and for thicker samples as prepared by high-pressure freezing. These sample preparation activities have meshed nicely with a separate LDRD project (Lai, 2010-183-R1) aimed at developing cryo x-ray microscopy instrumentation. We took on the task of preparing cryogenically frozen mouse fibroblast and algae samples, which were then provided to Lai's team for x-ray microscopy examination. We participated in the x-ray experiments by providing guidance on the best sample areas to examine and by evaluating the quality of the images obtained so as to guide improvements in the preparation of the next set of samples. In FY 2011, these activities with Lai's team using a cryogenic gas cooling system at beamline 2-ID-D at the Advanced Photon Source, showed that fluorescence scans of trace element distribution in biological samples could be obtained with improved sample fidelity relative to dried specimens.

In multivariate statistical analysis of spectrum imaging data, we entered FY 2011 having worked with the Mathematics and Computer Science Division (MCS) at Argonne to understand the mathematical underpinnings of the non-negative matrix factorization method we have been developing for spectromicroscopy data analysis. Before FY 2011, MCS helped us to better understand the desirability of including basic data processing constraints, such as spectral smoothness, in the cost function that is minimized in this analysis method, rather than adding it separately as an additional constraint applied during iterative processing.

In FY 2011, we issued a contract to a scientific software development firm to take legacy code written in the proprietary language IDL (ITT Visualization Systems) and convert it to an open-source Python language package, since development in Python is being encouraged by the Scientific Software Group at the Advanced Photon Source. This package, called Mantis, is now available on the web (code.google.com/p/spectromicroscopy). A PhD student supported under this project has been working on further development of the non-negative matrix factorization algorithm, including its incorporation into the framework provided by Mantis. Cost functions, including minimum absolute value second derivative (aimed at enforcing smoothness on reconstructed spectra), and data-matching and positivity constraints were developed. As this code is being developed, we have been working on validating the code by testing it on data involving the speciation of arsenic in

mail tailings, as well as on spectromicroscopy data for visualization of lignin and cellulose in biofuels materials as relevant to DOE's mission in energy research. This code development work was ongoing as FY 2011 ended.

Proposed Work for FY 2012

In FY 2012, the groundwork we have laid in developing cryo sample preparation protocols will play a key role in a new experimental program at the Advanced Photon Source: the first operation of the Bionanoprobe, a new x-ray microscope designed to work with frozen hydrated specimens for fluorescence imaging and tomography. This microscope is a first of its kind with robotic cryo specimen exchange. This project will prepare all cryogenic samples to be studied by using the Bionanoprobe. We will use the Bionanoprobe to provide feedback to improve our preparation methods and to develop protocols for cryo preparation of new sample types, such as HeLa cells incorporating titanium nanoparticles.

Our proposed work in FY 2012 in multivariate statistical analysis of spectrum imaging data is to finish the basic coding and verification of non-negative matrix factorization methods begun in FY 2011 and go on to build these capabilities into the open-source Python program Mantis (described above). We will then work on testing early versions of this enhanced program for the analysis of spectromicroscopy data acquired at the Advanced Photon Source; we have already had expressions of interest and early tests for the study of battery materials by using the transmission x-ray microscope (TXM) at the APS.

Seminars

Jacobsen, C. (2011). "X-ray Imaging for Environmental Science." Colloquium, Pacific Northwest National Lab, Richland, WA, Feb. 6–8, 2011.

Jacobsen, C. (2011). "X-ray Imaging." National School on Neutron and X-ray Scattering, Argonne National Laboratory, IL, June 2011.

Jacobsen, C. (2011). "4th Generation Light Source Applications in Microscopy." Higher European Research Course for Users of Large Experimental Systems (HERCULES), Orsay, France, Mar. 20–23, 2011.

Jacobsen, C. (2011). "Cryo: Samples, Damage, and Instruments." Biomedical Applications of X-ray Microprobes, Northwestern University, Evanston, IL, Aug. 11, 2010.

Tuning Electronic Structure at High Pressures: Toward Novel Materials Discovery from X-ray Science under Extreme Conditions

2011-023-NO

Daniel Haskel

Project Description

We seek to develop a state-of-the-art, x-ray spectroscopy capability that will enable researchers to conduct transformational studies of electronic and energy materials under the simultaneously extreme conditions of high pressure (1–2 Mbar), high field (10 Tesla [T]), and low temperatures (1–2 Kelvin [K]). The new capability will enable exploring changes in electronic structure and electronic ordering in a much larger (P,H,T) range than is currently available at any synchrotron facility. The expanded pressure range is of critical importance if we are to take the exploration of phase diagrams into uncharted territory, especially in systems with relatively small compressibility and large characteristic energy scales (~0.5–1 eV), such as complex oxides. The high-field capability will also enable studies at extreme pressure conditions of antiferromagnets and paramagnets — objects that are beyond the reach of current studies (only ferromagnets can be studied now).

Mission Relevance

This project is relevant to DOE's basic science mission. The new capability will provide information on electronic structures to be used as input in "materials by design" computational efforts. As stated in the DOE-Basic Energy Sciences report, *Materials under Extreme Conditions* (2007), some of the "grand challenges" for energy research on materials under extreme conditions include addressing such questions as the following:

Can the movement of electrons be predicted and controlled to form bonds under pressure? Are there totally new kinds of bonds in these regimes? Will the materials formed under these conditions have unique chemical (reactivity) and physical (electronic, magnetic, superconducting) properties?

We intend to create the capability to address some of these challenges with this project.

FY 2011 Results and Accomplishments

In FY 2011, our efforts focused on developing the cryostat/magnet system. This effort culminated in a final design and the acquisition of the cryostat part of the system. Details of the work that was involved follow:

- ▶ We studied cryogen-free and cryogenic options for cooling a superconducting magnet. We abandoned our initial preference for a cryogen-free design because vibrations could not be mitigated, even with pulsed-tube designs (experiments above 1 Mbar use sample sizes of ~20–30 microns, requiring ≤ 1 -micron stability).
- ▶ We examined cryogenic options for cooling the diamond anvil cell (DAC), including He-3 inserts and He-4 pumping. A variable temperature insert (VTI) with a 3-in. sample tube manufactured by Cryo Industries of America (CIA) was found to be suitable for cooling the DAC to 2.2 K (Lambda point), with the possibility of extending the temperature range down to 1.4 K. The static He loss rate is extremely low (0.16 L/h).
- ▶ We studied magnet solenoid versus split-coil magnet options. Solenoid magnets that are readily available yield large fields (14 T); however, the horizontal field geometry required for our measurements prevents us from using the vertically loading cryogenic VTI needed for low-T operation without vibrations. We pursued a split-coil magnet with a maximum field of 7 T. On the basis of the scientific case, we gave priority to low temperatures (i.e., 1.4–2.2 K) over high fields.
- ▶ The cryostat/dewar was designed with reentrant room temperature bores along the radial (split) direction to allow implementation of a Ruby optical system for *in situ* pressure calibration.
- ▶ The cryostat and magnet are being procured separately. A design was implemented in which the dewar/VTI was manufactured first (FY 2011), with a provision to allow insertion of the superconducting magnet into the dewar in FY 2012.

Proposed Work for FY 2012

We will test the cryostat's operation to 2.2 K (Lambda point), with thermal load of the CuBe DAC. We will explore operation down to 1.4 K. We will test performance of the membrane-driven DAC at 2.2 K (and possibly down to 1.4 K), ensuring proper piston motion at low temperatures. The cryostat will be shipped back to CIA so that installation of the superconducting magnet and inclusion of optical windows into the cryostat's shroud and shields can take place. While the system is being upgraded, we will work on implementing an annular photodiode detector into the DAC environment for taking the fluorescence measurements. We will obtain optical components for the Ruby system that will be placed in the reentrant bore of the magnet for *in situ* pressure calibration. Once the system returns from CIA, we will test operation at 6.5 T and 2.2 K and will carry out the first set of x-ray measurements exploiting the full capability of the system.

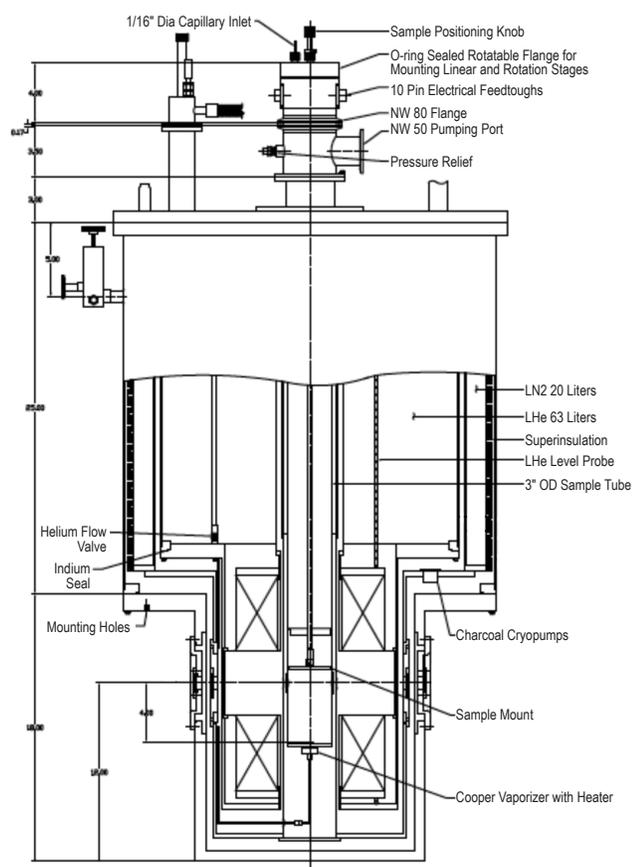


Figure 1. Custom-designed cryostat and split-coil superconducting magnet for x-ray spectroscopy experiments under extreme pressure conditions.

Development of *in situ* Radioactive Materials Probes Using High-Energy X-rays

2011-063-N0

Meimei Li, Jonathan Almer, Yiren Chen, Ali Mashayekhi, Ken Natesan, Dileep Singh, Leyun Wang, and Frank Westferro

Project Description

Hard x-ray science has made an extraordinary impact in many areas of materials science and engineering. The state-of-the-art synchrotron technology has drawn an increasing number of users — as well as demands for expanded capabilities that will enable researchers to conduct “new frontier” research. A fast-growing application field focuses on developing high-performance materials for advanced nuclear energy systems. Such materials, when exposed to intense irradiation, high thermal and mechanical loading, and chemical corrosion in nuclear energy systems, undergo physical and chemical transi-

tions at multiple length scales through their service life. Most of these transitions are detrimental for the materials’ performance, and can ultimately jeopardize the function of the entire nuclear system. Although this phenomenon has been studied for decades, a comprehensive description of how environmental factors (i.e., irradiation, temperature, loading, etc.) alter the nano- and micro-structure and in turn affect material performance is still missing. The main reason for this knowledge gap is the lack of appropriate experimental techniques to characterize the multi-scale structure evolution of the material in conditions which mimic the real nuclear reactor environment.

This project aims to develop and demonstrate an innovative post-irradiation, *in situ* high-energy x-ray scattering and imaging capability for the characterization of irradiated materials subjected to extreme conditions of temperature and stress. We are developing an experimental module that will enable us to make synchrotron-based x-ray measurements on irradiated samples at the Advanced Photon Source (APS). The experimental module will be connected to a mechanical testing frame at the 1-ID beamline, permitting the enclosed and irradiated sample to be characterized *in situ* by both small and wide angle x-ray scattering (SAXS/WAXS) and imaging under relevant thermal and mechanical loading conditions (e.g., tension, creep, and fatigue). An internal rotation mechanism is being developed to enable three-dimensional (3D) tomography of the irradiated specimen under load. With this capability, the evolution of internal stress, texture, and crystallographic defects in irradiated materials can be followed in real time during annealing and deformation, allowing the thermo-mechanical properties to be directly correlated with micro-structural information.

Mission Relevance

This project is directly relevant to DOE’s energy mission as exemplified in programs of the Office of Nuclear Energy, Office of Science (Basic Energy Sciences and Fusion Energy Sciences), and the National Nuclear Security Administration. It will also benefit other agencies, such as the U.S. Nuclear Regulatory Commission and the nuclear industry. First, the experimental module we are developing will be valuable for fundamental studies of the structure-property relationship of materials under various extreme conditions, particularly high irradiation. Second, the results obtained from these pioneering experiments will help us better understand the behavior of different types of reactor materials in nuclear environments. This will allow us to improve the material design of different structural components in nuclear reactors. In addition, these experimental results can be used to assess existing computational models for predicting materials performance in nuclear environment.

FY 2011 Results and Accomplishments

In FY 2011, we completed the design, feasibility study, and technical and safety evaluation of the experimental module. The module is composed of a vacuum chamber with infrared heating capability to 1200°C and a direct-loading mechanism of a subsized specimen to a mechanical test frame. The chamber is equipped with four x-ray windows that have been specially designed for maintaining optimum optical performance (i.e. high transmission to x-ray and visible light while high reflection against infrared waves for thermal uniformity in the chamber and to prevent overheating) and the mechanical integrity of the module. An integrated interior radiation shielding, as well as shield shutters for the x-ray windows, provides comprehensive protection from radiation exposure. This interior shielding is sufficient for handling low-activity specimens with minimal radiological control at the APS beamlines. A secondary external radiation shielding can be added for handling high-activity specimens, when needed. Another salient feature of the experimental module design is that it will achieve internal rotation that permits 3D x-ray tomography of a specimen under tensile loading. Significant effort is under way to test this design.

A confirmatory test was conducted to verify the performance of x-ray detectors under a high-radiation background. The response of the detector to an elevated radiation field was assessed by exposing a GE area detector to neutron-irradiated specimens under a “worst case” scenario. The recorded signal levels over typical synchrotron exposure timescales (i.e., from 1 to 10 s) were only slightly above background at the highest radiation activity, indicating an adequate performance of the x-ray detection system in the high radiation field. This is largely attributed to the energy sensitivity of the detector, which is highest in the 50–100-keV range (1-ID synchrotron source where experiments are conducted) whilst gamma emissions if irradiated specimens are at higher energies (>200keV) where sensitivity is lower. This test confirmed the feasibility of using the detector system for highly-radioactive samples.

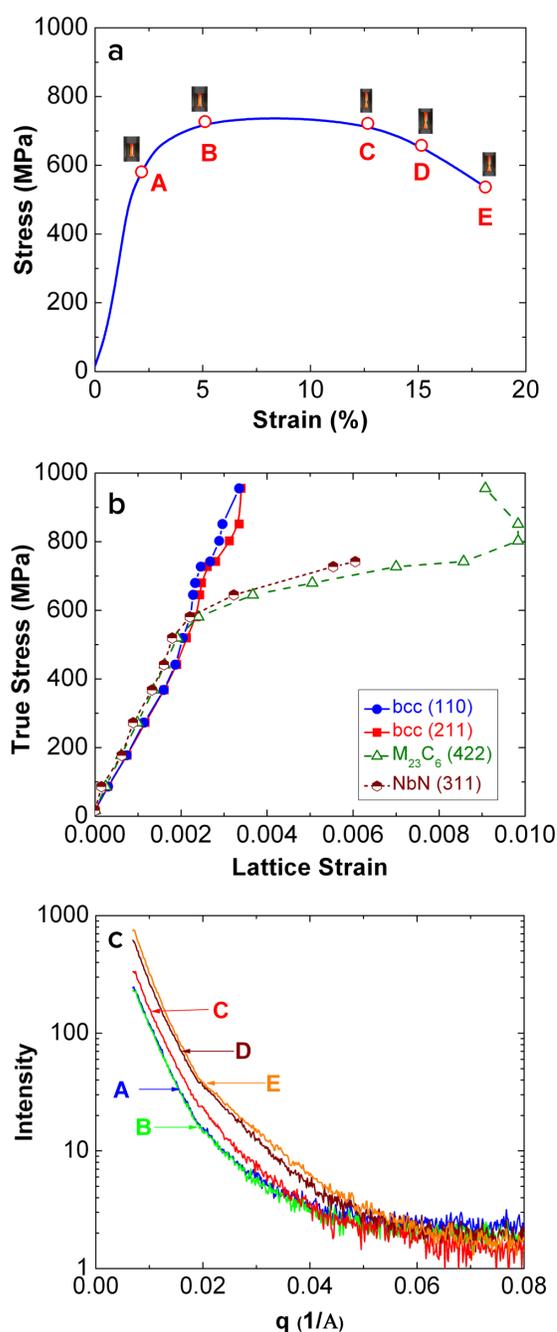


Figure 1. Simultaneous WAXS/SAXS is used to monitor the evolution of microstructure during the uniaxial tension of a ferritic-martensitic steel: (a) the engineering stress-strain curve shows the macroscopic response of NF616 ferritic-martensitic steel under tensile loading. Points A-E represent different steps during the tensile loading; (b) WAXS measurements provide the crystallographic-dependent deformation process of the body-centered-cubic (bcc) matrix and precipitate particles, particularly in the localized deformation region (from C-E) where the deformation mechanisms are not well understood, and (c) SAXS profile at different loading steps A-E shown in (a). The position of each scattering intensity curve is positively related to the total void volume in the specimen at that loading step. In particular, scattering intensity increased rapidly from C to D, indicating large amounts of voids developed during this stage before the specimen failed after step E.

An important element of the project is to conduct initial experiments using nonirradiated specimens to optimize the design of the *in situ* irradiated material probe. An experiment conducted at the 1-ID beamline used simultaneous WAXS/SAXS to monitor the evolution of microstructure during uniaxial tension of a ferritic-martensitic steel (Figure 1). WAXS measurements revealed the development of lattice strain, texture, and plastic deformation, whereas the SAXS data revealed void formation and growth, which are responsible for cracking and final fracture. Absorption data were taken along the gauge length to assess the shape change and to identify the flow localization and failure region (a critical problem in irradiated materials). This experiment demonstrated that simultaneous WAXS/SAXS is of remarkable value to studies of the failure mechanisms of engineering materials. Once the vacuum chamber is completed, we will examine irradiated specimens in the same test frame and by the same WAXS/SAXS technique, (combined with x-ray imaging), to study the correlation between irradiation-induced microstructural changes and material's degradation mechanisms.

Proposed Work for FY 2012

During FY 2012, we will focus on fabricating the experimental module. Following the completion of the module, we will conduct confirmative experiments on nonirradiated specimens and compare them with *ex situ* experimental data. We also plan to conduct testing of irradiated samples.

Fast X-ray Detectors Based on Multichannel Plates

2011-067-NO

Bernhard W. Adams, Klaus Attenkofer, Jeffrey W. Elam, Henry J. Frisch, Harold E. Gibson, and Zinetula Z. Insepov

Project Description

The goal of this project is to develop a novel type of x-ray photon detector with a two-dimensional spatial resolution on the order of 0.1 mm and with a time resolution of better than 1 nanosecond. The project runs concurrently with, but is distinct from, the large-area picosecond photon detector (LAPPD) programmatic project that is based at Argonne, and it leverages Argonne's atomic-layer-deposition (ALD) technology for x-ray-specific adaptations.

An LAPPD-type detector consists of a photocathode, a stack of microchannel plates (MCPs), and an array of microwave striplines inside of a vacuum vessel. Upon irradiation (using visible photons in the LAPPD proper and x-ray photons here), the photocathode emits photoelectrons. Each of these leads to the formation of a cascade of secondary electrons in the MCPs,

which hits one or more of the striplines, where it spreads in both directions as a pair of electromagnetic pulses. The time of the initial photoelectron emission and its location along the striplines are determined from the pulse-arrival times; in the other direction, the spatial resolution is given by the pitch of the striplines (with subdivision through interpolation).

The present project introduces several modifications of this concept. Most importantly, a thin-film, normal-incidence photocathode of the type used for visible photons would have a very low x-ray stopping power; and a combination of a scintillator with a visible-light LAPPD detector would have insufficient time resolution. Therefore, a dedicated MCP is used here as a photocathode with a large active area and is combined with grazing x-ray incidence (inside the pores, see Figure 1) to match the x-ray absorption to the electron escape depth. Leveraging the ALD technology, this MCP is optimized not as an amplifier but for its x-ray absorption. It is operated at a much lower electric bias than are the amplifier MCPs, thus opening the possibility of performing sub-nanosecond gating with pulses from a commercial microwave amplifier. An interesting application of this capability would be time-domain nuclear-resonance spectroscopy, where conventional detectors are blinded by the excitation pulse (the so-called prompt-pulse problem). Unlike most time- and spatially resolving x-ray detectors, this one does not derive its time resolution from gating and can deliver a continuous stream of time- and location-tagged photon detection events to create "movies" of images or spectroscopic data.

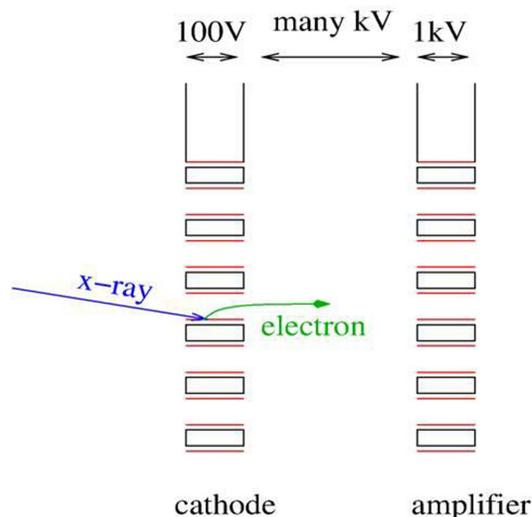


Figure 1. Schematic of the use of an MCP as an x-ray photocathode.

Mission Relevance

This project supports DOE's science mission directly and through its value to DOE's national user facilities. For example, this project is relevant to the Advanced Photon Source (APS) because it introduces a powerful new x-ray detection technique with numerous applications in imaging and spectroscopy.

copy. It is also relevant to the DOE-supported LAPPD project because it provides that project with an interesting application area. Beyond the immediate application in synchrotron environments, spin-off applications are to be expected in fields as diverse as medicine or homeland security.

FY 2011 Results and Accomplishments

Detailed studies of MCP gain and timing characteristics were performed using a pulsed laser at Sector 7 of the APS. These studies led to the optimization of the ALD process parameters (resistive layer and secondary-electron-emitter layer), as well as operational parameters (voltages on photocathode, MCPs, and gaps between them) that influence gain, sustainable event rate, and timing. In parallel, particle-tracking Monte-Carlo simulations were performed and compared to the experimental results, leading to a detailed understanding of MCP operation.

A dedicated vacuum chamber with microwave-signal connectors was fabricated to test a first design of the x-ray detector. The chamber has a large (20-mm diameter) diamond window to transmit both ultraviolet light and x-rays. It was tested at the 7-BM beamline, and signal pulses due to x-rays were seen (Figure 2). The pulses exhibit ringing because an optimized anode structure was not yet available at the time.

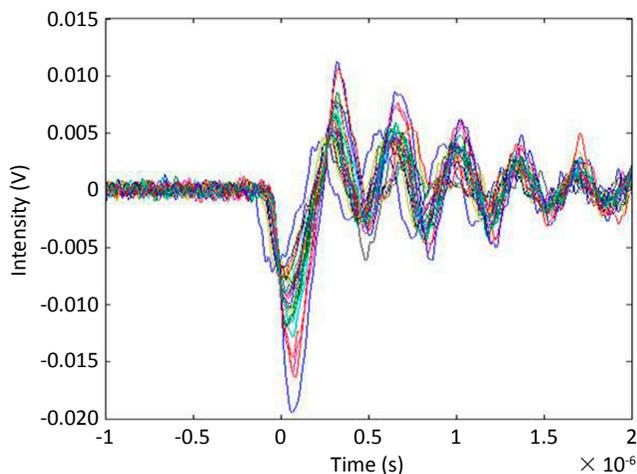


Figure 2. MCP pulses obtained from the x-rays.

An MCP coated by ALD with tungsten oxide was fabricated to serve as an x-ray photocathode. A high-power (50 W), wide-band (0.02 to 2.5 GHz) microwave amplifier was purchased to drive the cathode MCP pulsed bias, and preliminary tests of pulsed operation were performed.

Proposed Work for FY 2012

The goals for FY 2012 are to demonstrate:

1. Readout anodes optimized for high spatial resolution. The goal is to obtain a fine pitch of striplines for optimum spatial resolution in the transverse direction and to reduce the signal propagation speed along the striplines to obtain the best spatial resolution in the longitudinal direction (along striplines) for a given waveform sampling rate. One option to be explored is to use silicon or gallium-arsenide (GaAs) substrate material for its high dielectric constant, which allows narrow striplines (500 microns for a standard 635-micron wafer at 50 ohms) and slows down signal propagation. Silicon has the advantage of being less expensive and easier to handle. It can also easily be obtained in ultrathin sheets for correspondingly narrower striplines. GaAs has the advantage of lower loss at high frequencies (10 GHz). In addition to the choice of substrate, slow-wave structures, such as meandering striplines, will be tested. These different options will be compared for their potential to obtain the best spatial resolution.
2. Imaging with an anode optimized for high spatial resolution. The newly developed picosecond application-specific integrated circuit (PSEC-4 ASIC) will be used for parallel waveform acquisition.
3. Sub-nanosecond gating with a microwave power amplifier driving the photocathode MCP bias. In order to achieve several 100 V of bias voltage, a tapered stripline will be used on the MCP. Such a taper requires careful design to be able to operate over a wide bandwidth (DC to 2 GHz). Taper structures and ways to compensate for distortion through waveform synthesis will be studied.

X-ray Optics Fabrication with Self-Assembled Nanostructures

2011-104-N0

Yuxin Wang, Jeffery Elam, Joan Vila-Comamala, and Hsien-Hau Wang

Project Description

This project aims to develop techniques to fabricate a new generation of high-performance x-ray optics optimized for high efficiency and reliability, particularly at high energies (well above 20 keV). We are using a self-assembled nanostructure as the basis to fabricate Fresnel zone plate lenses with 20–30% efficiency and extremely high structural stability. The fabrication process involves preparation of an anodic aluminum oxide (AAO), metal deposition on the substrate, resist spin coating by e-beam lithography (EBL), EBL coating expo-

sure and development, heavy metal etching, and atomic layer deposition (ALD) with tungsten (Figure 1). The combined gains in efficiency, operating x-ray energy range, and stability will make these optics a critical fundamental technology for the operations of the Advanced Photon Source (APS) at Argonne.

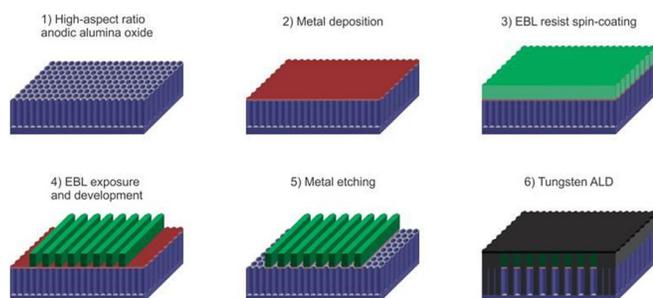


Figure 1. Illustration of the optics fabrication process. (1) High aspect ratio AAO membrane is prepared from pure aluminum disks; (2) A thin layer (2–5 nm) of Cr coating is deposited on top of the AAO membrane to seal the pores; (3) a layer of photoresist is coated over the Cr and (4) patterned with electron beam lithography techniques; (5) exposed Cr coating is removed; and finally (6) the exposed AAO pores are filled with atomic layer deposition (ALD) technique.

Mission Relevance

This project supports DOE's science mission through its expected benefit to DOE's national user facilities. For example, success of this project will supply a fundamentally critical technology to APS operation and R&D. In APS's imaging programs, for example, this technology will enable routine x-ray studies in five dimensions consisting of 3D space, x-ray energy (hence, material composition), and time. The goal is to completely characterize the 3D structure, 3D composition, and dynamic evolution in time of materials even under extreme operating conditions. In addition to microscopy and imaging applications at APS, this development will bring significant benefit to other facilities at DOE laboratories, including a wide range of other x-ray techniques (such as grating-based phase contrast imaging, protein crystallography, and micro-diffraction). For example, a zone plate with 100- μm -diameter and 40-nm resolution can generate over 1,000,000 times flux concentration at its focal point. Incorporating such a lens will dramatically transform their ability to study sub-micron features with high-speed dynamics and further enhance the capabilities of advanced methods, such as multi-wavelength anomalous diffraction (MAD). The combined gains in efficiency, operating x-ray energy range, and stability will supply a key technology for use at the APS and other DOE laboratories.

FY 2011 Results and Accomplishments

The key challenge of this project is the development of a complex process for fabricating nano-structures with high aspect ratios (Figure 1). During FY 2011, we focused on the substrate preparation and e-beam patterning. These two steps contain the most uncertainty and potentially require the most devel-

opment effort, while the remaining steps are relatively well known.

Substrate preparation: Our first attempt used a commercial Al plate. We treated the surface by an electro-polish process to produce a locally flat surface with roughness sufficient for photo-lithography but too rough for e-beam writing. We developed a mechanical polishing process capable of producing a substrate with significantly better roughness that is well-suited for EBL. As shown in Figure 2, this mechanical process reduced the surface roughness from 4.3 nm to 0.14 nm.

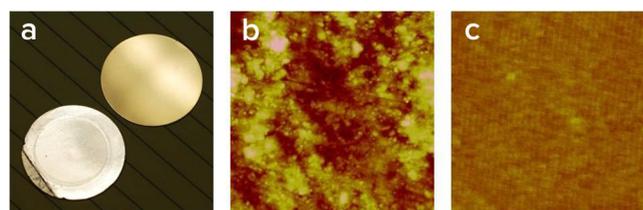


Figure 2. (a) Al substrate with 1 inch diameter prepared by (lower left) electro-polishing and (upper right) mechanical polishing; (b) atomic force microscopy (AFM) image of electro-polished sample with surface roughness of 4.3 nm over $1\ \mu\text{m} \times 1\ \mu\text{m}$ area; and (c) AFM image of mechanically polished sample with surface roughness of 0.14 nm over $1\ \mu\text{m} \times 1\ \mu\text{m}$ area.

AAO pore growth: We expect to add limited refinements to narrow this already well-developed process to optimize the pore structure through a depth of 5–20 μm . We used a process to produce small-pore AAO with 20–25 nm size. Some examples are shown in Figure 3.

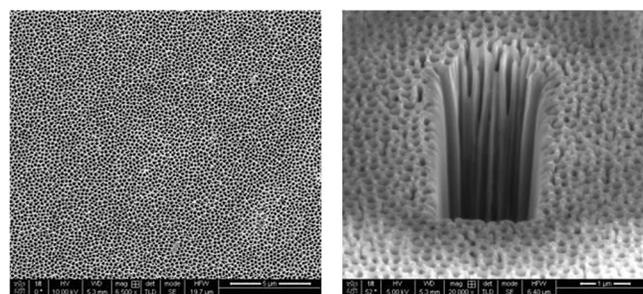


Figure 3. AAO substrate with 40 nm pore size – the vertical pore profiles are revealed from the center cross-sections cut by a focused ion beam machine (FIB).

Electron-beam patterning: We completed a series of e-beam runs with both Si and AAO substrates by using hydrogen-based silsesquioxane photoresist to both calibrate to the e-beam exposure process flow and produce the desired optics. To date, we prepared zone plates with 40-nm line width on Si substrate and 150-nm line width on AAO substrate, as shown in Figure 4.

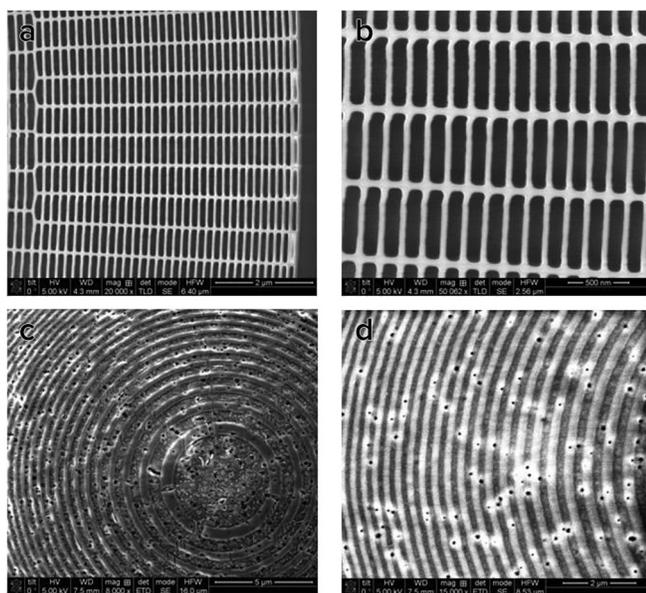


Figure 4. Zone plates with (a,b) 40 nm line width fabricated on Si substrate and (c,d) 150 nm line width fabricated on AAO substrate.

Resist development: The development of exposed resist was calibrated during the e-beam experiments using Si wafers. The same process will be tested with the AAO substrate.

Heavy metal deposition: We attempted ALD of tungsten onto unpatterned AAO with varying porosity and aspect ratio up to 500. Scanning electron microscopy showed satisfactory deposition near the sample top. Deposition deeper into the pores will be examined by using the focused ion beam at the Center for Nanoscale Materials.

Proposed Work for FY 2012

In FY 2012, we will perform the following tasks:

- ▶ Refine AAO fabrication techniques to optimize the process for smaller pore sizes, allowing finer feature patterning.
- ▶ Refine the e-beam fabrication process to reduce the AAO line width to less than 100 nm while maintaining 5- μ m thickness – achieving an aspect ratio of 50.

Next Generation Data Exploration: Intelligence in Data Analysis, Visualization, and Mining

2011-149-N0

Stefan Vogt, Lydia Finney, Mark Hereld, Chris Jacobsen, Sven Leyffer, Claude Saunders, Siwei Wang, Jesse Ward, and Stefan Wild

Project Description

In this project, we are developing a new generation of data analysis and visualization tools for multidimensional microscopy. The focus is on three capabilities: (1) software that can interpret data, identify and classify object types within datasets, and enable researchers to ask complex questions of a single but complex data set; (2) the ability to analyze datasets that represent the combined results of several instruments (e.g., to classify objects on the basis of all the available input data); and (3) data mining capabilities, through the integration of the developed software with database organization of datasets. The goal is to probe and correlate very large datasets, acquired over several years, spanning multiple instruments and researchers.

Mission Relevance

The scientific applications of the analysis methods developed in this project will impact areas crucial to DOE's missions, including basic science, environmental stewardship, and national security. These areas range from addressing issues related to bio-remediation of heavy metal or radionuclide contamination to investigating novel approaches toward efficient biofuels and to understanding nutrient cycling in the ocean and its impact on climate change. This project will also create a fundamental change in the scientific impact of imaging capabilities at the Advanced Photon Source (APS). We expect that these capabilities will directly enable new science in metallomics, cell biology, pathogenesis, novel therapeutic agents, bioremediation, biofuels, and nanoengineering and will be uniquely leveraged by Argonne's high-performance computing capabilities. Additionally, this work will establish a model and a framework that can be used for future projects targeting different areas of data analysis and support maintaining the APS as the premier hard x-ray science facility.

FY 2011 Results and Accomplishments

We developed a standard for a common HDF5-based file format that will be used for data storage and analysis. We then changed our established data analysis methods to make use of the new file format, facilitating data exchange. We started to port core analysis methods that we developed for single-CPU computing to parallel computing, in particular GPU-based

computing. We started developing a pipeline for data analysis that makes use of corresponding tools available in the Mathematics and Computer Science Division (MCS) and considered approaches to integrating these tools and setting up pipelines in the context of the APS data acquisition environment.

We evaluated different approaches to object classification, in particular unsupervised neural networks (self-organizing maps) as well as k-means cluster analysis, and found that since both approaches give very similar results, we can concentrate on just using cluster analysis in the future. Furthermore, we started to make use of a multi-phased approach (cf. [1]) for identifying and distinguishing different cells. We developed graph-based methods for image segmentation and investigated several different partitioning algorithms. We used this approach to correctly identify 95% of cells in an x-ray fluorescence micrograph with more than 500 cells.

Proposed Work for FY 2012

We plan to port the core analysis code we have used in the past (“MAPS”) into a more open programming platform (Python), so as to be better able to support it and make use of data analysis pipelines. We will be extending our development of cluster analysis, graph-based methods for image segmentation, and multivariate analysis to better make use of multiple image signals simultaneously. We will be carrying out experiments to acquire test datasets against which to test the identification and classification software packages we develop. We will make use of high-performance computational mathematics tools, such as parallel nonnegative matrix factorization techniques, and build parallel tools for support-vector machines. We will build our data analysis tools on top of the Toolkit for Advanced Optimization, which has been developed by MCS and has demonstrated parallel scalability on clusters such as Argonne’s Fusion cluster. We plan to integrate complementary imaging data, such as visible light microscopy, into the analysis and will prepare test experiments to evaluate the performance of our methods. We will develop a portal to a data and analysis repository, including web-based technologies that enable integrated collection, creation, management, annotation, analysis, and browsing of data from disparate sources (e.g., data from several APS beamlines, electron microscopy, and visible-light microscopy).

[1] “Efficient and Effective Clustering Methods for Spatial Data Mining” by Raymond Ng and Jiawei Han, Proceedings of 20th International Conference on Very Large Data Bases (VLDB 1994) September 12–15, 1994, Santiago de Chile, Chile; pages 144–155.

Seminars

Vogt, S. (2011). “Data Acquisition for Fluorescence Imaging and Spectroscopy.” NSLS User Meeting Brookhaven National Laboratory, Upton, NY, May 25, 2011.

Vogt, S. (2011). “X-ray Microscopy for the Life Sciences and Bio-Nanotechnology”, Northwestern University, Chicago, IL, Jan. 15, 2011.

Development of Grating Interferometers for Quantitative High-Energy X-ray Imaging and for Real-Time Wavefront Monitoring

2011-170-N0

Lahsen Assoufid, Francesco De Carlo, Ralu Divan, Kamel Fezzaa, Wah-Keat Lee, Albert Macrander, Derrick Mancini, Shashidhara Marathe, Alec Sandy, and Xianghui Xiao

Project Description

The aim of this project is to develop grating-based high-energy x-ray Talbot interferometry for applications including quantitative, high-speed, 2-D and 3-D phase contrast imaging and tomography; wavefront sensing; and at-wavelength characterization of optics. The interferometer exploits a well-known phenomenon called the Talbot effect, in which periodic structures such as gratings, illuminated with a coherent plane wave of light, are self-imaged at characteristic distances. When a specimen is placed behind or in front of a grating, the resulting self-image is distorted. The magnitude of the distortion is directly related to the composition and morphological properties of the specimen.

This concept has attracted attention because of its many advantages compared to other imaging methods, including simplicity, compactness, robustness, and the ability to image large specimens. Fast phase imaging relies on in-line holography techniques, which suffer from qualitative phase-contrast artifacts. Quantitative phase imaging based on grating interferometry will greatly reduce such artifacts and is uniquely suitable for imaging dynamical systems under real conditions and in real time. Grating-based interferometry is also well suited for high-speed wavefront sensing and correction and as a tool for at-wavelength optics characterization and diagnostics, which are essential to advancing Advanced Photon Source (APS) science.

Mission Relevance

This project supports DOE’s missions in energy sciences and in national user facilities. It will advance APS science and imaging capabilities, as well as optics development. Quantitative phase imaging is essential for the study of specimen morphology and component distribution. Grating techniques allow high-resolution phase imaging/tomography using highly

sensitive phase contrast, allowing for probing samples that have constituents which otherwise would be indistinguishable. Compared to other methods, in addition to providing phase contrast data, these techniques allow both traditional absorption contrast and dark-field images to be derived from a single set of measurements, with minimal exposure time and minimal radiation dose to the sample. Fast quantitative phase imaging could have profound implications for many applications requiring time-dependent imaging. Preserving incident wavefront shape and coherency is critical to advancing key APS experimental techniques.

FY 2011 Results and Accomplishments

In FY 2011, we focused on designing the interferometer and developing fabrication procedures for high-aspect-ratio 1-D and 2-D gratings, in collaboration with the Center for Nanoscale Materials (CNM). An interferometer was built and tested. We used gratings acquired from Microworks GmbH for 18- and 25-keV x-rays and a phase grating developed at CNM for 18-keV x-rays. We developed data analysis software for the stepping method and acquired single-shot fringe pattern processing software through the National Institutes of Health. We successfully tested the interferometer in single- and two-grating modes. The former is well suited for high-speed imaging and wavefront sensing, as it requires no scanning. We collected data on several specimens including a leaf, a mosquito, and a patterned resolution target (see Figure 1). We used Talbot imaging to evaluate coherence properties of multilayer optics in collaboration with the European Synchrotron Radiation Facility and the National Synchrotron Light Source.

Proposed Work for FY 2012

In FY 2012, we will (1) establish grating interferometry as a standard technique for optics testing and beam wavefront characterization, (2) further improve the interferometer and the analysis software, (3) develop fast 2-D/3-D imaging with application to both dynamics studies in materials science (e.g., *in situ* corrosion studies) and biological specimens, and (4) further improve current grating fabrication procedures and explore new fabrication methods. Improvements to the etching process will optimize the grating profile and allow fabrication of gratings for a spectrum of x-ray energies. We will explore soft x-ray lithography to fabricate a mold for Au electro-deposition for fabricating gratings with high aspect ratios.

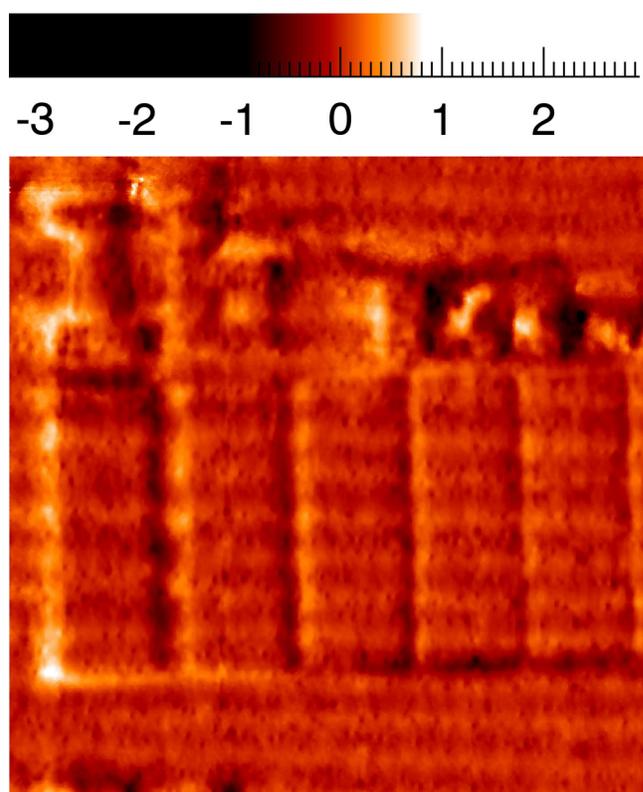


Figure 1. A differential phase contrast image of a patterned resolution target acquired with 25-keV x-rays.

Development of Revolver Undulator for APS

2011-204-N0

Efim Gluskin and John Grimmer

Project Description

Undulators are magnetic arrays designed to produce a vertical magnetic field that alternates direction depending on its position along the undulator axis. This magnetic field causes the 7-GeV electron beam at the Advanced Photon Source (APS) to wiggle horizontally, producing high-brilliance, hard x-ray beams. The x-ray energy can be tuned very precisely by adjusting the gap between the upper and lower magnet arrays. The minimum and maximum x-ray energies that can be produced by an undulator are a function of the period of the alternating field. The period is chosen either to provide maximum brilliance over a narrow (and possibly discontinuous) spectral range or to provide somewhat lower brilliance over a broader (and possibly continuous) range. This project seeks to develop a “revolver undulator” to provide the benefits of two undulators of different periods in the space currently required for one undulator. The revolver undulator will have two upper and

two lower magnet arrays of different periods; either period can be selected for use by rotating the revolver mechanisms. Undulators operate remotely for months at a time, and must do so reliably, safely, and precisely, while countering magnetic attractive forces exceeding 5,000 lb (22,241 N [newtons]). The performance of the existing gap separation mechanism used for undulators at the APS has been stellar. The challenge in developing a revolver undulator is to maintain this level of performance with an inherently more complex system. To achieve this goal, we designed two different revolver undulators, both based on the existing gap separation mechanism.

Mission Relevance

Revolver undulators are a key component in the APS; such undulators will meet demands for greater flexibility by providing the different periods of two undulators while occupying the footprint of only one; this will be accomplished without the schedule delays that would result from swapping undulators of different periods. Successful completion of this project will advance DOE's science mission to enable world-class science and technology by making Advanced Photon Source insertion devices more versatile and accessible to a broad spectrum of researchers.

FY 2011 Results and Accomplishments

In consultation with APS users and technical staff, we defined the range of magnet array periods, lengths, and minimum gaps to be served with revolver undulators. We also characterized the mechanical performance required of an APS revolver undulator and developed updated specifications for the undulators' magnetic performance. We pursued two different design avenues: one using a non-revolving "strongback" and the other a revolving strongback; the strongback is the structure that provides bending stiffness to the magnet arrays. For the non-revolving option, the strongback only revolves the magnet arrays and the structure that connects the arrays. This approach is shown in Figure 1. The other design uses a revolving strongback, as shown in Figure 2. In comparing the two approaches, the key advantage of the non-revolving strongback design is greater bending stiffness of the combined revolving and non-revolving structures resulting from the greater height available for the full-length structure. The key advantage of the revolving strongback design is greater torsional stiffness of the revolving structure resulting from its large, continuous diameter. As the designs evolved, we took steps to minimize the drawbacks in both designs. The non-revolving strongback design incorporates a revolver drive system about midway along the length to minimize differential torsional deflection under magnet loading. The revolving strongback design is effectively supported in four locations along the length, rather than two, to minimize differential deflection under magnet loading.

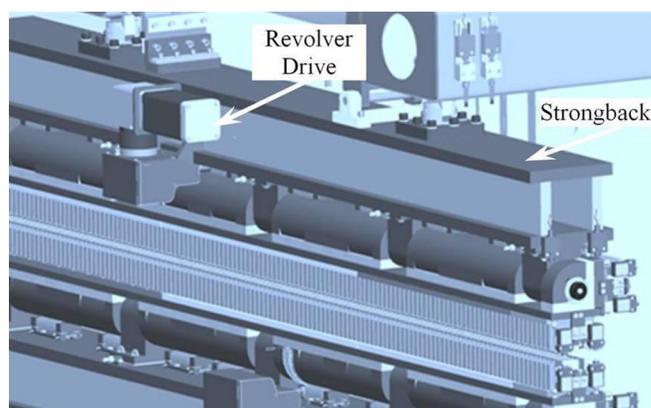


Figure 1. Non-revolving strongback design. Only the magnetic arrays and their mounting structures revolve. The revolver drive is located at the mid-point of the arrays to minimize differential torsional deflection of the arrays.

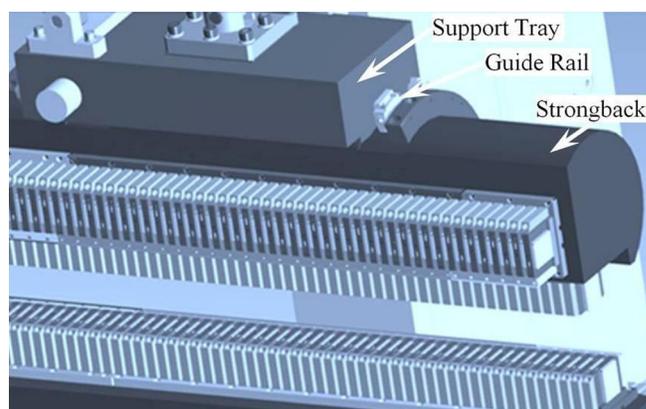


Figure 2. Revolving strongback design. The entire strongback revolves with the magnetic arrays. Two support trays (non-revolving) and four guide rails for each strongback minimize differential bending deflection of the arrays.

Parts for an early design version of the non-revolving strongback were assembled, aligned, and tested for accuracy and repeatability. The testing used representative support spacing, and the system was loaded so that deflection data could be scaled to correspond to conditions that would be observed under actual magnet forces. We further improved the design, integrating a revolver drive. The design can accept full-size undulator magnet structures and mounts directly to the existing APS gap separation mechanism. We also improved the initial design of the revolving-strongback concept. The new design uses a popular machine tool "linear" bearing system in a curved-rail format for revolver axis guidance and a duplex worm gear drive system, the variable pitch of which allows convenient backlash adjustment.

Proposed Work for FY 2012

During FY 2012, we will further evaluate the existing non-revolving and revolving strongback designs and fabricate two full-scale versions, each as a dual-magnet-structure revolver

top “jaw” paired to a single-magnet-structure (conventional) lower jaw. We will develop control system modifications to ensure safe operation of the devices and test the revolver motions without magnets. We will then install the magnetic arrays and measure and tune the undulators for optimal magnetic characteristics. The performance of each device will then be evaluated in absolute terms, relative to non-revolver undulators and relative to one another. One of the two devices will be selected for the final design based primarily on its long-term mechanical reliability and on the reproducibility of magnetic performance.

High-Power, Ultra-Stable Radio-Frequency Test Apparatus for Superconducting Radio-Frequency (SRF) Deflecting Cavity Testing and Development

2011-205-N0

Alireza Nassiri, Tim Berenc, Joel D. Fuerst, Douglas Horan, Michael P. Kelly, Terry Smith, and Geoff Waldschmidt

Project Description

Some users of the Advanced Photon Source (APS) require novel superconducting radio-frequency (SRF) deflecting cavities to provide the capability for short-pulse x-rays (SPX). Two types of deflecting cavities are currently under development; the cavity design that best meets APS storage ring beam stability requirements will be adopted for the SPX system. Radio frequency, thermal, and mechanical characterization of the test cavities is critical to ensure that the cavities meet the stringent SPX performance specifications. The goal of this project is to develop an instrumented, ultra-stable, mobile test system that would enable performance of precision cavity and cryomodule testing. The proposed apparatus, consisting of a 300-W continuous wave (CW) cavity characterization system (CCS) and a 5-kW (5,000 W) CCS, would greatly reduce the risks associated with development of a deflecting cavity.

Mission Relevance

This project supports DOE’s missions in basic sciences and in national user facilities. A critical issue related to the SPX development effort is the ability to perform high-power cavity testing of the deflecting cavities in liquid helium at a temperature of 2 K. The test apparatus will allow us to test and characterize a superconducting RF deflecting structure at full surface magnetic field, and we will have the ability to operate the cavities between 2 and 1.6 K at LHe temperature. This system has the flexibility to lock onto the main resonance frequency of a cavity under different power coupling conditions. This capa-

bility allows for quick recovery from faults and the effects of LHe bath temperature and pressure fluctuation.

FY 2011 Results and Accomplishments

Design, procurement, and assembly of the 300-W traveling wave tube RF amplifier system were completed, and the system has been relocated to the Argonne Tandem Linac Accelerator System (ATLAS) RF test stand. To accommodate vertical cold (2 K) integration of the first deflecting cavity (MARK-I) into an existing ATLAS-provided cryostat, we designed and fabricated a new cryostat top plate, a neck insert, a 2 K feedbox, and a feedbox dewar adapter; the system is now fully operational. A new vacuum system was installed and commissioned to support the SPX cavities vertical test.

High-Power RF Dampers for Superconducting RF Deflecting Cavities

2011-206-N0

Alireza Nassiri, Branislav Brajuskovic, Jie Liu, and Geoff Waldschmidt

Project Description

The goal of this project is to design, test and characterize the performance of silicon carbide as high-frequency radio frequency (RF) power absorbing material in RF deflecting cavities. High-power damping elements are required to design lower-order-mode (LOM) and higher-order-mode (HOM) waveguide dampers for superconducting radio frequency (SRF) deflecting cavities, such as those that might be used in the Advanced Photon Source (APS) storage ring. A dual-wedge design using a lossy dielectric material has been proposed for both applications. The high-power dampers for the SRF deflecting cavities will be required to operate in the cavity vacuum environment. It is critical to ensure that the dampers efficiently absorb and dissipate unwanted power in all non-deflecting mode frequencies during operation, without generating particulates that will contaminate the cavity and degrade or destroy its performance. It is also important to understand the quantity and nature of damper material particulate generation when ultimate strength limits are exceeded and the materials are stressed to the point of failure.

Mission Relevance

This project supports DOE’s mission in basic sciences and in national user facilities. APS researchers have long been interested in developing and implementing a means to produce short-pulse x-ray beams in one sector of the storage ring to open up new areas of scientific study. One possible means to accomplish this goal relies on use of SRF cavities that are operated in deflecting mode to shorten the electron bunches before they pass through the undulator. When developed

and implemented with enhanced controls and advanced diagnostics, such a system would potentially provide exciting new capabilities for APS users. Because the ability to damp unwanted resonant modes in the cavities is critical to success, this project addresses mitigation of the risks associated with the dampers.

FY 2011 Results and Accomplishments

The high-power LOM damper design evolved into a four-wedge waveguide damper (see Figure 1). Unlike the PEP-II design on which the short-pulse x-ray (SPX) dampers are based, the majority of power absorbed by the LOM damper is monochromatic at approximately four times the frequency of the dominant mode in the PEP-II design. As a result, the localized power density in the SPX dampers may become excessive, producing high stresses that could result in material failure. A symmetrically cooled four-wedge design, with silicon carbide (SiC) damping material, was optimized to distribute the RF loading over the damper volume to reduce the temperature gradient and stresses in the damper and to make the deformation more symmetrical.

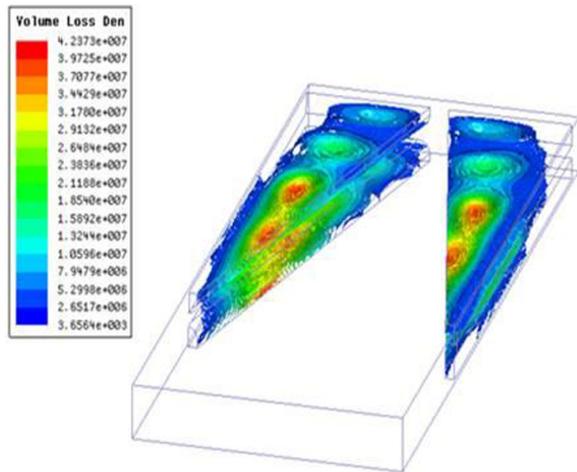


Figure 1. Power density in W/m^3 for a four-wedge rf damper.

The design of the dampers must account for two critical sources of stress and possible damper failure: (1) the fabrication process, which consists of brazing the damper material to a copper substrate, and (2) the operational conditions in the APS storage ring. Substantial RF and mechanical engineering (ME) analysis was performed to address these issues and optimize the damper materials. We completed, or are in the process of completing, the following analyses: (1) the effect of SiC tiles and gap size on RF and ME performance; (2) the effect of a pin bed, compared with a flat plate, for the copper substrate; (3) the effect of a realistic braze layer to alleviate stresses at the SiC/copper interface, and (4) parametric analysis of the LOM damper geometry. To improve the accuracy of these analyses, we conducted a documentation search to

obtain realistic, temperature-dependent, material properties of the investigated brazing materials.

We also analyzed the design of the HOM dampers to optimize them for broadband damping up to 8 GHz (see Figure 2) and determined the frequency-by-frequency dependence of the RF power loading of the dampers near the beam for the Mark-II SPX cavity (see Figure 3).

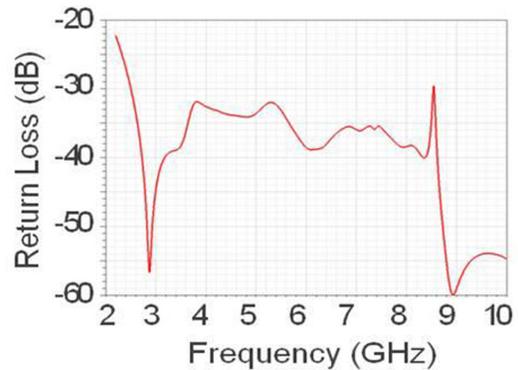


Figure 2. Broadband frequency response (return loss) of the 4-wedge damper design.

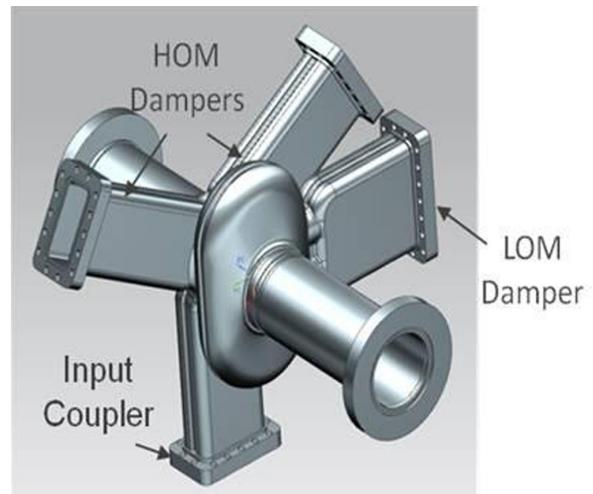


Figure 3. Mark II deflecting cavity equipped with lower- and higher-order mode waveguide dampers.

To reduce the risks inherent in using the high-power, high-frequency, monochromatic LOM damper, we aggressively pursued an alternate approach. Instead of relying on SiC vacuum loads, we are in the process of designing a double RF window and analyzing it for the LOM waveguide. By using this approach, we can implement greatly simplified and well-proven out-of-vacuum loads in place of the higher-risk LOM dampers.

Low-power and high-power testing of the dampers began by using a 5-kW klystron-based RF amplifier. Sample SiC damper material was received and machined, and several brazing tests of the SiC damper material to various copper substrates were completed; initial results are encouraging. We designed a copper cavity and expect to complete fabrication early in 2012. This cavity will be used to evaluate the effectiveness of the dampers in reducing the cavity impedance.

Proposed Work for FY 2012

Anticipated tasks for 2012 include the following:

- ▶ Final design of a high-power damper waveguide,
- ▶ Optimization of the RF/ME design for the LOM and HOM dampers,
- ▶ Fabrication and assembly of the LOM RF window,
- ▶ High-power testing of the LOM window assembly, and
- ▶ High-power testing of the LOM/HOM dampers.

Device Engineering for High-Performance Photocathodes

2011-207-NO

Marcel Demarteau, Klaus Attenkofer, Henry J. Frisch, and Junqi Xie

Project Description

Photocathodes are materials that release electrons through the photoelectric effect when the energy of the absorbed photon is larger than the material's work function. They are widely used for various applications in radiation detectors, photo-injectors, image-intensifying devices, and other devices. Although multi-alkali photocathodes are widely produced in industry, details about their growth mechanisms — such as structural formation, chemical composition, cathode thickness, and surface roughness and its relationship to overall quantum efficiency — are poorly understood. This project focuses on the development of new growth recipes for multi-alkali photocathodes. The initial goal is to better understand the relationship between the microscopic structural composition and the chemical composition of the photocathodes and their macroscopic properties. On the basis of this understanding, we will develop a theory-inspired growth recipe that results in substantially higher quantum efficiency and wavelength tunability and is compatible with conventional process technology in industry.

Mission Relevance

This project is relevant to DOE's basic science mission. Photo-detectors are used in a wide spectrum of applications, ranging from night-vision devices to monitoring of fuel cores of nuclear reactors to large-area neutrino detectors. A common

feature of these devices is that they are expensive and most have relatively low quantum efficiency. A better understanding of the growth process will be key to providing the tools to develop detectors with substantially higher quantum efficiency and wavelength tunability that will enable new science programs in support of DOE's mission to understand how our universe works at its most fundamental level at significantly lower cost.

FY 2011 Results and Accomplishments

In FY 2011 we acquired and commissioned an industrial cathode growth facility. By using a commercial photo multiplier tube (PMT) fabrication facility, we were able to grow conventional PMT cathodes, which are used in baseline experiments to study photocathode properties. Bialkali photocathodes with a peak quantum efficiency of 24% for small PMT housings were grown by using the PMT fabrication facility. We also designed an ultra-high-vacuum growth and characterization chamber to study the microscopic structure of cathodes and to optimize their functionality. This facility allows to simulate a wide range of known growth recipes, to develop new ones, and to probe the intermediate states *in situ* by using various optical and electrical measurements. The cathodes grown in the industrial facility, for example, can be replicated in the ultra-high-vacuum setup with the added capability of near continuous *in situ* characterization. A movable optical station with options for optical and electrical measurements that can be shared between different growth facilities within the laboratory was also commissioned.

In collaboration with Brookhaven National Laboratory, we studied the multi-alkali photocathode growth process through *in situ* x-ray scattering measurements, including x-ray diffraction (XRD) and x-ray reflectometry (XRR). Characterization during real-time growth revealed correlations between growth parameters and microscopic structural changes in the photocathode. XRD enabled selective observation of the growth of specific crystalline orientation during the deposition and evaporation of an antimony (Sb) layer. We also obtained measurements of a phase transition of the Sb layer. XRR revealed surface roughness changes during the growth process and permitted measurements of the layer thickness while the potassium (K) layer was evaporated on an Sb layer grown *ex situ*, in addition to measurements of *in situ* Sb layer growth.

Proposed Work for FY 2012

In FY 2012, we will focus on the study of multi-alkali photocathode growth processes through *in situ* optical and electrical measurements by using the facilities established during FY 2011. We will study the correlations between cathode growth parameters and macroscopic properties (optical and

electrical). Together with the *in situ* x-ray results, correlations between the cathode's microscopic and macroscopic properties may be revealed, yielding insight into the development of high-quantum-efficiency cathode growth recipes.

Studies of Thermomechanically Induced Fatigue in GlidCop® for Use in Photon Absorbers for High-Power-Density X-ray Beam Applications

2011-215-NO

John Quintana, Branislav Brajuskovic, Jeffrey Collins, Patric Den Hartog, Ali Khounsary, and Gary Navrotski

Project Description

GlidCop®, a dispersion-strengthened copper alloy, is the material most commonly used to fabricate x-ray absorbers for hard x-ray third-generation synchrotron facilities; unfortunately, the available thermo-mechanical and fatigue data for GlidCop® are very limited. Although the design criteria for stress and temperature limits of x-ray absorbers fabricated from GlidCop® at the Advanced Photon Source (APS) have been successful in avoiding component failures over the present life of the facility, several research studies suggest that these criteria, similar to those used at all third-generation synchrotron facilities, may be too conservative. As worldwide facilities, including the APS, contemplate upgrades that will result in higher total power and higher peak heat flux levels, the thermal load on x-ray absorbers will increase significantly, exceeding the existing design criteria limits for these devices in many cases. To define new design limit criteria for GlidCop®, we are pursuing an engineering research program based on the experimental determination of the thermo-mechanical conditions leading to crack formation and propagation. By using x-ray power from the APS, numerous GlidCop® samples have been subjected to 10,000 thermal loading cycles under various beam load conditions, and the samples have been metallurgically examined for crack presence and geometry. Data from these studies will be correlated with strain levels computed by finite element analysis (FEA) simulation so that the expected fatigue life of x-ray absorbers may be predicted.

Mission Relevance

This project supports DOE's missions in basic science and in national user facilities. The ability to accurately predict the thermal fatigue life of GlidCop® x-ray absorbers could justify the continued use of existing designs, leading to a significant cost savings for the APS and other synchrotron facilities. It will

also help support the development of operations procedures to prevent absorber failure from impacting facility reliability. A better understanding of the failure mechanism governing the fatigue life of GlidCop® will be beneficial to existing and proposed third- and fourth-generation x-ray synchrotron facilities.

FY 2011 Accomplishments and Results

The Sector 29 beamline at the APS was used throughout FY 2011 to test numerous GlidCop® AL-15 samples exposed to severe cyclic thermal loading at normal incidence. Several different power levels were chosen, and each sample was subjected to 10,000 thermal cycles with one-second heating and nine-second cooling times. *In situ* CCD (charge-coupled device) imaging was performed and data were collected from an acoustic emission system. So far, a total of 32 samples were tested, and the first 24 samples were metallurgically examined for surface roughness and crack presence/geometry, as shown in Table 1. The applied power level on groups of successive sample sets was adjusted in an attempt to isolate the region where no surface degradation occurs as a result of the cyclic thermal loading. Several failure mechanisms have been noted, including traditional deep cracking, fine cracking, ablation, and exfoliation. Figure 1 provides a metallurgical image of a sample that exhibits both deep cracking and exfoliation.

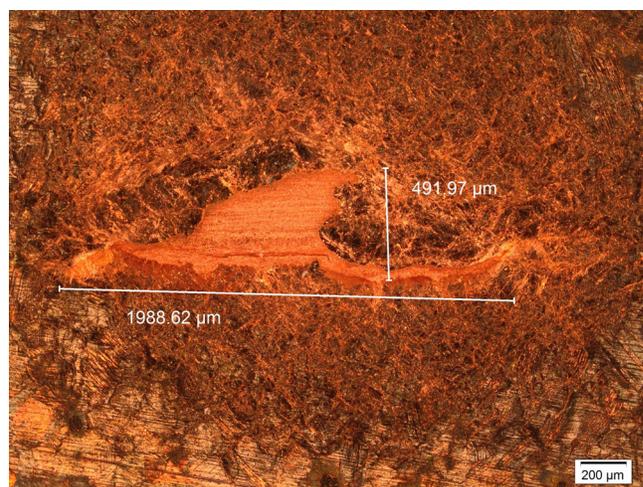


Figure 1. Optical metallurgical image (50X magnification) of a sample that exhibits both deep cracking and exfoliation.

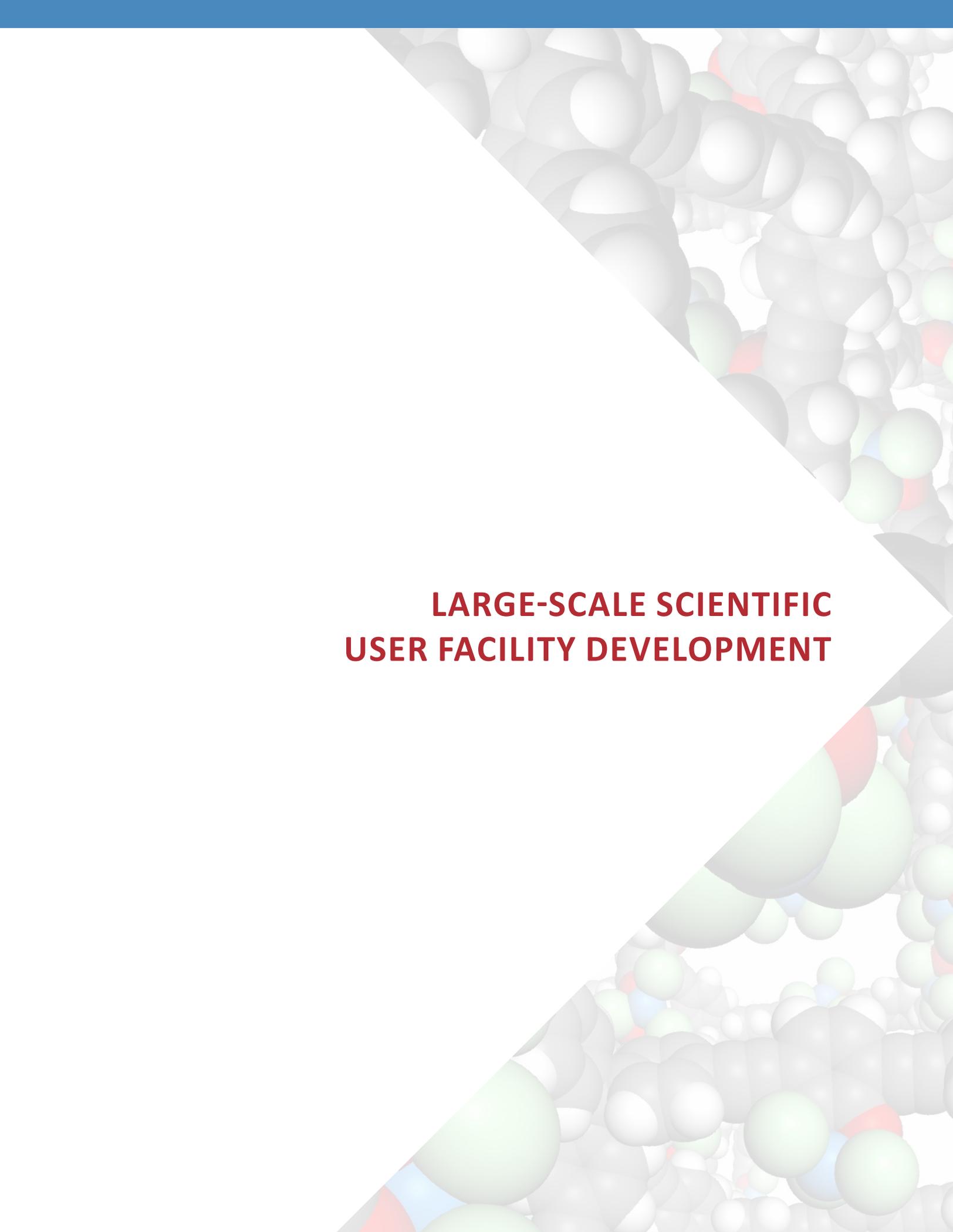
Sample Number	2- Undulator Gap (mm)	Peak temperature, 1.0 s heating (°C)	Largest Crack Length (µm)	Largest Crack Width (µm)	Approximate Exfoliated Area (mm ²)	Surface roughness, R _a (µin)	Comments
1	21.641	444.000	1815	11.01		7.3	3 horizontal "scratches"
2	20.958	491.000	1756	491	9.07	6.7	Exfoliation with crack
3	20.318	540.000	528	5.5	10.23	7.2	Exfoliation
4	19.715	590.000	4329	53		7.2	Crack
5	21.641	444.000			11.24	7.1	Exfoliation
6	20.958	491.000	2989	56		6.8	Crack
7	20.317	540.000	2531			7.0	Several horizontal "scratches"
8	19.715	590.000	4877	82		7.5	Crack
9	21.640	444.000	1238	32.3		11.3	Several vertical "scratches"
10	21.640	444.000	453	11.3		13.0	Several vertical "scratches"
11	21.640	444.000	565	16.95		11.9	Several vertical "scratches"
12	21.640	444.000			6.98	11.0	Exfoliation
13	21.243	471.000			8.93	13.5	Exfoliation
14	21.243	471.000	916	41		13.4	Crack
15	21.243	471.000			9.00	10.4	Exfoliation
16	19.715	590.000	3227	224		11.4	Many vertical "scratches"
17	22.070	417.000			5.87	20.0	Exfoliation
18	22.070	417.000			5.20	15.9	Exfoliation
19	22.070	417.000			5.83	15.8	Exfoliation
20	22.070	417.000				17.0	No surface degradation
21	22.070	417.000				13.7	No surface degradation
22	22.070	417.000	363	16		15.0	Crack
23	22.070	417.000				12.8	No surface degradation
24	22.070	417.000				14.6	No surface degradation

Table 1. Surface roughness and crack presence/geometry data from the metallurgical evaluation of the first 24 test samples.

In addition, a high-heat-load testing chamber was developed that uses as a heating source a coherent 400-W fiber optic laser with near-perfect Gaussian energy distribution. By using calorimetric methods, several coatings were tested to assess energy coupling efficiency into GlidCop®. We found that nanoparticle carbon conductive paint applied in a thin coat by using an air brush system coupled 91% of the laser power into our test samples.

Proposed Work for FY 2012

Additional samples will be tested at Sector 29 during FY 2012. Complete metallurgical examinations will be performed on all of the samples, and the data will be correlated and combined with elastic-plastic FEA analysis to yield a fatigue life model for APS absorbers. Additional tests will be performed by using the laser system in attempts to replicate the fatigue damage observed using the APS x-ray source. If these tests are successful, additional tests will be performed to evaluate the effects on fatigue life of different surface finishes, including electro-polishing and laser peening. Laminated samples with two layers of different ductility will also be studied to investigate crack arrest.



**LARGE-SCALE SCIENTIFIC
USER FACILITY DEVELOPMENT**

Large-Scale Beam Dynamics Optimization for More Efficient Operation of Large User Facilities

2009-071-R2

Peter Ostroumov, Brahim Mustapha, Jerry Nolen, and Richard Pardo

Project Description

Our goal for this project is to develop a realistic computer model that could be relied upon to operate an accelerator-based user facility. This effort requires that we devise a realistic three-dimensional (3-D) model for every element on the beamline and establish a good understanding of the initial beam parameters at the source by combining source models and beam measurements. In addition, we must implement specific interfaces between the beam diagnostic devices and the beam dynamics code, as well as develop 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 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 2011 Results and Accomplishments

Full 3-D Beam Dynamics Simulations of the ATLAS Upgrade Radio Frequency Quadrupole (RFQ): As we reported in FY 2009, the final design for the ATLAS upgrade RFQ combines sinusoidal vane modulation in the bunching section with trapezoidal modulation in the accelerating section. For the standard sinusoidal modulation, analytical formulas typically are used to calculate the voltage and field distributions. However, no analytical formulas exist for the trapezoidal case, and 3-D field distributions must be calculated numerically to be used for beam dynamics simulations. While the cell-by-cell 3-D field option already exists in the beam dynamics code, TRACK, the single-cavity option for a 4-m-long RFQ has yet to be developed. The single-cavity option provides a more consistent way to calculate the field in Microwave Studio and then export the 3-D field into TRACK for beam dynamics simulations. Figure 1 shows the TRACK graphics results for the beam dynamics along the RFQ, and Table 1 provides a comparison of the results for the cell-by-cell and the single-cavity simulations. We clearly

find a very good agreement between the two options in output beam energy, beam emittances, and transmission.

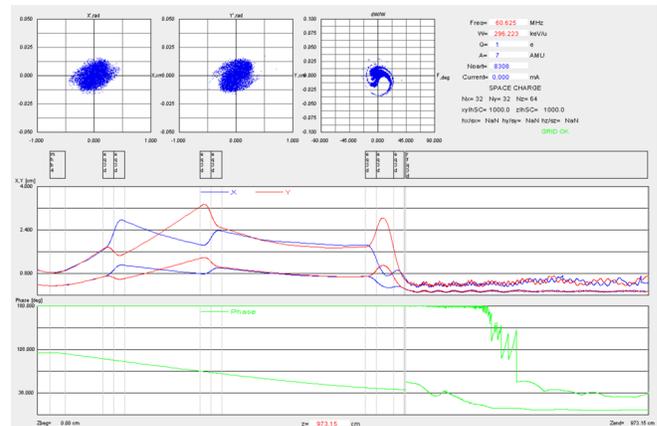


Figure 1. TRACK graphics results for the beam dynamics simulations along the medium-energy beam transport and RFQ. The three top plots show the beam phase space and the two bottom plots show the beam envelopes.

Table 1. Comparison of the Cell-by-Cell and Single-Cavity Beam Dynamics Simulations Results.

Quantity/Feature	EM-Studio Cell by Cell	MW-Studio Single Cavity
W-out (keV/u)	296.5	296.2
Transmission (%)	83	83
Longitudinal ϵ -rms (π deg.keV/u)	18.6	20.7
Transverse ϵ -rms (π mm.mrad)	0.21	0.22
Output beam	Symmetric	Almost symmetric

Full 3-D Design and Simulation of the Electron Beam Ion Source (EBIS) Injection Line for the CARIBU Upgrade: The CARIBU facility uses a californium fission source to produce neutron-rich rare isotopes. At present, an electron cyclotron resonance (ECR) ion source is used to enhance the charge state of the extracted ions for more efficient acceleration in the ATLAS accelerator. To improve the charge breeding efficiency and the extracted beam purity, an EBIS charge breeder is under development to replace the ECR. The californium source produces radioactive ions with masses from 80 to 160 atomic-mass-units at intensities of $\sim 10^7$ ions/s for the most abundant species. To achieve the highest overall efficiency of the system, the injection beamline between CARIBU and the EBIS charge breeder should be carefully designed to avoid ion beam losses and emittance growth. It should provide several differential pumping sections to achieve the necessary ultra-high vacuum in the EBIS and to match the ion beam to the phase space acceptance of the EBIS at the injection point. For

these purposes, a fully 3-D design approach was adopted. The 3-D fields for all the beamline elements were calculated by using Electro-Magnetic (EM) Studio software, and then they were extracted and incorporated into the 3-D TRACK simulations. The EM Studio was especially instrumental in the optimization of the accelerating tube and the switching chamber. By using 3-D TRACK simulations, a beamline design that satisfied all the requirements was developed. The reference ion beam was transported with no losses and minimal emittance growth, and it was appropriately matched to the acceptance calculated for the EBIS. Figure 2 shows the designed beamline along with the simulated beam envelopes.

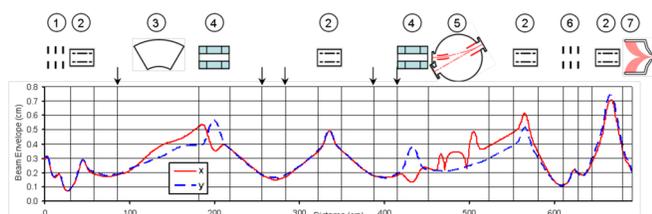


Figure 2. The designed EBIS injection beamline (top) and the simulated beam envelopes (bottom).

Photocathodes Development for Accelerator R&D

2009-076-R2

Zikri Yusof, Matthew Virgo, and Alexander Zinovev

Project Description

This project encompasses three broad areas: the development of a high-quantum-efficiency photocathode for the Argonne Wakefield Accelerator (AWA) photoinjector upgrade, the study of the physics of photocathodes, and the exploration of the gallium nitride family as a possible photocathode for an accelerator photoinjector.

Mission Relevance

Accelerator-based user facilities are a cornerstone of modern science and technology. The development of a high-quantum-efficiency photocathode supports DOE science missions by enabling the AWA facility to upgrade to a more powerful electron accelerator as part of the research and development of advanced accelerator concepts. The use of a high-quantum-efficiency photocathode enables the AWA to generate the high-charge, multi-bunch electron beam required to produce the necessary high-gradient acceleration. This ability is a vital component to produce the next generation of particle accelerators, especially for high-energy physics experiments.

The study of the physics of photocathodes provides valuable information on the performance of these photocathodes in

accelerators. Beyond that, this study also imparts insight into the physics of photocathodes in general. Furthermore, this study has important implications for other fields that involve these materials, such as the development of photodetectors.

Choosing an accelerator photocathode inevitably requires a compromise between the competing requirements of lifetime, quantum efficiency, and beam quality. One family of photoemissive materials, the group III-nitrides (gallium nitride, indium nitride, and aluminum nitride), shows great promise for accelerator applications, particularly when quantum efficiency and lifetime are the primary concerns. These materials could be strong candidates for future accelerator photocathodes, especially for their potential ability to use less demanding light sources to generate electrons from these photocathodes.

FY 2011 Results and Accomplishments

Cesium telluride photocathodes were consistently grown with a quantum efficiency of better than 10%. So far, 18 photocathodes were grown, with the highest reaching close to 20%, as shown in Figure 1. Therefore, the main aim to refine the growth recipe and to produce consistent results with high quantum efficiency was accomplished.

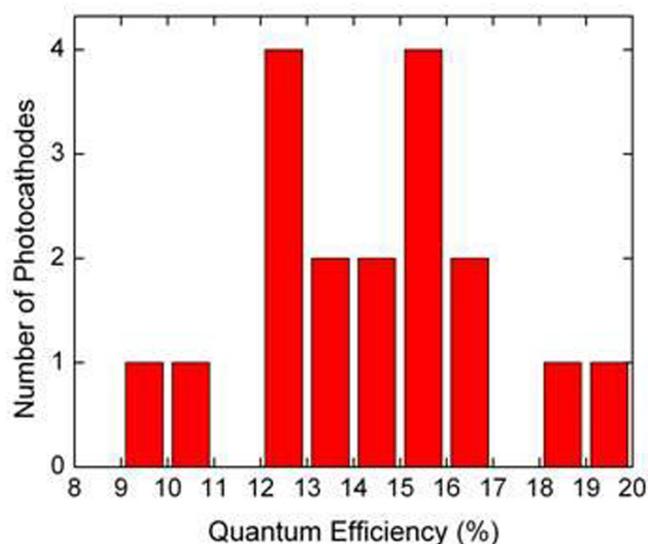


Figure 1. Distribution of the quantum efficiency of all the fabricated cesium telluride photocathodes.

A new mode of operation for gallium nitride cathodes was investigated. Conventionally, this material must be coated with cesium to function to reduce the surface barrier so that it may function effectively as a photoemitter. The strong electric field generated in a typical radio frequency electron gun also reduces the surface barrier, though to a lesser degree. This alternative mechanism of barrier lowering was studied. An experimental apparatus was developed to directly measure

this effect, but results were not obtained before the completion of the project.

A study on the work function/Fermi level of the cesium telluride photocathode was conducted. The study reveals the expected correlation between the work function and the quantum efficiency. On the other hand, it also reveals an unexpected behavior of the work function upon exposure of the photocathode to ultraviolet light.

Advances in 2 Kelvin Superconducting Cavities for Future Accelerators

2009-158-R2

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 superconducting radiofrequency (SRF) test cryostat for International Linear Collider (ILC)-type elliptical cells and transverse electromagnetic (TEM) superconducting cavities in order to develop advanced cavity designs for new electron and ion accelerators. 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 U.S. user facilities located at Argonne National Laboratory — the Advanced Photon Source (APS) and Argonne Tandem Linac Accelerator System (ATLAS) heavy-ion accelerator — will likely 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. There is also keen interest in building ion accelerators for applications of national interest, such as accelerator-driven systems for medical isotope production and ion interrogation for national security applications. For the next decade, SRF cavities will be the only viable technology that can meet these demands. By building and maintaining 2 K SRF cavity test capability and continuing to advance SRF cavity performance, we are supporting Project-X at Fermilab, the Soreq Applied Research Accelerator Facility (SARAF) at Soreq Nuclear Research Center, and the Facility for Rare Isotope Beams (FRIB) at Michigan State University. More-

over, in 2012 with program support, expansion of the 2 K cavity test capability will allow SRF cavities to be tested by using next-generation thin film technologies that employ atomic layer deposition (ALD) techniques.

FY 2011 Results and Accomplishments

Argonne is the world leader in SRF technology for reduced-velocity ($\beta < 1$) cavities. In FY 2009, we commissioned and operated the world's highest-performance section of superconducting heavy-ion linac in ATLAS. In FY 2010, we built and tested a moveable second sound cavity quench detector. In FY 2011, we demonstrated 4 MV of accelerating potential from a single low- β cavity. Both achievements were enabled by the new 2 K cavity test cryomodule capability supported under this project. The location of the quench in this cavity was determined to be on the cavity center conductor using the second sound quench detector.

To put these achievements in context, the voltage from a single Argonne cavity is more than two-thirds of the voltage that was achieved at TRIUMF (Vancouver, British Columbia) in 2006 when an entire six-cavity cryomodule was used. We also have new capabilities for processing and testing $\beta = 1$ cavities for particles moving at or near the speed of light. Elliptical-cell cavities with $\beta = 1$ now routinely exceed the very demanding ILC specification for an accelerating gradient of 35 MV/m and are among the world's best-performing cavities. The 2 K test capability developed here is being used to test the first superconducting cavities to be coated by using thin-film ALD for the next generation of superconducting cavities.

We recently made major advances in design, fabrication, and surface treatment technologies to produce a new, 72-MHz, quarter-wave cavity. The cavity was designed and built in just 17 months. A key technical development was the demonstration of a new horizontal electropolishing system, the first for any complete quarter-wave cavity. It was based heavily on elliptical cavity work done by Argonne and Fermilab scientists.

Results from 2 K tests demonstrated that the 72-MHz quarter-wave resonator (Figure 1) had the best performance to date of any cavity in this velocity range. The cavity had very low RF losses and achieved the highest accelerating gradient ever of any quarter-wave structure. Such results indicate that we are on the verge of demonstrating the breakthrough needed to realize a future compact proton or ion accelerator.

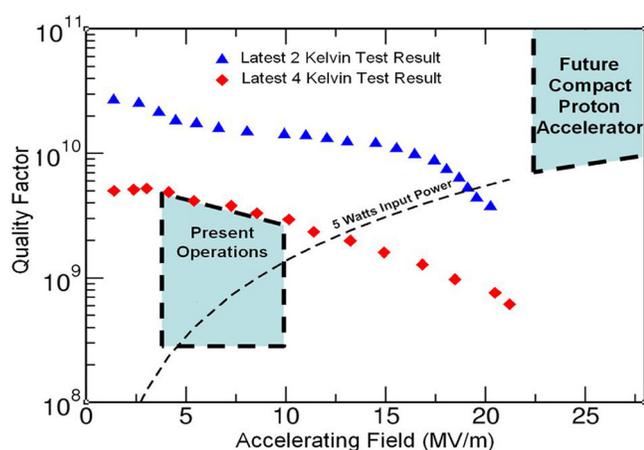


Figure 1. World-record quarter-wave cavity performance in 2 K and 4 K operation.

An array of second sound thermometers using both germanium crystals and oscillation superleak transducers performed sound detection at 2 K by using the 72-MHz cavity. The quench (performance-limiting) location was localized to a spot on the cavity's center conductor that was 30 cm down from the cavity's top. A new optical inspection tool based on a compact, high-resolution, optical boroscope is being used to study the cavity's electrical surface in order to identify any defects and extend this record performance in future cavities.

Development of High-Power Targets for Isotope Production with Low-Energy Beams

2010-181-R1

Jerry Nolen and Bradley Micklich

Project Description

The purpose of this project is to design and test a new target for the production of important isotopes for both nuclear medicine and fundamental research purposes. Such a target would significantly advance the state of the art of medical isotope production. The specific example ^{211}At , produced using a Bi target, was selected for this initial effort. It is known that an ideal beam for the production of this isotope is 30-MeV alpha particles. An alpha beam of this energy and high intensity, 3.3 mA (50 kW), can become available as the first stage of a high-power superconducting linac.

This target builds on the "tilted-target" concept developed under the FRIB (Facility for Rare Isotope Beams) R&D program for high-power targets for ISOL (Isotope Separation On-Line) -type radioactive-beam applications. The tilted-target concept has been used extensively for many years in the medi-

cal isotope production industry, but the concept has not been pushed to the high power densities required for the present more advanced applications (i.e., ~50-kW low-energy alpha beams vs. ~10-kW proton beams). The present concept also builds on the liquid-metal cooling technology developed at the Advanced Photon Source (APS) in the early 1990s and further developed for FRIB applications.

Mission Relevance

This project is relevant to DOE's science mission. ^{211}At is listed as an important radionuclide for clinical trials of therapeutic cancer treatment via targeted radio-immunotherapy. It is in short supply, even for the clinical-trial stage, because there are very few accelerators worldwide with the necessary high-current 30-MeV beam of alpha particles. There will be an even greater need for this isotope 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 to the effective production of a wide variety of isotopes that are required for use in the field of nuclear medicine as well as basic nuclear physics. Hence, the potential customer base is very large. This research also fits well within the current mission of the DOE Office of Nuclear Physics (ONP) in support of its Research Isotope Program.

FY 2011 Results and Accomplishments

During FY 2010, the target concept that used liquid metal cooling and the tilted foil geometry was modeled and shown to be viable for the required high-intensity alpha particle beams with power up to 50 kW. This concept is a significant advance in the state of the art.

In FY 2011, the main activity was to develop a design and plan for the production of ^{211}At at the existing ATLAS facility. The development of the plan for production of ^{211}At at ATLAS first required radiological simulations to determine the maximum alpha particle beam currents that can be run assuming a modest shielding upgrade of the facility. These simulations showed that alpha particle beam currents up to 80 electrical micro-amperes are acceptable within the planned shielding upgrade. This current is also well within the currents deliverable from an available electron cyclotron resonance ion source for ATLAS. The corresponding beam power of 1.2 kW is much less than the limit of the previous year's target design. Hence, a scaled-back target design that does not require liquid metal cooling is proposed for the ATLAS irradiation station. Also, during FY 2011, a design for the proposed new irradiation was developed with shielding wall thicknesses calculated to be adequate for the proposed beam current. On the basis of these designs, the yield of ^{211}At that can be produced routinely at ATLAS is 100 mCi per month for a 3-hour irradiation, which corresponds to a use of only 1% of the ATLAS beam time. Research in association with the University of Chicago Comprehensive Cancer Center is possible.

A background image featuring a large, stylized white arrow pointing from the top-left towards the bottom-right. The arrow is set against a field of numerous semi-transparent molecular models. These models consist of spheres in various colors (green, blue, red, grey) representing atoms, connected by lines representing chemical bonds. The models are arranged in a way that suggests a complex, interconnected network or a crystalline structure. The overall aesthetic is clean and scientific.

**MATERIALS AND MOLECULAR DESIGN
AND DISCOVERY (M2D2)**

Advancing the Frontiers of Computational Design of Materials

2009-180-R2

Larry Curtiss, Ian Foster, Jeffrey Greeley, Kalyan Kumaran, Nichols Romero, and Peter Zapol

Project Description

The objective of this project is to create a powerful new capability for designing materials with specific properties. It will include a database and new algorithms and data analysis methods. The work targets new catalytic materials — a research area that is in the forefront for energy applications. When this first step is successfully completed, it will be possible to extend the capability to many other types of materials.

Mission Relevance

The use of computers can make the search for new materials much more efficient, and it can have a major impact on science and engineering. The design and discovery of new materials are key components in developing many energy-related technologies and fulfilling DOE's energy security mission. This effort, which focuses on a design workbench for catalytic materials, is a first step toward a more general, theory-based design of materials with desired functional properties that will revolutionize the materials discovery process.

FY 2011 Results and Accomplishments

In research prior to FY 2011 we initiated the development of the materials design workbench including a database for storage of electronic structure data for surface reactions and molecules. We also started generating data for selected catalytic reactions to develop the algorithms needed for the design part of the workbench. This included density functional calculations of surface reactions and development of correlations for use in screening of candidate materials. The completion of this work on the development of the workbench and the selected reaction is described below.

In FY 2011, we finished developing our materials design workbench by establishing a web browser interface to the database of electronic structural information. We completed several demonstration projects that employed design principles that can be used as a basis for screening and predicting new catalysts, including catalysts for methanol decomposition and CO₂ reduction. We employed the Blue Gene/P and other computers to screen potential candidate materials. We are now obtaining feedback from experimental studies to validate our findings.

In our CO₂ reduction work, we carried out first-principles calculations to explore the mechanisms of the two-electron reduction

of CO₂ to HCOOH or CO in photochemical reactions catalyzed by the TiO₂ anatase (101) surface. Two energetically competitive reaction pathways to HCOOH were identified (Figure 1) that involve initial 1-electron (via bidentate) and 2-electron (via monodentate) reduction steps. The pathways for producing CO were also explored. From the electronic structure analysis, we showed the role of the anatase surface in facilitating electron and proton transfer in CO₂ reduction. On the basis of the determined rate-limiting step, we then screened substitutional surface cation doping and found metallic elements that could substantially lower the reaction barriers. A simple model describing the relationship between the activation barriers and the binding energies of CO₂⁻ ion to the dopant surface site is proposed and will be useful for further screening.

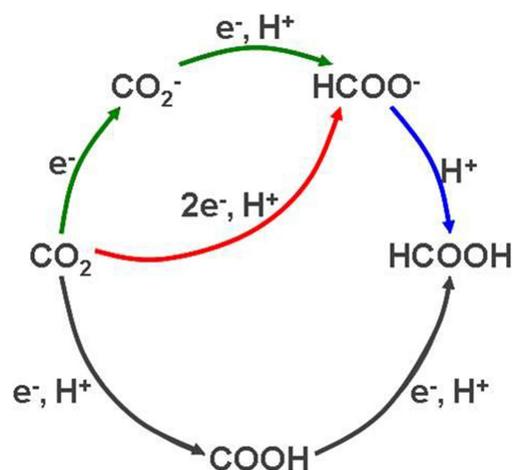


Figure 1. Schematic illustration of reaction pathways from CO₂ to formic acid HCOOH used for screening the catalyst. The green route and red route are the most energetically competitive, with reaction barriers below 1 eV; the black routes have much higher barriers.

In our methanol decomposition work, we used a combination of first-principles density functional theory calculations and scaling relationships to estimate the thermochemistry and kinetics of methanol decomposition on gas-phase subnanometer metal clusters. The method employs scaling relations between binding energies of various atomic and molecular species, determined on the pure metal clusters, to calculate the methanol decomposition thermodynamics for 17 pure and bimetallic clusters. In addition, activation energy barriers are estimated from Brønsted-Evans-Polanyi plots between transition-state and final-state energies on these clusters. The energetic results are combined with a simple microkinetically inspired rate expression to estimate reaction rates as a function of important catalytic descriptors, including the carbon and oxygen binding energies to the clusters. A volcano plot (Figure 2) was derived from the analysis to help find good candidates for catalysis. On the basis of this scheme, several alloy clusters were identified as promising candidates for the methanol decomposition reaction and proposed for experimental study.

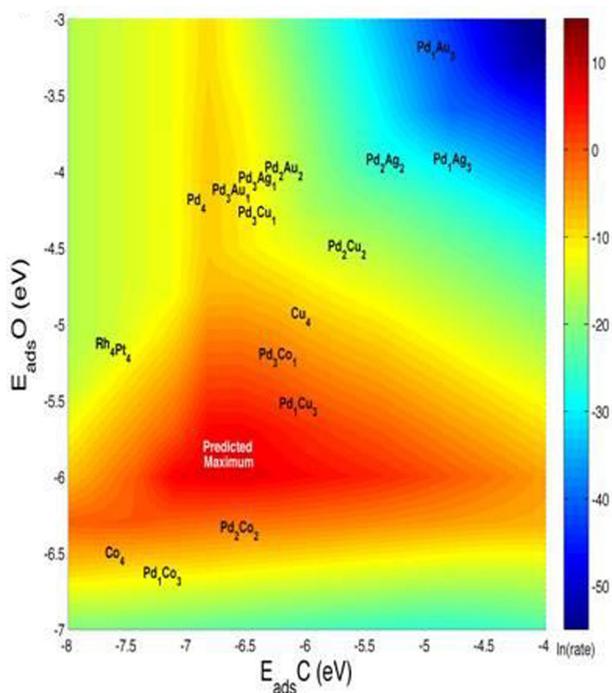


Figure 2. Volcano plot for methanol decomposition on four-atom subnanometer metal clusters based on oxygen and carbon adsorption energies. Red indicates the highest predicted rate; blue indicates the lowest rate. (Rate scale is shown at the right.)

Seminars

Curtiss, L. (2011). "Density Functional Studies of the Reactivity of Supported Metal and Metal Oxide Nanoclusters." Theory and Modeling of Nanoscale Materials Workshop, Albuquerque, NM, Oct. 14–15, 2010.

Curtiss, L. (2011). "First Principals Studies of Nanoscale Effects on Catalytic Activity and Selectivity." Workshop on Evolution and Control of Complexity Key Experiments Using Sources of Hard X-rays, Argonne National Laboratory, IL, Oct. 11–13, 2010.

Investigation of Novel Relativistic Quantum States in Iridates

2010-190-R1

Bum Joon Kim and John Mitchell

Project Description

Transition-metal oxides are renowned for a diverse spectrum of tunable physical properties ranging from superconductivity to colossal magneto-resistance, which result from competing interactions among charge, orbital, and spin degrees of freedom. It has recently been realized that the delicate

balance between spin and orbital degrees of freedom can be greatly altered by relativistic spin-orbit coupling to result in microscopic hopping processes and magnetic interactions that are quite different from the established picture of transition-metal oxides, opening a novel route to correlated electron physics and realizing novel quantum phases of matter, such as the Weyl semi-metal and topological Mott insulator, which have been recently predicted to exist when spin-orbit coupling is strong enough to induce certain magnetic order and band topology.

Our project focuses on systematic investigation of the role of spin-orbit coupling in the electronic and magnetic structures of 5d transition-metal oxides, with the goal of finding material realizations of this novel physics. This involves growth of high-quality single crystals of a number of candidate materials, characterizing them with standard transport and magnetization measurements, and performing more advanced studies on their magnetic order and excitations using resonant x-ray scattering and electronic structures using angle-resolved photoemission. We will investigate how the magnetic order affects electronic band structure, specifically how the magnetic order correlates with the structure of the Mott gap and topological properties of the electrons. The knowledge acquired from this study will provide guidance for engineering band topologies to realize novel quantum phases of matter.

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 understanding electron correlation and novel states of matter through control of materials structure. BES (DOE Basic Energy Sciences) has emphasized design and discovery of new materials to understand such new states of matter. The work proposed here is well aligned with this emphasis area.

FY 2011 Results and Accomplishments

Prior to FY 2011, we focused entirely on growing high quality single crystals of Sr_2IrO_4 by the flux method and characterizing them using standard tools. We were able to grow high-quality crystals of size up to $1 \times 1 \times 0.2 \text{ mm}^3$, which allowed us to proceed toward the next milestone.

In FY 2011, we studied magnetic excitations in Sr_2IrO_4 by using resonant inelastic x-ray scattering at the Ir L_3 absorption edge and uncovered two kinds of dispersive magnetic modes. One is a magnon mode that is present in all magnetically ordered systems. By mapping the magnon modes over an entire Brillouin zone, we showed that the interactions are indeed described by a two-dimensional antiferromagnetic Heisenberg model as expected from analysis of superexchange interactions, with a nearest-neighbor interaction J of about 60 meV, which is

about half of that found for superconducting cuprates. This observation implies that the low-energy effective physics can be described by the same model Hamiltonian as developed for superconducting cuprates and suggests that Sr_2IrO_4 could be a novel platform for high-temperature superconductivity.

We also discovered a new kind of magnetic collective excitation originating from strong spin-orbit coupling, involving coherent propagation of entangled spin-flip and orbital-flip excitations. This spin-orbit exciton mode is strongly renormalized by the low-energy magnon modes, and interestingly, its hopping process is analogous to that of the well-known problem of single-hole propagation in the antiferromagnetic background in high-temperature superconductors. As a result, the dispersion of the spin-orbit exciton mode becomes very similar to that found for a hole dispersion in parent cuprate insulators (Figure 1). This observation further reinforces the view that the low-energy spin and charge dynamics are much akin to that in the cuprates. Our study clearly reveals the entangled nature of spin and orbital degrees of freedom, which opens a new avenue for correlated electron physics.

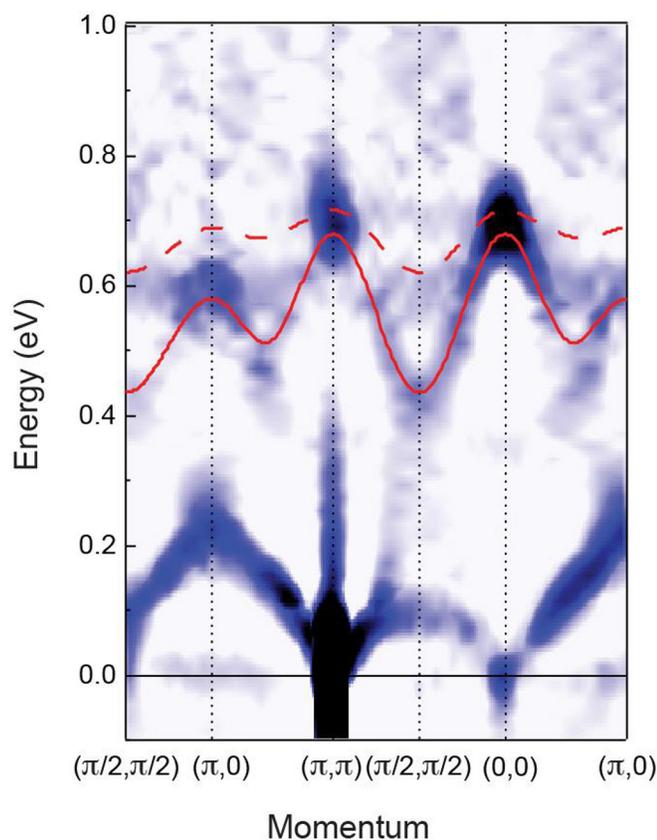


Figure 1. Image plot shows the second derivative of the raw experimental data, revealing two branches of magnetic modes. The low-energy branch (0–0.2 eV) shows the dispersion of the magnon mode, and the high-energy branch shows the dispersion of the spin-orbit exciton mode. Red solid and dashed curves show dispersions expected in the theoretical model.

Proposed Work for FY 2012

We will investigate how this magnetic order affects the electronic band structure and vice versa. Unlike the case of Mott insulators found in 3d transition-metal oxides, the size of the Mott gap is comparable to the energy scale for magnetic interaction J in 5d transition-metal oxides, from which a unique situation can arise: the magnon dispersion can overlap with the particle-hole continuum even in an insulating phase. A recent study performed on a series of cuprates shows that the magnon mode survives even deep into the overdoped regime, which suggests that magnons may be the mediator of the high-temperature superconductivity. Our observation of high-energy magnetic mode well inside the continuum also supports the idea that magnetic modes can survive dissipations due to overlapping with the charge continuum. We will study the momentum structure of the Mott gap and its correlation with the magnon lifetime to elucidate the strength of the interactions between magnons and electron-hole pairs.

The structure of the Mott gap itself is strongly affected by the presence and structure of the magnetic order. This finding is especially interesting with respect to the possibility that certain magnetic orders in certain lattice geometries may realize a topologically nontrivial phase of matter in the absence of time-reversal symmetry. We will perform angle-resolved photoemission spectroscopy to probe the electronic band structure and to study its dependence on the magnetic order. Specifically, pyrochlore iridates are predicted to host an array of new topological phases of matter. Again, the knowledge of cross-correlation between magnetic and electronic band structure is critical for searching for such a new quantum phase of matter.

Seminars

Kim, B.J. (2011). “Entangled Spin-orbital Waves in Sr_2IrO_4 .” Telluride Science Research Center Workshop, Telluride, CO, Jul. 18–22, 2011.

Kim, B.J. (2011). “Isospin Dynamics in Sr_2IrO_4 - Forging Links to High- T_c Superconductivity.” Swiss Light Source User Meeting, Paul Scherrer Institute, Villigen, Switzerland, Sep. 16–17, 2011.

Kim, B.J. (2010). “Zooming Into Electronic Fine Structure Using Resonant X-ray Scattering.” Seoul National Institute, Korea, Jun. 25, 2010.

Kim, B.J. (2010). “Mott transition in 2D Square Lattice: In-gap Kondo-like Quasiparticles, Negative Compressibility and Phase Separation”, Seoul National University, Mar. 5, 2010.

Molecular and Fluidic Transport in Nanostructured Soft Materials and Composites

2010-198-R1

Derrick C. Mancini

Project Description

The study of nanostructured soft materials is a burgeoning field of research with wide application. 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. The behavior, properties, and structure of the materials are governed by their interaction with the fluid or with chemical species or moieties transported within or through the nanoscale fluidic environments and complexes. Also, many of the systems self-assemble or organize, driven thermodynamically but still controlled by the same nanoscale transport phenomena.

This project involves using a multi-scale approach to simulation, from molecular dynamics (MD) through finite element methods, comparing these results with experimentally observed behavior, and relating them to the physical and chemical structure of the soft material systems. We will synthesize or obtain soft material systems and composites including hydrogels, hydrogel-nanoparticle composites, nanoparticles with organic chain functionalization, and composites of any of these materials to form more complex systems. Other molecules, macromolecules, ions, and clusters will be used to either incorporate into these systems or to interact with these systems in the aqueous phase. We will structurally characterize the soft material systems and composites by using optical microscopy, transmission electron microscopy (TEM) and scanning electron microscopy (SEM), dynamic light scattering (DLS), x-ray diffraction (XRD), small-angle x-ray scattering (SAXS), and ultra-small-angle x-ray scattering (USAXS); we will chemically characterize them by using Fourier transform infrared (FTIR), Raman, and ultraviolet visible (UV-vis) spectroscopies. 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, and also by using dynamic sensitive techniques like x-ray photon correlation spectroscopy (XPCS).

Mission Relevance

The development of modeling and simulations of nanoscale transport of fluids and ions in nanostructured polymeric and membrane systems will contribute to DOE's science, environment, and energy missions. These systems are ubiquitous and have applications in energy storage and conversion, environ-

mental systems and mitigation, sensor technology, and drug delivery.

FY 2011 Results and Accomplishments

We established DLS capabilities, prepared six applications for beamtime at the Advanced Photon Source (APS) and Spallation Neutron Source (SNS), and initiated tests at the APS. For our scattering studies, we identified the need to obtain polymers of well-defined size or narrow poly-dispersity index (PDI), especially to compare with computational results. PNIPAM-co-PAA (poly[N-isopropylacrylamide]-co-poly[acrylic acid]), with swelling characteristics similar to those of PNIPAM, was identified as the best copolymer to study pH sensitivity.

PNIPAM and PNIPAM-co-PAA nanogels of narrow size distribution and different sizes were successfully synthesized and purified. Atomic force microscopy (AFM), DLS, and USAXS were used to characterize these nanogels and study their swelling behaviors under varying temperature and pH conditions. We studied the aggregation behavior of linear PNIPAM with narrow molecular weight distribution in water, and we found that the formation of nearly monodispersed mesoglobules from PNIPAM above lower critical solution temperature (LCST) strongly depends on molecular weight, concentration, and heating history. We produced hydrogel nanoparticles with PDI=1.2, which can be extended to metal-core hydrogel composite nanoparticles. We also produced PNIPAM-coated magnetic nanoparticles to study the effect of external electromagnetic field on fluidic transport. Finally, we demonstrated that PNIPAM can be patterned by using soft x-ray contact lithography and extreme ultraviolet interference lithography, although further optimization of the chemistry is required.

We significantly advanced our modeling by using MD calculations of hydrogel oligomers. We focused on understanding the solvation dynamics and role of water, at the atomistic level, in defining the LCST of thermo-sensitive polymers. We also concentrated on PNIPAM as a classical thermo-sensitive polymer with an LCST of 32°C. MD simulations were carried out both below and above the LCST to determine the role of solvation dynamics and local ordering of water in inducing conformational transitions in PNIPAM oligomers through the LCST. We determined that chains of at least 30 monomers were required to observe collapsing behavior; this phenomenon is due to the breakdown of a rigid solvation cage above the LCST. We calculated the vibrational spectra contributions of proximal water PNIMAP as it undergoes conformational transition across LCST. Our calculations suggest that vibrational spectroscopy may be used to characterize the fundamental molecular behavior of the solvation effects previously modeled. We also modeled the agglomeration dynamics of PNIPAM oligomers across the LCST and determined that there is no significant difference for very short chains, but unusual behavior begins to appear for chains of more than 30 monomers.

Proposed Work for FY 2012

We will study the kinetics of swelling/collapse of PNIPAM nanogels by employing USAXS integrated with microfluidic devices. Small-angle neutron scattering (SANS) of nanogels will be used to probe the phase separation of backbone and side groups of PNIPAM in water. SANS of water/ethanol mixtures may help explain the origin of co-non-solvency. Time-resolved SAXS using laser heating will reveal the thermodynamics and kinetics of the conformational change between the random coil and fully collapsed globule for PNIPAM. Experimental results will be compared with the combined results of finite element method and MD calculations to relate phenomena to molecular mechanisms. Many of these studies will require controlled mixing or confined transport of polymer solutions to study the kinetics and dynamics of oligomers and nanoparticles using all of these techniques. We will design and build capillary and microfluidic systems to conduct these experiments. We will also model the fluidic transport by using FEM (finite element methods) and verify the transport function of the fluidic systems by comparing the models to observed behavior.

We will extend our MD calculations to include more complex transport phenomena that include specific effects, including:

1. Effect of salt ions (e.g., Na+ Cl-, Na+, Br-) on the ordering/cage of proximal water near the polymer surface and on the LCST of PNIPAM;
2. Effect of solvent mixtures on the LCST of PNIPAM (e.g., ethanol + water);
3. Simulations of PNIPAM at different temperatures and pH levels to evaluate hysteresis, if any; and
4. Simulations of hydrogels of PNIPAM at various pH levels with different cross-linkers in the presence of different ions.

We will continue to integrate our modeling results with experimental measurements to relate the molecular mechanisms to the observed behavior of these systems.

The Rational Synthesis of Kinetically Stabilized, Higher-Order Inorganic Materials for Catalysis

2010-202-R1

Adam Hock and Theodore Krause

Project Description

Major challenges exist to the large-scale adoption of solar energy as a significant contributor to our energy sources, whether the photon energy is used to directly generate electricity (photovoltaic devices) or to drive chemical reactivity

(photoelectrochemical devices). The diffuse nature of sunlight demands transformational improvements in our photon harvesting abilities. New photon harvesting technologies — 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 metal oxides and nitrides, are far more robust, physically and photochemically. One advantage the new photon harvesting technologies enjoy is that solution-phase chemical synthesis is extremely versatile, allowing rational variation, study, and improvement of material properties. However, the robust inorganic materials rely on high-temperature, thermodynamically driven solid state processes that make it difficult to control molecular structure. The lack of control over structures and interfaces (and, by extension, a lack of control over systematic improvements to photon harvesting ability) represents a major stumbling block in the adoption of solar energy.

We are developing well-defined vapor phase synthesis techniques to prepare materials and structures not possible with current technology. We use sequential, stoichiometric surface deposition chemistry, termed atomic layer deposition (ALD), to prepare new materials which are evaluated as potential photon harvesting materials. ALD is a specialized chemical vapor deposition process that uses alternately pulsed reactive gases that do not undergo uncontrolled thermal growth. Thus, the thickness and properties of the resulting films are tailored by controlling well-defined, stoichiometric, and sequential chemical reactions. Our unique method provides a mechanism for studying the effect of chalcogenide substitution upon physical (e.g., grain size, lattice structure, morphology), photoelectronic (e.g., absorption energy and ability, carrier concentration and mobility), and catalytic properties. The materials targeted are abundant and non-toxic, in contrast to other emerging photon harvesting materials, which contain rare and toxic Cd and Se.

Mission Relevance

This project is directly aligned with the DOE missions to support basic science, fortify energy supplies, and ensure energy security. Well-controlled synthetic methods to tailor composition and produce structurally engineered materials are needed for more efficient solar devices. Finally, dramatic improvements in light-driven catalysis are needed to shift the United States to a renewable solar-based chemical feedstock economy.

FY 2011 Results and Accomplishments

All laboratory facilities, including inert-atmosphere glove boxes, a solvent purification system, fume hoods, and other related equipment were brought fully on line. An ALD apparatus was set up. Our initial work focused on preparing FeO_x films by using a new iron ALD precursor that we developed. ALD-grown Fe₂O₃ is used for photocatalytic water splitting;

however, the growth rates of previously reported systems are extremely low and require extremely reactive ozone for film growth. Our novel precursor grows FeO_x films more rapidly with several co-reactants, including hydrogen peroxide, oxygen and ozone.

We also targeted the ternary material tantalum oxynitride (TaON), reported to photocatalytically split water under visible-light irradiation. Thus, we also prepared a variety of Ta complexes as potential ALD precursors. Vapor precursor development is ongoing and volatility has not yet been achieved. We, however, synthesized an unusually stable Ta complex, which can be recovered unchanged after being heated to temperatures greater than 170°C for several hours. Despite the compound's high stability, it is still extremely reactive towards water. Therefore, we are modifying the molecular architecture to synthesize complexes with less ligand bulk and consequently higher volatility. High thermal stability and reactivity are the most desirable characteristics of vapor precursors; thus, if sufficient volatility is not realized, we plan to explore the direct liquid injection method in the future.

Proposed Work for FY 2012

We plan to develop the FeO_x vapor deposition chemistry and optimize growth conditions. We also will utilize our Ta precursor, along with other Group 4 precursors, to synthesize thin films of Group 4 or 5 mixed oxides, nitrides, and sulfides designed to harvest visible light. Ta, Fe, and Group 4 vapor precursor development and testing will continue, focusing mostly on FeO_x and TaON. We anticipate that the stoichiometric material TaON will be more easily prepared than mixed metal oxy/sulfides; however, tuning band gaps by varying the oxygen-heteroatom ratio remains a goal for FY 2012. We will fully characterize our films for bulk composition and structure by x-ray and 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 and catalytic experiments will be pursued.

Soft Catalysts for Green Chemistry and Energy Applications

2011-060-NO

Marc J.A. Johnson, Lin X. Chen, Jeffrey W. Elam, Michael D. Hopkins, Joseph T. Hupp, Julius Jellinek, Di-Jia Liu, Elizabeth A. Mader, SonBinh T. Nguyen, Shengwen Yuan

Project Description

Given rising world energy demands — along with growing concerns over the long-term availability of crude oil and natural

gas resources and the negative environmental impact associated with their use — there is an urgent need to develop new catalysts that more efficiently transform existing resources (e.g., methane) and alternative raw materials (such as carbon dioxide) into fuels and chemical feedstocks. To address this need, we have designed and developed a new class of solid catalysts that integrates highly selective organometallic active sites into permanently porous organic polymers (POPs, Figure 1). This modular and tailorable class of catalysts is designed to combine the best aspects of homogeneous catalysts (high selectivity at low temperature, tunability) and heterogeneous catalysts (stability, ease of separation). This will lead to more efficient utilization of crude oil and natural gas supplies, and thus will significantly reduce both the demand for and the negative environmental impacts of their use. Furthermore, these catalysts will effect new transformations that lead to new chemistries that use carbon dioxide as a chemical feedstock — chemistries that cannot be realized with traditional catalyst technologies. The design principles developed here will have applications beyond the specific systems that we target. The initial focus has been the development of methods for (1) reproducibly and reliably synthesizing the needed POPs and (2) incorporating the catalytic metal sites into the POPs.

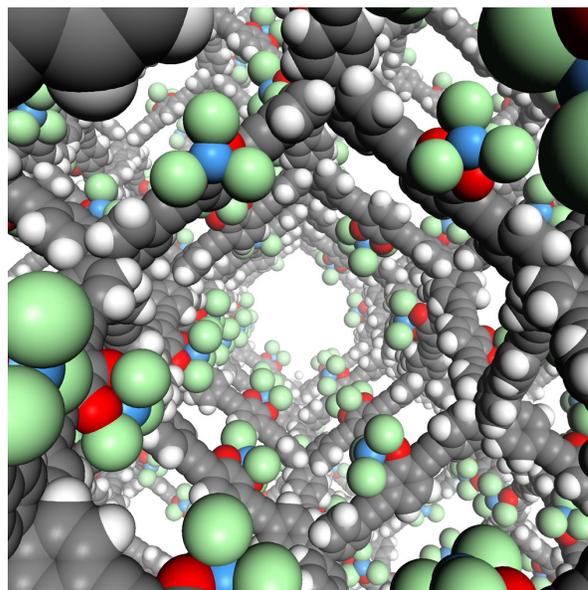


Figure 1. Calculated minimum-energy structure of an idealized catalytic POP, highlighting the high density of catalytic metal sites (blue) and their associated ligands (green, red) in wide channels in the porous network polymer.

Mission Relevance

This project is relevant to DOE's energy mission. Catalysis has an extraordinary impact on the U.S. economy as evident by U.S. Department of Commerce statistics, which estimate that nearly 90% of all processes in the chemical and petroleum industries and nearly 30% of all manufactured goods in the United States involve adopting one or more catalytic processes to maximize the rate and conversion of feedstocks

to the desired product(s), as well as to lower process energy requirements. New catalysts are urgently needed both to enable more efficient use of existing traditional resources, such as methane, and to permit the exploitation of alternative, renewable feedstocks and carbon dioxide. The proposed catalysts will complement traditional molecular and solid catalysts, enabling new chemical transformations.

FY 2011 Results and Accomplishments

Three new POPs were synthesized from pairs of molecular building blocks (BBs; to date, tetrahedral node BBs with linear strut BBs). These syntheses were accomplished by using two different types of metal-catalyzed, bond-forming reactions to link the tetrahedral node molecules with linear strut molecules (Figure 1). This approach validated two catalytic methods for synthesizing the POP network polymers. The new POPs each contain one of two different types of metal-binding sites. In addition, two control POPs that lack metal-binding sites were synthesized analogously. For the POPs containing each of the two metal-binding sites, two different chemical methods for introducing a transition metal were validated. To date, two different transition metals were incorporated in amounts exceeding 5 weight percent (wt%). Only trace metal incorporation was found in the case of the control POPs that lack the designed metal-binding sites. Surface areas of the metal-free and metal-containing POPs fell into the range of 300–1,300 m²/g. Pore size distributions were also determined. The POPs that are most thermally robust (i.e., stable at temperatures up to >350°C under nitrogen) are amorphous.

Proposed Work for FY 2012

At least two new metal-binding sites will be incorporated into POPs by using analogous synthetic methods. Infrared spectroscopy, nuclear magnetic resonance, electron paramagnetic resonance, x-ray absorption, and other spectroscopic methods will be used to characterize the structures of the POPs on a molecular level both before and after metallation. This effort will include identification and quantification of end groups. At least three different synthetic methods will be evaluated for their ability to produce robust and ordered (rather than amorphous) POPs, as a result of the expected advantages of ordered POPs. Additives will be assayed for their ability to produce large, regular pores during the synthesis of the POPs. The POPs will be evaluated as catalysts for reactions with small molecules for fuel synthesis (e.g., hydrogen, alkanes, olefins, arenes, carbon dioxide). The structures will be characterized under catalytic conditions using one or more beamlines at the Advanced Photon Source. The potentials needed for performing molecular dynamics simulations of the processes involved in the synthesis of metal-free and metal-containing POPs will be developed. Computational studies of the reaction pathways leading to observed and desired product molecules will be performed for explicative and predictive purposes. These

activities related to theory, simulation, and modeling will guide the synthesis of next-generation catalytic POPs.

Guided Discovery of Crystalline Molecular Materials for Advanced Energy, Information, and Communication Technologies

2011-083-N0

John Schlueter, Karena W. Chapman, Gregory Halder, Dean Miller, and Peter Zapol

Project Description

The overarching goal of this project is the design and crystallization of functional electronic molecular materials for applications in energy, information, and communication. We are using synthetic methods to control phase formation on a selective basis; stabilize new metastable phases; and perfect the crystallization methodology for the growth of large, single crystals suitable for performing detailed studies of electronic and magnetic properties. *In situ* x-ray methods at the Advanced Photon Source at Argonne — predominantly diffraction and pair distribution function techniques under precisely controlled sample environments — are being used to understand a range of crystal growth processes, such as hydrothermal and electrochemical syntheses.

Mission Relevance

Several key reports have recognized the importance of crystal growth capabilities as a key requirement for the continued development of basic energy sciences, and this project contributes to this important national goal. The electronic and magnetic molecular materials developed in this project will have application in various energy, communication, and information technologies (including superconductivity, solid state lighting, and spintronics) and will address outstanding issues in these fields that have been outlined in DOE's Basic Research Needs series. A fundamental approach to understanding aggregation and crystallization in molecular materials under both ambient and extreme conditions is needed so these materials can be developed to their full potential.

FY 2011 Results and Accomplishments

In the area of molecule-based magnetic materials, we recently described the crystallization of a novel bifluoride-bridged coordination polymer and the synthesis of the [Cu(HF₂)₂(pyrazine)]_n coordination polymer, which contains both $\mu_{1,3}$ and $\mu_{1,1}$ bifluoride bridging modes, as well as an understanding of the magnetic coupling through experimental and theoretical methods. One of the premises of our work is that competition for intermolecular interactions in molecular systems, such as

these, likely allows the stabilization of many polymorphic structures with similar energies. If the energy barrier between polymorphs is small, electronic/magnetic switching may be possible.

One objective of this project is the development of techniques for the growth of large, single crystals that would be suitable for characterization through advanced methods, such as neutron diffraction. In this regard, we developed a controlled vapor phase diffusion technique for the growth of large, single crystals of $[\text{Cu}(\text{d},\text{pyrazine})_2(\text{DF}_2)]\text{SbF}_6$ (see Figure 1). We also worked to perfect hydrothermal growth techniques and grew large, single crystals of $[\text{Cu}_2(\text{d},\text{pyrazine})_4\text{D}(\text{DF})(\text{DF}_2)](\text{SbF}_6)$ (also shown in Figure 1). Experiments are in progress to determine the nuclear and magnetic structures of these materials through neutron diffraction.

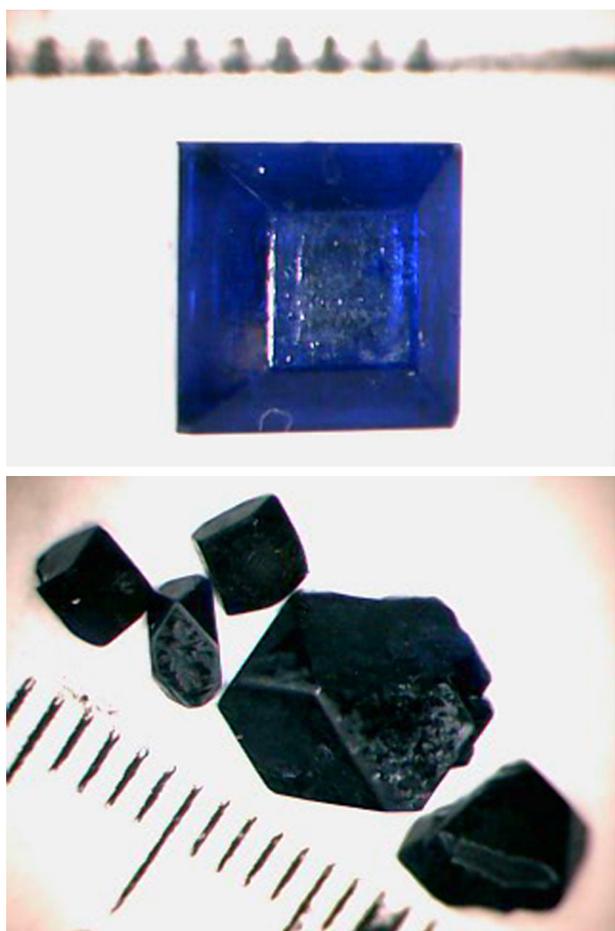


Figure 1. Photographs of deuterated single crystals of magnetic coordination polymers grown for neutron diffraction experiments: $[\text{Cu}(\text{d},\text{pyz})_2(\text{HF}_2)]\text{ClO}_4$ (top) and $[\text{Cu}(\text{d},\text{pyz})_2(\text{DF}_2)]\text{SbF}_6$ (bottom). The scales are in millimeters.

We also worked to understand the response of these molecular materials to external stimuli, such as external pressure. A striking example of how pressure can be used to control the mag-

netic properties of magnetic coordination polymers is exemplified by the $\text{CuF}_2(\text{H}_2\text{O})_2(\text{pyrazine})$ system. At ambient pressure, this system is characterized by two-dimensional $\text{CuF}_2(\text{H}_2\text{O})_2$ sheets within which the antiferromagnetic exchange is mediated through hydrogen bonds. To pressures up to ~ 1 GPa, the Jahn-Teller axis lies along the copper-pyrazine chains. As the pressure is increased above ~ 1 GPa, a structural phase transition results from the reorientation of the Jahn-Teller axis to lie along the copper-water direction. This pressure increase effectively eliminates magnetic superexchange through the $\text{F}-\text{OH}_2$ network, resulting in a one-dimensional magnetic structure with coupling through the copper-pyrazine chain. As the applied pressure approaches 3 GPa, the Jahn-Teller axis rotates once again to lie along the copper-fluoride direction. We also observed a third pressure-induced structural transition in this material near 5 GPa. Single-crystal x-ray diffraction studies indicated that in this phase, water is forced out of the copper coordination sphere and is stabilized by hydrogen bonding to fluoride ions.

In the area of molecule-based superconductors, we analyzed the structure and electronic properties of the $k-\alpha'$ - $(\text{BEDT-TTF})_2\text{Ag}(\text{CF}_3)_4(1,1,2\text{-trichloroethane})$ superconductor that we found to have a five-fold increase in superconducting transition temperature as compared to the parent $k-(\text{BEDT-TTF})_2\text{Ag}(\text{CF}_3)_4(1,1,2\text{-trichloroethane})$. Both of these materials were discovered and synthesized at Argonne National Laboratory. Consistent with our work on polymorphism in magnetic coordination polymers, we worked empirically to control phase formation. We found that the $k-\alpha'$ - $(\text{BEDT-TTF})_2\text{Ag}(\text{CF}_3)_4(1,1,2\text{-trichloroethane})$ polymorph preferentially grows under high current conditions and thus designated it as the kinetic phase. Through crystal structure analysis, we found that the α' -type layer is charge ordered, likely making this a highly two-dimensional superconductor. Electronic band-structure calculations confirmed this speculation.

Proposed Work for FY 2012

Research will be aimed at controlling polymorph formation in magnetic coordination polymers and conducting cation radical salts. This effort will be accomplished through the use of crystallization under such extreme conditions as pressure, temperature, and current. Theoretical methods will be used to understand the relative energies of polymorphs and *in situ* methods, such as pair distribution function (PDF) analysis, will be used to understand and control phase formation. Charge distribution analysis through x-ray diffraction and precise descriptions of hydrogen bonding through neutron diffraction will be pursued to understand the solid state transformations that have been observed. We are also working to develop the synthetic infrastructure to synthesize fluorinated molecular components that will be used as directional building blocks in molecular solids.

Reactive Synthesis of Metastable Materials

2011-101-NO

Peter Zapol, Paul Fuoss, Matthew Highland, and Peter Stair

Project Description

While the prediction and characterization of new materials structures with outstanding properties are key components of materials research and development, in many cases the primary challenge is to discover methods to synthesize these desired structures. Often the structure is metastable and must be grown through a non-equilibrium, kinetically controlled path. This project aims to address the fundamental science underlying synthesis of such metastable materials as InN — in particular, the mechanisms by which non-equilibrium chemical activities can be created and controlled during film growth from chemically reactive vapors. By using hard x-rays from the Advanced Photon Source to penetrate the reactive vapor phase and chamber walls, we will carry out *in-situ* scattering and fluorescence studies to observe the structure and composition during growth. We will simultaneously perform *in-situ* infrared spectroscopy to characterize the molecular species on the surface that determine the nitrogen activity. Multiscale theory and simulation, from first-principles calculations of the molecular reaction pathways and barriers to continuum modeling of the crystal nucleation and growth processes, will provide fundamental understanding and guidance for the experiments. Experiments and simulations where we vary surface properties (e.g., composition, crystal orientation and step density) will elucidate the mechanisms by which the high nitrogen activity is produced in this system, resulting in strategies to control the growth of metastable InN and its alloys. Demonstration of these methods will show how atomistic understanding of the reaction pathway and the role that different reaction intermediates play in the formation of metastable materials can enable the synthesis of new materials with previously unattainable properties (Figure 1).

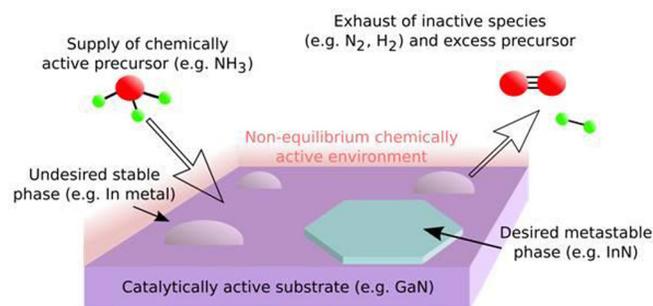


Figure 1. Schematic of reactive synthesis of metastable materials.

Mission Relevance

Development and application of pioneering *in-situ* experimental techniques and multiscale modeling to the science of materials synthesis will pave the way for new approaches to far-from-equilibrium materials synthesis and new fundamental programs related to the DOE missions in energy security and environmental quality. Our results will have broad applicability in the growth of metastable materials by chemical routes. The development of combined *in-situ* x-ray techniques and infrared spectroscopy will benefit multiple programs focused on surface reactivity, in both synthesis and catalysis focus areas. Advances in synthesis of high-quality In_xGa_{1-x}N alloy films with bandgaps spanning the visible and solar spectra will be applicable to applied programs in photocatalysis, solid-state lighting, photovoltaics, and optoelectronics.

FY 2011 Results and Accomplishments

As an initial step in predicting the mechanisms of metastable InN formation, first principles were used to calculate surface phase diagrams and reaction barriers in GaN and InN exposed to NH₃. We identified a new lowest-energy surface structure on InN that was not known. We have also simulated x-rays crystal truncation rod profiles for all the calculated structures to help identify those in *in-situ* x-ray experiments. Calculated barriers identified NH decomposition as a rate-limiting step and helped us to propose a new mechanism for the production of active nitrogen during film growth via decomposition of ammonia up to active NH species, which subsequently undergo hydrogen exchange with other species before forming nitrogen molecules.

As a high conductivity material with good reflectivity in the infrared region, ZrB₂ surfaces permit high-quality data to be obtained by reflection absorption infrared spectroscopy (RAIRS) of the clean surface and epitaxial thin films of the semiconductors GaN and InN. Exposure to ammonia with the crystal at room temperature produced no IR (infrared) peaks. With the help of computational results, we interpreted this finding as indicating complete dissociation. Exposures to hydrogen produced IR peaks were in excellent agreement with theoretical predictions. We also studied the surface of GaN as a function of temperature and chemical environment (N₂/NH₃ and N₂/H₂ gas mixtures) using *in-situ* x-ray scattering. Formation of measured off-specular crystal truncation rods of GaN on sapphire depended on the temperature and chemical environment. Crystal truncation rods of GaN in NH₃ at 500–700°C were reproduced when switching back from N₂ or H₂ to NH₃, indicating a reproducible adsorption of certain species onto GaN in an NH₃ environment.

Proposed Work for FY 2012

In determining which combinations of substrate properties will produce high nitrogen activities and high-quality InN films, we will rely on theoretical predictions as well as *in-situ*

experimental observations. To that end, we will integrate an IR spectrometer into an existing metal-organic chemical vapor deposition (MOCVD) system. Real-time IR spectroscopy measurements will track the decomposition of NH_3 and the formation of intermediate surface species such as NH_2 and NH . Surface x-ray scattering will be used to measure surface structure and dynamics of reconstructions, step morphology, and faceting as a function of vapor composition and temperature. These will be compared with first principles calculations of surfaces with step edges. By combining *in-situ* x-ray and IR spectroscopy measurements, we will determine the substrate orientation and composition dependence of the effective nitrogen activity for comparison with reaction models based on parameters determined from calculations. As the overall goal is to establish the mechanism of the underlying surface chemical reactions involved in the growth of gallium and indium nitride by MOCVD, it is important to explore the surface chemistry of both the nitrogen and metal-containing precursors. These results will be compared to the observed surface structure and composition variations in different growth regimes.

Next Generation Multicomponent Nanocatalysts: *in situ* Study of the Growth and Function

2011-123-NO

Elena V. Shevchenko, Jeffrey R. Guest, Julius Jellinek, Byeongdu Lee, Sungsik Lee, Xiao-Min Lin, and Tijana Rajh

Project Description

The goal of the project is to explore, understand, and characterize the complex correlations among the size, composition, structure (both interior and exterior), thermal responses, electronic properties, and catalytic characteristics of multicomponent nanoparticles (e.g., mixed, core-shell, and dumbbell-like). This research entails a combination of chemical synthesis, *in situ* characterization, and theory/modeling/simulation techniques.

One of the main objectives of the project is to understand and characterize the synthesis conditions/mechanisms that define the composition and structure of the resulting multicomponent nanoparticles (NPs). Based on this understanding, we will then synthesize novel multicomponent NPs with potentially superior characteristics. This effort is focused on understanding the mechanism of the nucleation and growth of nanosized core/shells and dumbbells, as this understanding is critical for further progress in material design. The contribution of different parameters that control synthesis of NPs will be investigated by *in situ* hard x-ray study of the synthesis of multicomponent catalysts. Simultaneous anomalous small-

and wide-angle x-ray scattering (SAXS and WAXS, respectively) are used to determine the number and size of nanoparticles and the compositional distribution of atoms over the growth of nanoparticles. The *in situ* variation of the lattice parameter of either shell or core metal due to alloying is of interest because it is directly related to the catalyst performance. The primary types of NPs that will be investigated are (i) ternary metallic core-shell and dumbbell-like systems, such as CoPt_3/Au , FePt/Au , $\text{Au}/\text{Fe}_2\text{O}_3$, and CoPd_2/Au , and (ii) hybrid semiconductor-based photocatalysts, such as a CdSe/CdS core/asymmetric shell with variable width of the shell decorated with Au.

The catalytic properties of the chemically synthesized NPs are being tested in reduction and oxidation reactions. The issues that we are addressing include (i) capping ligands that limit the availability of the surface of NPs for the reaction and can poison the catalysts and (ii) the effect on possible sulfur-containing interfaces between the constituents in multicomponent NPs.

Theory/modeling/simulation will explore and characterize a variety of structural forms, both isomeric (i.e., defined by the geometric packing) and homotopic (i.e., defined by the placement of different types of atoms between the sites of a given geometric form). This effort will also calculate the energetics, thermal stability and temperature-induced structural and phase transformations, electronic properties, and chemical/catalytic characteristics of the multicomponent NPs (in gas phase and in environment, e.g., deposited on supports). These structural forms will then be synthesized and explored experimentally.

Mission Relevance

This project is relevant to the DOE mission in transforming the nation's energy system. Catalysis is a key process in energy processing and production of different types of chemical products. Also, it has significant environmental aspects since it allows increasing the efficiency of industrial processes. High-performance catalysts play a central role in energy conversion and storage technologies. We expect that the knowledge gained through this project will greatly advance our ability to design and synthesize catalytic nanostructures with superior performance, avoiding the time- and labor-consuming activities of current empirical approaches.

FY 2011 Results and Accomplishments

- ▶ We developed a general approach to synthesize a variety of dumbbell-like NPs, such as Pt/Au , FePt/Au , and CoPt_3/Au . We found that redox ions, such as Co_{2+} or Pb_{2+} , located or adsorbed at the surface of seeds are key parameters that control the homogeneity of the nucleation of gold at the surface of Pt, FePt, and CoPt_3 NPs.

- ▶ We performed an *in situ* study of the nucleation and growth of CoPt₃/Au and Pt/Au dumbbells under realistic conditions (Figure 1). Aliquots of the sample were taken each minute by a syringe pump and then returned to the reaction flask. The nucleation and growth of dumbbells and changes in the seed materials were monitored by simultaneous synchrotron SAXS and WAXS. Blank experiments where the reactants are confined in the capillaries demonstrated completely different kinetics of nucleation and growth of dumbbells. These results emphasize the importance of *in situ* studies under realistic conditions, in this case in the flask where stirring and reactant diffusion clearly yield a different result.

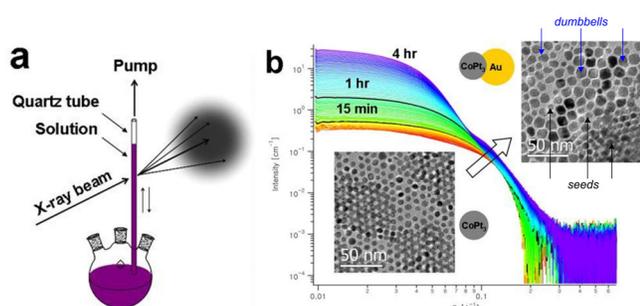


Figure 1. (a) Experimental setup used in *in situ* studies of nucleation and growth of nano-dumbbells; (b) SAXS data and micrographs showing the evolution of seeds and growth of CoPt₃/Au dumbbells. The arrows show examples of dumbbells and non-reacted seeds. Growth of gold appears as an increase of the peak intensity below 0.1 \AA^{-1} and developing of the peak around 0.1 \AA^{-1} .

- ▶ We performed systematic *ex situ* characterization of the catalytic properties of the synthesized seeds and their dumbbells by using room-temperature hydrogenation of octyne, butanal, and citral as model reactions. We found that CoPt₃ NPs are more efficient catalysts than conventional Pt particles deposited on carbon or chemically synthesized Pt NPs. The catalytic properties of dumbbells significantly depend on the oxidation state of the surface of the seeds and gold precursors used during the synthesis of nano-dumbbells. We assume that these two factors affect the mechanism of nucleation and growth of dumbbells, as well as the surface of seeds in dumbbells. We found that Pt/Au and CoPt₃/Au dumbbells synthesized with AuCl are catalytically less active in hydrogenation of octyne and very active in hydrogenation of butanal. These observations are important for the design of highly selective catalysts.
- ▶ As an initial density functional theory (DFT) study, we calculated the structural, energetic, and electronic characteristics of pure Pt and Co and mixed Pt/Co clusters with 13 and 55 atoms; these results were used as paradigmatic representations of systems investigated experimentally, such as CoPt₃ NPs. The study involved careful testing and justification of the computational framework (choice of the exchange-correlation functional

and pseudopotential/basis set). Among the issues that were explored are the effects of admixing Co to Pt clusters. We found that admixing of Co to Pt, or vice versa, leads to stabilization of clusters, indicated by an increase of their binding energy. Also, it is energetically preferred to have the surfaces of the clusters enriched in Pt atoms and their interiors enriched in Co.

- ▶ Since the surface of chemically synthesized NPs is covered with ligands, we tested the effect of ligands commonly used in synthesis of NPs on their catalytic activity (both conversion and selectivity) in hydrogenation of octyne and citral. Primary amines significantly improved the selectivity (Figure 2), despite the common perception about the “bad” influence of surface ligands on the catalytic properties of NPs.

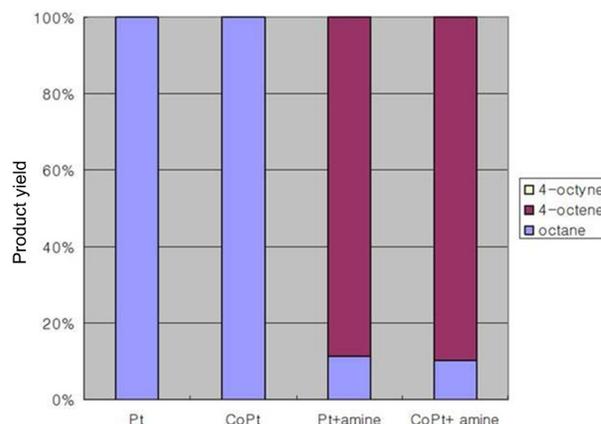


Figure 2. Conversion and selectivity of hydrogenation of octyne on clean and modified dodecylamine Pt and CoPt₃ NPs. In all cases we saw 100% conversion and as a result we do not see any traces of 4-octyne. This implies very high catalytic activity of Pt and CoPt₃ chemically synthesized nanoparticles. Samples modified with dodecylamine show significantly higher selectivity as it is evidenced by higher fraction of octene while in the case of non-modified samples, octyne was completely converted into octane.

- ▶ Also addressed by the theory/simulation component of the project was the energetics of adsorption of various hydrocarbons and amine groups on Pt nanoparticles (i.e., the systems explored in our experimental studies). The findings include the following: (1) the adsorption energies of alkenes (as represented by, e.g., C₈H₁₆) and amines (as represented by, e.g., C₈H₁₇NH₂) are close; (2) the adsorption energies of corresponding alkynes (as represented by, e.g., C₈H₁₄) are higher than those of either alkenes or amines; (3) in the case of coadsorption with amines, the strengths of adsorption of both alkenes and alkynes to the Pt nanoparticles are reduced, the source being the steric repulsion between the alkenes/alkynes and the amines; and (4) the reduction in the adsorption energy of alkenes is larger than that of alkynes. These findings are central for understanding the role of amines in affecting the selectivity of Pt nanocatalysts in hydrogenation of various unsaturated hydrocarbons.

Proposed Work for FY 2012

- ▶ Synthesis of multicomponent Au/iron oxide and FePt/iron oxide
- ▶ *In situ* SAXS and x-ray absorption spectroscopy of synthesized CoPt₃/Au and FePt/Au NPs
- ▶ Evaluation of selectivity switchers
- ▶ *In situ* CO oxidation
- ▶ Photoinduced synthesis of CdSe/CdSe/Au and comparison with chemical only approach
- ▶ Extension of the studies performed on pure Pt nanoparticles to bimetallic Pt-based nanoparticles, such as Pt-Co and Pt-Fe
- ▶ Extension of the studies to pure and alloy metal nanocatalysts of larger sizes
- ▶ Exploration of the comparative catalytic functionality of different faces [e.g., (100) vs. (110) vs. (111)] of the pure and alloy nanocatalysts

Inorganic Synthons: Toward Scalable Materials Design, Discovery, and Creation

2011-134-N0

Lynda Soderholm, Peter Chupas, Mercuri Kanatzidis, and John F. Mitchell

Project Description

This project seeks to develop a mechanistic approach for the directed syntheses of inorganic materials. At the core of our approach is the conceptual extension beyond atoms as core building blocks to inorganic functional groups — preorganized units call “synthons” — that self-assemble in molten or aqueous solution prior to crystallization. Synthons may take the form of well-defined fragments of covalent networks or merely exist as atomic correlations. If we can identify these preorganized bulk precursors and understand the general principles that guide their formation and condensation, we can move toward a mechanistic approach to the discovery and growth of new and targeted materials with energy relevance.

Mission Relevance

Our project fits squarely in the area of DOE’s science mission because it addresses the Grand Challenge of controlling the structure of matter at the atomic level. The knowledge we gain as a result of this project will effectively rewrite textbooks on inorganic synthesis, paving the way toward directed creation of inorganic solids with the precision of organic functional group synthesis and the high yields of solid-state reactions.

FY 2011 Accomplishments and Results

We began this project by focusing on two parallel lines of investigation, centering on atomic-correlation development in (1) a chalcogenide melt and (2) dissolved metal ions in aqueous solution.

Research indicates that the syntheses of polychalcogenides of the type A_2Q_x (A=alkali, Q=S, Se, Te) are preceded by different kinetic intermediates that may exist at various temperatures and flux compositions. These compounds are promising candidates for directed synthesis because they are often related by subtle changes in internal connectivity and conformation of M-Q linked building blocks. The resulting phases have distinct semiconducting properties. Studies here began with characterizing polysulfide chains in the melt, specifically mixtures of K_2S_3 and K_2S_5 powders. At room temperature, the Raman spectra simply show a combination of the K_2S_3 and K_2S_5 modes. Upon heating, mixtures of molten K_2S_3 and K_2S_5 cannot be reproduced by linear combinations of the starting-material modes (dashed blue lines in Figure 1). For example, the 50% mixture gives a distinct spectrum, which we assume to be molten K_2S_4 . The 25% and 75% molten spectra can be fit as combinations of K_2S_3 + K_2S_4 and K_2S_4 + K_2S_5 . So it appears that in the melt, K_2S_x behaves like line compounds, with chains of S_x^{2-} (where x is a single number if stoichiometry allows) greatly favored.

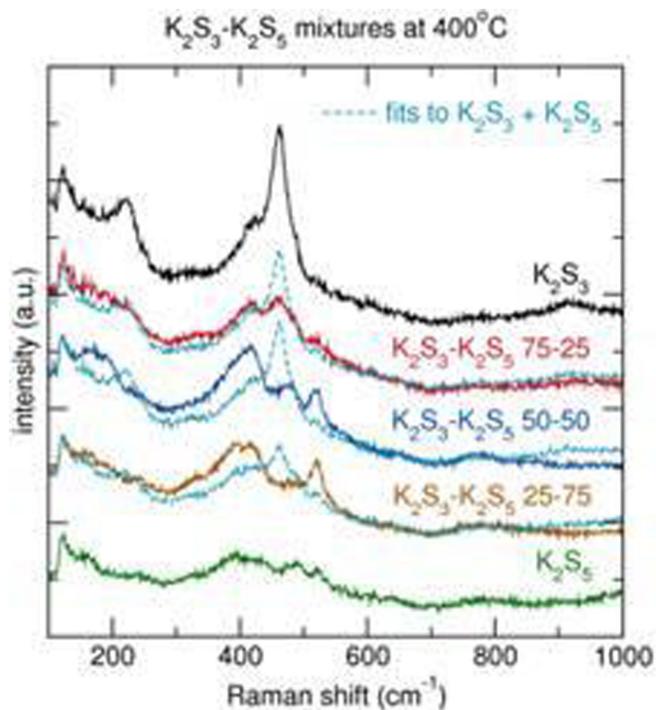


Figure 1. Raman spectral features used to characterize polysulfide chains in the melt, specifically mixtures of K_2S_3 and K_2S_5 powders. The room temperature spectrum simply shows a combination of the K_2S_3 and K_2S_5 modes. Upon heating, mixtures of molten K_2S_3 and K_2S_5 cannot be reproduced by linear combinations of the starting-material modes (dashed blue lines).

In parallel but related studies, we began to probe the formation of metal-oxide synthons in aqueous solution as a synthetic route to extended-oxide materials, thus stretching to the limit the concept of bonded clusters rather than continuing to view solid formation simply as the atom-by-atom development of long-range correlations. We undertook a systematic exploration of polynuclear Zr(IV) oxide cluster formation because of its potential as a basis for photochemical catalysis. Guided by concurrent theoretical studies of metal-oxide cluster stabilities, we can focus on determining conditions that optimize a monodisperse solution of Zr oligomers. The goal is to control solution conditions to tune and isolate size-selected Zr oxide synthons.

Our approach involved slowly raising the pH through *in situ*, controlled water electrolysis. Total x-ray scattering data were used to observe and quantify correlations. The results show formation of a monodisperse Zr-polymeric phase in solution, as depicted in Figure 2. Important to this work is clear evidence that the zirconyl ion $[\text{Zr}=\text{O}]^{2+}$ is *not* present in any of the samples, resolving a long-standing question in the literature. Single-crystal structures of precipitates formed following hydrolysis reactions confirmed the assignments of tetrameric clusters present in solution.

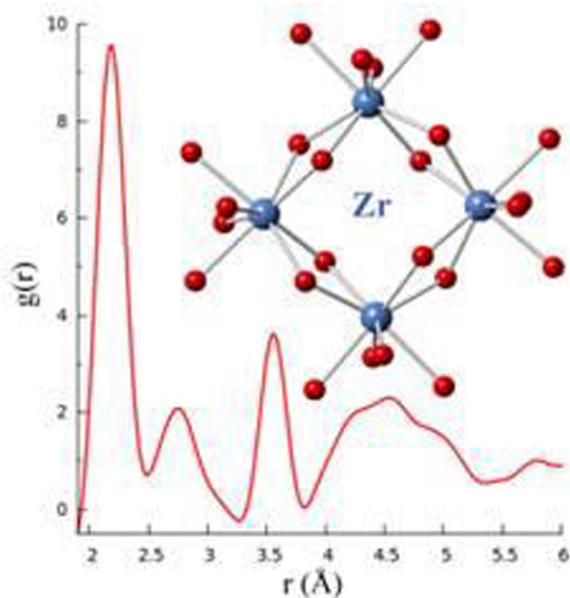


Figure 2. The Fourier transform of high energy x-ray scattering (HEXS) data obtained from an aqueous Zr solution. The peak positions and intensities are consistent with the monodisperse presence of the polynuclear structure depicted in the figure inset. This cluster can be precipitated as single crystals by manipulating solution conditions.

Proposed Work for FY 2012

The chalcogenide and aqueous oxide projects are fully engaged as *in situ* studies on the basis of results to date. Solutes will be included in the chalcogenide melts to study synthon formation as a function of temperature and its impact on

precipitate composition and structure. Transition-metal oxide correlations in aqueous solution will be further monitored as a function of solution conditions and choice of transition metal. We will continue our efforts to couple these experiments with computational studies of cluster growth in melts to determine synthons, establish additional pathways of synthons to transition metal structures, and begin exploring the role of solvent in structure growth. In addition, selected aqueous solutions showing strong evidence for the presence of clusters will be used to initiate studies employing the synthon concept to optimize thin-film growth.

Synthesis Science of Functional Layered Complex Oxides

2011-188-N0

John W. Freeland, Anand Bhattacharya, Jeffrey A. Eastman, Dillon D. Fong, Hawoong Hong, Julius Jellinek, Nenad M. Markovic, and Serge M. Nakhmanson

Project Description

Functional materials based on complex oxides offer new and exciting strategies for meeting many of our outstanding energy challenges. Materials theorists can now even design virtual crystals for specific applications and predict their properties. Unfortunately, synthesis of a new oxide material is typically difficult, particularly when there is a lack of quantitative feedback during growth. The goal of this project is to understand the growth of functional layered complex oxides, utilizing both computational studies of synthesis and an oxide molecular beam epitaxy (MBE) system with *in situ* x-ray scattering and spectroscopy capability. The *in situ* oxide MBE system will be the first of its kind and will allow an unprecedented level of control over both stoichiometry and structure. The associated coupling of theory and experiment are expected to significantly advance both growth science and our understanding of complex oxide phenomena as we harness these materials as model systems in the search for novel catalytic functionality.

Mission Relevance

This project is relevant to DOE's basic science mission. This project aims to develop the "science of synthesis" approach for the case of layered oxide thin films. The goal is to move quickly down the path from prediction to synthesis of novel energy materials by merging theory and experimental efforts from across the laboratory. Harnessing the ability to quickly isolate synthesis pathways will enable the study of novel materials for energy storage and conversion. In addition, this project involves the development of a unique capability at the Advanced Photon Source that, in the long term, will greatly benefit a wide community of users interested in oxide thin-film synthesis.

FY 2011 Results and Accomplishments

Layered oxide materials offer a broad range of functionalities, and the many recent advances in computational theory now allow the design of novel phases with potentially transformative properties in the field of energy technology. This project combines three key ingredients to develop a new approach to materials discovery: *in situ* characterization of the growth of layered oxides (see Figure 1), theory of synthesis in close interaction with experiment, and systematic exploration of the relationships between complex oxide structures and electro-catalytic behavior.

In FY 2011, we redesigned and assembled the world's first *in situ* ozone-assisted MBE system in Sector 33 of the Advanced Photon Source (APS). In order to synthesize the complex composition profiles for the class of novel materials known as layered oxides (see Figure 1), the growth flange accommodates multiple sources with integrated shutters for layer-by-layer growth control together with a high-purity ozone source that will deliver a jet of pure ozone for film oxidation during growth (see Figure 2). Our experiments will be able to simultaneously measure lattice structure and composition by using x-ray fluorescence with monochromatic x-rays.

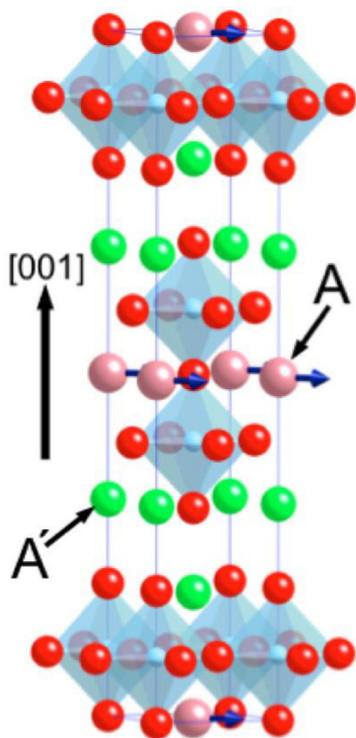


Figure 1. Crystal structure of a Ruddlesden-Popper type $\text{PbSr}_2\text{Ti}_2\text{O}_7$ superlattice, where $A=\text{Pb}$ and $A'=\text{Sr}$. In this structure, the Ti atoms (blue) are octahedrally coordinated by Oxygen (red).

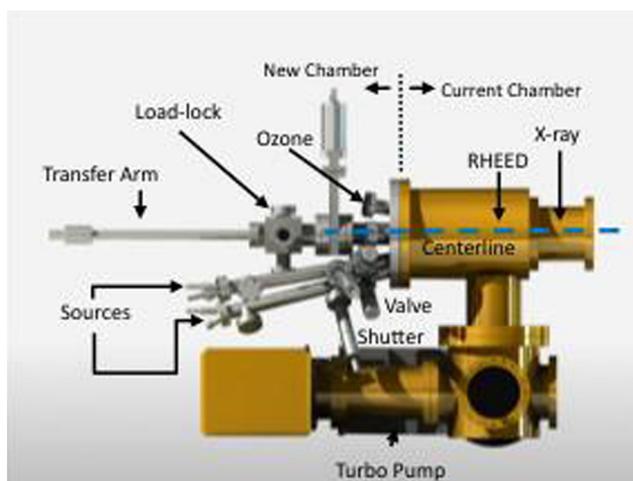


Figure 2. Drawing showing the oxide growth upgrade to the existing molecular beam epitaxy system in Sector 33 of the APS.

The experimental effort is coupled to a theoretical effort, the ultimate goal of which is to provide prescriptions for optimal growth conditions of compounds with desired structure and layer sequence. This goal is being achieved via extensive molecular dynamics (MD) and Monte Carlo simulations of oxide MBE growth, conducted as a function of the chemical identity of the depositing species and such operational conditions as epitaxial stress, temperature, and pressure.

Finally, to explore the utility of oxide surfaces for enhanced catalytic performance, these well-characterized systems were harnessed in electrochemical reactions. In order to design complex oxide catalysts for the oxygen reduction reaction and oxygen evolution reaction, we began by studying epitaxial thin films of SrRuO_3 on (100)-oriented niobium-doped strontium titanate and tracking both *in situ* catalytic activity and crystallographic structure with hard x-rays.

Proposed Work for FY 2012

During FY 2012, we will begin *in situ* growth studies of $\text{PbSr}_2\text{Ti}_2\text{O}_7$ and substitutionally doped variants of this material. Theoretical efforts will expand the capabilities of electronic structure calculations to integrate with the developed framework for molecular dynamics to optimize the interatomic potentials. The *in situ* studies of catalytic function will expand into conducting layered oxides.

Seminars

Freeland, J. (2011). "Emergent Correlated Electron States at Surface and Interfaces." Max Planck Institute for Solid State Research, Stuttgart, Germany, Dec. 3, 2010.

Freeland, J. (2011). "Emergent Correlated Electron States at Surfaces and Interfaces." Leibniz Institute for Solid State and Materials Research, Dresden, Germany, Dec. 2, 2010.

Freeland, J. (2011). "Understanding and Controlling Phases of Complex Oxides." Max Planck Research Department for Structural Dynamics, Hamburg, Germany, Nov. 29, 2010.

Multiscale Computational Molecular Science

2011-197-NO

Gregory A. Voth

Project Description

The objective of this project is to develop multiscale methods that rely on rigorous statistical mechanics to describe electrochemical processes and materials relevant to energy conversion and storage. Specifically, this work focuses on the transport of charged defects through, and morphological rearrangements within, ion-selective membranes for fuel-cell and battery technologies. The techniques being pursued include a unique reactive molecular dynamics (MD) method, based on multistate empirical valence bond (MS-EVB) theory, which extends classical MD to include chemical reactions in complex environments. In addition to modeling reactive processes at large simulation scales, new coarse-graining procedures are being developed to better connect resource-intensive *ab initio* simulations to large-scale classical MD. The results of such efforts will provide more accurate descriptions of materials without resorting to empirical fitting with experiment. Hence, these methods will retain the predictive capability to guide experiments.

Mission Relevance

This project is relevant to DOE's missions in basic science and energy. The continued development of energy conversion and storage systems is highly relevant to ensuring the leadership of the United States in energy storage technologies, as well as reducing the nation's dependence on oil. By combining the methods developed in this work, a consistent simulation tool is being investigated that will be capable of predicting materials properties relevant to device engineering based on molecular structure. Such a simulation method will be invaluable to the ongoing efforts to optimize batteries and fuel cells while avoiding costly "guess and check" approaches.

FY 2011 Results and Accomplishments

Several advances have been made in applying MS-EVB to modeling reactive processes in electrochemical membranes and to the coarse-grained description of charge transport in fuel cells. The code developed for reactive MS-EVB simulations (RAPTOR [Rapid Approach for Proton Transport and Other Reactions]) has been successfully generalized to explore reactive dynamics for both proton and hydroxide transport through

polyelectrolyte membranes, as well as more complicated reaction schemes involving the synthesis and decomposition of multiple molecules. A new force-matching algorithm was developed to define the reactive portions of a MS-EVB model with tabulated potentials. This algorithm was successfully used to model an excess proton and hydroxide ion based on *ab initio* simulations. The parallel performance of the RAPTOR code was also improved by implementing a multiple-program approach to reduce communication by evaluating short-range and k-space calculations simultaneously on separate partitions of processors.

A novel coarse-grained description of proton transport through fuel cell systems was developed that combines a coarse-grained model of the polymer electrolyte with a meso-scale fluid dynamics approach to study diffusive proton transport (see Figure 1). Combined with atomistic information, this approach allows for the study of proton conductivity in fuel cell membranes at a length scale previously inaccessible to atomistic simulations and allows for direct comparison with spectroscopically measured proton concentrations and conductivity data.

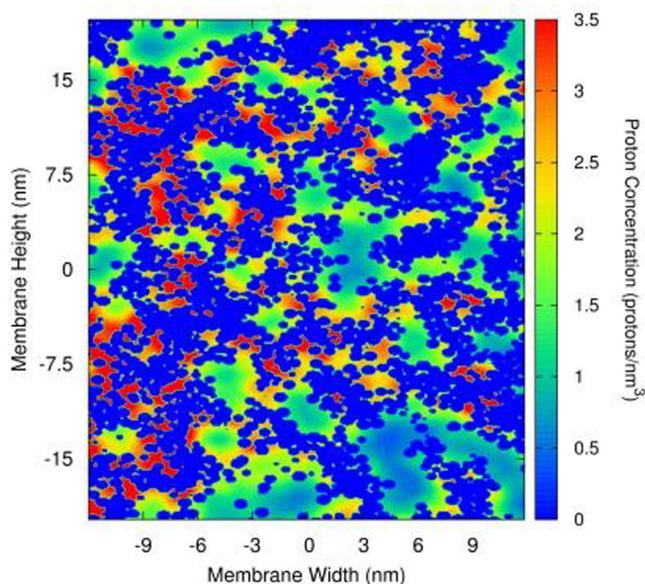


Figure 1. The simulated proton concentration profile at steady state through a portion of the Nafion 117 membrane frequently used in proton exchange fuel cells. The color bar indicates the intensity of proton concentration where the dark blue regions correspond to the excluded volume of the polymer backbone. Localization of protons around regions of the polymer demonstrates their attraction to the negatively charged sulfonate groups, resulting in the formation of complex double layers.

Proposed Work for FY 2012

Ongoing work is focused on optimizing the new parallelization strategy of RAPTOR and the LAMMPS (Large-Scale Atomic/Massively Parallel Simulator) MD codes on leadership-class computing resources (e.g., Intrepid [IBMBlue Gene/P]) available at the Argonne Leadership Computing Facility. The mul-

multiple-program approach will also be used to develop a new parallelization strategy for the efficient simulation of multiple reactive species in concentrated environments. In addition, further studies are also under way to include the mesoscale simulation of proton transport at larger length scales and improve the underlying coarse-grained model using results from simulations made possible with a DOE Innovative and Novel Computational Impact on Theory and Experiment (INCITE) award.

Fundamental Developments in Theory and Modeling of Nanoscale Systems and Phenomena

2011-198-NO

Julius Jellinek

Project Description

The field of nanoscience and nanotechnology represents a truly new research area, where the principal novelty extends not only to the systems and phenomena at hand, but also to the fundamental concepts, methodologies, and techniques, both experimental and theoretical, needed to study and characterize them. Whereas, by virtue of practical necessity, this is well recognized in experimental studies of nanosystems — the very ability to perform them hinges on and forces the development of new, highly sensitive “nanoprobes” — the overwhelming majority of theoretical explorations in the field still rely on concepts and methodologies originally developed for either the condensed phase or the gas phase of matter. These concepts and methodologies may not only be inefficient as applied at the nanoscale, but, more importantly, they may be limited or even inadequate for capturing, characterizing, and predicting principally novel properties and phenomena. Therefore, formulation of new fundamental theoretical concepts and methodologies and new theoretical tools of analysis and characterization that are specifically targeted at and tailored to nanoscale objects is central for the development of the entire field. The goal of this project is to initiate and execute a well-defined program of exploratory theoretical research that aims to develop such new concepts, methodologies, and analysis techniques in the general areas of dynamics and statistical mechanics of nanoscale (more generally, finite-size) systems.

Mission Relevance

This project falls under DOE’s basic science mission. Because advanced materials are ubiquitous throughout all technologies underlying energy, environment and national security, a new and better approach to understanding and prediction in

nanoscience and nanotechnology holds the potential to have a truly revolutionary impact on all mission areas of the DOE.

FY 2011 Results and Accomplishments

The main effort in FY 2011 was directed at conceptual/analytical developments targeting formulation of an exact methodology for computation of the vibrational densities of states for arbitrarily anharmonic systems. Knowledge of the density of states is essential, because it allows the theoretical/computational characterization of thermodynamical and statistical mechanical properties of a system.

In the case of harmonic systems (i.e., systems comprised of a finite number of harmonic oscillators), the vibrational density of states can be expressed exactly by an analytical formula. A major advance in the practical application of this formula was achieved when Beyer and Swinehart [T. Beyer and D.F. Swinehart, *Algorithm 448: Number of Multiply-Restricted Partitions*, *Commun. ACM* **16**, 379 (1973)] introduced their ingenious direct counting algorithm. Later, Stein and Rabinowitch [S.E. Stein and B.S. Rabinovitch, *J. Chem. Phys.* **58**, 2438 (1973)] generalized this algorithm to the case when some of the oscillators are anharmonic, but this generalization assumes that the oscillators are independent (i.e., there is no energy exchange between them). This is a severe restriction. All other generalizations still assume at most a weak coupling between the different modes. This assumption can be used only in application to nearly rigid systems. Our goal is to find a solution for the general case of an arbitrarily high degree of anharmonicity (i.e., strong coupling between the modes), including the limiting cases of highly floppy or even liquid-like systems. In working toward this goal, we made progress on two fronts.

The first abandons reliance on knowledge of the “natural” (i.e., low-energy) spectrum of vibrational frequencies of a system and replaces it with the power spectrum derived from information (specifically, the velocity correlation function) computed in the course of a molecular dynamics simulation. The simulation can be carried out at any energy, including very high energies, when the system is highly anharmonic and its vibrational modes are strongly coupled. The power spectrum, which accumulates all the frequencies experienced by the system in the course of its time evolution and which may have the form of a continuous distribution, is then discretized into a finite number of frequencies with their associated degeneracies. The discretization leads to non-integer degeneracies, which at first glance may appear non-physical and problematic.

Progress on the second front addresses and resolves this apparent difficulty. It is based on generalization of the notion of the factorial ($N!$), normally defined as a product of integers, to non-integer (i.e., real-valued) numbers using the so-

called gamma function. On the basis of this generalization, we developed a modification of the Beyer-Swinehart algorithm for harmonic systems that explicitly incorporates the possible degeneracy of the vibrational modes (the original algorithm is “blind” to the fact that some frequencies may have the same value). The modified algorithm is considerably more efficient than the original one in applications to harmonic systems with vibrational degeneracy. Even more importantly, the modified algorithm can also be used in cases when the degeneracies have non-integer values, as in our case described above. This new development is general (i.e., not limited only to the problem of vibrational densities of states), and we expect it to find many applications in a broad spectrum of disciplines, including in social sciences, especially in the context of statistical analyses of data.

Proposed Work for FY 2012

Our work in FY 2012 will focus on the following:

- ▶ “Merging” the power spectrum-based analysis and the modified algorithm described above and completing the formulation of the conceptual framework for exact characterization of the vibrational densities of states of arbitrarily anharmonic systems;
- ▶ Coding the new methodology and incorporating it into molecular dynamics programs;
- ▶ Performing large-scale numerical studies on highly anharmonic systems (e.g., atomic clusters at energies/temperatures corresponding to the transition from the solid-like to the liquid-like form), including computation of their vibrational densities of states;
- ▶ Extending our dynamical analysis methodology based on the so-called dynamical degrees of freedom — which has so far been applied only to homogeneous systems — to finite heterogeneous systems;
- ▶ Applying this extension in large-scale dynamical simulations targeting understanding and characterization of the intricacies of the melting-like transition in finite heterogeneous systems (e.g., bimetallic nanoparticles); and
- ▶ Using the computed densities of states to establish a correlation between the dynamical and statistical behavior at the nanoscale.

The ability to compute vibrational densities of states is of fundamental importance because the knowledge of this property allows one to define and characterize all the other thermodynamic properties of systems as a function of their energy or temperature.

Image Furnace Growth of Single Crystals

2011-199-N0

Kenneth R. Poeppelmeier and James A. Enterkin

Project Description

The goal of this project is to improve crystal growth capabilities, to grow large single crystals of interesting materials, and to understand how crystal structure is related to crystal properties. We will primarily use the optical floating zone technique, combined with a flux for difficult-to-grow crystals. The focus of this project is on developing these techniques and understanding how growth conditions affect bulk and surface structures while growing crystals of materials of interest, to achieve a better understanding of how bulk and surface structures are related and how structure affects properties. Metal oxides, mixed metal oxides, and mixed metal oxide halides will be investigated. Non-linear optical (NLO) materials were identified as an initial class of materials of interest. Cu_2O was identified soon after the project began as a second material of interest, due to its long exciton lifetime.

Mission Relevance

This project is relevant to DOE’s basic science mission. The fundamental knowledge gained from and technical results of this project will be of interest to DOE, the DOD, other agencies, and private industry for both basic and applied R&D activities. From a basic R&D viewpoint, the crystal growing community will benefit from a better understanding of crystal growth as a result of the fundamental research conducted in this project. From an applied R&D viewpoint, the ability to produce large single crystals with NLO properties will support the development of lasers with shorter wavelengths. These shorter-wavelength lasers are used in a number of advanced spectroscopic techniques that are routinely used in catalysis and materials research, including photoemission spectrometry, Raman scattering spectrometry, and scanning tunneling microscopy. Furthermore, the development of lasers with shorter wavelengths will allow data storage at higher densities than current Blu-ray technology.

FY 2011 Results and Accomplishments

In FY 2011, a new optical floating zone furnace was installed that is capable of elevating temperatures up to 3000°C in atmospheres of any composition from 10^{-5} torr to 10 bar (~7600 torr).

In collaboration with the S. Pan group (Xinjiang Technical Institute of Physics & Chemistry), we began investigations of several NLO borate materials, including $\text{Na}_3\text{V}_2\text{B}_6\text{O}_{13}$, $\text{Li}_3\text{Cs}_2\text{B}_5\text{O}_{10}$, $\text{Li}_6\text{CuB}_4\text{O}_{10}$, $\text{Bi}_2\text{ZnB}_2\text{O}_7$, and $\text{K}_3\text{B}_6\text{O}_{10}\text{Cl}$. We successfully synthesized each of these NLO materials and are at various stages of preparing and growing crystals for each material.

In collaboration with researchers at Northwestern University, we grew large crystals of cuprous oxide (Cu_2O) to study exciton behavior. Cuprous oxide experiences an extremely long exciton lifetime, up to 13 microseconds, which makes it an ideal material for studying exciton behavior via high-spatial-resolution exciton-mediated photovoltaic effect. This technique requires large, high-quality single crystals that can be oriented and cut along any desired face, allowing the electrodes to be deposited along any plane. Orientation is important because it determines optical selection rules.

We used 99.9% copper rods to grow crystals that were 8 mm in diameter and several centimeters in length (Figure 1). Low-purity copper was used first to gain experience with different growth rates and atmospheres, and to determine optimal growth conditions. The orientation of each crystal was determined by using the Laue method, and crystals were successfully oriented and cut. Photoluminescence experiments revealed impurities and copper vacancies; the impurities arise from impurities in the starting material, and the vacancies are likely due to growth conditions.

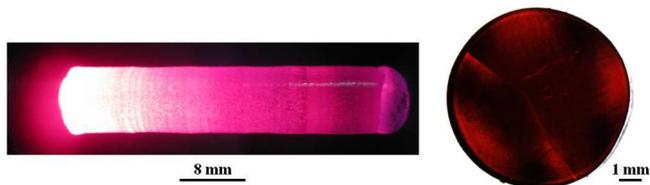


Figure 1. (Left) Cu_2O crystal cut on the left side and illuminated via a fiber light through the cut. (Right) Cu_2O crystal cut perpendicular to growth direction, showing a single grain boundary running from top left to bottom right.

In collaboration with Northwestern University Department of Materials Science and Engineering researchers, we established the relationship between bulk and surface crystal structures from the bond valence perspective. Chemical bonding is often overlooked by the surface science community, in part because bond strengths, lengths, and coordination geometries differ significantly from bulk to surface. We determined that chemical bonding plays a role in the structure of crystal surfaces analogous to that played in the bulk, and how the differences in bond strengths, lengths, and geometry can be readily understood through bond valence principles.

Proposed Work for FY 2012

We will continue to experiment with growth conditions for the five borate materials. Crystals of some can be grown from a self-melt and will be grown in the first part of FY 2012. Other materials require a flux for crystal growth. For these materials, we will investigate possible fluxes. Once suitable candidate flux systems are identified, we will continue with the growth of these materials. Following crystal growth, structure and properties, especially NLO properties, will be investigated. Observing the change in the wavelength of laser light pulsed

through oriented single crystals will allow measurement of second harmonic generation coefficients (d_{ij}). Monitoring crystal quality upon exposure to laser light will allow assessment of the damage thresholds.

We plan to optimize Cu_2O crystal growth conditions to minimize both copper and oxygen vacancies. We will then use higher-purity starting material (99.999% copper rods) to obtain the desired low level of impurities. Seed crystals will be used to control the orientation of the grown crystals, and crystals will be oriented and cut along the desired crystal facet. Electrodes will be deposited via electron beam lithography and excitons will be created via laser excitation. The electrodes will allow measurement of the voltage associated with exciton decay.

Novel Materials for Active Nanostructures

2011-200-N0

Daniel López and Liliana Stan

Project Description

The goal of the project is to fabricate and evaluate new-generation, high-performance active nanostructures incorporating novel active thin-film materials. Active materials optimized for maximum performance at nanoscale dimensions will be useful to develop more-sensitive, faster, and broader bandwidth devices that can be densely integrated into compact systems. In particular, we will deposit, mainly by sputtering, piezoelectric and ferroelectric thin films and their corresponding electrode materials for integration into both nano-electrical and nano-mechanical systems.

The focus of this work is on optimizing deposition conditions to maximize polarization while minimizing film thickness and controlling the residual stress and stress gradient in the entire film stack. The electrode materials will include metals and conducting oxides and will be optimized to maintain polarization while minimizing fatigue during operation. An important objective of this project is to understand the phenomena governing piezoelectric and ferroelectric response in active nanostructures. This information will guide the design and interpretation of nanoscale structures suitable for application in nano-electro-mechanical systems. We will develop a variety of designs for testing and incorporating the piezoelectric/ferroelectric materials into these active nanostructures. The approach builds on the ability to fabricate piezoelectric and ferroelectric nanostructures with superior physical responses using conventional semiconductor processes.

Mission Relevance

This project is relevant to DOE's basic science mission. Investigations coupling novel materials with active nanostructures will yield new scientific insights to the physics of these materials and their use in devices with novel functionality. The potential value of these results in the applications arena is also significant.

This project will develop novel piezo-resistive materials with enhanced response to external electrical fields. One of today's major limitations to manipulate nanostructures is associated with the lack of mechanisms to interface with the nano-world in order to control structures with dimensions smaller than 100 nm. These novel piezoelectric materials will allow large deformations at the nanoscale without large actuation voltages, providing a new mechanism to interact and sense nanostructures.

FY 2011 Results and Accomplishments

A novel sputter deposition system capable of handling 8-inch wafers (AJA International, Inc.) was installed, upgraded, and qualified. The system is fully functional, offering a variety of options with respect to deposition materials, substrate choices, and deposition conditions.

Recipes were developed for Ti, Pt, and SrRuO₃ (SRO) depositions. We explored different deposition conditions for Ti, Pt, and SRO film growth in order to optimize their characteristics. These films are intended to be used as an adhesion layer and bottom electrode layer. Ti and Pt films with good uniformity were achieved over the area of a wafer 20 cm in diameter. The Pt films grown on Ti/Si exhibit a strong (111) preferential orientation, which is a key factor in achieving polycrystalline Pb(Zr 0.2Ti_{0.8})O₃ (PZT) films with preferred out-of-plane orientation. Because the microstructure, preferred orientation, and ferroelectric properties of PZT films grown on Pt bottom electrodes depend strongly on the adhesion layer beneath the Pt layer as well as on the preparation conditions of Pt electrodes, we investigated these films in conjunction with PZT growth.

Epitaxial growth of PZT and SRO on SrTiO₃ (STO) single-crystal substrates was achieved. To optimize the PZT, we started by growing the films on single-crystal STO substrates. We achieved epitaxial growth of perovskite PZT films on SRO-buffered STO single-crystal substrates. Moreover, the ferroelectric properties of these films are good, which means they are ready to be integrated with the Si substrates.

We determined the appropriate temperature range for growing single-phase perovskite PZT films on Pt/Ti/Si. Applying the PZT deposition conditions from SRO/STO to Pt/Ti/Si was not a straightforward process. Because of interfacial reactions and interdiffusion between the layers, the PZT deposition condi-

tions had to be modified. The appropriate temperature range for growing perovskite PZT on Pt/Ti/Si was identified.

Proposed Work for FY 2012

Proposed work for FY 2012 includes the following:

- ▶ Identify other materials as buffers between the PZT and Si,
- ▶ Fabricate and test the first active nanostructures,
- ▶ Identify scaling methods to allow large-scale integration of active nanostructures, and
- ▶ Identify phenomena governing the piezoelectric response of active nanostructures.

Rare Earth Elements

2011-209-N0

John Hryn, Richard Brotzman, Jeffrey W. Elam, Sam Jiang, Xiao-Min Li, Yi Liu, and Angel Yanguas-Gil

Project Description

The goal of this project is to expand the general knowledge and capabilities associated with rare earth elements (REEs), which have recently been the focus of increased interest by DOE and other agencies. Prompting this interest is the use of REEs in many applications that contribute to increased energy efficiency and environmental benefits and an anticipated near-term shortage. REEs are used in high-energy-product (BH) magnets (B is flux density and H is magnetic field strength) for automotive light-weighting and wind power turbine applications, in phosphors for lighting applications (particularly light-emitting diodes [LEDs]), and in other energy-related applications. This project will allow us to combine capabilities in (1) magnet theory, nanosynthesis, and nanotechnology to begin developing processing technology for the synthesis of high-energy-product (BH) exchange spring magnets; and (2) rare earth chemistry and atomic layer deposition to begin developing high-energy efficient phosphors for increased luminescence.

Mission Relevance

This project is related to DOE's mission in energy security and science. REEs are of considerable interest to DOE and other agencies and have been the topic of several workshops and reports. The benefits of the project are expected to include more energy-efficient magnets, which will enable light-weighting of automobiles, and more energy-efficient wind turbines. Current magnets for these applications depend on Nd and Dy (REEs neodymium and dysprosium), which are predicted to be in short supply. The proposed alternative, Sm-Co (samarium cobalt) exchange-spring magnets, are more energy efficient and made of materials that are expected to be plenti-

ful, enabling energy savings in power generation (from wind power) and improved energy efficiency in transportation. In addition, phosphors developed during this project are expected to improve energy efficiency in upcoming LED applications. These developments would result in energy savings and, therefore, improved energy security by decreasing U.S. dependence on foreign sources of energy (e.g., oil from the Middle East).

FY 2011 Results and Accomplishments

In FY 2011, we initiated two specific projects, described below.

Design and Manufacture of Nanostructured “Exchange-Spring” Magnets

Method 1: We completed iron nanoparticle synthesis through decomposition of a pre-formed iron oleate complex at 380°C. Iron oxide (FeO) and aggregated iron nanoparticles were produced in the supernatant and attached to the magnetic stir bar, respectively. The synthesis will be repeated once the procedure is modified to remove the magnetic stir bar.

Method 2: We synthesized single-crystal iron nanoparticles from iron carbonyl, $\text{Fe}(\text{CO})_5$, at 200°C (Figure 1). Iron-cobalt nanoparticles (Fe/Co = 5/1) were synthesized by using the same procedure by adding a surface complexing agent to prevent cobalt nucleation and to control the rate of cobalt addition to iron nuclei. Metal nanoparticles were chemically passivated with silica shells by polymerizing tetraethylorthosilicate on the nanoparticle surface.

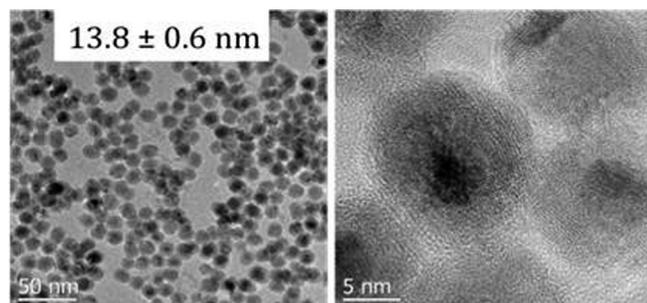


Figure 1. Iron nanoparticles of uniform size (13.8 ± 0.6 nm).

Synthesis of Improved Phosphors

This portion of the project involved synthesizing REE phosphors by using luminescent and optically active materials with higher doping efficiencies and controlling the dopant distribution. We control the spacing of the rare earth emitters by using surface-functionalized atomic layer deposition. This step reduces the growth per cycle and increases the spacing between rare earth emitters. This allows increased luminescence for the same amount of REE. We developed a methodology to incorporate the use of beta-diketonate and cyclopentadienyl precursors. This development opens the methodology to the whole lanthanide series because it uses the $\text{M}(\text{acac})_3$

and the $\text{M}(\text{Cp})_3$ and $\text{M}(\text{EtCp})_3$ precursors. We proved that the use of alkyl alcohols, carboxylic acids, and diketones (such as acetylacetone) reduces the growth per cycle in a wide range of oxide surfaces and that the process works with ozone as an oxygen source, which is crucial for phosphor materials to avoid the presence of hydroxyl groups known to quench photoluminescence. We synthesized $\text{Er}:\text{Al}_2\text{O}_3$ (erbium aluminum oxide) and $\text{Er}:\text{TiO}_2$ (erbium titanium dioxide) as model systems, and our first findings from EXAFS (extended x-ray absorption fine structure) characterization of the samples indicate a low degree of Er-Er clustering.

Proposed Work for FY 2012

The FY 2012 work on the magnet portion of the project will build on the efforts begun during FY 2011 and on exchange magnets. We will explore a core-shell approach to manufacturing the magnets. Initial experiments will include synthesis of the core-shell nanostructure in Argonne’s Center for Nanoscale Materials (CNM). The initial process that has been developed will be scaled to produce a green-body that will be subsequently sintered and superplastically deformed to produce an exchange magnet. The magnet will be tested to determine its energy product, and our research team will use the results to improve the process until a suitable magnet sample is produced. This portion of the project will focus on a new magnet system (Mn-Bi) that has the potential to replace Sm-Co and other rare-earth magnets in some energy applications.

The FY 2012 work on phosphors will apply the methodology developed during FY 2011 to the fabrication of red phosphors based on an Eu^{3+} (europium) emitter. The goals are to achieve luminescent red phosphors with a smaller amount of Eu and to study the influence of co-sensitization to further reduce the concentration of Eu while retaining the same luminescent properties.

In FY 2012, we will begin investigation of catalytic processes that involve mesoporous materials (e.g., SBA-15 and MCM-41), which hold significant promise for the cracking of heavy oils, such as those produced in Alberta, Canada (the largest source of imported crude oil in the United States). While promising, these materials cannot be used in fluid catalytic cracker (FCC) operations because of their low stability at high temperatures. We have shown that small (monolayer) coatings of certain transition metals into the pores of SBA-15 dramatically improve the materials’ stability. This catalyst could replace some of the rare-earth-exchanged zeolites normally used in FCCs, thereby reducing the need for rare earths in the refining industry.

Several other projects have been identified, including improved recycling of REE-containing phosphors, improved manufacture of metal REEs by using molten salt electrolysis

for more efficient use of REEs, and improved separation processes. We anticipate initiating several of these new projects in FY 2012.

Polyelectrolyte Brushes in Multivalent Ionic Media

2011-217-NO

Matthew Tirrell

Project Description

Our interest in multivalent interactions in polyelectrolytes spans the range from solutions containing trivalent metal cations to polyelectrolyte complexes formed by mixing solutions of oppositely charged polyelectrolytes. The main emphasis of this project is to develop new routes to self-assembly of aggregates and hydrogels based on fluid polyelectrolyte complexation, or coacervation. The need for robust and responsive hydrogels for use in numerous pharmaceutical, biomedical, and industrial applications has motivated intense research efforts on these important polymeric materials. The defining feature of hydrogels is that the vast majority of their mass consists of water, yet they still exhibit solid-like mechanical properties because of the presence of a three-dimensional network structure that, classically, is created through *in situ* covalent bond formation between multifunctional, reactive precursors.

Limitations of the covalent approach are that the hydrogels are not re-moldable once formed, have limited responsiveness to external stimuli, and may require organic co-solvents/reagents during their formation. To overcome these limitations, hydrogels formed through non-covalent physical associations arising from intermolecular interactions, in lieu of covalent crosslinks, have attracted significant interest recently, particularly as responsive materials and injectable gels. Typically, a drawback of such physically associated hydrogels is their poor mechanical properties, due to generally weak intermolecular interactions. In addressing new strategies to yield high-performance physically associated hydrogels, the role of dynamic materials formed via electrostatic interactions serves as a powerful model. The molecular model we are exploring is shown in schematic form in Figure 1.

Mission Relevance

This project is relevant to DOE's basic science mission. This work is relevant to the objective of producing strong, lightweight functional materials at low temperature via non-covalent bonding mechanisms and self-assembly processes. Specifically, this work addresses some of the principal issues raised in the Chapter 3 of the BESAC report: "Directing Matter and Energy: Five Challenges for Science and the Imagination."

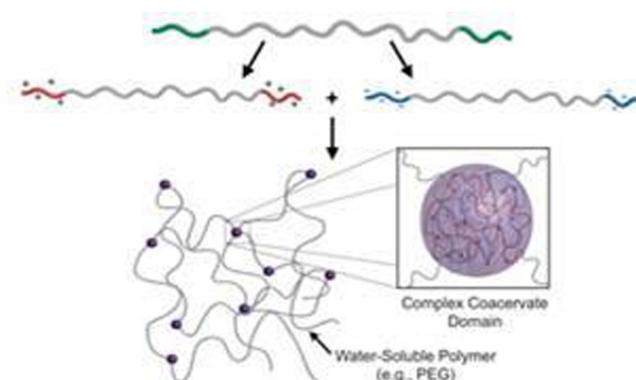


Figure 1. This figure represents a schematic route to making tri-block copolymers with a neutral (uncharged) middle block and either positively (red) or negatively (blue) charged end blocks. The idea is to make the backbone of the charged chains as similar as possible by using synthetic polypeptides, so that the charge differences are the dominant structural difference. These oppositely charged block then form complexes, such as the micellar domains illustrated in the inset, which tie the neutral middle blocks together via physical crosslinks.

Among the desired properties stressed explicitly in that report, which are present in the new class of materials we are developing, are self-healing, switchability or tunability in response to relevant environmental factors or control triggers, lightweight, and ease of processability via self-assembly. As our systems are built from synthetic polypeptides, this project also addresses Chapter 5 of the BESAC report in creating new self-assembled materials with properties found elsewhere only in naturally occurring biological systems.

FY 2011 Results and Accomplishments

A tri-block copolymer system, where the middle block is polyethylene oxide and the end blocks poly allyl glycidyl ether, can be functionalized post-polymerization to create otherwise identical anionic or cationic tri-blocks. Among our early findings are that, in media with low salt concentration (< 1M), equimolar mixtures of the anionic and cationic tri-blocks form elastic solids with BCC ordering of the ionic domains. The modulus can be reduced by adding salt, which weakens the polyionic interactions. At around 1M salt, the ordered structure dissolves and the mixtures become low-viscosity liquids. In the ordered state, application of sudden high shear strain "breaks" the structure, leading to a dramatic drop in modulus. Interestingly, the modulus recovers to a high value in minutes.

Proposed Work for FY 2012

Future experiments will explore the effects of block molecular-weight variation and off-stoichiometric mixing proportions in the multicomponent block copolymer systems. Referring to Figure 1, we will prepare a broad set of at least five triblock copolymers, spanning a range of chain lengths in each block, where the middle block in the figure will be an uncharged polypeptide (such as polyserine or polyglycine), and the end

blocks will be either polylysine (cationic) or polyglutamic acid (anionic). This synthesis work will take 3–4 months. We will then do rheological and small angle x-ray scattering measurements on, initially, balanced stoichiometric mixtures of the cationic and anionic polymers over a range of total polymer concentrations. Rheology will tell us how stiffness and elasticity develops in these materials; scattering will tell us how ordered structure develops in parallel. These rheo/optical studies will require 3–4 months, as well. The final phase of FY 2012 will address unbalanced stoichiometries, that is, how the material properties change when the total polymer concentration is constant, but the proportions of anionic and cationic polymers are not 50–50.



NATIONAL SECURITY

Molecular Characterization of Spore Coat Proteins

2010-093-R1

Daniel Schabacker and Paul 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 information on how or by whom the material was prepared. Neither can genetic means provide information on the resources available to the operator. Obtaining useful information requires 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 reliable enough to withstand legal challenges in court. The proteome, which is the set of expressed proteins in a given type of cell or 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 in order to provide detailed information on the methods used to culture, purify, and store the BTA. This methodology could help to identify not only the specific organism but also the facilities used to prepare it and the technical sophistication of the operator. *Bacillus anthracis* spores, which cause anthrax, are the model organisms for this research.

Mission Relevance

This project supports DOE's national security mission to reduce the global danger from weapons of mass destruction by enhancing our ability to attribute a BTA to individuals or organizations. This innovative approach is an improvement over 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, semiautomated platform that does not require a specialized laboratory or expensive mass spectral analysis.

FY 2011 Results and Accomplishments

The initial year of this research focused on developing the methods required for generating robust proteomic signatures. During this process, we discovered that our system was able to discern even slight variations in sample preparation. The addition of sugar-binding lectins allowed us to generate interactive signatures identifying variations in glycosylation of the proteins, thereby providing additional signatures supporting attribution.

Our research in FY 2011, focused on refining the methods needed to generate reproducible proteomic signatures. Because of our system's high sensitivity and resolving power, it was determined that slight variations in the proteomic signature will be present even in identical spore preparations of *Bacillus anthracis*. Such noninformative, inherent signature variations have not been characterized or even identified by today's less sensitive, lower-resolution proteomic tools. We began characterizing them to better understand our processes and to remove them from our analysis. We also expanded our analysis to non-sporulating bacteria, such as *E. coli*. Our initial analysis of *E. coli* preparations revealed that replicates had extremely similar (practically identical) signatures. Comparing *E. coli* proteome signatures from two growth media proved that our technological approach can provide extremely reproducible data while differentiating growth conditions. A major accomplishment in the project's second year was submitting a provisional patent application with our collaborators at the Loyola University Medical Center.

Proposed Work for FY 2012

In FY 2012, the project will focus on generating *B. anthracis* spore proteome signatures under two growth conditions to confirm we can differentiate between those conditions. We will continue characterizing the inherent noninformative signature variations in *B. anthracis* spore preparations to remove them from our analysis. We will also continue to generate data for non-sporulating bacteria by comparing *E. coli* cultured in two growth media. The data will be used to support the provisional patent application. In addition, we will explore the process of optimizing software and algorithms for automated comparative analysis.

Seminars

Schabacker, D. (2010). "An Ultrahigh Resolution Method for Identification and Attribution in Microbial Forensics." Private Meeting, Quantico, VA, Oct. 15, 2009.

Schabacker, D. (2010). "Method for Characterizing Protein Signatures in Food Technology." National Center For Food Safety and Technology, Summit-Argo, IL, Nov. 6, 2009.

Pravecek, T., D. Schabacker and A. Driks (2010). "Microbial Forensics and Signatures." Air Mobility Command, Scott Air Force Base, IL, Feb. 4, 2010.

Schabacker, D. and T. Pravecek (2010). "Characterizing Biological Matrices Through Proteomic Signatures." Air Force Research Laboratory, Dayton, OH, May 13, 2010.

Detection of Low Copy Number of Pathogenic Microbes by Litmus Strip

2010-175-R1

Qiaoling Jin, Liaohai Chen, and Daniel Schabacker

Project Description

A rapid and portable bioassay requiring the minimum engagement of sophisticated instruments and reagents, yet sensitive enough for early detection of pathogenic microbes, is a grand challenge for countering terrorism and preventing the spread of epidemic diseases. Although many of the commonly used approaches, including enzyme-linked immunosorbent assays and polymerase chain reaction, have very high sensitivity and specificity, they require advanced instruments or multiple reagents and thus are not suitable for field use or first responders. This project aims to develop a colorimetric assay for sensitively detecting pathogenic microbes by 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 under field conditions by simple visualization, and thus is directly relevant to the DOE mission in national security and public safety (countering bioterrorism threats and responding to epidemics). We expect the technology will also have great impact on early-stage disease diagnosis and basic biology and biomedical research.

FY 2011 Results and Accomplishments

In FY 2011, we focused on four main areas:

1. *Scale up the synthesis of the autocatalytic reactant tert-butyl 2-methyl-2-(p-toluenesulfonyloxymethyl) acetoacetate (BMTSAA):* We successfully synthesized the autocatalytic component BMTSAA in three steps: (1) monomethylation of *tert*-butyl acetoacetate, (2) hydroxymethylation with formalin under alkaline conditions, and (3) tosylation with *p*-toluenesulfonyl chloride. Since a large quantity of BMTSAA is needed for sensor platform development, we scaled up the synthesis to gram-scale. Specifically, we (a) simplified the first step of the purification procedure by using preparative flash chromatography to obtain *tert*-butyl 2-methyl-3-ketobutanoate in a higher yield and (b) optimized the reaction conditions in steps 2 and 3 by using toluene

as the solvent so that the reaction could be refluxed at higher temperature. As a result, the overall yield of the synthesis is now ~36%, and we were able to obtain gram-scale product for sensor development.

2. *Demonstrate the biosensor scheme based on the release of catalyst from polymeric micelles upon bio-recognition:* We first demonstrated the feasibility of the proposed sensor scheme in a model system in which an extremely low concentration of avidin protein molecules in solution was detected by using a spectrometer to detect the release of porphyrin catalyst molecules upon the recognition of biotin with avidin (Figure 1).

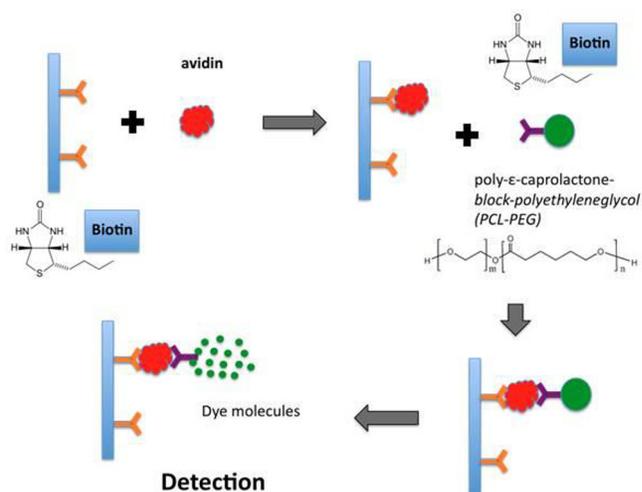


Figure 1. Biosensor scheme based on the release of catalyst from polymeric micelles upon bio-recognition.

The experiment started with the synthesis of two substrates: a biotin-modified glass substrate and biotin-labeled polymeric micelles that encapsulate porphyrin molecules. The synthesis of the biotin-modified glass substrate was achieved by first modifying a bare glass surface with 3-aminopropyltriethoxysilane, yielding a glass substrate with amine groups attached. The resulting substrate was then reacted with biotinyl-N-hydroxy-succinimide ester to generate the biotin-modified glass substrate.

In order to synthesize a biotin-labeled polymeric micelle, a new block co-polymer of poly-caprolactone–block–polyethyleneglycol (PCL-PEG) that had a carboxylic acid terminal group in the PEG end was synthesized in the lab. Polymeric micelles with carboxylic acid groups on the surface were then synthesized by adding deionized (DI) water to a solution of HOOC-PCL-PEG in dimethylformamide at a concentration of 11.4 mM at room temperature in the presence of porphyrin molecules in the solution and dialyzing against DI water overnight. The resulting polymeric micelles were subsequently reacted with biotin ethylene-

diamine in the presence of *N,N'*-dicyclohexylcarbodiimide as a catalyst to yield biotin-labeled polymeric micelles.

The detection of extremely low concentrations of avidin protein was achieved by first dipping the biotinylated glass substrate in the avidin solution, washing the substrate with water three times, and then dipping it into the biotinylated polymeric-micelle solution. Since one avidin molecule has four biotin binding sites, biotinylated polymeric micelles were attached to the glass substrate via the biotin-avidin interaction. The substrate was then dipped into a chemiluminescence reactant solution in which porphyrin, released from the micelles catalyzed the chemiluminescence reaction. The porphyrin is released because the organic solvent in the reactant solution can destroy the micelle structure. The chemiluminescence signals were recorded by a spectrometer. Figure 2 shows the signal output as a function of avidin concentration on both linear (left) and log (right) scales. The assay is extremely sensitive in the lower avidin concentration range. Even femtomolar avidin can be reliably detected. We thus demonstrated the biosensor scheme based on the release of porphyrin catalyst from polymeric micelles upon bio-recognition.

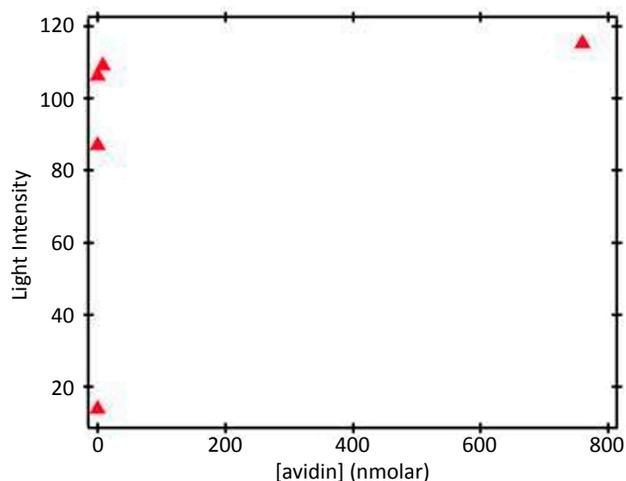
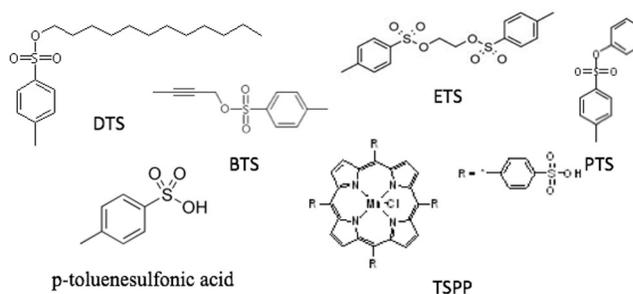


Figure 2. Sensor signal output as a function of avidin concentration.

3. *Develop autocatalytic reaction conditions suitable for visualization of sensor platform.* In FY 2010, we demonstrated the autocatalytic reaction of BMTSAA by following and quantifying the acid formation (pH value) during the reaction. An exponential increase of proton concentrations was observed in 90 minutes and proton concentrations reached a plateau in about two hours. For sensor applications, it is highly desirable for the reaction to be finished in minutes instead of hours. In FY 2011, we focused on optimizing the reaction conditions to shorten the reaction time and to decrease the initiator concentration.

We screened more than 20 organic acids to identify the best candidate for initiating the autocatalytic reaction, on the basis of the feasibility of encapsulation (by the polymeric micelle), acidity, and the efficiency of initiating the autocatalytic reaction. Figure 3 (top) shows the top six acid candidates and the minimum amount needed to initiate the reactions in different solvents. Among the candidates, *p*-toluenesulfonic acid has the highest sensitivity: one microgram of acid was able to initiate the reaction in 40- μ L solvent. The reaction can be easily followed by visualization after the addition of a pH indicator (Figure 3, bottom).



p-toluenesulfonic acid

TSPP

Acids	In ACN (mg)	In CHCl ₃ (mg)
DTS	0.01-0.03	0.02-0.04
ETS	0.03	>0.1
BTS	0.01	0.01
PTS	>0.1	>0.05
TSPP	0.001	
<i>p</i> -toluenesulfonic acid	0.001	

Samples	<i>p</i> -toluenesulfonic acid	BPB indicator
282	0.1mg	yellow
283	0.05mg	yellow
284	0.01mg	yellow
285	0.005mg	yellow
286	0.001mg	yellow
287	0.0005mg	blue
288	0.0001mg	blue
289	none	blue



Figure 3. Selecting suitable organic acids as initiator for the autocatalytic reaction.

In addition, when the acid initiator was encapsulated within the micelles, the organic-acid-loaded micelles could also trigger the reaction. As shown in Figure 4, as the concentration of Dodecyl *p*-toluenesulfonate (DTS) loaded micelle increased, the total acid generated by the reaction also increased exponentially within a one-hour reaction time frame.

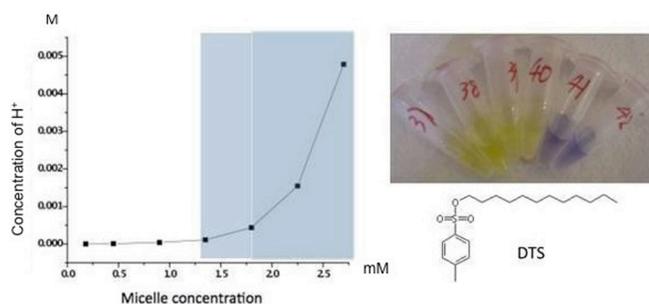


Figure 4. Acidity from the autocatalytic reaction as a function of concentration of DTS loaded micelles.

4. **Synthesize new block co-polymers that have the potential to form polymeric vesicles.** During FY 2011, it was found that water-soluble organic acids initiate the autocatalytic reactions with much higher efficiencies, and thus will make the sensor platform more sensitive. Since it is hard to encapsulate water-soluble molecules in polymeric micelles without leakage, we decided to synthesize new block co-polymers that can form polymeric vesicles so that water-soluble organic acids can be encapsulated. Two types of block-co-polymer were synthesized in our lab (Figure 5).

a) **Synthesis of COOH-PEG-PCL.** COOH-PEG-OH (0.22 g) and ϵ -caprolactone (1.14 g) were mixed in 80 mL toluene and stirred at room temperature. After adding $\text{Sn}(\text{Oct})_2$ (32 μg), the reaction mixture was stirred for 72 h at 130°C . The product was purified by repeated precipitation from dichloromethane into n-hexane.

The polymer was characterized by ^1H NMR (Figure 5) and the molecular weight of the PCL part was calculated to be 11800. Polymers with different molecular weight ratios were produced by varying the weight ratio between COOH-PEG-OH and ϵ -caprolactone while the molar ratio between ϵ -caprolactone and $\text{Sn}(\text{Oct})_2$ was maintained at 100000:1.

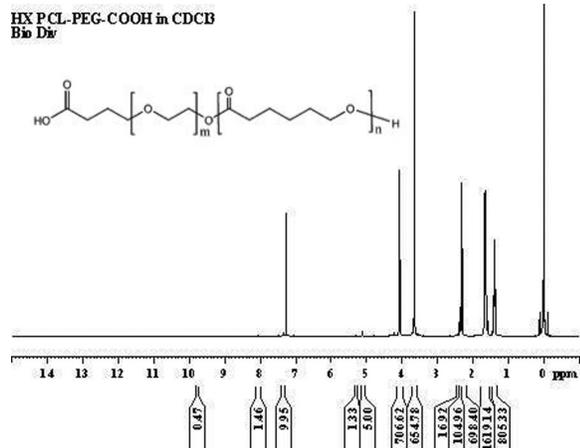


Figure 5. Chemical structures of newly synthesized polymers; ^1H NMR spectrum of COOH-PEG-PCL polymer.

b) **Synthesis of (PCL-PEG-S) $_2$.** (PEG-S) $_2$ (0.4 g) and ϵ -caprolactone (0.91 g) were mixed in 10 mL toluene, then the solvent was removed and the mixture was dried at 50°C for 3 h. After drying, 1 wt % $\text{Sn}(\text{Oct})_2$ in toluene was added. The reaction mixture was then refluxed under N_2 for 24 h. (PCL-PEG-S) $_2$ was precipitated in cold diethyl ether and purified by repeated precipitation from dichloromethane/ether.

The polymer was characterized by ^1H NMR (Figure 6) and the molecular weight of the PCL part was calculated to be 1000.

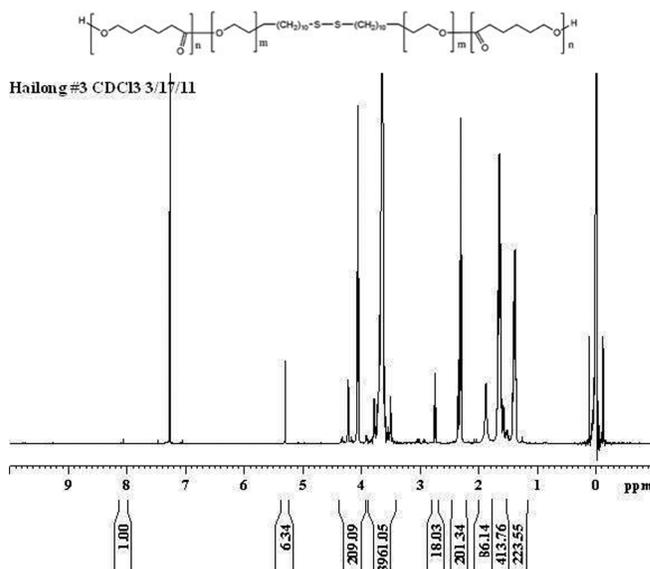


Figure 6. ^1H NMR spectrum of PCL-PEG-S-S-PEG-PCL polymer.

Polymers with different molecular weights were produced by varying the weight ratio between (PEG-S) $_2$ and ϵ -caprolactone while maintaining the molar ratio between ϵ -caprolactone and $\text{Sn}(\text{Oct})_2$.

Data Encryption and Compression for Cybersecurity Applications

2011-027-N0

Alexander Heifetz and Paul Raptis

Project Description

The objective of this research is to develop computationally efficient algorithms for data encryption and compression with a compressive sensing (CS) paradigm. In this project, we are examining the feasibility of CS-based encryption for cybersecurity applications. Using the CS approach, we are analyzing the encryption dependability of noisy measurements and of compressible signals that are not K -sparse. Data are sparse if they can be compressed or represented by very few non-

zero coefficients in some domain. For example, most signals are sparse in the wavelet domain, which is the principle of data compression. We are also investigating CS encryption reliability through simulation and will generate data through which cyber attack detection and mitigation strategies may be demonstrated. One application area of particular interest is the cybersecurity of control systems at a nuclear facility. We are investigating strategies for the detection and mitigation of cyber attacks on state estimators of the nuclear facility’s SCADA (supervisory control and data acquisition) system.

Technical approaches include the development of intelligent cybersecurity simulation algorithms offering the following options to the user: concealing a signal of interest into a form of untraceable noise or encrypting a signal of interest inside background noise. Concealment involves (1) seamlessly removing the signal from the data, (2) converting the signal into a form of background noise, and (3) seamlessly inserting the “converted noise” back into the data. On the other hand, encrypting the signal of interest by using background noise involves (1) seamlessly removing the signal from the data, (2) converting the signal into a form of “encrypted noise,” and (3) seamlessly inserting the “encrypted noise” back into the data. Modules for decryption and encryption algorithms using fractal analysis and wavelets are being developed. The learning part of the system is achieved by using a combination of artificial neural networks (ANNs), neural networks, and fuzzy if/then rules. ANNs offer a powerful means of learning hidden patterns from examples such that the patterns can be recognized immediately once they reappear. Moreover, they are capable of generalization, which is critically important because it is impossible to pre-postulate all scenarios in advance. Neural network architectures and suitable learning paradigms will be identified.

Mission Relevance

This project addresses the DOE mission in national security and nuclear nonproliferation. Users of the technology developed as an outcome of this project will be programs within the National Nuclear Security Administration’s Office of Nuclear Nonproliferation Research and Development (NA-22), such as the Simulations and Modeling (SAM) and Nuclear Safeguards programs. Other customers may include user agencies in the U.S. Department of Defense, the U.S. Department of Homeland Security, and the various government intelligence agencies. Secure networks for data gathering and management developed as an outcome of this project will benefit mission areas of programs mentioned above.

FY 2011 Results and Accomplishments

According to Shannon’s principle, a good cipher (encryption scheme) should provide data confusion and diffusion. In conventional encryption approaches, both requirements can be addressed by developing appropriate permutation and ran-

domization matrices. These matrices serve as encryption/decryption keys that have to be shared by the sender and the receiver prior to any information exchange. This imposes the requirement to develop secure key distribution protocols. In compressive sensing (CS), data is randomly sampled (which is data confusion) using a specially designed measurement matrix (which is data diffusion). Thus, the CS protocol satisfies good cipher requirements. Decryption of the received message is performed using CS methods of data recovery from incomplete information, which consists of a numerical solution of the optimization problem.

We have developed a CS-based data encryption which we describe below. The coding/decoding scheme for the transmission of information over unprotected channels is summarized in Figure 1. We chose to implement compressive sensing coding using a Hadamard Transform (HT). The sender and the receiver know ahead of time that HT will be used for data encryption. One of the advantages of using HT is that data encryption and decryption can be accomplished in a robust manner using simple matrix multiplication. Data encryption via multiplication by the *H* matrix (matrix implementation of HT) results in diffusion-type encryption of the original data. An *H* matrix can be generated in several ways. The method we selected consists of using a cyclic matrix *S*. In a cyclic matrix *S*, every row has the same elements as the row above it but the elements are circularly shifted by one position.

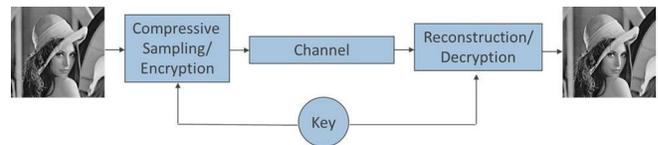


Figure 1. Coding/decoding scheme for information transmission.

The first row of *S* is 1110010 (see Figure 2). Successive rows of *S* are found by circularly shifting the elements in the above row by one position to the right. We have written MATLAB scripts to implement *S* matrix generation on a digital computer.

$$S = \begin{bmatrix} 1 & 1 & 1 & 0 & 0 & 1 & 0 \\ 0 & 1 & 1 & 1 & 0 & 0 & 1 \\ 1 & 0 & 1 & 1 & 1 & 0 & 0 \\ 0 & 1 & 0 & 1 & 1 & 1 & 0 \\ 0 & 0 & 1 & 0 & 1 & 1 & 1 \\ 1 & 0 & 0 & 1 & 0 & 1 & 1 \\ 1 & 1 & 0 & 0 & 1 & 0 & 1 \end{bmatrix} \begin{matrix} S_1 \\ S_2 \\ S_3 \\ S_4 \\ S_5 \\ S_6 \\ S_7 \end{matrix}$$

Figure 2. Example of cyclic matrix *S* for *n* = 3.

In a hypothetical data communication protocol, the matrix which contains coded information about the scene (known as cipher text), is transmitted over an unprotected channel. The reconstructed image Y is obtained by the receiver using the Inverse Hadamard Transform (IHT), which has a closed form analytic expression. Implementation of the IHT consists of trivial matrix multiplications. Therefore, performing encryption/decryption on a continuous stream of data using this scheme can be accomplished rapidly on a digital computer. An example of coding and decoding a 511×511 pixel image using a full set of Hadamard masks is shown in Figure 3. This numerical example was performed using scripts written in MATLAB environment. In the example shown, a full set of Hadamard masks is used for image coding, which represents a diffusion-only data encryption approach.

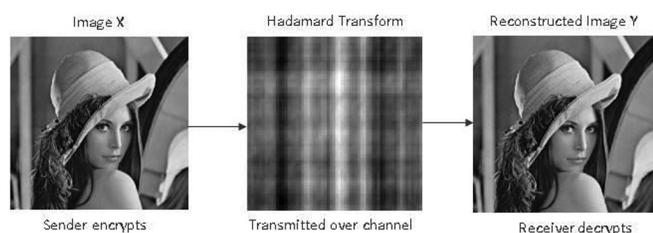


Figure 3. Example of coding->transmission->decoding scheme for 511×511 test image.

In compressive sensing, a subset of measurement vectors is used to code an image. Hence, the size of the matrix, which is transmitted over a narrowband channel, is smaller. At the same time, the reconstructed image size is the same as that of the original. This treatment is advantageous when one has to encrypt large geospatial images, such as the image shown in Figure 4. This image, taken by a satellite camera, has 11501×10807 pixels and occupies 355 MB of memory on a hard drive. (We have compiled a database of large geospatial images for this project to be used in CS-based encryption and compression research in FY 2012.) The reconstruction of a sub-sampled encoded image can be achieved by using CS iterative optimization algorithms. We downloaded and installed a shareware software package “L1magic” that implements one version of the CS reconstruction algorithm. We will use this package in FY 2012 work on this project

Proposed Work for FY 2012

Work and Expected Results. We will investigate CS encryption reliability by simulating a number of scenarios for large-scale cyber attacks including, but not limited to, situations where:

- a. Eavesdroppers intercept and decipher transmitted signals. By using learning algorithms developed in connection with the intelligent monitoring of deviations from equilibrium processes, we will monitor the transmission process and detect the presence of eavesdroppers with quantifiable uncertainty.

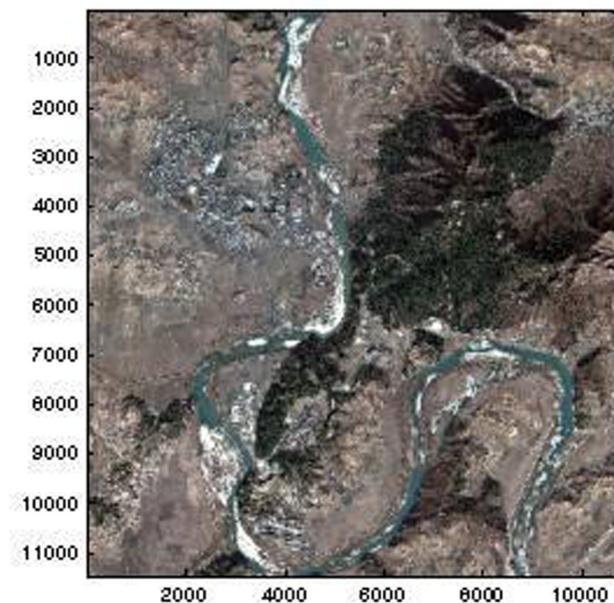


Figure 4. Example of a large (355-MB) geospatial image.

- b. Eavesdroppers actively corrupt the fidelity of the transmission process. Damage to the validity of the process will be detected and reported with quantifiable uncertainty.
- c. There are early signs of activities that may result in paralyzing the capacity of the network. This tool will detect incipient features of sabotage through analysis of the fractal structure of process noise.

Algorithm development, scenario identification, and quantifiable results from the above scenarios will be the main outcomes of our work in FY 2012.

Deliverables. Project deliverables will consist of CS-based encryption and compression algorithms. Intermediate technical milestones will consist of (1) benchmarks of CS encryption algorithm performance for various signals and (2) testing for robustness against various types of simulated cyber attacks in a number of scenarios with quantifiable uncertainties. Simulation results will be compiled by using the Receiver Operating Characteristics (ROC) curves: false positive, false negative, true positive, and true negative. Each of the four categories will be further subdivided into categories according to the number and type of intrusions present.

Milestones. Technical milestones are to include software development within six months, illustrative scenario development in nine months, and a technical report in 12 months.

Architectures and Algorithms for Protecting Sensitive Information in Mobile Wireless and Sensing Environments

2011-109-NO

Charles Catlett and Dane Skow

Project Description

An increasing amount of private information is being shared in social networks, particularly through mobile smartphones, yet social network privacy settings are typically complex, with defaults tending toward open disclosure rather than privacy. In this project, we are exploring information disclosure mechanisms that allow individuals to describe the conditions under which their private information can be disclosed. For example, an emergency capability could be developed that would give access to information about the location of individuals within a building, allowing emergency personnel to query the information to determine whether all employees and visitors have evacuated. Such a database would open the possibility for tracking the comings and goings of employees, raising serious privacy concerns. However, privacy could be preserved with appropriate and enforceable restrictions — such as regulating the frequency with which queries can be made (e.g., once per quarter, reset upon verification of emergency use). Similarly, protocols that enable individuals to tailor circles of trust would allow for collaborative applications that disclose different levels of detail based on trust settings. A user’s “inner circle” might have access to that user’s location information within a building, with a wider circle of collaborators seeing only that the user is “at the Laboratory,” with no location data provided to other users. Our focus will be specific to location information sharing.

Mission Relevance

This project is relevant to DOE’s national security mission. The line between personal and professional information sharing has been blurred with social networking tools. This situation has triggered agencies, research laboratories, companies, and other organizations to educate employees and develop usage guidelines. Location sharing, in particular, has implications to the physical security of individuals because, given the accumulation of data over time, it reveals patterns, habits, schedules, and acquaintances. Given that social engineering is one of the most powerful cyber attack methods, information of this type is extremely valuable to an attacker. Development of privacy-preserving location sharing mechanisms is, thus, of critical importance from a cyber security standpoint to DOE, other federal agencies, national laboratories, and other large organizations.

FY 2011 Results and Accomplishments

The work in 2011 involved two related tasks: (1) testing a simple location-sharing system using wearable sensors and wireless networks and (2) evaluating indoor location systems for use with smartphones. The first task involved exploring various methods for sensing location and proximity. The second task was aimed at deploying a test bed within which we could experiment with location-sharing methods and associated privacy mechanisms.

The first task explored the feasibility of using various wireless networking technologies (Bluetooth, 802.11 Wi-Fi, and 802.15 Zigbee) to sense proximity with other devices (e.g., via the Bluetooth discovery mechanisms). Given unique identifiers for each device, both worn and fixed, this information would indicate both proximity of people and physical location (sensor IDs were associated with either people or locations via a simple lookup table). Using a single design for both wearable and fixed-location units, we deployed fixed sensors in multiple rooms of a workshop venue (Pervasive Computing, July 2011) while workshop participants wore the mobile units. The sensor units transmitted location and other sensor data (e.g., sound levels, accelerometer readings) to an Internet server for graphing and analysis.

For the indoor location-sharing service project, we initiated collaborations with the UCLA Center for Embedded Networked Sensing and ETH-Zurich, both of whom had developed open source software for location sharing. We deployed the ETH-Zurich indoor location server, Redpin, and did extensive testing and evaluation with Android smartphones. Redpin exploits the fact that for each room in a building the signal strength readings from multiple Wi-Fi access points in the building provide a unique “signature.” Over time and with participant cooperation, the system can “learn” the signals for rooms in a building, providing an indoor location service. We found, however, that the variability in signal strength from Wi-Fi access points is high enough that over time the server develops many false positives. Consequently, we intend to explore alternatives in 2012.

Proposed Work for FY 2012

For FY 2012, we will be evaluating algorithms for location services with minimal information sharing while exploring various indoor location systems, including those developed at the University of Washington Ubicomp Laboratory and at Microsoft Research.

Seminar

Catlett, C. (2011). “Pervasive Computing and Privacy Research at Argonne National Laboratory.” ECE Weekly Colloquium, IIT, Chicago, IL, Sep. 30, 2011.

Multilevel Optimization Tools for the Simulation, Detection, and Mitigation of Cyber Attacks

2011-121-NO

Sven Leyffer, Ilya Safro, and Michael Skwarek

Project Description

We are developing a set of next-generation mathematical models and computational techniques to simulate, detect, and mitigate attacks on networks of computers. The main objectives are to enable network operators to better detect attacks, quantify the attack spread, and explore the trade-offs between threat levels and operability of the system. The detection of attacks includes the enhancement and extension of existing machine learning tools in order to detect cyber threats. We are developing computationally fast intrusion detection techniques that are robust to outliers and/or manipulation by an adversary.

In addition, we are developing techniques that allow network operators to choose a minimal set of computing resources that must be shut down to mitigate the effect of a cyber attack. Our tools allow operators to keep the operability of the network at a maximum, while reasonably containing the threat.

Mission Relevance

This project is relevant to DOE's national security mission. Attacks on the nation's cyber infrastructure impose an increasing cost on DOE and the nation. In the first half of 2009, for example, the Department of Defense spent more than \$100 million dollars repairing damage caused by cyber attacks. The results of our research will enable network operators to better detect attacks, quantify the attack spread, and explore the trade-offs between threat levels and operability of the system.

FY 2011 Results and Accomplishments

We formulated several network optimization problems that are based on mathematical models of the spread of epidemics in biological networks.

We developed the first version of a solver for optimal response to cyber attacks and epidemics. The solver was designed to handle large-scale networks and was tested on networks of up to 10 million nodes. In this version, we solve a model that is based on independent probabilities of the attack (infection) spread over the network links. In the heart of the solver is a multiscale framework that is based on an algebraic multigrid aggregation. The main objective of the multiscale framework is to construct a hierarchy of coarser problems, each approximating the original problem, but with fewer degrees of free-

dom. In our solver this is achieved by introducing a chain of successive Galerkin operators for projections of the network Laplacian matrix onto lower-dimensional spaces where the problem becomes more tractable. The multiscale framework has three key advantages that make it attractive for applying on modern large-scale instances: (1) it exhibits linear complexity (in the number of links and refinement stage complexity); (2) it is relatively easy to parallelize and implement, using standard matrix-vector operations; and (3) it is able to incorporate a variety of external optimization algorithms (at the refinement stage) at different scales. The multiscale framework is combined with MINOTAUR, a mixed integer nonlinear programming (MINLP) solver, to solve nonlinear integer problems at the coarse level and at each refinement stage.

We also developed an exact solver for another related formulation of the network response problem. The solver is based on the computational infrastructure for operations research (COIN-OR) open-source CBC solver for general mixed-integer optimization problems. Our solver for network response improves on the standard branch-and-cut algorithm for our particular problem; the improvement is due to two algorithmic novelties. The first involves the application of specialized cutting planes that tighten the upper bound on the optimal solution. The second is a specialized heuristic algorithm for quickly finding feasible solutions in the course of the branch-and-bound search. An exact optimal solution can be found for relatively dense networks with up to a hundred nodes, or for larger sparse networks.

A vast array of modeling and optimization problems in cyber security is formulated on networks that show the relationships between entities such as computers, routers, users and events. Developing a novel cyber security system that addresses such problems requires very intensive testing and simulation of adversary behavior. Such a procedure must validate the novel cyber security system on many networks, but this is often difficult because, usually, in any cyber system (of some organization) there is only one cyber network. In general, obtaining the required scientific data about the networks is often expensive or infeasible. Thus, the amount of available data may be insufficient for testing, verification, and validation of a multi-purpose cyber security system. In this situation, data should be inferred from a high-validity model, i.e., artificial networks, in order to anticipate the possible topology and behavior of the computer system in the future and under different circumstances. Generation of artificial networks with realistic properties is one of the central areas of modern network science. We introduced a novel strategy for generating artificial networks that captures unknown structural properties in the network generation process as well as takes into account self-dissimilarities across scales of the network. At the core of the strategy are methods adapted from the theory

of multigrid aggregation and its applications to combinatorial optimization.

Proposed Work for FY 2012

We are continuing to work on both exact and multilevel methods for several probabilistic variants of the network response problem to solve large-scale instances by further development and experiments with parallel computation. In the case of the exact method we will also investigate tighter continuous relaxations of the network-response MINLP formulation to further speed the computation. We will verify and validate the proposed response methods by using the attack-defense simulations on different types of real and artificial networks. Artificial networks will be generated by using our multiscale network generator, which we also plan to adapt for more specific cyber security needs.

We also plan to continue work on sparse classification and support vector machines (SVMs) for determining rules for detecting cyber threats. In particular, we are investigating novel convex relaxations of a sparse SVM MINLP formulation. In preliminary experiments this approach is demonstrating improved classification performance with benchmark datasets. We will compare the novel sparse SVM relaxation with state-of-the-art SVM methods, as well as methods that have been recently proposed in the literature for adversarial classification.

Enhancing Smart-Grid Cyber Security with Near-Real-Time Message-Passing Techniques

2011-169-NO

Jianhui Wang, Jiaxin Ning, Scott Pinkerton, and Zhi Zhou

Project Description

The objective of this project is to address cyber security issues in the smart grid by using statistical tools to validate the data passed between software modules. Principal Component Analysis (PCA), cross-correlations, profile analysis, and pattern recognition will be used to determine how much the data passed to a module deviates from its expected value. An agent-based power-system simulation platform will be developed to study the performance of the detection algorithms.

Mission Relevance

The project supports DOE's strategic goal of enhancing transmission reliability through enhanced smart-grid cyber security. The project 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. In sum, the proposed approach may significantly improve bulk power-system operation and planning by lowering system cost, reducing blackouts, increasing social welfare, and advancing research on power systems. The proposed method can realize the benefits of new energy sources and applications without compromising the reliability and security of power-system operations.

FY 2011 Results and Accomplishments

A detection algorithm was developed to determine whether data passed to the Optimal Power Flow (OPF) software module had been compromised. The OPF module was chosen because its output is used by power control centers to ensure that electrical flows and bus voltage magnitudes and angles are within acceptable limits while operating the power system as economically as possible. The standard OPF module (called AC-OPF) is a computer program that solves an optimization problem with nonlinear constraints for real and reactive power. Results from the AC-OPF model are often approximated through use of a simpler model called DC-OPF, which relies solely on real power constraints in a linear form. In our research, the PCA technique was used to monitor the data passing to the DC-OPF module. PCA is a powerful statistical technique used extensively in the social sciences to reduce the dimensionality of data and, more recently, in complicated multivariate analysis in fields such as face recognition and image compression. The technique transforms a typically large set of correlated variables into a smaller set of uncorrelated variables, called principal components. These variables are then ordered so that the first few principal components contain most of the variability contained in all of the original set of variables, while maintaining as much information as possible from the original data.

The algorithm we developed determines if the input data has been compromised by monitoring the output of the DC-OPF module. It separates the time-series variability into common-cause and assignable-cause variability. Common-cause variability is naturally occurring and inherent to the process, while assignable-cause variability is unnatural and due to a shock or disruption to the process. In a power system, common-cause variability might include the time of day or ambient temperature. On the other hand, assignable-cause variability might include equipment failure, operator error or introduced data-integrity issues. This type of variability cannot be accounted for by naturally occurring events and needs to be identified and corrected. The PCA technique provides a way to separate these two sources of variability by computing an orthogonal linear projection of the multivariate data. The orthogonal-linear-projection model is obtained from historical DC-OPF outputs (power flows), which are computed under common-cause system variability.

The PCA-based detection algorithm that we developed was tested by using a simple agent-based modeling and simulation (ABMS) platform coded in MatLab. The IEEE-24 Reliability Power System data, which consist of 38 transmission lines, 24 buses (of which 17 have load), and 33 generators, were used to study the performance of the algorithm. The ABMS was simulated for 168 hours under common-cause system variability to generate historical power-flow outputs. Generator failures were sampled according to a continuous-time two-state Markov chain. Next, the projection model was computed by using the PCA technique. In a second simulation, the detection algorithm monitored the output of the DCOPF module, checking for the occurrence of assignable-cause variability. Several types of tampered data passed to the DC-OPF were simulated. Each case was simulated for 575 hours under regular operation conditions that included load variability and generator outages. At hour 576, one of the following three cases was assumed to occur: (1) a line broke down, (2) the reactance of a line was maliciously reduced to 80% of its original value, or (3) the reactance of a line was maliciously increased to 120% of its original value. The detection algorithm correctly detected that there was no assignable-cause variability at hours 1 to 575 and correctly detected at hour 576 that there was indeed assignable-cause variability in the three assumed cases. These results show the potential of statistical methods, PCA in particular, for enhancing smart-grid cyber security.

Although the newly developed algorithm performed successfully, there are still many challenges to overcome. The computation of the orthogonal projection model presents the “curse of dimensionality,” since it requires the calculation of the eigenvectors of a data matrix with dimension dependent on the number of transmission lines. A more efficient way of calculating the eigenvectors will be needed for large power systems. In addition, the nonlinearity in the objective function and constraints of the AC-OPF will present challenges. Furthermore, an algorithm that can help with identifying the source of the anomaly is needed.

Mobile Device Vulnerability Research

2011-214-N0

Charles Catlett

Project Description

Our hypothesis is that the security of the individuals carrying mobile electronic communication devices, and by extension the security of their employers, can be significantly improved through (1) exposure and understanding of vulnerabilities and (2) human-computer interface techniques that are directly tied to device security settings and that provide feedback regarding the vulnerabilities of the device at any given time. Our objec-

tive is to develop a comprehensive vulnerability assessment capability for mobile devices as a guide to research aimed at (1) making the security of the device more apparent to the owner and (2) giving the owner intuitive methods for securing the device.

Mission Relevance

This project supports DOE’s national security mission. The cyber security vulnerabilities associated with rapidly proliferating mobile phones, tablets, and other devices — those associated with interactions among multiple mobile devices and/or between mobile devices and fixed sensor networks — are rapidly evolving. The consequences range from cyber security breaches at national laboratories and other facilities to loss of intellectual property through cyber espionage. Despite this evolving and increasing threat, there is very little research at DOE laboratories focused on understanding, characterizing, and ultimately countering these threats. This project seeks to support DOE missions by providing insight and strategies to address the security of mobile devices themselves and of facilities within which mobile devices are used.

FY 2011 Results and Accomplishments

To initiate the project, we first examined the mobile phone marketplace and surveyed the literature and the press regarding smartphone security circa early 2011. This study led us to the conclusion that a focus on Android rather than Apple iOS would be more fruitful and relevant for three reasons. First, the growth of Android in market penetration appears to be trending toward a market share greater than that of Apple iOS. Second, Apple retains tight control over applications permitted for iOS devices, in contrast to the open Android approach. By mid-2011, it became clear that the Android became a prime target for malware, given reports from security companies such as McAfee, Trustwave, and Whisper Systems, as well as papers and presentations at security conferences, such as BlackHat/DEFCON. Third, multiple decisions by the Department of Defense suggest that their platform of choice will be Android for both business systems and mobile warrior programs. Consequently, a focus on Android will have higher relevance to national security.

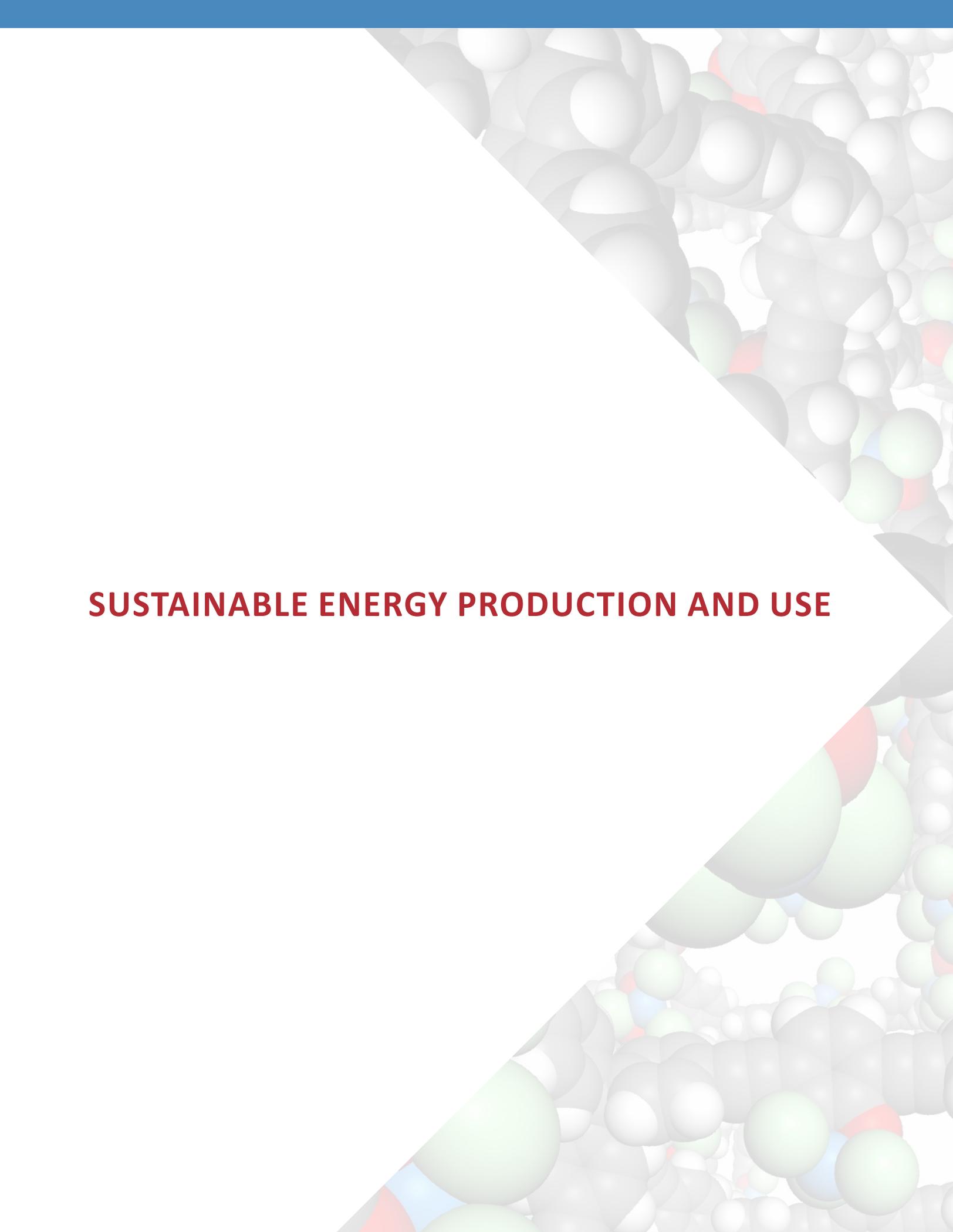
As part of this work, we consulted research teams and application developers in various industries to understand trends in the use of Android devices, yielding insight into attack modes in the field. To this end, as part of a workshop on mobile and pervasive computing that we organized in July 2011 (<http://icis.anl.gov/programs/summer2011-1b>), we engaged groups developing applications for medical use, navigation, and social networks to discuss trends in mobile applications and potential vulnerabilities affecting individual privacy and security. A report from this workshop is available from the principal investigator.

Of particular note, we found that one approach to malware development is to presuppose access to the device kernel, thus developing malware that will become effective in a manner that is dependent upon future vulnerabilities. Simply put, the malware community is not only targeting current/known vulnerabilities but also developing more powerful attacks that will be ready to use on the basis of future vulnerabilities.

Finally, we identified and are examining several Android software systems to understand the nature of vulnerabilities and of software intended to either address or exploit those vulnerabilities. These include software from Good Technologies, CarrierIQ, and Trustwave.

Proposed Work for FY 2012

Building on initial work to identify vulnerabilities and exploitation methods and tools, we plan to analyze exploitation tools and protective applications available from open and commercial sources in FY 2012. This analysis will establish the groundwork from which to develop a set of principles, methods, and approaches to provide information to device owners about the security status of their mobile devices and guidance to improve the security status of their devices.



SUSTAINABLE ENERGY PRODUCTION AND USE

Integrated Biofuel/Engine Design

2009-097-R2

Douglas E. Longman, Philip D. Laible, YuPo Lin,
Stephen T. Pratt, Seth W. Snyder, and Michael Q. Wang

Project Description

The efficient production of biofuels needs to be integrated 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. In this project, we are seeking to realize the full potential of the energy source (fuel) and conversion device (engine) by designing the fuel properties in coordination with engine research following a multi-disciplinary team approach. 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 reduction in emissions would have a global impact by providing sustainable energy. Success in this project will lay the groundwork for integrated pathways to design fuels and engines that reach their maximum potential. Beneficiaries include fuel manufacturers and other renewable energy companies.

FY 2011 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. Samples of the target fuel molecules being considered (and blends of the same) were then analyzed, modeled, and tested for physical and combustion properties in preparation for the final year of research reported here.

Substantial progress was made in the design, fabrication, and evaluation of new strains of photosynthetic bacteria employed in strategies to produce biodiesel surrogate molecules. Metabolic engineering efforts initially focused on the design of strains that produce phytol. However, efforts toward the pro-

duction of reduced forms of farnesol, geraniol, and isoprenol (branched C15, C10, and C5 alcohols, respectively) were also initiated. These related approaches will enable engine tests on a suite of related molecules that appear practical for spark-ignited or low-temperature combustion strategies.

Bioengineering efforts combined primary knock-out mutations (deleting genes *crtB*, *ispA*, and *bchG*) in photosynthetic bacteria, resulting in more than 10 multiply mutated strains that have two or more genes deleted. Data show that deletion of *crtB* is minimally requisite to our strategies and a valuable means for increasing phytol production.

Reduced hydrocarbons are the most valuable fuel targets, and expression vectors were constructed to augment the availability of an enzyme involved in maximally reducing branched hydrocarbons inside *Rhodobacter* cells. Here, when this gene, *bchP*, was produced at levels higher than standard, phytol levels were observed to increase. This strategy will be valuable in the future when comparing our approach with those of others where reduced fuels cannot be generated biologically.

Theoretical calculations were performed on the thermal decomposition of the C5 building block for phytol shown in Figure 1. The dominant decomposition pathway for this species is dehydration to produce the diene displayed in the figure. This pathway is disadvantageous in combustion systems, since diene production is generally associated with a significant increase in the production of soot. This observation suggests that modification of the C5 alcohol to produce the saturated alcohol, isopentanol, would be most advantageous. This transformation could in principle be achieved either in the feedstock generation by modification of the organism or in the separations process. Increasing the length of the hydrocarbon chain to the C10, C15, and C20 alcohols will progressively minimize the negative effects of the double bond, as thermal decomposition will produce increasingly larger amounts of alkanes, which have much better characteristics with respect to soot formation.

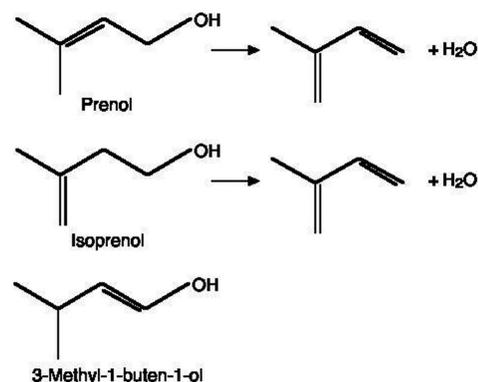


Figure 1. A primary decomposition pathway for prenil and isoprenol leads to the formation of a diene and water. This channel does not occur for the 3-Methyl-1-buten-1-ol isomer.

The density, viscosity, surface tension, vapor pressure, heat of combustion, heat of vaporization, and chemical composition of pure phytol and 5%, 10%, and 20% blends (by volume) with diesel fuel were measured. Overall, the properties of the phytol blends were in the vicinity with diesel fuel except for the viscosity and vapor pressure of pure phytol, which were significantly different from diesel. These differences in properties influence the flow development inside the injection system and thus affect the spray, combustion, performance, and emission behavior. Extensive inner nozzle flow modeling was performed to assess the potential of using phytol as a blending agent with diesel fuel. The cavitation, turbulence, and flow properties of phytol and the 5%, 10%, and 20% blends were modeled and compared in a production injection system provided by Caterpillar, Inc. No discernible difference was detected in the nozzle flow characteristics of the diesel and P5 blend. The P10 and P20 blend characteristics were similar to each other, but noticeably different from diesel. The nozzle flow characteristics of pure phytol were so significantly different from diesel fuel that it was decided to only engine test the blends.

Engine verification tests were conducted on a Caterpillar single-cylinder diesel truck engine. The engine testing focused on the C20 molecule, phytol. Blends of phytol by volume of 5%, 10%, and 20% were made (P5, P10, and P20, respectively) with standard, certification No. 2 diesel fuel. Each blend was evaluated for engine performance, exhaust emissions (regulated and unregulated), and combustion characteristics by using *in situ* imaging. The P5 and P10 showed no measurable effect on the engine performance. However, P20 began to exhibit degradation in the engine performance and exhaust emissions. This result confirmed the computational fluid dynamics (CFD) simulation results, where the higher viscosity of the P20 blend affected the fuel spray characteristics.

A preliminary well-to-wheels lifecycle analysis was performed by using the latest version of the Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation (GREET) model (GREET 1 2011). As a basis, the baseline algae fuels pathway recently added to GREET1 was used with the companion Algae Process Description tool. We then compared the developed phytol + lipid pathways with the algae lipid pathways. The main parameters that varied were the lipid fraction in the harvested organism (25% weight lipids is our baseline), the phytol fraction (10% weight), and the mass and energy

1 See Frank, E.D., J. Han, I. Palou-Rivera, A. Elgowainy, and M.Q. Wang, 2011. User Manual for Algae Life-Cycle Analysis with GREET (Report No. ANL/ESD/11-7 ANLESD), http://greet.es.anl.gov/publication-algae_life_cycle_manual; Frank, E.D., J. Han, I. Palou-Rivera, A. Elgowainy, and M.Q. Wang, 2011. Life-Cycle Analysis of Algal Lipid Fuels with the GREET Model (Report No. ANL/ESD/11-5 ANLESD115), http://greet.es.anl.gov/publication-algal_lipid_fuels.

balance to convert the extracted (lipid and phytol) fraction into diesel fuels via a transesterification to biodiesel or a hydroprocessing-based upgrade to renewable diesel. Greenhouse gas (GHG) emissions results showed some interesting improvements over the baseline algae fuel scenario. The key findings include the following:

- ▶ Our baseline process shows a reduction of GHG emissions over the algae baseline process of between 18% (biodiesel) and 30% (renewable diesel). Our new process has the potential to increase the fuel yield over the algae baseline because of the higher fraction of extractables (lipid plus phytol) at harvest time.
- ▶ Even if the effects of a potential higher extractables yield are neglected, obtaining a fuel molecule directly from the organism instead of from bio-oil in need of upgrading has significant benefits. A comparison of a more conservative version of our process with the baseline algae process shows GHG reductions of between 5% (biodiesel) and 20% (renewable diesel).
- ▶ Our biological baseline process improves GHG emissions from low-sulfur diesel fuel by 53% to 63%.

This work resulted in the following patent:

Laible, P., and S. Snyder, "Engineered Photosynthetic Bacteria, Methods of Manufacture of Biofuels," patent application filed June 2011. (Application # 13159340)

Seminars

Snyder, S.W. (2011). "Near Term Opportunities for Biorefineries: Critical Barriers to Bioenergy." Near-term Opportunities for Biorefineries, Champaign, IL, Oct. 11–12, 2010.

Advanced Cathode Materials for High-Performance Lithium-Ion Batteries

2009-115-R2

Jie Li, Khalil Amine, Zhijun Chen, Jeffrey W. Elam, Rachel Koritala, Yung Liu, Dean Miller, and Michael J. Pellin

Project Description

A lithium, manganese, and oxygen (Li-Mn-O) composite is potentially the best cathode material for batteries in future plug-in hybrid electric vehicles because of its higher working voltages and lower cost compared with other materials. However, the composite suffers from electrochemical instability: the Mn³⁺ ions dissolve into the electrolyte, and the reduced metallic Mn blocks the channels of the graphite anode, thereby leading to rapid battery degradation. Exploiting a film

coating to increase the electrical stability of cathode particles may enable industry-related applications of the Li-Mn-O composite. Until recently, the trade-off between the surface protection and the increased electrical impedance for the coated layers grown by using current technologies has prevented technological progress.

With its unique feature of self-terminated reactions, the atomic layer deposition (ALD) method is particularly well suited to synthesizing ultrathin, 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 (1) to demonstrate that significant improvements in battery performance can be achieved by applying ultrathin ALD nano-films to the granular cathode materials and (2) to develop an advanced material processing technology on a large scale.

Mission Relevance

This project supports DOE's mission in energy security. Because our research will result in the development of advanced ALD-coating technology in a fluidized bed reactor (ALD is one of five key areas identified), we expect this project to contribute to the DOE Industrial Technology Program in the area of nano-manufacturing. In addition, since this project involves the large-scale manufacture of advanced nano-structured cathode materials, it also will contribute to the DOE Material Discovery, Design, and Synthesis Program (Basic Energy Sciences) and the Battery R&D Program (under Vehicle Technology).

FY 2011 Results and Accomplishments

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 deposited by using ALD on either $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ -constructed cathodes or granular materials. Battery performance tests that used 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 was 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. Moreover, we demonstrated that the ALD Al_2O_3 and ZrO_2 coatings have positive impacts on cycling performance for the most promising Li-ion battery made of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) cathode material with the highest voltage (5 V vs. 3.7 V for the current Li-Co-O battery). Interestingly, we observed that with an increase in film thickness, the cycling curve is flat out (i.e., long lifetime). However, the initial battery capacitance is meanwhile reduced. The Al_2O_3 -coated cell battery is much more sensitive to the coated film thickness than the ZrO_2 -coated battery, especially

when the film is thicker than 5 nm. Because Al_2O_3 is an insulating material, while 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.

In addition, a coherently controlled gas-fluidized bed (CCGFB) reactor was fabricated, which can be operated under vacuum. In contrast to a conventional fluidized-bed reactor, the new reactor incorporates a nonlinear controlling technology. The technology was implemented by creating a standing fluid wave in the gas-fluidized bed to suppress flow instabilities, such as plug, clustering, and channeling fluidizations. We successfully demonstrated, for the first time, that 5–10- μm cathode powders, $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ and LNMO, can be uniformly fluidized in our CCGFB without using energy-intensive mechanical vibration/rotary approaches, thereby creating the condition necessary to enable a conformal ALD coating on each of the primary cathode particles at a large scale.

In FY 2011, various hydrodynamics and ALD powder-coating experiments for the ultrafine cathode materials were conducted in our newly fabricated gas-fluidized bed under the vacuum condition of about 1 torr (at the top bed). The reactor was constructed by using a stainless-steel column, the outer diameter of which measured 4 cm. Water and $\text{Zr}(\text{EtMeN})_4$ were used as the chemical precursors in the coating experiments. The mean particle size was 5–10 μm in diameter, and the typical particle loading for each coating experiment was 150 g. Pressures, concentrations of various gaseous species, and temperatures of the entire system were monitored by using pressure transducers, an on-line mass spectrometer, and thermal probes, respectively. The bed pressure-drop was used to monitor fluidization quality throughout the experiments.

The ALD-coated powders were characterized by using both the inductively coupled plasma/mass spectrometry analytic technique (for quantifying coated Zr) and the scanning electron microscopy/transmission electron microscopy (SEM/TEM) imaging technique (for visualizing the film morphology and measuring the thickness of the ALD-coated ultrathin film). Figure 1 depicts the SEM/TEM images of the ALD-coated cathode particles. The result indicates that the conformal and highly uniform ultrathin coating film on the cathode particle surface can be obtained. The energy-dispersive spectroscopy (EDS) (TEM) analysis of the particle surface, as shown in Figure 2, further confirms the existence of Zr besides the elements of Ni, Co, and Mn, which are attributed to the original $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode material. The preliminary test of the cycling performance of the battery made of such coated cathode material indicates an approximate 10% increase in its capacity retention compared with that for the cell made of the uncoated cathode material, as shown in Figure 3.

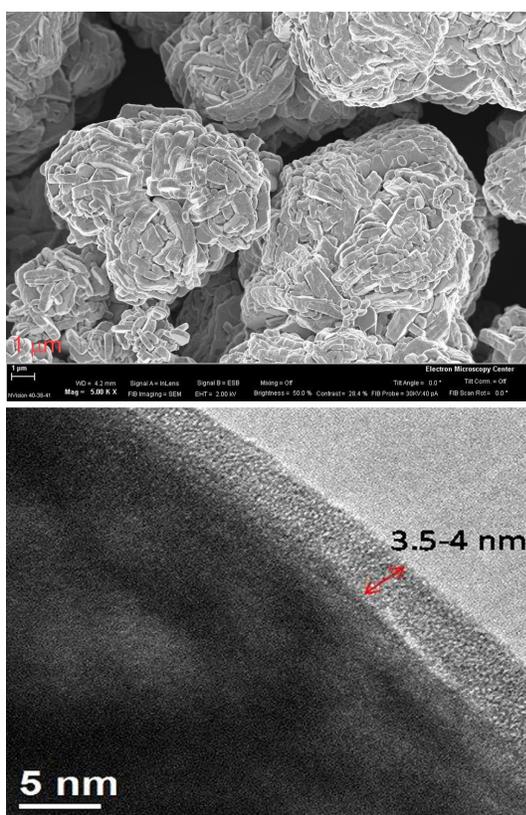


Figure 1. The SEM (top) and TEM (bottom) images of ALD-coated cathode particles in a gas-fluidized bed display a highly conformal and ultrathin ZrO_2 film.

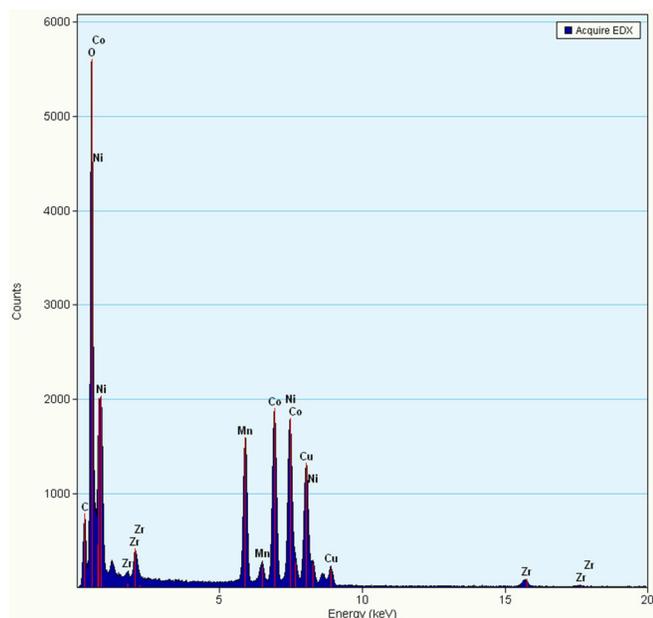


Figure 2. The EDS (TEM) analysis shows the existence of Zr peaks on the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ particle surface.

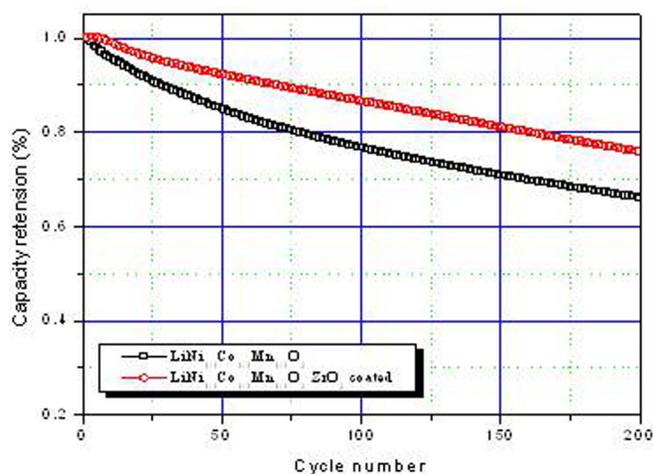


Figure 3. A comparison of the cycling performances of two cells, which are made of (1) uncoated and (2) ALD-coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode particle material, under accelerated test conditions indicates that coating can enhance the cycling performance of the cell.

Novel Power System Operations Methods for Wind-Powered Plug-in Hybrid Electric Vehicles

2010-044-R1

Jianhui Wang, Mihai Anitescu, Audun Botterud, Emil Constantinescu, Anant Vyas, and Victor Zavala

Project Description

This project addresses how power systems can incorporate large amounts of wind power and a high penetration of plug-in hybrid electric vehicles (PHEVs) into their operations, from a few days-ahead planning to real-time operations. We propose to develop a novel stochastic security-constrained unit commitment and dispatch algorithm for power system operations, as opposed to using the traditional deterministic method, which does not consider the uncertainties 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 to improve the protection and restorative capability of national and international critical energy infrastructure components. The proposed approach may significantly improve bulk power system's operation and planning by lowering the system's cost, reducing blackouts, improving social welfare, and advancing

research on power system and large-scale computing. The proposed method can leverage the benefits of new energy sources and applications without compromising the reliability and security of power system operations.

FY 2011 Results and Accomplishments

In FY 2010, we developed a computational framework for wind power forecasting and scenario generation by making use of a state-of-the-art numerical weather research and forecasting (WRF) model that is running on Argonne's high-performance computers. Using this framework, we (1) analyzed the economic impacts of advanced weather forecasting systems in grid operations and (2) evaluated their predictability, resolution, and computational limitations. One of the main conclusions of this study is that a dedicated grid-oriented weather forecasting system is required in next-generation operations. This system will require dedicated computational resources that are capable of (1) handling the required resolutions and (2) generating uncertainty information in forms that are consistent with advanced stochastic optimization solvers.

In FY 2011, we used it for forecasting wind speed and its uncertainty to generate wind speed and power scenarios. Because such simulations are computationally expensive, we carried out simulations on the Fusion cluster at Argonne. We were able to compute 24-hour forecasts in about 10 minutes by using 128 central processing units (CPUs). We used targeted resolutions for a stochastic unit commitment and economic dispatch (UC/ED) model over the state of Illinois and scaled it up to the Continental United States. By using a computational framework that integrates WRF and stochastic UC/ED models, we demonstrated that WRF generally provides accurate forecasts of wind speed.

We developed a new unit commitment model that can simulate the interactions among PHEVs, wind power, and demand response (DR). Four PHEV charging scenarios were simulated for the Illinois power system. Results showed that optimally dispatching the PHEV charging load could significantly reduce the system's total operating cost. When DR programs are in place, the operating cost can be reduced even more. We also reported on using a stochastic unit commitment model that considers the coordination of thermal generating units and PHEV charging loads as well as the penetration of large-scale wind power. Results show that a smart charging pattern can reduce a power system's operating costs and compensate for fluctuations in wind power.

We wrote the contingency algorithm, and the program was compiled and executed in the Linux environment. Results showed that the sequential contingency analysis for the IEEE 1168-bus system ran for 70 seconds. By implementing parallel computing for contingency screening and by synchronizing the variable reading and space allocation with the main function,

it took 32 processors about 12 seconds to compute the 1,168-bus case — much less time than that taken by the sequential program.

We implemented a stochastic UC/ED formulation using the Illinois transmission system and solved it with a new hybrid parallel version of our solver, PIPS (Parallel Interior Point Solver). The Illinois grid contains about 2,000 transmission nodes, 2,500 transmission lines, 900 demand nodes, and 300 generation nodes. Time horizons of up to 24 hours were used. This stochastic UC/ED problem is the largest one ever solved. The problem contains 1.4 billion variables. A strong scaling efficiency of 96% was obtained on 32 racks (131,072 cores) of the "Intrepid" Blue Gene/P system at Argonne. Solution times of less than an hour were achieved.

We used dynamic game theoretical models and predictive control theory to identify mechanisms that lead to long-term market instability and price volatility. In particular, we found that finite forecast horizons and incomplete gaming introduce spurious dynamics into the system that can ultimately lead to insufficient ramp capacity. We did an initial review of current operating reserve requirements in U.S. electricity markets and of the assumptions for operating reserves that were used in some wind integration studies. Furthermore, we conducted an initial investigation of how to derive a demand curve for operating reserves. As the project continues, the findings will support the development of advanced dispatch algorithms for co-optimized energy and operating reserve markets.

Proposed Work for FY 2012

We will extend our capabilities for stochastic optimization by developing scalable methods under a simplex solution paradigm. We will also address the fundamental limitation of capturing physical constraints in clearing formulations. We found that presence of physical constraints introduces strong biases in deterministic and stochastic clearing formulations and introduces price spikes; traditionally, the physical limits have been simulated in market models by using step cost functions. We want to understand this behavior at a more fundamental level and develop more consistent stochastic optimization formulations. In particular, we will try to prove that the explicit handling of constraints leads to more consistent risk premiums in day-ahead markets.

We will use advanced optimization techniques (e.g., robust optimization and chance-constrained programming) to investigate how to best integrate large amounts of wind power into power system operations. As opposed to deterministic and stochastic unit commitment, robust optimization can search for the worst-case scenarios in which wind fluctuates the most, while the probability at which a certain percentage of wind power will be used can be defined through chance-constrained programming.

We will integrate our developments in a single continuous-time stochastic clearing formulation. The framework will incorporate PHEV devices and detailed transmission systems. Our integration will, for the first time, enable researchers to understand price behavior induced by short-term storage devices. We will focus on determining the optimal levels of storage needed to mitigate volatility and maximize market efficiency in the presence of increasing wind supply.

Optimization of Luminescent Solar Concentrators

2010-047-R1

Seth B. Darling, George Crabtree, Jeffrey R. Guest, Roy Holt, Matthew Pelton, David Potterveld, Tijana Rajh, Elena V. Shevchenko, and Gary Wiederrecht

Project Description

We are developing an approach to address the challenges associated with large-scale solar energy harvesting by using a multilayer solar concentrator that is based on luminescent quantum dots (QDs). Solar concentrators are a promising means to reduce the cost of photovoltaic (PV) power, because concentrating solar radiation allows less active material to be used. Luminescent solar concentrators (LSCs) 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 [IR], where organic dyes fail) because of tunable band gaps, and can have significant Stokes shifts that reduce energy losses associated with light reabsorption. Other significant advantages come from a multilayer QD concentrator (Figure 1). It will provide major opportunities for developing flexible, economic, and efficient PV cells by accommodating the mismatch between the incident energy of the solar spectrum and the band gap of semiconductors used in PV devices.

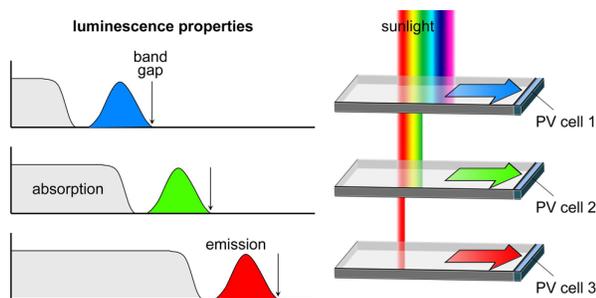


Figure 1. Three-layer luminescent solar concentrator. Each layer is optimized for a specific part of the solar spectrum. The figure on the left illustrates the absorption and emission spectra of three different nanocrystalline materials with three different band gaps, each of which is embedded in one 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 costs of solar energy is a very promising pathway to achieve this. Moreover, investigations of the luminescent solar concentrator will yield 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 2011 Results and Accomplishments

To direct synthetic efforts, in FY 2010 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. Single-layer and multilayer concentrators, with both ideal luminescent materials and with CdSe/CdS quantum nanorods, were simulated by using published absorption/emission data and variable Stokes shift and quantum yield (QY) to obtain a benchmark of performance.

Nanoparticles (NPs) of CdSe ranging from 2 to 6 nm (<5% size dispersion) were synthesized by using a high-temperature solution-based process. These monodisperse CdSe NPs were used as seed materials for further growth of an anisotropic CdS shell, the length and core size of which were variable. Such systems demonstrate Stokes shifts of up to 175 nm, thereby reducing self-absorption. Longer rods mean more absorption by the CdS shell than by the CdSe core, thereby minimizing reabsorption.

Both minimizing reabsorption and maximizing the QY of the nanocrystals are essential for realizing a high-performance LSC. The importance of reabsorption is reduced if the size of the CdS shell is increased relative to the size of the CdSe core; however, we observed that this also reduces the QY. To understand the reasons for this QY reduction, we measured time-resolved photoluminescence and ultrafast transient absorption on nanorods with different core and shell sizes. Results indicated that the main reason is a decreasing radiative recombination rate for nanorods with larger shells, which can be attributed to a delocalization of electrons throughout the CdS shell. These measurements were made by optically exciting the shell; subsequent measurements indicated that if the CdSe core is excited instead, the electrons can remain localized in the core (for large enough core sizes). Calculations indicate that this unexpected phenomenon can be attributed to the presence of separate electronic states that are located either in the core or the shell, with inhibited relaxation between the states. Together, these results provide guidelines for choosing the nanoparticle structure that optimizes the tradeoff between reabsorption and QY.

In FY 2011, LSC devices were fabricated by incorporating synthesized CdSe core/shell nanorods into polymer matrices (Figure 2). Ultraviolet polymerization led to more stable nanoparticle-polymer composites than did thermal polymerization, and it also led to less degradation of the nanoparticle QY. Measurements of luminescence from these composites indicated that reabsorption was nearly eliminated. Measurements are now being taken to determine the quantum efficiencies and concentration factors of these slabs. These measurements will be compared to the Monte Carlo simulations to validate the models and determine the maximum theoretical performance of an optimized device.

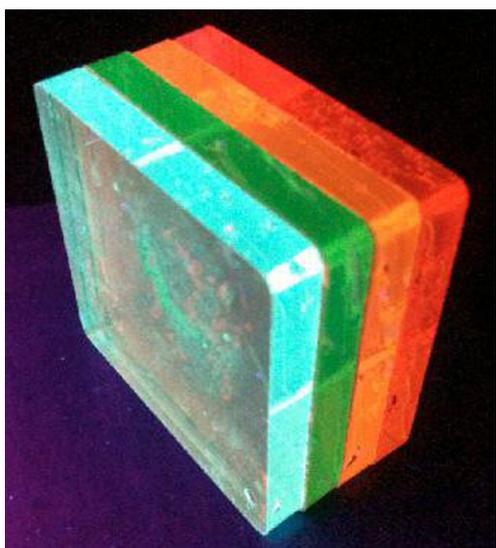


Figure 2. Four LSC slabs ($2 \times 2 \times 0.3$ cm) fabricated with luminescent nanoparticles of different sizes. The result was different emission wavelengths spanning the visible range. These slabs exhibit very low reabsorption losses.

Probing Catalytic Transient Intermediate in Ultrafast Time Domain

2010-167-R1

Di-Jia Liu and Lin X. Chen

Project Description

Catalyst development has traditionally been a time-consuming process. For practitioners in the field, catalyst synthesis is often regarded as “black magic” based on years of experience and know-how. To design catalysts rationally, it is vital to gain insight about 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 catalytic reaction pathways 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 optical and x-ray transient absorption spectroscopies (OTA and XTA), and terahertz spectroscopy, for the investigation of the time-dependent behavior of model catalytic systems and catalysts relevant to energy and environmental applications. The goal is to introduce 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 are directly linked to DOE missions. This project aims to develop innovative tools to promote better understanding, design, and discovery of catalyst materials.

FY 2011 Results and Accomplishments

This project was initiated in FY 2010. Using both optical and x-ray transient absorption methods, we have since investigated several Ru-, Rh-, and Pt-containing organometallic systems with significant implications in photocatalysis and homogeneous catalysis. Their time-dependent structural and dynamic behaviors were studied in both the laboratory and on an x-ray beamline at the Advanced Photon Source. We were able to identify intermediate structures at 100-ps time resolution that have not been observed before. As a result of these initial studies, we were able to select several promising systems for more in-depth investigation.

In FY 2011, we carried out two XTA experiments at beamline 11-ID-D of the APS. The first one investigated the reaction intermediates during photo-isomerization of (fulvalene) tetracarbonyl biruthenium, $(\text{RuFv})_2$, a novel energy storage material (sunlight in a bottle) developed at UC Berkeley. Upon photo-excitation, $(\text{RuFv})_2$ is converted from the cis- to the trans-isomer via multiple intermediate steps (Figure 1). The trans-isomer can be converted back to the starting cis-configuration through catalysis. A recent computational study has calculated the isomerization mechanism and predicted the release of ~ 20 kcal/mol thermal energy during the reversal process. These studies revealed an exciting possibility for $(\text{RuFv})_2$ as a medium to store solar energy in a bottle and release it thermally via catalysis.

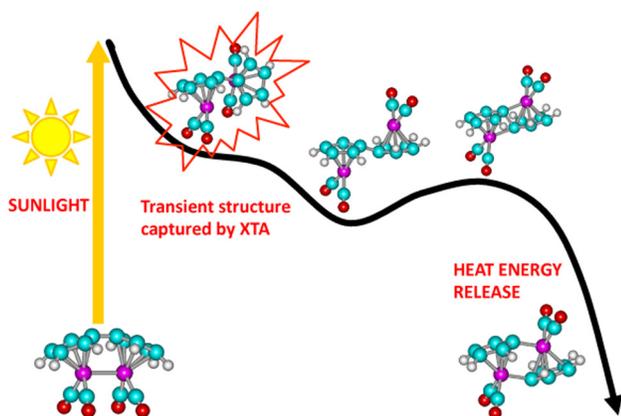


Figure 1. The reaction mechanism for the energy storage complex whereby the transient structure leads to the sunlight-to-heat energy conversion captured by the XTA study.

In our XTA study, we captured a transient structure within 100-psec after the laser excitation to mimic the absorption of sunlight. Detailed analysis indicated that this transient was one of the structures that evolved after the excited state, on the basis of quantum mechanical calculations. Its structure explains the reaction mechanism and identifies the possible reactions pathways. Meanwhile, we continued to analyze the data acquired from previous experiments on homogeneous catalytic systems, particularly triruthenium dodecacarbonyl [Ru₃(CO)₁₂]. This organometallic compound is a representative multinuclear molecular catalyst, mainly used for organic synthesis in the liquid phase triggered by heat or light. The CO dissociation from the trimetal cluster complex illustrates the dynamic process of a classical catalytic reaction. A manuscript is currently in preparation.

The second part of the project involves the construction of a terahertz (THz) system that will be used as a generic, non-photon trigger source to study the catalytic processes that are not light-induced. This work is at the forefront of chemical sciences. The approach is to use the THz excitation source to “shake” the low-frequency vibrational modes that are along the reaction pathways for catalytic reactions. These modes include long-range rocking and twisting of the molecule, such as those found in the isomerization of (RnFv)₂. A model THz setup was constructed during FY 2011; the system needs to be tested and fine-tuned in tandem with an existing laboratory laser system.

Proposed Work for FY 2012

During FY 2012, we will continue to follow the technical approaches and milestones outlined in our research plan. Specifically, we will test the recently fabricated THz pump-probe system in the laboratory as a new method to excite reactions through nuclear-electronic vibrational coupling. Once the fine-tuning and improvement process is completed,

we will apply it to investigate the transient spectroscopy of model catalytic systems, such as metal complexes and metal nanoparticles. We will also continue the XTA study by applying the APS to new systems, such as the photoinduced reduction of iron catalyst through electron transfer from dye molecules that harvest the light and funnel the electron density to the iron catalyst mimics.

Seminars

Harpham, M.R., M.W. Mara, J. Huang, A.B. Stickrath, X. Zhang, K. Attenkofer, G. Jennings, D.-J. Liu and L.X. Chen (2011). “Ultrafast X-ray Studies in Catalysis: Progress, Challenges and Perspectives.” 2011 Advanced Photon Source Center for Nanoscale Materials Electron Microscopy Center Users’ Workshop, Argonne, IL, May 2–5, 2011.

Homogeneous Catalysis of Water Oxidation for Photochemical Energy Storage

2010-184-R1

SonBinh T. Nguyen and Marc J. A. Johnson

Project Description

This project aims to design catalysts that can convert water into O₂ and H⁺ in the so-called water oxidation reaction (Figure 1, left), which is a critical half-reaction in the production of H₂, a clean energy source, from water using renewable energy sources such as sunlight. The generated H⁺ can then be reduced to hydrogen by an electron in a separate second half-reaction that is often called proton-coupled electron transfer.

Mission Relevance

This project is relevant to DOE’s science and energy missions. The demand for H₂ 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 ~95% of the H₂ 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 H₂ and current demands for natural gas for providing heat and generating power. Because SMR contributes to global warming by producing 7.3 tons of CO₂ per ton of H₂ produced, it is one of the largest sources of greenhouse gas emissions in the chemical industry. To meet the future demands for H₂, new sustainable catalyst technologies that utilize feedstocks (such as water) and renewable energy sources (such as wind or solar) must be developed.

FY 2011 Results and Accomplishments

Prior to FY 2011, our efforts were focused on setting up and equipping the laboratory for the proposed work. Once the laboratory was set up, we successfully synthesized three types of tridentate ligands (Figure 1, right). In FY 2011, we prepared complexes of these ligands with Mn, Co, Zn, and Re and characterized them fully. We subsequently surveyed these complexes for activity in the catalytic oxidation of water under electrochemical conditions using cyclic voltammetry (CV). In parallel with these activities, density functional theory was used to calculate the energies of key intermediates in the proposed catalytic cycles. Anticipated trends in the stability of a key terminal oxo complex were found. Catalytic oxidation of water was observed in the case of two cobalt-containing complexes; representative CV data for catalytic water oxidation by one of these complexes are depicted in Figure 2. However, the complexes themselves appeared to undergo decomposition to form a known solid cobalt-based catalyst for water oxidation. Water oxidation was also observed in one instance for a Mn-based catalyst. Metal complexes of monodentate ligands did not withstand the oxidation conditions used. Ligands based on N-heterocyclic carbenes were particularly susceptible to protonation, leading to their detachment from the metal center. Two new bulky tridentate ligands that incorporate acyclic aminocarbene units as the ligating groups were designed and synthesized. These ligands also proved unsuitable for the desired reactions. The targeted unimolecular complexes appear to be subject to low-energy decomposition accompanied by loss of one or more ligands under protic and/or oxidizing conditions, rendering them unsuitable as homogeneous catalysts for water oxidation; small metal-oxo clusters may be more appropriate synthetic targets.

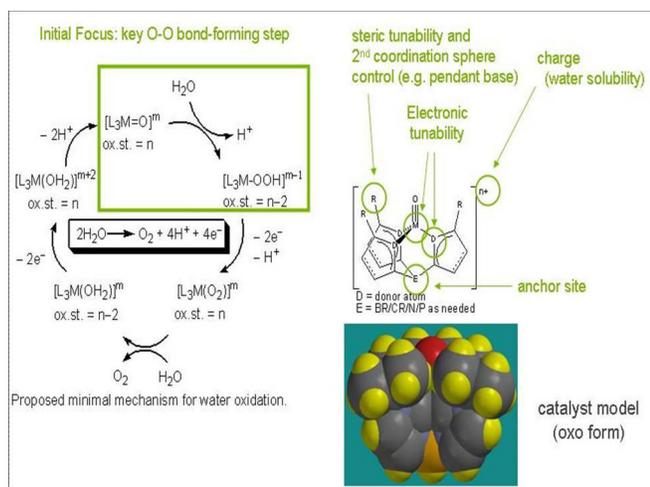


Figure 1. Left: Proposed mechanism for the oxidation of water into O_2 . Right: A proposed intermediate for a tripodal metal oxo catalytic intermediate that is capable of oxidizing water.

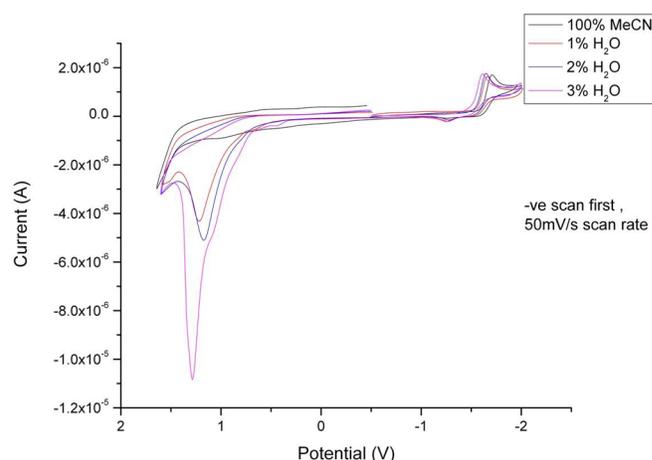


Figure 2. Representative cyclic voltammograms showing the catalytic oxidation of water by a Co-based complex in acetonitrile-water mixtures. Higher water amount leads to higher catalytic currents.

Seminars

Ahultz, A., O.K. Farha, S.H. Cho, T. Gadzikwa, J.T. Hupp and S.T. Nguyen (2010). "Metal-organic Frameworks and Polymer Organic Frameworks as a Versatile Platform for the Deployment of Catalysts." 2010 Catalysis: Advances and Perspectives Workshop, Heidelberg, Germany, Sep. 10, 2010.

Johnson, M.J.A. (2011). "Homogeneous Catalysis at Argonne National Laboratory." Bar Ilan University - Argonne Workshop, Argonne, IL, Oct. 12, 2010.

Johnson, M.J.A. (2010). "Tuning the Reactivity of Metal-nitrogen and Metal-carbon Multiple Bonds: Applications to Metathesis." University of Edinburgh, Scotland, September 6, 2010.

Johnson, M.J.A. (2010). "Tuning the Reactivity of Metal-nitrogen and Metal-carbon Multiple Bonds: Applications to Metathesis." Technical University of Munich, Munich, Germany, January 26, 2010.

Johnson, M.J.A. (2010). "Tuning the Reactivity of Metal-nitrogen and Metal-carbon Multiple Bonds: Applications to Metathesis." University of Chicago, Chicago, IL, Nov. 6, 2009.

Johnson, M.J.A. (2011). "Tuning the Reactivity of Metal-nitrogen and Metal-carbon Multiple Bonds: Applications to Metathesis." University of Ottawa, Ottawa, Ontario, Canada, Oct. 6, 2010.

Johnson, M.J.A. (2010). "Tuning the Reactivity of Metal-element Multiple Bonds for Applications in Metathesis." 2010 Catalysis: Advances and Perspectives Workshop, Heidelberg, Germany, September 3-4, 2010.

Johnson, M.J.A., A.M. Geyer, E.S. Wiedner, J.W. Kampf and J.B. Gary (2010). "Tuning the Reactivity of Metal-Nitrogen and Metal-Carbon Multiple Bonds: Applications to Metathesis." *Catalysis: Advances and Perspectives*, Heidelberg, Germany, Sep. 3, 2010–Sep. 4, 2010.

Mirkin, C.A., J.T. Hupp, R.Q. Snurr, L.J. Broadbelt, D. Tiede and S.T. Nguyen (2010). "From Functional Supramolecular Chemistry to Metal-organic Frameworks: Biomimetic Catalysts and Sensors." Technical University of Munich, Munich, Germany, Jan. 25, 2010.

Nanoscale Architectures for Energy Storage

2010-188-R1

Tijana Rajh, Klaus Attenkofer, Mahalingam Balasubramanian, Ralu Divan, Stephen Gray, Jeffrey Greeley, Christopher S. Johnson, Nenad M. Markovic, Matthew Pelton, Elena V. Shevchenko, and Vojislav Stamenkovic

Project Description

This project aims to develop novel nanoscale electrode materials that could lead to development of affordable and efficient rechargeable batteries. Whereas rechargeable Li-ion batteries offer the highest energy density of any present battery technology, they still have a number of limitations, such as cost, safety, and service life. Thus, the discovery, research, and development of a sustainable system that can provide an alternative to Li-ion batteries are essential for further advancement of energy storage materials. Sodium-based batteries are attractive because of the promise of low cost associated with the abundance of sodium and enhanced stability of non-aqueous battery electrolytes due to the lower operating voltages. We will focus on obtaining a fundamental understanding of chemical and physical processes that occur in nanoscale electrodes and electrode-electrolyte interfaces to improve the performance of the electrode materials for Li-ion as well as Na-ion batteries. From these initial considerations, we will design optimal electrode materials operating with transporting ions having different diameters and valence states. The special focus will be on polyvalent ions, such as Mg^{2+} , Ca^{2+} , or Be^{2+} , that can provide the higher energy densities needed for the development of compact batteries.

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 2012. 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 challenge facing energy storage.

FY 2011 Results and Accomplishments

In FY 2010 we developed nanoscale electrodes in the forms of nanotubes (TiO_2 and FeO_x , with outside diameter = 50-60 nm), nanoribbons (V_2O_5 and MnO_2 , 8-12 nm in diameter), and hollow nanoparticles (Fe_2O_3 , 5 nm) for Li- and Na-ion batteries and showed that they can operate with near theoretical reversible capacity in a half cell configuration. In FY 2011 we integrated them with standard microcrystalline electrodes for testing in a Li and Na ion full cell configuration. We found that nanostructured electrode materials have advantages over bulk materials for rechargeable batteries and can achieve (1) high energy (10^2 – 10^3 Wh/kg), because of efficient electronic and ionic transport properties; (2) high power (10^2 – 10^4 W/kg), enabled by the large contact area; and (3) good cycle life (~600 cycles), because of high mechanical strength at nanoscale sizes to accommodate volume change during operation. It was also found that hollow nanostructures contain very high concentrations of cation vacancies that can be efficiently utilized for Li intercalation without structural change and can operate like solid-state solutions with ~100% coulombic efficiency and excellent stability. We monitored the *in situ* and *ex situ* structural transformation of hollow nanostructures by using synchrotron x-ray adsorption and diffraction techniques that provided a clear understanding of the lithium intercalation and conversion processes during electrochemical cycling. We also showed that open-frame layered structures can be optimized to accommodate large-volume Na ions by adjusting the layer spacing upon exposure of the reduced layered structure to a high concentration of Na ions (Figure 1). The electrostatic attraction of electrochemically altered oxide layers provides a strong driving force for the diffusion of a large concentration of transporting ions into open-layer frameworks. This consequently leads to ordering of the overall structure, with the appearance of both short-range order within the layers and long-range order between the layers. Upon deintercalation of sodium, the long-range order is lost while the intralayer structure is still preserved.

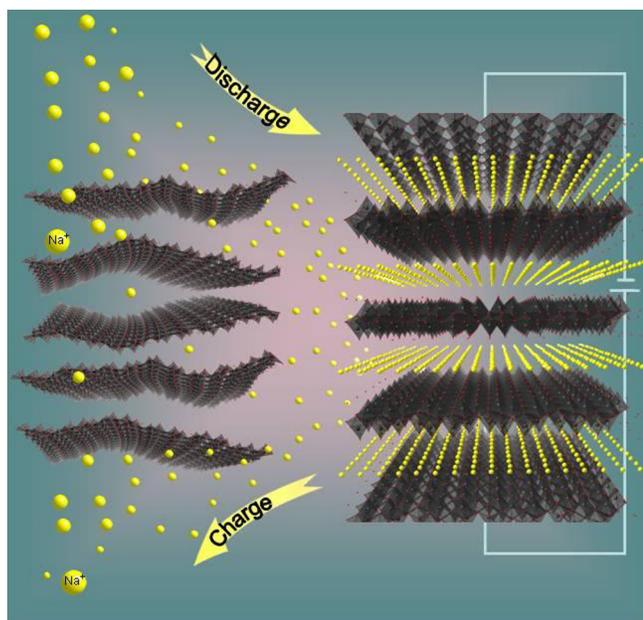


Figure 1. Ability of open-frame layered structures to accommodate large-volume Na ions by adjusting their layer spacing upon exposure to high concentrations of Na ions.

Inducing ordering of nanomaterials in operando allows realization of the highest possible electrode capacity by optimizing the balance of electrostatic forces. Molecular-dynamics and density functional theory calculations with a classical interaction potential were employed to obtain insights into the dynamical properties of Li ion transport in anatase and amorphous titania. All-nanoscale Li-ion and Na-ion full-cell-configuration batteries composed of nanoscale anodes (TiO_2) and cathodes (V_2O_5 and MnO_2) were investigated and were found to achieve the highest specific capacities and power densities reported to date. A specific achievement of this part of the work was the demonstration of a water-based full cell operating as a Na rechargeable battery.

Proposed Work for FY 2012

During FY 2012, we will 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 Ca, Be and Mg ion-based cells. We have already shown that all nanoscale anodes and cathodes investigated can operate with Na transporting ions; in some cases, even with larger capacities. We expect that our electrochemical methods for preparation of nanoscale electrodes can create 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.

Process Engineering Research for Scalable Energy Storage Materials

2010-191-R1

Gregory 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, parallel process engineering research is required to ensure that these materials can be consistently and cost-effectively manufactured in high-volume applications.

Mission Relevance

This project is relevant to DOE's energy mission. Scientists in the battery materials programs across the DOE complex refer to scale-up as synthesis of battery materials in gram quantities, but with time-consuming, multiple small-scale runs. There are no capabilities to scale up currently developed battery materials (primarily lithium-ion based batteries) to kilogram and tens-of-kilograms quantities at any DOE laboratory to support the transition of these technologies to industry. Moreover, there is no systematic engineering research capability or program across the DOE complex or in industry to identify and resolve constraints on development of cost-effective process technology for the high-volume manufacture of these advanced materials.

FY 2011 Results and Accomplishments

In FY 2010, work began with an initial feasibility study on the scale-up of the redox shuttle ANL-RS2 and proof-of-concept (10 g) experiments. Work continued in FY 2011 with the first-stage scale-up (100 g) and second-stage scale-up (1,000 g) experiments.

The three major accomplishments during FY 2011 are described below.

Electrolyte materials process scale-up development and system design

First-stage scale-up work was conducted, and 100-g batches of ANL-RS2 were synthesized and found to have analytical and electrochemical performance comparable to that of material synthesized at the proof-of-concept stage.

Mini-pilot-scale assembly for electrolyte materials development

An electrolyte materials scale-up laboratory was established in Argonne's building 362. A system consisting of a 20-L continuous stirred jacketed reactor for the synthesis of kilogram batches of electrolyte materials (such as ANL-RS2) was developed. This system also includes materials handling equipment capable of feeding reagents in an inert atmosphere and process monitoring capabilities.

Process optimization for electrolyte materials batch process development

The revised process to synthesize ANL-RS2 was optimized, the second-stage scale-up was completed, and a 1,576-g batch was synthesized. The material was found to be analytically and electrochemically identical to that generated at the 100-g scale. Samples of the material have been submitted to multiple industrial battery materials companies.

Proposed Work for FY 2012

In FY 2012, we will conduct process engineering research for the scale-up of a new cathode material, LiFePO_4 composite. Until now, this material has only been synthesized in small batches using 500-mL vessels, which produce approximately 50 g of material. The current process is labor-intensive and time-consuming, requiring approximately 1–2 weeks of a skilled chemist's effort to produce 50 g of material. Scaling up the process involves modification of the bench-scale process chemistry to allow for the continuous production of the LiFePO_4 composite, development of a process engineering flow diagram, design of a mini-scale system layout, fabrication of the experimental system, and experimental validation of the optimized process. The mini-system will be assembled by using an existing synthesis reactor system. Cathode materials produced will be analyzed to confirm material properties. In addition, we will develop a strategy for further scaling up battery materials and integration into manufacturing operations.

Microscopic Building Blocks of an Improved Lithium-Ion Battery

2010-192-R1

John F. Mitchell and Qiyin Lin

Project Description

Lithium-ion batteries are at the state of the art for deployed electrical-energy storage platforms, finding use in applications ranging from power cells for laptop computers to the electrical drive train of plug-in hybrid vehicles, such as the Chevrolet Volt. Moving Li-ion batteries toward higher capacities, better cycling performance, and higher power densities that are nec-

essary for widespread deployment of mobile storage stands as both a technical and scientific challenge. We are approaching this challenge from a very fundamental standpoint, creating well-defined crystalline substrates with which the key processes in charging and discharging batteries can be studied in pristine forms, isolated from extrinsic effects found in powders and composites. Specifically, we aspire to grow the highest quality single crystals of canonical cathode materials (e.g., LiCoO_2 , LiFePO_4), understand their intrinsic electronic and ionic transport characteristics, explore their performance in real-world as well as idealized battery environments, and correlate performance with underlying processes (Li-ion diffusion in the bulk and at the surface of the crystal, structural changes during charging, etc.). The outcome of such studies is expected to inform improvements of today's Li-ion cathode materials, as well as inspire design of next-generation Li-ion cathodes with improved functionality.

Mission Relevance

Expanding the role of energy technologies that can reduce fossil-fuel dependence and enhance U.S. energy security is a critical mission activity of the DOE. Research in advanced electrical-energy storage materials platforms directly targets this mission. All electrical energy storage platforms based on Li-ion technology depend on the motion of these ions through solid electrodes. Understanding the materials science of how this process occurs and how to improve its efficiency underpins the fundamental objective of this work.

FY 2011 Results and Accomplishments

Following successful growth of LiCoO_2 and LiFePO_4 crystals in FY 2010 and preliminary electrochemical characterization of these samples, our FY 2011 accomplishments centered on the development of a principally new method for growing crystals of LiCoO_2 , delithiating them, and exploring the structure of the material. A significant outcome of this work was (1) the convincing demonstration of defect-free LiCoO_2 crystals that reveal the intrinsic, highly insulating nature of this material and (2) strong evidence for inhomogeneous delithiation on the macroscale.

In the first of these results, we grew crystals by a vapor process that eliminates many of the extrinsic defects that are apparently present in crystals grown either in traditional ways or by powder synthesis where semiconducting behavior is found. The high electrical resistivity is consistent with simple pictures of the electronic structure of LiCoO_2 and furthermore argues that these defects are essential for effective charging. Because of this high resistivity, we were unable to electrochemically delithiate these defect-free crystals. Instead, we chemically removed Li and followed the process *in situ* with x-rays. In this way, we were able to demonstrate that the crystals can be delithiated without decomposing or breaking into polycrystalline form. Furthermore, this x-ray technique allowed us to

monitor the Li concentration over time, allowing us to selectively choose important compositions for electrical characterization. Using x-ray microdiffraction techniques, we showed clear evidence of inhomogeneous lithium distributions over micron scales in delithiated single crystals (Figure 1). While this finding shows that single crystals are not favorable for battery cathodes, it may also help to provide a length scale for practical cathode materials to overcome this inhomogeneous process.

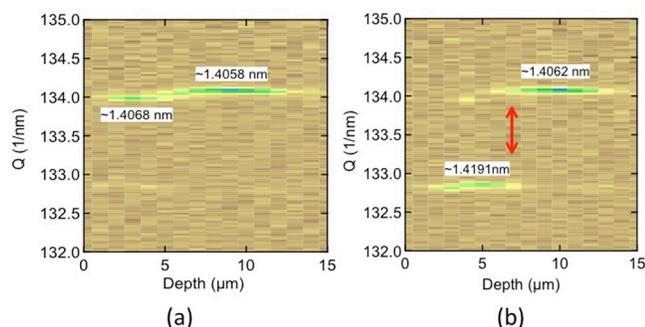


Figure 1. X-ray microdiffraction study of a stoichiometric (left) and a partially delithiated (right) Li_xCoO_2 single crystal of $\sim 15 \mu\text{m}$ thickness. The position of the $(0,0,30)$ reflection appears as a line of higher intensity. A single line demonstrates a homogeneous Li distribution in the pristine crystal. On the other hand, the delithiated crystal shows an evolution from a single phase at the surface to a biphasic region in the middle of the crystal (shown by the double-headed arrow). This is prima facie evidence of inhomogeneous lithium distribution established during delithiation.

Proposed Work for FY 2012

In the final year of the project, we will pursue three tracks. First, we will determine if the chemically delithiated single crystals can be charged (or cycled) electrochemically. The higher conductivity of these Li-deficient crystals may make this possible. If successful, it will make possible a range of *in situ* experiments under realistic conditions. Second, we will finish our studies of the LiCoO_2 system by systematically characterizing the electrical properties of chemically delithiated specimens. An electrical anomaly at $\sim 170 \text{ K}$ noted by others and seen by us as well has been attributed to ordering of $\text{Co}^{3+}/\text{Co}^{4+}$. This explanation seems unlikely, on the basis of the temperature dependence of the electrical conductivity. We will explore this behavior by using transport measurements that will be supplemented by spectroscopic studies of the electronic structure of Co in the region $x \sim 0.75$ in Li_xCoO_2 . Third, we will prepare and characterize materials targeted by the Argonne battery group for fundamental study of delithiation chemistry. This effort includes crystal growth of Li_2MnO_3 and attempts to fluorine-dope $\text{Li}_2(\text{Mn},\text{Co})\text{O}_3$ as a strategy to prevent voltage drops observed during repeated cycling of the oxide.

Atomistically Informed Mesoscale Simulation of Gradient Nuclear-Fuel Microstructure

2010-196-R1

Dieter Wolf

Project Description

In this project, we will incorporate the effects of the temperature and stress gradients present across nuclear fuels into an atomistically informed mesoscale phase-field modeling framework. 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. 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-level processes involved in radiation damage, including defect clustering. These processes will be elucidated 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 simulation model.

Mission Relevance

This project is relevant to DOE's energy mission, particularly 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 2011 Results and Accomplishments

Using computer time available through Argonne's Fusion cluster, we performed MD simulations on UO_2 and cerium dioxide (CeO_2) under ion irradiation in order to investigate the degree to which ceria can be used as a surrogate material for the investigation of radiation damage in UO_2 . Specifically, we (1) determined the kinetics of the clustering of irradiation-induced point defects and the initial formation of the extended defects and (2) compared the clustering mecha-

nisms in the two materials. Our simulations for CeO_2 revealed the formation of charge-neutral interstitial dislocation loops that are identical to those recently observed experimentally at Argonne's IVEM-Tandem (intermediate voltage electron microscope-tandem accelerator) facility by the group of Prof. J. Stubbins at the University of Illinois at Urbana-Champaign (UIUC). Our simulations revealed that these loops are formed by diffusion and clustering of both Ce and O interstitials. When Ce interstitial diffusion was suppressed by lowering the simulation temperature, *charged* clusters were formed. The formation of charged clusters is consistent with the simulations on UO_2 , where U interstitials are immobile on the time scale accessible to MD simulations. We concluded that clustering of point defects in CeO_2 and UO_2 is qualitatively identical and is controlled by the cation diffusivity.

A unique aspect of our approach to simulating radiation damage is the ability to insert vacancies and interstitials (so-called Frenkel pairs) on only one sublattice at a time, rather than simultaneously on both (as is the case in the conventional radiation-damage experiments and simulations). With this capability, we could identify the atomic-level mechanism of dislocation-loop formation. Remarkably, our simulations revealed a self-healing response of the perfect crystal to the radiation-induced defects. In fact, the lattice responds to point defects created during irradiation with the spontaneous creation of new point defects. These new "structural defects," with a negative energy of formation, neutralize the radiation-induced point-defect cluster by screening its long-range Coulomb potential, thereby lowering the overall energy and localizing the damage. A similar lattice response was previously also identified in simulations of magnesium oxide, although very different types of clusters were formed, suggesting that this self-healing screening response may be an intrinsic reaction of all ionic materials to irradiation.

Proposed Work for FY 2012

The above atomic-level simulations serve as input into meso-scale simulations using a phase-field approach to determine microstructure evolution under irradiation. Specifically, we will incorporate the coupling between stress- and temperature-gradient terms as driving forces into our phase-field code. This 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 also perform MD simulations of irradiation-induced defects and defect clustering in body-centered cubic Mo as a model metallic fuel material. In addition to the cluster-formation mechanism, we will determine defect formation and migration in a temperature gradient (so-called thermo-

migration, also known as the Soret effect). These simulations will provide important input to the mesoscale simulations in a temperature gradient.

Controlled Heterogeneity of Materials for Energy Applications

2010-197-R1

Marius Stan and Di Yun

Project Description

Materials for energy applications, such as nuclear fuels and electrical batteries, are multi-component ceramics or metals 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." To this end, we will develop theoretical and computational tools for the analysis of heterogeneity at the micro- and nanoscale levels in nuclear fuels (e.g., UO_2) and solid electrolytes for Li-ion batteries. Then, by performing simulations of heat, chemical, and electrical transport for a variety of heterogeneous features (point defect clusters, pores, gas bubbles, cracks), we will identify the optimal nano(meso)-structure and assist the design and synthesis of new materials.

Mission Relevance

This 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 beyond nuclear energy and energy storage. The project fosters theoretical and computational work resulting in new models, methods, and algorithms. It will result in innovative design experiments that can transform the understanding of materials, thus moving materials science from observation and analysis to prediction and control. All these features benefit both basic and applied scientific research and support the DOE Office of Science and Office of Nuclear Energy missions and strategies. This project will serve as seed for a multiscale (atomistic, meso-scale, and continuum) high-performance materials simulation program at Argonne that is

relevant to such DOE programs and resources as the Nuclear Energy Advanced Modeling and Simulation (NEAMS) Program, the Center for Electrical Energy Storage (CEES), and the Argonne-led Center for Exascale Simulation of Advanced Reactors (CESAR).

FY 2011 Results and Accomplishments

This project started in August 2010. In FY 2010, we defined the relevant geometry and boundary conditions for the coupled simulations of heat transport and chemical species diffusion in porous materials.

In FY 2011, we set up a simulation domain consisting of a cylindrical uranium oxide (UO₂) fuel pellet and steel cladding separated by a helium gap, 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. In the UO₂ pellet we placed a disc-shaped void, thus creating a low (few percent) porosity. The heat transport simulation showed that the presence of the void changed the local temperature by more than 100 K. Subsequent simulations involved a uniform distribution of smaller voids adding up to a similar total porosity. In this case, the effect on the temperature field was less severe but still noticeable. Current simulations are focused on heterogeneous (non-uniform) distributions of voids and preliminary results show that, for the same size distribution, the thermal field is most sensitive in the regions of large temperature gradients.

For the study of energy storage materials, we set up a simulation of the heat profile in an air-cooled cylindrical Li-ion battery, using COMSOL Multiphysics. The temperature field was first determined for a porosity-free material as a function of battery operating parameters and a fixed cooling regime. The goal of this component of the project is to study the effect of porosity on the temperature and the ionic and electronic transport properties of the electrodes to guide the design and synthesis of optimal materials.

Proposed Work for FY 2012

We will further study the effect of the size distribution, position, shape and orientation of voids on the heat and chemical transport in UO₂ and will analyze the information to determine the optimal distribution.

For energy storage materials, we will investigate the effect of heterogeneity on thermal transport and the potential impact on ionic and electronic transport in Li-ion batteries.

Seminars

Stan, M. (2011). "Materials Discovery and Design." Illinois Institute of Technology, Chicago, IL, Mar. 28, 2011.

Stan, M., B. Mihaila, A.D. Andersson, P. Cristea, S.Y. Hu, C. Ramirez, V. Tikare, P. Turchi and M. Samaras (2010). "Integration of Simulation Techniques for Nuclear Fuels." F-Bridge School, Karlsruhe, Germany, Sep. 28–Oct. 2, 2010.

Near-Term Spent Nuclear Fuel Disposal Using Accelerator Drive System

2010-201-R1

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Project Description

The first objective of this project is to characterize and develop an innovative accelerator-driven system (ADS) for disposing of the spent nuclear fuel (SNF) inventory of the United States. U.S. commercial SNF inventories continue to increase, currently amounting to ~60,000 MT and growing by ~2,000 MT per year. It is estimated that the SNF inventory will reach a total of 120,000 MT over the lifetimes of the currently operating commercial nuclear power plants. SNF contains ~1% transuranics (~700 MT), which include ~40 MT of minor actinides (MAs). The proposed ADS is intended to transmute/fission the MAs, thereby eliminating the long-term radiotoxicity of the SNF. The proposed system also utilizes existing proven technology as much as possible with minimum extrapolation, so it will be possible to deploy such systems in the near term.

Mission Relevance

In support of DOE's energy mission, our proposed system provides a disposal solution for SNF. This system significantly reduces the required geological repository capacity for nuclear waste and eliminates the need for a large storage facility such as the one that has been planned for Yucca Mountain, Nevada.

FY 2011 Results and Accomplishments

The accelerator required to drive the neutron production target was selected to be a continuous-wave superconducting proton linac with a beam energy of 1 GeV. For the engineering study phase, a beam power of 5 MW is appropriate, while for the production facility, a beam power of 25 MW per accelerator is required. During FY 2011, initial studies of these accelerators were carried out. End-to-end beam dynamics simulations were done to determine the number and types of superconducting cavities required, along with initial estimates of the liquid helium refrigeration and RF power supply specifications. For the 25-MW linac, there is research and devel-

opment to be carried out on the RF couplers, for which the requirements are beyond the present state of the art but not considered potential show-stoppers.

Considerable attention was given to the nuclear chemical engineering aspects of ADS development issues. Our efforts to date were devoted to exploring ways to understand the engineering of these systems and identifying solutions to facilitate their development. Specifically, the focus of our research and development activities falls into three general areas: developing a process flowsheet for partitioning actinides from used light water reactor (LWR) fuel for transmutation in the ADS, selecting a fuel system, and developing a flowsheet for fission product removal from the ADS fuel after MA transmutation.

Three ADS fuel systems were examined. These include two lead slurry fuels containing actinides suspended as either oxide or intermetallic compounds and one fluoride salt system with dissolved actinide fluorides. Each of these possible fuel types involves challenges, and the work to date focused on assembling background information on corrosion, slurry stability, fuel chemistry, and reprocessing methods. One of the key issues in considering use of a lead-based fuel is corrosion of container materials. To prevent oxidation, a reducing environment is needed, and that is provided by the addition of Mg. This approach appears to be a satisfactory method to mitigate lead corrosion of the structural materials.

Attention was given to reprocessing the fuel as the reaction proceeds, and reasonable progress was made on developing schemes for reprocessing lead slurry fuels. These methods are based largely on pyrochemical processes investigated at Argonne during the last forty years.

Regarding the subcritical core, the major activity in FY 2011 involved defining and optimizing the operating parameters. The fuel carrier chemistry defines the upper limit of the transuranics concentration as a function of the operating temperature range. In defining the system parameters, a transuranics concentration range was considered, but the upper value is lower than the chemistry value. The system is designed for an effective neutron multiplication factor of 0.98. To reach this neutron multiplication factor, a small fraction of the SNF plutonium is mixed with the MAs. For the 0.98 effective neutron multiplication factor, the change in the plutonium fraction in the transuranics results in changing the volume of the subcritical assembly and consequently the initial MA inventory. Figure 1 shows the required initial MA inventory as a function of the plutonium fraction in the transuranics for a 0.98 effective neutron multiplication factor. In the same figure, the corresponding fission blanket volume is shown to achieve an effective neutron multiplication factor of 0.98.

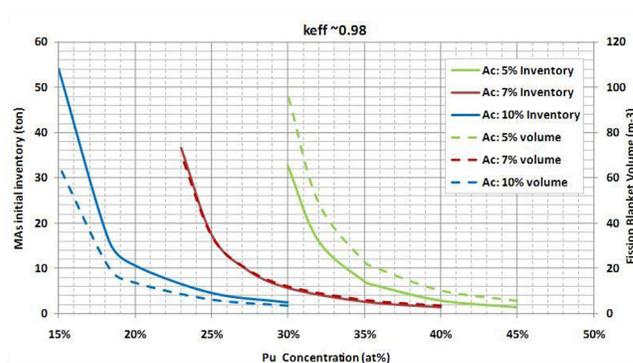


Figure 1. Initial inventory of the MAs and the fission blanket volume as a function of the plutonium concentration for 5, 7, and 10% actinide concentrations in the lead-bismuth eutectic.

The annual consumption rates of the transuranic materials, which are constant during the operation, are shown in Figure 2 for three actinide concentrations. The consumption rates of the MAs and the combined uranium and plutonium are also shown in Figure 2. The efficiency of the uranium separation process from the SNF is 99.995%. The transuranics have a very small uranium fraction, which is tracked in the analyses. The net transuranics consumption rate is constant during all the years. The subcritical assembly composition reaches a steady state after about 5–6 years of operation. On the basis of these results for a 7% actinide concentration, four subcritical systems, each with 3 GWt of output power, will consume the MAs of the 70,000 metric tons in the SNF inventory in less than 33 fuel power years.

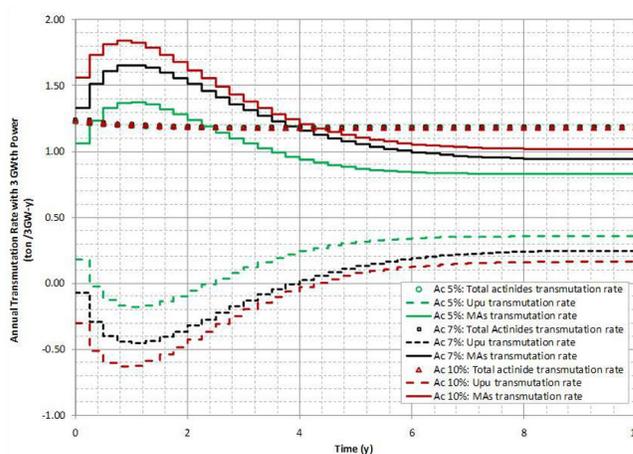


Figure 2. Annual transmutation rates of actinides, plutonium, and minor actinides for the ADS system (3 GW_t) with 5% (35.7% Pu), 7% (27.2% Pu) or 10% (20% Pu) actinide concentration in the lead-bismuth eutectic.

Proposed Work for FY 2012

RF couplers will be developed for the 5-MW implementation, and work will be done to investigate approaches for the 25-MW implementation.

System engineering will be done to develop a balanced flow-sheet for the system. Identification of wetting agents and appropriate concentration ranges will be investigated for the oxide slurry. Additionally, a method will be developed for achieving a stable slurry and maintaining that slurry under the relevant conditions while understanding the corrosive behavior of the slurry system.

Work is under way to start the development of the blanket configuration, utilizing a heterogeneous blanket design. We intend to remove the 3-GW thermal power and keep the design as simple as possible by utilizing one fuel zone, one feeding system, and one liquid-cleaning system.

Spin and Charge Dynamics in Oxide Heterostructures

2010-204-R1

Olle Heinonen

Project Description

This project increases our fundamental understanding of spin and charge dynamics in oxide and magnetic heterostructures, as well as our ability to design complex nanostructured materials systems with specific properties. The scope of the work is two-fold. 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. Another part of this work is directed at understanding magnetization behavior, both static and dynamic, in patterned magnetic thin films. Second, the effects of defect motion on charge transport in metal/oxide/metal nanostructures are studied through modeling and experiments, with a goal of understanding how resistive switching is influenced by defects and how the switching can be controlled, and, in a broader context, how oxygen defects affect the behavior in oxide heterostructures.

Mission Relevance

The project aligns with the DOE BES mission to support research in areas relevant to energy efficiency through use-inspired R&D on new materials for information storage. In particular, the research is relevant to the development of low-power electronics. There is a great need for research in this area, as was highlighted in the report "Gadgets and Gigawatts" by the International Energy Agency in 2009: by the end of year 2030, energy consumption due to consumer electronics and information technology is estimated to rise to 1,700 TWh. This level of consumption equals the combined current total residential electricity consumption in the United States and Japan.

FY 2011 Results and Accomplishments

In FY 2010, initial work was done on transport and structure of magnetic tunnel junctions, and on the magnetization dynamics in tunnel junctions.

The main accomplishments in FY 2011 were (1) elucidating the behavior of magnetic resonance modes in magnetic tunnel junctions and the behavior of driven resonances and (2) increasing the fundamental understanding of static and dynamic magnetization behavior in patterned magnetic thin-film structures.

The magnetization dynamics in circular magnetic tunnel junctions of diameter 240 nm were studied in conjunction with experimental work at the University of Gothenburg, Sweden in collaboration with Prof. Johan Åkerman's group. Three different branches of modes and their behavior in the presence of an applied magnetic field were studied. The frequency dependence of the different modes as a function of the applied field strength was explained on the basis of the different layers in which the modes were excited. Furthermore, the frequency dependence at fixed field but as a function of applied bias voltage was studied and explained. In one branch of modes, spin torque effects cause the frequency to depend linearly on bias voltage, while in another branch, Joule heating effects dominated, giving rise to a quadratic dependence of the mode frequency on bias voltage. Furthermore, it was demonstrated that under certain conditions, the magnetization motion can give rise to a frequency-doubling in the measured signal voltage. The mechanisms for de-coherence of driven modes, or auto-oscillations induced by spin torque from a dc bias current, were studied. It was shown for the first time that mode-hopping, in which the oscillations switch from one distinct mode to another, analogous to mode-hopping in lasers, can be a major cause of de-coherence of driven oscillations in magnetic tunnel junctions.

Patterned magnetic thin films can display complicated static and dynamic behavior that is controlled by shape effects and by interactions between and within the patterned structures. The static behavior and nanoscale magnetization structure of artificial spin-ice lattices were studied. Such systems consist of patterned mono-domain magnetic structures between which all interactions cannot be simultaneously minimized, leading to rich complex phase diagrams and quasi-static magnetization reversal behavior. The micromagnetic simulations of artificial spin-ice lattices were combined with aberration-corrected Lorentz transmission electron microscopy (ALTEM) and Monte Carlo methods to detail the nanoscale structure of topological magnetic defects and their effect on the magnetization reversal. Also, the magnetization behavior of trilayer discs was studied. The discs consisted of two layers of soft magnetic material (Permalloy) separated by a thin Cr layer, such that the interaction between the Permalloy layers was

weakly anti-ferromagnetic. Experimental studies using ALTEM revealed a novel behavior of the magnetization in response to a static magnetic field. Micromagnetic modeling showed that this behavior was due to the formation of a topological structure (a so-called meron) in the two magnetic layers. Finally, with collaborators at Northwestern University, the magnetization modes of magnetic thin film anti-dot arrays were studied. Experimental work at Northwestern University in conjunction with micromagnetic modeling showed that the spectrum of modes contains a novel mode due to magnetization motion confined to the edges of the holes in the anti-dot array.

In addition to the work on magnetic tunnel junctions and patterned magnetic thin films, a study was conducted at the Nanoprobe beamline at the Center for Nanoscale Materials (CNM) correlating the resistive behavior and structure of Pt/NiO/Pt heterostructures. Several devices were studied in both the as-deposited high-resistance state and the low-resistance electroformed state, as well as in high-resistance re-set and low-resistance set states. The data analysis is near completion, and it appears that the change in resistance is correlated with changes in the NiO (111) diffraction intensity on scales much larger than the grain size of the NiO.

Proposed Work for FY 2012

The dynamic behavior of artificial spin-ice lattices, as well as the “meron”-structures, will be studied by using micromagnetic simulations. A particular emphasis will be placed on how topological structures and defects affect the magnetization dynamics and magnetization modes.

First-principles methods will be used to study oxygen defects in metal/oxide/metal heterostructures. The behavior of such defects is closely related to important phenomena ranging from transport or resistive behavior to fatigue in ferroelectrics. An allocation on the ALCF Blue Gene/P platform was granted for large-scale first-principles studies of oxygen defects.

Seminars

Heinonen, O. (2011). “Spin Torque in Magnetic Tunnel Junctions.” Seminar at the University of Minnesota, Minneapolis, MN, Oct. 25, 2010.

Heinonen, O. (2010). “Spin Torque in Magnetic Tunnel Junctions.” Nordforsk Nanospintronics Workshop, Norrköping, Sweden, Sep. 22–24, 2010.

Heinonen, O. (2010). “Spin Torque in Magnetic Tunnel Junctions.” Colloquium, Dept of Physics, Case Western Reserve University, Cleveland, OH, Sep. 9, 2010.

Muduli, P.K., O.G. Heinonen and J. Akerman (2012). “Intrinsic Frequency Doubling in an MgO Based Spin Torque Oscillator.” 56th Annual Conference on Magnetism & Magnetic Materials (MMM 2011), Scottsdale, AZ, Oct. 30–Nov. 3, 2011.

Enzyme Processes in Energy Production

2011-203-N0

Jyotsana Lal

Project Description

An understanding of enzyme catalysis on a molecular level is of fundamental importance in biology and medicine. Enzymes play a key role in almost all biological processes, accelerating by many orders of magnitude a variety of metabolic reactions, as well as controlling energy transduction, the transcription and translation of genetic information, and signaling. The static structures are known for many enzymes, yet the functions of enzymes are governed ultimately by their dynamic character. Lately, several groups have explored this insight. The limiting factor in these studies is that the relevant dynamics may require characterization over even broader ranges of scale in time and length. The availability of state-of-the-art experimental facilities at the Spallation Neutron Source and the Advanced Photon Source provides an extraordinary combination of tools for addressing fundamental questions about the structure and dynamics of these systems. We intend to probe the effect of internal dynamics (on pico- to nanosecond timescales) of an enzyme undergoing active catalysis in solution. The second set of experiments is designed to probe the role of water molecules and hydration in protein dynamics for functional and enzymatic activity. Recent work has revealed the complexity of water itself and its role as an active participant in biological processes. In particular, we want to understand how cellulase enzymes degrade cellulose, the key to increasing the efficiency and lowering the cost of biofuels, such as ethanol.

This project involves demonstrating the use of neutron spin echo (NSE) techniques to probe the effect of internal dynamics on an enzyme that is undergoing active catalysis in solution. The second part of the project involves using the MISANS (Modulated Intensity Small Angle Neutron Scattering) technique to study biomolecule behaviors.

Mission Relevance

This project was undertaken in response to DOE’s grand challenges for Basic Energy Sciences (BES), which includes meeting the need for abundant, clean, and cheap energy. The fundamental studies we propose are aimed at characterizing the biological processes involved in energy capture, storage, and use. The goal is to provide insight into the design of synthetic systems for analogous processes. Our approach is to use of state-of-the-art techniques at the Spallation Neutron Source (SNS) and Advanced Photon Source (APS) facilities, which are enabled by BES.

FY 2011 Results and Accomplishments

We first studied prototypical carbonmonoxyhemoglobin (HbCO) then focused on adenylate kinase (ADK), a model enzyme system that plays an important role in cellular energy balance. ADK is a small, ubiquitous enzyme involved in maintaining a balance between the following metabolites: adenosine monophosphate (AMP), adenosine diphosphate (ADP), and adenosine triphosphate (ATP) ($2 \text{ ADP} \leftrightarrow \text{ATP} + \text{AMP}$). Once mixed with ADP as a starting reagent, ADK will catalyze, interconverting ADP, AMP, and ATP for at least 24 hours or more in a continuous cycle. Therefore it is a very convenient biochemical system for the study of enzymatic action. We also obtained preliminary NSE results from experiments on cellulases, which represent a large class of enzymes that are crucial to the degradation of biomass.

We also obtained complementary wide-angle x-ray solution (WAXS) scattering measurements of the changes in the internal structure of the enzyme. The results of WAXS studies provided the following insights into the dynamics of ADK during its catalytic cycle in solution: (1) the apo (open) and inhibited forms (locked with AP5A) are readily distinguished (see Figure 1), and (2) scattering under active cycling condition cannot be reconstructed as a linear combination of the data collected from the putative end-points of the cycling (open and closed), indicating that, when the enzyme is functioning, the abundance of intermediate forms is large enough to contribute significantly to the scattering pattern. These results gave us confidence that, under conditions required for collecting NSE scattering data, the kinetics of cycling are observable (Figure 2, data taken at IN15, ILL, Grenoble, France).

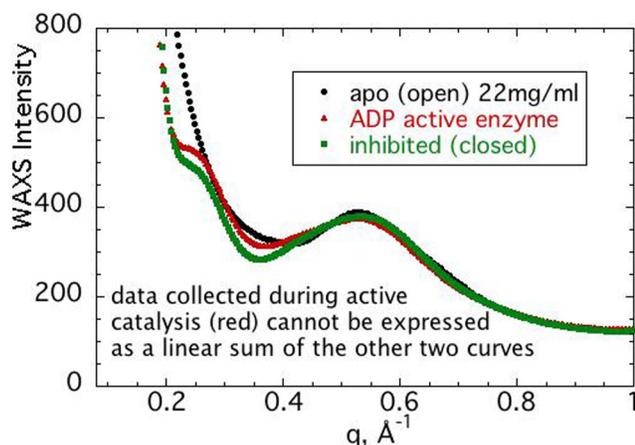


Figure 1. WAXS patterns of ADK (22 mg/ml) in apo (open) form (black); inhibited (closed) form (green); and while undergoing steady-state catalysis (red).

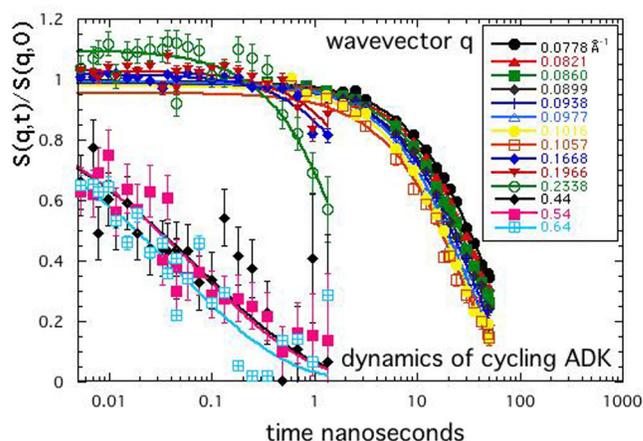


Figure 2. NSE patterns of ADK as it undergoes steady-state catalysis. These data shows the ADK relaxation rates from picoseconds to 100 of nanoseconds at nanometer-length scales.

The project also provided valuable information about the deconstruction of lignocelluloses, which is essential for the use of biomass as a feedstock in production of chemicals and fuels. Collection and analysis of initial WAXS data (from APS) and NSE data (from SNS-NSE BL-15 at Oak Ridge National Laboratory) on B-1-4 endocellulase (40 mg/ml) from *Costridium cellulovorans* and on cellulase from the National Renewable Energy Laboratory cellobiohydrolase I (Cel7A) from *Trichoderma reesei* contributed to this information.

Finally, we had great success in measuring the dynamics of skyrmion lattices in helimagnets. We successfully completed the first demonstration of MISANS at SNS and carried out experiments on a copper-nickel-iron alloy and pluronics using very long wavelengths at PF2, Institut Laue-Langevin, Grenoble, France.

Chemical Reactions in Lithium Air Batteries: Insight from Multiconfiguration Molecular Dynamics

2011-208-N0

Jessica Swanson

Project Description

The goal of this project is to develop a computational framework to describe the complex chemical reactions that occur in energy storage systems, such as the cathodic surface electrolyte interphase (SEI) in lithium-ion and metal air batteries. More broadly, the goal was to establish a foundation for continued efforts in theory, modeling, and simulation of energy storage systems. Although researchers recognize the importance of accurately modeling energy storage devices and have

identified a path toward these capabilities, the computational modeling of these systems has largely been approached from two extremes: calculation of molecular-scale properties for certain cell regions (often in fixed chemical or phase states) and phenomenological study of full-scale devices. Although both approaches have aided in the development of energy storage technologies, a significant gap remains between the studied scales. This gap inhibits the ability of the models to significantly impact the design process. This project addresses the need to incorporate molecular-scale phenomena (e.g., quantum mechanical bond breaking and formation) into multi-scale methods (e.g., multiconfiguration molecular dynamics) to allow thorough investigation of these systems (i.e., explicitly including heterogeneous energy storage materials and capturing free energy processes at temperature).

We identified a pathway to using multi-scale methods to translate chemical complexity into the prediction of experimental observations and to incorporate molecular-scale simulations into the complex mesoscopic scales in energy storage materials (i.e., several to tens of micrometers). This pathway is based on the following three guiding principles: (1) the connection of microscopic information (obtained at the electronic, atomistic, and molecular levels and leading to mechanistic insight) to full cell-level modeling and experimental measurements; (2) the inclusion of realistic system complexity (e.g., electronic transitions and phase transformations coupled to ion intercalation; heterogeneous electrode and interfacial regions resulting in charging layers and spatially dependent, yet coupled, charge transport and chemical transformations); and (3) the identification and design of materials with optimal properties (e.g., stable high-capacity electrodes; stable interfacial compositions that allow ion diffusion but limit electron transport and reactivity; and high-potential electrolytes).

Mission Relevance

The project is relevant to DOE's missions in science and energy. Advances in theory, modeling, and simulation are expected to play a pivotal role in energy storage research. Numerous DOE reports have highlighted the potential for theory to enable transformational breakthroughs in energy storage by providing insight into the complex physical and chemical processes that govern electrochemical systems and by identifying optimal energy storage materials. Researchers have been unable to obtain a clear understanding of the processes that occur in energy storage systems because of the incredible complexity of these systems. Batteries, for example, involve multiple types of matter (crystalline and amorphous solids, polymers, organic liquids, and heterogeneous interfaces) that interact with each other and change rapidly in early charging cycles and gradually over the lifetime of a cell. They are composed of incompletely characterized, heterogeneous materials that undergo unknown phase changes and chemical reactions under non-equilibrium operating conditions. Similar complexi-

ties plague all energy storage systems, from capacitors to flow batteries. Understanding these systems through experimental analysis has been limited by a lack of *in situ* characterization techniques. Gaining the insight needed to understand these processes will demand advances in complementary theoretical and experimental characterization. Ultimately, the theoretical effort will provide transformative predictive capabilities for energy storage device properties and functions.

FY 2011 Results and Accomplishments

This project led to a new line of research focusing on coupled charge transport (i.e., both ion and electron) through the SEI in Li-ion batteries. The focus in this case was on the graphitic anode. Along with experimental characterization, we explored highly ordered pyrolytic graphite (HOPG) with tailored SEI chemistry and developed a multi-scale description to (1) account for the solvation and desolvation of the Li ion explicitly as it crosses the interfacial region, (2) include interfacial heterogeneity, and (3) describe charge transfer and the influence of locally distinct electric fields. We did all of this within a molecular simulation that is capable of sampling statistically reliable thermodynamic and dynamic properties.

We employed the Anderson-Newns semi-empirical Hamiltonian to model charge transport across the SEI. This is a computationally flexible and much more efficient strategy for describing electron transfer in condensed phase systems than *ab initio* simulations. The Anderson-Newns model is being parameterized to reproduce quantum calculations. Similarly, an empirical reactive force field is being developed for the Li cations with the force matching methodology based on quantum calculations. The combination of the Anderson-Newns description of electron transfer and a reactive force field for ion movement will allow for polaron formation, a potentially important facet at the interface. This capability will also be verified with quantum calculations. Model development is ongoing. The final product will be a molecular dynamics methodology that is scalable and thus implementable on the Argonne Leadership Computing Facility.

Improving Catalytic Performance by Applying Electrochemical Control

2011-210-N0

Stefan Vajda

Project Description

This project aims at using an interdisciplinary approach to explore the effect of electrochemical potential on the activity of small cluster-based catalysts supported on novel carbon-based materials. The effort will emphasize the controlled syn-

thesis of atomically precise metal alloy and metal composite clusters by using synthesis techniques developed at Argonne and based on gas-phase physical cluster fabrication. The effort will also include state-of-the-art characterization for the understanding and design of the new materials.

Mission Relevance

This project is relevant to DOE's energy mission. The design of new catalytic materials, including the optimization of their size and composition at the sub-nanometer scale and fine-tuning of their properties via electrochemical potential, represents a fundamental new approach to solving energy-related problems by identifying environmentally friendly and efficient catalysts for the production of fuels and improved energy storage.

FY 2011 Results and Accomplishments

Since project initiation, we performed tests on the reactivity of size-selected cobalt clusters under electrochemical conditions, characterized their chemical composition, and completed initial studies of the stability of clusters at elevated temperatures. As support material for these studies, we chose ultrananocrystalline diamond (UNCD) film of about 100 nm thickness, with the goal of having an (electro)chemically inert support to avoid to the maximum extent any possible reactivity of the support. To ensure that no agglomeration of clusters takes place upon deposition, we deposited $\text{Co}_{27\pm 4}$ clusters at as low as 0.1 monolayer atomic coverage. X-ray absorption spectra revealed that after their exposure to air, the cobalt clusters turned into oxides. Complementary x-ray photon spectroscopy and absorption spectroscopy characterization performed at BESSY and the Advanced Light Source confirmed the oxidized character of the clusters. X-ray scattering data revealed high stability of the clusters; they withstand thermal treatments of several hours' duration without noticeable signs of agglomeration/size change.

Next, the inertness of the UNCD support was tested in an electrochemical cell, under oxygen evolution reaction conditions. Figure 1 shows a practically inert support material in comparison with any other reported or used carbon-based support material. To characterize the activity of the cobalt clusters, two samples were tested: one "fresh" sample that had not yet been used in a reaction and a sample that had been tested for stability at catalytically relevant temperatures. The results are plotted in Figure 2 and show that within measurement error, there is no difference in the activity of the "fresh" and pre-treated samples.

The most important outcome from these initial experiments is to demonstrate the feasibility of performing studies of sub-nanometer-size clusters under electrochemical conditions and at extremely low metal loadings/surface coverage. To the best of our knowledge, these are the first such electrochemical experiments on sub-nanometer-size clusters.

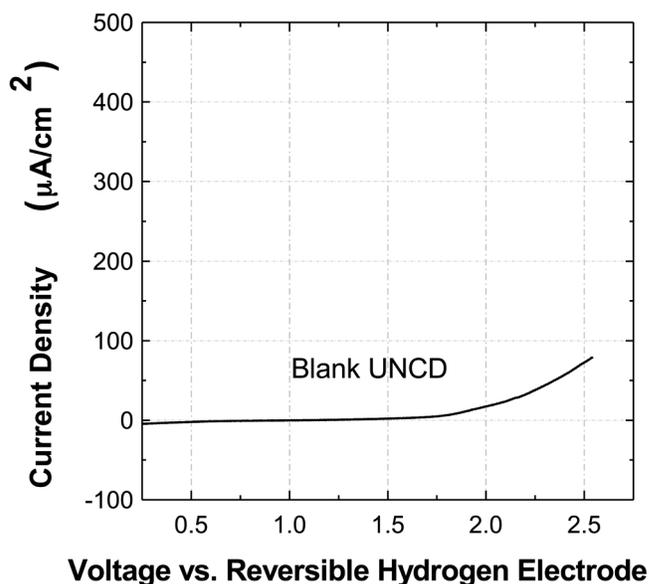


Figure 1. Electrochemical characterization of the UNCD support (without the catalytic cobalt clusters) reveals that it is electrochemically inert, showing only negligible reactivity at the highest voltages applied. (Voltage in units of Volt.)

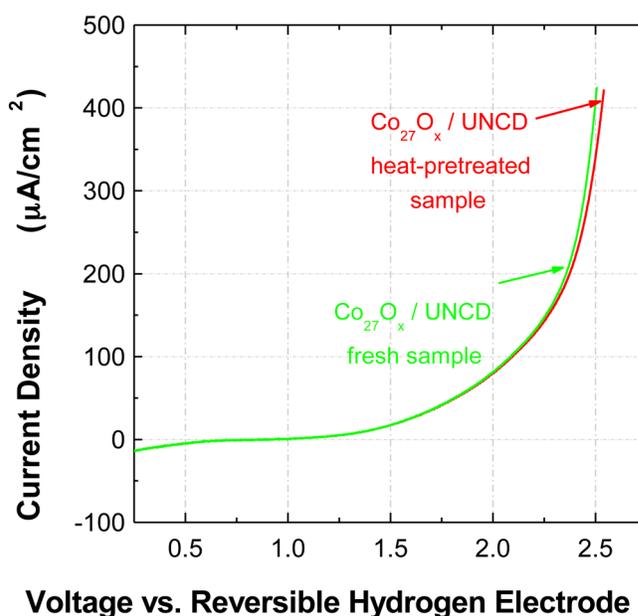


Figure 2. Electrochemical characterization of the UNCD-supported sub-oxide cobalt clusters (red: heat-pretreated sample, green: fresh sample, voltage in units of Volt.). The identical reactivities observed confirm that heat treatment does not affect the size of the sub-nanometer clusters and does not alter their electrochemical activity.

This work resulted in the following invention:

Vissers, D., L. Curtiss, O. Auciello, K. Amine, and S. Vajda, "Materials for Ion Transport," invention report submitted August 2011. [ANL-IN-11-071]

Proposed Work for FY 2012

- ▶ Extend studies to cobalt clusters containing fewer than 27 atoms, including thermal stability of the clusters on various oxides that may later serve as protectants against agglomeration of the clusters in harsh reaction environments.
- ▶ Initiate studies of clusters of other metals, such as nickel and copper.
- ▶ Include the use of chemically modified/structured UNCD supports.

Research and Development of Advanced Energy Storage Methodologies

2011-212-NO

Dieter M. Gruen

Project Description

Materials breakthroughs are required in storage and conversion methodologies to help bring about the large-scale, economical use of sustainable energy sources. Both of these areas can benefit substantially from new research and development efforts in nanocarbon materials. As a result of pioneering work in the field of nanocarbons, which culminated in the discovery of ultrananocrystalline diamond (UNCD) films, we are developing a new class of mechanically and thermally stable, highly electrically conducting nanocarbon materials consisting primarily of hollow polyhedral stacks of 5–7 graphene sheets enclosing volumes of 300–500 cubic nanometers. These unique nanocarbon structures have the potential to function as high-performance cathodes in lithium-air batteries, and so we have measured the storage capacity of this material in a cell. We discovered that the high storage capacity, near 5-kWh/kg carbon, when coupled with the temporally remarkably stable electrochemical potential (3.38–2.8 V), warrants detailed study to enable the optimization of the performance of such cathodes. The considerable challenges that must be overcome to make lithium-air batteries viable include, but are not limited to, controlling the porosity of the electrode for higher storage capacity, designing catalysts for improving the charge and discharge kinetics, developing electrolytes that resist the aggressive chemical environment of the cell and reduce the overpotential, and preventing lithium dendrite formation.

In this project, experiments will yield data on new nanocarbon material, called ultrananocrystalline graphene (UNCG). Specific results will include the clarification of the interrelationship among capacity, discharge current, and voltage, which will enable the optimization of the performance of this

material. In addition, the project will result in high-resolution transmission electron microscopy (HRTEM) characterization as a function of UNCG composition, synthesis conditions, and annealing temperatures. The research is expected to also result in the correlation of (1) the details of the carbon nanostructure with the location, confinement, and composition of the discharge product and (2) the details of the reaction of Li_2O_2 with electrolytes, the carbon support, and with encapsulated catalyst particles. An important outcome of the project will be findings from an evaluation of the stability of various electrolytes, particularly ionic liquid electrolytes, with respect to attack by Li_2O_2 , as well as the identification of electrochemical intermediates and gaseous charging products and the effect of electrolytes on the morphology of electrodeposited lithium. Finally, an important question concerning the use of ionic liquids as electrolytes involves the preservation of high diffusion coefficients, which are compromised by structuring effects due to the presence of lithium ions. Thus, as a result of the proposed research, we expect to gain an understanding of the effect on the overpotential of bringing MnO_2 into more intimate contact with Li_2O_2 by making use of the unique nanostructure of UNCG. This understanding will enable us to maximize the overall efficiency of energy storage in Li-air batteries.

Mission Relevance

The proposed project is relevant to DOE's missions in energy and national security. When coupled with a new generation of electrolytes, bulk nanocarbons are expected to advance the search for high-capacity rechargeable lithium-air batteries. The prosperity and, indeed, the survival of our complex technological civilization depend on the availability of economical energy inputs. In particular, energy in the convenient form of electricity is highly desired and in demand in ever-increasing amounts, and so the project will be of particular interest to several national laboratories that are conducting research and development on sustainable energy efforts in general and on problems related to storage and generation in particular. This project will help to create novel storage materials that are expected to demonstrate breakthrough performance characteristics, which will be of high value to DOE, the nation, and the international community.

FY 2011 Results and Accomplishments

Catalytic synthesis of graphene was found to occur when methane gas reacts with cubic SiC nanopowder at 1,000–1,200 K. The nanoensemble created under these relatively mild experimental conditions consists primarily of cylinders with diameters ranging from 4 to 30 nm with aspect ratios near unity and walls composed of 10–20 layers of graphene surrounding nano-SiC particles. Sputtering by electron irradiation sequentially removes the graphene shells, thus exposing the SiC cores. Electron and x-ray diffraction studies reveal the highly crystalline nature of the graphene shells, which constitute 90 mol% of the ensembles. Raman data support a model

involving growth of graphene on carbon rather than on silicon-terminated SiC. This finding means that in all likelihood, the multilayer graphene cylinders preserve the electronic characteristics of single-layer graphene because rotational faulting decouples the multilayers from each other.

To the degree that structure determines function, one can expect that UNCG will display a high energy storage capacity.

Proposed Work for FY 2012

The reaction rates for the growth of the graphene cylinders will be measured. The data will be used to determine the order of the reaction. The measurements will give us insight into the mechanism of this highly unusual reaction involving a gaseous molecule — methane — decomposing at temperatures far lower than those expected to yield a solid graphene material.

Milestone: Determination of reaction rate and reaction mechanism of methane with nanosilicon carbide at 900°C.



OTHER NOVEL R&D

NEMS-Based Nanosensors for Basic Science Research

2008-195-R3

Daniel López and Derrick 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. These probes are nano-electro-mechanical-systems (NEMS) actuators capable of sub-nanometer 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. This effort will 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. The project is aligned with the DOE mission 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 2011 Results and Accomplishments

The goal of this project is to develop novel NEMS devices to manipulate optical forces in the nanoscale. During the first year of the project, we designed and fabricated a variety of NEMS actuators optimized to detect the Casimir force and near-field plasmonic forces. During FY 2010, a novel nanofabrication process to integrate nanoparticles and nanostructures onto the actuators was developed.

During FY 2011, we optimized the process of integrating nanoparticles onto nanomechanical devices. In parallel, we optimized the optical setup required to detect the light scattered by these nanoparticles. This activity was very time consuming, since detecting the light scattered by 100-nanometer particles required the use of a dark-field microscope, where the background radiation is minimized by several orders of magnitude, the polarization of the incident light is precisely controlled, and the temperature variations are considerably

reduced. After optimization of the optical setup, we measured the scattered spectrum of the static gold nanoparticles for calibration purposes. Subsequently, we measured the scattered spectrum of the nanoparticles incorporated into the actuators. We demonstrated that the optical response of these nanoparticles can be manipulated in a controllable and reproducible manner.

The results obtained during FY 2011 are summarized below:

- ▶ We designed and fabricated NEMS-based actuators capable of nanometer position control of nanostructures.
- ▶ We developed and demonstrated a novel nanofabrication process capable of incorporating nanometer-size structures onto micro-electro-mechanical-systems 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 one nanometer or better.
- ▶ We performed the first optical measurements of the light scattered from these nanometer-size nanostructures.

In addition, we are currently performing real-time manipulation of the optical interaction between these nanostructures.

Explosive Nucleosynthesis of Heavy Elements

2009-035-R2

James Truran, David Chamulak, and Craig 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 envi-

ronments and thereby tested stellar and supernova model predictions; in this way, we have significantly constrained the nature of the earliest stellar populations in the universe. 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 analyze aspects of theory and expand our 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 National Academy of Sciences report, "Connecting Quarks to the Cosmos," which identifies one of the outstanding physics challenges for the new century: *How were the heavy elements from iron to uranium made?* (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.

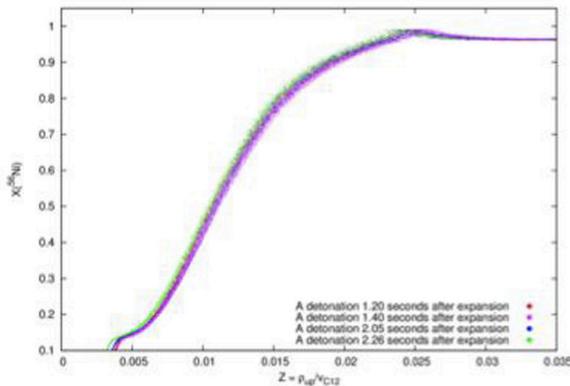
FY 2011 Results and Accomplishments

The project has achieved significant progress in several areas: thermonuclear (Type Ia) supernovae, core collapse (Type II) supernovae, classical novae, and equations of state.

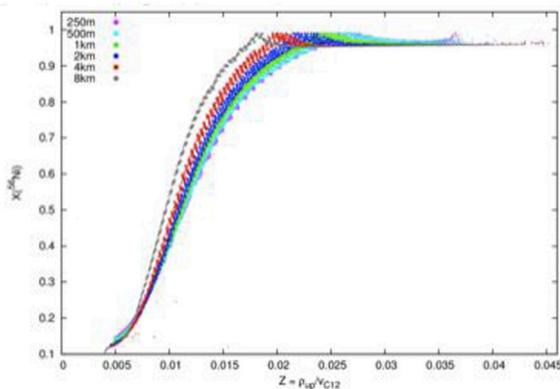
Thermonuclear supernovae. The emphasis of research was on modeling the outbursts of SNe Ia. The significance of these events arises from their brightness at maximum, enabling their use as distance indicators, tied to the powering of their light curves by the production and subsequent decay of ^{56}Ni 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 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 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, and 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 worked with University of Chicago Flash Center researchers to examine the nucleosynthesis implications and constraints for recent hydrodynamic models. We performed one-dimensional, spherically symmetric simulations for six different resolutions (250 m, 500 m, 1 km, 2 km, 4 km, and 8 km). For 500-m resolution, we studied the detonation mechanism for four different ignition conditions. These four conditions differ in the velocity profile of the star at the time of detonation. We obtained different velocity profiles by pulsating the star to mock up the stellar motion during the deflagration phase and then detonating the star at different times. We found that the mass fraction of ^{56}Ni is very tightly related to an empirical variable $Z = \rho_{\text{up}}/v_{12c}$, where ρ_{up} is the mass density immediately upstream of the detonation wave and v_{12c} is the velocity at the end of carbon burning. These fluid variables were obtained from Lagrangian tracer particles that were embedded in the simulations. The mass fraction of ^{56}Ni was obtained from the post-process nucleosynthesis by using the temperature and density histories recorded by the tracer particles. Above $Z \sim 0.005$, which corresponds to the temperature of about 4.5×10^9 K, this relation between ^{56}Ni mass fraction and the empirical variable also appears to be robust for all four different simulations (Figure 1, top). This indicates that in one-dimensional, detonating supernova models, one can predict the final yields of ^{56}Ni without performing post-process nucleosynthesis if both the upstream density and the velocity at the end of carbon burning are known.

Likewise, we find the relation between the ^{56}Ni yields and the empirical variable converges as the resolution increases (Figure 1, bottom). However, the physical descriptions during the supernova explosion are now understood to be more complicated as the new observations show that the explosions occur in non-spherically symmetric forms. Therefore, the verification of this relation in the two- and three-dimensional simulations is imperative. If the behavior of ^{56}Ni yields with the empirical variable, Z , is also valid in the higher-dimensional settings, this would represent a major breakthrough. With this empirical indication, we would be able to estimate the mass fraction of ^{56}Ni with an accuracy of $\sim 10\%$ or less without post-processing the thermodynamic trajectories by the tracer particles to calculate nucleosynthetic yields, which is computationally expensive. Additionally, we would be able to effectively push the resolution of the current multidimensional simulated ^{56}Ni yields from 4 km down to 500 m. The physical interpretation of the variable Z and the possibility that other variables other than the mass density and the velocity might be involved are under investigation. It is also conceivable to extend the scaling relation to the intermediate mass elements, the products of the incomplete nuclear burning, such as ^{28}Si , ^{32}S , ^{36}Ar and ^{40}Ca .



Mass fraction of ^{56}Ni as a function of the ratio of mass density immediately upstream of the detonation wave and the velocity at the end of carbon burning for different initial conditions. A detonation was initiated at different times after the star was led to expand: 1.20, 1.40, 2.05, and 2.26 seconds.



Mass fraction of ^{56}Ni as a function of the ratio of mass density immediately upstream of the detonation wave and the velocity at the end of carbon burning for six different resolutions: 250 m, 500 m, 1 km, 2 km, 4 km, and 8 km. The initial velocity profile is the same for all resolution runs.

Figure 1. (top) Mass fraction of ^{56}Ni as a function of the ratio of mass density immediately upstream of the detonation wave and the velocity at the end of carbon burning for different initial conditions; (bottom) Mass fraction of ^{56}Ni as a function of the ratio of mass density immediately upstream of the detonation wave and the velocity at the end of carbon burning for six different resolutions.

We studied 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 also are working with University of Chicago Flash Center researchers on the nucleosynthesis “post-processing” of the temperature/density trajectories recovered from hydrodynamic models of SNe Ia. The purpose of this aspect of the research is 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.)

We were also concerned with the consequences of the asymmetry on the nucleosynthetic signatures of nearly edge-lit detonations in white dwarf cores. Most of the leading explosion scenarios for Type Ia supernovae involve the nuclear incineration of a white dwarf star through a detonation wave. Several scenarios have been proposed as to how this detonation may actually occur, but the exact mechanism and environment in which it takes place remain unknown. We explored the effects of an off-center initiated detonation on the spatial distribution of the nucleosynthetic yield products in a toy model – a pre-expanded near Chandrasekhar-mass white dwarf. We find that a single near edge-lit detonation results in asymmetries in the density and thermal profiles, notably the expansion timescale, throughout the supernova. We demonstrate that this asymmetry of the thermodynamic trajectories should be common to off-center detonations where a small amount of the star is burned prior to detonation. The asymmetry stems from the fact that in one hemisphere, the propagation direction of the detonation wave is largely in the direction of final (radial) expansion, whereas in the other hemisphere it is largely opposing it. The sensitivity of the yields on the expansion timescale results in an asymmetric distribution of the elements synthesized as reaction products. We tabulate the shift in the center of mass of the various elements produced and find an odd-even pattern for elements past silicon. We find a clear compositional asymmetry, in coordinate as well as in velocity space, in regions of the white dwarf that do not burn to nuclear statistical equilibrium.

Type-Ia simulations by groups worldwide will benefit from the in-depth study of energetics made possible by our involvement. We also worked with the supernova group at The Hebrew University, Jerusalem, on studies of possible signatures of helium detonations in systems in which helium accretion onto carbon-oxygen (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 the ^{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. In particular, we undertook a detailed investigation of the nucleosynthesis processes that are understood to be responsible for the origin of the heavy elements. The r-process continues to represent perhaps the most signifi-

cant challenge to our understanding the synthesis of nucleosynthesis theory. We have as yet neither unambiguously identified the r-process site nor detailed the manner in which it operates. Fortunately, however, observations of metal deficient halo stars provide a means of scrutinizing heavy element ($A > 100$) abundance patterns at a stage of galactic abundance evolution prior to either the realization of high concentrations of iron-peak elements (the lines of which dominate the spectra) or the emergence of any significant s-process element contamination.

Scrutiny of the heavy element patterns in these extreme halo population stars at metallicities below $Z \sim 10^{-2} Z_{\odot}$ reveal three significant features that constrain r-process modelers:

1. The abundances in the mass range from barium to platinum/lead ($138 < A < 210$) are pure r-process products.
2. The r-process patterns in the range ($138 < A < 210$) in these extreme halo stars are *robustly* in accord with the r-process patterns in Solar System matter.
3. There exists a subclass of these r-process enriched halo stars – the actinide “boost” stars – that shares the same robust r-process pattern in the mass range ($138 < A < 210$) but has elevated levels of abundances of iron to uranium under explosive conditions in supernova events and/or thorium relative to Solar System abundances.

We interpret both the 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 the conditions that are required to reproduce the extraordinary robustness of the r-process ($138 < A < 210$) pattern over billions of years of Galactic history and the occurrence of the boost stars as compelling evidence for the role of fission recycling in the r-process. Using the known fission rates, we find that fission can, indeed, impact the abundance levels of the actinides at the levels observed in the boost stars without significantly altering the agreement of the barium-to-platinum r-process pattern with Solar Abundances.

We and colleagues at the University of Chicago also investigated the “neutrino-p process.” In this process, 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 – Breakout. Classical nova explosions are a consequence of thermonuclear runaways in accreted hydro-

gen 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 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 $^{15}\text{O}(\alpha,\gamma)^{19}\text{Ne}$ 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 to thermonuclear runaway of classical novae. The high levels of such elements as carbon, oxygen, and neon in nova ejecta led to the conclusion that these enrichments must be a consequence of dredge-up of core matter into the accreted envelopes. The composition of nova ejecta (nebular shells) predicted by these hydrodynamic studies, when compared with observations, impose important constraints on nova models. In this we seek also an understanding of the mechanism by which the accreted hydrogen envelopes of novae are enriched to 20–30% by mass in C-O-Ne nuclei from the underlying white dwarf. (Such mixing may also hold extremely important implications for some classes of Type Ia supernova models, as well as the brightness distribution of SNe Ia’s in diverse stellar populations, as discussed in the preceding section on supernovae.) Our recent efforts in this regard were concerned with the occurrence of mixing and its effects for white dwarfs in nova binary systems that involve either ONeMg white dwarfs or helium white dwarfs. Since mixing with carbon enhances the hydrogen burning rates dramatically, one should question whether significant enrichment of the ejecta is possible also for other compositions (He, O, Ne) predicted by stellar evolution models. We simulated several non-carbon cases and found significant amounts of those underlying materials in the ejected hydrogen layer. Despite large differences in rates, time scales, and energetics that might distinguish the cases, our results show that the convective dredge-up mechanism predicts significant enrichment in all our non-carbon cases, including helium enrichment in recurrent novae. The results are consistent with observations.

Materials Theory

2009-214-R2

Alexei Abrikosov, Konstantin Matveev, and Michael Norman

Project Description

This project consists of research on (1) the transport properties of quantum wires, (2) local order in transition metal oxides, and (3) fluctuation effects in high-temperature superconductors.

Mission Relevance

This project supports the DOE science mission and, 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). In particular, the work on quantum wires has direct implications for future device technologies. The work on local order supports experimental programs that develop diffuse scattering capabilities at Argonne's Advanced Photon Source (APS) and Oak Ridge's Spallation Neutron Source (SNS). The work on superconductors also addresses science challenges associated with the next-generation energy grid.

FY 2011 Results and Accomplishments

In previous years we explored the effect of equilibration of weakly interacting electrons on transport properties of quantum wires, studied Nernst effect in cuprates above the superconducting transition, and calculated the electronic contribution to the longitudinal and Hall conductivities in the pseudogap phase of cuprates.

Our accomplishments for FY 2011 are described below.

Transport Properties of Quantum Wires: We studied the effect of the equilibration of the electron liquid on the conductance of quantum wires. We considered the regime of arbitrarily strong interactions between the electrons, when their properties are described by the so-called Luttinger liquid theory. We added the effect of equilibration to this theory phenomenologically and found the resulting conductance of a quantum wire as a function of its length and the equilibration rate. The experiment showed that in the limit of a long wire, the correction to the conductance associated with the equilibration processes shows a quadratic dependence on the temperature.

We also developed a theory of the equilibration rate of Luttinger liquids. Unlike previous theories, in which the equilibration was treated microscopically in the limits of either very weak or very strong interactions between electrons, our project focused on a more phenomenological approach valid at

any interaction strength. The resulting equilibration time is expressed in terms of the spectrum of hole-like excitations in the Luttinger liquid. Our expression reproduces previously known limits and enables one to study equilibration for any system with a known excitation spectrum.

Finally, we studied thermal transport in quantum wires. We considered the case of relatively short wires, in which full equilibration does not occur because the backscattering of the electrons is exponentially suppressed. Still, the right- and left-moving electrons can exchange energy, resulting in corrections to the thermal conductance of a quantum wire. We evaluated the correction as a function of the length of the wire. As the wire becomes longer, the relative correction to the thermal conductance becomes quadratic in temperature. Our thermal conductance results illustrate the violation of the Wiedemann-Franz law in interacting electron systems.

Local Order in Transition Metal Oxides: We determined that in the relevant part of the phase diagram where charge ordering could be present, high-temperature superconducting cuprates should exhibit unidirectional (stripe) order, not 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 in checkerboard order. As a function of the interaction potential due to charge order, checkerboard order occurs in a region of the phase diagram between that where stripe order is stable and that where charge ordering with a diagonal wave vector occurs instead. Experiments on cuprates indicated that the real materials are near the phase boundary between stripe and checkerboard order; in fact, checkerboard order was recently proposed as a way to understand the nature of the Fermi surface in underdoped cuprates, as revealed by quantum oscillation experiments.

Fluctuation Effects in High-Temperature Superconductors: The Nernst effect (transverse current response to a magnetic field in the presence of a temperature gradient) is a sensitive test of superconducting fluctuations, and a large Nernst signal has been seen in high-temperature superconducting cuprates, particularly in the pseudogap phase where an energy gap exists above the superconducting transition temperature. We calculated the Nernst effect by generalizing the Gaussian theory for the fluctuational Nernst signal to account for the reduced electronic density of states due to the pseudogap. In our model, the amplitude of the Cooper pairs is fixed in magnitude, but the pairs have a finite relaxation time proportional to temperature. The resulting Nernst signal picks up an extra factor of $1/T^3$ relative to Gaussian theory because of the suppression of the current caused by the pseudogap. This enhanced temperature dependence agrees remarkably well with experimental data on underdoped cuprates.

Multifunctional Polymers for Regulating Membrane Function

2011-202-NO

Millicent A. Firestone

Project Description

The goal of this work is to design and synthesize biologically inspired multifunctional polymers that target selected signal transduction pathways and induced changes in biomembrane structure and function. The main objectives of the proposed work are twofold: (1) to generate synthetic polymers that interact with natural (living) systems in a predictable fashion by regulating natural communication pathways and (2) to harness the fundamental principles of quorum sensing for the dynamic assembly and reconfiguration of materials. Ultimately, this research will help establish the link between synthetic polymer-induced changes in biomembrane physicochemical characteristics and cell biochemistry. If this connection can be successfully made, these findings will represent a significant advance in using synthetic polymers for the inhibition/regulation of chemical communication and signal transduction.

Mission Relevance

This project is relevant to DOE's basic science mission. The research focused 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, basic physical sciences in the synthesis and characterization of bioactive polymers are coupled with life sciences. This scientific effort offers the unique opportunity to advance soft materials research and further enhances the biomolecular materials effort directed at solving energy-related challenges.

FY 2011 Results and Accomplishments

Polymers that regulate quorum sensing or chemical communication between prokaryote cells were synthesized and characterized. Bacterial intercellular communication included detection of the population density/environment via signaling molecules and receptors, resulting in controlled gene expression. The addition of exogenous organo-phosphate was found to regulate the *Pseudomonas* quinolone signal (PQS) biochemical pathway, shifting the behavior of bacteria from that of a lethal pathogen to an indolent colonizer. Moreover, we determined that the method used to add the organo-phosphate is important. Studies directed at understanding the architecture of the polymer carrier of the organo-phosphate were performed.

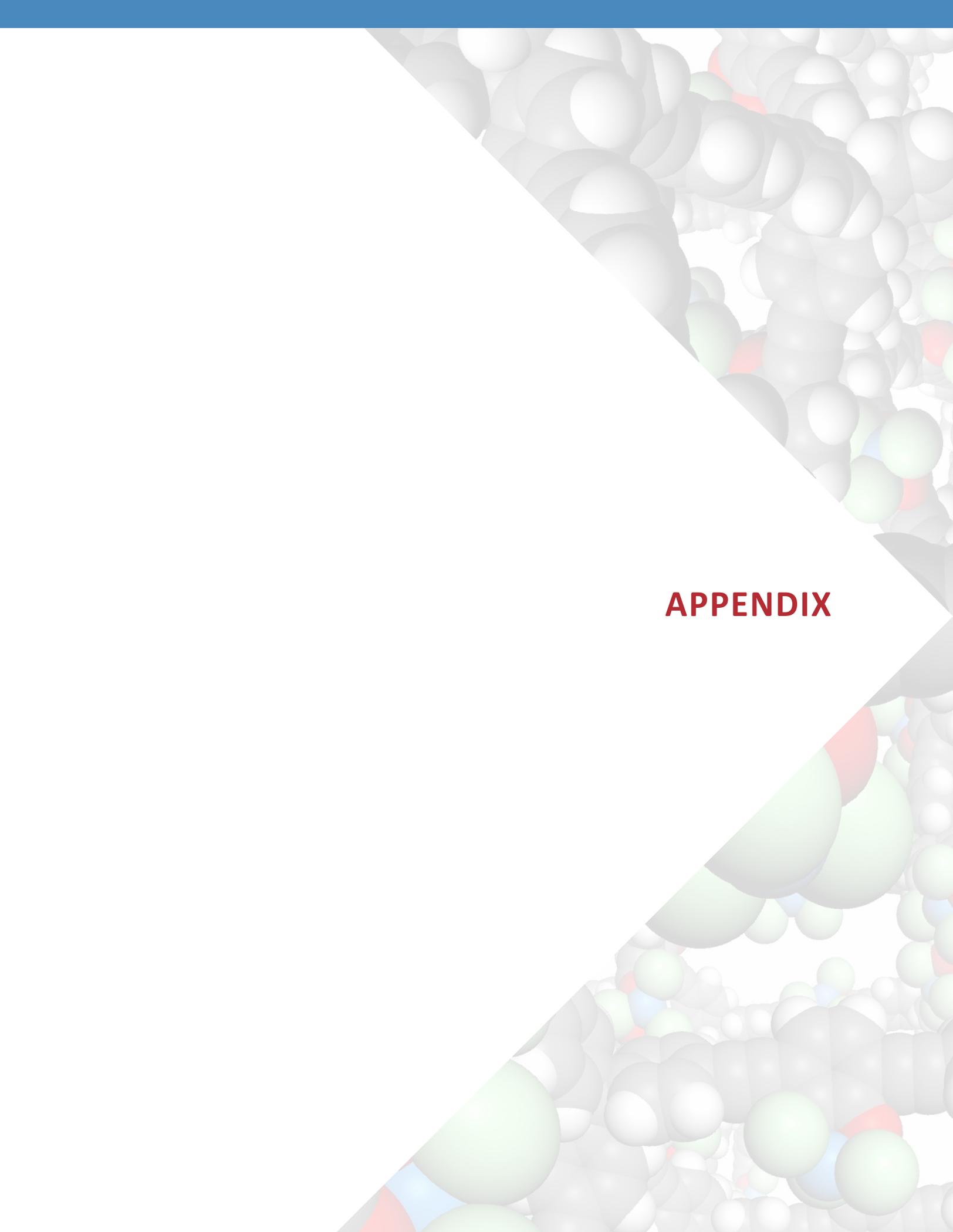
Three phosphate end-derivatized nonionic polymers were synthesized. Specifically, phosphate was successfully added to two poly(ethylene-oxide)-poly(propylene-oxide)-poly(ethylene-oxide) (PEO-PPO-PEO) triblock copolymers — which had previously been determined to associate with model biological membranes through either transmembrane insertion (F88, PEO₁₀₃-PPO₃₉-PEO₁₀₃) or harpoon insertion (F68, PEO₇₅-PPO₃₀-PEO₇₅) — and a diblock PEO-PPO coupled through a bisphenol-A (BPA) linkage. Phosphorous-31 nuclear magnetic resonance (NMR) spectroscopy corroborated the proton NMR findings and was used to determine the amount of phosphate added to the PEO-PPO-PEO.

Small-angle x-ray scattering studies conducted at the Advanced Photon Source indicated that the terminally charged phosphate moieties significantly alter the polymer interactions with model biological membranes (lipid bilayers). Addition of the terminal phosphates on the transmembrane inserted polymer (F88) lessens the steric pressure on the membrane, making the bilayer less rigid. Conversely, the harpoon-associated polymer (F68) carrying phosphate strengthens the steric pressure membrane rigidity. The observed changes in the membrane structure upon addition of the polymeric phosphates correlate well with the observed changes in the biochemical pathways.

Proposed Work for FY 2012

During FY 2012 we will continue with our efforts to reconstitute the chemically modified polymers into model membranes and perform x-ray scattering studies. Electron density analysis of the data will be performed to determine details about polymer-membrane interactions. The analysis procedure will yield near molecular level details of the location and conformational state of the phosphate-modified or phosphate-iron-modified polymers in the bilayer and/or water domains. It is anticipated that these studies will yield insights into the location and accessibility of the end-derivatized chemical moieties. In addition, these studies will provide information on how the modified polymer-membrane association alters the physical characteristics of the bilayer (bilayer stiffness, hydration layer thickness, etc.). Detailed structural analysis is an important component of this research effort, ultimately allowing for structure-function correlations to be made. The fundamental physicochemical studies will be done in parallel with *in-vitro* and *in-vivo* experiments examining the phosphate-modified polymer effectiveness at de-activating bacterial virulence. The multifaceted approach, involving synthesis of tailored polymers and x-ray scattering studies, coupled with *in-vitro* and *in-vivo* experiments, is expected to significantly advance our understanding of how chemically modified polymers influence not only cell membrane structure and properties but also complex biochemical pathways. This component of our research project will serve to establish the link between synthetic polymer-induced changes in biomembrane physico-

chemical characteristics and cell biochemistry. If this connection can be successfully made, these findings would represent a significant advance in using synthetic polymers for the inhibition regulation of chemical communication and signal transduction.



APPENDIX



PUBLICATIONS AND PRESENTATIONS I
(DERIVED FROM LDRD PROJECTS
ACTIVE IN FISCAL YEAR 2011)

Director's Competitive Grants

2009-068-R2

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

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Makowski, L. and J. Lal (2009). "Biomedical Applications of Cellular and Structural Imaging." APS Users' Meeting: Imaging Structural Hierarchy in Biological Systems, Argonne, IL, May 6, 2009.

Makowski, L., J. Lal and R. Harder (2011). "X-ray Coherent Diffraction Imaging of Cellulose Fibrils In-situ." 33rd Annual International IEEE EMBS Conference, Boston, MA, Aug. 30–Sep. 3, 2011.

2009-083-R2

Chien, T.Y. (2010). "Controllable Local Modification of Fractured Nb-doped SrTiO₃ Surfaces." 2010 American Physical Society March Meeting, Portland, OR, Mar. 15–19, 2010.

Chien, T.Y. (2011). "Cross-sectional Scanning Tunneling Microscopy and Spectroscopy of Fractured Oxide Surfaces and Heterostructure Interfaces." American Physical Society March Meeting, Dallas, TX, Mar. 2011.

Chien, T.Y. (2011). "Cross-sectional Scanning Tunneling Microscopy and Spectroscopy of Fractured Oxide Surfaces and Heterostructure Interfaces." New Functional Materials: Synthesis, Properties, and Methods, Manali, Himachal Pradesh, India, Jun. 2011.

Chien, T.Y. (2011). "Probing Complex Oxide Interfaces." SPIE Photonic West, Oxide-based Materials and Devices International Conference, San Francisco, CA, Jan. 2011.

Chien, T.Y. (2010). "Probing Complex Oxide Interfaces." International Workshop on Scanning Probe Microscopy for Energy Applications, Oak Ridge National Laboratory, Sep. 2010.

Chien, T.Y. (2010). "Probing Complex Oxide Interfaces by Cross-sectional Scanning Tunneling Microscopy." 2010 American Physical Society March Meeting, Portland, OR, Mar. 15–19, 2010.

Chien, T.Y. (2011). "Probing Complex Oxide Interfaces." Novel Emergent Phenomena Created by Spatial Confinement, Louisiana State University, Baton Rouge, LA, Oct. 2010.

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Chien, T.Y., J.W. Freeland and N.P. Guisinger "Morphology Control of Fe Films Using Ordered Termination on SrTiO₃ Surfaces." *Appl. Phys. Lett.* **98**: 256102.*

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Freeland, J.W. (2011). "Manipulating Orbital and Magnetic Structure at Oxide Interfaces." Multifunctional Materials 6, Kodiak, Alaska, Aug. 1–4, 2011.

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2009-111-R2

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Vlasko-Vlasov, V., A. Joshi-Imre, J.T. Bahns, L. Chen, L. Ocola and U. Welp (2010). "Liquid Cell with Plasmon Lenses for Surface Enhanced Raman Spectroscopy." *Appl. Phys. Lett.* **96**(20): 203103.*

2009-146-R2

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 (2010). "First Deployment of an Electron Beam Ion Trap at an Advanced Source of Hard X-rays." American Physical Society/ American Association of Physics Teachers Meeting (2010 APS/AAPT), Washington, DC, Feb. 13–17, 2010.

Silver, E., J.D. Gillaspay, P. Gokhale, E.P. Kanter, N.S. Brickhouse, R.W. Dunford, K. Kirby, T. Lin, J. McDonald, D. Schneider, S. Seifert and L. Young (2011). "Work Toward Experimental Evidence of Hard X-ray Photoionization in Highly Charged Krypton." Proceedings of the 21st Int. Conf. on Application of Accelerators in Research and Industry, Fort Worth, TX, Aug. 8–13, 2010. *AIP* **1336**: 146–149.

2009-190-R2

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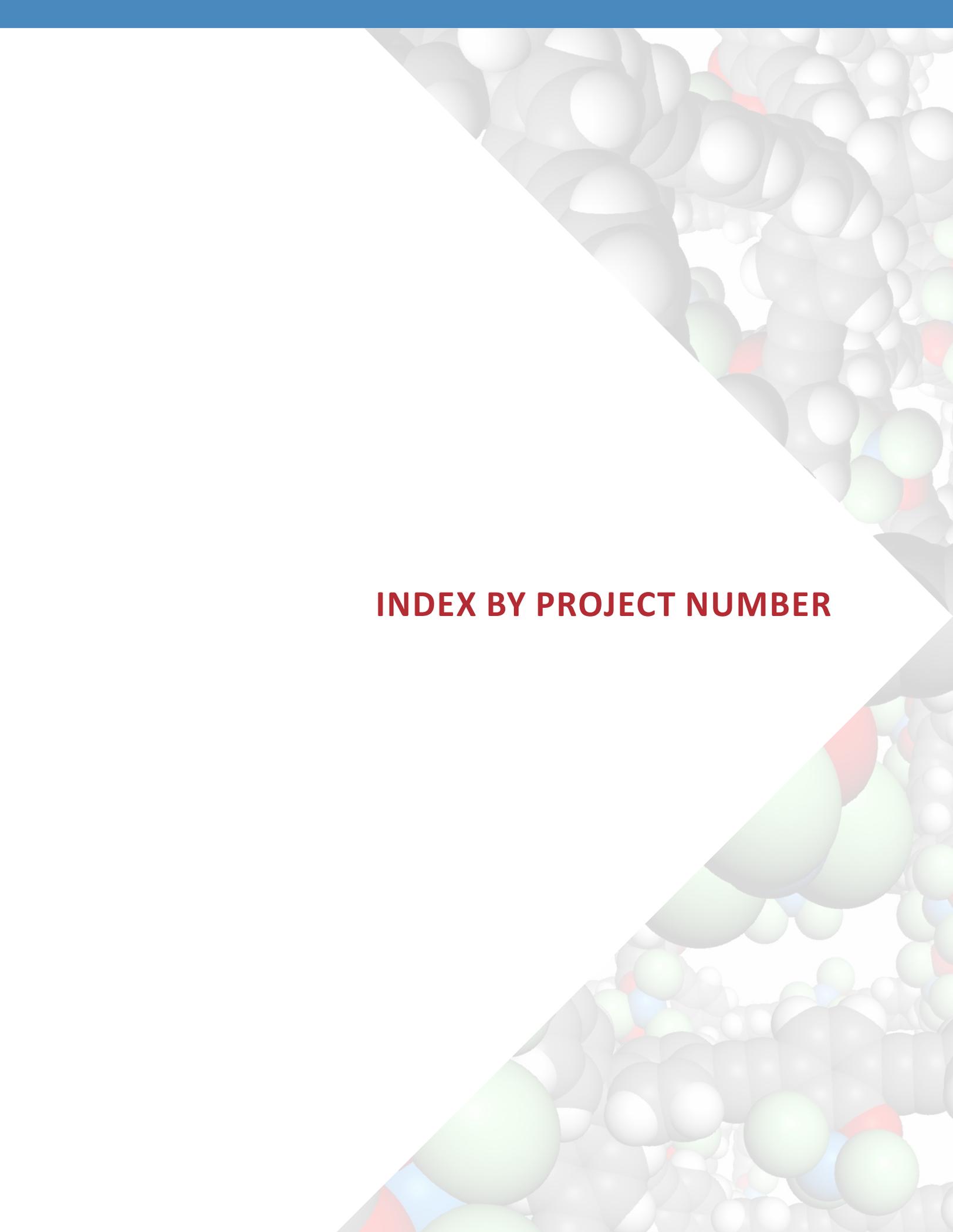
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Welp, Ulrich	2010-010-R1.....	15			
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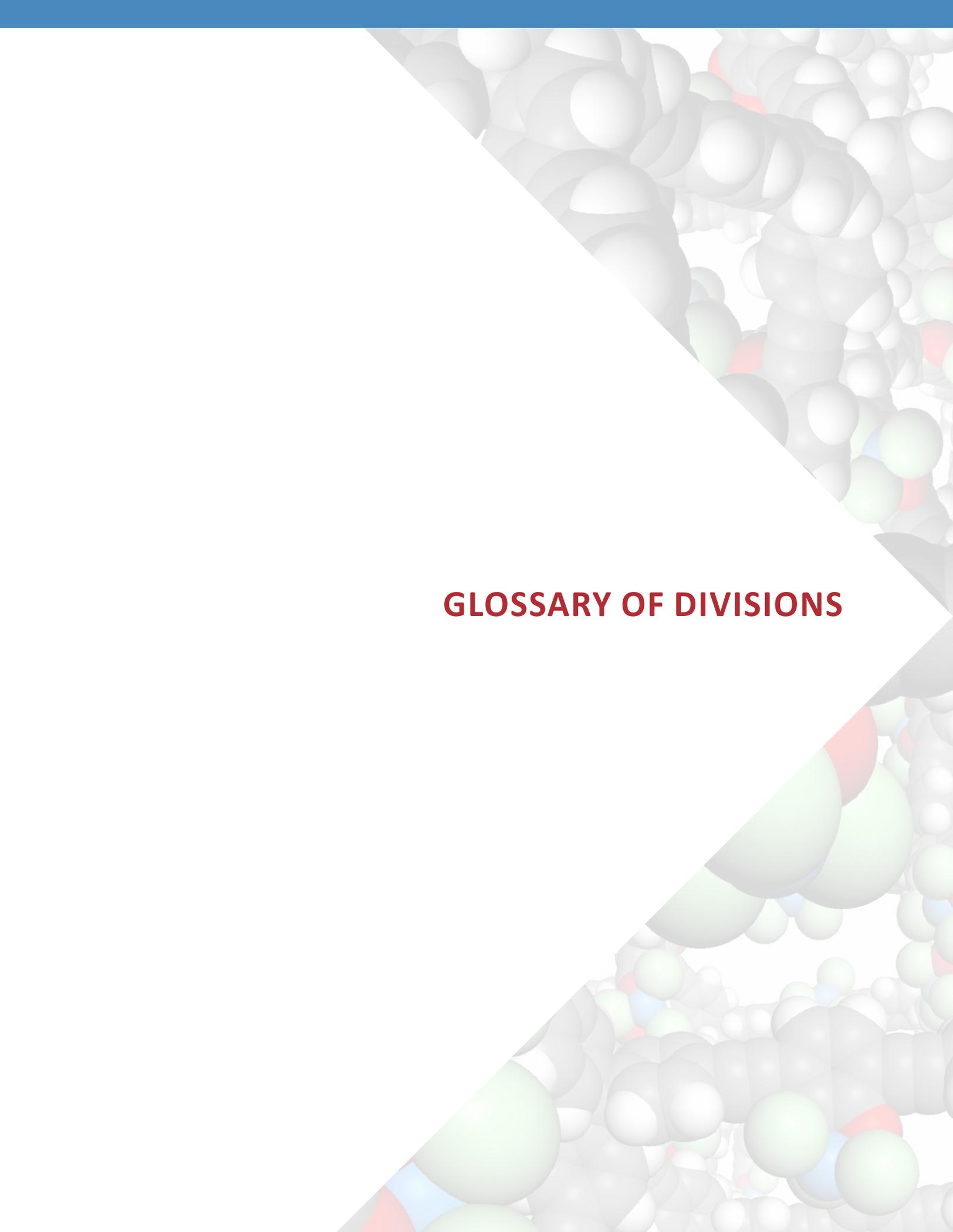
FY 2012 NEW START PROJECTS

FY 2012 New Start Projects

LDRD #	Project Title	Lead Investigator
2012-012-N0	New High-Energy Rechargeable Li Batteries Based on Selenium and Selenium-Sulfur Composite (SexSy) Electrodes	Ali Abouimrane, CSE
2012-015-N0	Mesoscale Elastic Problems	Olle Heinonen, MSD
2012-016-N0	Knowledge Discovery in Microbial Community Composition and Metabolite Turnover Using Satellite Remote Sensing Data	Jack Gilbert, CELS
2012-052-N0	Developing New Ce-Based, High-Efficiency Light-Conversion Phosphors	Guokui Liu, CSE
2012-055-N0	Development of a Close-Packed LaBr ₃ (Ce) Detector Array for Nuclear Physics Applications	Michael Carpenter, PHY
2012-061-N0	Revealing Lithium-Based Battery Performance by in Situ Characterization	Dean Miller, MSD
2012-072-N0	Graphene-Enabled Superlubricity: Vanishing Friction and Wear in Static and Sliding Contacts	Anirudha Sumant, CNM
2012-074-N0	Carbon Flux from Thawing Permafrost: Development of a Predictive Model Linking Microbial Activity and Biogeochemistry with Carbon Metabolism	Julie Jastrow, BIO
2012-082-N0	A Novel Low-Level Software Architecture for Exascale Nodes	Kamil Iskra, MCS
2012-087-N0	Rechargeable Nanofluids Technology for Electrical Energy Storage	Elena Timofeeva, ES
2012-114-N0	Extreme-Scale Electromagnetic Modeling with Nanoscience Applications	Mi Sun Min, MCS
2012-180-N0	Novel Noncarbon Catalyst Support for PEMFCs	Xiaoping Wang, CSE
2012-181-N0	Curing Cancer with the Power of Fireflies	Tijana Rajh, CNM
2012-197-N0	Development of Wavefront-Preserving Mirrors for Extreme-Heat-Load X-ray Beamlines	Ali Khounsary, AES
2012-199-N0	High-Heat-Load Hard-X-ray Monochromators	Al Macrander, XSD
2012-202-N0	Future for Energy-Efficient General-Purpose Computing Based on Heterogeneity	Andrew Chien, MCS
2012-203-N0	Biofuel Chemical Kinetic Experiments to Advance the Modeling of Advanced IC Engine Combustion	Scott Goldsborough, ES
2012-204-N0	Membrane-Bound, Broad-Spectrum, Photo-Driven Protein Devices	Stephan Rosenkranz, MSD

FY 2011 New Start Projects (continued)

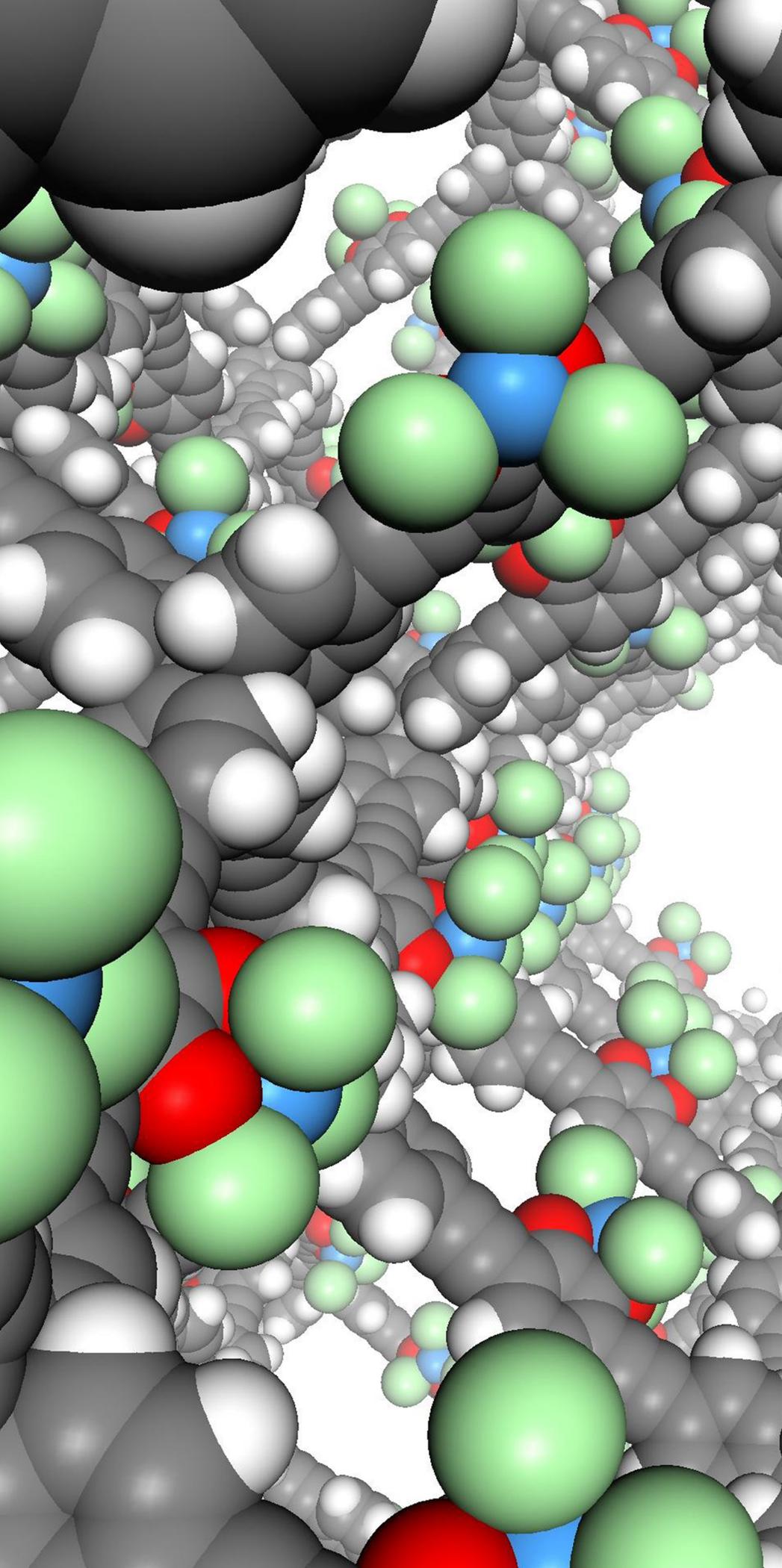
LDRD #	Project Title	Lead Investigator
2012-205-N0	Modeling the Interactions of Biophysical, Biogeochemical, and Microbial Dynamics in Permafrost-Affected Soils: From Pore Scale to Regional Scale	Zhaosheng Fan, BIO
2012-206-N0	Developing, Improving, and Testing Methods for Predicting Spatial and Vertical Distributions of Soil Organic Carbon at Regional Scales	Umakant Mishra, EVS



GLOSSARY OF DIVISIONS

Glossary of Divisions

AES	APS Engineering Support
BIO	Biosciences
CELS.....	Computer, Environment, and Life Sciences
CNM	Center for Nanoscale Materials
CSE	Chemical Sciences and Engineering
ES	Energy Systems
EVS	Environmental Sciences
MCS.....	Mathematics and Computer Science
MSD	Materials Science
PHY.....	Physics
XSD.....	X-ray Sciences



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