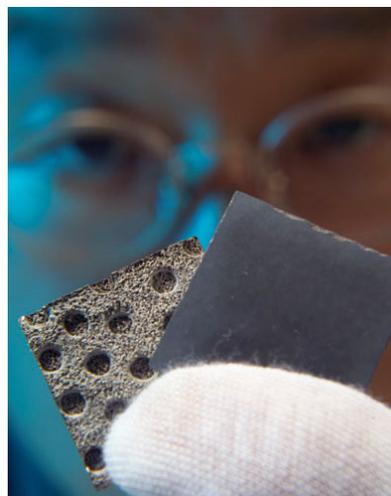


Chemical Engineering Division Annual Technical Report 2002



Chemical Engineering Division
Engineering Science Innovation



Argonne National Laboratory

This tiny rechargeable battery (left) powers a BION® microstimulator (right) that can be implanted near target nerve areas to help patients with a variety of medical conditions, including stroke, Parkinson's disease, and urinary urge incontinence. The battery chemistry, which is key to the system, was developed by the Chemical Engineering Division and the University of Wisconsin.

The Chemical Engineering Division is studying the copper-chlorine thermochemical cycle, in which chemicals are combined with water and heated to cause chemical reactions that produce hydrogen (and oxygen) at 500°C—a temperature compatible with current power plant technologies. The chemicals are not consumed, and are recycled in a closed system.

A revolutionary process developed by Argonne's Chemical Engineering Division could enhance the storage options for economically disposing of thousands of tons of spent nuclear fuel now in temporary storage at commercial nuclear power plants across the United States. In one step, the technology converts spent commercial fuel, which is a ceramic oxide, into a metallic form for processing with Argonne's pyroprocessing technology. This technology can greatly reduce the amount of waste that needs disposal in a repository.

The Chemical Engineering Division has developed a unique solid oxide fuel cell design that holds great promise for use as auxiliary power units in tractor-trailers. Such units would provide electricity for operational needs, such as cargo refrigeration, and comfort, such as cabin heating and cooling. The key is the TuffCell's innovative metal-supported design, which provides easy fabrication and high mechanical strength at a cost considerably lower than current SOFC designs.

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2002

Chemical Engineering Division
Annual Technical Report

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April 2003

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Introduction

The Chemical Engineering Division is one of eight engineering research divisions within Argonne National Laboratory, one of the U.S. government's oldest and largest research laboratories. The University of Chicago oversees the laboratory on behalf of the U.S. Department of Energy (DOE). Argonne's mission is to conduct basic scientific research, to operate national scientific facilities, to enhance the nation's energy resources, and to develop better ways to manage environmental problems. Argonne has the further responsibility of strengthening the nation's technology base by developing innovative technology and transferring it to industry.

The Division is a diverse early-stage engineering organization, specializing in the treatment of spent nuclear fuel, development of advanced electrochemical power sources, and management of both high- and low-level nuclear wastes. Although this work is often indistinguishable from basic research, our efforts are directed toward the practical devices and processes that are covered by Argonne's mission. Additionally, the Division operates the Analytical Chemistry Laboratory; Environment, Safety, and Health Analytical Chemistry services; and Dosimetry and Radioprotection services, which provide a broad range of analytical services to Argonne and other organizations.

The Division is multidisciplinary. Its people have formal training as ceramists; physicists; material scientists; electrical, mechanical, chemical, and nuclear engineers; and chemists. They have experience working in academia; urban planning; and the petroleum, aluminum, and automotive industries. Their skills include catalysis, ceramics, electrochemistry, metallurgy, nuclear magnetic resonance spectroscopy, and petroleum refining, as well as

the development of nuclear waste forms, batteries, and high-temperature superconductors.

Our wide-ranging expertise finds ready application in solving energy and environmental problems. Division personnel are frequently called on by governmental and industrial organizations for advice and contributions to problem solving in areas that intersect present and past Division programs and activities.

Currently, we are engaged in the development of several technologies of national importance. Included among them are:

- Advanced lithium-ion and lithium-polymer batteries for transportation and other applications,
- Fuel cells, including the use of an oxidative reformer and gasoline as the fuel supply,
- Stable nuclear waste forms suitable for storage in a geological repository, and
- Aqueous and pyrochemical processes for the disposition of spent nuclear fuel.

Our programs in basic science are engaged in smaller research projects, such as catalysis, hydrogen production, and superconductivity, that have the potential to impact future energy systems.

The Division also serves as a source of technical support for national security, radiochemical analysis and characterization, and other areas requiring specialized expertise.

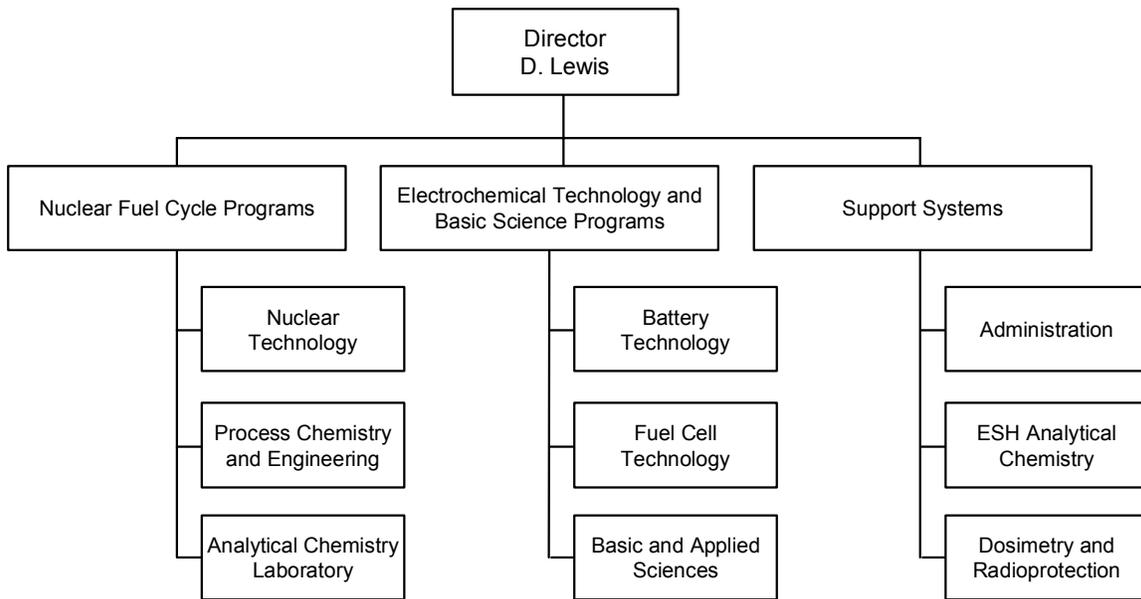
During fiscal year 2002, CMT had an annual operating budget of approximately \$36 million.

Introduction

Of that, 83% was from DOE and the remainder from other government agencies and private industry. The level of full-time staffing during the past year was 175 full-time, and 35 part-time.

Displayed below is an organization chart of the Division. A complete organization chart appears at the end of this report.

In this annual report we present an overview of the technical programs together with representative highlights. The report is not intended to be comprehensive or encyclopedic, but to serve as an indication of the condition and status of the Division.



Batteries

Rechargeable lithium batteries have become very popular as power sources for consumer electronic devices, because of their high energy density (the energy that can be obtained per unit of weight or volume) relative to nickel cadmium and nickel metal hydride batteries. Cellular telephones, digital cameras, camcorders, laptop computers, and other electronic devices currently use high-energy lithium-ion batteries. Due to their success in these applications, they have been under development for other applications such as energy storage devices for electric vehicles, hybrid electric vehicles, and specialty battery applications, since the mid-1990s.

Transportation: A Historical Perspective

The Chemical Engineering Division (the Division) has been involved in the development of advanced lithium batteries for transportation applications since 1994. Our early work was on lithium-polymer batteries, which employ metallic lithium negative electrodes, a polyethylene oxide solid electrolyte, and a metal oxide positive electrode. This technology was being developed for use in electric vehicles (EVs) under a cooperative research and development agreement, or CRADA, with 3M Corporation and Hydro-Quebec. The U.S. Advanced Battery Consortium (comprising DaimlerChrysler, Ford Motor Company, and General Motors Corporation) and the U.S. Department of Energy (DOE) sponsored this research and development (R&D) from 1994 to 2001. Under this program, the Division provided technical support in three main areas: electrochemical characterization and modeling of advanced cell designs, testing and evaluation of prototype hardware, and the development of advanced electrode materials.

In 1998, the Division helped DOE to organize and initiate a new multi-national-laboratory R&D program on high-power lithium-ion batteries. Lithium-ion batteries employ a liquid or gel-polymer electrolyte and lithium insertion compounds in both the positive and negative electrodes. The development of high-power lithium-ion batteries for hybrid electric vehicle (HEV) application was begun under the Partnership for a New Generation of Vehicles (PNGV) Program. This program was a federal government/U.S. auto industry partnership to develop low-emission full-size passenger vehicles with an 80-mile-per-gallon fuel economy. The PNGV Program focused on the development of HEVs, which employ an energy storage device to level the load on the prime power source and recapture regenerative braking energy. The new multilaboratory R&D program, denoted the Advanced Technology Development (ATD) Program, was initiated to assist PNGV industrial developers of high-power lithium-ion batteries overcome the barriers of life, abuse tolerance, and cost for this promising technology. The ATD Program covers a broad range of R&D activities associated with understanding the mechanisms that limit life and

Chemical Engineering Division Battery R&D

Transportation (Hybrid/Fuel-Cell Electric Vehicles)

- Understand life and safety limiting mechanisms
- Develop novel materials and advanced cell chemistries to enhance power, life, and safety, while reducing cost
- Develop innovative approaches for reducing battery cell packaging costs

Specialty Applications

- Develop long-life secondary batteries for biomedical applications
- Initiating R&D on high-energy secondary batteries for military and space applications

Batteries

abuse tolerance, as well as evaluating and developing advanced materials that are designed to overcome these limitations, while simultaneously reducing material costs. It also involves the development of novel approaches for reducing cell packaging costs.

Transportation Research Today

In 2002, the PNGV Program was replaced by a new auto industry/federal government partnership, denoted the FreedomCAR Partnership. It expands on the PNGV Program, with a long-term focus on the development of fuel cell electric vehicles (FCEVs), while it continues to support the development of HEV technologies in the nearer term. DOE's ATD Program continues to address the high-power lithium-ion battery needs for HEV applications and is initiating similar R&D support in the development of high-power lithium-ion batteries for use in FCEVs. The Division continues work under the FreedomCAR Partnership and the ATD Program.

Additionally, the Division conducts longer-range, but focused, research on advanced materials for lithium batteries. These longer-range research activities seek to develop novel new materials that can enhance the performance, life, and/or safety of advanced lithium batteries, while reducing cost. In recent years, a new family of intermetallic negative electrode materials was discovered, as was a new family of layered metal oxide positive electrode materials. We continue our efforts to develop optimal electrode compositions.

Specialty Applications

The Division works collaboratively with industry on rechargeable lithium batteries for specialty applications. In a major project funded by the Department of Commerce, National Institute of Standards and Technology, Advanced Technology Program, the Division is under contract to the industrial leader of the project to develop advanced cell chemistries for long-life rechargeable lithium microbatteries. The microbatteries will be used as the power

source in an injectable microstimulator implant known as a BION®.

These microstimulators will be used to treat patients suffering from stroke, epilepsy, urinary incontinence, eyelid droop, sleep apnea, and other conditions involving impaired nerves and/or muscles. The primary cell chemistry involves a new polymer electrolyte that has high ionic conductivity at room temperature, while the back-up chemistry employs a more conventional long-life liquid electrolyte system.

The Division plans to initiate new battery R&D projects with the goal of developing more optimal secondary lithium batteries for use in other specialty applications. These applications include long-life high-energy portable power sources for military and space applications.

The Division operates the Electrochemical Analysis and Diagnostics Laboratory, which was established by DOE to conduct independent evaluations of advanced battery systems for applications such as EV, HEV, FCEV, and stationary energy storage. This facility has been cited as a valuable resource by battery users, developers, and DOE program managers, who must evaluate and make choices regarding competing battery technologies and research directions. Since it was established more than two decades ago, the laboratory has tested more than 4,000 cells and batteries, ranging from individual 4-Wh cells to 50-kWh batteries, representing numerous technologies and battery developers. The test facility has expanded to include the testing and evaluation of fuel cell stacks and fuel cell systems up to 50 kW.

For More Information

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High-Power Lithium-Ion Batteries for Transportation

Safer, longer-lived and less costly batteries for hybrid electric vehicles

Batteries are an essential component of the hybrid electric vehicle (HEV) systems currently under development internationally for light-duty transportation applications. Although a few production HEVs have been introduced into the automotive market, no current battery technology has demonstrated an acceptable combination of efficiency, calendar life, safety, and cost for large-scale commercialization of HEVs.

As part of the FreedomCAR Partnership between the U.S. Department of Energy (DOE) and the major automobile manufacturers, Argonne's Chemical Engineering Division (the Division) and four other DOE laboratories are conducting research and development to help industrial battery developers reduce the cost and enhance the calendar life and inherent safety of high-power lithium-ion HEV batteries. Our approach is to develop longer-life and safer high-power cell chemistries, that employ low-cost materials; incorporate them into sealed cells; conduct well-defined thermal abuse and accelerated aging tests on the cells; and then employ a suite of sophisticated diagnostic tools and techniques to identify the main factors that control life and abuse tolerance. The diagnostic results are used by the Division to identify and develop more optimal materials and cell chemistries for this high-power application.

This year we developed a low-cost cell chemistry that offers a 44% reduction in material costs compared with our second-generation baseline cell chemistry.

2002 Research Highlights

During 2002, we completed most of the accelerated aging of second-generation baseline cells (their chemistry is shown in Table 1). Also, many new and aged second-generation cells underwent detailed diagnostic evaluations.

Table 1. Chemistry Incorporated in Second-Generation Baseline Cells

Component	Material
Anode	92 wt% MAG-10 graphite 8 wt% PVDF binder
Cathode	84 wt% $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ 4 wt% SFG-6 graphite 4 wt% carbon black 8 wt% PVDF binder
Electrolyte	1.2M LiPF_6 in EC:EMC (3:7)

PVDF = polyvinylidene fluoride, EC = ethylene carbonate, EMC = ethyl methyl carbonate

Additionally, we identified several advanced materials that seem to offer cost, life, and safety advantages over those that were used in our second-generation baseline cells.

Data from accelerated aging tests indicate that the second-generation cells exhibit a much slower rate of power fade than our first-generation cells; however, the rate is still too high. The 5% Al dopant appears to have partially stabilized the positive electrode, but it remains the major source of impedance rise in cells that underwent accelerated aging (see Fig. 1).

Electrochemical transport modeling indicates three possible causes: (a) preferential isolation of small active particles, (b) surface films, and/or (c) oxide surface layers on the electrochemically active particles. Extensive diagnostic studies show evidence of (a) and (b). Figure 2 shows that surface films are formed during the initial formation cycle and then change their chemical nature during aging. Also, the second-generation chemistry exhibits inadequate thermal abuse characteristics, as determined by differential scanning calorimetry and accelerating rate calorimetry studies.

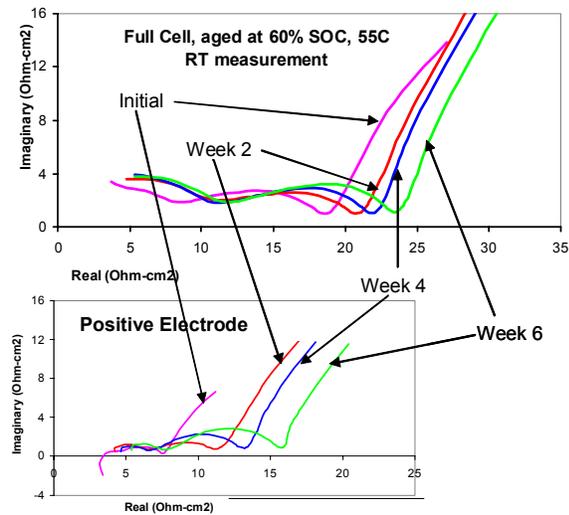


Fig. 1. Electrochemical impedance spectroscopy on cells with reference electrodes show that the cathode interface is the main source of impedance rise during aging.

During the past year, Division researchers identified a low-cost cell chemistry that employs a $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ spinel cathode as the system that offers the most promise for simultaneously meeting the FreedomCar performance, life, safety, and cost goals. The main components of this cell chemistry are: (a) a carbon-coated round-edge natural graphite anode, (b) the spinel cathode, and (c) a lithium bis-oxoborate salt in a PC-based electrolyte solvent system. The Division's battery-level cell-winding materials cost model indicates that this cell chemistry offers a 44% reduction in material costs compared with the second-generation chemistry. A portion of the cost savings results from the higher rate capability of the spinel cathode, which allows the use of a smaller-capacity cell and reduces the quantities of all materials used in the cell windings. Also, at \$7.40 per kg, spinel is the lowest-cost cathode material.

The Division is working with the Army Research Laboratory and Idaho National Engineering and Environmental Laboratory to develop an optimal solvent system for a new low-cost (\$33 per kg) lithium bis-oxoborate salt. This salt does not form HF in the presence of water, as does LiPF_6 , thereby suppressing Mn^{2+} dissolution and extending the life of cells that use $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ spinel cathodes. Finally,

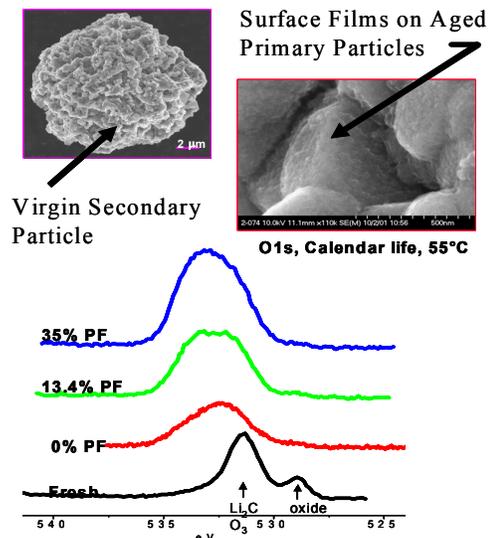


Fig. 2. High-resolution transmission electron microscopy images show surface films form on cathode particles and x-ray photoelectron spectroscopy shows these polymeric films change in their chemical composition with aging.

the use of low-cost (\$10 per kg) carbon-coated round-edge natural graphite allows the use of a low-cost (\$16 per L) PC-based electrolyte solvent system. This chemistry also exhibits thermal abuse characteristics superior to those of our second-generation cell chemistry.

This research is funded by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, FreedomCAR and Vehicle Technologies Office. Other participating DOE laboratories are Brookhaven, Idaho National Engineering and Environmental, Lawrence Berkeley, and Sandia National Laboratories.

Research Participants

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Advanced Electrode Materials for Lithium-Ion Batteries

Finding new materials to optimize electrochemical reactions

Materials play a key role in the development of advanced lithium-ion batteries for transportation and other special applications. The Chemical Engineering Division conducts long-range research aimed at the development of novel new materials that can enhance the performance, life, and safety of lithium batteries while reducing cost. In recent years, the Division has discovered several new intermetallic negative electrode materials and modified layered metal oxide positive electrode systems. We are continuing our efforts to develop these materials—and to discover new ones—to provide optimal electrode compositions and performance that developers require in lithium-ion batteries.

2002 Research Highlights

Layered lithium metal oxides LiMO_2 ($M = \text{Co}, \text{Ni}, \text{Mn}$) and LiMn_2O_4 (spinel) have been widely studied as positive electrodes for lithium-ion cells. These cells are assembled in the discharged state to avoid safety problems and the inconvenience of handling charged and highly reactive electrode materials, such as a lithiated graphite negative electrode or a delithiated lithium metal-oxide positive electrode. When assembled in the discharged state, all of the lithium that is transported between the positive and negative electrodes during charge and discharge is initially contained in the positive electrode. On the initial charge of a lithium-ion cell, some of the lithium that is deposited at the graphite electrode reacts irreversibly with various electrolyte components in the cell: the organic solvent, such as ethylene carbonate or dimethyl carbonate; a component of the electrolyte salt, such as a fluoride ion derived from LiPF_6 ; and trace amounts of water. These reactions form a passive protective layer on the lithiated graphite particles, preventing further reaction between the lithiated graphite electrode and the electrolyte. Consequently, the lithium trapped in the protective layer is unavailable for further electrochemical reaction

and cannot be transported back to the delithiated $\text{Li}_{1-x}\text{CoO}_2$ electrode during discharge, which results in an irretrievable capacity loss from the lithium-ion cell. It stands to reason that positive “over-discharged” electrodes, which contain an excess of lithium, can be used to compensate for the capacity loss of lithium-ion cells, particularly the loss that occurs on the initial charge/discharge cycle. Our research has focused on finding new materials with a surplus of lithium that can be used sacrificially during the initial charge of lithium-ion cells.

As part of our investigations of $x\text{LiMO}_2 \bullet (1-x)\text{Li}_2\text{M}'\text{O}_3$ “composite” electrodes with layered structures, we have discovered that when $M = \text{Mn}$ and Ni , and $M' = \text{Ti}$, the electrodes deliver substantial capacity not only at high voltage (4.3–3.5 V) but also at low voltage (2.0–1.25 V) as shown for $x = 0.95$ in Figure 1. The electrochemical reactions are fully reversible; they provide a high electrode capacity of >250 mAh/g. X-ray absorption spectroscopy (XAS) data of the starting electrode [which can be written in layered notation as $\text{Li}(\text{Mn}_{0.46}\text{Ni}_{0.46}\text{Ti}_{0.05}\text{Li}_{0.02})\text{O}_2$] for $x = 0.95$ showed that the manganese and nickel oxidation

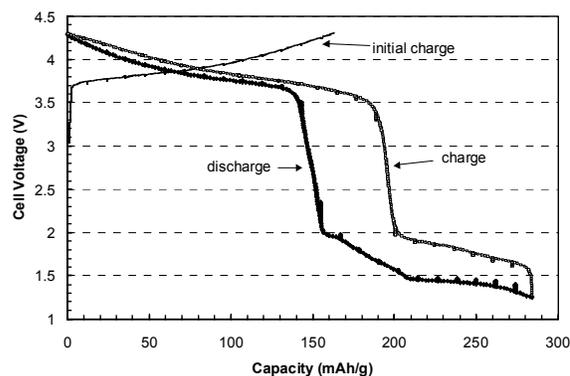


Fig. 1. Charge/discharge profile of $\text{Li}/\text{Li}(\text{Mn}_{0.46}\text{Ni}_{0.46}\text{Ti}_{0.05}\text{Li}_{0.02})\text{O}_2$ cell at 50°C between 4.3 and 1.25 V. When $M = \text{Mn}$ and Ni , and $M' = \text{Ti}$, the electrodes deliver capacity at both high (4.3–3.5 V) and low voltage (2.0–1.25 V).

states are predominantly 4^+ and 2^+ , respectively; it was presumed that the titanium ions are tetravalent. It has been established from a combination of *in situ* XAS and x-ray diffraction data that lithium extraction is accompanied predominantly by the oxidation of Ni^{2+} to Ni^{4+} and that lithium insertion is accompanied by the reduction of Mn^{4+} to Mn^{2+} . The apparent absence of any significant amount of the Jahn–Teller ions, Ni^{3+} and Mn^{3+} , during charge and discharge is believed to be a factor that contributes to the excellent structural and electrochemical stability of these electrodes. Of particular significance is the process that occurs at low voltage, during which a first-order transition occurs to yield a layered Li_2MO_2 structure from the parent LiMO_2 electrode. This finding demonstrates that for some electrodes, the layered MO_2 framework can remain stable over a very wide compositional range and voltage window.

In layered LiMO_2 structures, such as LiCoO_2 , LiNiO_2 and $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$, the lithium and M ions occupy the octahedral sites in adjacent layers of the cubic-close-packed (ccp) rock-salt structure (Fig. 2a). By contrast, in Li_2MO_2 structures, the oxygen ions are arranged in a hexagonal-close-packed (hcp) array; the M ions are located in all the octahedral sites of one layer, whereas the Li ions are located in all the tetrahedral sites of adjacent layers (Fig. 2b). Therefore, the transition from a layered LiMO_2 structure to layered Li_2MO_2 necessitates (1) insertion of one Li per formula unit, (2) displacement of the lithium ions from their octahedral positions to neighboring tetrahedral sites, and (3) concomitant shear of the ccp oxygen layers to hcp stacking. Although this crystallographic transformation appears straightforward, a high cell impedance associated with the $\text{LiMO}_2 - \text{Li}_2\text{MO}_2$ transition implies that the transformation is kinetically hindered. In this respect, the presence of any manganese or nickel ions in the lithium layers of the parent $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ structure would severely restrict the transition from occurring, because a lithiated hcp $\text{Li}_2\text{Mn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ structure (which is derived from an imperfect

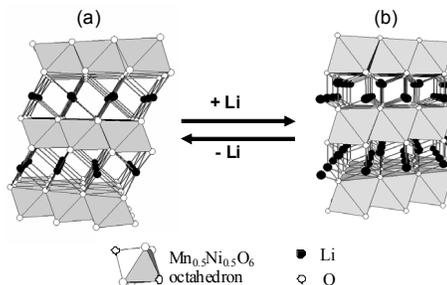


Fig. 2. Illustrations of (a) layered LiMO_2 structure and (b) layered Li_2MO_2 structure (M = Mn, Ni).

$\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ structure) would require the simultaneous occupation of the edge-shared tetrahedra in the Li-rich layer by Li^+ ions and Mn^{2+} - or Ni^{2+} ions, which would be energetically unfavorable. In Li_2MnO_2 , the $\text{Li}_{(\text{tet})}-\text{Li}_{(\text{tet})}$ distance is only 2.177 Å. Our conclusion is that a perfectly layered LiMO_2 structure, which we believe might be obtained with a composition such as $\text{Li}(\text{Mn}_{0.46}\text{Ni}_{0.46}\text{Ti}_{0.05}\text{Li}_{0.02})\text{O}_2$, would be more likely to facilitate the formation of a Li_2MO_2 structure than one containing some transition metal ions within the lithium layers. In this respect, it is well known that layered LiNiO_2 and LiMnO_2 structures tend to contain a small amount of nickel and manganese in the Li layers.

The identification of new layered Li_2MO_2 electrodes in which the MO_2 framework is stable to lithium extraction therefore holds promise for their exploitation as lithium reservoirs for lithium-ion cells that operate at higher potential.

This research is funded by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, and Office of Science.

Research Participants

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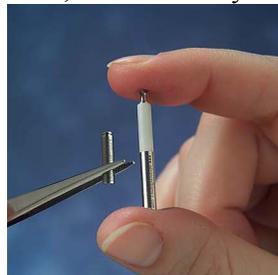
High-Energy Batteries for Biomedical and Specialty Applications

New materials enable tiny, long-lived rechargeable batteries to do big jobs

Lithium-ion batteries are of interest to developers of many types of consumer and biomedical devices. Biomedical devices, in particular, could be powered by rechargeable lithium-ion batteries, but the limited calendar life and inherent safety limitations of current lithium-ion batteries prevent their use in this application. A more chemically stable system is needed, and one alternative is a lithium battery that employs a solid polymer electrolyte.

Implantable microstimulators powered by long-life, rechargeable lithium-ion batteries offer hope for victims of stroke, Parkinson's disease, epilepsy, urinary urge incontinence, eyelid droop, and many other conditions involving muscular impairment. An estimated 7 million Americans suffer from conditions that could benefit from treatment with muscle microstimulators. Muscle function can be restored in such patients by a programmable electronic implant called a BION®.

In collaboration with several partnering organizations, the Chemical Engineering Division (the Division) has developed a tiny, long-lived rechargeable lithium-ion battery system to power BIONs (manufactured by Advanced Bionics). Our partners are Quallion LLC, the University of Wisconsin, the Alfred E.



for the battery.

The expertise that has enabled Division researchers to develop the remarkable microbattery is being applied to the development of high-energy rechargeable batteries for other

Mann Foundation, Lithchem International and Valtronic USA. Our research has focused on development of the polymer electrolyte and cathode material

applications, including consumer and military use.

2002 Research Highlights

Advanced polymer electrolyte: Working with Quallion and the University of Wisconsin, the Division has developed a new poly(ethylene oxide) grafted siloxane polymer for use in long-lived batteries. These siloxane-based polymers are superior to any other polymers with respect to their chemical and thermal stability, resistance to oxidation and reduction reactions, and low toxicity.

We recently isolated a new siloxane phase with an ionic conductivity of near 10^{-3} Scm^{-1} at room temperature, when used with lithium bis-trifluoromethane sulfonyl imide salt (see Fig. 1). The conductivity of this polymer, which is similar to that of conventional liquid organic electrolytes used in lithium ion batteries, is the highest ever reported for any polymer electrolyte. Also, this polymer is nonflammable and exhibits outstanding electrochemical stability up to 5.2 V (see Fig. 2).

The polymer closest to this in performance oxidizes at 3.5 V, limiting the choice of cathode materials to low-voltage VO_x . The large voltage

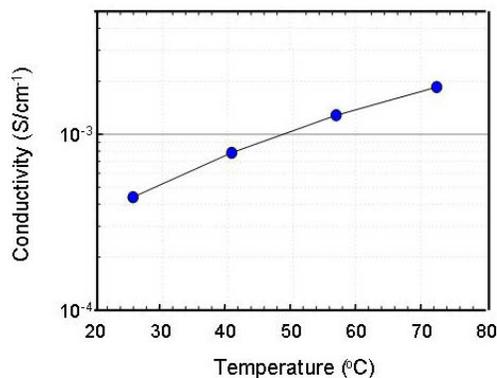


Fig. 1. Lithium ion conductivity of siloxane polymer with temperature—the highest reported for any polymer electrolyte.

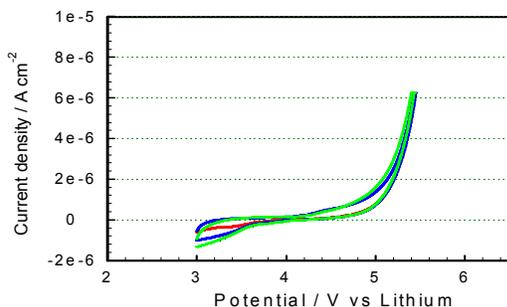


Fig. 2. Cyclic voltamogram showing the outstanding electrochemical stability of siloxane up to 5.2 V. This polymer is nonflammable.

stability window of the siloxane polymers (high resistance to oxidation and reduction) offers the opportunity to use state-of-the-art high capacity density layered cathode materials that offer ≥ 250 mAh/g capacity density at 4.5 V. Furthermore, a preliminary safety study, using accelerated rate calorimetry of the viscous liquid siloxane in the presence of metallic lithium, shows very minor reactions taking place at very high temperatures (360°C) (see Fig. 3). Conventional organic liquid electrolytes, mixed with metallic lithium, show a series of exothermic reactions at low temperature (150°C) that are orders of magnitude higher than those observed with siloxane, indicating that this polymer is very stable thermally and should provide the safety and long life needed in batteries for implantable medical devices. The high ionic conductivity of this polymer also makes it a viable candidate for other applications such as satellites, consumer electronics, and smart cards.

Advanced cathode materials: Lithium-ion batteries with layered $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ as the

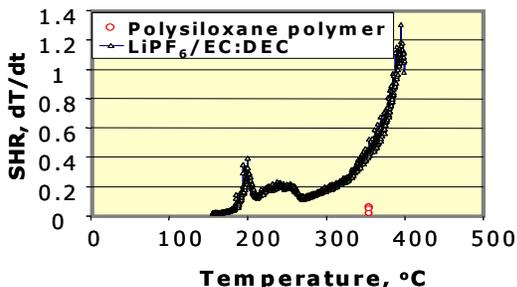


Fig. 3. ARC data showing the limited reactivity of lithium metal with siloxane and $\text{LiPF}_6/\text{EC}:\text{DEC}$ electrolyte.

cathode material have higher energy density than other secondary batteries. However, this cathode material exhibits significant capacity fade, due to its high surface reactivity with the organic electrolytes and the well-known phenomenon of divalent nickel displacement to the lithium sites. The displaced divalent nickel causes rapid capacity fade by blocking the path for lithium ions to shuttle into and out of the cathode, resulting in a corresponding large irreversible capacity loss.

The Division is developing a new cathode material based on the olivine LiFePO_4 . This olivine is more stable in the presence of the electrolyte and safer than the more conventional $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ system. However, the olivine material is insulating and the Division has been investigating new methods for improving its conductivity. Preliminary results have shown improvement in capacity and excellent cyclability at relatively high rates (Fig. 4).

This research is funded under the National Institute of Standards and Technology, Advanced Technology Program.

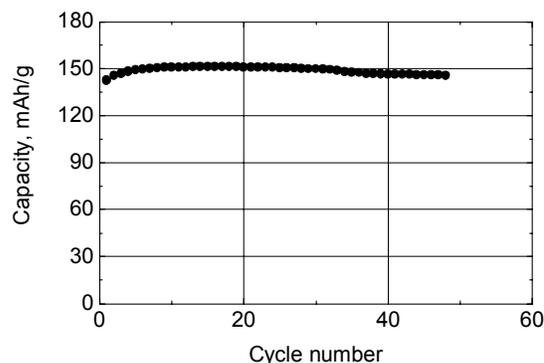


Fig. 4. Capacity density vs. cycle number for discharges at 37°C using carbon-coated olivine LiFePO_4 .

Research Participants

Khalil Amine, Ilias Belharouak, Gary L. Henriksen, Bookeun Oh, Sang Young Yoon, and Donald R. Vissers. For more information, contact Khalil Amine (630-252-3838, amine@cmt.anl.gov).

Battery Testing and Evaluation

Providing standardized, independent evaluations of advanced batteries

The Electrochemical Analysis and Diagnostics Laboratory (EADL) in the Chemical Engineering Division has been providing battery developers with reliable, independent, and unbiased performance evaluations of their cells, modules, and battery packs since 1976. These evaluations have been performed for the U.S. Department of Energy (DOE), government and industry consortia, and industrial developers to provide insight into the factors that limit the performance and life of advanced battery systems. Recently, our capabilities have expanded to fuel cell testing (see “Fuel Cell Testing and Evaluation” in the Fuel Cells section of this report).

The EADL is an extensive facility designed to test large numbers of both small and large batteries and fuel cells designed within and outside of Argonne National Laboratory. It is now the only known facility with capabilities to conduct 120 concurrent advanced battery studies under operating conditions that simulate electric-vehicle (EV), electric-hybrid vehicle (HEV), utility load-leveling and standby/uninterruptible power source applications. Each battery is independently defined, controlled and monitored to impose charging regimes and discharge load profiles that simulate the types of dynamic operating conditions found during actual use. The testing of groups of cells/batteries is controlled by computers that communicate over high-speed networks with central servers and are controlled by other PC workstations.

The EADL has evaluated many different battery technologies, such as Na/S, LiAl/FeS, LiAl/FeS₂, Li/polymer, Li-ion, Zn/Cl₂, Zn/Br₂, Ni/Fe, Ni/Zn, Ni/MH, Ni/Cd, and Pb-acid. These represent technologies from battery developers throughout the world.

2002 Research Highlights

In our HEV work with Li-ion batteries, we characterized and tested prototype lithium-ion batteries made under DOE’s Advanced Technology Development Program. At present, lithium-ion technology exhibits exceptional power capability and long cycle life, but very poor calendar life. One of the goals for this project is to gain an understanding of the effect of cell chemistry on calendar life. For this work, two cell chemistries were used; the cell chemistry differed in the composition of the cathode. Group A cells contained a LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ cathode and Group B, LiNi_{0.8}Co_{0.15}Al_{0.10}O₂. Accelerated calendar life tests were used at 45°C (Groups A and B) and 55°C (Group A only) at 60% state of charge (SOC).

Initially, the average C/25 capacities for groups A and B were 1.03 ± 0.03 and 0.97 ± 0.02 Ah, respectively. As the cells age, the C/25 capacity fades. The capacity fade data were plotted as a function of $t^{1/2}$, yielding straight lines with reasonable values of regression coefficients, r^2 (see Fig. 1). From the graph, we can infer that the rate of C/25 capacity fade for both groups of

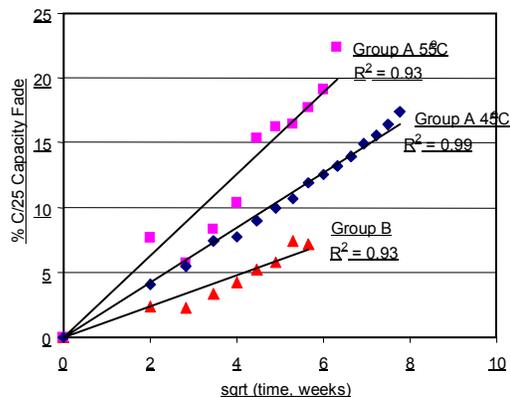


Fig.1. % C/25 capacity loss vs. square root of time.

Batteries

cells followed $t^{1/2}$ kinetic laws at both test temperatures and that the capacity fade rate of Group B cells is less than that of Group A cells.

The initial average area specific impedance (ASI) values at 60% state of charge were 28.41 ± 1.36 and 34.68 ± 2.77 m Ω for Groups A and B, respectively, and these values changed with time during the experiment. Figure 2 shows the change in average ASI values with time.

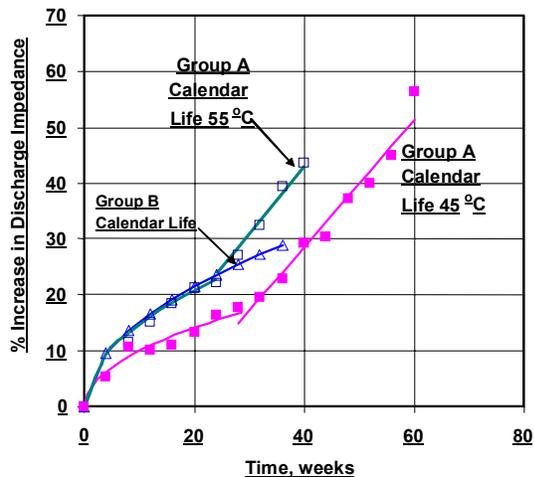


Fig. 2. % increase in discharge impedance as a function of time for Groups A and B.

The impedance rise was sensitive to the Al concentration. At 45°C, the Group B cells displayed higher overall impedance rise and power fade at 45°C than the Group A cells. The time dependence of the impedance rise in Group A displayed two distinct kinetic rate laws; the initial portion depended on $t^{1/2}$ and the final, t . At about 36 weeks, the rate law for impedance increase in Group B was simpler and depended only on $t^{1/2}$. While the higher Al content decreased capacity fade, it was detrimental to the cell impedance.

The EADL was established by DOE's Office of Energy Efficiency and Renewable Energy, FreedomCAR and Vehicle Technologies Office.

Research Participants

Ira D. Bloom, Daniel J. Andrekus, Scott A. Jones, Edward G. Polzin, Benjamin G. Potter, and Carl E. Webster. For more information, contact Ira Bloom (630-252-4516, bloom@cmt.anl.gov; visit our web site at <http://www.cmt.anl.gov/facilities/eabl.shtml>).

Selected Publications and Presentations

Journal Articles, Books, and Book Chapters

- Surface Changes on $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ Particles during Testing of High-Power Lithium-Ion Cells
D. P. Abraham, R. D. Twisten, M. Balasubramanian, I. Petrov, J. McBreen, and K. Amine
Electrochem. Commun. **4**, 620–625 (2002)
- An Accelerated Calendar and Cycle Life Study of Li-ion Cells
I. Bloom, B. W. Cole, J. J. Sohn, S. A. Jones, E. G. Polzin, V. S. Battaglia, G. L. Henriksen, C. Motloch, R. A. Richardson, T. Unkelhaeuser, D. Ingersoll, and H. L. Case
J. Power Sources **101**, 238–247 (2001)
- Symmetric Cell Approach Towards Simplified Study of Cathode and Anode Behavior in Lithium-Ion Batteries
C. H. Chen, J. Liu, and K. Amine
Electrochem. Commun. **3**(1), 44–47 (2001)
- Low-Cost Flexible Packaging Materials
A. N. Jansen, K. Amine, A. E. Newman, D. R. Vissers, and G. L. Henriksen
J. Mater. **54**(3), 29–32 (2002)
- The Role of Li_2MO_2 Structures (M = Metal) in the Electrochemistry of $(x)\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2 \bullet (1-x)\text{Li}_2\text{TiO}_3$ Electrodes for Lithium-Ion Batteries
C. S. Johnson, J.-S. Kim, A. J. Kropf, A. J. Kahaian, J. T. Vaughey, and M. M. Thackeray
Electrochem. Commun. **4**, 492–498 (2002)
- Layered $\text{Li}(\text{Ni}_{0.5-x}\text{Mn}_{0.5-x}\text{M}'_{2x})\text{O}_2$ ($\text{M}' = \text{Co}, \text{Al}, \text{Ti}; x = 0, 0.025$) Cathode Materials for Li-ion Rechargeable Batteries
S.-H. Kang, J. Kim, M. E. Stoll, D. P. Abraham, Y. K. Sun, and K. Amine
J. Power Sources **112**, 41–48 (2002)
- Layered $x\text{LiMO}_2 \bullet (1-x)\text{Li}_2\text{M}'\text{O}_3$ Electrodes for Lithium Batteries: A Study of $0.95\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2 \bullet 0.05\text{Li}_2\text{TiO}_3$
J.-S. Kim, C. S. Johnson, and M. M. Thackeray
Electrochem. Commun. **4**, 205–209 (2002)
- A Comparative Study on the Substitution of Divalent, Trivalent, and Tetravalent Metal Ions in $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$ ($\text{M} = \text{Cu}^{2+}, \text{Al}^{3+}, \text{and Ti}^{4+}$)
J. Kim and K. Amine
J. Power Sources **104**, 33–39 (2002)
- The Effect of Tetravalent Titanium Substitution in $\text{LiNi}_{1-x}\text{Ti}_x\text{O}_2$ ($0.025 \leq x \leq 0.2$) System
J. Kim and K. Amine
Electrochem. Commun. **3**, 52–55 (2001)

Batteries

An *In-Situ* X-Ray Absorption Spectroscopy Study of InSb Electrodes in Lithium Batteries

A. J. Kropf, H. Tostmann, C. S. Johnson, J. T. Vaughey, and M. M. Thackeray
APS Forefront **1**, 113–116 (2001)

Papers Presented at Scientific Meetings

Nanocomposite Based Coatings and Films

D. J. Chaiko

Presented at the Polymers, Laminations, Adhesives, Coatings & Extrusions (PLACE)
Conf., Boston, MA, September 8–12, 2002

The Colloid Chemistry of Organoclays

D. J. Chaiko

Presented at the SAMPE Conf.: Polymer Nanocomposites, Long Beach CA,
May 12–16, 2002

Diagnosis of Power Fade Mechanisms in High-Power Lithium-Ion Cells

D. P. Abraham, J. Liu, C. H. Chen, Y. E. Hyung, M. Stoll, and K. Amine

Presented at the 11th Int. Meeting on Lithium Batteries, Monterey, CA June 23–28, 2002

New Polysiloxane Polymer Electrolyte for Lithium Batteries

K. Amine, B. Oh, Y. Hyung, D. R. Vissers, R. West, and H. Tsukamoto

Presented at the 10th Power Source Meeting, Cherry Hill, NJ, June 10–13, 2002

LiNi_{0.5}Co_{0.5}O₂ as a Long-Lived Positive Active Material for Lithium-Ion Batteries

I. Belharouak, H. Tsukamoto, and K. Amine

Presented at the 11th Int. Meeting on Lithium Batteries (1MLB), Monterey, CA,
June 23–28, 2002

An Investigation of the Resistance Rise and Power Fade in High-Power Li-ion Cells

I. Bloom, S. A. Jones, V. S. Battaglia, G. L. Henriksen, C. Motloch, J. Christophersen, J. Belt,
R. Wright, R. Jungst, H. Case, and D. Doughty

Presented at the 19th Seminar and Exhibit on Primary and Secondary Batteries,
Fort Lauderdale, FL, March 11–14, 2002

Flame-Retardant Additives for Lithium-Ion Batteries

Y. E. Hyung, D. R. Vissers, and K. Amine

Presented at the 11th Int. Meeting on Lithium Batteries, Monterey, CA, June 23–28, 2002

Structural and Electrochemical Evaluation of (1-x)Li₂TiO₃•(x)LiMn_{0.5}O₂ as an Electrode Material for Lithium Batteries

C. S. Johnson, J.-S. Kim, A. J. Kropf, A. J. Kahaian, J. T. Vaughey, and M. M. Thackeray

Presented at the 11th Int. Meeting on Lithium Batteries, Monterey, CA, June 23–28, 2002

Comparative Study of $\text{Li}(\text{Mn}_{0.5-x}\text{Ni}_{0.5-x}\text{M}'_{2x}(\text{O}_2 (\text{M}'=\text{Mg,Al,Co,Ni,Ti}; x=0,0.25)$ Cathode Materials for Rechargeable Lithium Batteries

S.-H. Kang, J. Kim, Y. K. Sun, and K. Amine

Presented at the 11th Int. Meeting on Lithium Batteries (IMLB), Monterey, CA, June 23–28, 2002

The Electrochemical Behavior of $x\text{LiNiO}_2 \bullet (1-x)\text{Li}_2\text{RuO}_3$ and $\text{Li}_2\text{Ru}_{1-y}\text{Zr}_y\text{O}_3$ Electrodes in Lithium Cells

G. J. Moore, C. S. Johnson, and M. M. Thackeray

Presented at the 11th Int. Meeting on Lithium Batteries (IMLB), Monterey, CA, June 23–28, 2002

Status of Aging and Life Analyses of Generation 2 Advanced Technology Development Lithium-Ion Cells

C. G. Motloch, J. P. Christophersen, R. B. Wright, C. D. Ho, I. Bloom, S. A. Jones,

V. S. Battaglia, R. Jungst, H. Case, R. A. Sutula

Presented at the 19th Int. Seminar on Primary and Secondary Batteries, Ft. Lauderdale, FL, March 11–14, 2002

New Interpenetrating Network-Type Poly(siloxane-g-ethylene oxide) Polymer Electrolyte for Lithium Battery

B. Oh, D. R. Vissers, Z. Zhang, R. West, H. Tsukamoto, and K. Amine

Presented at the Int. Meeting. on Lithium Batteries, Monterey, CA, June 23–28, 2002

Alternative Anode Materials for Lithium-Ion Batteries: A Study of Ag_3Sb

J. T. Vaughey, L. Fransson, H. A. Swinger, K. Edström, and M. M. Thackeray

Presented at the 11th IMBL Meeting, Monterey, CA, June 23–28, 2002

Using Raman Microscopy and Diffraction Space Mapping Techniques to Explore Epitaxy, Strain and Twinning in $\text{Mba}_2\text{Cu}_3\text{O}_{7-x}$ Coated Conductor Embodiments

K. Venkataraman, A. J. Kropf, C. U. Segre, Q. Jia, S. R. Foltyn, A. Goyal, A. K. Cochran,

S. Chattopadhyay, and V. A. Maroni

Presented at the Mater. Res. Soc. Int. Workshop on Processing and Applications of Superconductors, Gatlinburg, TN, August 1–2, 2002

Fuel Cells

Fuel cells continue to be viewed as a significant new power source for transportation applications, including vehicle traction power as well as auxiliary power for the vehicle's hotel and accessory loads such as air conditioning/heating, mobile office, navigation, and entertainment. Under the FreedomCAR Partnership involving the major U.S. automobile manufacturers and the U.S. Department of Energy, fuel cells are a central technology to be developed and commercialized for automotive applications.

Fuel cells are also being developed for residential and distributed stationary power generation, often for combined heat and power applications. The U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy (DOE/EE), has recently been restructured into eleven offices, of which the Office of Hydrogen, Fuel Cells, and Infrastructure Technologies brings together all of DOE/EE's programs in hydrogen (production, distribution/fueling infrastructure, end-use applications, and on-board storage) and fuel cell technology development efforts. We are working closely with that Office, and with the DOE/Fossil Energy's SECA (Solid state Energy Conversion Alliance) program, to help develop materials, processes, and systems for fuel cells in a variety of applications.

While hydrogen is being pursued as the ideal energy carrier in the long term, the near-term use of fuel cells to power automobiles and residential/distributed power generators will require the use of gasoline and other conventional (natural gas, diesel) or alternative (methanol, ethanol, propane, bio-diesel) fuels. In the near term, therefore, fuel cell systems will need fuel processors to convert the available fuel to hydrogen or a hydrogen-containing gas mixture.

The development of catalysts, processes, and reactor designs for fuel processing is a significant portion of our fuel-cell-related research and development. For effective use of such fuel processors in fuel cell systems, and for the effective use of fuel cell systems in the desired varied applications, system integration, startup, and dynamic response are key issues that are being addressed by our fuel cell systems design and analysis activities, working with staff from Argonne's Nuclear Engineering Division.

Chemical Engineering Division Fuel Cell R&D

- Development of catalysts, processes, and reactor designs for fuel processing using conventional fuels
- Diesel reforming for use with solid oxide fuel cells
- Development of new polymer electrolyte materials for fuel cells
- New alloy materials for metallic interconnects in solid oxide fuel cells

Other research and development activities in the Chemical Engineering Division's Fuel Cell Department include the development of new polymer electrolyte materials for use in fuel cells that operate at 120–150°C that are of interest in transportation and stationary power generation; diesel fuel reforming for use in solid oxide fuel cells; new alloy materials for metallic interconnects for these solid oxide fuel cells operating at 650-800°C; and a novel, metal-supported solid oxide fuel cell and stack concept that offers the potential to be thermally and mechanically rugged and of lower cost in materials and fabrication processes. We are collaborating with three university teams to address some of the materials and chemical processing issues.

Fuel Cells

For More Information

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technology/fuelcells/](http://www.cmt.anl.gov/science-technology/fuelcells/)

Fuel Processor Engineering

Making the transition to hydrogen-powered fuel cells

Successful deployment of fuel cell power will be contingent upon the ability to economically produce hydrogen at or near the point of consumption. For the near term, it is anticipated that the hydrogen will be produced either on-board the vehicles from liquid fuels such as gasoline, ethanol, etc., or at distributed plants from natural gas, propane, or petroleum-derived fuels. The objective of this work is to evaluate, develop, and define innovative approaches to engineering implementation of fuel processor technologies, and ultimately to transfer the technology to the private sector.

2002 Research Highlights

Transient heat transfer studies of monoliths: During the startup of a fuel processor, heating up of the catalysts and containment hardware is by heat transfer from a hot gas to a cold solid surface. We are using experimental measurements and computational fluid dynamics (CFD) to characterize the primary transient heat transfer processes during startup and to help define and evaluate component designs and operating conditions. Figure 1 shows that the modeled (solid) and measured (dotted) thermal responses of a monolith block initially at 23°C to hot air flow are in close agreement. The test reactor and the CFD modeling can be used to evaluate other catalyst structures and reactor geometries.

Diesel reforming in a multi-kilowatt autothermal reformer (ATR): This work is addressing the technical challenges in an engineering-scale demonstration of sustained high conversions of diesel fuel and its constituents. Because of the difficulty of vaporizing the fuel, a liquid injection nozzle has been designed to operate with the requisite feed rates of diesel, air, and steam. In the first step of the investigation, specific components of commercial diesel fuels have been tested, such as paraffins (dodecane and hexadecane), aromatics (xylene and

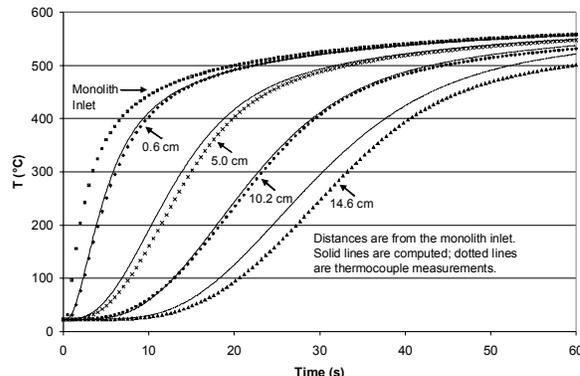


Fig. 1. The CFD model and experimental observations agree closely for the heatup of a monolithic catalyst structure during fuel processor startup.

methylnaphthalene), and naphthene (t-butyl cyclohexane). The effects of varying the oxygen-to-carbon (O/C) and the steam-to-carbon (H₂O/C) ratios on the extent and efficiency of fuel conversion have been examined. The ATR reactor achieved stable operation with nearly complete fuel conversion and excellent H₂ and CO yields with varying fuel input rates, as shown in Figure 2. The different diesel components could be reformed with good efficiency; however, the needed O/C and H₂O/C were different, as was the tendency to form carbon deposits during the ATR reaction.

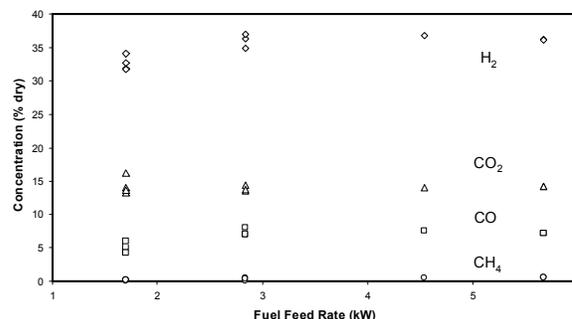


Fig. 2. The ATR reactor shows stable performance for the reforming of hexadecane, a major constituent of diesel fuels, with varying fuel feed rates.

Integrated fuel processor: As part of our effort to transfer technology to the private sector, we have established a cooperative research and development agreement with H2fuel LLC of Mount Prospect, Illinois, to develop a commercially viable version of our compact and efficient fuel processor. A 12.5-kWth (for a 5-kWe fuel cell) nominal capacity, 23-cm dia by 42-cm tall integrated fuel processor (ATR, sulfur removal, and water-gas shift) is being tested in our laboratory. The processor recently concluded 2,300 hours of continuous operation with commercial-grade natural gas. Figure 3 shows the stable product composition during the test, while Figure 4 shows the reforming efficiency as a function of fuel processing rate. The fuel processor is presently being tested for liquid fuels, including ethanol and gasoline.

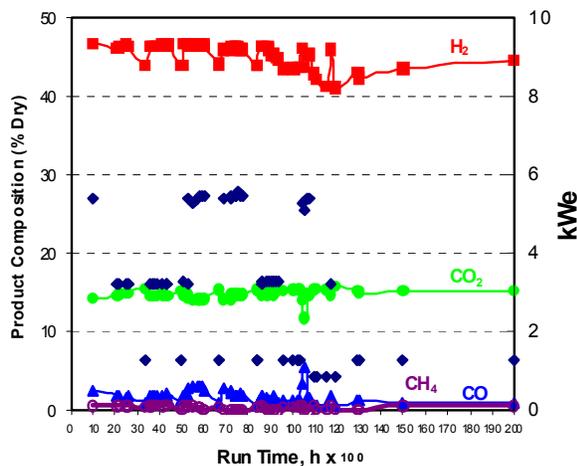
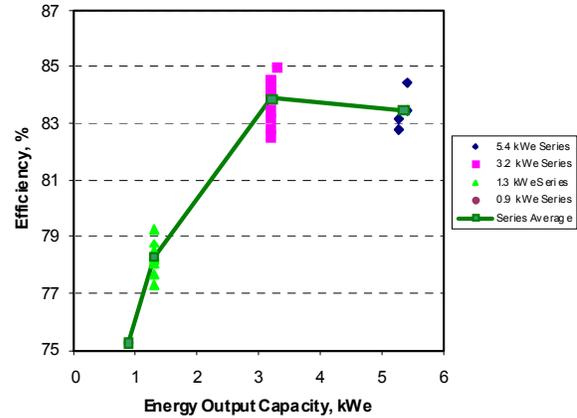


Fig. 3. Product composition from the reforming of commercial-grade natural gas was stable over the 2000-h test in the integrated fuel processor.



kWe	O ₂ /C	H ₂ O/C
5.4	0.57	1.22
3.2	0.58	1.23
1.3	0.62	1.18
0.9	0.62	1.19

Fig. 4. Fuel conversion efficiency increased with increasing processing rate over the 2,000-h test as the O₂/C ratio decreased and the H₂O/C ratio increased.

This research is funded by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Office of Hydrogen, Fuel Cells, and Infrastructure Technologies. Part of the work on the integrated fuel processor was supported by H2fuel.

Research Participants

Shabbir Ahmed, Sheldon H. D. Lee, Di-Jia Liu, Hsiu-Kai Liao, Dennis D. Papadakis, and Steven A. Lottes (Energy Systems Division, Argonne National Laboratory). For more information, contact Shabbir Ahmed (630-252-4553, ahmed@cmt.anl.gov).

Fuel Processor Catalysis

Catalysts to enable gasoline-powered fuel cells for vehicles

Autothermal reforming of gasoline and other conventional or alternative fuels has been identified as the most promising approach for on-board generation of hydrogen for automotive fuel cell systems. In our past work, we have developed novel catalysts that are exceptionally effective for converting gasoline and a variety of other conventional and alternative transportation fuels to hydrogen. These catalysts use transition metals, such as Pt, Rh, Ni, or Ru, supported on an oxide-ion conducting substrate, such as ceria or zirconia. The support may be doped with a small amount of a non-reducible oxide, such as gadolinium, samarium, or yttrium.

Certain formulations of these catalysts have also been shown to be resistant to sulfur poisoning. Süd-Chemie, Inc., of Louisville, Kentucky, currently supplies these catalysts under a licensing agreement. In addition to developing these catalysts further, we have recently started investigating perovskites—mixed metal oxides with the structure ABO_3 . We are focusing on perovskite compositions that do not contain costly precious metals, such as Pt and Rh. The benefit is that these catalysts would be less expensive than the precious metal-based catalysts. Lanthanum nickelate ($LaNiO_3$) has been shown to generate near-equilibrium predicted yields of hydrogen for autothermal reforming of a variety of hydrocarbon fuels; however, its stability under reducing conditions is a concern. Doping $LaNiO_3$ on the B-site with certain elements, such as Cr, has been shown to improve the material's stability, while doping on the A-site with elements such as Ca increases its catalytic activity.

2002 Research Highlights

A primary focus of our research effort this year has been to determine the performance of the doped ceria catalysts coated on a honeycomb monolithic structure for reforming commercial-

grade gasolines. This work is being conducted under a cooperative research and development agreement with Süd-Chemie, Inc.

For autothermal reforming of a Chevron-Phillips sulfur-free (<450 ppb sulfur) gasoline, a composition referred to as ANL-A performed better than a composition referred to as ANL-B. ANL-A and ANL-B differ in the nature of the transition metals supported on the doped-ceria substrate, generating almost four times more H_2 per mole of gasoline at a temperature of $\sim 700^\circ C$ and a gas-hourly space velocity (GHSV) of $27,000\ h^{-1}$. As shown in Figure 1, the H_2 yield observed for ANL-B was not significantly greater than that observed in the absence of a catalyst. Mechanistic studies have shown that for autothermal reforming, oxidation reactions involving molecular oxygen, which produce no H_2 , occur at a lower temperature than steam reforming reactions, which produce H_2 . Although ANL-B has been shown to be better than ANL-A at catalyzing the oxidation reaction, ANL-A is better at catalyzing the steam reforming reaction at lower temperatures. Although not shown, there is little difference in the H_2 yield with the ANL-A catalyst as the

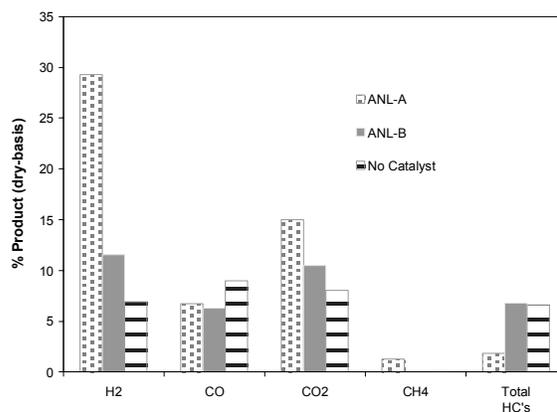


Fig. 1. ANL-A yields much more hydrogen than ANL-B in the autothermal reforming of a commercial sulfur-free gasoline. Conditions: $700^\circ C$, $O_2:C = 0.5$, and $H_2O:C = 1.8$.

GHSV is increased from 27,000 to 110,000 h⁻¹, demonstrating that ANL-A is a very active catalyst. Long-term (~1,000-h) tests indicate a deactivation of this catalyst. Current effort is directed toward improving the long-term stability of the ANL-A catalyst.

Figure 2 shows the H₂, CO, CO₂ and CH₄ yields from the autothermal reforming of a sulfur-free benchmark gasoline fuel mixture using a Ca- and Cr-doped LaNiO₃ perovskite catalyst over 300 hours. The product yield is stable over this period without any significant catalyst deactivation. When a benchmark fuel containing 50 ppm sulfur is introduced, however, the yield of H₂ decreases by 30–50% over the first few hours, followed by a much slower rate of decrease at longer times. Continuing work will focus on improving the sulfur tolerance of the perovskite catalysts.

This research is funded by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Office of Hydrogen, Fuel Cells, and Infrastructure Technologies.

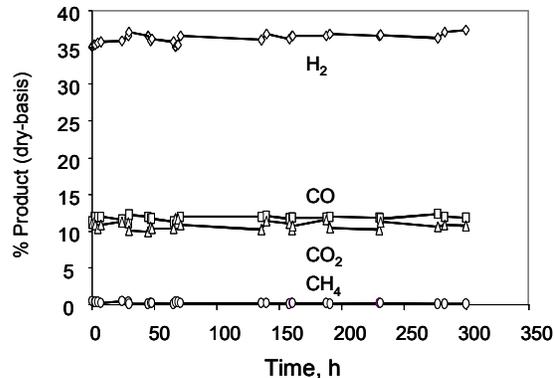


Fig. 2. A Ca- and Cr-doped LaNiO₃ perovskite catalyst shows stable autothermal reforming of the benchmark gasoline over 300 h. Conditions: 700°C, O₂:C = 0.4, and H₂O:C = 1.5.

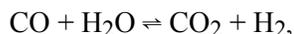
Research Participants

Theodore R. Krause, Jennifer R. Mawdsley, Cecile C. Rossignol, and Magali S. Ferrandon. For more information, contact Theodore Krause (630-252-4356, krause@cmt.anl.gov).

Water-Gas Shift Catalysis

Fine-tuning catalysts that will work “under the hood”

On-board reforming of hydrocarbon fuels, such as gasoline, is one option being considered for supplying hydrogen, or H_2 , to automotive polymer electrolyte fuel cells (PEFCs). The fuel gas initially produced from the reforming of such fuels can contain 10–15% carbon monoxide, or CO, depending on the fuel and the reforming process used. Because the performance of the PEFC can be degraded by as little as 100 ppm CO, the CO in the fuel gas is reduced by conversion to carbon dioxide, or CO_2 , and additional H_2 via the water-gas shift (WGS) reaction,



to ~1%. The CO is further reduced to trace levels by preferential oxidation or methanation. In industrial practice, the WGS shift reaction is carried out in two stages, using two different catalysts—iron-chromium (Fe-Cr) and copper-zinc (Cu-Zn). These catalysts require well controlled startups and shutdowns and are not suitable for automotive applications.

We are developing new shift catalysts based on a bifunctional mechanism, where one component, typically a metal, adsorbs CO and the other component, typically a reducible metal oxide, dissociates water. One such catalyst uses platinum supported on a doped ceria substrate. We are also working on copper-based shift catalysts that are not pyrophoric and suffer little or no loss of activity upon exposure to air or high temperatures.

2002 Research Highlights

In addition to high activity and stability to air exposure, the WGS catalysts must maintain adequate activity over an operating lifetime of 5,000 h or more. Thus, the long-term stability and sulfur tolerance of the shift catalysts is a major concern. For Pt supported on a doped-ceria substrate, the catalyst deactivates more

rapidly at 250°C than at 300°C, as shown in Figure 1. Based on the decline in activity, deactivation rate constants of $2 \times 10^{-4} \text{ h}^{-1}$ and $1.1 \times 10^{-3} \text{ h}^{-1}$ were calculated at 250°C and 300°C, respectively. Although the deactivation rate is still too high for automotive applications, it is less than the rate of $8 \times 10^{-3} \text{ h}^{-1}$ for Pt-ceria catalysts reported in the literature. The presence of 3–4 ppm of H_2S had essentially no effect on our catalyst's WGS activity, indicating that this catalyst is tolerant to sulfur at concentrations present in reformat produced by the autothermal reforming of low-sulfur gasoline (~30 ppm). It is possible that carbonate formation is responsible for the higher deactivation rate at the lower temperature.

Work is in progress to clarify the mechanism for deactivation and to develop measures to reduce or overcome the loss in activity.

In a second approach, copper deposited on substrates consisting of Cu(I)-based oxides with the delafossite structure are being investigated

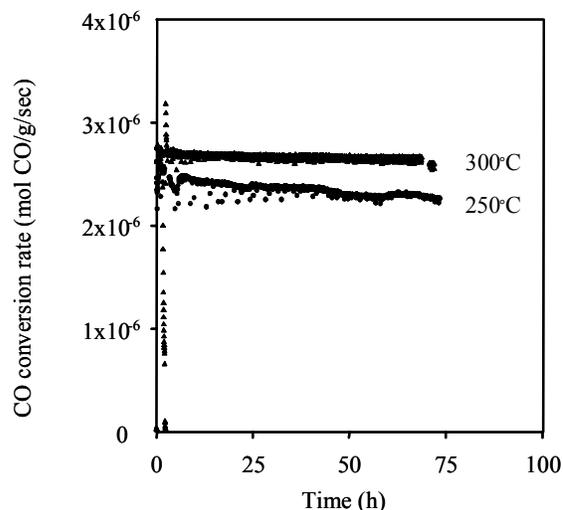


Fig. 1. The Pt-on-doped-ceria water-gas shift catalyst deactivates faster at 250°C than at 300°C, possibly due to increased carbonate formation at the lower temperature.

for their WGS activity. As shown in Figure 2, one such composition (Cu/Oxide_A (1) and Cu/Oxide_A (2), which represent two separate syntheses) exhibits shift activity similar to that of the commercial Cu-Zn catalyst (LTS). X-ray diffraction analysis of Cu/Oxide_A suggests that the oxide substrate is actually a mixture of the delafossite and spinel phases. Brief exposure to air at 300°C resulted in a decrease in activity.

Work is continuing on improving the activity and the air stability of this family of catalysts.

This research is funded by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Office of Hydrogen, Fuel Cells, and Infrastructure Technologies.

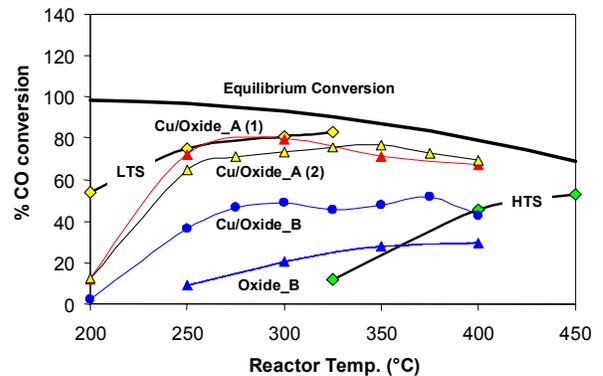


Fig. 2. The Cu(I)/delafossite-based catalyst exhibits water-gas shift activity comparable to that of the commercial low-temperature shift catalyst.

Research Participants

Theodore R. Krause, Deborah J. Myers, John F. Krebs, Sara Yu Choung, and Razima Souleimanova. For more information, contact Theodore Krause (630-252-4356, krause@cmt.anl.gov).

Fuel Cell Systems Analysis

Finding the right balance of efficiency, cost, and performance for automotive use

The use of fuel cells to power automobiles will require the use of gasoline and other conventional (natural gas, diesel) or alternative (methanol, ethanol, propane, bio-diesel, etc.) fuels. Such systems will need fuel processors to convert the available fuel to hydrogen or a gas mixture that contains hydrogen. While various developers are addressing improvements in individual components and subsystems in automotive fuel cell propulsion systems (such as cells, stacks, fuel processors, and balance-of-plant components), we are using modeling and analysis to address issues of thermal and water management, design-point and part-load operation, and component-, system-, and vehicle-level efficiencies and fuel economies. Such analyses are essential for effective system integration. We use Argonne's GCtool software package to devise and analyze system configurations and operation.

This year we analyzed the pressurized direct hydrogen automotive fuel cell system for water and thermal management issues, as well as for factors that affect parasitic power consumption in the system. One interesting result from these analyses was that both the condenser and the air heater/humidifier have their maximum heat duties at part load, not at rated power.

2002 Research Highlights

During 2002, one of our major activities was to model and analyze an 80-kW pressurized direct hydrogen fuel cell system, potentially for use in a sport-utility vehicle. The modeled system used compressed hydrogen fuel and operated at 3 atm, 80°C, and a cell potential of 0.7 V at the rated power point. The modeled fuel cell system was analyzed for water and heat management issues, and parasitic losses at normal and high ambient temperatures and elevations.

Water and heat management: At the rated power, the dew point of the cathode exit gas that

is needed to maintain water self-sufficiency is higher than the stack operating temperature, so no water condensation is needed from the exhaust gas. At part load, however, the required dew point decreases below the stack temperature at pressure ratios <1.8, requiring condensation of water from the exhaust to maintain water self-sufficiency. The needed dew point as a function of the pressure ratio is shown in Figure 1 for the base case of 25% relative humidity and 1 atm pressure (at mean sea level), as well as for 100% relative humidity and 0.75 atm ambient pressure (at elevated locations).

The corresponding heat duty of the condenser, shown in Figure 2, increases with decreasing pressure ratio and reaches a maximum at a pressure ratio of ~1.2. At still lower pressure ratios, the condenser duty decreases due to the reduced air flow rates. Figure 2 also shows that the condenser heat duty increases with decreasing oxygen utilization; the maximum condenser duty more than doubles as the oxygen utilization is decreased from 60% to 40%.

Similarly, the maximum heat duty for the cathode feed air heater/humidifier occurs not at the rated power point but at a part-load pressure ratio of ~1.6, as shown in Figure 3. At higher pressure ratios, the compression itself provides

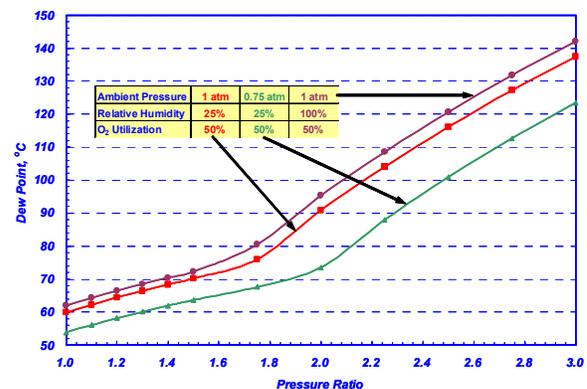


Fig. 1. Although not needed at the rated power, a condenser is required at partial loads where the pressure ratio is less than 1.8.

Fuel Cells

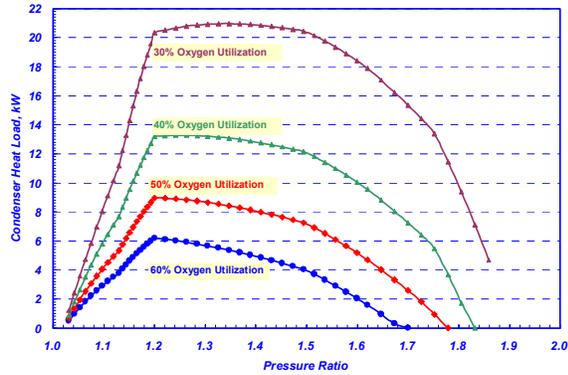


Fig. 2. The system condenser must be designed for maximum heat duty not at the rated power but at partial loads where the pressure ratio is 1.2–1.3.

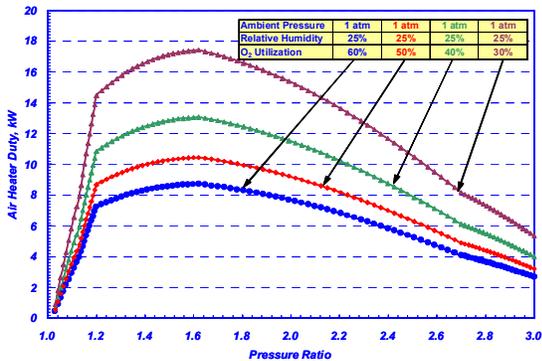


Fig. 3. The heat duty for the cathode air heater/humidifier is highest at partial loads where the pressure ratio is approximately 1.6.

the major portion of the heating and humidification heat duty. The compressor contributes a successively lesser fraction of the needed heating as the pressure ratio decreases. Figure 3 also shows that the maximum heat duty increases with decreasing oxygen utilization.

Parasitic losses: In this system, the two major parasitic power consumers are the compressor-

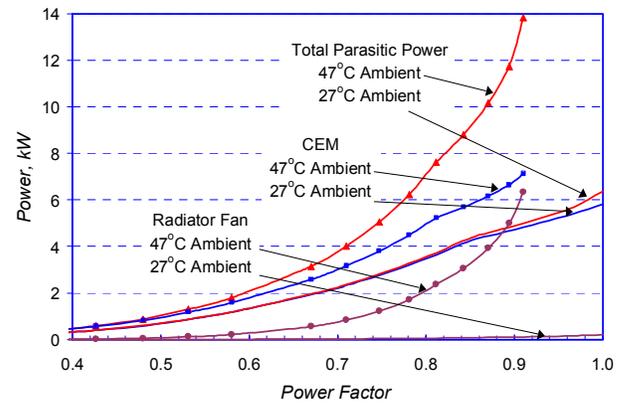


Fig. 4. The parasitic power consumption by the air compressor and the radiator fan increases greatly as the ambient temperature increases from 27°C to 47°C.

expander module (CEM) and the radiator fan. This parasitic load becomes significantly greater as the ambient temperature increases from the nominal 27°C to 47°C, as shown in Figure 4. At the higher ambient temperature, the system is unable to deliver the full rated power of 80 kW. At 90% of the rated power, the CEM and the radiator fan each consume more than 6 kW.

This research is funded by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Office of Hydrogen, Fuel Cells, and Infrastructure Technologies.

Research Participants

Romesh Kumar and E. Danial Doss and Rajesh Ahluwalia (Nuclear Engineering Division, Argonne National Laboratory). For more information, contact Romesh Kumar (630-252-4342, kumar@cmt.anl.gov).

Materials for Solid Oxide Fuel Cells

Reducing cost and improving performance of SOFCs

A major trend in solid oxide fuel cell (SOFC) development, particularly in the development of planar cells and stacks, is toward lower temperatures, compared with the 1,000°C operating temperature of conventional SOFCs. At operating temperatures below about 800°C, it becomes feasible to consider metallic components for ease of fabrication and lower costs.

One component of special interest is the interconnect, which is exposed to oxidizing conditions on the cathode side and to humid reducing conditions on the anode side. Ferritic stainless steels have been the primary candidates investigated for this application as they have coefficients of thermal expansion (CTE) comparable to that of the zirconia-based SOFC electrolyte. In the commercially available steels, however, chromium migration from the interconnect to the cathode and anode electrocatalysts poisons the fuel cell and degrades its performance.

We are developing new alloys and coatings that inhibit chromium volatilization and migration, while maintaining low corrosion rates and high electronic conductivity of the scales that are formed. We are using mechanical alloying and powder metallurgy techniques to prepare any desired alloy composition, as well as to vary that composition within the interconnect as desired for optimum performance and least cost.

2002 Research Highlights

The work on interconnect materials has focused on two areas: modified ferritic stainless steels and ferritic alloys without chromium. Several new alloys have been prepared by mechanical alloying and powder metallurgy processing. Once the alloys are fabricated, corrosion tests are conducted on specimens by exposing them to flowing humidified air for up to 400 h at 800°C.

The weight gain is used as a measure of the corrosion rate, while the increase in area specific resistance (ASR) provides a measure of the conductivity of the oxidized specimens at 800°C. Figures 1 and 2 show the weight gain and the ASR for several of the alloys prepared in our laboratory along with the same measurements for some commercially available wrought ferritic stainless steels. In general, a larger weight gain is accompanied by a higher ASR, but this is not always the case. Some of the alloys produced had higher weight gains but lower resistances, indicating a more electrically conductive oxide scale.

Typically, the removal of chromium greatly reduces the corrosion resistance of ferritic alloys, but one new Cr-free alloy developed

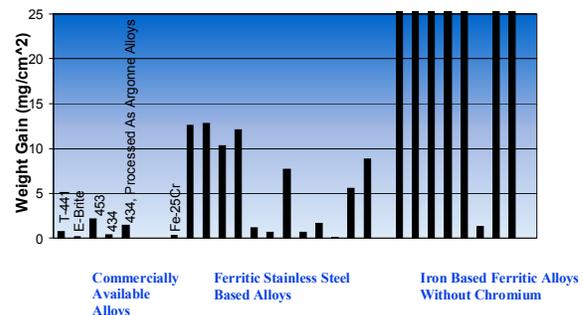


Fig. 1. Some of the prepared alloys show corrosion comparable to or less than that for commercial materials after 400 h exposure to humidified air at 800°C.

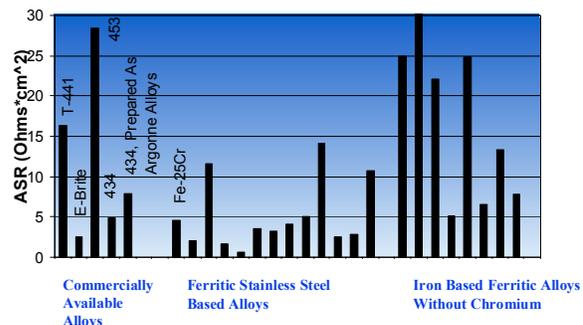


Fig. 2. Some of the new alloys exhibit lower resistivities than commercial alloys after 400 h in humidified air at 800°C.

shows a reasonably high oxidation resistance, while two of them show fairly good electrical conductivity of the scales. We are continuing work on both groups of alloys, those with and without chromium.

Using the powder metallurgy approach, compositionally and functionally graded sample plates have been produced consisting of similar alloys, different alloys (for tailoring of residual stresses), and cermet layers. Figure 3 shows three samples of different combinations that have been produced to demonstrate this concept.

This research is funded by the U. S. Department of Energy, National Energy Technology Laboratory.

Research Participants

Terry A. Cruse and Michael Krumpelt. For more information, contact Michael Krumpelt (630-252-8520, krumpelt@cmt.anl.gov).

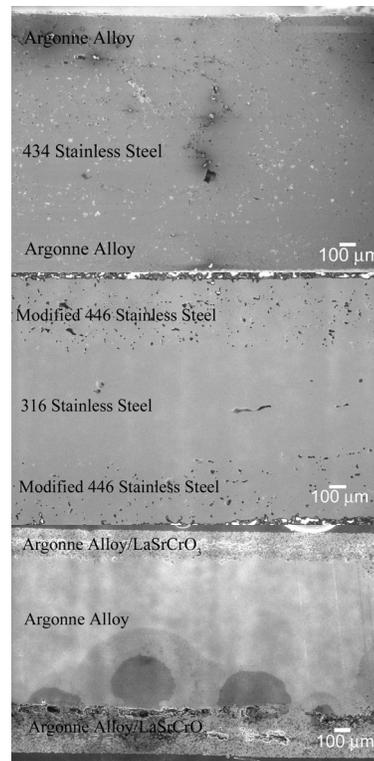


Fig. 3. Different alloy combinations have been prepared for potential application as SOFC interconnect materials.

Fuel Cell Testing and Evaluation

Providing standardized, independent analyses for fuel cell developers



Fuel cell developers, fuel cell users, automakers, and government and private agencies all need some way to obtain an unbiased assessment of the fuel cell technologies currently being developed for transportation. Argonne National Laboratory's Fuel Cell Testing Facility can fill that bill, providing independent, standardized testing and evaluation.

The Facility draws on Argonne's extensive experience evaluating batteries and battery test equipment, and provides the same high-quality testing for fuel cells. Equipped with extensive and specialized hardware and computing power, the Facility is ideally suited to the complex task of testing fuel cell systems, including how well fuel cell stacks and supporting components interact. The Facility provides a standard test environment for benchmarking new fuel cell stacks and systems. Since the evaluations are independent as well as standardized, the test results help validate the capabilities of a particular fuel cell technology and allow for its direct comparison with competing fuel cell technologies.

Designed to Automotive Power Criteria

The Fuel Cell Test Facility has been specifically designed to automotive power criteria. It is

equipped to test fuel cell stacks and systems up to 80 kW, the size needed for a passenger car.

The brain of the facility is a computer-controlled electronic load system that can simulate the power demands of a vehicle. The heart of the facility is a sophisticated gas management system that supplies air and fuel to the fuel cell with precise control of flow rate, pressure, temperature, and humidity and can simulate the rapid gas-flow changes found in actual driving conditions, as cars accelerate and brake. The fuel can be hydrogen, gasoline or simulated reformat. (Reformat is the output gas of a device that produces hydrogen from other fuels, such as methanol, gasoline, or natural gas.)

Most recently, Argonne's Fuel Cell Test Facility has begun testing fully integrated fuel cell systems that incorporate their own fuel processing and air supply subsystems.

In our fuel cell work, we have evaluated stacks and complete systems from many developers. These ranged from 0.72-kW stacks (hydrogen-fueled) to a 50-kW complete system (gasoline-fueled).

The Fuel Cell Test Facility is part of the Electrochemical Analysis and Diagnostics Laboratory (EADL). The EADL was established by DOE's Office of Energy Efficiency and Renewable Energy, FreedomCAR and Vehicle Technologies Office.

Research Participants

Ira Bloom, Dan Andrekus, Scott Jones, Edward Polzin, Ben Potter, and Carl Webster. For more information, contact Ira Bloom (630-252-4516, bloom@cmt.anl.gov; visit our web site at <http://www.cmt.anl.gov/facilities/eadl.shtml>).

Fuel Cell and Battery Technical Analyses

Supporting U.S. Department of Energy research and development

Argonne's Chemical Engineering Division (the Division) provides technical and programmatic support to the U.S. Department of Energy's (DOE's) Office of Hydrogen, Fuel Cells, and Infrastructure Technologies and to the FreedomCAR and Vehicle Technologies Office. In this capacity, Division technical experts participate in reviews to evaluate contractor progress, provide feedback to DOE and its contractors, prepare input for program plans and work statements, organize technical workshops, and evaluate the technical merit of proposals. Some representative activities carried out in 2002 are described below.

2002 Highlights

Hydrogen storage workshop: On-board hydrogen storage is a key enabling technology for fuel cell vehicles because current storage technologies are too bulky, thereby limiting driving range. The Division organized and hosted a Hydrogen Storage Workshop in August 2002 (see <http://www.carttech.doe.gov/new.html>) to discuss approaches to increasing the capacity and reducing the cost of hydrogen storage technologies. Sessions were held on carbon technologies, advanced/complex hydrides, chemical storage, and advanced concepts. Participants included representatives of industry, academia, and DOE national laboratories. The research recommendations from the workshop will be implemented in a hydrogen storage solicitation that is planned for 2003.

Fuel cells for buildings and stationary applications: The Division participated in a workshop with DOE and industry stakeholders in April 2002 to identify the issues related to fuel cells for buildings and stationary applications (see <http://www.carttech.doe.gov/research/fuelcells/index.html>). Based on the workshop discussions, the Division provided recommendations on research topics for the

2003 solicitation ("Research and Development for Fuel Cells for Stationary and Automotive Applications" at <http://e-center.doe.gov>).

Portable and off-road fuel cell power applications: Division representatives attended a joint DOE/industry Portable Power Workshop in January 2002. The focus of the workshop was portable fuel cells for low-power (sub-watt to 20- to 50-W) applications such as consumer electronics and high-power (1- to 10-kW) applications such as auxiliary power units (APUs) for hotel and refrigeration loads for long-haul trucks and recreational vehicles (see <http://www.carttech.doe.gov/pdfs/FC/205.pdf>). A DOE solicitation is planned for 2003 to demonstrate the market readiness of the proposed consumer electronics or auxiliary power unit fuel cell systems and to help expedite the commercial introduction of fuel cells ("Research, Development, and Integration of Energy-Efficient Technologies in Portable Power, Auxiliary Power Units, and Offroad Fuel Cell Applications" at <http://e-center.doe.gov>).

World fuel cell survey: Division technical experts represented DOE on extensive visits to organizations involved in fuel cell, hydrogen, and enabling technology research and development in Canada, Europe, and Asia. The organizations comprised government, industry, academia, and national laboratories. Information gathered from the visits is being compiled into a report to provide insight into the commercialization strategies and approaches of non-U.S. fuel cell development efforts and to identify potential areas of cooperation.

Fuel cell report to Congress: The United States Congress directed DOE to submit two reports addressing the status of fuel cell technologies. Division personnel participated in preparing and editing these reports. The first report addressed the need for two public/private partnerships to

demonstrate the use of fuel cells in commercial-scale applications by 2012—one for stationary and distributed generation and the other for transportation and infrastructure. The second report details the technical and economic barriers to the use of fuel cells in transportation, portable power, and stationary and distributed generation applications. The report also includes recommendations on program adjustments that are needed for the commercial use of fuel cells for stationary and transportation applications by 2012. DOE combined the reports into a single report, “Fuel Cell Report to Congress,” which is available at <http://www.eere.energy.gov/hydrogenandfuelcells/>).

Fuel cell codes and standards: The Division actively participates in the Society of Automotive Engineers (SAE) Fuel Cell Standards Committee that is developing recommended practice guides and standards for fuel cell vehicles in the following areas: safety, performance, fueling interface, emissions and fuel economy measurement, and recyclability. The SAE activity is coordinated with other national and international standards-setting organizations.

Batteries for advanced transportation technologies: The Division provides technical expertise and coordination of long-term battery research that is sponsored by DOE’s FreedomCAR Office and conducted at universities and the national laboratories. The program is developing novel electrochemical technology for advanced batteries for hybrid electric vehicles, electric vehicles, and fuel cell electric vehicles. In addition to work on low-cost, high-energy-density materials, advanced diagnostic techniques that can enable *in situ*

studies of electrochemical cells are being developed. Mechanisms for observed performance degradation are being studied, and the program has identified and synthesized a new nonflammable electrolyte for lithium-ion batteries. The more fundamental work in this program directly supports the applied development and testing of advanced cells under DOE’s Advanced Technology Development Program, described below.

Advanced Technology Development Program: DOE’s Advanced Technology Development (ATD) Program was initiated to focus research and development at the national laboratories that addresses the critical barriers preventing the introduction of advanced batteries into the automotive sector. Those barriers include poor calendar life, poor abuse tolerance, and high cost. The Division provides technical direction and coordination of the ATD research activities. We also coordinate the annual DOE Merit Review. The program has demonstrated that the materials currently used by battery developers cannot meet cost goals of the U.S. Advanced Battery Consortium. It has identified the primary causes of both life and power fade in representative battery chemistries and has begun to investigate novel materials, such as manganese spinels, that can meet the performance targets for high-power batteries.

Participants

Walter F. Podolski, Vincent S. Battaglia, Thomas G. Benjamin, Brian T. Concannon, Robert D. Sutton, and William M. Swift. For more information, contact Walter Podolski (630-252-7558, podolski@cmt.anl.gov).

Patents and Selected Publications and Presentations

Patents

Steam Reforming Catalyst

K. W. Kramarz, I. Bloom, S. Ahmed, R. Kumar, R. Wilkenhoener, and M. Krumpelt
U. S. Patent No. 6,303,098 B1, issued October 16, 2001

Proceedings Papers

Materials for Low Temperature Solid Oxide Fuel Cells

M. Krumpelt, J. M. Ralph, T. A. Cruse, and J.-M. Bae
Proc. of the 5th European Solid Oxide Fuel Cell Forum, Ed. J. Huijsmans, European Fuel Cell Forum, Switzerland, p. 215 (2002)

Papers Presented at Scientific Meetings

Integrated Fuel Processor Development Challenges

S. Ahmed, C. Pereira, S. H. D. Lee, T. D. Kaun, and M. Krumpelt
Presented at the 10th AIChE Spring National Meeting, New Orleans, LA,
March 10–14, 2002

Fuel Cell Testing at Argonne National Laboratory

I. Bloom, E. G. Polzin, and W. M. Swift
Presented at the 224th Am. Chem. Soc. National Meeting, Boston, MA,
August 18–22, 2002

Water Balance in Fuel Cells Systems

J. P. Kopasz, S. Ahmed, R. Kumar, and M. Krumpelt
Presented at the 10th AIChE Spring National Meeting, New Orleans, LA,
March 10–14, 2002

Fuel Requirements for Fuel Cell Systems

J. P. Kopasz, T. R. Krause, S. Ahmed, and M. Krumpelt
Presented at the 224th Am. Chem. Soc. National Meeting, Boston, MA,
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Catalytic Autothermal Reforming of Hydrocarbon Fuels for Fuel Cell Systems

T. R. Krause, J. P. Kopasz, C. Rossignol, J. D. Carter, and M. Krumpelt
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Fuel Cells

Materials Challenges in Solid Oxide Fuel Cells

M. Krumpelt, J. M. Ralph, and T. A. Cruse

Presented at the Mater. Res. Soc. Spring Meeting, San Francisco, CA, April 1–5, 2002

Using Advanced Solid Oxide Fuel Cells in Zero Emission Coal Systems

R. Kumar and M. Krumpelt

Presented at the 27th Int. Technical Conf. on Coal Utilization and Fuel Systems, Clearwater, FL, March 3–7, 2002

The Road Ahead for Fuel Cell Cars (With a Look in the Rearview Mirror)

R. Kumar and W. F. Podolski

Presented at the Electrochem. Soc. Meeting, Philadelphia, PA, May 12–17, 2002

Investigation of Catalytic Autothermal Reforming of Diesel Surrogate Fuels

D.-J. Liu, T. D. Kaun, H.-K. Liao, and S. Ahmed

Presented at the 3rd Department of Defense Logistic Fuel Reforming Conf., Panama City Beach, FL, August 27–28, 2002

Metal/Ceria Water-Gas Shift Catalysts for Automotive Polymer Electrolyte Fuel Cell Systems

D. J. Myers, J. Krebs, J. D. Carter, R. Kumar, and M. Krumpelt

Presented at the 10th AIChE Spring National Meeting, New Orleans, LA, March 10–14, 2002

Fuel Processor for Fuel Cell Systems

C. Pereira, S. H. D. Lee, T. D. Kaun, S. Ahmed, and M. Krumpelt

Presented at the AIChE Annual Meeting, Reno, NV, November 4–9, 2001

Role of Metal-Support Interactions on the Activity of Pt and Rh Catalysts for Reforming Methane and Butane

C. Rossignol, T. R. Krause, and M. Krumpelt

Presented at the 10th AIChE Spring National Meeting, New Orleans, LA, March 10–14, 2002

Process Chemistry and Engineering

The Chemical Engineering Division conducts research on the treatment and disposal of nuclear wastes generated at Department of Energy (DOE) sites and by commercial light water reactors. Our research falls into two primary areas: (1) the behavior of waste materials following their disposal in the proposed Yucca Mountain repository, and (2) methods of separating wastes for further treatment to reduce overall toxicity, fissile content and volume.

Waste Form Behavior

DOE will submit a license application to the Nuclear Regulatory Commission in December 2004 to construct a geological repository at Yucca Mountain. We are providing key input to the development of performance assessment models for commercial spent nuclear fuel (CSNF) and defense high-level waste (DHLW). Our work also supports the qualification and long-term performance assessment of ceramic and metal waste forms from electrometallurgical treatment of spent sodium-bonded Experimental Breeder Reactor-II (EBR-II) fuel.

Performance assessment models for CSNF and DHLW glass: We are developing models for the degradation and radionuclide release rate from commercial spent fuel and DHLW glass. In support of this effort, we have conducted waste glass and spent fuel tests under repository-relevant unsaturated conditions. Tests in humid air have shown that deliquescent salts in, or released from, these waste forms can have important effects. Our work has led to the identification of the waste form reactions that occur under repository-relevant test conditions, estimates for the rates of these reactions, and identification of the important role of alteration products in sequestering radionuclides.

EBR-II waste forms: Spent sodium-bonded fuel from EBR-II must be treated before disposal in the repository. Two waste forms will be used to immobilize wastes from electrometallurgically

treated fuels: a ceramic waste form (radioactive salts) and a metallic waste form (contaminated cladding hulls). Laboratory tests are being conducted to address qualification requirements with regard to both waste forms and their impact on the disposal system.

Thorium-uranium dioxide fuels: We have investigated the corrosion behavior of irradiated (Th,U)O₂ fuel samples from the Shippingport Light Water Breeder Reactor. The results from these studies show that the dissolution rate of irradiated thoria-uranium fuels in near-neutral, oxidizing aqueous solutions are at least two orders of magnitude lower than those measured for UO₂ spent fuels under similar test conditions.

Chemical Engineering Division Process Chemistry and Engineering R&D

- Develop means to convert ⁹⁹Mo production from high- to low-enriched uranium.
- Develop processes and equipment for safe and economic treatment of nuclear waste.
- Develop industrial separations
- Characterize leaching/degradation mechanisms for nuclear waste forms in the environment.
- Develop a scientific basis for repository performance.
- Develop waste form acceptance criteria.

Waste Separation

Our work focuses on (1) the use of low-enriched uranium (LEU) in the production of molybdenum-99 (⁹⁹Mo), (2) research and development support for Savannah River Site's (SRS) Salt Processing Project, and (3) developing separation technologies for the safer long-term disposal of spent nuclear fuel in support of the Advanced Fuel Cycle Initiative (AFCI).

Use of low-enriched uranium in ^{99}Mo production: Production of medical-grade ^{99}Mo by thermal neutron fission of ^{235}U , generally in high-enriched uranium (HEU) targets, accounts for a significant fraction of U.S. HEU exports. ^{99}Tc , the daughter of ^{99}Mo , is the most commonly used medical radioisotope in the world. To reduce nuclear-proliferation concerns, the U.S. Reduced Enrichment for Research and Test Reactors (RERTR) program is working to limit the use of HEU by substituting LEU fuel and targets. The program is international in scope. The substitution of LEU in targets requires approximately five times more total uranium to produce a given amount of ^{99}Mo , necessitating modifications to the target design and recovery/purification steps. Our work this year concentrated on (1) improvements to target digestion and purification/recovery for the CNEA process in Argentina and (2) addressing the impact of the increased solid waste volume generation from LEU substitution at MDS Nordion in Canada.

Research and development support for SRS Salt Processing Project: During 2002, three projects supported this effort: (1) Sr and transuranic (TRU) removal using magnetite, (2) testing of modified solvent for Cs removal for the caustic side solvent extraction (CSSX) process, and (3) recovery of solvent entrained during the CSSX process with coalescers. Magnetite was demonstrated to be superior to the monosodium titanate (MST) process, whose performance was identified as a technical and cost risk by DOE. The use of magnetite also could allow costs savings by reducing the plant footprint. Performance of the modified solvent in the CSSX process was found satisfactory. Recovery of entrained solvent using coalescers was found feasible, with potential cost savings of \$5M per annum, based on a 20-gpm plant.

Separation technologies for safer long-term disposal of spent nuclear fuel: Research under DOE's AFCI program is developing safer alternatives to long-term disposal of spent nuclear fuel to enhance the performance of the repository. Current strategy focuses on the separation of dissolved commercial light water

reactor fuel into three streams: (1) a TRU product stream that will be converted to fuel or transmuted by fissioning to generate electrical power, (2) separate ^{99}Tc and ^{129}I streams that will be fabricated into targets for transmutation, and (3) a uranium product stream that will be solidified and disposed of as low-level waste. Solvent extraction processes can provide the large-scale, selective, efficient separations required for these three product streams. In 2001, a demonstration of the Uranium Extraction Process (UREX) was conducted using simulated feed. This year research focused on analyzing the results of the UREX demonstration, refining the Argonne Model for Universal Solvent Extraction to develop a flowsheet for the a UREX demonstration with commercial spent fuel at SRS, and expanding the spent-fuel treatment process to separate short-lived fission products from the long-lived actinides remaining in the UREX raffinate.

Spinoff Research

In collaboration with scientists at the University of Florida, we are investigating solvent alternatives for the separation of actinides from lanthanides. We also are evaluating the removal of volatile organic compounds from groundwater using vegetable oils. In addition, we have begun development of a new technology for biotoxin removal using biostabilized magnetic nanoparticles. Specific toxins or pathogens can be removed from the blood by functionalized magnetic nanoparticles. The focus of the investigation is on particle characteristics that avoid immune system response and retain specific antibodies, *in vitro* testing of particles, and *in vivo* demonstration of removal of a biotinylated enzyme.

For More Information

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UREX Process Demonstration

Improved separations lead to safer long-term disposal of spent nuclear fuel

Transmutation of waste is a process in which long-lived radioisotopes are converted to short-lived radioisotopes. If the transmutation of radionuclides technology can be successfully implemented, the volume, toxicity, and fissile content of waste now requiring repository disposal will be reduced. New processes can reduce the risk of proliferation associated with components of spent fuel. The end result would be a safer, simpler geologic repository.

One of the technical issues is the adequate separation of uranium and transuranic (TRU) and long-lived fission-product elements from spent fuel. Research under the U.S. Department of Energy's Advanced Fuel Cycle Initiative (AFCI) Program is addressing this issue by separating dissolved commercial fuel into three streams:

- A transuranic (TRU) product stream that will be further processed, converted to fuel, and transmuted by fissioning to generate electrical power,
- Separate ^{99}Tc and ^{129}I streams that will be fabricated into targets for transmutation to short-lived nuclides, significantly reducing the dose from the parent isotopes, and
- A uranium product stream that will be disposed of as low-level waste.

Solvent extraction processes can provide the large-scale selective, efficient separations required for these three product streams.

The Chemical Engineering Division (the Division) has developed a process for uranium extraction (UREX) with the use of a computer model, Argonne Model for Universal Solvent Extraction, or AMUSE. In 2001 a demonstration of the process was conducted using simulated feed (described in the Division's 2001 annual

report, ANL-02/14). This year the research focus has been on analyzing the results of the UREX demonstration, refining the AMUSE model to develop a flowsheet for the demonstration of the UREX process with commercial spent fuel at the Savannah River Site, and expanding the spent-fuel treatment process to separate short-lived fission products from the long-lived actinides remaining in the UREX raffinate.

2002 Research Highlights

In the UREX process, $\geq 99.9\%$ of the uranium and $>95\%$ of technetium are separated from the other fission products and actinides into separate uranium and technetium streams. This separation is achieved by the addition of acetohydroxamic acid (AHA) to the scrub section of the process. The AHA greatly diminishes the extractability of plutonium and neptunium. Because plutonium is not separated from neptunium, the minor actinides, and fission products, the UREX process provides greater proliferation resistance than the PUREX process, where both plutonium and uranium are separated from the other waste components.

Results of the UREX demonstration with a simulated dissolved spent fuel feed confirmed the successful separation of the uranium and technetium from the other waste components. The uranium and technetium concentration profile in the contactor stages demonstrated the expected performance based on the AMUSE calculations. Table 1 gives the measured uranium, technetium, plutonium, and neptunium fractions in each of the product streams. As can

Table 1. Measured Component Recoveries from UREX Cold Demonstration

	% U	% Tc	% Pu	% Np
Raffinate	0.00033	5.2	99.7	99.7
Tc Strip	0.00039	>94.7	0.16	<0.003
U Strip	99.999	<0.1	0.13	<0.3

be seen from the table, the uranium and technetium product concentrations achieved the desired concentration targets. However, the results showed that an improved algorithm was required in AMUSE to predict Pu(IV) complexation by AHA.

Based on the results of this demonstration, AMUSE was improved and a revised process flowsheet was developed in support of the demonstration of the UREX process with dissolved spent fuel at the Savannah River Site (SRS). The new flowsheet, developed with the AMUSE code, was required to accommodate the equipment in place in the hot cell at SRS. Changes in the number of stages were required in all of the sections, notably to the extraction and scrub sections. The goal was to demonstrate the ability of the UREX process to generate the three desired product streams that meet the programmatic targets from a dissolved commercial spent fuel feed. The demonstration at SRS, conducted in August of 2002, met all process goals.

The long-term goals of the AFCI program include recovery of Pu, Np, and minor actinides for transmutation, Cs and Sr for decay storage, and long-lived or stable fission products for geologic disposal. Recovery of these products in

separate process streams is required. As part of this effort, potential multi-tier aqueous processes for waste recovery and purification based on solvent extraction were evaluated for their potential to achieve AFCI process targets. Figure 1 is a simplified schematic of an expanded process to treat spent fuel using UREX as a head-end process. The product streams would be converted to fuel for a transmuter or waste forms for both short-term and long-term disposal.

Additional improvements were done to the AMUSE model to prepare a flowsheet for demonstration of an expanded UREX process with both simulated feed and dissolved commercial spent fuel. Both demonstrations will be conducted by the Division in 2003.

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Research Participants

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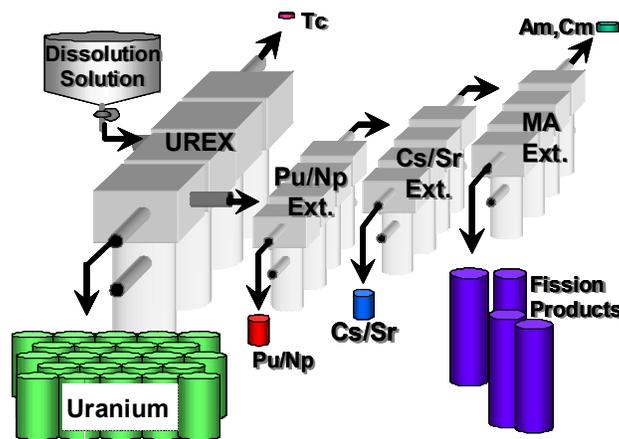


Fig. 1. Expanded UREX-based process for separation of plutonium, neptunium, and short-lived fission products from dissolved spent nuclear fuel.

New Developments in Molybdenum-99 Production from Low-Enriched Uranium

Reducing the proliferation risks of making medical isotopes

The mission of the Reduced Enrichment for Research and Test Reactors (RERTR) program is to facilitate the conversion of research and test reactors from the use of high-enriched uranium (HEU, $\geq 20\%$, typically 93% ^{235}U) to low-enriched uranium (LEU, $< 20\%$ ^{235}U). The focus of work in the Chemical Engineering Division (the Division) is to convert molybdenum-99 (^{99}Mo) production from HEU to LEU targets.

Molybdenum-99, a fission product, decays to $^{99\text{m}}\text{Tc}$, which is the most commonly used medical radioisotope in the world. The use of LEU targets requires approximately five times more total uranium than for HEU targets to produce a given amount of ^{99}Mo and, therefore, requires modification to the target and the process to recover and purify Mo-99. Our work over the last year with Argentine Comisión Nacional de Energía Atómica (CNEA) in Argentina has shown that their conversion to LEU foil targets can improve their production efficiency. Specific processing steps will be demonstrated in 2003. Our work over the last year with MDS Nordion in Canada has addressed the issue of solid waste volume, and we have proposed two alternatives for minimizing the impact of their conversion to LEU targets on the solid waste volume. In both cases, progress has been made toward the ultimate conversion from HEU to LEU targets.

2002 Research Highlights

Several ^{99}Mo producers digest irradiated high-enriched uranium aluminide/aluminum dispersion plates in alkaline solution. These producers include CNEA, Institut National des Radioéléments, Mallinckrodt, and the South African Nuclear Energy Corporation Limited. The Division is cooperating with CNEA to convert its process to LEU metal foil targets. In the proposed CNEA process, irradiated LEU-foil

targets are digested in alkaline solution. We have researched and proposed improvements in the CNEA process digestion and purification/recovery steps that will significantly improve the efficiency of their process.

A new digester (Fig. 1) was designed and built to accommodate the proposed process, and specifically to be used in the CNEA hot cell facility.



Fig. 1. Digester designed and built by the Chemical Engineering Division for use in the CNEA process.

Previous work with the CNEA process has used a two-step digestion. The first step uses NaOH to digest the target and precipitate uranium as UO_2 . The second step uses O_2 gas to oxidize the UO_2 to U(VI), which allows complete release of Mo-99 into solution. The Mo-99 is then recovered by anion-exchange purification. Studies of three alternative digestion procedures are underway. Final recommendations will depend on the results of tests conducted before the end of the calendar year.

The proposed process is expected to use less than 10-20% of the volume needed to digest HEU targets. Therefore, the anion-exchange columns used to purify the ^{99}Mo product can be

significantly smaller. Column sizing studies were done to determine the optimal sizes to be used in a demonstration next spring at CNEA. The use of these smaller columns will generate far less liquid waste and will reduce processing time considerably. We are planning a demonstration in spring 2003 for all aspects of the proposed process.

The Division is cooperating with MDS Nordion, Atomic Energy of Canada Ltd. (AECL), and Société Générale pour les techniques Nouvelles (SGN, France) to develop a process for converting ^{99}Mo production at Chalk River, Ontario, Canada to LEU. When LEU targets are dissolved in nitric acid, the dissolver solution will contain approximately five times more U than HEU targets for the same ^{99}Mo yield. Consequently, the waste solution from target digestion will have more uranium and perhaps a greater volume than that generated from the current process. At the Chalk River facility, that waste solution must be stabilized as a solid. Therefore, conversion to LEU targets may impact their waste handling and storage. The path the Division chose to address these potential problems is to (1) study the limits of the current direct evaporation/calcination of the nitric-acid/uranium-nitrate solution and (2) study the use of oxalate precipitation to eliminate the formation of molten uranium nitrate hexahydrate (UNH).

The direct calcination process was shown to be feasible for the treatment of UNH/ HNO_3 solutions generated during an LEU process, by altering the process to minimize the volume of the final calcined product. However, sputtering was observed that could result in equipment contamination. If these results can be achieved in a production facility, then the direct calcination process could be adapted for use with LEU targets.

The oxalate precipitation process appears promising for the treatment of UNH/ HNO_3 solutions in bench-scale tests and in our laboratory-scale calciner. Relative to the direct calcination process, the oxalate precipitation process would allow for less uranium in each calciner cup in the absence of an additional compaction step. No sputtering was observed during the oxalate precipitation process. Therefore, the oxalate precipitation process provides a promising alternative to the direct calcinations process.

We have worked with MDS Nordion toward conversion of their process to LEU targets. Our research and development (R&D) on direct calcinations suggests that this process could be adapted for LEU targets. Our R&D on oxalate precipitation suggests that the process is a promising alternative to direct calcinations. In the near future, Division research will support the pilot demonstrations by SGN.

The Division continues to partner with ^{99}Mo producers from Argentina, Australia, Canada, and Indonesia to convert targets from HEU to LEU for production of medical grade ^{99}Mo . We will continue to pursue building active programs with other ^{99}Mo producers in Belgium, the Netherlands, South Africa, and South Korea.

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Research Participants

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R&D Support for Savannah River Site's Salt Processing Project

Helping to meet goals for processing and safely disposing of high level waste

Nearly 34 million gallons of radioactive high-level waste (HLW) are currently stored in tanks at the Savannah River Site (SRS) in South Carolina. This waste, which is a product of the cold-war era, contains a significant inventory of hazardous radioactive isotopes. These include cesium (Cs), strontium (Sr), uranium (U), and transuranic elements (TRU) plutonium, americium, and neptunium (Pu, Am, and Np). Because of the high cost associated with disposal of the HLW, it is essential to reduce its volume. The current SRS plan, referred to as the "Salt Processing Project" or SPP, is to separate most of the radioactive isotopes into a concentrated small fraction of the waste, which will be treated as HLW. The remaining majority of the waste, with the isotopes removed from it, will then be treated as low-level waste (LLW) using a less expensive method.

Researchers in the Chemical Engineering Division were involved in three projects supporting the SPP during 2002:

- Sr and TRU removal using magnetite
- Recovery of entrained solvent in the caustic side solvent extraction (CSSX) process using coalescers
- CSSX flowsheet test with modified solvent for Cs removal

Data were provided to SRS for the design and operation of the treatment plant and its preliminary design has been started.

The first of the three projects involved studying magnetite, an iron oxide, for separating Sr and TRU elements from the HLW. Magnetite could replace the currently used material, monosodium titanate (MST), whose performance was identified as a technical and cost risk by the

U.S. Department of Energy. Our tests have shown that magnetite performance is superior to MST. We estimate that by using magnetite, SRS will be able to cut costs by reducing the plant footprint while safely achieving process goals.

In the second project, we evaluated the performance of the modified solvent in the CSSX process. The new solvent was satisfactory and met SRS criteria.

In the third project, we studied the use of coalescers for recovering entrained solvent in the CSSX process. Recovery of this solvent can produce a potential cost savings of \$5 million annually, based on a plant processing rate of 20 gallons per minute (gpm).

2002 Research Highlights

Use of in-situ formed magnetite for Sr and TRU removal: The boundaries for this experimental work were defined based on an operational envelope developed in collaboration with SRS. Decontamination factor (DF) values were measured for both magnetite and monosodium titanate (MST). Magnetite DF values were found to be superior to MST for all isotopes studied. DF values for Pu, Np, and Sr achieved within 30 minutes of magnetite formation were orders of magnitude larger than the needed values. DF values for U and Am were less than the former three but still acceptable, and greater than MST. Figure 1 is a comparison of DF values for Sr using magnetite and MST, where magnetite DF values are orders of magnitude higher than MST.

CSSX flowsheet test using modified solvent: A modified solvent was developed by Oak Ridge National Laboratory for the CSSX process that removes Cs from the SRS tank waste. The new solvent was developed to replace a previous version that was super-saturated and caused

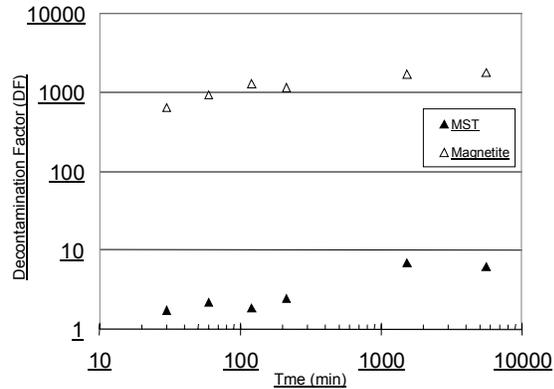


Fig 1. Magnetite performance is superior for Sr decontamination compared with MST.

early precipitation. The modified CSSX solvent was evaluated for the same CSSX flowsheet, SRS simulant, and 33-stage 2-cm centrifugal contactor that had been used to test the previous CSSX solvent. As with the previous solvent, the key process goals were achieved: (1) Cs was removed from the waste with DF values greater than 40,000 (Fig. 2) and (2) the recovered Cs was concentrated by a factor of 15 in dilute nitric acid. Thus, the modified solvent can be used in place of the previous super-saturated

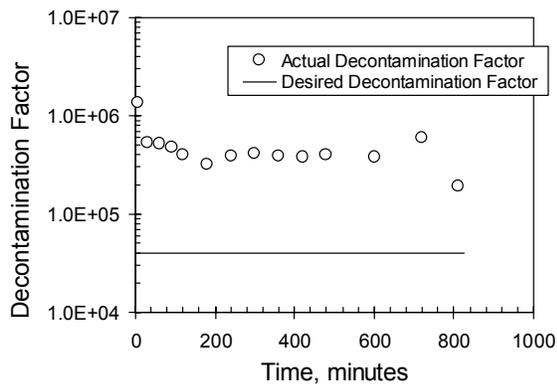


Fig 2. The DF remained above 40,000 for the CSSX process test using the modified solvent.

solvent while maintaining satisfactory hydraulic performance and achieving process requirements.

Recovery of entrained CSSX solvent using coalescers: The cost of solvent used in the CSSX process is about \$1,900 per liter. Some of this solvent gets entrained in the aqueous solution during the extraction process, causing significant loss. This work focused on recovering the entrained solvent.

The entrainment of the solvent components in the SRS simulant during the operation of a 4-stage contactor unit was quantified. The chemical stability of several candidate commercial coalescing media in the caustic simulant was examined. A laboratory-scale coalescer was operated in tandem with a four stage 4-cm contactor unit. Results indicated that a 90% recovery of the entrained solvent can be achieved using a commercial coalescer equipped with appropriate media and at appropriate operating conditions. This represents a potential savings of \$5 million annually, based on a plant processing rate of 20 gpm.

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Research Participants

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Waste Forms Qualification Testing

Meeting requirements for high-level waste storage

Spent sodium-bonded fuel from the Experimental Breeder Reactor II must be treated prior to disposal in the federal high-level waste repository. Two waste forms will be used to immobilize wastes from electrometallurgically treated fuels for disposal: a ceramic waste form (CWF) will be used to immobilize radioactive salts and a metallic waste form (MWF) will be used to immobilize contaminated cladding hulls. Laboratory tests are being conducted to address qualification requirements with regard to both the waste forms and their impact on the disposal system.

Several waste product specifications are identified in the DOE Waste Acceptance System Requirements Document (WASRD). These include requirements regarding the physical, chemical, and radiological stability of the waste form, the consistency of waste forms and their production, imposed radionuclide concentration limits, etc. A primary focus of recent research has been to establish acceptable methods for tracking waste form product consistency.

The impact of disposed waste forms on the ability of the disposal system to contain the radioactive waste must also be evaluated in performance assessment calculations that will be conducted for the Yucca Mountain repository license application. These calculations will be used to show that the system of natural and engineered barriers combined with the integrity of the waste forms themselves will meet groundwater protection requirements over the regulated service life of the repository. The Chemical Engineering Division is developing a method to account for the CWF and MWF in these calculations.

2002 Research Highlights

The CWF is a multi-phase material composed primarily of sodalite inclusions bound in a

borosilicate glass matrix. The primary role of the sodalite is to contain chloride from the salt. Small amounts of halite and various oxide and silicate inclusions are also present. The most abundant radionuclide in the CWF will be Pu-239, which will be sequestered as (U,Pu)O₂ inclusions in the glass. Small amounts of fission products will be contained in the sodalite, glass, and halite phases. The release of radionuclides from the CWF will require prior degradation of the sodalite/glass matrix.

A wide range of tests and analyzes have been conducted to measure the CWF degradation behavior. Recent work has focused on measuring the consistency of CWF products, which is a key requirement in the WASRD. All CWF materials will be made with about 67 mass % Zeolite A, 25 mass % borosilicate glass, and 8 mass % waste salt. Only the salt composition will vary. Sodalite forms during processing by reaction of Zeolite A with salt. The method used to track the consistency of high-level waste (HLW) glasses, namely, the product consistency test (PCT) was evaluated as a possible method to track the consistency of the CWF. The PCT is specified in the WASRD for measuring the consistency of HLW glasses. This method was expected to be appropriate because the dissolution mechanism of HLW glass is the same as that of the sodalite and binder glass phases in the CWF. The PCT is conducted by immersing crushed glass in demineralized water at 90°C for seven days, then using the concentrations of soluble components (e.g., alkali metals, boron, and silicon) in the test solution as a measure of the chemical durability. Besides tracking the consistency of the CWF chemical durability, application of the PCT can be used to track the amount of halite and the sodalite/glass mass ratio in the CWF, which provide evidence of process control.

Issues that were studied regarding use of the PCT with the CWF included possible phase fractionation due to crushing and sieving, the ability to discriminate between dissolution of the halite, sodalite, and glass phases, and the precision of the method. The different phases were found not to fractionate due to crushing and sieving, and the crushed CWF material was representative of the bulk material. This was confirmed by chemical dissolution and analysis of different size fractions. The amount of halite is measured by immersing the crushed material in demineralized water for about 1 minute at room temperature to dissolve halite from the surface of the particles, then measuring the chloride concentration in the solution. This is referred to as the rapid water soluble test (RWS).

A series of CWF materials was made using different processing conditions to generate different amounts of halite. As shown in Figure 1, the chloride concentration from the RWS is correlated with the amount of halite measured to be in the bulk CWF with x-ray diffraction. Another series of CWF materials was made with different zeolite/glass ratios to determine the sensitivity of the PCT test solution. The results (Fig. 2) indicate that the

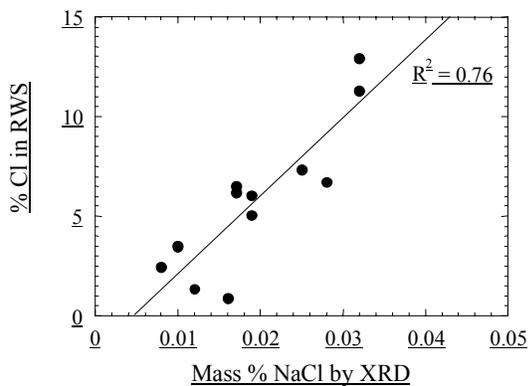


Fig. 1. Correlation between chloride in the PCT wash solution and halite in the bulk CWF measured by x-ray diffraction.

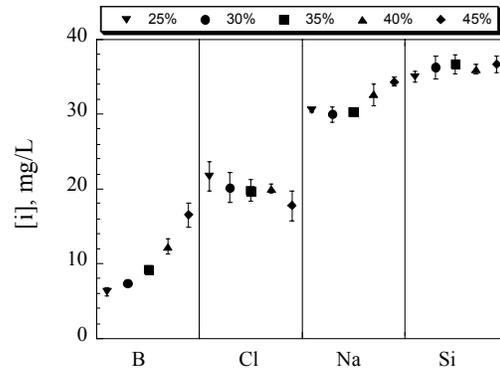


Fig. 2. Sensitivity of PCT solution concentrations to sodalite/glass ratio in CWF (mean \pm 1 σ for triplicate PCT).

boron concentration can be used to discriminate CWF with different amounts of glass, but the concentrations of Na, Cl, and Si cannot. This is because boron is present only in the binder glass, whereas the other components are present in both the glass and sodalite phases. An interlaboratory study was conducted to measure the precision with which the PCT can be conducted with CWF. The results indicated that the same precision can be attained for PCT conducted with CWF as with borosilicate glasses. As a result of these studies, the scope of the PCT has been revised to specifically state its applicability to glass-ceramic materials, with reference to the CWF.

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Research Participants

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Combining XAFS and EELS to Understand the Fate of Neptunium during the Corrosion of Spent Fuel

Building a repository safety case

Interest in mechanisms that may control the release of radioelements from corroded commercial spent nuclear fuel (CSNF) has been heightened by the selection of the Yucca Mountain site in Nevada as the repository for high-level nuclear waste in the United States. Weathering of natural uranium deposits has served as a model for understanding long-term behavior of spent fuel. However, natural-analog studies are of limited value for predicting the behaviors of transuranic elements, such as neptunium (Np), an important contributor to long-term dose. Recently, researchers proposed that certain transuranics, particularly Np, may be incorporated into solid alteration phases that are likely to form during CSNF corrosion. Initial data had been reported that seemed to corroborate the use of this model, and on this basis an empirical Np solubility model was proposed that assumes Np is incorporated into U(VI)-solids (e.g., dehydrated schoepite, $\text{UO}_3 \cdot 0.8\text{H}_2\text{O}$). To test this hypothesis, we initiated research using synchrotron x-ray absorption spectroscopy (XAS) and electron energy loss spectroscopy (EELS) to study specimens of uranyl oxyhydroxide alteration phases derived from CSNF to learn about the possible fate of neptunium during CSNF corrosion.

2002 Research Highlights

The details of XAS structure near a particular absorption edge are determined by the local environment of a specific atomic species, including distances to near neighbors, types and numbers of neighboring atoms, the charge state of the central atom, and the site symmetry. Several XAS measurements from CSNF were performed at the Materials Research Collaborative Access Team (MR-CAT) insertion device beamline located at sector 10 of the Advanced Photon Source (APS), a third-

generation x-ray synchrotron source located at Argonne National Laboratory. The brightness of the APS facility in the high-energy x-ray regimes makes it ideal for investigating radionuclide systems.

A fundamental difficulty in detecting and measuring the hard x-ray absorption spectra of small quantities of neptunium in a uranium matrix is the small energy separation of the fluorescent x-ray spectral lines (about 330 eV between the $L \alpha_1$ lines). Quantities as small as 1 part in 100 can be detected easily. However, detecting smaller quantities and measuring useful spectroscopic information requires that the background from the matrix uranium be substantially decreased. We chose an experimental approach for a narrow bandwidth detector based on diffractive optics. One such diffractive geometry is the Laue configuration, where x-rays are transmitted through the crystal, which is bent to the form of a logarithmic spiral to match the diffraction condition across its entire surface.

Specimens of uranyl oxyhydroxide alteration phases were taken from two different CSNF Approved Testing Materials that had been exposed to 100% relative humidity at 90°C for 104 months. Fluorescence yield as a function of incident energy was obtained using a bent-Laue configuration as described above. The yellow alteration rind that coated the CSNF was confirmed by XAS near-edge structure in each case to be uranium (VI)-based, likely dehydrated schoepite (Fig. 1). Neptunium fluorescence was not observed, however, and detailed analyses firmly established upper limits for Np incorporation of less than 1 part in 5000, which is significantly below previously reported concentrations in the alteration phases, and less than about half the value in the unaltered fuels.

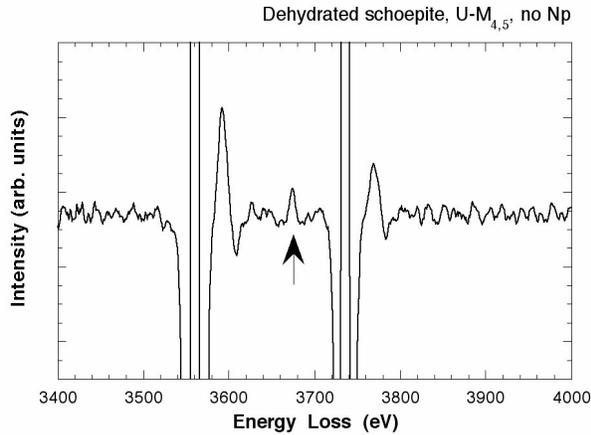


Fig. 1. Uranium L-III XAS from CSNF corrosion products shows structure consistent with uranyl (U^{6+}) chemistry.

Based on these XAS results, we re-examined incorporation and attribute the discrepancy to a previous EELS-based claims of neptunium peculiar plural-scattering event in uranium that creates a spurious electron energy loss peak at the Np-M₅ energy (3666 eV). The source of this peak is combined losses from the U-O_{4,5} edge (~110 eV), and the U-M₅ edge at 3551 eV. We also show that similar EELS peaks could be observed in uranium specimens known to be free of neptunium (Fig. 2).

This work has demonstrated the utility of XAS for clarifying the role of alteration phases in sequestering radioelements that are important in assessing the performance of a geologic repository containing spent nuclear fuel.

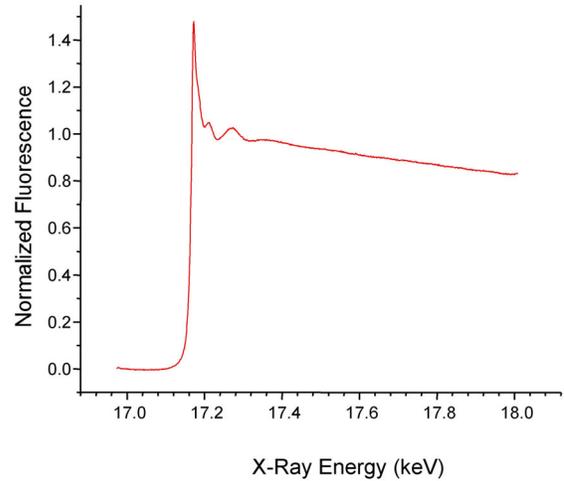


Fig. 2. Second-difference EELS spectrum of Np-free dehydrated schoepite shows a feature at ~3666 eV that had been attributed to Np, but which clearly must have another origin, such as plural scattering of electrons, in this case.

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Research Participants

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U.S. and European Fuel Corrosion Studies

Lessons learned from comparing underground and underwater disposal

Disposal of used nuclear fuel is an international problem for which different countries have selected vastly different solutions. In the United States, we look to Yucca Mountain, Nevada, for permanent underground disposal in a remote desert repository. Meanwhile, several European countries plan to store their spent fuel submerged deep under water. Both approaches are viable because corrosion of the fuel and mobilization of its radionuclides require both water and oxygen to proceed at an appreciable rate.

While Yucca Mountain has atmospheric oxygen levels, its rate of water infiltration is very slow. Conversely, deep water-saturated repositories have copious water but their oxygen content is near zero. Corrosion-testing experiments are conducted by each country under conditions that test the limits of their proposed repository environment. In tests conducted by the Chemical Engineering Division (the Division) for the Yucca Mountain Project, spent nuclear fuel is corroded with oxygenated groundwater at infiltration rates at and above the maximum rates expected in the desert environment over the next 10,000 years. Similarly, Swedish experimenters explore the limits of their repository environment by corrosion-testing water-submerged segments of spent nuclear fuel in an environment with atmospheric oxygen levels.

Taken together, these tests represent non-overlapping test conditions that probe the mechanisms by which spent fuel rods may eventually corrode and release their nuclides. Comparison of the results from these studies provides interesting insights into the process by which spent fuel is likely to corrode in the presence of any amount of water.

2002 Research Highlights

The results of two corrosion tests performed by the Division with spent nuclear fuel from the

same rod were compared with the results of a corrosion test performed by the Swedish Royal Institute of Technology (SKB) with a similar spent fuel. One of the Division's tests subjected crushed, de-clad fragments of commercial spent fuel to periodic injections of modified groundwater. The second test permitted drainage of modified groundwater through short, vertical segments (3 to 9 cm long) of clad spent nuclear fuel rods. Both experiments were performed at 90°C and allowed the water to oxidize and leach soluble components from the ceramic fuels. The resulting leachates were periodically collected and analyzed.

The Swedish tests were conducted with shorter (2 cm) segments of clad commercial spent nuclear fuel. As in the Division's clad segment tests, the Swedish segments were cut at both ends, allowing water to contact both exposed fuel surfaces. These tests were performed at room temperature with the segments submerged in 200 mL of simulated groundwater open to the air in order to maintain atmospheric O₂ levels. Although the SKB tests were conducted with 16 different segments of fuel, each with a different burnup value, two of the segments closely bracket the burnup of the segments and fragments used in the Division's tests and provide the basis for this comparison.

Results from these tests for ¹³⁷Cs are shown in Figure 1. During irradiation, Cs is volatilized and migrates along thermal gradients from its source in the fuel matrix to the cooler regions of the fuel rod, including the fuel grain boundaries, the gap between the fuel and cladding, and the plenum region at the axial ends of the rods. From characterization of the Argonne test fuel (ATM-103), we know that the fuel/clad gap region contains approximately twice as much Cs as the grain boundaries for that fuel. When the rod segments are exposed to either intermittent trickles of water (as in the Division's segment

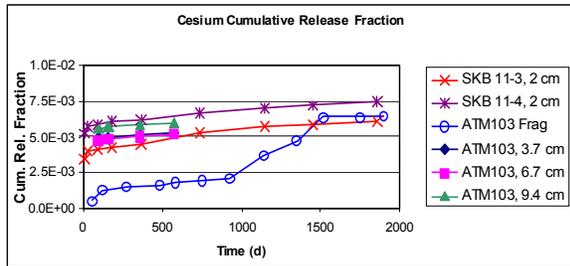


Fig. 1. Cesium release from clad rod segments and de-clad fuel fragments.

tests) or submerged (as in the SKB tests), the fuel/clad gap region is preferentially leached and Cs release is high. This can be observed in Figure 1, which shows higher release of Cs from the clad rod segments than from the de-clad fuel fragments during the first four years. By the fifth year of testing, the leached fragments had released Cs from their grain boundaries, resulting in release equivalent to that from the gap region of the clad segments.

By comparing these patterns of Cs release we learned several important facts and can construct a working paradigm for fuel corrosion in a repository. First, we learned that the preferred path of water in clad fuel is through the fuel/clad gap region rather than through cracks or channels through the fuel matrix. This is extremely important because the distribution of elements in spent fuel is highly heterogeneous but predictable. Knowing the path of water through the fuel rod enables us to predict the potential for water exposure and therefore leaching and release of radionuclides of interest.

Second, by comparing results of the Division and SKB rod segment tests, we learned that the water path is the same whether the segments are

submerged in pools of water or are exposed to only intermittent trickles of water. This important fact allows us to extrapolate fuel corrosion models over a range of water infiltration conditions possible for the repository.

Third, we observed that cladding significantly slows corrosion of the fuel matrix and subsequent release of nuclides from grain boundaries. Release of Cs from grain boundaries, observed as a sharp increase in slope for fuel fragments in Figure 1, occurred after three years for the fuel fragments but has not yet occurred for the Division's rod segments nor after five years for the SKB segments. Continued testing of the Division's rod segments will enable determination of the protective effect of clad on fuel corrosion and nuclide release.

Finally, we learned that the anticipated precipitation of fuel (uranyl) oxidation products and concurrent volume expansion within the clad segments are not sufficient to breach the cladding between room temperature and 90°C. Continued testing at 90°C will determine the integrity of the cladding at longer times and enable better assessment of the "cladding credit" that may be assumed in repository models.

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Research Participants

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R. A. Leonard
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R. A. Leonard, S. B. Aase, H. A. Arafat, C. Conner, J. R. Falkenberg, D. B. Chamberlain,
M. C. Regalbuto, and G. F. Vandegrift
ANL-02/11 (May 2002)

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R. A. Leonard, S. B. Aase, H. A. Arafat, C. Conner, J. R. Falkenberg, M. C. Regalbuto, and
G. F. Vandegrift
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ANL-02/18 (December 2001)

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M. A. Lewis, M. C. Hash, A. S. Hebden, and W. L. Ebert
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Monitoring the Consistency of Multiphase Waste Forms

W. L. Ebert, M. A. Lewis, and S. G. Johnson

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Corrosion Tests of LWR Fuels—Nuclide Release

P. A. Finn, Y. Tsai, and J. C. Cunnane

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P. A. Finn, Y. Tsai, and M. M. Goldberg

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J. A. Fortner, S. B. Aase, and D. T. Reed

Presented at the Fall Meeting of the Mater. Res. Soc., Boston, MA, November 26–30, 2001

A High Surface Area-To-Solution Volume, Static Test of IBR-II Irradiated Mixed-Oxide Fuel

J. A. Fortner, P. A. Finn, and M. M. Goldberg

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Corrosion of Metallic Uranium Fuel in a Hydrologically Unsaturated Environment

J. A. Fortner, M. M. Goldberg, and C. S.-Davis

Presented at the Fifth Topical Meeting of the Am. Nucl. Soc., Charleston, SC, September 17–20, 2002

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J. A. Fortner, M. M. Goldberg, and C. Shelton-Davis

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S.-Y. Jeong and W. L. Ebert

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S.-Y. Jeong, L. R. Morss, A. J. Morgan, and W. L. Ebert

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M. D. Kaminski and L. Nunez

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Experimental Verification of Caustic-Side Solvent Extraction for Removal of Cesium from Tank Waste

R. A. Leonard, S. B. Aase, H. A. Arafat, D. B. Chamberlain, C. Conner, M. C. Regalbuto, and G. F. Vandegrift

Presented at the 12th Symp. on Separation Science and Technology for Energy Applications, Gatlinburg, TN, October 15–18, 2001

Simulant Flowsheet Testing with Modified Solvent (2-cm Scale)

R. A. Leonard, S. B. Aase, H. A. Arafat, C. Conner, M. C. Regalbuto, and G. F. Vandegrift

Presented at the 12th Symp. on Separation Science & Technology, Gatlinburg, TN, October 10–15, 2001

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M. A. Lewis, M. Serban, C. L. Marshall, and D. Lewis

Presented at the Am. Nucl. Soc. Winter Meeting, Reno, NV, November 11–15, 2001

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L. Nunez, G. F. Vandegrift, D. L. Bowers, J. Sedlet, S. F. Wolf, and Y. Tsai

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M. Serban, M. A. Lewis, C. L. Marshall, and R. D. Doctor

Presented at the 224th Am. Chem. Soc. National Meeting, Boston, MA, August 18–22, 2002

RERTR Progress in ⁹⁹Mo Production from LEU

G. F. Vandegrift, C. Conner, S. B. Aase, A. J. Bakel, D. L. Bowers, E. Freiberg, A. V. Gelis, K. J. Quigley, and J. L. Snelgrove

Presented at the 6th Int. Topical Meeting on Research Reactor Fuel Management, Gent, Belgium, March 17–20, 2002

Development of the AMUSE Code for Designing Solvent Extraction Flowsheets

G. F. Vandegrift, J. M. Copple, and M. C. Regalbuto

Presented at the 26th Actinide Separations Conf., Berkeley, CA, June 3–6, 2002

Nuclear Technology

Pyrochemical process development and demonstration in the Chemical Engineering Division extends from the reprocessing technologies developed in the 1960s for the Experimental Breeder Reactor II through the Electrometallurgical Treatment (EMT) Program to the Advanced Accelerator Applications (AAA) Program. Within the AAA Program, treatment of spent light water reactor (LWR) fuel is of paramount importance. Implementing a spent LWR fuel treatment technology would enhance the capability of the planned Yucca Mountain repository as well as provide long-term energy security for the United States. To this end, the Department initiated the development of innovative treatment technologies—one for the conversion of oxide fuel to metal (see “Oxide Reduction to Convert Spent Oxide Fuel to Metal Fuel” in this report section) and another for recovering transuranic elements—and continued the advancement of uranium electrorefining. These treatment technologies, together with Argonne’s established waste form technologies, provide the foundation for Argonne’s pyroprocessing flowsheet to treat spent LWR fuel.

We are pursuing the development of an electrolytic process to recover transuranic elements from molten salts for subsequent recycle into advanced reactor systems. The electrolytic process comprises the electro-deposition of metallic transuranic elements, along with any residual uranium initially present in the salt as molten chlorides, at the cathode of the cell and the evolution of chlorine gas at the anode, which could be recycled to produce oxidant for the electrorefining process. Theoretical analysis of the fundamental electrochemistry of the process is complete, preliminary cell concepts are evaluated, and an initial cell concept has been selected for fabrication and testing.

Advancement of the uranium electrorefining process occurred in several areas. Testing of a transitional basket anode for the Mark V electrorefiner provided valuable insight into the mechanism by which uranium agglomerates in the space between the anode and cathode modules. Uranium agglomeration leads to reduced electrorefiner efficiency and, consequently, lower throughput. High throughput—much higher than that required for the treatment of metallic fast reactor fuel—is essential for the treatment of spent LWR fuel. Thus, testing began with a new advanced high-throughput anode system. The high-throughput anode system consists of a set of high surface-area-to-volume anode baskets to contain the fuel and an electrically isolated set of rods for stripping tightly adhering uranium from the cathode of the cell.

Chemical Engineering Division Nuclear Technology R&D

- Pyrochemical process development and demonstration
- Fuel and materials development and evaluation
- Recovery of transuranic elements from molten salts for recycle into advanced reactor systems
- Development of high-throughput anode system for uranium electrorefining
- Evaluation and preliminary design of a parallel plate electrorefiner concept to aid in selection of electrorefiner design concepts for use in a spent LWR fuel treatment facility.

Preliminary test results with this system revealed a profound difference in the morphology of the uranium deposit on the cathode and that found in the product collector compared with the uranium

collected with previous designs; also, no agglomerates of uranium were observed. In addition, no scraping was required to remove the uranium from cathode surface or the stripper rods. Electrochemical data from this high-throughput anode will guide the design of the high-throughput electrorefiner. Finally, evaluation and preliminary design of a parallel plate electrorefiner concept began in the later part of the year. Data from this system will be used to compare electrorefiner design concepts (parallel plate vs. concentric cylinder) proposed for use in a spent LWR fuel treatment facility.

Beyond pyroprocess development, the Division continues its efforts in the development of cermet nuclear fuels for use in advanced reactor systems and studies of liquid metal coolant/materials interactions. In cermet fuel development, important achievements made during the year include establishing a fluidized-bed oxide microsphere coating capability and the fabrication of cermet fuel rods with the powder-in-tube method.

The powder-in-tube fabrication method is a simple low-temperature alternative to elevated temperature methods used for fuel fabrication. In this process, oxide microspheres (50 to 1,000 μm diameter) and zirconium metal powders (~ 44 μm nominal diameter) are dry-mixed, loaded into stainless steel or Zircaloy drawing tubes and vibratory-packed. The powder-containing tube is drawn through a die to reduce the diameter and compact the powder into a dense matrix. Annealing the metals

between 500°C and 1,000°C removes strain hardening and strengthens interfacial bonding. Multiple cycles are used with sequentially decreasing die sizes to achieve complete densification.

Liquid metal coolants proposed for use in fast neutron spectrum reactors designed for energy production as well as heat sources for hydrogen production lead to corrosion of the structural components of the reactor. The Division established a test facility to evaluate the effect that heavy liquid metal coolants such as lead or lead-bismuth eutectic solutions have on structural materials (e.g., steel alloys and ceramics). One of the recent tests involved exposing silicon carbide to liquid lead at 800°C, a coolant-temperature regime suggested for hydrogen production. Results of these tests indicate that silicon carbide shows considerable promise for use in high-temperature liquid metal coolant systems.

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Light Water Reactor Fuel Treatment

Easing the repository burden and recovering value from spent reactor fuel

Commercial nuclear reactors generate about 2,000 metric tons initial heavy metal (MTHM) of spent oxide fuel annually in the United States, adding to the current inventory of 44,000 MTHM that is destined for geologic repository storage. The Chemical Engineering Division is developing technologies to minimize the burden on the repository associated with spent fuel components and to recover the energy value of the actinides in this fuel.

2002 Research Highlights

A pyrochemical process for the treatment of spent light water reactor (LWR) fuel, as depicted in Figure 1, is being developed. In the process, fuel oxides are converted to metals; uranium and transuranic elements are separated and recovered as metal products for fuel fabrication; and the fission products are stabilized in waste forms qualified for geologic repository storage. Three core technologies—direct electrolytic reduction, high-throughput uranium electrorefining and uranium/transuranic (U/TRU) recovery by electrolysis—are being developed to achieve these objectives. Integration of the individual unit operations into a commercially viable, cost-competitive process has also been a focus of the work.

In the process under development, fuel assemblies are chopped, shredded and loaded into fuel baskets. The fuel baskets are transferred to the direct electrolytic reduction vessel where fuel oxides are converted in-situ to metals at the cathode, generating oxide ions that dissolve in the electrolyte and diffuse to the anode. Oxygen gas is evolved at the non-consumable anode. Development work on this process has emphasized cell design, anode materials and cathode reduction kinetics.

The reduced metal from the electrolytic reduction step is retained in the fuel baskets and routed to the uranium electrorefiner. In this process, the fuel baskets serve as the anode. The separation of uranium is achieved by anodic dissolution and electrotransport to the cathode where it is reduced back to a metal and recovered as product. Our development of this technology builds on our experience with electrorefining spent fuel from the Experimental Breeder Reactor II, with particular focus on high-throughput designs.

The transuranic elements and some fission products anodically dissolve and concentrate in the electrorefiner salt. This salt is treated by electrolysis to recover a mixture of uranium and

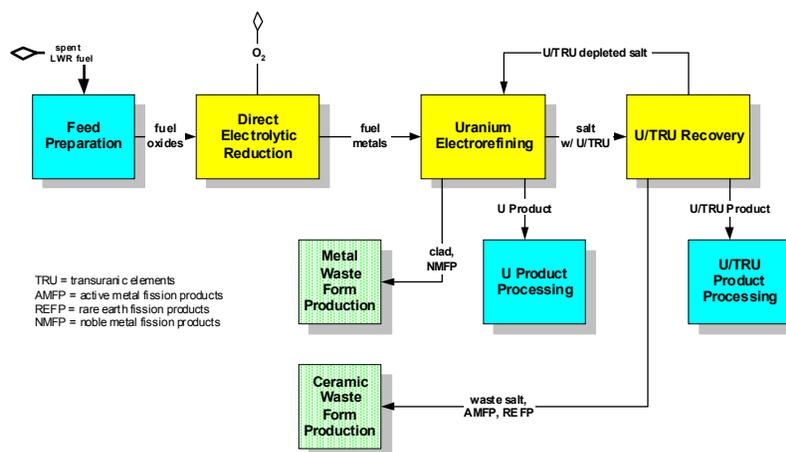


Fig. 1. Spent Light Water Reactor Fuel Treatment Flowsheet.

transuranic metals at the cathode, generating chlorine gas at a graphite anode. Molten salt electrolysis is industrially practiced in the manufacture of several metals, most notably magnesium. Development of this technology for application to U/TRU recovery has been initiated this year with promising early results.

A conceptual design for a demonstration plant with a capacity to treat 100 MTIHM/yr spent LWR fuel has been generated in cooperation with other Argonne research divisions. A concept drawing of the hot cell facility is shown in Figure 2. We are currently refining the design and estimating the costs for the recycling facility.

Research Participants

Mark A. Williamson, Diane J. Graziano, James L. Willit, Sean M. McDevitt, David B. Chamberlain, John P. Ackerman, Arthur A. Frigo, Karthick Gourishankar, William E. Miller, and Michael K. Richmann. For more information, contact Diane Graziano (630-252-6903, graziano@cmt.anl.gov).

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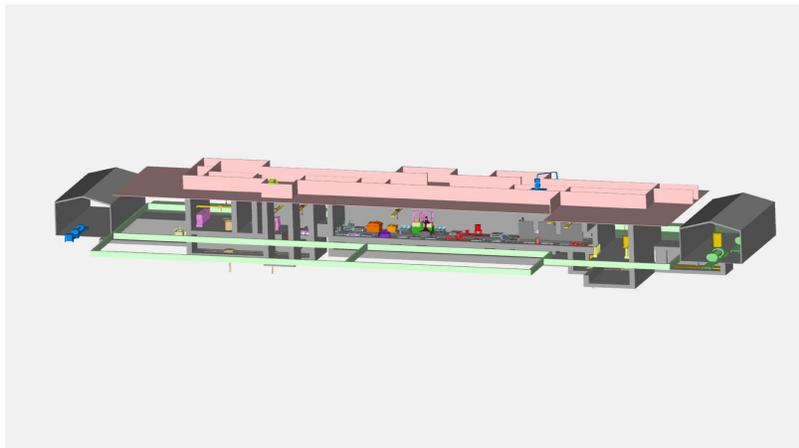


Fig. 2. Conceptual Spent Fuel Treatment Facility.

Oxide Reduction to Convert Spent Oxide Fuel to Metal

Saving repository space and creating new fuel for advanced reactors

Operation of commercial nuclear power plants in the United States has resulted in the accumulation of more than forty thousand tons of spent oxide fuel. This fuel is scheduled for burial in the Yucca Mountain repository. Initially, the radioactivity of spent fuel is mostly due to fission products, but the main constituent of the spent fuel is actinides: unconsumed uranium and heavier elements. These actinides are responsible for nearly all the radioactivity of the spent fuel after a few hundred years. It is probably even more significant that these same actinides can be re-used in advanced reactors if separated from most of the fission products and other constituents of spent fuel.

The Chemical Engineering Division is developing a direct electrolytic reduction process to convert this spent fuel to new metal fuel for advanced reactors and to durable waste forms suitable for disposition in the repository. Our goals are twofold: to radically reduce the long-term burden on Yucca Mountain and any future repositories, and to salvage the actinides, thereby providing sufficient fuel to generate many tens of times as much energy as was obtained in the first use of this commercial fuel.

2002 Research Highlights

Recent work in development of this process has focused on three major areas: (1) cathode studies, which investigate the fundamentals of reduction rate, and hence process cost; (2) cell design studies, intended to define a device that best meets the economic and other criteria for a commercial process, and (3) development of materials for the anode of the electrolytic cell that remain usable for long periods of time under commercial operating conditions.

Cathode studies: The cathode studies have demonstrated rapid and complete reduction of actinide oxides in batches ranging from a few

tens of grams to more than 300 grams; larger tests are underway. Uranium makes up roughly 99% of the actinide content of the spent fuel, and it requires fewer security and safety precautions to work with; thus initial work in cathode studies used uranium oxide feeds. Complete conversion of uranium oxide can be routinely achieved within the analytical uncertainty of less than ~0.5%, and reduction rates are very rapid. Figure 1 shows a uranium cathode product that is completely reduced.



Fig. 1. Fuel Basket Cross-Section Showing a Completely Reduced Cathode Product

It is not sufficient to reduce uranium oxide. In order to radically decrease the long-term hazard of the material sent to the repository, it is necessary to also reduce the oxides of the elements heavier than uranium. These are mainly plutonium and americium, with small amounts of curium and neptunium. After complete reduction of uranium oxide became routine, we began studies with a $\text{UO}_2\text{-PuO}_2$ feed containing 5% plutonium and small amounts of its daughter, americium, to determine the feasibility of PuO_2 reduction. Initial results show that the electrolytic reduction process is also very effective at reducing both PuO_2 and AmO_2 . Chemical analysis on initial cathode product samples showed that the average conversion of the minor oxide components PuO_2

and AmO₂ in the fuel was >98%. One of the objectives of our ongoing cell design and cathode development work is to demonstrate complete reduction of all the actinides.

In the course of the cathode development work, it was necessary to develop several research tools. These include development of a Ni-NiO reference electrode that is sensitive to oxide concentration in the salt, and several analytical methods that are sensitive and versatile enough to evaluate the oxygen and metal contents of the products from all the various test cells. The analytical tools include an ignition-based method, a method based on oxidation with bromine and ethyl acetate, and a Leco analysis method that is very sensitive to the last traces of oxygen in the product. These techniques are described elsewhere in this report.

Cell design studies: In the cell design task, we are evaluating a novel alternative concept intended to allow both cathode and anode to operate at near-optimum conditions at all times. The initial small (21 g UO₂) experiment with this cell design showed the behavior expected for its electrode configuration, and yielded complete reduction of uranium oxide. Development work has led to a concentric cylindrical electrode arrangement that gave complete reduction of 79 grams of UO₂ with very rapid kinetics; it was necessary to limit the applied voltages to avoid power supply overload (>20 amperes). A second cell of this configuration was run with 315 grams of UO₂. This cell also showed very rapid reduction, but it was obvious that the large amount of oxygen evolved, which was not isolated from the cathode and structural cell parts, had nearly destroyed all stainless steel parts in the hot zone and adversely affected the gold anode. Although both steel and gold were used strictly as an experimental convenience, we also believe that a

mechanism involving re-reduction of product oxygen at the cathode and consequent oxide release to the electrolyte supported large background currents, thereby reducing cell efficiency. The next cell to be tested will use a variant of the cylindrical geometry that allows isolation of the anode gases from the rest of the cell and sparging of the anode with inert gas to sweep away the oxygen.

Anode materials studies: Inert anode materials are being evaluated to develop the best material and anode configuration design for the electrolytic reduction process. The initial screening activities included materials selection, thermodynamic calculation, chemical compatibility tests, high-temperature electrical conductivity measurements, and in-cell electrochemical performance testing. A selection of metals and conductive ceramic oxides were evaluated with the most promising being tested under service-relevant electrochemical environments. At present, strontium-ruthenium oxide (SrRuO₃) appears to be the best-available inert ceramic anode for this application and efforts are underway to develop fabrication methods for practical configurations and to evaluate its long-term performance.

Research Participants

Mark A. Williamson, Karthick Gourishankar, John P. Ackerman, Dennis Dees, Diane J. Graziano, Sean M. McDeavitt, Len Leibowitz, Laurel Barnes, Andy Hebden, James L. Willit, David B. Chamberlain and Arthur A. Frigo. For more information, contact Mark Williamson (630-252-9627, williamson@cmt.anl.gov).

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Cermet Nuclear Fuels for Advanced Fuel Cycles

Improving the performance of nuclear fuels

Zirconium matrix cermet nuclear fuels are being developed by the Chemical Engineering Division under two separate, related programs in collaboration with Purdue University, other national laboratories, and other Argonne National Laboratory research divisions. Cermets have demonstrated the potential to enhance fuel performance because the high thermal conductivity of the metal matrix maintains low internal temperatures, which has beneficial performance and safety implications.

We are presently working on two different cermet concepts: (1) thorium-uranium oxide microspheres in a dense zirconium matrix, and (2) coated transuranic (TRU) microspheres in a low-density zirconium matrix.

2002 Research Highlights

Thorium-uranium oxide cermet fuel: This nearly completed project is a collaboration with Purdue University's School of Nuclear Engineering under the U.S. Department of Energy's 1999 Nuclear Energy Research Initiative (NERI). The principal goal of this project is to demonstrate the feasibility of a zirconium-matrix cermet fuel containing (Th,U)O₂ microspheres that can achieve high actinide burnup with improved irradiation stability due to low internal fuel temperatures, low fuel failure rates, and minimal waste treatment. In the baseline cermet fuel concept, the fuel "meat" is composed of a fine dispersion of (Th,U)O₂ microspheres that have a theoretical density between 70 and 99% and a uranium enrichment below 20% U-235. Nominal values for the microsphere diameter, ThO₂-to-UO₂ ratio, fuel-to-matrix ratio, and U-235 enrichment were selected as ~50 μm, 50:50, 50:50, and ~19.5%, respectively.

Important achievements made in this project include the following:

- The development of the powder-in-tube method and equipment for the fabrication of cermet rods,

- The establishment of lab-scale fabrication equipment for (Th,U)O₂ microspheres by spray drying,
- The creation of a detailed thermal model to simulate the behavior of cermet fuel, and
- The design and simulation of nuclear reactor fuel cycle behavior and economics.

Computer simulations revealed excellent behavior and, after some initial simulation, a boiling water reactor (BWR) core with a tight-pitch hexagonal lattice was developed using the nominal (Th,U)O₂ cermet. The BWR moderator-to-fuel area was reduced and the conversion ratio increased from ~0.6 to more than 0.9, resulting in a substantial increase in fuel burnup. Another notable simulation was made using a standard BWR lattice with burnable absorbers built into the fuel matrix. Figure 1 illustrates that the excess fuel reactivity is well controlled (with no significant penalty to the achievable burnup) when the zirconium matrix contains ~5 atom % boron in 1 of every 20 fuel rods.

In the laboratory activities, spray drying and sintering were demonstrated to produce stable, dense, and homogeneous microspheres. A

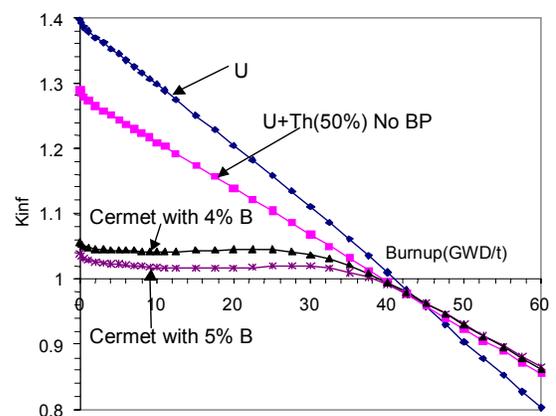


Fig. 1. Reactivity vs. burnup for a BWR fuel assembly with burnable absorbers built into the cermet matrix (Purdue University).

representative picture of the final sintered microspheres is shown in Figure 2. Also, the powder-in-tube fabrication method was demonstrated as a low-temperature alternative to elevated temperature methods. In this process,

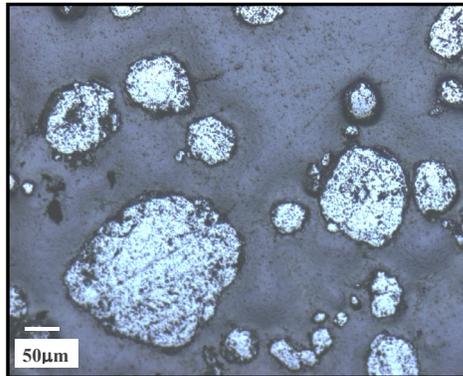


Fig. 2. Spray-dried and sintered (U,Th)O₂ microspheres (Purdue University).

oxide microspheres and zirconium metal powders are dry-mixed and loaded into stainless steel drawing tubes and drawn to form a dense matrix (Fig. 3).

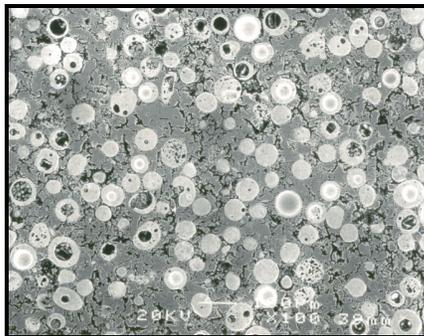


Fig. 3. Electron micrograph of microspheres in a zirconium matrix fabricated by powder-in tube drawing.

Coated actinide cermet fuel: Cermet fuels were also being developed for use in the multi-laboratory Advanced Accelerator Applications (AAA) program of Fiscal Year 2002. In this program, fuel materials were being developed for the transmutation of transuranic (TRU) elements from commercial light-water reactors in an accelerator-driven system. The goal of our particular project was to develop a method for coating the TRU microspheres to enable fission product containment and thermochemical stabilization in the zirconium matrix.

A fluidized bed-chemical vapor deposition (FB-CVD) method was selected to deposit a niobium metal coating onto the TRU microspheres. Niobium was selected as the refractory metal of choice because of its favorable nuclear properties, its relative ductility and workability, and its chemical compatibility with the TRU oxides and zirconium metal. The FB-CVD method is a commercially demonstrated technology and the focus of this task was to translate this established technology into a specific form that can be carried out in a remote-operation hot cell.

The FB-CVD coating system was assembled in a controlled area laboratory and the initial coating demonstrations were completed. Figure 4 is a photograph of fluidized ZrO₂ microspheres before the coating operations were initiated. Final coating experiments were underway at the writing of this report. With the demonstration of this FB-CVD coating method and the emergence of the Advanced Fuel Cycle Initiative, this project is now complete.



Fig. 4. Zirconium oxide (ZrO₂) microspheres in the FB-CVD vessel.

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Research Participants

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Corrosion of Structural Materials by Heavy Liquid Metal Coolants

Finding materials to enhance the performance of fast reactors

A particular set of advanced nuclear reactor systems use liquid lead and lead-bismuth eutectic (LBE) alloys as the system coolant. Common designations for lead-based coolants are HLM (heavy liquid metal) or HLME (heavy liquid metal coolant). Such coolants are especially useful for reactors with fast neutron spectra, or fast reactors, and high coolant temperatures, such as those proposed for the thermochemical production of hydrogen.

In all HLME systems, liquid metal corrosion is a primary performance issue. The Chemical Engineering Division has been testing candidate materials for natural-circulation HLME systems. The goal of this research is to select and evaluate promising structural materials, building on a large international database from the early days of nuclear research. Our relatively modest scope is focused on the effects of specific variables at low oxygen content and various temperatures.

This work started in support of the STAR-LM natural-circulation, fast reactor design, which uses LBE coolant with a maximum temperature of $\sim 550^{\circ}\text{C}$. Recently, research has been carried out to support a similar, higher-temperature lead-cooled system for a Nuclear Energy Research Initiative (NERI) project. The NERI project is focused on the generation of hydrogen using a nuclear-powered heat source, with the specific reactor design being a natural-circulation HLME fast reactor operating with a maximum coolant temperature of $\sim 800^{\circ}\text{C}$.

2002 Research Highlights

We have installed a test system to expose candidate materials to flowing lead and lead-bismuth under a temperature gradient at a controlled oxygen potential. The gradient is essential for discerning preferential dissolution and transport of alloy components. Alloy samples are sealed within a quartz harp (Fig. 1),

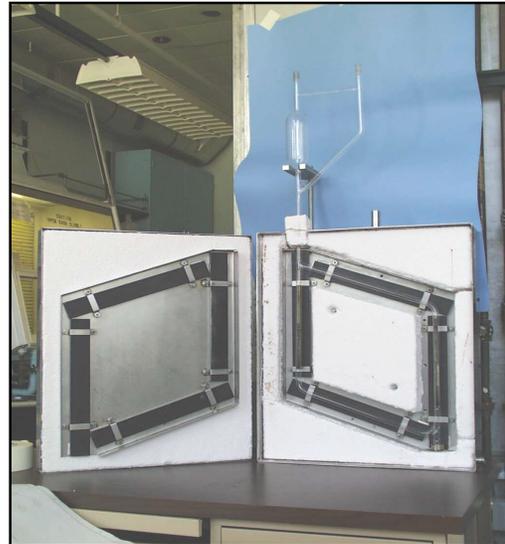


Fig. 1. Quartz harp installed in furnace enclosure utilized to test various material samples.

which is filled with molten metal; natural circulation induces liquid metal flow. Stainless steels alloys have been tested at $550^{\circ}\text{C}/\sim 400^{\circ}\text{C}$ (hot leg/cold leg) to simulate the operating environment of the STAR-LM natural-circulation fast reactor. A silicon carbide sample tube was tested in a quartz harp this year in flowing molten lead at $800^{\circ}\text{C}/650^{\circ}\text{C}$ to simulate the operating environment of a natural circulation HLME fast reactor.

Initial experiments were performed using lead-bismuth eutectic (LBE) coolant in contact with various stainless steel alloys. It was observed that the alloy constituents exhibited selective corrosion attack in lead and lead alloys at the test temperatures up to 550°C with end-grain and surface asperities the preferred sites of attack (Fig. 2). Intrusion of the liquid metal occurred along chromium-rich phases in the stainless steel. Mass transport of iron-rich phases occurred along the LBE/Cr phase interface.

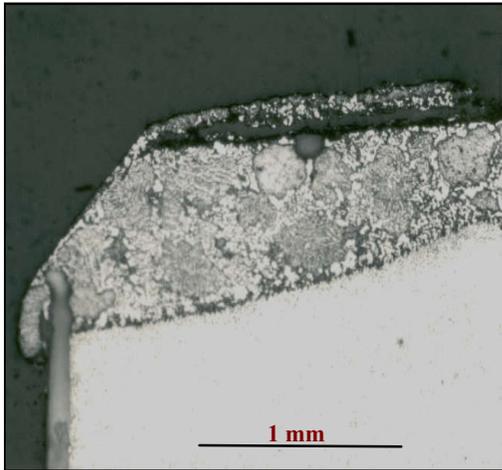


Fig. 2. Selective attack of HT-9 steel in flowing lead-bismuth eutectic alloy at 550°C.

As noted above, a natural-circulation corrosion test was performed using lead and silicon carbide as part of the NERI hydrogen project. It is well documented that, at temperatures proposed for hydrogen generation (about 800°C), stainless steel and other metal alloys exhibit creep, loss of strength, sensitization and other high-temperature exposure phenomena. With this in mind, ceramics became the next logical choice of test materials.

In addition to its thermodynamic compatibility with lead, silicon carbide was selected as our first test material because of the well documented radiation stability of β -SiC, the low neutron activation of Si and C, excellent mechanical and thermal properties of SiC, and a rich history of application in aerospace components as monolithic ceramics and composites.

Experimental results after 1,000 hours exposure at 800°C revealed no evidence of lead interaction with the SiC sample. The ceramic surfaces exhibited an as-processed appearance with no evidence of wetting (Fig. 3). The lead exhibited no evidence of interaction with the SiC and pulled away from the sample as it cooled.



Fig. 3. (Top) Representative pretest photo of SiC sample tube. (Bottom) Longitudinal metallographic cross section prepared through the SiC tube sample after exposure to the molten lead for 1,000 hours at 800°C.

Adherent drops of lead exhibited non-wetting, demonstrated by very high contact angles.

The results clearly indicate that SiC shows promise for application in high-temperature HLMC systems. Future work will focus on establishing other structural materials for hydrogen-generating HLM nuclear systems at temperatures up to 800°C. Testing will include samples made from vanadium-4 titanium-4chromium alloy and silicon carbide composites.

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Research Participants

Jude M. Runge, Leonard Leibowitz, Laurel A. Barnes, and Sean M. McDevitt. For more information, contact Sean M. McDevitt (630-252-4308, mcdevitt@cmt.anl.gov).

Patents and Selected Publications and Presentations

Patents

Method and Apparatus for the Clean Replacement of Contaminated HEPA Filters
S. G. Wiedmeyer, A. A. Frigo, D. E. Preuss, E. F. Bielick, and R. F. Malecha
U. S. Patent No. 6,364,923 B1, issued April 2, 2002

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J. E. Indacochea, S. M. McDeavitt, and G. W. Billings
J. Adv. Eng. Mater. **3**(11), 895–901 (2001)

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Thoria-Based Cermet Nuclear Fuel: Neutronics Fuel Design and Fuel Cycle Analysis
T. J. Downar, S. M. McDeavitt, T. K. Kim, S. Revankar, and A. A. Solomon
Proc. of the ICONE10 10th Int. Conf. on Nuclear Engineering, Arlington, VA,
April 14–18, 2002, Paper No. ICONE10-22305 (2002)

A Positive Approach for Leak Testing Negative-Pressure Gloveboxes
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Orlando, FL, August 19-21, 2002 (2002)

Corrosion of Stainless Steels by Lead-Based Reactor Coolants
L. Leibowitz, V. A. Maroni, S. M. McDeavitt, A. G. Raraz, and A. J. Kropf
Proc. of the Am. Nucl. Soc. Winter Meeting, Reno, NV, November 11–15, 2001, ANS
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Thoria-Based Cermet Nuclear Fuel: Sintered Microsphere Fabrication by Spray Drying
A. A. Solomon, S. M. McDeavitt, V. Chandramouli, S. Anthonysamy, S. Kuchibhotla, and
T. J. Downar
Proc. of the ICONE 10 10th Int. Conf. on Nuclear Engineering, Arlington, VA,
April 14–18, 2002, Paper No. ICONE10-22445 (2002)

Papers Presented at Scientific Meetings

Thoria-Based Cermet Nuclear Fuel: Neutronics Fuel Design and Fuel Cycle Analysis

T. J. Downar, S. M. McDeavitt, A. A. Solomon, and T. K. Kim

Presented at the ICONE 10 10th Int. Conf. on Nuclear Engineering, Arlington, VA,
April 14–18, 2002

A Structural Study of Neptunium-Bearing Uranium Oxides

R. J. Finch

Presented at the Am. Geophysical Union Spring Meeting, Washington, DC,
May 28–31, 2002

Precipitation of Crystalline NpO_2 During Oxidative Corrosion of Neptunium-Bearing Uranium Oxides

R. J. Finch

Presented at the Fall Meeting of the Mater. Res. Soc., Boston, MA,
November 26–30, 2001

Neptunium Incorporation in Uranium(VI) Compounds Formed During the Aqueous Corrosion of Neptunium-Bearing Uranium Oxides

R. J. Finch, E. C. Buck, and S. F. Wolf

Presented at the Fall Meeting of the Mater. Res. Soc., Boston, MA,
November 26–30, 2001

The Development of a Standard of Practice for the Design and Fabrication of Containment Gloveboxes for Materials that Emit Low-Penetrating Ionizing Radiation

A. A. Frigo

Presented at the 16th Annual Conf. and Exposition of the Am. Glovebox Soc. Meeting,
Orlando, FL, August 19–21, 2002

A Positive Approach for Leak Testing Negative-Pressure Gloveboxes

A. A. Frigo and J. K. Basco

Presented at the 16th Annual Conf. and Exposition of the Am. Glovebox Soc. Meeting,
Orlando FL, August 19–21, 2002

Electrochemical Reduction of Metal Oxides in Molten Salts

K. V. Gourishankar, L. Redey, and M. A. Williamson

Presented at the 131st TMS Annual Meeting, Symp. on Molten Salt Processing
Technology, Seattle, WA, February 17–21, 2002

Electrochemical Reduction of Oxides

K. V. Gourishankar, M. A. Williamson, L. Redey, and D. G. Graczyk

Presented at the Fifth Topical Meeting of the Am. Nucl. Soc., Charleston, SC,
September 17–20, 2002

Ceramic-Metal Interfaces in Nuclear Materials Application

S. M. McDeavitt

Presented at the Am. Nucl. Soc. Annual Meeting, Hollywood, CA, June 9–13, 2002

The Role of Interfaces in Ceramic-Metal Bonding

S. M. McDeavitt, G. W. Billings, and J. E. Indacochea

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Ceramic-Metal Interface Stability

S. M. McDeavitt, G. W. Billings, and J. E. Indacochea

Presented at the ASM Int. Materials Solution Conf., Indianapolis, IN, November 5–8, 2001

Cermet Fuel for the Thorium Fuel Cycle

S. M. McDeavitt, T. J. Downar, and A. A. Solomon

Presented at the Am. Nucl. Soc. Annual Meeting, Hollywood, FL, June 9–13, 2002

Thoria-Based Cermet Nuclear Fuel: Cermet Fabrication and Behavior Estimates

S. M. McDeavitt, M. C. Hash, A. A. Solomon, T. J. Downar, S. Revankar, and A. S. Hebden

Presented at the ICONE 10 10th Int. Conf. on Nuclear Engineering, Arlington, VA, April 14–18, 2002

The Role of Ceramic-Metal Interfaces as an Enabling Technology in Nuclear Energy Applications

S. M. McDeavitt, J. E. Indacochea, and G. W. Billings

Presented at the 104th Annual Meeting of the Am. Ceram. Soc. Int. Symp. on Ceramic Joining, April 28–May 1, 2002

Corrosion of HT9 Stainless Steel by Lead-Based Reactor Coolants

S. M. McDeavitt, L. Leibowitz, V. A. Maroni, J. M. Runge, L. A. Barnes, and C. T. Snyder

Presented at the Am. Nucl. Soc. Winter Meeting, Reno, NV, November 14, 2001

Thoria-Based Cermet Nuclear Fuel: Sintered Microsphere Fabrication by Spray Drying

A. A. Solomon, S. M. McDeavitt, V. Chandramouli, S. Anthonysamy, S. Kuchibhotla, and T. J. Downar

Presented at the ICONE 10 10th Int. Conf. on Nuclear Engineering, Arlington, VA, April 14–18, 2002

Development of Pyrochemical Separations Technologies for Partitioning and Transmutation Systems

M. A. Williamson

Presented at the Am. Nucl. Soc. Annual Meeting, Hollywood, FL, June 9–13, 2002

Engineering Aspects of Electrorefining Development

J. L. Willit, R. J. Blaskovitz, V. Goss, and E. C. Gay

Presented at the Fifth Topical Meeting of the Am. Nucl. Soc., Charleston, SC, September 17–20, 2002

Development of High Throughput Uranium Electrorefining

J. L. Willit and E. C. Gay

Presented at the Symp. on Molten Salt Processing Technology, 131st TMS Annual Meeting, Seattle, WA, February 17–21, 2002

Basic and Applied Sciences

The Chemical Engineering Division conducts forefront research on fundamental issues involving chemistry and materials functionality in systems that are relevant to energy efficiency enhancement, electric power distribution, chemical manufacturing, and clean air technologies.

These studies embrace (1) the processing and characterization of selected classes of ceramic oxides with high superconducting critical temperatures, (2) novel approaches to heterogeneous catalysis, (3) new vistas in homogeneous catalysis, and (4) the details of ion transport mechanisms in operating electrochemical devices and during metal corrosion. This research makes use of cutting-edge synchrotron x-ray and nuclear magnetic resonance facilities at Argonne National Laboratory, including the Advanced Photon Source.

Our investigations of high-temperature superconducting (HTS) ceramics have two main areas of emphasis, one directed at the optimization of processing conditions for the silver-sheathed $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ (Ag/Bi-2223) composite superconductor, and the other at the characterization of HTS-coated conductor embodiments employing biaxially textured $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_7$ (YBCO) in thick-film form as the superconducting medium.

During the past year we completed an extensive series of Raman microscopy studies on a wide variety of YBCO-coated conductor embodiments. From this work we developed criteria for evaluating important chemical and structural details inherent to the various processing methods under investigation and development in the U.S. Department of Energy's (DOE's) applied superconductivity program. These studies provided (1) concrete evidence for the

occurrence of orthorhombic/tetragonal phase separation in the YBCO, (2) insights into the causes for degradation of critical current with increasing YBCO film thickness, and (3) critical guidance in the optimization of processing conditions for the pulsed laser deposition of YBCO on roll-textured silver substrates.

Chemical Engineering Division Basic and Applied Research

- Processing and characterization of ceramic oxides with high superconducting critical temperatures
- Heterogeneous and homogeneous catalysis
- Ion transport mechanisms in operating electrochemical devices and during corrosion
- Hydrogen production

Our research on homogeneous catalysis continues to explore regimes of elevated pressure and the effects of solvent polarity on reaction kinetics for important industrial processes, such as the hydroformylation of olefins. We have also continued our efforts to extend the scope of this research in directions that combine features of nanoscience, multiphase media approaches, and surfactant technology, with the goal of developing a new class of catalysts exhibiting the beneficial characteristics of homogeneously and heterogeneously induced chemical reactivity.

Using state-of-the-art high-pressure nuclear magnetic resonance (NMR) methods developed by and in place in the Chemical Engineering Division, we have conducted in-depth investigations of the effects of CO pressure, temperature, and solvent medium polarity on the

phosphine-modified cobalt catalyzed hydroformylation of selected olefins. The results of this research showed that a salt-like Co(I) phase tends to form and subsequently precipitate in polar media. The formation of this salt-like phase can be discouraged by reducing the basicity of the phosphine ligand, reducing CO pressure, and increasing temperature.

Development and application of NMR-based toroid cavity imaging devices has continued in the past year. Methods devised for the elucidation of ionic transport phenomena in battery systems have been extended to the study of corrosion and subsurface defect formation in the types of lithium alloys (e.g., Li-Al) used for the manufacture of high-performance jet aircraft wings. An NMR-based detection device suitable for controlled environment studies has been successfully tested as a probe of the spatial disposition, mobility, and chemical reactivity of lithium in the interface region of variably treated Li-Al alloy specimens.

The heterogeneous catalysis research program in the Chemical Engineering Division continues to address a broad range of forefront issues in relation to chemical production, energy efficiency, and environmental air quality. Studies aimed at discovering a one-step method for the production of phenol from, e.g., benzene, have focused on the role of the Cu-based catalyst Cu-ZSM-5 in determining reactivity and selectivity during the direct oxidation of benzene to phenol using air as the oxidant. The results of this study showed that stabilization of the Cu(II) state was critical to maintaining reactivity and selectivity and that lower copper loadings and

better dispersion favored Cu(II) stabilization. The utilization of the Advanced Photon Source was vitally important to the achievement of this new understanding.

Hydrogen production for energy-efficient fuel cells has become a leading mission of DOE. Investigations performed during the past year in the heterogeneous catalysis program have demonstrated that liquid metals, like Pb and Sn, can be used to pyrolytically convert methane into H₂ and carbon (a highly marketable side product). A salient feature of this work is that heavy liquid metals are a contending candidate for the coolant in the next generation of nuclear reactors.

Our work on improved catalysts for reduction of NO_x emissions has continued. An additive-assisted bifunctionalized form of Cu-ZSM-5 has been developed and tested with considerable success. The new (proprietary) formulation yields improved selectivity to N₂ formation, greater resilience, and enhanced water tolerance relative to the standard Cu-ZSM-5 material.

For More Information

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Characterization of Superconductor Embodiments Using Raman Microscopy

Studying how superconductor properties affect current-carrying capacity

The Chemical Engineering Division has carried out extensive Raman microscopy studies to develop a conclusive understanding of the implications of Raman spectral features recorded during the characterization of $\text{M}\text{Ba}_2\text{Cu}_3\text{O}_x$ thin films (MBCO, where $\text{M} = \text{Y}$ or a rare earth element) on textured substrates. The intention of this work is to develop a rapid, nondestructive, and informative method for interrogating chemical and microstructural details that influence the performance of the MBCO high-critical-temperature superconductor deployed in coated conductor embodiments.

In the course of this work, issues related to laser penetration depth, excitation wave-length, and orientation with respect to the MBCO crystal axes have been codified to the point where it is possible to obtain a wide variety of substantive information about MBCO film specimens from their Raman spectra. This information generally includes phase composition, texture quality, and atomic ordering effects.

2002 Research Highlights

Observation of a band near 450 cm^{-1} in Raman spectra of YBCO coated conductor specimens from several collaborating institutions has prompted a systematic investigation of its origin. Spectra of two YBCO films on buffered metal substrates that contained this mode as a prominent spectral feature are presented in Figure 1, together with the spectrum of a melt processed bulk YBCO sample known to be tetragonal YBCO. Both supposedly orthorhombic YBCO films (deposited by colleagues at Los Alamos National Laboratory using pulsed laser deposition methods) appear to contain domains of tetragonal YBCO, suggesting that oxygenation of YBCO films may in some cases be either incomplete or somehow inhibited during fabrication of coated conductor films.

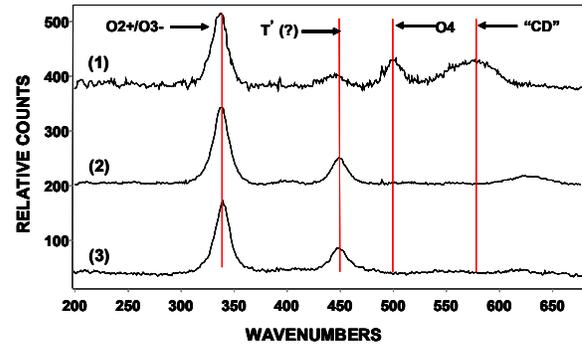


Fig. 1. (1) YBCO/CeO₂/YSZ/Hastelloy C, (2) YBCO/CeO₂/YSZ/CeO₂/textured Ni; and (3) bulk/melt-processed/ textured tetragonal YBCO.

The extent to which this phase separation acts to degrade critical current density, J_c , or contributes in a beneficial way to flux pinning is currently under investigation.

In related research, Raman spectra were recorded for a series of pulsed laser deposited (PLD) YBCO films of varying thickness on SrTiO_3 substrates prepared by colleagues at the Oak Ridge National Laboratory. The purpose of this study was to investigate changes in film composition and c axis alignment as YBCO film thickness is increased. The results, shown in Figure 2, indicate that the onset of tilted YBCO grain growth begins to occur at thickness values between 0.4 and $0.7\ \mu\text{m}$. (This is determined by the increase in intensity of the O4 mode of YBCO at 500 cm^{-1} relative the O2+/O3- mode at 340 cm^{-1} .) Note in Figure 2 that the J_c initially drops off with increasing film thickness but eventually reaches a relatively constant value for YBCO thicknesses greater than $1.0\ \mu\text{m}$.

Raman microscopy is also being used to monitor phase evolution and texture quality during the deposition of PLD YBCO on rolled silver substrates. Correlations have been observed

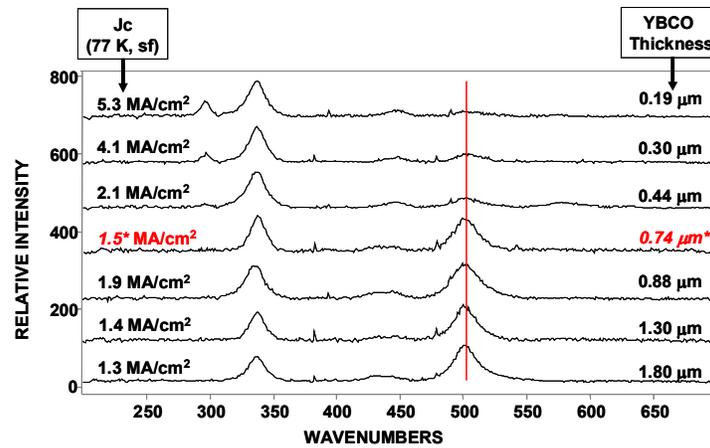


Fig.2. Raman spectra of PLD-type YBCO films of varied thickness on SrTiO₃ single crystal substrates. The 0.74-µm film is on a LaAlO₃ substrate.

between YBCO film J_c and processing parameters. Critical temperatures (T_c) and magnetization-based driving currents for four YBCO films on textured silver substrates containing varied amounts of Cu are plotted in Figure 3. Also plotted in Figure 3 is the value of I₅₀₀/I₃₄₀ from the Raman spectrum of each film, which reaches a minimum at Ag-0.2 at.% Cu.

Based on the criterion for high texture quality (i.e., I₅₀₀/I₃₄₀ → 0), it is clear that the YBCO film on Ag-0.2 at.% Cu exhibits the least evidence of tilted YBCO grains. (The Raman spectrum of this film also presented the least evidence of cation disorder and second phases.) A companion study of the effect of laser pulse energy density on the performance of the deposited YBCO film produced a similar correlation with texture quality. I₅₀₀/I₃₄₀ values obtained from the Raman spectra reached a minimum at the same energy density (138 mJ/cm²) that yielded the best performing YBCO/Ag-0.2 at.% Cu specimen.

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Research Participants

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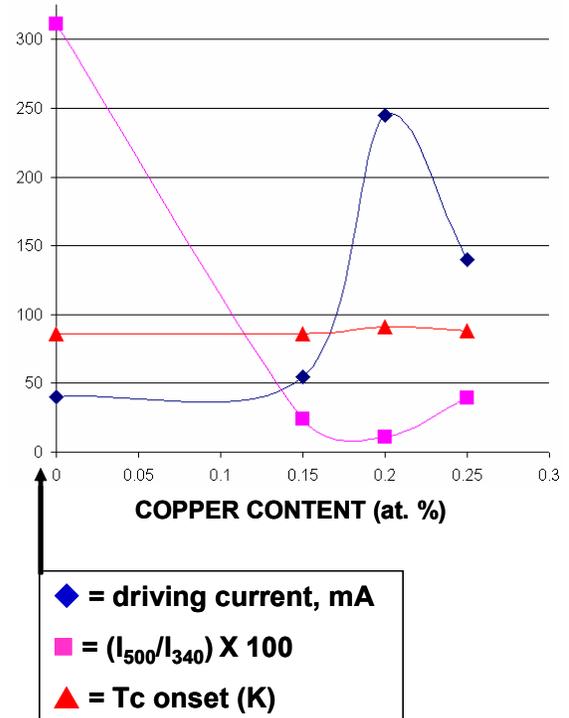


Fig. 3. Plot of magnetization-based driving currents, critical temperatures (T_c), and I₅₀₀/I₃₄₀ values (from Raman spectra) for four PLD-type YBCO films on roll-texture silver substrates containing varied amounts of copper.

Reducing Emissions of Nitrogen Oxides

Coating improves water stability and activity of an important class of catalyst

The removal of nitrogen oxides (NO_x) from emissions streams has become a global concern. NO_x can lead to smog and acid rain and is considered a major greenhouse gas. Pending governmental regulations in the next decade will force the use of NO_x removal systems on stationary and mobile sources to abate emissions. Several possible lean-burn NO_x reduction systems have been proposed. Selective catalytic reduction (SCR) of NO_x by ammonia is currently the most widely used technology in commercial applications. However, this process requires the storage of either ammonia or urea—typically not available for many chemical plants and a drastic consideration for mobile sources. Additionally, the process must be designed to avoid ammonia slippage into the atmosphere.

Because of these concerns, alternative mechanisms of NO_x reduction have been investigated. The most promising replacement technology appears to be the selective catalytic reduction of NO_x with hydrocarbons (HC-SCR). In this process, a slipstream of the combustion fuel can be used as the reductant for SCR, thus removing the storage problem. Furthermore, the slippage of hydrocarbon is more environmentally benign than ammonia, although it is still necessary to minimize the slippage. Transition metal-exchanged zeolites, such as Cu-ZSM-5, exhibit very high activities for HC-SCR, but tend to suffer negative effects if water is present in the emissions stream. Thus, efforts have been made to identify other possible catalysts for this process.

2002 Research Highlights

In our laboratory, we have been working on new additives to extend the life of catalysts such as Cu-ZSM-5. One of these additives (patents applied for) is not just effective for eliminating the water stability problem for Cu-ZSM-5, but actually improves its activity. The best additives

create new catalyst systems that are bifunctional; the additive catalyzes one reaction while the zeolite catalyzes a separate one. The synergy of the two components allows us to fine-tune each to optimize the overall chemistry.

While these bifunctional materials are somewhat less active than the base metal-zeolite component under dry conditions, there is a significant activity improvement for our catalysts at low temperatures in the presence of water. With some of our materials, at a space velocity of $30,000 \text{ hr}^{-1}$, we have been able to achieve approximately 50% conversion of NO with >99% selectivity to N_2 in the presence of water at 250°C using propylene as reductant; comparatively, under identical conditions Cu-ZSM-5 will reach only 60% conversion at 350°C with similar selectivity. NO conversions above 90% can be reached at the same temperatures over the bifunctional catalysts by lowering the space velocity without altering the nitrogen selectivity. Furthermore, the tested hydrocarbons are fully oxidized to CO_2 over these new materials, reducing CO emissions to a minimum compared with Cu-ZSM-5.

Table 1 shows the activity of the native Cu-ZSM-5 for reducing NO_x along with the additive at low and high loadings. As can be seen, the additive selectively removes NO, converting it to N_2 . Only very small quantities of undesirable by-products such as NO_2 or N_2O are observed.

The additive effectively coats the outside of the zeolite particle. We have used field emission scanning electron microscopy (FESEM) and x-ray diffraction (XRD) to identify the nano-scale structure of these samples. In general, we have found that our preparation methods produce small nano-particles of the oxide decorated on the outside of the metal-exchanged zeolite, with possible additional phases yet not fully

Table 1. Activity of Cu-ZSM-5 and Cu-ZSM-5 with Additive under Wet Conditions at 250°C

	Cu ZSM5 Only	Cu-ZSM-5 with Low Concentration of Additive "A"	Cu-ZSM-5 with High Concentration of Additive "A"
NO conversion	15.20%	32.20%	52.70%
NO ₂ and N ₂ O selectivity	3.80%	1.50%	0.60%
CO selectivity	30.90%	11.60%	8.30%

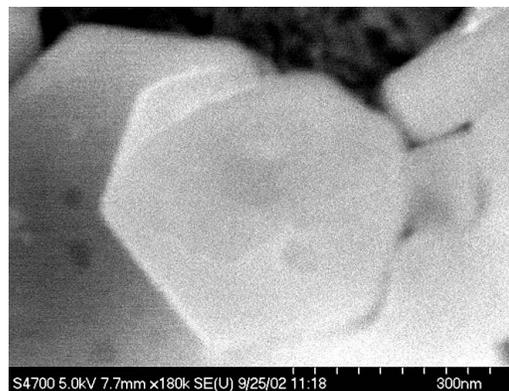
identified. We propose that the close proximity of the two phases allows short-lived HC-SCR intermediates generated by one phase to interact with the other phase and therefore improve the activity. Figure 1 shows FESEM micrographs of the normal zeolite and an optimized catalyst with the externally applied coating. Uniform coatings appear to be a crucial component for low temperature activity and high selectivity.

Work so far has focused on propylene as the reductant for these bifunctional systems. However, recent changes in regulations have placed propylene on the list of undesirable highly reactive volatile organic chemicals (HRVOCs). Therefore, new work will concentrate on using paraffins such as propane, alone or mixed with propylene. Alternatively, readily-available methane would be an ideal reductant for many coal-burning plants. For diesel systems, heavier hydrocarbons such as hexane will be present in the fuel, and could also be used as reductants. The target systems will be tested for these alternative reductants and modified, if necessary, to perform under the new conditions. In addition, the effects of SO₂ on the long term activity of the catalyst will also be studied.

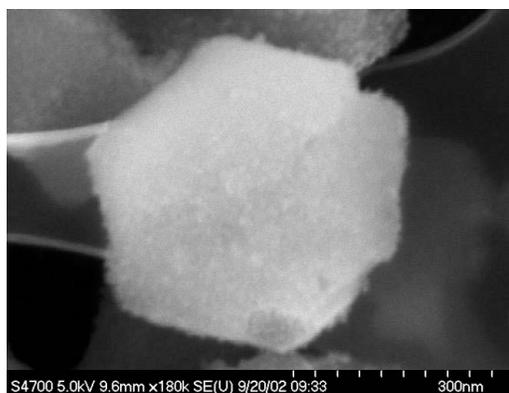
This research is funded in part under a cooperative research and development agreement with BP Corporation.

Research Participants

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(a)



(b)

Fig. 1. (a) The native Cu-ZSM-5 catalyst, which is unstable under wet conditions. (b) A uniform, optimized coating over the surface of the Cu-ZSM-5 imparts high activity and selectivity to the catalyst even at high moisture contents.

Producing Hydrogen by Methane Pyrolysis

Finding a “greener” way to produce hydrogen for energy

Currently petroleum refining is by far the biggest consumer of pure hydrogen, but the major petroleum companies and vehicle manufacturers are orienting their industries toward a hydrogen economy. Motivations for exploring hydrogen as the leading alternative energy are to help assure a future energy supply through a renewable energy source, and to lessen global environmental problems by reducing carbon dioxide (CO₂) emissions and improving air quality. It is predicted that the world demand for hydrogen will grow by 10% annually over the next five years, from the present level of 10-12 billion standard cubic feet per day (scf/d).

The thermal decomposition of methane (breaking it down into chemical elements and compounds using heat) has great potential for producing hydrogen without CO₂ and carbon monoxide (CO) emissions, but it can be of practical interest only if a thermally efficient process is developed and an efficient way is found to dispose of the carbon by-product generated during the reaction. We propose to use the heat energy contained in the liquid metal coolant of next-generation (Generation IV) nuclear reactors to produce hydrogen and carbon from methane or natural gas by direct-contact pyrolysis (DCP), which does not produce greenhouse gases.

In DCP, methane or natural gas is bubbled through a bed of either low-melting-point metals such as lead or tin, or through a mechanical mixture of metal and solid media such as silicon carbide. The main advantage of this proposed system is that the carbon by-product that is generated can be easily separated from the heat transfer media (the metals or metal/solid media) because carbon is lighter, presumably floating on top of the heated media.

Our experiments are providing a foundation, including the needed technical expertise, for producing pure hydrogen cost-effectively by using the heat energy from Generation IV nuclear reactors when they are built in approximately 25-30 years. Such reactors will operate at much higher temperatures than existing nuclear reactors, opening the door for processes such as DCP.

This year we showed that DCP with either methane or natural gas is possible, and the only gaseous product is hydrogen.

2002 Research Highlights

Our experiments this year showed that natural gas was converted selectively to carbon and hydrogen at temperatures ranging from 600 to 900°C. No other gaseous products besides hydrogen were observed in the effluent stream. Figure 1 shows a typical result for the thermal decomposition of natural gas bubbled through a 1/4-in. feed tube into a 4- or 8-in.-high bed of molten Pb at 750°C. Methane and ethane conversions increased with decreasing flow rate and increasing heat transfer bed height—in other

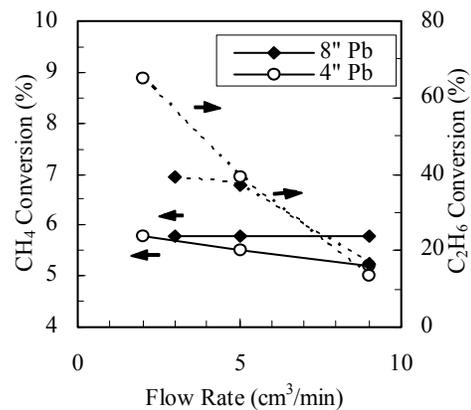


Fig. 1. CH₄ and C₂H₆ conversions in the natural gas pyrolysis over 4 in. (○) and 8 in. (◆) of molten Pb. T = 750°C.

words, with increasing the contact time between the natural gas and the molten metal.

To optimize the process, we used porous metal filters (Mott Corporation) with two different porosities (0.5 and 2 μm) as feed tubes, to minimize the size of the gas bubbles, thus facilitating better heat transfer between the natural gas and the heated media. Figure 2 depicts a comparison of the hydrogen concentrations (vol %) obtained in the natural gas pyrolysis, bubbled through a range of heat transfer media at 750°C and different volumetric flow rates. It is apparent that the most efficient systems used for the pyrolysis process are the ones using the Mott porous filters. This is comparable to the activity reported for Ni- and Fe- based catalysts, considered to be among the most active and commonly used for the catalytic decomposition of hydrocarbons. Additionally, the potential ease of separation of carbon by-product from the reaction mixture makes the technique proposed in this paper more advantageous compared with the catalytic process.

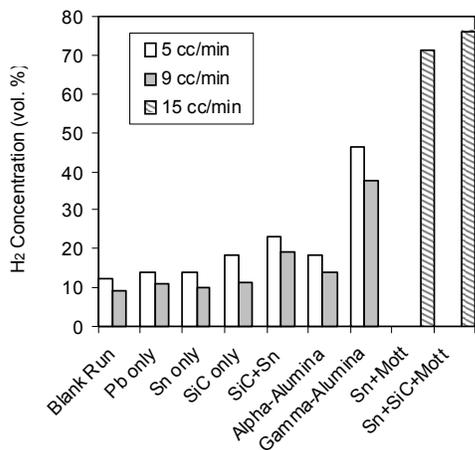


Fig. 2. Comparison of concentrations of hydrogen (vol. %) produced in natural gas pyrolysis, bubbled through different heat transfer media.

The carbon by-product generated during the pyrolysis process has great market potential in traditional industries (as a reducing reagent for the production of SiC in rubber, plastics, inks, etc. and as a carbon additive/carburizer in the

steel industry) as well as in emerging ones such as the carbon/air fuel cell, a process currently under development at Lawrence Livermore National Laboratory.

Figure 3 shows SEM images of the carbon collected after experiments with Pb and Sn. In the pyrolysis of methane, two forms of carbon are generated — pyrocarbon (Fig. 3a) as solid carbon deposits resulting from surface reactions, and finely divided carbon (soot) (Fig. 3b). Pyrocarbon was found to cover the entire heated section of the reactor, irrespective of the heat transfer media used in the pyrolysis experiments.

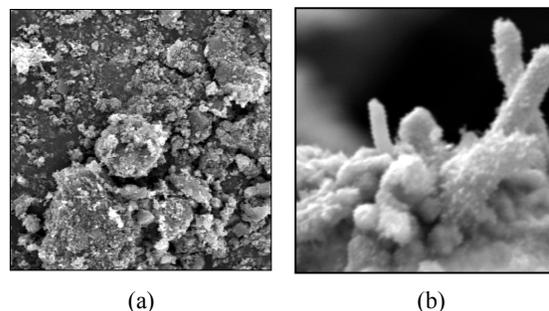


Fig. 3. SEM images of carbon samples collected after experiments with Pb (a) and Sn (b).

Elemental analysis of carbon samples generated during the pyrolysis experiments indicate that the C:H atomic ratios (on a molar basis) are within the range of 1 C atom per 0.06 H atom for all samples analyzed (i.e., nearly all of the hydrogen has been stripped from the methane). The hydrogen atom balance calculated after each experiment confirms the above reaction stoichiometry. XRD spectra reveal that the carbon by-product is graphitic in nature, with an average particle size of 120 Å.

Research Participants

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Selective Oxidation of Aromatics to Commodity Chemicals

Finding a one-step method for making phenol

Catalytic chemical synthesis accounts for 60% of today's chemical products and 90% of the current chemical processes. Given this dominance, catalytic oxidation has been targeted by the U.S. Department of Energy as one of the most significant areas for advancement in the chemical industry. Catalytic oxidations are the lifeblood of the chemical industry. The products of oxidation are the required intermediates for many industrial chemicals and organic polymers. As such, selective oxidation is an important element for future development of the chemical industry.

The direct oxidation of benzene to phenol has been the focus of work by numerous investigators over the last thirty years. However, most of these investigations were exploratory in nature. To our knowledge, there is no known, one-step process using molecular oxygen that selectively converts benzene to phenol with high yield.

Currently, phenol is produced at a rate of about 4.5 billion pounds per year in the U.S. and ~11 billion worldwide. Phenol is used primarily to produce phenol-formaldehyde resins. The three-step cumene process produces about 95% of the phenol used in the world. Starting from benzene, the cumene process involves:

- Alkylation of benzene with propene to form cumene, catalyzed by phosphoric acid or aluminum chloride.
- Oxidation of cumene to cumene hydroperoxide using molecular oxygen.
- Cleavage of cumene hydroperoxide to phenol and acetone, catalyzed by sulfuric acid.

Argonne's Chemical Engineering Division is conducting research aimed at finding a one-step method of producing phenol.

2002 Research Highlights

Reactions were carried out using air as the oxidant. At 400°C benzene conversion was 10-15% and phenol was produced at 0.83% yield with 9% selectivity. The addition of water improved both the phenol yield (2.3%) and selectivity (21%). The controlled reduction of Cu^{2+} to Cu^+ in H_2 demonstrated that Cu^{2+} is necessary for the formation of phenol. When Cu^+ was the starting material, the initial yield to phenol was almost zero. Once Cu^+ oxidized to Cu^{2+} under the reaction conditions, the yield to phenol increased dramatically.

So far, this reaction required at least 400°C to occur. By adding water to the reaction, we were able to produce phenol at temperatures as low as 200°C. At this temperature, the selectivity to phenol increased notably (70%), but the conversion was rather low.

The Cu content and the Si/Al ratio in Cu-ZSM-5 were varied in order to identify the best catalyst composition. These reactions were carried out at 200°C, at this temperature secondary reactions promoted by the acidity of the support are minimum. Table 1 shows the selectivity to phenol and CO_2 at different Si/Al ratios and different Cu loadings. The catalyst with a Si/Al ratio of 25 and a Cu loading of 0.85 wt% gave the best selectivity to phenol. Higher Cu loadings favored the formation of CO_2 . Previous reports on Cu-ZSM-5 proposed two different Cu sites: one predominates at low Cu loadings (<100% exchanged) and the second predominates at high Cu loadings. CuO is formed in Cu-ZSM-5, exchanged at more than the 100% level; this catalyst is far more selective to CO_2 formation.

Temperature-programmed reduction of the Cu-exchanged zeolites showed that the high-temperature reduction peak (Cu^+ to Cu^0) shifts

Table 1. Cu-ZSM-5 Selectivity to Phenol and CO₂

	Si/Al Ratio				
	15	25	40	40	
Cu loading (wt %)	0.85	0.85	1.5	1.9	0.85
Selectivity to phenol (%)	59	70	25	20	52
Selectivity to CO ₂ (%)	22	14	55	65	21

to higher temperatures as the Cu loading decreases. During this second reduction step, the metallic Cu migrates to form small clusters; more dispersed Cu ions require higher temperatures for the reduction.

In-situ XANES temperature-programmed reduction (Fig. 1) agreed with these results. Preliminary analysis of the data indicated that $\text{Cu}^{2+} \rightarrow \text{Cu}^+$ reduction is insensitive to Cu loading. However, high Cu loadings resulted in low-temperature reduction of $\text{Cu}^+ \rightarrow \text{Cu}^0$. This indicates that at low loadings, the Cu sites are isolated and promote phenol formation. In-situ EXAFS followed the formation of Cu-Cu bonding as a function of Cu loading and reduction temperature.

This research is funded by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Office of Industrial Technologies, and through a cooperative research and development agreement with ABB Lummus, Engelhard Corporation, and Northwestern University.

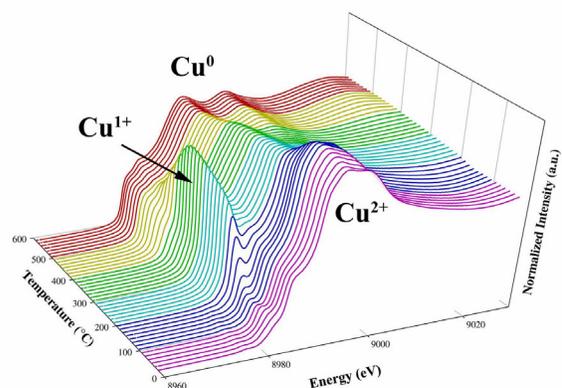


Fig. 1. Normalized XANES spectra of Cu-ZSM-5 collected during the temperature-programmed reduction in 4% H₂/He.

Research Participants

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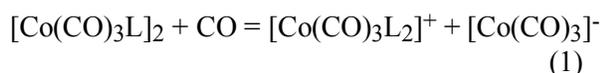
Ionic Species in Cobalt-Catalyzed Hydroformylation

Finding insight into the occurrence of cobalt(I) salts in the Shell Process

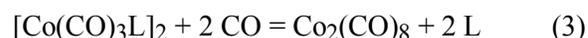
High-pressure nuclear magnetic resonance (NMR) spectroscopy was used to study reactions of carbon monoxide with cobalt complexes of the type $[\text{Co}(\text{CO})_3\text{L}]_2$, where L = tertiary phosphine, that are used as catalysts in the phosphine-modified hydroformylation of olefins. For the case where L is the relatively basic phosphine $\text{P}(\text{n-C}_4\text{H}_9)_3$, high pressures of carbon monoxide typically used in olefin hydroformylation cause CO addition and disproportionation of the catalyst to produce a catalytically inactive cobalt(I) salt with the composition $[\text{Co}(\text{CO})_3\text{L}_2]^+[\text{Co}(\text{CO})_4]^-$. The reaction is exothermic in benzene solution with $\Delta H = -14.1 \pm 0.1$ Kcal/mol and $\Delta S = -48.6 \pm 0.2$ eu. Salt formation is favored by polar solvents, and for the case where L is the water-soluble phosphine $\text{P}(\text{CH}_2\text{CH}_2\text{CH}_2\text{OH})_3$, cobalt(I) salt formation proceeds essentially to completion in water. For the case where L is the weakly basic phosphine $\text{P}(\text{C}_6\text{H}_4\text{CF}_3)_3$, high pressures of carbon monoxide do not result in salt formation; instead, displacement of the phosphine ligand occurs with the formation of mixtures of $[\text{Co}(\text{CO})_4\text{L}]_2$, $\text{Co}_2(\text{CO})_7\text{L}$, and $\text{Co}_2(\text{CO})_8$.

2002 Research Highlights

Phosphine-modified cobalt catalysts are used in the Shell Process for the large-scale production (400,000 tons per year) of long-chain alcohols via hydroformylation and further reduction of terminal/internal olefin substrates. Here, we describe reactions of CO at high pressures with phosphine-modified catalysts of the Shell type, i.e., $[\text{Co}(\text{CO})_3\text{L}]_2$, where L = tertiary phosphine. Dependent upon the choice of L, solvent, and reaction temperature, CO reacts with the catalysts to produce a cobalt (I) salt by CO addition and disproportionation, as shown in Equation 1,



or it reacts by displacement of one or both phosphines in the catalyst as shown in Equations 2 and 3.



Although CO is a necessary ingredient in hydroformylation, both the disproportionation and the ligand displacement reactions shown in these equations are detrimental to the overall catalytic process. Disproportionation decreases the catalyst available for reaction with H_2 to form the necessary hydridic species, $\text{HCo}(\text{CO})_3\text{L}$, required in the catalytic process. Displacement of the phosphine ligand, to the extent that the products of Equations 2 and 3 lead to the formation of unsubstituted $\text{HCo}(\text{CO})_4$, decreases the selectivity of the process to produce the more desirable linear alcohol product favored by the steric bulk of the tertiary phosphine ligand.

For the phosphine-modified cobalt catalyst based on highly basic tri-n-butylphosphine, formation of the Co(I) salt by CO addition and disproportionation is thermodynamically favorable and exothermic even in nonpolar benzene solution. With use of this ligand, salt formation is more favorable in the more polar solvent 1,4-dioxane. In contrast, displacement of the tri-n-butylphosphine with CO to form free ligand is not significant even at relatively high CO pressures. For this highly basic ligand, salt formation can best be minimized with the use of high temperatures, which disfavors the salt due to the reaction's exothermicity, and the use of as-low a CO pressure and the least polar solvent possible. On the other hand, for catalysts using the less basic $\text{P}(\text{C}_6\text{H}_4\text{CF}_3)_3$ ligand, salt formation is not significant even at high CO pressures in toluene solution; instead, large excesses of added ligand are needed to avoid

facile displacement of the phosphine by CO. For the catalyst system based on water-soluble $\text{P}(\text{CH}_2\text{CH}_2\text{CH}_2\text{OH})_3$, salt formation, with the structure shown in Figure 1, is complete in aqueous solution and no other complexes could be detected in this highly polar solvent even at low pressures of CO.

This research is funded by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences.

Research Participants

Jerry W. Rathke, Robert J. Klingler, Michael J. Chen, and Rex E. Gerald II. For more information, contact Jerry Rathke (630-252-4549, rathke@cmt.anl.gov).

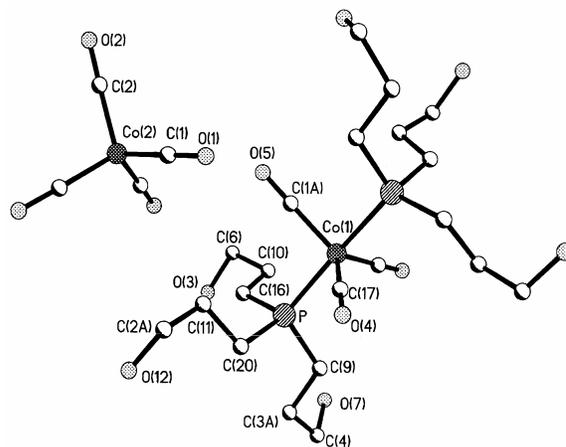


Fig. 1. Crystal Structure of the Co(I) Salt Produced with the Ligand $\text{P}(\text{CH}_2\text{CH}_2\text{CH}_2\text{OH})_3$.

Subsurface Spectroscopic Imaging of Metal Corrosion

Understanding the chemistry of corrosion in high-performance alloys during production

Lithium-aluminum alloys are used for high-performance jet wings because of their superior strength and low density. Corrosion of the surface layer of these and other important alloys leads to surface pitting and blistering, which results in poor adhesion of paint or protective coatings.

The chemistry of corrosion and the formation of defect inclusions (pits and blisters) during alloy processing are poorly understood because surface layer tests conducted during the production of these alloys are difficult to perform with existing spectroscopic tools. Argonne scientists have developed a detector that will provide spectroscopic identification and spatial location of the chemical species present in the surface corrosion layer of a metal structure under processing conditions.

2002 Research Highlights

Aluminum alloys, including the 8000 series Al(Li, Mg) alloy and the 2000 series Al(Cu, Li) alloy, exhibit a depletion of the alkali metal near the surface during the fabrication process. In the case of the 8000 series, the depletion of Li is more severe than the depletion of Mg, and results in defect inclusions. It has been proposed that oxygen, water, and heat play a role in this deleterious process. In the Mg-containing alloys, subsurface layers of magnesium oxide (MgO) are formed. These layers are up to 25 microns in depth and are thought to be due to the reaction of Mg with atmospheric oxygen at elevated temperatures. Alloy materials with MgO layers lack the physical and mechanical properties desired by the aerospace industry. The alkali depletion problem is magnified under conditions of high humidity and reduced pressure. Further understanding of the redox chemistry that takes place during specific stages of the manufacturing process would aid metals manufacturers in designing processes to

minimize or eliminate surface corrosion. Characterization tools that can be used to identify the chemical species and chemical transformations that lead to subsurface defects during the fabrication processes of the alloys are sought. The data obtained from novel characterization tools could impact the design of new and existing fabrication equipment and conditions that are directed toward circumventing surface corrosion.

NMR is a powerful tool that is useful for identifying chemical species and elucidating chemical reactions. Thus, it is highly desirable to perform NMR analyses of metal samples, especially under actual fabrication conditions. However, if a metal object is placed inside a commercial NMR detector, then severe distortions in the NMR spectra are observed. These distortions occur because the probing radio frequency field and the externally applied magnetic field are affected by the presence of electrically conductive objects. The exploitation of NMR analyses for metals is atypical, and when it has been accomplished was performed on finely divided metal powders suspended in oil or wax. What is needed is an NMR detector that can probe the subsurface layer of a macroscopic metal structure with a simple geometrical form, such as a rod, tube, or sheet. Since surface oxide pitting extends to depths of 10-30 μm , the NMR apparatus should be capable of probing the composition and reactions of chemical species within this depth range, while exhibiting insensitivity to the bulk sample.

We have developed an NMR toroid cavity imaging device and technique that permit the monitoring of the reaction products of a wide range of chemical species in the subsurface layer of a metal. In addition, for a cylindrical rod sample the spectroscopic data can be mapped according to the depth from the surface with

micrometer resolution. Because the metal sample also functions as the NMR inductor, it does not distort the radio frequency field and the externally applied magnetic field. The cylindrical design of the toroid cavity probe affords a simple means for analyzing the surface layer of macroscopic metal samples, and provides a high-pressure vessel that is used to expose the metal surface of the sample to a controlled atmosphere of gaseous or liquid reagents. Figure 1 is a photograph of the toroid cavity NMR detector designed for metal rod samples.



Fig. 1. Photograph of a toroid cavity NMR detector with an Al-Li alloy cylindrical rod sample incorporated as the central conductor. A rectangular rod sample is also shown.

The imaging device was used to map the concentration of lithium in a well characterized aluminum alloy that was free of surface defects. Figure 2 depicts the first ${}^7\text{Li}$ -NMR image of lithium atoms in the Al-Li alloy sample. The subsurface layer of the sample exhibits a uniform distribution of lithium atoms across the

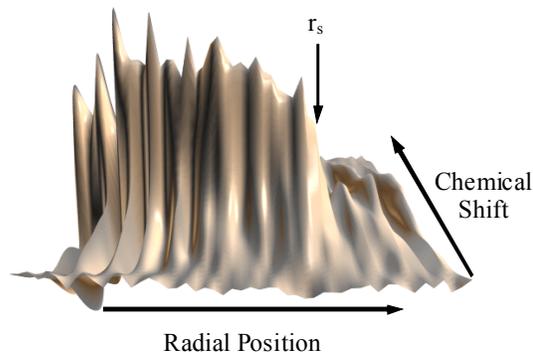


Fig. 2. NMR image of the lithium nuclei near the outer surface of the Al-Li alloy rod shown in Figure 1. The outer radial dimension of the alloy sample is indicated by r_s .

surface layer of 20 μm . In future experiments, the image profile will be monitored as lithium atoms are leached from the surface and react to form oxide products. The application of the novel NMR device to the investigation of the spatial disposition, mobility, and chemical reactivity of lithium and other constituent atoms in Al-Li alloys should answer questions about the kinetics of mass transport of atoms and the underlying corrosion reaction mechanism(s) that occur during alloy processing.

This research is funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences.

Research Participants

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Selected Publications and Presentations

Journal Articles, Books, and Book Chapters

Investigation of a Multi-Set-Point First Heat Treatment Methodology for the Silver-Sheathed (Bi,Pb)₂Sr₂Ca₂Cu₃O_x Composite Conductor

R. M. Barceanu, V. A. Maroni, N. N. Merchant, A. K. Fischer, M. J. McNallan, and R. D. Parrella

Supercond. Sci. Technol. **15**, 1167–1175 (2002)

Time Evolution of Phase Composition and Microstructure in the Ag/Bi-2223 Composite Superconductor Heat-Treated at Specific pO₂/Temperature Set Points

R. M. Barceanu, V. A. Maroni, N. N. Merchant, A. K. Fischer, M. J. McNallan, and R. D. Parrella

Supercond. Sci. Technol. **15**, 1160–1166 (2002)

Kinetics, FTIR and Controlled Atmosphere EXAFS Study of the Effect of Chlorine on Pt Supported Catalysts during Oxidation Reactions

F. J. Gracia, E. E. Wolf, J. T. Miller, and A. J. Kropf

J. Catal. **209**, 341–354 (2002)

An *In-Situ* X-Ray Absorption Spectroscopy Study of InSb Electrodes in Lithium Batteries

A. J. Kropf, H. Tostmann, C. S. Johnson, J. T. Vaughey, and M. M. Thackeray

APS Forefront **1**, 113–116 (2001)

(Co)MoS₂/Alumina Hydrotreating Catalysts: An EXAFS Study of the Chemisorption and Partial Oxidation with O₂

J. T. Miller, C. L. Marshall, and A. J. Kropf

J. Catal. **202**, 89–99 (2001)

In Situ EXAFS Analysis of the Temperature Programmed Reduction of Cu-ZSM-5

M. K. Neylon, C. L. Marshall, and A. J. Kropf

J. Am. Chem. Soc. **124**(19), 5457–5465 (2002)

Formaldehyde Determination in Supercritical CO₂

J. W. Rathke, L. M. Wojcinski, R. J. Klingler, M. J. Chen, and R. E. Gerald II

The Chemist **78**(4), 7–10 (2001)

Low Temperature Steam Reforming of Methanol over Layered Double Hydroxide-Derived Catalysts

S. R. Segal, K. B. Anderson, K. A. Carrado, and C. L. Marshall

Appl. Catal. A, General **231**, 215–216 (2002)

An EXAFS Study of the Coordination Chemistry of Hydrogen Hexachloroplatinate (IV): 1. Speciation in Aqueous Solution

W. A. Spieker, J. Liu, J. T. Miller, A. J. Kropf, and J. R. Regalbutto

Appl. Catal. A:General **232**, 219 (2002)

Investigation of Metal-Dusting Mechanism in Fe-Base Alloys Using Raman Spectroscopy, X-Ray Diffraction, and Electron Microscopy

Z. Zeng, K. Natesan, and V. A. Maroni
Oxid. Met. **58**, 1–2 (2002)

Proceedings Papers

EXAFS and Activity Studies of the Poisoning Effect of Cl on Pt/Al₂O₃ Catalysts during Oxidation Reactions

F. Gracia, E. E. Wolf, J. T. Miller, and A. J. Kropf
Proc. of the 9th Int. Symp. on Catalyst Deactivation, Studies in Surface Science and Catalysis, Lexington, KY, October 7–10, 2001, Vol. 139, pp. 471–478 (2001)

Papers Presented at Scientific Meetings

Catalytic Carbonylations in Supercritical Fluids

M. J. Chen, R. J. Klingler, and J. W. Rathke
Presented at the 223rd National Meeting of the Am. Chem. Soc., Orlando, FL, April 7–11, 2002

Gas Phase Hydroxylation of Benzoic Acid to Phenol

V. Duma, K. Popp, M. C. Kung, S. Ohyama H. H. Kung, and C. L. Marshall
Presented at the ACS Meeting, Division of Industrial and Engineering Chemistry “Green Chemistry”, Orlando, FL, April 7–11, 2002

Characterizing Toroid Cavity Detectors for Investigations of Thin Films

R. E. Gerald II, S. Heckmann, and J. W. Rathke
Presented at the 43rd Experimental Nuclear Magnetic Resonance Conf., Pacific Grove, CA, April 14–19, 2002

In Situ NMR of Electrochemical Systems

R. E. Gerald II, R. J. Klingler, and J. W. Rathke
Presented at the 8th Int. Symp. on Polymer Electrolytes, Santa Fe, NM (Invited) May 19–24, 2002

Toroid Cavity NMR Detector Applications at Low and High Magnetic Fields

R. E. Gerald II, R. J. Klingler, J. W. Rathke, and M. A. ter Host
Presented at the 42nd Experimental Nuclear Magnetic Resonance Conf., Orlando, FL, March 11–16, 2001

Thin Film NMR

R. E. Gerald II, J. W. Rathke, L. E. Iton, and G. S. Schade
Presented at the Int. Workshop on Nanocomposites: Materials, Neutrons, and Data Interpretation, Argonne National Laboratory, Argonne, IL, March 28–30, 2002

Advances in ENMR of Solid-State Electrolytes

R. E. Gerald II, J. Sanchez, R. J. Klingler, and J. W. Rathke

Presented at the 44th Rocky Mountain Conf. on Analytical Chemistry, Denver, CO, poster session, July 28–August 3, 2002

Electrochemical/NMR Detectors

R. E. Gerald II, J. Sanchez, R. J. Klingler, and J. W. Rathke

Presented at the 8th Int. Symp. on Polymer Electrolytes, Sante Fe, NM, May 19–24, 2002

In Situ NMR of Thin Films

R. E. Gerald II, J. Sanchez, R. J. Klingler, and J. W. Rathke

Presented at the Analytical Chemistry Seminar Series, Department of Chemistry, University of North Carolina, Chapel Hill, NC (Invited) February 7–10, 2002

In Situ X-ray Absorption Spectroscopy of Intermetallic Electrodes for Lithium Batteries

A. J. Kropf

Presented at the Valparaiso Physics Dept. Seminar Series, Valparaiso, IN, April 5, 2002

Direct Contact Pyrolysis of Methane Using Nuclear Reactor Heat

M. A. Lewis, M. Serban, C. L. Marshall, and D. Lewis

Presented at the Am. Nucl. Soc. Winter Meeting, Reno, NV, November 11–15, 2001

Applications of Molecular Spectroscopy Methods to the Study of Metal Dusting Corrosion

V. A. Maroni

Presented at the Int. Workshop on Metal Dusting, Argonne National Laboratory, Argonne, IL, September 26–28, 2001

Heat Treatment Strategies for the Next Generation of Ag/Bi-2223 Composite Conductor

V. A. Maroni, R. M. Baurceanu, K. Venkataraman, Y. Tang, C. Segre, R. D. Parrella, Y. Huang, and G. N. Riley, Jr.

Presented at the US/Japan Workshop on High-Tc Superconductors, Santa Fe, NM, December 2–5, 2001

Applications of FTIR Spectroscopy to Problems in Materials Science

V. A. Maroni, S. A. Johnson, K. T. Wu, and P. D. Maroni

Presented at the 40th Eastern Analytical Symp. and Exposition, Atlantic City, NJ, October 1–4, 2001

Hydrogen Production by Direct Contact Pyrolysis of Natural Gas

M. Serban, M. A. Lewis, C. L. Marshall, and R. D. Doctor

Presented at the 224th Am. Chem. Soc. National Meeting, Boston, MA, August 18–22, 2002

Ride'n Ript—Difference Images Combined for Compensation of Acoustic Ringing in Toroid Cavity Detectors

P. Trautner, H. G. Niessen, K. Woelk, and R. E. Gerald II

Presented at the 22nd North Rhine Westfalia Spring Symp. on Magnetic Resonance, Dortmund, Germany, March 26, 2002 (The title of this document has been translated from the German Language.)

Analytical Chemistry Laboratory

The Analytical Chemistry Laboratory (ACL) operates in the Argonne system as a full-cost-recovery service center, but its mission also includes a complementary research and development component in analytical chemistry and its applications. Because of the diversity of research and development work at Argonne, the ACL handles a wide range of analytical problems in its technical support role. It is common for Argonne research and development programs to generate unique problems that require significant development of methods and adaptation of techniques to obtain useful analytical data. Thus, much of the support work done by the ACL is very similar to applied research in analytical chemistry.

Some routine or standard analyses are done, but the ACL usually works with commercial laboratories if high-volume production analyses are required by its clients.

Organizationally, the ACL is in Argonne's Chemical Engineering Division (the Division). The ACL provides technical support not only for programs in the Division (its major client) but also for the other research divisions and programs at Argonne.

The ACL comprises three groups:

- Inorganic Analysis
- Radiochemical Analysis
- Organic Analysis

The skills and interests of staff members cross group lines, as do many projects within the ACL. The ACL receives about 800 jobs

annually, many of which involve multiple samples.

The Inorganic Analysis Group uses wet-chemical and instrumental methods for elemental, compositional, and isotopic determinations in solid, liquid, and gaseous samples and provides specialized analytical services.

The Radiochemical Analysis Group uses nuclear counting techniques to determine the radiochemical constituents in a wide range of sample types, from environmental samples with low radioactivity to samples with high radioactivity that require containment.

The Organic Analysis Group uses a number of complementary techniques to separate organic compounds and measure them at trace levels. The group is also involved with chemical agent determination and the Waste Isolation Pilot Plant Head Space Gas Performance Demonstration Program.

Together, the ACL groups have a full range of analytical capabilities for performing inorganic, organic, and radiochemical analyses.

In addition to a wide spectrum of advanced analytical instruments, the ACL has a sample-receiving system that allows efficient processing of environmental samples and hazardous and mixed-waste samples, including those requiring chain-of-custody procedures. The ACL also has quality assurance and control systems in place to produce analytical data packages that meet the reporting requirements of the U.S. Department of Energy, the U.S. Environmental Protection Agency, the U.S. Army Corps of Engineers, and other organizations.

Analytical Chemistry Laboratory

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Analysis of Simulated Headspace Gases for the Waste Isolation Pilot Plant Project

Helping the Nation to permanently dispose TRU waste

The Waste Isolation Pilot Plant (WIPP), a DOE installation, is the nation's first repository for the permanent disposal of defense-generated transuranic radioactive (TRU) waste left from research and production of nuclear weapons at the various DOE sites. The WIPP site, located in southeastern New Mexico, consists of large interconnecting rooms hollowed out of an ancient, stable salt formation approximately 600 meters underground. WIPP began to receive waste on March 26, 1999. It received its 500th shipment in January 2002. Over the next 35 years, WIPP is expected to receive about 3,700 shipments of waste.

Before being shipped to the site, wastes must be characterized to identify the presence of any hazardous materials in addition to the radioactivity. Other nondestructive assays also are conducted, including the analysis of headspace gas for specified volatile organic compounds. The U.S. Department of Energy, Carlsbad Area Office, National TRU Program Office has established a performance demonstration program (PDP) for laboratories that will participate in the analysis of headspace gas to be shipped to the WIPP site. The Carlsbad Area Office grants approval to laboratories for analysis of headspace gases that are successful in analyzing blind audit samples of simulated headspace gases. The Analytical Chemistry Laboratory (ACL) was selected as the laboratory to prepare, analyze, and distribute samples for the headspace gas PDP.

2002 Research Highlights

During Fiscal Year 2002, Cycle 16A of Headspace Gas Performance Demonstration Program (HSGPDP), 14 sets of HSGPDP samples were prepared. Each set consisted of five 6-L SUMMA[®] canisters at 6 psig containing low, high, special and duplicate mixtures of analytes. A blank containing Ultra Zero grade air was also included in the set. Two sets of HSGPDP samples were sent to the Rocky Flats Environmental Technology Site and Westinghouse Savannah River Company (WSRC). One set was sent to Los Alamos National Laboratory, the ECL at Idaho National Engineering and Environmental Laboratory, the Central Characterization Project at Savannah River (mobile vendor), the Central Characterization Project at the Nevada Test Site (mobile vendor), the Central Characterization Project at Argonne-Illinois (mobile vendor), the BNFL Lindsay Office, and Fluor Hanford. Two sets were prepared as backup samples and one set was prepared for Argonne-Illinois verification analysis.

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Research Participants

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Plutonium Metal Exchange Program

Checks and balances in measuring plutonium

With the closure of the Rocky Flats Production site, the Department of Energy's National Nuclear Security Administration no longer has the ability to manufacture plutonium pits. Los Alamos National Laboratory (LANL) has been given the mission to duplicate, on a limited scale, the Rocky Flats facility at LANL's New Mexico site. LANL's Analytical Chemistry Group is responsible for various measurements on the pits and at several points in the production process. These measurements are vital due to the stringent quality requirements of the material.

As part of ensuring that analytical determinations are valid, LANL has asked several outside laboratories to participate in a plutonium metal exchange. The exchange entails sending small pieces of the same plutonium metal to be evaluated by each laboratory. The exchange is repeated two to three times per year using different plutonium material. Data from the participating laboratories are used to identify strengths and weaknesses of particular analytical procedures. The exchange program is also designed as an opportunity for the laboratories to collaborate and learn new techniques that are available at other organizations.

2002 Research Highlights

The Analytical Chemistry Laboratory continued to be a participant in the second year of the

program. In 2002 we reported the results of our analysis of the exchange samples and attended a meeting of participants at LANL to review the data.

We had determined the isotopic composition of the plutonium by thermal ionization mass spectrometry (TIMS) and assayed the metals for plutonium using TIMS measurements and the isotope dilution technique. We also analyzed the plutonium samples for metal impurities using chemical separation and inductively coupled plasma-atomic emission spectrometry (ICP-AES), and determined ^{241}Am using alpha spectrometry. Uranium content was determined by separation and using the TIMS method.

The results of these determinations, along with the results of other participants, are compiled. Results from these analyses are then used to improve methods where there may be deviancies.

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Research Participants

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Tritium Target Qualification Project

Helping the Nation to produce tritium

The U.S. Department of Energy (DOE) has selected light-water-reactor irradiation of tritium-producing burnable absorber rods (TPBARs) as its preferred option for tritium production over the next 40 years. Each TPBAR contains columns of ^6Li -enriched lithium aluminate (LiAlO_2) ceramic pellets that generate tritium while maintaining criticality control in the reactor core.

The Tritium Target Qualification Project (TTQP) at Pacific Northwest National Laboratory (PNNL) is developing a national capability to mass-produce the needed LiAlO_2 pellets. Since 1997, the Analytical Chemistry Laboratory has been providing vital support to the TTQP by:

- Developing and validating modern methods for needed analytical chemistry measurements,
- Characterizing or preparing reference materials for method qualification and control,
- Transferring methods to a commercial analysis laboratory, and
- Providing analysis services for pellet manufacturing processes until a commercial capability is qualified.

2002 Research Highlights

Methods development: Specifications for the LiAlO_2 pellets require determination of the ^6Li enrichment, lithium and aluminum content, and the Li/Al atom ratio. Also required are numerous impurities, including carbon, halides, and 24 cationic elements. Our earlier work on needed methods produced several notable developments that have been reduced to standard practice, translated into detailed operating procedures,

and validated for acceptable precision, bias, range, and sensitivity with program-specified test materials.

The methodology we established included:

- A microwave-accelerated procedure for dissolving the highly refractory LiAlO_2 ceramic with acid,
- A procedure using inductively coupled plasma-optical emission spectrometry (ICP-OES) for very precise, simultaneous measurement of lithium, aluminum, and the Li/Al ratio,
- A conventional ICP-OES procedure for simultaneously measuring all 24 cation impurities using the same solution as the major-constituent determinations, and
- New methods for decomposing the ceramic to allow halide measurements with ion chromatography.

This year, our methods were applied to the analysis of large-scale production-lot pellets. One modification was needed in the microwave dissolution procedure to accommodate small amounts of a very refractory phase (LiAl_5O_8) formed under the conditions used in sintering the large lots of pellets. All the other methods performed satisfactorily.

Standards for method qualification and control: Because reference materials from nationally or internationally recognized agencies such as the National Institute of Standards and Technology (NIST) are not available for pertinent measurements, we characterized or prepared several working reference materials needed for system calibration, qualification of new laboratories, and tracking long-term continuity of results.

The “Highly Enriched Working Reference Material” (HEWRM) is a batch of 95% ^6Li -enriched lithium carbonate that supplements NIST SRM 924a as a calibration standard for the high-precision ICP-OES method. It is needed because the ICP-OES system shows different sensitivity for the ^6Li and ^7Li isotopes and must be calibrated for both to handle isotopic variation in the LiAlO_2 ceramics. This year, PNNL validated our characterization of this material to establish its lithium assay, isotopic composition, and homogeneity so it could be used as a program reference material.

Our characterization of the lithium aluminate control material (LACM), a lithium aluminate powder produced by the TTQP as a laboratory control sample, was also documented and validated. A portion of this material is to be analyzed with every batch of pellet samples processed by a laboratory over the program’s lifetime. Results contribute to the laboratory’s quality control program and track consistency of results over time.

Isotopic reference materials that we prepared by gravimetrically mixing certified standards were made available for distribution. We also made a set of check standards for testing laboratory performance in measuring lithium isotopes and prepared a set of standards simulating solution from the microwave-assisted dissolution of LiAlO_2 . These solutions were provided to a candidate commercial laboratory so they could qualify their ability to meet bias requirements at the ends of the calibration range for the ICP-OES method.

Technology transfer: The ultimate goal of our support to the TTQP was to transfer our methods to a commercial laboratory that will analyze production lot pellets. This year, that goal was achieved when a laboratory contracted by DOE successfully completed an extensive

qualification exercise. The qualification entailed multiple analyses of the LACM, isotopic reference materials, and blind standard solutions that we provided. Along the way, we helped the commercial facility resolve some instrument problems and other difficulties. Now qualified, the commercial laboratory has responsibility for all final-inspection measurements on production-lot pellets. They have processed the 40-pellet test samples from several lots, with excellent results.

Measurements for manufacturing-process development: Capabilities established as we developed methods for the TTQP also allowed us to provide data to producers of the LiAlO_2 ceramics as they scaled up processes for pellet production. We analyzed a large number of samples related to powder precursors from which pellets are sintered and to the pellet-making process. While the commercial laboratory pursued qualification, we analyzed inspection-pellet groups from three production batches and verified batch conformance to program specifications. Analyzing these real-world samples allowed us to improve our procedures and to encounter the kinds of problems that the commercial laboratory would face in its production support. This experience was invaluable in our role as advisor to the commercial facility.

This work was funded by the U.S. Department of Energy through the Tritium Target Qualification Project at Pacific Northwest National Laboratory.

Research Participants

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Methods for Analysis of Oxide Reduction Products

Providing analytical chemistry data to track progress in developing a new technology

Direct electrolytic reduction is a process that converts metal oxides directly to the corresponding metal by a solid-state transformation at the cathode of an electrochemical cell. Researchers in the Chemical Engineering Division (the Division) are studying the direct-electrolytic-reduction technology as a key step in a pyrochemical process for recovering the uranium and transuranic value of spent oxide fuels from nuclear reactors.

To determine the yield, reduction rate, and efficiency of the process, and to provide data for scale-cell design, the Division's engineers need reliable quantitative chemical-analysis data to characterize the oxide-reduction products and cell chemistry. The Analytical Chemistry Laboratory implemented methods for separating reduction products from the cell's electrolyte matrix, for determining the relative amounts of metal and oxide components in the products, and for describing minor constituents in the electrolyte and products.

2002 Research Highlights

In bench-scale experiments involving uranium, the oxide reduction is carried out in a molten $\text{LiCl-Li}_2\text{O}$ electrolyte at 650°C . The oxide feed is contained in a fuel-basket cathode constructed from stainless steel wire mesh. An oxygen-evolving electrode such as platinum and a reference electrode are also present in each cell. During the process, the oxide fuel in the basket is reduced to metal; oxide ions that dissolve into the electrolyte are transported to the anode and liberated as oxygen gas. Some lithium metal is produced at the cathode as the oxide reduction occurs.

Chemical data typically desired from each test cell included (1) the amounts of lithium oxide, lithium metal, and other constituents in the electrolyte salt; and (2) the composition of

material in the cathode basket, including the amount of electrolyte salt, lithium oxide, lithium metal, and the relative amounts of oxide and metal in the cathode product. The feed material in most experiments was uranium oxide; other tests were carried out with rare-earth metal oxides (Nd, La, Ce) and with a uranium/plutonium oxide mixture.

Analysis of samples taken from the electrolyte salt normally began by dissolving the salt in deionized water. To determine lithium metal, the dissolution was done in a closed vessel connected to a gas buret such that evolved hydrogen could be measured. Lithium oxide in the salt was determined by titrating a portion of the salt solution with standard acid, which provides a measure of the sum of lithium oxide and lithium metal in the salt. The water solution was also analyzed using inductively coupled plasma-atomic emission spectrometry (ICP-AES) to determine lithium, uranium, stainless steel constituents, and other elements of potential interest for a given test. Chloride in the water solution could be determined with ion chromatography (IC).

Chemical characterization of the cathode composition was a challenging task. At the end of each experiment, Division engineers removed the cathode basket from the test cell and sectioned it into segments for analysis. Each segment contained varying amounts of metal, residual oxide, and entrained salt. The main goal in analyzing these cathode products was to determine the extent to which the oxide feed had been converted to metal but other parameters were also of interest, including the salt content, the amounts of lithium metal and lithium oxide, and the amounts of other constituents that might be present.

In analyzing the cathode products, we first separated the metal and oxide phases from surrounding salt by washing with either

methanol or water. Both solvents were effective in removing lithium chloride from the cathode products. Initially we favored methanol because it seemed less likely to react with the product metals and increase the apparent oxide concentration. However, we found that with uranium under the washing conditions, no discernable reaction with water occurred. Using water allowed the washing to be done in the apparatus connected to the gas buret and allowed measurement of lithium metal. The vapor pressure of methanol is too high and too dependent on temperature for gas evolution measurements to be made over it. We separated the wash solution from the insoluble product phases by filtering under an argon purge and dried the products by rinsing with a small amount of methanol and drawing argon over the product on the filter. The wash solution was then analyzed like the solutions produced from the electrolyte salt. The product phases could be examined by other appropriate means.

With uranium, we devised three different techniques for determining the relative amounts of metal and oxide present in the isolated product. Choosing one method or another depends on the nature of the product composition and the extent to which the oxide feed was reduced to metal. The first technique used with uranium is the "ignition" method, in which a weighed portion of the product is converted to U_3O_8 by ignition in air at 900°C . Assuming that the sample consists solely of a U metal/ UO_2 mixture, the relative amounts of metal and oxide can be calculated from the measured mass of the ignited sample. Relatively large samples can be processed to give a good bulk average value for the extent of reduction. Errors can arise if impurity phases are present in the sample. This method cannot differentiate between very small amounts of oxide (e.g., 98 vs. 99 % metal).

The second technique for uranium is a direct measurement of oxygen in the product using a LECO TC-136 Oxygen Determinator. This approach is very sensitive and can measure trace oxygen levels in the cathode product. It is limited to fairly small samples (1 g) but one can easily run many samples for average data.

The third approach for uranium uses selective dissolution of the product metal with elemental bromine in methanol or ethyl acetate. In our use of this process, the cathode product is submerged in the solvent, a small amount of MgO is added to neutralize acidic byproducts, liquid bromine is added, and the mixture is stirred at room temperature. The metal dissolves and the oxide does not. The oxide residue is collected on a filter and then the uranium in the filtrate (metal) and filter cake (oxide) is determined by any suitable method (we use ICP-AES). This method gives excellent sensitivity at any metal/oxide ratio and is very suitable for analyzing products that contain multiple metal/metal-oxide couples. We applied the method to products involving several rare earths as well as plutonium and americium.

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Research Participants

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Determination of Nitroaromatics in Soil and Water Samples

Finding traces of explosives in soil and water

The Analytical Chemistry Laboratory (ACL) performs a wide range of analyses to meet the needs of our clients. Recently we were asked to determine selected nitroaromatics (high explosives) in surface and ground waters and in soils. The request was to analyze the list of target compounds of EPA SW-846 Method 8330.

2002 Research Highlights

For the groundwater samples we set up a method for extraction using divinyl-benzene-based solid phase disks. The high performance liquid chromatography (HPLC) method was performed, using a C-18 reversed phase column as the primary identification column and a Cyano HPLC column for confirmation. The mobile phase consisted of 50:50 water:methanol.

The detection was at 254 nm. The detection limits for water samples were approximately 0.4 ppb while for soil samples the detection limits were approximately 0.5 ppm. The surface water samples were extracted using the salting out method; the soil samples were extracted using the sonication method.

Many of the water samples were found to contain some of the target compounds. However, the soil samples did not contain the target compounds above the detection limits.

Research Participants

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