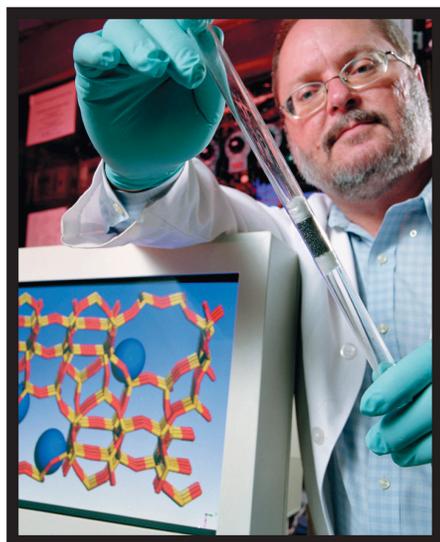


Chemical Engineering Division

Annual Technical Report



2003

Chemical Engineering Division
Engineering • Science • Innovation

Argonne National Laboratory





Scientists in the Chemical Engineering Division have developed an energy-efficient cerium-based catalyst that can remove up to 95-100% of the nitrogen oxide emissions in exhaust. Moreover, unlike many other catalysts, it works at normal exhaust temperatures and is *more* effective with water vapor present.



The UREX+ aqueous solvent extraction process, being developed by the Chemical Engineering Division, is one of two Argonne technologies being developed to reduce by more than 95 percent the mass of high-level waste slated to be stored in the Yucca Mountain nuclear waste repository. The goal is to delay or avoid the need for a second repository. The work is part of the Advanced Fuel Cycle Initiative.



The FASTER (Feasibility of Acceptable Start Time Experimental Reformer) project at Argonne National Laboratory is a collaborative project with three other National Laboratories, and academic and commercial organizations. The project is designed to study the feasibility of fast-starting gasoline fuel processors for automotive fuel cell systems, and to provide data and recommendations for DOE's Go/NoGo decision to continue on-board fuel processor development.

Argonne National Laboratory, with facilities in the states of Illinois and Idaho, is owned by the United States Government and operated by The University of Chicago under the provisions of a contract with the Department of Energy.

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2003

**Chemical Engineering Division
Annual Technical Report**

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March 2004

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Introduction

The Chemical Engineering Division is one of six divisions within the Engineering Research Directorate at 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, to promote national security, 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. Additionally, the Division operates the Analytical Chemistry Laboratory, which provides a broad range of analytical services to Argonne and other organizations.

The Division is multidisciplinary. Its people have formal training in chemistry; physics; materials science; and electrical, mechanical, chemical, and nuclear engineering. They are specialists in electrochemistry, ceramics, metallurgy, catalysis, materials characterization, nuclear magnetic resonance, repository science, and the nuclear fuel cycle. Our staff have experience working in and collaborating with university, industry and government research and development laboratories throughout the world.

Our wide-ranging expertise finds ready application in solving energy, national security, 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 with gasoline as the fuel supply,
- Production and storage technologies critical to the hydrogen economy,
- Stable nuclear waste forms suitable for storage in a geological repository,
- Threat attribution and training relative to radioactive dispersal devices ("dirty bombs"), and
- Aqueous and pyrochemical processes for the disposition of spent nuclear fuel.

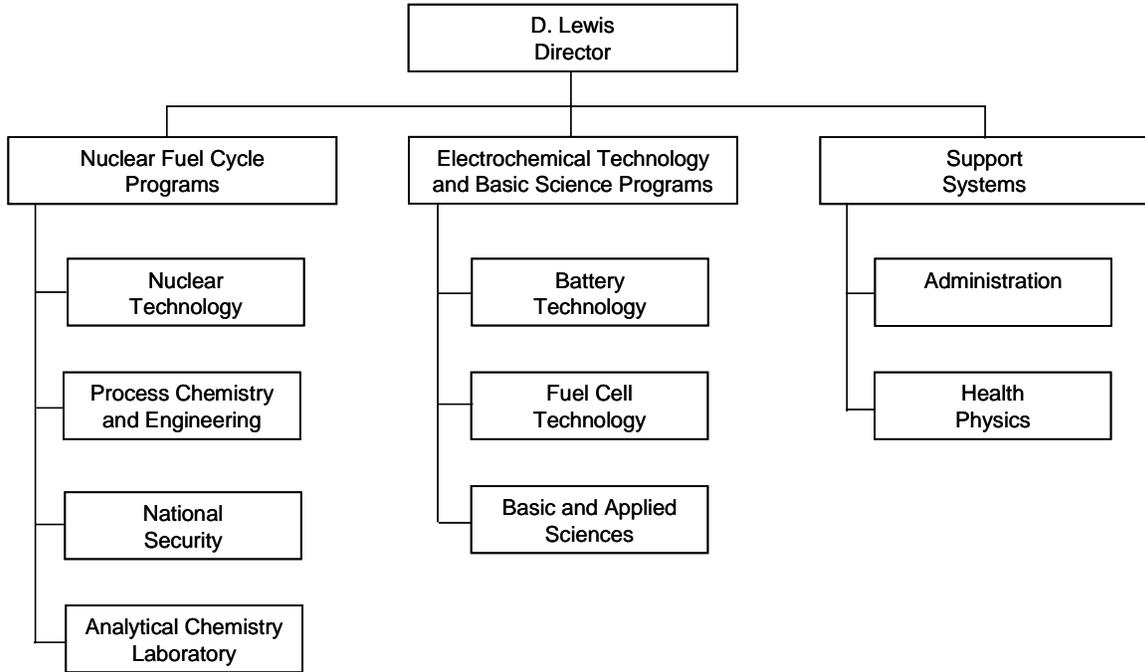
Other important programs are focused in superconductivity, catalysis, nanotechnology, and nuclear materials.

During fiscal year 2003, CMT had an annual operating budget of approximately \$36 million. Of that, more than 90% was from DOE and the remainder from other government agencies and private industry.

Displayed below is an overview 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.

Introduction



Batteries

Rechargeable lithium batteries have become very popular as power sources for consumer electronic devices, because of their high energy density (energy per unit 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 lithium-ion batteries. Due to their success in these applications, they are under development for other applications such as energy storage devices for electric vehicles, hybrid electric vehicles, and specialty battery applications.

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 that employed 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.

In 1998, the Division helped DOE to organize and initiate a new multi-national-laboratory R&D program (the Advanced Technology Development or ATD 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) applications 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 internal combustion engine and recapture regenerative braking energy. The 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 abuse tolerance, as well as evaluating and developing advanced materials designed to overcome these limitations, while simultaneously reducing material costs. It also involves the development of novel approaches for reducing cell packaging costs.

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 advanced lithium battery chemistries for biomedical, space, and military applications
- Develop advanced electrolyte systems with more stable salts

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,

Batteries

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 and FCEV applications. The Division continues work on the ATD Program under the FreedomCAR Partnership and is expanding its efforts to study low-temperature performance.

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 for both high-power and high-energy lithium batteries for use in transportation applications.

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, 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 neuromuscular microstimulator implants known as bions®.

These microstimulators may be used to treat patients suffering from stroke, Parkinson's disease, epilepsy, urinary urge incontinence, and many other conditions involving muscular impairment. 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.

During the last year, the Division implemented three new industrial contracts. One of the contracts deals with the development of a new salt-based electrolyte system for use in lithium-ion batteries. A second contract deals with the development of a more optimal cell chemistry for use in military applications. The third contract deals with the development of electrolyte additives that can stabilize the cell chemistries used in secondary lithium batteries being developed for satellite applications.

Additionally, 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 80 kW.

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High-Power Lithium-Ion Batteries for Transportation

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

Better high-power batteries are needed to level the load and recapture regenerative braking energy in hybrid electric vehicle (HEV) and fuel cell electric vehicle systems, currently under development internationally for transportation applications. Although a few production HEVs have been introduced into the automotive market, no current battery technology demonstrates an acceptable combination of efficiency, 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 U.S. 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 more stable cell components and chemistries that employ lower-cost materials; incorporate them into sealed cells; conduct well-defined abuse, low-temperature performance, 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.

2003 Research Highlights

This year we made significant progress in understanding the factors that limit the life of our second-generation baseline cell chemistry. This cell chemistry is shown in Table 1. Average cell aging data are provided in Figure 1. Many of the aged second-generation cells underwent detailed diagnostic evaluations to understand the aging mechanisms in this cell chemistry.

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

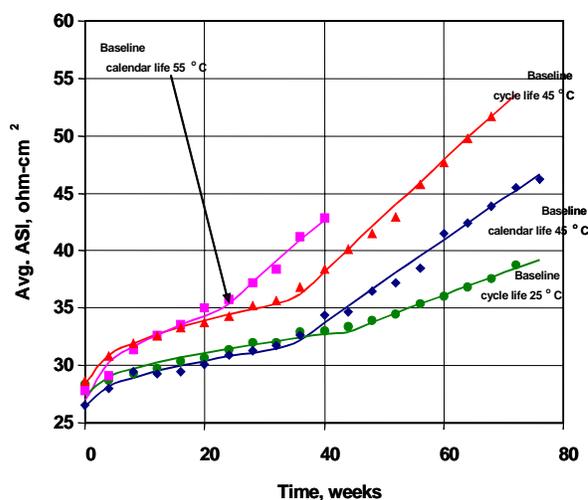


Fig. 1. Average cell aging characteristics—impedance vs. aging time at temperature.

Prior reference electrode studies, showed that the majority of the cell impedance rise during aging occurred at the cathode and our diagnostic studies focused on this electrode. Electrochemical impedance spectroscopy (EIS) of new and aged cathodes showed different phenomena during the early (low-rate impedance rise) stage vs. the late (high-rate impedance rise) stage of cell aging. During the early stage, most of the impedance rise is associated with an increase in the mid-frequency arc (see Fig. 2), which is an interfacial impedance. During the late stage, the

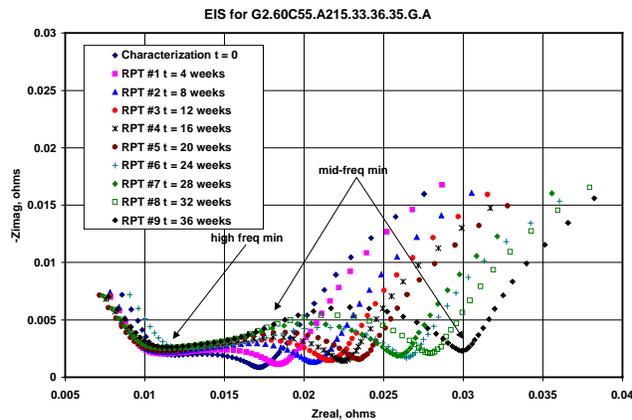


Fig. 2. Early-stage EIS data on aged cells.

low-frequency tail (see Fig. 3) becomes dominant. This low-frequency tail is associated with diffusional phenomena. ANL's cell transport model was used to study both features of the EIS data and to identify responsible phenomena.

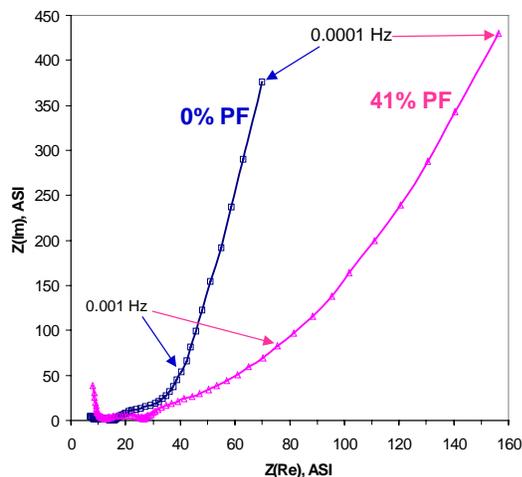


Fig. 3. Late-stage EIS data on aged cells

The main phenomenon identified and studied extensively is the development of organic surface films on the cathode. These films were observed via high-resolution scanning electron microscopy and transmission electron microscopy (HR-TEM). X-ray photoelectron spectroscopy studies showed that chemical changes in these films occur in a manner that directly correlates with the amount of cell impedance rise and power fade. Scraping of the cathode surfaces was found to re-expose the cathode active material, thereby verifying the presence of films covering the active cathode material in aged cells.

Various other diagnostic studies were performed on cathodes that were harvested from new and aged cells. X-ray diffraction studies showed that the structure of the bulk cathode material was essentially unchanged during the aging process. HR-TEM studies showed limited evidence of particle cracking in cathodes harvested from cells with extreme (>50%) power fade. HR-TEM and EELS showed that the virgin cathode material contains a thin (5- to 10-nm) NiO crust (outer layer) on the surface of the cathode particles and the thickness of this crust remained constant (did not increase) during the aging process.

Based on these results, it appears that the organic surface films on the cathodes are playing a significant role in the impedance rise and power fade of these high-power cells. It is possible that these films impede Li^+ diffusion/migration to the surface of the cathode where the electron exchange reaction occurs. As the surface of the active cathode particles becomes more thoroughly covered by these films, the impedance of the cathode increases. Additional studies are being performed to verify the role that these films play in the impedance rise and power fade of the cathode during aging.

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 include 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 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 has improved the electrochemical properties of metal oxide positive electrodes by compositional modification of their structures or surface treatment. We are continuing our efforts to develop these materials—and to discover new ones—to provide optimal electrode performance that developers require in lithium-ion batteries.

2003 Research Highlights

Stabilized LiMn_2O_4 Spinel Electrodes

Despite its superior rate capability and structural and thermal stability compared with layered LiCoO_2 and LiNiO_2 electrodes, the solubility of LiMn_2O_4 spinel electrodes in lithium-ion battery electrolytes has precluded their widespread use in commercial cells.

Recent technological advances have been made in improving the cycling stability of LiMn_2O_4 (i.e. $\text{A}[\text{B}_2]\text{O}_4$ spinel structure) electrodes by either A-site and/or B-site substitution in combination with metal-oxide coating of the material. This dual approach combats the solubility problems and instability encountered by the spinel electrode in application.

We have used colloidal metal-oxide suspensions of zirconia, alumina and silica to coat LiMn_2O_4 - and substituted $\text{Li}_{1.05}\text{M}_{0.05}\text{Mn}_{1.9}\text{O}_4$ ($\text{M} = \text{Al}, \text{Ni}$) powders. The coated powders are annealed at $400\text{ }^\circ\text{C}$ and then made into electrodes. Using this technique, it is possible to control the surface

architecture of the coating in terms of thickness and porosity. Our initial results have shown that ZrO_2 -coated spinel electrodes consistently provide superior performance compared with those coated with SiO_2 or Al_2O_3 . The inferior electrochemical behavior of SiO_2 and Al_2O_3 -coated electrodes is attributed to a sintering reaction that occurs between the LiMn_2O_4 particles and the nanosized SiO_2 ($\sim 2\text{ nm}$) and Al_2O_3 ($< 20\text{ nm}$) particles during the annealing step, which apparently does not occur when ZrO_2 ($< 4\text{ nm}$) particles are used.

The voltage profiles for the initial discharge of $\text{Li}/\text{LiMn}_2\text{O}_4$ - and $\text{Li}/\text{Li}_{1.05}\text{M}_{0.05}\text{Mn}_{1.9}\text{O}_4$ cells, cycled between 4.3 and 3.3 V at $50\text{ }^\circ\text{C}$, with uncoated spinel electrodes and electrodes coated with 4 wt% ZrO_2 are compared in Figure 1. The specific capacity of coated electrodes (based on the mass of the active spinel electrode and the ZrO_2 coating) is lower than that of uncoated electrodes, as expected, because the coating is electrochemically inert and should increase polarization effects at the electrode surface during electrochemical discharge. The point of inflection that occurs approximately halfway along the discharge curve of the $\text{Li}/\text{LiMn}_2\text{O}_4$ cell is attributed to Li^+ - and electronic ordering of the manganese ions when the spinel electrode reaches the composition $\text{Li}_{0.5}\text{Mn}_2\text{O}_4$; this inflection is smoothed in cells with substituted electrodes, consistent with earlier reports in the literature. In these instances, the voltage profile adopts greater single-phase character in the higher voltage region, in contrast to the two-phase behavior of $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ electrodes for $0.5 \leq x \leq 1$, supporting the argument that substitution for Mn by the M ions in $\text{Li}_{1.05}\text{M}_{0.05}\text{Mn}_{1.9}\text{O}_4$ electrodes disrupts the long-range atomic and electronic order within the spinel structure, thereby suppressing the ordering process during the electrochemical extraction and reinsertion of lithium.

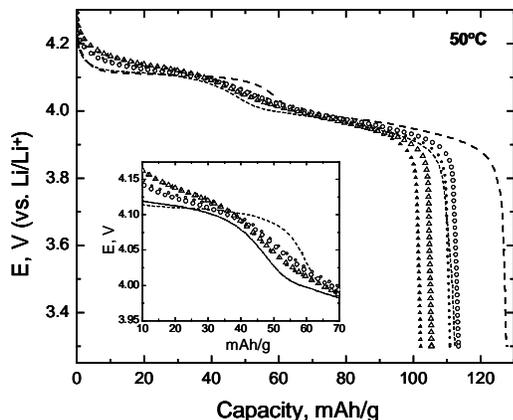


Fig. 1. Initial discharge profiles of lithium cells at 50 °C with uncoated (large symbol) and coated (small symbol) LiMn_2O_4 (-), $\text{Li}_{1.05}\text{Al}_{0.05}\text{Mn}_{1.90}\text{O}_4$ (Δ) and $\text{Li}_{1.05}\text{Ni}_{0.05}\text{Mn}_{1.90}\text{O}_4$ (\circ) spinel electrodes.

Capacity vs. cycle number plots of Li/spinel cells containing uncoated LiMn_2O_4 , ZrO_2 -coated LiMn_2O_4 and ZrO_2 -coated $\text{Li}_{1.05}\text{Ni}_{0.05}\text{Mn}_{1.90}\text{O}_4$ electrodes are shown in Fig. 2 (50 °C). The data demonstrate that the coated, substituted spinel electrode provides greater cycling stability than both coated and uncoated LiMn_2O_4 electrodes.

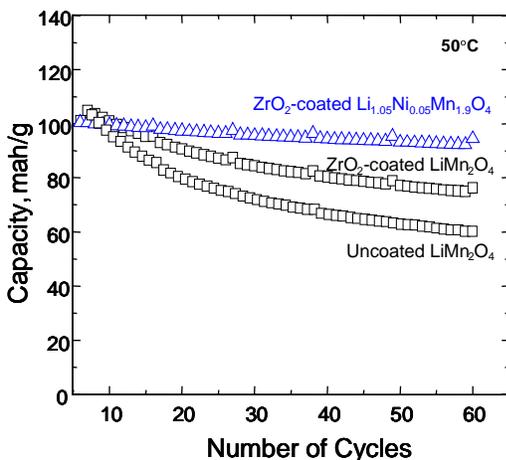


Fig. 2. Capacity vs. cycle number plots for lithium cells cycled between 4.3 and 3.3 V at 50 °C : uncoated LiMn_2O_4 ; ZrO_2 -coated LiMn_2O_4 ; and ZrO_2 -coated $\text{Li}_{1.05}\text{Ni}_{0.05}\text{Mn}_{1.90}\text{O}_4$.

Coatings deposited from colloidal suspensions feature thicknesses that vary over a wide range, typically from 10 to 50 nm. A high-resolution

transmission electron microscope (TEM) image of a ZrO_2 -coated LiMn_2O_4 electrode that had been annealed at 400 °C provides little evidence of ZrO_2 reaction with, or fusion to, the spinel particles (Fig. 3). A magnified image, inset in Figure 3, shows that the coatings consist of a porous conglomerate of ZrO_2 primary particles less than 4 nm in dimension. The combination of a porous coating that allows access of the electrolyte to the spinel electrode, and the high surface area of the ZrO_2 particles and their affinity for scavenging HF and H_2O molecules from the electrolyte appear to be among the reasons why ZrO_2 coatings are proving to be most effective in stabilizing the cycling stability of LiMn_2O_4 spinel electrodes. Products of ZrO_2 reacted with HF/ H_2O could result in oxonium-zirconium-fluoride-hydrate structures, such as $[\text{ZrF}_5 \cdot \text{H}_3\text{O}^+ \cdot 2\text{H}_2\text{O}]$. This product is reformulated as a $\text{ZrO}_2 \cdot 5\text{HF} \cdot \text{H}_2\text{O}$ compound (component notation) in order to emphasize the stabilizing properties that an amphoteric ZrO_2 coating provides.

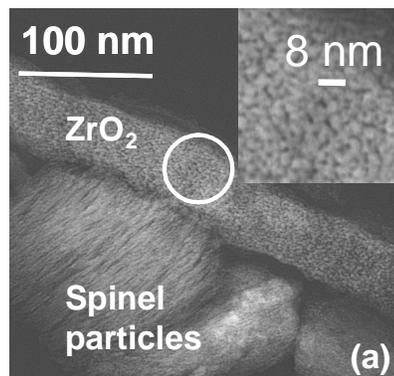


Fig. 3. High-resolution TEM image of ZrO_2 -coated LiMn_2O_4 spinel particles.

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

Advanced materials help meet the requirements of several specialty applications

During the last year, the Chemical Engineering Division (the Division) was involved in several contracts with outside organizations (Work for Others, or WFO, contracts) to develop advanced cell chemistries and cell components for high-energy lithium batteries. The largest of the contracts is a 4-year NIST-ATP project with Quallion LLC. This project consists of developing battery chemistries for long-life rechargeable lithium polymer battery systems to power advanced micro-stimulators, such as the bion®.

Two other WFO contracts are directed at developing long-life rechargeable lithium polymer and lithium ion batteries for use in military and space applications, respectively. In both cases, the Division is developing cell chemistries. A fourth project involves the development of optimal solvent systems for an industrial firm that has developed a new Li^+ conducting salt that is thermally, chemically, and electrochemically more stable than the conventional LiPF_6 salt. These new projects were initiated only recently and will not be reported on this year.

The remainder of this subsection provides selected advances on the WFO project to develop a long-life high-energy lithium-polymer battery for use with bions. Implantable bions offer hope for victims of strokes, Parkinson's disease, epilepsy, urinary urge incontinence, and similar conditions involving neuromuscular impairment.

2003 Research Highlights

Advanced polymer electrolyte: Working in collaboration with Quallion and the University of Wisconsin, the Division is developing new poly(ethylene oxide) grafted siloxane polymers. These siloxane-based polymers exhibit very

good electrochemical, chemical, and thermal stability, as well as low toxicity. Our prior work showed that these polymer electrolytes possess very good room-temperature ionic conductivities, are stable over a wide voltage window, and exhibit significantly enhanced thermal stability relative to the conventional liquid electrolyte systems used in lithium ion cells and batteries.

New siloxane phases with ionic conductivities near 10^{-3} S/cm at room temperature are being synthesized and characterized. Figure 1 shows the conductivity of one of these new siloxane polymers as a function of temperature. These conductivities are similar to those for conventional liquid organic electrolytes used in lithium ion batteries. The outstanding electrochemical stability of these polymer electrolytes offers the opportunity to use them with advanced high capacity layered cathode materials with ≥ 250 mAh/g capacity density at 4.5 V. Figure 2 provides a cyclic voltamogram on one of the new siloxane polymers, showing the material is

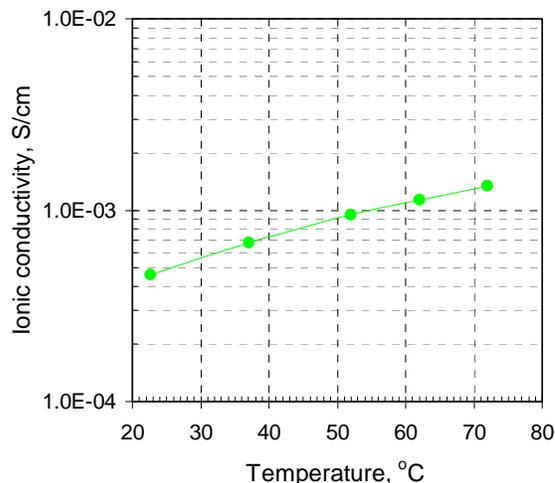


Fig. 1. Lithium ion conductivity of siloxane polymer electrolyte as a function of temperature.

Batteries

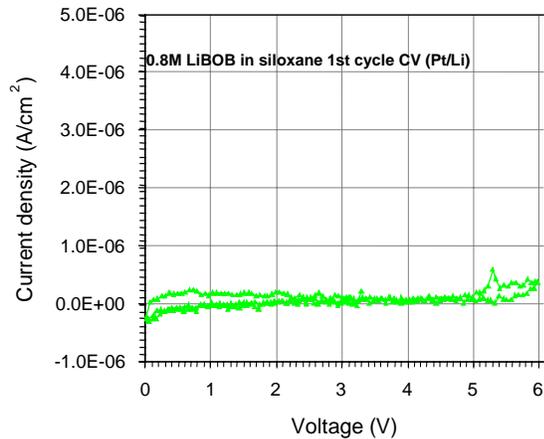


Fig. 2. Cyclic voltamogram showing the electrochemical stability of siloxane polymer between 0 and 6 V vs. lithium.

extremely stable between 0 and 6 volts vs. lithium. Additionally, these materials are nonflammable and non-toxic. These features combine to make the siloxane polymer electrolytes attractive for use in long-life batteries for implantable medical devices. Also, their high ionic conductivities make them viable candidates for other applications, e.g., satellites, consumer electronics, and smart cards.

Advanced cathodes: During the last year, we refined our LiFePO₄ cathode material for use in the new long-life battery system for the bions. The olivine cathode materials have greater chemical and thermal stability in the presence of conventional electrolytes and they exhibit better safety characteristics relative to the LiNi_{1-x}Co_xO₂ type cathode materials. The olivine materials are electronically insulating and we have optimized the performance of our material using a new process for coating the olivine with carbon at the particle level.

Stable cell performance: Recent data on cells that employ a LiNi_{1-x}Co_xO₂ type cathode, a siloxane polymer electrolyte system, and a graphite anode show excellent stability. Figure 3 provides capacity density and coulombic efficiency data on a cell of this type. The high coulombic efficiency provides further verification of the stability of the siloxane polymer electrolyte. Beginning early in the project, we were able to achieve stable performance from cells that employed lithium metal anodes and during the last year we have succeeded in transferring this level of performance stability to cells that employ graphite anode materials.

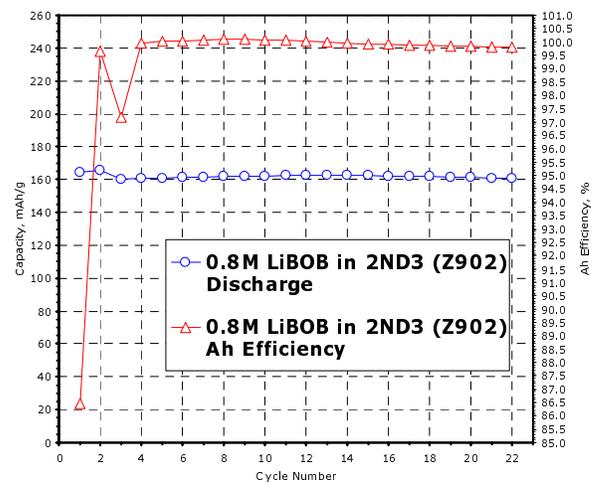


Fig. 3. Capacity density and efficiency vs. cycle number for a graphite/siloxane polymer/LiNi_{1-x}Co_xO₂ cell.

Research Participants

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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.

2003 Research Highlights

In a portion of our HEV work with Li-ion batteries, we continued the calendar life evaluation of prototype lithium-ion batteries made under DOE's Advanced Technology Development (ATD) Program. These batteries were designed for use in hybrid electric vehicles. At present, lithium-ion technology exhibits exceptional power capability and long cycle life, but has insufficient 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_{0.10}Al_{0.10}O₂. Accelerated calendar life tests were used at 45 (Groups A and B) and 55°C (Group A only) at 60% state of charge.

Initially, the average C/25 capacities for Groups A and B were 1.03 ± 0.03 and 0.97 ± 0.02 Ah, respectively. As 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 for both groups of 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.

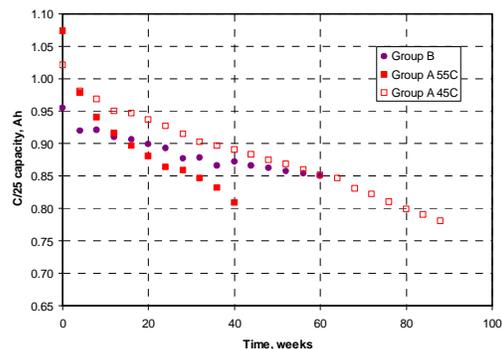


Fig. 1. C/25 capacity vs. time for Groups A and B.

The initial average ASI values at 60% SOC were 28.41 ± 1.36 and $34.68 \pm 2.77 \text{ } \Omega\text{-cm}^2$ 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.

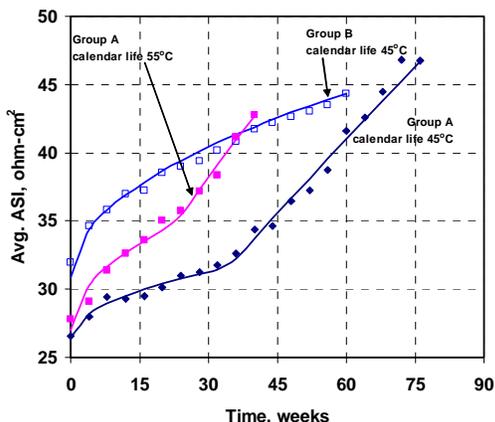


Fig. 2. Discharge impedance as a function of time for Groups A and B.

The impedance was sensitive to the Al concentration. At 45°C, the Group B cells displayed higher overall impedance and power fade at 45°C than did the Group A cells. The time dependence of the impedance 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 in Group B was simpler and depended on $t^{1/2}$ only. While the higher Al content decreased capacity fade, it was detrimental to cell impedance.

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

Research Participants

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Fuel Cells

Almost all of the major automobile manufacturers in the U. S. and abroad have exhibited prototype fuel cell-powered cars. Fuel cells are viewed as a clean, efficient power source for transportation applications, including vehicle traction power as well as auxiliary power for the vehicle's hotel and accessory loads. Fuel cells operating on hydrogen, as well as on clean hydrocarbon fuels, are a major thrust of development under the FreedomCAR program involving the major U. S. automobile manufacturers and the U. S. Department of Energy (DOE). Fuel cells are also being developed for residential and distributed stationary power generation, often for combined heat and power applications. The Chemical Engineering Division is working closely with the DOE Office of Energy Efficiency and Renewable Energy, Hydrogen, Fuel Cells and Infrastructure Technologies Program, and with the DOE Office of Fossil Energy, 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, etc.) fuels. In the near term, therefore, fuel cell systems will need fuel processors (reformers) to convert the available fuel to hydrogen or a hydrogen-containing gas mixture. Thus, a significant portion of our fuel-cell-related R&D has the objective of developing catalysts, processes, and reactor designs for fuel processing in integrated fuel cell power systems.

A major project in this effort is the FASTER (Feasibility of an Acceptable Start Time Experimental Reformer) project, under which we will design, fabricate, and test a gasoline

reformer that can start up in 60 seconds or less. Working with staff from Argonne's Nuclear Engineering Division, we are using GCtool and related software to design and analyze fuel cell systems. Such analyses are useful in devising system integration approaches that permit effective use of fuel processors in fuel cell systems, and for the effective use of fuel cell systems in the desired varied applications. The analyses address key issues of system efficiency and performance, system integration, startup, and fuel economy for direct-hydrogen- as well as reformat-fueled fuel cell systems.

Chemical Engineering Division Fuel Cell R&D

- Development of catalysts, processes, and reactor designs for fuel processing of conventional and alternative fuels
- Design, fabrication, and testing of a fast-startup (60 s or less) gasoline fuel reformer
- 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 R&D activities include the development of new polymer electrolyte materials for use in fuel cells that operate at 120–150°C or higher that are of interest in transportation and stationary power generation; diesel fuel reforming for use in solid oxide fuel cells operating at 650°C or higher; new alloy materials for metallic interconnects for these solid oxide fuel cells; and a metal-supported solid oxide fuel cell and stack concept that offers the potential to be thermally and mechanically rugged and of low cost in materials and fabrication processes. In addition, we are collaborating with three different University teams to address some of the materials and fuel processing issues.

Fuel Cells

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Fuel Processor Engineering

Making the transition to hydrogen-powered fuel cells

Fuel-cell-powered vehicles will require a hydrogen-refueling infrastructure and on-board hydrogen storage capacities that can offer driving ranges comparable to those available with today's gasoline-fueled internal combustion engine cars. The transition to the hydrogen infrastructure can be bridged with the use of on-board fuel processors that can convert available fuels (such as gasoline) to hydrogen. The demanding requirements of the automotive application, together with the sensitive nature of the polymer electrolyte fuel cell, contribute to a fuel processor design that is complex.

The Chemical Engineering Division has developed technologies and designs for on-board fuel processors. A key requirement for these on-board fuel processors is their rapid start capability. The U.S. Department of Energy (DOE) has targeted start-up times of 60 seconds for the year 2005, and 30 seconds by 2010 at normal ambient temperatures. Reducing the large thermal mass of the fuel processor, most of which must be heated to several hundred degrees Celsius, will enable rapid start and also reduce the energy (fuel) consumed during startup.

2003 Research Highlights

Feasibility of Acceptable Start-Time Experimental Reformer (FASTER): We are leading a collaborative program to design, fabricate, and demonstrate rapid start-up of a laboratory-scale (10-kWe, ~30-kWt) fuel processor. Contributing organizations include Los Alamos (LANL), Oak Ridge (ORNL), and Pacific Northwest (PNNL) National Laboratories and several universities and private organizations.

The FASTER design (Fig. 1) consists of an autothermal reformer (ATR) followed by a 4-stage water-gas shift (WGS) reactor and a 3-stage preferential oxidation (PrOx) reactor. Reformate temperatures are maintained at desired levels with the help of six heat exchangers. Water injected before the fourth WGS stage helps cool the reformate and favor CO conversion in WGS4. HE1, the heat exchanger between the ATR and WGS1, is a microchannel heat exchanger designed and fabricated by PNNL. The five other heat exchangers are of carbon foam construction, designed and fabricated by ORNL. The preferential oxidation reactors are designed and fabricated by LANL.

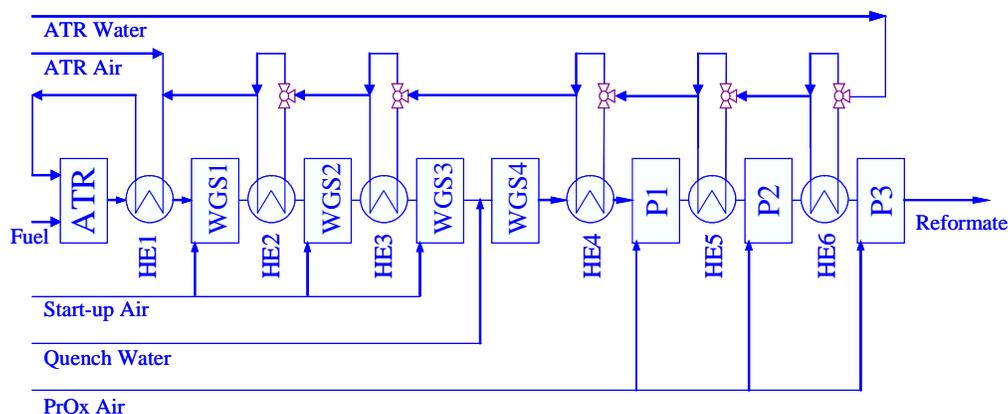


Fig. 1. FASTER consists of a sequence of reactors and heat exchangers provided by the various project team members.

The FASTER startup strategy relies on the ATR component reaching its operating temperature very quickly. This is achieved by operating at a high O/C [ratio of oxygen (from air) to carbon in the fuel] ratio. The resulting reformat, which contains combustible gases (H₂, CO, and light hydrocarbons) will be oxidized just ahead of WGS1, WGS2, and WGS3 by injecting controlled amounts of air. For initial production of fuel-cell-quality fuel gas, only the ATR and the first three zones of the shift reactor must be brought up to temperature. The PrOx units have been sized to compensate for the higher CO (up to 4%) from the shift reactor during startup.

Readying the ATR to produce combustible gases requires rapid heating of the front edge of the ATR catalyst. Figure 2 shows that with a 400-W electric heating coil placed just ahead of the catalyst, it took ~66 seconds to heat the catalyst inlet face to 300°C. Introducing the fuel and air mixture onto the catalyst surface at that time initiated the oxidation reactions, which led to a rapid rise in catalyst temperature.

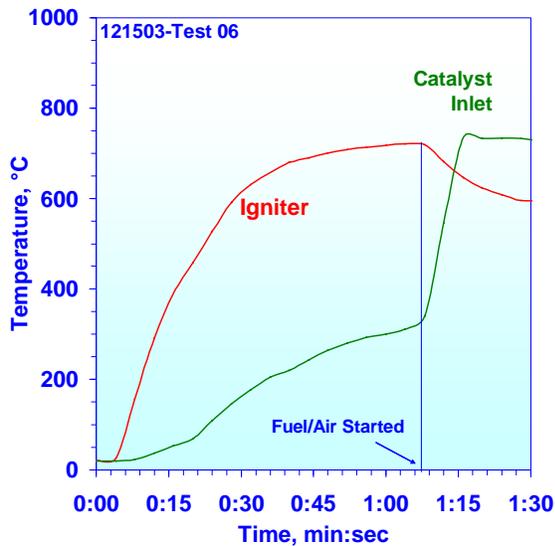


Fig. 2. With a 400-W [1/16-in dia. heater rod] electric “igniter,” the inlet edge of the ATR catalyst reached the light-off temperature of 300°C in 66 s.

Start-up can be accelerated if the power to the heater can be increased. A commercially available heater element (www.emitec.com) rated for higher power input, could be heated to

500°C in 10 seconds, by applying 1.6 kW of electric power (Fig. 3). Adapting such an element for the ATR process has the potential to accelerate ATR readiness. Similarly, the ability to inject vaporized fuel will lower the catalyst temperature at which the fuel/air mixture can be injected. These and other options are being investigated to further accelerate start-up.

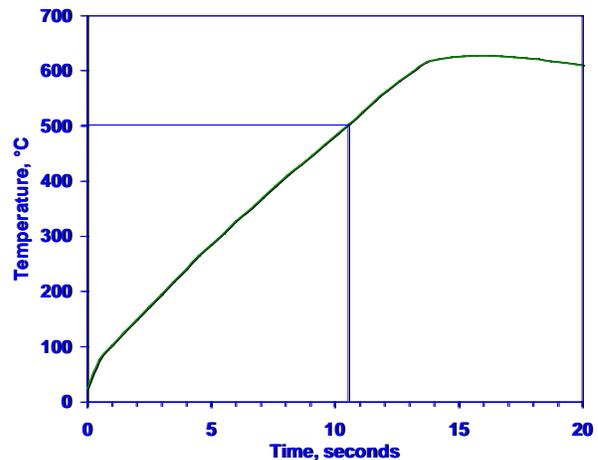


Fig. 3. A commercial electric heater can achieve surface temperatures of 500°C and higher in about 10 s using an input power of 1.6 kW.

FASTER components have been received from suppliers and are being integrated into the fuel processor containment vessel. Experimental data generated from the operation will be used to validate models and project fuel processor designs that can meet constraints such as size, weight, start-up time, and fuel consumption for automotive gasoline fuel processors.

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

Research Participants

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Fuel Processor Catalysis

Catalysts to enable fuel cells to operate on today's fuels

Reforming of gasoline, natural gas, and other conventional or alternative fuels is one option being pursued for supplying hydrogen for automotive and stationary polymer electrolyte fuel cell (PFEC) systems. Reforming involves reacting the fuel with oxygen, generally supplied as air, and water in the presence of a catalyst at 600–1000°C to produce a hydrogen-rich gas, referred to as reformat. In addition to hydrogen, reformat contains significant amounts of nitrogen, carbon dioxide, and carbon monoxide. Nitrogen and carbon dioxide do not affect the anode catalyst in the fuel cell stack; however, carbon monoxide “poisons” the anode catalyst and degrades the performance of the fuel cell. To maintain an acceptable level of performance, the concentration of carbon monoxide in the reformat must be reduced to <10 ppm. Two reactions, the water-gas shift ($\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$) and preferential CO oxidation ($\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$), are used to reduce the concentration of carbon monoxide to acceptable levels. Collectively, the catalysts used for the reforming, water-gas shift, and preferential CO oxidation reactions are referred to as fuel processing catalysts. Available commercial catalysts are not suitable for use under the demanding operating conditions in automotive or small-scale residential fuel cell power systems. Our research is focused on developing new reforming and water-gas shift catalysts specifically tailored for use in these emerging fuel cell applications.

2003 Research Highlights

Autothermal Reforming Catalysis: A primary focus of our research is to develop catalysts that are not poisoned by the sulfur present in conventional fuels. For example, even after new regulations take effect in 2006, the average sulfur content of gasoline would still be 30 ppm by weight (compared with 150 ppm in 1999). The sulfur content of natural gas is

approximately 30 ppm by volume. At these levels, sulfur severely poisons the Ni-based steam reforming catalysts used in the industrial production of hydrogen. Typically, sulfur poisoning occurs due to the adsorption of sulfur on, and the consequent blocking of, the catalytically active sites. The extent of surface coverage by sulfur decreases with increasing temperature. Thus, higher reaction temperatures promote sulfur tolerance. This requires, however, that the catalyst be thermally stable at these higher reaction temperatures.

We have developed a reforming catalyst based on Rh dispersed on a lanthanum-modified alumina substrate that has been shown to exhibit high fuel conversion, high selectivity for hydrogen, and low hydrocarbon breakthrough when reforming a variety of hydrocarbon fuels. As shown in Figure 1, this catalyst produced a reformat containing 60 vol% H_2 (dry, N_2 -free basis) from a sulfur-free (<450 ppb S) gasoline at 700°C over a period of 100 h on stream. With gasoline containing 34 ppm sulfur, the catalyst severely deactivated at 700°C with the H_2

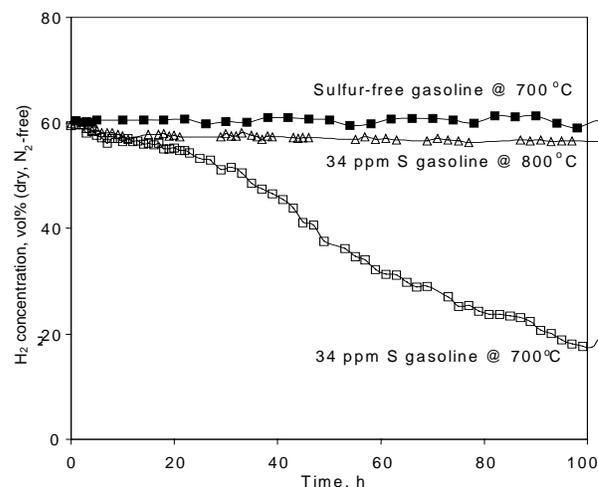


Fig. 1. The rhodium-lanthanum-alumina autothermal reforming catalyst is resistant to poisoning by sulfur at 800°C for the reforming of gasoline for automotive fuel cell systems.

concentration in the reformat decreasing from its initial value of 60 to 18 vol% after 100 hours on stream. By increasing the reaction temperature to 800°C, however, only a slight decrease in the H₂ concentration was observed during first 20 h, with the H₂ concentration remaining steady over the next 80 h. We are continuing these tests to verify long-term (>1000 h) stability of this catalyst with sulfur-containing fuels.

Water-Gas Shift Catalysis: We are developing water-gas shift catalysts that do not exhibit the loss in performance observed with commercial iron-chromium and copper-zinc oxide shift catalysts when used in fuel cell systems due to the rapid startups, frequent shutdown/startup cycles, and frequent and rapid power variations experienced during normal operation. Our new shift catalysts are based on platinum (Pt) dispersed on a reducible cerium oxide substrate. These catalysts are more stable than the commercial catalysts, but their cost is a major concern. We are attempting to reduce the costs of these catalysts by increasing their shift activity without increasing the platinum loading.

Our kinetic studies, as well as studies by other research groups, suggest that the shift activity of Pt-ceria catalysts can be improved by increasing the rate of dissociation of water, which is the rate-controlling elementary reaction step in the catalyzed water-gas shift reaction. For this purpose, we are investigating the addition of rhenium (Re) in the Pt-ceria catalyst. As shown in Figure 2, the addition of Re to Pt increases the rate of CO conversion per gram of catalyst by

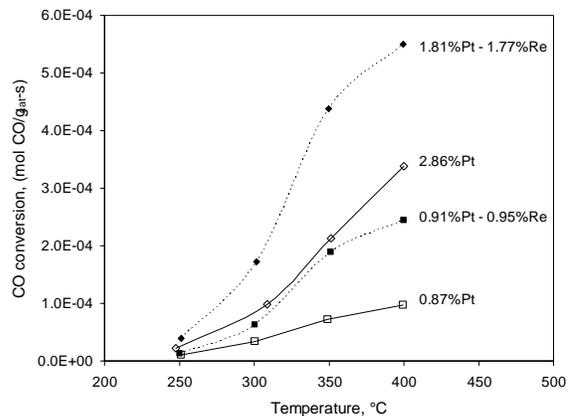


Fig. 2. The Pt-Re catalyst is 2.5 times as active as the Pt alone catalyst for the water-gas shift reaction at temperatures of 300°C or higher.

more than a factor of two with equivalent Pt loading at temperatures of 300°C or higher. Our current effort is focused on evaluating the long-term stability of these binary catalysts, for which we are conducting characterization studies to determine the nature of the interaction between Pt and Re.

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

Research Participants

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Fuel Cell Systems Analysis

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

While different developers are addressing improvements in individual components and subsystems in automotive fuel cell propulsion systems (e.g., cells, stacks, fuel processors, 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, performance, efficiency, and fuel economy.

2003 Research Highlights

We have analyzed conceptual pressurized direct hydrogen fuel cell systems (FCS) for a hybrid mid-size SUV. In such systems, the FCS alone must be able to meet the vehicle's power demand under all sustained driving conditions, such as 100 mph on a level road, or 55 mph on a 6.5% grade. In addition, the vehicle must be able to accelerate from zero to 60 mph in 10 s, using battery assist if needed.

We analyzed three systems with different levels of hybridization (i.e., fuel cell power versus battery power) to meet these requirements. Table 1 lists the significant attributes of the three systems. The sustained top speed necessitates a minimum fuel cell power of 80 kW. FCS-1 is a 100-kW system with only a compressor, no expander; FCS-2 is 100-kW system with a compressor/expander/motor module (CEM); and FCS-3 is a 160-kW system with a CEM. Without the expander to recover the energy in the pressurized exhaust, the compressor in FCS-1 needs a rather large 27-kW motor. With the expander in FCS-2, the CEM motor power is only one-third that of the motor in FCS-1. Both FCS-1 and FCS-2 require battery assist to meet the 0-60-mph acceleration requirement. FCS-3 is

Table 1. Vehicle/fuel cell system parameters for the hybrid mid-size SUV

Mid-Size All Wheel Drive SUV			
Gross Vehicle Wt, kg	2400		
Frontal Area, m ²	2.46		
Rolling Friction Coeff.	0.0084		
Drag Coefficient	0.41		
Traction Power, kWe:			
0–60 mph in 10 s	160		
100 mph, level	80		
55 mph, 6.5% grade	70		
Fuel Cell Systems			
	FCS-1	FCS-2	FCS-3
Rated Power, kWe	100	100	160
Comp/Exp/Motor	w/o Exp	w/ Exp	w/ Exp
CEM Power, kWe	27.3	9.5	15.1
System Efficiency, %,			
@ Rated Power	47	54	54
@ 80 kWe	52	56	59
@ 20 kWe	62	63	64

large enough to power the SUV without a battery assist. At the rated power as well as at part load, FCS-3 has the highest efficiency while FCS-1 offers the lowest efficiency.

Stack Performance: Figure 1 shows the performance of the stack in FCS-2 at cold (startup) and warm conditions. At 80°C, the design operating temperature, the stack generates ~105 kWe and 0.7 V/cell at the rated power point. At a cold start from 20°C, the power produced is 20% lower, along with a lower cell voltage of 0.55 V. During startup from –20°C, the maximum stack power is reduced by 35% and the cell voltage is further lowered to 0.45 V. The lower cell voltages lead to proportionately lower fuel cell efficiencies.

Heat Rejection System: Our analyses show that the size of the heat rejection system for the SUV is determined by the performance requirement on a 6.5% grade, rather than the top sustained speed; a radiator sized for the heat duty at

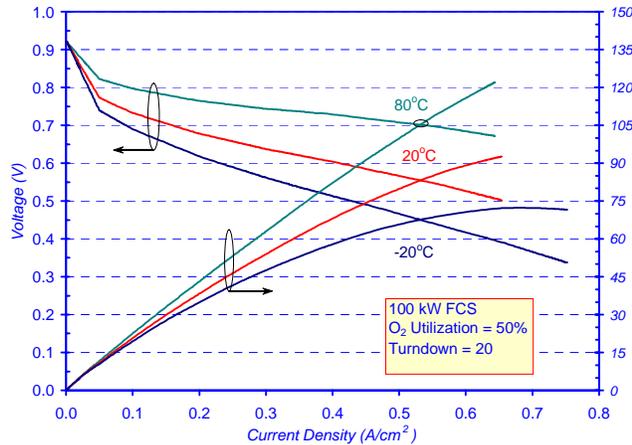


Fig. 1. Fuel cell stack performance as a function of temperature for the 100-kWe stack in FCS-2. The available power is reduced by 20–35% during cold starts.

55 mph on a 6.5% grade can meet the systems’ heat rejection requirements at all speeds. Further, in the case of the FCS-3, no heat rejection is needed at speeds of less than 60 mph, indicating that the fuel cell stack cannot be maintained at 80°C at low speeds. The trend for the radiator heat duty is similar for FCS-2, but the maximum heat load is nearly twice as large, even though the fuel cell system is almost 40% smaller. Unlike the radiator, however, the condenser for the 100-kW system is smaller than the one for the 160-kW system.

CEM Idle Speed: We also examined the air management system for issues of idle speed and maximum turndown. The CEM plays an important role in determining the transient response, cold start-up, and part-load performance of a pressurized FC system. For a high-speed, matched, turbo compressor/expander module, we found that with an expander the maximum turndown can be as high as 20; without an expander, however, the maximum allowable turndown may be no greater than about 5.

Fuel Cell System Efficiency: The system efficiency at part load and the dynamic fluctuations in efficiency during a drive cycle depend on the maximum CEM turndown and the presence or absence of an expander in the system. Figure 2 shows the effect of CEM

turndown on the efficiency of FCS-2 when the vehicle is driven on the Federal Urban Driving Schedule (FUDS). Differences in efficiency are evident at low loads for maximum CEM turndowns of 5 and 20, respectively. Both give efficiencies in excess of 60% on FUDS, but with a turndown of 20, the peak efficiency can exceed 70% at low loads. The scatter in dynamic efficiency is largely due to acceleration demands from idling speeds. Figure 2 also shows the contribution of the expander to system efficiency. Differences in efficiency at high loads are due to the significant power generated by the expander; at low loads, the significant differences in efficiency are due to the higher turndown available with an expander in the system.

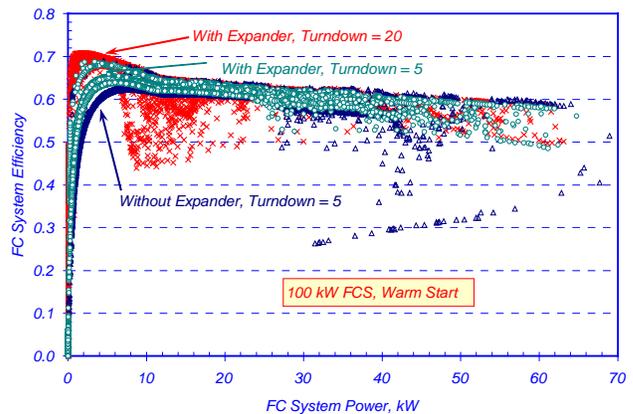


Fig. 2. The pressurized direct hydrogen fuel cell systems offer efficiencies of $\geq 60\%$ at part loads. The dynamic efficiencies can be significantly lower, particularly with systems without an expander.

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

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Hydrogen and Fuel Cell Materials

Materials development to enable commercialization

Fuel cell power systems have been demonstrated for applications as varied as milliwatt-level cell phones and kilowatt-level vehicle traction. Now that it has been demonstrated that fuel cell systems can deliver the necessary power with improved fuel efficiency, the technology development focus is on lowering cost, improving durability, and reducing system size and weight. Materials advances are needed in many system components to achieve these goals. Research in the Chemical Engineering Division aims to address materials issues for polymer electrolyte and solid oxide fuel cell systems to enable their widespread commercialization.

The state-of-the-art electrolyte for the polymer electrolyte fuel cell, being developed for vehicle traction and residential power, requires humidification to conduct protons and thus its operating temperature is limited to $<100^{\circ}\text{C}$ (typically 80°C). This requirement adds complexity, size, weight, and cost to the fuel cell power system. Argonne's approach to developing membrane electrolytes with high proton conductivity at low relative humidity and temperatures above 100°C is to utilize sulfonated polyaryl ether dendrimers (highly branched macromolecules). The polyaryl ether dendrimers were chosen as the membrane building blocks because they have a high density of proton-conducting functional groups, are thermally stable, and are expected to be stable in the fuel cell environment.

Solid oxide fuel cells (SOFCs) are attractive power sources for vehicular auxiliary power applications because they exhibit high power densities and efficiencies, have simplified fuel reforming requirements, and are fuel-flexible. These SOFC-based power systems are viewed as being ideal for auxiliary power units (APUs) for light- and heavy-duty vehicles. The SOFCs presently being developed use the anode or electrolyte as the cell support. We have

developed an SOFC design concept, TuffCell, that uses a metallic bipolar plate as the cell and stack support. The TuffCell offers an inherently more rugged design than the anode- or electrolyte-supported designs, and the potential for much lower manufacturing costs.

2003 Research Highlights

Polymer Electrolyte Development: The high density of ionic groups on the dendrimer electrolyte building blocks renders them soluble in water, the product of the fuel cell reaction. Our approach to forming water-insoluble membranes is to cross-link the dendrimers or attach them to insoluble polymer backbones. Our efforts this year have been focused on synthesizing significant quantities of the polyaryl ether dendrimers up to generation four (four levels of branching), shown in Figure 1, and attaching them to water-insoluble polymer backbones, such as polyepichlorohydrin. Thermal gravimetric analysis has shown that membranes formed by attaching the generation two dendrimer to polyepichlorohydrin are thermally stable up to 240°C . Initial measurement of the proton conductivity of this membrane showed a conductivity of 0.1 S/cm at

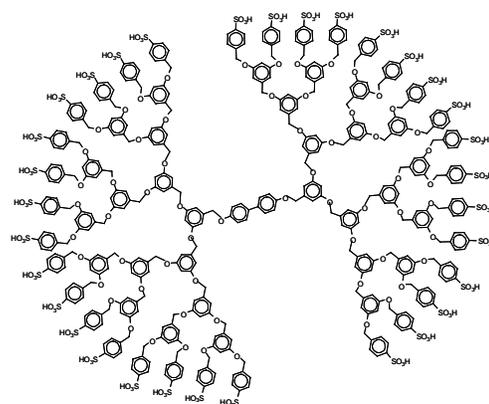


Fig. 1. A polyaryl ether dendrimer (generation 4 shown here) is the building block of a new polymer membrane electrolyte for fuel cells.

76°C and 6% relative humidity, a conductivity comparable to that of the currently used commercial polymer electrolyte under 100% relative humidity conditions. Measurements at higher temperature are underway.

The focus of future work will be on identifying and synthesizing suitable cross-linking molecules. In addition we will investigate the effects of dendrimer size, degree of cross-linking and length of the cross-linking molecules on membrane characteristics, including ionic conductivity, membrane morphology and thermal stability. The ultimate goal of this project is to develop a polymer with the required high proton conductivity (>0.1 S/cm) at temperatures up to 150°C and low humidity conditions and to demonstrate this polymer in an operating fuel cell.

Metallic Bipolar Plate-Supported Solid Oxide Fuel Cell (TuffCell): During 2003, we built and tested several cells of the TuffCell design (Fig. 2). TuffCell's superior mechanical properties were proven in impact tests and in four-point bending tests that showed these cells to have failure strengths four times higher than those of commercial anode-supported cells. The maximum power density achieved with single cells operating on hydrogen/air at 800°C was increased this year from 30 mW/cm² to more than 250 mW/cm² (Fig. 3) through improvements in the cathode material and the anode structure. This electrochemical performance was not degraded by several temperature cycles between room temperature and 800°C at 10°C/min.

In addition to improving the design and materials to increase power density, future work will focus on increasing the individual cell size, building short stacks of cells, testing these stacks using hydrogen and simulated reformat, and determining start-up time, ability to cycle the

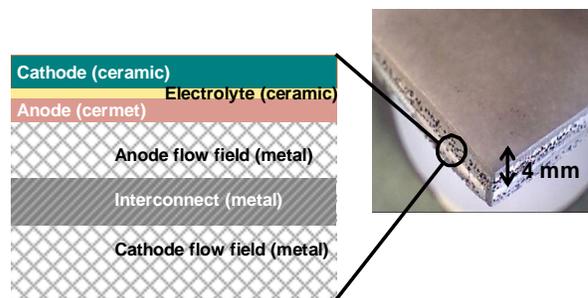


Fig. 2. The TuffCell's metallic bipolar plate serves as the support for the ceramic cell components, making it mechanically and thermally robust.

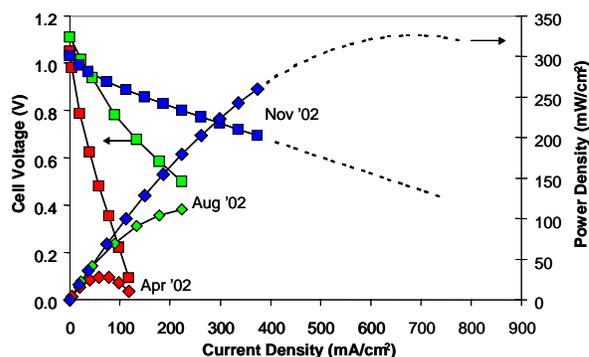


Fig. 3. The maximum power density achieved with single TuffCells has been increased to >250 mW/cm² through improvements in the cathode material and the anode structure (800°C, hydrogen/air).

temperature, and cell durability. The ultimate goal of this research is to develop rugged, high-power-density, low-cost stack units made by a commercially viable manufacturing process.

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

Research Participants

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Solid Oxide Fuel Cells

Finding new materials and catalysts to improve fuel cell performance

The Solid State Energy Conversion Alliance (SECA) is a U.S. Department of Energy (DOE) program aimed at developing fuel cell power modules of 3-10 kW electrical capacity based on solid oxide fuel cells. The Chemical Engineering Division is contributing to this program as a Core Technology participant, addressing three issues of generic nature.

2003 Research Highlights

The Division is engaged in addressing three distinct issues in solid oxide fuel cell development: (1) improving the corrosion resistance of metallic bipolar plates, (2) investigating poisoning of cathodes by chromium, and (3) exploring new sulfur-tolerant catalysts for diesel fuel reforming. These three tasks are part of the Core Technology program of the SECA initiative, whose objective is to develop modular SOFC systems of 5 kW capacity.

To improve the corrosion resistance of steels in the SOFC environment, we are pursuing an innovative technique of functionally grading the composition of the steels. Using a tape-casting technique, we can vary the composition from one side of a plate to the other and enrich components that have improved corrosion resistance on either the air or the fuel side. Figure 1 shows a cross section of a SS430 steel with a substantial amount of lanthanum chromite in the surface. The latter offers protection against oxidation by hot air and steam, as is encountered on the air side of the fuel cell. The lanthanum chromite can be enriched in the surface by tape-casting the powder together with stainless steel powder. Work is continuing to make the lanthanum chromite layer dense.

Poisoning of cathodes by chromium has been noticed by several groups developing planar solid oxide fuel cells using ferritic stainless steels as interconnect materials. When testing

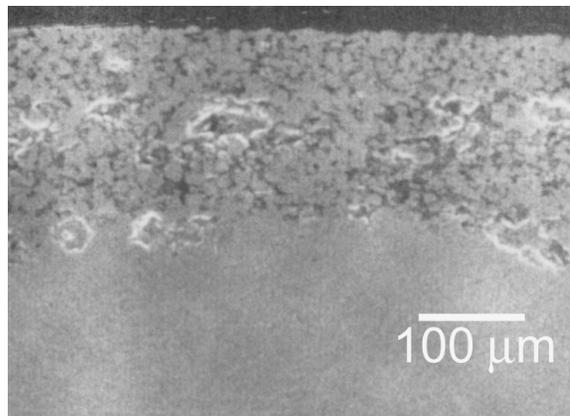


Fig 1. Stainless steel enriched with lanthanum chromite at the surface.

such cells, the cell potential declines within a few days by more than 20% and chromium deposits are found in the cathodes. Argonne was asked by DOE to investigate the phenomenon.

We operated several cells with three different steels and two different cathode materials and confirmed the observations of others. Figure 2 shows the chromium content in a cathode that had been operated for 250 hours at 700°C. Between 1 and 3.5 % chromium is found in the cathode, with higher concentrations near the electrolyte where the electrochemical reactions occur. Clearly, chromium is lost from the interconnect material and is being transported through the cathode to the electrochemically active area, where it interferes with the normal hydrogen oxidation reaction. We are now working on methods to prevent this migration from occurring.

Small solid oxide fuel cell systems of about 5 kW capacity are potentially applicable as auxiliary power units for heavy-duty vehicles such as tractor-trailer trucks. The diesel fuel used in these vehicles needs to be converted into a hydrogen-rich gas before it can be used in the fuel cell. Catalysts for converting diesel fuel deactivate in less than 100 hours due to the high

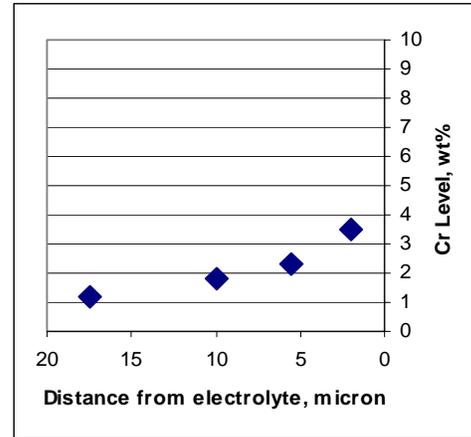
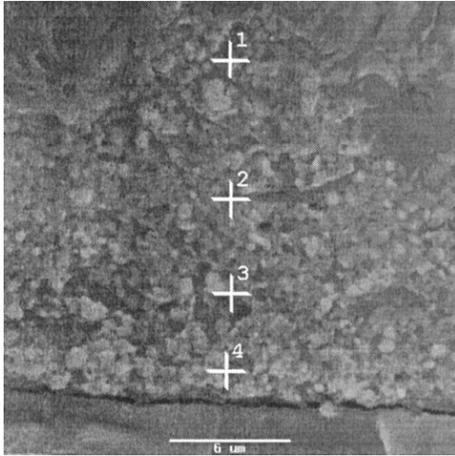


Fig. 2. SEM of LSF Cathode having 430 SS Interconnect from SOFC (#14) at 700°C.

temperature and sulfur content of the fuel. The Division is exploring a new generation of catalysts that may overcome these problems.

In the past 12 months, we were able to show that perovskites such as LaCrO_3 and LaAlO_3 when doped on the B-site with certain elements perform very well.

Figures 3 and 4 show the hydrogen yield per mole of fuel that is obtained with the aluminite and chromite catalysts. The catalysts perform similarly and are as active as previously known noble-metal catalysts.

The observation of good reforming activity from the B-site doped aluminite is intriguing and unexpected. It is known that undoped alumina

shows little POX or SR catalytic activity in hydrocarbon reforming, contrary to the case of chromite. The oxidation state of Al^{+3} is also too stable under either reducing or oxidizing conditions to participate in any redox reaction. The catalytic activity is therefore related to the B-site dopant.

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

Research Participants

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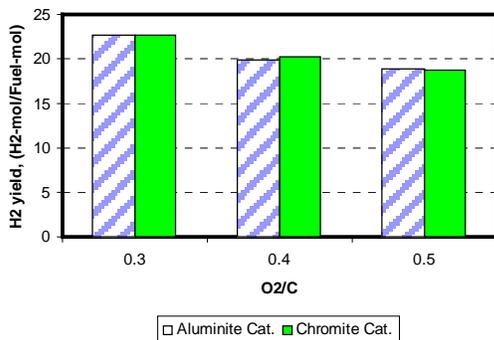


Fig. 3. Hydrogen yield during ATR reforming of dodecane at different O_2/C ratio over aluminite and benchmark chromite ATR catalysts.

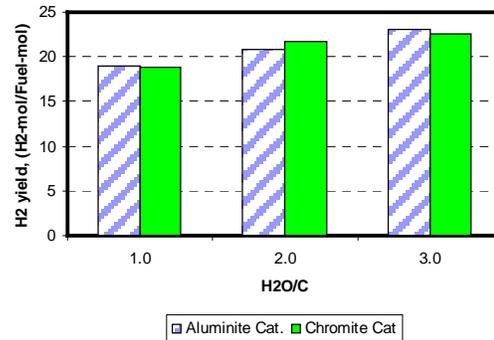


Fig. 4. Hydrogen yield during ATR reforming of dodecane at different $\text{H}_2\text{O}/\text{C}$ ratio over aluminite and benchmark chromite ATR catalysts.

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 meet that need, 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). We have also evaluated a partial fuel cell system consisting of the complete system minus the fuel cell stack.

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

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Fuel Cell Technical Analysis

Supporting U.S. Department of Energy research and development

Argonne's Chemical Engineering Division (the Division) provides technical and programmatic analysis for the U.S. Department of Energy, Hydrogen, Fuel Cells, and Infrastructure Technologies, and FreedomCAR and Vehicle Technologies Programs. 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. Representative activities carried out in 2003 are described below.

2003 Highlights

Non-platinum electrocatalyst workshop: Platinum group metal (PGM) electrocatalysts are currently used on the polymer electrolyte membrane (PEM) fuel cell anode and cathode to facilitate electrochemical reactions (hydrogen oxidation and oxygen reduction, respectively). The use of these catalysts contributes significantly to the overall cost of the fuel cell stack as well as to the overall system cost. There is also some concern about future production capability, reserves, and cost of these PGM catalysts. Hence, there is national interest in the development and use of non-PGM catalysts in the PEM fuel cell, particularly on the cathode side. The Division helped to organize a Non-Platinum Electrocatalyst Workshop in March 2003 (see http://www.eere.energy.gov/hydrogenandfuelcells/electrocatalysts_workshop.html) to discuss approaches to developing electrocatalysts that do not contain PGMs. Sessions on inorganic and organic approaches were held. Participants included representatives of industry, academia, and DOE national laboratories.

Fuel cells for stationary and automotive applications: Division personnel assisted in drafting the Statement of Work in a DOE

solicitation "Research and Development of Fuel Cells for Stationary and Automotive Applications." The solicitation covered a wide range of topics, including the development and demonstration of stationary fuel cells for building and back-up/peak shaving applications, the development of natural gas fuel processing systems, the development of improved stack and system components, the development of platinum recycling technology and non-precious metal catalysts, and the economic analysis of PEM fuel cell systems. We participated in the proposal review process and advised DOE during the proposal selection process. The solicitation resulted in the selection of 13 firms and educational institutions in 12 states to receive \$75 million in cost-shared awards to fund new research in advanced fuel cell technology for vehicles, buildings and other applications

Portable and off-road fuel cell power applications: Division staff drafted a Statement of Work for the DOE solicitation "Research, Development, and Integration of Energy-Efficient Technologies in Portable Power, Auxiliary Power Units, and Offroad Fuel Cell Applications." The solicitation addressed 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. The purpose of the research is 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. The solicitation was issued in 2003, and the Technical Analysis Group reviewed proposals and served as technical support for the Source Evaluation Board. Announcement of awards is expected in 2004.

On-board fuel processing decision: The transition to a hydrogen economy will take decades. During this transition, technologies that use the current liquid and gaseous fueling infrastructure will be needed to provide the hydrogen to power fuel cell vehicles. Many options are being considered, such as fuel reforming on-site at fueling stations or fuel reforming on-board the vehicle. Truly renewable sources of hydrogen are the long-term goal. The DOE has funded R&D of on-board fuel-flexible reforming technologies for the past 10 years. Based on the current state of technology development, it is uncertain that on-board fuel processing technologies will meet the technical criteria (start-up/transient time, energy consumption, durability, and cost) by 2010 to support the hydrogen transition phase. Division representatives are actively engaged in DOE's analysis of the prospects for successful attainment of the goals and the decision to continue R&D in this area.

Compressor/expander/motors: DOE continues to evaluate compressor/expander/motor and motor controller (CEMM) devices for fuel cells. Division experts are actively engaged in definition of key operating parameters and quantification of performance goals as well as technical management of the following programs. Development is underway at UTC Fuel Cells, Honeywell Engines and Systems, and Mechanology, Inc. UTC's blowers (for air

delivery to the fuel cell as well as to the fuel reformer) for a 50- to 75-kW_e fuel cell have been fabricated and will be tested by Argonne National Laboratory (at the compressor test stand that is located at Mechanology, Inc., in Attleboro, Massachusetts). Mechanology's test rig is one of the few in the nation that has the capability to independently run such devices. Mechanology is allowing Argonne no-cost private access, following familiarization with the test stand, to conduct the acceptance tests for DOE.

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.

Participants

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Process Chemistry and Engineering

The Chemical Engineering Division (the 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) methods of separating wastes for further treatment to reduce overall toxicity, fissile content and volume, and (2) the behavior of waste materials following their disposal in the proposed Yucca Mountain repository

Waste Separation

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

Separation technologies for safer long-term disposal of spent nuclear fuel – UREX+ process demonstration: Research under the DOE's AFCI program is developing safer alternatives to the long-term disposal of spent nuclear fuel to improve the performance of the geological repository. Current strategy focuses on spent fuel separation into five streams: (1) a uranium product stream that will be solidified and disposed of as low-level waste, (2) a technetium product that will be transmuted, (3) an electrical power generator TRU product stream, consisting of a Pu/Np product that will be converted to mixed oxide fuel and Am/Cm product that will be transmuted by fissioning, (4) a cesium and strontium product for interim decay storage, and (5) a long-lived fission product that will be incorporated in superior waste forms for disposal in a geological repository. The UREX+ process consists of five solvent extraction processes. The entire process was demonstrated in 2003 with a hot simulant

and actual dissolved spent fuel. Excluding the effects of process upsets, product specifications were met for disposal of uranium as non-transuranic low-level waste, technetium fissile content, Pu/Np mixed oxide fuel fabrication concentration requirements, and interim storage requirements for Cs/Sr product.

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. 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, reducing proliferation concerns. The substitution of LEU in targets requires approximately five times more total uranium, requiring modifications to the target design and recovery/purification steps necessary. In 2003, we demonstrated processing steps at the laboratory scale to improve the efficiency of the converted LEU process with Argentine Comisión Nacional de Energía Atómica (CNEA). A full scale demonstration is planned in Argentina during 2004. Also we developed two alternatives for the treatment of uranium-rich acid waste for MDS Nordion in Canada and ANSTO in Australia by direct calcination and oxalate precipitation. Direct calcination generates primarily UO_3 and NO_x , while oxalate precipitation generates primarily UO_2 and CO_2 products.

Research and development support for SRS Salt Processing Project: Nearly 34 million gallons of radioactive high-level waste (HLW) are currently stored in tanks at the Savannah River Site in South Carolina. Because of the high cost associated with disposal of the HLW, it is desirable to reduce its volume. Division researchers are developing a process to remove

Sr and TRU from tank waste using *in-situ*-formed mixed iron oxides (IS-MIO) that could replace the current baseline process, which uses monosodium titanate (MST). This year's studies demonstrated that the iron loading can be reduced with no penalty to the process and that the solids formed could be filtered by the current benchmark process.

Waste Form Behavior

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

Spent Fuel from Commercial Reactors and DHLW Glass for the Yucca Mountain Project:

We have been selected to develop models to calculate the degradation and radionuclide release rates from the commercial spent fuel and DHLW glass for performance assessment. To support the modeling effort, we have conducted tests under a range of environmental conditions, including repository-relevant unsaturated conditions. Tests conducted in humid air have recently shown that deliquescent salts in the waste can have important effects. The fission product inventory of deliquescent fission product salts (e.g., CsI) in the fuel/cladding gap region may promote condensation of water and cause aggressive conditions that break down the passive film and promote active corrosion of the fuel and cladding. Experimental work has identified waste form reactions and estimated their rates for long disposal times, and demonstrated the role of alteration products in sequestering radionuclides. We have also shown how x-ray absorption spectroscopy can be used to characterize the crystal chemistry of trace elements in spent fuel and its alteration products.

EBR-II Waste Forms: Spent sodium-bonded fuel must be treated prior to disposal in the waste repository. Two waste forms will be used to immobilize wastes from electro-metallurgically 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.

Spinoff Research: Human-Detoxification System

We are developing a human-detoxification system based on biocompatible and injectable nanospheres as a novel portable method of protecting people from acute exposures to biological, chemical or radiological toxins. Specific toxins or pathogens can be removed from the blood circulation by functionalized magnetic nanoparticles. These particles are then removed from the body using a magnetic filtration system. The focus of the initial investigation is on (1) nanoparticle development, (2) filtration system design and (3) testing of a prototype system in animal models. The importance of encapsulated oils in the microspheres as a way to increase magnetic nanoparticle loading and avoid clustering has been identified and specialized polymers have been synthesized that allow direct binding to the receptors. A prototype magnetic separator to study separation of magnetic nanospheres in blood was constructed and *in vivo* studies of the pharmacokinetics of the system were initiated.

For More Information

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UREX+ Process Demonstration

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

The safe and economical disposal of spent fuel from commercial nuclear reactors will help to ensure a stable energy supply for the future. As currently envisioned, this spent fuel will be placed directly into a geologic repository. However, if key radionuclides present in the spent fuel can be sufficiently separated from the remaining components, the volume, toxicity, and fissile content of spent fuel now requiring repository disposal can be reduced. Uranium, the major component by volume can potentially be disposed as low-level waste. Long-lived transuranic elements can be transmuted in nuclear reactors, while short-lived but highly radioactive elements can be isolated and allowed to decay prior to permanent disposal. The end result would be a safer, simpler geologic repository and would avoid the need for a second repository. New processes can also reduce the risk of proliferation associated with components of spent fuel.

The U.S. Department of Energy's Advanced Fuel Cycle Initiative (AFCI) Program is trying to achieve these goals by separating dissolved spent commercial fuel into five streams.

- A uranium product stream that will be solidified and disposed of as low-level waste,
- A technetium product that will be transmuted,
- An electrical power generator TRU product stream, consisting of a Pu/Np product that will be converted to mixed oxide fuel and Am/Cm product that will be transmuted by fissioning,
- A cesium and strontium product for interim decay storage, and
- A long-lived fission product that will be incorporated in superior waste forms for disposal in a geological repository.

The Chemical Engineering Division (the Division) has developed a solvent extraction process, UREX+, that will achieve all of the separations required by the AFCI program. The process builds on the uranium extraction (UREX) process, which recovers uranium and technetium, and was first demonstrated at Argonne National Laboratory in 2001. Four additional solvent extraction steps were added to recover the three remaining key radionuclides streams. In 2003, the research focus was on designing all five of the UREX+ process flowsheets, designing and fabricating the equipment required for the process, and demonstrating the entire process with actual spent nuclear fuel.

2003 Research Highlights

The UREX+ process consists of five solvent extraction processes as shown in Figure 1. The entire process was demonstrated in 2003 with a hot simulant and actual dissolved spent fuel. The UREX process separates uranium (U) and technetium (Tc) from the dissolved spent fuel. Cesium (Cs) and strontium (Sr) are separated in the chlorinated cobalt dicarbollide / polyethylene glycol (CCD/PEG) process. NPEX separates Pu and Np, while TRUEX and Cyanex separate the minor actinides from the lanthanides and the remaining fuel components. The UREX, NPEX, TRUEX, and Cyanex process flowsheets were developed with a computer model, the Argonne Model for Universal Solvent Extraction, or AMUSE. The CCD/PEG flowsheet was developed by scientists at the Idaho National Engineering and Environmental Laboratory.

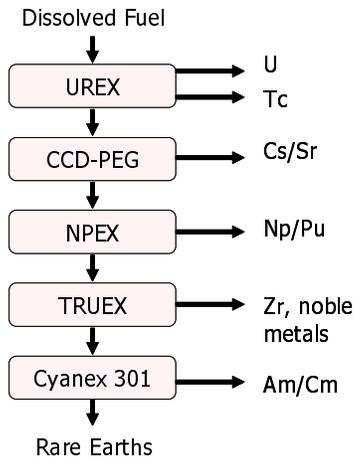


Fig. 1. UREX+ process for separation of uranium, technetium, Cs/Sr, Pu/Np, and Am/Cm from dissolved spent nuclear fuel.

The complete UREX+ process was demonstrated in a centrifugal contactor, a very high-efficiency solvent extraction device originally developed at Argonne in the early 1970s. Because it was necessary to run most of the process segments in a shielded cell facility, a completely new centrifugal contactor was fabricated. The unit was designed so that all components could be accessed from the front of the unit with manipulators (robotic arms) as access was not possible from other directions due to space restrictions. Additional refinements to the design were made to improve efficiency and hydraulic performance. Because of differences in the relative densities of the organic and aqueous phases in the various processes, a key design requirement was that the unit allow the direction of flow of the aqueous and organic streams to be reversed. A photo of the contactor is shown in Figure 2.

The process was run successfully twice: first with a simulated dissolved spent fuel, and then with an actual spent fuel that had been dissolved in nitric acid. The spent fuel was obtained as a chopped spent fuel rod and dissolved in nitric acid at an elevated temperature and pressure in a sealed vessel. The dissolved fuel was filtered and diluted before it was used as the feed to the UREX process. Dissolution was successful; chemical analysis of the filtered solids indicated that essentially all of fuel had been dissolved.



Fig. 2. Centrifugal contactor designed for the UREX+ demonstration.

The simulant composition was based on the expected composition of the dissolved fuel.

Results of the UREX+ demonstration with simulated dissolved spent fuel feed were used to confirm the results predicted by AMUSE. Refinements to several process flowsheets were done. These refinements, small changes in feed flow rates and relative feed locations, were implemented in the hot fuel test.

Results of the hot fuel test indicated that the refinements made to the process flowsheet following the simulant runs were successful. Excluding the effects of process upsets, product specifications were met for disposal of uranium as non-transuranic low-level waste, the technetium fissile content, the Pu/Np mixed oxide fuel fabrication concentration requirements, and the interim storage requirements for the Cs/Sr product.

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

Research Participants

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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 of ^{235}U , 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 the amount of total uranium used for HEU targets to produce a given amount of ^{99}Mo . Therefore, modifications to the target and to the ^{99}Mo recovery process are required. In addition, the larger amount of uranium will impact the waste handling processes.

2003 Research Highlights

Our work over the last year with Argentine Comisión Nacional de Energía Atómica (CNEA) in Argentina show that its production efficiency can be improved. The CNEA process has already successfully converted to LEU. Specific processing steps were demonstrated at the laboratory scale this year and will be demonstrated at full scale in Argentina during 2004. We have also addressed the treatment of uranium rich acid waste for MDS Nordion in Canada and ANSTO in Australia. Last year we proposed two alternative processes, direct calcination and oxalate precipitation. Direct calcination generates primarily UO_3 and NO_x , while oxalate precipitation generates primarily UO_2 and CO_2 products.

The Division is cooperating with CNEA to increase the efficiency of their process with LEU metal foil targets. We have proposed and

developed improvements in the CNEA process digestion and purification/recovery steps.

For the digester step, it was determined that a new digester design was needed. An appropriate vessel is manufactured by Berghof™ (Fig. 1). We have tested this digester during this past year and have shown it to be reliable and relatively easy to use. We conducted digestion tests with four low-burnup depleted uranium targets irradiated in the Intense Pulsed Neutron Source at Argonne National Laboratory.

The goal of these tests was to evaluate the effectiveness KMnO_4 as an oxidant during uranium metal dissolution. Three different processes were tested, each of which resulted in high (93-99%) Mo recoveries. The uranium metal in the targets was oxidized to U(VI); at the same time, KMnO_4 was reduced to insoluble MnO_2 . The formation of MnO_2 results in a larger amount of solid waste. The digestion generates a suspension containing uranium salts and MnO_2 . The solids settle to the bottom of the vessel, making their recovery difficult. To solve this problem, we are adding a stirrer to the digester. We expect that stirring will prevent the solids from settling out, and will make their removal easier. As an additional benefit, mixing during digestion might increase digestion efficiency and decrease process time. This work will be completed prior to the planned demonstration in spring 2004.

We are also cooperating with two ^{99}Mo producers [MDS Nordion (Canada) and the Australian Nuclear Science and Technology Organization] that dissolve UO_2 targets in nitric acid solutions. During the last year, the Division has developed improved processes for treating uranium-rich acidic liquid waste generated by these producers. When LEU targets are dissolved in nitric acid, the dissolver solution



Fig. 1. Digester manufactured by Berghof™ for use in the CNEA process.

contains 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. Therefore, the conversion to LEU target is expected to impact waste treatment and storage.

Two processes were examined last year for the treatment of uranium-rich acidic liquid waste—direct calcination and uranyl oxalate precipitation. The direct calcination process was shown to generate primarily UO_3 solid and NO_x gas. The oxalate precipitation process appears promising for the treatment of uranium-rich HNO_3 solutions. The primary products are UO_2 solid along with CO and CO_2 gas. The oxalate precipitation process provides a promising alternative to the direct calcinations process. The main advantage of the oxalate precipitation

process is that it does not generate the undesirable NO_x gas product; instead, it regenerates HNO_3 suitable for recycle.

The Division continues to partner with ^{99}Mo producers from, 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.

This research is funded by the U.S. Department of Energy, Office of Nuclear Nonproliferation.

Research Participants

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R&D Support for Savannah River Site 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 desirable 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.

Researchers in the Chemical Engineering Division are developing a process to remove Sr and TRU from tank waste using *in-situ*-formed mixed iron oxides (IS-MIO). In the IS-MIO process, a mixture of iron oxides and hydroxides is formed when a solution containing Fe(II) and Fe(III) ions is added to alkaline tank waste. The iron-bearing solids that are formed adsorb or occlude Sr and TRU elements present in the HLW. The solids are then recovered by filtration and incorporated into glass for eventual disposal in a geologic repository.

IS-MIO could replace the current baseline process, which uses monosodium titanate (MST). Our tests have shown that IS-MIO is superior to MST in removing both Sr and TRU elements from HLW. The pre-cursors for the IS-MIO process are also much less expensive and easier to fabricate than MST. We estimate that by using IS-MIO, SRS will be able to cut costs by reducing the processing time required to treat the waste and potentially reducing the plant footprint, with no detrimental effects on plant safety.

2003 Research Highlights

Decontamination Studies: The boundaries for this process demonstration were defined based on an operational envelope developed in collaboration with SRS. Decontamination factor (DF) values were measured for both IS-MIO and MST. In previous studies, IS-MIO DF values were found to be superior to MST for all isotopes studied. More recent work has focused on reducing the quantity of iron added to the tank waste. This work has demonstrated that DF values for Pu, Np, Am, and Sr achieved within 0.5 to 2 hours of solids formation was still significantly higher than the values required by SRS, even at reduced iron loadings. At short contact times, DFs were higher than those achieved with MST. Figure 1 is a comparison of DF values for Sr using IS-MIO and MST.

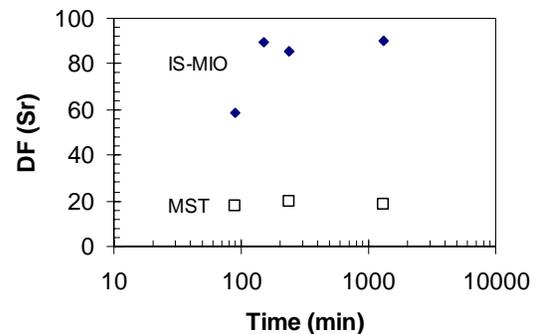


Fig. 1. IS-MIO performance is superior for Sr decontamination compared with MST.

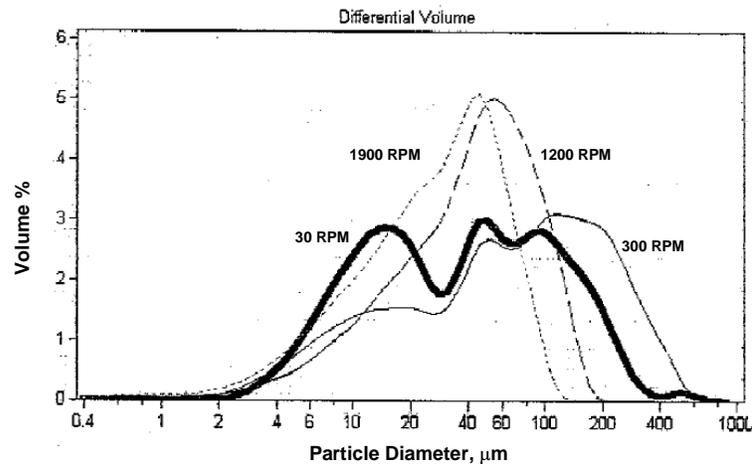
Mixing Intensity Studies: At SRS, the iron solutions will be added to a large stirred tank containing the HLW. The IS-MIO solids will then be passed through a cross-flow filter to separate the solids and treated waste. In 2004, SRS will conduct tests to determine how effectively IS-MIO solids can be filtered from HLW tank waste after treatment with the existing equipment developed for MST. In support of these studies, we examined the effect of mixing intensity and time on the particle size

distribution obtained for IS-MIO. Fe(II)/Fe(III) solution was added to stirred simulated HLW solution. Figure 2 shows the change in the particle size distribution as the stirring speed is changed. Results indicate that filtration is feasible with a cross-flow filter.

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Research Participants

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1 Hour of Mixing

Fig. 2. IS-MIO particle size distribution as a function of mixing speed.

Crystal Chemistry of Trace Elements in Spent Nuclear Fuel

Providing input to the Yucca Mountain repository license application

As part of our scientific support for the Yucca Mountain Repository Development Project we developed a model that is to be used to assess the long-term radionuclide release rate from commercial spent nuclear fuel in support of the repository license application. This model is based on the conservative assumption that radionuclides embedded in the fuel lattice will dissolve when the fuel's UO_2 matrix is oxidized and dissolved. However, as illustrated in Figure 1, our test results have indicated that a fraction of the inventory of important radionuclides (for example, technetium-99) may not dissolve when the fuel is oxidized and converted to U(VI) alteration phases. This is because a fraction of the technetium (Tc) is incorporated into corrosion-resistant noble metal alloy "epsilon" particles that do not readily corrode under repository-relevant test conditions. The Department of Energy is interested in evaluating the extent of the conservative bias in the current model. This requires characterizing the complex chemistry of trace fission products and transuranium actinides in the fuel matrix and in its alteration products.

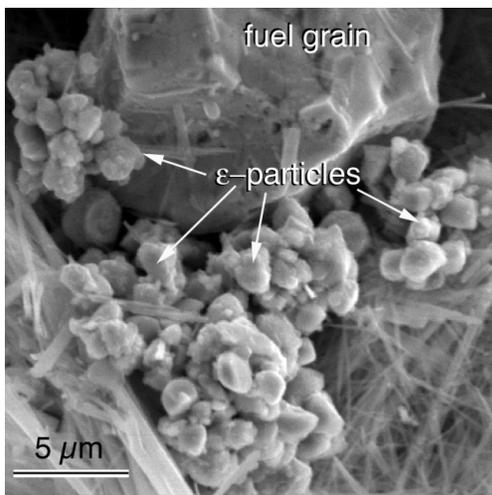


Fig. 1. Scanning electron micrograph of CSNF showing Mo- and Tc-rich epsilon (ϵ) particles concentrated on the surface of a corroded fuel grain.

2003 Research Highlights

Few techniques have proven more effective than x-ray absorption spectroscopy (XAS) for determining oxidation states and structural environments of elements in solids. Chemical Engineering Division researchers, using a novel "bent-Laue analyzer" detection scheme developed in collaboration with the Illinois Institute of Technology, have obtained detailed XAS information from trace elements in specimens of commercial spent nuclear fuel (CSNF). 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). The brightness of the APS facility in the high-energy x-ray regimes makes it ideal for investigating radionuclide systems, which have relatively high-energy absorption edges, and which must be carefully encapsulated for radiological safety. This approach, for the first time, has allowed direct observation of oxidation state, coordination environment, and site symmetry of fission product and actinide elements in CSNF. Figure 2 shows molybdenum (Mo) K-edge XAS from uncorroded CSNF. Details of the spectral edge and extended fine structure indicate a mixture of metallic and oxidized Mo in this specimen. In Figure 3, a line scan across a different specimen shows the amount of Tc and Mo relative to the uranium matrix in a corroded fragment of fuel. Note the similarity of the concentrated Mo and Tc to the collection of particles in Figure 1. These findings suggest that a substantial portion of the Tc may be in a form that is much more stable than originally modeled.

In addition to near-term applications that will allow a better understanding of radionuclide release from corroding waste in the Yucca Mountain Repository, this advance is expected

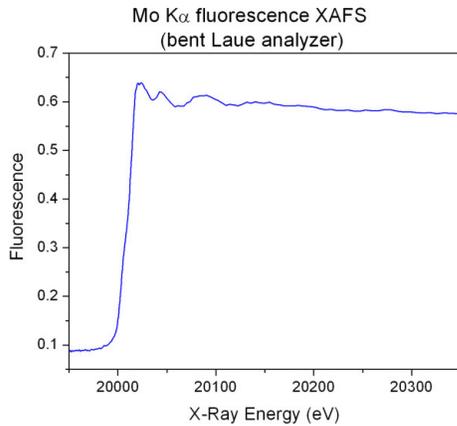


Fig. 2. Molybdenum K-edge XAS from CSNF using Bent-Laue analyzer detection at the Advanced Photon Source. The molybdenum is present in the fuel at only 0.3 wt%. It is the ability of the Bent-Laue analyzer to resolve these weak features in the presence of a strong background that makes the XAS analysis of trace elements in CSNF possible.

to find applications in understanding fission product behavior in advanced fuel cycles (e.g. fission product behavior in nuclear fuels operating at high temperatures).

This research is funded by the U.S. Department of Energy (DOE), Office of Civilian Radioactive Waste Management, Yucca Mountain Program. Use of the Advanced Photon Source was

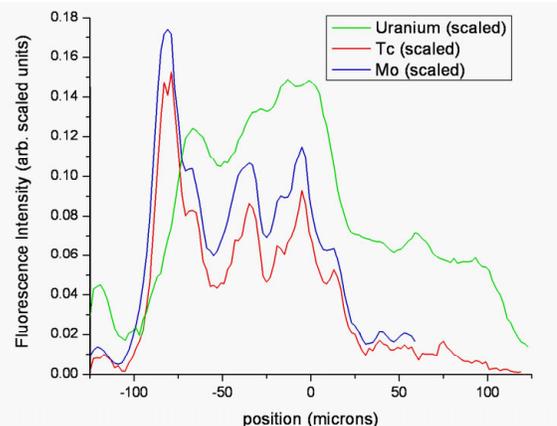


Fig. 3. X-ray line scans for uranium, technetium (Tc), and molybdenum (Mo), scaled to relative concentration in the CSNF. These show an anomalous enrichment of Mo and Tc at the surface of a uranium fuel fragment that had been corrosion-tested for more than 8 years.

supported by the DOE's Office of Energy Research, Basic Energy Sciences.

Research Participants

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EBR-II Waste Forms Qualification Testing

Meeting requirements for high-level waste storage

Spent sodium-bonded fuel from the Experimental Breeder Reactor II (EBR-II) must be treated prior to disposal in the high-level radioactive waste repository at Yucca Mountain. Two waste forms will be used to immobilize wastes from electrometallurgically treated fuels for disposal: a ceramic waste form (CWF) for radioactive salts and a metallic waste form (MWF) for contaminated cladding hulls. Laboratory tests are being conducted to support qualification of the CWF and MWF for disposal at Yucca Mountain. Our approach is to show that these waste forms meet the acceptance requirements specified for the standard borosilicate high-level waste (HLW) glass waste forms, and that their disposal will not adversely impact the performance of the disposal system.

The performance of the integrated barriers of the repository system is being modeled to show that regulatory requirements for containment of radionuclides will be met. Work is in progress to show that the model that will be used in repository performance assessment to calculate the release of radionuclides due to HLW glass degradation can also be used to represent the release of radionuclides from the CWF and MWF, thereby avoiding the need for separate source term models.

2003 Research Highlights

The CWF is a multiphase material composed of about 70% sodalite, 3% halite, and 2% various oxides encapsulated in 25% borosilicate binder glass. Degradation of the CWF is dominated by the dissolution of the sodalite and binder glass phases, which can be modeled using the same rate expression developed for borosilicate HLW glasses. This is because dissolution of the sodalite and binder glass occurs through the same mechanism as HLW glass, namely, surface dissolution through hydrolysis of Si-O bonds. The dissolution rate is a function of pH,

temperature, and the dissolved silica concentration. Dissolution rates and model parameter values measured for the separate sodalite and binder glass phases and for the composite CWF are well represented by the HLW glass degradation model.

The MWF is a composite of nearly equal amounts of a stainless steel phase and a Laves intermetallic phase. In contrast to the CWF, the degradation mechanism of the MWF is different from that of HLW glasses, and involves both oxidation and dissolution steps. Our approach to showing that the degradation rate calculated for HLW glasses can be used to represent the MWF is based on direct comparison of the rates measured for MWF with those calculated with the HLW glass degradation model.

The release rate of radionuclides from HLW glasses is calculated as the product of the specific degradation rate (mass glass per unit surface area, per unit time), the surface area, and the radionuclide inventory in the glass (curies per unit mass glass). The inventory that will be used for HLW glasses is a weighted average for all HLW waste from all waste form producers, and includes radionuclides to be immobilized in the CWF and MWF. Therefore, tests were conducted to determine if the product of the specific degradation rate and surface area for a HLW glass waste form was representative of the corresponding product for the MWF.

Tests were conducted to allow direct comparison of the release of radionuclides from a MWF with the release calculated for HLW glasses over the range of pH and temperature values that could occur in a breached waste package. A surrogate MWF containing about 10% uranium was used in the tests, and the degradation rate was calculated based on the release of uranium. Coupons were cut and polished to a 600-grit surface finish.

Tests were conducted in buffer solutions to provide a range of pH values. In addition, NaCl was added to the leachants to generate 1,000 ppm Cl^- to represent the dissolution of halite from CWF that will be co-disposed with the MWF. The MWF surface area-to-leachant volume ratio was about 200 m^{-1} in all tests. The solution was completely replaced and analyzed after test durations of 14, 28, and 70 days. The solutions were replaced to minimize feedback effects and track any effects of the formation of a passivating layer on the degradation rate. It also refreshed the air in the test vessel so that the availability of oxygen did not restrict the MWF degradation rate. The degradation rate was calculated from the cumulative release of uranium through 70 days and the geometric surface area of two MWF ingots, which is 0.76 m^2 based on nominal dimensions. One or two MWF may be disposed in a canister with CWF.

The HLW glass degradation model includes a rate coefficient variable that represents the combined uncertainty in the concentration of dissolved silica and the amount of water contacting the glass, and a surface exposure factor variable that represents the uncertainty in the extent of fracturing and the accessibility of water to glass within cracks. Values of the rate coefficient and surface exposure factor variables are selected from ranges between defined maximum and minimum values for use in performance assessment calculations. Different ranges in the rate coefficient are used for acidic and alkaline solutions.

The MWF degradation rates measured in tests at 50, 70, and 90°C and at various pH values are plotted in Figure 1 (discrete points) along with the rates calculated for HLW glass as a function of pH at 20, 50, 70, and 90°C (lines). The rates for both are in units of mass waste form degraded per day. The HLW glass rates were calculated using the maximum values of the rate coefficient and the minimum value of the surface exposure factor (which gives a surface area of 30 m^2). The rate using the minimum values of the rate coefficients are also shown for 20°C .

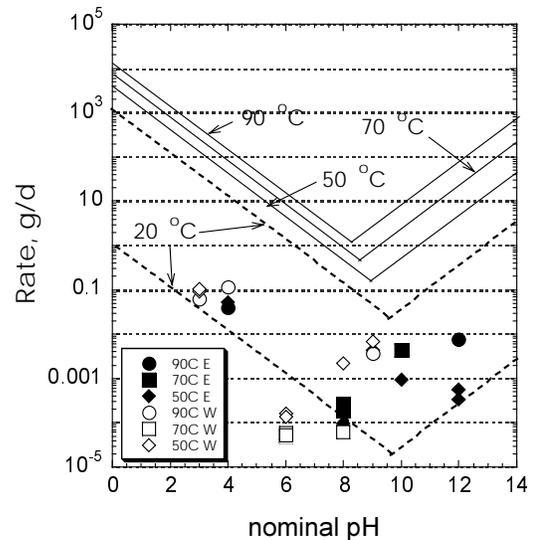


Fig. 1. Comparison of measured dissolution rates of MWF (discrete points) with calculated rates from HLW glass model (lines). Dotted lines show maximum and minimum rates at 20°C . The E and W suffixes in the legend distinguish tests conducted at Argonne-East and Argonne-West.

The MWF degradation rates at all temperatures are well represented by the range rates calculated for HLW glass at 20°C over the pH range. This simple approach does not explicitly account for the electrochemical and diffusion processes that probably control MWF degradation. Some of those effects are taken into account by the measured rate, while other effects are not. For example, galvanic coupling occurs between the stainless steel and intermetallic phases during the tests, but the passivation layers formed on the test coupons over the 70-day test period are too thin to provide a significant diffusion barrier. The measured rates are probably conservatively high due to the negligible effect of the passivating layer.

This research is funded by the U.S. Department of Energy, Office of Nuclear Energy Research, Science and Technology.

Research Participants

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Human-Detoxification System

Engineering injectable magnetic nanospheres for selective removal of blood-borne toxins

The Chemical Engineering Division is developing a human-detoxification system based on biocompatible and injectable nanospheres as a novel portable method of protecting people from acute exposures to biological, chemical or radiological toxins. These nanospheres, which contain magnetic nanophases, are made of the same plastics as sutures for internal use. The nanospheres chase down toxins circulating within the human bloodstream. Receptors attached to the nanospheres bind to these toxins and fix them to their surfaces. Blood is then withdrawn from the body to be filtered through a small hand-held device containing a magnetic filter that captures the polymer spheres with their bound toxins. Initially sponsored by the Defense Advanced Projects Agency, this work was established to aid military personnel in the field. In addition to its military and civilian application for treating exposure to biological, chemical or radiological weapons, the system also is expected by researchers to aid physicians in diagnosing and treating a range of diseases, including certain cancers and autoimmune diseases. Further, the small hand-held blood filtering device shows promise as a blood-cleansing treatment, similar to hemodialysis, for certain disorders such as autoimmune disease.

2003 Research Highlights

The program is divided into three main areas of research. The first is the design and synthesis of magnetically responsive nanospheres composed of biodegradable, FDA-approved polymers. The nanospheres (one hundred to several hundred nanometers in diameter) are biochemically inert. Magnetic nanophases (10- to 20-nm crystallites) imbedded in the polymer determine the spheres' magnetic responsiveness. Receptors attached to the surface of spheres are used to identify and bind to blood-borne toxins. Our research is focused on developing the procedure that

produces the best nanospheres – i.e., smooth spherical shape that are highly magnetic, with proper surface chemistry, a high density of receptors, and of uniform size.

The second area of research is designing a compact, magnetic filtration unit that would separate the magnetic nanospheres from the blood after tapping into a vein or artery. The unit would allow blood to enter passively or actively. Magnets inside the unit separate the nanospheres from the blood and return the clean blood to the body.

The third area of research is testing of prototype systems in the animal model. We have made significant progress in all three areas of research. We have identified the importance of encapsulated oils in the microspheres as a way to increase magnetic nanophase loading and avoid clustering (see Fig. 1). We have synthesized specialized polymers that will allow us to directly bind the receptors. We have been successful in removing more than 70% of model toxins from *in vitro* systems containing normal saline (0.9%) and whole rat blood. We have constructed a prototype magnetic separator to

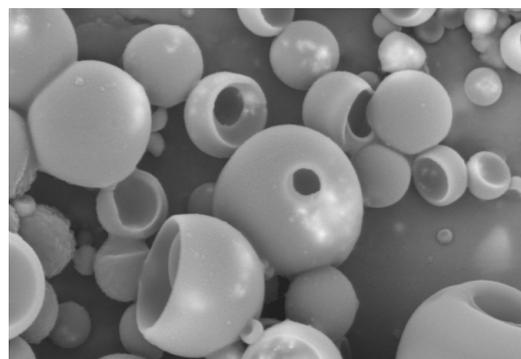


Fig. 1. Electron micrograph of magnetic nanophase cluster (bright spots) on the surface of poly(lactic acid) microspheres. Note the distinct clustering of the magnetic phases.

study separation of magnetic nanospheres in blood (Fig. 2). We are currently identifying the filter efficiency as a function of blood flow rate and magnetization and size of the nanospheres. Finally, we have begun *in vivo* studies to study the pharmacokinetics of the total system.

Potential benefits of this technology are:

- Early diagnosis of exposure to toxins
- Treatment of victims of acute toxin exposure
- Diagnosis of conventional disease (e.g., early metastatic cancer), and
- Treatment of conventional disease (e.g., auto-immune disease like lupus or rheumatoid arthritis).

This work is supported by the Defense Advanced Research Projects Agency (DARPA) Defense Science Office, The Department of Energy, the Cancer Research Foundation, and the Brain Research Foundation of The University of Chicago.

Research Participants

At Argonne, Michael Kaminski (co-lead), Carol Mertz, Martha Finck, and Vivian Sullivan (Chemical Engineering Division), Fred Stevens (Biosciences Division), Kenneth Kasza (Energy Technology Division), and Paul Fischer (Mathematics and Computer Science Division). At The University of Chicago, Axel Rosengart (co-lead), Sandra Guy, Peter Pytel, Lydia Johns, and Loch McDonald, Haitao Chen, Yumei Xie, and Patricia Caviness. For more information, contact Michael Kaminski, (630-252-4777, kaminski@cmt.anl.gov).

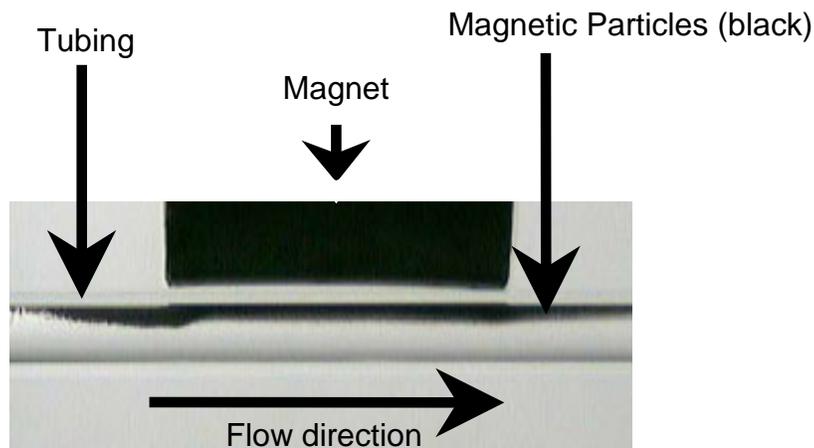


Fig. 2. Optical image of the capture of magnetic microspheres in flow by a permanent magnet. Magnetic nanospheres loaded with toxins are trapped by the magnetic force, allowing the clean blood to return to the body.

Nuclear Technology

The *National Energy Policy*, approved by the President in May 2001, recommends the continued development of an advanced nuclear fuel recycling technology commonly known as pyroprocessing. The Policy specifically states:

. . . United States should reexamine its policies to allow for research, development and deployment of fuel conditioning methods (such as pyroprocessing) that reduce nuclear waste streams and enhance proliferation resistance. In doing so, the United States will continue to discourage accumulation of separated plutonium, worldwide.

The United States should also consider technologies (in collaboration with international partners with highly developed fuel cycles and a record of close cooperation) to develop reprocessing and fuel treatment technologies that are cleaner, more efficient, less waste intensive, and more proliferation resistant.

The National Energy Policy Group went on to recommend the development of advanced nuclear systems to meet the United States' projected energy needs over the next several decades including the growing demand for electricity and production of alternative fuels such as hydrogen. The U.S. Department of Energy, through its integrated Generation IV (Gen IV) and Advanced Fuel Cycle Initiative (AFCI) programs will develop and demonstrate the next generation of advanced nuclear systems, to meet future needs for safe, economic, sustainable, proliferation-resistant and environmentally responsible fuel cycles and energy production.

The Chemical Engineering Division (the Division) leads pyrochemical process research, development and demonstration for the Gen IV and AFCI programs. Over the past year, the emphasis of our work has been on the treatment of spent light water reactor fuel to recover the

actinides for use in advanced reactor systems and to encapsulate fission products in durable waste forms for storage in a geologic repository. These same technologies are also applicable to the treatment of oxide-based fuels discharged from advanced nuclear power systems. Throughout the process development activities, our focus has centered on the development of commercially viable technologies—technologies that produce a high-quality product, are scalable and have promise of high throughput, integrate seamlessly with the other process steps and the facility, and are economic.

In this section of the Division's annual report, you will find a description of our main pyroprocess development activities over the past year. We continued advancement of the electrolytic reduction technology for the conversion of spent oxide fuels to the base metals by conducting kilogram-scale tests to evaluate cell design features and identify key design criteria needed for larger cells. Additionally, improvements in the manufacture and operation of inert anode materials led to the selection of a preferred material for use in the reduction cells.

Experimental results from the high-throughput anode system, which provided an experimental test-bed for evaluating product morphology as a function of cell operating parameters (Figs. 1 and 2), guided the development of a planar electrode electrorefiner (PEER) concept for the recovery of uranium from spent fuels. A prototype of PEER is being designed and fabricated so that we can assess the electrochemical performance of a planar electrode system and continuous or semi-continuous product recovery techniques for high-throughput operation. Although designed for the treatment of light water reactor fuel, the concept also could be used to increase the rate of treatment of blanket fuel from the Experimental Breeder Reactor II.

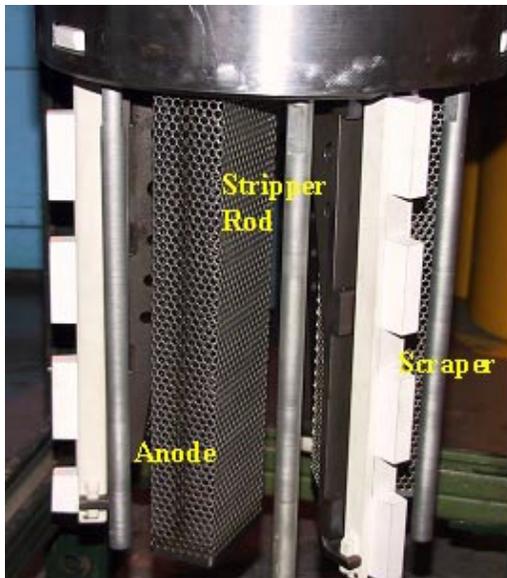


Fig. 1. High-throughput anode system.



Fig. 2. Dendritic uranium growth on stripper rods of high-throughput anode.

We also demonstrated actinide recovery from molten chloride salt via electrowinning. Initial tests with the electrolysis cell produced a mixed uranium and plutonium product at the cell cathode and chlorine gas at the anode. Chemical analysis of the cathode deposit from the first electrolysis experiment revealed that the uranium to plutonium ratio was 2:1 in the

metallic deposit. The ratio of uranium to plutonium in the molten salt phase at the start of the experiment was 0.75:1. Additional testing will be performed to determine the relationship between cell operating parameters and product morphology and quality as well as to identify optimum cell operating conditions, which are essential for scale-cell design.

In collaboration with the Korean Atomic Energy Research Institute, we began evaluating materials of construction for use in an electrolytic reduction system. The electrolytic reduction process occurs in a chemical environment that is too aggressive for most common structural materials. However, commercially available high-temperature alloy materials as well as new candidate systems based on functional barrier coatings may be suitable for the process; several of these materials are being evaluated in the corrosion test apparatus.

Finally, we participated in a study focused on commercialization of our pyroprocessing technology. A facility design concept was developed from equipment concepts that were generated from a detailed set of requirements for each unit operation. The processing facility was sized to treat approximately 100 metric tonnes of spent fuel per year with the major process equipment designed to treat 500 kg of heavy metal per day. An operations model of the facility will be used to identify necessary modifications to the fuel treatment flowsheet and further refine the facility design concept.

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Oxide Reduction to Convert Spent Oxide Fuel to Metal

Saving repository space and creating new fuel for advanced reactors

The U.S. Department of Energy (DOE) has more than 40,000 tons of spent oxide fuel from commercial reactors in its inventory that is scheduled for burial in a geologic repository. Spent oxide fuel contains valuable actinides that could be extracted and fabricated into fuel for use in advanced reactors. In addition, the extraction of actinides from the spent fuel will significantly reduce the radioactivity of the spent fuel and the volume of spent fuel to be buried in the repository. Thus, an effective process of actinide extraction from spent oxide fuel will result in the efficient use of a valuable resource—actinides—for generating electricity while minimizing the burden on the repository.

The Chemical Engineering Division is developing a molten-salt-based direct electrolytic reduction process to convert the spent oxide fuel to metal, which can then be further processed for extraction of uranium and transuranic elements by electrorefining and electrowinning operations, respectively. The overall process also produces durable, compact waste forms that are suitable for disposition in the repository. Our goals are two-fold: to radically reduce the long-term burden on the repository and any future repositories, and to salvage the actinides for reuse in reactors, thereby realizing the actinides' full energy potential.

2003 Research Highlights

Laboratory-scale experiments have shown that direct electrolytic reduction is a very promising approach to reducing actinide oxides to metals. Recent work in the development of this process has focused on (1) understanding the effects of scale-up on cell design, process electrochemistry, and cell operation, (2) understanding the behavior of fission products in the spent fuel, and (3) development of non-consumable oxygen electrodes for long-term sustained operations in molten LiCl at 650 °C.

High Capacity Reduction (HCR) Cells: In order to gain a strong fundamental insight into the scale-up effects on the electrochemistry of the process, the cell operation, and the cell design, we designed high-capacity reduction (HCR) cells with a 1-kg UO₂ capacity (this is about 50 times the capacity of the bench-scale cells that have been operated up to this point) and conducted three kg-scale UO₂ reduction runs during this year. Several design parameters were varied in each experiment to better understand the operation of the electrolytic reduction process as well as the requirements for a large-scale electrolytic reduction cell.

Typically the high-capacity reduction cells consisted of a rectangular fuel basket containing UO₂ particles (0.075 mm–2.8 mm in size) as the cathode, one or two anode assemblies, an off-gas system, and a provision for one or more reference electrodes. Each anode assembly consisted of a platinum electrode, a MgO shroud and a provision for sweeping out the evolved oxygen with argon sweep-gas. The off-gas system consisted of a pump, piping, copper cooling coils, and an oxygen meter. The experiments were performed at 650 °C in a LiCl-1wt% Li₂O melt using a stainless steel crucible and an argon atmosphere.

In general, the overall results from these experiments were extremely encouraging, suggesting that the electrolytic reduction process is a robust system that can yield a high-quality product at high throughput. The cathode products were generally highly reduced with the product in the third HCR experiment, showing a conversion of greater than 99.5%. The cells could support sustained high-current operations with average current in the range of 40-50 A. The cell response was stable and generally predictable. No major corrosion of cell components or degradation of platinum anode was observed. Major improvements in cell

design and operation were observed in each sequential HCR experiment. Average current efficiencies for the complete reduction campaign in the third HCR experiment was 65%, a relatively high value for these kinds of electrochemical operations.

Anode Material Studies: Inert anode materials are being evaluated to develop the best material and anode configuration design for the electrolytic reduction process. Strontium-ruthenium oxide (SrRuO_3) has been identified as a promising inert anode conductive phase. Production of SrRuO_3 has been standardized and considerable effort was put into developing a method for testing that would allow self-consistent and reliable results. Efforts have continued in the development of fabrication methods for practical configurations and to evaluate long-term performance of this material.

The anode with which we have most testing experience is derived from SrRuO_3 with a silicate binder. The SrRuO_3 -based anode demonstrated stable performance throughout typical 4-hr oxygen generation tests, showing no signs of attack (Fig. 1). The estimated current density is $1\text{A}/\text{cm}^2$. Neither experiments generating chlorine nor exposures to Li-metal-saturated salt demonstrate apparent adverse effects to the anode. In addition to anode tests conducted in our electrochemical cell, several samples were produced and provided to independent experimenters for testing. These samples will be tested in larger cells and are expected to provide information on longer test periods.

We are looking at other systems such as SrRuO_3 with a Ca-Ti-O binder system. The anode materials demonstrated positive results, not showing any obvious signs of attack following extended operation in oxygen-generating conditions. The current density of the SrRuO_3 and Ca-Ti-O sample was on the order of $0.5\text{A}/\text{cm}^2$.

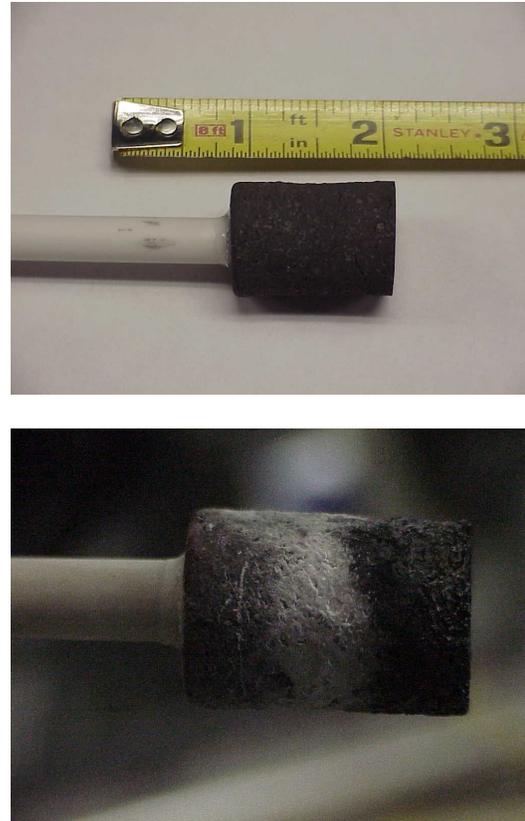


Fig. 1. SrRuO_3 -based anode before (above) and after (below) testing demonstrates inertness of material.

Progress has been made in identifying candidate materials and testing them in increasingly challenging environments. High current density, potentiostatic stability, and retention of physical integrity are the primary response variables to gauge electrochemical performance. The SrRuO_3 samples show promise in all of these areas.

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

Research Participants

Mark A. Williamson, Karthick Gourishankar, Laszlo Redey, Argentina A. Leyva, Dennis W. Dees, Len Leibowitz, Mark C. Hash, Laurel A. Barnes, Andrew S. Hebden, James L. Willit, and Arthur A. Frigo. For more information, contact Mark Williamson (630-252-9627, williamson@cmt.anl.gov).

Structural Materials to Enable Electrolytic Reduction of Spent Oxide Nuclear Fuel in a Molten Salt Electrolyte

Materials for effective, cost-efficient, and proliferation-resistant nuclear fuel technology

The Chemical Engineering Division (the Division) is currently collaborating with the Korea Atomic Energy Research Institute (KAERI) to develop advanced structural materials for use in a new technology enabling the electrolytic reduction of spent nuclear fuel in a molten salt electrolyte. The principal objectives of this three-year project are to assess and select commercially available candidate materials for service in the electrolytic reduction process, and to develop new candidate material systems (e.g., functional barrier coatings) for service in the electrochemical reduction process vessel. The materials solutions developed here will benefit the U.S. Department of Energy's Advanced Fuel Cycle Initiative (AFCI) program for the reduction of transuranic and fission product oxides, and KAERI's Advanced Spent Fuel Conditioning Process for conditioning spent fuel for long-term storage and eventual disposal.

The electrolytic reduction of spent nuclear fuel involves the liberation of oxygen in a molten lithium chloride electrolyte, resulting in a chemically aggressive environment that is too corrosive for typical structural materials. The electrochemical process vessel, structural cell components, and the electrical supply materials must be resilient in the presence of oxygen, molten salt components, and various impurities at 650°C to ensure high processing rates and extended service life. The successful implementation of this project will provide an enabling solution for the effective management of spent fuel, and contribute to the establishment of a nuclear fuel cycle technology that is proliferation-resistant and cost-effective. Our recent corrosion testing has contributed to this effort by revealing those commercial alloys displaying the most corrosion resistance under simulated process conditions and showing

promise for use as base structural materials in the electrochemical reduction process.

2003 Research Highlights

The project began with a coordination meeting in March to discuss the experimental approach and areas of technical expertise relevant to the project. Subsequent to this meeting, the Division and KAERI independently developed an initial list of high-temperature alloys, based on a combination of high-temperature strength and corrosion resistance properties. Each organization also developed an apparatus for corrosion testing of metal alloy samples. Previous immersion corrosion studies in hot molten salt conducted by the Division indicated that preferential dissolution of elements and/or compounds from container material, adjacent samples, or any material in contact with the molten salts may contribute to chemical reactions related to corrosion mechanisms. For this reason, we designed our testing apparatus to contain three independent vessels, each with a separate gas sparge tube and sample hanger, to eliminate any spurious sources of corrosion. The completed testing apparatus is shown in Figure 1.



Fig. 1. Completed corrosion test apparatus.

The expected conditions in the electrochemical process vessel during operations are ~625°C to 725°C, 1-6% lithium oxide in lithium chloride, and ~10% oxygen; our test conditions simulated this environment. Corrosion testing began in July and thus far we have tested 44 samples from eight alloys. The sample coupons were immersed to half their length in the molten salt mixture to assess the corrosion effects of submersion and exposure of the alloys to the salt/oxygen vapors. Samples were evaluated for 3- to 9-day intervals, at temperatures ranging from 625 to 725°C, in molten salt containing 3 and 6% lithium oxide in lithium chloride, with argon - 10% oxygen percolating through the molten salt mixture.

Post-test characterization and analyses were performed at University of Illinois at Chicago under the direction of Professor J. Ernesto Indacochea. Preliminary examination of selected samples indicated formation of a thin adherent corrosion scale representing a single corrosion front with uniform penetration to ~100-120 μm. Metallographic images of the microstructure of Inconel 690 are shown in Figure 2. Micrographs (a) and (c) were taken at 200X and (b) and (d) at 500X. Micrograph (a) is an image of a sample area suspended above the level of the molten salt and contacted only by molten salt vapor and escaping oxygen gas.

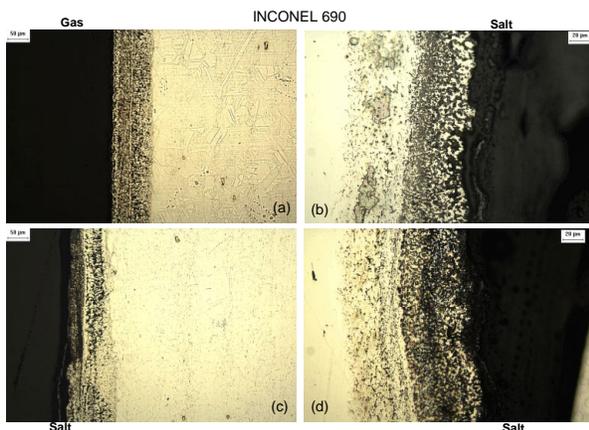


Fig. 2. Corrosion scale formation on surface with penetration into underlying metal alloy.

The corrosion scale has areas of breakage and separation from the specimen and may be a consequence of the thickness of the surface scale, motion of the molten salt, and thermal expansion coefficient mismatch between the scale product and the metal substrate. In this instance, the corrosion has penetrated below the surface of the corrosion scale and progressed along grain boundaries as shown in Figure 3. The micrograph was taken at 500X.

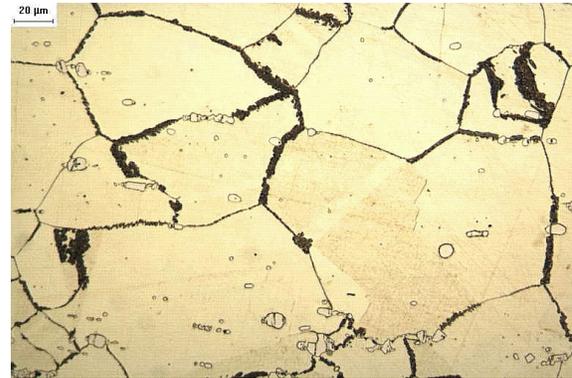


Fig. 3. Preferential corrosion attack at grain boundaries.

A joint presentation highlighting the first year's work was given in November at the United States Department of Energy International Nuclear Energy Research Initiative Program Annual Review in Seoul, South Korea.

This research is funded by the United States Department of Energy, Office of Nuclear Energy, Science and Technology, International Nuclear Energy Research Initiative program.

Research Participants

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Pyroprocess-Based Treatment of Spent Nuclear Fuel: Process and Equipment Integration

Integrating operations to provide an economical process

There is a growing consensus in the United States and abroad that a significant growth in nuclear energy must occur and that it must be accompanied by the development of advanced fuel cycles that are proliferation-resistant and decrease the amount and long-term hazards of nuclear waste. This policy direction is reflected in the National Energy Policy, which recommends development of advanced nuclear fuel cycles. In accordance with this policy, both the Advanced Fuel Cycle Initiative (AFCI) and the Generation IV Program within the U. S. Department of Energy (DOE) Office of Nuclear Energy, Science and Technology support the recycle of spent nuclear fuel. Specifically, AFCI is focused on recycle of spent fuel to optimize use of the first geological repository. DOE currently has about 40,000 tonne (heavy metal) of spent oxide fuel in inventory and this quantity is growing at the rate of about 2,000 tonne per year. Under AFCI, new recycle technologies are required that are more proliferation-resistant and cost-competitive than existing alternatives. Among the technologies being developed to meet these goals are pyroprocesses that build on the success of the demonstration of Experimental Breeder Reactor II metallic fuel treatment at Argonne National Laboratory.

2003 Research Highlights

A primary thrust of research in the pyroprocess area prior to this year has been the development of the individual unit operations required to treat spent fuel. General process flowsheets and most of the viability demonstrations have been completed. However, detailed mass balances are needed to provide the basis for sizing the various pieces of equipment and facilities housing them. The individual operations must then be integrated to provide an economical overall process.

Our efforts during the past year focused on the development of a detailed process flowsheet

with mass balances, the generation of facility and equipment conceptual designs, and the determination of step-by-step operational details for an operational model of the facility. One of the key results has been the reduction in the floor-space-area requirements for the process cell within the facility of more than 50% compared with an earlier informal conceptual facility design generated in 2002.

Detailed Process Flowsheet: A detailed process flowsheet (Fig. 1) has been developed for a facility to treat 100 tonne/yr of initial heavy metal. Mass balances have been determined for each operation. The process includes 17 principal operations:

1. Fuel assembly chopping, shredding, and loading into baskets.
2. Treatment of the off-gases from Operation 1 to sequester fission gases (e.g., krypton and xenon). The oxygen from Operation 4 and the chlorine from Operations 12 and 13 also will be treated.
3. Long term storage of the fission gases.
4. Direct electrolytic reduction of the fuel oxides to metals.
5. Recovery and recycle of carry-over electrolyte salt from the Operation 4 product.
6. Electrorefining of the metal product from Operation 4 to recover uranium.
7. Production of the oxidant (uranium trichloride) required for the electrorefiner operation.
8. Processing of the uranium product from Operation 6 to separate the uranium from any electrolyte that has adhered to the uranium and consolidate the uranium dendrites into an ingot.
9. Handling and routing of the uranium ingot from Operation 8.
10. Production of metal waste form to stabilize the noble metal fission products and cladding from the spent fuels, and to recover residual actinides.

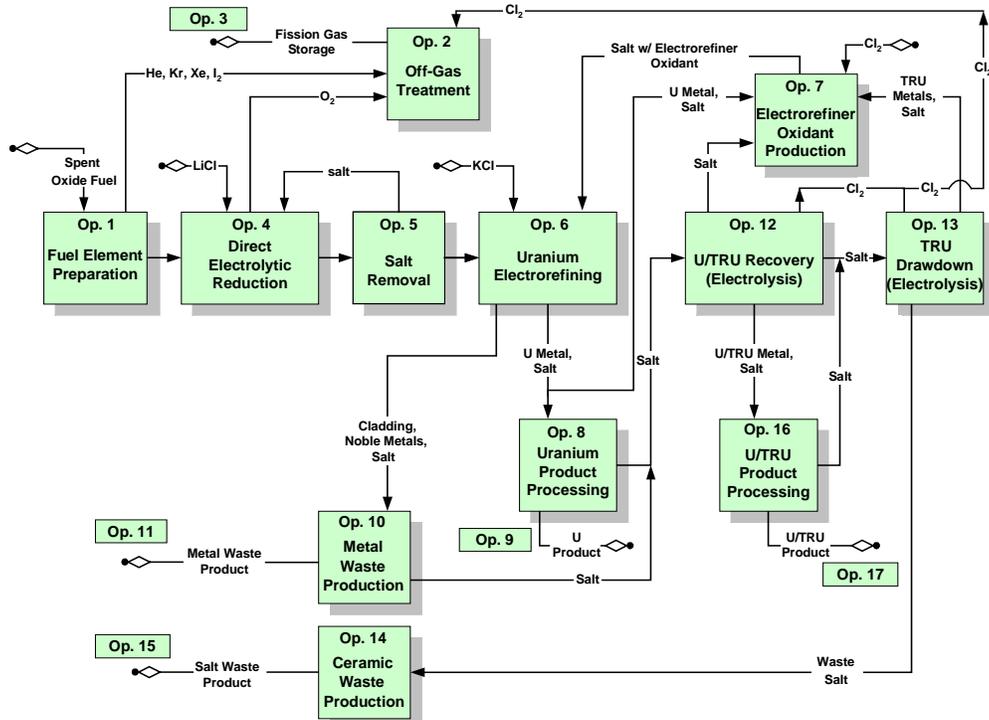


Fig. 1. Process Flowsheet.

11. Handling and routing of the metal waste form product generated during Operation 10 for ultimate repository disposal.
12. Electrolytic recovery of transuranic elements and residual uranium metal from process chloride salts produced during electrorefining. This operation will recover about 98% of the transuranics and all of the residual uranium.
13. Recovery of the remaining transuranics using an electrolysis drawdown operation.
14. Production of ceramic waste form to immobilize any chloride salts that contain fission products and residual actinides.
15. Handling and routing the ceramic waste-form product generated during Operation 14 for ultimate repository disposal.
16. Processing of the uranium and transuranic products from Operation 12 to separate the uranium and transuranics from any electrolyte salt that has adhered to them.
17. Handling and routing of the uranium and transuranic product from Operation 16.

Facility Layout: A conceptual design of a facility is being developed and refined using operational modeling techniques. The main operational floor layout for this facility is shown

in Figure 2. A three-dimensional depiction of the facility is presented in Figure 3.

Equipment Design: Equipment is being designed to meet the mass-balance requirements associated with the flowsheet. Two of the cornerstone operations of the pyroprocess-based facility are direct electrolytic reduction of the spent oxide fuel to metal and electrorefining of this metal product to recover uranium. The conceptual designs of these equipment items are shown in Figs. 4 and 5.

Research Participants

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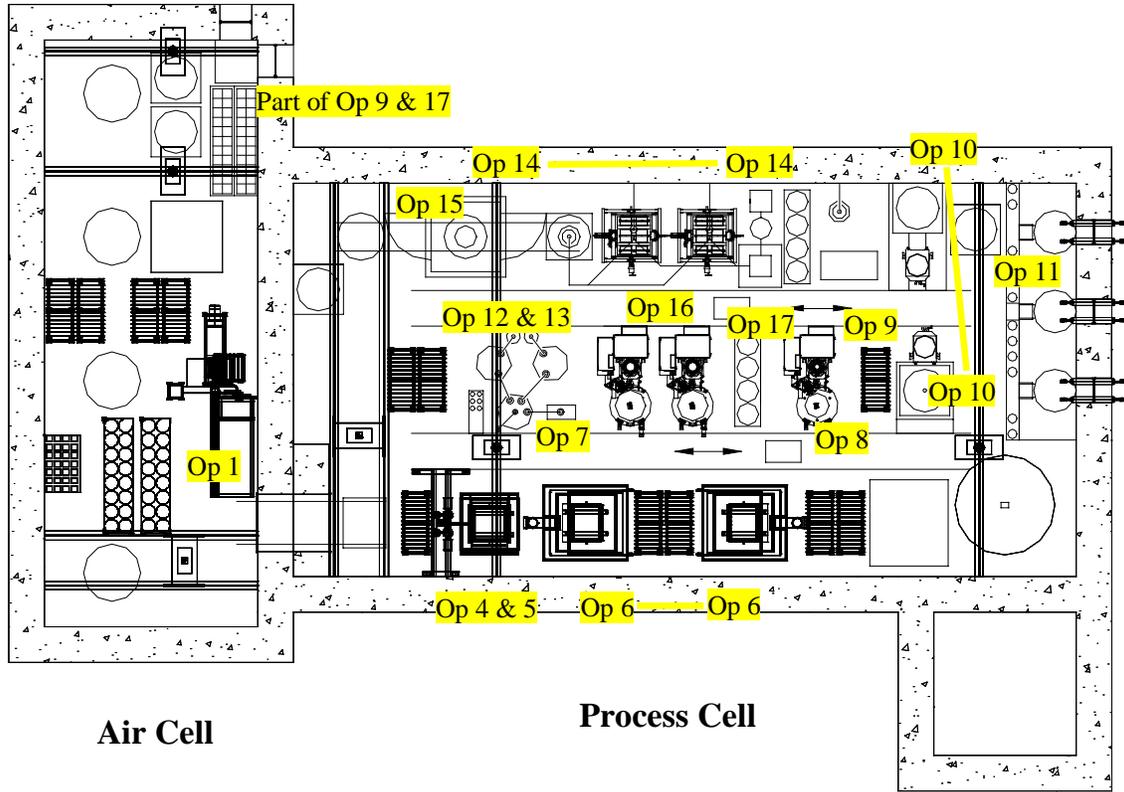


Fig. 2. Layout of Main Operational Floor of Treatment Facility.

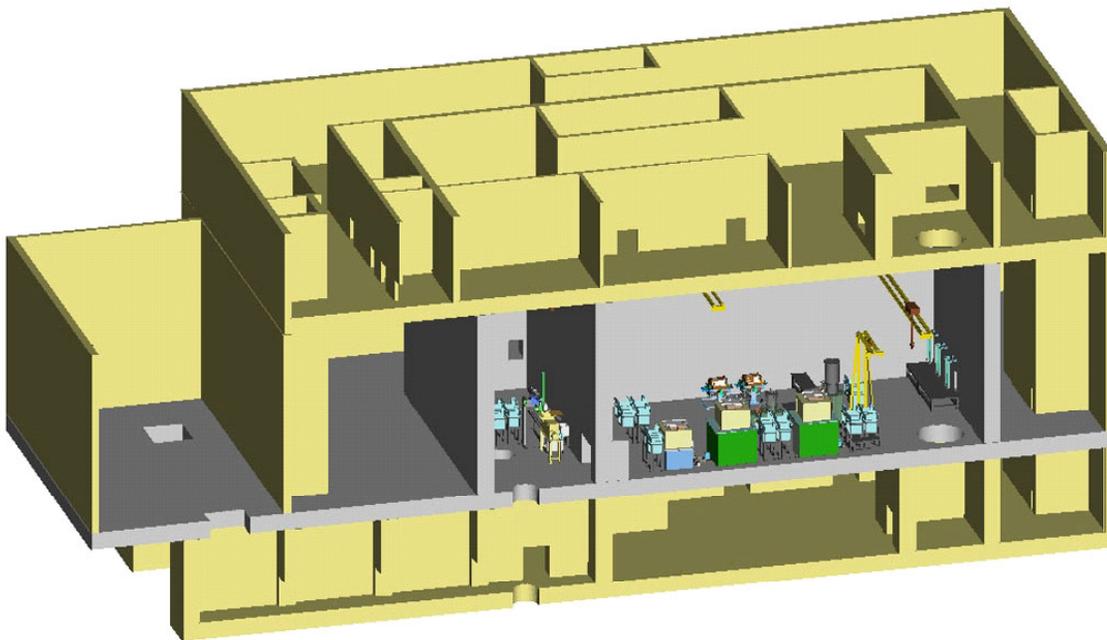


Fig. 3. Three-Dimensional View of Treatment Facility.

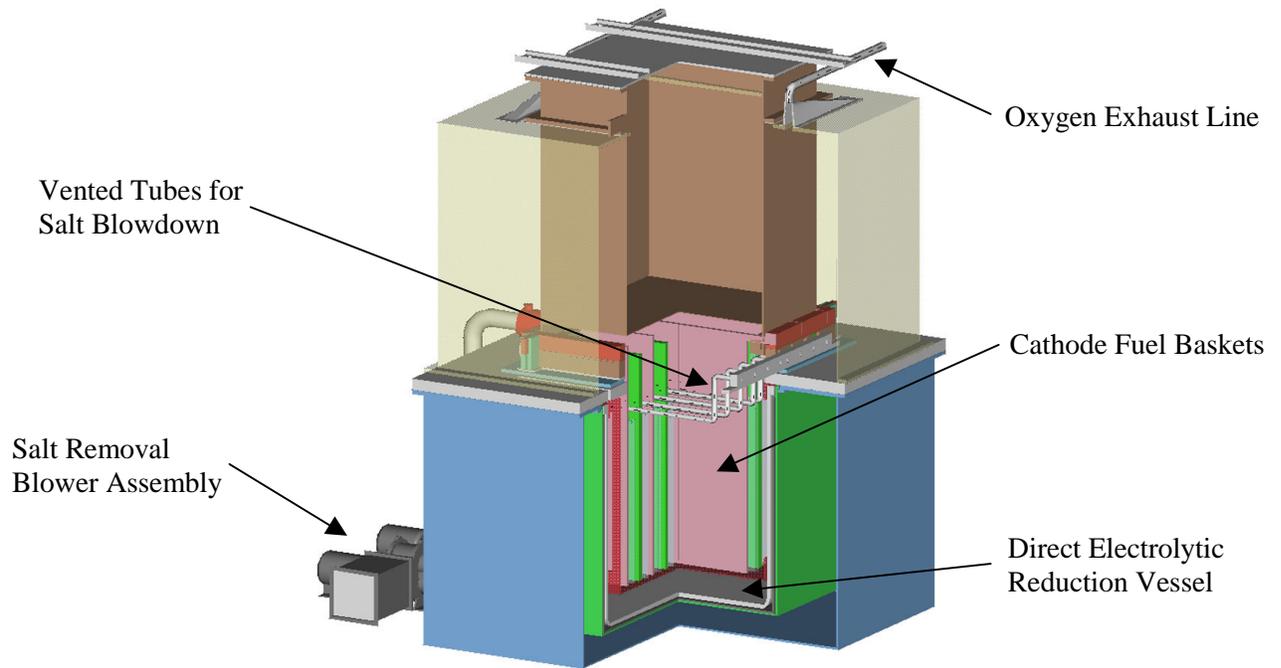


Fig. 4. Direct Electrolytic Reduction Equipment Concept.

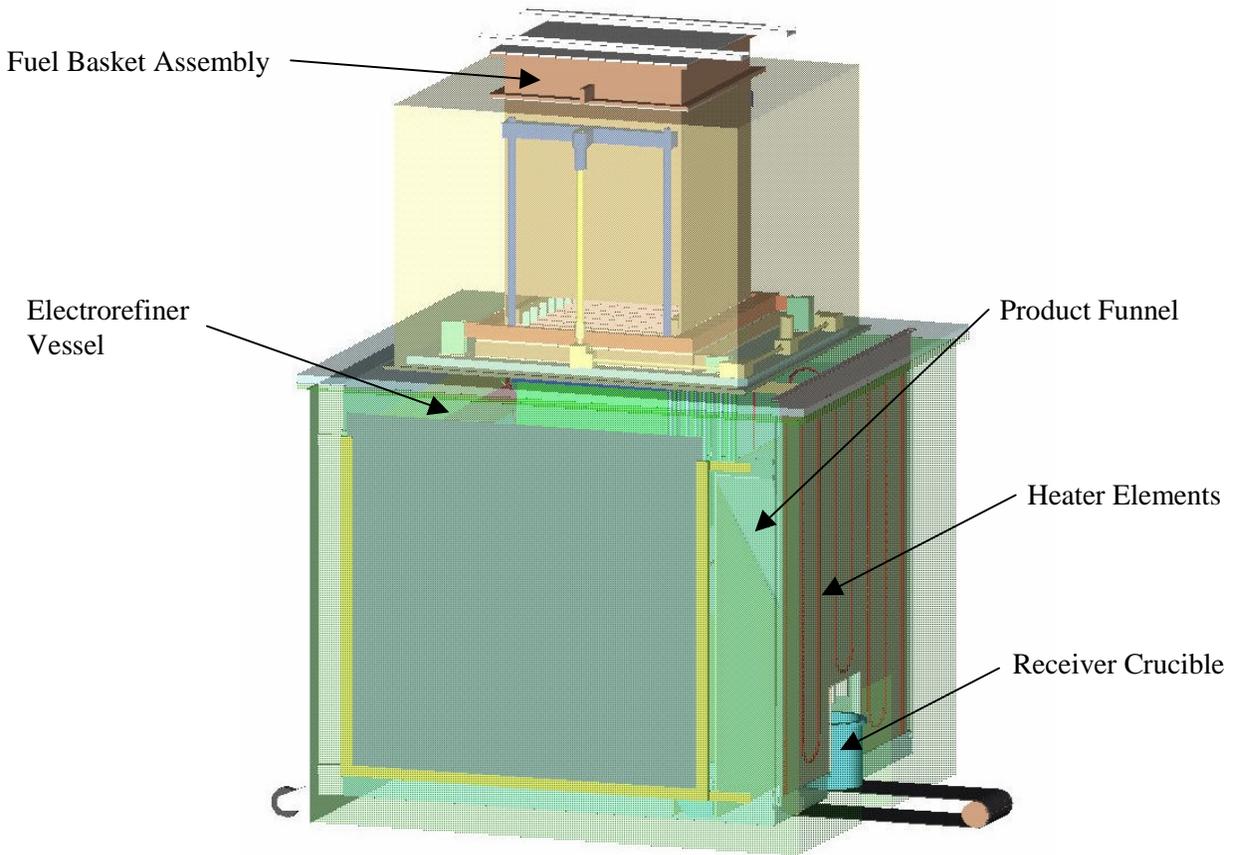


Fig. 5. Electrorefiner Equipment Concept.

Pyroprocess-Based Treatment of Spent Nuclear Fuel: Planar Electrode Electrorefiner Development

Scaling up electrorefining technology

The high-throughput uranium electrorefiner (concentric cylinder electrodes) that was developed for treating spent Experimental Breeder Reactor II fuel was scaled for treating up to 5 tonnes of spent fuel per year. Adapting this technology to treating the much larger volume of light-water reactor fuel requires a major increase in scale (factor of 10 to 100) and efficiency. This challenge is being addressed as part of the Department of Energy's Advanced Fuel Cycle Initiative (AFCI) program.

2003 Research Highlights

Our experience with the Mark-V electrorefiner that is presently being used to treat EBR-II blanket fuel in the Fuel Cycle Facility at Argonne-West has provided some of the data needed for scale-up and has identified key inefficiencies that must be addressed.

Because electrorefining is an electrochemical process, throughput is directly proportional to cell current and electrode area. At 100% efficiency we have demonstrated an electrorefining rate of 1.75 kg/hr/m^2 of anode basket area. Allowing for handling time and a lower voltage limit required by zircaloy cladding common to light water reactor fuel, electrorefining 100 metric tons in one year (200 days) requires $\sim 22 \text{ m}^2$ of anode basket area. The present Mk-V design has only $\sim 2 \text{ m}^2$ of anode area and has major inefficiencies with respect to scraping the electrodeposited uranium off the cathode and removing the electrorefined uranium product from the electrorefiner.

Motivated by the need for higher throughput and guided by our experience with the Mark-V, we developed a new conceptual planar electrode electrorefiner (PEER) design (Fig. 1) with the following key features

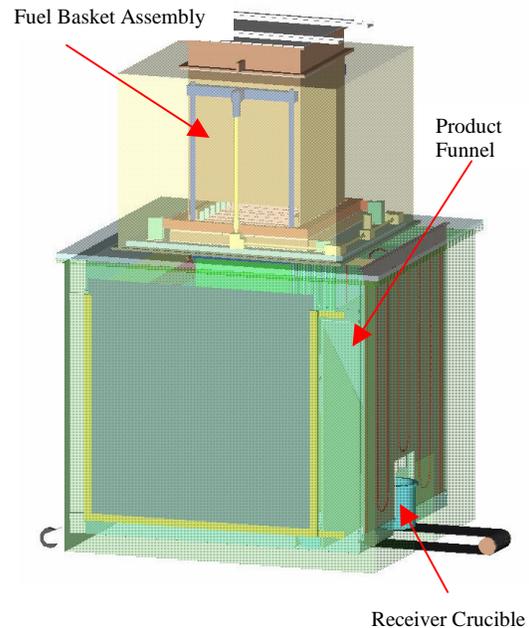


Fig. 1. Conceptual PEER Design.

- Parallel, planar anode baskets
- Intermittent scraping of cathodes
- Independent removal of uranium dendrites
- Direct delivery of uranium dendrites to cathode processor crucible

Electrodeposited uranium is scraped off the planar cathodes by vertical-motion scrapers. The dislodged uranium slides down the sloping bottom of the vessel into a collection basket. The collection basket periodically is raised and inverted, dumping the product down the product funnel into the receiver crucible. Preliminary results indicate that periodic scraping of the cathode is much more efficient at removing the electrodeposited uranium than continuous scraping as in the Mk-V electrorefiner.

In order to evaluate the feasibility of the PEER concept and to acquire the necessary data with respect to parameters such as scraping frequency, scraper design, cathode design, optimum electrode spacing, product density, and cathode current density, a smaller prototype module has been designed. This test module, shown in Figure 2, has a single anode basket, vertical motion scrapers, and variable electrode spacing. Scrapers and cathodes are replaceable in this prototype so we can evaluate different cathode and scraper designs.

Design, fabrication, and installation of this prototype module will be completed by summer 2004 and testing can then begin.

Research Participants

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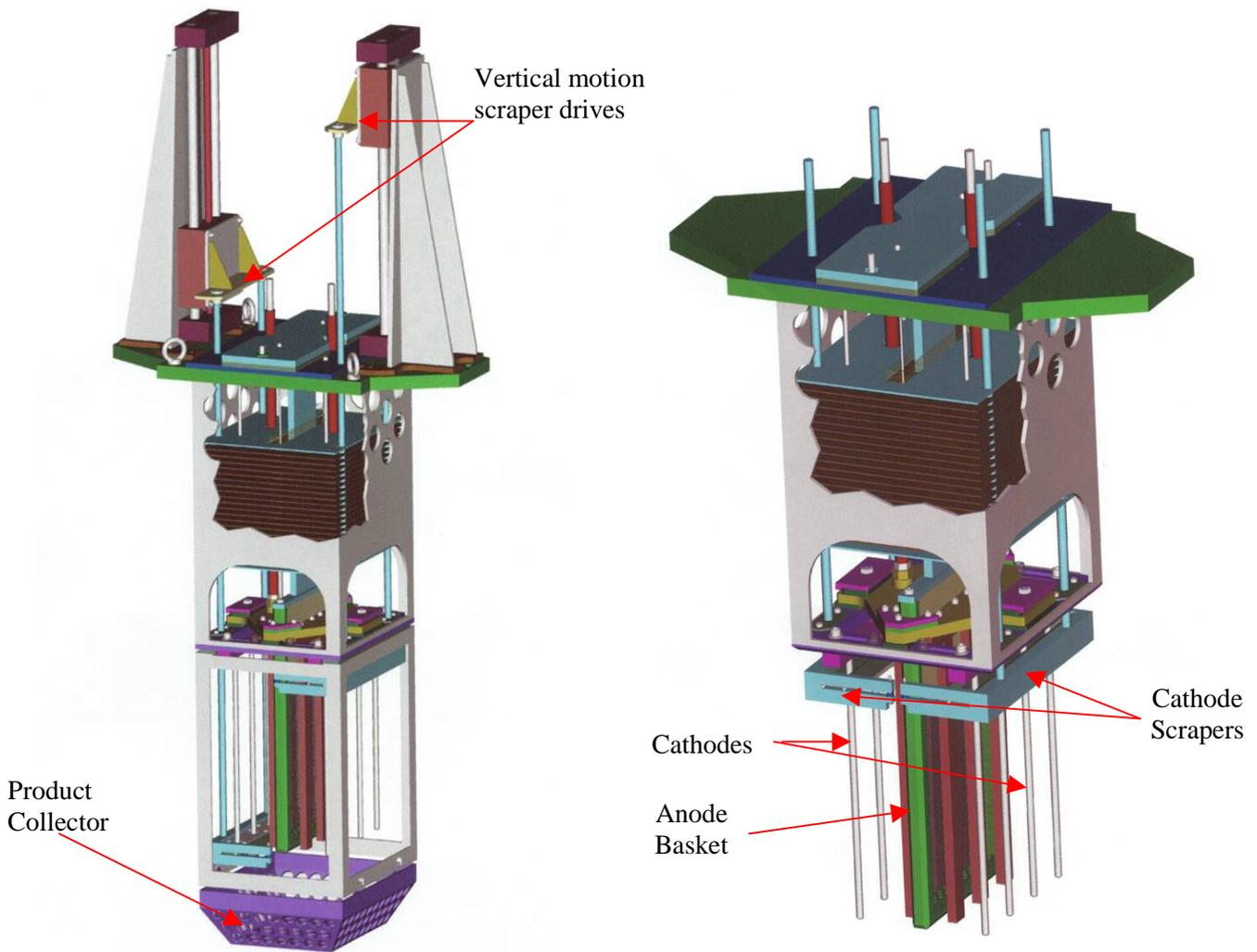


Fig. 2. Drawings of PEER prototype test module showing entire module (left) and close up of electrodes (right).

Recovery of Actinides from Spent Fuel by Electrolysis

Reducing the quantity of nuclear waste and related storage costs

The proposed geologic repository has a legislated capacity limited to approximately 63,000 tonnes of initial heavy metal in commercial spent nuclear fuel (CSNF); however, the 103 commercial reactors currently operating in the U.S. will produce this quantity of CSNF by 2014. A primary goal of the Advanced Fuel Cycle Initiative (AFCI) is to develop new ways to treat nuclear waste generated by commercial nuclear power plants that may greatly reduce both total quantity and radioactive hazards of nuclear waste, and may significantly reduce the cost of disposing radioactive waste in a remote underground repository. The recovery of transuranic elements from spent fuels is a key element of AFCI, and pyrochemistry has many recognized benefits in the treatment of spent nuclear fuels, including dramatic reductions in the waste stream ultimately destined for geologic disposal. This project focuses on pyrochemical treatment of spent light-water-reactor oxide fuels, in which the fuels are reduced and the bulk of the uranium is recovered via electrorefining. In a subsequent process step, the actinides (transuranic [TRU] elements and residual U) are recovered from the molten salt as a metal product by electrolysis. The resulting mixture of actinides is suitable feed material for advanced reactors. A major focus of Argonne's effort in this field is to develop a solid cathode technology for the co-deposition of a readily recoverable actinide-metal product.

2003 Research Highlights

In order to evaluate the viability and value of recovering actinides on a solid cathode by electrolysis, we are determining whether: (1) the actinide-metal product can be efficiently harvested from the solid cathode on a commercial scale and (2) the recovered product meets quality specifications for advanced reactor

fuel fabrication. The ability to harvest the actinide-metal product will depend most strongly on morphology of the deposit, and several experimental variables can affect product morphology (including voltage, current density, composition, and temperature); the overall quality of the product also depends on salt composition and recovery method (e.g., single-pass recovery or a multi-stage configuration). Project goals include:

- Maximizing the TRU content of deposited U, while minimizing deposition of fission products (primarily rare earth elements),
- Depositing U and TRU within a practical amount of time,
- Investigating the effects of system variables on U/TRU product morphology, and
- Investigating the durability of materials used to construct the electrochemical cell.

The first series of experiments resulted in the successful deposition of U and Pu on a solid cathode along with a minor amount of neodymium, Nd, and, possibly, gadolinium, Gd; potentially due to instabilities in cell current and/or voltage. Note that the experiments used plutonium to represent the series of the transuranic elements from neptunium to curium, all of which have known thermodynamic properties that can be related to those of plutonium. A representative current / voltage trace and photograph of a typical product are shown in Figures 1 and 2, respectively. Another significant positive result of the first experiments was the successful operation of the electrolysis cell, which performed as expected without problem or incident; component corrosion has also been minimal. The corrosivity of hot chlorine gas required several special

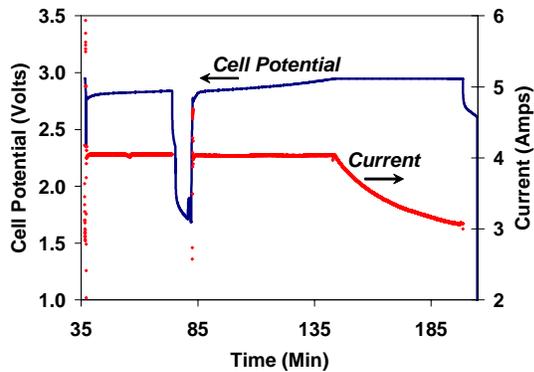


Fig. 1. Trace showing cell potential (volts) and current (amps) measured under current control with a voltage limit (≈ 2.95 V).



Fig. 2. Photograph of cathode deposit following constant-current run. Central hole is where sample was removed for further analysis (visible at left).

design and operating accommodations. Other results from the first year of experimental runs have also indicated avenues for further study for optimizing cell configuration and operating conditions, such as determining the effect, if any, of parasitic reactions that may reduce cell efficiency.

Culmination of this effort will be to define operating parameters and design concepts for a commercial-scale electrolysis cell.

This research is funded by the U.S. Department of Energy, Office of Nuclear Energy Research, Science and Technology.

Research Participants

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National Security

The Chemical Engineering Division (the Division) is conducting research programs aimed at developing U.S. capability to attribute the detonation or deployment of radioactive material, and to enhance the “hands-on” ability of Department of Defense personnel whose missions involve potential interactions with highly radioactive materials such as those found in radiological dispersal devices, or “dirty bombs.”

In work funded by the Department of Defense’s Defense Threat Reduction Agency (DTRA), under the Domestic Nuclear Event Attribution (DNEA) Program, the Division is leading an effort to develop the capability to attribute the detonation or deployment of radioactive material in the United States to a hostile nation or terrorist group. The program comprises experts at U.S. Department of Energy (DOE) and Department of Defense research and development laboratories, Law Enforcement Agencies such as the Federal Bureau of Investigation, and other governmental agencies. At Argonne, the DNEA project focuses on two main areas. The first is establishing the capability to receive and analyze samples collected from an RDD device or event. Argonne currently is developing laboratory capabilities and procedures, and has completed several demonstrations of our analytical capabilities. The second major focus area is evaluating the data collected in the laboratory and using these data for attribution.

Chemical Engineering Division personnel helped establish a training program and are now helping to provide this training to Department of Defense personnel whose missions involve potential interactions with highly radioactive materials such as those found in dirty bombs. The training is conducted as a five-day instructional program at Argonne National Laboratory-West (located in Idaho), and includes classroom lectures, laboratory exercises, and facility tours. The laboratory exercises include a suite of radioactive materials in controlled settings for measurements. These teams have extensive training relative to nuclear devices and other weapons of mass destruction (chemical and biological), but little training and no hands-on experience with highly radioactive materials. These exercises clearly demonstrate the operation (or shortcomings, if present) of their instruments in measuring highly radioactive materials.

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Domestic Nuclear Event Attribution Program

Tying nuclear devices and "dirty bombs" to hostile groups

The Chemical Engineering Division manages a national security program sponsored by the Department of Defense's Defense Threat Reduction Agency (DTRA). The purpose of the Domestic Nuclear Event Attribution (DNEA) Program is to develop the capability to attribute the detonation or deployment of radioactive material in the United States to a hostile nation or terrorist group. This program is supported by experts drawn from U.S. Department of Energy (DOE) and Department of Defense research and development laboratories, Law Enforcement Agencies such as the Federal Bureau of Investigation, and other governmental agencies.

The DNEA Program is focused on two types of events. The first is attribution of an event involving a nuclear device. Expertise for these events is drawn from the DOE weapons laboratories, primarily Los Alamos and Livermore. The second type of event is the attribution of a radioactive dispersal device (RDD), or "dirty bomb". Because of Argonne's expertise in the nuclear fuel cycle, we have been assigned the lead for activities involving RDDs.

Although the program at Argonne is managed by the Chemical Engineering Division, project efforts are supported primarily by staff from the Nuclear Technology and Nuclear Engineering Divisions. DOE's New Brunswick Laboratory also plays a key role in the program.

2003 Research Highlights

The DNEA project at Argonne focuses on two main areas. The first is to establish the capability to receive and analyze samples that were collected from an RDD device or event. Laboratory capabilities and procedures are currently being developed and several demonstrations of our analytical capabilities

have been completed. The second major focus area is evaluating the data collected in the laboratory and using these data for attribution. To accomplish this goal, several databases are being developed that will include the necessary (or available) data on radioactive materials. One database will focus on spent fuel; the second on sealed sources. Existing databases on research reactors and spent fuel have been tapped as input data. A Nuclear Regulatory Commission database was used to start the development of the sealed-source database. Discussions are underway with two source manufacturers and third with a company that refurbishes sealed sources to obtain this signature information. In addition, specific sealed sources are being collected for analysis in our laboratories to verify or determine this signature information.

In addition to these two activities, we are participating in the development of a DNEA Program quality assurance plan, sample collection in the field using robotics, and the development of operation plans that would be used in an actual event. In FY 2004, we will continue to expand the data included in the databases and we will participate in round-robin sample exchanges. These sample exchanges are important, as they will demonstrate our capabilities to analyze and interpret these types of samples.

This research is funded by the Defense Threat Reduction Agency.

Research Participants

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Radiological Dispersive Device Materials Training Program

Providing "hands on" experience to defense personnel

Chemical Engineering Division personnel helped establish a training program and are now helping to provide training for Department of Defense personnel whose missions involve potential interactions with highly radioactive materials such as those found in radiological dispersal devices (RDDs).

2003 Research Highlights

The training is conducted as a five-day instructional program at Argonne National Laboratory-West (located in Idaho), and includes classroom lectures, laboratory exercises, and facility tours. The laboratory exercises include a suite of radioactive materials in controlled settings for measurements. These teams have extensive training relative to nuclear devices and other weapons of mass destruction (chemical and biological), but little training and no hands-on experience with highly radioactive materials. These exercises clearly demonstrate the operation (or shortcomings, if present) of their instruments in handling highly radioactive materials.

The focus of this course is to introduce a broad spectrum of RDD-related materials to military customers. These materials include spent fuel, dissolved fuel, waste solutions, medical isotopes, and industrial sources. Our goals are to (1) focus our instruction on how this information is applicable (or not) to their instruments and procedures and the new environment of RDDs; (2) provide practical demonstrations and exercises with their instruments and these materials; and (3) provide an interface to a new set of technical experts. For some teams, exercises may focus on search activities (Fig. 1), while for others radiography is emphasized (Fig. 2).



Fig. 1. Department of Defense personnel conducting an outdoors search exercise.



Fig. 2. Department of Defense personnel setting up equipment for a radiography exercise.

In 2003, four classes were held for Department of Defense personnel; ten additional classes are scheduled for FY 2004. In addition, one team from the National Guard (Georgia Weapons of Mass Destruction, Civil Support Team) has scheduled a four-day course, and other civil support teams are considering participating in this course. Other potential customers include first responders such as fire department personnel, coast guard, and state and national transportation security and investigative organizations.

Research Participants

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Basic and Applied Sciences

The Basic and Applied Sciences Department of the Chemical Engineering Division conducts research on a broad range of fundamental issues involving chemistry and materials functionality in systems that are relevant to electric power distribution, energy efficiency enhancement, chemical manufacturing, and clean air technologies.

These studies embrace (1) the processing and characterization of high-critical-temperature superconductors (HTSs), (2) novel approaches to heterogeneous catalysis, (3) new vistas in homogeneous catalysis, and (4) the details of ion transport mechanisms in operating electrochemical devices. Some aspects of this research make use of cutting-edge synchrotron x-ray, nuclear magnetic resonance, and transmission electron microscopy facilities available at Argonne National Laboratory, including the Advanced Photon Source.

In recent years, our investigations of HTS materials have focused on the characterization of coated conductor embodiments employing biaxially textured $M_1Ba_2Cu_3O_7$ films (MBCO, $M = Y$ or a rare earth metal) as the superconducting medium. Much of this work is performed as part of longstanding collaborations with industries and other national laboratories.

In the past year we developed and implemented a technique for performing detailed Raman microscopy measurements on long-lengths (1 to 10 m) of YBCO coated conductor tape prepared using textured metal substrates. These studies have (1) shed new light on the mechanisms involved in the transformation of the MBCO precursor to the superconducting phase, (2) revealed important insights about the relationship between phase composition and conductor performance, and (3) led to the development of Raman-based diagnostic concepts suitable for on-line monitoring of the MBCO coated conductor fabrication process.

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
- Hydrogen production and storage

The heterogeneous catalysis research program in the Chemical Engineering Division seeks to address a broad range of forefront issues in relation to chemical production, energy efficiency, and environmental air quality. Our work on improved catalysts for reduction of NO_x emissions has led to a new selective catalytic process that offers a promising alternative to established de- NO_x technology. A CeO_2 -doped bifunctionalized form of Cu-ZSM-5 has been developed and tested with considerable success. This new formulation yields improved selectivity to N_2 formation, greater on-line resilience, and enhanced water tolerance relative to the standard Cu-ZSM-5 material. The process developed to date uses propylene as the reducing agent. Current work is focused on the study of alternative reducing agents that are safer and more readily available to the particular application, e.g., gasoline constituents for automobiles, diesel fuel for heavy vehicles, and methane for coal-fired burners.

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 the state-of-the-art high-pressure nuclear magnetic resonance (NMR) capability developed by (and in place within) the Chemical Engineering Division, we have made the first observations of the cobalt carbonyl hydride catalyzed hydrogenation of carbon monoxide in a supercritical medium (carbon dioxide). The reaction kinetics were investigated in detail and the key reaction products (which included methanol and methyl formate) were identified. Important new insights concerning the effects of solvent polarity were gleaned from the results of these experiments.

In our research on in-situ NMR imaging of functioning lithium battery electrodes, we have made significant enhancements to our coin-cell-NMR detection probes that were designed to improve electrode-electrolyte contact. Using this new coin-cell device, we have made seminal observations that reveal a transient lithium phase

in the graphite anode compartment during the first charge cycle and have made significant progress toward identifying this phase. Detailed studies of lithium intercalation/de-intercalation in carbonaceous materials with well-defined structures are underway to characterize the lithium binding sites and to elucidate the binding mechanism.

During the past year, the staff members of the Basic and Applied Sciences Department have been actively engaged in laying groundwork for new programs that will support prominent Department of Energy initiatives in nanoscience/nanotechnology and the development of hydrogen as a fuel.

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Reel-to-Reel Raman Microscopy of Long-Length Superconducting Tapes

Studying the precursor-to-superconductor phase transformation process

Rapid progress is being made in the development of the $\text{M}\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ (MBCO) superconductor on long-length substrates. There is a growing expectation that functional, reliable MBCO-based conductor ($\text{M} = \text{Y}$ or a rare earth element) in lengths exceeding 100 meters will be available in three to five years. The coated conductor manufacturing process consists of a series of film deposition steps that must be monitored to assure compositional and structural uniformity together with product quality control. One of the routes to long-length YBCO coated conductor involves electron beam deposition of a Y-BaF₂-Cu precursor on long-length, biaxially textured substrates. YBCO films formed from this precursor have yielded critical current densities (J_{cs}) in excess of 1.0 MA/cm^2 . In this report we describe experiments performed on differentially heat-treated Y-BaF₂-Cu precursors deposited on meter-long buffered substrates. These experiments, performed in collaboration with Oak Ridge National Laboratory (ORNL), were conducted to investigate the evolution of the YBCO phase as a function of time at a fixed precursor conversion temperature and in a fixed processing atmosphere. The thermal processing and subsequent examination of these tapes were conducted in a reel-to-reel (R2R) mode that permitted the creation of a time-synchronized composition gradient in the reeling direction.

2003 Research Highlights

In prior years, we demonstrated that Raman microscopy is easily implemented and extremely useful for examining chemical composition and microstructure evolution after MBCO phase formation. The production of MBCO coated conductor in lengths approaching 100 meters made necessary the development of methods for applying Raman microscopy to long lengths of tape, hence, during the past year we integrated R2R methodologies into our Raman microscopy

apparatus (see Fig. 1). This technique provides substantive information when used to examine fully processed tapes, but we also find it especially useful for characterizing phase evolution in tapes that have been processed to obtain a gradation of transformed precursor states. A colleague at ORNL developed a method for creating such tapes that consists of reeling a precursor-coated substrate into a preheated furnace at a controlled rate such that each increment of the precursor spends a different amount of time at the selected precursor transformation temperature. The tape feed rate is controlled so that the leading edge of the precursor is over-processed, the trailing edge is essentially unprocessed, and an entire spectrum of phase conversion states exists in between. When the leading edge of the coated section reaches the end of the hot zone, the tape is rapidly back-reeled out of the furnace to quench the existing phase states.

During the past year, we performed Raman microscopy measurements on two of these time-gradient-processed tapes produced at ORNL. Both were meter-length YBCO/CeO₂ (150 nm)/



Fig. 1. Picture of the reel-to-reel (R2R) device used to feed and control long-length coated conductor tapes during Raman microscopy measurements. The device is shown in position on the stage of the Raman microprobe.

YSZ (200 nm)/Y₂O₃ (15 nm)/Ni (1 μm)/Ni-W (50 μm) embodiments. The specimens were coated with varying thicknesses of precursor to produce two different thicknesses of YBCO, i.e., one 300 nm and the other 1,000 nm thick.

The series of Raman spectra in Fig. 2 provide an overview of phase transformation along the portion of the 300 nm YBCO tape that experienced a precursor conversion temperature of 740°C. On the right hand side of Fig. 2, we correlate each spectrum with the elapsed time at 740°C to provide a global view of the overall reaction kinetics. In just a few minutes at 740°C, broad Raman bands (not shown) associated with the amorphous precursor are completely gone and evidence of CuO plus several other crystalline phases is clearly present. In a little over ten minutes, phonons attributable to BaF₂ and BaCeO₃ are apparent, YBCO is starting to form, and bands due to several key intermediate phases appear transiently in the spectra. In a little over 30 minutes the spectra are dominated by tetragonal YBCO phonons; in fact, the last vestiges of CuO are seen at the 34-minute point. It is important to note that x-ray diffraction (XRD) scans of this region (obtained at ORNL) detected the in-growth of BaF₂ and BaCeO₃ and the formation of YBCO (not specifically the “T” form) but not the CuO or other new phases.

The Raman microprobe results (1) allowed us to detect/track key intermediate phases, which included not only CuO but also Y₂Cu₂O₅, and barium cuprates and (2) provided information on the phase state of the YBCO (orthorhombic versus tetragonal). The type of graphic representations derived from the Raman data for the time gradient processed tapes from ORNL are shown in Figure 3. Using the combined information from ORNL’s XRD measurements and our Raman measurements, we were able to deduce the optimum heat treatment times for the two different tapes, which were confirmed by critical current measurements on similarly processed samples. In addition, we were able to determine the consequences of over-heat treating and to develop a plausible/testable model for the YBCO formation mechanism that has as its basis a series of simple binary reactions fully supported by the XRD and Raman results.

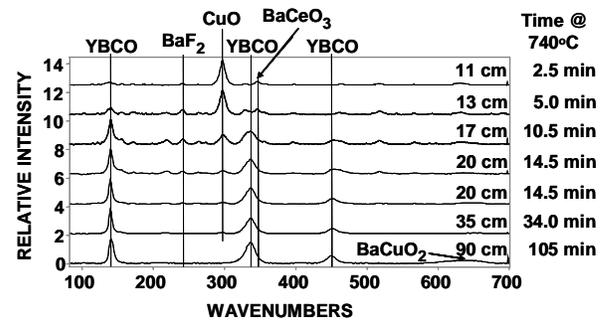


Fig. 2. Raman spectra of increments along the portion of the 300 nm time-gradient-processed YBCO tape that experienced the precursor conversion temperature (740°C). The time each increment spent at 740°C prior to the quench is indicated along the right side of the plot.

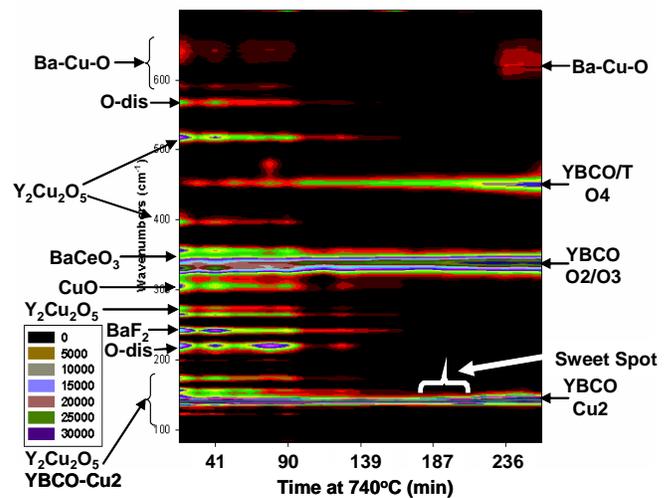


Fig. 3. Top view of the Raman frequency-reaction time plane (with intensities in color scale format) for the ca. 1,000-nm time-gradient-processed tape. The time domain covered is the early through late soak period at 740°C. All Raman band intensities are normalized to the intensity of the Cu₂ mode of YBCO at ca. 145 cm⁻¹.

This research was sponsored by the U.S. Department of Energy, Office of Electric Transmission and Distribution, as part of a DOE program to develop electric power technology.

Research Participants

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Bifunctional Catalyst to Reduce 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.

2003 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

(CeO_2 coated on the external surface of the zeolite) 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. At a space velocity of $30,000 \text{ hr}^{-1}$ using propylene as reductant, 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 ; 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 without altering the nitrogen selectivity over the bifunctional catalysts by lowering the space velocity. Emissions of carbon monoxide are also lowered for the coated material.

Table 1 shows the activity of the native Cu-ZSM-5 for reducing NO_x along with low and high loadings of CeO_2 . 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 (common in less efficient catalysts) are observed with this material.

The additive effectively coats the outside of the zeolite particle. We have used scanning electron microscopy (SEM) 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 nanoparticles of CeO_2 decorated on the outside of the metal-exchanged zeolite, with possible additional phases yet not fully identified. We

Table 1. Activity of Cu-ZSM-5 and Cu-ZSM-5 with CeO₂ Additive under Wet Conditions at 250°C

	Cu ZSM5 Only	Cu-ZSM-5 with 10% of CeO ₂ Additive	Cu-ZSM-5 with 20% of CeO ₂ Additive
NO conversion	15.2%	32.2%	52.7%
NO ₂ and N ₂ O selectivity	3.8%	1.5%	0.6%
CO selectivity	30.9%	11.6%	8.3%

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 SEM 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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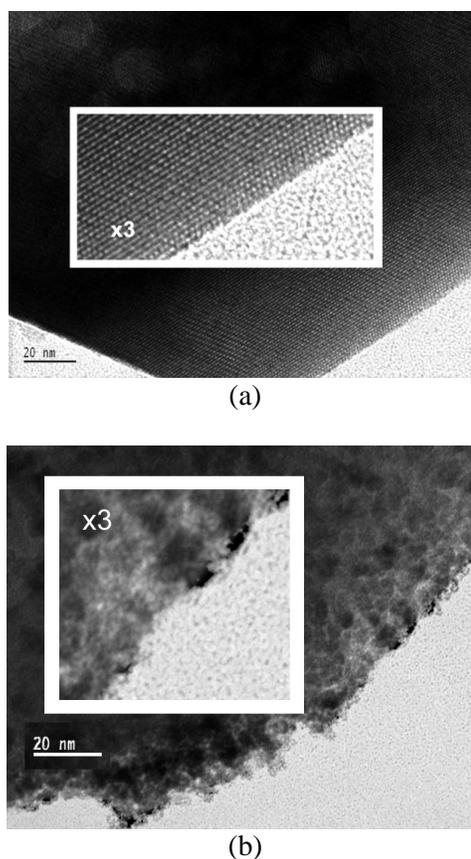


Fig. 1. (a) The native Cu-ZSM-5 catalyst, which is unstable under wet conditions. Note the sharp edge of the zeolite crystallite without the additive. (b) A uniform, optimized coating of CeO₂ over the surface of the Cu-ZSM-5 imparts high activity and selectivity to the catalyst even at high moisture contents. The layer thickness is about 20 nm.

Supercritical Carbon Monoxide Hydrogenation

Studying a mechanistically important catalytic reaction

The Chemical Engineering Division has accomplished cobalt carbonyl hydride catalyzed hydrogenation of carbon monoxide in a homogeneous supercritical carbon monoxide medium for the first time.

Considerable research on homogeneous catalysts for the hydrogenation of CO was undertaken in several laboratories in the late 1970s and early 1980s. The most studied of homogeneous CO hydrogenation catalysis systems is the cobalt carbonyl catalyzed reaction, which has been shown to follow a rate law that is first order in both $\text{HCo}(\text{CO})_4$ and H_2 pressure. The reaction is believed to proceed through an early coordinated formaldehyde intermediate that produces, dependent upon the reaction conditions and solvent, variable amounts of methanol, methyl formate, and ethylene glycol as initial reaction products. In the proposed mechanism, higher alcohols and higher formate esters are produced by secondary homologation and transesterification reactions associated mainly with the initially produced methanol and methyl formate.

Since most of the early kinetic studies on these systems were accomplished using high-pressure autoclaves, it seems possible that recent advances in high-pressure spectroscopic techniques that would allow in situ scrutiny of these systems might provide more information on them. We recently tested the use of a high-pressure toroid nuclear magnetic resonance (NMR) probe on the cobalt carbonyl catalyzed CO hydrogenation in supercritical carbon monoxide medium for the first time.

2003 Research Highlights

We used a single-phase homogeneous supercritical system containing catalyst and reactant gases to avoid gas-liquid mixing problems that might otherwise interfere with

kinetic studies in an unstirred NMR pressure vessel using conventional liquid media.

The reaction rate and products and the cobalt containing species associated with the catalytic reaction were measured in situ at 180 and 200 °C and at total pressures of hydrogen and carbon monoxide near 260 atm using a high-pressure NMR probe. The second order rate constant at 200 °C, $12 \times 10^{-8} \text{ s}^{-1} \text{ atm}^{-1}$, measured in supercritical carbon monoxide, is close to the reported value for the nonpolar solvent benzene ($15 \times 10^{-8} \text{ s}^{-1} \text{ atm}^{-1}$) and considerably smaller than that reported in the more polar solvent 2,2,2-trifluoroethanol ($84 \times 10^{-8} \text{ s}^{-1} \text{ atm}^{-1}$). The products of the reaction including methanol and methyl formate were quantified by in situ ^1H NMR, while in situ ^{59}Co NMR revealed cobalt carbonyl hydride and dicobalt octacarbonyl as the only detectable cobalt species. Separate experiments established that the homologation of methanol, the pathway for production of higher alcohols under CO hydrogenation conditions in polar solvents, did not occur to a measurable extent in the nonpolar supercritical CO medium used here.

The results in Table 1 show that the rate of CO hydrogenation in supercritical carbon monoxide medium is comparable to that measured in nonpolar benzene solution and considerably slower than that in the more polar media, 1,4-dioxane and trifluoroethanol. Rate measurements at 180 and 200 °C also show a strong temperature effect in supercritical carbon monoxide.

Methanol homologation to produce higher alcohols and the production of ethylene glycol are reactions favored by highly polar media and did not proceed to any measurable extent in the nonpolar supercritical CO medium. Our results also establish that kinetic studies of the homogeneous hydrogenation of carbon

Table 1. Second-Order Rate Constants, $k(2)$, for CO Hydrogenation in Various Solvents

Solvent	Temperature, °C	P (H ₂), atm	P (CO), atm	$k(2)$, atm ⁻¹ s ⁻¹
Benzene	200	145	145	15 x 10 ⁻⁸
1,4-dioxane	196	148	148	25 x 10 ⁻⁸
CF ₃ CH ₂ OH	200	153	153	84 x 10 ⁻⁸
scCO ₂	200	103	156	12 x 10 ⁻⁸
scCO ₂	180	103	156	4.8 x 10 ⁻⁸

monoxide are feasible in a supercritical medium in a high-pressure NMR probe. This is the case even though CO hydrogenation with the HCo(CO)₄ catalyst normally requires long reaction times under severe pressure and temperature conditions.

In future work on this system, accurate determinations of such parameters as activation barriers and kinetic isotope effects, afforded by high-pressure NMR in a gas-like medium that is highly amenable to theoretical calculations, will allow scrutiny of the early steps in this important reaction. The earlier work with autoclaves had established a strong temperature coefficient and a significant isotope effect on this system, but the uncertainties and complexities associated with sampling from autoclaves discouraged attempts to accurately determine these

parameters with the high-pressure techniques available at that time. Evaporation of the volatile HCo(CO)₄ into the autoclave headspace increased by removal of liquid samples, and uncertain quenching of samples containing this unstable species, are problems associated with autoclave sampling methods that are alleviated by the high-pressure NMR technique used here.

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

Research Participants

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In Situ NMR Analysis of Graphite Insertion Electrodes

Characterizing the structure and dynamics of lithium binding sites

This research seeks to obtain fundamental insight into the nature of the lithium binding sites and the mechanisms for lithium ion transport in important solid-state ion conductors. A component of this project involves the development of unique in situ NMR/electrochemical devices and NMR imaging methods for use with solid-state electrodes. The resultant compression cell imager allows the first true in situ NMR observations to be made on lithium insertion electrodes during the actual charge/discharge process. Theoretical computations of the lithium ion binding energies and the electric field anisotropy are performed by collaborators in the Argonne Chemistry Division for use in interpreting the NMR spectral details.

2003 Research Highlights

We have made significant enhancements to the original 2032-sized coin cell NMR detector, which was the first such device to simultaneously function as an electrochemical coin cell and a wide-line NMR detector. The resulting modified device, depicted in Figure 1, is referred to as the compression cell and its salient feature is a threaded plunger that applies active pressure to the electrode stack. Importantly, the plunger design and construction material were carefully selected to minimize distortions in the static magnetic field homogeneity to avoid adversely affecting the NMR line widths. The resulting improvement in the electrode-electrolyte contact allows more complete utilization of all the insertion electrode material as required for a true in situ spectroscopic device. We have tested the electrochemical performance metered by the ratio of theoretical to observed electrode capacity as a function of the charging rate. The entire cross section of the insertion electrode material is lithiated using the compression cell. Furthermore, the long-term viability of this

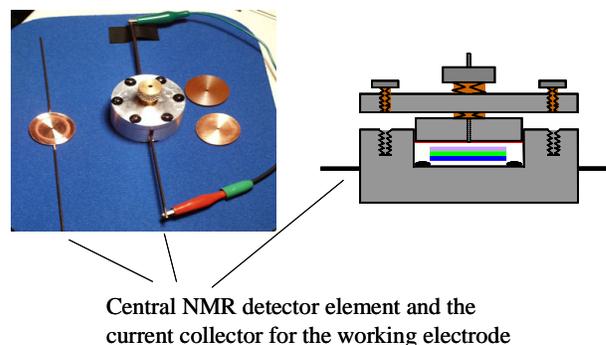


Fig. 1. Compression cell for in situ NMR analysis with simultaneous electrochemical cycling of standard 2032-sized coin cell battery stacks. At left, a photograph of an assembled cell and at right, a schematic depicting a typical electrochemical cell stack inside the compression cell.

device is remarkable for a cell that uses a single O-ring seal. One of these compression cells has been continuously cycled for more than a year with minimal capacity fade.

This device has sufficient NMR spectral resolution to simultaneously distinguish and follow the development of all of the lithium-containing species in the cell. The covalently bound lithium species that form at the solid-electrolyte interphase are spectrally well resolved near ± 6 ppm from the intercalated lithium species in the 10-150 ppm region of the spectrum. In addition, the ${}^7\text{Li}$ electric quadrupole satellite singularities in the NMR powder pattern for lithium ions at the hexagonally symmetric sites in graphite are readily observable using the compression cell yielding an absolute value of the nuclear electric quadrupole (e^2qQ/h) interaction, 45.1 kHz, that is similar to previously reported values. All of these ionic lithium spectral features are well resolved from the metallic lithium that is used as the counter electrode, which is observable at a Knight shift of 260 ppm.

Using this cell we have found evidence for a transient response for graphite insertion electrodes that has not been described previously. During the initial cycle of lithium insertion we observed a ^7Li NMR resonance feature that grows in near 17 ppm. This feature is reversible. It decays during the subsequent lithium deinsertion process upon reversing the current. In addition, this spectral feature is not observed on the second cycle. In contrast, we find on the second cycle only the formation of the standard ^7Li NMR signature for intercalated graphite near 47 ppm. Importantly, using the in situ method, we find that the transient feature at 17 ppm does not emerge below 0.16 V until nearly 17% lithium uptake has occurred. While ^7Li spectral features near 17 ppm are sometimes associated with irreversibly bound lithium, others have also proposed edge sites and high-stage lithiated graphite. The reversibility of the NMR resonance is sufficient to rule out the first possibility of irreversibly bound lithium while additional work on model compounds, described below, will be required to distinguish between the last two possibilities.

Carbonaceous materials have been extensively investigated for their ability to intercalate lithium. However, these materials are complex and very little is understood about the fundamental binding sites for lithium in these carbons. Our approach in future work toward

understanding the key issues that affect lithium binding is to conduct in situ ^7Li and ^{13}C NMR investigations on a series of model carbons with well-defined structures. Substrates such as pyrene, phenanthrene, and corannulene can be isotopically labeled with ^{13}C or ^2H to enhance the NMR measurements. We feel that there is a dearth of ^{13}C NMR chemical shift information for these materials and that the carbon nucleus should be a particularly sensitive probe of changes in the carbon hybridization (sp^2 versus sp^3) that can occur with lithium intercalation. The compression cell NMR probe is well suited for the analysis of carbonaceous materials because it is equally sensitive to amorphous as well as crystalline areas of the substrates. In addition, these experimental NMR studies will be compared with theoretical calculations on the same carbon systems, as has already been done by collaborators in the Chemistry Division for lithium complexes to anthracene and naphthalene.

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

Research Participants

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Analytical Chemistry Laboratory

The Analytical Chemistry Laboratory (ACL) operates in the Argonne National Laboratory 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 technical 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 handles about 500 jobs annually, most of which involve multiple samples.

The Inorganic Analysis Group uses wet-chemical and instrumental methods for elemental, compositional, and isotopic determinations in solid and liquid samples and provides specialized analytical services. Major instrumentation includes: inductively coupled plasma / atomic emission spectrometer; inductively coupled plasma / mass spectrometer; thermal ionization mass spectrometer; mercury analyzer; Karl Fischer titrator; C, H, N, and O analyzers; ion chromatograph, and microwave and muffle furnace digestion units.

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. Depending on the level of radioactivity, the work is performed in hot cells, gloveboxes, radiochemical hoods, and bench tops. Major instrumentation includes Inductively Coupled plasma/atomic emission spectrometer, ion chromatograph, alpha spectrometers, several gamma counters, beta scintillation counter, x-ray diffraction spectrometer, scanning electron microscope, and energy dispersive x-ray fluorescence apparatus.

The Organic Analysis Group uses a number of complementary techniques to separate organic compounds and measure them at trace levels. Analysis of volatile and semivolatile organic compounds and PCBs is performed in radioactive and non-radioactive samples. The group is also involved with chemical agent determination and the Waste Isolation Pilot Plant Headspace Gas Performance Demonstration Program. Major instrumentation includes purge-and-trap/gas chromatograph/mass spectrometer, gas chromatograph/mass spectrometer for semivolatiles, gas chromatographs with electron capture detectors for polychlorinated biphenyls, Fourier

Transform Infrared spectrometer with a microscope attachment, Fourier Transform Raman spectrometer, accelerated solvent extraction system, and automated supercritical fluid extraction system.

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, and quality assurance system that allows efficient processing of environmental samples and hazardous and mixed-waste samples, including those requiring chain-of-custody procedures.

In this year's annual report, four ACL projects are highlighted: (1) preparation of simulated samples of headspace gas that will occur in the waste-bearing containers destined for disposal in the Waste Isolation Pilot Plant, (2) the Tritium Target Project, (3) K_d determination for selected nuclides in soils, and (4) the isotopic analysis of high-burnup spent nuclear fuel.

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Performance Demonstration Program for 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 U.S. Department of Energy (DOE) installation, is the nation's first repository for the permanent disposal of defense-generated transuranic radioactive (TRU) waste generated from research and production of nuclear weapons at various DOE sites. The WIPP site is located in southeastern New Mexico, 26 miles east of Carlsbad and 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. Over the next 35 years, WIPP is expected to receive about 19,000 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. Among other characterizations of waste destined for WIPP, analysis of headspace gas for specified volatile organic compounds is required. The National TRU Program Office of DOE's Carlsbad Area Office has established a performance demonstration program (PDP) for laboratories that participate in the analysis of headspace gas to be shipped to the WIPP site. The Carlsbad Area Office grants approval to laboratories to analyze headspace gases if the laboratories are successful in analyzing blind audit samples of simulated headspace gases. The Chemical Engineering Division's Analytical Chemistry Laboratory (ACL) was selected as the laboratory to prepare, analyze, and distribute samples for the headspace gas PDP.

2003 Research Highlights

During 2003, Cycle 17A of the Headspace Gas Performance Demonstration Program (HSGPDP), 15 sets of HSGPDP samples were prepared. Each set consisted of five 6-L SUMMA[®] canisters at 6 psig containing mixtures of analytes at concentrations classified as: low, high, and special. A duplicate sample and a blank sample (containing ultra zero grade air) were also included in the set. Two sets of HSGPDP samples were sent to Rocky Flats Environmental Technology Site and two were sent to Los Alamos National Laboratory. One set each was sent to the following laboratories: Idaho National Engineering and Environmental Laboratory (INEEL) Environmental Chemistry Laboratory, INEEL Advanced Mixed Waste Treatment Project, the Central Characterization Project at the Savannah River Site (mobile vendor), the Central Characterization Project at the Nevada Test Site (mobile vendor), the Central Characterization Project at Argonne National Laboratory (mobile vendor), and Fluor Hanford. Four sets were prepared as backup samples and one set was prepared for verification analysis at Argonne National Laboratory-East

This work was funded by the U.S. Department of Energy, Waste Characterization Program, Carlsbad Field Office.

Research Participants

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Tritium Target Qualification Project

Helping the Nation to produce tritium

The 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.

Over the past four years, the Tritium Target Qualification Project (TTQP) at Pacific Northwest National Laboratory (PNNL) has developed a national capability to mass-produce the needed LiAlO_2 pellets. Since 1997, the Analytical Chemistry Laboratory in the Chemical Engineering Division has provided 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 was qualified.

2003 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 is the determination of 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.

Methodologies we established include a microwave-accelerated procedure for dissolving the refractory LiAlO_2 ceramic with acid; an inductively coupled plasma-optical emission spectrometry (ICP-OES) procedure 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. For the past year and a half, our methods were routinely applied by a qualified commercial analytical chemistry laboratory to the analysis of large-scale-production-lot pellets.

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 calibration, qualification of laboratories, and tracking the continuity of results over time.

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. Last 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. It is routinely used by the commercial laboratory in preparing its calibration standards.

Our characterization of the lithium aluminate control material (LACM), a LiAlO_2 powder produced by the TTQP as a control sample, was also validated last year. 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. Portions of the LACM that have been analyzed with every batch of inspection pellets evaluated by the qualified laboratory have shown notably consistent results.

Isotopic reference materials that we prepared by gravimetrically mixing certified standards were also provided to the qualified commercial laboratory. In addition, we sent them a set of check standards for testing laboratory performance in measuring lithium isotopes. These standards and check standards helped verify that the laboratory meets bias requirements for the lithium isotopic measurements.

Technology Transfer: The ultimate goal of our support to the TTQP was to transfer our methods to a commercial laboratory that would analyze production lot pellets. That goal was achieved last year when a laboratory contracted by DOE successfully completed an extensive qualification exercise, which entailed multiple analyses of the LACM, isotopic reference materials, and blind standard solutions that we

provided. Now qualified, the commercial laboratory has already processed the 40-pellet test samples from about nine lots, with excellent results. Some of the pellets from these lots have been incorporated into TPBAR assemblies, which were delivered in early September 2003 to the reactor in which they will be placed. This milestone event is documented in the photograph in Figure 1. It stands as a tribute to the success of the project, and that of our relatively modest but important role.



Fig. 1. Tritium-producing burnable absorber rods being delivered for installation in the nuclear reactor where they will be irradiated.

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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Distribution Coefficients Measurements of Soils

Helping to understand radionuclide migration

The Analytical Chemistry Laboratory (ACL) was requested to measure the distribution coefficients (K_d values) of several radionuclides in site specific soils. The definition of K_d is the equilibrium constant that describes the partition of a radionuclide or other analyte by adsorption between a solid phase (soil) and a liquid phase (groundwater). This relationship is expressed in units of L/Kg.

The results of the measurements are used in a variety of applications. For example, K_d values may be used for waste site suitability or remediation plans. Also, powerful modeling tools such as RESRAD (developed by Argonne National Laboratory) incorporates K_d along with other parameters as hydrology, precipitation rate, soil porosity, bulk density, and vadose zone thickness to understand radionuclide migration at specific sites.

2003 Research Highlights

The tests are performed in batches with a weighted portion of soil and known volumes of groundwater spiked with the pertinent isotopes. Typical suites of requested isotopes include

^{237}Np , ^{99}Tc , ^{239}Pu , ^{238}U , and ^{241}Am . The client supplies soil and groundwater that is spiked, added to a container and mixed for a proscribed time. The containers are centrifuged to separate most of the soil from the water. The water is also filtered through a 0.2- μ filter to further remove small particles.

The filtrate samples are analyzed primarily by inductively coupled plasma-mass spectrometry or by gamma spectrometry. The data show the ratio of the initial and final concentrations in each test. The amount of a spike analyte that is reduced is indicative of the adsorption qualities of the soil for that particular analyte.

The ACL has measured soils received from DOE facilities, including the Ashtabula site, and U.S. Ecology, a private-sector nuclear waste repository owner.

Research Participants

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Isotopic Analysis of High-Burnup Spent Nuclear Fuel

Providing data to benchmark codes for predicting nuclide inventories and fuel properties

As nuclear fuel is irradiated, its isotopic composition changes through depletion of fissile isotopes, accumulation of fission products and neutron-capture products, and decay of radioactive isotopes. After being removed from the reactor, the fuel's isotopic composition continues to change as radioisotopes decay. This history- and time-dependent nuclide composition of irradiated nuclear fuel determines its neutronic properties and radiological characteristics. Computational codes that accurately predict the nuclide inventory of nuclear fuels as a function of time and history are a mainstay of the nuclear industry and are used to evaluate such issues as (1) the neutron multiplication factor in criticality safety, (2) decay heat sources for thermal analysis, (3) neutron and gamma-ray sources for shielding and dose-rate analysis, and (4) radionuclide toxicity in waste management.

Interest among nuclear power producers has grown over the past few decades in higher utilization of nuclear fuel, which translates to achieving higher burnup (a measure of the number of fuel atoms that underwent fission). For this reason, the U.S. Nuclear Regulatory Commission (NRC) has fostered research to better understand the physical and compositional properties of high-burnup fuel and how these properties affect safety in handling spent fuel. Argonne's Energy Technology Division (ET) has worked with the NRC for several years to investigate materials issues related to storage of high-burnup fuel, including studies of hydrogen migration in cladding, thermal creep, and mechanical performance. Among other issues of interest to NRC is determining the reliability of existing computational codes for predicting nuclide inventories at burnup levels beyond those that are already validated (to about 40 GWd/MtU). Experimental data for isotopes in fuels with burnup higher than 40 GWd/MtU are limited. Data for some isotopes that are important to a concept called "burnup credit" are

very rare. Burnup credit refers to an allowance in safety analysis calculations for decreased reactivity in the fuel as a result of actinide depletion and a presence of neutron-absorbing irradiation products (poisons) that reduce the fuel's ability to achieve criticality. At high burnup, the decrease in reactivity can be substantial and might allow significant increases in the quantity of spent fuel that can be safely stored or transported in a single container, which could reduce storage and transportation costs.

Some fuel rods used in the ET studies have exceptionally high burnup (66 GWd/MtU, rod average) and, also important, have very well-documented histories. These fuel rods provide a special opportunity for generating isotopic data that might be compared with computational-code results at very high burnup. The Chemical Engineering Division has undertaken the task of analyzing specimens of fuel from these rods to determine actinide and fission product isotopes. The primary interest of NRC in these analyses was for isotopes needed to assign an experimental burnup value to the fuels, and for isotopes related to burnup credit considerations. Because the effort required to measure an array of additional isotopes is incremental, the analysis goals were extended to include isotopes that affect heat load, shielding, and criticality evaluations. An analysis scheme that can produce data for about 75 isotopes from a small number of operations has been applied to two very-high-burnup specimens.

2003 Research Highlights

In a first phase of our experimental work, we implemented procedures to dissolve irradiated uranium oxide fuel in our hot-cell facility, and accurately measure actinide and fission product isotopes needed for determining fuel burnup. The procedures were used to analyze a specimen of boiling water reactor fuel having a calculated burnup of 64 GWd/MtU. The objective of the

measurement was to produce an experimental burnup value that would allow a benchmark test of the code calculation. Abundances of U, Pu, and Nd isotopes were measured by thermal ionization mass spectrometry (TIMS) using elemental fractions isolated from the fuel solution with ion-exchange methods. Quantities of each element were determined by isotope dilution after mixing weighed portions of the fuel solution and a triple-spike solution containing ^{233}U , ^{242}Pu , and ^{150}Nd separated isotopes. The U and Pu spikes were standardized against certified reference materials (New Brunswick Laboratory) and the Nd spike against natural Nd. The fission product ^{148}Nd was used for calculating the burnup in accordance with the ASTM designation E-321. The code-predicted burnup value agreed well with that derived from our isotopic data.

In a second phase of our task, two specimens of fuel that had been irradiated to very high burnup (estimated at 72 GWd/MtU) in a pressurized water reactor were dissolved and analyzed. The analysis scheme for these specimens again used TIMS and isotope dilution to achieve high accuracy for the U, Pu, and Nd isotopes. When the Nd fraction for TIMS analysis was isolated, we selectively eluted fractions containing Sm, Eu, and Gd, which were analyzed with inductively coupled plasma-mass spectrometry (ICP-MS) to obtain isotope abundances for each of these rare earths. A diluted portion of the raw fuel solution was also analyzed by ICP-MS to quantify individual isotopes that are free of isobaric interferences (i.e., do not have the same mass number as an isotope of another element). Because the list of isobar-free nuclides includes at least one isotope of Sm, Eu, and Gd, the quantitative ICP-MS data could be combined with the ICP-MS isotopic data for these elements to quantify all of their isotopes. Gamma spectrometry measurements with a portion of the dissolved fuel provided data for ^{106}Ru , ^{125}Sb , ^{134}Cs , ^{137}Cs , ^{144}Ce , ^{154}Eu , ^{155}Eu , and ^{241}Am . Alpha pulse height analysis was carried out on a portion of the raw fuel solution, on the separated plutonium fraction, and on a fraction containing Am and Cm eluted from the same ion exchange column used for separating the rare

earths. Because the amounts of ^{239}Pu and ^{240}Pu in each fuel were accurately known from the TIMS data, alpha activity ratios in these spectra allowed reliable quantitation of ^{238}Pu , ^{244}Cm , and ^{241}Am , and a fairly good measurement of ^{243}Am . Analyzing the Am/Cm fraction with the TIMS gave a better estimate of ^{243}Am as well as values for ^{245}Cm , ^{246}Cm , ^{247}Cm , ^{248}Cm , and ^{250}Cm .

With the relatively few operations involved in the TIMS/isotope dilution, gamma, ICP-MS, and alpha spectrometric measurements, data were developed for burnup-credit isotopes, radiation source isotopes, and heat-load sources.

This work has demonstrated that a great deal of information is obtainable with fairly reasonable effort by using currently available methodology, if moderate accuracy can be tolerated. The ICP-MS proved to be a particularly productive tool in determining the many stable or very long-lived isotopes of interest for burnup credit applications. Some of the isotopes we measured (^{103}Rh , ^{95}Mo , ^{101}Ru) have not been reported previously for high burnup fuels.

Compilation and review of the data are still in progress. An early estimate of the fuel burnup from the isotopic data suggests agreement with the calculated prediction of 72 GWd/MtU. Several isotopes that were measured by more than one method showed good consistency. For example, ^{143}Nd and ^{145}Nd from the ICP-MS agreed with the TIMS data. ^{154}Eu and ^{155}Eu from the ICP-MS agreed well with gamma results. And ^{241}Am from gamma agreed with that from the alpha spectra.

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Research Participants

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Presented at the Int. Conf. on Powder Metallurgy and Particulate Materials, Las Vegas, NV, June 8–12, 2003

Preparation of Uranium Chloride

A. A. Frigo, L. S. Chow, J. K. Basco, J. L. Willit, and W. E. Miller

Presented at 27th Actinide Separations Conference, Argonne, IL, June 9-12, 2003

Stabilization of LiMn_2O_4 Spinel Electrodes for Lithium Batteries

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

Presented at the Int. Conf. on Polymer Batteries and Fuel Cells, Jeju Island, Korea, June 1–6, 2003

Effects of Multicomponent Fuels, Fuel Additives, and Fuel Impurities on Fuel Reforming

J. P. Kopasz, L. E. Miller, and D. V. Applegate

Presented at the Int. Future Transportation Technology Conf., Costa Mesa, CA, June 23–25, 2003

Transition Metals on Oxide Ion Conducting Supports as Reforming Catalysts for Fuel Cell Systems

T. R. Krause, C. Rossignol, M. Ferrandon, J. P. Kopasz, J. Mawdsley, and J.-M. Bae

Presented at the 18th North Am. Catalysis Soc. Meeting, Cancun, Mexico, June 1–6, 2003

Patents and Selected Publications and Presentations

In-Situ X-Ray Absorption Spectroscopy of Electrochemically Induced Phase Changes in Lithium-Doped InSb

A. J. Kropf, C. S. Johnson, J. T. Vaughey, and M. M. Thackeray
Presented at the 12th Int. Conf. on X-Ray Absorption Fine-Structure Spectroscopy (XAFS XII), Malmö, Sweden, June 22–27, 2003

XAFS Analysis of Layered $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$ ($0 < x \leq 2$) Electrodes for Lithium Batteries

A. J. Kropf, C. S. Johnson, J. T. Vaughey, and M. M. Thackeray
Presented at the 12th Int. Conf. on X-ray Absorption Fine-Structure Spectroscopy, Malmö, Sweden, June 22–27, 2003

A Bent Silicon Crystal in the Laue Geometry to Resolve X-ray Fluorescence for X-ray Absorption Spectroscopy

A. J. Kropf, C. Karanfil, C. U. Segre, L. D. Chapman, and G. Bunker
Presented at the 12th Int. Conf. on X-Ray Absorption Fine-Structure Spectroscopy (XAFS XII), Malmö, Sweden, June 22–27, 2003

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

A. J. Kropf, J. T. Miller, and C. L. Marshall
Presented at the 12th Int. Conf. on X-Ray Absorption Fine-Structure Spectroscopy (XAFS XII), Malmö, Sweden, June 22–27, 2003

Diesel Reforming in a Kilowatt Scale Autothermal Reformer with Liquid Injection

D.-J. Liu, H.-K. Liao, L. E. Miller, and S. Ahmed
Presented at 2003 Future Transportation Technology Conference, Costa Mesa, CA, June 23-25, 2003

Diesel Reforming for Fuel Cell Application in a 1- to 5-Kilowatt ATR Reformer

D.-J. Liu, H.-K. Liao, L. E. Miller, and S. Ahmed
Presented at 18th North American Meeting of the North American Catalysis Society, Cancun, Mexico, June 1-6, 2003

Sono Synthesis and Characterization of Nanophase Hydrodesulfurization Catalysts

D. Mahajan, M. J. Castagnola, C. L. Marshall, A. J. Kropf, M. Serban, and J. Hanson
Presented at 18th North American Catalysis Society Meeting, Cancun, Mexico, June 1-6, 2003

Desulphurization of Gasoline, Distillate, and Heavy Feeds to Meet the Environmental Needs of the 21st Century

C. L. Marshall
Presented at the 18th North Am. Catalysis Soc. Meeting, Cancun, Mexico, June 1–6, 2003

Modeling the Performance of Lithium-Ion Batteries for Fuel Cell Vehicles

P. A. Nelson, D. W. Dees, K. Amine, and G. L. Henriksen
Presented at International Future Transportation Technology Conference, Society of Automotive Engineers, Costa Mesa, CA, June 23-25, 2003

Bifunctional Catalysts for the Selective Catalytic Reduction of NO by Hydrocarbons

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

Presented at the North Am. Catal. Soc. 18th Annual Meeting, Cancun, Mexico, June 1–6, 2003

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

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

Presented at the 12th Int. Conf. on X-ray Absorption Fine-Structured Spectroscopy

$\text{Ln}_{1-x}\text{Sr}_x\text{CoO}_3$ (Ln=Gd, Pr) as a Cathode for Intermediate-Temperature Solid Oxide Fuel Cells

C. Rossignol, J. M. Ralph, J.-M. Bae and J. T. Vaughey

Presented at 14th International Conference on Solid State Ionics, Monterey, CA, June 22-27, 2003

Efficiency Improvements and Scale-up for Uranium Electrowinning

J. L. Willit, R. J. Blaskovitz, and J. Figueroa

Presented at 27th Actinide Separations Conference, Argonne National Laboratory, Argonne, IL, June 9-12, 2003

Metallic Bipolar Plate Supported Solid Oxide Fuel Cell ("TuffCell")

J. D. Carter, T. A. Cruse, R. Kumar, and D. J. Myers

Presented at 2003 Hydrogen and Fuel Cells Merit Review Meeting, Berkley, CA, May 19-22, 2003

Water-Gas Shift Catalysis

S. Y. Choung, J. Krebs, M. Ferrandon, R. Souleimanova, D. J. Myers, and T. R. Krause

Presented at 2003 Hydrogen and Fuel Cells Merit Review Meeting, Berkeley, CA, May 19-22, 2003

A Glovebox System for Handling Materials that Emit Low-Penetrating Ionizing Radiation

A. A. Frigo

Presented at 2003 American Glovebox Society Standards Development Committee and Outreach Meeting, Oak Ridge, TN, May 7, 2003

LiFePO_4 as Cathode Material for Rechargeable Lithium-Ion Batteries

L. Agyarko, I. Belharouak, and K. Amine

Presented at the 30th Annual Conference of the Organization for the Professional Advancement of Black Chemists and Chemical Engineers, Indianapolis, IN, April 13-19, 2003

Structured Catalysts for Autothermal Reforming of Hydrocarbon Fuels

J.-M. Bae, S. Ahmed, R. Kumar, and E. Doss

Presented at the Conf. on Fuel Cell Science, Engineering and Technology, Rochester, NY, April 21–23, 2003

Patents and Selected Publications and Presentations

Application of Cathode Materials to Co-Sintered Metal Supported SOFC

J. D. Carter, T. A. Cruse, J.-M. Bae, J. M. Ralph, C. Rossignol, D. J. Myers, R. Kumar, and M. Krumpelt

Presented at American Ceramic Society Annual Meeting, Nashville, TN, April 27-30, 2003

Electroactive Poly-Dilithium Phthalocyanine Coatings for Lithium Battery Materials

N. P. Fackler and C. S. Johnson

Presented at 203rd Electrochemical Society Meeting, Paris France, April 28-May 2, 2003

Electrochemical Investigation of the Uranium Exchange Current Density in LiCl-KCl

V. Goss

Presented at the Annual Meeting of the National Organization for the Professional Advancement of Black Chemists and Chemical Engineers, Indianapolis, IN, April 15, 2003

Enhanced Electrochemical Stability of Colloidal Metal Oxide Coated Spinel LiMn_2O_4 Electrodes

C. S. Johnson, K. Lauzze, D. P. Abraham, N. L. Dietz, and M. M. Thackeray

Presented at the 203rd Electrochem. Soc. Meeting, Paris, France, April 27–May 2, 2003

XAFS Analysis of Layered $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$ ($0 < x \leq 2$) Electrodes for Lithium Batteries

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

Presented at 12th Users' Meeting for the Advanced Photon Source, Argonne, IL, April 29-May 1, 2003

Fuel Processing for Mobile Fuel Cell Systems

M. Krumpelt, T. R. Krause, and J. P. Kopasz

Presented at First International Conference on Fuel Cell Science, Engineering and Technology, Rochester, NY, April 21-23, 2003

An In-Situ, Real-Time XANES and EXAFS Characterization of Noble Metal Catalyst Perovskite Catalysts for Producing Hydrogen Using Gasoline Fuel

J. R. Mawdsley, T. R. Krause, and J. P. Kopasz

Presented at the 105th Annual Meeting & Exposition of the Am. Ceram. Soc., Nashville, TN, April 27–30, 2003

Perovskite Catalysts for Producing Hydrogen from Gasoline Surrogates

J. R. Mawdsley, T. R. Krause, J. P. Kopasz, and J. Critchfield

Presented at 105th Annual Meeting of the American Ceramic Society, Nashville, TN, April 30, 2003

Liquid Metal Interactions on Ceramic Surfaces in Advanced Nuclear Energy Applications

S. M. McDeavitt, J. M. Runge, L. Leibowitz, J. E. Indacochea, and L. A. Barnes

Presented at ICONE 11, Eleventh International Conference on Nuclear Engineering, Tokyo, Japan, April 20-23, 2003

The Role of A-Site Deficiency in the Performance of Sr-Doped Lanthanum Ferrite Cathodes for SOFCs

J. M. Ralph, C. Rossignol, and J. T. Vaughey

Presented at 105th Annual Meeting & Exposition of the Am. Ceram. Soc., Nashville, TN, April 27–30, 2003

Using In-Situ Formed Magnetite for the Removal of Sr and Actinides from Tank Waste at the Savannah River Site

H. A. Arafat, S. B. Aase, A. V. Gelis, M. C. Regalbuto, J. Sedlet, and G. F. Vandegrift

Presented at the AIChE Spring 2003 National Meeting, New Orleans, LA, March 30–April 3, 2003

Removal of Sr and Actinides from Alkaline Tank Waste Using In Situ Formed Mixed Iron Oxides (IS-MIO)

H. A. Arafat, S. B. Aase, A. V. Gelis, M. C. Regalbuto, J. Sedlet, and G. F. Vandegrift

Presented at the AIChE Spring 2003 National Meeting, New Orleans, LA, March 30–April 3, 2003

Glass Degradation Model for Contact by Humid Air, Dripping Water, and Immersion

W. L. Ebert, R. A. Olson, J. A. Fortner, and N. L. Dietz

Presented at the Am. Nucl. Soc. Int. High-Level Radioactive Waste Management Conf., Las Vegas, NV, March 30–April 2, 2003

Re-evaluating Neptunium in Uranyl Phases Derived from Corroded Spent Fuel

J. A. Fortner, R. J. Finch, A. J. Kropf, and J. C. Cunnane

Presented at the 10th Int. High-Level Radioactive Waste Management Conf. (IHLRWM), Las Vegas, NV, March 30–April 3, 2003

Re-evaluating Neptunium in Uranyl Phases Derived from Corroded Spent Fuel

J. A. Fortner, R. J. Finch, A. J. Kropf, and J. C. Cunnane

Presented at the 225th Am. Chem. Soc. National Meeting & Exposition, New Orleans, LA, March 23–27, 2003

Aqueous Colloids from Corrosion of Metallic Uranium Fuel: A SAXS and TEM Study

J. A. Fortner, C. J. Mertz, M. M. Goldberg, and S. Seifert

Presented at the 225th Am. Chem. Soc. National Meeting & Exposition, New Orleans, LA, March 23–27, 2003

Toroid Cavity Detectors for Homogeneous Catalysis Studies in Supercritical Fluids

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

Presented at the 44th Experimental Nuclear Magnetic Resonance Conf., Savannah, GA, March 30–April 4, 2003

Electrochemical Investigation of the Uranium Exchange Current Density in LiCl-KCl Eutectic

V. Goss, K. V. Gourishankar, and J. L. Willit

Presented at the 132nd TMS Annual Meeting and Exhibition, San Diego, CA, March 2–6, 2003

Patents and Selected Publications and Presentations

Electrochemical Reduction of Spent Oxide Fuel

K. V. Gourishankar, L. Redey, and D. J. Graziano

Presented at the 132nd TMS Annual Meeting and Exhibition, San Diego, CA, March 2–6, 2003

Dissolution Behavior of Irradiated Thoria-Urania Fuel in Oxidizing Groundwater at 90°C

J. L. Jerden and J. C. Cunnane

Presented at the 2003 Int. High-Level Radioactive Waste Management Conf., Las Vegas, NV, March 30–April 2, 2003

Effects of Additives and Impurities on the Reforming of Gasoline

J. P. Kopasz, L. E. Miller, D. V. Applegate and S. Ahmed

Presented at the AIChE Spring National Meeting, New Orleans, LA, March 30–April 3, 2003

Pt, Rh, and Ni Supported on Oxide-Ion-Conducting Substrates as Catalysts for Generating H₂ for Fuel Cells

T. R. Krause, C. Rossignol, M. Ferrandon, J. P. Kopasz, and J.-M. Bae

Presented at the AIChE Spring 2003 National Meeting, New Orleans, LA, March 30–April 3, 2003

Challenges of Converting Diesel Fuel to Hydrogen-Rich Reformate

M. Krumpelt, J. P. Kopasz, and D.-J. Liu

Presented at Fuel Cells 2003 Conference, Stamford, CT, March 31–April 1, 2003

Study of the Hydroxocarbonate Speciation of Plutonium(VI) in Alkaline Media

I. Laszak, A. V. Gelis, M. P. Jensen, and K. L. Nash

Presented at the 225th ACS National Meeting, New Orleans, LA, March 23–27, 2003

Cermet Nuclear Fuel Fabrication by Powder Metallurgy Methods

S. M. McDeavitt, M. C. Hash, A. S. Hebden, J. M. Runge, C. T. Snyder, and A. A. Solomon

Presented at the 132nd TMS Annual Meeting and Exhibition, San Diego, CA, March 2–6, 2003

Pyrochemical Separations of TRU and Fission Product Content from Metal Alloy Fuels

M. K. Richmann, W. E. Miller, Z. Tomczuk, and D. J. Graziano

Presented at the 132nd Annual Meeting and Exhibition, San Diego, CA, March 2–6, 2003

Progress in Coal Liquefaction Including a Discussion of Wilsonville Data

A. M. Valente and D. C. Cronauer

Presented at the 225th Am. Chem. Soc. National Meeting & Exposition, New Orleans, LA, March 23–27, 2003

Sulfur Removal from Reformate

X. Wang, T. R. Krause, and R. Kumar

Presented at the 225th Am. Chem. Soc. National Meeting & Exposition, New Orleans, LA, March 23–27, 2003

Recent Advances in Uranium High Throughput Electrorefining

J. L. Willit, G. A. Fletcher, R. J. Blaskovitz, J. Figueroa, and M. A. Williamson

Presented at the 132nd TMS Annual Meeting and Exhibition, San Diego, CA, March 2–6, 2003

TEM Analysis of an Actinide-Bearing Sorbent: Monosodium Titanate

N. L. Dietz, M. C. Duff, and D. T. Hobbs

Presented at the VII InterAmerican Congress on Electron Microscopy, Microscopy and Microanalysis 2003 Conf., San Antonio Convention Center, San Antonio, TX, August 3–7, 2003

ANL UREX+ Lab-Scale Demonstration Results

G. F. Vandegrift, M. C. Regalbuto, S. Aase, H. Arafat, A. Bakel, D. Bowers, J. P. Byrnes, M. A. Clark, J. W. Emery, J. R. Falkenberg, A. V. Gelis, C. Pereira, L. Hafenrichter, Y. Tsai, K. J. Quigley, and M. H. Vander Pol

Presented at Advanced Fuel Cycle Initiative Semi-Annual Meeting, Santa Fe, NM, August 26-28, 2003

AMUSE Code Update

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

Presented at Advanced Fuel Cycle Initiative Semi-Annual Meeting, Santa Fe, NM, August 26-28, 2003

Development of Engineering Product Storage Concepts

M. D. Kaminski, G. F. Vandegrift, J. Laidler, E. Bakker, and W. Culbreth

Presented at Advanced Fuel Cycle Initiative Semi-Annual Meeting, Santa Fe, NM, August 26-28, 2003

Interfacial Aspects of Ceramic-Metal Brazing

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

Presented at the AWS-ASM Int. IBSC Brazing and Soldering Conf., San Diego, CA, February 17–19, 2003

Fuel Cell Vehicle Developments

W. F. Podolski and P. Davis

Presented at the Fuels, Lubricants, and Engineers Conf., Charleston, SC, February 25–26, 2003

NMR Technology for *In Situ* Analyses of Coin Cells

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

Presented at the 5th IBA-HBC Yeager Memorial Symp., Waikoloa Beach, HI, January 7–10, 2003

Electrode Development for Solid Oxide Fuel Cells

J. M. Ralph, C. Rossignol, D. J. Myers, and R. Kumar

Presented at the 5th IBA-HBC Yeager Memorial Symp., Waikoloa Beach, HI, January 7–10, 2003

Patents and Selected Publications and Presentations

Development of the AMUSE Code

M. C. Regalbuto, G. F. Vandegrift, A. J. Bakel, J. M. Copple, and C. Pereira
Presented at the Advanced Nuclear Fuel Cycle Initiative Quarterly Review,
Albuquerque, NM, January 21–24, 2003

Bipolar Plate-Supported Solid Oxide Fuel Cells for Auxiliary Power Units

J. D. Carter, T. A. Cruse, J.-M. Bae, J. M. Ralph, D. J. Myers, M. Krumpelt, and R. Kumar
Presented at the Mater. Res. Soc. Fall 2002 National Meeting, Boston, MA, December 2–
6, 2002

The Behavior of Light Water Reactor Fuel After the Cladding Is Breached Under Unsaturated Test Conditions

J. C. Cunnane, J. Fortner, and R. J. Finch
Presented at the Mater. Res. Soc. Fall 2002 National Meeting, Boston, MA, December 2–
6, 2002

Accounting for EBR-II Metallic Waste Form Degradation in TSPA

W. L. Ebert, M. A. Lewis, T. L. Barber, and S. G. Johnson
Presented at the Mater. Res. Soc. Fall 2002 National Meeting, Boston MA, December 2–
6, 2002

Neptunium Substitution into the Structure of Alpha-U₃O₈

R. J. Finch and A. J. Kropf
Presented at the Mater. Res. Soc. Fall 2002 National Meeting, Boston, MA, December 2–
6, 2002

Observations on Aqueous Colloid Formation during High Level Waste Glass Corrosion

J. A. Fortner, C. J. Mertz, and J. C. Cunnane
Presented at the Mater. Res. Soc. Fall 2002 National Meeting, Boston, MA, December 2–
6, 2002

Natural Groundwater Colloids from the USGS J-13 Well in Nye County, NV: A Study Using SAXS and TEM

J. A. Fortner, C. J. Mertz, and P. R. Jemian
Presented at the Mater. Res. Soc. Fall 2002 National Meeting, Boston, MA, December 2–
6, 2002

Radionuclide Release Rates From Spent Fuel Rod Segments

M. M. Goldberg and Y. Tsai
Presented at the Mater. Res. Soc. Fall 2002 National Meeting, Boston, MA, December 2–
6, 2002

Effects of Iron and pH on Glass Dissolution Rate

S.-Y. Jeong and W. L. Ebert
Presented at the Mater. Res. Soc. Fall 2002 National Meeting, Boston, MA, December 2–
6, 2002

Dissolution Behavior and Fission Product Release from Irradiated Thoria-Urania Fuel in Groundwater at 90°C

J. L. Jerden and J. C. Cunnane

Presented at the Mater. Res. Soc. Fall 2002 National Meeting, Boston, MA, December 2–6, 2002

High-Pressure NMR in Homogeneous Catalysis

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

Presented at the Workshop on Selectivity in Catalysis, Argonne National Laboratory, Argonne, IL, December 3, 2002

Dissolution of a Multiphase Waste Form

M. A. Lewis, N. L. Dietz, and T. H. Fanning

Presented at the Mater. Res. Soc. Fall 2002 National Meeting, Boston, MA, December 2–6, 2002

Ceramic Waste Form Dissolution Behavior in Silicate Groundwater

M. A. Lewis, N. L. Dietz, and T. H. Fanning

Presented at the Fall Meeting of the Mater. Res. Soc., Boston, MA, December 2–6, 2002

Understanding the Behavior and Stability of Some Uranium Mineral Colloids

C. J. Mertz, J. A. Fortner, and Y. Tsai

Presented at Mater. Res. Soc. Fall 2002 National Meeting, Boston, MA, December 2–6, 2002

Diffraction Space Mapping of Epitaxy, Strain, and Twinning in $Mb_{a_2}Cu_3O_{7-x}$ Thin Films on $SrTiO_3$ (100) Substrates

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. Fall 2002 National Meeting, Boston, MA, December 2–6, 2002

Argonne National Laboratory (ANL) Progress in Minimizing Effects of LEU Conversion on Calcination of Fission Product ^{99}Mo Acid Waste Solution

A. J. Bakel, K. J. Quigley, and G. F. Vandegrift

Presented at the 24th Int. RERTR Meeting, San Carlos de Bariloche, Argentina, November 3–8, 2002

Improved Materials and Cell Design for Mechanically Robust Solid Oxide Fuel Cells

J. D. Carter, J. M. Ralph, J.-M. Bae, T. A. Cruse, C. Rossignol, M. Krumpelt, and R. Kumar

Presented at the 2002 Fuel Cell Seminar, Palm Springs, CA, November 18–21, 2002

A Novel Approach to Making Metallic Interconnects for Planar Solid Oxide Fuel Cells

T. A. Cruse, J.-M. Bae, J. D. Carter, R. Kumar, and M. Krumpelt

Presented at the 2002 Fuel Cell Seminar, Palm Springs, CA, November 18–21, 2002

Auto-thermal Reforming Catalysis

T. R. Krause, J. Mawdsley, J. D. Carter, M. Krumpelt, C. Rossignol, and J. P. Kopasz
Presented at the 2002 Fuel Cell Seminar, Palm Springs, CA, November 18–21, 2002

Hydrogen Generation via Fuel Reforming

J. Krebs
Presented at the Int. Workshop on Hydrogen in Materials & Vacuum Systems,
Newport News, VA, November 11–13, 2002

Argonne National Laboratory Progress in Developing a Target and Process for Converting CNEA Molybdenum-99 Production to Low-Enriched Uranium

G. F. Vandegrift, A. V. Gelis, S. B. Aase, A. J. Bakel, E. Freiberg, Y. Koma, and C. Conner
Presented at the 24th Int. RERTR Meeting, San Carlos de Bariloche, Argentina,
November 3–8, 2002

High-Power Lithium-Ion Batteries with Improved Calendar Life and Safety

K. Amine, J. Liu, Y. Hyung, I. Belharouak, and G. L. Henriksen
Presented at the 43rd Battery Symp., Fukuoka, Japan, October 12–14, 2002

An Investigation of the Impedance Rise and Power Fade in High-Power, Li-Ion Cells

I. Bloom, S. A. Jones, V. S. Battaglia, E. G. Polzin, G. L. Henriksen, C. G. Motloch,
J. P. Christophersen, J. R. Belt, C. D. Ho, R. B. Wright, R. G. Jungst, H. L. Case, and
D. H. Doughty
Presented at the 19th Int. Electric Vehicle Symp. (EVS-19), the Answer for Clean
Mobility, Busan, South Korea, October 19–23, 2002

Characterization of Actinide Removal Mechanisms for High-Level Waste Treatment: Application of X-ray Absorption Fine Structure (XAFS) Spectroscopic Techniques

M. C. Duff, D. B. Hunter, D. T. Hobbs, M. J. Barnes, S. D. Fink, Z. Dai, J. P. Bradley,
N. L. Dietz, and J. A. Fortner
Presented at the 29th Annual Meetings of the Federation of Analytical Chemistry and
Spectroscopy Societies (FACSS), Providence, RI, October 13–17, 2002

Phase Transitions in Lithiated Intermetallic Anodes for Lithium Batteries—In Situ XRD Studies

L. Fransson, K. Edstrom, J. T. Vaughey, and M. M. Thackeray
Presented at the 202nd Electrochem. Soc. Fall Meeting, Salt Lake City, UT, October 20–
25, 2002

Synthesis and Electrochemical Properties of Layered $\text{Li}(\text{Ni}, \text{MnM}')\text{O}_{2-y}\text{F}_y$ ($\text{M}' = \text{Al}, \text{Co}, \text{Ti}$, $0 \leq y \leq 0.1$) Cathode Materials

S.-H. Kang, Y. K. Sun, and K. Amine
Presented at the 202nd Electrochem. Soc. Fall Meeting, Salt Lake City, UT, October 20–
25, 2002

Electrochemical Evaluation of $x\text{Li}_2\text{TlO}_3 \bullet (1-x)\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ ($0 \leq x \leq 0.31$) Electrodes for Lithium-Ion Batteries

J.-S. Kim, C. S. Johnson, J. T. Vaughey, A. J. Kropf, and M. M. Thackeray
Presented at the ECS Fall Meeting, Salt Lake City, UT, October 20–25, 2002

Improved Spinel Lithium Manganese Oxide as Cathode for High Power Battery for HEV Application

J. Liu, K. Xu, T. R. Jow, and K. Amine

Presented at the 202nd Electrochem. Soc. Fall Meeting, Salt Lake City, UT, October 20–25, 2002

The Role of Interfaces in Ceramic-Metal Bonding

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

Presented at ASM International Materials Solutions 2002, International Conference on Joining of Advanced and Specialty Materials 5, Columbus, OH, October 8-9, 2003

Low-Temperature Powder Metallurgy Method for the Fabrication of Cermet Inert Matrix Fuels

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

C. T. Snyder, and L. A. Barnes

Presented at the Inert Matrix Fuel 8th Meeting, JAERI Tokai, Ibaraki, Japan, October 16–18, 2002

Development of Advanced Fuel Processors for Fuel Cell Vehicles

J. F. Miller, S. Ahmed, R. Kumar, S. H. D. Lee, and C. Pereira

Presented at the 19th Int. Battery, Hybrid and Fuel Cell Electric Vehicle Symp. and Exhibition, Seoul, Korea, October 19–23, 2002

Use of a Model to Delineate Sources of Impedance Rise in Two Li-ion Cell Chemistries

B. G. Potter, S. A. Jones, G. L. Henriksen, C. Motloch, J. Christophersen, J. Belt, and I. Bloom

Presented at the 202nd Electrochem. Soc. Meeting, Salt Lake City, UT, October 20–25, 2002

Electrode Materials for Solid Oxide Fuel Cells

J. M. Ralph, C. Rossignol, and R. Kumar

Presented at the 202nd Electrochem. Soc. Fall Meeting, Salt Lake City, UT, October 20–25, 2002

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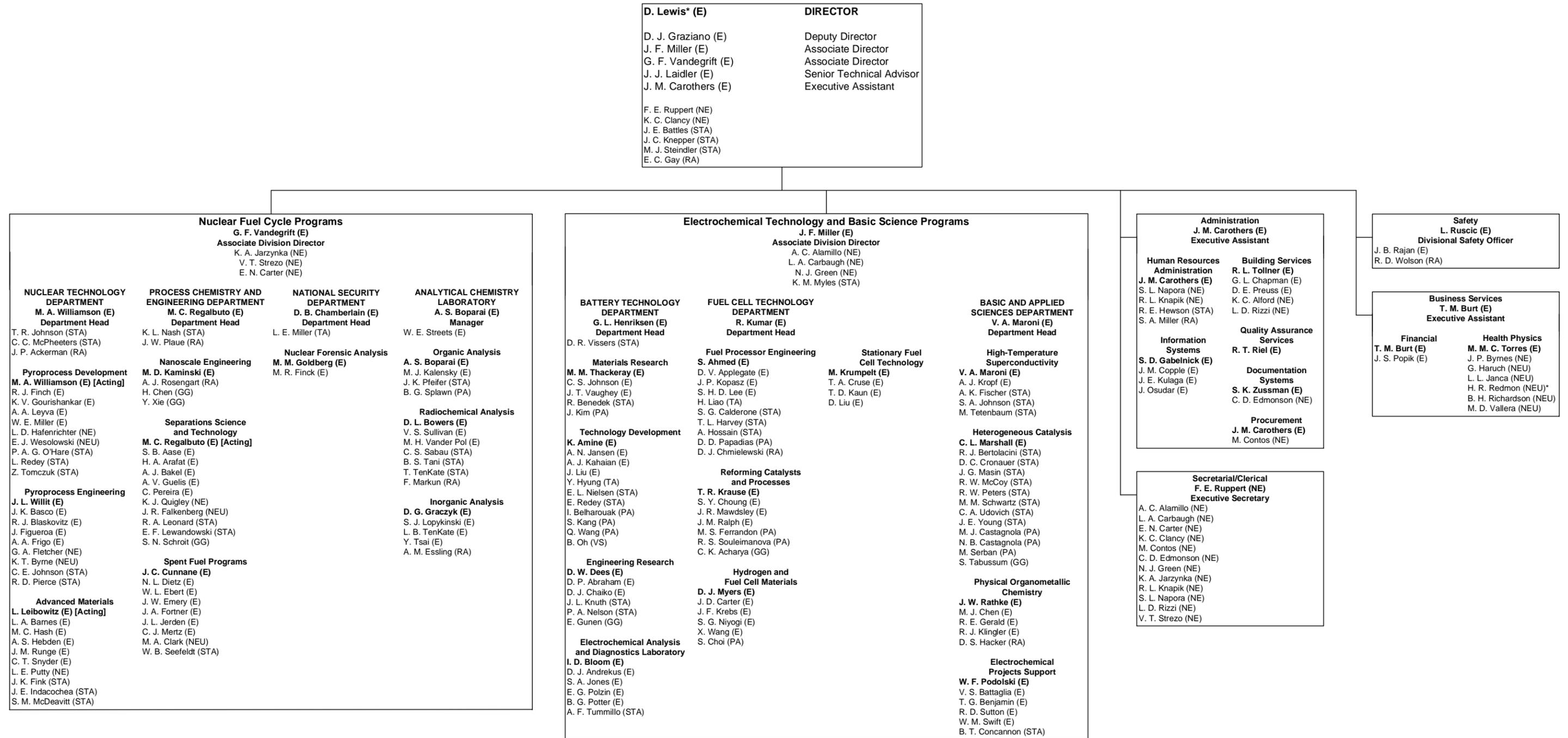
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