ABSTRACTS

Poster Session
for
Materials Science Division

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Hosted by
Chemical Engineering Division
David Lewis, Director

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CATALYSIS

Catalytic Destruction of Chemical Threats in Human-Occupied Spaces

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In this project, we are investigating the use of catalysts to purify an air supply after a chemical attack. Traditionally, adsorbent beds are utilized to remove chemical agents from the air supply, however, this type of protection has several limitations. Adsorbents have a limited capacity, and common air contaminants like smoke, can further decrease the capacity for the toxic agents. In addition, after use the adsorbent beds must be disposed of as highly toxic waste, since the adsorbent concentrates the toxic agent. Catalytic destruction breaks the chemical agents down to non-toxic components. Most catalysts are easily poisoned by the chemical agents, rendering them inactive. The Argonne catalyst has demonstrated resistance to poisoning and in early tests, demonstrated destruction efficiencies of > 99.9999

New Supports for the Catalytic Removal of Sulfur from Heavy Oils

Christopher L. Marshall, Manuela Serban, and Lillian Ruscic

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Hydrodesulfurization (HDS) represents a crucial component of current petroleum refining operations in terms of both environmental and economic considerations. At the same time that crude oils are becoming heavier, with increasing amounts of sulfur, product regulations are becoming increasingly more stringent. Therefore, new support materials and new active phases for high-performance HDS catalysts are needed. In the early 1990s a new material, MCM-41, a mesostructured molecular sieve was developed. This material has a uniform, one-dimensional and hexagonal pore structure in the range of 20-100 Å. Because of its large pore diameter and uniform pore distribution, MCM-41 was being investigated as a size-selective support for HDS catalysis. Tests of the optimized catalyst with a high-sulfur, heavy oil show that the catalyst is effective for desulfurization of these heavier materials. The catalyst appears to break aliphatic bonds in the first step, allowing the DBT-like molecular species to enter the pores for desulfurization.

Bifunctional Catalysts for the Selective Catalytic Reduction of NOx by Hydrocarbons

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Novel bifunctional catalysts combining two active phases, typically Cu-ZSM-5 and a modifier, were prepared and tested for the selective catalytic reduction of nitrogen oxides using propylene in order to overcome the hindering effects of water typically seen for single-phase catalysts such as Cu-ZSM-5. Chemical characterization by temperature-programmed reactions, DRIFTS and x-ray absorption spectroscopy indicated strong interaction between the two phases, primarily producing materials that exhibited lower reduction temperatures. Two improvements in NOx reduction activity were seen for these catalysts compared

with Cu-ZSM-5: a lower temperature of maximum NOx conversion activity (as low at 250°C) and an enhancement of activity when water was present in the system. The use of a second phase provides a way to further tailor the properties of the catalyst in order to achieve the mechanistic conditions necessary to maximize NOx remediation.

HYDROGEN

Lightweight and Robust Hydrogen Storage Materials for Automotive Fuel Cells

Robert J. Klingler, John F. Krebs, Jerome W. Rathke, and Deborah J. Myers

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The critical properties that a hydrogen storage material must possess include a high hydrogen storage capacity and facile reversible hydrogen absorption kinetics at low pressures and temperatures. In addition to these requirements, hydrogen storage materials used for automotive fuel cell systems must have high gravimetric and volumetric hydrogen storage capacities. Alane has the desirable properties of containing 10 wt% hydrogen and its volumetric hydrogen content (148 g/L) is twice that (70.8 g/L) for liquid H_2 at 20°K. Improvements are needed in the thermodynamics and kinetics of hydrogen addition to bulk aluminum for alane to become a viable hydrogen storage material. The energetics of aluminum surface layers are anticipated to be significantly more favorable for reversible hydrogen addition than the bulk material. Accordingly, a potential means to exert control over the thermodynamics and kinetics for the hydrogenation of aluminum to alane is through variations in the substrate size on the nanometer scale where the entire substrate has surface-like properties. This Chemical Engineering Division project focuses on the development of nanoparticulate aluminum and aluminum-containing compounds with structures that can maintain the size of the alane hydride phase within the nanometer regime. One such compound is AlB_2, whose structure comprises alternating aluminum and boron sheets. The described technology can easily be extended to include compounds composed of alkali or alkaline earth metals. Based on their low formula weights, the proposed hydrogen storage materials are expected to have hydrogen capacities several factors larger than commercially available hydrogen storage materials.

Production of Hydrogen from Water with Low-Temperature Thermochemical Cycles

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The Chemical Engineering Division is exploring the possibility of producing hydrogen with low-temperature thermochemical water-splitting cycles operable with heat derived from nuclear or solar heat sources. The research effort focuses on identifying, developing and commercializing thermochemical cycles with a maximum temperature of less than 550°C. The temperature limitation is imposed mainly because potential heat source options around this temperature are proven and reliable and because material issues are less severe. The most promising candidate has proved to be a family of three hybrid cycles based on copper and chlorine chemistry.

Fuel Processing Catalyst Development

Theodore R. Krause, Jennifer F. Mawdsley, Magali Ferrandon, James M. Ralph, Razima Souleimanova, John F. Krebs, and Mario J. Castagnola

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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 systems. Although commercial catalysts are available for producing hydrogen, these 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. For reforming, we are developing two families of catalysts: (1) precious metals dispersed on an oxide substrate such as a refractory alumina or a reducible ceria and (2) a purely oxide-based catalyst consisting of oxides with the perovskite structure. These catalysts have been shown to exhibit high fuel conversion, high selectivity for hydrogen, and low hydrocarbon breakthrough in the reforming of a variety of hydrocarbon fuels. A major challenge is to develop a sulfur-tolerant catalyst. For the precious-metal catalysts, we are exploring bimetallic formulations to improve sulfur tolerance. For water-gas shift, we are developing catalysts that do not exhibit the loss in performance observed with commercial iron-chromium and copper-zinc oxide 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 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 cost of these catalysts by increasing their shift activity through the use of bimetallic formulations containing platinum.

Oxidation States of Pt in Ceria-supported Pt Water-Gas Shift Catalysts

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Ceria-supported platinum has received considerable interest as a catalyst for the water-gas shift ($CO + H_2O \leftrightarrow CO_2 + H_2$) reaction. The changes in the oxidation state of platinum supported on a gadolinium-doped ceria ($Pt/Ce_{0.8}Gd_{0.2}O_{1.9}$, Pt/CGO) and a zirconia-doped ceria ($Pt/Ce_{0.8}Zr_{0.2}O_2$, Pt/CZO) during temperature-programmed reduction were monitored by *in situ* x-ray absorption spectroscopy. Using principal component analysis of the Pt L_3-edge in the XANES region of the spectra in combination with fitting of the EXAFS region revealed that Pt(IV) oxide was initially present on both doped-cerias, and that the Pt(IV) was reduced to Pt(II) before being completely reduced to Pt(0). Pt/CGO underwent reduction from Pt(IV) to Pt(II) at a lower temperature (100°C) than Pt/CZO (150°C). In the case of Pt/CGO, the reduction of Pt(IV) to Pt(II) occurred at a lower temperature (50°C) if the sample was reduced in hydrogen and then reoxidized after the initial calcination. This effect was not observed with Pt/CZO. Analysis of the Ce L_3-edge of a sample of Pt/CGO showed that only a small fraction (<5%) of cerium was reduced from Ce(IV) to Ce(III) at 250°C, with no further reduction observed below 500°C, which suggested that only cerium located in the surface layers was reduced.

NANO-MATERIALS

Using Nanoscale Technology to Help Stroke Victims: Prototype Nanoparticles for Future Magnetically Guided, Targeted Tissue Plasminogen Activator Stroke Therapy

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A novel strategy for acute stroke treatment based on nanoscale technology could combine the advantages of non-invasive and targeted delivery of tissue plasminogen activator (t-PA). In such a system, non-toxic magnetic spheres are loaded with tPA (tPA-encapsulation), then intravenously injected and concentrated at the site of the vascular occlusion by an external magnetic field (targeted lysis), thereby, potentially improving clot lysis efficiency, reducing side effects, and extending the therapeutic time window. In this study we have identified the first building blocks of the proposed therapy--the development of tPA-encapsulated magnetic nanocarriers. Biodegradable poly(lactic-co-glycolic) acid microspheres were synthesized to encapsulate dye, protein, and magnetic nanocrystals.

Searching for Improved Treatment Options for Human Internal Decontaminations: A Nanoscale Approach

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We seek to develop, design, and demonstrate a novel, integrated system based on magnetic nanoparticles for selective and rapid removal of biological, chemical, and radioactive biohazards from humans. Magnetic nanospheres are developed that are biostabilized with long-chain hydrophilic polymers to avoid rapid bioclearance, are biodegradable and non-toxic, and present a variety of specific toxin-binding receptors. These nanospheres are injected directly into the bloodstream of exposed humans. Once injected, the nanospheres circulate freely, offering selective capture and sequestration of blood-borne toxins to the surface receptors. The magnetic separator allows blood to pass through a closed-loop system containing tubular micro-channels designed to optimize blood flow and particle removal. Small magnets within the device trap the particle-toxin complexes at the tube walls and the detoxified blood is returned to the body. After the procedure, the toxin-bound particles can be flushed from the removable tubing and used as an analyte in further testing.

HIGH-TEMPERATURE MATERIALS

Anode Development for Electrolytic Reduction of Spent Oxide Fuel

Laurel Barnes, Andrew S. Hebden, Mark C. Hash, and Leonard Leibowitz

An electrochemical treatment method is being developed in for spent light water reactor fuel. In this process, conducted in molten LiCl, the oxide fuel reduced to metal at the cathode and oxygen is evolved at the anode. Under some conditions chlorine may also be evolved at the anode. Long anode lifetimes are required for this process to be feasible. This requirement, combined with the severe conditions (high temperature, oxygen and potentially chlorine generation, lithium exposure, and molten salt electrolyte) make selection of suitable anode materials challenging. Potential materials were selected based in thermodynamic data and assessed with some simple screening tests. Promising materials have been tested in an electrochemical test cell. Several promising materials have been identified and are undergoing further testing to determine which is most suitable based on scalability, current density, potentiostatic stability, and corrosion resistance.

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Chemical Vapor Deposition of Niobium Coating on Microspheres

Christine T. Snyder, Larry E. Putty, Thomas C. Carter, Jude M. Runge, , Andrew S. Hebden, Bryce W. Campbell, Leonard Leibowitz, and Sean M. McDeavitt (Purdue University)

The Chemical Engineering Division is supporting the Department of Energy's Advanced Fuel Cycle Initiative program in its mission to develop and demonstrate the technologies needed to transmute the long-lived transuranic (TRU) actinide isotopes contained in spent nuclear fuel into shorter-lived fission products. One area in which we are involved is the development of fuels for higher-actinide transmutation systems. As part of this support effort, one of our objectives is the development of methods for coating TRU microspheres to ensure fission product containment and thermochemical stabilization in a metal matrix, and to fabricate experimental cermet fuel pins containing the coated TRU microspheres. Recent method development experiments using non-radioactive materials included laboratory coating experiments using chemical vapor deposition to deposit a niobium coating onto 100- to 300-µm zirconium oxide microspheres. The spheres were examined by scanning electron microscopy, and subsequent energy dispersive spectroscopy confirmed that the coating was niobium. The coating method will ultimately be adapted for use in a glovebox to remotely coat (Pu,Np,Am) O_2 fuel particles.

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

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The Chemical Engineering Division is 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 development project are (1) to assess and select commercially available candidate materials for service in the electrolyte reduction process and (2) 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 DOE's Advanced Fuel Cycle Initiative program for the reduction of transuranic and fission product oxides, and the Advanced Spent Fuel Conditioning Process (ACP) of the Korea Atomic Energy Research Institute for the conditioning of 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 will 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 properties under process-simulated conditions and showing promise for use as base structural materials in the electrochemical reduction process.

Performance of Structural Materials in Lead-Based Reactor Coolants at Temperatures up to 800°C

Jude Runge, Leonard Leibowitz, Victor Maroni, Laurel Barnes, Christine Snyder,
and Sean M. McDeavitt; Alberto Polar and Francisco Rumiche (University of Illinois-Chicago)

The Lead-Cooled Fast Reactor System (LFR) is one of the six advanced nuclear reactor systems selected by the Generation IV International Forum to meet challenging technology goals for advanced nuclear energy systems. The LFR system is a fast-spectrum reactor utilizing lead or lead/bismuth eutectic (LBE) liquid metal coolant and a closed fuel cycle for efficient conversion of uranium and management of actinides. The LFR is cooled by natural convection and has a reactor outlet temperature of 550°C, which could possibly range up to 800°C with advanced materials. Of significant concern is the compatibility of structural materials with LBE coolants at high temperatures. To evaluate candidate structural materials, we used a thermal-convection-based test method to expose these materials to molten lead and lead-bismuth flowing under a temperature gradient. The temperature gradient is essential for natural circulation that induces liquid metal flow, as well as for discerning preferential dissolution and transport of alloy components. Results from the analysis of interactions of various selected structural alloys (HT-9 and V - 4Cr - 4Ti alloy with flowing molten lead over a temperature range of 650-800°C) showed that the level of dissolution and mass transport

depends upon base metal chemistry, microstructure and surface finish. In addition to the corrosion test results that contraindicated the use of the selected metal alloys at high temperatures, it is well documented that mechanical properties change at the high-end LFR temperatures required for hydrogen generation, about 800°C. Stainless steel and other metal alloys exhibit creep, loss of strength, sensitization and other high-temperature-exposure phenomena. Thus, ceramics became the next logical choice of test material. Additional experiments were performed in flowing molten lead over the 650-800°C range, with monolithic silicon carbide ceramic and SiC–SiC Nicalon® fiber-reinforced composite materials. The absence of reaction between the liquid lead and the SiC indicates the promise of ceramic materials in high-temperature applications. Research into manufacturing various structural components from SiC and SiC composites has indicated feasibility. The results of these high-temperature tests help in the selection of advanced materials for the LFR and other advanced nuclear reactor systems.

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Large-Scale Production of Uranium Chloride for Use in Pyroprocessing Spent Nuclear Fuels

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The electrolyte in electrorefiners that will be used to separate uranium from spent nuclear fuel by pyroprocessing is a 59 mol% lithium chloride (LiCl) - 40 mol% potassium chloride (KCl) - 1 mol% uranium chloride (UCl_3) ternary salt. The UCl_3 is the oxidant that provides the transport ion required for the uranium in the spent fuel to move from the electrorefiner anode to its cathode. Metallic fission products, bond sodium, and transuranics (TRUs) react with the UCl_3 to form metal uranium and sodium chloride (NaCl), fission product chlorides, and TRU chlorides. Thus, to maintain the UCl_3 concentration needed for electrotransport, UCl_3 must be periodically added to the electrolyte. This replenishment is accomplished by the addition of 46 mol% LiCl - 24 mol% KCl - 30 mol% UCl_3 eutectic ternary salt to the electrolyte salt. The high-throughput electrorefiner requires that no cadmium be present in the system. A series of experiments were conducted to demonstrate the ability to safely prepare cadmium-free UCl_3 in a ternary eutectic salt. The test apparatus consisted of a heated well containing a crucible. The crucible contained a pool of molten LiCl-KCl salt on top of a liquid cadmium layer at a temperature of about 600°C. Into the molten LiCl-KCl salt, a fuel basket containing uranium metal was submerged within the molten salt layer. Chlorine gas was sparged into the liquid cadmium pool to produce cadmium chloride ($CdCl_2$), which rose to the salt/cadmium interface because it was lighter than the liquid cadmium. Cadmium chloride dissolved in the molten salt and reacted with the uranium in the fuel basket to produce UCl_3. The final product salt was a ternary salt of 46 mol% LiCl - 24 mol% KCl - 30 mol% UCl_3. The process temperature of 600°C was maintained to prevent the presence of solid $CdCl_2$, which could have plugged the chlorine gas nozzle ($CdCl_2$ melts at 568°C). The results of the UCl_3 experiments conducted with this test apparatus demonstrated that the UCl_3 salt-production test apparatus, including the chlorine-gas system, could be safely used to prepare a LiCl-KCl-UCl_3 salt; the rate of heat generation by the exothermic reactions of cadmium with chlorine and $CdCl_2$ with uranium did not cause an excessive temperature rise in the apparatus; there was excellent agreement between the calculated and measure amounts of chlorine gas and uranium used; the final product with a ternary eutectic salt composition could always be obtained by a final composition adjustment with the

proper chemicals; the UCl_3 salt conversion test apparatus could be used for future small-scale production of the LiCl-KCl-UCl_3 ternary salt without modification of the apparatus; and scaling up of the UCl_3 salt-production test apparatus for larger production runs will be a relatively straightforward effort.

ELECTROCHEMICAL MATERIALS

Non-Precious Metal Electrocatalysts for Polymer Electrolyte Fuel Cells

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One of the main barriers to commercialization of polymer electrolyte fuel cell power systems is cost. The cost of the membrane-electrode assembly constitutes approximately 84% of the total fuel cell stack cost (~$180/kW), with the anode and cathode contributing ~$82/kW. This high cost is largely due to the use of platinum-containing electrocatalysts. In the past decade, there have been significant advances in reducing the platinum metal loading of both the anode and cathode. However, any further substantial cost reductions will require the replacement of platinum with a less costly electrocatalytic material. The objective of this new project is to develop non-platinum cathode catalysts for polymer electrolyte fuel cells. Based on stability diagrams and past cathode electrocatalyst work, we have identified several materials that may be active for oxygen reduction and stable in the acidic fuel cell environment. These are transition metal nitrides and carbides that are isoelectronic with tungsten carbide and chromium-based transition metal spinels (e.g., $FeCr_2O_4$, $ZnCr_2O_4$, and $CuCr_2O_4$). We have constructed an apparatus for evaluating the kinetics of oxygen reduction on the candidate materials and verified the operation of this apparatus using the state-of-the-art carbon-supported platinum catalyst. We have also initiated the evaluation of potential electrocatalysts using this apparatus.

Metallic Bi-polar Plate-Supported Solid Oxide Fuel Cell (TuffCell)

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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.

High-Voltage $Li[(Ni_{0.5-x}Co_x)Mn_{1.5}]O_4$ ($0 \leq x \leq 0.5$) Spinel Oxide Cathodes for Lithium Batteries

Christopher S. Johnson, A. Jeremy Kropf, John T. Vaughey, Xiaoqing Qian, Roy Benedek, and Michael M. Thackeray

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Higher-voltage batteries coupled with multi-electron transfer reactions can yield large amounts of energy storage per mole of battery material, and current research is aimed at exploring the electrochemistry and structures of such electroactive materials. In the $Li[Ni_{0.5}Mn_{1.5}]O_4$ spinel electrode, which provides approximately 4.7 V against metallic lithium, the nickel and manganese ions are formally divalent and tetravalent respectively. Analogous to the charge-compensation mechanism in the novel layered $Li[Ni^{II}_{0.5}Mn^{IV}_{0.5}]O_2$ electrode (see Metal Oxide Electrode Multi-Electron Transfer Processes, MRCAT poster), a Ni(II/IV) two-electron redox couple also occurs on cycling the spinel electrode (between 5.0 and 3.7 V) during which the Mn(IV) remains electrochemically inert. In this work, a series of Co-substituted spinel compounds $Li[Co_xNi_{0.5-x}Mn_{1.5}]O_4$ (x=0, 0.1, 0.2, 0.4, and 0.5) were synthesized by solution-precipitation methods and characterized. Rietveld profile refinements of powder XRD patterns for the cubic, cation-ordered spinels (space group $P4_332$) were used to calculate the lattice parameter, *a*, and non-lithium (Ni, Co) occupancy of the 8c tetrahedral site. The lattice parameter decreases linearly with the amount of substituted Co in the spinel structure, consistent with solid-solution behavior and the direct substitution of the slightly smaller Co(II) ions for Ni(II) ions. Ni, Co and Mn XANES data were collected to determine the nominal oxidation states of the transition metal ions in each of the compounds. For x=0.1, the cobalt ions are divalent, the Mn ions tetravalent, and Ni ions divalent. For higher values of x, charge-transfer to Mn occurs, creating Mn(III) with Co(III), while Ni(II) persists. First principles calculations were performed at various values of x to compare the theoretically-predicted electronic structures, and charge-ordering in $Li[Co_xNi_{0.5-x}Mn_{1.5}]O_4$ spinels with that determined experimentally.

High-Temperature Polymer Electrolyte Membranes

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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°C (typically 80°C). This requirement adds complexity, size, weight, and cost to the fuel cell power system. Our approach to developing membrane electrolytes with high proton conductivity at low relative humidity and temperatures above 100°C is based on the assembly of dendritic macromolecules into network structures. Using this approach enables control over the pore size, end-group functionality, and ion transport properties of the membrane. Such materials should have high thermal stability, while retaining high ionic conductivity at temperatures to 150°C and higher, without the need for humidification. In addition, we are investigating organic-inorganic hybrid materials based on sulfonated macromolecules and silica.

Dopant-Induced Stabilization of Rhombohedral $LiMnO_2$ against Jahn-Teller Distortion

Roy Benedek and Michael M. Thackeray

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Dopants on the Mn sublattice of layered $LiMnO_2$, a candidate cathode material for lithium batteries, tend to suppress the Jahn-Teller-driven monoclinic distortion in favor of a layered rhomobohedral structure, which has superior Li insertion/extraction cycling properties. First-principles calculations, within the local-spin-density approximation-generalized-gradient approximation (LSDA-GGA) framework, using the VASP code, have been performed for the dopants Cr, Fe, Co, Ni, Cu, Mg, and Al, to assess their relative effectiveness in the stabilization of the rhombohedral structure. Antiferromagnetic and ferromagnetic structures were assumed for the monoclinic and rhombohedral structures, respectively. The selected solutes were all found to adopt the same oxidation state (divalent or trivalent) in both the monoclinic and the rhombohedral structures. The relatively early transition elements Cr and Fe are trivalent, whereas the late transition metals Co, Ni, and Cu are divalent. Although a divalent solute oxidation state, which results in the oxidation of a Mn neighbor to the (non-JT-active) 4+ state, is generally favorable for rhombohedral structure stabilization, other dopant properties (e.g., size mismatch, covalency) evidently also play a role in determining the relative effectiveness of a given solute as a stabilizer. Thus, divalent Co and Cu are about equally effective as stabilizers as are trivalent Fe, Cr, and Al. Most effective are Mg and Ni.

Electron Transfer at the Border Between Intermetallic and Zintl Phases

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Over the past decade a significant amount of work has gone into optimizing electrode materials seeking cheaper, faster, and better alternatives to the currently used components. Whereas numerous cathode materials and electrolyte mixtures have been successfully developed, few advances outside of optimized carbon formulations have been tested for anodes. The graphitic carbons work well, but at very low potential so they must be closely monitored to avoid lithium plating onto the anode surface, a safety hazard during overcharge or battery abuse conditions. Alternative electrode materials that operate a few hundred millivolts above lithium plating potential that we have been investigating are main group metal-containing intermetallics. Historically lithium Zintl phases, e.g. Li_xSn, Li_xSi, and Li_xAl, have been studied as possible replacement anodes but problems arising due to volume expansion, phase transitions, irreversible capacity, and poor kinetics of lithium insertion have outweighed the benefits of higher densities and capacities. Our approach has been to use intermetallics as insertion electrodes rather than "lithium sinks", thus limiting the volume expansion and phase transitions. Recent studies using Cu-Sn, Cu-Sb, and Mn-Sb alloys have shown that electrochemically filling interstitial vacancies in certain classes of alloys with lithium can be a viable alternative to carbon. For example the alloy Cu_2Sb displays a very efficient reversible reaction at room temperature with lithium as it shuttles between the parent alloy material and a Li_2CuSb/Cu composite electrode.

Coated Lithium Battery Materials: Toward Improvement in Interfacial Electrochemistry

Christopher S. Johnson, Michael M. Thackeray, John T. Vaughey, Arthur J. Kahaian, Jeom-Soo Kim, and Giselle Sandí (Chemistry Division)

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The electrochemical performance of battery materials can be dramatically modified by a surface or interfacial coating. The coating can cause improvements in the electrode kinetics from a favorable electronic conductivity increase or from advantageous current distribution effects. Coatings can also increase the chemical stability of the electroactive material by stopping corrosion into the battery electrolyte. Li ionic pathways through the coating are critical to electrochemical performance of the underlying material. Two examples are provided in this work, where (1) metal oxides were coated on lithium battery cathodes and (2) graphite anodes were coated with carbon or copper. Metal-oxide coatings with amphoteric properties are applied to $LiMn_2O_4$ spinel and layered $LiMO_2$ (M=Li, and/or first row transition metals) oxides to stabilize the electrochemical interface against the electrolyte. A colloidal deposition process was implemented that results in nanoscopic domains of metal-oxide (e.g., ZrO_2) intimately adhered to the bulk powder electrode. Carbon coating was accomplished from a propylene vapor decomposition in inert atmosphere on the powder electrodes, and Cu metallization-coating was done by a fluidized bed method. Ni metallization and Ag coating has also been carried out and these are done by a proprietary solution process. Performance improvements over uncoated electrodes are observed in both examples, and TEM characterization of coatings has provided insight as to the morphology and protective mechanism of the coatings.

Battery Materials for Implantable Bions

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Working in collaboration with Quallion LLC and the University of Wisconsin, the Chemical Engineering 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. Conductivities are similar to those for conventional liquid organic electrolytes used in lithium ion batteries. The outstanding electro-chemical stability of these polymer electrolytes offers the opportunity to use them with advanced high-capacity layered cathode materials with $\geq$250 mAh/g capacity density at 4.5 V. The material is extremely stable between 0 and 6 volts compared with 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.

Measurement of Unknown Optical Rotatory Properties of CB Agents and Simulants Using Optical Polarimetry
Bryan G. Splawn

Most bio-surveillance technologies employ polymerase chain reaction (PCR), laser-induced fluorescence, and immunoassay methods of detection. These methods are sensitive and provide accurate confirmation; however, they are highly technical, expensive, specific, non-handheld, and time- consuming because sample preparation is often required. In an attempt to circumvent these limitations, a new method for characterizing the chemical and physical properties of chemical and biological (CB) agents and CB simulants is proposed that uses the principles of optical polarimetry. This optical method is simple, inexpensive, broad-spectrum, handheld-capable and requires no chemical derivatization. *It is important to note that very few data exist on the optical rotatory properties of CB agents.*

Contact: Bryan G. Splawn (2-7906)

NUCLEAR MAGNETIC RESONANCE

Catalytic Olefin Hydroformylation in Supercritical Carbon Dioxide
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The Fluid Catalysis Program explores catalysis mechanisms, new catalytic species, and new catalytic reaction chemistry using an array of *in situ* spectroscopic and kinetic techniques at the high pressures and temperatures that are frequently used in industrial chemical processes. The first in situ NMR studies of several high-pressure carbonylation reactions are described. High-pressure probes that incorporate toroid detectors for optimal sensitivity were employed to investigate the oxo reaction for the catalytic hydroformylation of olefins in supercritical carbon dioxide solution. The *in situ* measurements required pressures as high as 0.5 kbar at 250 ^{o}C. Reaction rates and steady-state concentrations of catalytic species in the hydroformylation of propylene in supercritical CO_2 were found to be comparable to those measured for typical liquid hydroformylation media. However, because only one phase is present in the supercritical system, stirring to achieve gas-liquid mixing was found to be unnecessary, and an improved yield of linear product was achieved in CO_2 even without stirring. Processes involving the tetracarbonylcobalt radical, $\cdot Co(CO)_4$, dominated the NMR observable high-temperature chemistry of the oxo catalyst. Thermodynamics for the dissociation of $Co_2(CO)_8$ into two $\cdot Co(CO)_4$ radicals were measured using NMR magnetic susceptibility determinations in supercritical CO_2.

Gas Phase Micelles as Minireactors for Catalysis

Robert J. Klingler, Jerome W. Rathke, and Rex E. Gerald II

This research explores the benefits of a new type of environmentally benign reaction medium formed by dispersing micelles with high-density aqueous cores in a low-density supercritical fluid phase. This unique combination of properties holds promise to facilitate catalytic and electron transfer reactions. In addition, this new type of reaction medium could improve existing industrial technologies by replacing conventional organic solvents with carbon dioxide, thereby reducing our dependency on fossil fuels. The method uses a specialized family of surfactants that are tailored for use in supercritical carbon dioxide ($scCO_2$) to combine the efficient mass transfer characteristics of a gas-like medium with the solvating advantages of a high-density aqueous reaction environment. The system is investigated using Argonne-developed high-pressure *in situ* NMR imaging techniques. The NMR spectral observations have provided the first conclusive evidence for the presence of homogeneously dissolved surfactants in the low-density supercritical medium.

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Investigations of Electrochemical Systems Using Novel Detectors: Toroid Cavity NMR Imagers

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Three NMR detectors developed at Argonne for investigations of electrochemical systems will be reviewed. The first detector, *Near Electrode Imager*, was designed to create ion concentration gradients in cylindrical samples of PEO-based polymer electrolytes *in situ*, and to study the temporal and spatial evolution of the ions and polymer host by several ^{7}Li, ^{19}F, and ^{1}H NMR methods. One-dimensional radial concentration profiles (1D-images) of cations and anions have been recorded by ^{19}F and ^{7}Li NMR for a standard polymer electrolyte. The sequence of images recorded at different stages of cell polarization depicts the depletion of charge carriers adjacent to the cathode. The images open an avenue for quantifying the mass transport of ions in a heterogeneous system. The second detector, *Compression Coin Cell Battery Imager*, was invented to study the intercalation mechanisms of lithium ions in carbonaceous electrode materials used as anodes in lithium-ion batteries. This device was designed to accommodate graphitic electrodes that are cast as flat laminates on metallic current collectors. A third detector, *SAMs Imager*, is a highly sensitive detector for NMR investigations of the molecular architecture and dynamics of self-assembled monolayer films on atomically flat metal surfaces. We have employed this detector to study self-assembled thin films of alkane thiols on a pool of mercury by proton NMR spectroscopy. Examples of experiments conducted with each of these detectors are presented.

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SYNCHROTRON RADIATION AND MR-CAT

Non-Destructive Transmission X-Ray Diffraction Analysis of the Silver-Sheathed Bi-2223 Composite Superconductor

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The most advanced high-critical-temperature superconductor embodiment available today is the silver-sheathed $(Bi,Pb)_2Sr_2Ca_2Cu_3O_x$ (Ag/Bi-2223) composite conductor, which can now be manufactured in kilometer lengths suitable for devices such as motors, generators, transmission lines, and fault current limiters. A key step in Ag/Bi-2223 manufacturing process is the heat treatment that transforms the ceramic powder mixture enclosed in the precursor billet into the superconducting Bi-2223 phase. Monitoring of this process as a function of process variables requires direct examination of the samples. The primary methods employed in virtually all cases today are x-ray diffraction (XRD) with a laboratory source and scanning electron microscopy coupled with energy-dispersive spectroscopy. With both of these methods, the sample must be sectioned and the silver polished away to expose the superconducting ceramic cores, i.e., both methods involve destructive sectioning of the sample. As an alternative to the conventional XRD method that avoids the need to abrade away the silver and also, in principle, avoids the need to section long lengths of composite wire, we have investigated transmission XRD at x-ray energies high enough to fully penetrate the silver-sheathed composites. We have found that this can be done very effectively at the Advanced Photon Source (Materials Research Collaborative Access Team beamline) by working at 25 keV (0.49594 Å), an energy that lies below the silver K edge. Using this technique, we have been able to determine the phase content of as-rolled, partially heat-treated, and fully heat-treated Ag/Bi-2223 specimens without any damage to the specimen itself. This allows us to investigate the same specimen at progressive stages of the deformation/heat treatment process. We find that the Bi-2223 grain colonies form with a fiber texture, that a lead-rich residual second phase is clearly detectable in all samples, and that the fully processed samples still contain detectable quantities of the Bi-2212 and Bi-2201 phases.

The Nature of Molten Chloride Salt Occlusion by Zeolite 4A

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A glass-zeolite ceramic waste form is being developed for the disposal of radioactive waste salts. The typical waste salt is the LiCl-KCl eutectic salt with variable amounts of fission product and actinide chlorides, e.g., CsCl, $SrCl_2$, UCl_3, $NpCl_3$, and $PuCl_3$. A key step in the production of the waste form is the occlusion of the waste salt by zeolite 4A at 823 K. The properties of the waste form critically depend upon the detailed mechanism of the occlusion process. Hence, as a first step in understanding the occlusion of the waste salt by zeolite 4A, an investigation by simultaneous differential scanning calorimetry / synchrotron powder X-ray diffraction (DSC/XRD) was undertaken of the occlusion of the LiCl-KCl eutectic salt by zeolite 4A.

Metal Oxide Electrode Multi-Electron Transfer Processes

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Multi-electron transfer reactions can yield larger amounts of energy storage per mole of battery material, and current research is aimed at exploring the electrochemistry and structures of such materials. X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS) experiments were used to study chemical and electrochemical Li insertion and extraction reactions of $LiNi_{0.5}Mn_{0.5}O_2$. These results, along with galvanostatic cycling data, show that $LiNi_{0.5}Mn_{0.5}O_2$ layered electrodes in lithium batteries operate predominantly off two-electron redox couples, Ni^{4+}/Ni^{2+}, between approximately 4.5 and 1.25 V and Mn^{4+}/Mn^{2+} between 1.25 and 1.0 V versus metallic Li, respectively. The retention of a stable layered framework structure and the apparent absence of Jahn–Teller ions Ni^{3+} and Mn^{3+} in the high- or low-voltage region is believed to be responsible for the excellent structural and electrochemical stability of these electrodes. The $LiNi_{0.5}Mn_{0.5}O_2$ layered oxide reversibly reacts chemically or electrochemically with Li to form an air-sensitive, dilithium compound, $Li_2Ni_{0.5}Mn_{0.5}O_2$ with a hexagonal structure analogous to Li_2MnO_2. The cycling behavior of $Li/LiNi_{0.5}Mn_{0.5}O_2$ cells over a large voltage window (4.6 to 1.0 V) and with very slow rates shows that rechargeable capacities greater than 500 mAh/g can be obtained. These materials have great utility to store excess lithium for use to combat the capacity-loss problems at graphite, metal-alloy, or intermetallic negative electrodes against lithium metal-oxide positive electrodes of conventional lithium-ion cells.

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

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We have conducted in-situ x-ray absorption fine-structure (XAFS) spectroscopy studies on phase transformations of the III-V semiconductor InSb induced by electrochemical insertion of Li and extrusion of indium in lithium-battery coin cells. Upon discharging the cell, indium is extruded from the zinc-blend-type InSb structure and replaced by Li. Although up to 90% of the indium can be displaced, the Sb fcc sublattice remains stable at all degrees of lithiation. This process is largely reversible. However, in the fully charged state, about 40% of the In remains outside the matrix as In metal, leaving a corresponding number of Schottky vacancies in a $In_{1-y}Sb$ defect structure. Our discussion focuses on the ease and reversibility of the phase changes in InSb electrodes, which is attributed to the stability of the Sb fcc sublattice at all states of charge, to the lattice compatibility of the different phases, and to the absence of significant charge gradients. These processes are corroborated by low-temperature ex-situ studies of battery electrodes.

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

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In situ EXAFS during temperature-programmed reduction was performed on Cu-ZSM-5 in order to examine the state of copper under reaction conditions. A continuously scanning monochromator coupled with rapid acquisition rates facilitated observation of characteristic pre-edge features from various Cu oxidation states. EXAFS fitting and factor analysis of the XANES were performed in an attempt to determine the number and type of Cu species present. The data suggest that initially only Cu^{2+} is present, but in two different locations on the zeolite; both states reduce to Cu^{1+} in both H_2 and CO, but under different conditions. Under H_2 conditions, migration of Cu^{1+} to Cu^0 clusters is observed at 450°C, while no metallic state is observed during CO reduction.

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

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A highly-strained, curved silicon crystal in the Laue geometry has been used as a large area x-ray fluorescence analyzer for x-ray absorption spectroscopy. The analyzer is able to resolve the Lα fluorescence lines for neighboring actinide elements, which are separated by about 150 eV. A large gain in the signal-to-background ratio has been demonstrated for small quantities of Np in the presence of U compared with other detection techniques (such as solid-state detectors); the U fluorescence peak approached 1000 times the magnitude of the off-peak background, while, for 0.5 wt.% Np in U_3O_8, the Np L_3-edge signal-to-background ratio was 3.5.

Using Raman Microscopy and X-ray Diffraction Space Mapping Techniques to Explore Epitaxy, Strain, and Twinning in $MBa_2Cu_3O_{7-x}$ Coated Conductor Embodiments

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The microstructure of an $MBa_2Cu_3O_{(7-x)}$ (M = Yttrium or a rare earth metal) thin film has a profound influence on the superconducting properties of the conductor embodiment. Key aspects of the thin film microstructure, such as strain, epitaxy, layer tilt, twinning and orthorhombicity can be qualitatively and quantitatively studied by mapping the diffraction space of the $MBa_2Cu_3O_{(7-x)}$ film layers and the substrate. The details and results of recent experimental studies of $EuBa_2Cu_3O_{(7-x)}$ and $YBa_2Cu_3O_{(7-x)}$ films deposited on strontium titanate (100) substrates using diffraction space mapping (DSM) are presented. DSM was carried out in

symmetric and asymmetric reflection geometries using the MRCAT insertion device beamline at the Advanced Photon Source. Our results indicate a greater extent of layer relaxation in the superconducting film when a buffer layer is utilized between the film and the substrate, in contrast to the case of an $MBa_2Cu_3O_{(7-x)}$ film deposited directly on the substrate. In the latter case, strain at the film/substrate interface appears to induce a pseudo-tetragonal disorder accompanied by a reduction in observable twinning relative to the $MBa_2Cu_3O_{(7-x)}$ film on the buffered substrate.

In Situ Real-Time XAFS Characterization of Noble Metal Catalyst Impregnation

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Using x-ray absorption spectroscopy, we have characterized dilute solutions (200 ppm and above) of noble metal catalyst precursors such as H_2PtCl_6 (chloroplatinic acid or CPA), $NaAuCl_4$, Na_2PtCl_4 and $(NH_3)_4PtCl_2$, and Na_2PdCl_4 and $(NH_3)_4PdCl_2$. The changes in coordination chemistry of these materials upon adsorption appear to be consistent with a totally electrostatic adsorption mechanism as opposed to one invoking “chemical” interactions or surface ligand exchange. The Au(III) solutions show little dependence on Au or excess Cl- concentration. In addition, the Au-Cl coordination numbers for the adsorbed samples, if plotted versus the equilibrium bulk pH at which the sample was prepared, fall below the species in solution. If they are plotted versus the pH at the adsorbed layer, however, the chloride coordination numbers of the adsorbed complexes overlap with the coordination of the liquid phase species. This is to say that the adsorbing complexes speciate as if in the liquid solution, but at the local conditions of the adsorption plane. A chemical mechanism has been cited for CPA adsorption over carbon. We used time-dependent, in-situ XANES to try to determine if Pt reduction accompanied adsorption, or occurred after it. CPA was adsorbed onto carbon black at an initial pH below 3.0. Results indicate an almost complete reduction of Pt^{+4} to Pt^{+2} over a time span of two hours or less. The reduction kinetics was dependent on the type of carbon. The reason for these differences is under investigation.

NUCLEAR MATERIALS CHARACTERIZATION

Neptunium Substitution into the Structure of Alpha-U_3O_8

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We synthesized powder samples of $Np_xU_{3-x}O_8$ with x between 0 and 0.33. Analyses of solids by x-ray absorption spectroscopy indicate that Np occupies U sites and is predominantly tetravalent. Lattice parameters vary smoothly as a function of Np concentration. The ***a*** and ***b*** parameters (parallel to structural sheets in U_3O_8) depend strongly on Np concentration below $x = 0.3$; however, extrapolation of a least-squares fit up to $x = 1$ (the maximum value of x if Np is tetravalent) suggests little expected change in ***a*** or ***b*** for values of x greater than approximately 0.5. The ***c*** cell parameter (perpendicular to the plane of the sheets) shows relatively little dependence on Np concentration for all values of x. The ***a*** and ***b*** cell parameters vary in a complementary fashion, such that the a-b

plane and unit-cell volumes remain nearly constant for small x (below ~0.2). The projected volume increase at higher x may be accommodated by expansion along ***c***; the maximum volume expansion for $Np_xU_{3-x}O_8$ is projected to be less than 0.2% up to $x = 1$. Our results demonstrate that $Np_xU_{3-x}O_8$ forms a homogeneous solid solution up to (at least) $x = 0.33$, and that a complete solid solution may exist between α-U_3O_8 and NpU_2O_8; however, the structure of NpU_2O_8 may resemble that of β-U_3O_8.

Trace Element Chemistry in Spent Nuclear Fuel Using X-Ray Absorption Spectroscopy
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Knowledge of the chemical states of fission products and transuranium actinides in spent nuclear fuel (SNF) and related materials provides a first line of understanding that may benefit waste disposal in a geologic repository, fuel reprocessing, transmutation/recovery, and remediation of sites from weapons-related activities. Few techniques have proven more effective than x-ray absorption spectroscopy (XAS) for determining oxidation states and structural environments of elements in solids. Several XAS measurements from SNF 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 at high x-ray energy makes it ideal for investigating radionuclide systems, which have relatively high-energy absorption edges, and which must be carefully encapsulated for radiological safety. Using a novel “bent-Laue analyzer” (BLA) detection scheme, we have obtained detailed XAS information from trace elements (Pu, Np, Mo, and Tc) in specimens of SNF. The BLA provides unprecedented rejection of the intense uranium fluorescence background, yielding spectral information from elements present at concentrations of 10^{-4}. These data have allowed the first direct observation of oxidation state, coordination environment, and site symmetry of fission product and actinide elements in SNF.

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Transmission Electron Microscropy

Transmission Electron Microscopy in the Chemical Engineering Division
Nancy L. Dietz

The Chemical Engineering Division utilizes transmission electron microscopy as an analytical tool for many different applications, throughout its programs. Selected applications will be discussed.

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