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May 20, 2004

Mr. Tien Q. Duong
5G-030, EE-32
Forrestal Building
U.S. Department of Energy
Washington D.C. 20585

Dear Tien:

Here is the second-quarter FY 2004 report for the Batteries for Advanced Transportation Technologies (BATT) Program. This report and prior Program reports can be downloaded from http://berc.lbl.gov/BATT/BATT.html.

Sincerely,

Frank McLarnon
Manager
BATT Program

cc:	J. Barnes	DOE/OFCVT
	D. Howell	DOE/OFCVT
	E. Wall	DOE/OFCVT
	K. Abbott	DOE-Oakland

LBID-2495 (2)

BATT TASK 1
CELL DEVELOPMENT

TASK STATUS REPORT

PI, INSTITUTION: K. Striebel, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Cell Development - Cell Fabrication and Testing

SYSTEMS: Low-cost Li-ion and high-power Li-ion

BARRIER: Inconsistent evaluation of the merits of candidate novel materials.

OBJECTIVES: The primary objective is to establish a test vehicle for the evaluation of new materials for high-power and low-cost Li-ion cells.

APPROACH: The testing of novel materials in a standard cell with preset protocols will provide the necessary link between the invention of novel battery components and the diagnostic evaluation of failure modes, and will accelerate the development of EV's, HEV's and FCEV's. Novel components will be developed in BATT Program Tasks 2, 3, and 4 (anodes, electrolytes, and cathodes) for baseline cell chemistries. These components are incorporated into a standardized cell, and then tested using a consistent protocol to determine cell capacity, energy, power, and lifetime characteristics. Tested cell components are then delivered to appropriate investigators involved with BATT Program diagnostic projects.

STATUS OCT. 1, 2003: The benchmarking of the low-cost Li-ion cell with $LiFePO_4$ and natural graphite in liquid and gel electrolyte for room temperature operation was completed. A comparison of the performance of $LiFePO_4$ from seven different labs was completed with the aid of modeling efforts of J. Newman. Many approaches to improve the stability of the natural graphite anode in the presence of the $LiFePO_4$ cathode were compared.

EXPECTED STATUS SEPT. 30, 2004: Further benchmarking of the low-cost Li-ion baseline cell including high-temperature aging will be carried out with larger cell sets to demonstrate reproducibility. Diagnostic analysis of cell components from this study will be combined with those from previous cells to lend insight into the degradation mechanism occurring on the natural graphite electrode in the presence of $LiFePO_4$. Performance measurements on the candidate sources of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ will be carried out and the best incorporated into Graphite/$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ pouch cells. Room temperature benchmarking of this baseline chemistry will be completed. In addition, half-cell studies of $LiMn_2O_4$ in LiBOB-containing electrolyte for the high-power baseline cell will be carried out. Electrodes and cells will be prepared and tested in support of specific modeling and diagnostic studies, and for the evaluation of new materials for the various baseline cells will be evaluated as they are received.

RELEVANT USABC GOALS: Specific power 300 W/kg, 10 year life, <20% capacity fade.

MILESTONE:

(a)	Prepare 16 $LiFePO_4$/natural graphite cells for evaluation	2/04
(b)	Benchmark $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$/$LiPF_6$:PC:EC:DMC/Grcell	6/04

PROGRESS TOWARD MILESTONES

The primary objective of the project is to benchmark the performance of new materials for low-cost, high-energy and high-power Li-ion cells capable of meeting the USABC and FreedomCAR goals for energy density, power density, cost, and cycle life. In FY2004, we continued our studies of the performance and failure modes of the natural graphite(NG)/$LiFePO_4$ baseline cell and began the benchmarking of the natural graphite/$LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ baseline cell.

The performance of six different sources of $LiFePO_4$, with varying amounts and types of *in-situ* carbon, was compared with the help of a mathematical model of the electrochemistry of this material (in collaboration with Srinivasan/Newman). Several important conclusions regarding matrix conductivity and particle morphology for $LiFePO_4$ electrodes were made (see Task 6). In addition, the model was able to predict that this system, with the carbon-coated current collector, is capable of meeting the goals of the HEV application. In LBNL $LiFePO_4$/NG pouch cell studies, the rate of capacity fade was reduced from about 0.27 to 0.1%/cycle with the addition of the carbon-coated current collector and other cell modifications. Electrodes from the cycled cells showed no electrochemical deterioration of the active materials. However, Raman spectroscopy of the cycled anodes revealed the presence of iron species, as well as an increase in the relative disorder of the graphite. The presence of iron was confirmed with TEM/EDX analysis. The location and morphology of the iron-containing species appears similar to that observed for Mn deposition on the anode of the $LiMn_2O_4$/graphite cell cycled in $LiPF_6$-containing electrolytes. Sixteen $LiFePO_4$/NG cells were assembled from electrode films supplied by Hydro Quebec (Zaghib) and three different electrolytes, including a LiBOB electrolyte, received courtesy of Ferro Chemical Company. Aging and cycling studies of these cells are underway at room temperature and 45°C. The room-temperature cells are still cycling but are showing rates of capacity fade comparable to those with the LBNL electrodes. However, the cells with the LiBOB electrolyte show somewhat better capacity retention when compared with the $LiPF_6$-electrolyte cells, especially at elevated temperature.

Benchmarking of the $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ and spinel/NG cells is underway. Cathode films were prepared from four sources of $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ (Mitsui, Tanaka and Seimi) and a highly Li-doped spinel from Toda. Half-cell studies have been carried out with the following conclusions: The L333 (Seimi) $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ showed the best high-rate performance and was selected for initial baseline studies. In addition, this material had a discharge capacity of 230 mAh/g when charged to 4.7 V vs. Li/Li^+ without severe degradation. Spinel and $LiFePO_4$ cathodes were used in half-cell evaluations of novel electrolytes from Ferro Chemical and Clemson University (Creager), respectively. The LiBOB-containing electrolytes from Ferro showed superior stability with the spinel cathode at 55°C, compared to the $LiPF_6$ electrolyte cell. The new $CF_3SO_2N(Li)SO_2(CF_2)_4SO_2N(Li)SO_2CF_3$ salt from Clemson showed comparable stability to the LiTFSI salt in EC/DEC solvent with a $LiFePO_4$ cathode. Initial $Ni_{0.33}Mn_{0.33}Co_{0.33}O_2$ /NG pouch cells showed good capacity but poor cycling stability due to non-uniformities in the electrode thickness and hence poor C/A ratios.

TASK STATUS REPORT

PI, INSTITUTION: T.J. Richardson, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Cell Development - Materials Characterization, Overcharge Protection, Cathode Development

SYSTEMS: Low-cost, high-energy Li-ion

BARRIER: Short lithium battery lifetimes, inadequate capacity.

OBJECTIVES: Support cell development through structural characterization of active electrode components before, during, and after cycling. Investigate inexpensive, self-actuating overcharge protection mechanisms. Synthesize and evaluate alternative electrode materials.

APPROACH: Address primary causes of capacity and power fading by correlating them with changes in the composition and structure of electrode active materials. Techniques employed include x-ray diffraction (XRD), vibrational spectroscopy, and electroanalytical testing. Develop an internal overcharge protection mechanism based on a separator component that will internally short an overcharged cell. Discover improved cell systems through a limited program of synthesis and evaluation of alternative components.

STATUS OCT. 1, 2003: Phase transformations and accumulation of decomposition products in cycled and aged electrodes from Task 1.1 were identified and correlations made with cell performance characteristics. The utility of electroactive polymers for overcharge protection in lithium ion batteries was demonstrated. Potentially useful new low-cost, high capacity electrode materials were prepared and evaluated.

EXPECTED STATUS SEPT. 30, 2004: Further composition and structural analyses of BATT Task 1.1 electrodes will have contributed to our understanding of the failure and degradation modes in the baseline systems. Electroactive conducting polymers capable of providing overcharge protection in lithium ion cells with cathode potentials of at least 3.5 V (e.g., $LiFePO_4$) will have been characterized. New cathode materials will have been synthesized and evaluated for introduction into BATT chemistries.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES: Demonstrate reversible overcharge protection utilizing an electroactive conducting polymer in 3.5 V or higher lithium-ion cells. (July 2004)

PROGRESS TOWARD MILESTONE

This task addresses a number of issues important to development of safe, cost-effective, lithium ion batteries with adequate energy and power densities and extended lifetimes. These include overcharge protection, general issues of component structure and stability, and exploratory work on alternative electrode materials.

Given the susceptibility of lithium-based batteries to energetic venting and even explosion following severe overcharging, a reliable overcharge-protection mechanism is an indispensable requirement for large cell assemblies. Ideally, this would be achieved with a minimum of added weight, volume, and cost. We showed last year that electroactive polymers whose conductivity depends upon their state of charge can provide overcharge protection in lithium batteries by means of a reversible, self-actuating, low-resistance internal shunt that allows overcharge currents to pass harmlessly through a cell while maintaining its discharge capacity and allowing the rest of the cell stack to operate normally. The feasibility of this approach was first demonstrated in low-voltage Li-TiS_2 cells using a polymer that began to short the cells at around 3.2 V. In FY 2004 we have succeeded in protecting higher-voltage cells containing the 3.5 V cathode $LiFePO_4$ and even $LiMn_{0.33}Ni_{0.33}Co_{0.33}O_2$, which operates above 4 V. In addition, we have shown that the mechanism works as well with carbon anodes as with lithium, that the temporary internal short does not cause significant self discharge at the end of charging, that the presence of the polymer does not compromise the conductivity of the electrolyte, and that the polymer can be used in an external protection circuit as well as inside the cell.

Nickel-rich cathodes, such as the former baseline material $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$, when exposed to air become contaminated with Li_2CO_3. Cells made with these electrodes have low capacity and power characteristics. We have shown that the formation of a thick carbonate coating on the active particle surfaces causes electronic isolation of a significant portion of the active material. Since this phenomenon is especially noticeable in Ni-containing cathodes, we studied the new baseline material $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ to evaluate its resistance to degradation in air. The tendency to form Li_2CO_3 is considerably diminished in the new composition.

We reported previously that an iron (III) phosphate, $Fe_{1.2}PO_4X$, where X is F, OH, or H_2O, synthesized hydrothermally, showed good cyclability in a single-phase system, $Li_yFe_{1.2}PO_4X$, with *y* up to at least 1. Structural characterization of this system has been completed. Substitution of titanium for iron gave a material with good capacity and cyclability, but a reduced discharge potential. Substitution by manganese was difficult to achieve. Since particle size reduction by high-energy ball milling and by reduced synthesis times failed to increase the rate capability, no further work is planned on this material. Progress in synthesis and evaluation of other phosphate compounds, including some iron vanadates with capacities up to 200 mAh/g will be reported.

TASK STATUS REPORT

PI, INSTITUTION: K. Zaghib, Hydro-Québec (IREQ)

TASK TITLE - PROJECT: Cell Development - Lithium-Ion Polymer Batteries with Low-Cost Materials

SYSTEMS: Low-cost Li-ion

BARRIER: High cost of Li-ion batteries

OBJECTIVES: Fabricate Li-ion/polymer cells (4 cm^2 area) using cell chemistries proposed by DOE, and send 50% of the total cells to LBNL for testing. Investigate phenomena at the anode/separator and cathode/separator interfaces in Li-ion/polymer cells, and determine the cycle life of Li-ion/polymer cells at various temperatures (55°C to 0°C) and self-discharge rates. Synthesize low-cost graphite anodes and $LiFePO_4$ cathode materials for Li-ion/polymer cells.

APPROACH: Our approach is to synthesize and coat electrodes (both anode and cathode) with low-cost materials, and use these materials to assemble prismatic cells. Additional work will be focused on gel polymers, as well as studies of pressure effects and interfacial phenomena at the polymer/electrode interfaces.

STATUS OCT. 1, 2003: Electrochemical characterization of carbon-coated $LiFePO_4$ and graphite will be tested in gel polymer electrolytes by using LiFSI salt. We investigated the thermal properties of the gel electrolyte by thermal gravimetric analysis. Several Li-ion gel-type cells were prepared, and 15 cells were sent to LBNL for evaluation. In addition, cathodes and anodes containing $LiFePO_4$ (2µm) and carbon fibers MCF and Vapor grown carbon fiber (VGCF) and there mixture with natural graphite, respectively, were coated.

EXPECTED STATUS SEPT. 30, 2004: We will determine the composition of the anode (natural graphite and fibers) and cathode material as a function of the water-soluble binder (WSB) (no fluoride) by reducing the amount of binder in the electrodes by 50% compared to the standard PVDF type. In order to reduce the amount of the binder and the cost of the coating, we will use a new process by using WSB in both the anode and cathode. Also we expect to investigate the effect the soluble WSB on other baselines chemistries ($LiMn_2O_4$, $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$).
Cryogenic methods coupled with SEM will be developed to improve the homogeneity of the active material-binder-electronic conductor, the adhesion between the electrode and the current collector and to optimize the thickness of the electrode to obtain suitable porosity.
We will study electrode flexibility by using PVDF versus WSB in order to improve the safety aspect of the battery. We expect to provide primary cycling data evaluated in Li-ion polymer cells, by introducing WSB and low-cost lithium salt, namely, LiFSI, developed by the University of Montreal (UM). We will continue using the carbon-coated $LiFePO_4$ with 2µm particle size from Phostech.

RELEVANT USABC GOALS: Specific power 300 W/kg, 10-year life, < 20% capacity fade.

MILESTONES:
(a) Identify low-cost water-soluble binder for Li-ion polymer cells. December 2003.
(b) Deliver 30 cells to LBNL at 10 cells every 4 months.

PROGRESS TOWARD MILESTONE

Studies on the effect of the polymer on the gel electrolyte (x% polymer-(1-x)%EC-GBL-1.5M LiTFSI) were completed. This polymer contains tetrafunctional terminal acryloyl-modified alkylene oxide polymer (four-branch polymer). Two significant findings from this study are: *i*) the vapor pressure decreases with a decrease in the amount of GBL, and *ii*) at high temperature (100-125°C), the vapor pressure decreases when the polymer content increases. This effect helps improve the battery safety characteristics.

TGA analysis was used to investigate the influence of the polymer content [100%, 30%, 20% and 10% by weight] in the gel on the weight loss of the electrolyte at higher temperatures. The results show an increase in the polymer content produced a decrease in the weight loss of the gel.

Optimization studies of the gel composed of x% polymer and (1-x)% [EC-GBL-1.5M LiFSI showed that a 10/90 polymer/liquid ratio by weight yielded good mechanical properties, and with only 20% swelling. The ionic conductivity decreased linearly from 10.1 to 3.50 mS/cm with increasing polymer content in the gel with pure liquid electrolyte and a 35/65 wt% polymer/liquid ratio.

Oxidation of the gel polymer was investigated as a function of various additives (PMMA, TiO_2, SiO_2). The additives PMMA and SiO_2 showed comparable results, with an improvement in oxidation stability with a mixture. However, with TiO_2 additive the oxidation stability was reduced compared to the polymer alone.

Accomplishments

- Completed evaluation and safety studies of low-cost $LiFePO_4$ cathode in Li-ion polymer cells (First quarter, Fiscal Year 2003)

- Completed physicochemical characterization (conductivity, vapor pressure, mechanical property (swelling) and oxidation stability) of the gel polymer electrolyte with EC-GBL. (First quarter, FY 2003)

- Observed that lithium bis(fluorosulfonyl) LiFSI has higher thermal stability than other Li salts and demonstrated good cycle life with LiFSI/EC + GBL

- Identified that stainless-steel packaging yielded cells with low cycle life due to sealing problems and electrolyte leakage; this effort was abandoned and work will be focused on metallized plastic.

- Preliminary studies indicated that Sumitomo metallized plastic is an acceptable packaging material for Li-ion polymer cells, but further development is required. The optimum sealing conditions are 220˚C for 5 sec.

- Several Li-ion gel-type cells were prepared and 30 cells were delivered to LBNL for evaluation. In addition, positive ($LiFePO_4$) and negative (natural graphite) electrodes were sent to LBNL.

BATT TASK 2
ANODES

TASK STATUS REPORT

PI, INSTITUTION: M. Thackeray, Argonne National Laboratory

TASK TITLE: Anodes - Non-Carbonaceous Materials

SYSTEMS: Low-cost Li-ion

BARRIER: Cost and safety limitations of Li-ion batteries

OBJECTIVES: To replace carbon with an alternative inexpensive anode material that will be compatible, in particular, with low-cost manganese oxide cathodes. The project also addresses the need for improved safety of Li-ion cells.

APPROACH: Our main approach over the past few years has been to search for inexpensive intermetallic electrodes that provide 1) an electrochemical potential a few hundred mV above the potential of metallic Li, and 2) a capacity of 300 mAh/g and ~2000 mAh/ml. Our results suggest that matrix reactions when combined with insertion reactions may have a stronger chance of success than when topotactic reactions are used alone. We will therefore focus our future efforts predominantly on composite Al-, Si-, Sn-, and Sb-based electrodes. At the same time, we will continue our search for alternative metal oxide negative electrodes that was initiated in FY2003. Our focus will be layered, low-valence metallic oxides, such as $LiVO_2$. We will complement this search with structural modeling of the electrodes by first principles calculations to predict whether the reactions occur by lithium insertion or by displacement.

STATUS OCT. 1, 2003: Ag_3Sb was used as a model intermetallic compound to study the differences in electrochemical behavior and stability between topotactic and matrix reactions. Although it was possible to achieve the performance target of 300 mAh/g, the major limiting factor of intermetallic electrodes is their irreversible capacity loss on the initial cycle (typically >30%). This capacity loss was attributed to the formation of a thick SEI layer, as observed by TEM and XPS of Cu_6Sn_5 and Cu_2Sb electrodes. Studies of metal oxide negative electrodes, such as an electronicallyconducting Mg-substituted $Li_4Ti_5O_{12}$ spinel electrode (used together with a high-potential spinel cathode, $LiMn_{1.5}Ni_{0.5}O_4$) and a Mo-based electrode had been initiated.

EXPECTED STATUS SEPT. 30, 2004: AlSb and composite intermetallic electrodes will have been investigated. Modeling of the reaction between lithium and AlSb will be completed. Low-potential metallic oxides such as $LiVO_2$ will have been screened. SEI layers that form on intermetallic and metal oxide electrodes below and above 0.7 V vs. Li^0 will have been compared.

RELEVANT USABC GOALS: 10-year life, <20% fade over a 10-year period.

MILESTONES: By Sept 2004: 1) Composite intermetallic electrodes: more than 100 cycles with capacities in excess of 300 mAh/g in lithium half-cells with less than 20% capacity fade on the initial cycle; 2) Oxide electrodes: 50 cycles below 1 V vs. Li^0 with a capacity comparable to that of $Li_4Ti_5O_{12}$ (150 mAh/g); 3) Characterization of SEI layers on intermetallic and metal oxide electrodes by TEM and XPS. By April 2004: 4) Modeling of the $Li_{1+x}VO_2$ system.

PROGRESS TOWARD MILESTONES

During FY2004, the emphasis of our research changed from intermetallic electrodes, such as Cu_6Sn_5 and Cu_2Sb, that operate by topotactic reactions to composite electrodes containing one (or more) metal components within a graphite matrix, for example, C/Sn and C/Sb systems. When the metal component is restricted to approximately 10 atomic percent, capacities of approximately 400 mAh/g have been achieved for 100 cycles, thereby meeting our FY 2003 target. We plan to repeat these studies at 0°C during the next contract period to determine if the metal component improves the rate capability of the graphite electrode at low temperatures. We have also explored metal oxide electrodes such as Li_2MoO_3 and $LiVO_2$ in an attempt to find an alternative electrode to $Li_4Ti_5O_{12}$ that *i*) operates at lower potential (0-1 V vs. Li) than $Li_4Ti_5O_{12}$ (1.5 V vs. Li)) and *ii*) provides at least an equivalent practical capacity as the spinel electrode (~150 mAh/g). Theoretical first-principles calculations have shown that $LiMO_2 \rightarrow Li_2MO_2$ lithium insertion reactions occur between 2.0 and 1.0 V *vs*. Li and are favored only for M=Mn and Ni; displacement reactions are favored for M=V, Co, and Cr. Experimental results have confirmed theoretical predictions. Although Li_2MoO_3 could deliver 200 mAh/g for more than 50 cycles, thereby meeting our FY2004 target, the electrode exhibited (like many other metal oxides) an unacceptably high capacity loss during the initial charge/discharge cycle. Our cathode research, however, has shown that composite electrodes with a Li_2MnO_3 component may compensate for such initial capacity losses. In FY 2005 we will focus on this approach and, in addition, on a new technique to prelithiate anodes to reduce capacity loss effects.

TASK STATUS REPORT

PI, INSTITUTION: M.S. Whittingham, SUNY at Binghamton

TASK TITLE - PROJECT: Anodes - Novel Materials

SYSTEMS: Low-cost Li-ion battery and gel battery

BARRIER: Cost, safety and volumetric capacity limitations of Li-ion batteries

OBJECTIVES: To replace the presently used carbon anodes with safer materials that will be compatible with manganese oxide cathodes and the associated electrolyte. In particular, we will investigate Mn-tolerant anode materials.

APPROACH: Our anode approach is to explore, synthesize, characterize, and develop inexpensive materials that have a potential around 500 mV above that of pure Li (to minimize the risk of Li plating and thus enhance safety) and have higher volumetric energy densities than carbon. We will place emphasis on simple metal alloys/composites. All materials will be evaluated electrochemically in a variety of cell configurations, and for thermal and kinetic stability.

STATUS OCT. 1, 2003: We showed that vanadium and manganese oxides, in their highest oxidation states, are not prime candidates. Pure aluminum was found to have a high capacity and react readily with lithium, but its capacity faded rapidly on cycling in carbonate-based electrolytes; aluminum-based alloys show inferior behavior to pure aluminum. Tin-containing materials, such as $MnSn_2$ cycle well for a few cycles before capacity fade sets in. Pure tin anodes cycle better than pure aluminum or $MnSn_2$, but the cell impedance was found to increase markedly after about ten cycles.

EXPECTED STATUS SEPT. 30, 2004: From our program to understand capacity fade of tin on cycling, we expect to have defined the key parameters determining capacity loss, to have determined the impact of tin morphology on capacity fade, and as a result to have identified several additional non-aluminum binary alloys; and to have improved the electrochemical performance of the materials identified.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES: (a) We will design a program to identify, understand and mitigate the capacity loss on cycling of simple alloy systems. This will result in a milestone to understand and define the key parameters determining capacity fade in pure tin by June 2004, and to propose a means of remediating that fade. (b) Another major milestone is to identify by September 2004 a new simple material (a binary alloy) that has the potential of higher volumetric capacity than carbon at about 0.5 V relative to pure Li.

PROGRESS TOWARD MILESTONES

The goals of this project are to find improved transition metal oxide cathode materials for lithium batteries and to gain a better understanding of what limits the use of simple alloys as the anode. In the cathode area major effort is being focused on stabilized layered manganese dioxides, and on building a base-case cathode system using $LiFePO_4$ against which the manganese and other cathodes will be compared. In the anode area, the focus is being placed on tin materials, with the initial experiments being on pure tin foils.

NOVEL ANODE MATERIALS

Metal-Based Anodes. The presently used graphitic carbon anode used in lithium cells has a relatively low capacity, and can pose safety problems under high charge rates. As a result a number of alloy-forming metals have been studied. We are studying the behavior of bulk metal foil, wherein there is no need for conductive diluent or binder, and therefore minimum likelihood of side reactions. This allows a better understanding of what causes capacity fade in metal anodes. The electrochemical cycling of the metal foils are being compared with expanded metal grids (supplied by K. Zaghib of HQ) where the expansion upon reaction can be better accommodated. Tin foil, even at cycling rates of 3 mA/cm^2, is comparable to alloys such as Cu_6Sn_5, formed *in-situ* by heating a tin film electrodeposited on copper. The expanded tin foil shows better performance than the tin foil, and in the case of aluminum expanded grids, the performance is comparable to that of graphite. We also continue to investigate simple metal oxides as hosts for lithium anodes.

LiBOB Electrolyte. We have begun the investigation of electrolyte salts that do not contain fluoride to determine if they allow the better cycling of anodes: for example, what is the difference between $LiPF_6$ and LiBOB in the EC/DMC mixed solvent? In this solvent the lithium ion forms a tetrahedrally coordinated $Li(EC)_4$ complex for both salts. It is the only solvent with which LiBOB forms a tetrahedral lithium complex. Initial results show lower power capability but less capacity loss during cycling. We will attempt to make purer LiBOB and look at variants of it, and evaluate for cyclability of simple metal anode systems. LiBOB is very sensitive to moisture forming a 1:1 adduct, and decomposes in excess water.

Collaborations and discussions are being held with Professor A. Angell (Arizona State) and Dr. Karim Zaghib (IREQ Hydro-Québec).

Publications:

1. S. Yang, P.Y. Zavalij and M.S. Whittingham, “Anodes for Lithium Batteries: Tin Revisited,” *Electrochem. Commun*. **5,** 587-590 (2003).

2. P.Y. Zavalji, S. Yang and M.S. Whittingham, “Crystal Structures of Potassium, Sodium and Lithium *bis*(Oxalato)Borate Salts from Powder Diffraction Data,” *Acta Cryst*, **B59**, 753-759 (2003).

BATT TASK 3
ELECTROLYTES

TASK STATUS REPORT

PI, INSTITUTION: N. Balsara, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Electrolytes - Polymers for Li Metal Electrodes and Low-Cost Polymer Gel Cells

SYSTEMS: Li/polymer and low-cost Li-ion

BARRIERS: Short Li battery lifetimes, poor ambient-temperature performance for polymer electrolytes, and low energy and power densities due to instability to 4 V.

OBJECTIVES: 1) Determine the feasibility of the Li metal electrode with organic electrolytes and provide operating conditions that prevent dendrite growth. 2) Determine the limitations on Li-ion transport in polymer electrolytes and composite electrodes and develop new materials capable of ambient-temperature operation with Li metal. 3) Determine the limits of stability of organic electrolytes at high-voltage cathode materials (*e.g.*, 4 V) and develop materials and methods to increase stability.

APPROACH: To obtain a fundamental understanding of charge transport in polymers through polymer characterization and the synthesis of new materials. Polymers will be characterized by methods such as neutron scattering, dielectric relaxation spectroscopy, and light scattering to obtain new insights into the rate-limiting transport processes.

STATUS OCT. 1, 2003: We completed an *in situ* study of dielectric relaxation of polyethylene oxide (PEO)/salt mixtures under shear flow using a new rheo-dielectric instrument. These measurements give fundamental insight into the nature of Li^+ migration in PEO matrices. A manuscript describing these effects will be submitted for publication by fiscal year end. The capability of synthesizing monodisperse PEO homopolymers and PEO-containing block copolymers will be established. A cell for measuring the conductivity of our samples in controlled environments was built and tested. Physical characterization and electrical conductivity measurements on nanostructured electrolytes made from PEO block copolymers was started.

EXPECTED STATUS SEPT. 30, 2004: Rheo-dielectric studies of PEO/LiTFSI and polytri- and polytetra-methyleneoxide/LiTFSI (PTMO/LiTFSI) mixtures will be measured and analyzed. The conductivity of nanostructured PEO-PI films with oriented cylinders will be studied. Promising films will be used in cell performance studies. We will begin collaborating with John Kerr and other members of the BATT Program on the thermodynamic and rheological characterization of polymer gel electrolytes. In a separate study [Hahn *et al*., *Phys. Rev. Lett*., 2003], we have characterized novel gels composed of block copolymers. We will use the knowledge gained there to help the BATT Program.

RELEVANT USABC GOALS: 10 year life, <20% capacity fade over a 10-year period, 1000 cycles, operating environment –40 to 65°C, specific energy >170 Wh/kg, specific power >300 W/kg, <150$/kWh @ 20K/year.

MILESTONE: a) Study effect of salt and electrolyte molecular structure on Li mobility *via* rheo-dielectric measurements on polymer mixtures 9/04; b) Establish conditions for aligning PEO in diblock copolymers 9/04

PROGRESS TOWARD MILESTONES

The dielectric properties of poly(ethylene oxide) (PEO) melts containing lithium perchlorate ($LiClO_4$) under steady shear flow were measured using a home-built rheo-dielectric instrument. The instrument also enabled measurement of the linear and non-linear rheological properties and the quiescent dielectric properties of the PEO/$LiClO_4$ mixtures. A significant increase in the zero-shear viscosity η_0 is observed upon addition of $LiClO_4$ to PEO. This is due to Li^+–mediated intermolecular bridging of the PEO chains. Significant shear thinning was observed under fast shear, suggesting the flow-induced break-up of the intermolecular bridges and the flow-induced liberation of Li^+ ions. The presence of liberated ions was detected directly by dielectric dispersion experiments under steady shear flow. The dielectric dispersion curves shift to higher frequencies, ω, with increasing shear rate, indicating an increase in ionic conductance. Dispersion curves obtained at different shear rates collapse onto a single master curve when plotted against a reduced frequency $\lambda^{-1}\omega$ where λ is a shear rate-dependent normalizing factor. The shear rate dependence of λ^{-1} and η/η_0 is identical. This establishes the quantitative connection between shear thinning, observed in the rheological experiments, and the shear-induced increase in the electrical conductivity, observed in the dielectric experiments. This work, which provides fundamental insight into the mechanism of ion transport in polymer electrolytes, has been published (Y. Matsumiya, N.P. Balsara, J.B. Kerr, and H. Watanabe, *Macromolecules*, vol. 37, p.544-553, **2004**).

We are continuing to work with the Kerr group on rheo-dielectric characterization of polymer electrolytes. We have measured the rheological properties of comb branched poly(trietra methylene oxide) (PTMO) polymers containing LiTFSI. We have compared these measurements to the characteristics of PEO/LiTFSI mixtures. Zero shear viscosity measurements on the linear PEO and PTMO polymer electrolyte systems indicate a much lower activation energy for lithium ion transport in the PTMO polymer matrix. These measurements, together with measurements of conductivity and salt diffusion coefficients, indicate that the mobility of Li^+ ions in PTMO is substantially greater than that in PEO, due to a decrease in the activation energy for the Li^+/polymer complex in the two systems. A paper based on these results is being written (G. Liuao *et al.*).

The limitations of PEO as a polymer electrolyte in Li-ion batteries are well established. In an attempt to combine the positive attributes of PEO and overcome the limitations, we have embarked on a program of studying nanostructured polymer electrolytes obtained from polyethyleneoxide-polyisoprene (PEO-PI) block copolymers. We have successfully synthesized a series PEO-PI block copolymer samples. Our objective is to create rubbery membranes with conducting PEO channels that run through the membranes. We are using electric fields to align the PEO channels and monitoring the alignment by in-situ birefringence measurements. We have also established the infrastructure necessary to examine polymer electrolytes by transmission electron microscopy.

We continue to collaborate with members of the BATT program on rheological and structural characterization of polymer electrolyte systems.

TASK STATUS REPORT

PI, INSTITUTION: J. Kerr, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Electrolytes - R&D for Advanced Lithium Batteries

SYSTEMS: Li/polymer and low-cost Li-ion

BARRIER: Short Li battery lifetimes, dendrite growth, poor ambient temperature performance for polymer electrolytes and low energy and power densities due to poor interfacial ion transport and instability to 4 V.

OBJECTIVES: 1) Determine the feasibility of the Li metal electrode with organic electrolytes and provide operating conditions that prevent dendrite growth. 2) Determine the limitations on Li-ion transport in polymer electrolytes and composite electrodes and develop materials capable of high power operation at ambient temperature with Li metal and high capacity cathode materials. 3) Determine the limits of stability of organic electrolytes at high-voltage cathode materials (*e.g.*, 4 V) and develop materials and methods to increase stability.

APPROACH: A physical organic chemistry approach is taken to electrolyte design, thereby ensuring that not only are the sources of poor performance and failure pinpointed but also the problem can be corrected through materials design and synthesis.

STATUS OCT. 1, 2003: Effects of filler particles and cross-linking on transport and mechanical properties were quantified for polymer electrolytes, and polymer electrolyte gels. Initial tests of surface modification of lithium anodes and carbon nano-particles were completed. Tests for dendrite-free operation of Li metal electrodes in full cells (Li/V_6O_{13}) and half-cells (Li/Li) were completed.

EXPECTED STATUS SEPT. 30, 2004: Characterization of mechanical, transport, electrochemical, and chemical properties of cross-linked comb-branch and linear polymers and polyelectrolytes will be completed for both dry polymer electrolyte used with lithium metal and polymer gel electrolytes used with carbon. Modifications of lithium metal surfaces and conducting carbon particles will be assessed.

RELEVANT USABC GOALS: 10 year life, <20% capacity fade over a 10-year period, 1000 cycles, operating environment –40 to 65°C, specific energy >170 Wh/kg, specific power >300 W/kg, <150$/kWh @ 20K/year.

MILESTONES:

1. Demonstrate dendrite-free cycling of lithium metal electrodes in full cells (Li/V_6O_{13}) and half-cells (Li/Li) for >4000 coulombs of charge (goal > 8,000 coulombs) at > 0.5 mA/cm^2 and discharge capacities of 8 coulombs/cycle with polarizations of <200mV (full cell) and < 50mV (half-cell) at ≤60°C. (09/30/2004)
2. Complete assessment of polyelectrolyte vs. polymer electrolyte gel systems in carbon anode Li-ion cells. (09/30/2004)

PROGRESS TOWARD MILESTONE.

Work has continued to focus on the behavior of polymer electrolyte materials at surfaces. These surfaces include lithium metal electrodes, composite electrodes and fillers such as carbon black and ceramic nanoparticles. The polymer electrolytes include linear and comb branch polymers, either cross-linked or not, in combination with a variety of salts and solvents to form "dry" and gel electrolyte systems. Polyelectrolyte single ion conductor materials are also under study. The surface interactions of these polymer electrolyte systems are under investigation in order to understand their role in a variety of phenomena that limit the performance of lithium batteries, including dendrite initiation and growth at lithium metal anodes, interfacial polarization at a variety of electrodes leading to limitations on power and energy density as well as limitations on transport phenomena and capacity fade.

Dendrite Initiation and Growth at Lithium Metal Anodes. Studies have been carried out on both symmetrical lithium/lithium and full Li/V_6O_{13} cells using linear and comb-branch polymer materials, with varying levels of cross-linking and added filler material to vary the mechanical properties of the polymer electrolyte. We have found that dendrite initiation is completely inhibited if the cell polarization is kept sufficiently low. Typical successful polarizations are less than 20 mV for 0.1 mA/cm^2. Higher current densities can be applied provided the duration of the polarization does not allow establishment of steady–state conditions. The polarization is minimized by use of thin cells (<50 microns), use of electrolytes with good transport properties and minimization of the interfacial impedance. Studies have been carried out on the effects of pre-forming the lithium passive layer by reaction with nitrogen, CO_2, alkylene glycol ethers, and alcohols to provide a more reproducible interface. It has been noted that extended cycling at current densities above a critical value appears to lead to increases in the apparent salt diffusion coefficient and the interfacial impedance. This is consistent with transport effects that lead to salt concentrations at the electrodes that differ from the bulk. Different surface concentrations also lead to variations in the exchange current densities that alter the charge transfer impedance. These effects can be more effectively controlled by use of electrolytes with better transport and mechanical properties.

New Polymer Structures for Improved Performance. We have continued to study the structure-function relationships for both linear and comb-branch polymer systems. The introduction of the trimethylene oxide (TMO) link into the polymer chains clearly increases the polymer mobility. However, the TMO appears to lower the dielectric constant of the medium resulting in increased ion pairing and a decrease in the concentration of free charges to carry current. Combination of the large anions such as TFSI and BETI with TMO-containing polymers leads to better ion dissociation that combined with increased chain flexibility gives better transport. This includes the preparation of single ion conductor materials that can use even larger anions (*cf.* Creager and DesMarteau, Clemson U.) to give practical conductivities with no concentration polarization. The synthesis of a comb polymer system that contains only TMO solvation units, even in the backbone, has been initiated. Studies are also under way on the curing chemistry of polymers for gel and "dry" polymer and polyelectrolyte systems.

TASK STATUS REPORT

PI, INSTITUTION: S.A. Khan, P.S. Fedkiw, North Carolina State University;
G.L. Baker, Michigan State University

TASK TITLE - PROJECT: Electrolytes - Composite Polymer Electrolytes for Lithium and Lithium-Ion Batteries

SYSTEMS: Li/polymer

BARRIER: Short lithium battery lifetimes and high costs

OBJECTIVES: The ultimate objectives are to develop composite polymer electrolytes that are low-cost, have high conductivities, impart electrode-electrolyte interfacial stability, and yield long cycle life.

APPROACH: Our approach is to use surface-functionalized fumed silica fillers in BATT-baseline and candidate systems to determine the effects of filler type and concentration on interfacial stability and cell cycling. We correlate these electrochemical characteristics with mechanical properties and materials chemistry (*e.g.*, silica-type or PEO-type, synthesized by Baker or Kerr, respectively). Data collected include elastic and viscous moduli, ionic conductivity, transference number, Li cycling efficiency, Li-electrolyte interfacial resistance, and full-cell cycling capacity using 3-V cathodes.

STATUS OCT. 1, 2003: We established that fumed silica-based composite electrolytes with low-molecular weight (MW) PEOs exhibit desirable mechanical properties characteristic of solid electrolytes (e.g., elastic modulus G' $>10^5$ Pa), yet have the processability of liquids and display conductivities rivaling liquid electrolytes ($\approx 10^{-3}$ S/cm at 25°C). Fumed silica stabilizes the lithium/electrolyte interface, and effectively suppresses lithium dendrite growth. We found that addition of fumed silicas into low-molecular weight PEOs significantly improves charge-discharge cycle performance, coulombic and energy efficiencies, rate capabilities, and self-discharge performance of Li/V_6O_{13} cells. We further determined that adding fumed silica improves the rheological properties of both high-MW and mixed-MW polymer electrolytes, but can be either beneficial or detrimental to ion-transport behavior. In this regard, adding fumed silica also improves the interfacial stability of lithium/electrolyte (both high-MW and mixed-MW PEO) interface and cycle performance of Li/V_6O_{13} cells.

EXPECTED STATUS SEPT. 30, 2004: We will explore effects of blend composition, that is, the mass ratio of low-MW component (*e.g.*, PEG-dM 250) to high-MW component (*e.g.*, 600K), on rheological and transport properties of mixed-MW polymer electrolyte. We will further study the role of fumed silica in attenuating aluminum corrosion. We will collaborate with Drs. DesMarteau and Creager and study their new imide salts and single ionic conductor in fumed silica compositions.

RELEVANT USABC GOALS: Specific power 300 W/kg, 10 year life, < 20% capacity fade.

MILESTONES: (a) Investigate effects of mass ratio of low- to high-MW polymer in blends of fumed silica based composite electrolytes on transport and rheological properties; study the role of fumed silica in aluminum corrosion. September, 2004. (b) Investigate conductivity, interfacial stability, and rheological properties of new lithium imide salts developed by Drs. DesMarteau and Creager through personnel and sample exchange. May, 2004.

PROGRESS TOWARD MILESTONES

During FY 2004 we focused our efforts in four areas: *i*) nanocomposite electrolytes consisting of lithium salt + fumed silica (FS) + mixtures of low- and high-MW PEO solvents; *ii*) reactivity of aluminum current collectors in electrolytes containing FS; *iii*) FS modified with anionic groups as a means to effect single-ion conduction; and *iv*) electrolytes containing FS with salts other than TFSI (including salts from BATT-funded Clemson group).

We measured conductivity and rheology of $P(EO)_{20}$LiTFSI (lithium bis(trifluoro-methylsulfonyl)imide) + 10% A200 fumed silica electrolytes with different mass ratios of polyethylene oxide (PEO, MW=600K) to polyethylene glycol dimethylether (PEG-dM, MW=250): 100/0, 80/20, 67/33, 50/50, 33/67, and 20/80. Conductivity increases with amount of low-MW component but the heat of fusion as well as melting and crystallization temperatures decrease. Surprisingly, the corresponding moduli of the blends are higher than the composite containing the high-MW component, and the elastic modulus and yield stress show a maximum in concentration with PEG-dM. These results are important since it was expected that the low-MW component would plasticize the high-MW PEO and produce a monotonic decrease in elastic modulus. Lithium dendrite formation was investigated via *in-situ* microscopy at 65 and 80°C using mixed-MW $P(EO)_{20}$LiTFSI (PEO (600K):PEGdm (250)=50:50) electrolytes. Dendrites that have a current density-dependent morphology form in the electrolyte but addition of fumed silica suppress their growth considerably.

We studied the effect of fumed silica on aluminum corrosion using low-MW PEO electrolyte (PEGdM (250) + LiTFSI; Li:O=1:20). The open-circuit voltage for cells with fumed silica-based electrolytes was more stable than that for the baseline liquid electrolyte, and the current density was lower, as assessed by cyclic voltammetry (2.0-5.0 V) and chronoamperometry (4.3V). In EIS measurements, the electrolytes containing FS have a large phase lag over a wide frequency range, which does not exist for the baseline liquid electrolyte. These phenomena may be interpreted as a film-coating behavior.

We have begun to study new lithium salts: lithium bis(perfluoroethylenesulfonyl) imide (LiBETI), lithium bis(oxalato)borate (LiBOB), and dilithium bis(perfluoromethylsulfonyl) (perfluoroethylenesulfonyl) imide (Li dianionic). Electrolytes composed of PEGdM (250) + lithium salt with Li:O=1:20 with and without fumed silica were evaluated. LiBOB has the highest conductivity and Li dianionic has the lowest. Dynamic rheological properties of FS-containing electrolytes are similar for both LiBETI and Li dianionic salts.

We studied new fumed silica-based single-ion conductors, which were synthesized by covalently attaching lithium-exchanged anionic groups [lithium 2-acrylamido-2-methyl-1-propanesulfonate (LiAMPS)] to surface acrylates on Degussa R711 fumed silica (R711-pLiAMPS). Conductivity and transference number measurements were performed. A maximum Li^+ transference number of 0.78 is achieved at room temperature for R711-pLiAMPS at a surface Li^+ surface content of 4.2 nm^{-2} and a Li:O mole ratio of 1:20 (48.5 wt% filler) with a conductivity of 2.2×10^{-6} S cm^{-1}. Adding LiTFSI to the samples enhances room-temperature conductivity by more than 2 orders of magnitude while still maintaining a high Li^+ transference number.

TASK STATUS REPORT

PIs, INSTITUTION: D. DesMarteau and S. Creager, Clemson University

TASK TITLE - PROJECT: Electrolytes - New Battery Electrolytes based on Oligomeric Lithium bis((perfluoroalkyl)sulfonyl)imide Salts

SYSTEMS: Li/polymer

BARRIER: Poor electrolyte transport properties, low power density, short lifetime

OBJECTIVES: (1) Synthesize new battery electrolytes based on oligomeric bis((perfluoroalkyl)sulfonyl)imide anions having high ionic conductivity and high lithium transference. (2) Characterize solid polymer and gel electrolytes made from the target salts with respect to structure, transport properties (conductivity, salt diffusion, transference), mechanical properties, reactivity with electrodes and current collectors, and performance in test cells.

APPROACH: Salts will be synthesized using variants of methodologies developed at Clemson over the last 15 years (D. DesMarteau, *J. Fluorine Chem*. 1995, **72**, 203-208). Transport properties will be measured using impedance combined with restricted diffusion, DC polarization, and concentration cell techniques. Rheological properties, reactivity studies with electrodes and current collectors, and half-cell and full-cell testing will be performed using standard techniques with assistance from and/or in collaboration with other BATT researchers.

STATUS OCT. 1, 2003: Small quantities (<5 g each) of Li salts of general structure $CF_3SO_2[N(Li)SO_2R_fSO_2]_nN(Li)SO_2CF_3$, n=1,3,7,17, were synthesized. Ionic conductivity, salt diffusion, Li transference, glass transition, and PEO crystallinity measurements on SPEs made from the target salts in high-MW PEO hosts were completed. Small quantities of allyl ether salts of structure $CH_2{=}CHCH_2OCF_2CFHOCF_2CF_2SO_2$-X, with X=O(Li) and $N(Li)SO_2CF_3$ suitable for use in making single-ion conductors were synthesized.

EXPECTED STATUS SEPT. 30, 2004: Studies of ion transport, electrode reactivity and corrosion, mechanical properties, and cell testing using oligomeric imide salts will be completed. Methods for making single-ion conductors by grafting imide-based salts onto supports will be demonstrated, and preliminary ion transport data acquired.

RELEVANT USABC GOALS: 10 year life, <20% capacity fade, specific power 300 W/kg.

MILESTONE:
(a) Synthesize salts of structure $CF_3SO_2[N(Li)SO_2R_fSO_2]_nN(Li)SO_2CF_3$, $R_f = (CF_2)_4$ and n = 4 and ~20 in sufficient quantities to provide other BATT workers with materials for a variety of tests including rheological, reactivity, and cell tests -May 2004.
(b) Synthesize sulfonimide-based salts with terminal allyl ether and allyl epoxide groups, and use the salts with reactive hosts including PEO comb polymers provided by BATT task 3.2 (Kerr) to prepare single-ion conductors, which will be characterized in dry and gel form - Dec. 2004.

PROGRESS TOWARD MILESTONES:

Research objectives in the June 2003 - May 2004 reporting period were to synthesize new lithium salts based on the bis((perfluoroalkyl)sulfonyl)imide anion, and to characterize polymer electrolytes prepared using the salts. Characterization included work performed at Clemson to measure conductivity, salt diffusion, and lithium transference. Salts were also provided to BATT co-workers for studies of reactivity with electrodes and current collectors (*e.g.*, aluminum corrosion), conductivity and rheological testing in composite electrolytes containing low-MW PEG fortified with inorganic oxide additives, transference number measurement using the potentiostatic polarization technique, and cell testing.

A dianionic salt of structure $CF_3SO_2N(Li)SO_2(CF_2)_4SO_2N(Li)SO_2CF_3$ was provided to BATT coworkers for testing as follows: Kathy Striebel, LBNL, for half-cell and full-cell cyclic experiments; Tom Devine, LBNL / UCB, for aluminum corrosion testing; and Peter Fedkiw / Saad Khan, NCSU, for conductivity, voltammetry, and rheology testing in composite electrolytes. Cell testing is still underway but early indications are that half-cells prepared using a 1:1 EC:DEC solution of the salt with a $LiFePO_4$ cathode and lithium reference and counter electrodes undergo reversible galvanostatic cycling at voltages comparable to those obtained previously for similar cells prepared using monoanionic electrolytes, e.g., LiTFSI. Voltammetry studies in a composite PEG-dm(250) electrolyte indicate a voltage window of 5.2 V, comparable to that of LiBETI in the same host. Corrosion testing is on hold pending resolution of issues associated with water content in electrolyte solutions. In addition, an oligomeric salt of structure $CF_3SO_2[N(Li)SO_2(CF_2)_4SO_2]_nN(Li)SO_2CF_3$, $n \approx 24$, was provided to BATT coworkers Fedkiw and Khan for Li transference testing. Transference numbers near 0.5 were obtained for lithium in SPEs prepared using a hi-MW PEO host and measured at 90°C, higher than for a monoanionic salt but still short of the 1.0 value needed to derive maximum benefit in a battery.

A working hypothesis in this research has been that the use of low-lattice-energy salts with large and/or oligomeric anions would provide a favorable combination of high ionic conductivity and low anion mobility. Transport studies performed at Clemson and also at NCSU focusing on salt diffusion and lithium transference indicate that the motion of oligomeric anions in polyether hosts is slow relative to that of monomeric anions but not slow enough to prevent salt polarization in cells under charging / discharging conditions. This finding has led us to focus our synthetic efforts on methods for immobilizing fluorosulfonimide anions in polyether hosts. In this regard, allyl-ether-modified salts of structure $CH_2{=}CHCH_2OCF_2CFHOCF_2CF_2SO_2$-X, with X=O(Li) and $N(Li)SO_2CF_3$ were synthesized for local use at Clemson and also provided to BATT co-worker Kerr at LBNL for use in synthesizing single-ion conductors using comb-branch polyether hosts. Coupling reactions between allyl-ether-modified salts and hydrosilyl-modified polyethers were evaluated at Clemson. Based on combined ^{1}H and ^{19}F NMR data, we believe that attack at fluorocarbon bonds can occur during coupling reactions under certain circumstances. Ongoing work will seek to identify appropriate catalysts/conditions for this chemistry to occur cleanly. Coupling reactions between trifluorovinylether-modified salts and simple hydroxyl-terminated polyether oligomers proceeded cleanly, and preliminary conductivity studies on the resulting ionic liquids are very promising.

TASK STATUS REPORT

PI, INSTITUTION: G.D. Smith and O. Borodin, University of Utah

TASK TITLE - PROJECT: Electrolytes - Molecular Modeling of Solid Polymer Electrolytes, Single Ion Conductors and Gel Electrolytes

SYSTEMS: Li/polymer and low-cost Li-ion

BARRIER: Poor cation transport properties in solid polymer electrolytes and single ion conductors

OBJECTIVES: Gain molecular-level understanding of cation transport mechanisms in single-ion conductors and gel electrolytes. Develop tools and methodologies for accurate prediction of structural and dynamic properties of solid polymer electrolytes, single-ion conductors and gel electrolytes. Use these tools to understand ion complexation and transport mechanisms in polymer electrolytes, single-ion conductors and gel electrolytes. Perform virtual design of novel electrolytes with high conductivity and transport number.

APPROACH: Develop *ab initio* quantum chemistry based force fields for solid polymer electrolytes, single ion conductors, and gel electrolytes. Validate ability of the developed force fields to accurately predict cation environment and ion transport by comparing results of molecular dynamics (MD) simulations against available experimental data. Synergistically use MD simulations data and experimental results (conductivity, transference number, structure factor, etc) to obtain detailed understanding of the cation transport mechanism. Based upon understanding of the ion transport mechanism, virtually design novel electrolytes and predict their properties using MD simulations. Recommend the most promising virtually designed electrolytes for experimental synthesis.

STATUS OCT. 1, 2003: *Ab initio* quantum chemistry-based force fields were developed for the PEO-based comb-branched polymer with and without TFSI anions attached to the side chains. Computational experiments were initiated on the single-ion conductor at one salt concentration and temperature with and without ethylene carbonate plasticizer using molecular dynamics simulations.

EXPECTED STATUS SEPT. 30, 2004: Predictive capabilities of the developed force fields will be evaluated through comparison of predicted ion transport, thermodynamic, and structural data with the available experimental data. Molecular-level understanding of the effect of polymer structure and amount of plasticizer on ion transport mechanism in single-ion conductors and gel electrolytes will be obtained. Novel single-ion conductors and gel electrolytes with improved conductivities will be developed.

RELEVANT USABC GOALS: Specific power 300 W/kg, operating environment –40 to 65°C.

MILESTONE: (a) Complete investigation of the effect of plasticizer on ion transport properties - March 2004
(b) Obtain molecular-level understanding of the effect of the polymer structure on ion transport in single-ion conductors. Develop novel single-ion conductors with improved ion transport properties - September 2004

PROGRESS TOWARD MILESTONES

The transport and mechanical properties of polymer and gel electrolytes and single-ion conductors depend on numerous parameters that include the polymer structure, choice and amount of plasticizer, Li salt concentration, and choice of counterion (anion). Experimental investigation of this vast parameter space is expensive and is further complicated by a lack of fundamental understanding of property-structure relationships in general and cation transport mechanism in particular. Molecular dynamics (MD) simulation methods are well suited for gaining fundamental understanding of the mechanisms for Li^+ cation mechanism in existing electrolytes and thereby providing strategies for a search of novel electrolytes with improved transport properties.

Our research has focused on developing tools (MD codes that use state-of-the-art potentials, force field fitting tools) and methodologies for accurate prediction of structural and dynamic properties of solid polymer electrolytes (SPEs), single-ion conductors (SICs), and gel electrolytes. We use these tools to assist experimental efforts (Kerr, Khan, Creager) in understanding ion environment and transport mechanisms in SPEs, SICs, and gel electrolytes and to perform virtual design and characterization of novel electrolytes with high conductivity and transport number. We have developed a new generation quantum-chemistry-based accurate potential energy functions (force field) for predicting thermodynamic, structural, and dynamic properties of numerous polyethers and carbonates doped with LiTFSI salt. MD simulations using developed force fields predict static and dynamic structure factors, self-diffusion coefficients, ionic conductivity, and degree of ion association in excellent agreement with experiments performed on oligomers of PEO, carbonates (EC, PC, DMC), and their solutions with LiTFSI. MD simulations of a SIC gel electrolyte based upon poly(epoxide ether)–TFSI-Li^+/ethylene carbonate (EC) with Li:EC:EO=1:4:6 predict high ionic conductivity of 10^{-2} S/cm and a reasonable degree of ion ionic dissociation of 0.2-0.4 at 393 K, indicating that gel electrolytes and SICs of this type have promising ionic transport properties for Li-ion batteries. Thus, MD simulations support experimental efforts by the Creager and Kerr groups directed toward synthesis and characterization of these promising electrolytes.

The influence of the PEO conformational (local) dynamics on Li^+ and $TFSI^-$ diffusion has also been investigated by varying barriers for PEO conformational transitions. We found that local PEO dynamics are coupled not only with the Li^+ cation mobility but also with the $TFSI^-$ anion mobility. This result has important ramifications for strategies of rational design of new electrolytes: *i.e.*, one cannot expect to increase only Li^+ dynamics and not $TFSI^-$ anion dynamics by selecting a polymer with more rapid local dynamics.

MD simulations of poly(epoxide ether) with side chains of long ether repeat units ($PEPE_5$) doped with LiTFSI, EO:Li=20:1, T=393 K showed that Li^+ is complexed primarily by ether oxygens from the side chains and not by ether oxygens from the main chain. This data explains why the ionic conductivity (measured by the Kerr group) of a number of PEO-based comb-branched copolymers doped with LiTFSI was independent of the chemistry of the groups connecting side chains to the main chain.

The structure and dynamics of the Li^+ first coordination shell in liquid electrolytes such as DME and EC were also examined in detail. Lithium cations were found to be complexed by 4 EC and 2-3 DME molecules. Average residence times of EC and DME molecules around a Li^+ ion were ~1 ns, whereas average residence times of $TFSI^-$ were about an order of magnitude longer.

BATT TASK 4
CATHODES

TASK STATUS REPORT

PI, INSTITUTION: M. Thackeray, Argonne National Laboratory

TASK TITLE: Cathodes - Novel Materials

SYSTEMS: High-energy, high-voltage (Li-ion); Low-cost (Li-ion); High-power (Li-ion)

BARRIER: Cost and safety limitations of Li-ion batteries

OBJECTIVES: To develop low-cost manganese oxide cathodes to replace $LiCoO_2$.

APPROACH: Our approach is to search for, characterize, and develop low-cost manganese oxide electrodes for Li-ion cells. We will continue to focus on high-capacity layered lithium-manganese oxide structures that are represented by the composite formula $xLi_2M'O_3 \bullet (1-x)LiMO_2$ in which M′ = Mn, Ti, Zr, Ru and M = Li, Mn, Ni, Co. Some of these electrodes are showing excellent promise to replace $LiCoO_2$ as the cathode material of choice in lithium-ion cells. In conjunction with our anode project (Task 2.1), we will continue to explore the electrochemical properties of high-potential (4.0-5.0 V) layered and spinel electrodes against low-potential metal oxide anodes. Such electrochemical couples can provide a cell voltage between 2.5-3.5 V.

STATUS OCT. 1, 2003: Investigations of $xLi_2M'O_3 \bullet (1-x)LiMO_2$ composite electrodes in which a $Li_2M'O_3$ component (M′=Mn, Ti, Zr) was used to stabilize layered $LiMO_2$ electrode structures, particularly $LiMn_{0.5}Ni_{0.5}O_2$, were undertaken. These electrodes provide an exceptionally high reversible capacity (~300 mAh/g) when cycled over a wide voltage window (4.6-1.45 V) due to the formation of a layered Li_2MO_2 structure at low voltage. The instability of Li_2MO_2 compounds in air makes it difficult to fabricate over-discharged cells to combat the irreversible capacity loss at graphite and intermetallic negative electrodes. The BATT project on the stabilization of 4 V spinel electrodes was transferred to the ATD program.

EXPECTED STATUS SEPT. 30, 2004: Improvements in the electrochemical performance of $xLi_2M'O_3 \bullet (1-x)LiMO_2$ electrodes will have been achieved. High-capacity $xLi_2M'O_3 \bullet (1-x)LiMO_2$ electrodes and high-rate (5 V) spinel electrodes will have been evaluated against metal oxide anodes in ~3 V cells. We will have provided samples of high-capacity VO_x samples to J. Kerr at LBNL for evaluation in Li/polymer cells.

RELEVANT USABC GOALS: 10-year life, <20% fade over a 10-year period.

MILESTONES: (a) Evaluate $xLi_2M'O_3 \bullet (1-x)LiMO_2$ composite electrodes against a technical target of 180 mAh/g for 100 cycles between 4.5 and 3.0 V vs. Li^0 at room temperature and 50°C; (b) reduce the irreversible capacity loss of $xLi_2M'O_3 \bullet (1-x)LiMO_2$ electrodes, which is observed during the first cycle when the upper voltage limit is set at 4.5 V, to 10-15%; (c) develop a spinel electrode that provides 110 mAh/g between 4.0 and 5.0 V for 100 cycles; and (d) evaluate the electrochemical properties of composite $xLi_2M'O_3 \bullet (1-x)LiMO_2$ and spinel electrodes against metal oxide negative electrodes that operate at <1.5 V *vs*. Li^0 - September 2004.

PROGRESS TOWARD MILESTONES

Novel Cathodes

We have continued to develop high-capacity and high-rate $xLi_2M'O_3 \bullet (1-x)LiMO_2$ "composite" electrodes (M′=Ti, Mn, Zr; M=Mn, Ni) with the goal of achieving 180 mAh/g for 100 cycles between 4.5 and 3.0 V. During FY 2004, we obtained 170-180 mAh/g at 50°C for 100 cycles from $0.03Li_2ZrO_3 \bullet 0.97LiMn_{0.5}Ni_{0.5}O_2$ electrodes, thereby almost meeting our targeted capacity. Our most-recent data show that capacities >200 mAh/g are achievable. Despite the strong structural compatibility between $Li_2M'O_3$ and $LiMO_2$ components, XRD data, in combination with NMR data (C. Grey, SUNY, Stony Brook) and HRTEM data (S. Hackney, Michigan Technological University, Houghton), showed unequivocally that the structures are not simple solid solutions but consist rather of complex atomic and compositional arrangements, yielding domains with short-range order. Acid treatment of electrodes containing a Li_2MnO_3 component significantly reduced the irreversible capacity loss of the initial charge-discharge cycle when cells were charged to 4.6 V without compromising the overall capacity (200 mAh/g). Progress in operating spinel electrodes between 5.0 and 3.5 V *vs*. Li for high-rate applications will be highlighted, as will our recent efforts to use coatings deposited from colloidal metal oxide suspensions to stabilize the surface of high-potential (4.5-5.0 V) layered and spinel electrodes (research transferred from the BATT Program to the ATD Program).

TASK STATUS REPORT

PI, INSTITUTION: M.S. Whittingham, SUNY at Binghamton

TASK TITLE - PROJECT: Cathodes – Novel Materials

SYSTEMS: Li/polymer/gel and low-cost Li-ion

BARRIER: Lower-cost, higher-capacity and safer cathodes

OBJECTIVES: The primary objective is to find lower-cost and higher-capacity cathodes, exceeding 200 Ah/kg, that are based on benign materials.

APPROACH: Our cathode approach is to place emphasis on manganese dioxides, both pure and modified with other transition metals, using predominantly low-temperature synthesis approaches. These materials will be synthesized and characterized, both structurally and for thermal and chemical stability. All will be evaluated electrochemically in a variety of cell configurations.

STATUS OCT. 1, 2003: We determined that layered manganese dioxides can be structurally stabilized, and that their electronic conductivity and cycling can be significantly enhanced by the addition of other transition metals. The vanadium-stabilized $LiMnO_2$ was shown to have insufficient power capability to be interesting, but we plan to show the effectiveness of conductive coatings for enhancement of capacity. We completed an evaluation of $LiFePO_4$ as a base-case low-cost cathode, and we showed that hydrothermal synthesis is not a viable approach. We are continuing work to show that vanadium oxides can also be stabilized by the addition of manganese ions to attain capacities over 200Ah/kg.

- $LiFePO_4$: > 120 Ah/kg for 100 cycles at 1 mA/cm^2.
- Layered $Li_xCo_zNi_yMn_{1-y-z}O_2$: 180 - 200 Ah/kg for 10 cycles
- Layered $A_zMn_{0.1}V_2O_5$ (A= NH_4 or TMA): ≥ 200 Ah/kg for 6 cycles.

EXPECTED STATUS SEPT. 30, 2004: For low-cost Li-ion cells, we expect to identify the changes in stabilized $LiMnO_2$ structures as a function of current density and substitution level in $Li_xMn_{1-y-z}Ni_yMn_zO_2$, to determine the optimum substitution level and the role of cobalt, to determine the conductivity and lithium diffusion. For Li/polymer cells we expect to complete the evaluation of the manganese-stabilized δ-vanadium oxides, to investigate other vanadium oxides and phosphates and to compare them to the iron phosphates. We will also have evaluated possible variants on iron phosphate as base-case cathodes. Emphasis in all cases will be placed on understanding the reasons for capacity fade.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES: Our major milestones this year are: (a) to characterize the stabilized (electronically) manganese oxide, determine the optimum substitution of Mn to obtain a capacity of 200 Ah/kg, and to compare the best samples with iron phosphates by September 2004, and (b) to complete the characterization of manganese-stabilized vanadium oxides by December 2003 and compare the best samples with lithium iron and other phosphates for polymer or gel batteries.

PROGRESS TOWARD MILESTONES

The goals of this project are to find improved transition metal oxide cathode materials for lithium batteries and to gain a better understanding of what limits the use of simple alloys as the anode. In the cathode area major effort is being focused on stabilized layered manganese dioxides, and on building a base-case cathode system using $LiFePO_4$ against which the manganese and other cathodes will be compared. In the anode area, the focus is being placed on tin materials, with the initial experiments being on pure tin foil.

(see also our summary under the anode section, presented earlier in this report)

NOVEL CATHODE MATERIALS

Lithium Iron Phosphate. In 2003/2004 our study was completed on lithium iron phosphate as a base-case system. $LiFePO_4$ is a stable cathode material above 1.5 volts, and it cycles exceptionally well; the capacity may be enhanced to 100% by either raising the temperature or lowering the power output. Several vanadium and manganese compounds are now being studied to increase the operating potential.

Stabilized Layered Manganese Dioxides. The layered nickel/manganese system $LiNi_yMn_yCo_{1-2y}O_2$ has been studied for $0.33 \leq y \leq 0.5$ to determine the optimum composition, the nature of the electrochemically active specie, the role of cobalt, and to compare capabilities against $LiFePO_4$. Physical and electrochemical characterization of these materials shows that they may best be described as stabilized nickel oxides. The composition $LiNi_{0.4}Mn_{0.4}Co_{0.2}O_2$ gave the best capacity even though it contained some nickel in the lithium layer, exceeding 180 mAh/g for 20 cycles. They show superior capacity performance relative to $LiFePO_4$ at all current densities. Their chemical and thermal stability has been determined, and coatings will be studied to enhance the chemical stability in fluoride-based electrolytes. There is minimal volume change during cycling. Extensive cycling under partial discharge conditions will be carried out during the next year.

Delta-Phase Vanadium Oxides. In 2003/2004 our study came close to completion on the vanadium oxides, which show the largest capacities but poor capacity retention at high rates. In 2004/2005 we will complete a study on one compound, which is showing a low polarization.

Collaborations and discussions have been held with Professors C. Grey (SUNY Stony Brook), G. Ceder (MIT), and A. Angell (Arizona State).

<u>Publication:</u>

1.J. Katana Ngala, N.A. Chernova, M. Ma, M. Mamak, P.Y. Zavalij, M. Stanley Whittingham, “The Synthesis, Characterization and Electrochemical Behavior of the Layered $LiNi_{0.4}Mn_{0.4}Co_{0.2}O_2$ Compound,” *J. Mater. Chem.*, **14** 214-220 (2004).

TASK STATUS REPORT

PI, INSTITUTION: M. Doeff, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Cathodes - Synthesis and Characterization of Cathode Materials for Rechargeable Lithium and Lithium-Ion Batteries

SYSTEMS: Li/polymer and low-cost Li-ion

BARRIERS: Cost, cycle life, safety, and energy density

OBJECTIVES: To develop low-cost cathodes based on benign materials (*e.g.*, manganese oxides, lithium iron phosphates) having electrochemical characteristics (*e.g.*, cycle life, energy and power densities) consistent with the goals of the USABC and/or PNGV.

APPROACH: Cathode materials are synthesized using both conventional solid-state techniques and solution methods (*e.g.*, sol-gel, glycine-nitrate combustion). The microstructures and atomic structures of the materials are determined by relevant methods, and electrochemical analysis is carried out in a variety of cell configurations. Emphasis is placed on low-cost, structurally stable materials such as manganese oxides and lithium iron phosphate, as well as novel materials with the potential for high energy density.

STATUS OCT. 1, 2003: Initial screening of $Li_xNi_yMn_{1-y}O_{2+z}$ O2/O3 intergrowths was completed. Experiments showing the correlation of $LiFePO_4$ performance with residual surface carbon structure were completed.

EXPECTED STATUS SEPT. 30, 2004: Study of O2/O3 intergrowths will be expanded to the $Li_xAl_yMn_{1-y}O_{2+z}$ system. Optimization of coatings from candidate aromatic or polymeric additives on $LiFePO_4$ will be underway.

RELEVANT USABC GOALS: 10-year life, < 20% capacity fade over a 10-year period.

MILESTONES:

(a) Go/no go decision on optimization process for coating $LiFePO_4$	4/04.
(b) Determine optimum O2/O3 ratios for $Li_xAl_yMn_{1-y}O_{2+z}$	6/04

PROGRESS TOWARD MILESTONE (a)

The objectives of this project are to develop low-cost cathodes based on benign materials having electrochemical properties consistent with the goals of the USABC and/or FreedomCAR. Next-generation materials ($LiFePO_4$ and $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$) are synthesized and studied with a goal of overcoming performance limitations. Exploratory work is directed at novel manganese oxides with the potential of lowering cost and improving safety without compromising energy density. Diffusion coefficient studies on $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ composite cathodes are underway with V. Srinivasan (modeling). Conventional synthesis routes (mixed hydroxide method) cannot be used to make thin-film electrodes so alternative synthesis routes were explored this year. Direct synthesis from nitrate precursors and calcination at temperatures ≥900ºC results in well-crystallized, phase-pure products with electrochemical performances similar to that of a good commercial sample (Tanaka lot # LNCMO-30301) but with decreased irreversible capacity on the first cycle and improved overall cycling.

Strategies to overcome low rate capability in $LiFePO_4$ (*e.g.*, carbon coating) often result in lowering the energy density to an unacceptably low level. Recent work (with R. Kostecki, diagnostics) is directed toward optimizing the structure of *in situ* carbon produced during $LiFePO_4$ synthesis. Carbons with low D/G ratios (disordered/graphene) have higher electronic conductivities and result in improved electrochemical performance, even when present in small amounts (≤ 1 wt%). In FY 2004, ways to promote formation of low D/G ratio carbon were explored, including using additives during synthesis. Best results were obtained with pyromellitic acid (PA). The role of iron impurities in catalytic graphitization was also investigated. The addition of small amounts of iron nitrate and PA during synthesis improves carbon structure and inhibits sample oxidation, as shown by thermogravimetric analyses.

Work on layered manganese oxide intergrowths continued in FY 2004, but emphasis switched from Ni and Co substituents to Al, which is expected to have cost and safety advantages. The O3 component is associated with higher capacity but is unstable with respect to formation of spinel. In contrast, O2 is stable, but exhibits lower capacity. Intergrowths are intermediate in behavior and represent a possible route to high energy density, stable, layered manganese oxide electrodes, if properly designed. This year, numerous Al-substituted compositions were synthesized; of these, 29 were phase-pure O2 or O3, or intergrowths of O2/O3. As Al content increases, the resistance to spinel conversion increases in O3 compounds but capacity also decreases. O2/O3-$Li_xAl_{0.15}Mn_{0.85}O_2$, in contrast, delivers more than 150 mAh/g and cycles with little capacity fading. After 100 cycles, there is some evidence of spinel formation, but full phase conversion is inhibited by the presence of the O2 component.

Publication (spring 2004)

F. Hu and M.M. Doeff, "Electrochemical Characterization of Manganese Oxide Cathode Materials based on $Na_{0.4}MnO_2$," *J. Power Sources*, **129**, 296 (2004).

TASK STATUS REPORT

PI, INSTITUTION: J.B. Goodenough, University of Texas at Austin

TASK TITLE - PROJECT: Cathodes - Novel Materials

SYSTEMS: Li secondary battery

BARRIERS: Cost, cycle life, safety, and energy density

OBJECTIVES: To evaluate alternative layered oxides as cathode materials for a Li-ion battery.

APPROACH: Layered $Li_{1-x}Ni_{1-y}Co_yO_2$ oxides have been shown to exhibit a high Li^+-ion mobility. On the other hand, these oxides are metastable and decompose on removal of a large fraction of lithium from between the host MO_2 layers. Moreover, transition-metal ions M that do not have a strong octahedral-site preference migrate to vacancies in the Li layer, which limits the choice of transition-metal atom. Ohsuku and Mikimura reported a capacity that approaches 150 mAh/g over the range 2.5 to 4.3 V *vs.* Li for 30 charge/discharge cycles with $Li_{2-x}Ni(II)Mn(IV)O_4$, but only with a low current density. We undertook an investigation of this system to determine (1) whether we could increase the capacity at higher current densities by coating the particle with carbon and (2) the role of the Mn(IV) ions since $Li_{2-x}Ni(II)Ti(IV)O_4$ did not appear to be a good cathode material. Other layered oxides would also be explored.

STATUS OCT. 1, 2003: Well-ordered $Li_2Ni_{1-x}Mn_xO_4$ was prepared and battery testing with and without a carbon coating was in process. Single phase Li_2VOSiO_4, and $Li_2(V_{0.9}Ti_{0.1})OSiO_4$ were prepared and preliminary attempts to chemically extract lithium were completed. A new class of layered oxides isostructural with Li_2CuO_2 was under investigation.

EXPECTED STATUS SEPT. 30, 2004:

- Layered $LiNi_{1-x}Mn_xO_2$ with no, or few, transition-metal atoms M in the Li layers will have been battery tested to give a final determination on whether access to the Ni(IV)/Ni(III) couple is possible in the presence of the Mn(IV) ion.
- Ion exchange of Li for Na to determine whether the inability to extract Li form Li_2VOSiO_4 is due solely to low electronic conductivity or is intrinsic to the structure. If the latter is the case, a model will be devised to guide future cathode design.
- Substitution into the Li_2CuO_2-system will be explored in an attempt to suppress the structural transition induced by lithium extraction.

RELEVANT USABC GOALS: 10-year life, < 20% capacity fade over a 10-year period.

MILESTONES:

- Evaluation of $Li_{2-x}NiMnO_4$ to be completed by Feb. 2004
- Evaluation of $Li_{2-x}VOSiO_4$ to be completed Aug. 2004
- Evaluation of other layer-like oxides to be completed by Aug. 2004

PROGRESS TOWARD MILESTONES

New Structures. Two new structures were explored, a layered Li_2VOSiO_4 and a Li_2CuO_2 structure consisting of ribbons of edge-shared square-coplanar $CuO_{4/2}$ units separated by rows of Li^+ ions. The Li^+-ion mobilities in both structures were too low to be of practical interest.

$LiMO_2$ structure. The layered $LiMO_2$ compounds with M = Co or $Ni_{1-x}Co_x$ are used commercially; but cobalt is expensive, and operation on the Co^{4+}/Co^{3+} and/or the Ni^{4+}/Ni^{3+} couples results in oxygen evolution when more than half of the Li is removed. The $LiNi^{2+}{}_{1-x}M^{4+}{}_xO_2$ compounds with M = Ti or Mn do not contain cobalt and should allow operation on the Ni^{3+}/Ni^{2+} redox couple without loss of voltage. However, the performance with M = Ti is poor whereas that with M = Mn was fair. Because the layered $LiMO_2$ structure offers the best chance for high Li^+-ion mobility together with a capacity in excess of 150 mAh/g, we decided to resolve the problems with $LiNi^{2+}{}_{1-x}M^{4+}{}_xO_2$ compounds.

First, we used a criterion for monitoring from x-ray diffraction data the degree of ordering of the Li^+ ions into alternate (111) layers of the rock-salt structure. We then noted that the critical parameter driving the cation ordering was the ratio of the ionic radii of the alkali ion and the mean radius of the transition-metal ions. A smaller ratio makes ordering yield a larger reduction in elastic strain energy. For example, well-ordered $NaFeO_2$ has the ionic radius ratio IRR = 0.63 whereas disordered $LiFeO_2$ has an IRR = 0.87. Because $LiNi^{2+}{}_{0.5}Ti^{4+}{}_{0.5}O_2$ has an IRR = 0.88, it becomes clear that $LiNi_{0.5}Ti_{0.5}O_2$ cannot be well ordered whereas $LiNi^{2+}{}_{0.5}Mn^{4+}{}_{0.5}O_2$ has an IRR = 0.83, which makes it easier to obtain a high degree of cation order. Placement of an M atom in the Li layer blocks Li^+-ion motion and reduces the free volume for Li^+-ion movement by clamping the separation of the oxide-ion sheets bordering the Li layers. In order to lower further the IRR while retaining a large fraction of Ni^{2+} ions, we chose to study $LiNi_{0.6}Mn_{0.4}O_2$. The third task was to develop a synthetic procedure that would yield molecular-level mixing of the Mn and Ni atoms prior to calcinations. We were able to monitor the influence on cathode performance of the Li^+-ion ordering. We also demonstrate that there is no voltage step on passing from the Ni^{3+}/Ni^{2+} to the Ni^{4+}/Ni^{3+} couple. We are now able to supply LBNL for further testing cathodes containing no cobalt having a performance equal to or superior to that of our $LiCoO_2$ reference. At a C/23 rate, the cathode has an average voltage *vs*. Li of 4V and a capacity of 170 mAh/g if operated over the range 4.3-2.75 V, and there was no capacity fade within experimental error after 50 cycles.

Future work: The lack of progress in development of new cathode materials since the conception of $LiFePO_4$ has convinced us that a radically new approach is needed. We therefore propose development of a new cathode material based on a composite structure consisting of the electrolyte and a conducting polymer backbone to which a molecular, or nano particle-based redox unit is covalently anchored. This approach is attractive as it allows great flexibility in modification of the backbone and in the choice of anchored redox units. Moreover, the composite structure allows high Li^+-ion mobilities to and from the redox unit.

TASK STATUS REPORT

PI, INSTITUTION: A. Manthiram, University of Texas at Austin

TASK TITLE - PROJECT: Cathodes - Superior Capacity Retention, High Rate Spinel Manganese Oxide Compositions

SYSTEMS: Low-cost, high-rate Li-ion

BARRIERS: Cost, cycle life, safety, power density, and energy density

OBJECTIVES: To develop low-cost spinel manganese oxide compositions that can offer excellent capacity retention, high rate, low irreversible capacity loss, and good storage characteristics at elevated temperatures.

APPROACH: Our approach is to develop a firm scientific understanding of the factors that control/influence the electrochemical performance of the spinel oxide cathodes and utilize the knowledge gained to design and develop high-performance spinel manganese oxide compositions. In this regard, a variety of single and multiple cationic substitutions as well as an optimization of the microstructure and morphology are being pursued.

STATUS OCT. 1, 2003: New project initiated on 4/1/04.

EXPECTED STATUS SEPT. 30, 2004: A variety of cationic substitutions in $LiMn_2O_4$ to give spinel $LiMn_{2-y-z-\eta}M_yLi_zM'_\eta O_4$ (M and M' = transition and non-transition metal ions) compositions, an evaluation of their electrochemical performance, and a correlation of the electrochemical properties to some basic materials parameters such as initial lattice parameter, initial manganese valence, and the lattice parameter difference Δa between the two cubic phases formed during the charge-discharge process will have been completed. Such a correlation is expected to help to identify optimum cathode compositions.

RELEVANT USABC GOALS: 10-year life, < 20% capacity fade over a 10-year period.

MILESTONES: (a) Optimization of the microstructure and electrochemical properties of the $LiMn_{2-y-z}Ni_yLi_zO_4$ system, and (b) exploration of the $LiMn_{2-y-z-\eta}M_yLi_zM'_\eta O_4$ (M and M' = transition and non-transition metal ions) systems.

PROGRESS TOWARD MILESTONES

A systematic study of several singly and doubly substituted spinel manganese oxide compositions in our laboratory reveals that there is a clear correlation between the capacity fade and a number of sample characteristics such as initial lattice parameter, initial manganese valence, degree of manganese dissolution, and lattice parameter difference Δa between the two cubic phases formed during cycling. Moreover, other electrochemical performance parameters such as rate capability, storage performance, and irreversible capacity (IRC) loss during the first cycle also bear a relationship to the sample characteristics. Our study reveals that the lattice parameter difference between the two cubic phases formed during the discharge-charge process and the consequent microstrain play a major role in controlling the electrochemical properties. The samples exhibiting good capacity retention are characterized by a high initial Mn valence of > 3.58+, and low initial lattice parameter *a*, IRC, and Δa. The low Δa minimizes the microstrain and leads to a maintenance of good crystallinity with sharp diffraction peaks upon cycling. For example, the doubly substituted $LiMn_{2-y-z}Ni_yLi_zO_4$ samples satisfy these criteria and exhibit a combination of superior capacity retention, rate capability, and storage characteristics with low IRC compared to $LiMn_2O_4$ despite a similar amount of Mn dissolution.

However, the doubly substituted composition $LiMn_{1.85}Ni_{0.075}Li_{0.075}O_4$ exhibits a lower capacity of about 95 mAh/g. Our preliminary experiments show that the capacity values can be increased further by optimizing the microstructure and an incorporation of additional cations such as Cu^{2+}. For example, $LiMn_{2-y-z}Ni_yLi_zO_4$ compositions synthesized by heating a commercial $Li_{\sim 0.5}MnO_2$ precursor with appropriate amounts of lithium hydroxide and nickel hydroxide exhibit higher capacity and better capacity retention than the corresponding samples prepared by the conventional solid-state method due to a larger and more-uniform size of the particles. Also, the triply substituted compositions such as $LiMn_{2-y-z-\eta}Ni_yLi_zCu_\eta O_4$ exhibit higher capacity than the doubly substituted $LiMn_{2-y-z}Ni_yLi_zO_4$. We are in the process of evaluating the rate capability and storage characteristics of the $LiMn_{2-y-z-\eta}Ni_yLi_zCu_\eta O_4$ compositions. In parallel, we are also focusing on eliminating the $Li_xNi_{1-x}O$ impurity phase in the 5 V spinel cathode system, $LiMn_{1.5}Ni_{0.5}O_4$, *via* suitable cationic substitutions and an evaluation of their cycle life and rate capability.

BATT TASK 5
DIAGNOSTICS

TASK STATUS REPORT

PI, INSTITUTION: R. Kostecki, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Diagnostics - Electrode Surface Layers

SYSTEMS: Graphite/$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (high-energy, high-voltage Li-ion), Graphite/$LiFePO_4$ (low-cost Li-ion), and Graphite/LiBOB+γBL:EA/$LiMn_2O_4$ (high-power Li-ion)

BARRIER: Short lithium battery lifetimes

OBJECTIVE: Establish direct correlations between electrode surface chemistry, interfacial phenomena, and cell capacity or power decline.

APPROACH: Our approach is to use *in situ* and *ex situ* Raman microscopy, scanning probe microscopy (SPM), ellipsometry, and standard electrochemical methods to characterize cell components taken from baseline BATT Program cells, fresh electrode materials, and thin-film model electrodes. Data to be collected include changes in electrode surface morphology, structure, electronic conductivity, electrode surface chemistry, and SEI thickness and composition, all of which may accompany cell cycle-life tests.

STATUS OCT. 1, 2003: We developed an understanding of the key elements for good electrochemical performance of $LiFePO_4$ cathode, *i.e.*, the role of residual carbon on the performance of the composite $LiFePO_4$ cathode. We determined and understood the effects of various synthesis routes, carbon coating, and impurities on the performance of $LiFePO_4$ cathodes. We provided preliminary data from *in situ* Raman spectroscopy and current-sensing atomic force microscopy of individual particles of BATT baseline electrode materials. We concluded our model ellipsometric diagnostic studies of thin-film $LiMn_2O_4$ cathodes.

EXPECTED STATUS SEPT. 30, 2004: We expect to develop a full understanding of the mechanism of carbon retreat in composite $LiAl_{0.05}Ni_{0.8}Co_{0.15}O_2$ cathodes and its impact on the cathode electrochemical performance upon cycling and storage in $LiPF_6$-EC-EMC electrolyte at elevated temperatures. We intend to identify and characterize the physico-chemical processes that are responsible for this effect, and establish possible links with other detrimental phenomena. The correlations between electrode history, electrode surface properties, and temperature for baseline $LiAl_{0.05}Ni_{0.8}Co_{0.15}O_2$ cathodes will be developed. We expect to determine and verify the key elements for realizing acceptable high-rate performance of $LiFePO_4$ composite cathodes, *i.e.*, the effect of residual carbon and solid-solution doping by metals supervalent to Li^+. We will initiate fundamental studies of dendrite growth on the Li/polymer electrolyte interface.

RELEVANT USABC GOALS: 10 year life, 1000 cycles life - 80% DOD, < 20% capacity fade over a 10-year period.

MILESTONES: (a) Determine the mechanism of carbon retreat from the composite cathodes in Li-ion cells - March 2004. (b) Evaluate the effect of residual carbon and solid-solution doping on high-rate performance of $LiFePO_4$ cathodes - June 2004.

PROGRESS TOWARD MILESTONES

We determined and verified the key elements necessary for high-rate performance of $LiFePO_4$ composite cathodes. We continued to collaborate with M. Doeff (BATT Task 4.3) to study the effect of controlled carbon doping on the electrochemical performance of the composite $LiFePO_4$ cathode. We confirmed that utilization of solid-state or sol-gel prepared $LiFePO_4$ samples used as cathodes in lithium cells depends primarily upon the structure of the residual carbon (0.5-2%) co-produced from either inorganic or organic precursors during the synthesis process. Carbon coatings with low disordered/graphene and sp^2/sp^3-coordinated carbon ratios were produced deliberately by adding small amounts of functionalized organic precursors. Significantly improved utilization and better rate capability correlated well with a larger ratio of sp^2-coordinated carbon, which exhibits better electronic properties than disordered or sp^3-type carbonaceous materials, although the total residual carbon in the samples remained lower than 2 wt%.

To characterize the effect of $LiFePO_4$ solid-solution doping by metals supervalent to Li^+ on the material performance, we examined samples of highly conductive Nb-doped $LiFePO_4$ material from Prof. Yet-Ming Chiang (MIT). A comparative current-sensing AFM (CSAFM) and Raman microscopy diagnostic study of surface electronic conductivity, composition, and structure was carried out at nanometer-scale lateral resolution. Surface analysis of 1% Nb-doped and pristine $LiFePO_4$ samples indicated: (*i*) significantly higher carbon content in the Nb-doped $LiFePO_4$ than in the pristine sample; (*ii*) a non-uniform distribution of carbon at the sample surface; (*iii*) no electronic conductance in the pristine $LiFePO_4$ sample; and (*iv*) non-uniform conductivity of the Nb-doped $LiFePO_4$. Importantly, the carbon distribution at the cathode surface corresponds to the observed conductivity pattern. Thus, the doping effect (if any) is masked by the residual carbon from organic precursors. The higher carbon content in the 1% Nb-doped $LiFePO_4$ is most likely responsible for improved conductivity and electrochemical performance.

In collaboration with Kathryn Striebel (BATT Program Task 1.1) we investigated the mechanism of carbon retreat in composite cathodes. Electrochemical tests of a pure carbon black electrode indicated that carbon black is electrochemically active toward the EC:EMC, 1M $LiPF_6$ electrolyte at elevated temperatures (57°C) at potentials above 3.8V. Reversible processes such as PF_6^- anion intercalation-deintercalation into carbon and carbon surface oxidation-reduction are likely to contribute to the observed current. Raman analysis showed that the structure and electronic properties of the carbon additive undergo significant changes upon cycling in $LiPF_6$-containing electrolytes. Carbon displacement was observed in the cycled cells; and carbon particles were detected on the surface of the lithium anode.

The potential role of carbon retreat/redistribution on cathode impedance rise and capacity loss was demonstrated in our diagnostic studies of $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$, $LiFePO_4$ and $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathodes from tested cells. Surprisingly, they display similar symptoms of degradation, *i.e.*, (*i*) loss of surface electronic conductivity, (*ii*) surface composition changes (carbon retreat), (*iii*) a non-uniform state of charge of active material at the end of testing. The loss of a direct electronic path through the carbon matrix leads to an increased resistance within the electrode and, eventually, total isolation of some particles.

TASK STATUS REPORT

PI, INSTITUTION: X.-Q. Yang, Brookhaven National Laboratory

TASK TITLE - PROJECT: Diagnostics - Battery Materials: Structure and Characterization

SYSTEMS: High-power Li-ion, high-energy Li-ion

BARRIER: Short lithium battery lifetimes

OBJECTIVES: The primary objective is to determine the contributions of electrode materials changes, interfacial phenomena, and electrolyte decomposition to cell capacity and power decline.

APPROACH: Our approach is to use a combination of *in situ* and *ex situ* synchrotron techniques to characterize electrode materials and electrodes taken from baseline BATT Program cells. Techniques that are sensitive to both bulk and surface processes will be used. This will include both K and L-edge x-ray absorption spectroscopy. Exploratory work will be done on other techniques such as non-resonant inelastic x-ray scattering (NRIXS).

STATUS OCT. 1, 2003: In FY 2003 we completed an *in situ* x-ray diffraction (XRD) and a combination of *in situ* and *ex situ* x-ray absorption spectroscopy (XAS) studies of the initial charging processes in $LiNi_xMn_{1-x}O_2$, $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$, and $LiFePO_4$. We also completed *in situ* XRD studies on carbon-coated Si and Ge_3N_4 anodes. We also demonstrated the feasibility of O K edge studies using non-resonant inelastic x-ray scattering (NRIXS) with hard x-rays.

EXPECTED STATUS SEPT. 30, 2004: We expect to complete the XAS and XRD work on $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$. We also expect to complete our studies of the SEI products on cathodes cycled in electrolytes with different salts. We expect to develop time-resolved XRD techniques using position-sensitive detectors (PSD), image-plate detectors (IPD) and charge-coupled devices (CCD). A combination of synchrotron techniques and TEM will be used to study coatings on cathode materials. We expect to provide preliminary data on the effect of new electrolytes and additives on the stability of $LiMn_2O_4$ electrodes at elevated temperatures.

RELEVANT USABC GOALS: 15-year life, <20% capacity fade over a 10-year period.

MILESTONES: (a) Complete *in situ* XAS and XRD $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$, during cycling, by April 2004. (b) Complete development work on new-time resolved XRD techniques, by June 30, 2004.

PROGRESS TOWARD MILESTONES

The primary objective is to develop and apply advanced diagnostic techniques, with sensitivity to bulk and surface process, to monitor degradation process in lithium batteries, to determine the contributions of electrode materials changes, interfacial phenomena, and electrolyte decomposition to cell capacity and power decline. Our approach is to use a combination of *in situ* and *ex situ* synchrotron-based x-ray absorption and diffraction techniques to characterize new electrode materials and electrodes taken from baseline BATT Program cells. Techniques that are sensitive to both bulk and surface processes will be used. This will include both K and L-edge x-ray absorption spectroscopy using both fluorescence yield (FY) and electron yield (EY) detection modes. Exploratory work will be carried out on other techniques such as Transmission Electron Microscopy (TEM), and EELS.

Up to May 2004, we have completed *in situ* x-ray diffraction (XRD) and a combination of *in situ* and *ex situ* x-ray absorption spectroscopy (XAS) studies of the initial charging processes in $LiNi_xMn_{1-x}O_2$, $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ and $LiFePO_4$.

We have developed and applied a new technique, using time-resolved XRD to study the thermal decomposition of Gen 2 cathode materials, $Li_{1-x}Ni_{1/2}Mn_{1/2}O_2$, and $Li_{1-x}Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathodes at different charged states. XRD studies were carried out in the time-resolved mode during heating from 25ºC to 450ºC. For a Gen 2 cathode charged to 50% SOC ($Li_{0.67}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$), decomposition occurs at about 280°C. This temperature decreases with increasing SOC. The presence of electrolyte also can decrease the decomposition temperature even further. Comparing the XRD spectra, it was found that the decomposition temperature is about 265ºC for $Li_{0.33}Ni_{0.5}Mn0.5O_2$. This temperature is about 200°C for the Gen 2 ($Li_{0.33}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$) cathode, which is higher than the 170°C for $Li_{0.33}NiO_2$.

The oxidation states of the transition metals in different charged states are studied using synchrotron-based x-ray absorption techniques. The *K*-edge absorption spectra were studied *in situ* and the *L*-edge absorption spectra for transition metals were studied *ex situ* using the soft x-ray source at the BNL NSLS. Soft x-ray absorption measurements were performed on cathodes extracted from cells charged to different states. Ni and Mn L edges as well as oxygen K edges were recorded, all having energies between 500 and 900 eV. These measurements were carried out in both the electron yield (EY) mode and the fluorescence yield (FY) mode. The EY mode probes to a depth of ~50 Å and the FY mode to a depth of ~2000 Å. Therefore, the EY data have surface sensitivity, whereas the FY mode probes the electrode bulk. For the $Li_{1-x}Ni_{1/2}Mn_{1/2}O_2$ cathodes, it was found that the charge compensation was obtained through oxidizing the Ni^{2+} to Ni^{4+}, while the Mn cations remaining at the Mn^{4+} state during charge. For the $Li_{1-x}Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathodes, the oxygen contribution to charge compensation becomes a very interesting issue, through oxygen K-edge studies.

In situ XRD studies on the oxygen-rich Al-doped spinel cathodes showed the structural stability of this material when cycled at 55°C.

TASK STATUS REPORT

PI, INSTITUTION: P.N. Ross, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Diagnostics – Interfacial and Reactivity Studies

SYSTEMS: High power battery

BARRIER: Short battery lifetime

OBJECTIVES: The primary objective is to establish direct correlations between electrode surface changes, interfacial phenomena, and cell failure.

APPROACH: Our approach is to use *in situ* Fourier transform infrared (FTIR) spectroscopy to study the *interfacial chemistry* in model electrode/electrolyte systems. The spectrometer optics and spectroelectrochemical cell have a special design that enables any electrode material to be studied. Model systems to be studied this year include new Mn-based cathode materials and new Sb-based anodes. The FTIR spectroscopy will be accompanied by classical electroanalytical methods such as cyclic voltammetry and the rotating ring-disk electrode (RRDE).

STATUS OCT. 1, 2003: Experiments confirmed the mechanisms and standard potentials calculated for the electrochemical oxidation of alkyl carbonate solvents of interest. The standard oxidation potentials for Li-ion battery solvents are more than 1 V above the 4.2 V cut-off normally used. Solvent oxidation does not contribute to gas evolution or power fade/capacity loss in Gen 2 Li-ion cells.

EXPECTED STATUS SEPT. 30, 2004: Determine the oxidative stability of Li-ion battery electrolytes with new Mn-based cathodes materials. Determine the oxidation and reduction chemistry of new Li-ion battery electrolyte salts, such as LiBOB. Establish the stability of the SEI layer on Sb-based anodes in PC-based electrolyte.

RELEVANT USABC GOALS: 15-year life, < 20% capacity fade over a 15-year period.

MILESTONE: Establish the possible advantage of a Sb-based anode *vs.* a carbon anode for the high-power battery application. September 2004

PROGRESS TOWARD MILESTONES

The chemistry of the SEI layer formed on graphite anodes cycled in propylene carbonate (PC) – lithium bis(oxolato)borate (LiBOB) electrolyte was studied by *ex-situ* Fourier Transform Infrared Spectroscopy (FTIR) analysis in the attenuated total reflection (ATR) mode. The vibrational spectra clearly show that electrochemical reduction of the BOB anion is a part of the SEI layer formation chemistry. The reduction reaction changes the oxygen coordination around the B atom from tetrahedral BO_4 to trigonal BO_3, *e.g.* esters of boric acid, and changes the symmetry of the O-C-O bonding closer to that in esters of oxalic acid. BOB anion reduction appears to prevent PC co-intercalation into graphite and allows for cycling of graphite anodes without exfoliation.

The surface films formed on commercial $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ cathodes (ATD Program Gen 2) charged from 3.75V to 4.2V *vs*. Li/Li^+ in EC:DEC - 1M $LiPF_6$ were analyzed using the *ex-situ* FTIR-ATR) technique. A surface layer of Li_2CO_3 is present on the fresh cathode, probably from reaction of the active material with air during the cathode preparation procedure. The Li_2CO_3 layer disappeared after soaking in the electrolyte, indicating that the layer dissolved into the electrolyte possibly even before potential cycling of the electrode. IR features arising only from the binder (PVdF) and a trace of polyamide from the Al current collector were observed on the surfaces of cathodes charged to below 4.2 V, *i.e.* no surface species from electrolyte oxidation. Some new IR features were, however, found on the cathode charged to 4.2 V and higher. An electrolyte oxidation product was observed, and it appeared to contain dicarbonyl anhydride and (poly)ester functionalities. The reaction appears to be an indirect electrochemical oxidation with overcharging (removal of > 0.6 Li ions) destabilizing oxygen in the oxide lattice, resulting in oxygen transfer to the solvent molecules.

TASK STATUS REPORT

PI, INSTITUTION: G. Ceder, Massachusetts Institute of Technology
C. Grey, SUNY at Stony Brook

TASK TITLE - PROJECT: Diagnostics - First-Principles Calculations and NMR Spectroscopy of Cathode Materials with Multiple Electron Transfers per Transition Metal

SYSTEMS: Cation-doped lithium nickel manganese oxides

BARRIERS: High voltages, low electronic conductivity, stability, and limited electrochemical testing of cathode performance

OBJECTIVES: To engineer high-capacity, stable cathode materials by working with redox-active metal ions that can exchange multiple electrons in a narrow voltage range, focusing initially on the Ni^{2+}/Ni^{4+} couple. Determine the effect of structure and cation doping on the Li deintercalation/ intercalation mechanisms and the Ni^{2+}/Ni^{4+} couple.

APPROACH: Use solid-state NMR and XAS to characterize local structure and oxidation states of the nearby cations (in the 1st and 2nd cation coordination spheres) as a function of state of charge and number of charge cycles. Use first-principles calculations (density functional theory) to identify redox-active metals, relative stability of different structures, the effect of structure on cell voltages, and to identify promising cathode materials for BATT applications. Anticipate possible instabilities in materials by using calculations and NMR to identify low-activation-energy pathways for cation migration. Investigate the effect of doping on conductivity.

STATUS OCT. 1, 2003: The analysis of the TEM data for $Li[NiMn]_{0.5}O_2$ was completed, and preliminary analysis of the neutron diffraction data was performed.

EXPECTED STATUS SEPT. 30, 2004: $Li[Li_{(1-2x)/3}Ni_xMn_{2/3-x/3}]O_2$ extended cycling studies will have been completed, and the effect of cycling on cathode local structure will have been determined experimentally and compared with predictions from 1st principles calculations. Extensions to related materials with two-electron redox couples will be ongoing. Applications of NMR and calculation methodology to other relevant systems under investigation by members of the BATT Program will be ongoing.

RELEVANT USABC GOALS: Specific power 300 W/kg, 10 year life, < 20% capacity fade

MILESTONES:
(a) November 1, 2003: Complete structural (diffraction, transmission electron microscopy (TEM) and NMR) and computational studies of members of the pseudobinary $Li[Li_{(1-2x)/3}Ni_xMn_{2/3-x/3}]O_2$.

(b) May 1, 2004: Complete structural studies (NMR, XAS, diffraction) of extended cycling for $Li[Li_{(1-2x)/3}Ni_xMn_{2/3-x/3}]O_2$. Determine how a series of dopants affects structure and electrochemistry of these cathodes, by using a combination of calculations and experiment. Complete studies of Ti^{4+}-, Co^{3+}-, and Ni^{3+}- doped material with other members of the BATT Program (Thackeray, Whittingham, and Goodenough).

PROGRESS TOWARD MILESTONES

We have continued to focus on the development and characterization of materials that access the Ni^{2+}/Ni^{4+} redox couple. Using results from first-principles computations, NMR, TEM, XRD, and neutron diffraction, we are now able to explain many of the structural and electrochemical observations in $\mathbf{Li[Ni_xMn_{(2-x)/3}Li_{(1-2x)/3}]O_2}$. The cations in the transition metal layer are long-range ordered, even in the $Li(Ni_{1/2}Mn_{1/2})O_2$ material, previously suspected to have no cation ordering. Ordering occurs in supercells of $\sqrt{3} \times \sqrt{3}$ (or multiples of this cell) and contains Li in specific sites in the transition metal layer. Hence, the substantial Li-Ni disorder, previously attributed to processing, is an integral component of the stable structure of this material, and it is unlikely that it can be reduced. The Li-Ni-Mn ordering in the transition metal layer explains the strong dependence of electrochemical behavior on processing in these materials. When the ordering is well formed, Li from the transition metal layer can be electrochemically extracted or migrate to tetrahedral sites. This is likely to influence the Li diffusion kinetics.

Using NMR as a detailed probe into the local structure of $Li[Ni_xMn_{(2-x)/3}Li_{(1-2x)/3}]O_2$ materials, we have focused on two different areas that impact the utility and performance of this material. NMR studies of the $Li[Ni_xMn_{(2-x)/3}Li_{(1-2x)/3}]O_2$ system with x = 1/2 and 1/3, and cycled between 3 and 4.8V, show that the materials become increasingly disordered over time. By 20 cycles, no Li^+ ions are observed in the transition metal layers for both nickel compositions. X-ray diffraction of these materials show that the superstructure peaks assigned to ordering of the Li, Mn, and Ni in the transition metal layers disappear very rapidly. In the second project we have investigated the effect of temperature and annealing conditions on structure and property. The structure of these materials is under investigation by using NMR, diffraction, TEM, and pair distribution function analysis.

In order to understand how structure affects the electrochemistry of these systems, we used two new experimental methods. First, we used electron spin resonance (ESR) to follow oxidation state change. Although x-ray absorption spectroscopy is typically used to track the oxidation state of the electrochemically active cation, when multiple changes of oxidation state are involved (*e.g.*, Ni^{2+} to Ni^{4+} or V^{3+} to V^{5+}) it's often difficult to determine whether the oxidation process occurs directly or whether intermediate oxidation states are involved. ESR provides a second method for identifying ion oxidation states, and is very sensitive to the presence of Ni^{3+}. Our experiments show that the amount of Ni^{3+} formed as a stable intermediate upon charging $Li[Ni_xMn_{(2-x)/3}Li_{(1-2x)/3}]O_2$ is less than expected based on two simple one-electron reactions $Ni^{2+} \rightarrow Ni^{3+} \rightarrow Ni^{4+}$, and for x>1/3, the oxidation process does not involve Ni^{3+} as a stable intermediate.

We have also been trying to enhance the capacity of $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$. Using first-principles computations it was found that upon charge, Ni^{2+} oxidizes to Ni^{4+} before the Co^{3+}/Co^{4+} redox couple is activated. The Co^{3+}/Co^{4+} capacity sits a quite high potential making it unlikely that it can be completely used in practical battery applications, thereby limiting the capacity enhancements that can be achieved with this material. Computations predicted the effect of various substitutions on the voltage curve of this material. Substitution of Mn^{4+} by Ti^{4+} and Zr^{4+} were all found to increase the Co^{3+}/Co^{4+} redox potential. Only direct substitution of part of the Co by Fe was found to reduce the potential at the end of charge. Partially substituted materials have been synthesized. Initial electrochemical testing confirms the lowered potential, but also indicates poor cycling performance. The development of first-principles methods to predict electronic conductivity, in such important materials as $LiFePO_4$ and other phosphates, is underway.

TASK STATUS REPORT

PI, INSTITUTION: T.M. Devine, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Diagnostics - Corrosion of Current Collectors

SYSTEMS: Gr/LiFePO4, Low-cost Li-ion

BARRIER: Uncertain and possibly inadequate corrosion resistance of Al current collectors

OBJECTIVES: Predict the long-term corrosion performance of Al current collectors in Gen 2 cells based on statistical analyses of corrosion of Al current collectors in batteries tested in the BATT and ATD Programs. Determine the mechanism of passivation and identify the passive film responsible for the corrosion resistance of Al current collectors in Gen 2 and in electrolytes of multi-component salts that are optimized for battery service and that are noncorrosive to Al current collectors. Determine the influence of the level of purity of Al on its corrosion resistance in Gen 2 and in multicomponent, noncorrosive electrolytes.

APPROACH: The research project consists of three tasks. In the first task, the Al current collectors taken from many tens of batteries that have been life-tested following well-defined testing protocols are inspected for corrosion damage. The results of the failure analyses are analyzed by Extreme Value Statistics to predict 10-year and 15-year performance of Al current collectors in Li-ion batteries. Another objective of the failure analyses is to identify the mechanism of corrosion of the Al current collectors. In the second task, the passive films that are responsible for the corrosion resistance of Al, which has been rendered free of its air-formed film, will be identified in (*i*) Gen 2 and (*ii*) multicomponent noncorrosive electrolytes. In the third task, virgin coin cells will be charged and overcharged and the type and extent of corrosion of Al current collectors will be identified.

STATUS OCT. 1, 2003: Completed failure analyses of Al current collectors from 33 batteries that were life-tested by M. Doeff. The severity of pitting corrosion of Al current collectors was related to the type of cathode ($LiFePO_4$ and $LiMn_2O_4$), the number of cycles, and the magnitude of the charging current density. The influence of impurities in the electrolyte and in Al on the corrosion of Al current collectors was investigated by potentiodynamic anodic polarization tests of Al in 1 M $LiPF_6$/EC + DMC. Lastly, the influence of applied potential and the effect of partial removal of the air-formed oxide film on the corrosion of Al in Gen 2 and 1M $LiPF_6$/EC + DMC were determined.

EXPECTED STATUS SEPT. 30, 2004: The mechanism of Al passivation o and the identity of the passive film will be determined in Gen2 electrolyte and in at least one electrolyte containing multi-component, noncorrosive salts. The mechanism(s) of corrosion of Al current collectors in life-tested batteries will be determined. 10 and 15 year performances of Al current collectors in Gen 2 electrolyte will be estimated using Extreme Value Statistical Analyses of the data obtained in the inspections of life-tested batteries.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade.

MILESTONES: (a) The influence of Al composition (purity) its resistance to pitting and crevice corrosion in Gen 2 electrolyte will be determined by August 31, 2004.
(b) 10-year and 15-year performance of Al current collectors in Gen2 batteries will be predicted based on Extreme Value Statistical Analyses of life-tested batteries by August 31, 2004.

PROGRESS TOWARD MILESTONES

In the previous quarter we reported a small but possibly significant incidence of corrosion of aluminum current collectors in lithium-ion batteries that had been life tested by Marca Doeff (MD). Our immediate objective has been to determine the cause(s) of the corrosion. It has been difficult to duplicate in electrochemical corrosion tests the corrosion that occurred to aluminum current collector during MD's battery charging/overcharging. To determine why corrosion sometimes occurs to current collectors, we have looked into the factors that are responsible for the generally good corrosion resistance of aluminum in battery electrolytes. Identifying the factors necessary for corrosion resistance might help to explain why corrosion sometimes occurs.

A combination of potentiodynamic polarization tests, electrochemical quartz crystal microbalance tests, and ac impedance spectroscopy have indicated the following. First, Al is susceptible to severe corrosion in EC+DMC that is free of $LiPF_6$ and that contains a small amount of water as a contaminant. Decreasing the water concentration decreases the amount of corrosion. Varying the relative amounts of EC and DMC does not prevent corrosion, but adding a minimum of 0.02 M $LiPF_6$ prevents significant corrosion. Second, the $LiPF_6$ causes the formation of a protective film of AlF_3. The thinner the air-formed film of Al_2O_3, the more readily AlF_3 forms. Third, when the air-formed film of Al_2O_3 is completely removed, the film of AlF_3 forms at the very low potential of 1.0 V *vs*. Li/Li^+. Since AlF_3 can form at 1.0 V *vs*. Li/Li^+, its formation does not depend on (*i*) oxidation of the solvent, which is stable to potentials above 4.0 V, or (*ii*) voltage breakdown of PF_6^-, which is stable to potentials as high as 5.0 V. Fourth, either very little water contamination, or possible no water at all, is needed to provide F- for forming the film of AlF_3. The protective film of AlF_3 is formed in 1 M $LiPF_6$ 1:1 EC+DMC that was dehydrated by exposure to high surface area alumina powder. If AlF_3 forms in the complete absence of water, thermal decomposition of PF_6^- might be the source of F^- needed for the formation of AlF_3. The results to date indicate that water contamination is not harmful to corrosion resistance of Al provided a small concentration (*i.e.,* 0.02 M) of $LiPF_6$ is present.

BATT TASK 6
MODELING

TASK STATUS REPORT

PI, INSTITUTION: J. Newman, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Modeling - Improved Electrochemical Models

SYSTEMS: Li/polymer and low-cost Li-ion

BARRIERS: Dendrite formation, capacity fade

OBJECTIVES: Develop experimental methods for measuring transport, kinetic, and thermodynamic properties. Model electrochemical systems to optimize performance, identify limiting factors, and mitigate failure mechanisms.

APPROACH: Develop model of dendrite formation on lithium metal. Use simulations to improve understanding of the SEI layer. Develop improved experimental methods for measuring transference numbers in liquid and polymer electrolytes.

STATUS OCT. 1, 2003: Molecular dynamics simulations of diffusion coefficients were completed. Simulation of the behavior of conductive polymers for overcharge protection was completed. Modeling of dendrite growth and initiation was continuing. The effect of linear-elastic stresses on electrode current densities was evaluated for periodically roughened surfaces. The shear modulus of the electrolyte phase was varied to determine shear stress near deforming lithium/polymer interfaces. Modeling of the SEI layer and comparison with experimental results was continuing. Measurement of thermodynamic and transport properties in liquid electrolytes was continuing. Modeling of the iron phosphate/natural graphite baseline and its performance optimization was completed and the optimized designs supplied to the Cell Development group.

EXPECTED STATUS SEPT. 30, 2004: Modeling of dendrite growth will be ongoing. A stability analysis will be completed that determines practical conditions under which dendrite growth can be inhibited or eliminated by mechanical means. Comparison of SEI simulations with experimental results and refinement of the model will be ongoing.

RELEVANT USABC GOALS: Specific Energy, 150 Wh/kg, Specific power 300 W/kg

MILESTONES: In March 2004, we will know what elastic properties, if any, inhibit dendrite initiation.

PROGRESS TOWARD MILESTONES

Dendrite Initiation and Propagation We have accomplished our dendrite modeling milestone, to determine elastic properties that inhibit dendrite initiation. Our goal was to determine if a pure lithium anode was feasible in polymer-electrolyte systems, or if failure by dendritic deposits was an insurmountable obstacle. Our model helped us determine the bulk properties that are necessary for the polymer to inhibit interfacial roughening by mechanical action. Present polymer research has focused on materials with elastic moduli in the megapascal range. We found that polymers require shear moduli in the gigapascal range in order to inhibit interfacial roughening, providing a useful technical target for scientists in materials development. The general kinetic model we developed has broad utility, and can be employed to treat interfacial roughening in many systems. The results in the lithium/polymer system were somewhat surprising because there has been a great deal of theoretical work in liquid electrolyte systems, which has shown that interfacial roughening cannot be prevented.

The Solid Electrolyte Interphase We have completed a mathematical model of the Solid Electrolyte Interphase (SEI) on the negative electrode. Results indicate that film growth and impedance rise are greater at lower electrode potentials, indicating that failure may be accelerated for systems in which the cell is fully charged. Current efficiency increases with the charge rate. The potential of the negative electrode with respect to a lithium reference electrode drops to zero before the electrode is fully charged, indicating that the electrode capacity is not fully utilized. This effect is enhanced at higher rates of charge, confirming that the SEI has a detrimental impact on rate capability. Parameter estimation will allow us to compare simulations with experimental results.

Transport Property Measurement We have developed a novel method, based upon the galvanostatic polarization technique, for measuring transference numbers in electrolytes that have practical application to lithium-ion batteries. We have begun measuring transport properties (conductivity, transference number, and diffusivity), as well as the thermodynamic factor, in a ternary system ($LiPF_6$ in PC), over a range of salt concentrations. We will compare these properties to those of LiBOB in several solvent systems. Preliminary measurements indicate that the conductivity of LiBOB-based electrolytes depends upon the solvent choice, and may be greater than or less than that of $LiPF_6$ in PC. For more-complex electrolytes (*e.g*. those with multiple solvents or additives), we will devise a methodology for estimating $(1/2)n(n-1)$ independent transport properties, where n is the number of components in the electrolyte.

TASK STATUS REPORT

PI, INSTITUTION: V. Srinivasan and J. Newman, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Modeling - Modeling of BATT Program Baseline Chemistries

SYSTEMS: Low-cost Li-ion cells

BARRIER: Capacity fade, low power capability

OBJECTIVES: Model BATT Program baseline systems to optimize performance, identify limiting factors, and understand failure mechanisms. Measure relevant thermodynamic, kinetic, and transport parameters for use in the models.

APPROACH: Develop models for BATT Program baseline chemistries. Use models to improve understanding of performance limitations and identify promising design options to maximize performance. Compare optimized cells to identify promising baselines that satisfy DOE goals. Incorporate life-limiting mechanisms into baseline models and study their effects on performance.

STATUS, OCT. 1, 2003: Optimization of natural graphite/iron-phosphate cell to maximize performance was completed. Modeling of baseline spinel cathodes was initiated.

EXPECTED STATUS SEPT. 30, 2004: Modeling of all BATT Program baseline cells, along with optimization studies, will be competed. A model-based performance comparison of the three baseline cells will be ongoing. Incorporation of phenomena that affect the cycle life of these cells will be ongoing.

RELEVANT USABC GOALS: Specific energy, 150 Wh/kg, specific power 300 W/kg

MILESTONES: Develop models for $LiMn_2O_4$ and $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ baseline cells and determine performance limitations for each by May 2004 and August 2004, respectively.

PROGRESS TOWARDS MILESTONES

The goal of this project is to understand the behavior of the three BATT Program baseline systems, namely, $LiFePO_4$, $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$, and $LiMn_2O_4$ spinel, using mathematical models. The approach taken is to develop mechanistic models for each chemistry and combine them with controlled half-cell experiments in order to understand limiting mechanisms. This understanding is then used to suggest changes to the materials and quantify the improvements. In addition, full-cell models with a natural graphite negative electrode are used to perform cell design and optimization studies to evaluate the maximum possible performance of these chemistries and compare them to the DOE/FreedomCAR goals for both EV and HEV applications.

$LiFePO_4$ Baseline: A model was developed for this chemistry in the prior fiscal year, and it was concluded that both transport limitations in the solid phase and conductivity in the matrix phase limited its high-power capability. In order to explore these effects further and to understand the cause for the wide differences in performance among the materials reported by various groups, a combined model-experimental approach was taken, in collaboration with Kathryn Striebel, whereby six different iron phosphates from various laboratories were analyzed. The model allowed for the differences in loading and thickness in each of these electrodes to be normalized, whereby the intrinsic differences between each of the materials were exposed. The study revealed that both the carbon coating and extra added carbon are critical to performance and that small particles and uniform particle sizes are preferable. Subsequently, the model was used to perform optimization studies wherein we maximized the specific energy by changing the thickness and porosity. The optimization was performed for discharge-times ranging from 10 h to 2 min, thereby spanning both the EV and HEV goals. This approach showed that this baseline system does show promise in high-power applications.

$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ Baseline: Comparison of a model, developed in this reporting period, to experimental data show that the main potential drops were caused by kinetic and transport losses in the solid particles. This suggests that decreasing the particle size, whereby both the diffusion length is decreased and the surface area for reaction is increased, would be very helpful in improving the cell performance. Subsequently, the same optimization studies, as detailed above, were conducted on this baseline for two charging voltages, 4.3 and 4.5 V. The model results show that this baseline exhibits as much as 20% higher specific energy and specific power when charged to 4.3 V compared to the $FePO_4$ baseline system. An additional 10% increase in performance was seen when charged to 4.5 V owing to the higher capacity at higher charging voltages.

Spinel Baseline: Work has been initiated to model and optimize this baseline system and compare it to the other two. Experimental data with various rates are being collected, which will then be compared to an existing model for this chemistry. Cells with $LiPF_6$ electrolyte will be compared to those with LiBOB to quantify any loss in performance.

Future tasks will concentrate on making the models more robust by measuring relevant transport and kinetic properties (with Marca Doeff) and studying the performance of the baseline systems for HEV applications.

TASK STATUS REPORT

PI, INSTITUTION: A.M. Sastry**,** University of Michigan

TASK TITLE - PROJECT: Modeling and Experimentation – Electrochemical Materials

SYSTEMS: Li/polymer and low-cost Li-ion

BARRIER: Short lithium battery lifetimes

OBJECTIVES: Predict the role of conductive and mechanical failures on reduced performance in the baseline systems, by tightly coupled experimental and simulation studies of microscale transport and mechanics phenomena.

APPROACH: Use simulations to design combinations of conductive additives to improve battery performance, and specifically reduce irreversible capacity losses (ICL). Perform complete studies of electrode (both anode and cathode) conduction, with cell testing to confirm the materials' effect on battery performance. Show improvement in performance of baseline materials with strategic additives, as determined by simulation.

STATUS OCT. 1, 2003: Confirmed structure/function relationships in carbon additives in baseline systems. Determined effect of lamination on contact resistance in baseline systems. Determined initial relationship between ICL and conductivity of anode. Initiated testing of cathodes. Initiated simulations of cathode conductivity.

EXPECTED STATUS SEPT. 30, 2004: Experiments (LBNL and UM) and simulations on conduction in baseline anodes and cathodes, with correlations developed relating material composition and cell capacity losses will be completed. Modeling of other BATT Program baseline cell chemistries will be ongoing.

RELEVANT USABC GOALS: Specific power 300 W/kg, 10 year life, < 20% capacity fade

MILESTONES:
(a) Identification of improvements possible in additive carbon layers in anodes (between current collectors and active materials) - May 2004.

(b) Simulations of local mechanical loads in pressed anodes - June 2004.

PROGRESS TOWARD MILESTONES

We have developed a technique for nondestructive determination of the electronic conductivity and contact resistance of each sublayer in composite $LiFePO_4$ cathodes. We have used our approach to experimentally determine electronic conductivity of $LiFePO_4$ cathodes with carbon additives, in close collaboration with other BATT Program researchers (Striebel, Zaghib). Composite $LiFePO_4$ cathodes with varying amounts (3 to 12 wt%) and types of conductive carbon additives were pressed onto carbon-coated current collectors patented by Hydro-Québec; this compression was carried out to reduce the contact resistance between active materials and current collectors. Sample cathodes were tested and the data obtained were sent to LBNL (Striebel) for comparison with electrochemical conduction performance. Our conduction experiments (four-point probe) were analyzed using a numerical approach to solve for conductivity of each layer in the composite electrodes, and contact resistances between layers.

Our conductivity data confirm that carbon additives significantly improve overall $LiFePO_4$ cathode electrical conductivities. For example, measured resistivity dropped from 176 to 67 $\Omega\cdot$cm as carbon black increased from 3 wt% to 10 wt% in the materials studied. Carbon black provided better overall improvement of conductivity than graphite, among carbon-type additives. This may be due to the intrinsic material properties of carbon black and graphite, or their morphologies in the final, pressed electrode.

As part of our efforts, we developed a computer code equipped with a user-friendly interface for the use of BATT Program researchers to obtain conductivities and contact resistances within multilayered electrodes. The code simulates the in-line four-point-probe technique, and utilizes a closed-form numerical method to obtain results for the internal conductivity of electrode sub-layers.

Our next efforts will be focused on investigation of the relationship between electrode thickness, and power and energy of composite $LiFePO_4$ cathodes, using 3D finite-element modeling. We found that 3D packing effects play a significant role in the electrochemical conductivity of the other relevant program electrochemistries, due to the size of particles used for conduction relative to electrode thickness. Furthermore, because pressing electrodes can result in improved conductivity, but can also severely damage the cathode, we will also generate a general guideline for pressing electrodes for optimized conductivity.

PROPOSALS UNDER REVIEW

ORGANIZATION *(Principal Investigator)*	TITLE	STATUS
SUNY Binghamton *(M.S. Whittingham)*	Novel Anode Materials and Novel Cathode Materials	Renewal Proposal- Under Negotiation
MIT *(G. Ceder)*	High Capacity, Stable Cathode Materials with Multiple Electron Transfer per Transition Metal	Renewal Proposal- Under Negotiation
SUNY Stony Brook *(C. Grey)*	High Capacity, Stable Cathode Materials with Multiple Electron Transfer per Transition Metal	Renewal Proposal- Under Negotiation

BATTERIES FOR ADVANCED TRANSPORTATION TECHNOLOGIES (BATT)

CALENDAR OF RECENT AND UPCOMING EVENTS

March 2004

7 - 10	First International Seminar on Fuel Cell Development and Deployment, Program Chairman, Nigel Sammes, University of Connecticut, School of Engineering, 44 Weaver Road Unit 5233, Storrs, CT 06269, Tel: 860.486.9204, Fax: 860.486.8378, E-mail: sammes@engr.uconn.edu. (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; ecs@electrochem.org; http://www.electrochem.org/meetings/meetings.htm)

May 2004

9 - 14	205th Electrochemical Society Meeting – San Antonio, TX (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; ecs@electrochem.org; http://www.electrochem.org/meetings/meetings.htm)
25	Anode Symposium - Berkeley, CA (A.R. Landgrebe and M.S. Whittingham, co-chairs)
26-27	BATT Program Annual Review Meeting - Berkeley, CA (F. McLarnon, chair)

June 2004

1 - 4	4th International Advanced Automotive Battery Conference (AABC-04) – San Francisco, CA (530-692-0140; fax: 530-692-0142); AAABC04@advancedautobat.com – http://www.advancedautobat.com/aabc.html; The Renaissance Parc 55 Hotel
21-22	ATD Program Meeting, Argonne, IL
27 – July 2	12th International Meeting on Lithium Batteries, IMLB12 – Nara, Japan (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; imlb12@electrochem.org; http://www.electrochem.org/meetings/meetings.htm)

September 2004

19 - 24	55th Annual Meeting of the International Society of Electrochemistry – Thessaloniki, Greece (Prof. E. Theodoridou) http://www.isechemistry.gr/

October 2004

3 - 8	206th Electrochemical Society Meeting – Honolulu, HI (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; ecs@electrochem.org; http://www.electrochem.org/meetings/meetings.htm)

May 2005

15 - 20 207th Electrochemical Society Meeting – Quebec City, Canada (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; ecs@electrochem.org; http://www.electrochem.org/meetings/meetings.htm)

23 - 29 Lithium Battery Discussion Meeting, LiBD2004 – Arcachon France (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; ecs@electrochem.org; email: Josh.Thomas@mkem.uu.se; http://www.icmcb.u-bordeaux.fr/libd)

September 2005

25 - 30 56th Annual Meeting of the International Society of Electrochemistry – Busan, Korea (Contact: H Kim; hasuckim@plaza.snu.ac.kr)

October 2005

16 - 21 208th Electrochemical Society Meeting – Los Angeles, CA (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; ecs@electrochem.org; http://www.electrochem.org/meetings/meetings.htm)

May 2006

7 - 12 209th Electrochemical Society Meeting – Denver, CO (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; ecs@electrochem.org; http://www.electrochem.org/meetings/meetings.htm)

23 - 29 Lithium Battery Discussion Meeting, LiBD2004 – Arcachon France (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; ecs@electrochem.org; email: Josh.Thomas@mkem.uu.se; http://www.icmcb.u-bordeaux.fr/libd)

October 2006

29 - Nov. 3 210th Electrochemical Society Meeting – Cancun, Mexico (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; ecs@electrochem.org; http://www.electrochem.org/meetings/meetings.htm)