Batteries for Advanced

Transportation Technologies

(BATT) Program

for

Electrochemical Energy Storage

1st Quarter Report

FY 2004

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March 5, 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 first-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
	V. Battaglia	LBNL
	K. Abbott	DOE-Oakland

LBID-2495

BATTERIES FOR ADVANCED TRANSPORTATION TECHNOLOGIES (BATT) PROGRAM

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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

(a) Prepare 16 $LiFePO_4$/natural graphite cells for evaluation 2/04

NTT (Japan) has reported excellent cycle life with the $LiFePO_4$/graphite cell. However, in our prior work we observed a significant capacity fade with this cell that was attributed to a side-reaction at the anode which acts to consume the cycleable lithium. This behavior has been observed with three different natural graphite anodes. The natural graphite anodes, removed from previous cells, were evaluated with Raman Spectroscopy (Kostecki). The anodes cycled against $LiFePO_4$ showed evidence of an, as yet unidentified, Fe species that was not observed on identical anodes cycled against $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ cathodes. These results along with the need to switch to a PC-containing electrolyte necessitated the evaluation of two coated natural graphites, GDR LA-2-2 from Mitsui Mining and SLC1015 from Superior Graphite, to replace our standard SL20. In addition, modifications have been made to our coater in an effort to scale-up our process for the application of a uniform carbon black/PVdF coating to the current collector, prior to coating the $LiFePO_4$. When these evaluations are complete, we will assemble several batches of eight identical cells for performance and aging studies at elevated temperatures.

(b) Benchmark $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$/$LiPF_6$:PC:EC:DMC/Gr cell 6/04

Four candidate $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$'s, received from Tanaka, Seimi and Mitsui, show acceptable cycling stability at C/2, in half-cell studies, as shown in Fig. 1.

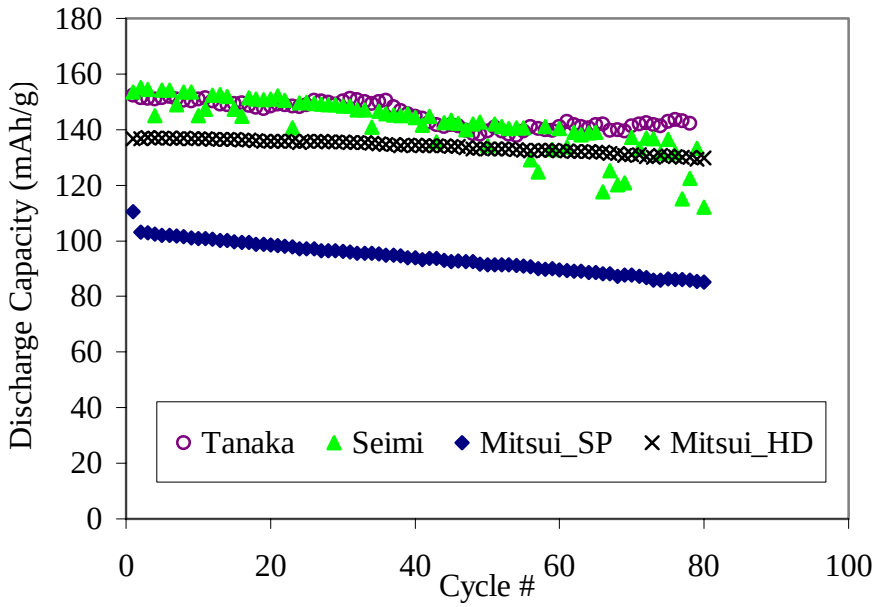


Figure 1. Comparison of C/2 Cycling for four different types of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$.

First-cycle inefficiencies for the Tanaka and Seimi cathodes were about 10-11%, with somewhat higher values for the Mitsui materials. Due to better high-rate performance and general availability, the Seimi L333 has been chosen as the baseline $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ and cathodes made from this material have been delivered to the modeling and diagnostic tasks. Studies of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ / natural graphite pouch cells are underway.

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

Electroactive polymers whose conductivity depends upon their state of charge can provide substantial overcharge protection in lithium batteries. We first showed that Li-TiS_2 cells containing poly-3-butylthiophene-impregnated separators were reversibly shorted internally at a cell potential of about 3.2 V. We are now working to increase the onset potential of the overcharge protection mechanism by using different polymers and making changes in the separator loading and polymer microstructure. Poly-3-phenylthiophene is oxidized at a potential about 0.5 V higher than poly-3-butylthiophene, and was therefore a candidate for protecting cells containing the olivine $LiFePO_4$ cathode. It was found, however, that this polymer was unstable at low potentials and degraded when in contact with the anode of a lithium or lithium ion cell. By preparing a composite separator with poly-3-phenylthiophene on the cathode side and poly-3-butylthiophene on the anode side, reversible shorting at nearly 4.0 V was achieved, sufficient to demonstrate protection of 3 V Li-MnO_2 cells and 3.5 V $LiFePO_4$ cells. Since most conductive polymers are only stable in a limited potential range, polymers with oxidation potentials suitable for 4 V lithium batteries are generally unstable at the Li anode potential. The approach of incorporating a lower voltage polymer as a protection layer between the higher voltage polymer and the anode has greatly expanded the field of polymer candidates for overcharge protection.

We are also studying the behavior of cells containing only the conducting polymer-impregnated separator and an anode for use as external overcharge protection devices. In many cases, it is possible to increase the shorting potential relative to that of an internal separator. This may also allow the use of alternative electrolytes and other components in the external device.

OTHER PROGRESS:

We previously showed that the iron (III) phosphate, $Fe_{1.2}PO_4X$, where X is F, OH, or H_2O, synthesized by a hydrothermal method, 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. It was hoped that particle size reduction by high energy milling, or by reduced synthesis times, would increase the rate capability of this material. Unfortunately, this was not realized, and no further work is anticipated on this cathode material. Synthesis and evaluation of other phosphate compounds, especially ones containing manganese, continue. Two possibly new phases with stoichiometry $LiFePO_4F$ and $LiMnPO_4F$ have been prepared by solid state reactions at 750°C. These are M^{III} compounds and may be able to sustain both insertion and extraction of lithium.

$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ cathodes exposed to air for long periods contain large quantities of Li_2CO_3. Cells made with these electrodes have low capacity and poor power characteristics. We have shown that the formation of a thick carbonate coating on the active particle surfaces causes isolation of a significant portion of the active material. Since this phenomenon is especially noticeable in Ni-containing cathodes, we will study the new baseline material $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ carefully to evaluate its resistance to degradation in air.

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

During this quarter, we studied the swelling and conductivity of a gel polymer electrolyte as a function of liquid electrolyte content. The gel is composed of x% polymer and (1-x)%EC-GBL-1.5M LiFSI. The conductivity decreased linearly from 10.1 to 3.50 mS/cm with increasing polymer content in the gel, *i.e.*, pure liquid electrolyte and 35/65 wt% polymer/liquid ratio (Table1), respectively.

Table 1: Conductivity of the gel electrolyte as a function of the polymer content.

Polymer (wt%)	EC-GBL(wt%) 1.5M LiFSI	Conductivity (mS/cm)
0	100	10.10
10	90	9.35
15	85	7.68
20	80	6.18
25	75	5.01
30	70	4.17
35	65	3.50

Optimization studies of the new HQ gel electrolyte showed good mechanical properties at 10/90 polymer/liquid ratio by weight. A 20% variation in swelling was observed with this polymer.

Our second objective was to evaluate half cells and Li-ion cells by using a new low-cost lithium salt bis(fluorosulfomyl)-LiFSI, developed by The University of Montreal. The discharge capacity of cells containing LiFSI was 10% higher than that with $LiBF_4$ at C/1 rate. Tests indicate that EC-GBL showed a comparable performance to EC-PC-DMC in Li-ion cell with LiFSI salt.

We have studied the oxidation stability of the gel polymer as a function of additives (PMMA, TiO_2, SiO_2). The additives PMMA and SiO_2 show comparable results, with an improvement in polymer oxidation stability (see Fig.1). However, addition of TiO_2 yielded a slight decrease in stability compared to the polymer alone.

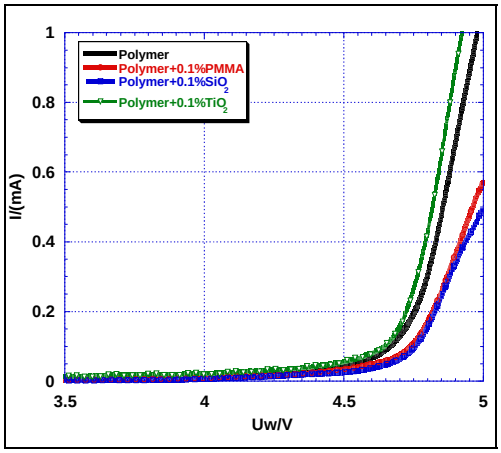


Figure 1. Additive effect on the gel polymer oxidation stability.

We have developed a new design for sealing machine which will be used to study the effect of trapped gas in the cell.

Our last goal to deliver 10 Li-ion gel cells, which contained composite anode (graphite and fiber) and $LiFePO_4$ as cathode, to LBNL by the end of December 2003 was achieved.

We have identified Zeon (Japan) as an appropriate supplier of low-cost water-soluble binders (WSB) for use in both negative and positive electrodes. We will develop an optimized coating process for the WSB in cooperation with Zeon. This essentially meets our December 2003 milestone on this subject.

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

Accomplishments

We have initiated studies on graphite-metal and graphite-intermetallic composite electrodes with the strategy of using the metal or intermetallic component to increase the specific and volumetric electrode capacities of pure graphite (372 mAh/g and 818 mAh/ml, respectively), and to take advantage of the structural stability of the carbon component to buffer volumetric expansion and to maintain good electronic contact between particles. In particular, we are using a solution route as an alternative method to making small metal or intermetallic particles at room temperature for these composite electrodes. Our solution-route approach is analogous to that reported recently by Dailly *et al.* in which Sb metal was deposited onto graphite by reduction of $SbCl_5$ with potassium-intercalated graphite (KC_8). We have also continued our search for high capacity metal-oxide negative electrodes.

Our initial work on graphite-metal and graphite-intermetallic composites has been based on systems containing Sb, Si, Sn, and Ag. For example, our preliminary data on graphite-Sn and graphite-Sb composites electrodes, fabricated from intimate mixtures of the components, show that a specific capacity above the theoretical value for pure graphite can be achieved without compromising electrochemical stability (Fig. 1). For example, over the first 7 cycles, a Sn-graphite composite electrode provides a steady 377 mAh/g, whereas a Sb-graphite electrode provides 457 mAh/g. (These cells are still on test.) Moreover, the irreversible capacity loss observed on the initial cycle is only 8% for the Sb-graphite electrode; it is slightly higher for Sn-graphite (14%). These data hold promise for future developments.

We are investigating the structural morphology and electrochemical properties of Cu_2Sb, Ag_3Sb and InSb intermetallic electrodes, synthesized at room temperature by the solution route. Metals or intermetallic compounds produced by this technique tend to crystallize with high-surface-area dendritic structures, as shown in Fig. 2 for an InSb sample. Attempts are currently being made to crystallize these structures onto graphitic substrates, and to evaluate their electrochemical properties.

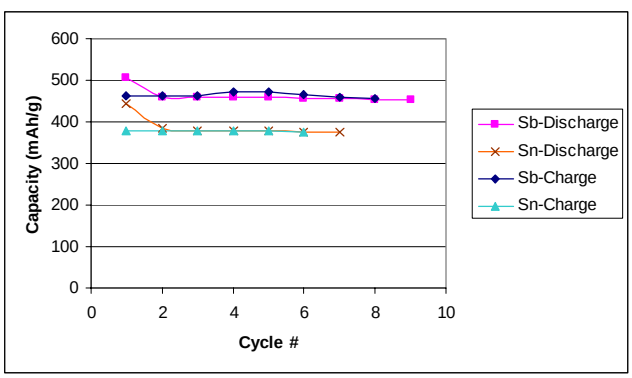


Figure 1. Capacity *vs*. cycle no. plots for Sb-graphite and Sn-graphite composite electrodes.

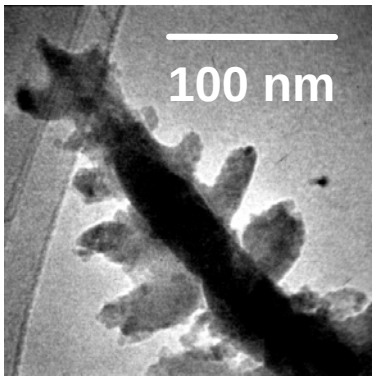


Figure 2. TEM image showing the dendritic morphology of InSb formed from a solution route.

Our studies of metal-oxide negative electrodes are currently focused on layered Li_2MO_3 and low-potential $Li_{1+x}MO_2$ systems. Although the theoretical capacity Li_2MnO_3 (918 mAh/g) could be achieved in a lithium cell by fully reducing the manganese ions to their metallic state during the initial cycle, only 400 mAh/g could be cycled in the range 1.2 – 0.0 V, consistent with the hysteresis and high irreversible capacity loss observed in related metal-oxide systems.

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

In the previous report we discussed our program to understand the cause of capacity fade for tin foil as the anode in lithium batteries. An analysis of our data showed that, after a break-in period, the amount of lithium inserted into the tin foil is equal to the amount of lithium removed in the previous half-cycle. This indicated that freshly formed tin is essentially inert in the electrolyte used. This behavior was essentially the same whether a fluoride electrolyte salt, like $LiPF_6$, or a fluoride-free salt, like LiBOB, was used; however, the initial capacity was lower for the LiBOB salt. Capacity fade must thus be associated with the lithium-tin phase after lithium insertion. Two possible options are: (1) some of the lithium in the tin reacts irreversibly with the electrolyte, this becoming unavailable for subsequent use, and (2) some of the Li_xSn alloy becomes physically and electronically detached from the electrode so it can no longer participate.

To help determine the impact of the electrolyte salt on the capacity fade, we have made a study of the solvent coordination in $LiPF_6$ and LiBOB EC/DMC electrolytes. For the LiBOB salt, the lithium is tetrahedrally coordinated by four EC molecules; the DMC is not coordinated to the lithium. The BOB^- ion is not coordinated in the solid state to any solvents. The structure is shown in Figure 1. Ethylene carbonate is the only solvent we have found to date that tetrahedrally coordinates the lithium. All other solvents not only give a higher lithium coordination number, but the BOB^- ion is also in the lithium coordination sphere, and often the lithium is present in dimers or chains of O-Li-O-Li- units. Interestingly the lithium is also tetrahedrally coordinated in the ethylene carbonate complexes of $LiPF_6$ and $LiAsF_6$, and the DMC again is not involved in the immediate coordination sphere.

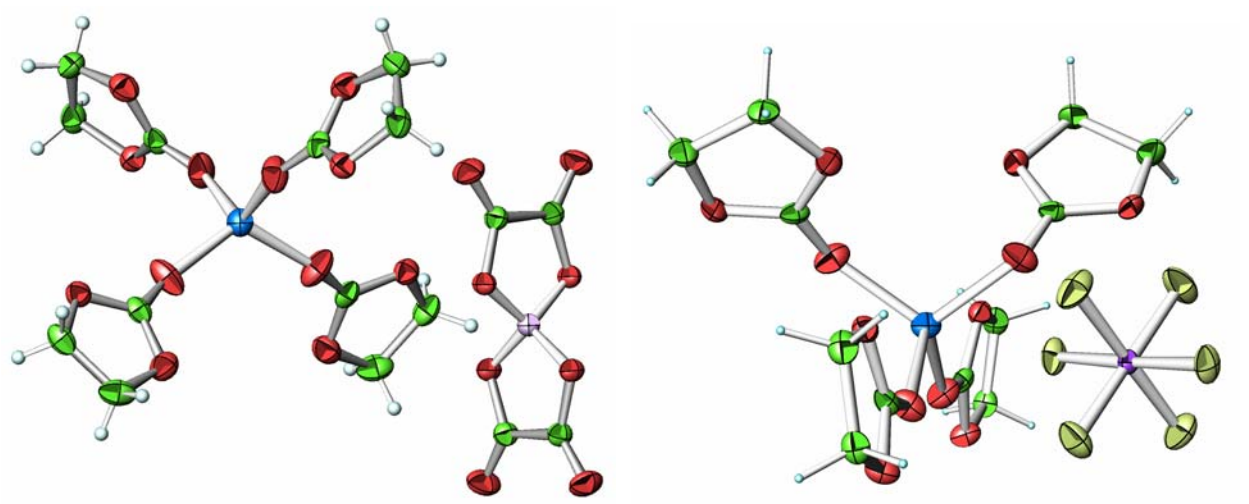


Figure 1. Left): The structure of LiBOB in ethylene carbonate, and right) the structure of $LiPF_6$ in ethylene carbonate both precipitated from an EC/DMC electrolyte.

Further plans to meet or exceed milestones: None
Reason for changes from original milestones: No changes

Publications and Presentations resulting from the work.

1. Peter Y. Zavalij, Shoufeng Yang and M. Stanley Whittingham, "Structures of potassium, sodium and lithium bis(oxalato)borate salts from powder diffraction data," *Acta. Cryst.* **B59**, 753-759 (2003).
2. M. Stanley Whittingham, Yanning Song, Shoufeng Yang, Samuel Lutta, Katana Ngala, Natasha Chernova and Peter Y. Zavalij, "Recent trends in lithium battery research," presented at the Taipei Power Forum, Taipei, Taiwan, December 1, 2003.

TASK STATUS REPORT

PI, INSTITUTION: G.A. Nazri and M.D. Curtis, University of Michigan
T. Malinski, Ohio University

TASK TITLE – PROJECT: Anodes - Novel Composite Anode for Lithium-ion Batteries

SYSTEMS: Low–cost Li-ion

BARRIER: Safety, irreversible capacity loss, and self-discharge

OBJECTIVES: Develop a low-cost and safe composite anode plate with no intrinsic irreversible capacity loss (ICL) and with higher gravimetric and volumetric energy density than the current carbonaceous anodes. Improve the kinetics of the Li insertion-extraction process in the composite anodes for application in high-power Li-ion cells.

APPROACH: Prepare alternative composite anodes *via* reactive mechano-milling of anode materials with lithium or lithium hydride to eliminate inherent irreversible capacity loss of metal-oxide anodes. Form a desirable synthetic SEI layer *via* the mechano-reduction of oxide anodes in presence of electrolyte, and improve kinetics of lithium insertion - extraction process by optimization of anode particle size to nanoscale.

STATUS OCT. 1, 2003: The optimization of mechano-milling process parameters for reactive reduction of metal oxide, nitride and phosphides anodes was completed. The chemical nature of the SEI formed on metals and alloys due to reduction of their oxides, nitrides, and phosphides were studied . An electrochemical study of the composite anode in baseline electrolyte (EC-DMC containing 1M $LiPF_6$) was carried out.

EXPECTED STATUS SEPT. 30, 2004: A well-controlled process basedon reactive mechano-milling will be introduced for the preparation of composite anodes from various oxides, nitrides, and phosphides. Full characterization of the composite anodes in terms of their chemical composition, particle size, and nature of their SEI layer will be completed. Electrochemical tests will be performed to determine charge-discharge behavior of the composite anodes in terms of their voltage profile, reversibility, and overall capacity. Cycle-life tests of the composite anodes at several levels of active material loading will be continued and accumulated cycle numbers and remaining capacity will be reported.

RELEVANT USABC GOALS: Exceeding 10-year life, high-power battery electrode, low cost battery and high safety.

MILESTONES: (a) A new class of anode material with high capacity, high rate of charge discharge will be developed by April 2004. (b) Electrochemical tests including charge-discharge cycle life of composite anodes formed by reactive milling of oxides and nitrides and phosphides will be completed by August 2004.

PROGRESS TOWARD MILESTONES

The process of mechanomilling activation of anode materials has been introduced by our group and applied to various oxides, nitrides and phosphides to remove their first cycle irreversible capacity loss. This process is applied to SnO, SnO_2, PbO, and transition metal oxides, nitrides and phosphides with emphasis on low-cost $LiFe_2P$. In general, we have observed a large overpotential (about 1 V) during lithium extraction from most reduced transition metal oxides. Therefore, we have focused on the development of a practical composite anode with less than 0.5 V hysteresis between charge-discharge voltage profiles. The prelithiation of transition metal phosphides-halide compounds was considered. We have synthesized the copper phosphide iodide as a promising new anode material for rechargeable lithium cell. The new anode was ball milled with lithium, lithium hydride and lithiated graphite. For each test, sampling material from the ball mill jar during the ball milling process monitored the extent of reaction between lithium and copper phosphides iodide. Formation of lithium iodide and lithium phosphides was confirmed by Raman, IR and ^{7}Li NMR spectroscopy. The ^{7}Li NMR spectra clearly show the two mobile lithium sites on the Li_3P phase. Based on material analysis results and electrochemical charge-discharge cycles, we propose the following reversible reaction for the activated metal phosphides halides.

$$[aLi_3P + M + bLiX]_{composite} \longrightarrow Li_bX_bMP + 3aLi^+ + 3a(e)^-$$

e where M= Cu and X = I. The post analysis of the active material at the end of charge and discharge indicates that the reversible phase is only the Li_3P phase in the presence of nano metal particles. The high rate capability of the sample also indicates excellent ionic and electronic conductivities for anode plates constructed from activated copper phosphides iodide and lithiated graphite. For electrode with 10-micron thickness, full capacity is achievable at the 5C rate. Thermal analysis of lithiated (charged) samplesafter removal of electrolyte and salt has shown no exothermic peaks below 150 C.

Further plans to meet or exceed milestones.
Our future plan is to monitor the charge-discharge reactions using in-situ Raman spectroscopy.

Reason for changes from original milestones. N/A

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

Our objective is to build nanostructured polymer electrolytes with polyethyleneoxide channels embedded in a polyisoprene matrix. We have synthesized a series of polyisoprene-b-polyethyleneoxide copolymers and are studying the morphology of thin films of these copolymers on silicon substrates. Previous studies using Atomic Force Microscopy (AFM) revealed cylinders oriented parallel to the surface of our substrate. These AFM studies show a roadmap topology that is consistent with widely accepted theories on the balance of enthalpic, entropic, and surface interaction energy of thin block copolymer films. This orientation is not desired because it does not allow the conduction of ions between the electrodes through the polyethyleneoxide cylinders. For this reason, we will attempt to align the polyethyleneoxide cylinders perpendicular to the electrode surface. To achieve this goal, we will apply an electric field across the polymer film sandwiched between two electrodes. We believe that the polarizability of the polyethyleneoxide chains will lead to the orientation of the cylinders in the desired direction. We expect a selective orientation of the PEO chains because of the difference in the dielectric constants of polyisoprene and polyethyleneoxide.

We have designed and built a cell to conduct the electric field alignment experiments. The cell consists of two parallel plate electrodes connected to a high voltage source capable of ~2000V output. Because of the high voltage required, several safety measures have been instituted to protect operators from accidental discharge. The cell will provide temperature control and will enable heating the polymer in an inert gas atmosphere.

Following alignment, we will use AFM to probe the surface structure of our films. In addition, as AFM only investigates the surface morphology of our samples, we will employ Transmission Electron Microscopy (TEM) to explore the orientation through the thickness of our polymer films. The TEM studies will be performed at the National Center for Electron Microscopy (NCEM) at LBNL.

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.

1. Polymer Electrolytes for Lithium Metal Electrodes (Li/Polymer/Metal Oxide)
1.1. Cycling of lithium/lithium symmetrical cells with comb-branched, network, and linear polymer electrolytes has been carried out to study dendrite growth. These tests have demonstrated that dendrite growth or surface roughening is absent under conditions of low overpotential and shallow cycling. With cells that exhibit low overpotential, there appears to be little or no limit on the amount of charge that can be passed with no initiation of roughening. Low overpotential is achieved through minimization of the cell thickness (reduce ohmic and concentration polarization) and by minimization of the interfacial impedance. Ohmic and concentration polarization are also minimized by better transport properties of the electrolyte (conductivity and salt diffusion coefficient). Low current densities ($<I_L/10$) favor low overpotential. Increase of the current density immediately led to roughening. It has also been noted that limited depth of discharge appears to suppress dendrite growth. Li/Li cell cycling that did not allow the overpotential to reach steady state conditions showed little sign of surface roughening, despite operation at relatively high current densities($>I_L/10$). An increase in the cycle capacity that reached the steady state plateau immediately led to surface roughening. These results indicate that cells may be operated without surface roughening at low current densities for deep cycling and at high current densities for shallow cycling. Tests conducted under these conditions are continuing but necessarily take a long time to complete.

Experiments have been carried out to modify the surfaces of the lithium electrodes in order to minimize the interfacial impedance and provide more reproducible surfaces. Lithium electrodes are prepared by manual polishing and then reacted with compounds to pre-form the SEI layer. These compounds include nitrogen, CO_2, glyme, methyl-capped ethylene, propylene and trimethylene glycols. To date, the treatment of the lithium surfaces appears to lead to reduction in the interfacial impedance under some conditions and this contributes to less dendrite growth due to a reduction in the overpotential described above.

1.2. Transport measurements have been made on a variety of salts with TMO-containing polymers. These measurements, in conjunction with results from single-ion conductor studies (NASA PERS program), show that the extra carbon in the TMO polymers unquestionably leads to higher polymer mobility. However, the same carbon group apparently induces a decrease in the dielectric constant of the medium resulting in an increase in ion-pairing. It is noted that the conductivities of Li Triflate and $LiBF_4$ solution in PTMO are much lower than those of these salts in PEO, despite the fact that the PTMO systems have much lower T_g values. The conductivity of LiTFSI in PTMO is slightly lower than in PEO while that of LiBETI is higher. This indicates that the degree of ion dissociation is less affected in the large delocalized anions by the lower dielectric constant of the PTMO and indicates that the large anions presently being synthesized at Clemson (Task 3.4) may provide best performance with the lower dielectric constant but more mobile TMO-type polymers. More detailed transport measurements are continuing.

2. Gel Polymer Electrolytes and PolyElectrolytes. (Gel Polymer Cell). Polyelectrolyte gels have been prepared and tested in Li/Li and Li/V_6O_{13} cells. The full cells have been successfully discharged but charging is abnormal due to high interfacial impedances.

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

Accomplishments toward milestones over last quarter:

We are using conductivity measurements as a tool to develop protocols for incorporating fumed silica in the mixed-MW PEO system. We have measured conductivity for $P(EO)_{20}LiTFSI$ + 10% A200 composite with different mass ratios of PEO (600K):PEG-dM (250): 100/0, 80/20, 67/33, 50/50, 33/67, and 20/80. The conductivity increases with amount of low-MW PEG-dM in the temperature span of 15 to 90 °C, with the increase being more pronounced in the lower portion of the range. A significant aspect of our findings is that the corresponding moduli of the blends are higher than the composite consisting of the high-MW component. Dynamic rheological results for the composite mixed-MW systems reveal that the elastic modulus increases and s passes through a maximum as the concentration of PEG-dM increases in the blends. These results are significant and interesting since it was expected that the low-MW component would plasticize the high-MW component and produce a monotonic decrease in elastic modulus. These trends will be more thoroughly analyzed as additional data are collected; there seems to be a synergistic mechanism of network formation among the high-MW PEO, fumed silica, and low-MW PEG-dM that remains to be explored.

We have also undertaken a systematic study of the melting and crystallization temperatures of mixed-MW composite polymer electrolytes. We have recorded differential scanning calorimetry (DSC) data for the composite mixed-MW PEO electrolytes with different mass ratio of the two polymers, and we find that the melting and crystallization temperatures decrease with the amount of low-MW PEG-dM. The heat of fusion follows the same trend. We have also collected DSC data for $P(EO)_{20}LiTFSI$ (PEO (600K):PEG-dM (250); Li:O=1:20) with and without fumed silicas. The addition of A200 (hydrophilic) or R805 (hydrophobic) fumed silica increases the melting and crystallization temperature and decreases the heat of fusion. Since melting enthalpy is an indication of the degree of crystallinity, our results indicate that adding fumed silica into mixed-MW PEO electrolytes decrease the crystallinity. This trend is also observed in the high-MW PEO electrolytes, which we have been previously reported. The conductivity of the $P(EO)_{20}LiTFSI$ (PEO (600K):PEG-dM (250)=1:1 (mass); Li:O=1:20) electrolytes increases considerably in the temperature range where a decrease in the elastic modulus is observed. In the same temperature range, the DSC data show that melting is occurring.

Further plans to meet or exceed milestones: We will begin collaboration with BATT investigators Drs. DesMarteau and Creager to test their new imide salts and single-ion conductors.

Reason for changes from original milestone: N/A

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:

Excellent progress has been made in synthesizing salts of structure $CF_3SO_2[N(Li)SO_2R_fSO_2]_nN$-$(Li)SO_2CF_3$, $R_f = (CF_2)_4$ in sufficient quantities that the salts may be provided to BATT co-workers to conduct rheological, reactivity, and cell tests. Seven grams of a dimeric salt (n=1 above) have been synthesized and samples are being shipped to coworkers Striebel (BATT task 1.1) for cell testing, Devine (BATT task 5.5) for aluminum corrosion testing, and Khan (BATT task 3.3) for rheology and other testing. Synthesis of hexa-anionic (n=5) and poly-anionic (n ~23) salts is in progress and should be completed in the first quarter of CY 2004.

Allyl ether salts of structure $CH_2{=}CHCH_2O\text{-}CF_2CFHO\text{-}CF_2CF_2\text{-}X$, with $X{=}SO_3(Li)$ (sulfonate, salt C) and $X{=}SO_2N(Li)SO_2CF_3$ (sulfonimide, salt D) were synthesized and approximately five grams of each salt were provided to coworker Kerr (BATT task 3.2) in October 2003 for use making single-ion conductors by coupling the allyl ether groups on the salts to reactive comb polymer hosts using hydrosilyl coupling chemistry. Continuing work at Clemson has focused on improving the synthesis of both salts, including changing the solvent from acetonitrile to tetrahydrofuran and adjusting the reaction temperature to dramatically reduce the amount of colored by-products that are produced during synthesis. Elimination of by-products eliminates the decolorization step that currently is required to produce pure materials.

Work at Clemson is also focusing on developing the coupling reactions needed to link these salts to polyether hosts using hydrosilyl coupling methods. Hydrosilyl-functionalized polyethers were prepared in good yields by conversion of short-chain PEG monomethyl ethers into allyl ethers using allyl bromide (rxn 1), after which allyl groups were converted into propyl-dimethyl-hydrosilyl groups by reaction with dimethylchlorohydrosilane (rxn 2) followed by conversion of chlorosilane to hydrosilane with excess $LiAlH_4$ (rxn 3). A new method using controlled aqueous hydrolysis to remove residual $LiAlH_4$ was developed and shown to effective even in the presence of hydrosilyl groups which are normally hydrolytically sensitive. This method offers a substantial improvement on prior methods for making hydrosilyl-derivatized polymers in which removal of residual $LiAlH_4$ proved difficult. The product of rxn (3), a hydrosilyl-derivatized PEG oligomer, was produced in good yield in tens-of-gram quantities.

(1) $\text{PEG-OH} + \text{Br-CH}_2\text{-CH=CH}_2 \rightarrow \text{PEG-O-CH}_2\text{CH=CH}_2$

(2) $+ \text{H-Si(CH}_3)_2\text{-Cl} \rightarrow \text{PEG-O-CH}_2\text{CH}_2\text{CH}_2\text{-Si(CH}_3)_2\text{-Cl}$

(3) $+ \text{LiAlH}_4 \text{ (excess)} \rightarrow \text{PEG-O-CH}_2\text{CH}_2\text{CH}_2\text{-Si(CH}_3)_2\text{-H}$

All of our initial attempts at accomplishing platinum-catalyzed coupling of hydrosilyl-derivateized PEG to allyl groups in salts C and D failed. A wide range of catalysts (including Karstedt's catalyst and hexachloroplatinic acid, two commonly used catalysts for hydrosilyl coupling reactions) and conditions were tried, all to no effect. We hypothesized that anionic groups in the salts were deactivating the catalysts, and with this idea in mind we tried exchanging lithium cations for organic cations, specifically triethylammonium, reasoning that a large hydrophobic cation might shield the anionic groups thereby preventing them from deactivating the platinum catalyst. Early indications are that this strategy is succeeding, and work in progress will seek to confirm this indication and exploit it to prepare sulfonate- and sulfonimide-derivatized polyethers for use as single-ion lithium conductors.

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

Our group has concentrated on two major tasks this quarter: (a) further validation of the new improved force field for polyethers, carbonates and their interactions with the $Li^+/TFSI^-$, (b) investigation of the Li^+ transport mechanism in poly(epoxide ether) (PEPE)–TFSI-Li^+ single-ion conductors and poly(epoxide ether)–TFSI-Li^+/ethylene carbonate (EC) gel electrolytes.

The ability of molecular dynamics simulations with the developed force field to accurately predict transport properties of pure ethers, carbonates and their solutions with LiTFSI is of major interest. Experimental NMR data are available in the literature for the self-diffusion coefficient of 1,2-dimethoxyethane (glyme), diglyme, triglyme, ethylene carbonate and also two normal alkanes (n-decane and n-tridecane). MD simulations were performed at the experimental conditions (T,P), and self-diffusion coefficients were measured for the above solutions. The RMS deviation of the self-diffusion coefficients measured in MD simulations from NMR data was 8% with a maximum deviation of 26 %. This is excellent accuracy for predicting self-diffusion coefficients, considering that no transport properties were used in force field parameterization. MD simulations of the EC/LiTFSI (EC:Li=20:1) electrolyte at 313 K were also performed, and they yielded the EC, Li^+ and $TFSI^-$ self-diffusion coefficients within 30 % of experimental values, indicating the ability of the force field to accurately predict ion self-diffusion in the electrolyte of interest.

MD simulations of the $(PEPE)_5$–TFSI-Li^+ (ether oxygen:Li=6:1) single-ion conductor were performed at 363 K for 4 ns. The Li^+ ion transport mechanism was studied. We found two major types of events that contribute to the Li^+ transport: (a) cation dissociation from the $TFSI^-$ anions affixed to the side chains accompanied by complexation by ether side-groups; (b) cation hopping from one side chain to another. The Li^+ cation hopping from one side chain to another occurred by almost simultaneous decomplexation from 2-3 ether oxygens and complexation with the other 3 ether oxygen atoms from another side chain. This mechanism is different from the previously observed one in solid polymer electrolytes such as linear PEO/Li-salt, where Li^+ motion occurred by moving along PEO chains one ether oxygen atom at a time. The spatial distribution of anions was also studied. A snapshot of the anion distribution in the simulations box is shown in Fig. 1. Anions were found to be distributed non-homogeneously, but no large aggregates of anions were observed.

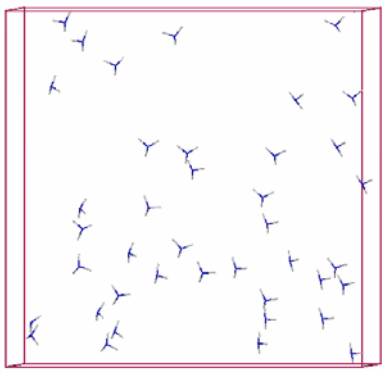


Figure 1. Snapshot of the simulations box of $(PEPE)_5$-$TFSI^-/Li^+$. Only anions are shown as CF_3 groups.

Reasons for changes from original milestones: N/A

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.

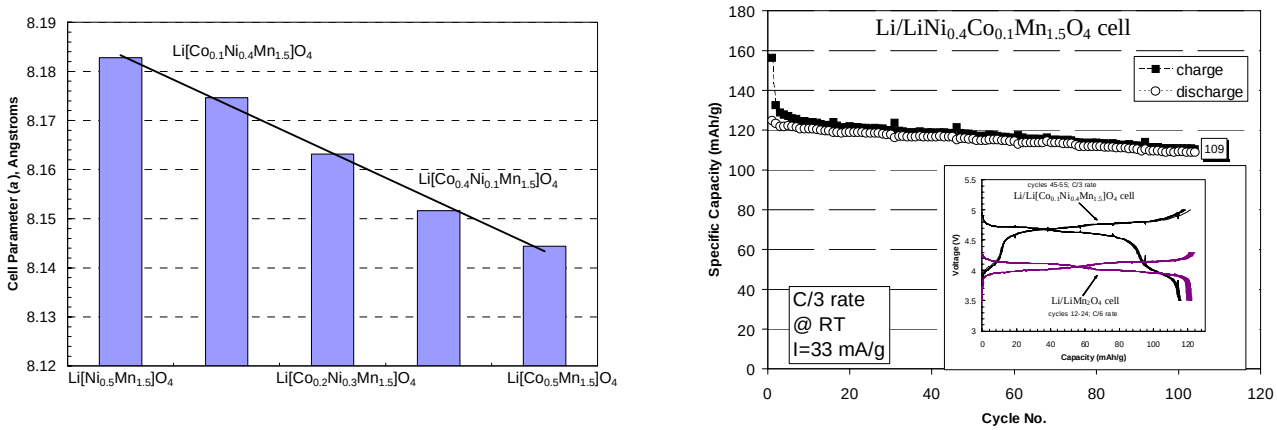
RELEVANT USABC GOALS: 10-year life, <20% fade over a 10-year period.

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

The substitution of Co for Ni and Mn in layered $Li[Ni_{0.5}Mn_{0.5}]O_2$ to form $Li[Ni_{0.33}Co_{0.33}Mn_{0.33}]O_2$ is known to improve the electrochemical behavior of the material. The formal oxidation states of the transition metals in $Li[Ni_{0.33}Co_{0.33}Mn_{0.33}]O_2$ are nickel (II), cobalt (III) and manganese (IV). The mixed-valent metals in the structure enhance d-band overlap, thereby improving electronic conductivity. This effect translates to lower impedance in the cathode and superior performance at high rates.

In a $Li[Ni_{0.5}Mn_{1.5}]O_4$ spinel electrode, which provides nearly 5 V against metallic lithium, the nickel ions are divalent and the manganese ions are tetravalent. Crystallographic studies of $Li[Ni_{0.5}Mn_{1.5}]O_4$ show a cation and charge ordering similar to that in layered $Li[Ni_{0.5}Mn_{0.5}]O_2$. Therefore, by analogy to the layered system, we are pursuing Co substitution in $Li[Ni_{0.5}Mn_{1.5}]O_4$ in an attempt to improve the electrochemical properties of the spinel, and particularly its electronic conductivity. A series of substituted spinels $Li[Co_xNi_{0.5-x}Mn_{1.5}]O_4$ (x=0, 0.1, 0.2, 0.4, and 0.5) were synthesized by solution-precipitation methods and characterized by powder X-ray diffraction. Rietveld profile refinements of the cubic, cation-ordered spinel structure (space group $P4_332$) were used to calculate the lattice parameter, *a*, and the non-lithium (Ni, Co) occupancy of the 8c tetrahedral site. As shown in Fig. 1a, *a* decreases linearly with the amount of substituted Co in the structure, consistent with solid-solution behavior and the direct substitution of the slightly smaller Co(II) ions for Ni(II) ions. Ni, Co and Mn XANES data of the spinel compounds have been collected at the Advanced Photon Source at ANL. These data are still to be analyzed; the oxidation states of the Ni-, Co- and Mn ions obtained experimentally will be compared to theoretical predictions made by first principles methods.



(a) (b)

Figure 1. (a) Lattice parameter variation in $Li[Co_xNi_{0.5-x}Mn_{1.5}]O_4$ (x=0, 0.1, 0.2, 0.4, and 0.5) spinel samples; (b) Cycling stability of a $Li/Li[Co_{0.1}Ni_{0.4}Mn_{1.5}]O_4$ cell and, inset, voltage profiles comparing $Li/Li[Co_{0.1}Ni_{0.4}Mn_{1.5}]O_4$ (5 V) to $Li/Li[Mn_2]O_4$ (4 V) spinel cells.

It is possible that the occupation of the 8c sites by Ni or Co, albeit small (<10%), may retard Li-ion diffusion within the interstitial space of the spinel framework. The $Li[Co_{0.1}Ni_{0.4}Mn_{1.5}]O_4$ spinel, which showed the lowest occupancy of the 8c site (3.7%), has therefore been selected for electrochemical evaluation and is currently under test in Li coin cells. For a high-potential electrode, the initial results are extremely promising; this electrode yields 109 mAh/g after 104 cycles at a C/3 rate (Fig. 1b), thereby meeting milestone (c) for this task. Work is in progress to improve the cycling stability of these spinel cathodes.

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

(b) Manganese-stabilized vanadium oxides. This Quarter, we completed our milestone to evaluate stabilized vanadium oxides, and to make a comparison of them with other cathode materials. Our study of other phosphates continues. We found that the delta vanadium oxide structure, which contains two vanadium oxide sheets per layer, is more stable than conventional vanadium oxide. The two-sheet structure is also a major component of V_6O_{13} and is found in xerogels. We have synthesized these vanadium oxides using manganese and organic species as stabilizing units. For comparison, we also made a vanadium oxide containing only lithium ions, LiV_4O_{10}.

All of the stabilized vanadium oxides showed a high capacity, seen in Fig. 1 below. In contrast, the un-stabilized lithium vanadium oxide showed less capacity and more fade on cycling due to structural reorganization. It is clear that these oxides can attain capacities exceeding 200 Ah/kg over several cycles at low current densities, such as 0.1 mA/cm^2. The ammonium-stabilized compound showed the best electrochemical behavior. However, increasing the current density results in significant capacity loss, so that by 1 mA/cm^2, they have lower capacity than the layered oxides $LiMn_{0.4}Ni_{0.4}Co_{0.2}O_2$. Moreover, the polarization increases, resulting in a still lower energy storage capability. Thus, we conclude that, at the present time, these vanadium oxides cannot attain the power densities to be of further interest to the BATT program.

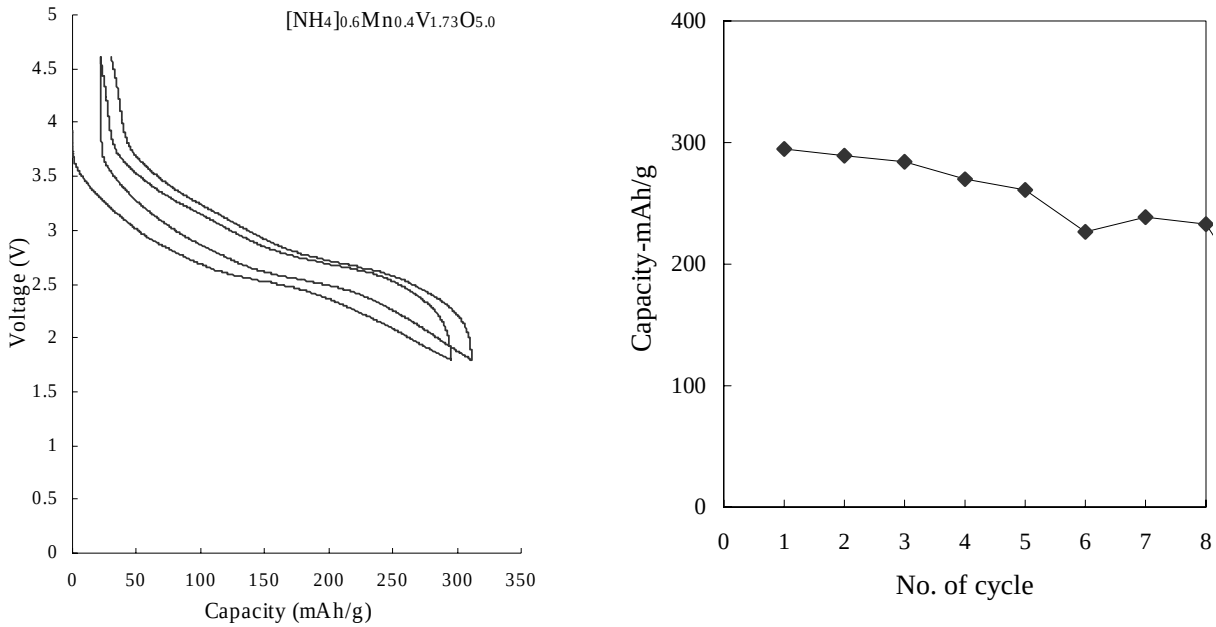


Figure 1. (Left) Discharge and recharge of first cycles of $[NH_4]_{0.6}Mn_{0.5}V_2O_5$ at 0.1 mA/cm^2; (right) the capacity as a function of cycle number.

Further plans to meet or exceed milestones: None
Reason for changes from original milestones: No changes

Publications and Presentations resulting from the work.

1. Katana Ngala, Natasha Chernova, Miamiao Ma, Marc Mamak, Peter Y. Zavalij and 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. Materials Chem.* **14,** 214-220 (2004).
2. M. Stanley Whittingham, Yanning Song, Shoufeng Yang, Samuel Lutta, Katana Ngala, Natasha Chernova and Peter Y. Zavalij, "Recent trends in lithium battery research," presented at the Taipei Power Forum, Taipei, Taiwan, December 1, 2003.
3. Miaomiao Ma, J.Katana Ngala, Peter Y. Zavalij and M Stanley Whittingham, "Carbon-coated layered $LiNi_yMn_yCo_{1-2y}o_2$ (y=0.4) for lithium batteries," Materials Research Society, Boston, December 2003.

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)

We recently discovered that $LiFePO_4$ electrochemical performance was strongly correlated to the structure of surface carbon on the particles. Coatings with lower D/G (disordered/graphene) and higher sp^2/sp^3 ratios as determined by Raman microprobe spectroscopy (Kostecki and McLarnon) have higher electronic conductivities, and allow better utilization of the $LiFePO_4$ electrode. Experiments carried out this quarter were directed towards understanding how graphene-containing carbon is formed on $LiFePO_4$. Results from thermogravimetric analysis (TGA), Raman microprobe spectroscopy, and elemental analysis on samples indicate that addition of an easily decomposed organic molecule during synthesis (e.g., pyromellitic acid, PA) improves carbon structure, although it may not actually increase overall carbon content. Losses due to evaporation and/or oxidation to CO and CO_2 during synthesis are not easily controlled and reduce the overall carbon content in the product. A beneficial effect of the PA additive, however, is the suppression

of $LiFePO_4$ oxidation at elevated temperatures (Figure 1). Interestingly, adding iron nitrate appears to amplify this effect.

It is well documented in the carbon nanotube literature that transition metal compounds such as iron oxides promote the formation of graphene from volatile carbon-containing precursors at relatively low temperatures (≥500°C) compared to typical graphitization temperatures of ~2700-3000°C. This suggests that trace iron oxide impurities may play a role in the formation of sp^2 carbon during $LiFePO_4$ synthesis. To test this theory, we processed samples containing both PA and iron nitrate additives (iron nitrate decomposes to form iron oxide upon heating). Raman microprobe spectroscopy showed a dramatic decrease in D/G ratios for these samples (*i.e.*, improved carbon structure). The relatively large amounts of iron nitrate used (0.7-1 wt %) resulted in a visible red iron oxide impurity that had a negative impact on performance, however. Experiments for next quarter will be directed towards optimization of iron nitrate/PA ratios and further investigation of the role of iron-containing promoters on the formation of sp^2 carbon in $LiFePO_4$ samples.

A series of O2 and O2/O3 $Li_xAl_yMn_{1-y}O_2$ ($0.6 \leq x \leq 0.8$, $0 \leq y \leq 0.3$) samples were synthesized from their P2 or P2/P3 sodium-containing precursors and are currently being characterized electrochemically. As with the $Li_xNi_yMn_{1-y}O_2$ system, only pure O3 materials are obtained for high y, whereas O2/O3 intergrowths are obtained for low y (Figure 2). This is significant because O3 layered compounds have higher capacity than O2, but may convert to spinel upon cycling. Intergrowths show intermediate behavior.

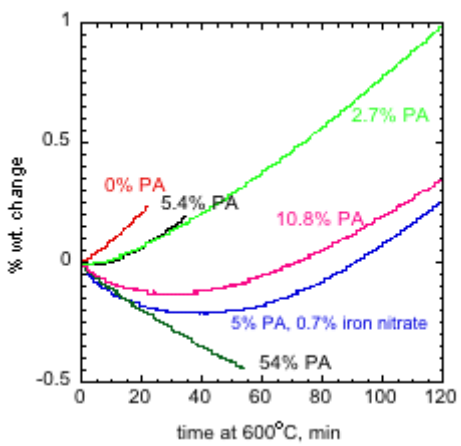


Figure 1. Weight change profiles of $LiFePO_4$ samples containing pyromellitic acid (PA) and iron nitrate (isothermal, 600°C). $LiFePO_4$ oxidation results in a net weight gain.

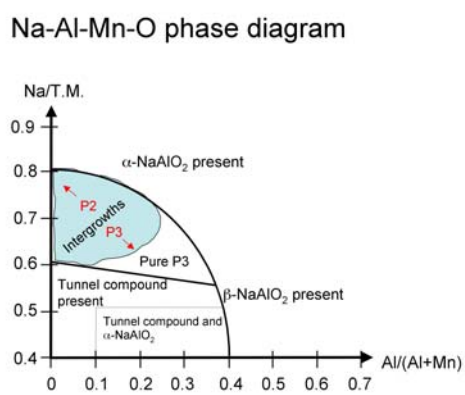


Figure 2. Phase diagram for the Na-Al-Mn-O system, from which $Li_xAl_yMn_{1-y}O_2$ compounds are derived.

OTHER WORK:

$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ was successfully synthesized directly from nitrate precursors and also by a glycine-nitrate combustion process. The first method will be used to make thin films for diffusion coefficient measurements, once synthesis conditions are optimized.

PUBLICATIONS AND PRESENTATIONS

"Influence of Substitution on the Structure and Electrochemistry of Layered Manganese Oxides", Tom A. Eriksson, Young Joo Lee, Joel Hollingsworth, Jeffrey A. Reimer, Elton J. Cairns, Xiao-feng Zhang, and Marca M. Doeff, *Chem. Mater.*, **15**, 4456 (2003).

"Electrochemical Performance of Aluminum-substituted Layered Manganese Oxide Intergrowth Structures", Marca M. Doeff, Joel Hollingsworth, and Mickael Dollé, *Electrochem. Soc. Meeting*, Orlando, FL, Vol. 2003-2, abstract 334 (2003).

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

- **Accomplishments towards milestones over the last quarter.**

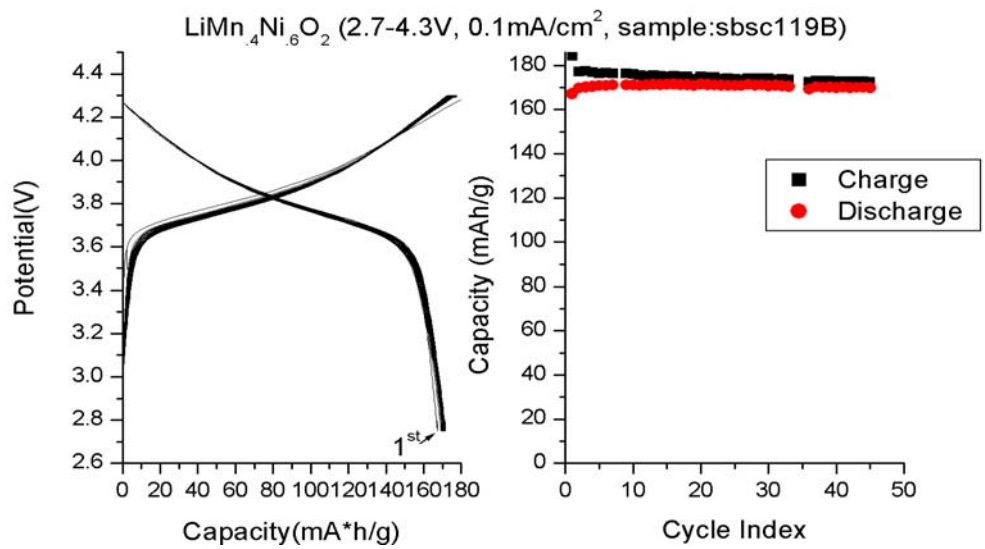
Evaluation of $Li_{2-x}NiMnO_4$

The Ni(III)/Ni(II) and Ni(IV)/Ni(III) redox couples are pinned at the top of the O^{2-}:$2p^6$ band as antibonding states containing a large admixture of O-2p and Ni-3d orbitals. Electrochemical data show that the Ni(IV)/Ni(III) redox couple is not accessible in $Li_{2-x}NiMnO_4$, but it is accessible in $Li_{1-x}NiO_2$. In order to access the Ni(IV)/Ni(III) redox couple, it is necessary to go to the smaller values of y in $Li_{1-x}Ni_{1-y}Mn_yO_2$, which has motivated a comparative study of compositions $0.2 \leq y \leq 0.5$ in order to obtain a greater capacity.

Low capacity is also associated with cation disorder, which appears to increase with increasing temperature. There is, therefore, an optimal sintering temperature that allows cation order as well as chemical reaction. To find this optimal temperature, which is expected to be unique to x in $LiMn_xNi_{1-x}O_2$ due to the lower mobility of Mn^{4+} vs. Ni^{3+}, a series of material has been synthesized by sintering at different temperature. The electrochemical data for optimized $LiMn_{0.4}Ni_{0.6}O_2$ shown in Fig. 1 clearly suggest that this series is worth pursuing. Samples of $LiMn_{0.4}Ni_{0.6}O_2$ have therefore been sent to K. Striebel at Lawrence Berkeley National Laboratory for further testing.

Evaluation of $Li_{2-x}VOSiO_4$

The structure of Li_2VOSiO_4 consists of Li^+-ion sheets between slabs of square-pyramidal $V{=}OO_{4/2}$ units sharing corners with tetrahedral $SiO_{4/2}$ units. Phase-pure samples of Li_2VOSiO_4 and $Li_2(V_{0.9}Ti_{0.1}O)SiO_4$ were prepared. Since the parent compounds are insulating, chemical, rather than electrochemical, Li extraction was attempted. Although the structure remained stable when exposed to I_2 or Br_2, there appeared to be little or no lithium extraction. In order to determine whether the inability to extract Li is due to poor electronic conduction or poor ionic conduction, a Na/Li ion-exchange experiment was preformed. The Li ions were found to be unexpectedly immobile. We have therefore started a collaboration with G. Ceder at MIT in an attempt to understand these results.



- **Reason for changes from original milestones:** N/A

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

Our first objective was to determine and verify the key elements necessary for 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 continued o 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. Carbon coatings with low D/G (disordered/graphene) and sp^2/sp^3 coordinated carbon ratios were produced deliberately by adding small amounts of functionalized aromatic or ring-forming compounds such as pyromellitic acid, naphthalene-tetracarboxylic-dianhydride, and poly(acrylonitrile). 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. % . 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.

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 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. Raman microprobe surface imaging of 1% Nb doped and pristine $LiFePO_4$ samples indicated that: (i) carbon content in the Nb-doped $LiFePO_4$ is significantly higher than in the pristine sample and (ii) carbon is non-uniformly distributed at the surface of the samples. CSAFM images showed no electronic conductance in the pristine $LiFePO_4$ sample. On the other hand, surface electronic conductance images of the Nb-doped $LiFePO_4$ showed areas of excellent conductivity located in the intergranular spaces and deep crevices between agglomerates. the surfaces of Nb-doped $LiFePO_4$ primary particles appeared completely non-conductive. Interestingly, surface composition Raman maps indicated that carbon distribution at the surface corresponds to the observed conductivity pattern at the CSAFM images (Fig. 1). Thus, 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 the improved conductivity and electrochemical performance. This concludes our effort toward milestone B.

Our second objective (milestone A) was to investigate the observed carbon retreat in composite cathodes. Preliminary electrochemical tests have indicated that a pure carbon electrode is electrochemically active toward the EC:EMC, 1M $LiPF_6$ electrolyte at elevated temperatures (57°C) at potentials above 3.8V. In-depth diagnostic studies of the mechanism of this process are currently underway.

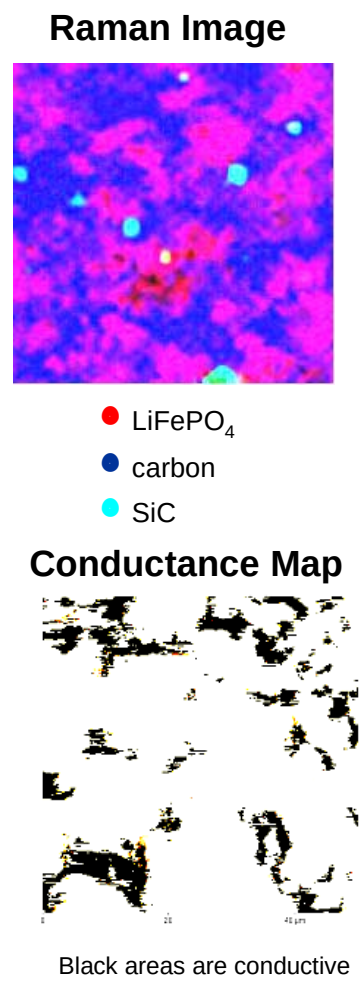


Figure 1. Raman and CSAFM 50x 50 μm images of 1% Nb doped $LiFePO_4$.

TASK STATUS REPORT

PI, INSTITUTION: J. McBreen, 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

In this quarter, *in situ* x-ray diffraction (XRD) and a combination of *in situ* and *ex situ* x-ray absorption spectroscopy (XAS) was used to study the phase changes and redox processes in $LiNi_xMn_{1-x}O_2$ and $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$. XAS was carried out at the K and $L_{2,3}$ edges of Ni, Co, and Mn and at the O K edge. In the case of $LiNi_xMn_{1-x}O_2$ and LiFePO4 studies weree performed during charge and discharge. Preliminary in situ XRD studies have been carried out on $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ during cycling and deep discharges.

XRD studies of thermal decomposition of $Li_{1-x}Ni_{1/2}Mn_{1/2}O_2$ cathodes from charged cells were carried out in the time-resolved mode during heating from 25ºC to 450ºC. The time-resolved XRD studies were carried out on $Li_{0.8}Ni_{1/2}Mn_{1/2}O_2$ (30% SOC nominal) in the presence and absence of electrolyte, respectively. In the absence of electrolyte no changes are seen until about 400ºC, which is much higher than that observed for Gen-2 material under the similar condition. In the presence of electrolyte, decomposition reactions can be seen at lower temperature around 300ºC, which is also much higher than that observed for Gen-2 material.

Preparations for the following studies are also underway:

Using soft x-ray XAS, at the B, O, F, and P K-edges to study decomposition products on electrodes and separators from cycled cells. This will include electrodes from cells with $LiPF_6$, $LiBF_4$, and LiBOB electrolytes. The diagnostic work will include studies of materials obtained from various sources and materials prepared at BNL. In addition, the diagnostics will be applied to electrodes tested at BNL and materials from baseline BATT Program cells. The techniques will also be used to identify SEI products from electrolytes with new salts and additives.

A combination of *in situ* XRD and *ex situ* soft x-ray XAS and TEM will be used to study the mechanism of the beneficial effect of inorganic coatings on cathode stability. This will be coupled with a study of the effect of electrolyte composition on cathode stability.

Exploratory work will be undertaken to identify new electrolytes to stabilize $LiMn_2O_4$ electrodes at elevated temperatures. Previous preliminary work at BNL, in this area, appears promising. This will be coupled with studies of the SEI layers

Selected publications

1. H. S. Lee, Z. F. Ma, X.-Q. Yang, X. Sun, and J. McBreen "Synthesis of a New Series of Fluorinated Boronate Compounds as Anion Receptors and Studies of Their Use as Additives in Lithium Battery Electrolytes", *J. Electrochem. Soc*., Accepted.
2. Mahalingam Balasubramanian, Won-Sub Yoon, Xiao-Qing Yang, James McBreen, and J. Hanson "Time Resolved X-ray Diffraction Study of the Thermal Degradation of Cathode Materials Used in Li-ion Batteries", submitted to the proceedings for the 2004 Meeting of the Electrochemical Society, Orlando, Florida, October 12-16, 2003.
3. Xiao-Qing Yang, Won-Sub Yoon, Mahalingam Balasubramanian, James McBreen, B. H. Deng, X. Q. Wang, M. Yoshio, M. Okada, "The Relationship between the Structural Changes and the Capacity Retention of Oxygen-Rich $LiMn_2O_4$ Type Cathode Materials during Cycling Studied by *In Situ* X-Ray Diffraction", submitted to the proceedings for the 2004 Meeting of the Electrochemical Society, Orlando, Florida, October 12-16, 2003.

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

FTIR Analysis of Electrolyte Stability

The first experiments were conducted with our new FTIR spectrometer and spectroelectrochemical cell, which has the capability of *in-situ* as well as *ex-situ* analysis of the electrode/electrolyte interface. Initially these studies will utilize ideal electrodes such as glassy carbon and Au or Pt, but may be extended to other BATT Program electrode materials. These model studies will examine the stability of the surface layers as a function of the cycling conditions, *e.g*., current density, potential, and temperature. The first experiments used glassy carbon and dry Gen 2 electrolyte, and showed conclusively that no oxidation occurs below 5 V. Above 5 V, CO_2 does appear as an oxidation product along with a surface film that could not be identified. Addition of water (> 150 ppm) caused CO_2 to appear at much lower potentials, *e.g*., below 4 V, in agreement with the report by Joho and Novak, *Electrochim. Acta* **45** (2000) 3589 also using FTIR. The reaction of water with the salt may also play a role in catalyzing the oxidation of the solvent. The next experiments used a Gen 2 cathode *in-situ* instead of glassy carbon and produced very different results. These experiments need to be repeated, but clearly the first experiments show some reaction of the electrolyte even at 3.8 V. Previous experiments with *ex-situ* FTIR analysis of Gen 2 cathodes showed oxidation beginning at *ca*. 4.2 V. It appears, as expected, that the increased sensitivity of *in-situ* analysis enables us to determine the onset potential (same reaction) more accurately.

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

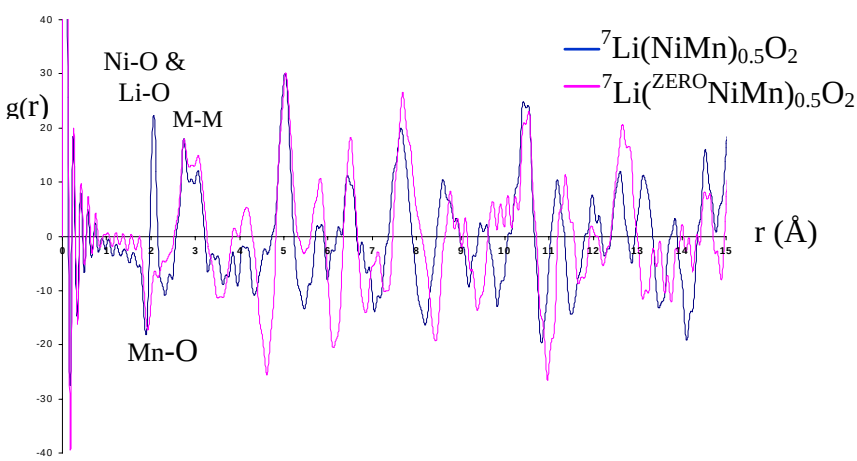
MILESTONES:
(a) November 1, 2003: Complete structural (diffraction, transmission electron microscopy (TEM) and NMR) and computational studies of members of the pseudobinary $Li[Li_{(1-2x)/3}Ni_xMn_{2/3-x/3}]O_2$.

(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

A combined NMR and first-principles study describing the local structures in the materials $Li[Li_{(1-2x)/3}Ni_xMn_{2/3-x/3}]O_2$ is in press.[1] A second paper describing the use of TEM to characterize long-range ordering in these materials is also in press.[2] Here, we, in collaboration with Y. Shao- Horn (MIT), demonstrate that cation-ordering schemes, with similar cation-ordering in the transition metal layers as that found in Li_2MnO_3, but differing in how the layers stack in the c-direction, are observed in some of these materials.[2] A third paper describing the effect of cycling on the structure of $Li[Li_{(1-2x)/3}Ni_xMn_{2/3-x/3}]O_2$ has been submitted for publication.[3] Li ions in both the transition metal layers and Li layers participate in the electrochemistry. A mechanism for Li extraction from the transition metal layers is proposed based on the calculations. A paper describing EXAFS work on this system, performed in collaboration with J.McBreen's group has been published.[4] This completes the work for the Nov. 1 2003 Milestone.

Neutron diffraction (ND) data sets were collected on the GEM instrument at ISIS (UK) for $^6Li(NiMn)_{0.5}O_2$, $^7Li(NiMn)_{0.5}O_2$ and $^7Li(^{ZERO}NiMn)_{0.5}O_2$. The last sample, $^7Li^{ZERO}Ni_{0.5}Mn_{0.5}O_2$, was prepared with an appropriate ratio of natural abundance Ni and ^{62}Ni, so that there is no scattering from the Ni atoms in the ND experiment. Rietveld refinements were performed and reasonable fits to the data were obtained when using the layered framework with the α-$NaFeO_2$ structure (space group R) as the structural model. A small proportion of Li atoms was found in the transition metal layers, associated with a Ni^{2+} substitution in the lithium layers (10.6(1)% for $^7Li(NiMn)_{0.5}O_2$) in agreement with our ^6Li MAS NMR experiments. The figure below displays the PDF plot for $^7Li(NiMn)_{0.5}O_2$ and $^7Li(^{ZERO}NiMn)_{0.5}O_2$). The (negative) peak at 1.93 Å corresponds to the Mn^{4+}-O distance. The Li^+-O and Ni^{2+}-O distances are so similar that the two peaks corresponding to these distances are not resolved in the PDF plot for $^7Li(NiMn)_{0.5}O_2$. The Ni^{2+}-O bond is clearly resolved in the Ni-only data, and a bond length of 2.07 Å was determined. At least three peaks were seen at around 2.9 Å, which correspond to the M-M interatomic distances. The data clearly illustrate that analysis of the diffraction data, with structural models based on the α-$NaFeO_2$ (R) structure are too simplistic, and a full analysis of this material will require that cation local ordering be included in the model. This is analysis is now being performed with the Reverse Monte-Carlo method and by using ordering schemes based on those suggested from TEM and first-principles studies.



Publications

1. W.-S. Yoon, S. Iannopollo, C. P. Grey, D. Carlier, J. Gorman, J. Reed and G. Ceder, Electrochem. Solid St. Lett., in press.
2. S. Meng, G. Ceder, C.P. Grey, W.-S. Yoon, Y.Shao-Horn, Electrochem. *ibid*, in press.
3. C.P. Grey, W.-S.Yoon, J Reed and G. Ceder, *ibid*, submitted.
4. W-S. Yoon, C.P. Grey, M. Balasubramanian, X.-Q. Yang, J. McBreen, Chem. Mater., 15, 3161 (2003).

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

Al current collectors from another 29 Li-ion cells, which were life-tested by M. Doeff, were inspected by optical microscopy for evidence of corrosion. All cells employed an electrolyte of 1 M $LiPF_6$/EC + DMC. 16 of the 23 current collectors that were coated with $LiFePO_4$ cathodes exhibited pitting corrosion. In two instances the pitting corrosion was extensive. Pitting corrosion was detected in the Al current collectors of two of the three cells with cathodes of $LiLi_{0.5}Mn_{0.5}O_2$ and in one of the three cells with $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ cathodes.

Although pitting corrosion was detected in the Al current collectors from cells life-tested by M. Doeff, pitting corrosion did not occur in laboratory tests of bare Al (*i.e.*, not coated with a cathode) in 1M $LiPF_6$/EC+DMC, which is the electrolyte used in the life-tested batteries.

Laboratory tests suggest that the cathode might have an adverse effect on the corrosion of Al current collectors. Corrosion of Al was detected in a small area ($7x10^{-4}$ mm^2) that was stripped of $LiFePO_4$ and subjected to an anodic current density of 0.1 mA/cm^2 for 36 h. in Gen 2 electrolyte. In addition, pitting corrosion was detected in parts of the Al surface that had been covered by cathode. Presumably, the pitting corrosion occurred at pores/cracks in the cathode. A second laboratory test also suggested that the cathode might play a role in the corrosion of the Al current collector. Three samples were tested. In the first, the Al was covered with $LiFePO_4$. In the second sample, half of the surface of Al was stripped of the coating of $LiFePO_4$. The third sample of Al was completely free of $LiFePO_4$. The potentials of the three samples were measured as anodic current densities ranging from 0.002 to 1.0 mA/cm^2 were applied. The anodic currents dramatically increased the potential of the bare Al sample. An anodic current of only 0.002 mA/cm^2 raised the potential of bare Al to approximately 6V vs. Li+/Li. An anodic current of 1 mA/cm^2 increased the potential of bare Al to over 30V. The response of the Al samples that were fully coated or only half coated with $LiFePO_4$ was very different from the response of bare Al. Even at current densities as high as 0.1 mA/cm^2, the potential of the fully coated sample was less than 4 V, and the potential of the half-coated sample was increased to only ≈ 6V. At 1 mA/cm^2, the potential of the half-coated Al was raised to 26 V and the potential of the fully coated sample was increased to 12 V. The results suggest that at cathode defects such as cracks and pores the potential of Al might be locally raised to high values, which result in pitting corrosion. Since very high potentials did not cause pitting corrosion of bare Al, we speculate that oxidation of the electrolyte occurs near the surface of the cathode and generates products that are corrosive to Al . Hopefully, analyses of the corrosion products will shed light on the mechanism by which the cathode might cause corrosion of Al.

The results of potentiodynamic anodic polarization tests suggest the critical role of fluoride in the formation of a protective film on the surface of aluminum in $LiPF_6$/EC+DMC. Samples of bare Al were tested in EC+DMC with different concentrations of $LiPF_6$. In pure EC+DMC the Al sustained severe pitting corrosion. Significant pitting corrosion also occurred in EC+DMC with 10^{-4} M and 10^{-3} M of $LiPF_6$. However, 0.01M $LiPF_6$ was nearly as effective as 1M $LiPF_6$ in preventing pitting corrosion of Al.

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 were 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

Past theories of electrode stability assume that surface-tension forces counter the amplification of surface roughness at cathodes, and have shown that at lithium/liquid interfaces, the instability cannot be prevented. Last quarter, lithium electrodes and solid polymer electrolytes were treated by linear elasticity theory, and the effect of deformation on deposition reaction rate was evaluated. To inhibit dendrite initiation by mechanical action, a polymer was found to require a shear modulus two to three orders of magnitude greater than the crosslinked poly(ethylene oxide) materials presently under research. Investigation of the role of local concentration and potential variations on this stability requirement is ongoing.

A model of the solid electrolyte interface (SEI) layer has been developed to understand how transport through the SEI layer affects battery operation. Simulations have been run at different charging rates to examine the effect of current density on the ohmic and charge transfer resistances of the SEI. New film-formation mechanisms will be reviewed and implemented in the coming months.

Previous attempts at transference-number measurement were limited in accuracy by side reactions and the inability to solve independently for activity coefficient and transference number values. New experimental methods are being developed to avoid these issues. To avoid side reactions, a negative electrode of a more moderate potential than lithium is being investigated. This negative electrode is reversible to lithium ions; when paired with a positive electrode reversible to anions in the electrolyte, activity coefficients can be measured independently. Improved transport-property measurement will assist in modeling of baseline chemistries.

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

In the previous quarter, we reported on the optimization of the natural-graphite/iron-phosphate baseline undertaken to maximize performance under a wide range of discharge times. In order to gauge the impact of extra mass in the cell arising from, for example, device packing or added electronics, the optimization was redone for another value of the residual mass. The study showed that while less residual mass results in better performance, the improvements are not significant. In other words, changes to the electrode thickness and porosity can be used to offset extra weights in the cell. However, the optimized thickness and porosity would be different for different values of the residual mass.

For both optimizations, the thickness of the electrode for very slow discharge times (10 h) was in the order of 400 μms. However, such large thicknesses were thought to pose difficulties during calendaring of the electrode. Suggestions on the ranges for the thickness and porosity that are known to be amenable to existing manufacturing techniques were solicited from Keith Kepler (Farasis Energy, Inc.) The optimization studies were redone with these limits, and the effects of these practical restrictions evaluated.

In order to complement the model for the $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ baseline cell, Swegelok cells were fabricated using materials made by Seimi Chemical Co., in collaboration with the BATT Program cell development group (K. Striebel). The equilibrium potential of the material and the performance at various rates have been measured. These data will now be used with the intercalation model, previously developed in the Newman group, in order to understand performance limitations.

OTHER ACCOMPLISHMENTS

The model for the iron-phosphate electrode, developed over the last year, was used to compare the materials made by six different research groups in order to understand why some materials perform better than others. The model was used to extract the matrix-phase resistance and the particle size for each of the materials by keeping material properties (kinetic parameters and diffusion coefficient) constant. Subsequently, the materials were compared by simulating their performance for a constant design (*i.e.*, porosity and thickness). The study, when interpreted with the recent studies on the role of carbon conducted by BATT investigators Kostecki and Doeff, suggests that a coating of graphitic carbon on the particles is critical in minimizing ohmic drops. In addition, smaller particles, and a narrow distribution of particle sizes, are important to enhance the utilization with increasing rate. The excellent performance of the samples prepared by MIT can be attributed to the use of small particles. The comparison shows that the best performance is achieved using the cathodes prepared by Hydro-Québec, among the materials studied.

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

- **Accomplishments toward milestone over last quarter**

Various carbon-type additives are used in thin, multilayered electrodes to reduce conduction losses within active materials (K. Striebel). Usage of a novel carbon-coated current collector was expected to reduce the contact resistance at the interface of active material and current collector. In order to verify this, new experimental techniques and analytical models for conduction loss have been developed in this quarter. A numerical reduction method for determination of conduction in multilayered sheets was tested, against data obtained from a multilayered electrode (Striebel). To reduce the need for direct, finite-element simulations, an analytical solution for conduction in multilayered structure sheets was attempted, and refinements are ongoing. The analytical approach will be tested against direct finite-element simulations. An analytical approach would prove far more useful/tractable for other DOE researchers, and thus is being pursued vigorously.

Numerical codes for data reduction of four-point-probe experimental data on multilayered electrodes are being developed, equipped with a user-friendly graphical user interface (GUI) to ease their application by other DOE researchers (initially, Striebel and co-workers).

Conductions properties of cathodes ($LiFePO_4$) with various carbon additives were investigated using the modified four-point-probe technique developed by our group. Conductive properties of various designs of current collectors [provided by LBNL (Striebel) and Hydro-Qubéc] were also investigated.

- **Further plans to meet or exceed milestone**

We will continue to provide all codes for analysis of multilayered electrodes to other DOE workers, and plan to integrate new materials manufactured by Striebel into our theoretical studies, both as validation of models, and in order to continue to provide guidance on selection/design of materials.

- **Reason for changes from original milestone: N/A**

PROPOSALS UNDER REVIEW

ORGANIZATION *(Principal Investigator)*	TITLE	STATUS
MIT *(Y.-M. Chiang)*	Olivine Cathodes: Thermochemistry, Defect Properties, and Electrochemical Performance	Unsolicited Proposal-rejected
Columbia University *(A. West)*	An Investigation of the Stability of the Lithium Metal Interface	Unsolicited Proposal-rejected
ANL *(K. Amine)*	Development of Polysiloxane-Based Solid Electrolyte for Lithium Batteries	Unsolicited Proposal-rejected
NREL *(S.-H. Lee and J.A. Turner)*	High-Capacity/ Stability Nano-structured Manganese Oxide Cathodes For Lithium Batteries	Unsolicited Proposal-rejected
ANL and INEEL *(A. Kahaian and K. Gering)*	A Systematic Development of Room-Temperature Ionic Liquids for Lithium-Ion Batteries	Unsolicited Proposal-rejected
Univ. of Texas @ Austin *(A Manthiram)*	Superior Capacity Retention, High-Rate Spinel Manganese Oxide Compositions for Lithium-Ion Batteries	Unsolicited Proposal - In Negotiation
Brigham Young University *(D.R. Wheeler and J.N. Harb)*	Design, Optimization, and Fabrication of High-Performance Electrodes for the Next Generation of Li-Ion Batteries	Unsolicited Proposal-rejected

BATTERIES FOR ADVANCED TRANSPORTATION TECHNOLOGIES (BATT)

CALENDAR OF RECENT AND UPCOMING EVENTS

October 2003

12 - 17	204th Electrochemical Society Meeting – Orlando, FL (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)

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 Workshop - 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
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)