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July 30, 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 third-quarter FY 2004 report for the Batteries for Advanced Transportation Technologies (BATT) Program. This report and prior Program reports can be downloaded from http://berc.lbl.gov/BATT/BATT.html.

Sincerely,

Frank McLarnon
Manager
BATT Program

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

LBID-2495 (3)

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/Gr cell	6/04

PROGRESS TOWARD MILESTONES

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

Sixteen $LiFePO_4$/graphite cells were assembled from anodes and cathodes, received from K. Zaghib at Hydro Quebec, IREQ (HQ). Cells were filled with electrolytes based on either $LiPF_6$ or LiBOB in carbonate solvents. Most of the cells were tested at room temperature with 100% DOD cycling at a rate of C/2. Four cells were tested at 45°C. Post-test diagnostic evaluations were carried out on components from several of the cells, including electrochemical diagnostics, Raman spectroscopy and TEM. The $LiFePO_4$/graphite cells showed initial ASI curves very similar to those observed from the HQ-supplied cells, namely on the order of 150 Ω-cm^2. In previous work, we showed that while $LiFePO_4$ cathodes with the HQ carbon-coated current collector showed significantly better performance than the same electrode mix cast onto bare Al, cells with an ASI as low as 45 Ω-cm^2 were achievable with the LBNL-prepared carbon black-coated Al. Work is continuing on the scale-up of this current-collector and with the development of an in-house method for measurement of the contact resistance between the active mix and the current collector, based on our collaboration with Ann Marie Sastry (U. Michigan).

The lowest room temperature capacity fade rates for this batch of cells were 0.1%/cycle and 0.05%/cycle for the $LiPF_6$ and LiBOB-electrolytes, respectively. This low fade rate was maintained for at least 80 cycles before cell disassembly for post-test diagnostics. The rates of capacity fade at 45°C were significantly higher, however, the LiBOB cells again outperformed the $LiPF_6$ cells. Electrochemical analysis of the electrodes removed from these cells showed that capacity fade is primarily due to the loss of cycleable lithium from the cell. The cathode active material was essentially unchanged when cycled against a source of lithium (Li foil in the half-cell). In addition, an increase in cell impedance is responsible from some of the capacity fade.

In previous cells, various iron oxide species have been detected on anode samples removed from $LiFePO_4$ cells, by Raman spectroscopy (R. Kostecki) and confirmed with TEM (X. Song). In this more recent batch of cells, it is clear that LiBOB greatly influences the nature of the anode SEI layer. More work will be required to understand fully the Raman spectrum from this anode. However, no clear peaks from the Fe-oxide region were observed in preliminary spectra from anodes removed from $LiFePO_4$ cells cycled with LiBOB electrolyte.

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

The baseline $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ has been defined as one containing cathode-active material from Seimi Chemical (L333) and the LA-2-2 (GDR) carbon-coated graphite from Mitsui Mining. Anodes prepared from the GDR graphite were purchased from Quallion Corp. and used as received with dual-side coating of the current-collector. Cathodes were made in several coating thicknesses in order to match the capacity of the anode. Several cells have been prepared with PC-containing electrolyte (1.0M $LiPF_6$ /EC/PC/DMC, 1:1;3) . At room temperature, the best performing cells (benchmark for the BATT program) show a fade rate of 0.55%/cycle during C/2 cycling and an ASI at 50% SOC of about 136 ohm-cm^2. At 45 °C, this fade rate increases to 0.9%/cycle. Single electrode ASI tests suggest that a major portion of this impedance arises from the cathode and the increase in this impedance is responsible for the capacity fade. Several cell components have been delivered for Raman and XRD analysis. Further studies on the capacity retention of this cathode at voltages higher than 4.3V are underway with the L333 material and some experimental material received from Seimi.

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

The milestone was achieved in March 2004. We have now succeeded in using electroactive polymers to protect against moderate-rate overcharging in cells containing cathode with potentials above 4.0 V, including the BATT baseline material, $LiMn_{0.33}Ni_{0.33}Co_{0.33}O_2$ and ATD Gen2 $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$. In addition, we have shown that the mechanism works as well with carbon anodes as with lithium, that the temporary internal short does not cause significant self discharge at the end of charging, that the presence of the polymer does not compromise the conductivity of the electrolyte, and that the polymer can be used in an external protection circuit as well as inside the cell.

It has become clear that the morphology and distribution of the conducting polymer within the separator strongly influences the overcharge current density that can be maintained at a given cell voltage. When cast onto a fibrous, non-woven separator with large pores, a stable current density of more than 1 mA/cm^2 can be achieved, while the same polymer on Celgard 2500 may pass only 0.1 mA/cm^2.

We are currently making cells in which the overcharge protection portion of the separator is in direct contact with one or both current collectors. This is expected to improve the long-term stability of the electroactive polymers.

OTHER PROGRESS:

$LiFePO_4$, $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ and $LiCoO_2$ electrodes were found to be resistant to reaction with air to form Li_2CO_3. This is in contrast to the behavior of $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$, in which formation of a thick carbonate coating on the particle surfaces may cause isolation of a significant portion of the active material.

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 focused on our major target of producing an electrode coating from a water-soluble polymer binder (WSB). We developed an experimental coating plan with different polymer concentrations to optimize the slurries. Anodes containing a mixture of fiber and graphite, and $LiFePO_4$ cathodes, were coated with WSB of different thicknesses. The amount of binder in the electrodes was reduced by more than 50%. A "scotch-tape" test was used to evaluate the adhesion of the coating, and the results show that the cathodes and anodes have good adhesion properties. Our second objective is to optimize new cathode films based on other BATT baselines chemistries ($LiMn_{0.5}Ni_{0.5}O_2$, $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$). Different thicknesses of these cathode materials were coated. By April 2004, several of these cathode films were sent to LBNL for evaluation.

We studied the thermal stability of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ by Accelerating Rate Calorimetry (ARC). The cathode materials, from hydro-Quebec, were tested by Prof. Dahn at Dalhousie University (Halifax, Canada). Two samples; A (2 µm), and B (10 µm) of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ in cathodes were studied. The cathodes were first charged to 4.2V vs. Li. Figure 1 shows the self-heating rate versus temperature for $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (samples A and B) in EC/DEC (1:2 by volume) solvent and in 1M $LiPF_6$ EC/DEC or 0.8M EC/DEC electrolytes. In EC/DEC solvent, the onset temperatures for self-sustained exothermic reactions are 180˚ and 200˚C for samples A (2 µm) and B (10 µm), respectively. In 1 M $LiPF_6$ EC/DEC both samples show the same stability to 180°C. For both samples, the reactivity with LiBOB EC/DEC is more severe than with $LiPF_6$ EC/DEC, the onset temperatures are 140˚ and 150˚C for sample A and B, respectively. This result confirms the higher thermal stability of $LiFePO_4$[1,2] compared to $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ in LiBOB EC/DEC.

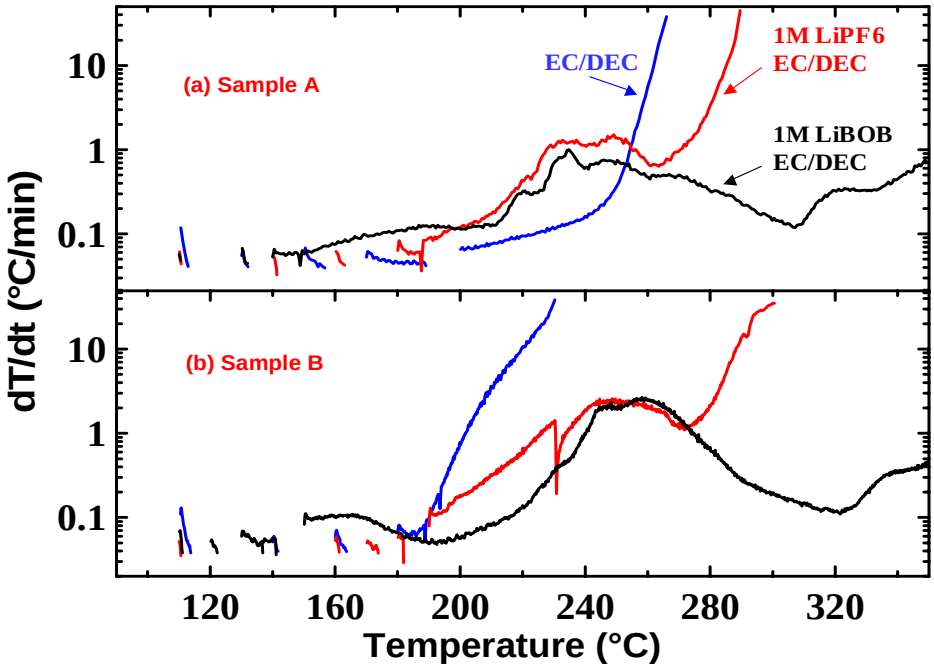


Fig. 1: Self-heating rate of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ samples with two particles size A(2 µ) and B(10 µ) in EC/DEC (1:2 by volume) solvent and in 1M $LiPF_6$ EC/DEC or 0.8M EC/DEC electrolytes.

Our last goal is to deliver to LBNL 10 Li-ion gel cells with composite anode (graphite and fiber) and $LiFePO_4$ cathode using water soluble polymer binder by July 2004.

[1]: K. Zaghib et al., J. Power Sources, Vol. 134-1 (July 2004), 129-134.
[2]: J. Dahn et al., IMBL 12 Meeting, NARA, Japan (2004), The Electrochemical Society, Abs. 299

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 Li 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

We have focused our work on electrochemical evaluations of oxide-based anode systems and on metal-graphite composite anodes. We have continued to explore Li_2MO_2 systems that operate below 2V vs. Li^0 and, in particular, $LiCoO_2$ and $LiNiO_2$. These efforts are built on our earlier studies of $Li[Mn_{0.5}Ni_{0.5}]O_2$ in which it was demonstrated that an extra Li could be accommodated by electrochemical insertion into the Li layers to form $Li_2[Mn_{0.5}Ni_{0.5}]O_2$ without destroying the $[Mn_{0.5}Ni_{0.5}]O_2$ framework. Our theoretical modeling calculations of the $Li_{1+x}CoO_2$ system have predicted that, under thermodynamic equilibrium, Li_2CoO_2 does not form. Lithiation of $LiNiO_2$ to form Li_2NiO_2 is not easily accomplished because the Li layers are generally contaminated by some Ni. We have therefore investigated $LiCoO_2$ and $LiNiO_2$ as anode materials at potentials below 1 V in order to access electrochemical capacity by reduction of the transition metals to the metallic state, following the approach taken recently by Tarascon et al in their studies of MO compounds such as CoO.

For $LiCoO_2$, we observed a high electrode capacity in the voltage window 3.0 to 0 V. Although the initial cycle displayed a large irreversible capacity loss, part of which is attributed to the formation of a Li-rich SEI phase, continued cycling gave a reversible capacity of 550 mAh/g, corresponding to the reaction of 2.0 Li per $LiCoO_2$ unit (Fig. 1). Most of this capacity is discharged below 500 mV vs. Li^0 (Fig. 1a). In-situ X-ray diffraction analysis of a $LiCoO_2$ electrode during electrochemical discharge in a Li cell showed that the $LiCoO_2$ electrode was reduced first to CoO and thereafter to Co with the concomitant formation of Li_2O in both stages, in agreement with our theoretical predictions. On subsequent charge, the Co is oxidized only as far as CoO. $LiNiO_2$ electrodes behave in a similar manner, yielding a reversible capacity of ~500 mAh/g, which corresponds to the reaction of ~1.8 Li per the initial $LiNiO_2$ unit (Fig. 1b).

Work on metal- or intermetallic-graphite composite electrodes is continuing. We are focusing our efforts predominantly on composite electrodes with Sn and Sb to provide systems with superior gravimetric and volumetric capacities to graphite. We are also continuing our efforts to improve the cycling stability of Cu_6Sn_5 electrodes by improving inter-particle contact and maintaining electronic connectivity and conductivity in the electrode at all times.

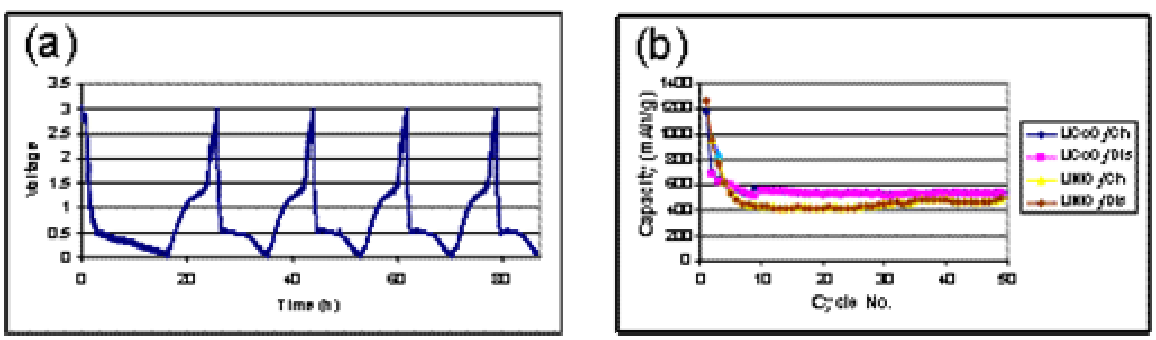


Figure 1. (a) Discharge and charge profiles of a $Li/LiCoO_2$ cell (3.0 to 0.0 V) and (b) Capacity vs. cycle no. plots for $Li/LiCoO_2$ and $Li/LiNiO_2$ cells.

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 previous reports we discussed the electrochemical behavior of tin foil as the anode in lithium batteries. Recently we have obtained expanded tin and aluminum grids from Karim Zaghib at Hydro-Québec, to determine if their open structure will mitigate the capacity fade. Figure 1 shows the electrochemistry of the tin grids. It shows a cycling behavior similar to tin foil, with a slightly higher initial discharge capacity. After the first discharge, three plateaus corresponding to $Li_{0.4}Sn$, LiSn, $Li_{2.33}Sn$ respectively appear in the following lithium intercalation and deintercalation. Compared with tin foil, the grid has a slightly better electrochemical performance beyond 10 cycles. We will pursue composite electrodes of this type with Hydro-Quebec in the next quarter.

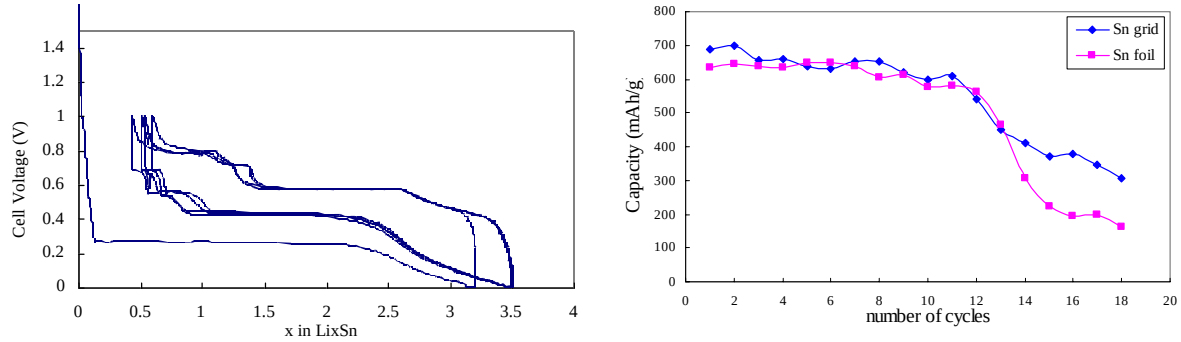


Figure 1. (Left) cycling of expanded tin grid, and (right): the discharge capacity compared with tin foil

Karim Zaghib also provided three aluminum grids whose behavior is displayed in Figure 2. All of them show the formation of LiAl during cycling, and an initial high capacity of ~1Ah/g, followed by a fast dropping off to ~400mAh/g, which is still higher than the capacity of the graphite anode. Although this behavior is significantly better than aluminum foil, it still shows that aluminum cannot be cycled extensively in carbonate electrolytes.

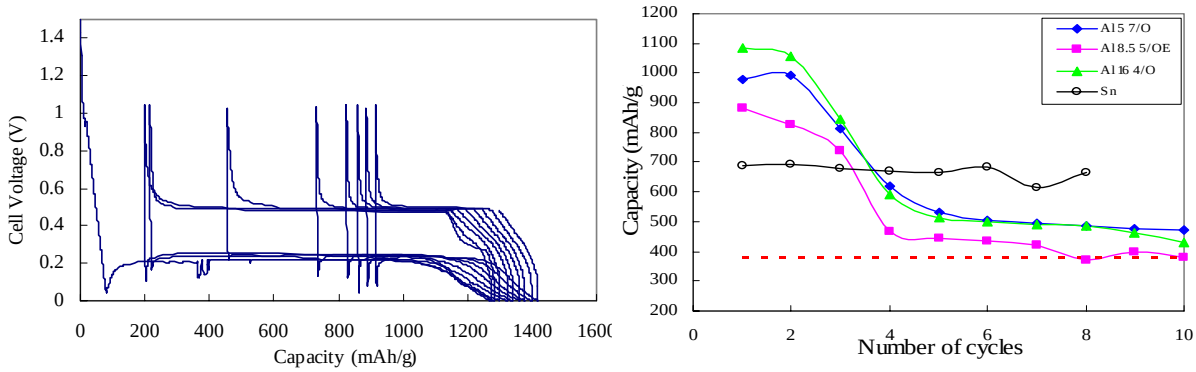


Figure 2. Left: cycling of expanded aluminum grid; Right: discharge capacity comparison of aluminum and tin grid

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

TASK STATUS REPORT

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

TASK TITLE - PROJECT: ANODES – NOVEL COMPOSITE ANODES FOR LITHIUM-ION BATTERIES

SYSTEMS: Low-cost Li-ion battery, Improved safety, long cycle and calendar life

BARRIERS: Poor cycle life, poor safety, self-discharge, and electrolyte decomposition

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.

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

EXPECTED STATUS SEPT. 30, 2004: A well-controlled process based-on 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 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 focus of our work has been the development of a composite anode with superior performance with respect to the current graphitic anode technology. In our previous work we have established a general prelithiation process to activate various anode materials and eliminate their initial irreversible capacity loss during charge-discharge cycling. After successful completion of this work, which includes an optimized chemical reduction process of anode materials before electrode fabrication, we have worked to improve the overall gravimetric and volumetric capacity of our composite anodes. Among various oxides, nitrides and phosphides, which have been tested before, we have focused on optimization of SnO_2. We have successfully reduced the oxide to nano-sized metallic Sn by mechanomilling of SnO_2 in presence of metal hydrides according to the following general reaction scheme:

$$SnO_2 + LiH \text{ (or NaH)} \xrightarrow{\text{Mechanomilling}} \text{Sn (nano-sized)} + LiOH \text{ (or NaOH)}.$$

In a second process we removed the inactive by-products to produce impurity free nano-sized Sn. The nano-sized Sn was ball milled with a flexible conductive matrix (composite of conductive carbon black 80 wt% and graphite fiber 20 wt%), and electrodes with 10-15 mg/cm^2 were fabricated using a non-fluorinated rubber binder. The engineering of electrode fabrication with good adhesion to pre-coated copper substrate was also optimized. The capacity of the composite anode was studied at various levels of lithium insertion. The electrochemical testing of the electrode at 1, 2, and 5 mA/cm^2 were performed. Engineering of the electrode was further optimized for better utilization of Sn particles. The capacity of the electrode at 1 mA/cm^2 was in excess of 850 Ah/Kg, (more than twice the capacity of the current graphite anode). A stable capacity in the range of 680 mA/cm^2 was achieved after 5-10 charge-discharge cycles. Charge-discharge cycles of several cells are in progress. A similar process will be applied to other promising low cost and safe anode materials in large size batteries for transportation application.

● Further plans to meet or exceed milestones.

Our future plan is to further optimize the formulation of active material (nano-sized Sn) with flexible conductive matrix and non-fluorinated rubbers to improve stable charge-discharge cycles in the range of 800 AH/Kg. We will also apply the above process to other promising low cost and safe anode materials.

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

The dielectric properties of poly(ethylene oxide) (PEO) melts containing lithium perchlorate ($LiClO_4$) under steady shear flow was measured using a home-built rheo-dielectric instrument. A significant increase in the zero-shear viscosity η_0 is observed upon addition of $LiClO_4$ to PEO. This is due to Li^+–mediated intermolecular bridging of the PEO chains. Significant shear thinning was observed under fast shear, suggesting the flow-induced break-up of the intermolecular bridges and the flow-induced liberation of Li^+ ions. The presence of liberated ions was detected directly by dielectric dispersion experiments under steady shear flow. Our experiments established the quantitative connection between shear thinning, observed in the rheological experiments, and the shear-induced increase in the electrical conductivity, observed in the dielectric experiments. This work, which provides fundamental insight into the mechanism of ion transport in polymer electrolytes, has been published (Y. Matsumiya, N.P. Balsara, J.B. Kerr, and H. Watanabe, *Macromolecules*, vol. 37, p.544-553, **2004**).

We have recently conducted small angle neutron scattering experiments to determine the nature of polymer electrolytes. These experiments suggested the presence of a periodic structure with a length scale of 40 nm. Such a structure has not been anticipated from any of the pervious work, either theoretical or experimental.

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

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

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. Dendrite Initiation and Growth at Lithium Metal Anodes. During cycling tests of lithium/lithium symmetrical cells with comb-branched, network and linear polymer electrolytes it has been noted that there are critical current densities and cell polarizations below which no surface roughening occurs. The lithium metal may be cycled indefinitely with no apparent change in the concentration polarization or the interfacial impedance.

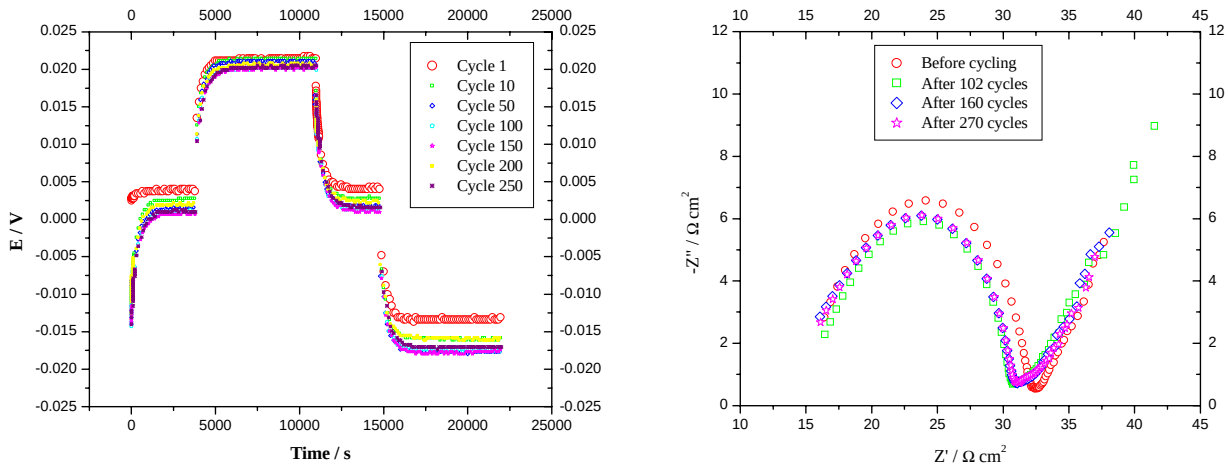


Figure. Li cycling profile and evolution of impedance for a lithium cell based on LiTFSI /$PEPE_4$-co-$AllylE_2$ electrolytes (EO/Li=20) at 85°C at a current density of 100μA cm^{-2}.

Increase of the current density or a decrease in the temperature to values where the transport properties can no longer relax the concentration gradients quickly enough results in increases in the interfacial and concentration impedances. This leads to steadily increasing cell polarizations and surface roughening. The LiTFSI and LiBETI imide salts are able to sustain 100μA cm^{-2} indefinitely. However, salts with poorer transport properties, LiMethide and LiTriflate, cannot sustain these current densities while a variety of salts appear to react with the lithium metal during cycling. These include $LiBF_4$, $LiPF_6$, LiBOB and $LiClO_4$, which all show large increases in interfacial impedances upon cycling. $LiPF_6$ appears to be particularly unsuitable as would be consistent with the reaction of PF_5 on the PEO-type polymer. Post-mortem analyses of the cells by GC/MS confirms the reactions on the polymers by the lithium metal by detection of the side chain fragments from the comb polymers.

Impedance measurements as a function of temperature have also been made to estimate the exchange current densities at lithium metal electrodes using a linear cross-linkable polymer from Zeon Corporation, ZTP500. This is a co-polymer of ethylene oxide, propylene oxide and allylglycidylether and is similar to the material used by 3M/HQ in the USABC program. The transport and mechanical properties and exchange current densities have been measured for both the linear polymer and various levels of cross-linking. Cross-linking clearly leads to a decrease in both the transport properties and the exchange current densities. Thus, any non-uniformity in the polymer cross-linking will lead to non-uniform polarization and immediate surface roughening. These effects may be alleviated by an increase in transport properties which can be improved by addition of solvents to prepare gel polymer electrolytes.

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

We have started to evaluate the effects of processing on the rheological properties and conductivities of mixed-molecular weight (MW) polymer electrolytes. The composite electrolytes consisted of polyethylene oxide (PEO, 200K) + polyethylene glycol dimethylether (PEG-dM, 250) (mass ratio 4:1) + LiTFSI (lithium bis(trifluoromethylsulfonyl)imide) (Li:O=1:20) + hydrophilic fumed silica (10 wt% A200). Two processing methods were employed: melt mixing and solvent mixing. Solvent mixing was carried out by dispersing and dissolving the polymer, salt, and filler in acetonitrile at room temperature; melt mixing was carried out in a co-rotating twin screw extruder (Haake Mini melter) at 90 °C. All the samples were kept under vacuum at room temperature until tested. Dynamic rheological experiments at 80 °C showed higher elastic and viscous moduli for the solvent-cast samples with and without filler compared to the melt-processed analogs. This suggests differences in the dispersion and distribution of the components since thermal and/or mechanical degradation in the melt mixed samples was tested and ruled out. We also found the melt-mixed samples to show slightly higher ionic conductivities than the solvent-cast materials. The effects of processing conditions are continuing to be explored.

We have evaluated the potential windows of $P(EO)_{20}$LiTFSI + 10% A200 composites with different mass ratios of PEO (MW=600K): PEG-dM (MW=250)=100/0, 80/20, 67/33, 50/50 using Li/electrolyte/SS (stainless steel) cells. The experiments were conducted at 75 ºC, scanning from 2 to 6 V at 1mV/s rate. We found that the mass ratio had no effect on the potential windows, with all samples exhibiting degradation about 5.1 V.

We have begun to study the thermal stabilities of different lithium salts: lithium bis(perfluoroethylenesulfonyl) imide (LiBETI), lithium bis(oxalato)borate (LiBOB), and dilithium bis(perfluoromethylsulfonyl) (perfluoroethylenesulfonyl) imide (Li dianionic, collaboration with Clemson University) by using thermogravimetric analysis (TGA). The TGA measurements were done from room temperature to 600 ºC at a heating rate of 5 ºC/min under nitrogen. Preliminary results indicate that the thermal stabilities of LiBETI and Li dianionic salts are better than that of LiBOB. We have evaluated the potential windows of these three types of lithium salts both in liquid (PEG-dM 250) and gel (PEG-dM 250 + 10% R805) states. Fumed silica has no effect on the potential window; LiBETI and LiBOB have slightly higher potential windows (~ 5.3 V) than Li dianionc (~ 5.2 V).

We have studied the interfacial stability with lithium of single-ion conducting fumed silica [Degussa R711-poly(lithium 2-acrylamido-2-methyl-1-propanesulfonate), R711-pLiAMPS, surface Li^+ content $\gamma = 4.2\ nm^{-2}$] + PEGdm (MW = 250, Li:O = 1:20) composite electrolytes both at open-circuit and lithium deposition–dissolution cycling conditions. Lithium cycling was conducted by applying a current of 0.05 mA cm^{-2} on Li/electrolyte/Li cells, and the current was reversed every 1 h (180 mC cm^{-2}). The lithium-electrolyte interface of R711-pLiAMPS + PEGdm electrolyte is stable at open-circuit, however, the average voltage of Li/electrolyte/Li cell increases dramatically during the first few cycles, indicating an unstable interface. Adding LiTFSI as additional ion carrier decreases interfacial resistance at open-circuit and stabilizes the cell voltage during cycling. For example, R711-pLiAMPS + LiTFSI (59 mol% in total ion carriers) + PEGdm (Li:O = 1:20) electrolyte shows no appreciable voltage increase after 350 cycles.

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:

Progress continues on the 2004 project milestones of supplying new sulfonimide-based Li salts to BATT coworkers, and synthesizing new sulfonimde-based lithium salts for use in preparing single-ion conductors. Major effort has also been directed at a new class of lithium salts consisting of fluorosulfonate and fluorosulfonimde anions covalently linked to short polyether chains which serve to solvate the lithium and provide a matrix for Li transport.

Salts were supplied in spring 2004 to BATT coworker Kathy Striebel for tests in a half-cell configuration with a $LiFePO_4$ cathode with the salt dissolved in a 1:1 EC:DEC solvent mixture. Compatibility of salt solutions with the $LiFePO_4$ cathode was established, with little or no capacity fade over many tens of cycles. Further half-cell testing using lithiated graphite anodes is planned for fall 2004, and salt synthesis for those tests is underway. Salts were provided to BATT coworker Tom Devine for use in Al corrosion testing, which is underway. SPEs were fabricated using a series of salts of structure $CF_3SO_2[N(Li)SO_2R_fSO_2]_nN\text{-}(Li)SO_2CF_3$, $R_f = (CF_2)_4$, n=0, 1, 5, and 24, and the SPEs were provided to BATT coworkers Fedkiw and Khan at NCSU for approximate Li transference testing using the potentiostatic polarization method. Results of those tests will be combined with tests performed at Clemson using low-frequency EIS to measure Li transference, and also using restricted-diffusion methods to measure salt diffusion, over a wide range of anion sizes. These combined studies will lend insight into the relationship between anion size and charge, and anion transport, in lithium SPEs.

Substantial progress has been made synthesizing and characterizing polyether-based ionic melts consisting of fluorosulfonate and fluorosulfonimide anions linked to polyethers, with lithium cations solvated by the polyether chains. The reaction used for these syntheses is as follows: $PEG\text{-}OH + CF_2{=}CFO\text{-}CF_2CF_2\text{-salt} \rightarrow PEG\text{-}O\text{-}CF_2\text{-}CHFO\text{-}CF_2CF_2\text{-salt}$ (salt = SO_3Li or $SO_2N(Li)SO_2CF_3$). We note that while these materials are not themselves intrinsic single-ion conductors, they should behave as single-ion conductors when used in a Li-ion battery for which both electrodes are blocking for anions but non-blocking for lithium. Coupling reactions run with trifluorovinylether salt as limiting reagent (to avoid side reactions) were found by ^{19}F NMR to proceed cleanly and in high yield with no detectable side-products. Preliminary conductivity data acquired on a material with lithium fluorosulfonate attached to a 350 MW PEG monomethyl ether chain, which still contained some excess unmodified PEG, were quite promising, e.g., room-temperature conductivity was above 10^{-4} S/cm and was only slightly less than that of LiTFSI dissolved in 350 MW PEG monomethyl ether at the same EO:Li ratio. Methods are being developed to remove the excess PEG, e.g. by heating under vacuum and/or by selective solvent extraction, and also to eliminate sodium impurities which AA analysis showed were present and which probably derive from the NaH used to deprotonate PEG-OH prior to addition to the trifluorovinylether. Replacement of NaH with LiH should solve this problem. Experiments aimed at preparing and evaluating purified samples (free of sodium, unmodified PEG, and/or excess free salt) with fluorosulfonate and fluorosulfonimde anions are in progress.

Finally, preliminary work aimed at synthesizing fluorosulfonate and fluorosulfonimide-functionalized organic epoxides, for synthesizing lithium single-ion conductors by ring-opening polymerization has begun. Epoxidation using hydrogen peroxide and various organic peroxides has been attempted, and other epoxidizing agents are being evaluated.

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

During this quarter our group concentrated on prediction of structural and dynamic properties of two classes of materials schematically shown in figure 1: a) dry single ion conductors; b) ionic liquids. Molecular dynamics (MD) simulations have been performed on the PEPE-m-20-TFSILi, m=5,10,20 (see figure 1 for notation) single ion conductors and the LiTFSI-EO_n-TFSILi ionic liquids for n=12,20,40 at 423 K for 1 ns after 1 ns equilibration. The main goal is to find optimal length of the side chain or polyether connector in these materials.

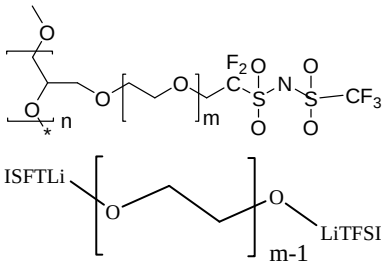


Figure 1. Schematic structures of the polyepoxyde ether (PEPE-m-n)/TFSILi single ion conductor and LiTFSI-EOn-TFSILi ionic liquid used in MD simulations.

Conductivity of the PEPE-m-20-TFSILi and LiTFSI-EO_n-TFSILi electrolytes have been estimated at 423 K and are shown in figure 2. These data indicate that the most optimal number of ether oxygen units in a side chain is ~10-12 for the PEPE-m-20-TFSILi electrolyte, and 20 for the LiTFSI-EO_n-TFSILi ionic liquid. A drop in conductivity with side chain decrease from 10 to 5 ether oxygen repeat units in the PEPE-m-20-TFSI electrolyte is associated with a sharp decrease of the fraction of "free" Li^+ charge carriers from ~60% to ~30% and slowing down of the polymer and Li^+ local dynamics with the decrease of the length of the side chains.

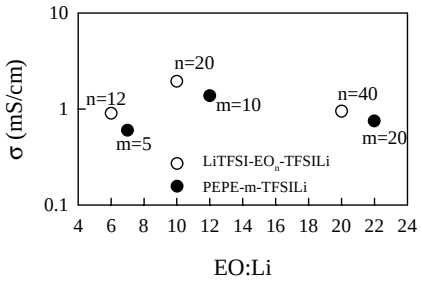


Figure 2. Conductivity of the PEPE-n-(20) and LiTFSI-EOn-TFSILi electrolytes at 423K.

We also initiated MD simulations of the single ion conductors with the structure shown in figure 3. These polymers have rather short side chain of length five EO repeat units, with the TFSI anion attached to side chains every 2,4,8 repeat units. Due to short side chain length (5 EO), these single ion conductors are not expected to crystallize but could exhibit transport properties even better than those shown in figure 2. Initial estimates of transport properties from short simulations indicate rather high conductivities ~1 mS/cm at 423 K. Accurate predictions at structural and transport properties at this and lower temperatures are expected within 1-2 months.

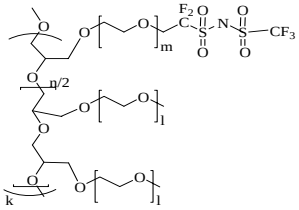


Figure 3. Schematic structure of the single ion conductors used in studies of the effect of salt concentration on conductivity.

Further Plans To Meet Or Exceed Milestones We initiated studies of the LiTFSI-EO_n-TFSILi ionic liquids that are currently investigated by Clemson group within BATT program. We expect to provide guidance into the most optimal design of these materials and molecular level understanding of the Li^+ cation transport mechanism in them.

BATT TASK 4
CATHODES

TASK STATUS REPORT

PI, INSTITUTION: M. Thackeray, Argonne National Laboratory

TASK TITLE: Cathodes - Novel Materials

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

BARRIER: Cost and safety limitations of Li-ion batteries

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

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

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

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

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

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

PROGRESS TOWARD MILESTONES

Novel Cathodes

We have continued to explore the cycling stability of composite $xLi_2M'O_3 \bullet (1\text{-}x)LiMO_2$ electrodes at high potentials vs. Li^0. Electrodes with composition $0.3Li_2MnO_3 \bullet 0.7LiMn_{0.5}Ni_{0.5}O_2$ (x=0.3) yield capacities >200 mAh/g if charged and discharged between 4.6 and 2.0 V in lithium cells. These electrodes suffer a large irreversible capacity loss (~20-25%) on the initial cycle when charged to 4.6 V as a result of oxygen loss and/or reaction with the electrolyte; thereafter, the electrodes cycle with >99% coulombic efficiency (Fig. 1a, b).

The irreversible capacity loss on the initial cycle is attributed to a concomitant two-stage reaction whereby Li_2O is removed from the electrode structure during charge. It is believed that extraction of lithium from the Li_2MnO_3 component is accompanied by removal of electrons from the oxygen 2p band; the resulting oxidized surface is consequently stabilized by the loss of oxygen. These reactions can be represented:

$$Li_2MnO_3 \rightarrow 2\,Li^+ + Mn^{4+}O_3^{4-} + 2e \qquad \textit{electrochemical process} \qquad (1)$$

during which electrons are removed from the oxygen 2p band to form an unstable $Mn^{4+}O_3^{4-}$ configuration. This process is accompanied by a chemical redox reaction that stabilizes the electrode surface:

$$2\,Mn^{4+}O_3^{4-} \rightarrow 2\,MnO_2 + O_2 \qquad \textit{chemical process} \qquad (2)$$

The formation of a MnO_2 species, which remains structurally integrated at the surface of layered $xLi_2MnO_3 \bullet (1-x)LiMn_{0.5}Ni_{0.5}O_2$ composite electrodes during the initial charge is consistent with the high capacities that have been obtained from these electrodes on subsequent charge/discharge cycles between 4.6 and 2.0 V (Fig. 1a, b). For example, the theoretical capacity of a $0.3Li_2MnO_3 \bullet 0.7LiMn_{0.5}Ni_{0.5}O_2$ electrode is 184 mAh/g if the Li_2MnO_3 component is not electrochemically activated by the processes described above whereas, in practice, more than 200 mAh/g is delivered by the electrode. The removal of Li_2O from these electrodes can be used to offset the first-cycle capacity loss of graphite and intermetallic negative electrodes in Li-ion cells.

Reaction of Li_2MnO_3 with acid removes Li_2O from the structure; this process is accompanied by some H^+-Li^+ ion-exchange. We are therefore investigating the reactions of composite $0.3Li_2MnO_3 \bullet 0.7LiMn_{0.5}Ni_{0.5}O_2$ electrodes with acid with the hope of removing some Li_2O from the electrode to reduce the irreversible capacity loss on the first cycle to a desired level. Preliminary results indicate that this may indeed be possible; the first–cycle capacity loss of an untreated electrode is 22%, whereas it is only 5% for an acid-treated electrode (Fig. 1c, d).

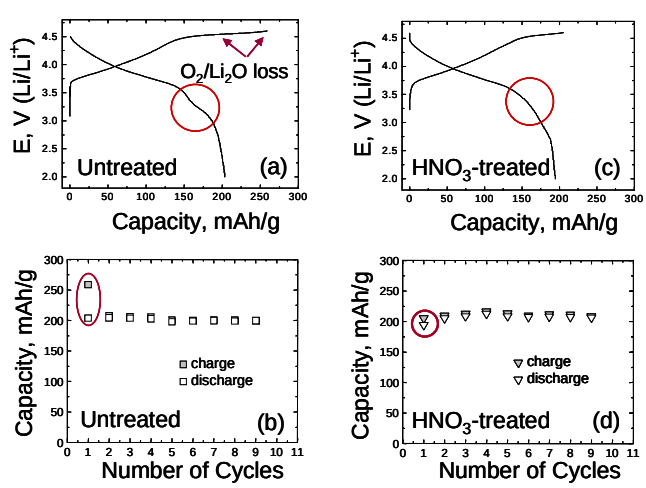


Figure 1. Electrochemical data of lithium cells with untreated- and acid-treated $0.3Li_2MnO_3 \bullet 0.7LiMn_{0.5}Ni_{0.5}O_2$ electrodes (4.6-2.0 V).

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

(a) Stabilized Manganese Oxides. This Quarter, we completed the evaluation of the structure of layered $LiMn_{0.4}Ni_{0.4}Co_{0.2}O_2$ at room temperature for both the starting material and as a function of the degree of electrochemical deintercalation. Our studies of other compositions and of the thermal stability of these compounds continue. A combined x-ray and neutron diffraction study showed that the three transition metals, Mn, Ni, and Co, are randomly distributed at room temperature in the TM layer. Only nickel of the three migrates to the lithium layer, and the degree of migration is related to the cobalt content and the temperature of synthesis.

Several positive conclusions have been found:

1. The volume changes by less than 2% as the lithium is removed, which should minimize any mechanical decrepitation of the electrode.
2. The structure of $LiNi_{0.4}Mn_{0.4}Co_{0.2}O_2$ does not change on lithium removal unlike $LiCoO_2$ where all the CoO_2 slabs/blocks slide going from the 3-block to the 1-block structure. There is only a trace of the 1-block structure, unlike $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ where our initial data indicates that structural change occurs. This may be related to the 2-3% nickel in the lithium layers pinning the structure. Thus, it might be advantageous to leave some nickel disorder in the compound.

The capacity over extended cycling exceeds 160 mAh/g at a 1 mA/cm^2 charge/discharge rate when cycling up to cut-off of 4.4 volts. Capacities as high as 200 mAh/g can be attained if the cut-off voltage is raised to 4.6 volts – more extensive testing in this range will be carried out next quarter as will be some high rate pulse testing. Thus, we conclude that at the present time these layered $Li_xMn_{1-y-z}Ni_yCo_zO_2$ compounds can attain high power and energy densities and being stable are of great future interest to the BATT program.

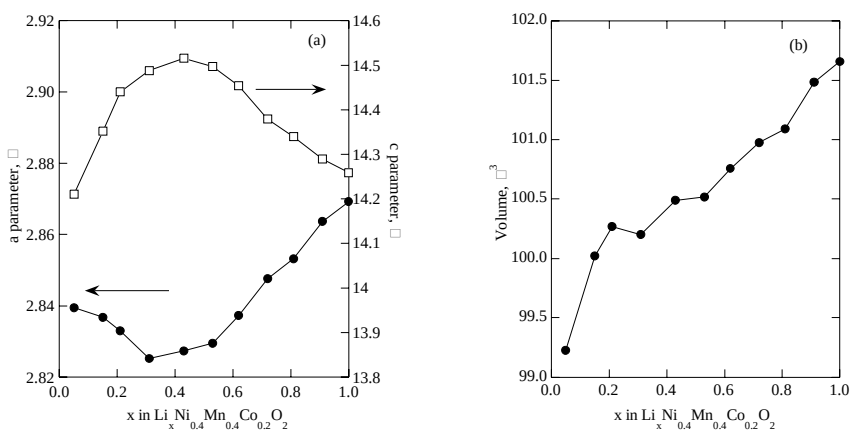


Figure 1. (a) Lattice parameters and (b) cell volume as a function of lithium content.

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 and M. Stanley Whittingham: Structure Determination for Powder Diffraction Data-Challenging Battery Materials, *The Rigaku Journal*, 2004, 21:2-14.
2. Miaomiao Ma, Natasha Chernova, Peter Y. Zavalij and M Stanley Whittingham: Cathode Materials for HEV Lithium-Ion Batteries: Layered $LiMn_{0.4}Ni_{0.4}Co_{0.2}O_2$. *Solid State Chemistry Gordon Conference*, New London, New Hampshire, July, 2004.

TASK STATUS REPORT

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

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

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

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

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

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

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

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

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

MILESTONES:

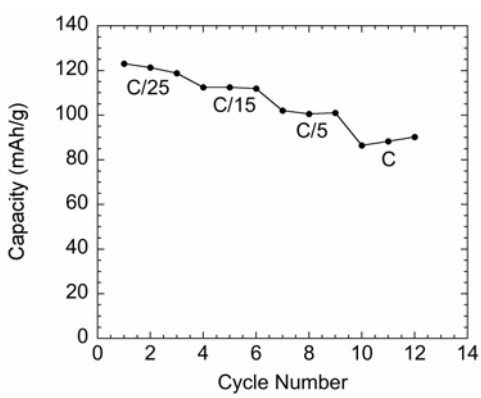
(a) Go/no go decision on optimization process for coating $LiFePO_4$	4/04.
(b) Determine optimum O2/O3 ratios for $Li_xAl_yMn_{1-y}O_{2+z}$	6/04

PROGRESS TOWARD MILESTONE (a)

Work continues on optimization of the carbon coating on $LiFePO_4$; the goal is to produce carbons with low D/G ratios (disordered/graphene) so that a minimal amount may be used to improve conductivity. Addition of pyromellitic acid (PA) during synthesis improves carbon structure, resulting in better rate performance. Surface Fe(III) oxides promote formation of G-type carbon, but must be kept to very low levels or else utilization is adversely affected. This quarter, we varied the amount of PA (2-8%) added to samples during synthesis and used two different partial pressures of O_2 in the furnace, by employing either a Ti powder or a Cu mesh "getter" during heating. Results were much better when Cu was used. This suggests a role for trace amounts of oxygen in the formation of G- type carbon during synthesis because Cu is a less efficient getter than Ti.

Best results were obtained when PA amounts between about 2-6 wt. % were used. The amount of residual carbon, in all cases, is less than 1 wt. % and does not necessarily track the amount of PA added. Carbon structure is more important than amount in determining performance. Figure 1 shows cycling data for one of the samples synthesized (6% PA, Cu). Although utilization is lower than theoretical at low current densities, the rate capability is good. Decreasing the particle size and using carbon coated current collectors should improve the low rate utilization. Future work includes evaluation of electrodes containing conductive polymers, and a systematic study of the effect of iron promoters upon *in situ* carbon structure.

Evaluation of the $Li_xMn_{1-y}Al_yO_2$ system is nearly complete. Figure 2 shows cycling data for Li cells containing O3 phases. Substitution levels of 12-18% Al give the highest capacity electrodes.



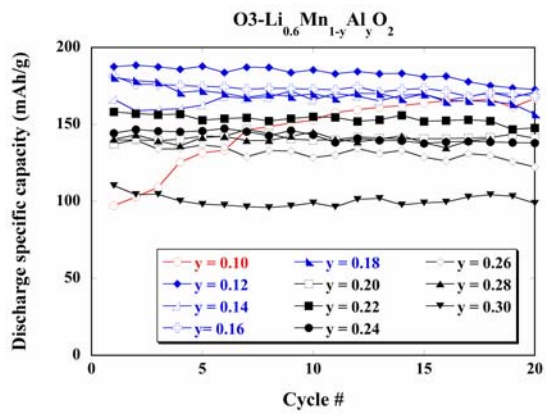


Figure 1 (left) Cycling and rate data for a Li/$LiFePO_4$ cell. **Figure 2 (right)** Cycling data for Li/O3-$Li_{0.6}Mn_{1-y}Al_yO_2$ cells.

Further plans to meet or exceed milestones N/A

Reason for changes from original milestones Milestone 4.3b has been postponed until 9/04, due to the large number of samples and data needed to complete the analysis.

Publication

"Direct Synthesis of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ from Nitrate Precursors," Sébastien Patoux and Marca M. Doeff, *Electrochem. Commun.*, **6/8**, 767 (2004).

TASK STATUS REPORT

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

TASK TITLE - PROJECT: Cathodes - Novel Materials

SYSTEMS: Li secondary battery

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

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

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

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

EXPECTED STATUS SEPT. 30, 2004:

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

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

MILESTONES:

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

PROGRESS TOWARD MILESTONES

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

Our efforts during the past quarter has been divided between our two main research efforts A) fabrication of cathodes based on $LiNi_{1-x}Mn_xO_2$ and B) testing the feasibility of cathodes based on redox pairs tethered to a conducting polymer.

<u>The $LiNi_{1-x}Mn_xO_2$-system:</u>

Similar to $LiCoO_2$, this material is based on the α-$NaFeO_2$ structure. Here the redox units are both the $Ni^{2+/3+}$ and $Ni^{3+/4+}$, which are pinned at the top of the O-2p band to give a working potential of ~4 V vs. Li^+/Li, with no potential step between the two redox pairs. We have previously shown that this electrode material can be cycled extensively at low rates, thus our efforts in this quarter have been focused on showing the rate limitations. The outcome of these investigations are summarized below. It has become clear that there is a capacity drop upon increased discharge rates. The capacity loss is reversible upon returning to low-rate testing and is accompanied by a large iR drop. This combined with data from previous studies of $LiCoO_2$ [Abraham *et al*. *J. Electrochem.Soc*. 145(1998)p.482] have led us to believe that our commercial semi-permeable separator, which was chosen based on mechanical rather than conductivity criteria may be limiting the capacity rather than the cathode. We are therefore examining other membranes that may be employed in a laboratory setting when testing at high rates are required. With this new membrane, we hope to improve upon the already large 5C capacity of ~110 mAh/g.

<u>The polymer tethered redox pair-system:</u>

The motivation for exploring this system is a desire to avoid the low Li^+-ion mobilities found in most solid-state structures and to introduce a structure that can be tailored by solution chemistry techniques rather than high-temperature sintering. Like the solid-state counterparts, this system is designed to immobilize the redox pair in a matrix were both electrons and Li^+ ions may be delivered without resistance. We plan to accomplish this by choosing an electrolyte-permeable conducting polymer scaffolding (poly-pyrrole) onto which we plan to covalently anchor the redox units (Ferrocene).
Towards this end, we have, during the past quarter, synthesized a small amount (~0.5 g) of a monomer unit containing both ferrocene and pyrrole. To prepare the cathode will require electrochemical polymerization and we have designed an electrochemical cell that will allow us to prepare and characterize the electrode separately from the battery cell. In preliminary trials, this cell combined with a potentiometric technique have already been shown to produce self-supporting polymer films that can be removed from the electrolyte, dried, and characterized before installation in the battery assembly. However, due to our limited supply of the redox-tethered monomer, these trials were completed with a commercially available mock monomer not suited for battery application. Work is now underway to improve our success rate so that sheets of the target polymer may be produced for testing.

- **Further plan to meet or exceed milestones N/A**
- **Reason for changes from original milestones N/A**

TASK STATUS REPORT

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

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

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

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

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

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

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

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

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

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

PROGRESS TOWARD MILESTONES

From our previous work, we identified that doubly substituted spinel oxide compositions such as $LiMn_{1.85}Ni_{0.075}Li_{0.075}O_4$ exhibit a combination of superior capacity retention, rate capability, and storage characteristics with low irreversible capacity (IRC) loss compared to $LiMn_2O_4$. The better electrochemical performance is due to a low lattice parameter difference Δa between the two cubic phases formed during the charge-discharge process and the consequent low microstrain. However, the $LiMn_{1.85}Ni_{0.075}Li_{0.075}O_4$ composition exhibits a lower capacity of about 95 mAh/g. With an objective to increase the capacity values, we have focused on incorporation of other additional cations such as Cu^{2+} into $LiMn_{2-y-z}Ni_yLi_zO_4$. The triply substituted spinel compositions $LiMn_{2-y-z-\eta}Ni_yLi_zCu_\eta O_4$ exhibit slightly higher capacity values than the doubly substituted $LiMn_{2-y-z}Ni_yLi_zO_4$. For example, $LiMn_{1.85}Li_{0.075}Ni_{0.04}Cu_{0.035}O_4$ and $LiMn_{1.88}Li_{0.06}Ni_{0.03}Cu_{0.03}O_4$ compositions synthesized by conventional solid state methods exhibit capacity values of around 100 mAh/g. It is found that the substitution of Cu^{2+} for Ni^{2+} does not degrade the rate capability. We are currently in the process of evaluating the storage characteristics of the triply substituted $LiMn_{2-y-z-\eta}Ni_yLi_zCu_\eta O_4$ compositions and an exploration of the substitution of other cations such as Mg^{2+} and Zn^{2+} for Ni^{2+}.

In parallel, we have also been focusing on the 5 V spinel cathode $LiMn_{1.5}Ni_{0.5}O_4$ as well. We have identified that the $Li_xNi_{1-x}O$ impurity phase that is normally encountered during the synthesis of $LiMn_{1.5}Ni_{0.5}O_4$ could be eliminated by keeping the Ni content (y in $LiMn_{2-y}Ni_yO_4$) at ≤ 0.42. We have also found that the capacity retention of the 5 V spinel can be improved by a substitution of other transition and non-transition metal ions as in $LiMn_{1.5}Ni_{0.42}M_{0.08}O_4$ ($M^{2+} = Mg^{2+}$, Cu^{2+}, and Zn^{2+}) and $LiMn_{1.42}Ni_{0.42}M_{0.16}O_4$ ($M^{3+} = Al^{3+}$, Cr^{3+}, Fe^{3+}, and Co^{3+}) while maintaining the Mn valence at 4+. For example, $LiMn_{1.42}Ni_{0.42}Co_{0.16}O_4$ exhibits a capacity retention of 98 % after 50 cycles at a current density of 0.5 mA/cm^2 compared to 92 % for $LiMn_{1.5}Ni_{0.5}O_4$. Additionally, with an aim to develop a better understanding of the factors that control the electrochemical performance of the 5 V spinel oxide cathodes, we have focused on the structural characterization of the chemically delithiated $Li_{1-x}Mn_{1.5-y}Ni_{0.5-z}M_{y+z}O_4$ samples that were obtained by stirring the parent $LiMn_{1.5-y}Ni_{0.5-z}M_{y+z}O_4$ spinel compositions with an acetonitrile solution of the oxidizer NO_2BF_4 under argon atmosphere for 2 days. Rietveld analysis of the X-ray diffraction data indicates that three cubic phases are formed during the charge-discharge process in the 5 V region of $Li_{1-x}Mn_{1.5-y}Ni_{0.5-z}M_{y+z}O_4$. An analysis and comparison of the lattice parameter values of the phases reveal that the cation substituted $Li_{1-x}Mn_{1.5-y}Ni_{0.5-z}M_{y+z}O_4$ spinel oxides exhibit a lower lattice parameter difference Δa between the cubic phases formed during the charge-discharge process compared to $Li_{1-x}Mn_{1.5}Ni_{0.5}O_4$, resulting in a better capacity retention for the former. This observation is similar to that found by us with the 4 V spinel oxide cathodes.

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 primary objective in the third quarter of FY04 was to carry out in-depth diagnostic studies of the mechanism of carbon retreat in composite cathodes and determine its impact on cathode electrochemical performance upon cycling and storage in $LiPF_6$-EC-EMC electrolyte at elevated temperatures. The observed carbon retreat was determined and verified in the composite $LiAl_{0.05}Ni_{0.8}Co_{0.15}O_2$, $LiFePO_4$, and $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathodes and it was clearly linked with other detrimental phenomena that led to the observed cell degradation.

In collaboration with Kathryn Striebel (Task 1.1) we investigated the mechanism of carbon retreat. Thin film carbon black electrodes, 90% carbon, 10% PVDF, d=20mm, were prepared on Al current collector. Carbon electrodes were characterized and then stored or cycled vs. Li-metal in 1.2M $LiPF_6$ EC/EMC (3:7) electrolyte at 57°C. Electrochemical tests of a pure carbon black electrode have indicated that carbon black is electrochemically active toward the electrolyte at elevated temperatures at potentials at which most composite cathodes operate in Li-ion cells. The voltammetric scans show large anodic and cathodic currents above 3.8V and below 2.9V, respectively. Strong temperature effect was observed. Interestingly, electrochemical response from carbon electrode changes during cycling. The intensity of anodic and cathodic peaks increases during initial cycles. However, the peak current starts to decrease gradually after ~20 cycles to vanish completely after 130 cycles.

We observed substantial surface morphology changes in the electrodes cycled between 2.5 and 4.4 V (Figure 1).The particles of carbon black appear larger and the carbon film seems less densely packed, compared to the fresh carbon electrode or the electrode that was just stored in the electrolyte at 57°C. Deconvolution of Raman spectra of the cycled carbon electrode showed significant D and G band broadening and new bands characteristic for sp^3-type (non-conductive) carbon, which suggests that the structure and electronic properties of carbon black undergoes severe degradation upon cycling in $LiPF_6$ containing electrolytes. Reversible processes such as PF_6^- anion intercalation-deintercalation into carbon and thin film formation are likely to contribute to the observed effect. Carbon displacement was observed in the cycled cells; carbon particles were detected in the Celgard® separator and on the surface of the lithium anode. Further detailed studies of the mechanism of carbon degradation are currently under way.

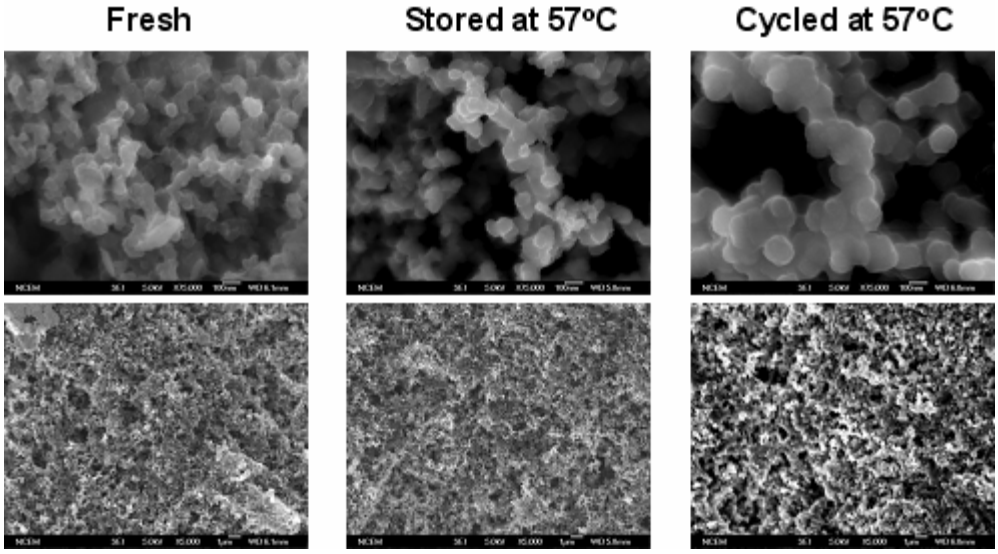


Figure 1. SEM images of carbon black electrodes that were tested in 1.2 M $LiPF_6$, EC:EMC electrolyte at 57°C.

TASK STATUS REPORT

PI, INSTITUTION: W.-S. Yoon, 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

We have used time-resolved XRD to monitor structural changes in charged cathode materials in the presence of electrolyte as a function of temperature. The structure of the cathode materials with electrolyte show dramatic changes with increasing temperature compared to that of the cathode materials without electrolyte. The onset temperature of thermal decomposition reactions is dependent on the lithium content in the structure. As the degree of Li-ion deintercalation increases, the thermal decomposition takes place at less elevated temperatures. The time resolved XRD studies were done on $Li_{0.0}Ni_{1/2}Mn_{1/2}O_2$ (overcharged up to 4.8 V) in the presence of electrolyte. The interesting point is, when the cell was charged to 4.8 V, overcharged cathode does not show the (002) graphite (used as conducting additive) peak at ambient temperature. This might be the result of the disorder caused by the intercalation of PF6- into the graphite layer structure. At around 95ºC the intercalated PF6- apparently moved out and the graphite (002) peak appears.

Comparative studies between Gen2 ($LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$) cathode and $LiMn_2O_4$ spinel cathode were made using in situ X-ray diffraction (XRD) technique. Both cathodes were cycled at room temperature and 55 ºC. The kinetics of the structural changes at different temperatures for Gen2 and spinels are quite different. For Gen2, more structural changes were observed at room temperature, showing the controlling factor is the lithium ion diffusion rate, which is higher at higher temperatures. On the other hand, for spinel materials, more phase separations were observed after cycling at high temperatures, indicated that the damaged surface structure restricted the lithium ion insertion. This surface damage is caused by high temperature (high voltage) cycling for spinels.

Collaborations and discussions with other members of the BATT program (C. Grey, M. Thackeray, S. Whittingham, and J. Goodenough) are ongoing.

Selected publications

1. K. Y. Chung, W.-S. Yoon, H. S. Lee, X.-Q. Yang, J. McBreen, B. H. Deng, X. Q. Wang, M. Yoshio, R. Wang, J. Gui, and M. Okada "Comparative Studies between Oxygen Deficient $LiMn_2O_4$ and Al-doped $LiMn_2O_4$", *J. Power Sources*., Submitted.

2. W.-S Yoon, M. Balasubramanian, X.-Q Yang, J. McBreen, and J. Hanson "Time Resolved XRD Study on the Thermal Decomposition of $Li_{1-x}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ Cathode Materials for Li-ion Batteries", *Electrochem. Solid-State Lett.*, submitted.

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 electrochemical stability of the GEN2 electrolyte additive vinyl ethylene carbonate (VEC) is under study using both electrochemical and ex-situ FTIR spectroscopic methods. Reduction of VEC is being studied with graphite anodes while oxidation is being studied using GEN2 oxide cathodes. Gen2 cathodes ($LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$) were cycled (C/20 rate) in Swagelok cell vs. Li/Li^+ under identical conditions (3.5 – 4.1 V) except for additives in the electrolyte. IR measurements were performed on unwashed samples. The surface of Gen2 cathode cycled in electrolyte without additive is covered by solvate (Li^+:EC), as seen by the strong features at 1700 – 1820 cm^{-1} in curve A of Figure 1. Unlike the cathode cycled in electrolyte without the additives, much less solvate was found on those cathodes cycled in electrolyte either with 2% VC (curve B) or 2% VEC (curve C). The cathode cycled in 2% VEC gives rise to the least strong infrared absorbance, indicating the least amount of solvate. It is not clear why there is less solvate on the cathodes after cycling, or what the implications are. From comparison of those spectra, new features appear in spectra B and C that could be attributed to oxidation of the additive (either VC or VEC). There was some electrochemical evidence for oxidation of the additives in the 3.8 – 4.1 V region. Previously, we had calculated the oxidation potential of VC using DFT to be 4.06 V (Zhang et al. *JECS* **148** (2001) E183), which would be consistent with the observation here. The results are still being interpreted.

Publications

K.A. Striebel, J. Shim, E.J. Cairns, R. Kostecki, Y-J.Lee, J. Reimer, T.J. Richardson, P.N. Ross, X. Song, G.V. Zhuang, "Diagnostic analysis of electrodes from high-power lithium-ion cells cycled under different conditions", *J. Electrochem. Soc.* **151**, A857-A866, 2004.

S.-W. Song, G.V. Zhuang, P.N. Ross, "Surface Film Formation on $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ Cathodes Using Attenuated Total Reflection IR Spectroscopy", *J. Electrochem. Soc.* **151**, A1162-A1167, 2004

G.V. Zhuang, K. Xu, T.R. Jow, P.N. Ross, "Study of SEI Layer Formed on Graphite Anodes in PC/LiBOB Electrolyte Using IR Spectroscopy", *Electrochem. and Solid-State Lett.* **7**, A224-A227, 2004

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

Our earlier work has shown that the "transition metal" layers of $Li[Li_{(1-2x)/3}Ni_xMn_{2/3-x/3}]O_2$ materials contain Ni, Mn and Li, even for x = 0.5; subsequent work has shown that the ordering of the ions in the (predominantly) transition metal layers is far from random, Li ions in these layers occupying sites near more Mn^{4+} ions than expected in the random model. Computations have identified a plausible structure for the x = 1/2 material, which is consistent with the available experimental information. Electrochemical modeling of the structure to understand the relationship between battery performance and ordering is currently underway. NMR spectra and X-ray diffraction (XRD) patterns have been obtained for the x = 1/2 and 1/3 materials as a function of cycle number which demonstrate that the local structure surrounding Li slowly becomes more disordered. After 5 cycles, Li is still present in the transition metal layers surrounded predominantly by Mn. In contrast, the long range order decreases rapidly on cycling, the "superstructure" peaks in the x = 1/3 material, which are indicative of ordering in the transition metal layers, disappearing after 5 cycles. After 20 cycles, the concentration of Li in the layers (as seen by NMR) has dropped by more than 75%. Similar results are seen for x = 1/3 (Figure 1). The results suggest that Li vacancies in the transition layers, formed on charge, may provide a mechanism for Mn/Ni disordering following multiple cycles, leading to a reduction of sites for Li in these layers.

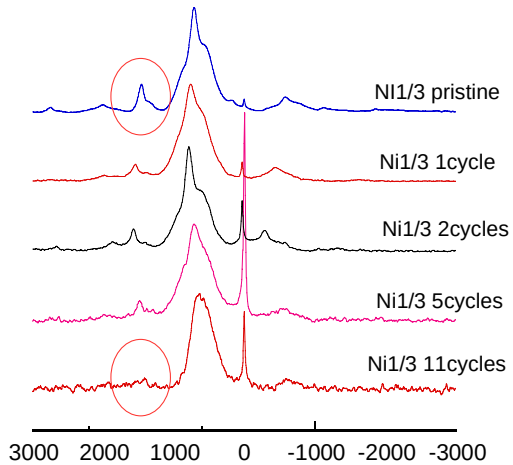


Figure 1. ^{6}Li spectra of x = 1/3 as a function of cycling, showing the gradual decrease in the intensity of the resonance assigned to Li in the transition metal layers (circled in the top and bottom spectra).

Synthesis and electrochemical testing of members of the pseudobinary $xLiCoO_2 – (1-x) Li(Ni_{2/3}Nb_{1/3})O_2$ have been performed. Diffraction results indicate that the even for compositions comprising 50% $LiCoO_2$ and 50% $Li(Ni_{2/3}Nb_{1/3})O_2$ (x = 0.5), the structure maintains the $Li(Ni_{2/3}Nb_{1/3})O_2$ structure, and no evidence for a layered structure is seen. This result is mirrored in the electrochemistry, where $LiCoO_2$ doping actually decreases the electrochemical performance. This is consistent with the ordering in the rock-salt derived material, $Li(Ni_{2/3}Nb_{1/3})O_2$, which in contrast to $LiCoO_2$, contains transition metals (Nb^{5+} and Ni^{2+}) in all the metal layers. A cubic rocksalt structure is seen for x = 0.7, which also suffers from poor electrochemical performance. The results are in agreement with Madelung (electrostatic) calculations on similar systems, which highlight the importance of the strong Nb^{5+}-Nb^{5+} coulombic repulsions in stabilizing the $Li(Ni_{2/3}Nb_{1/3})O_2$ structure. Work on the Ti^{4+}-doped materials has now been published.[1,2] The study of the Li_2TiO_3-$Li(NiMn)_{0.5}O_2$ solid solution was performed in collaboration with M. Thackeray's group.[2] NMR spectra of the Ni excess materials prepared by J. Goodenough's group have been performed. Analysis of the data is in progress. This completes the milestone for May 2004.

References:

1. K. Kang, D. Carlier, J. Reed, E. M. Arroyo, G. Ceder, L. Croguennec, and C. Delmas, *Chem. Mater.*, **15**, 4503 (2003).

2. J.-S. Kim, C. S. Johnson, J. T. Vaughey, M. M. Thackeray, S. A. Hackney, W. C. Yoon, and C. P. Grey, *Chem. Mater*, **16**, 1996 (2004).

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

The previous report focused on two aspects of our research. First, aluminum current collectors of life-tested coin cells were examined by optical and scanning electron microscopy for evidence of corrosion. Second, the passivation of aluminum was investigated in $LiPF_6$-containing battery electrolytes. During the most recent quarter, the role of aluminum oxides on the corrosion behavior of aluminum was studied in several battery electrolytes. In particular, we looked into the influence of three different surface conditions of aluminum on aluminum's corrosion: (1) aluminum covered with an air-formed oxide, (2) aluminum covered with a thick oxide, prepared by anodization in sulfuric acid, and (3) bare aluminum, which was stripped of its air-formed film by *in-situ* abrasion in the battery electrolyte.

The electrochemical behavior of aluminum covered by surface films of alumina (Al_2O_3) of different thickness was characterized by cyclic current-voltage (C-V) curves in $LiPF_6$-containing battery electrolytes. The voltage spanned the range between the corrosion potential and 5V vs. Li^+/Li. The corrosion potential increased with the thickness of Al_2O_3 and was approximately 2.5 V for aluminum with an air-formed film of Al_2O_3. There were two main effects of oxide thickness on the C-V curve. As the oxide thickness increased, (1) the current during the first cycle decreased, and (2) the voltage, at which the oxidation rate during the first cycle abruptly increased, was raised. EQCM experiments indicated that the abrupt increase in current was caused by the formation of another surface film, which was most likely AlF_3. The AlF_3-type film appeared to form on top of the film of Al_2O_3, as opposed to replacing the film of Al_2O_3. The AlF_3-type film provided additional protection against corrosion and its thickness increased with the applied voltage.

The additional protection against corrosion provided by greater thickness of Al_2O_3 was investigated by potentiodynamic and potentiostatic anodic polarization experiments in 1.0M LiTFSI/EC+DMC. Interestingly, a 48 µm thick anodized film of Al_2O_3 significantly increased the corrosion resistance of aluminum during potentiodynamic polarization tests in the highly corrosive 1.0M LiTFSI. However, considerable corrosion of aluminum occurred when potentials of 5V and 6V were applied for 20 hrs. Although it is unlikely that aluminum current collectors would experience potentials greater than approximately 4.2V, the fact that severe pitting corrosion of aluminum occurred at 5V suggests that corrosion could occur at 4.2V after long times. Inspection by scanning electron microscopy of anodized samples polarized at 6.0V for 20 hrs indicated that the thick, anodized Al_2O_3 film itself was not corroded. Rather, aluminum was corroded beneath the anodized film. This result suggests that current collectors covered by thin, air-formed films of Al_2O_3 corrode in a similar way. That is, corrosion initiates at defects in the air-formed film and then attacks the aluminum beneath the air-formed film.

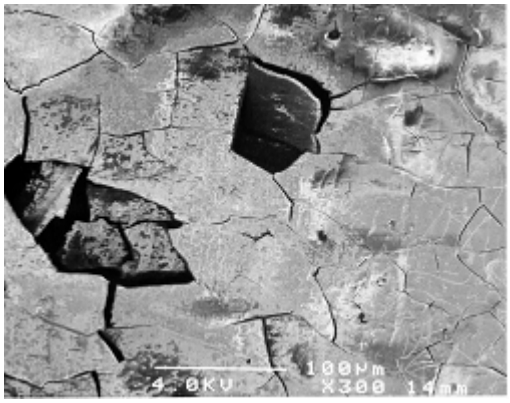


Figure 1. Typical morphology of aluminum with 48 um thick Al_2O_3 film in 1.0 M LiTFSI/EC+DMC after 20 hours at 6.0V.

BATT TASK 6
MODELING

TASK STATUS REPORT

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

TASK TITLE - PROJECT: Modeling - Improved Electrochemical Models

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

BARRIERS: Dendrite formation, capacity fade

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

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

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

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

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

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

PROGRESS TOWARD MILESTONES

Dendrite Initiation and Propagation

We have accomplished our dendrite modeling milestone, to determine elastic properties that inhibit dendrite initiation. Our goal was to determine if a pure lithium anode was feasible in polymer-electrolyte systems, or if failure by dendritic deposits was an insurmountable obstacle. Our model helped us determine the bulk properties that are necessary for the polymer to inhibit interfacial roughening by mechanical action. Present polymer research has focused on materials with elastic moduli in the megapascal range. We found that polymers require shear moduli in the gigapascal range in order to inhibit interfacial roughening, providing a useful technical target for scientists in materials development.

The general kinetic model we developed has broad utility, and can be employed to treat interfacial roughening in many systems. The results in the lithium/polymer system were somewhat surprising because there has been a great deal of theoretical work in liquid electrolyte systems, which has shown that interfacial roughening cannot be prevented.

The Solid Electrolyte Interphase

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

Transport Property Measurement

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

TASK STATUS REPORT

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

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

SYSTEMS: Low-cost Li-ion cells

BARRIER: Capacity fade, low power capability

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

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

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

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

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

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

PROGRESS TOWARDS MILESTONES

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

Spinel Baseline: A model has been developed for this baseline and experimental half-cell data has been collected on cells with different electrode thickness and using two different salts ($LiPF_6$ and LiBOB). Comparison of the model to data suggests that contact resistance drops between the current collector and the active material may be an important limiting factor in the cells tested. This completes the milestone related to this baseline. The Cell Development group (Striebel) is currently fabricating carbon-coated current collectors, which, it is thought, would help in decreasing the contact resistance. These electrodes should allow us to test the predictions by the model and complete the characterization of the system. In addition, optimization studies and comparison to the other two baselines will be undertaken.

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

• Accomplishment toward milestone over last quarter

We performed experimental studies to determine electronic properties of multilayered $LiFePO_4$ cathodes, in order to quantify reductions in $LiFePO_4$ matrix resistivity and/or contact resistances between matrices and current collectors by addition of carbon black and graphite. With the aim of extracting these layerwise and interlayer properties, we extended the Schumann-Gardner approach to analysis of a four-point probe experiment, and solved the resulting coupled nonlinear equations numerically. We studied five cathodes in close collaboration with other BATT researchers (Striebel, Zaghib) with varying amounts (3-12wt%) and types (carbon black, graphite) of conductive additives patented by Hydro-Québec. $LiFePO_4$ particles within the electrodes were pre-coated with carbon before mixing with additives and binder.

Experimental results showed reductions of ~62% in electrical resistivities of $LiFePO_4$ matrix with addition of carbon black increased from 3 to 10wt%. On the other hand, addition of graphite additives produced only small reductions. For concentrations above 6wt% of conductive additives, homogeneous electronic resistivities were observed. Contact resistances at interfaces between $LiFePO_4$ matrix and carbon coating of current collector, and between carbon coating and current collector were similar in all cases, indicating consistency in manufacturing. Based on results here, we suggest that addition of ~3vf% carbon black significantly improves electronic conductivity of $LiFePO_4$ composite cathodes.

• Further plans to meet or exceed milestone

Our next efforts will be focused on investigation of the relationship between electrode thickness and electrochemical performance of composite $LiFePO_4$ cathodes, using numerical modeling. We found that 3D packing effects play a significant role in electrochemical performance of both ionic diffusion among electrolyte, and electronic transport among active materials, due to the size of active material particles used for conduction relative to electrode thickness. Furthermore, since pressing electrodes can result in improved conductivity, but it can also severely damage the cathode particles and hinder the ionic diffusion. We are developing a mathematical model with the capability of including realistic morphology of electrode and transport mechanisms; with this new capability, we hope to be able generate general guidelines for pressing electrodes and selection of conductive additive for improvement of cathode rate performance.

• Reason for changes from original milestone: N/A

PROPOSALS UNDER REVIEW

ORGANIZATION *(Principal Investigator)*	TITLE	STATUS
SUNY Binghamton *(M.S. Whittingham)*	Novel Anode Materials and Novel Cathode Materials	Renewal Proposal- Contract Placed
MIT *(G. Ceder)*	High Capacity, Stable Cathode Materials with Multiple Electron Transfer per Transition Metal	Renewal Proposal- Contract Placed
SUNY Stony Brook *(C. Grey)*	High Capacity, Stable Cathode Materials with Multiple Electron Transfer per Transition Metal	Renewal Proposal- Contract Placed
Univ. of Texas @ Austin *(A Manthiram)*	Superior Capacity Retention, High-Rate Spinel Manganese Oxide Compositions for Lithium-Ion Batteries	Unsolicited Proposal - Contract Placed
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- In Negotiation
Carnegie Mellon University *(P. Kumta)*	High Capacity, Reversible Encapsulated Porous Nanocomposite Anodes for Lithium-Ion Batteries	Unsolicited Proposal- Under Review

BATTERIES FOR ADVANCED TRANSPORTATION TECHNOLOGIES (BATT)

CALENDAR OF RECENT AND UPCOMING EVENTS

May 2004

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

June 2004

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

September 2004

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

October 2004

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

May 2005

15 - 20	207th Electrochemical Society Meeting – Quebec City, Canada (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; ecs@electrochem.org; http://www.electrochem.org/meetings/meetings.htm)
23 - 29	Lithium Battery Discussion Meeting, LiBD2004 – Arcachon France (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; ecs@electrochem.org; email: Josh.Thomas@mkem.uu.se; http://www.icmcb.u-bordeaux.fr/libd)

September 2005

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

October 2005

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

May 2006

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

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

October 2006

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