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March 20, 2003

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

Dear Tien:

Here is the first-quarter FY 2003 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,

A handwritten signature in black ink that reads "Frank McLarnon".

Frank McLarnon  
Manager  
BATT Program

cc: J. Barnes DOE/OAAT  
R. Kirk DOE/OAAT  
V. Battaglia ANL  
K. Abbott DOE-Oakland

LBID-2454

**BATTERIES FOR ADVANCED TRANSPORTATION TECHNOLOGIES  
(BATT) PROGRAM**

**QUARTERLY REPORT**

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# BATT TASK 1 CELL DEVELOPMENT

## TASK STATUS REPORT

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

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

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

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

**OBJECTIVES:** The primary objective is to benchmark the performance of new materials for low-cost and high-power 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 a battery-powered EV. Novel components will be developed in BATT Program Tasks 2, 3, and 4 (anodes, electrolytes, and cathodes) for baseline liquid and gel electrolyte 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. Fabrication of baseline polymer-electrolyte cells is carried out in BATT Program Task 3.2.

**STATUS OCT. 1, 2002:** The analysis of capacity and power fade mechanisms for Li-ion cells with Gen 2 materials was completed in coordination with the ATD Program. The initial benchmarking of the low-cost Li-ion cell with  $\text{LiFePO}_4$  and natural graphite in liquid and gel electrolyte was completed.

**EXPECTED STATUS SEPT. 30, 2003:** Efforts on the low-cost Li-ion baseline cell will be focused on  $\text{LiFePO}_4$  cathodes, various gel electrolyte components applied to Celgard separators, and the evaluation of the available natural graphites. Characterization of  $\text{LiFePO}_4$  materials prepared *via* different synthetic processes will be compared. Electrode compositions will be optimized for electronic and ionic conductivity with the aid of collaborative modeling studies (J. Newman and A.M. Sastry). New materials for the base line cells will be evaluated including, doped  $\text{LiFePO}_4$ ,  $\text{Li}(\text{Ni},\text{Mn})\text{O}_2$ ,  $\text{Li}_{0.44}\text{MnO}_2$ , and intermetallic anodes.

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

**MILESTONE:** (a) Benchmark the performance of the  $\text{LiFePO}_4$ (UdM)/natural graphite cell with liquid electrolyte - December 2002. (b) Compare performance of  $\text{LiFePO}_4$  from different sources - May 2003. (c) Evaluate cycle performance and power capability of the  $\text{LiFePO}_4$  / gel polymer electrolyte / natural graphite cell - August 2003.

## PROGRESS TOWARD MILESTONES

The room-temperature performance and cycle life of the LiFePO<sub>4</sub>(U. d'Montreal)/natural graphite (SL20, Superior Graphite) cell has been benchmarked with a LiPF<sub>6</sub>/carbonate electrolyte, thus completing Milestone 1. The characteristics for this cell and the LiFePO<sub>4</sub>/gel electrolyte cell from Hydro-Québec(HQ) are compared in Table 1. The two cells contain the same cathode-active powder from U. d'Montreal. The gel cells are prepared at HQ (see their report) with an HQ carbon-coated Al current collector, the HQ spherical natural graphite and their ex-situ crosslinked gel electrolyte. The liquidelectrolyte cell contains the new, LBNL-prepared, carbon-coated Al current collector, an SL20 natural graphite (Superior Graphite) anode and LP40 electrolyte. The benchmark numbers are on a cell basis. The power numbers are calculated from the OCV and the ASI, measured during the initial RPT characterization, with the formula:

$$\text{Power [W/cm}^2\text{]} = V_{\text{lim}} (\text{OCV} - V_{\text{lim}}) / \text{ASI}$$

The power numbers are especially high for these cells in part because of the flat voltage profile combined with the wide voltage limits (2.5 to 4.0V). The ASI of the liquid-electrolyte cell was dropped from around 500 to 50 Ω-cm<sup>2</sup> by the incorporation of the carbon-coated current collector. The rated capacity of the cells is taken as 80% of the first discharge capacity measured during the formation of the cell at C/25. The cycle life (to 80% rated capacity) is calculated from the measured capacity fade rate during C/2 100%DOD cycling. The fade rates for both cell technologies are much higher than expected from half-cell data. Our current efforts are focused on understanding this phenomenon; it probably arises due to an instability in the anode SEI caused by iron cations coming from the cathode, similar to what is observed in the Mn/C, system. These benchmark numbers will continuously be updated, in addition to being modified next quarter to fit with the newly released USABC goals.

**Table 1 Gap Chart for LiFePO<sub>4</sub>/NG Low-Cost Baseline Cell**

USABC Goals	Units	Mid-Term	Long-Term	HQ Gel	LBNL Liq.
Power Density <sup>1</sup>	W/l	250	600	618	2230
Specific Power, Dischg	W/kg	150	400	252	709
Specific Power, Regen <sup>2</sup>	W/kg	75	200	574	1523
Energy Density	Wh/l	135	300	155	158
Specific Energy	Wh/kg	80	200	63	50
Life	years	5	10	NA	NA
Cycle Life <sup>3</sup>	cycle	600	1000	83	75
Power & Capacity Degradation	% rated	20	20	20	20
Price (10,000 units @ 40 kWh)	\$/kWh	150	100	NA	NA
Operating Environment	°C	-30 - 65	-40 - 85	25	25
Normal Recharge Time	hours	6	3 to 6	2	2
Fast Recharge Time	minutes	15	15	NA	NA
Continuous Dischg. in 1 hr	% rated energy	75	75	NA	NA
Cell Weight .	mg/cm <sup>2</sup>			27	44
Cell Volume	cm <sup>3</sup> /cm <sup>2</sup>			0.011	0.014
Rated Capacity .	mAh/cm <sup>2</sup>			0.57	0.63

1. 18s, at 80% DOD , 2. 10s at 20% DOD, 3. during 100%DOD cycling

## 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 an electrolyte or 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, 2002:** Phase transformations and accumulation of decomposition products (if any) in cycled electrodes from BATT Program Task 1.1 have been identified and correlated with cell performance characteristics. Efforts to assess the utility of electroactive polymers for overcharge protection in Li-ion batteries are ongoing. Some potentially useful new low-cost, high-capacity electrode materials have been prepared and evaluated.

**EXPECTED STATUS SEPT. 30, 2003:** Composition and structural analyses of BATT Program Task 1.1 electrodes will have contributed to our understanding of the failure and degradation modes in the baseline systems. The switching behavior of electroactive conducting polymers incorporated in Li-ion cells will have been characterized, and an assessment of their potential for providing overcharge protection will be underway. Additional new cathode materials will have been prepared and evaluated.

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

**MILESTONES:** Construct and test an overcharge protection device utilizing an electroactive conducting polymer. (July 2003)

## PROGRESS TOWARD MILESTONES

Efforts are currently underway to prepare and test electroactive polymer membranes to determine their switching potentials, limiting currents, and resistivities in their neutral states. The pores of polypropylene separators are partially filled with conducting polymers using chemical or electrochemical methods. During normal cycling of Li-ion cells, these separators remain resistive, becoming conductive only when the normal voltage limit is exceeded.

Li-TiS<sub>2</sub> cells containing separators were modified by solution deposition of 0.4 mg/cm<sup>2</sup> of poly-3-butylthiophene. The resistance to overcharging was measured at moderate charge rates of 0.4 mA/cm<sup>2</sup>. The potential of an unprotected cell rose rapidly at the end of charge to more than 4V, and the subsequent discharge capacity was severely reduced. In a protected cell, the cell potential rose only to about 3.2 V and held at this value indefinitely. The discharge capacity of the protected cell was preserved, and its behavior under normal cycling conditions was largely unaffected by the small amount of polymer required.

In support of this task, a model is being developed by K. Thomas and J. Newman to aid understanding the reactions that occur in the polymer at different states of charge. This model will also help to determine the optimum loading to achieve maximum protection with minimum effect on cost and performance.

## TASK STATUS REPORT

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

**TASK TITLE - PROJECT:** Cell Development - Research on Lithium-Ion Polymer Batteries Utilizing Low-Cost Materials

**SYSTEMS:** Low-cost Li-ion

**BARRIER:** High cost of Li-ion batteries

**OBJECTIVES:** (a) To fabricate Li-ion polymer cells (4 cm<sup>2</sup> area) using cell chemistries proposed by DOE. Cells (50% of the total cells) will be sent to LBNL for testing. (b) To investigate interfacial phenomena at the anode/separator and cathode/separator in Li-ion polymer cells. (c) To determine the cycle life and self-discharge rates of Li-ion polymer cells at different temperatures (55°C to 0°C). (d) To synthesize low-cost graphite anodes and LiFePO<sub>4</sub> 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, 2002:** Studies were completed on the effect of different amounts of conductive carbon (1% to 15%) on the performance of LiFePO<sub>4</sub> electrodes. The results indicated that 6% carbon added to LiFePO<sub>4</sub> provides a good compromise for energy and power, while still achieving a reversible capacity of 65% at 2C rate and 62% at 3C rate. The effect of solvent mixture and the type of Li salt on the performance of Li-ion polymer cells were determined. The electrochemical performance of a Hydro-Québec (HQ) solvent (TESA) mixed with EC (3/1) was comparable to GBL-EC (3/1). Thirty cells were provided to LBNL in FY 2002 for evaluation.

**EXPECTED STATUS SEPT. 30, 2003:** Coating of cathodes based on LiFePO<sub>4</sub> with different ratios of conductive carbon (from 3 wt% to 15 wt%) will be completed. The investigation of phenomena at the cathode/separator interface in Li-ion/polymer cells containing LiFePO<sub>4</sub> by *in situ* SEM will be ongoing. Analyses of the effects of carbon-coated LiFePO<sub>4</sub> cathode materials with different particle sizes on Li-ion polymer cell rate capability and cycle life will be ongoing. Fabrication of Li-ion/polymer cells (4 cm<sup>2</sup> area) using cell chemistries proposed by DOE will be complete, and 50% of the total cells will have been sent to LBNL for testing.

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

**MILESTONES:** (a) Production of 60 Li-ion polymer cells (4 cm<sup>2</sup> area) by using highly viscous electrolyte based on GBL ( $\gamma$ -butyrolactone), TESA (tetraethylsulfamide), or mixed electrolytes will be completed by March 2003, with 50% of the total cells sent to LBNL. (b) Impedance and *in situ* SEM investigations of phenomena at the anode/separator and cathode/separator interfaces in Li-ion/polymer cells will be completed by May 2003. (c) Synthesis of low-cost carbon-coated LiFePO<sub>4</sub> cathode material for Li-ion/polymer cells will be completed by August 2003.

## PROGRESS TOWARD MILESTONES

(a) During this quarter we studied the effect of solvent mixture and the type of Li salt on the performance of Li-ion polymer cells. The electrochemical performance of a Hydro-Québec (HQ) solvent (TESA) mixed with EC (3/1) was comparable to GBL-EC (3/1). With a mixed salt (1 M LiTFSI + 0.5 M LiBF<sub>4</sub> in EC/GBL), a higher capacity fade was observed compared to cells containing the same molar concentration of the single salt (LiTFSI or LiBF<sub>4</sub>).

(b) The stability of gel electrolytes used for *in situ* studies in the vacuum chamber of an SEM was investigated. The gel electrolyte was tested at temperatures ranging from -10°C to 20°C, and pressures from 20 to 120 Pa. We conclude that the best operating conditions to avoid problems with the vapor pressure of the gel electrolyte are temperatures from -10 to 10°C and pressure of 50 Pa. A special cell was designed for *in-situ* scanning electron microscopy (SEM) of Li-ion cells containing the new gel polymer. Charge-discharge cycling and impedance measurements will be conducted in the cell while operating in the SEM. Our preliminary results demonstrated that it is possible to cycle the cell without adverse affects from the vapor pressure of the polymer electrolyte.

(c) An effort was directed at determining the effect of particle size on the performance of LiFePO<sub>4</sub>. Electrodes containing LiFePO<sub>4</sub> of three different particles sizes (2, 7 and 10 μm) were fabricated using a coating process. The electrodes were tested in a cell with Li metal (Li/gel/LiFePO<sub>4</sub>) at the C/24 rate. The data in Fig. 1 show the cell reversible capacity for the first two cycles with these electrodes. The electrode with the smallest particle size shows the best performance at the C/24 rate. The reversible capacity was 131 mAh/g with 2-μ particles, and only 108 mAh/g with the 7-μm particles. The capacity varies in the following order: 2 > 10 > 7 μm. The relation does not vary linearly with particles size. These results will be compared with LiFePO<sub>4</sub> of similar particle sizes (2, 7, 10 μm) obtained by a new synthesis method.

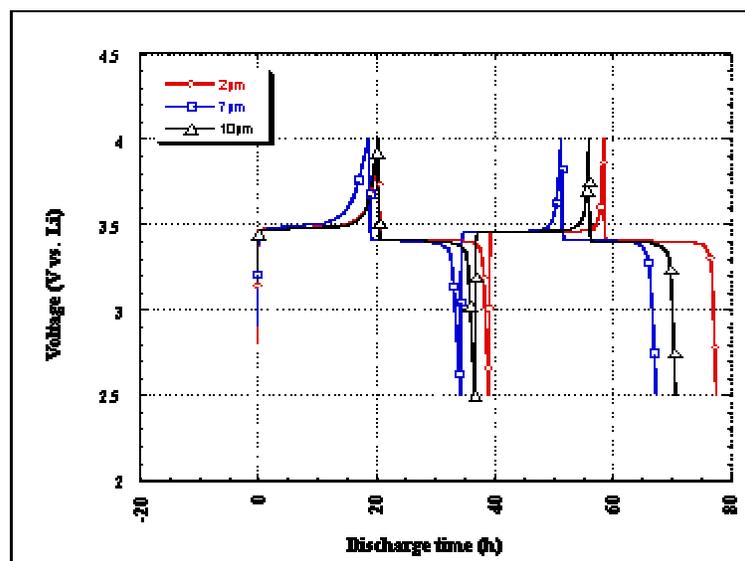


Figure 1. Effect of LiFePO<sub>4</sub> particle size

## 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 approach has been to search for and develop inexpensive intermetallic electrodes that provide an electrochemical potential a few hundred mV above that of metallic Li, and capacities of 300 mAh/g and ~2000 mAh/ml (the theoretical capacities for graphite are 372 mAh/g and 818 mAh/ml, respectively). The approach will be broadened in FY 2003 to include investigations of standard  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  and electronically-conducting Li-, Mg-, and Al-doped  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  anodes against high-voltage layered and spinel cathodes. Such Li-ion cells, which should be inherently safe compared to conventional Li-ion cells, provide a voltage of ~3 V and may find application in high-power batteries for HEVs.

**STATUS OCT. 1, 2002:** We have identified several intermetallic compounds that react topotactically with Li, and by reversible Li insertion/metal extrusion processes. The major focus has been placed on  $\text{Cu}_{6-x}\text{M}_x\text{Sn}_5$ ,  $\text{Cu}_2\text{Sb}$  and  $\text{MnSb}$  electrodes. Although these systems operate reversibly within strictly defined voltage limits, they still suffer from an unacceptably large irreversible capacity loss (ICL) on the initial cycle. Oxide surface layers, the choice of electrolyte, and the identity of the binder were determined to have a small effect on lowering the capacity loss, whereas the loss of extruded metal during the initial cycle and electronic isolation were determined to be major contributing factors in the loss of cell capacity.  $\text{MnSb}$  electrodes showed an ICL of 15-20% (similar to graphite electrodes) compared to  $\text{Cu}_{6-x}\text{M}_x\text{Sn}_5$ ,  $\text{Cu}_2\text{Sb}$  and  $\text{InSb}$  electrodes (25-40%) and delivered a steady 300 mAh/g for 20 cycles.

**EXPECTED STATUS SEPT. 30, 2003:** We expect to increase the cycle life of intermetallic electrodes based on tin and antimony to more than 100 cycles with capacities in excess of 300 mAh/g (~2000 mAh/ml) in Li half-cells. We will have completed our initial investigations of standard  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  and Li-, Mg-, and Al-doped  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  anodes that are coupled against high-voltage layered and spinel cathodes.

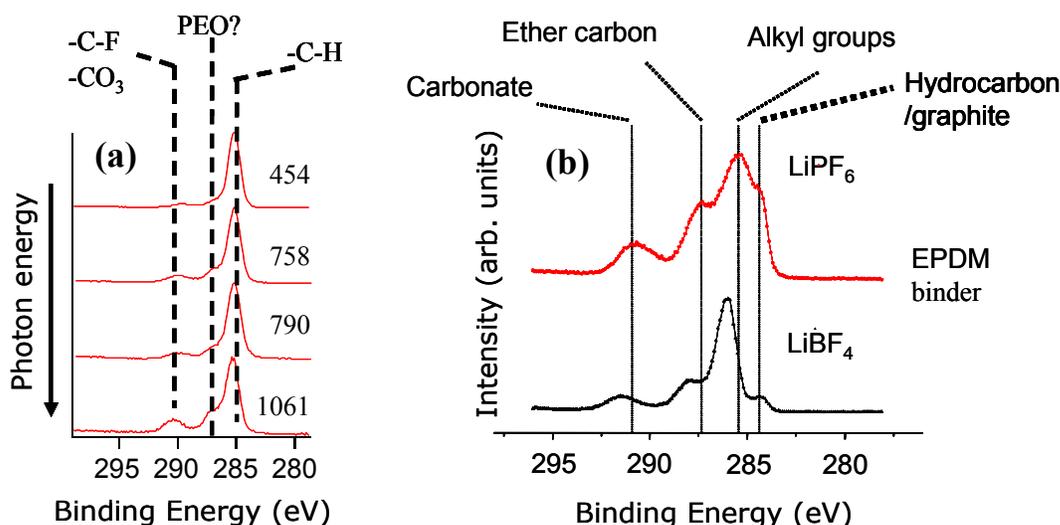
**RELEVANT USABC GOALS:** 10-year life, <20% fade over a 10-year period.

**MILESTONES:** (a) a reversible electrochemical capacity of tin- or antimony-based intermetallic electrodes in excess of 300 mAh/g (~2000 mAh/ml) for 100 cycles: September 2003.  
(b) 100 cycles from ~3 V cells containing a  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -type anode and a high-voltage layered or spinel cathode (September 2003).

## PROGRESS TOWARD MILESTONES

We have extended our non-carbonaceous anode work to a more in-depth study of the morphological features and the SEI layer of Sn- and Sb-based anode systems in an attempt to understand the reasons for the high capacity fade of intermetallic electrodes that is typically observed during the initial cycle. The SEI studies are being performed on  $\text{Cu}_6\text{Sn}_5$ , SnSb and  $\text{Cu}_2\text{Sb}$  electrodes by TEM analysis at ANL, and by synchrotron photoelectron spectroscopy (PES) in a collaborative effort with K. Edström at Uppsala University, Sweden.

The PES data provide evidence that the surface species relating to C-, O-, F- and P-containing compounds at intermetallic and graphite electrodes are similar as shown, for example, in the C1s spectra of  $\text{Cu}_2\text{Sb}$  and graphite in Fig. 1a and b, respectively. An advantage of using synchrotron PES is that photon energy can be varied (in the range 150-1360 eV) thereby allowing a non-destructive depth-profiling of the SEI layer from an enhanced cross section of the elements (Fig. 1a). The preliminary data obtained from  $\text{Cu}_2\text{Sb}$  electrodes suggest that the SEI layer with carbon-containing (polymeric?) species is thicker than it is with graphite. It is possible that this finding may be correlated to a greater reactivity of high-surface-area intermetallic electrode particles (that are generated during the initial charge/discharge cycle) with the electrolyte, which leads to a higher irreversible capacity loss compared to graphite. The PES analyses also suggest that the reaction between  $\text{Cu}_2\text{Sb}$  electrodes and  $\text{LiPF}_6$  to form a LiF surface layer is not as strong as it is with graphite electrodes.



**Figure 1.** C1s PES spectra for a)  $\text{Cu}_2\text{Sb}$  and b) graphite.

During the past contract period we have initiated work on oxide-based anode systems, e.g., Li- and Al-substituted  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  electrodes that are coupled with 5V spinel electrodes. Investigations of Si-based anodes have also been initiated to search for compounds that show a strong structural relationship with their lithiated products to complement the approach that we are adopting in studies of Sn and Sb-based systems.

## TASK STATUS REPORT

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

**TASK TITLE - PROJECT:** Anodes - Novel Materials

**SYSTEMS:** Low-cost Li-ion battery and gel-electrolyte 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 about 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, 2002:** We have shown that vanadium and manganese oxides, in their highest oxidation states, are not prime candidates. Pure Al was found to have a high capacity and react readily with Li, but its capacity faded rapidly upon cycling in carbonate-based electrolytes; Al-based alloys show behavior inferior to that of pure Al. Tin-containing materials, such as  $\text{MnSn}_2$ , cycle well for a few cycles before capacity fade sets in. Pure Sn anodes appear to cycle better than  $\text{MnSn}_2$ .

**EXPECTED STATUS SEPT. 30, 2003:** We expect to have designed a program to understand and remediate capacity fade upon cycling, and as a result to have identified several additional non-Al 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.

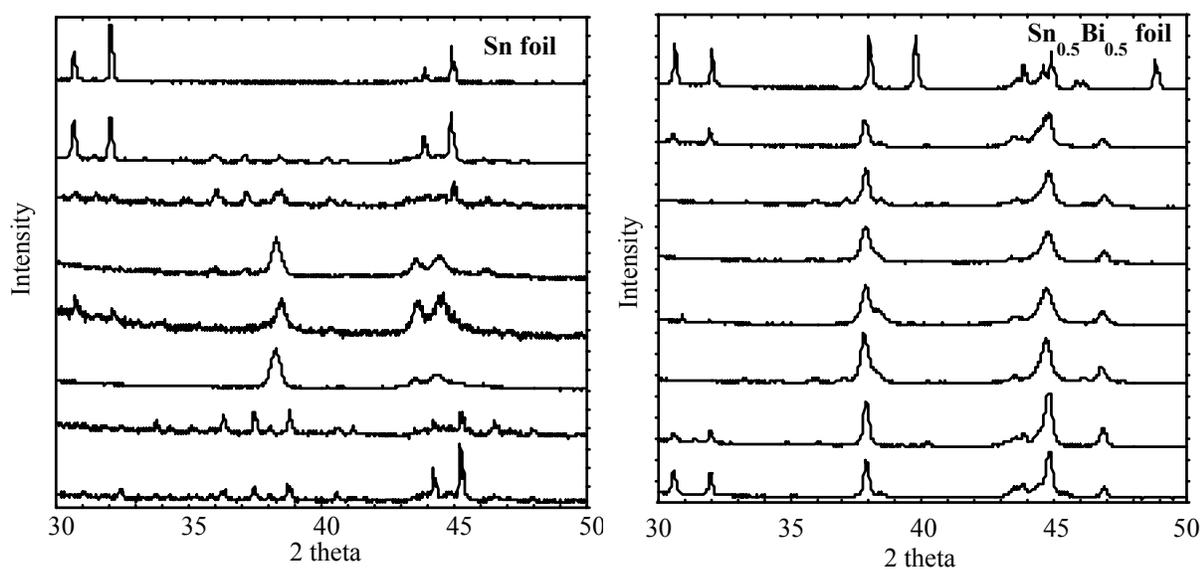
**MILESTONES:** (a) We will design a program to identify, understand, and mitigate the capacity loss upon cycling of simple alloy systems. This will result in a milestone to understand the cause of capacity fade in pure tin by June 2003, and to propose a means of remediating that fade.

(b) Another major milestone is to identify by September 2003 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

(a) Last quarter, we reported on the cycling behavior of pure tin foil and showed that the high initial capacity was maintained for at least ten cycles. This quarter we have determined the phases formed upon Li reaction into pure tin and into a 50:50 tin:bismuth mixture, and also determined the grain size of the tin foil before and after Li cycling.

Figure 1 shows the x-ray diffraction patterns of the tin and the tin/bismuth compounds as Li is inserted and then removed. During Li insertion into tin foil, the tin converts to LiSn, then to the phases  $\text{Li}_{2.33}\text{Sn}$ - $\text{Li}_{2.6}\text{Sn}$  and finally to  $\text{Li}_{3.5}\text{Sn}$ . The process is then reversed upon Li removal, with mostly pure tin being observed after complete recharge, with a small amount of  $\text{Li}_{0.4}\text{Sn}$ . In the case of  $\text{Li}_x\text{Sn}_{0.5}\text{Bi}_{0.5}$ , when discharged to  $1.5\text{Li}/\text{Sn}_{0.5}\text{Bi}_{0.5}$ , only diffraction lines associated with the  $\text{Li}_3\text{Bi}$  phase and pure tin are observed. As additional Li is added,  $\text{Li}_{0.4}\text{Sn}$  is observed (the peak at  $31.5^\circ$ ), then LiSn, followed by the more Li-rich phases with their broad peaks around  $38^\circ$  two-theta. As the Li is removed the reverse is observed with essentially pure Sn and pure Bi being formed. The Sn formed upon Li removal is essentially Bi free as expected from the phase diagram.



**Figure 1.** Left): XRD of  $\text{Li}_x\text{Sn}$  at different lithiation levels, from bottom to the top, the  $x$  value was 0.83, 1.00, 2.33, 3.54, 2.33, 1.11, 1.00 and 0.4. The last four were obtained during the recharge. Right): XRD of  $\text{Li}_x\text{Sn}_{0.5}\text{Bi}_{0.5}$  at different lithiation levels, from bottom to the top,  $x = 1.50, 2.00, 2.50, 3.40, 2.50, 2.00, 1.51, 0.10$ .

An analysis of the line widths of the diffraction lines for the tin sample shows that the initial grain size in the Sn foil is about 500 nm. As cycling proceeds the tin grain size decreases to about 100 nm after 10 cycles. As the capacity does not change during these ten cycles, particle size is not a key factor in determining capacity. This size is comparable to that reported by Schleich et al for Sn formed from tin oxide electrodes (JACS 120, 1, 1998). The diffusion coefficient of Li in Sn is very high, about  $10^{-7} \text{ cm}^2/\text{sec}$ , so the grain size of Sn is not expected to be important despite the commonly quoted concern about Sn grain growth.

### Publication

“Sn and SnBi Foil as Anode Materials for Secondary Lithium Battery”, Shoufeng Yang, Peter Y. Zavalij and M. Stanley Whittingham, *Mater. Res. Soc. Proc.* **756**, EE8.4 (2003). [Presented December 2002].

## TASK STATUS REPORT

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

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

**SYSTEMS:** Low-cost Li-ion

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

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

**APPROACH:** Prepare composite anodes *via* reactive mechano-milling to eliminate large ICLs of metal-oxide anodes that occur during initial Li charge-discharge cycles. Form a desirable synthetic SEI layer *via* the mechano-reduction of oxide precursors and reduce the anode particle size to nanoscale to improve rate capability.

**STATUS OCT. 1, 2002:** The optimization of mechano-milling process parameters for reactive reduction of metal oxide anodes was in progress. The chemical nature of the SEI formed on metals and alloys after reduction of their oxide precursors was studied. An electrochemical study of the composite anode in baseline electrolyte (EC-DMC containing 1M LiPF<sub>6</sub>) was ongoing. The process of developing composite anodes from mixed metal nitrides and oxides was in progress.

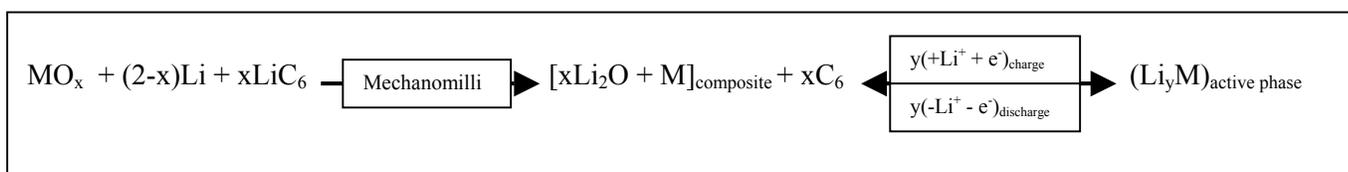
**EXPECTED STATUS SEPT. 30, 2003:** A well-controlled process based on reactive mechano-milling will be introduced for the preparation of composite anodes from various oxide or nitride precursors. Full characterization of the composite anodes in terms of their chemical composition, particle size, and nature of their SEI layer will be completed. Electrochemical tests of charge-discharge behavior of the composite anodes in terms of voltage profile, reversibility, and overall capacity will be completed. 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, low capacity loss (< 20%), good safety and high reliability (no toxic and flammable gas formation).

**MILESTONES:** (a) Optimization of process parameters for reactive mechano-milling of *sp* metal oxides completed by January 2003. (b) Electrochemical tests including charge-discharge cycle life of composite anodes formed by reactive milling of oxides and nitrides completed by August 2003.

## PROGRESS TOWARD MILESTONES

This work has been focused on the development of a safe composite anode with higher energy density and rate capability for high-power Li batteries. We have performed batch synthesis of mechanochemical reduction of oxides and nitrides. The reduced oxides and nitrides to metallic (or close to metallic) states are used to prepare active anode material for Li cells. In order to enhance the electronic conductivity of the final composite, two approaches have been examined. In the first approach, conductive carbon was added to the oxide during the mechanomilling process with metallic Li. In the second approach the lithiated graphite fiber was added for partial reduction of oxide and also for the enhancement of electronic conductivity of the final composite anode. It was observed that the addition of lithiated graphite for reduction of oxides produces a lower impedance electrode. Therefore we have focused on the production of lithiated graphite in our lab for the purpose of making composite anodes. The chemical lithiation of graphite fiber has been optimized, and batches of 100 to 120 grams were made successfully. The process involves the mechanomilling of oxides and nitrides with Li-containing precursors to make electronically conductive active anodes according to the following reactions:



The condition for high-yield preparation of lithiated graphite was obtained. The structural characterization of the product by x-ray diffraction (Fig. 1) shows good control of synthesis parameters. The energy required for production of lithiated graphite is low due to the low melting point of the Li sample, and the exothermic process of graphite lithiation.

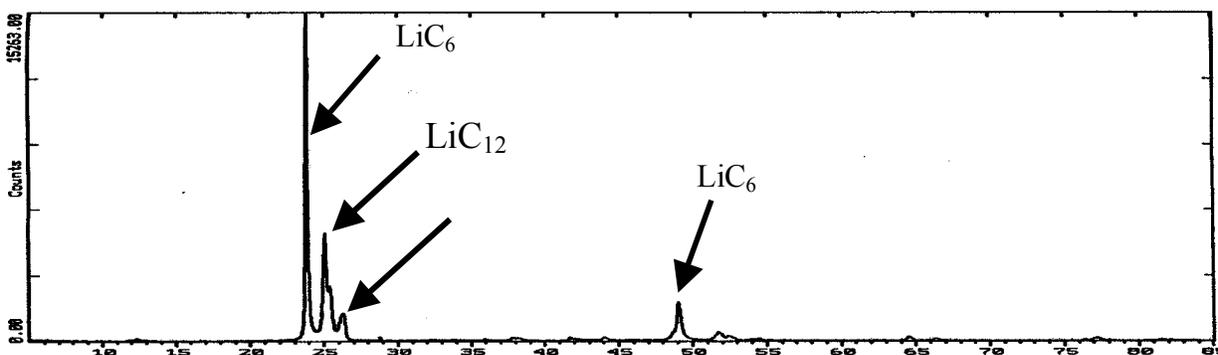


Figure 1. X-ray diffraction of chemically lithiated graphite prepared for prelithiation of oxides.

**Further plans to meet or exceed milestones:** Our future plan is to optimize the prelithiation of composite anodes by including conductive carbon during the mechanomilling process. A study of the effect of electrolyte addition to the milling process before the completion step is also in progress.

**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:**

- Determine the feasibility of the Li metal electrode with organic electrolytes and provide operating conditions that prevent dendrite growth.
- 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.
- 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, 2002:** New investigator.

**EXPECTED STATUS SEPT. 30, 2003:** The utility of neutron scattering, dielectric relaxation spectroscopy, light scattering, and rheological measurements will be fully explored for dry and gel polymers. A combination of polymer synthesis; physical, chemical, and electrochemical measurements; and theoretical calculations will be used to develop a working hypothesis on the limiting mechanism for Li-ion mobility.

**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:** Establish a working hypothesis for the rate-limiting step of Li-ion mobility in polymer electrolytes/polyelectrolytes (09/30/03).

## PROGRESS TOWARD MILESTONES

We have built a unique rheo-dielectric apparatus for probing the fundamental dynamical properties of polymer electrolytes and gel systems. The apparatus consists of a conventional ARES rheometer with a specially machined cone-and-plate fixture that allows the application of electric fields and the measurement of dielectric properties. The cone and plate are connected to a frequency analyzer through a dielectric interface (Solartron). This instrument has been rigorously tested and we have just begun studying the properties of PEO/salt mixtures.

The electrochemical properties of poly(ethylene oxide)(PEO)/lithium perchlorate ( $\text{LiClO}_4$ ) mixtures are governed by the motion of  $\text{Li}^+$  ion. This motion is inextricably linked to that of the PEO segments. This cooperative motion has been studied extensively under quiescent equilibrium; the motion of the PEO chains is modified by changing temperature. Of course, changing temperature also introduces other changes in the system. It is likely, for example, that ion dissociation, binding between ions and chains, and the average size of ionic clusters are also affected by temperature. In recent studies it has been shown that the intrinsic motion of polymer chains can be altered at constant temperature by the application of shear flow [Matsumiya et al., *Macromolecules*, 2002]. Our objective is thus to alter the mobility of PEO chains at constant temperature by the application of flow and measure the effect on the mobility of the  $\text{Li}^+$  ions using dielectric spectroscopy.

Preliminary rheo-dielectric measurements on pure PEO (MW=1,000) and PEO/ $\text{LiClO}_4$  with O:Li = 10:1 samples have been conducted. The measured dielectric loss  $\epsilon''$  gives the conductivity  $\sigma$  [ $\sigma = \epsilon''\epsilon_0\omega$ , where  $\epsilon_0$  is permittivity of free space, and  $\omega$  is the angular frequency of electric field]. The viscosity  $\eta$  of these samples was measured simultaneously.  $\sigma$  can be expressed in terms of charge  $q$ , number  $v$  and mobility  $\mu$  of all ionic species,

$$\sigma = qv\mu \propto \frac{1}{\zeta(T)} \exp\left(-\frac{\Delta H}{kT}\right)$$

where  $\zeta(T)$  is friction coefficient,  $\Delta H$  is enthalpy difference for dissociation of ionic species, and  $k$  is Boltzmann constant and  $T$  is temperature. The factor  $1/\zeta(T)$  is related to the  $\mu$ , and the factor  $\exp(-\Delta H/kT)$  to the  $v$ . We have observed the often-reported (approximately) inverse relationship between  $\sigma$  and  $\eta$ . It is, however, not possible to distinguish between the effect of friction ( $\zeta$ ), dissociation ( $\Delta H$ ), and other thermal effects based on these measurements.

**Further plans to meet milestone.** The rheo-dielectric experiments will be complemented by small angle X-ray scattering (SAXS) experiments. Our proposal to conduct these experiments at the Stanford Synchrotron Radiation Laboratory has been accepted and our first experiments are scheduled for Feb 20, 2003. Our objective is to study the temperature dependence of the cluster sizes at equilibrium directly. We will combine the SAXS and dielectric results to elucidate the role of friction, ionic dissociation, and polymer chain motion in PEO/salt mixtures. We will also continue to collaborate with the Kerr group on rheological and structural characterization of polymer electrolyte systems that they are studying.

## 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, poor ambient temperature performance for polymer electrolytes and low energy and power densities due to instability to 4 V.

**OBJECTIVES:** Determine the feasibility of the Li metal electrode with organic electrolytes and provide operating conditions that prevent dendrite growth. Determine the limitations on Li-ion transport in polymer electrolytes and composite electrodes and develop materials capable of ambient temperature operation with Li metal. 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, 2002:** Best polymer electrolyte transport and mechanical properties completed for TMO-containing comb polymers/LiTFSI or LiBETI (85°C:  $t_+^0=0.3$ ,  $D_s > 5 \times 10^{-12} \text{ m}^2/\text{s}$ ,  $\sigma = 10^3 \text{ S/cm}$ ; 25°C:  $t_+^0=0.2$ ,  $D_s > 10^{-12} \text{ m}^2/\text{s}$ ,  $\sigma \sim 10^{-4} \text{ S/cm}$ ,  $E_g(\text{compression}) > 10^6 \text{ Pa}$ ). Less-costly salts (LiTf, LiPF<sub>6</sub> and LiBF<sub>4</sub>) will also be measured and the cost vs. performance will be assessed. Dendrite-free cycling for > 500 coulombs in full cells at 0.2 mA/cm<sup>2</sup> [Lab cell (4cm<sup>2</sup>)]. Lithium/polymer cell testing at a larger cell size (e.g., 12.5 or 25cm<sup>2</sup> area) will be established

**EXPECTED STATUS SEPT. 30, 2003:** Effects of filler particles and cross-linking on transport and mechanical properties will be quantified for polymer electrolytes, polyelectrolytes, and polymer gels. Full and half-cell cycling and calendar tests will be used to quantify chemical side reactions and physical changes that limit battery life.

**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:** Demonstrate dendrite-free cycling of Li metal electrodes in full cells (Li/V<sub>6</sub>O<sub>13</sub>) and half-cells (Li/Li) for >1000 coulombs of charge (USABC goal >8,000 coulombs) at >0.5 mA/cm<sup>2</sup> with cell polarizations of <200mV(full cell) and <50mV(half-cell) at ≤60°C (09/30/03).

### PROGRESS TOWARD MILESTONES

We have investigated the effects of atmospheric exposure of polymer electrolyte membranes and composite electrodes (V<sub>6</sub>O<sub>13</sub>) in order to determine whether the Li metal/polymer cell components may be prepared outside of the glove box. We have shown that drying at elevated temperature (>60°C) under vacuum over a desiccant such as P<sub>2</sub>O<sub>5</sub> can restore the ion transport properties after exposure to moisture. Li/Li half cell cycling is affected by the presence of moisture resulting from such exposure. However, addition of fumed silica (A200) appears to restore the performance of wet PEO-LiTFSI to that of the dried electrolyte and no significant difference in cycling behavior is observed. With PEO-LiTf the interfacial behavior between wet and dry electrolytes is significant with the dry electrolytes exhibiting higher interfacial impedance. The wet material exhibits a higher salt diffusion coefficient, particularly when fumed silica filler is

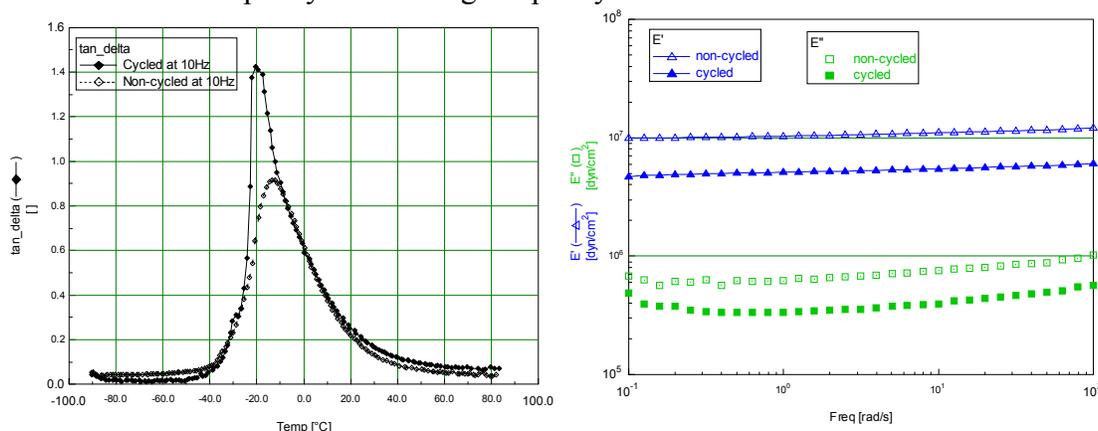
added while with dry electrolyte the diffusion coefficient is reduced by the addition of filler material. This implies that the moisture is closely bound to the filler material surface thereby providing an alternative conduction pathway that is consistent with many of the literature reports on the effects of added fillers. Exposure of composite  $V_6O_{13}$  cathodes to moisture through assembly of full Li/PEO-LiTFSI/ $V_6O_{13}$  cells with wet electrolyte leads to more rapid capacity fading which is also consistent with moisture adsorption on the solid surfaces.

*These experiments indicate that cell components may be prepared in a dry room or under ambient atmospheric conditions followed by drying prior to cell assembly without significant impact on cell performance. Further experiments are planned to confirm these conclusions.*

Studies of dendrite growth have been carried out with linear PEO and cross-linked linear and comb polymers. Initial results with PEO (M.Wt >200K) demonstrate that dendrite initiation is inhibited with Ultrapure PEO which has all of the impurities removed (fumed silica, calcium oxide/amide, BHT). The silica and calcium salts appear to play a more significant role than the BHT. These studies are continuing with the modeling group and careful measurements are being made of viscosity, shear and storage moduli and dielectric relaxation behavior to determine the effects on dendrite initiation. Purification of a number of M.Wt. samples of PEO has been undertaken with the assistance of the manufacturer.

Dendrite studies and Li/Li cycling with cross-linked comb branch PEPE<sub>3</sub>-LiTFSI have been carried out. (PEPE<sub>3</sub> is a PPO backbone with side chains that have three ethylene oxide units and a methyl end group). These studies are aimed at determining the applicability of the cross-linking chemistry. Our experiments demonstrate that thicker films (>300  $\mu\text{m}$ ) are necessary to inhibit dendrite growth. Since the current densities employed for the thinner films are much lower than the limiting currents, we attribute this behavior to non-uniformity in the polymer layer which is more critical for the thinner membranes. We noted changes in polymer conductivity, morphology and rheology during cycling. The initial polymer was sticky and adherent but we found no difficulty in removing the polymer from the Li electrode after cycling. Rheological analysis (Fig. 1) indicates that the modulus decreased after cycling and the area under the  $T_g$  transition in the  $\tan \delta$  measurement increased and the  $T_g$  decreased indicating that the polymer was more mobile. A shoulder appeared on the low-temperature side of the cycled  $T_g$  indicating the appearance of a  $\beta$ -transition. We attribute this behavior to bond-breaking of the back-bone, cross-links and side chains. Chemical analysis by GC of the electrolyte showed the presence of monomethyl triethylene glycol and other small fragments consistent with breaking bonds in the side chains. We are working on improvements to the curing process to improve the membrane uniformity.

Introduction of blends of cross-linked PEO and high M.Wt. PEO into full cell Li/ $V_6O_{13}$  cell cycling has significantly increased capacity retention. We believe that some of this effect is due to better efficiency during charging. The effect of salt concentration, M.Wt. and cross-linking in the membrane and composite cathodes indicates that the electrolyte transport properties are limiting the accessible capacity in these high-capacity cathodes.



**Figure 1.** Rheology measurement of cycled and non-cycled composite X-PEPE electrolyte (O:Li=20:1) (a) compression modulus at 85°C (b) glass transitions measurements in dynamic mechanical thermal analysis.

## 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, 2002:** We have established that fumed silica-based composite electrolytes with low-molecular weight (MW) PEOs exhibit conductivities exceeding  $10^{-3}$  S/cm at 25°C and have electrochemical properties decoupled from mechanical properties. We have determined that fumed silica stabilizes the Li/electrolyte interface, and effectively suppresses Li dendrite growth. We have 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<sub>6</sub>O<sub>13</sub> cells. We have determined that adding fumed silica improves the rheological properties of high-MW polymer electrolytes, but can be either beneficial or detrimental to ion-transport behavior. We have also found that adding fumed silica improves the interfacial stability of Li/electrolyte (high-MW PEO) interface and cycle performance of Li/V<sub>6</sub>O<sub>13</sub> cells.

**EXPECTED STATUS SEPT. 30, 2003:** Using mixed-MW (high- + low-MW) PEOs + LiTFSI as the base electrolyte, we expect to determine the effect of fumed silica on conductivity and electrolyte/Li interfacial stability and how these results vary with type of fumed silica surface group.

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

**MILESTONES:** (a) Interfacial stability and full-cell cycle studies of mixed polymer system completed by September 2003. (b) Rheological data for mixed-MW polymer system acquired for correlation with electrochemical stability by September 2003

## PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestones over last quarter:**

We have measured conductivities of homogeneously dispersed fumed silica in mixed-MW polymer materials and find the following: (1) In P(EO)<sub>10</sub>LiTFSI electrolytes (PEO (600K):PEG-dM (250)=1:1 (mass), O:Li=10), the conductivity at temperatures from 15 to 90°C decreases with addition of hydrophilic A200 or hydrophobic R805 fumed silica; (2) In (PEO)<sub>20</sub>LiTFSI electrolytes (PEO (600K):PEG-dM (250)=1:1 (mass), O:Li=20), the conductivity at temperatures from 15 to about 30°C increases with the addition of the fumed silica but above 30°C decreases; (3) In (PEO)<sub>20</sub>LiTFSI electrolytes (PEO (600K):PEG-dM (250)=2:1 (mass), O:Li=20), the conductivity at temperatures from 15 to about 40°C increases with the addition of the fumed silica but above 40°C decreases.

We have measured the dynamic rheology at 80°C of mixed-MW PEO (PEO (600K):PEG-dM (250)=1:1 (mass), without salt) containing 0 and 10 wt% A200. These results are similar to the earlier results for the high-MW PEO sample in that the presence of fumed silica produces an elastic gel above the melting point of the PEO matrix.

Adding nanoparticles of fumed silica improves the rheological properties of mixed-MW PEO electrolytes, while the addition of fillers can be either beneficial or detrimental to ion-transport behavior, which is the same trend as observed in high-MW PEO electrolytes. More importantly though, the mixed-MW PEO *composite* electrolytes have higher conductivities than the high-MW PEO *composite* electrolytes. At about 40°C, the mixed-MW PEO composite electrolytes have conductivities above 10<sup>-4</sup> S/cm, whereas the high-MW PEO composite electrolytes have conductivities just about 10<sup>-5</sup> S/cm. If the transference number for mixed-MW PEO composite electrolytes is improved, this sort of electrolyte is promising with its acceptable mechanical properties. At the same time, it is expected to lower the operating temperature for Li/polymer batteries.

- **Further plans to meet or exceed milestones:** We continue to characterize composite mixed-MW polymer electrolyte by differential scanning calorimetry, investigate the transference number, and study the interfacial stability of composite mixed-MW polymer electrolyte using Li/CPE/Li cycling.

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

## TASK STATUS REPORT

**PI, 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) Develop methods for synthesizing oligomeric ionene Li salts based on the bis((perfluoroalkyl)-sulfonyl)imide anion. (2) Develop methods for preparing solid polymer electrolytes (SPEs) from the target salts. (3) Provide data on transport properties, especially ionic conductivity and Li ion transference, for target SPEs at variable temperature and composition.

**APPROACH:** Salts will be synthesized using methodologies developed at Clemson over the last 15 years (D. DesMarteau, *J. Fluorine Chem.* 1995, **72**, 203-208). SPEs will be prepared from crosslinked low-MW polyethylene glycol (PEG) and also non-crosslinked PEG for comparison. Transport properties will be measured using electrochemical impedance spectroscopy combined with other electrochemical techniques including restricted diffusion, DC polarization, and concentration cell techniques.

**STATUS OCT. 1, 2002:** A series of dimeric Li salts with different perfluorinated chains linking sulfonyl imide anions together, and selected oligomeric ionene salts utilizing perfluoroalkyl linkers in longer chains, were synthesized. SPEs from the salts will be fabricated in polyether matrices, and their ionic conductivities measured at various temperatures and compositions.

**EXPECTED STATUS SEPT. 30, 2003:** Synthetic methods will be refined for tetra-anionic imide Li salts with a range of different perfluoroalkylene chains linking imide groups, and for oligomeric imides. Ionic conductivities will be measured for SPEs made using all new salts. For salts that exhibit especially favorable behavior a more complete set of transport data including transference and salt diffusion measurements will be made, initially in collaboration with other BATT Program participants and later at Clemson. Salts that exhibit especially favorable properties will also be synthesized in larger quantities and made available to other BATT Program participants for further testing.

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

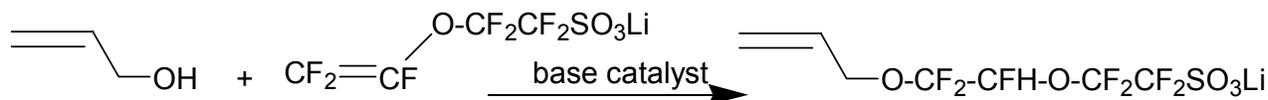
**MILESTONE:** (a) Prepare oligomeric Li salts of the type  $\text{CF}_3\text{SO}_2[\text{N}(\text{Li})\text{SO}_2\text{R}_f\text{SO}_2]_n\text{N}(\text{Li})\text{SO}_2\text{CF}_3$  with variable fluorocarbon linkers and systematic variation of the average  $n$  values. Refine synthetic methodology to improve yields, purity, and ease of the multi-step syntheses. (b) Perform a full transport properties study including measurement of conductivity and Li transference across a range of salt concentrations for a representative oligomeric imide salt. Milestones to be completed by September 2003.

## PROGRESS TOWARD MILESTONES

(a) Synthetic work on the target oligomeric imide Li salts progressed well in the October - December 2002 quarter. Robust synthetic methods are now available for producing salts with  $n=1,3,5$ , and 17 and  $R_f = (CF_2)_x$  with  $x=4,6,8$ . See previous quarterly / annual reports for details. In this quarter, fresh quantities of salt with  $n=1$  (dimer),  $R_f = (CF_2)_4$ , and  $n=5$  (hexamer),  $R_f = (CF_2)_x$ ,  $x=4$  and 6, were synthesized in 0.5 - 3 gram quantities, to replenish supplies consumed in routine testing and to provide adequate amounts of material for the planned full transport property testing.

(b) Work aimed at making a full transport property study, particularly emphasizing Li transference, in SPEs of the target Li salts is progressing. Samples of SPEs fabricated using the  $x=8$  dimeric Li imide salt were provided to Prof Steve Greenbaum at CUNY in the previous quarter, where they will be studied using pulsed-field-gradient  $^6Li$  and  $^{19}F$  NMR to determine Li and anion self-diffusion coefficients. These data will be used as an input parameter for planning and executing a galvanostatic DC polarization experiment, the results of which will be used (along with data from concentration cells) to obtain a full set of transport properties using the model developed by Newman and co-workers. Efforts aimed at making the required galvanostatic DC polarization and concentration cell measurements, and at using the model of Newman to interpret the data, are being pursued in collaboration with LBNL scientists who helped in developing the model.

Additional synthetic and SPE characterization work was also pursued in this quarter. Regarding synthetic work, a new route was devised to prepare an allyl ether Li salt which is targeted for use by Kerr at LBNL in the final synthetic step of an effort aimed at preparing true single-ion polymeric Li conductors. The proposed route to a Li sulfonate salt is as follows:



The resulting sulfonate salt could then be used to prepare the corresponding imide salt using methods presently being used to synthesize oligomeric imide salts. The target allyl ether is not the same as that proposed in the FY 2003 operating plan (e.g., this material is not fully perfluorinated), however it is quite similar and should have similar properties to the molecules originally proposed. An advantage of the proposed new route and material is that both the reactants are commercially available and thus the salt could be produced relatively inexpensively in reasonably large quantities.

Some work was pursued this quarter on ionic conductivity in Li salt SPEs prepared from high-MW PEO and LiTFSI also containing variable amounts of two different fumed silica additives (Aerosil 200 and 300, surface areas of 200 and 300 m<sup>2</sup> / g respectively, obtained from Degussa). Within experimental error we find that the effect of additives on conductivity for this combination of salt and host is minimal, which confirms what was also reported by Khan in the BATT annual review in July 2002. Work in progress is examining the effect of silica additives on conductivity in SPEs prepared using high and low MW PEO / PEG as host, and using selected salts from the oligomeric imide series.

## TASK STATUS REPORT

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

**TASK TITLE - PROJECT:** Electrolytes - A Molecular Dynamics Simulation Study of the Influence of Polymer Structure on Complexation Thermodynamics, Kinetics and Transport of Lithium Cations in Polyether-based Solid Polymer Electrolytes

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

**BARRIER:** Poor cation transport properties in solid polymer electrolytes

**OBJECTIVES:** Study the influence of polymer structure on ion complexation, dynamics and transport properties of polyether-based polymer electrolytes. Estimate the success of various strategies for the design of solid polymer electrolytes with improved transport properties.

**APPROACH:** Employ ab initio quantum-chemistry calculations to obtain energetics of polyether complexes with Li-salts and use these data to develop classical force fields for polyether/LiBF<sub>4</sub>. Extend these studies to single-ion conductors and gel electrolytes. Use atomistic molecular dynamics simulations of polyether-based Li polymer electrolytes for parametric investigation of the influence of polyether structure, strength of the polyether-Li and Li-anion interactions and barrier of conformational isomerization reaction on ion transport.

**STATUS OCT. 1, 2002:** Force fields for poly(ethylene oxide)/LiBF<sub>4</sub>, poly(oxymethylene)/LiBF<sub>4</sub>, poly(propylene oxide)/LiBF<sub>4</sub>, and poly(trimethylene oxide)/LiBF<sub>4</sub> were developed. Molecular dynamics simulations of these linear polyethers were performed.

**EXPECTED STATUS SEPT. 30, 2003:** A force field for the poly(ethylene oxide-trimethylene oxide) (EO-TMO) alternating copolymer doped with LiBF<sub>4</sub> will be developed. Molecular dynamics simulations of linear polyether-based polymer electrolytes will be completed, including EO-TMO. Parametric studies of the influence of PEO-Li<sup>+</sup> interaction of structural and dynamic properties will be completed. A force field for comb-branch copolymers with polyether side chains will be developed and validated. The mechanism of ion transport in comb-branch copolymers with polyether side chains will be determined. Molecular modeling of gel electrolytes and single ion conductors will be initiated. MD simulations will be performed on liquid electrolytes (EC/LiTFSI) and initiated for comb-branched PEO based gels with EC plasticizer and TFSI<sup>-</sup> anion attached to side-chains.

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

**MILESTONE:** (a) Complete studies of linear polyether-based polymer electrolytes doped with LiBF<sub>4</sub> and parametric studies of the influence of PEO-Li<sup>+</sup> interaction of structural and dynamic properties (February 2003)  
(b) Develop quantum chemistry based force field for ethers/LiTFSI perform analysis of ion transport in comb-branch copolymers with polyether side chains (July 2003)  
(c) Initiate MD simulations of PEO-based single ion conductors and gel electrolytes (September 30, 2003).

## PROGRESS TOWARD MILESTONE (a)

Our objective was to validate the developed force fields and to use them for investigation of the relation between the polymer structure and ion complexation and dynamics in polymer electrolytes. The ability of the ether-Li<sup>+</sup> ab initio quantum chemistry force fields with many-body polarization interactions to predict the Li<sup>+</sup> complexation energetics with various ether oligomers was evaluated through comparison of the Li<sup>+</sup>/(ether oligomers) complexation energy from the force fields with those from the ab initio calculations performed in the L. Curtiss group (*J. Power Sources*, 2002, **110**, 401). A set of Brownian dynamics simulations with the gradually decreasing temperature following the energy minimization routine was used to calculate the Li<sup>+</sup>/(ether oligomers) complexation energy using many-body polarizable force fields. The resulting Li<sup>+</sup>/(ether oligomers) complexation energies are shown in Fig.1(a). The Li<sup>+</sup> complexation energy is the highest for the ethylene oxide-trimethylene oxide (EO-TMO) alternating copolymer/Li<sup>+</sup> complex and for ethylene oxide (EO), following by the trimethylene oxide (TMO), propylene oxide (PO) and methylene oxide (MO) oligomers (-50.2 kcal/mol for 8 methylene oxide oxygen atoms complexed to a Li<sup>+</sup>, not shown in Fig. 1). The Li<sup>+</sup>/ethers complexation energies from ab initio quantum chemistry calculations are shown in Fig. 1(b). Although the force field predicts slightly lower Li<sup>+</sup>/ethers complexation energies compared to those from quantum chemistry calculations, it captures the relative complexation energies between various compounds reasonably well. The Li<sup>+</sup>/(ether oligomers) complexation energy was found to correlate well with the ability of the oligomers to wrap around a Li<sup>+</sup> cation and the conformational energetics of ethers.

MD simulations have been performed on P(EO-TMO) copolymer, PEO, PTMO, PPO(atactic), PMO doped with LiBF<sub>4</sub>, EO:Li=15:1 at 393 K using a two-body force field and a many-body polarizable force field (except for PPO and PMO). The fraction of “free” Li<sup>+</sup> cations was found to depend on the polymer matrix and follows the order: P(EO-TMO), PEO, PTMO, PPO, PMO with the largest fraction of “free” cations found for polymer electrolytes using a P(EO-TMO) matrix and no “free” cation found for the PMO matrix. These results correlate well with the Li<sup>+</sup>/ether complexation energies shown in Fig. 1. Initial estimates of conductivity indicated that the conductivities of P(EO-TMO), PEO, PTMO doped with LiBF<sub>4</sub> are within a factor of two from each other with the conductivity of P(EO-TMO)/LiBF<sub>4</sub> being the highest and conductivity of PTMO/LiBF<sub>4</sub> being the lowest. The conductivity of PPO(atactic)/LiBF<sub>4</sub> was approximately an order of magnitude lower than that for PEO/LiBF<sub>4</sub>, whereas the PMO/LiBF<sub>4</sub> conductivity was too insignificant to determine.

**Reasons For Changes From Original Milestones:** The milestones have been changed in response to suggestion of DOE reviewers to initiate investigation of gel electrolytes.

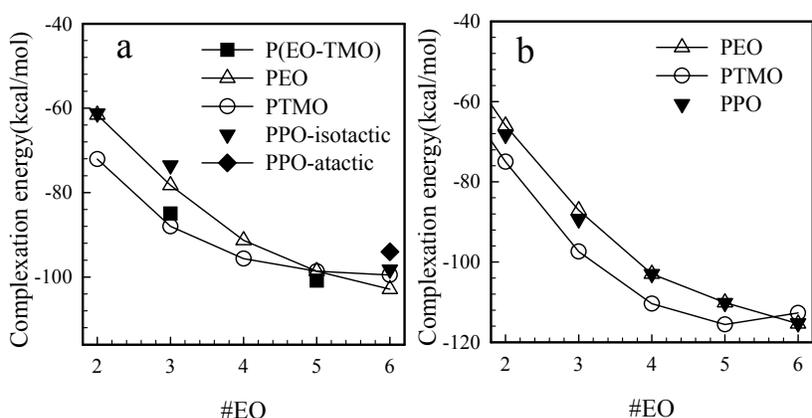


Figure 1. The Li<sup>+</sup>/ethers complexation energy calculated using a many-body polarizable force field (a) and from ab initio quantum chemistry calculations at HF/6-31G\* level from Larry Curtiss group (*J. Power Sources*, 2001, 110, 401).

## BATT TASK 4 CATHODES

### TASK STATUS REPORT

**PI, INSTITUTION:** M. Thackeray, Argonne National Laboratory

**TASK TITLE:** Cathodes - Novel Materials

**SYSTEMS:** Low-cost (Li-ion) battery

**BARRIER:** Cost and safety limitations of Li-ion batteries

**OBJECTIVES:** To develop low-cost manganese oxide cathodes to replace LiCoO<sub>2</sub>.

**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 composite layered lithium-manganese oxide structures that are represented by the general formula  $x\text{Li}_2\text{M}'\text{O}_3 \bullet (1-x)\text{LiMO}_2$  in which  $\text{M}' = \text{Mn, Ti, Zr, Ru}$  and  $\text{M} = \text{Li, Mn, Ni, Co}$  are showing excellent promise to replace LiCoO<sub>2</sub> as the cathode material of choice in Li-ion cells. In conjunction with our anode project, we will explore the electrochemical properties of high-potential layered and spinel electrodes against Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> and substituted, electronically-conducting Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> anodes in 3 V Li-ion cells that should be inherently safe.

**STATUS OCT. 1, 2002:** Preliminary investigations of  $x\text{Li}_2\text{M}'\text{O}_3 \bullet (1-x)\text{LiMO}_2$  composite electrodes in which a Li<sub>2</sub>M'O<sub>3</sub> component (M=Mn, Ti, Zr) was used to stabilize layered LiMO<sub>2</sub> electrode structures, particularly LiMn<sub>0.5</sub>Ni<sub>0.5</sub>O<sub>2</sub>, were undertaken. These electrodes tend to show a relatively large irreversible capacity loss (ICL) during the initial cycles, but thereafter cycle with good electrochemical reversibility, and provide a rechargeable capacity of approximately 140 mAh/g between 4.6 and 2.5 V at room temperature and 160-170 mAh/g at 50 °C. These electrodes can accommodate extra Li to form Li<sub>2</sub>MO<sub>2</sub> compounds with remarkable reversibility and without destroying the integrity of the layered structure; this finding has implications for using the surplus Li in Li<sub>2</sub>MO<sub>2</sub> structures to combat the ICL at graphite and intermetallic negative electrodes.

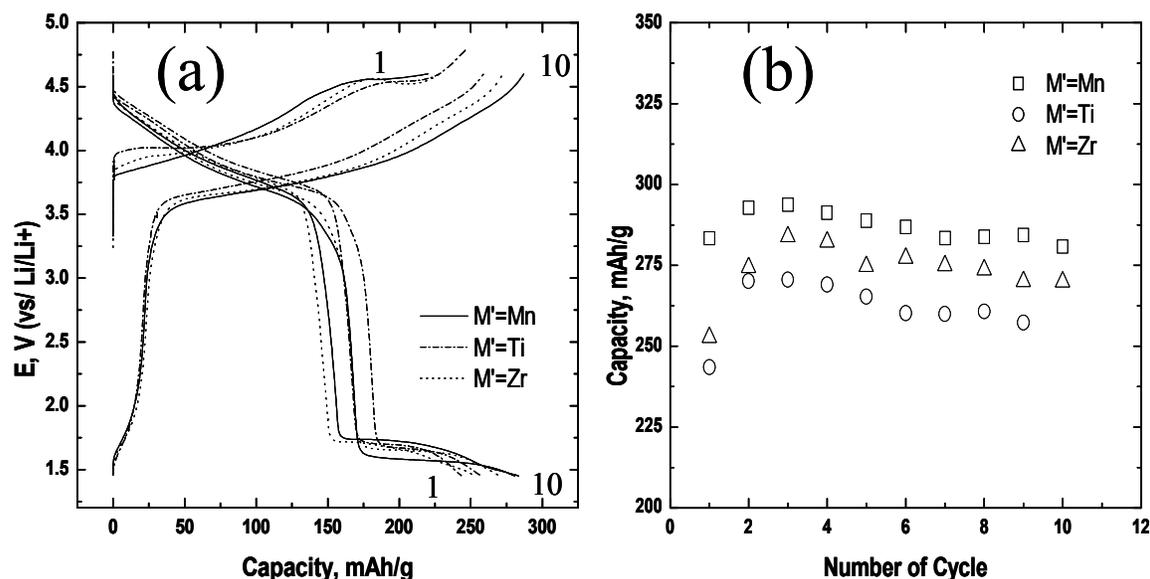
**EXPECTED STATUS SEPT. 30, 2003:** Improvements in the electrochemical performance of  $x\text{Li}_2\text{M}'\text{O}_3 \bullet (1-x)\text{LiMO}_2$  electrodes will have been achieved; the targeted performance goal is 190 mAh/g for 100 cycles at 50°C in Li-ion cells. The feasibility of using overdischarged electrodes (with Li<sub>2</sub>MO<sub>2</sub> structures) as a reservoir for Li to combat ICL effects in Li-ion cells will have been determined. Composite  $x\text{Li}_2\text{M}'\text{O}_3 \bullet (1-x)\text{LiMO}_2$  electrodes and spinel electrodes will have been evaluated against Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> and substituted Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> electrodes in ~3 V cells.

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

**MILESTONES:** (a) Evaluate  $x\text{Li}_2\text{M}'\text{O}_3 \bullet (1-x)\text{LiMO}_2$  composite electrodes against a technical target of 190 mAh/g for 100 cycles at 50°C, and determine the feasibility of using overdischarged electrodes as a reservoir for Li; and (b) evaluate the electrochemical properties of composite  $x\text{Li}_2\text{M}'\text{O}_3 \bullet (1-x)\text{LiMO}_2$  and spinel electrodes against modified Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> electrodes. (September 2003)

## PROGRESS TOWARD MILESTONES

We have continued our studies of  $x\text{Li}_2\text{M}'\text{O}_3 \bullet (1-x)\text{LiMO}_2$  composite electrode structures in an attempt to stabilize a  $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$  electrode at high potentials and to increase the rechargeable capacity to our targeted 190 mAh/g. We are in the process of comparing the relative electrochemical behavior of  $x\text{Li}_2\text{M}'\text{O}_3 \bullet (1-x)\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$  electrodes in which M' is Ti, Zr and Mn for the range  $0 < x < 0.3$ . We find that, for Ti and Mn, it is possible to achieve a product that shows apparent “single-phase” behavior in their X-ray diffraction patterns over the full range of x, whereas we have only been able to achieve such behavior for Zr up to  $x=0.05$ . The relative electrochemical behavior of  $\text{Li}/x\text{Li}_2\text{M}'\text{O}_3 \bullet (1-x)\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$  cells at room temperature when cycled over a wide voltage range (4.6 to 1.45 V) is shown in Fig. 1.



**Figure 1.** Electrochemical data of  $\text{Li}/0.05\text{Li}_2\text{M}'\text{O}_3 \bullet 0.95\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$  cells ( $\text{M}'=\text{Mn}, \text{Ti}, \text{Zr}$ ) at RT.

The voltage profiles of the various cells are similar. During the initial cycle, the charged electrodes all show an interaction with the electrolyte (believed to be associated with a loss of oxygen from the structure) that manifests itself as a voltage plateau at approximately 4.6 V. This phenomenon is not observed upon subsequent cycling and is attributed to a more stable, reduced electrode surface. Extremely high capacities ( $>260$  mAh/g) are obtained from these electrodes in the order  $\text{Mn} > \text{Zr} > \text{Ti}$  when cells are discharged to 1.45 V due to the formation of layered  $\text{Li}_2\text{MO}_2$ -type structures, for example,  $\text{Li}_2\text{Mn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ , as discussed in earlier reports. Of particular note is that all three  $0.05\text{Li}_2\text{M}'\text{O}_3 \bullet 0.95\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$  electrodes ( $\text{M}'=\text{Mn}, \text{Ti}, \text{Zr}$ ) provide a rechargeable capacity of 165 mAh/g in the high-voltage range (4.6-2.5 V) after 10 cycles. Increasing the M' content above  $x=0.05$  reduces the delivered capacity and does not appear to contribute to any significant enhancement in stability. The superior capacity delivered by Zr-substituted over Ti-substituted electrodes between 4.6 and 1.45 V raises the question about the role that Zr plays in enhancing the performance of  $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$  electrodes. With this in mind, as well as the superior performance that we have recently obtained from  $\text{ZrO}_2$ -coated spinel electrodes, we have initiated studies of  $\text{ZrO}_2$ -coated  $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$  electrodes (and derivatives thereof) in an attempt to increase their capacity and cycling stability in the high-voltage range.

## 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, 2002:** We have 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. We will show the effectiveness of conductive coatings for enhancement of capacity. We will have completed an evaluation of  $\text{LiFePO}_4$  as a base-case low cost cathode, and have shown that hydrothermal synthesis is not a viable approach. We will also have shown that vanadium oxides can also be stabilized by the addition of manganese ions to attain capacities greater than 200 mAh/g. In summary:

- $\text{LiFePO}_4$ : > 120 mAh/g for 100 cycles at 1 mA/cm<sup>2</sup>.
- Layered  $\text{Li}_x\text{Co}_z\text{Ni}_y\text{Mn}_{1-y-z}\text{O}_2$ : 180-200 mAh/g for 5 cycles
- Layered  $\text{A}_z\text{Mn}_{0.1}\text{V}_2\text{O}_5$  (A=  $\text{NH}_4$  or TMA):  $\geq 200$  mAh/g for 6 cycles.

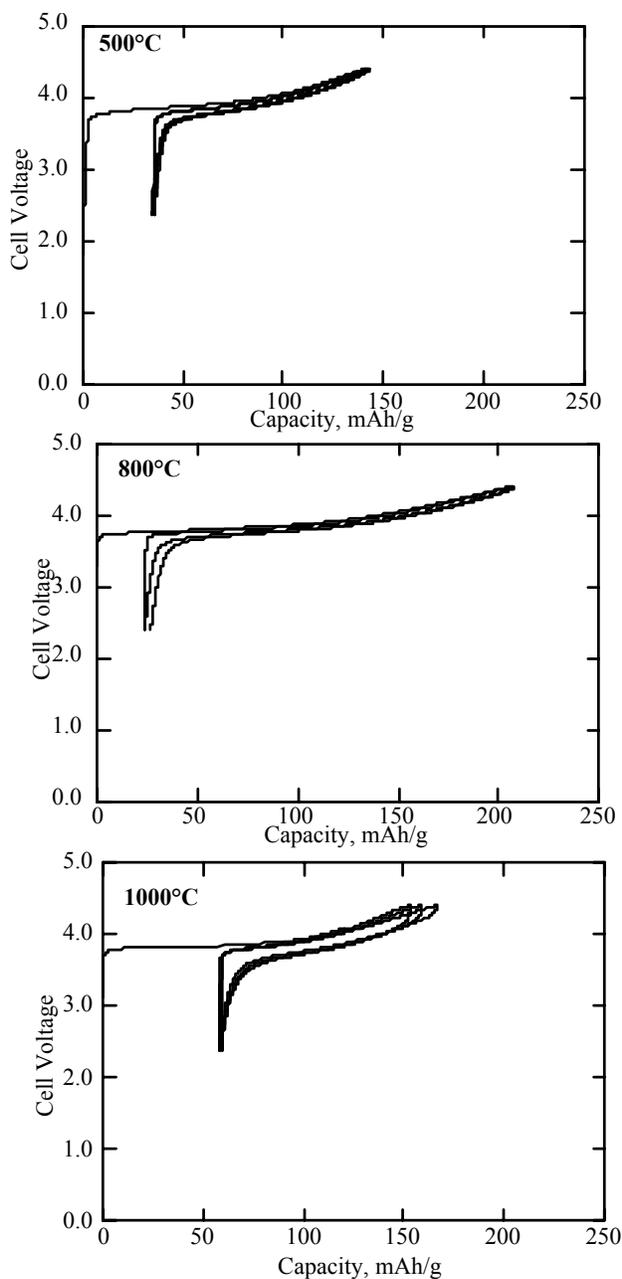
**EXPECTED STATUS SEPT. 30, 2003:** For low-cost Li-ion cells, we expect to identify the changes in stabilized  $\text{LiMnO}_2$  structures as a function of current density and substitution level in  $\text{Li}_x\text{Mn}_{1-y-z}\text{Ni}_y\text{Co}_z\text{O}_2$ , to determine the optimum substitution level and the role of cobalt, to determine the structure and composition of the vanadium stabilized  $\text{LiMnO}_2$  and to increase its electrochemical capacity. For Li/polymer cells we expect to complete the evaluation of the manganese stabilized  $\delta$ -vanadium oxides 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:** (a) To characterize the stabilized (geometrically and electronically) manganese oxide, determine the optimum substitution of Mn to obtain a capacity of 200 mAh/g, and to compare the best samples with iron phosphates. (b) To complete the characterization of manganese-stabilized vanadium oxides by June 2003 and to compare the best samples with lithium-iron and other phosphates for use in polymer or gel batteries.

## PROGRESS TOWARD MILESTONES

(a) Electronic Stabilization of Manganese oxide. This quarter's effort has continued on characterizing and understanding the mixed manganese-nickel oxides, which have a stable layered lattice that does not convert to spinel-like phases upon Li removal. Our emphasis continues to be on the compound  $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$ , which we showed earlier to have optimum behavior. These compounds show very little polarization during cycling. However, the temperature of synthesis has a marked impact on the capacity loss during the first cycle and on the subsequent cycling capacity. We studied three temperatures, 500°C, 800°C and 1000°C; the polarization on the 1000°C sample is by far the largest probably due to a larger particle size. Of the three



temperatures studied, 800°C shows the best behavior. Further work will thus focus on materials formed at this temperature.

Earlier, we reported on the positive impact of carbon coatings formed in-situ from carbon gels on the rate capability of these layered nickelates (BATT 1Q2002). We will explore the impact of such coatings on this 442 composition.

The presence of cobalt has a positive effect on the capacity and cycling of these electrodes, and in an effort to determine the role of the cobalt we

have begun a study of the electrical resistance of these layered materials. Earlier we showed that the conductivity of the layered manganese oxides was improved by two orders of magnitude by the addition of 2 to 5 % cobalt. An initial measurement of the 442 composition indicates a conductivity of about  $10^{-5}$  S/cm at 25°C.

Last quarter we reported on the initial XPS data on the layered compound  $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$ . Further analysis of the data has shown that the cobalt is trivalent, that the manganese is mostly tetravalent with about 20% trivalent, so that most of the nickel is divalent. However, the 20% Mn(III) and Ni(III) could be surface related.

**Figure 1.** Cycling of  $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$  synthesized at different temperatures. In each case the electrode contained 80% active material, 10% carbon black and

10% Teflon. Cycling was at  $0.1 \text{ mA/cm}^2$ .

**Further plans to meet or exceed milestones:** None

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

## 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, 2002:** Initial electrochemical characterization of sol-gel LiFePO<sub>4</sub> samples and O<sub>2</sub> layered manganese oxides will be complete. *In situ* XRD experiments on Li/tunnel MnO<sub>2</sub> cells will be underway.

**EXPECTED STATUS SEPT. 30, 2003:** Evaluation of Fe-substituted tunnel MnO<sub>2</sub> will be complete. Fundamental studies (*in situ* XRD analysis, diffusion coefficients, thermodynamic measurements, *etc.*) on unsubstituted tunnel MnO<sub>2</sub> will be complete.

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

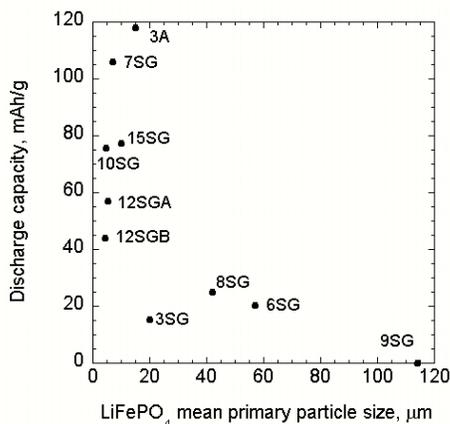
### MILESTONES:

(a) Go/no-go decision on sol-gel LiFePO<sub>4</sub> by April 2003.

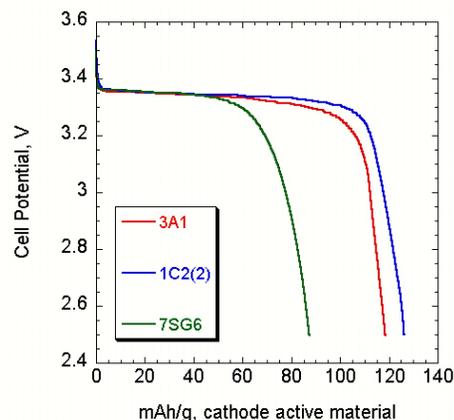
(b) Analysis of *in situ* XRD results on Li/tunnel MnO<sub>2</sub> cells will be complete by September 2003.

## PROGRESS TOWARD MILESTONES

The effect of processing variables on the electrochemical properties of sol-gel produced samples of  $\text{LiFePO}_4$  are being studied.  $\text{LiFePO}_4$  made by solid state reaction from iron acetate is being used for comparison purposes. All samples tested are phase-pure according to their x-ray diffraction patterns. The relationship between particle size and capacity obtained during slow cyclic voltammetry experiments is shown in Figure 1 for several sol-gel (SG) and acetate (A) samples.



**Figure 1.** Discharge capacities of Li/LiFePO<sub>4</sub> cells as a function of the LiFePO<sub>4</sub> primary particle size. LiFePO<sub>4</sub> samples are designated A (for acetate precursors) or SG (for sol-gel materials).



**Figure 2.** Discharges at 0.055 mA/cm<sup>2</sup> of Li cells containing LiFePO<sub>4</sub> made from acetate (3A1), made by sol-gel (7SG6), and a carbon-coated sample made by sol-gel (1C2(2)).

Particle growth is much less rapid at for sol-gel samples processed at 600°C (e.g., 7SG) than at 700°C (e.g., 9SG). Planetary milling after synthesis reduces the particle size (10SG) and restores some capacity, but not to that seen for 7SG. Furthermore, there is no clear correlation between utilization and particle size for primary particles smaller than about 20 μm. An investigation of surface species by Raman microprobe spectroscopy carried out by R. Kostecki (BATT task 5) indicates that materials with better electrochemical performance had evenly distributed coatings of residual carbon with a relatively higher graphitization ratio than lower capacity materials. The nature of the carbon coating is dependent upon sample heating time, intermediate milling steps, and synthesis method of the LiFePO<sub>4</sub> sample. A well-distributed carbon coating with a high graphitization ratio is produced when 2 wt% organic additive is added during preparation of a sol-gel sample processed the same way as 7SG. This results in a significant improvement in electrochemical performance (Fig. 2). In contrast, sol-gel samples doped with 1% Ti or Mg were phase pure according to XRD analysis, but did not appear to have increased electronic conductivity or improved electrochemical performance. This suggests that the high electronic conductivity and good rate capability exhibited by doped samples made by Chiang et al. at MIT may be associated with the nature of the carbon that is produced by that specific synthesis method.

### Publications and Presentations

“Synthesis and Characterization of a Copper-substituted Manganese Oxide with the Na<sub>0.44</sub>MnO<sub>2</sub> Structure”, M.M. Doeff, T.J. Richardson, J. Hollingsworth, C.-W. Yuan, and M. Gonzales, *J. Power Sources*, **112/1**, 294 (2003).

“Electrochemical Performance of Sol-Gel Synthesized LiFePO<sub>4</sub> in Lithium Batteries,” M. Doeff, R. Fiñones, and Y. Hu, *Electrochem. Soc. Meeting*, Salt Lake City, Utah October 2002, Vol. 2002-1, abstract 121.

“Exploiting the Na-Mn-O Phase Diagram to Make Novel Lithium Battery Electrodes,” *International Battery Association/Hawaii Battery Conference 2003*, Waikoloa, HI, January 2003.

## TASK STATUS REPORT

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

**TASK TITLE - PROJECT:** Cathodes - Novel Materials

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

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

**OBJECTIVES:** To evaluate alternative layered oxides as cathode materials for a Li-ion battery that operates between Ni(II) and Ni(IV).

**APPROACH:** Layered  $\text{LiMO}_2$  oxides have been shown to exhibit a high  $\text{Li}^+$ -ion mobility once a fraction of the Li is removed. On the other hand, these oxides are metastable and decompose upon removal of a large fraction of Li from between the host  $\text{MO}_2$  layers.  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$  contains Mn(IV) and removal of Li operates on the Ni(III)/Ni(II) and Ni(IV)/Ni(III) couples, both of which are pinned at the top of the  $\text{O}^{2-}:2p^6$  band. Ohzuku and Mikimura have demonstrated a capacity over the range 2.5 to 4.3 V vs Li that approaches 150 m Ah/g for 30 charge/discharge cycles at room temperature. We have found that the capacity decreases sharply at higher current densities, which we suspect is the result of poor conductivity. We will investigate (1) whether we can increase the capacity at higher current densities by coating the particles with carbon and (2) the role, if any, of the Mn(IV) ions. Since small particle sizes are probably necessary, sol-gel synthetic routes will be employed.

**STATUS OCT. 1, 2002:** New project initiated 8/1/02.

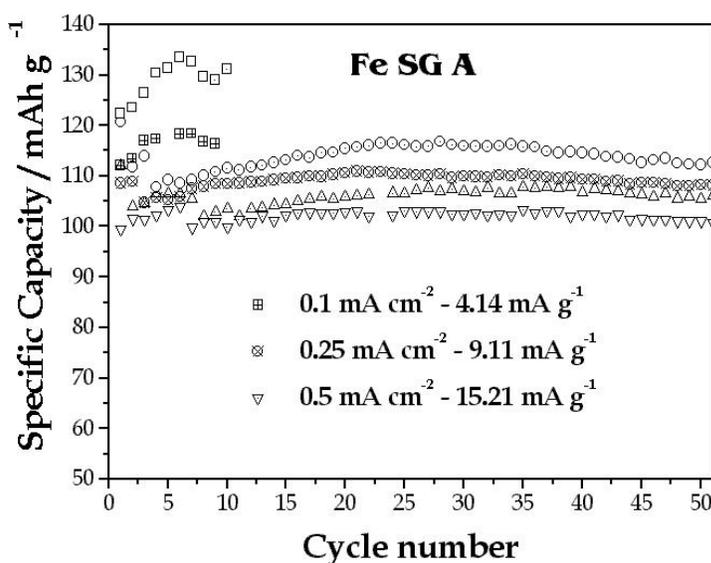
**EXPECTED STATUS SEPT. 30, 2003:**  $\text{Li}_2\text{NiMnO}_2$  samples with and without carbon will have been prepared and tested. Preliminary data will have been collected on other materials.

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

**MILESTONES:** (a) Test the influence of carbon coating on layered and spinel  $\text{Ni}^{2+}$ ,  $\text{Mn}^{4+}$  compounds operating on  $\text{Ni}^{3+}/\text{Ni}^{2+}$  and  $\text{Ni}^{4+}/\text{Ni}^{3+}$  couples and assess the role of  $\text{Mn}^{4+}$  in these compounds. September 30, 2003. (b) Investigation of  $\text{Mn}^{4+}$  ion by substitution of other  $\text{M}^{4+}$  ions. January 31, 2003.

## PROGRESS TOWARD MILESTONES

Last quarter we reported preliminary data comparing the performance of layered  $\text{Li}_2\text{MnNiO}_4$  cathodes vs. a Li anode with and without a carbon coating. However, careful analysis of our x-ray data showed a small shoulder on one of the main peaks that was not present in the material reported by Ohsuku and Mikimura. Several other laboratories have investigated  $\text{Li}_2\text{MnNiO}_4$  as a cathode material with results no better than ours; but all results are inferior to the performance initially reported by Ohsuku and Mikimura. There thus appears to be a trick in the synthesis of this compound with no transition-metal ion in the Li layers. We believe an improved synthesis route can give superior performance. However, the departure of Brian Cushing and a delayed arrival of Steen Schougaard to replace him prevented an early attack on an improved synthesis. Therefore, I report work with Michele Piana to investigate a new sol-gel synthetic route to prepare single-phase phospho-olivines  $\text{LiMPO}_4$  ( $M = \text{Fe}$  or  $\text{Mn}$ ). Triethyl phosphite (TEP) was used as a phosphate organic precursor with absolute ethanol as solvent. The sol-gel synthesis ensured homogeneity of the precursors at the nanometric scale, which improves reactivity; we were able to obtain products with very small agglomerates and crystal grain size. Several carbon sources were used to coat the particles in order to improve electrochemical performance. Galvanostatic cycling tests of the cathodic materials were made on coin cells with Li metal as anode in order to study the influence of the synthesis and the structural-morphological characteristics on the electrochemical performance of a phosphate/C composite. All  $\text{LiFePO}_4$  cathodes prepared by sol-gel method showed a specific capacity above  $100 \text{ mAh g}^{-1}$  of active material when cycled at the highest current density used ( $0.5 \text{ mA cm}^{-2}$ ) (Fig. 1).



**Figure 1.** Galvanostatic cycling tests at various current densities of  $\text{LiFePO}_4$  prepared by sol-gel synthesis (sample A).

## BATT TASK 5 DIAGNOSTICS

### TASK STATUS REPORT

**PI, INSTITUTION:** R. Kostecki and F. McLarnon, Lawrence Berkeley National Laboratory

**TASK TITLE - PROJECT:** Diagnostics - Electrode Surface Layers

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

**BARRIER:** Short lithium battery lifetimes

**OBJECTIVE:** Establish direct correlations between electrode surface changes, interfacial phenomena, and cell capacity/power decline.

**APPROACH:** Our approach is to use 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 and structure, electrode surface chemistry, and SEI thickness and composition, all of which accompany cell cycle-life tests.

**STATUS OCT. 1, 2002:** We defined relationships between electrode history, electrode surface properties, and temperature for baseline  $\text{LiAl}_{0.05}\text{Ni}_{0.8}\text{Co}_{0.15}\text{O}_2$  cathodes. We completed our studies of structural disordering of graphite anodes during cycling at elevated temperatures and correlated the mechanism of SEI reformation upon cycling with graphite structural degradation.

**EXPECTED STATUS SEPT. 30, 2003:** We expect to develop good understanding of the key elements for good electrochemical performance of  $\text{LiFePO}_4$  cathode, *i.e.*, identify the mechanism of electrode degradation in terms of changes of surface morphology and chemistry upon cycling and storage in BATT Program electrolytes. We will identify and confirm material limitations and specific degradation modes. We expect to determine and understand the effects of various synthesis routes, carbon coating, and impurities on the performance of  $\text{LiFePO}_4$  cathodes. We will continue to investigate the effect of carbon disordering to determine its impact on long-term Li-ion cell performance. We expect to provide preliminary data from *in situ* Raman spectroscopy and current-sensing atomic force microscopy of individual particles of BATT baseline electrode materials. We plan to provide full diagnostic results for model thin-film  $\text{LiMn}_2\text{O}_4$  cathodes.

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

**MILESTONE:** (a) Determine the effect of structure, morphology, carbon coating, and surface impurities on the electrochemical performance of  $\text{LiFePO}_4$  electrodes - January 2003.

(b) Develop capabilities to carry out *in situ* Raman spectroscopy and current-sensing atomic force microscopy of individual particles of BATT baseline electrode materials - June 2003.

### PROGRESS TOWARD MILESTONES

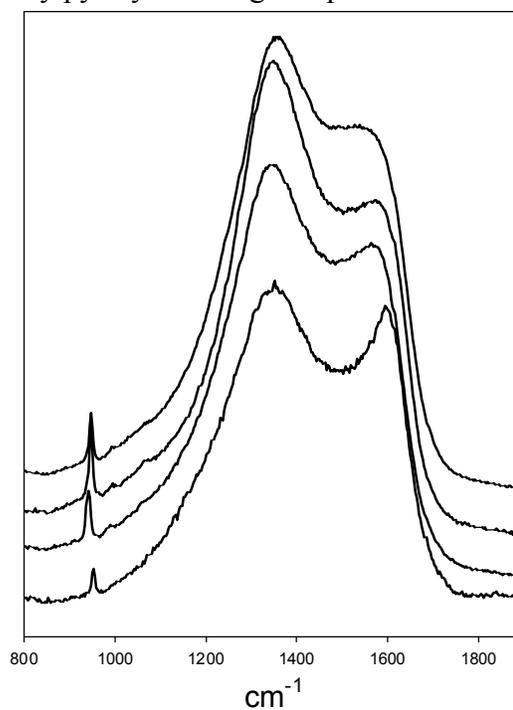
Our first objective during this quarter was to characterize processes that occur in baseline  $\text{LiFePO}_4$  cathodes and to continue studies of baseline  $\text{LiAl}_{0.05}\text{Ni}_{0.8}\text{Co}_{0.15}\text{O}_2$  cathodes cycled in  $\text{LiPF}_6$ -EC-DEC electrolytes. We used *ex situ* and *in situ* Raman microprobe spectroscopy and scanning probe microscopies analyze the chemical composition, grain size, and structure of electrodes from BATT baseline cells, which were provided by BATT task 1.1 (Striebel). We looked for evidence of corrosion, dissolution-precipitation processes, active-material phase

segregation, and new phase formation upon cycling in  $\text{LiPF}_6\text{-EC-EMC}$  electrolyte and possible correlations with the electrochemical properties of  $\text{LiFePO}_4$  and  $\text{LiAl}_{0.05}\text{Ni}_{0.8}\text{Co}_{0.15}\text{O}_2$  cathodes. Our routine diagnostic analysis of the BATT cells fully confirmed our previous results that carbon additives in composite  $\text{LiFePO}_4$  and  $\text{LiAl}_{0.05}\text{Ni}_{0.8}\text{Co}_{0.15}\text{O}_2$  cathodes recede from the surface at significant rates. This process is greatly accelerated at elevated temperatures and very likely responsible for degradation of both cell power and cell energy. We plan to carry out a model experiment with a thin-layer carbon electrode to investigate the mechanism of this process as well as determine its specific role in the degradation of cathode performance.

Our second objective was to focus on the role of elemental carbon additive with special emphasis on  $\text{LiFePO}_4$  because of its intrinsic low electronic conductance. Recent work of Y-M. Chang (MIT) demonstrated that solid-solution doping of  $\text{LiFePO}_4$  by metals supervalent to  $\text{Li}^+$  increases the electronic conductivity of  $\text{LiFePO}_4$  by a factor of  $\sim 10^8$ . However, the effect of residual carbon (which was present in all samples) on the material conductivity of his materials remains unclear. We analyzed a few samples of raw  $\text{LiFePO}_4$  powders, *i.e.*, before they were purposely mixed with carbon, from different suppliers including BATT Program participants, and we concluded that all of them contain significant amounts of residual carbon (0.5-1.5% wt.). The structure of this residual carbon is highly amorphous because of the relatively low temperature of final heat treatment (600-700°C) typically used when  $\text{LiFePO}_4$  is synthesized from organic precursors such as iron or lithium acetates or alkoxides. We learned from our earlier studies that electronic conductivity of amorphous carbons produced by pyrolysis of organic precursors

increases by 4 orders of magnitude for pyrolysis temperatures between 600 and 800°C. We then carried out an extensive analysis of  $\text{LiFePO}_4$  raw powders in search of a correlation between the residual carbon structure/conductivity and cathode electrochemical performance. These studies were performed in collaboration with BATT task 4.3 (Doeff), who provided raw samples of  $\text{LiFePO}_4$  synthesized under different conditions and determined their electrochemical behavior. Figure 1 shows Raman spectra of these raw powders, with labels which correspond to their measured discharge capacity. All samples showed a relatively small peak at  $940\text{ cm}^{-1}$ , which corresponds to  $\text{PO}_4$  stretching vibration, compared to intense bands that arise from significant amounts of residual carbon. Interestingly, improved utilization of  $\text{LiFePO}_4$  was correlated with residual carbon with higher graphitization ratio, *i.e.*, carbon which shows two distinct bands at  $1350$  and  $1580\text{ cm}^{-1}$ . We concluded that the electrochemical behavior of  $\text{LiFePO}_4$  is highly dependent upon details of processing and that the physico-chemical

properties of post-synthesis residual carbon determine the  $\text{LiFePO}_4$  electrochemical performance. Further mixing of  $\text{LiFePO}_4$  with carbon does not appear to have a significant effect on the electrode performance. We recommend the development of a synthesis route to produce a uniform and consistently “good” carbon coating on the  $\text{LiFePO}_4$  based on an optimized final heat-treatment, or the use of inorganic precursor materials followed milling with graphite or acetylene black. This completes our work on Milestone (a).



**Figure 1.** Raman spectra of  $\text{LiFePO}_4$  powders. Cathode capacities (from the uppermost to the lowermost curve) are 58, 96, 106, and 120 mAh/g, respectively.

## TASK STATUS REPORT

**PI, INSTITUTION:** J. McBreen, Brookhaven National Laboratory

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

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

**BARRIER:** Short lithium battery lifetimes

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

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

**STATUS OCT. 1, 2002:** We completed extensive *in situ* XRD on  $\text{LiMn}_2\text{O}_4$  in the 4.1 V region. This included several new findings on the phase behavior and the effect of Li and O stoichiometry on electrode stability. The work also showed that electrolyte composition had major effects on the stability of  $\text{LiMn}_2\text{O}_4$  at elevated temperatures. Work was also completed on the development of techniques for XAS studies of phosphorous decomposition products in cycled cells, and the techniques was applied to the ATD Program. Structural studies of new high-capacity cathodes and anodes will be ongoing. This includes XAS and XRD work on cathode materials such as  $\text{LiFePO}_4$ ,  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ , and  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ . Anode work includes XRD on carbon-coated Si and  $\text{Ge}_3\text{N}_4$ .

**EXPECTED STATUS SEPT. 30, 2003:** We expect to complete the XAS and XRD work on the cathode materials,  $\text{LiFePO}_4$ ,  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ , and  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ . XRD on carbon-coated Si and  $\text{Ge}_3\text{N}_4$  will also be completed. Exploratory work on non-resonant inelastic x-ray scattering NRIXS will be initiated. We expect to provide preliminary soft x-ray XAS data on various cathode materials, at the B, F, O, and P K edges and at the  $L_3$  and  $L_2$  edges of the transition metals.

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

**MILESTONES:** (a) Complete *in situ* XAS and XRD studies of  $\text{LiFePO}_4$ ,  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$  and  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  by April 2003. (b) Complete *in situ* XAS and XRD studies of Si and nitride-based anode materials by June 2003.

## PROGRESS TOWARD MILESTONE (a)

The *in situ* XAS and XRD studies of  $\text{LiFePO}_4$ ,  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$  and  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  are on schedule. Papers have been submitted on the work on  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$  and  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ . We have also carried out *ex situ* XAS at the Fe K edge on  $\text{LiFePO}_4$  cathodes, charged to various states of charge, in both the transmission and electron yield modes. The transmission data probe the bulk, whereas the electron yield data probe the outer few hundred-angstrom-layer of the  $\text{LiFePO}_4$  particles. So far the data do not support the “onion-type” two-phase model of Padhi *et al.* The experiments will be repeated. It is important to verify this because it may have implications regarding the rate capability of the  $\text{LiFePO}_4$  cathodes. *In situ* XRD indicates that the phase behavior of both on  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$  and  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  is very similar to that of Co-substituted  $\text{LiNiO}_2$ . *In situ* XANES results, at the Ni and Co K edges, of  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  are also very similar to that found for Co-substituted  $\text{LiNiO}_2$ .

## TASK STATUS REPORT

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

**TASK TITLE - PROJECT:** Diagnostics – Interfacial and Reactivity Studies

**SYSTEMS:** High power Li-ion

**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 to provide the basis to interpret more complex spectra recorded from ATD Program cell materials. For this year, we will add in-situ differential electrochemical mass spectrometry (DEMS) as a technique for studying *gas generation* from electrolyte decomposition reactions. These spectroscopies will be accompanied by classical electroanalytical methods such as cyclic voltammetry and the rotating ring-disk electrode (RRDE).

**STATUS OCT. 1, 2002:** Vinylene carbonate added (5 mol%) to PC-based electrolyte was found to prevent graphite exfoliation that normally occurs in PC-based electrolyte. The electrochemical oxidation of the saturated alkylcarbonate solvents used in Li-ion batteries occurs in dry (<20 ppm water) electrolytes only above 5 V. Water added to dry electrolyte causes the oxidation to occur at much lower potentials, e.g., <4 V.

**EXPECTED STATUS SEPT. 30, 2003:** Determine the oxidative and thermal stability of electrolytes with various electrode materials and impurities, e.g., water. Identify routes to improved stability *via* electrolyte additives and/or electrode pre-treatment.

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

**MILESTONE:** Identify at least one route to improved electrolyte stability *via* electrolyte additives and/or electrode pre-treatment.

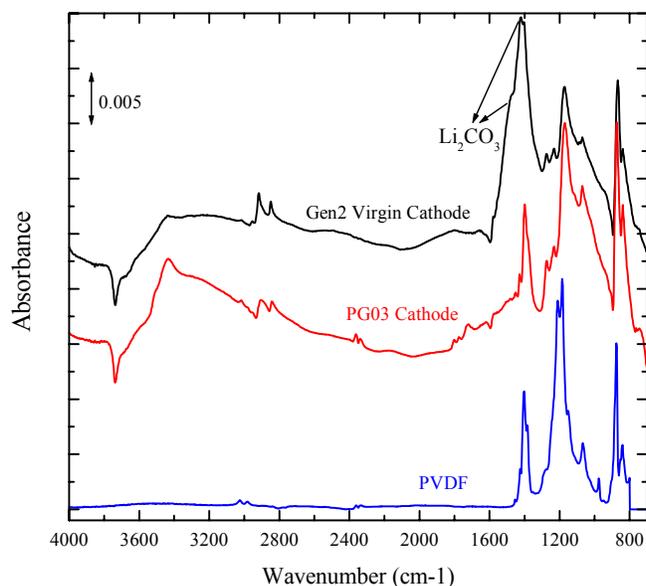
### PROGRESS TOWARD MILESTONES

Both anodes and cathodes harvested from four BATT Program pouch cells, PG 03, PG04, PG06 and PG13, were analyzed by ATR- FTIR. The components were “washed” by soaking in DMC for 24 hrs. followed by solvent evaporation in the glove box prior to spectroscopy analysis. The electrodes were then transferred from the glove box to the He-purged FTIR spectrometer sample chamber.

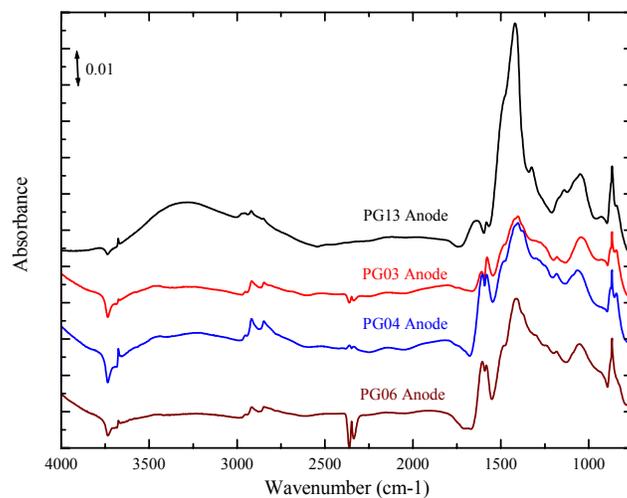
The infrared spectrum of the PG03 cathode after DMC washing is shown in Fig.1. The FTIR spectra from all four cells were essentially identical (the backgrounds were different due to differences in surface morphology). Although weak peaks at  $1804\text{ cm}^{-1}$  and  $1774\text{ cm}^{-1}$ , characteristic of the carbonyl group in EC, were still discernable, features in the spectral regions between  $1300\text{ cm}^{-1}$ – $700\text{ cm}^{-1}$  are the most prominent. Most of the features could be readily assigned to PVDF, via comparison with a reference spectrum from a PVDF powder (may not be the exact same PVDF used as the binder). Interestingly, the spectral difference in the  $1600\text{ cm}^{-1}$  to  $1300\text{ cm}^{-1}$  region between the virgin cathode (before assembly) and that after cycling in the cell, was quite striking. The strong peak at  $1422\text{ cm}^{-1}$  and a shoulder at  $1479\text{ cm}^{-1}$  are the C-O asymmetric and symmetric stretching modes of  $\text{Li}_2\text{CO}_3$ . To confirm the assignment definitively,

there should also a sharp peak at  $870\text{ cm}^{-1}$  associated with the  $(\text{CO}_3^{-2})$  group bending mode. Unfortunately, this peak is superimposed on a sharp peak at  $875\text{ cm}^{-1}$  from the PVDF. However, we have previously reported XPS analysis of ATD Program Gen2 virgin cathodes that showed definitively that  $\text{Li}_2\text{CO}_3$  is present in this material. However, no lithium carbonate could be detected by FTIR from the cathode of cycled cells, as clearly indicated by the absence of strong peak at  $1422\text{ cm}^{-1}$  and its shoulder at  $1479\text{ cm}^{-1}$ . The fate of the  $\text{Li}_2\text{CO}_3$  during cycling is still unknown.

Figure 2 shows the spectra obtained from anodes of four cycled pouch cells. These spectra were qualitatively similar, but quantitatively different. Specifically, the relative ratio of features between  $1700\text{--}1550\text{ cm}^{-1}$  and those between  $1550\text{--}1140\text{ cm}^{-1}$  vary significantly among these cells. However, the overall spectra features from different cells could be fit with the same mixture of Li compounds. The FTIR spectrum from PG04 anode in Fig.2 was simulated by superposition of individual spectra for lithium carbonate ( $\text{Li}_2\text{CO}_3$ ), lithium succinate ( $\text{LiO}_2\text{CCH}_2\text{CH}_2\text{CO}_2\text{Li}$ ), lithium oxalate ( $\text{Li}_2\text{C}_2\text{O}_4$ ) and lithium methoxide ( $\text{LiOCH}_3$ ). Succinate is merely a model compound for any number of carboxylates, e.g., formate, acetate, propionate, etc., that have the same strong features in the  $1700\text{--}1550\text{ cm}^{-1}$  from the  $-\text{COOLi}$  functional group. The features in the  $1674\text{--}1550\text{ cm}^{-1}$  spectral region arise exclusively from lithium carboxylates and lithium oxalate, whereas those in the  $1550\text{--}1140\text{ cm}^{-1}$  region arise mainly from lithium carbonate. The peak ratio variation in the two spectral regions reflects the abundance of carboxylate and oxalate relative to lithium carbonate in the layer. The vibrational features from of the PG13 anode clearly indicates that the passive layer on the anode of the high-temperature cycled cell PG13 (cycled at  $60^\circ\text{C}$ ) is quantitatively different from the cells cycled at lower temperature, i.e., the layer is nearly purely inorganic carbonate. Because this cell had much higher power fade than the other cells, the absence of organic species in the passive layer would appear to be correlated to the power fade, i.e., an organic component is needed to have sufficient Li-ion conductivity.



**Figure 1.** ATR-FTIR spectrum of a cathode from the PG03 pouch cell compared to that of a virgin cathode. Spectrum of a pure binder material shown for reference.



**Figure 2.** ATR-FTIR spectra of anodes from a series of BATT program pouch cells.

## TASK STATUS REPORT

**PI, INSTITUTION:** E.J. Cairns, Lawrence Berkeley National Laboratory

**TASK TITLE - PROJECT:** Diagnostics - Synthesis and Characterization of Electrodes

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

**BARRIER:** Rapid capacity fade

**OBJECTIVES:** The primary objectives are (1) to directly observe Li in BATT Program cathode materials, (2) characterize the Li atomic and electronic local environment, (3) determine changes in this environment with cycling, and (4) use this information to identify causes of capacity loss and propose improved electrode materials.

**APPROACH:** Our approach is to use  $^7\text{Li}$  MAS-NMR to characterize BATT Program electrodes before and after cycling. Data to be collected are isotropic chemical shift, linewidth, and relaxation times for each species of Li. XRD, magnetic susceptibility, and other data will also be used, as appropriate. NMR data on model failure mechanisms will be used to interpret the spectra. Structural information and information on the local Li environment will be gathered to improve our ability to design new electrode materials. This work will be carried out in collaboration with investigators who prepare and cycle electrode materials (*e.g.*, M. Doeff, K. Striebel, and others).

**STATUS, OCT. 1, 2002:** We obtained  $^7\text{Li}$  MAS NMR spectra for several  $\text{LiMPO}_4$  (M=Fe, Ni, Mn, Co) and  $\text{Li}[\text{Mn}_x\text{Fe}_{1-x}]\text{PO}_4$  olivine compounds and established the hyperfine shift mechanism. This information will help elucidate the structural changes during electrochemical cycling. We identified the change in the Ni and Ni-containing environment as a significant mechanism of capacity fade in Gen2 electrodes. We identified the various local environments of Li in the layered  $\text{Li}_y[\text{M}_{0.11}\text{Mn}_{0.89}]\text{O}_2$  materials and clarified the correlation between the local environments and electrochemical performance.

**EXPECTED STATUS SEPT. 30, 2003:** We anticipate that we will have completed an investigation of the capacity fade of several members of the family of layered  $\text{Li}_y[\text{M}_{0.11}\text{Mn}_{0.89}]\text{O}_2$  materials. We will also complete our investigation of  $\text{LiAl}_{0.05}\text{Ni}_{0.80}\text{Co}_{0.15}\text{O}_2$  material in terms of the changes that occur during cycling, and the changes that accompany capacity loss and power loss. We will continue our investigations of the  $\text{Li}(\text{Fe},\text{M})\text{PO}_4$  family of materials. As new materials are brought into the program, we will initiate NMR studies of these.

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

**MILESTONES:** (a) Complete NMR investigation of layered  $\text{Li}_y[\text{M}_{0.11}\text{Mn}_{0.89}]\text{O}_2$  materials by August 2003. (b) Complete investigation of the  $\text{LiAl}_{0.05}\text{Ni}_{0.80}\text{Co}_{0.15}\text{O}_2$  material in terms of changes that occur during cycling, and changes that accompany capacity and power loss by June 2003.

## PROGRESS TOWARDS MILESTONES

The spin-lattice relaxation time ( $T_1$ ) of  $\text{Li}_y[\text{M}_{0.11}\text{Mn}_{0.89}]\text{O}_2$  was measured in order to help assignments of the Li NMR resonances. Short  $T_1$  values of 1.94, 1.45, and 2.87 ms were measured for the resonances at 700, 300, and 100 ppm, respectively, and a relatively long  $T_1$  value of 1.54 s was measured for the resonance at  $-5$  ppm. A short  $T_1$  value is a characteristic of paramagnetic material, which confirms our previous assignments of the resonances at 700, 300, and 100 ppm to the Li cations in the O2, T2, and O3 type environments, respectively. In contrast, the long  $T_1$  at  $-5$  ppm indicates that the resonance arises from the Li cations residing on the grain surface instead of the inside the lattice structure. This suggests that the ion-exchange process used for preparing the material is not complete, leaving residual Li cations on the surface. The Li cations on the surface do not participate in the oxidation/reduction reactions, making no contribution to the capacity. The change in the local environment of  $\text{Li}_y[\text{M}_{0.11}\text{Mn}_{0.89}]\text{O}_2$  during and after charging /discharging was also investigated by Li NMR (Figure 1). No noticeable change is observed during charging (Figure 1(a)-(c)) and after one cycle (Figure 1(e)); three resonances at 700 (O2-type Li), 120 (O3-type Li), and  $-5$  (surface Li) ppm are observed. As shown in Figure 1(d), the resonance shifts to 400 ppm when the electrode is discharged to 2 V, indicating the lower oxidation state of Mn. After 62 cycles, a dominant broad resonance at 570 ppm is seen, which can be assigned to Li in the O2 structure. Note that the peak position is shifted to lower frequency due to the slightly discharged state of the cell (The OCV is 3.12 V in comparison to 3.5 V of the fresh cell). In contrast, it appears that the resonance at 120 ppm (Li in the O3 environment) disappears after 62 cycles. This suggests that Li is preferentially removed from the O3 environment during repeated cycling. Formation of a new phase or environment, which would have given rise to an additional resonance, is not seen for any of the materials. This is contrary to the situation for the O3 type layered compound, which shows a crystalline spinel phase after several cycles. These results show the greater stability of the O2 material.

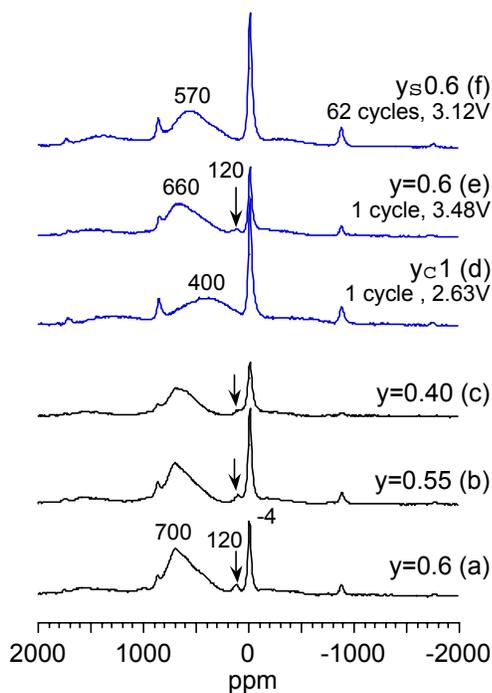


Figure 1.  $^7\text{Li}$  MAS NMR spectra of O2- $\text{Li}_y[\text{Al}_{0.11}\text{Mn}_{0.89}]\text{O}_2$  during and after electrochemical cycling.

## 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  $\text{Ni}^{2+}/\text{Ni}^{4+}$  couple. Determine the effect of structure and cation doping on the Li deintercalation/ intercalation mechanisms and the  $\text{Ni}^{2+}/\text{Ni}^{4+}$  couple.

**APPROACH:** Use solid-state NMR and XAS to characterize local structure and oxidation states as a function of state of charge and number of charge cycles. Use first-principles calculations (density functional theory) to identify redox-active metals, determine the relative stabilities of different structures and the effect of structure on cell voltages, and identify promising cathode materials for BATT Program applications. Use calculations and NMR to identify low-activation-energy pathways for cation migration and to investigate the effect of doping on conductivity.

**STATUS OCT. 1, 2002:** The analysis of the NMR data for  $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{0.5}]\text{O}_2$  and  $\text{Li}[\text{Li}_{1/9}\text{Ni}_{1/3}\text{Mn}_{5/9}]\text{O}_2$  during the first electrochemical cycle have been completed and compared with results from first-principles calculations. Investigation of multiple-cycled materials by NMR and calculations of the  $\text{Li}_2\text{MnO}_3$ -NiO phase diagram are on going. Exploratory syntheses of  $\text{Nb}^{5+}$ -doped systems have been initiated.

**EXPECTED STATUS SEPT. 30, 2003:** NMR data for  $\text{Li}[\text{Li}_{(1-2x)/3}\text{Ni}_x\text{Mn}_{2/3-x/3}]\text{O}_2$   $x = 1/2, 1/3, 1/10$  as a function of charging cycle will have been acquired and the analysis completed. XAS studies of the  $x = 1/2$  and  $1/3$  samples will be completed. A preliminary phase diagram for  $\text{Li}_2\text{MnO}_3$ -NiO will have been calculated. Studies of cation doping (e.g.,  $\text{Nb}^{5+}$ ,  $\text{Ti}^{4+}$ ,  $\text{Co}^{3+}$ ) on local structure and cell potential 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) Determine the site energies and voltages of the different Li environments in  $(1-x)\text{Li}[\text{Ni}_{0.5}\text{M}_{0.5}]\text{O}_2 \bullet x\text{Li}[\text{Li}_{1/3}\text{M}_{2/3}]\text{O}_2$  ( $M = 4+$ ) by first-principles calculations. Also determine the Li local environments and nickel oxidation state as a function of state of charge in  $(1-x)\text{Li}[\text{Ni}_{0.5}\text{M}_{0.5}]\text{O}_2 \bullet x\text{Li}[\text{Li}_{1/3}\text{M}_{2/3}]\text{O}_2$  ( $M = 4+$ ) by NMR spectroscopy and XAS. (Nov. 2002)  
(b) Synthesis and preliminary characterization (powder diffraction and NMR) and electrochemical testing of the  $\text{Nb}^{5+}$ -doped materials. Perform initial calculations on the effect of cation doping (e.g.,  $\text{Nb}^{5+}$ ) on the  $\text{Ni}^{2+}/\text{Ni}^{4+}$  couple. Perform (proton and Li) NMR studies of cation locations of iron phosphates and doped lithium (nickel) manganates in collaboration with S. Whittingham (SUNY Binghamton) and M. Thackeray (ANL). Complete XAS studies (with J. McBreen, BNL) of lithium nickel manganates. (May 2003)

## PROGRESS TOWARD MILESTONES

A detailed investigation of the structures of the as-prepared cathode materials  $\text{Li}[\text{Ni}_x\text{Mn}_{(2-x)/3}\text{Li}_{(1-2x)/3}]\text{O}_2$ , using NMR and calculations has been completed. Two sets of resonances are observed by NMR for the  $x = 1/2, 1/3$ , and  $1/10$  samples, which are assigned to Li in the predominantly Li layers and in the Ni/Mn layers. Based on the intensities of the resonances, the tendency for  $\text{Ni}^{2+}$  to replace  $\text{Li}^+$  in the predominantly Li layers, to form “anti-sites”, is shown to decrease with decreasing nickel content (Table 1). A model for cation ordering was proposed, which is based on the ordering found in the manganese  $[\text{Li}_{1/3}\text{Mn}_{2/3}]$  layers of  $\text{Li}_2\text{MnO}_3$ : Occupancies of 2:1 are obtained for  $\text{Ni}^{2+}$  substitution in the  $\text{Li}^+$  and  $\text{Mn}^{4+}$  sites in the ordered  $[\text{Li}_{1/3}\text{Mn}_{2/3}]$  layers, so as to maintain charge balance and to minimize the number of  $\text{Li}^+$  ions in the Mn/Ni layers with  $\text{Ni}^{2+}$  cations in their 1<sup>st</sup> cation coordination sphere.  $\text{Ni}^{2+}$  ions in the  $\text{Mn}^{4+}$  sites tend to cluster, particularly in the samples containing higher  $\text{Ni}^{2+}$  contents, so as to produce regions that are closer to the composition of  $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{0.5}]\text{O}_2$  (Figure 1).

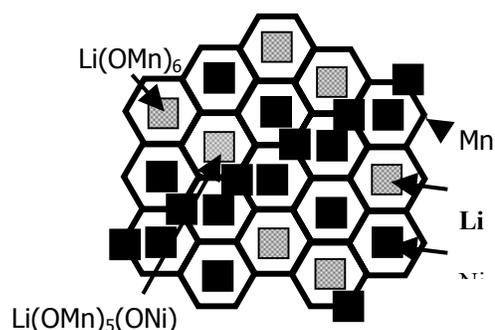
First principles calculations were used to estimate the “anti-site” energy and show that this decreases with  $\text{Ni}^{2+}$  content, consistent with the NMR results. A wide variety of unit cells were constructed with different cation ordering schemes and  $\text{Ni}^{2+}$  contents ( $x = 1/2, 1/3, 1/4, 1/6$ , and 0). These calculations showed (1) that antiferromagnetic interactions between Ni and Mn are important in determining the energies of these structures, (2) some tendency for the  $\text{Ni}^{2+}$  and  $\text{Mn}^{4+}$  ions to order in alternating zig-zag rows of  $\text{Ni}^{2+}$  and  $\text{Mn}^{4+}$ , particularly for the  $x = 1/2$  sample, (3) evidence for local phase segregation to form  $\text{Li}_2\text{MnO}_3$  and  $\text{Li}(\text{NiMn})_{0.5}\text{O}_2$ -like local environments, for  $x < 1/2$ , (4) a preference of the Li in the Ni/Mn layers to occupy environments that are surrounded by predominantly  $\text{Mn}^{4+}$  ions. The lower energy structures predicted by calculations are consistent with the NMR ordering model.

NMR and XAS studies (with J. McBreen) of the 1<sup>st</sup> cycle for the  $x = 1/3$  and  $1/2$  samples have been completed. Voltages for Li removal from different Li sites have been calculated for the different cells, completing our work on Milestone (a). Investigations of the effect of cation-doping (e.g.,  $\text{Co}^{3+}$ ,  $\text{Nb}^{5+}$ ) and multiple charge cycles on local structure are underway. Cation-doped samples have been provided by M. Thackeray for NMR studies.

Nickel Content (x)	Li content in T.M. layers (%)	
	Predicted	Experiment
1/2	0	7(1.5)
1/3	8	10(2)
1/10	20	19(2)
0	25	22(3)

**Table 1.** Predicted vs. experimentally-determined Li contents in the Ni/Mn layers, as a percentage of the total Li content, for  $\text{Li}[\text{Ni}_x\text{Mn}_{(2-x)/3}\text{Li}_{(1-2x)/3}]\text{O}_2$ . Errors in the experimentally-determined values are given in parenthesis.

**Figure 1.** Li, Mn and Ni arrangements in the predominantly transition metal layers. The Li and Ni ions are represented by light and dark gray squares. Mn ions are present on the corners of the hexagons that surround each Li (or Ni) ion. Clustering of  $\text{Ni}^{2+}$  to form zig-zag chains is illustrated.



## TASK STATUS REPORT

**PI, INSTITUTION:** J. Evans and T. Devine, Lawrence Berkeley National Laboratory

**TASK TITLE - PROJECT:** Diagnostics - Corrosion of Current Collectors

**SYSTEMS:** Low-cost Li-ion

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

**OBJECTIVES:** Characterize the long-term corrosion performance of Al current collectors in Gen 2 chemistry baseline cells. Determine the mechanism of passivation in Gen 2 electrolyte and identify the passive film responsible for the corrosion resistance of Al current collectors in Gen 2 cells. Identify electrolytes of multi-component salts that are optimized for battery service and that are noncorrosive to Al current collectors.

**APPROACH:** Inspect for corrosion damage the Al current collectors taken from the many tens or hundreds of batteries that have been life-tested following a well-defined testing protocol. ATD Program cells are the most likely source of data. Analyze by Extreme Value Statistics the results of the failure analyses and predict 10-yr and 15-yr performance of Al current collectors in Li-ion batteries. Use a combination of electrochemical tests (anodic and cathodic polarization and concurrent measurement of mass change using electrochemical quartz crystal microbalance; electrochemical impedance spectroscopy) and surface analytical techniques (optical and scanning electron microscopy, energy dispersive x-ray analyses and Raman spectroscopy) to investigate the mechanism of corrosion and passivation of Al in baseline electrolyte and in other electrolytes relevant to Li-ion batteries (*i.e.*, electrolytes of multi-component salts that are noncorrosive and are optimized for battery service).

**STATUS OCT. 1, 2002:** Life-tested batteries that are to be autopsied for corrosion-related damage of current collectors have been identified and grouped according to the identities of the electrolytes, cathode materials, and testing protocol. Inspection of the current collectors from life-tested batteries has begun. Preliminary electrochemical experiments to investigate passive film formation on Al in Gen 2 electrolyte has been completed.

**EXPECTED STATUS SEPT. 30, 2003:** Characterization of the performance of Al current collectors in life-tested batteries will be complete. The 10-yr and 15-yr performances of Al current collectors in Gen 2 electrolyte will be calculated using Extreme Value Statistical Analyses. The accuracy of the predictions will be a function of the quantity and quality of the data acquired from the failure analyses. The mechanism of Al passivation in Gen 2 electrolyte will be determined. The mechanism of Al passivation in electrolytes of multi-component, non-corrosive salts will be well underway.

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

### MILESTONES:

- (a) 10-year and 15-year performance of Al current collectors in Gen 2 batteries will be predicted based on Extreme Value Statistical Analyses of life-tested cells by August 2003.
- (b) Mechanism of Al passivation in Gen 2 electrolyte will be determined by August 2003.

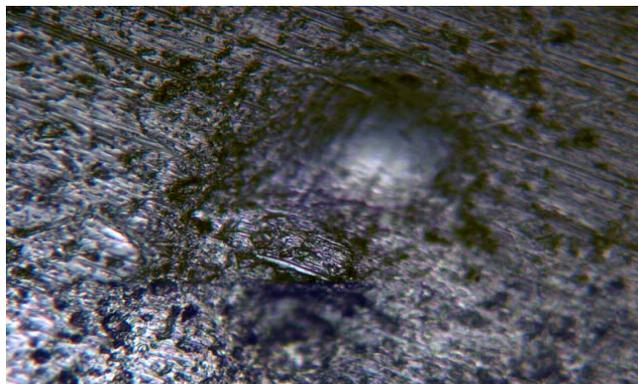
## PROGRESS TOWARD MILESTONES

In the past quarter, we collected and disassembled some used cells made at LBNL and commercial Li-ion batteries, corrosion was found on the surfaces of current collectors. In the most serious case, the current collector was fully corroded. The corrosion of Al foil in the cells can be classified from the morphology as uniform or localized corrosion (the latter being the pitting corrosion and crevice corrosion). The corresponding techniques for characterizing the corrosion are the EQCM and microscopy. Along with images of corrosion pits, the depth and the width of the pits as well as the ratio between the pit and sample area can be indices to evaluate the localized corrosion degree on the surface of the Al foil used as a current collector. Figure 1 shows the typical pits due to the corrosion on the surface of the current collector.

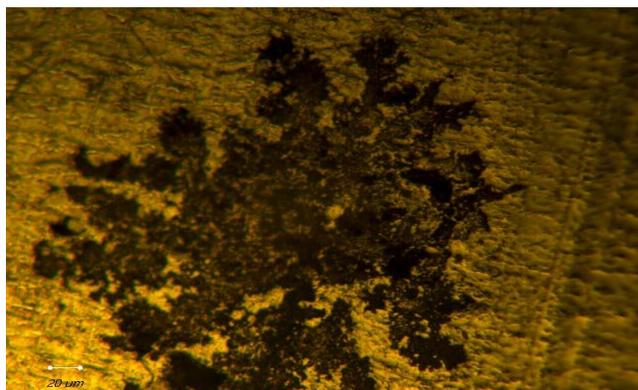
In the lab, we investigated the passivation and corrosion behavior of Al in 1.0 M  $\text{LiPF}_6/\text{EC}+\text{DMC}$  and 1.0 M  $\text{LiTFSI}/\text{EC}+\text{DMC}$  by EQCM and electrochemical methods. During the electrochemical measurement of Al in  $\text{LiPF}_6/\text{EC}+\text{DMC}$  electrolyte, mass increased due to the formation of corrosion products (or passivation). In  $\text{LiTFSI}/\text{EC}+\text{DMC}$  electrolyte, the corrosion product on the surface of Al showed no protection against the corrosion of Al. Under a potential of 5.0 V (vs. a Li reference) for 50000 secs, all the Al with the thickness of 1  $\mu\text{m}$  in 1.0 M  $\text{LiTFSI}/\text{EC}+\text{DMC}$  was corroded, while Al sample in  $\text{LiPF}_6/\text{EC}+\text{DMC}$  showed no obvious corrosion.

The influence of applied potential and current density on the corrosion of Al in 1.0 M  $\text{LiPF}_6/\text{EC}+\text{DMC}$  was studied. When the applied potential on the Al is over 7.5 V (an extreme potential) and the current is over  $3 \mu\text{A}/\text{cm}^2$  for 50000 secs, pitting and crevice corrosion occurred on the surface of the Al. The coating of graphite, active composite ( $\text{LiFePO}_4$ ) and PVC showed some inhibition of the corrosion of in 1.0 M  $\text{LiPF}_6/\text{EC}+\text{DMC}$ , while with some detachment of these coating, pitting corrosion also occurred on the surface without coating at high charging current density.

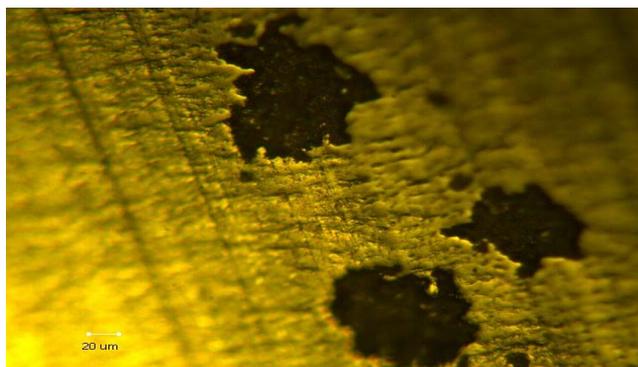
In the next quarter, we plan to make the Raman cell for the analyses of the passivation layer and corrosion products on the surface of Al in the battery electrolyte, then the mechanism of passivation of Al can be recognized. The analyses of corrosion from the used battery will be continued.



Commercial mobile phone battery, QualcoMM (the pit width is approximately 115  $\mu\text{m}$ )



LBNL-made Battery: 1SgAg8 (pit width is 400  $\mu\text{m}$ ; the depth is 8.8  $\mu\text{m}$ )



Part of the surface of Al foil without cathode composites in  $\text{LiPF}_6/\text{EC}+\text{DMC}$  (depth of the pits range from 8 to 10  $\mu\text{m}$ )

**Figure 1.** Typical pits on the surface of current collector.

## 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:** Side reactions, dendrite formation, low capacity, safety

**OBJECTIVES:** Develop experimental and computational methods for measuring and predicting 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 Li metal. Use simulations to improve understanding of the SEI layer. Use simulations to understand performance limitations of baseline BATT chemistries and to identify promising design options.

**STATUS OCT. 1, 2002:** Analysis of the effect of side reactions on measurements of transport properties is completed. Molecular-dynamics simulations of diffusion coefficients in multicomponent electrolytes such as  $\text{LiPF}_6$  in EC:DMC will be nearing completion. Diagnostic experiments of the SEI layer on lithium-tin electrodes are completed. Modeling of dendrite growth and initiation will be ongoing. Modeling of the SEI layer will be ongoing. Modeling the performance of baseline BATT chemistries  $\text{LiFePO}_4$  and  $\text{Li}_{0.4}\text{MnO}_2$  will be in progress. A preliminary model to describe the concentration and voltage profiles in polymer laminates will be completed.

**EXPECTED STATUS SEPT. 30, 2003:** Molecular dynamics simulations of diffusion coefficients will be completed. Modeling dendrite initiation in viscous and elastic electrolytes will be ongoing. Comparison of SEI simulations with experimental results and refinement of the model will be ongoing. Modeling of the performance limitations of  $\text{LiFePO}_4$  will be completed, and modeling of other BATT baseline chemistries will be ongoing. Simulation of the behavior of conductive polymers for overcharge protection will be completed. The model for the behavior of polymer laminates will be completed and compared to experimental data.

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

**MILESTONES:**

1. Develop model of electronically conducting polymers for overcharge protection by May 1, 2003.
2. Model of  $\text{LiFePO}_4$  and determination of performance limitations by August 1, 2003.

## PROGRESS TOWARD MILESTONES

Milestone 1: Experimental work was commenced to measure the equilibrium potential of the  $\text{LiFePO}_4$  material and obtain discharge data at various rates, in order to complement the previously developed mathematical model. The experimental results have allowed us to quantify the narrow single-phase regions through which diffusion of Li occurs. Comparing the model to the data shows that both the ohmic drop in the matrix phase and kinetic limitations contribute significantly to the total potential drop in the cell. However, the model shows that the most important contribution to the drop in accessible capacity at high rates is the *diffusion limitation* in the solid phase, which limits the capacity of the cell. These results explain why decreasing the particle size has a large effect on accessible capacity. Simulations are continuing to study the  $\text{LiFePO}_4$ /natural graphite baseline cell in order to gauge the maximum achievable specific energy and power.

Milestone 2: Experiments conducted by Guoying Chen with Tom Richardson have shown that electroactive polymers such as polythiophene can be mixed into the separator and used to protect cells against overcharge. The polymers become electronically conductive in the presence of a highly oxidizing potential such as occurs on overcharge. A model has been developed to understand how the short works. Essentially, the cell is transformed from a battery into a resistor whose resistivity varies with position across the separator. The resistor is then transformed back into a battery after the charging current is turned off. The simulations show that the polymer's degree of oxidation varies across the separator, being more oxidized (and thus more conducting) closer to the positive electrode, and confined to the neutral (insulating) state in a submicrometer-thick region adjacent to the negative electrode. Correspondingly, there is a large gradient in potential in the polymer adjacent to the negative electrode. The result is that the cell voltage is constant during overcharge, and this voltage depends *only* on the properties of the polymer short and is independent of the positive electrode chemistry. A simple analytic equation describes how the shorting voltage can be controlled by the separator thickness, the open-circuit potential and electronic conductivity of the polymer as functions of degree of oxidation, and the current density. The model matches experimentally observed trends of the effects of polymer conductivity and current density. Future work will analyze alternative configurations for the polymer short.

### Other Progress

Experiments are in progress (with John Kerr) to determine the effect of solvent molecular weight (and thus viscosity) on dendrite initiation, using PEO of varying molecular weights at  $85^\circ\text{C}$ . In addition, a stability analysis is being developed to theoretically elucidate the conditions necessary to prevent dendrite initiation.

A model of the SEI layer has been developed to understand how transport through the SEI layer affects battery operation. Modifications to the model are being made. A change of variables has been performed with hopes of accounting for space-charge regions in the film and improving the model's precision. Model performance with the variable change will be verified in the coming weeks.

## 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, 2002:** Confirm structure/function relationships in carbon additives in baseline systems. Determine effect of lamination on contact resistance in baseline systems. Determine initial relationship between ICL and conductivity of anode. Initiate testing of cathodes. Initiate simulations of cathode conductivity.

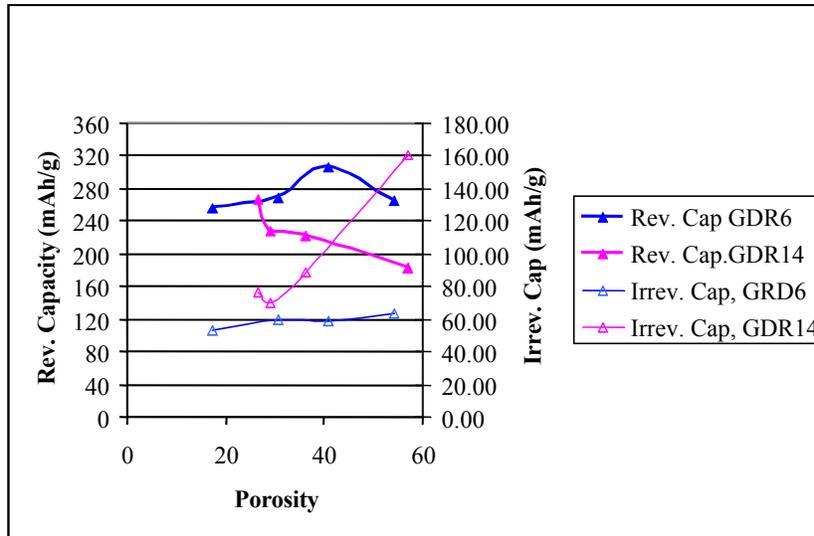
**EXPECTED STATUS SEPT. 30, 2003:** Experiments (LBNL and UM) and simulations on conduction in baseline anodes and cathodes, with correlations developed relating material composition and cell capacity losses will be completed. Modeling of other BATT Program baseline chemistries will be ongoing.

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

**MILESTONES:** (a) Determine relationship of ICL to electrode conductivities by May 2003.  
(b) Carry out simulations of conduction in cathodes with experimental verification by June 2003.

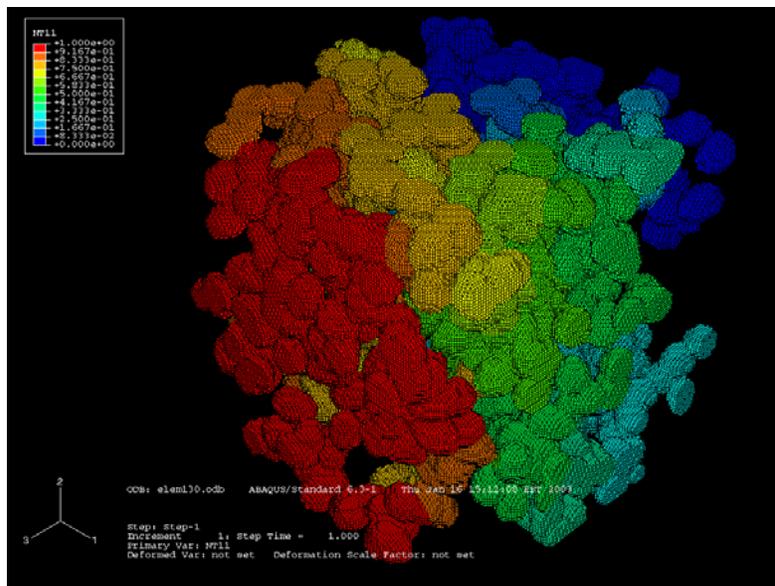
## PROGRESS TOWARD MILESTONES

This quarter, we completed initial analyses comparing performance to porosity in LBNL electrodes, per Fig. 1. We are thus near completion on milestone (a).



**Figure 1.** Reversible and irreversible capacities for GDR electrodes.

SEM image analysis suggests that lower porosities achieved via pressing of GDR14 electrodes may induce particle breakup, which results in increased irreversible capacity. We are presently investigating this hypothesis using detailed image analysis and comparison between conduction models assuming good and poor interfaces. We have also continued work on three-dimensional modeling of conduction in electrodes, since our analysis suggests that this may be important for cathodes (Fig. 2). The completion of this modeling work will allow us to complete milestone (b).



**Figure 2.** Pixillated model using 1M elements.

## PROPOSALS UNDER REVIEW

<b>ORGANIZATION</b> <i>(Principal Investigator)</i>	<b>TITLE</b>	<b>STATUS</b>
University of Utah <i>(G.D. Smith)</i>	A Molecular Dynamics Simulation Study of the Influence of Polymer Structure on Complexation Thermodynamics, Kinetics and Transport of Li Cations in Polyether-Based SPEs	Renewal Proposal- Contract Placed
Clemson University <i>(D. DesMarteau, S Creager)</i>	New Battery Electrolytes Based on Oligomeric Lithium bis((perfluoroalkyl) sulfonyl)imide Salt	Renewal Proposal- Contract Placed
North Carolina State Univ. <i>(S.A. Khan)</i>	Composite Polymer Electrolytes for Use in Lithium and Lithium-Ion Batteries	Renewal Proposal- Contract Placed
Hydro-Québec <i>(K. Zaghib)</i>	Research on Lithium-Ion Polymer Batteries Utilizing Low-Cost Materials	Renewal Proposal - Under Review
University of Texas at Austin <i>(J.B. Goodenough)</i>	Cathodes - Novel Materials	Renewal Proposal - Under Review
Massachusetts Inst. of Tech. <i>(G. Ceder)</i>	High Capacity, Stable Cathode Materials in Lithium and Lithium-Ion Batteries	Renewal Proposal - Under Review
SUNY @ Stony Brook <i>(C. Grey)</i>	An Investigation of the Stability of the Lithium Metal Interface	

# **BATTERIES FOR ADVANCED TRANSPORTATION TECHNOLOGIES (BATT)**

## **QUARTERLY REPORT FOR OCTOBER – DECEMBER 2002**

### **CALENDAR OF UPCOMING EVENTS**

#### October 2002

- 15 - 18 17<sup>th</sup> International Electric Vehicle Symposium & Exposition – Montreal, Canada (Ms. Pam Turner, EVS-17 Symposium Manager; (650) 365-2802; fax: (650) 365-2687; [electricevent17@aol.com](mailto:electricevent17@aol.com)).
- 6 - 11 202nd Electrochemical Society Meeting – Salt Lake City, UT (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; [ecs@electrochem.org](mailto:ecs@electrochem.org))

#### April 2003

- 27 - May 2 203rd Electrochemical Society Meeting – Paris France (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; [ecs@electrochem.org](mailto:ecs@electrochem.org); <http://www.electrochem.org/meetings/meetings.htm>)

#### June 2003

- 1 - 6 1st International Conference on Polymer Batteries and Fuel Cells (PBFC-1) – Jeju Island, Korea (Conference Headquarters Office, Department of Chemical and Biomolecular Engineering, KAIST, 373-1, Guseong-dong, Yuseong-gu, Daejeon, 305-701, KOREA; 82-42-869-3925; fax: 82-42-869-3910; [pbfc@pbfc.kaist.ac.kr](mailto:pbfc@pbfc.kaist.ac.kr); <http://pbfc.kaist.ac.kr>)
- 22 - 27 14th International Solid State Ionics Meeting - Monterey, CA (Turgut Gur, Stanford University, [turgut@stanford.edu](mailto:turgut@stanford.edu); <http://www.ssi-14.net/>), Asilomar

#### August 2003

- 31 – Sept. 5 54th ISE – Florianopolis, Brazil (Prof. L.A. Avaca)

#### September 2003

- 17 – 20 High Energy Density Electrochemical Power Sources – Nice, France (Marcelle Gaune-Escard, HEDEPTS 2003, Polytech'Marseille, IUSTI, 5 rue Enrico Fermi, 13453 Marseille cedex 13, France; 33 4 91 10 68 82; fax: 33 4 91 11 74 39; email: [battery@polytech.univ-mrs.fr](mailto:battery@polytech.univ-mrs.fr); <http://iusti.univ-mrs.fr/HEDES2003/index/html>)

#### October 2003

- 12 - 17 204th 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](mailto:ecs@electrochem.org); <http://www.electrochem.org/meetings/meetings.htm>)

#### May 2004

- 9 - 14 205th Electrochemical Society Meeting – Orlando, FL (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; [ecs@electrochem.org](mailto:ecs@electrochem.org); <http://www.electrochem.org/meetings/meetings.htm>)

September 2004

55th ISE – Thessaloniki, Greece (Prof. E. Theodoridou)

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](mailto:ecs@electrochem.org); <http://www.electrochem.org/meetings/meetings.htm>)