Ernest Orlando Lawrence
Berkeley National Laboratory
1 Cyclotron Road, 70R0108B, Berkeley CA 94720-8168
(510) 495-2679; fax: (510) 486-4260

February 24, 2006

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 2006 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/BATTreports.html.

Sincerely,

Venkat Srinivasan
Manager
BATT Program

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

BATT TASK 1
CELL DEVELOPMENT

TASK STATUS REPORT

PI, INSTITUTION: V. Battaglia, Lawrence Berkeley National Laboratory

TASK TITLE: Cell Development - Cell Fabrication and Testing

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

BARRIERS: Li-ion systems meeting performance, abuse, and life targets.

OBJECTIVES: Establish cell fabrication capability to evaluate BATT-developed, low-cost materials designed for high-power or high-energy.

APPROACH: Test novel materials in standard cells with preset protocols to provide the necessary link between the invention of novel battery components and the diagnostic evaluation of failure modes, and thereby accelerate the development of EVs, HEVs, and FCEVs. Incorporate novel components developed in the BATT Program into standardized cells, and test using a consistent protocol to determine cell capacity, energy, power, and lifetime characteristics. Optimize electrode configurations based on modeling results (task 6). Deliver tested cell components to appropriate investigators involved with BATT Program diagnostic projects (Task 5).

STATUS OCT. 1, 2005: The ability to make low-impedance cells repeatably should be in hand. Most materials that go into a battery, *e.g.*, active material and conductive additives, should be characterized with respect to BET, PSA, and SEM analysis. BATT Cell fabrication and test protocol will be released.

EXPECTED STATUS SEPT. 30, 2006: The ability to make cells with minimal introduction of contaminants should be in hand. Initial performance testing of an advanced high energy and an advanced high power system from materials from the BATT Program should be completed.

RELEVANT USABC GOALS: EV: specific energy of 300 Wh/L fully burdened. HEV: power density of 780 W/L fully burdened.

MILESTONES:
(1) January 2006 – Demonstrate batch-to-batch cell repeatability.
(2) June 2006 – Develop a test vessel optimized for BATT materials.
(3) June 2006 – Benchmark an advanced spinel system.
(4) September 2006 – Benchmark an advanced EV system

PROGRESS TOWARD MILESTONES

(a) Completed – During the last quarter of FY05 we showed we could make cells repeatably from batch-to-batch. Four new cells were fabricated that showed the same impedance and the same capacity as cells reported last May. The cells fabricated last May were tested in June and analyzed in July to have lost 50% of their capacity. We believed at the time that this was due to water intrusion. To test this theory, two of the four cells built in August were encapsulated in glass and tested side-by-side to two cells without the glass encasement. The glass encasement consisted of sandwiching the cells between two plates of glass and applying epoxy around the edges. After aging the cells for four weeks at 45°C, all four cells performed similarly, demonstrating a 50% loss of capacity. We now believe that the water is introduced during the fabrication process. This was further supported from trips to MSA, Yardney, and Quallion during the month of August where the need to keep water out of the cells during fabrication was emphasized. With this new found information we requested and were granted capital equipment money from FY05 to purchase a glove box into which we intend to move our battery components mixer and electrode fabrication table. The box arrived at the end of this quarter. It is our hope to have the box up and running by mid-February.

(b) On Schedule – Besides the glove box ordered in November, we also ordered two table-top boxes and acquired a new pouch sealer. We intend to move all of our cell fabrication equipment (mixer, coater, calender, punches, tab welding, and cell sealing equipment) into boxes under an inert atmosphere. We hope to have this reorganization of the lab completed by mid-February. Pouches with only electrolyte were made with the new pouch sealer and put in an oven at 45°C. After six months the pouches have shown no measurable weight loss. We believe by June we will have cells that are free of, and impermeable to, water. These cells will make for good vessels for studying BATT materials as they would be produced in an environment similar to that by a major cell manufacturer.

As we re organized the lab, we used some of the time during the last quarter to finish the basic characterization of the possible BATT baseline cell components. That involved completing the SEMs, BETs, and PSAs of twelve different cell components, including five cathode materials, four anode materials, and three conductive additives. Each analysis was performed three times to assure repeatability. A new website is being designed to allow for easy access of this ever growing database of component, half-cell, and full cell data.

(c) On Schedule – As part of the characterization of the Mn-spinel system, we intend to measure the solubility of the spinel in different electrolyte mixtures. Our hope is to provide a fundamental understanding of the solubility issue. Once our cell making capability is in place, we hope to test a material from Toda and compare it with a material from Manthiram's group.

(d) **On Schedule** – The highest energy density system of the BATT baselines is the one based on the 3 3rds material. Once our cell making capability is in place, we hope to make a cell designed for high energy and evaluate its cycle life.

TASK STATUS REPORT

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

TASK TITLE: Cell Development - Cathode, Anode, and Cell Development

SYSTEMS: Gr/$LiPF_6$+EC:DEC/$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (high-voltage, high-energy); Gr/LiBOB+γBL:EA/$LiMn_2O_4$ (high-voltage, high-power); Gr/$LiPF_6$+EC:DEC/$LiFePO_4$ (low-voltage, high-stability)

BARRIERS: Specific energy 150 Wh/kg, energy density 230 Wh/L, 30 ohm-cm^2 area-specific impedance.

OBJECTIVES: Synthesize and evaluate alternative electrode materials with improved energy density, safety, and stability. Support cell development and diagnostics tasks through chemical and structural characterization of cell components. Investigate mechanisms contributing to impedance rise in composite electrodes.

APPROACH: Identify candidate electrode compositions by systematic comparison of phase diagrams and literature reports. Prepare electrodes with novel materials and/or unique structures for evaluation in small cells. Employ x-ray diffraction (XRD), *in situ* microscopy, vibrational spectroscopies, and electroanalytical techniques to determine the applicability of the new materials to BATT chemistries. Investigate particle isolation mechanisms and their influence on power characteristics of composite electrodes.

STATUS OCT. 1, 2005: Composition and structural analyses of BATT electrodes will have contributed to our understanding of failure and degradation modes in the baseline systems. Overcharge protection for lithium ion cells with cathode potentials above 4.0 V will be achieved using electroactive conducting polymers. Operation of the overcharge protection mechanism at low temperatures and stable performance over 100 cycles will be demonstrated.

EXPECTED STATUS SEPT. 30, 2006: Potentially useful low-cost, high capacity electrode materials will have been prepared and evaluated. A detailed investigation of the mechanism and limitations presented by the $LiFePO_4$/$FePO_4$ phase transformation will be completed.

RELEVANT USABC GOALS: Specific energy 150 Wh/kg, energy density 230 Wh/L, 30 ohm-cm^2 area-specific impedance

MILESTONES: July 2006 – Determine capacity and cycling stability of lithium-magnesium alloy electrodes in liquid electrolyte cells.

PROGRESS TOWARD MILESTONES

Solid Solution Alloy Anodes: The large volume changes and substantial atomic rearrangements that accompany first-order phase transitions in conventional alloy electrodes result in exposure of fresh surfaces to the electrolyte, disconnection and isolation of active material, and inhomogeneous charge distribution. Cycling of a lithium alloy within a solid solution range (with a sloping potential vs. composition profile) may avoid these conditions and allow use of metal foil electrodes in rechargeable cells without formation of dendrites. In the lithium-magnesium system, a solid solution with the bcc lithium structure exists between 30 and 100 at % lithium, with an open circuit potential as high as 200 mV vs. Li. Although this alloy has been promoted extensively in the patent literature, very little has been published on the cycling behavior in lithium electrolytes, primarily due to the difficulty of obtaining and handling high quality samples.

$Li_{0.8}Mg_{0.2}$ foil was fabricated by melting the metals under argon in an open crucible and cold rolling the resulting ingot to a thickness of 0.5 mm. The alloy foil is bright and smooth, somewhat harder than lithium, but easily bent or cut. Preliminary cycling studies indicate that this composition resists dendrite formation and polarization at low current densities, but some diffusion limitations exist. Alloys with higher Mg content may show improved performance. Because these require higher processing temperatures, alternative synthetic routes may be useful. We have shown that cermets containing the desired alloy and an inert ceramic phase can be made by a simple and convenient metathesis reaction. This route may also be used to produce porous, but well-connected metal anodes with higher surface areas than foils.

Two-phase Cathodes: Although the “shrinking core” model for the $LiFePO_4$/$FePO_4$ system has found great popular appeal, it is physically incompatible with the known structure and chemical properties of the phases involved. We have prepared high quality single crystals of $LiFePO_4$ (Fig. 1) and are investigating the orientation and mechanism of propagation of the phase boundary using XRD along with microscopic, and spectroscopic techniques. In addition, we are seeking evidence for intermediate phases or solid solutions that may play a part in the phase transition.

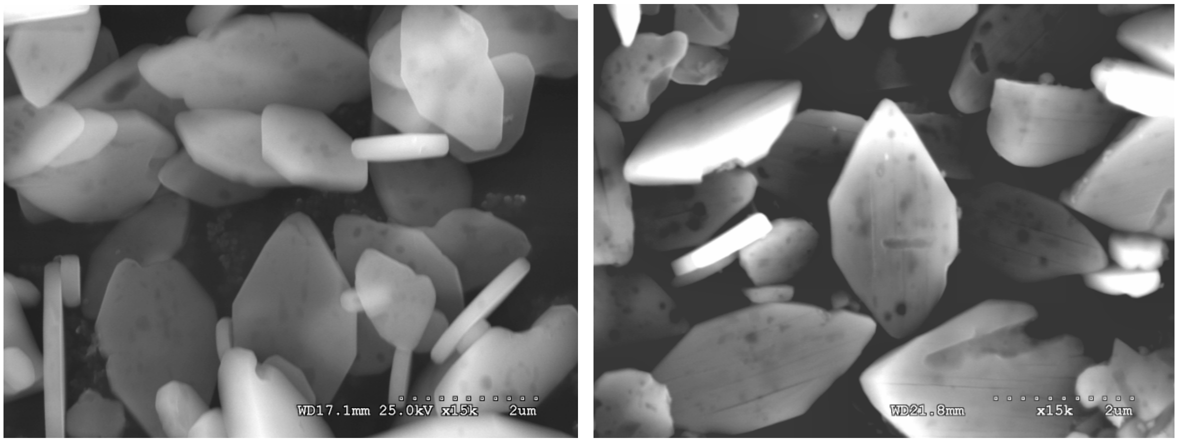


Figure 1. Hydrothermal crystals of $LiFePO_4$ (left) and $FePO_4$ (right).

TASK STATUS REPORT

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

TASK TITLE: Cell Development - Li-ion Polymer Batteries with Low-Cost Materials

SYSTEMS: Low-cost Li-ion

BARRIERS: High costs of Li-ion batteries

OBJECTIVES: Fabricate Li-ion/polymer cells using cell chemistries proposed by DOE and send cells to LBNL for testing. Optimize gel formation as a function of the % plasticizer content, optimize the thermal cross-linked temperature by using a new polymer with different molecular weights (2500, 5000 and 8000). Determine the conductivity of gel electrolytes as a function of plasticizer content, particularly, at low temperature. Study the interface of gel electrolyte in contact with the active electrode materials. Actively collaborate with polymer teams in the BATT Program. Continue developing water-soluble binder (WSB) for use in the anode and cathode. Continue a limited study on ionic liquid systems.

APPROACH: Synthesize and coat electrodes (both anode and cathode) with low-cost materials; evaluate these materials in Li-ion/polymer cells. In addition, focus on gel polymers, as well as studies to identify an appropriate salt and solvent to increase the performance and charge/discharge rate of Li cells at low temperatures. The gel electrolyte will be compared to a liquid electrolyte by measurements in half cells and Li-ion polymer cells at low temperatures.

STATUS OCT. 1, 2005: We will optimize the composition of anode and cathode materials in the electrodes as a function of the WSB (containing no fluoride), with the goal of reducing the amount of binder by 50% compared to standard electrodes with PVDF. To reduce the amount of binder and the cost of the coating, we will demonstrate a new coating process using the WSB in the anode and cathode with focus on $LiFePO_4$. Also, we expect to show the effect of the WSB on other baselines chemistries ($LiMn_2O_4$, $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$). Effort will be focused to understand the difference between WSB and PVDF electrodes in term of reversible and irreversible capacity. A limited effort will be focused on the effect of electrode drying; and the influence of temperature, time, and atmosphere in collaboration with LBNL (Kostecki). We expect to evaluate primary cycling data (including the PNGV protocol) from Li-ion/polymer cells containing WSB.

EXPECTED STATUS SEPT. 30, 2006: The cell configuration will be changed from the flat stainless-steel to metal-plastic type. HQ and LBNL teams will collaborate closely to fabricate better cells, beginning with a planned visit by the HQ team to LBNL in September 2005. We expect to show results on the effect of WSB (binder content, slurry viscosity, adhesion) on the cathode and the anode. The reversible and irreversible capacity of electrodes based on WSB will be compared to PVDF electrodes. Our collaboration with LBNL (Kostecki) on diagnostics will provide a better understanding of the effect of WSB and its difference with PVDF. Three different types of polymers, based on polyether as matrix, for gel electrolytes will be studied. Results will be obtained on optimizing gel formation as a function of plasticizer content and the cross-link conditions (temperature and time) after cell sealing. We expect to provide cycling data, including the PNGV protocol, in Li-ion polymer cells that contain gel electrolyte based on polymer-ionic liquid, polymer-liquid electrolyte and 100% liquid electrolyte.

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

MILESTONES: 1) Dec. 2005, Study the effect of drying temperature in WSB and understand the ICL loss *vs*. PVDF; 2) Dec. 2005, Deliver $LiFePO_4$ cells with WSB to LBNL for testing; 3) April 2006, Deliver cells with WSB in both of anode and cathode for testing.

PROGRESS TOWARD MILESTONES

During this quarter we continued efforts to optimize the assembly protocol, with particular emphasis on resolving problems in the cell assembly procedure. Some steps were modified and others were introduced in the protocol. Now, we are able to control all the assembly steps for laminated Li-ion cells. We plan to visit LBNL before April 2006 to discuss the new developments at HQ on cell assembly. The exchange of information is beneficial for HQ and LBNL to accelerate progress.

The second goal was focused on the water soluble binder (WSB) and $LiFePO_4$. A new generation of $LiFePO_4$ powder material was received from Phostech. This powder has a small particle size; the primary particles are less than 200 nm. This $LiFePO_4$ was recently introduced in our electrodes. The coating of this new generation of $LiFePO_4$ electrodes by using water soluble binder was successfully realized. Graphite anodes were also coated using WSB. Both cathode and anode were evaluated separately in coin-type cells in ECDEC-$LiPF_6$ with Li metal.

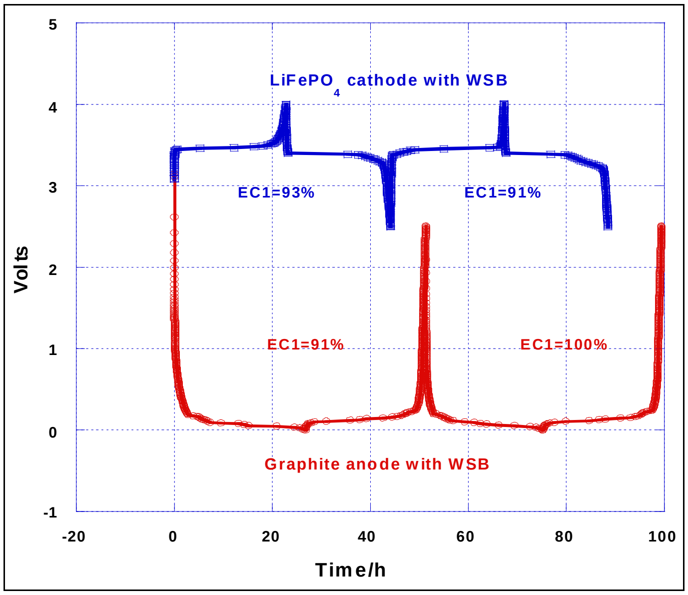


Figure 1. First two cycles at C/24 of $LiFePO_4$/Li and graphite/Li cells in ECDEC-$LiPF_6$, both electrodes are made with WSB.

The first two cycles at C/24 rate for the anode and cathode are shown in Fig. 1. The initial coulombic efficiency was 93% for $LiFePO_4$ cathode and 91% for graphite anode. The reversible capacities were 160 mAh/g and 370 mAh/g, respectively for the cathode and anode material. These encouraging data confirm the benefit of using WSB in both the anode and the cathode. Furthermore, this allows us to make a WSB Li-ion battery without using any fluorinated binder. Cells based on theses electrodes will be prepared and delivered to LBNL in January 2006.

For the third goal, we studied the effect of gel polymer formation on cell performance. Three cases were considered. In the first case, the gel was crosslinked before formation in the Li-ion cell. In the second case, the gel was crosslinked after cell formation. In the third case, the cell was first formed in liquid electrolyte, and the gel polymer was added after degassing. This experimental plan shows very beneficial data for cell performance with gel polymer. The cell where gel was introduced after formation in liquid media showed the best electrochemical results.

The milestone for January 2006 is to send Li-ion cells to LBNL for evaluation. Ten cells are under formation at HQ and will be sent shortly after degassing is complete.

TASK STATUS REPORT

PI, INSTITUTION: D. Wheeler and J. Harb, Brigham Young University

TASK TITLE: Cell Development - Design, Optimization, and Fabrication of Li-ion Electrodes for High Power Applications

SYSTEM: Low-voltage, high-stability: Gr/$LiPF_6$+EC:DEC/$LiFePO_4$

BARRIERS: Electrode impedance that limits power density and cycle life

OBJECTIVES: Improve battery power and life through novel electrode structures. Increase understanding of how electrode morphology influences performance. Develop tools to analyze high-rate performance of electrolytes.

APPROACH: We will explore methods for maximizing the high-power performance of low-cost $LiFePO_4$ composite cathodes. Our efforts will include the use of carbon fibers as conductivity additive in order to improve high-rate performance and diminish capacity fade due to loss of conductivity/connectivity. We will also seek to improve point-to-point electronic connections between the fibers, active material particles, and current collector. In addition, as part of our efforts to optimize ionic conduction, we will conduct Hall-effect experiments and molecular dynamics (MD) simulations in order to determine transport properties for liquid electrolytes.

STATUS OCT. 1, 2005: We will have demonstrated the power improvements possible with carbon fibers added to $LiFePO_4$ cathodes. Processing steps for the mixing and application of improved cathode slurries will also have been demonstrated. Construction of apparatus for obtaining electrolyte transference number using the Hall Effect will be nearly complete. New intermolecular potentials for MD simulations of the transport properties of $LiPF_6$ in liquid carbonate electrolytes will be nearly ready for use.

EXPECTED STATUS SEPT. 30, 2006: We will have optimized for the power improvements possible with use of carbon fibers in low-cost $LiFePO_4$ cathodes, and identified the additional factors that limit performance. We will have shown proof-of-concept results for obtaining the electrolyte transference number using the Hall Effect. MD simulations of the transport properties of $LiPF_6$ in liquid carbonate electrolytes, as a function of temperature and concentration, will be completed.

RELEVANT USABC GOALS: HEV goals of 30 $\Omega\text{-cm}^2$ ASI, discharge power around 650 W/kg for 10 s, and sufficient cold-cranking power.

MILESTONES:
(1) January 2006 – Demonstrate that Hall Effect can be used to reliably measure electrolyte transference numbers.
(2) May 2006 – Optimization of $LiFePO_4$ cathode by varying active-material loading, carbon-fiber length, and amount of conductivity additive.

PROGRESS TOWARD MILESTONES

Our primary tasks are to fabricate and test cells in order to determine the optimal compositions with respect to high-rate HEV performance for carbon-fiber containing $LiFePO_4$ cathodes, and to better understand the associated physical processes. As described more fully below, during the first quarter of FY2006 we began testing the interaction of carbon fibers with the carbon-coated aluminum current collector. We also began training a student on an AFM/STM instrument in order to explore the nature of the point-to-point connections between carbon fibers and $LiFePO_4$ particles. The remainder of our activities concern developing diagnostics for understanding ion transport in liquid electrolytes. We made modest progress on developing a new set of intermolecular potentials to simulate ion transport in mixed-carbonate solvents by molecular dynamics. We continue to work through instrumentation challenges that arise in the completion of a new Hall-effect-based tool to directly measure ion transference numbers—a mass-transport property that is difficult to obtain—as a function of composition and temperature. The challenges include corrosion of electrodes under operation and the presence of significant noise on the output signal. Completion of Milestone (a) will be delayed until the challenges can be overcome.

We have begun a set of experiments to examine possible advantages of fibers beyond simply increasing power density of electrodes. Figure 1 shows preliminary results for ASI tests of half-cells utilizing carbon-coated $LiFePO_4$ cathode material and (in some cases) carbon-coated current collector, both supplied by Hydro-Québec. The cathodes contained a total of 7.8% (by dry weight) carbon additives to promote electronic conductivity. “Fibers only” cells contained no conductivity additive other than carbon nanofibers from Pyrograf Products, Inc. The remaining cells contained equal mass amounts of carbon black and graphite (CB+GR) as conductivity additives. As expected, the cells without carbon-coated current collector (CCCC) show higher ASIs as compared to cells with CCCC. However, the advantageous effect of the carbon-coated current collector is significantly less in the fiber-containing cells and the performance of non-CCCC fiber-containing cells appears to be less variable than the baseline case. These results seem to indicate that carbon fiber partially compensates for the lack of a CCCC. We are currently testing other fiber compositions with the hope that the CCCC may be made redundant, which would simplify cathode fabrication.

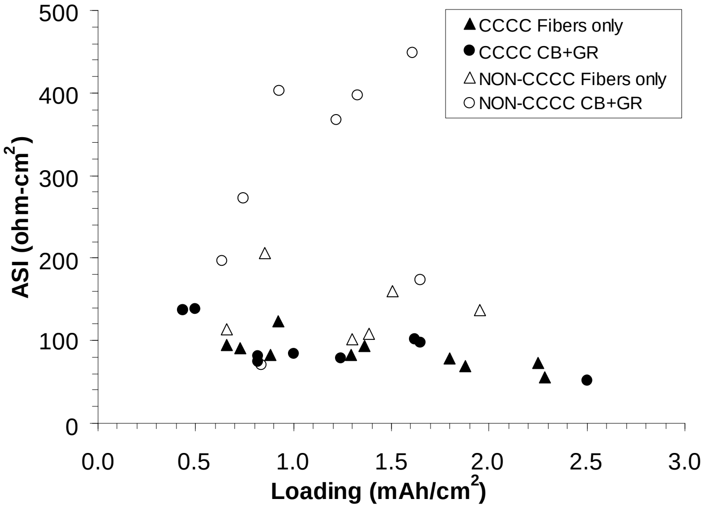


Figure 1. Area-specific impedance (ASI) *vs.* loading for fiber and non-fiber (CB+GR) cells, with and without the carbon-coated current collector (CCCC). Tests were conducted at 50% depth of discharge at 5C-rate discharge for 10 s.

BATT TASK 2
ANODES

TASK STATUS REPORT

PI, INSTITUTION: M. Thackeray, Argonne National Laboratory

TASK TITLE: Anodes - Non-Carbonaceous Anode Materials

SYSTEMS: Graphite/$LiPF_6$+EC:DEC/$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$; Graphite/LiBOB+$\gamma$BL:EA/$LiMn_2O_4$

BARRIER: Cost, low temperature- and abuse tolerance limitations of Li-ion batteries

OBJECTIVES: To replace graphite with an alternative inexpensive anode material that will be compatible, in particular, with low-cost manganese oxide cathodes. The project addresses the need to improve the capacity, rate capability and irreversible capacity losses of intermetallic electrodes as well as the low temperature operation and abuse tolerance of Li-ion cells.

APPROACH: Our approach over the past few years has been to search for inexpensive intermetallic electrodes (powder laminates rather than thin films) that provide 1) an electrochemical potential a few hundred mV above the potential of metallic Li, and 2) a capacity of at least 300 mAh/g (>1000 mAh/ml). We are focusing predominantly on Sn-based systems that appear to have a good chance of success in practical cells (cf. Sony 'Nexelion' cells). We will continue to study Sb and Si systems as these systems provide valuable information about reaction mechanisms and first-cycle irreversible capacity loss. We will continue our studies of FMC Corporation's stabilized lithium metal powder product (Lectro^{TM} Max Powder) in an attempt to eliminate first-cycle irreversible capacity loss. Promising electrodes will be evaluated in full cells against the high capacity metal oxides of our cathode project (Task 4.1).

STATUS OCT. 1, 2005: Studies of Lectro^{TM} Max powder (formally called SLMP) were initiated. Tentative conclusions from the studies were: 1) Lectro^{TM} Max reacts more readily with insertion compounds (e.g., graphite and $Li_4Ti_5O_{12}$) than with those that operate by displacement reactions (Cu_6Sn_5, Cu_2Sb, SnO), and 2) that Lectro^{TM} Max was more effective in countering the first-cycle capacity loss of graphite electrodes than intermetallic electrodes (*e.g.*, Cu_2Sb) and metal oxide electrodes (*e.g.*, SnO_x). Rate studies showed that Cu_6Sn_5 performs better then Cu_2Sb at room temperature and at 0°C.

EXPECTED STATUS SEPT. 30, 2006: Progress will have been made in reducing the first-cycle capacity loss of Sn-based intermetallic electrodes with Lectro^{TM} Max; capacity retention on cycling will have been improved and the performance of the intermetallic electrodes against the metal oxides of Task 4.1 in full cells determined. A comparison of the low temperature behavior and rate capability of intermetallic electrodes *vs*. graphite electrodes will have been made.

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

MILESTONES:
(1) September 2006 – Achieve less than 10% first-cycle capacity loss of Sn-based intermetallic electrodes and >300 mAh/g for more than 100 cycles. Determine low temperature capability
(2) September 2006 – Evaluate performance of intermetallic/lithium metal oxide

PROGRESS TOWARD MILESTONES

Accomplishments

We are studying the low temperature electrochemical properties of intermetallic electrodes. Specifically, we have investigated the low temperature properties of Cu_6Sn_5 and Cu_2Sb anodes in full cells (2032 coin-type) with ATD Gen 2 cathodes ($LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$) and Gen 2 electrolyte (1.2 M $LiPF_6$ in EC:EMC, 3:7 weight ratio).

Tests were conducted on $Cu_6Sn_5/LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ cells from room temperature to -30°C (Figs. 1 and 2). Cells were cycled between 4.1 and 2.1 V, ensuring that the potential of the Cu_6Sn_5 electrode did not fall below 0 V *vs.* Li^0. Capacity versus temperature data for 1.6 mAh cells showed the expected drop-off in capacity as the cell operating temperature was lowered. This behavior, which also occurs in Li half-cells with Cu_6Sn_5 and carbon anodes, and in full ATD Gen 2-type cells, is attributed to poor Li diffusion at the electrolyte/SEI interface as the temperature decreases, particularly below 0°C. Possible factors that may limit Li^+-ion diffusion at low temperature include a stronger solvation sphere around the lithium cations, crystallization or partial crystallization of an electrolyte-solvent polymeric species in the SEI layer, or restricted anionic motion in the SEI layer. HPPC tests (evaluated at ~0.4 mAh discharge; 10-sec discharge pulse; 2-sec charge pulse) showed a significant increase in ASI at lower temperatures, reaching ~1000 ohm-cm^2. Cells with Cu_2Sb anodes displayed similar behavior (Figs. 3 and 4). It is unlikely that Li plating occurred on the Cu_6Sn_5 and Cu_2Sb electrodes during these HPPC tests because they discharge their capacity several hundred mV above the Li^0 potential.

In addition to these low temperature studies, work continues on Sony-type cobalt-tin intermetallic electrodes, and on studies of stabilized Li metal powder (SLMP, Lecto^{TM} Max) electrodes in collaboration with FMC Corporation.

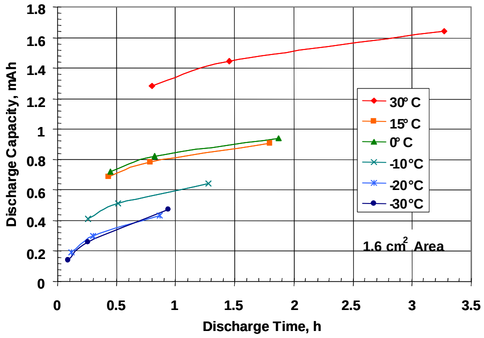


Figure 1. Cu_6Sn_5 cells: Capacity *vs.* discharge time at various temperatures.

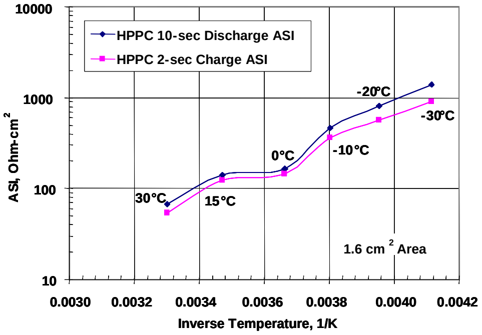


Figure 2. Cu_6Sn_5 cells: HPPC test as a function of temperature.

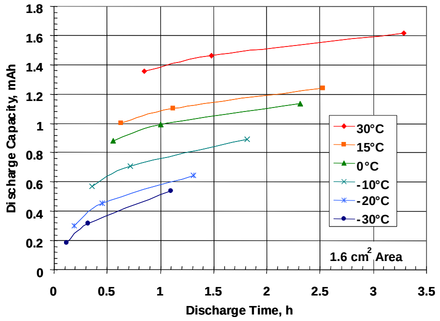


Figure 3. Cu_2Sb cells: Capacity *vs.* discharge time at various temperatures.

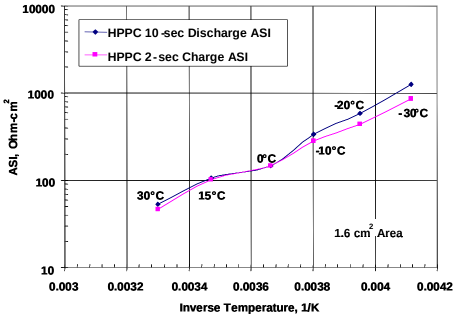


Figure 4. Cu_2Sb cells: HPPC test as a function of temperature.

TASK STATUS REPORT

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

TASK TITLE: Anodes - Novel Materials

SYSTEMS: Li-Ion: all systems.

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

OBJECTIVES: To replace the presently used carbon anodes with safer materials that will be compatible with low cost manganese oxide and phosphate cathodes and the associated electrolyte.

APPROACH: Our anode approach is to explore, synthesize, characterize and develop inexpensive materials that have a potential around 500 mV above that of pure lithium (to minimize risk of lithium 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, 2005: We have shown that bulk vanadium and manganese oxides, in their highest oxidation states, are not prime candidates. Pure aluminum foil, expanded metal and aluminum alloys were found to have a high capacity, react readily with lithium but their capacity faded rapidly on cycling in carbonate-based electrolytes. Tin containing materials such as $MnSn_2$ cycle well for a few cycles before capacity fade sets in. Pure tin foil anodes of grain size below a micron cycle better, but the cell impedance was found to increase markedly after about ten cycles.

EXPECTED STATUS SEPT. 30, 2006: From our program to understand capacity fade of tin on cycling, we expect to have defined the key parameters determining capacity loss, to have determined the impact of tin morphology on capacity fade, to have studied electrical connectivity by using a reactive support, and to have improved the electrochemical performance of the materials identified. Specifically we will know how the surface of tin changes on cycling, and what impact the depth of discharge has on capacity retention. We will also have begun to have an understanding of whether going nano will help solve the anode issues or exacerbate them.

RELEVANT USABC GOALS: 300,000 shallow discharge cycles, and abuse tolerance to cell overcharge and short circuit

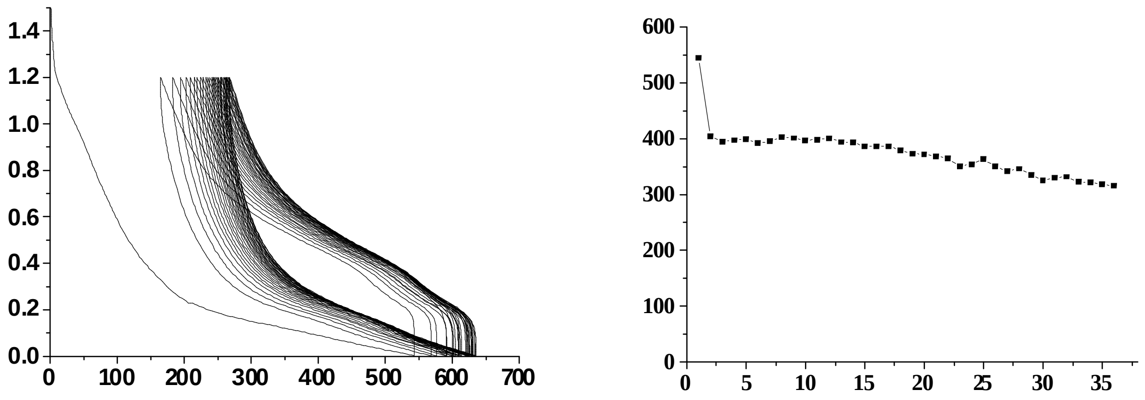
MILESTONES:
(1) July 2006 – Identify the surface changes on tin foil during cycling and as a function of the electrolyte working collaboratively with LBNL.
(2) August 2006 – Define the key parameters determining capacity fade in pure tin and its alloys, and determine and understand impact of depth of cycling on capacity fade (HEV *vs*. EV).

PROGRESS TOWARD MILESTONES

In previous quarters we reported the electrochemistry of tin foil and expanded tin grids, and showed that they had higher capacities than graphite as the host for lithium. However, the capacity rapidly decays after 10 to 15 cycles to values comparable to that of graphite. Earlier we discussed the cycling of the Sn_2Mn and Sn_2Co phases, which showed initially a high capacity that fell off just as for tin itself.

This quarter we continued our evaluation of the impact of using an amorphous tin material of nano-particle size, to determine if our project should place more emphasis on amorphous rather than crystalline anode materials. We obtained a commercial tin-cobalt anode material and evaluated its electrochemical behavior. It was found to be essentially amorphous, with no obvious crystalline phases; electron microprobe analysis indicated a tin to cobalt ratio consistent with the composition Sn_2Co plus a little titanium, the carbon content was low if any was present. A TEM analysis showed grain sizes of the order of 10 nm.

The electrochemical behavior of this amorphous tin-cobalt anode is shown in Fig. 1, for cycles at 1 mA/cm^2. The discharge and charge curves show none of the two-phase behavior typical of crystalline tin; rather they show behavior typical of a single-phase reaction. The first lithium insertion approaches the theoretical maximum of around 610 mAh/g if all the tin reacts to give $Li_{3.5}Sn$ as with tin foil. Around 200 mAh/g is lost after the first cycle and we are exploring to see whether this is due to an impurity or inherent in this material. In both cases a significant fraction of the reacted lithium could not be recovered on the charging cycle. After this first cycle loss, however, the capacity is retained much better than found for the crystalline tin samples which leads us to believe that the decrepitation of the electrode (and the resulting impedance increases) is much diminished by using nano-sized particles which have no long-range crystalline ordering.



(a) (b)

Figure 1. Electrochemical behavior of amorphous Sn_2Co; (a) smooth cycles showing single phase type behavior and (b) capacity retention on cycling; both were cycled at a current density of 1 mA/cm^2.

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

Publications and Presentations resulting from the work.

1. Quan Fan, Peter Y. Zavalij and M. Stanley Whittingham, "New Anode Materials for Lithium Batteries," Mater. Res. Soc. Meeting, Boston, December 2005.

TASK STATUS REPORT

PI, INSTITUTION: A. West, Columbia University

TASK TITLE – PROJECT: Anodes - An Investigation of the Stability of the Lithium Metal Interface

SYSTEMS: Li/Polymer/$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$

BARRIERS: Interfacial instability (dendrite formation) during charge of Li metal anodes leads to limited cycle life

OBJECTIVES: Understand the influence of electrolyte composition, deposition rate, and applied potential on interfacial stability of Li in liquid and polymer electrolytes. Investigate the root causes (mechanisms) of dendrite formation.

APPROACH: Dendrite formation and growth will be monitored by electrochemical and optical methods as a function of electrolyte composition and applied potential. In an attempt to study the cause or causes of dendrite formation, the impact of pulse plating parameters on dendrite formation will be considered. Furthermore nucleation and growth of Li deposits will be characterized by electrochemical methods.

STATUS OCT. 1, 2005: Glove box and other laboratory equipment will be purchased and assembled.

EXPECTED STATUS SEPT. 30, 2006: An investigation of the impact of deposition conditions on dendrite formation and growth in select liquid electrolytes will be completed. Methodologies for characterization of dendrite formation will have been evaluated. Plans to transition the work to include polymer electrolytes and to test theoretical stability models will be on-going.

RELEVANT USABC GOALS: Specific Energy = 200 Wh/kg and Specific Power = 400 W/kg; Energy Density= 300 Wh/l and Specific Power= 600 Wh/l; 1000 cycles

MILESTONES:
(1) March 2006 – Establish Columbia University experimental setup and evaluate methods of characterizing dendrite formation.
(2) September 2006 – Quantify the influence of electrolyte properties and deposition conditions on dendrite formation and grown.

PROGRESS TOWARD MILESTONES

This is a new project, commencing in September 2005. Based on discussions with and feedback from BATT Program investigators, we have established the preliminary methodology for building lithium metal batteries. Furthermore, an existing student, Owen Crowther, has been transitioned to this project. Hence significant progress toward milestone 1 has been made.

We have coordinated with Gao Liu at LBNL to build the laboratory set-up needed to conduct the necessary Li deposition experiments. We have purchased and set up a glove box (with the exception of a humidity sensor). A swagelok cell has been built, and data from cyclic voltammetry experiments using the cell with a Ni/$LiPF_6$ in DMC/Li system match published results. It has been determined that the high water content of the electrolyte led to a large ohmic resistance so high-purity electrolyte that will be used to accomplish our second milestone has been purchased from the Ferro Corporation. Furthermore, the cell will be modified to permit three-electrode measurements.

Also, rudimentary linear stability analysis theory has been studied to establish a framework to approach Li dendrite formation under pertinent conditions. It is our goal to correlate the theory to experimental data to better understand Li dendrite formation. An extensive literature survey is in progress to determine the best electrochemical methods to study lithium dendrite formation and growth.

Also, a trip has been planned to visit A. Ghosh-Dastidar and Susan Babinec at Dow Chemical Company during February to discuss their Li battery research. It is our hope that these discussions will possibly lead to new research collaboration.

BATT TASK 3
ELECTROLYTES

TASK STATUS REPORT

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

TASK TITLE: Electrolytes - Development of Polymer Electrolytes for Advanced Lithium Batteries

SYSTEMS: Li/polymer/$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$

BARRIERS: Dendrite formation in Li-metal batteries leading to short lifetimes.

OBJECTIVES: Study the stability of PS-PEO electrolytes against Li electrodes. Synthesize PS-PEO diblock copolymers to obtain electrolytes with high ionic conductivity and shear modulus. Establish a laboratory dedicated for sample preparation and physical characterization of dry polymer electrolytes

APPROACH: Synthesize and characterize robust nanostructured dry polymer electrolytes with high conductivity and high shear modulus that resist dendrite growth during cell cycling. Synthesize polymer and characterize salt/polymer mixtures using AC impedance spectroscopy. Test promising candidates for stability against Li electrodes and in Li cells in collaboration with members of the BATT Program. Fully characterize the materials of interest using additional methods such as neutron and light scattering, rheology, and transmission electron microscopy.

STATUS OCT. 1, 2005: A series of polystyrene-polyethyleneoxide (PS-PEO) block copolymers have been synthesized. Mechanical and electrical properties of a 60 kg/mol, 0.38 volume fraction PS-PEO copolymer with added $Li[N(SO_2CF_3)_2]$ will be measured using rheology and AC impedance spectroscopy. The morphology of the systems will be fully characterized by X-ray scattering and electron microscopy.

EXPECTED STATUS SEPT. 30, 2006: Continued characterization of nanostructured PS-PEO electrolytes including stability tests against Li electrodes and cell testing. Better understanding of polymer structure using microscopy and scattering. Examine dependence of parameters such as molecular weight, volume fraction, sample thickness, and rheological properties on behavior of solid polymer electrolyte. Build a new laboratory at Lawrence Berkeley National Lab for physical characterization and preparation of dry polymer electrolytes. Equipment will be a top-of-the-line glovebox containing an automated sample press, a rheometer, AC impedance measurement, and a Li electrode deposition system.

RELEVANT USABC GOALS: Specific Energy = 200 Wh/kg and Specific Power = 400 W/kg; Energy Density= 300 Wh/l and Specific Power= 600 Wh/l; 1000 cycles

MILESTONES:
(1) February 2006 – Determine stability of current dry polymer electrolyte against Li electrodes.
(2) September 2006 – Characterize new dry electrolytes.

PROGRESS TOWARD MILESTONES

Nanostructured Polymer Electrolytes.

We have established that by using a polystyrene-b-polyethyleneoxide (PS-*b*-PEO) diblock copolymer we can combine the mechanical stability of PS with the ionic conductivity of PEO. Since then, we have made conductivity measurements on a range of PS-*b*-PEO diblock copolymers in order to understand and optimize the ionic conductivity in these materials. The diblock copolymers were synthesized to access a large range of PEO molecular weight and volume fraction in the diblock system. We have characterized these systems by using GPC, NMR, and SAXS. We have also made AC impedance measurements on Li salt/copolymer mixtures. These measurements have shown very interesting results. The data indicate a lack of correlation between the ionic conductivity of these electrolytes and the volume fraction of PEO in the system, but a positive correlation between the ionic conductivity and the PEO molecular weight in the copolymer (Fig. 1: each set of data represents a different copolymer). This result, although somewhat counterintuitive, is very encouraging as it allows us to optimize the ionic conductivity of the electrolyte by simply changing the molecular weight of the PEO block in the copolymer.

We have also tried to address the engineering issues with the processing of the electrolyte for the fabrication of a scalable membrane electrode assembly. One of the challenges with the implementation of our PS-*b*-PEO-based electrolyte is its brittleness. We have solved this problem by synthesizing a polystyrene-b-polyisoprene-b-polyethyleneoxide (PS-*b*-PI-*b*-PEO) triblock, thereby adding a rubbery polymer to the matrix and making it more flexible without any significant loss of ionic conductivity (Fig. 1).

In order to characterize the PS-*b*-PEO based electrolytes we have performed a few experiments with non-blocking Li electrodes using both DC and AC voltages. With the help of these experiments we have been able to identify a good design for the membrane electrode assembly (MEA), and its fabrication process. We have designed MEAs that allow us a direct way of introducing a reference electrode for all DC measurements. We have also designed a hermetic chamber that can hold up to 30 such MEAs in an argon atmosphere for a parallel analysis. We have also established the process of depositing Li directly onto our electrolyte films, minimizing the interfacial resistance issues. For this quarter, we are focusing on DC measurements in order to establish the electrode-electrolyte stability (interfacial resistance and dendrite formation) and cycling efficiency.

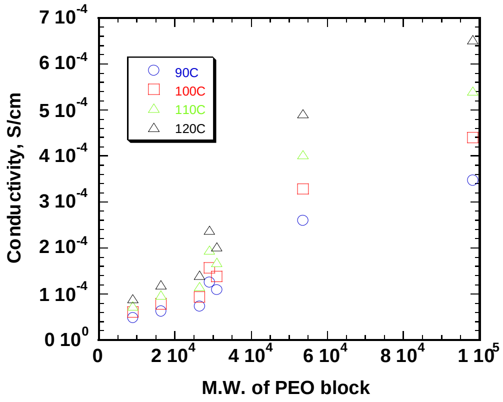


Figure 1. Ionic conductivity of electrolytes based on PEO containing copolymers *vs.* the molecular weight of PEO block in the copolymer. The [LiTFSI]/[EO] ratio is approximately 0.02 for all the electrolytes. The lowest PEO MW copolymer is PS-*b*-PI-*b*-PEO triblock.

TASK STATUS REPORT

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

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

SYSTEMS: Gr/$LiPF_6$+EC:DEC/$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (high-voltage, high-energy); Gr/LiBOB+γBL:EA/$LiMn_2O_4$ (high-voltage, high-power); Gr/$LiPF_6$+EC:DEC/$LiFePO_4$ (low-voltage, high-stability)

BARRIERS: Poor electrolyte transport and low power, particularly at low temperatures, short life due to power and capacity fade, low abuse tolerance.

OBJECTIVES: Determine and quantify the improvement (if any) in abuse tolerance of polymer gel electrolytes over liquid electrolytes. Determine the limitations on Li-ion transport in polymer gel electrolytes and the electrolyte component of composite electrodes and develop materials capable of high power operation at ambient temperature with lithiated carbons/Li metal alloy anodes and high voltage cathode materials. Determine the feasibility of the use of Li metal and lithium alloy electrodes with polymer gel electrolytes and provide operating conditions that prevent dendrite growth and provide high coulombic efficiencies (>99.9%) at HEV rates as well as under EV cycling conditions.

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, 2005: The effects of gels on abuse tolerance and transport properties will be determined. The transport performance of single-ion conductor gels will be compared with the binary systems. Compatibility of the polymer electrolyte and polyelectrolyte gels with lithium metal, graphite electrodes and composite cathodes will have been explored, with particular reference to the interfacial impedance.

EXPECTED STATUS SEPT. 30, 2006: The effects of impurities such as water on the impedance behavior of liquid and polymer gel cells will be determined for both calendar and cycle life cells. The effects of polymer gels on the impedance behavior of base line cells will be ascertained for gels that do not penetrate the composite electrodes. Exploratory experiments will be carried out for lithium alloy anodes with elastic binders.

RELEVANT USABC GOALS: 15 year life, <23% power fade, 30 ohm-cm^2 area-specific impedance, cold cranking capability to -30^oC, 300,000 shallow discharge cycles, and abuse tolerance to cell overcharge, short circuit and high temperatures (>60^o).

MILESTONES:
(1) September 2006 – Quantify the effect of impurities such as water on interfacial properties for liquid and gel electrolytes.
(2) September 2006 – Quantify the effect of gel polymer electrolytes on interfacial properties relative to liquid electrolytes.

PROGRESS TOWARD MILESTONES

1. Abuse Tolerance of Electrolytes. DSC measurements are in progress on base line electrolytes and electrolyte components with and without the presence of electrode components (anodes, cathodes, current collectors and electrode powders). The effect of impurities such as water (see 4 below) and the influence of the salt anion (PF_6 *vs.* BOB, TFSI) on the thermal stability are under study by DSC, aging and follow-up chemical analysis. For example, samples of EC/EMC with 1.2M $LiPF_6$ and added PEGDME 250 and 500 solidified after three months in an oven at 85°C while identical samples with the $LiPF_6$ replaced with LiTFSI remain liquid and clear after the same treatment. Chemical analysis of these samples is still pending. Kinetic experiments are planned to compare the stability of the base-line liquid electrolytes, gelled electrolytes, phase separated gels (PVDF) and single ion conductor polyelectrolyte gel electrolytes. In addition to DSC measurements, ARC calorimeter measurements are in preparation.

2. Transport Properties of Polymer Gels. Transport properties of polymer gel electrolytes are measured as a function of temperature. This includes a range of temperature from -30°C to + 60°C as well as the effects of accelerated calendar life and the presence of additives such as fumed silica that simulate the effect of the electrode surfaces on the mobility of the electrolyte components. Typical measurements are conductivity, salt diffusion coefficients and concentration cell potentials. In general, electrolytes which are gelled with fully swollen polymers exhibit slower ion transport properties than the corresponding liquid electrolytes.

3. Interfacial Impedance Behavior of Electrolytes. Impedance measurements of baseline electrolytes, gelled electrolytes and single ion conductor gel electrolytes at lithium metal and composite cathodes show increasing interfacial impedance as the mobility of the anion decreases. Studies of carbon anode electrodes are also planned once the method for measurement of the water content is completed.

4. Effects of impurities, particularly water, on interfacial behavior of electrolytes. Karl-Fischer titration measurements using a new oven attachment and methods developed at EMD/Mettler-Toledo will be used to accurately measure the water content of the cells and electrode components. Work is proceeding on method development. It is planned to determine the relationship between water content and electrochemical behavior (ASI, corrosion, capacity fade, etc.).

5. Mechanical Properties of Polymer Gel Electrolytes. Polymer gels provide opportunities for cost savings. They can act as the separator and eliminate the need for Celgard. They also provide adhesion for the electrodes thereby eliminating the need for pressure and expensive metal can packaging. To do this correctly requires knowledge of the mechanical properties of the polymer gels. Some of these systems are candidates to form protective films on lithium metal electrodes as well as highly elastic binders for large volume expansion alloy electrodes. Methods to measure the mechanical properties are under development using a Triton DMA which is capable of measurements of materials while completely immersed in solvent.

TASK STATUS REPORT

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

TASK TITLE: Electrolytes - Composite Polymer/Gel Electrolytes for Lithium and Lithium-ion Batteries

SYSTEMS: Low Cost Electrolytes for lithium-ion and lithium systems

BARRIERS: Short lithium battery lifetimes, poor polymer transport properties, and high costs

OBJECTIVES: Develop composite polymer/gel electrolytes that are low cost, mechanically strong, have high conductivities, impart electrode-electrolyte interfacial stability, and yield long-cycle life.

APPROACH: Use surface-functionalized fumed silica fillers in BATT-baseline systems (lithium-ion batteries for HEV) to determine the effects of filler type and concentration on interfacial stability and cell capacity upon cycling. Fumed silica-based polymer gel electrolytes are also examined for possible utility in rechargeable lithium systems (EV application). We attempt to correlate these electrochemical characteristics with mechanical properties and materials chemistry (e.g., silica-type, salt, or PEO-type, with novel materials supplied by G. Baker, D. DesMarteau, or J. Kerr). Data collected include modulus, ionic conductivity, interfacial resistance, lithium cycling efficiency, and full-cell cycling capacity.

STATUS OCT. 1, 2005: The effects of adding fumed silica into low-molecular weight (MW) polymer on the charge-discharge cycle performance, electrochemical efficiency, rate capabilities, and self-discharge performance of Li/V_6O_{13} cells have been completed. Rheological properties, conductivity, and interfacial stability of fumed silica-based electrolytes of high-MW polymer and mixed-MW (low- + high-MW) polymer gel have been investigated. The variation of mass ratio of low- to high-MW polymer in blends of fumed silica-based composite electrolytes reveals a maximum in elastic modulus and yield stress. Dendrite-inhibition effect by fumed silica in low-MW and mixed-MW PEO solvents have been demonstrated by electrochemical and in-situ microscopy. The attenuation effect of aluminum corrosion by fumed silica has been demonstrated. Single-ion conducting fumed silica (R711-poly(lithium 2-acrylamido-2-methyl-1-propanesulfonate, R711-pLiAMPS) has been synthesized with a maximum lithium transference number 0.78. The electrochemical studies show that 1M LiBETI/EC:PC:DEC:DMC (1:1:1:1) + 10%R805 gel electrolyte is a promising electrolyte candidate for lithium-ion batteries used in hybrid electric vehicles.

EXPECTED STATUS APRIL 30, 2006: We will study LiBOB (lithium bis(oxalato)borate) salt-based liquid electrolyte using γ–butyrolactone(GBL) + ethyl acetate (EA) + ethylene carbonate (EC) as cosolvents. We will expand the scope of our work to explore effects of adding fumed silica into the above electrolytes for lithium-ion systems including rheological and transport properties. We will write a final report.

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

MILESTONES:
(1) April 2006 – Investigate the effects of salt amounts, solvent compositions, and silica amounts and types of LiBOB/GBL+EA+EC liquid electrolytes on transport and rheological properties.
(2) April 2006 – Complete a final report.

PROGRESS TOWARD MILESTONES

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

We continued our research on BATT baseline liquid electrolytes: lithium bis(oxalato)borate (LiBOB)/ γ–butyrolactone(GBL): ethyl acetate (EA): ethylene carbonate (EC). We have studied the temperature dependence (0~60°C) of conductivity for LiBOB in GBL+EA+EC mixtures at different EC contents (GBL:EA:EC=1:1:0, 1:1:0.1, 1:1:0.5, and 1:1:1 (wt ratio)). The conductivity increases with temperature for all salt concentrations and solvent compositions. As the temperature decreases, the difference in conductivity between electrolytes with different EC content becomes more pronounced. The electrolyte composition with the highest conductivity at high temperature does not necessarily have the highest conductivity at low temperature. For example, at 60°C the electrolyte with GBL: EA: EC composition of 1:1:0.1 is the best while the electrolyte with composition of 1:1:0 has a lower conductivity. At 0 °C, however, the trends are reversed with composition of 1:1:0 having a higher conductivity than that of 1:1:0.1. The molar conductivity also decreases with decrease in temperature for all solvent compositions and salt concentrations.

According to our investigations, the conductivity behavior with temperature of LiBOB/ GBL+EA+EC electrolytes is non-Arrhenius, but it can be fitted to the Vogel-Tamman-Fulcher (VTF) equation:

$$\sigma = \frac{A\exp[-B/R(T-T_0)]}{\sqrt{T}}$$

where, *A*, *B*, and T_o are constants determined through data fitting. The fitted results show that *A* increases then decreases with salt concentration which supports the supposition that *A* is related to the mobility and association of ions; *B* decreases with salt concentration, which can be rationalized from Debye-Huckel theory. As salt concentration increases, the Debye length, which is defined as the effective radius of the ionic cloud that surrounds the reference ion, decreases. As the Debye length decreases, the potential decreases. This means that the energy required to move an ion is less, which explains why *B* decreases with increase of salt concentration. T_o increases as the LiBOB concentration increases. Since T_o is related to the glass transition temperature of the solution, any increase in glass transition temperature will increase T_o. The increase of the salt concentration leads to an increase in viscosity which in turn increases the glass transition temperature. These results (*A, B, and* T_o) agree with the trends for these parameters reported in the literature (I.I. Olsen et al, *J. Electrochem. Soc.,* 1996,143, 570).

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

TASK STATUS REPORT

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

TASK TITLE: Electrolytes - New Battery Electrolytes Based on Lithium Fluorosulfonate and Fluorosulfonimide Salts

SYSTEMS: Graphite/$LiFePO_4$ (Low-voltage, high-stability)

BARRIERS: Poor electrolyte transport, low power, short life, abuse tolerance.

OBJECTIVES: (1) Continue synthesizing ionic-melt electrolytes with low-lattice-energy anions attached to suitable a plasticizer, scaffold or solvating matrix (e.g. polyether oligomer); (2) Characterize the resulting electrolytes with respect to structure, transport properties, reactivity, and especially charge-discharge behavior in Graphite / electrolyte / $LiFePO_4$ cells.

APPROACH: Salts will be synthesized using variants of methods developed at Clemson over the last 20 years, with recent focus on attachment of fluorosulfonate and fluorosulfonimide anions onto polyether alkoxides. Transport properties will be measured using impedance combined with potentiostatic and galvanostatic polarization and restricted diffusion techniques. Half-cell and full-cell cycle testing will be performed in-house at Clemson on small (e.g. Swagelok) cells in collaboration with BATT coworkers who will provide materials (laminated electrodes) and help with transfer of test protocol knowledge.

STATUS Oct. 1, 2005: Plasticized ionic melt electrolytes of general structure (X)-O-CF_2CHFO-CF_2CF_2-salt where salt = SO_3Li or $SO_2N(Li)SO_2CF_3$ and X = polyether will have been synthesized and characterized with respect to structure, purity, and ionic conductivity. Preliminary cell testing in collaboration with BATT coworkers at NCSU will have been completed. Reactivity / abuse testing is on hold pending cell testing which will provide materials from disassembly of charged cells for thermogravimetric and calorimetric analysis.

EXPECTED STATUS SEPT. 30, 2006: In-house testing of small cells made using ionic melt electrolytes and tested under various charge/discharge rates and conditions will be complete. Reactivity testing on materials from disassembled charged cells will be complete. A new generation of ionic melt electrolytes of general structure [polyether-OC_6H_4-salt] where salt = -$SO_3(Li)$ or -$SO_2N(Li)SO_2Rf$, and composite electrolytes comprised of solid-state Li ion conductors dispersed in ionic melts, will be synthesized and characterized.

RELEVANT FREEDOMCAR GOALS: 15 year life, <23% power fade, specific power 625 W/kg at the system level.

MILESTONES:

(1) May 2006 - Develop in-house cell testing capabilities for small (Swagelok) cells and use those capabilities to do variable-rate charge-discharge cell testing of Graphite/electrolyte/ $LiFePO_4$ cells with ionic melt electrolytes already in hand.

(2) September 2006 - Synthesize and characterize new ionic melts of general structure [polyether-OC_6H_4-salt] where salt = $SO_3(Li)$ or $SO_2N(Li)SO_2Rf$ with Rf = CF_3 or C_4F_9.

PROGRESS TOWARD MILESTONES

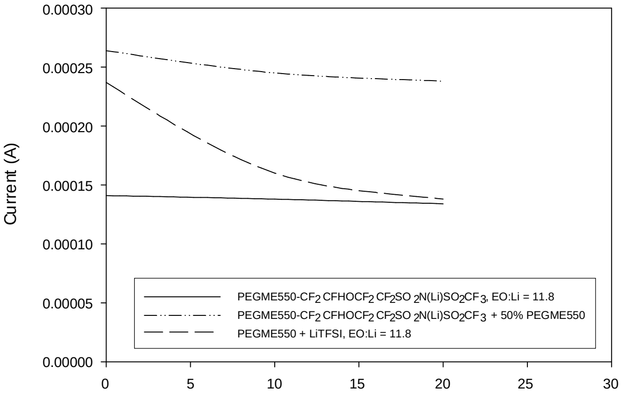


Figure 1. Current-time traces following DC potentiostatic polarization (E_{appl} = 0.3 volts) in $Li_4Ti_5O_{12}$ | electrolyte | $Li_4Ti_5O_{12}$ cells. Solid, polyether ionic melt only. Dashed, LiTFSI in polyether; dash-dot, mixture of polyether ionic melt with polyether plasticizer. EIS shows minimal change in interfacial impedance before and after polarization.

DC polarization studies on ionic melt electrolytes of general structure PEG-OCF_2CFH-OCF_2CF_2-salt where salt = SO_3Li or $SO_2N(Li)SO_2CF_3$ are being pursued to test whether the electrolytes show the expected resistance to salt concentration polarization as current is passed through them. Excellent progress was made during the reporting period due mostly to a switch from reactive lithium metal electrodes to electrodes made from lithium titanate ($Li_4Ti_5O_{12}$) supported on a metal foil current collector. Electrodes were provided by BATT coworker Karim Zaghib. Figure 1 presents some illustrative data showing current obtained in response to a 0.3 V potentiostatic polarization in three different $Li_4Ti_5O_{12}$ | electrolyte | $Li_4Ti_5O_{12}$ cells. Decreases in current following polarization are a consequence of salt concentration polarization. (EIS reveals little change in interface impedance before and after polarization.) Substantial polarization is observed for a LiTFSI-in-PEG electrolyte (dashed line) however almost no polarization is seen for the pure ionic melt electrolyte (solid line). Adding 50% by weight PEG plasticizer to the ionic melt electrolyte improves conductivity (data not shown) while the effect on salt concentration polarization (as indicated by the drop in current following polarization) is modest. Galvanostatic and potentiostatic polarization studies were performed in parallel on selected electrolytes to ensure internal consistency in the behavior. Similar behavior was found for several different ionic melt electrolytes including fluorosulfonimides and fluorosulfonates over a range of PEG molecular weights and Li:EO ratios. These are quite promising findings which we plan to follow up with full-cell cycle testing in the coming months.

On the synthetic front we have developed a means of synthesizing melt electrolytes of general structure PEG-OC_6H_4-salt where salt = $SO_3(Li)$ or -$SO_2N(Li)SO_2Rf$ (Rf = CF_3 or C_4F_9). Our initial proposed route involving reactants of structure Y-C_6H_4-salt where Y = I or N_2^+ did not work, however salts of structure F-C_6H_4-salt, where F is the leaving group, worked well. Conductivity testing is in progress and reactivity testing is planned. We have also completed studies on melts of structure PEG-OCF_2CFH-$OCF_2CF(CF_3)OCF_2CF_2$-salt where salt = SO_3Li or $SO_2N(Li)SO_2CF_3$. Synthesis proceeded cleanly and conductivities are good but consistently lower by 2-3X relative to comparable melts without the hexafluoroisopropoxy group in the linkage between the anion and the polyether. A paper reporting on this finding is in progress.

Finally we have received our new battery tester (Arbin BT-4, purchased with Clemson University funds) and installation and testing are in progress. We are fabricating a new generation of Swage-style cells with temperature-controlling and three-electrode capability (i.e. with internal reference electrodes). When these activities are complete, cycle testing of cells containing ionic melt electrolytes with active electrodes will commence.

TASK STATUS REPORT

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

TASK TITLE: Electrolytes - Molecular Modeling of Electrolytes and Their Interaction with Electrodes

SYSTEMS: Low-Cost Li-Ion

BARRIERS: Poor cation transport properties of single ion conductor gel electrolytes at ambient temperatures. Poor transport through SEI layer.

OBJECTIVES: Gain molecular level understanding of the cation transport mechanism in liquid electrolytes, single ion conductor gel electrolytes, and ionic liquids. Investigate transport properties of novel gel electrolytes and ionic liquids with improved lithium transference number. Understand lithium transport through the SEI layer and outer SEI layer/electrolyte interface.

APPROACH: Perform virtual synthesis and detailed characterization of a number of single ion conductor electrolytes, ionic liquids and liquid electrolytes using molecular dynamics simulations with developed many-body polarizable force fields. Investigate transport mechanism in electrolytes in details. Based upon learned information about transport mechanism, suggest improved electrolyte chemistries. Perform MD simulations of the SEI layer and SEI/electrolyte interface to predict structural and transport properties in these battery components.

STATUS OCT. 1, 2005: A detailed study of the influence of comb-branched copolymer architecture and EC plasticizer concentration on structural and transport properties of single ion conductor gel electrolytes as a function of temperature will be investigated for the following parameters: the length of side chains and their spacing, salt concentration, and amount of EC plasticizer. The structure and transport properties of the dilithium ethylene dicarbonate model SEI compound will be investigated. Barriers for lithium transport from electrolyte towards model electrolyte-electrode interface will be investigated for liquid electrolytes and dry single ion conductors.

EXPECTED STATUS SEPT. 30, 2006: A number of promising ionic liquids and gel electrolytes based on $TFSI^-$ anion anchored to polymer side-chains and oligomers chain ends will be investigated. Various ether-based and carbonate-based polymer and plasticizer couples will be explored in order to minimize electrolyte temperature dependence and improve room temperature conductivity. Barriers for Li^+ transport near SEI layer and in SEI layer will be studied for gel single ion conductors.

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

MILESTONES:

(1) May 2006 – Simulate a number of gel single ion conductors with new plasticizer/polymer couples that have cation transport by vehicular mechanism.

PROGRESS TOWARD MILESTONES

Li^+ Transport through Interfacial Electrolyte and SEI Layer

In FY2005 we investigated free energy barriers for Li^+ transport from liquid binary electrolytes, dry and gel single ion conductors toward the model interface. We found that the free energy barrier for a Li^+ approaching the surface is the lowest for liquid EC/LiTFSI electrolytes and the highest for the dry single ion conductor of (trifluoromethansulfonyl) imide anion immobilized on the comb-branched polymer-host side chain. At the next stage of the project, we have introduced additional realism to the model system. Specifically, we initiated a study of SEI/EC/LiTFSI interface, where SEI layer is represented by dilithium ethylene dicarbonate (Li_2EDC). We have inserted a slab of Li_2EDC in the EC/LiTFSI, Li:EC=10 electrolyte at 393 K and equilibrated the system. Currently, we are performing equilibrium MD simulations of this system; however, if timescales for the Li^+ exchange between electrolyte and Li_2EDC are found to be too long to access in conventional MD simulations we will utilize potential of mean force calculations with ~20 replicas to investigate free energy profile for the Li^+ exchange between electrolyte and Li_2EDC.

Li^+ Transport in Ionic Liquids and Plasticized Ionic Liquids

Conductivity of ionic liquids with the structure $Li^+/H(CH_2OCH_2)_{12}CF_2SO_2NSO_2CF_3$ (denoted as $EO_{12}TFSI/Li^+$) without a plasticizer and with 50 mol% plasticizer $H(CH_2OCH_2)_{12}H$ predicted from MD simulations are compared in Fig. 1 on the right with results of conductivity measurements performed by Clemson group (P.I.-Creager). MD simulations conductivity predictions are slightly lower than conductivity measured experimentally, but we consider the quality of MD simulation predictions good indicating reliability of MD simulations with developed many-body polarizable force field in predicting electrolyte transport properties.

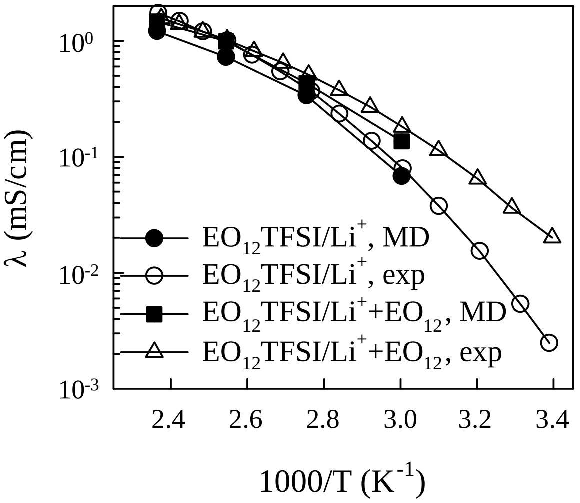


Figure 1. Conductivity of $EO_{12}TFSI^-/Li^+$ ionic liquid and $EO_{12}TFSI^-/Li^+$ plasticized with 50mol% electrolyte from MD simulations (Utah) and conductivity measurements performed by Clemson group (P.I. S. Creager)

Reasons for Changes from Original Milestones

Studies of pyrolidinium and imidazolium-based ionic liquids doped with LiTFSI have been initiated in order to understand transport mechanisms in these promising electrolytes. Many-body polarizable force fields have been developed for pyrolidinium/$TFSI^-$ and imidazolium/$TFSI^-$ ionic liquids.

BATT TASK 4
CATHODES

TASK STATUS REPORT

PI, INSTITUTION: M. Thackeray, Argonne National Laboratory

TASK TITLE: Cathodes - Novel Cathode Materials

SYSTEMS: Gr/$LiPF_6$+EC:DEC/$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (high-voltage, high energy), Gr/LiBOB+gBL:EA/$LiMn_2O_4$

BARRIER: Cost and abuse tolerance of Li-ion batteries

OBJECTIVE: To develop low-cost, high-energy and high-power Mn-oxide-based cathodes.

APPROACH: Our approach is to search for, characterize, and develop low-cost manganese oxide cathodes for Li-ion cells. Our work will continue to focus on high-voltage, high-capacity electrodes with two-component 'composite' structures, e.g., 'layered-layered' $xLi_2M'O_3\bullet(1-x)LiMO_2$ and 'layered-spinel' $xLi_2M'O_3\bullet(1-x)LiM_2O_4$ electrodes in which M′ is predominantly Mn and M is selected predominantly from Mn, Ni and Co. We will evaluate these electrodes in full cells against graphite and intermetallic anodes in conjunction with our anode project (Task 2.1).

STATUS OCT. 1, 2005: Rechargeable capacities greater than 230 mAh/g were achieved from composite 'layered-layered' $xLi_2MnO_3\bullet(1-x)LiMn_{0.5}Ni_{0.5}O_2$ electrodes (for x=0.3) in lithium half-cells for approximately 50 cycles between 4.8 and 2.75 V at 50 °C when low rates were used ($0.25mA/cm^2$). Composite 'layered-spinel' electrode structures, in which a layered component (Li_2MnO_3) was structurally integrated with a spinel component ($Li_4Mn_5O_{12}$), were also fabricated, the composition of the spinel component could be modified within the range $Li_{1+x}Mn_{2-x}O_4$ ($0<x<0.33$) by adjusting the processing temperature. Preliminary data showed that $xLi_2MnO_3\bullet(1-x)Li_4M_5O_{12}$ 'layered-spinel' electrodes provided a high initial capacity (>250 mAh/g) at low rates but that they did not cycle as well as 'layered–layered' $xLi_2MnO_3\bullet(1-x)LiMn_{0.5}Ni_{0.5}O_2$ electrodes.

EXPECTED STATUS SEPT. 30, 2006: Improvements in the electrochemical performance (*i.e.*, capacity, power and cycling stability) of $xLi_2M'O_3\bullet(1-x)LiMO_2$ electrodes and $xLi_2M'O_3\bullet(1-x)LiM_2O_4$ will have been achieved. Promising electrode compositions will have been evaluated against graphite and metal oxide negative electrodes.

RELEVANT USABC GOALS: 300,000 shallow discharge cycles (HEV requirement); 10 year life, <20% fade over a 10-year period.

MILESTONES: (1) September 2006 - Evaluate compositionally-modified 'layered-layered' $xLi_2M'O_3\bullet(1-x)LiMO_2$ and 'layered-spinel' $xLi_2M'O_3\bullet(1-x)LiM_2O_4$ electrodes with a high Mn content in Li half cells against a technical target of 200 mAh/g for 100 cycles between 4.8 and 2.5 V *vs.* Li^0 at room temperature and at 50°C. (2) September 2006 - Determine the rate capability and low-temperature behavior of the electrodes and evaluate them in full cells against graphite anodes and the intermetallic anodes of Task 2.1. (3) September 2006 - Probe the interplay between H^+ and Li^+ in highly charged and acid-treated electrodes.

PROGRESS TOWARD MILESTONES

Accomplishments

We have continued our studies of Li-rich metal oxide electrodes with composite structures, focusing this time on the $xLi_2MnO_3 \bullet (1-x)LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ system. Such an approach provides the possibility of significantly increasing the manganese content in the BATT baseline chemistry of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ electrodes. Several compositions were synthesized over the range $0 \leq x \leq 0.7$. Electrodes were evaluated in Li half cells. Cells were charged and discharged between 4.6 and 2.0 V at 0.1 mA/cm^2 (~C/20 rate) at room temperature and at a higher rate 0.3 mA/cm^2 (~C/3 rate) at 50°C. Charging the electrodes to 4.6 V activates the Li_2MnO_3 component by loss of Li_2O at this potential, thereby introducing an electrochemically active MnO_2 component into the electrode structure. Figure 1 shows the initial charge/discharge curves of RT cells with electrodes in which x = 0, 0.1, 0.3, 0.5 and 0.7; their cycling stability over the first 16 cycles is shown in Fig. 2. The rechargeable capacity of the standard BATT electrode $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (x=0) and an electrode with x=0.1 is relatively low (170-180 mAh/g). The capacity of the electrode increases with Li_2MnO_3 content. For x=0.7, a stable 210 mAh/g was achieved; increasing the operating temperature to 50°C and the charge/discharge rate from C/20 to C/3 does not markedly affect the discharge capacity of this electrode, which was maintained above 200mAh/g for at least 37 cycles (Fig. 3). These data auger well for the development of high capacity, Li-rich, and manganese-rich electrodes for Li-ion cells.

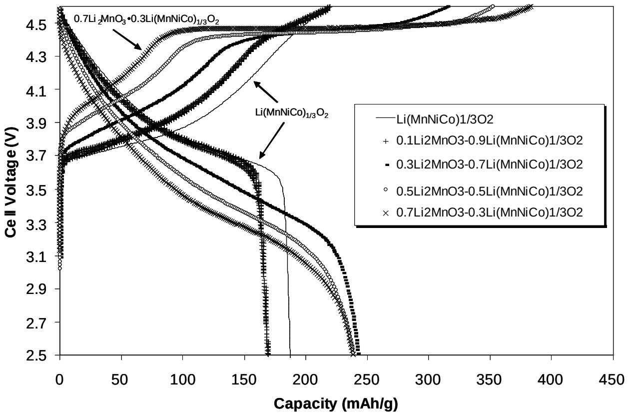


Figure 1. Initial charge/discharge profiles of a RT $Li/xLi_2MnO_3 \bullet (1-x)LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ ($0 \leq x \leq 0.7$) cell (4.6-2.0 V, C/20).

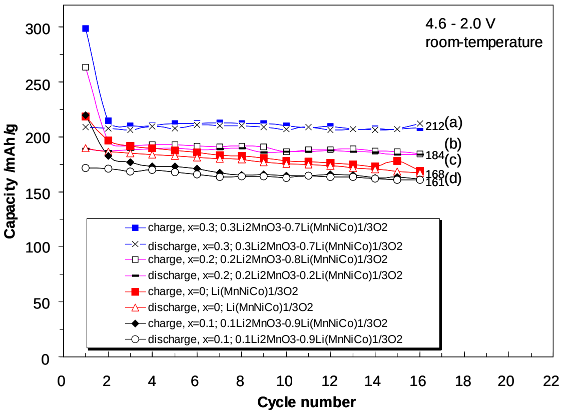


Figure 2. Capacity vs. cycle no. plot for the cells of Fig. 1.

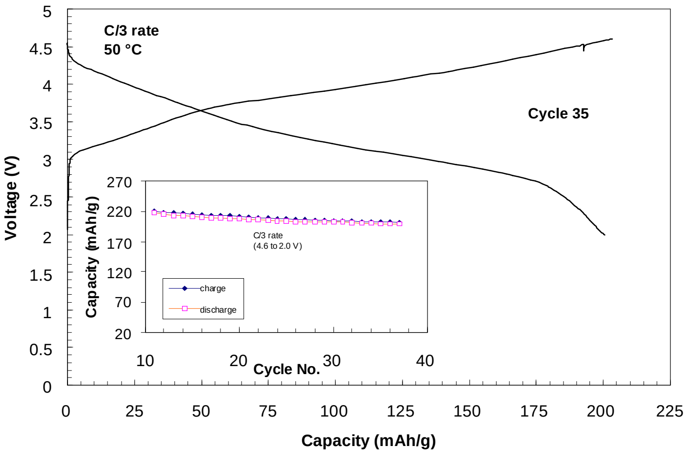


Figure 3. Voltage profile (35th cycle) and cycling stability of a $Li/0.7Li_2MnO_3 \bullet 0.3LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ cell at 50°C (C/3 rate).

TASK STATUS REPORT

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

TASK TITLE: Cathodes - Novel Cathodes

SYSTEMS: Li-Ion high-voltage, high energy and low voltage-high stability

BARRIER: Lower-cost, higher power, higher-capacity and abuse-tolerant safer cathodes

OBJECTIVES: The primary objectives are to find (a) lower-cost and higher-capacity cathodes, exceeding 200 Ah/kg, and (b) high-rate HEV compatible cathodes, both of which are based on environmentally 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, 2005: 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. Addition of other transition metals also prevents structure change at low lithium content to one-block or spinel structures, and changes oxygen evolution behavior. We have completed an electrochemical and thermodynamic evaluation of $LiFePO_4$ as a base-case low cost cathode, and shown that we can synthesize it hydrothermally at ≤ 200 °C. We have also studied other iron phosphates, none of which have both a 3.5 V discharge and a capacity exceeding 160 mAh/g.

- $LiFePO_4$: > 120 Ah/kg for 100 cycles at 1 mA/cm^2.
- Layered $Li_xCo_zNi_yMn_{1-y-z}O_2$: 160 and 150 Ah/kg for 60 cycles at 1 and 2 mA/cm^2 respectively.
- Layered $A_zMn_{0.1}V_2O_5$ (A= NH_4 or TMA): ≥ 200 Ah/kg for 6 cycles.

EXPECTED STATUS SEPT. 30, 2006: For low-cost Li-Ion cells, we expect to identify the changes in (a) electrochemistry, (b) oxygen evolution (abuse tolerance), (c) high rate capability (HEV), (d) coating effectiveness and (e) the electronic conductivity of $LiMnO_2$ structures as a function of substitution level as in $Li_xMn_{1-y-z}Ni_yCo_zO_2$, so as to determine the optimum minimum substitution level at increased manganese oxide levels. We will also have evaluated the electrochemical behavior of low temperature synthesized iron phosphate as base case cathodes, and explored some higher capacity next generation cathodes.

RELEVANT USABC GOALS: 300,000 shallow discharge cycles, and abuse tolerance to cell overcharge and short circuit

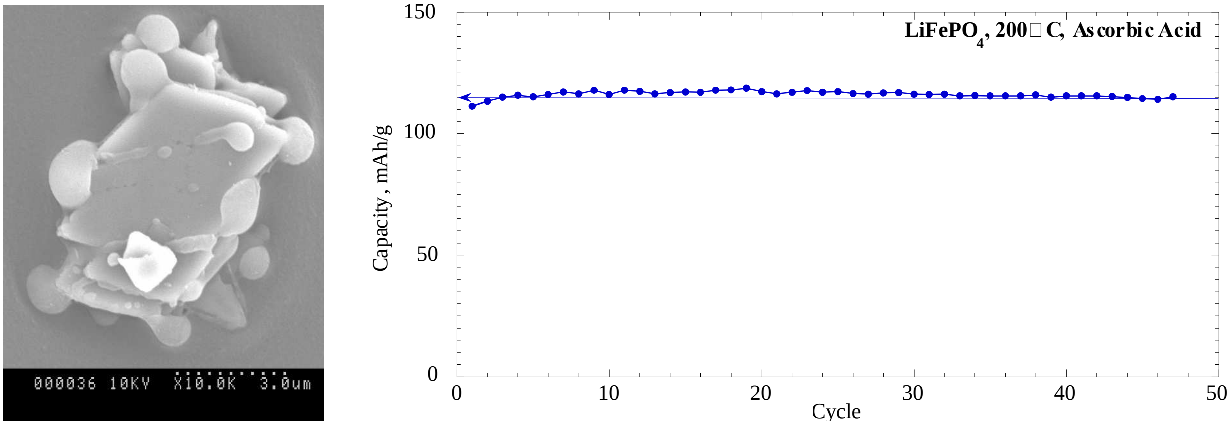
MILESTONES:
(1) July 2006 – Characterize the electronically stabilized manganese oxide, determine a higher optimum substitution of Mn to obtain a stable high rate abuse tolerant cathode (including application to HEV), and compare the best samples with the base case cathodes.
(2) July 2006 – Evaluate low temperature iron phosphates and compare them with high temperature $LiFePO_4$.

PROGRESS TOWARD MILESTONES

Low Temperature Formation of Lithium Iron Phosphate. This quarter we extended our studies of a low cost method for forming high quality lithium iron phosphate. In 2001 we reported the hydrothermal synthesis of the olivine phase for the first time. That paper generated a lot of interest, and we revisited this mass production method to see if we could improve the electrochemical behavior of the product formed. We have made a number of findings which are listed below which have significantly improved the electrochemical behavior:

1. The temperature of formation should preferably be over 175°C. This gives material with the same lattice parameters and cell volume as that formed at 700°C. We are now using temperatures of 190-200°C.
2. A reducing agent should be added to the hydrothermal reaction medium to minimize any oxidation of the iron to ferric in the aqueous environment. Ascorbic acid and sugar have been successfully used. Their presence also results in smaller particle sizes. Hydrazine has also been used, as reported in the literature for other iron phosphates, but secondary phases were found unless the pH was carefully controlled. The ferrous content was determined by complete oxidation, when a weight increase of 5% is expected for 100% ferrous.
3. The incorporation of carbon in the hydrothermal reaction medium either in solution as with ascorbic acid and sugar, or as carbon black or nanotubes provides a black product with increased electronic conductivity.

Figure 1 (left) shows $LiFePO_4$ crystallites with carbon globules on their surface; although non-optimized these black crystallites show much enhanced electronic conductivity over carbon-free hydrothermal product. Another sample, produced at 200°C in the presence of ascorbic acid, showed excellent retention of capacity when deep cycled as shown in Fig. 1 (right); this material has not been heat treated above 200°C. There is no apparent loss of capacity over these 50 cycles. Although the capacity of 115-120 mAh/g is lower than desired, it shows that hydrothermal product is electrochemically stable. Another sample has shown a Li cycling capacity of 80% of the theoretical 179 mAh/g, and we expect to be able to cycle optimized hydrothermal material at close to theoretical capacity.



(a) (b)

Figure 1. (a) Cycling of Li^+ in $Li_y(Mn_{0.45}Ni_{0.45}Co_{0.1})_{2-y}O_2$ for y=0.9 and (b) the capacity on cycling of $Li_y(Mn_{0.45}Ni_{0.45}Co_{0.1})_{2-y}O_2$ as a function of y; both at 0.5 mA/cm^2 from 2.5 to 4.6 volts.

Further plans to meet or exceed milestones: None

Reason for changes from original milestones: No changes

TASK STATUS REPORT

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

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

SYSTEMS: Low-voltage, high-stability ($LiFePO_4$), high-voltage, high energy ($LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$, new manganese oxides), and high voltage, high-power (new manganese oxides)

BARRIERS: Cost, cycle life, abuse-tolerance, energy density, and power 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 FreedomCAR.

APPROACH: Cathode materials are synthesized by various means. Physical and electrochemical properties (*e.g.*, structure, surface characteristics) are measured in conjunction with members of the diagnostic group. 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, 2005: Initial screening of novel manganese oxides for manganese dissolution and cycling performance at elevated temperatures has been completed. Tunnel-MnO_2s are superior to layered materials in terms of abuse-tolerance and are recommended for high power applications. Significant improvement in $LiFePO_4$ performance was observed when materials were processed with 4-8 wt% pyromellitic acid and 0.5-1 wt% ferrocene (a graphitization catalyst) due to the improved structure of the carbon coating.

EXPECTED STATUS SEPT. 30, 2006: An investigation of the high-voltage capacity of tunnel-MnO_2s will be carried out to determine if these materials are also suitable for high energy density applications, as well as work directed towards their high-power performance. Work on carbon-coated $LiFePO_4$ will continue, with emphasis placed on how distribution of carbon affects performance. Some effort will be directed towards co-synthesis of $LiFePO_4$ with carbon nanotubes. New manganese oxide structures without Ni or Co substituents for high-energy density applications will continue to be surveyed.

RELEVANT USABC GOALS: High power, abuse-tolerance (HEV); High energy density cathode materials that do not contain Ni or Co (EV).

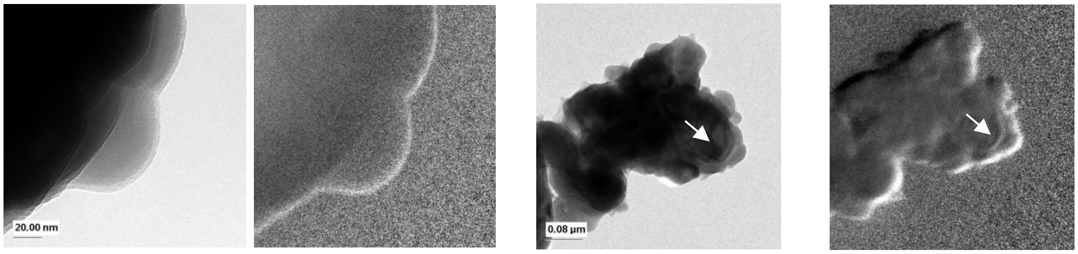
MILESTONES:
(1) (Sept. 2005-postponed until Dec. 2005) – Recommend the most abuse-tolerant manganese oxide structures for potential HEV applications, and highest energy density manganese oxides containing no Ni or Co for potential high energy applications.
(2) June 2006 – Determine feasibility (go/no go) of co-synthesizing $LiFePO_4$ and carbon nanotubes.
(3) September 2006 – Complete survey of tunnel-MnO_2 structures

PROGRESS TOWARD MILESTONES

4.3b (postponed from FY2005) Postmortem analysis was conducted on manganese-containing electrode materials that had been stored in 1M $LiPF_6$ in EC/DMC for up to eight weeks at 55ºC, and the results correlated with the cycling behavior in lithium cells. Layered manganese oxides and $LiNi_{0.5}Mn_{0.5}O_2$ form solvate phases, in which components of the electrolytic solution intercalate between the transition metal layers, under these conditions. The tendency is strongest with O2 layered structures, and leads to exfoliation. This, rather than Mn dissolution, which does not occur for the O2 structure, is the cause of the observed capacity fading in Li cells. $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ and tunnel compounds do not form solvates, but Mn dissolution occurs for the latter. Ti substitution has a protective effect against Mn dissolution and $Li_xTi_yMn_{1-y}O_2$ ($y>0.33$) cycles well even at elevated temperatures. This milestone is now complete and no further work is planned.

4.3a (FY2006) The coating on a high-rate $LiFePO_4$ was examined by EFTEM (Fig. 1) and positively identified as carbon (with H. Gabrisch of U. of New Orleans). In spite of the low carbon content (1.45 wt. %) and the heterogeneous particle morphology, a coating about 5 nm thick covers all surfaces. A TEM study of cycled powders shows that these coatings crack. Powders from cells in which capacity fading occurred are now being compared to those that cycled well. A survey of carbon nanotube synthesis methods is also underway.

4.3b (FY2006) Electrochemical characterization of tunnel manganese oxides in conventional electrolytes is now underway. Up to 180 mAh/g can be achieved when cells are charged to 4.8V, but some fading occurs upon cycling possibly due to electrolyte oxidation. A materials transfer agreement with CSIRO (Dr. Adam Best) in Australia has been successfully negotiated, and their ionic liquid electrolytes with high voltage stability will be sent to LBNL for evaluation in $Li/Li_xTi_yMn_{1-y}O_2$ cells.



(a) (b) (c) (d)

Figure 1. (a) TEM of $LiFePO_4$ particle. (b) EFTEM showing carbon distribution (white edge). (c) TEM of $LiFePO_4$ agglomerate. Arrow shows edge of a primary particle. (d) EFTEM showing carbon distribution. Arrow shows that carbon is present on the surface of the primary particle.

Further plans to meet or exceed milestones N/A

Reason for changes from original milestones Milestone 4.3b from FY05 was postponed until Dec. '05 to finish evaluation of storage and cycling tests. It has now been completed.

Publications and Presentations

"Towards a High-Rate $LiFePO_4$," J.D. Wilcox and M. M. Doeff, **Electrochem. Soc. Meeting,** Los Angeles, CA, Vol. 2005-2, abstract 154.

TASK STATUS REPORT

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

TASK TITLE: Cathodes - Novel Materials

SYSTEMS: Li secondary battery

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

OBJECTIVES: To evaluate alternative *cathode* materials for a lithium-ion battery.

APPROACH: The universal motif of cathodes in rocking chair Li-ion batteries is one of immobilized redox centers that are accessible to electrons from the current collector and Li^+ ions from the electrolyte. Immobilization ensures that the redox units do not transfer to and subsequently poison the anode. Our research is centered around high-power cathodes for the purpose of EVs and HEVs. This translates into pure or composite materials which allow for transfer of electrons *and* Li^+ ion with little or no resistance. We are currently pursuing three different avenues of research: (1) New materials based on conventional oxide structures with proven high rate capabilities, (2) new cathode schemes based on conductive polymers which may serve as a new conductive binder in more conventional composite cathodes, and (3) Substitution into the environmentally benign and cost effective $LiFePO_4$ to improve rate capabilities.

STATUS OCT. 1, 2005: Substitution of polypyrrole (PPy) for carbon and PTFE binder in $LiFePO_4$/PPy composite cathodes was shown to give an increased capacity and rate capability compared to a $LiFePO_4$/C/PTFE composite. This innovative approach shows promise of being extendable to other cathode materials.

EXPECTED STATUS Sept. 30, 2006: $LiFePO_4$ nanoparticles and $LiNi_{2/3}Mn_{1/3}O_2$ nanowires will be fabricated and tested in button cells. Analysis of the importance of carbon coating and of crystalline orientation in the nanowires will be under investigation. Fabrication of $LiNi_{2/3}Mn_{1/3}O_2$ with PPy will have been explored.

RELEVANT USABC GOALS: 30 ohm-cm^2 area specific impedance, cold cranking capability to –30°C, 300,000 shallow discharge cycles, abuse tolerance to short-circuit and cell overcharge.

MILESTONES:
(1) February 2006 – Synthesize, test, and evaluate $LiNi_{2/3}Mn_{1/3}$ nanowires
(2) February 2006 – Synthesize, test, and evaluate $LiFePO_4$ nanoparticles without and with Al substitution for Fe
(3) September 2006 – Electrochemically characterize the most promising cathode materials fabricated with/without PPy

PROGRESS TOWARD MILESTONES

In our previous work, we optimized the condition for fabrication of $LiFePO_4$/polypyrrole(Ppy) cathode by electrochemical deposition and also noted that a carbon coating of the particles is needed for binding to the Ppy. In the past quarter, we further investigated the dependence of composite capacity on Ppy weight content and tested fast charging of the $LiFePO_4$/Ppy cathode.

The Ppy content was analyzed by accurately weighting the $LiFePO_4$/Ppy film before and after it was burnt out at 700°C in Ar. As shown in Fig. 1, with increasing Ppy content, the composite capacity first increases and then decreases. The maximum capacity is attained when the Ppy content is around 20 wt%. If the Ppy content is larger than 25 wt%, the capacity is even lower than that of $LiFePO_4$. For the $LiFePO_4$/Ppy cathode with Ppy content of around 20 wt%, both discharging and charging rate capabilities are greatly improved. An important feature of the composite cathode is that it exhibits excellent fast charging performance. Figure 2 shows composite capacity *vs.* voltage at various charge rates. When the cathode was charged at a rate of 2C, the discharge composite capacity reached 110 mAh/g at a discharge rate of C/5. Even when it was charged at rates of 10C (6 min) and 20C (3 min), the capacity was still as high as 80 mAh/g. Moreover, it is stable over redox cycling under high charge/discharge rates. Therefore, our results show that the $LiFePO_4$/Ppy composite cathode is promising for HEVs with a fast charging performance.

In order to prepare good $LiFePO_4$/Ppy and other oxide/Ppy cathodes, carbon coating on the active cathode materials is necessary. We have tried several different techniques to coat carbon onto $LiFePO_4$ and $LiNi_{2/3}Mn_{1/3}O_2$. This work is still being carried out.

In the next quarter, we will further investigate fast charging performance of $LiFePO_4$/Ppy composite cathodes and a carbon coating technique for other oxides in order to incorporate Ppy by electrodeposition.

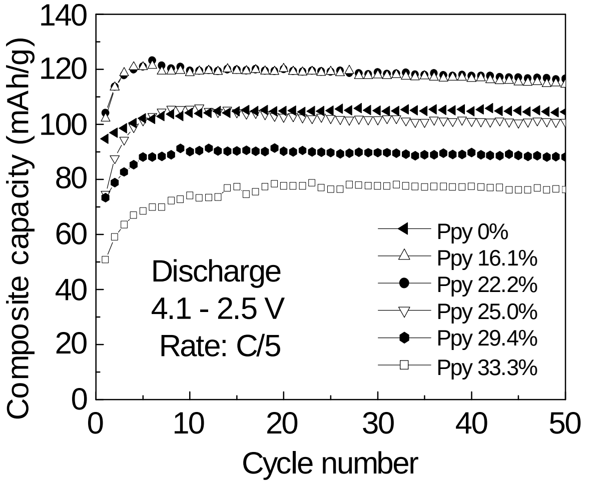


Figure 1. Discharge composite capacity over cycling for the $LiFePO_4$/Ppy composite cathode with different Ppy content. Note: Ppy 0% had C+PTFE.

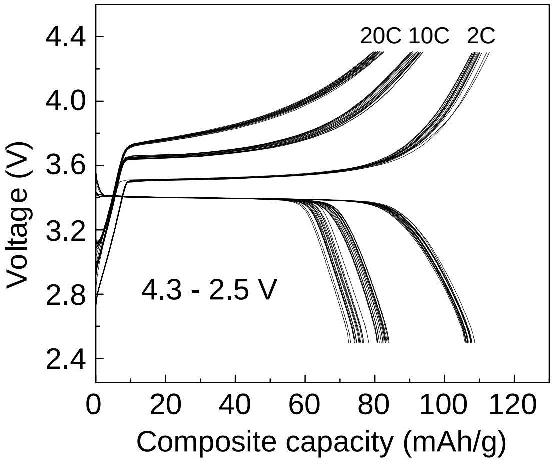


Figure 2. Composite capacity *vs.* voltage at high charge current for $LiFePO_4$/Ppy. Charge rate: 2C, 10C and 20C, discharge rate: C/5.

TASK STATUS REPORT

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

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

SYSTEMS: Spinel manganese oxides

BARRIERS: Cycle life, elevated temperature storage, power density, and energy density

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

APPROACH: Our approach is to develop a firm scientific understanding of the factors that control/influence the electrochemical performance of the spinel oxide cathodes and utilize the knowledge gained to design and develop high performance spinel manganese oxide compositions. In this regard, a variety of single and multiple cationic substitutions for manganese, anionic substitutions for oxygen, and an optimization of the microstructure and morphology are being pursued. The spinel oxide compositions are characterized by diffraction, spectroscopic, and electrochemical techniques to establish a structure-composition-property-performance relationship.

STATUS OCT. 1, 2005: Evaluation of the optimized $LiMn_{2-x-y}Li_xNi_yO_4$ and $LiMn_{2-x-y-z}Li_xM_yM'_zO_4$ (M and M' = transition and non-transition metal ions) spinel oxide compositions (4 V) in Li-ion cells, identification of the factors that control the electrochemical performances of the cation-substituted 5 V spinel oxide system $LiMn_{1.5}Ni_{0.5}O_4$, and a comparison of the factors with those of the 4 V spinel oxide cathodes.

EXPECTED STATUS SEPT. 30, 2006: Optimization of the synthesis and processing conditions as well as compositions of the spinel oxyfluoride cathodes, their characterization and electrochemical evaluation, monitoring and comparison of manganese dissolution at different depths of discharge in various spinel cathodes with and without Mn^{3+} and fluorine (4 and 5 V cathodes), comparison and effect of transition metal ion dissolution in spinel, layered, and olivine cathodes.

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

MILESTONES:
(1) March 2006 – Optimization of the synthesis conditions of oxyfluoride spinels
(2) September 2006 – Comparison and consequences of metal ion dissolution in various cathodes

PROGRESS TOWARD MILESTONES

Our previous investigation showed that (i) fluorine substituted spinel oxide compositions exhibit superior electrochemical performance compared to the oxide analogs and (ii) a low temperature approach involving the firing of the already synthesized cation-substituted spinel oxides $LiMn_{2-y-z}Li_yM_zO_4$ with ammonium hydrogen fluoride at ~ 450 °C for a short period of 5 h helps to maximize the fluorine content in the spinel lattice. With an aim to identify the origin of the enhancement in capacity retention, we have monitored (i) the evolution of the cubic to cubic phase transition and the two-phase region that occurs at $(1-x) \approx 0.3$ to 0.5 during the charge-discharge process of the spinel cathodes and (ii) the amount of manganese dissolution. It is found that both the cationic and fluorine substitutions lower the lattice parameter difference Δa between the two cubic phases formed, and the capacity fade at elevated temperatures (60°C) decreases with decreasing Δa (Fig. 1). Also, the cationic and fluorine substitutions decrease the amount of manganese dissolution that was measured by soaking the sample powders in 1 M $LiPF_6$ in ethylene carbonate/diethyl carbonate electrolyte at 55 °C for 7 days, and the capacity fade at 60°C decreases with decreasing manganese dissolution (Fig. 1). It is interesting to note that some cationic substitutions such as the co-substitution of Li and Ni are more effective in lowering Δa and manganese dissolution compared to that of Li and Ti. Interestingly, with a given cationic substitution, the anionic substitution with fluorine causes a further reduction in both the Δa and the amount of manganese dissolution. More importantly, manganese dissolution bears a clear relationship to the lattice parameter difference Δa. The amount of manganese dissolution decreases with decreasing Δa, which in turn leads to a decrease in the capacity fade as seen in Fig. 1. The reduced interfacial lattice strain due to the smaller Δa together with a passivation by the more ionic Mn-F bond compared to the Mn-O bond appears to lead to a suppression of manganese dissolution. Attempts to incorporate more than ~0.2 fluorine into the cation-substituted spinel oxides resulted in the formation of Mn_5O_8 as an impurity phase and a decrease in the initial capacity.

Additionally, in collaboration with Drs. Xiao-Qing Yang and Won-Sub Yoon at the Brookhaven National Laboratory, we have compared the *in situ* X-ray diffractions patterns of $Li_{1.04}Mn_{1.96}O_4$, $LiMn_{1.85}Li_{0.075}Ni_{0.04}Al_{0.035}O_4$, and $LiMn_{1.8}Li_{0.2}O_{3.79}F_{0.21}$ during the first charge. The *in-situ* data also show a reduction in Δa on going from $Li_{1.04}Mn_{1.96}O_4$ to $LiMn_{1.8}Li_{0.2}O_{3.79}F_{0.21}$ and $LiMn_{1.85}Li_{0.075}Ni_{0.04}Al_{0.035}O_4$, supporting the relationship between capacity fade and Δa.

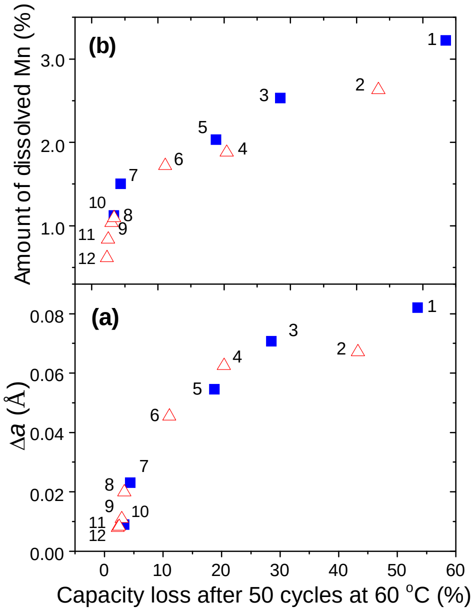


Figure 1. Correlation of the capacity fade in 50 cycles at 60°C to the (a) lattice parameter difference Δa between the two cubic phases formed during the charge-discharge process and (b) degree of manganese dissolution. Closed squares and open triangles refer, respectively, to the oxide and oxyfluoride cathodes.

1: $LiMn_2O_4$
2: $LiMn_2O_{3.92}F_{0.08}$
3: $LiMn_{1.8}Li_{0.1}Ti_{0.1}O_4$
4: $LiMn_{1.8}Li_{0.1}Ti_{0.1}O_{3.9}F_{0.1}$
5: $LiMn_{1.8}Li_{0.1}Cu_{0.1}O_4$
6: $LiMn_{1.8}Li_{0.1}Cu_{0.1}O_{3.9}F_{0.1}$
7: $LiMn_{1.8}Li_{0.2}O_4$
8: $LiMn_{1.8}Li_{0.2}O_{3.88}F_{0.12}$
9: $LiMn_{1.8}Li_{0.2}O_{3.79}F_{0.21}$
10: $LiMn_{1.8}Li_{0.1}Ni_{0.1}O_4$
11: $LiMn_{1.8}Li_{0.1}Ni_{0.1}O_{3.9}F_{0.1}$
12: $LiMn_{1.8}Li_{0.1}Ni_{0.1}O_{3.8}F_{0.2}$

BATT TASK 5
DIAGNOSTICS

TASK STATUS REPORT

PI, INSTITUTION: R. Kostecki, LBNL

TASK TITLE: Diagnostics - Electrode Surface Layers

SYSTEMS: Gr/$LiPF_6$+EC:DEC/$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (high-voltage, high-energy); Gr/LiBOB+γBL:EA/$LiMn_2O_4$ (high-voltage, high-power); Gr/$LiPF_6$+EC:DEC/$LiFePO_4$ (low-voltage, high-stability)

BARRIER: Short lithium battery calendar/cycle lifetimes.

OBJECTIVES: The primary objective is to establish direct correlations between electrode surface chemistry, morphology, topology, interfacial phenomena, and cell power or capacity decline.

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

STATUS OCT. 1, 2005: We expect to define relationships between electrochemical performance and limitations of BATT baseline systems and cell history, abuse tolerance, electrodes surface properties and interfacial phenomena. We intend to develop good understanding of the key elements for good electrochemical performance of $LiFePO_4$ and $LiMn_2O_4$ and $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ composite cathodes. We expect to complete the study of the effect of electrode pre-treatment on the evolution of interfacial impedance of electrodes stored in the electrolyte at elevated temperatures. We anticipate completing preliminary experiments to study graphite disordering phenomena in the composite anodes and carbon retreat/rearrangement in the composite cathodes.

EXPECTED STATUS SEPT. 30, 2006: We plan to optimize the microwave plasma-assisted carbon-coating process to obtain electronically conductive and uniform thin films of graphitic carbon directly on $LiFePO_4$ raw powders. The effect of carbon coating on the cathode electrochemical performance will be evaluated. We expect to develop full understanding of the mechanism of carbon retreat/rearrangement in the composite cathodes and graphite disordering in the carbonaceous composite anodes. We plan to determine their impact on the electrodes' electrochemical performance upon cycling and storage in $LiPF_6$-EC-EMC electrolytes at ambient conditions and at elevated temperatures. We expect to characterize physico-chemical processes which are responsible for these effects, and establish possible links with other detrimental phenomena.

RELEVANT USABC GOALS: 15 year life, 30 ohm-cm^2 area-specific impedance, 300,000 shallow discharge cycles.

MILESTONES: June 2006 – Full evaluation of microwave plasma-assisted synthesis of graphitic carbon matrix for composite cathodes.

PROGRESS TOWARD MILESTONES

We continued to study in detail the role of carbon additive in composite BATT baseline cathodes and its implications for battery high-rate performance. A new set of ^{13}C-enriched composite LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ cathodes were manufactured and characterized. The electrodes consisted of 84% of LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$, 4% ^{12}C graphite, 4% ^{13}C carbon black, and 4% PVDF binder. A new type of ^{13}C soft carbon, which emulates physico-chemical properties of acetylene black, was used. Electrochemical cycle life tests at C/10 rate of the cathode were carried out at room temperature in Swagelok cells vs. Li-metal anode in 1.2 M LiPF$_6$ in EC/DEC (3:7 vol. %) electrolyte. The cell lost ~80% of discharge capacity at C/10 and ~30% discharge capacity at C/20 after 180 cycles. A micro-Raman surface composition map of a fresh ^{13}C-enriched LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ cathode (Fig. 1a) shows a fairly uniform distribution of electrode components. However, post-mortem Raman analysis of the tested cathode shows a noticeably higher surface concentration of the active material. This result is in concert with our earlier diagnostic observations from commercial Li-ion batteries and model BATT cells.

A qualitative post mortem analysis of the cell components was carried out to determine the possible carbon rearrangement/movement in the cell. The surface of the Li anode was found free of carbon contaminants that could originate from the cathode. However, we identified and characterized a modest amount of fine carbon particles trapped in the Celgard 2300 separator and also traces of carbon additives in the electrolyte. The Raman spectra clearly show contributions from both ^{12}C and ^{13}C D and G carbon bands. Interestingly, all carbon particles found in the separator and electrolyte were highly amorphous unlike the original graphite and ^{13}C carbon black (Fig. 2). These amorphous carbons could originate from the graphite and ^{13}C carbon black additives as a natural carbon contaminant. Also, amorphous carbons could be generated from original carbon additives during electrode manufacture as a result of mechanical processing. Electrochemical cycling could also lead to gradual graphite particle degeneration due to PF$_6^-$ anion intercalation-deintercalation. In summary, we postulate that the changes in the carbon additive distribution in composite cathodes upon cycling have a great impact on the electrochemical performance of the electrode. Only small and insignificant amounts of fine carbon particles are carried away from the cathode.

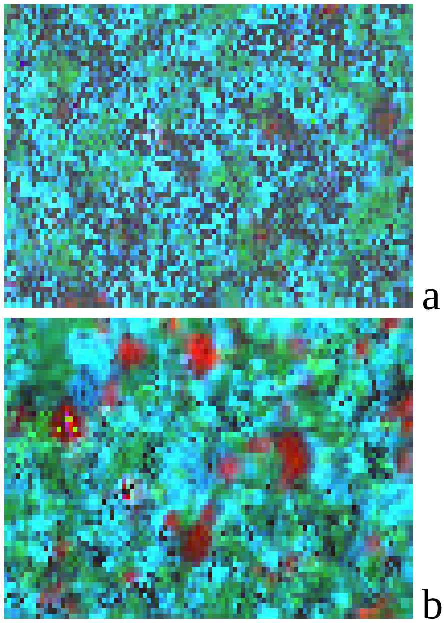


Figure 1. 50x80 μm Raman maps of a) fresh and b) cycled ^{13}C-enriched composite cathodes. Red, green and blue color corresponds to LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$, graphite and 13C additive, respectively.

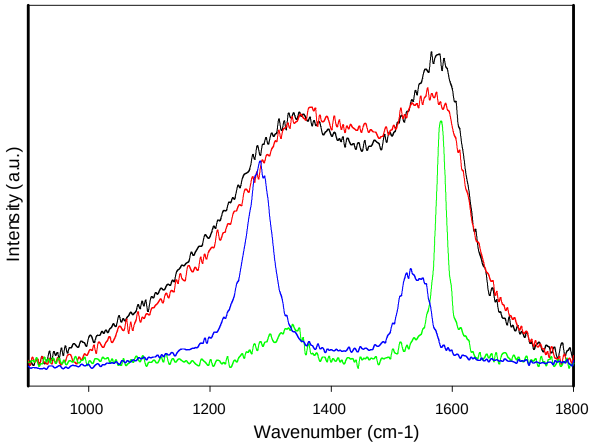


Figure 2. Raman spectra of — ^{12}C graphite, — ^{13}C carbon black, and —— carbon particles trapped in the separator .

TASK STATUS REPORT

PI, INSTITUTION: W-S. Yoon and X-Q. Yang, Brookhaven National Laboratory

TASK TITLE: Diagnostics - Battery Materials: Structure and Characterization

SYSTEMS: $Gr/LiPF_6+EC:DEC/LiCo_{1/3}Mn_{1/3}Ni_{1/3}O_2$ (high-voltage, high-energy); $Gr/LiPF_6+EC:DEC/LiFePO_4$ (low-voltage, high-energy)

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, ex situ* and time resolved synchrotron based x-ray techniques to characterize electrode materials and electrodes taken from baseline BATT Program cells. *Ex situ* soft X-ray absorption spectroscopy (XAS) will be used to distinguish the structural differences between surface and bulk of electrodes using both electron yield (EY) and fluorescence yield (FY) detectors. Time-resolved X-ray diffraction technique will also be used to understand the reactions that occur in charged cathodes at elevated temperatures in the presence of electrolyte. Hard and soft XAS will be used to elucidate the charge compensation mechanisms for cathode materials during electrochemical cycling. *In situ* x-ray diffraction will be used to monitor the structural changes of the electrode materials during charge-discharge cycling at different conditions.

STATUS OCT. 1, 2005: In FY 2005, in *situ* x-ray diffraction (XRD) and a combination of *in situ* and *ex situ* x-ray absorption spectroscopy (XAS) studies of the structurally stabilized $LiAl_{0.15}Mn_2O_4$ spinel materials cycled at different temperatures have been completed, the studies of the effects of new electrolytes and additives on the stability of $LiMn_2O_4$ electrodes at elevated temperatures were also completed. Using newly developed time resolved XRD technique, a systematic study of the structural changes of a series of cathode materials during heating with the presence of electrolyte has been completed. The formation of Li_2CO_3 was observed. The implication on the thermal stability of this newly reported observation has been studied and reported.

EXPECTED STATUS SEPT. 30, 2006: We expect to complete the *in situ* XRD work on $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ cathode materials cycled at elevated temperatures. We also expect to complete the *in situ* XRD and XAS studies of $LiFePO_4$ obtained from different sources during cycling at different charge-discharge rates. Soft X-ray XAS using partial electron yield and fluorescence yield detectors will be applied to various cathode materials at the O, F, and P K edges and at the L_3 and L_2 edges of the 3d transition metals.

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

MILESTONES:

(1) April 2006 – Complete *in situ* XRD studies of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ cathode material cycled at elevated temperatures

(2) September 2006 – Complete the *in situ* XRD and XAS studies of $LiFePO_4$ obtained from different sources during cycling at different charge-discharge rates.

PROGRESS TOWARD MILESTONES

We have continued to investigate the electronic structure for the electrochemically Li-ion deintercalated $Li_{1-x}Co_{1/3}Ni_{1/3}Mn_{1/3}O_2$ materials using soft X-ray absorption spectroscopy (XAS) at O K-edge and metal $L_{II,III}$-edge in the soft x-ray region, in combination with metal K-edge XAS spectra in hard x-ray region. The major charge compensation mechanisms in the $Li_{1-x}Co_{1/3}Ni_{1/3}Mn_{1/3}O_2$ electrode system on Li-ion deintercalation are established.

The major charge compensation at the metal site during charge is achieved by the oxidation of Ni^{2+} ions, while the manganese ions remain mostly unchanged in the Mn^{4+} state. The shaded area in Fig. 1 is the integrated pre-edge intensity assigned to oxygen p character hybridized with the transition metal 3d band. Figure 2 shows variations of pre-edge peak intensity for the O K-edge XAS spectra in FY mode for $Li_{1-x}Co_{1/3}Ni_{1/3}Mn_{1/3}O_2$ electrode during charge. The pre-edge peak intensity continuously increases in the range of $0 \leq x \leq 2/3$ in $Li_{1-x}Co_{1/3}Ni_{1/3}Mn_{1/3}O_2$. The spectral weight increases by ~37% from x = 0 to x = 0.7 in $Li_{1-x}Co_{1/3}Ni_{1/3}Mn_{1/3}O_2$ compared to that of pristine $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ indicating that a large portion of the holes that compensate the lithium ion deintercalation are located in O 2p states. In contrast, our previous O K-edge results of $Li_{1-x}Ni_{0.5}Mn_{0.5}O_2$ system showed relatively small change (~10% for x = 0 to 0.8 in $Li_{1-x}Ni_{0.5}Mn_{0.5}O_2$) in the pre-edge intensity during charge. $LiNi_{0.5}Mn_{0.5}O_2$ and $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ can be considered as a member of $Li[Ni_xCo_{1-2x}Mn_x]O_2$ series. The major difference between $LiNi_{0.5}Mn_{0.5}O_2$ and $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ systems is the later contains Co. Therefore, the increased pre-edge peak intensity observed is clearly due to the content of Co. Therefore, the major contribution on the increased pre-edge peak intensity is due to the content of Co. In contrast, the contribution of Ni-O covalency on the charge compensation is much less, based on the fact that a much less changes in weight of pre-edge peak (10%) was observed in $Li_{1-x}Ni_{0.5}Mn_{0.5}O_2$, comparing with the 37% observed in $Li_{1-x}Co_{1/3}Ni_{1/3}Mn_{1/3}O_2$. It is concluded that a large portion of the charge compensation during Li-ion deintercalation is achieved on the oxygen sites which are associated with Co.

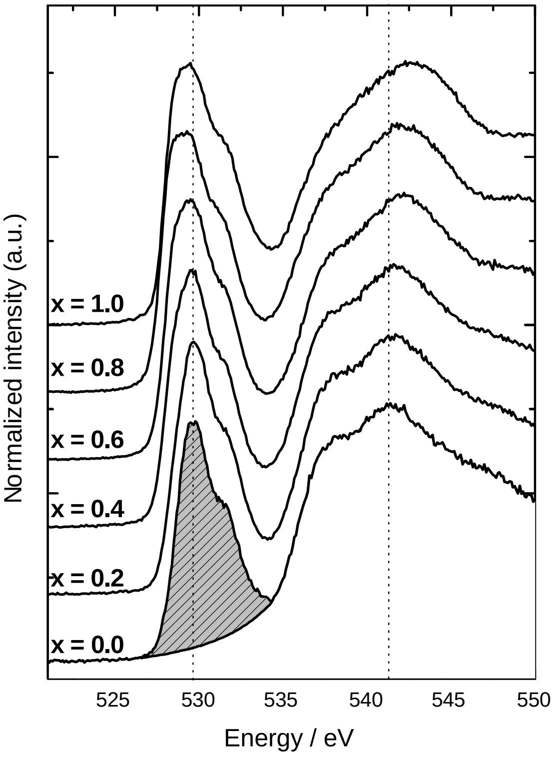


Figure 1. The O K-edge XAS spectra in FY mode for electrochemically Li-ion deintercalated $Li_{1-x}Co_{1/3}Ni_{1/3}Mn_{1/3}O_2$ electrode during charge.

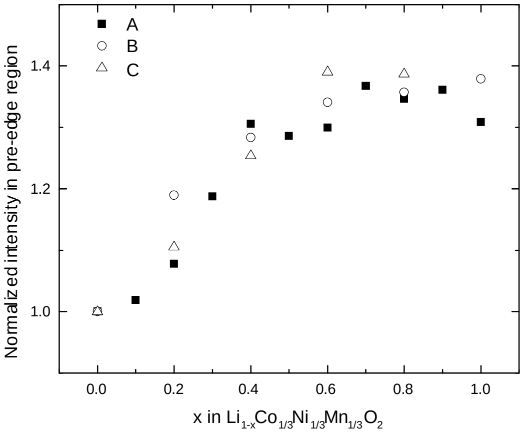


Figure 2. Variations of pre-edge peak intensity for the O K-edge XAS spectra in FY mode for $Li_{1-x}Co_{1/3}Ni_{1/3}Mn_{1/3}O_2$ electrode during charge.

TASK STATUS REPORT

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

TASK TITLE: Diagnostics - Interfacial and Reactivity Studies

SYSTEMS: High Power Battery

BARRIER: Short battery lifetime; Low temperature performance

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

APPROACH: Our approach is to use *ex-situ* and *in-situ* Fourier transform infrared (FTIR) spectroscopy to study the *interfacial chemistry* in model electrode/electrolyte systems. The spectrometer optics and spectroelectrochemical cell have a special design that enables any electrode material to be studied. The FTIR spectroscopy will be accompanied by classical electroanalytical methods such as cyclic voltammetry and ac impedance.

STATUS OCT. 1, 2005: Irreversible changes to graphite anodes due to charging (regen) at low temperature will be determined and correlated to cell chemistry.

EXPECTED STATUS SEPT. 30, 2006: The correlation between impedance rise in graphite anodes at low temperature and composition/structure of the SEI layer determined by FTIR will be established.

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

MILESTONES: September 2006 – Establish correlation between impedance rise in graphite anodes at low temperature and composition/structure of the SEI layer determined by FTIR.

PROGRESS TOWARD MILESTONES

Interfacial Chemistry and the Impedance Rise at Low Temperature

As recommended by the Review Committee in the 2005 Annual Review, we will continue on the study of interfacial chemistry in Li-ion batteries at low temperature in FY2006. The continuing study will address the origins of large polarization and the mechanism of Li deposition. Specifically, we are going to investigate: a) critical role of electrolyte composition in LT performance; b) Li-ion conductivity of the SEI layer; c) temperature dependence of Li-ion diffusion in graphite. Swagelok cells with battery electrodes and a three-electrode electroanalytical cell with microelectrodes will be used with a combination of ac impedance, CV and FTIR spectroscopy.

As a start on the use of ac impedance measurements with graphite anodes, we measured the impedance characteristics of SEI-related pure Li compounds, specifically Li oxalate, Li ethylene carbonate, and Li ethylene dicarbonate. We used stainless steel blocking electrodes in a Swagelok-type cell in our new glovebox. The sample were thin (0.02–0.1 mm) disks from compacted (1 tonne) crystals/powders. Qualitatively the characteristics of all three compounds were very similar, and characteristic of that for pure Li ion conductors. As an example, the Nyquist plot for Li oxalate in Fig. 1 consists of a single semi-circle with a characteristic spur at low frequency which points on blocking of Li ions at the stainless steel electrodes. The compound with the highest conductivity was as expected Li ethylene dicarbonate. The Bode plot for resistivity and phase angle are shown in Fig. 2.

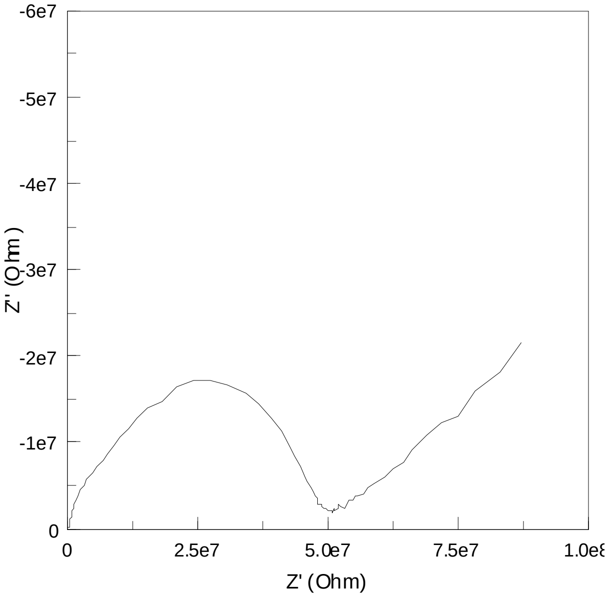


Figure 1. Nyquist plot of complex impedance of Li oxalate at ambient temperature

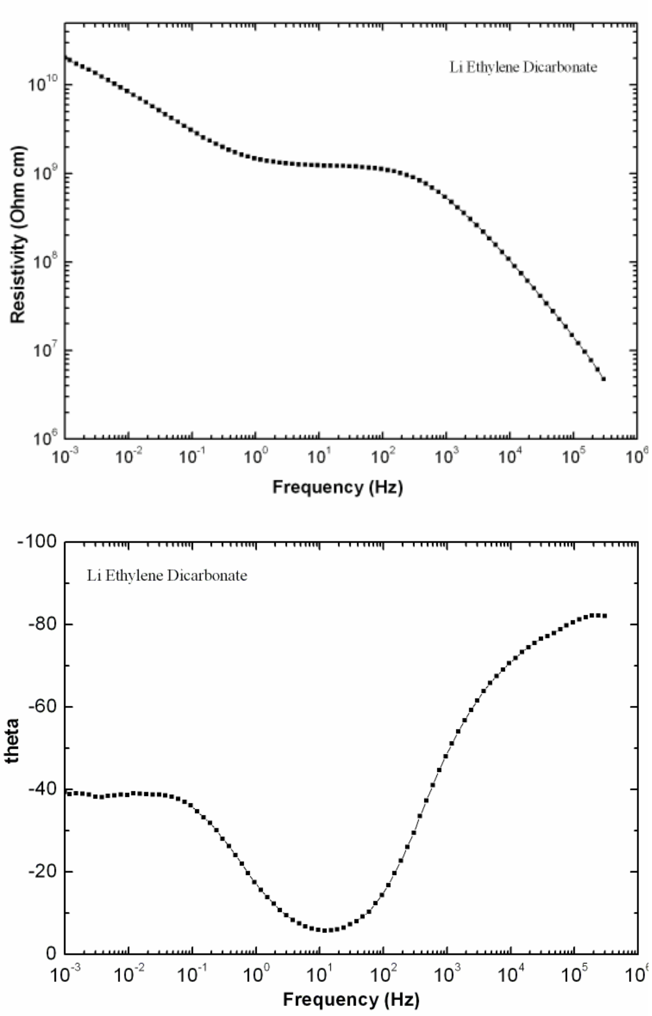


Figure 2. Bode plots of the resistivity and phase angle ($\propto$ dielectric constant) for Li ethylene dicarbonate at ambient temperature

The dispersion of conductivity with frequency in the high frequency range indicates a frequency independent dielectic constant. The low frequency dispersion is characteristic of compounds that become oriented in the electric field of the electrode and accumulate ions at the electrode interface, i.e. a relatively high double layer capacitance. The impedance behavior of these compounds is also qualitatively similar to that of Li ion conducting glasses like Li_2O-V_2O_5-P_2O_5 (*Sol. State Ionics* 176 (2005) 2163) and PEO electrolytes below the glass transition temperature (*Sol. State Ionics* 176 (2005) 2065). However, the absolute value of the conductivity is 1 – 2 orders of magnitude lower in these compounds. Nonetheless, if the SEI layer thickness is of the order of magnitude suggested by many studies, *e.g.,* 10 – 100 nm, the conductivities are high enough to transport Li ions at high rate (1 mA/cm^2 real) with only a small potential drop (10 – 100 mV) at ambient temperature. The temperature dependence of the conductivity is currently being measured.

TASK STATUS REPORT

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

TASK TITLE: Diagnostics - First Principles Calculations and NMR Spectroscopy of Cathode Materials

SYSTEMS: Doped lithium nickel manganese oxides; lithium iron phosphates; layered materials

BARRIERS: Low rate capabilities, high cost, poor stability.

OBJECTIVES: Determine the effect of structure on stability of cathodes. Explore rate limitations and relation to structure.

APPROACH: Use solid state NMR to characterize local and diffraction/TEM for long range structure, as a function of sample preparation method, state of charge, and number of charge cycles. Use first principles calculations (density functional theory) to identify redox-active metals, relative stability of different structures, and the effect of structure on cell voltages and identify promising cathode materials for BATT applications. Anticipate possible instabilities in materials at high states of charge by using calculations. Use calculations and NMR to identify low activation energy pathways for cation migration and to investigate electronic conductivity.

STATUS OCT. 1, 2005: $LiFePO_4$ studies by NMR will be ongoing. NMR studies of local structure of $Li[Li_{(1-2x)/3}Ni_xMn_{2/3-x/3}]O_2$ following cycling to high voltages will have been completed. Conductivity and transport modeling in $LiFePO_4$ will be ongoing. Development of methodology to predict stability of electrodes will be started.

EXPECTED STATUS SEPT. 30, 2006: Neutron diffraction studies of charged $Li[Li_{(1-2x)/3}Ni_xMn_{2/3-x/3}]O_2$ $x = 0.5$ cells will be completed. Results will have been compared with predictions from calculations. Applications of NMR and calculation methodology to other relevant systems under investigation by members of the BATT Program will be ongoing. Stability and conductivity models will have been tested.

RELEVANT USABC GOALS: 10 year life, < 20% capacity fade; 30 ohm/cm^2 area-specific impedance.

MILESTONES:

1. November 2005 – Initiate studies on conductivity in $LiFePO_4$ (NMR).
2. November 2005 – Acquire neutron diffraction data for the charged materials $Li_{1-x}[Li_{(1-2x)/3}Ni_xMn_{2/3-x/3}]O_2$ and initiate data analysis
3. November 2005 –Perform initial tests with methodology for stability prediction.
4. May 2006 – Complete analysis of the structure of $Li_{1-x}[Li_{(1-2x)/3}Ni_xMn_{2/3-x/3}]O_2$ during and after charging (by diffraction) and relate to performance.
5. May 2006 – Develop modeling and optimization approaches for rate capability of Ni-Mn based layered materials and $LiFePO_4$.

PROGRESS TOWARD MILESTONES

A full neutron diffraction analysis of the structure of Li[$Ni_{0.5}Mn_{0.5}$]O_2 as a function of state of charge has been completed; this work complements our earlier ^{6}Li MAS NMR studies of the same system (see Q4_2005). The work shows that significant structural rearrangements occur charging the samples, which are not necessarily reversible, particularly following charging to high voltages. The significant migrations of the Ni^{2+} ions in the Li layers, following charging to above 4.6 V. These Ni ions migrate to sites in the transition metal layers that have been vacated by Li^+. On subsequent discharge, only a subset of the Ni ions return to their initial site in the Li layers. The change in the c parameter as function of state of charge (Fig. 1) clearly demonstrates that structural changes are occurring at high voltage. No Li^+ returns to the transition metal layers following charge to 5.0V. Li does return if the material is charged to only 4.6 V. Calculations have been performed to explore the mechanisms for Ni migration and the structural features that stabilize Ni occupancy in the Li *vs.* transition metal layers. Magnetic susceptibility measurements performed in collaboration with S. Whittingham's group are consistent with Ni migrations following charging. This completes the work for the Nov 2005 milestone.

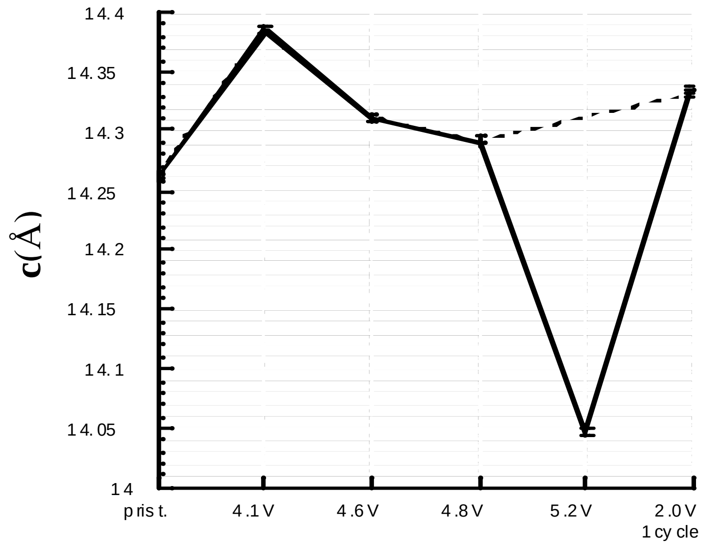


Figure 1. The change in the c-parameter on cycling. The dashed line indicates the data for the sample that was cycled to 4.8 V and then discharged to 2.0 V.

We now are using a combination of diffraction and NMR methods to investigate the effect of processing conditions on cation ordering. High resolution and intensity synchrotron radiation data strongly indicates that the development of cation ordering in the transition metal layers, in the Li[$Ni_{0.5}Mn_{0.5}$]O_2 and Li[$Ni_{1/3}Mn_{5/9}Li_{1/9}$]O_2 depends strongly on the length of heat treatment. Predictions from our joint experiment and theory studies are currently being used to help guide our synthetic efforts to synthesize materials with different cation orderings, to explore correlations between cation ordering and electrochemical performance. High-temperature NMR studies on $Li_{1-x}FePO_4$ are in progress.

TASK STATUS REPORT

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

TASK TITLE: Corrosion of Current Collectors

SYSTEMS: Gr/$LiPF_6$+EC:DEC/$LiFePO_4$ and Gr/$LiPF_6$+EC:DEC/$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$

BARRIERS: Inadequate corrosion resistance of aluminum current collectors

OBJECTIVES: Confirm the susceptibility of Al current collectors to underdeposit corrosion (udc), which is a form of crevice corrosion, in $LiPF_6$ electrolytes by inspecting the current collectors of ~50 additional life-tested coin cells. Determine the mechanism of udc and, in particular, determine the effect of temperature (25 to 60°C) and the influence of cathodes, such as $LiFePO_4$ and $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$, in causing udc. Establish the effectiveness of remedial actions, such as modifications to Al surface film and the addition of inhibitors on crevice corrosion resistance. Determine the effect of remedial actions against udc on the battery's discharge capacity and power.

APPROACH: The research proposed for FY2006 consists of five tasks: (1) determine the mechanism of udc of Al current collectors, in particular determine role of cathodes and temperature on udc; (2) evaluate remedial actions, which consist of modifying the Al surface and adding inhibitors to the electrolyte; (3) develop a short-time laboratory test of udc (for mechanistic study and for evaluating remedial actions); (4) assess effects of most effective remedial action(s) on performance of battery; (5) microscopically inspect (for evidence of corrosion) Al current collectors of ~50 additional coin cells previously charge/discharge tested by Marca Doeff (to bolster earlier conclusions regarding practical importance of corrosion and to confirm that corrosion occurs by udc.).

STATUS OCT. 1, 2005: Short-term udc test will be developed (Task 3). Udc tests of aluminum with different crevice formers will be underway (Task 1). Aluminum electrodes with anodized films formed in sulfuric acid (to produce 1-10nm thin layer of Al_2O_3) and in battery electrolytes (to produce duplex film with outer layers of AlF_3 or $AlBO_3$) will be prepared and coated with cathodes of $LiFePO_4$ (Tasks 2 and 4). Inspection of current collectors from life-tested coin cells will continue (Task 5).

EXPECTED STATUS SEPT. 30, 2006: The contribution of corrosion of current collectors to a battery's overall loss of capacity and the improvements due to remedial actions will be quantified. The mechanism of crevice corrosion of Al and the role of cathodes and temperature in causing corrosion of Al current collectors in electrolytes with $LiPF_6$ will be identified.

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

MILESTONES:
(1) August 2006 – Determine the specific role of cathodes such as $LiFePO_4$ and $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ in causing crevice corrosion of aluminum current collectors in battery electrolytes with salts of $LiPF_6$.
(2) August 2006 – Determine the effects of remedial actions against corrosion on a battery's loss of capacity.

PROGRESS TOWARD MILESTONES

During the past quarter, work was focused on (1) inspecting Al current collectors in life-tested ATD batteries for evidence of corrosion, and (2) determining the details of the mechanism of corrosion of Al current collectors in Li-ion batteries.

We have examined 19 ATD batteries out of 31 (with GEN2 electrolyte) that were previously charge/discharge tested at different temperatures ranging from ~25-60ºC. Microscopic inspection of Al current collectors of the ATD batteries was undertaken to confirm results of earlier laboratory corrosion tests of Al and the results of microscopic inspection of life-tested Li-ion coin cells. Both the laboratory corrosion tests and the inspections of the coin cells' current collectors indicated Al current collectors were susceptible to a type of crevice corrosion called underdeposit corrosion (udc).

Initial inspections indicate extensive localized corrosion of the Al current collector in all 19 cells even in ATD cells tested at room temperature (25ºC) for a short period of time (4 weeks). The results strongly suggest udc of the Al current collectors. We have begun performing a statistical analysis of the severity of corrosion, and preliminary results show that in one ATD cell tested at 45ºC without cycling, there are 2 corroded regions; one with 1.66% corroded area (STDEV 0.95%) and a second with 5.16% corroded area (STDEV 1.17%). Another analysis of a cell cycled at 50ºC for 20 weeks (until 50% power fade was reached), shows an average corroded area of 5.88% (STDEV 2.82%). Microscopic investigation of the surfaces of Al current collectors in life tested cells shows the corrosion consists of a large number of pits. The pits are distributed all over the current collector, and their size is around ~10 microns in diameter. Some of the Al foils contain pits that are filled with corrosion products, and identification of the corrosion products is an essential step in elucidating the mechanism of the corrosion process. We have just submitted a proposal to the National Center for Electron Microscopy in LBNL (NCEM) to characterize the corrosion products using TEM combined with EDX, and we hope to begin this study soon.

In addition, in order to elucidate the role of each cathode component on the Al's corrosion, we conducted galvanostatic measurements with different kinds of coatings on Al; 1. Al coated with only carbon black (poor coverage), 2. Al coated with only the polymeric binder (PVdF), 3. Al coated with only carbon black and the polymeric binder (PVdF) (1 and 2 um thick, good coverage), 4. Al/Cathode with an active material of $LiFePO_4$, 5. Al/Cathode with an active material of $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$, 6. Al/Cathode with an active material of $LiFePO_4$ without graphite, but with a higher concentration of carbon black. Underdeposit corrosion was found in samples 3-6. This study is incomplete, and we intend to further investigate the influence of the cathode components on the udc corrosion. Preliminary results suggest that the udc of Al might occur provided that the coating contains both carbon black and PVdF.

We plan to test the role of the water content in PVdF in the breakdown of the passivation film of Al, and to galvanostatically test Al covered with a matrix of PVdF with micro-particles of $LiFePO_4$. We are currently in the process of testing the validity of the hypothesis that localized corrosion of Al current collectors is due to the generation of PF_5. In order to investigate the effect of concentration of PF_5, we are studying the resistance of Al in electrolytes with different weight ratios of EC: EMC (from 1:7 to 2:7). We plan to continue this study in collaboration with John Kerr, and to use his system to produce PF_5 to evaluate its effect on Al. We also intend to investigate the compositional changes of the solution, after udc is formed in the Al current collector.

BATT TASK 6
MODELING

TASK STATUS REPORT

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

TASK TITLE: Modeling - Improved Electrochemical Models

SYSTEMS: Gr/$LiPF_6$+EC:DEC/$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (high-voltage, high-energy); Gr/LiBOB+γBL:EA/$LiMn_2O_4$ (high-voltage, high-power); Gr/$LiPF_6$+EC:DEC/$LiFePO_4$ (low-voltage, high-stability)

BARRIERS: Poor transport properties, capacity, and power fade

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

APPROACH: Use simulations to improve understanding of limitations in cell performance. Develop improved experimental methods for measuring transport properties in liquid electrolytes.

STATUS OCT. 1, 2005: Work is completed on a model for calculating stress distributions in electrode materials during intercalation. Full characterization of transport in $LiPF_6$ electrolytes is ongoing. Optimization of the lithium titanate spinel electrode has begun.

EXPECTED STATUS SEPT. 30, 2006: Optimization of lithium titanate spinel in various systems will be ongoing. Full characterization of transport in $LiPF_6$ electrolytes will be ongoing. Incorporation of side reactions into dualfoil for lithium-ion cells will begin. A new project will begin, possibly on the distribution of resistance between active materials connected to a current collector.

RELEVANT USABC GOALS: 30 ohm-cm^2 area-specific impedance, Cold cranking capability to -30°C, 300,000 shallow discharge cycles, Abuse tolerance to cell overcharge and short circuit

MILESTONES: May 2006 – Fully characterize transport in a binary electrolyte.

PROGRESS TOWARD MILESTONES

Transport Property Measurement

A new method is being developed in order to avoid the effects of side reactions in diffusion-coefficient measurements. A modified version of restricted diffusion is being used to measure diffusion coefficients in solutions of $LiPF_6$ in acetonitrile that does not require the use of lithium electrodes. The experimental setup now allows for temperature control. The new method is now starting to be applied to Gen 2 electrolyte as well. Preliminary results indicate that the diffusion coefficient for $LiPF_6$ is one order of magnitude higher in acetonitrile than in baseline electrolytes. Diffusion coefficient results will be combined with conductivity and concentration-cell measurements in order to characterize transport in binary electrolytes.

A modeling effort has begun, investigating the effect of various parameters including particle size and porosity on the high-charge rate behavior of lithium titanate spinel.

TASK STATUS REPORT

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

TASK TITLE: Modeling - Understanding the Behavior of Advanced Li-ion Chemistries Using Mathematical Modeling

SYSTEMS: $LiFePO_4$, $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$, and $LiMn_2O_4$ all *vs.* graphite

BARRIERS: Poor low-temperature operation, low power capability, capacity/power fade.

OBJECTIVES: Understand and quantify the behavior of the BATT chemistries. Use models to quantify the performance of new electrolytes and cathodes made in the program. Develop methodologies to estimate transport properties in cathodes

APPROACH: Develop mathematical models for various Li-ion chemistries. Design experiments to test theoretical predictions and to estimate properties needed for the models. Use models to compare various chemistries with each other and assess their ability to meet EV and HEV goals.

STATUS OCT. 1, 2005: The fast charge capability of the $LiFePO_4$ cathode will be quantified. Experiments that are designed to understand the phase behavior of the $LiFePO_4$ cathode will be ongoing.

EXPECTED STATUS SEPT. 30, 2006: A comprehensive quantification of the phase behavior of the $LiFePO_4$ system will be complete. A quantification of the low-temperature behavior of the $LiFePO_4$ cathode will be complete. Efforts to understand the spinel-L333 mixture materials will be on going. Development of models for the advanced materials synthesized in the BATT Program will be ongoing.

RELEVANT USABC GOALS: ASI =30 Ω-cm^2, Cold cranking capability to -30^{o}C, 300,000 shallow discharge cycles

MILESTONES:

(1) December 2005 – Quantify the impact of the phase behavior of $LiFePO_4$ cathode during HEV operation

(2) May 2006 – Complete model for the spinel-layered mixture material.

PROGRESS TOWARD MILESTONES

Path dependence in $LiFePO_4$: Previously, we have described the existence of path dependence in the $LiFePO_4$ system, whereby the high-rate electrochemical behavior at a particular State of Charge (SOC) depends on the history by which the electrode was brought to that SOC. Since these preliminary experiments, we have conducted an extensive study to understand the implications of this behavior when operating under HEV conditions. For example, the ASI calculated from a 3C pulse for 10 s at 50% SOC during charge is either 50 Ω-cm^2 or 70 Ω-cm^2, depending on the cycling history by which the electrode was brought to 50% SOC. The lower value occurs when the electrode is brought to 50% from the fully-charged state and the higher value when the electrode is brought to 50% from the fully-discharged state. Further, for the same cycling history, the ASI is different for discharge than for the regen pulse. More interestingly, while the value is higher for the regen pulse compared to the discharge pulse when the electrode is brought to 50% SOC from the fully-discharged state, the value is lower for the regen when the electrode is brought to 50% SOC from the fully-charged state.

The implication of this study is that predicting the power capability of the $LiFePO_4$ system is not straightforward and a clear understanding of the cycling history is necessary. In other words, battery management systems that are developed for this chemistry would need to account for the path dependence described here. In addition, reporting values of ASI in this material does not necessarily give you all the needed information; what is needed is the cycling conditions under which this value was obtained. This concludes Milestone 1.

Future work will concentrate on using the previously developed mathematical model along with this experimental data to understand the path dependence.

High-power Graphite Anodes for HEVs: We have also finished collecting experimental data on a high-power graphite anode (Mag 10). The data clearly shows the much higher power capability of this anode when compared to the previously studied SL20 anode. Simulations have begun to extract the properties that characterize this anode. Once this is complete, we anticipate repeating the optimization study to quantify the impact of this anode under various operating conditions.

TASK STATUS REPORT

PI, INSTITUTION: A.M. Sastry, University of Michigan, Ann Arbor

TASK TITLE: Modeling - Scale-Bridging Simulations of Active Materials in Li-ion Batteries, and Validation in BATT Electrodes

SYSTEMS: Low-cost Li-ion batteries

BARRIERS: Short lithium battery lifetimes

OBJECTIVES: Determine superior composition and processing conditions of electrodes for conductivity enhancement, especially for the LiFePO4 cathode. Develop scale-bridging simulations which will allow identification of the best particle morphologies for both energy- and power-dense systems. Develop superior anodes and cathodes by altering the content and morphologies of conductive materials.

APPROACH: Using new simulations developed to model conductivity of the particle networks within both anodes and cathodes, we will expand our investigations with three major new thrusts: 1) development of scale-bridging models to determine likely electrochemical performance of cathode materials, taking direct account of the effects of particle shape and connectivity; 2) determination of the effect of mechanical compression on real batteries, accounting for both multiple layers and cell compression, and 3) extensive experimental and numerical simulation of conduction in new materials synthesized by other BATT workers (Battaglia, Zaghib, Wheeler), and provision of guidance concerning the best morphologies to use.

STATUS OCT. 1, 2005: Experiments (LBNL and UM) and simulations on conduction and electrochemical perfomance in baseline anodes and cathodes, with correlations developed relating material composition, SEI layer formation and cell capacity losses will be completed. Modeling of other BATT Program baseline chemistries will be ongoing.

EXPECTED STATUS SEPT. 30, 2006: Correlation of cathode performance with particle morphology, including fiber additives will be made. Completion of conductivity and mechanical experiments to quantify losses under realistic loads will be made.

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

MILESTONES:
(1) December 2005 – Predict conductivity in electrodes fabricated by Battaglia at LBNL, develop optimized electrodes for minimum resistivity, minimum mass, maximum failure strength.
(2) January 2006 – Development of coupled electrochemical/mechanical simulations of small arrays within cathodes, with prediction of charge densities in particles.
(3) June 2006 – Expansion of algorithms to allow prediction of electrochemical performance of available particle shapes and sizes, in collaboration with Battaglia, Srinivasan.
(4) June 2006 – Experimental verification of conductivity, reactivity of cathode materials *via* AFM.

PROGRESS TOWARD MILESTONES

• Accomplishment toward milestone over last quarter

Modeling—Electrochemical Performance: In this quarter, we have built a 3D finite element model to simulate electrochemical performance. This model was based on our own prior work [1,2,3], and those of Newman and others [4,5]. In our initial test case, a lithium-manganese oxide-polymer cell tested in Macklin et al. [6] was used. A realistic microstructure of the porous electrode was first generated, based on the collision algorithm developed in our prior work [1]. The diffusivity and conductivity of ions, conductivity of electrons, and other parameters required in the model were estimated from the literature. Our initial results indicate that resistive loss due to the SEI layer is responsible for the capacity loss for the lithium-polymer cell used in the work of Macklin et al. [6].

• Further plans to meet or exceed milestone

We will continue developing mathematical tools for analysis of baseline materials, and integrate with other DOE workers as validation of models, and in order to continue to provide guidance on selection/design of materials. With other BATT workers (Battaglia, Srinivasan), we will test the electrodes prepared at LBNL to identify the superior design, by which electrodes can achieve minimizing resistivity, mass density, and maximum failure strength. Both of our prior modeling approaches and codes will be used to experimental system and to map electrode's conductivity. We will also collaborate with them to test cells in order to validate our proposed 3D finite element model.

• Reason for changes from original milestone: N/A

References

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[5] R.E. Garcia, Y.-M. Chiang, W. C. Carter, P. Limthongkul, and C. M. Bishop, Microstructural Modeling and Design of Rechargeable Lithium-Ion Batteries, *Journal of the Electrochemical Society* **152**, 1, A255-A263 (2005).

[6] Macklin, W.J., Neat, R.J. and Powell, R.J., 1991. "Performance of Lithium Manganese Oxide Spinel Electrodes in a Lithium Polymer Electrolyte Cell," Journal of Power Sources, **34**(1): pp. 39-49.

PROPOSALS UNDER REVIEW

ORGANIZATION *(Principal Investigator)*	**TITLE**	**STATUS**
Massachusetts Institute of Technology *(Y. Shao-Horn)*	TEM and AFM studies of nanoparticle coating on lithium battery materials: its effect on electrode stability, battery cycle life and battery safety	Unsolicited Proposal- Contract Placed
Clemson University *(D. DesMarteau/S. Creager)*	New Battery Electrolytes Based on Lithium Fluorosulfonate and Fluorosulfonimide Salts	Renewal Proposal- In Negotiation
HydroQuébec *(K. Zaghib)*	Li-ion Batteries with Low Cost Materials	Renewal Proposal- In Negotiation
University of Texas @ Austin *(J.B. Goodenough)*	Cathodes-Novel Materials	Renewal Proposal- In Negotiation
University of Texas @ Austin *(A. Manthiram)*	Superior capacity retention, high rate spinel manganese oxide compositions for lithium ion batteries	Renewal Proposal- In Negotiation

BATTERIES FOR ADVANCED TRANSPORTATION TECHNOLOGIES (BATT) CALENDAR OF RECENT AND UPCOMING EVENTS

October 2005

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

May 2006

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

15 - 19 The Sixth International Advanced Automotive Battery and Ultracapacitor Conference and The Second International Symposium on Large Lithium Ion Battery Technology and Application- Baltimore, MA, Tel: (530) 692-0140 E-mail: info@advancedautobat.com, http://www.advancedautobat.com/AABC/

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

June 2006

6 - 9 The Batteries for Advanced Transportation Technologies Annual Review- Berkeley, CA, http://berc.lbl.gov/BATT/BATT.html

October 2006

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