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July 28, 2008

Mr. David Howell
EE-2G/Forrestal Building
U.S. Department of Energy
1000 Independence Ave., S.W.
Washington D.C. 20585

Dear Dave:

Here is the third-quarter FY 2008 report for the Batteries for Advanced Transportation Technologies (BATT) Program. This report and prior Program reports can be downloaded from http://batt.lbl.gov/.

Sincerely,

Venkat Srinivasan
Manager
BATT Program

cc:	J. Barnes	DOE/OFCVT
	P. Davis	DOE/OFCVT
	T. Duong	DOE/OFCVT
	J. Krupa	DOE-BSO
	J. Muhlestein	DOE-BSO

BATT TASK 1
CELL ANALYSIS

TASK STATUS REPORT

TASK 1.1 - PI, INSTITUTION: Vincent Battaglia, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Cell Analysis - Cell Fabrication and Materials Characterization

SYSTEMS: High-voltage, high-energy: Gr/$LiPF_6$+EC:DEC/$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$

BARRIERS: Insufficient energy density, poor cycle life.

OBJECTIVES: 1) Provide a comprehensive, independent assessment of promising materials developed in the BATT program with regard to meeting high power or high energy performance targets. 2) Bring fundamental understanding to the area of electrode fabrication.

GENERAL APPROACH: Objective 1) is achieved through the identification and application of key diagnostic techniques that allow for the physical, chemical, thermal, and electrochemical characterization of materials as they relate to battery performance. Objective 2) is accomplished through engineering design analysis of each of the steps of the electrode fabrication process.

STATUS OCT. 1, 2007: The lithium doped Mn-spinel from Toda and a modified Mn-spinel synthesized within the BATT program will be fully characterized. This includes the physical, chemical, thermal, and electrochemical characteristics in a graphite based cell.

EXPECTED STATUS SEPT. 30, 2008: A matched set of cathode and anode electrodes will be designed and fabricated. Characterization of the electrodes against lithium foil will be completed and full cell performance characterization will be in progress.

RELEVANT USABC GOALS: PHEV: 144 Wh/l, 3000 deep-discharge cycles

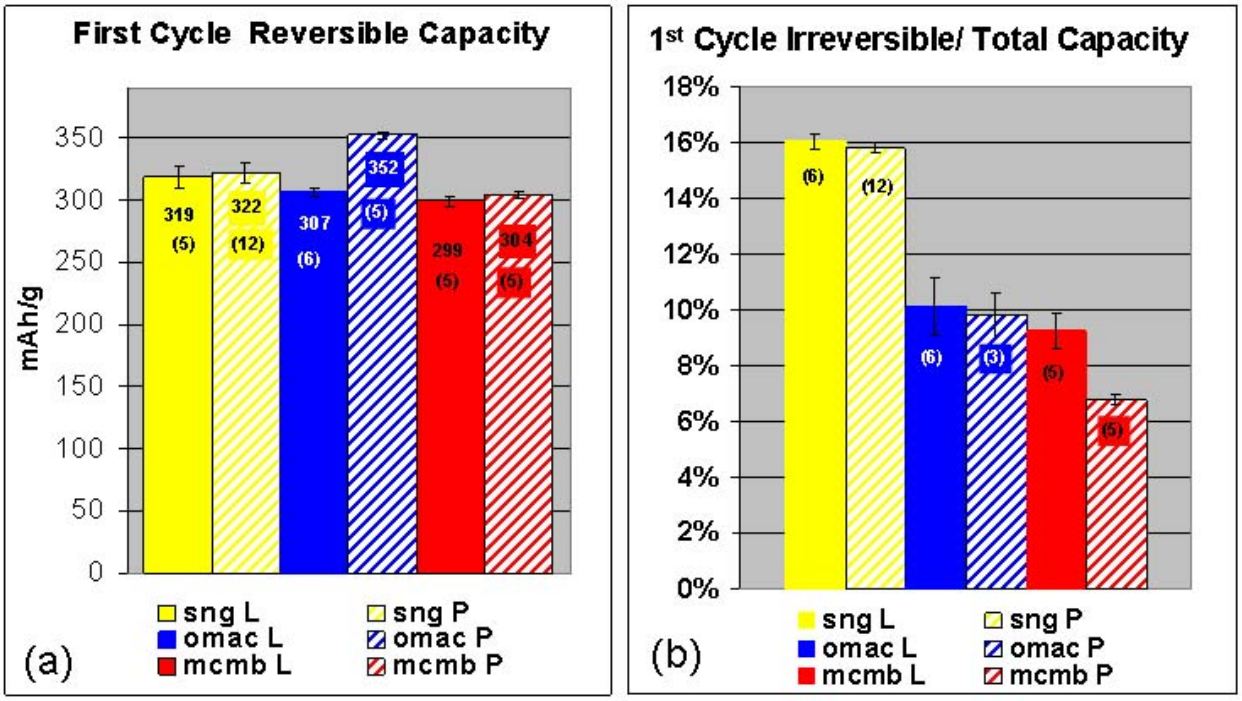
MILESTONES:
(a) Complete the physical characterization of all electrode components (Dec. 07). **Complete**
(b) Complete the cathode development (Jun. 08). **Complete**
(c) Complete the anode development (Aug. 08). **On schedule**
(d) Complete the chemical characterization of NCM (Sep. 08). **On schedule**

PROGRESS TOWARD MILESTONES

(a) Complete the physical characterization of all electrode components, (Dec. '07). **Met**. See the second quarterly report FY08 for details.

(b) Complete the cathode development, (Jun. '08). **Met**. Work on the cathode this quarter included assessing the levels of carbon, binder, porosity, and electrode thickness necessary for making an electrode capable of meeting the PHEV-40 energy density goal. The work showed that electrodes of ~140 microns and 35% porosity with standard ATD electrode formulations should meet the PHEV-40 power/energy requirements. Energy densities of 60% improvement could be achieved by using much less binder and conductive additive. (Data was sent to **Wheeler/Harb** at BYU for modeling.) The ultimate evaluation is the cycling capability as a function of carbon and binder content and the electrode porosity. This assessment will require a cycleable anode, the focus of the next milestone, as the lithium counter electrode used thus far is not a valid electrode to use for long term cycling tests.

(c) Complete the anode development, (Aug. '08). **On schedule**. Three graphites were evaluated to determine which is most appropriate for further development. (Laminates were supplied by **Zaghib** of HQ.) Reversible and irreversible capacities were measured as well as the rate of the side reaction after formation. The results of this initial characterization are provided in the figure and suggest that MCMB-1028 provides the best combination of reversible and irreversible capacity. Since we already have experience with MCMB and enough on-hand to last us through this analysis, we will continue to use this material in our initial assessment of the Graphite/NCM system for PHEV-40 applications.



Value in parentheses is the number of cells cycled. L: anode laminates made at HQ; P: anode laminates made at LBNL.

(d) Complete the chemical characterization of NCM, (Sep. '08). **On schedule.** An ICP-OES was purchased last year and arrived this quarter. The lab is still being reconfigured to allow for the set-up of this equipment. In the meantime, techniques are being established using a Berkeley campus instrument and samples are being prepared and stored.

TASK 1.2 - PI, INSTITUTION: Thomas Richardson, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Cell Analysis - Cathodes, Alloy Anodes, Diagnostics

SYSTEMS: High-voltage, high-energy: Gr/$LiPF_6$+EC:DEC/$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$
High-voltage, high-power: Gr/$LiPF_6$+EC:DEC/$LiMn_2O_4$
Low-voltage, high-stability: Gr/$LiPF_6$+EC:DEC/$LiFePO_4$

BARRIERS: PHEV: Low available energy, poor cycle life; EV: Low energy, poor cycle life.

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 that may contribute to impedance rise in composite electrodes or that may lead to better electrode design.

GENERAL APPROACH: Identify candidate electrode compositions by systematic analysis of phase diagrams and literature reports. Synthesize novel materials and/or unique structures for evaluation. Employ X-ray diffraction (XRD), *in situ* microscopy, vibrational spectroscopies, and electroanalytical techniques to determine the applicability of the new materials to BATT chemistries.

STATUS OCT. 1, 2007: Further details of the solid state chemistry of Li_xFePO_4 have been elucidated. In particular, the roles of intermediate phases and solid solutions have been clarified. Certain line phases, with x = 0.60 and x = 0.34 can be stabilized indefinitely in highly crystalline samples that also contain the end members. The convenient synthetic route to alloy cermets developed for the Li-Mg system has been extended to Li-Si. The observed higher rate capability in Li-Mg-Mg_3N_2 cermets relative to Li-Mg foils appears to be due to the greater surface area of the former.

EXPECTED STATUS SEPT. 30, 2008: The techniques used to study Li_xFePO_4 will have been applied to the Li_xMnPO_4 system.

RELEVANT USABC GOALS: *PHEV*: 96 Wh/kg, 5000 cycles; EV: 200 Wh/kg; 1000 cycles (80% DoD).

MILESTONES:
(a) Report rate and cycling performance of Li alloy and/or cermet electrodes with capacity exceeding 400 mAh/g. (Jun. 08) **Complete**
(b) Report results of phase transition, rate, and stability studies of Li_xMnPO_4 cathode materials. (Jul. 08) **Delayed – will be completed by Sep. 08**

PROGRESS TOWARD MILESTONES

High Voltage Cathodes: We are addressing the challenge of improving the rate, utilization, and stability of $LiMnPO_4$ electrodes by studying the inherent properties of the phases involved. Previously, we found chemical delithiation of $LiMn_{1-x}Mg_xPO_4$ proceeded to a greater degree for higher values of *x*. When $x = 0.2$, complete delithiation was achieved in a short time, whereas for lower values, long reaction times were needed. Possible explanations for the effect of Mg substitution include reduced macroscopic strain due to better lattice matching and decreased internal stresses due to the smaller concentration of Jahn-Teller ions and the intermediate ion radius of Mg^{2+} between those of Mn^{2+} and Mn^{3+}. The inability of Mn^{3+} decomposition products to accommodate Mg^{2+} may also inhibit decomposition of the substituted phases when oxidized. A paper entitled "Improving the performance of lithium manganese phosphate through divalent cation substitution" has been submitted to *Electrochemical and Solid State Letters* and is in the final stage of revision.

To compare these results with electrochemical charging, electrodes were fabricated by ball milling $LiMg_{0.1}Mn_{0.9}PO_4$ and $LiMnPO_4$ crystals with 20 wt% carbon black, then mixing with 10 wt% PVdF, 5 wt% SFG-6 graphite, and an additional 5 wt% acetylene black. The slurries were spread onto carbon-coated aluminum foil current collectors and dried at 120°C *in vacuo* for 10 h. Swagelok cells with Li foil anodes and reference electrodes were charged potentiostatically at 4.5 V *vs.* Li/Li^+. The specific current profiles for the two cells are shown in Fig. 1. The substituted electrode exhibited higher currents throughout the 20 h of charging, delivering nearly 120 mAh/g of active material despite its lower theoretical capacity, 157 mAh/g (Fig. 2). The unsubstituted electrode delivered only about 75 mAh/g (theoretical capacity 171 mAh/g).

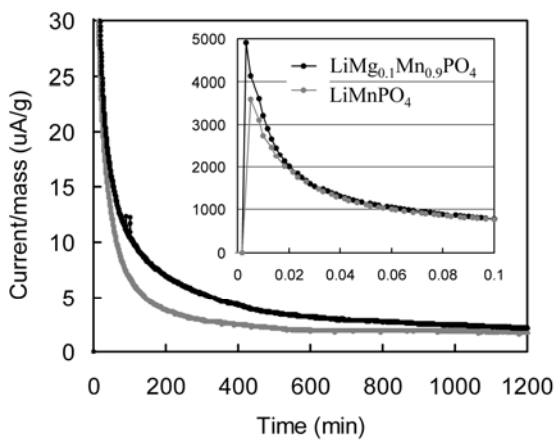


Figure 1. Charging current at 4.5 V.

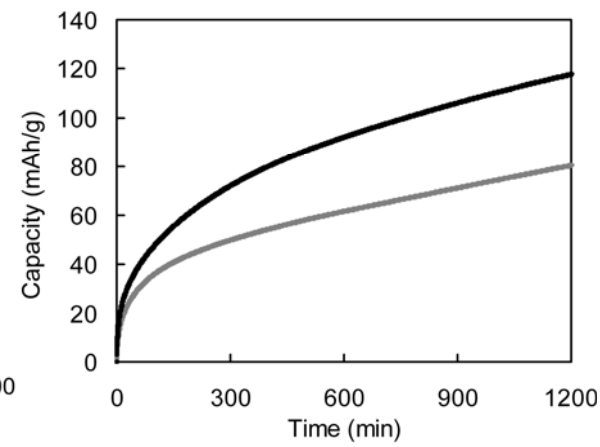


Figure 2. Capacity *vs.* time at 4.5 V.

High Capacity Anodes: Progress on this task has been delayed due to shifting of postdoc responsibilities to other work. We anticipate that the milestone will be completed in September 2008.

Collaborations this quarter: Kostecki, Grey, Yang, Doeff.

TASK 1.3 - PI, INSTITUTION: Karim Zaghib, Hydro-Québec (IREQ)

TASK TITLE - PROJECT: Cell Analysis - Interfacial Processes: SEI Formation and Stability on Cycling

SYSTEMS: Low-cost Li-ion

BARRIERS: Low energy and poor cycle/calendar life

OBJECTIVES: Identify suitable graphite materials for anodes that meet the requirement for low cost. Fabricate Li-graphite anode half cells and Li-ion cells by using cell chemistries proposed by DOE, and send 50% of the total cells to LBNL for testing. Graphite anode will be the main focus of this work. Electrodes based on different carbon materials will be coated, evaluated and supplied to other BATT Program team members. We will continue the development of water-dispersed binder (WDB) for the carbon-based anodes. The lithium titanate spinel ($Li_4Ti_5O_{12}$), which yields a passivation-free electrode, will also be considered in this project. Experiments will be conducted to understand the properties of the SEI layer that forms on different graphite electrodes fabricated using different binder and additives.

GENERAL APPROACH: Our approach is to coat anode electrodes based on low-cost graphites. Since MCMB graphite has demonstrated a stable SEI layer, it will be considered as the baseline anode material. Optimization of the anode coating processes will be considered because new carbons have different physical characteristics; this changes the coating parameters that must be used. Electrochemical evaluation of graphite anodes in a half-cell configuration will be employed and compared to the MCMB anode in EC-based standard $LiPF_6$ electrolyte. The effect of the binder will also be addressed (PVDF versus water dispersed binder).

STATUS OCT. 1, 2007: MCMB anode will be coated and evaluated in Li half cells. A new carbon obtained from Osaka Gas, which is reported to be an alternative to MCMB, will be coated and evaluated. The performance, *i.e.,* coulombic efficiency, reversible capacity and cycling, will be compared to SNG graphite. This work will help us to optimize the anode configuration for long cycle life and high-power requirement.

EXPECTED STATUS SEPT. 30, 2008: We expect to improve our technology to identify the optimum anode structure with a stable SEI layer. The water-dispersed binder from Zeon (Louisville, KY) will be evaluated in the electrodes. The coating process will be optimized with the graphites, MCMB and alternative graphite from Osaka Gas, containing PVDF and WDB to obtain suitable film with good adhesion and uniformity. The electrochemical performance (reversible and irreversible capacity) of these anodes will be determined. In addition, electrochemical performance results will be obtained with vinyl carbonate (VC) in cells containing graphite anodes. Cells and coated electrodes will be sent to LBNL to evaluate the physicochemical properties of the SEI layer that forms under different conditions.

RELEVANT USABC GOALS: *Specific power*: 750 W/kg, 5000 cycles, 15 year life (at 40°C).

MILESTONES:
(a) Complete fabrication and characterization of MCMB, alternative graphite from Osaka Gas and SNG anodes based on PVDF in standard electrolyte. (Dec. 07) **Complete**
(b) Identify the effect of water-dispersed binder with different anodes. (Feb. 08) **Complete**
(c) Evaluate VC additive and its content in the electrolyte on anode performance. (May 08) **Complete**

PROGRESS TOWARD MILESTONES

In the last quarter, we evaluated a new graphite (OMAC from Osaka Gas) and compared its performance with SNG12 (HQ) in standard electrolyte 1M $LiPF_6$–EC/DEC with additives VC and VEC. We found that the first coulombic efficiency (CE) was affected when a small amount of additives (2%) was introduced. The improvement was more significant with SNG12 than with OMAC15. The best additive was 2% VEC, witch gives an increase of 1CE from 85% to 93%, however the reversible capacity decreased by 7%.

In this quarter we have completed evaluation of OMAC-12 with water-dispersed binder. The results are comparable to PVDF binder electrodes, with 95% CE in the first cycle (1CE), and 352 mAh/g reversible capacity. However, this performance is higher than that for SNG12 (Fig. 1) - 92% 1CE and 315 mAh/g reversible capacity.

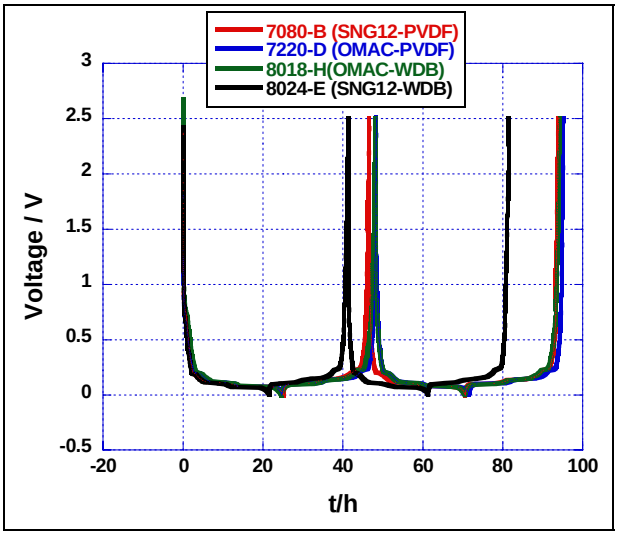


Figure 1. First cycle of Li/Graphite cells in 1M $LiPF_6$ 1M-EC/DEC with different binders.

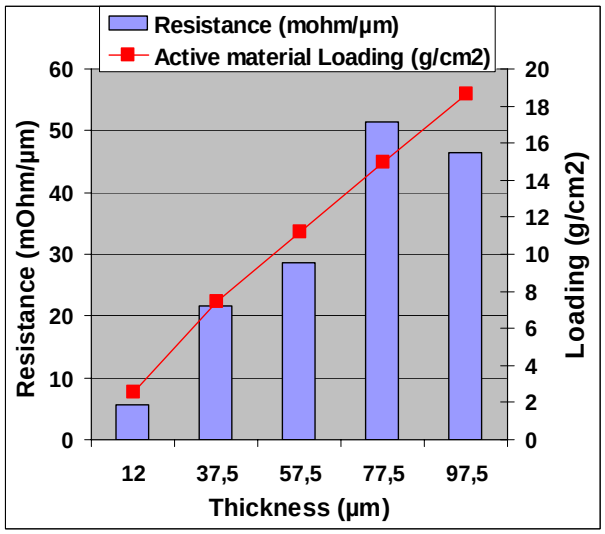


Figure 2. $LiFePO_4$-PVDF electrode resistance as in function of thickness.

In this quarter, we evaluated the resistance of cathodes made with different thickness of $LiFePO_4$ and PVDF ranging from 12µm to 100µm. A four-point probe apparatus was used to measure the resistance after calendaring the electrode at 2 g/cc. The results show a linear increase in the electrode resistance with increasing electrode thickness (Fig. 2). The electrode resistance shows a maximum at an electrode thickness of 77 µm. This result indicates that the power performance of the cell can be affected when thicker electrodes are used.

HQ continues collaborating with the different laboratories in the BATT program by supplying cells and components for evaluation; Li-bag cells with thick $LiFePO_4$ electrodes and commercial 18650 Li-ion-$LiFePO_4$ cells (Dr. Venkat Srinivasan, LBNL); graphite and $LiFePO_4$ electrodes for Arc-test (Dr. Peter Roth, Sandia Lab); and a second delivery this year of 10 cells, aluminum-bag Li/Graphite cells with VC and VEC as additives (Dr. Vince Battaglia, LBNL).

TASK 1.4 - PI, INSTITUTION: Dean Wheeler and John Harb, Brigham Young University

TASK TITLE – PROJECT: Cell Analysis - Design and Fabrication of High-performance Lithium-ion Electrodes for PHEVs

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 modeling tools to analyze and predict high-rate performance.

GENERAL APPROACH: We will explore, through experiments and modeling, different strategies for maintaining high-power performance while increasing energy performance of low-cost $LiFePO_4$ composite cathodes and other materials as they become available, such as $LiMnPO_4$. Our modeling efforts will lead to a more realistic electrode-morphology sub-model in existing state-of-the-art electrochemical models.

STATUS OCT. 1, 2007: We will have built a working cell model that better describes how cell performance depends on different conductivity additives and that is validated by experiment. We will use the model and the associated experiments to better understand the factors that limit performance for the $LiFePO_4$ cathode.

EXPECTED STATUS SEPT. 30, 2008: We will have a set of experimental results to better understand the liquid- and solid-phase transport limitations to high-power and energy density for $LiFePO_4$ cathodes. We will achieve a more predictive quantitative model of liquid-phase transport inside the porous electrode.

RELEVANT USABC GOALS: *Energy*: 56 Wh/kg (10 mile) and 96 Wh/kg (40 mile); *10-s discharge power*: 750 W/kg (10 mile) and 316 W/kg (40 mile).

MILESTONES:
(a) Use improved cell model and experiments to suggest optimal cell-fabrication parameters for use of baseline $LiFePO_4$ material in PHEVs. (Mar. 08) **Complete**
(b) Validate predictive model of liquid-phase transport in porous electrodes. (Jul. 08) **Delayed – will be completed by Aug. 08.**

PROGRESS TOWARD MILESTONES

We continued our work to refine a suite of experimental and modeling tools to better understand the relationship of cell morphology and the resulting impedance. In this quarter, we used our detailed computer model combined with unique experiments to evaluate the transport properties in porous cathodes and separators. This work is toward Milestone (b), which is on track for completion in August 2008.

We tested cells to quantify liquid-phase transport resistance in the separator and the cathode. Figure 1 shows one such model-experiment comparison of a polarization-interrupt experiment in a porous cathode film. Excellent agreement between model and experiment is obtained. Our work suggests that the liquid-phase resistance in the cathode is larger (by a factor of around 6) than predicted by the oft-used Bruggeman relation. This is in agreement with the expectation that for the particle distributions typical of lithium-battery electrodes, the liquid resistance will be larger than that predicted by Bruggeman relation. This work will soon be submitted for publication.

Work is continuing to correlate the effective liquid-phase transport resistance with cathode morphology, such as porosity and carbon fraction. For this, necessary experiments are being performed. Our collaborations with the Battaglia group to model and better understand performance of the $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ baseline cathode material for PHEV are ongoing.

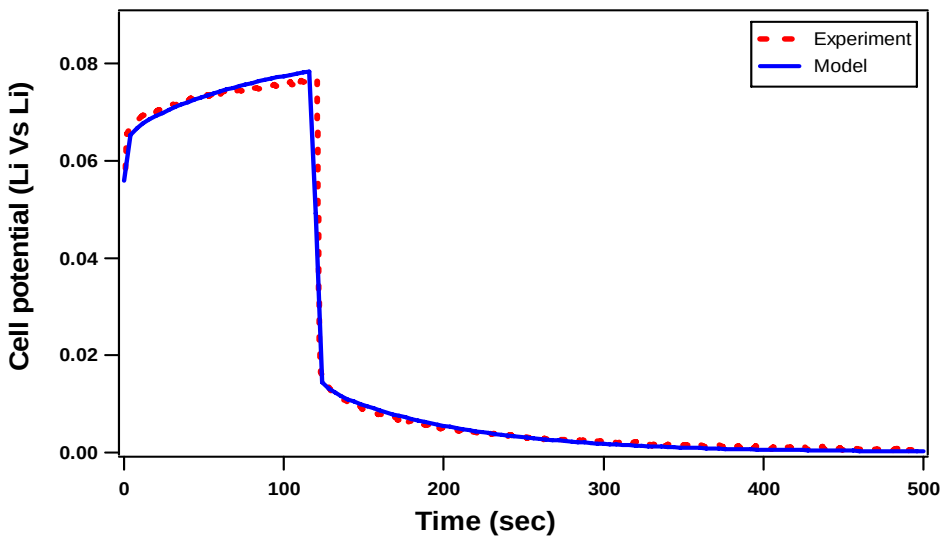


Figure 1. Model-experiment comparison of polarization-interrupt in a symmetric cell containing a porous cathode film.

TASK 1.5 - PI, INSTITUTION: Nancy Dudney, Oak Ridge National Laboratory

TASK TITLE – PROJECT: Cell Analysis - Investigation of Metallic Lithium Anode and Graphite Current Collector for Advanced Batteries

SYSTEMS: High-voltage, high-energy: Gr/$LiPF_6$+EC:DEC/$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$
Low-voltage, high-stability: Gr/$LiPF_6$+EC:DEC/$LiFePO_4$

BARRIERS: Poor cycle life, poor abuse tolerance, low energy density.

OBJECTIVES: Study the initiation of Li roughening upon cycling with an organic liquid or polymer electrolyte. Use these fundamental studies to identify new strategies to stabilize the Li interface. Investigate the use of highly conductive graphite as the current collector for the cathode. Evaluate battery lifetime and thermal management.

GENERAL APPROACH: Study the Li-electrolyte interface in contact with the electrolyte, including the SEI layer formation upon initial contact with the electrolyte and then during the early stage of roughening or dendrite formation. Investigate how SEI formation depends on composition and structure of the Li metal surface. Study the processing and properties of Li-ion battery cathodes, such as $LiFePO_4$, coated onto graphite current collectors in the form of high surface area foams or fibers. Assess the cycling performance of the cathode and the stability of the cathode/graphite interface.

STATUS OCT. 1, 2007: From baseline experiments, we have established that the SEI layer formed at a fresh Li surface submerged in $LiPF_6$+EC:DEC becomes increasingly resistive with the soak time. Techniques to characterize the interface, SEI formation, and the Li morphology upon initial cycling will be developed and tested. Graphite foam pieces have been successfully coated with $LiFePO_4$ plus a small carbon additive. Good electrical and mechanical bonds have been formed by sintering. Batteries formed with a liquid electrolyte and Li anode have shown good cycling with reasonable capacity utilization.

EXPECTED STATUS SEPT. 30, 2008: We expect to advance our understanding of the kinetics of the SEI formation and how the formation and properties vary for modifications in the Li structure and surface passivation layer. We will characterize the cathode/graphite bond as-formed and after-cycling of the cathode. With additional cycling performance results, we will project the performance of cells with graphite foam or graphite fiber current collectors for comparison with traditional battery design.

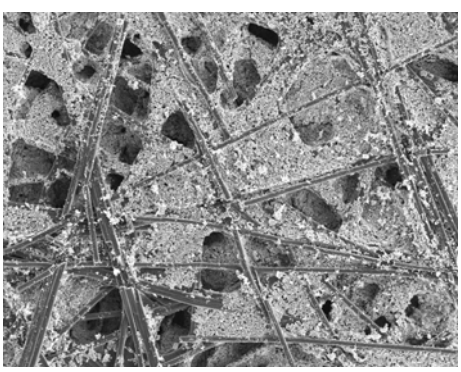
RELEVANT USABC GOALS: Energy density of 150 Wh/kg at C/3, 1000 cycles at 80% DOD, and operating environment to 50 or 85°C.

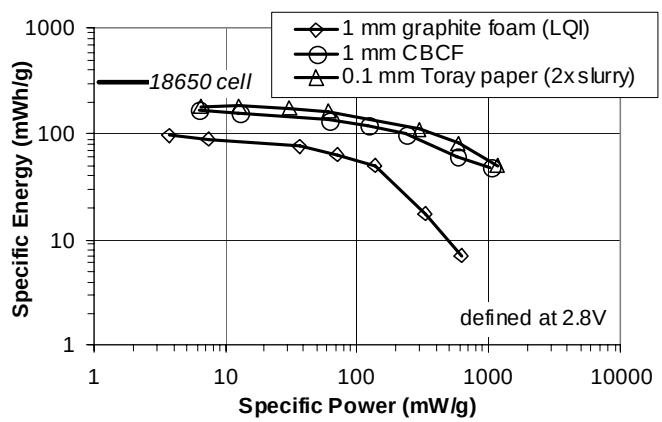
MILESTONES:
(a) Evaluate the SEI formation for Li in the organic electrolyte. (Sep. 08) **On schedule**
(b) Characterize the bond formed by heat treatment of cathode particles with a graphite current collector. (Sep. 08) **On schedule**
(c) Project the energy and power densities for batteries with graphite foam or graphite fiber current collectors. (Sep. 08) **Complete**

PROGRESS TOWARD MILESTONES

Porous graphite current collectors:
Highly conductive foams and fibers are being evaluated as cathode current collectors. This work was presented at the Phoenix ECS meeting and will be published in ECS Transactions. Recent work has shifted toward examination of $LiFePO_4$ supported with carbon fibers. Carbon-bonded carbon fibers (CBCF) and commercially available carbon fiber papers (Toray) have been evaluated with good results. The energy and power are higher for these 3D fiber-scaffolds than for the graphite foams reported earlier likely because of the more open structure. In addition, the fiber cathodes are more robust and easily assembled into a battery. Although these fiber structures have a lower thermal conductivity than the graphite foams, with proper choice of materials this property can likely be improved. Even so, projections of $LiFePO_4$-filled Toray paper indicate that the carbon fiber will support comparable loading and provide heat transport equal to that of Al foil. The figures show specific energy and power, based on the total weight of cathode+fibers, and a SEM micrograph of $LiFePO_4$ bonded to Toray paper by a 700°C anneal. For scale, the Toray fibers are 10 µm diameter.

In this quarter we have also addressed concern about the lower than expected $LiFePO_4$ utilization, which has been 72-82% for most samples. SEM and TEM investigations reveal that the carbon loading is likely significantly higher than original 2 wt% estimated from the slurry composition. Continuing TGA, EDX, XRD, and quantitative analysis will identify all sources for the residual carbon, quantify the amounts, and hopefully reduce the content to a more acceptable level. Upon completion, investigation of the particle and fiber bonds formed at 700° will continue and $LiFePO_4$-coated Toray samples will be fabricated for testing in Vince Battaglia's facility at LBNL. We can easily meet and exceed the 3mAh loading for testing in the 2325 coin cell configuration.





Lithium anode investigation:
The surface of our smooth, vacuum deposited, thin lithium films does not appear to passivate when soaked in EC-containing electrolytes. The SEI layer appears to become quite thick and highly resistive over several days. This differs from reports of lithium anodes formed of commercial ribbon or by electrodeposition from an electrolyte solution. The effect of an addition of vinylene carbonate to the electrolyte is now being evaluated as Alan West and others have found reduced dendritic growth with this additive. Plans are underway to investigate the SEI formed at both graphite and lithium electrodes using *in situ* cells for electron microscopy in collaboration with Karren More and other researchers at the ORNL High Temperature Materials Laboratory.

BATT TASK 2
ANODES

TASK STATUS REPORT

Task 2.1-PI, INSTITUTION: Michael Thackeray, Argonne National Laboratory

TASK TITLE: Anodes: Non-Carbonaceous Anode Materials

SYSTEMS: High voltage, high energy: Gr/$LiPF_6$+EC:DEC/$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$
High voltage, high power: Gr/$LiPF_6$+EC:DEC/$LiMn_2O_4$

BARRIERS: Low energy, poor low temperature operation and abuse tolerance limitations

OBJECTIVES: 1) Replace graphite with an alternative, inexpensive anode material that will be compatible, in particular, with low-cost manganese oxide cathodes. 2) Improve the capacity and cycle life limitations of intermetallic electrodes and their abuse tolerance in cells.

GENERAL APPROACH: Our approach is 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 400 mAh/g (>1500 mAh/ml). We are focusing predominantly on Sn- and Si-based systems that appear to have a good chance of success in practical cells, and we are capitalizing on a collaborative project with industry to aid us in this process. Promising electrodes will be evaluated in full cells against the high-capacity metal oxides of our cathode project. We are attempting to design electrodes in which electronic contact between particles is maintained at all times and to understand the stability and electrochemical behavior of nano-sized particles and the nature of the SEI layers formed thereon.

STATUS OCT. 1, 2007: Initial studies of ternary M-Cu-Sn (M= Fe, Co, Ni, Zn) intermetallic electrodes based on substituted $M_xCu_{6-x}Sn_5$ compounds were completed. It was established that electrodes from the Co-Cu-Sn system, in particular, provided an electrochemical capacity of 400 mAh/g during the early cycles of Li cells. A collaboration with Primet Precision Materials (Ithaca, NY) was established to access and evaluate nanosized intermetallic electrode particles. An investigation of the SEI layers on these materials was initiated in collaboration with Uppsala University (Sweden).

EXPECTED STATUS SEPT. 30, 2008: Progress will have been made in fabricating nano-sized intermetallic anode powders and in evaluating and improving their electrochemical properties. Promising compositions will have been evaluated against our high capacity cathodes of Task 4.1. SEI studies by XPS will have been undertaken; NMR studies will have been initiated.

RELEVANT USABC GOALS: 200 Wh/kg (EV requirement); 96 Wh/kg, 316 W/kg, 3000 cycles (PHEV 40 mile requirement). *Calendar life*: 15 years. Improved abuse tolerance.

MILESTONES:
(a) Synthesize, characterize, and evaluate Sn- and Si-based and related electrodes. (Sep. 08) **On schedule**
(b) Investigate SEI layers. (Sep. 08) **On schedule**
(c) Electrochemically evaluate intermetallic/lithium metal oxide cells. (Sep. 08) **On schedule**

PROGRESS TOWARD MILESTONES

Collaborators: L. Trahey (Argonne/Northwestern University), J. Vaughey (Argonne), H. Kung (Northwestern University)
Milestone addressed: (a) Synthesize, characterize and evaluate Sn-based electrodes

Accomplishments

Intermetallic compounds are being investigated as alternative anodes to graphitic carbon in Li-ion batteries for reasons of structure, overall capacity and safety. These anodes offer significantly higher capacity (both gravimetric and volumetric), various reaction potentials (*vs.* Li metal) and depending on their constituents, improved safety. Problems to be overcome before these anodes can compete with graphitic carbons include: 1) combating the first-cycle, irreversible capacity loss by developing an understanding of capacity fade mechanisms, and 2) controlling the dramatic volume expansion and contraction that occurs during cycling, which leads to loss of electrical contact between particles and short cycle life.

We have initiated studies of Cu_6Sn_5 electrodes when synthesized by electrochemical deposition on high surface area copper foams in an attempt to circumvent problem 2, in particular. This synthetic technique, which allows the creation of nanostructured intermetallic electrode materials on a highly porous, electronically-conducting substrate, is being adopted in an attempt to make use of the pores to accommodate the volume expansion and to use the interpenetrating copper network to ensure good electrical contact of the electrode particles at all times during electrochemical cycling. Cyclic voltammograms are being used to determine deposition parameters for controlling the composition of electrochemically-deposited Cu-Sn compounds from the deposition baths. For example, Fig. 1 shows that copper and tin reduction from chloride solutions occurs at approximately -300 mV and -650 mV, respectively, *vs.* a reference saturated calomel electrode (SCE). As-grown and annealed Cu-Sn thin films were analyzed by X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDS). An example of a microporous copper foam current collector, also synthesized by an electrochemical method prior to Cu and Sn deposition, is depicted in Fig. 2.

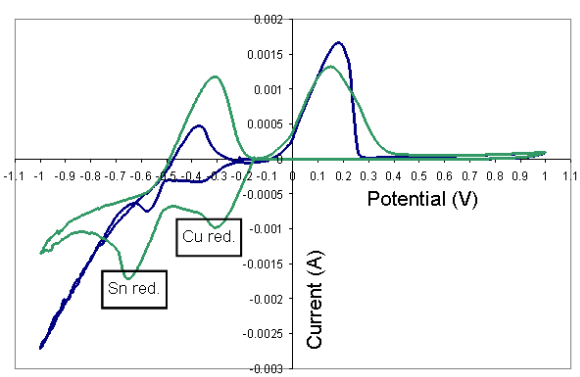


Figure 1. Cyclic voltammogram of cupric- and stannous-chloride solution (SCE reference electrode).

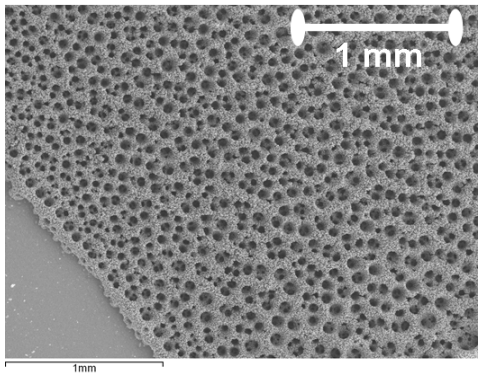


Figure 2. SEM image of a microporous copper foam current collector before electro-deposition of an active Cu-Sn layer.

We are still in the process of optimizing the reaction conditions for obtaining our desired Cu_6Sn_5 electrode composition. Details of our synthesis procedures will be presented and discussed in a future report, as will the electrochemical data of these types of electrodes.

TASK 2.2 - PI, INSTITUTION: M. Stanley Whittingham, SUNY at Binghamton

TASK TITLE - PROJECT: Anodes - Anodes: Novel Materials

SYSTEMS: Li-ion: all systems.

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

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

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

STATUS OCT. 1, 2007: We have shown that bulk crystalline metals have a high capacity and react readily with Li, but their capacity faded rapidly after several cycles in carbonate-based electrolytes. Tin-containing materials such as $MnSn_2$ and CoSn cycle well for a few cycles before capacity fade sets in. Pure Sn foil anodes of grain size below a micron cycle better, but the cell impedance was found to increase markedly after about ten cycles. In contrast we have shown that amorphous nano-size Sn alloys have a high capacity and maintain it on cycling, when stabilized with elements like Co. Both bulk and nano Sn hold capacity well when shallow cycled. We have concluded that our efforts should shift away from bulk crystalline Sn. We have also shown that nano-size manganese oxides, unlike crystalline vanadium and manganese oxides, are possible candidates, but have a first-cycle capacity loss issue.

EXPECTED STATUS SEPT. 30, 2008: From our program to understand capacity fade of Sn and Sn compounds on cycling, we expect to have defined the key parameters determining capacity loss, to have determined the impact of Sn 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 structure and surface of Sn changes on cycling, and what impact the depth of discharge has on capacity retention. We will also have a better understanding of how and if nano and/or amorphous materials, both alloys and oxides, will help solve the anode issues.

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

MILESTONES:
(a) Identify the structural and surface changes of Sn anodes during cycling working collaboratively with LBNL. (May 08) **Delayed – will be completed by Dec. 08**
(b) Determine and understand impact of depth of cycling on capacity fade (HEV *vs*. EV) for both crystalline and amorphous Sn. (Sep. 08) **On schedule**
(c) Explore nano-size Sn alloys and oxides to identify their cycling characteristics, and determine if Co-free materials are viable. (Sep. 08) **On schedule**

PROGRESS TOWARD MILESTONES

This quarter we continued our investigation of novel anode materials. Earlier we reported on our study of two nanosized/structured anode materials: the SONY Sn-Co-Ti-C anode and nano-oxides of manganese. A challenge with all nano-sized materials is their low tap density, which will result in a poor volumetric energy density. We therefore decided to see if we could produce $Li_4Ti_5O_{12}$ in a micron-size that would be effective electrochemically and have a high tap density; this material would be a good base case for the use of oxides. Unlike the manganese oxides, this material reacts by an intercalation reaction with no major structural change. As a result the charge/discharge curve is almost flat with a redox couple around 1.5 volts. This will make it much more feasible to use in Li cells, even though it will come with a substantial energy loss because of the 1.5 volt potential. Ideally, we want similar behavior but with a potential around 0.5 – 0.8 volts.

Last month we showed the cycling curve of this new micron-size $Li_4Ti_5O_{12}$ (Fig. 1). This material has a conductivity six orders of magnitude higher than the nano-sized material. We have evaluated it in a series of electrolytes; it shows essentially 100% capacity and 100% efficiency over extended cycling, as indicated in Fig. 2a. It is also showing reasonable power capability as shown in Fig. 2b. Impedance studies over 22 cycles show no increase of the impedance, even when using a Li anode. Even better performance should be possible on optimization of the synthesis method, and we will determine the effective tap density of this material.

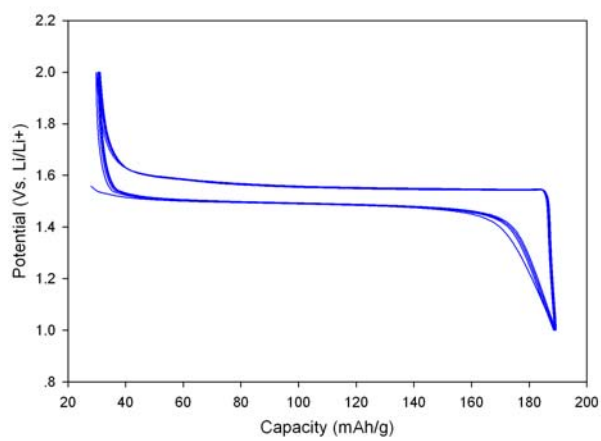
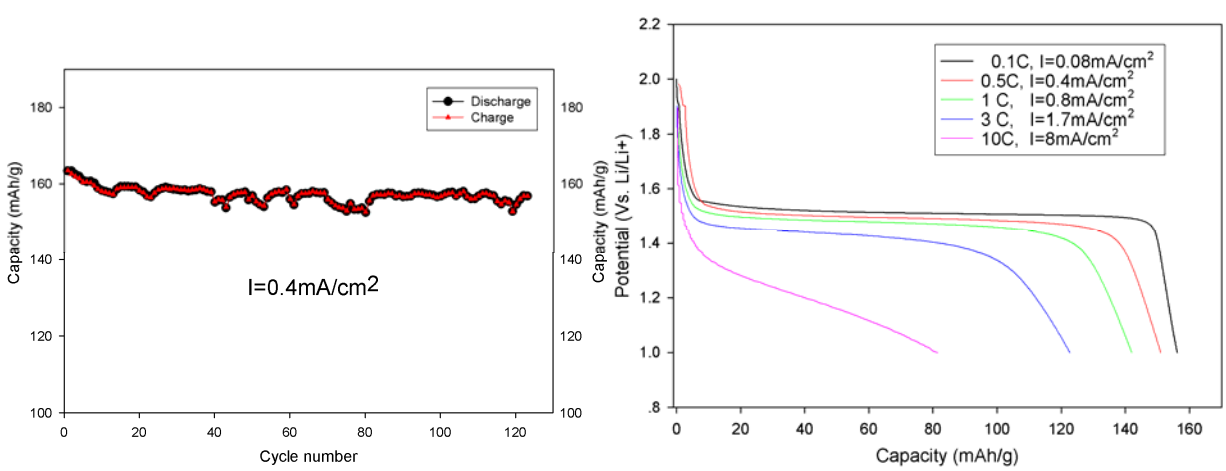


Figure 1. Cycling curve of $Li_4Ti_5O_{12}$.



(a) (b)

Figure 2. (a) Retention of capacity of $Li_4Ti_5O_{12}$, as a function of cycling at a C/2 rate, and (b) the rate capability of a $Li/Li_4Ti_5O_{12}$ cell.

This task was done in collaboration with Robert Kostecki.

TASK 2.3 - PI, INSTITUTION: Alan 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.

GENERAL APPROACH: Dendrite formation and growth is be monitored by electrochemical and optical methods as a function of electrolyte composition and current density. Microfluidic flow cells are used to minimize electrolyte use, increase repeatability, and study effects of additives.

STATUS OCT. 1, 2007: Characterization of Li deposits in liquid electrolytes will be completed. The experiments will show the effects of electrolyte composition, current density, and pulse plating parameters on the morphology of the deposited Li. Also, experiments will be finished that show the effect of additives on deposit morphology.

EXPECTED STATUS SEPT. 30, 2008: Characterization of Li deposits in common solid polymer electrolytes (SPE) will be completed. Electrochemical studies using microfluidic cells with insertion electrodes will be continuing.

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

MILESTONES:
(a) Characterize the effect of electrolyte composition and deposition conditions on Li morphology in the Li/liquid electrolyte system. (Oct. 07) **Delayed – will be completed by Sep. 08**
(b) Complete the design/fabrication of two cells that will be used prominently in future research. The first cell is a microelectrode cell used for optical observations of dendrite growth in the Li/polymer system. The second cell is a microfluidic flow cell to electrochemically study SEI effects in the Gr or alloy/liquid electrolyte system. (Feb. 08) **Delayed – will be completed by Sep. 08**

PROGRESS TOWARD MILESTONES

This quarter we were attempting to quantify the observation that dendrites propagate at a slower rate in electrolytes containing vinylene carbonate (VC). However, we were having trouble obtaining repeatable results with a side view that could be used to measure the dendrite growth. Our previous setup used 0.19 mm Cu electrodes that were electropolished prior to deposition. The quality of our Li deposition videos as well as the repeatability was improved by using larger electrodes (1.0 mm diameter) that were polished mechanically. Figure 1 shows a side-view deposition of Li from 1.2 M $LiPF_6$ in EC:EMC (3:7 by weight) at a rate of 1.25 mA cm^{-2} after 30 minutes. We are measuring the 2-D area of dendritic deposition with imaging software. Figure 2 is the 2-D dendrite area as a function of time for a sample deposition using the conditions stated above. The t_{FOD} is within the error bars of our previous cell using the smaller electrodes. This experiment was repeated 4 times and the t_{FOD} was 293 s with a standard deviation of 29 s while the dendritic area after 30 minutes of deposition was 0.062±0.0063 mm^2. We are currently testing the additives VC and VS at current densities of 1 and 4 mA cm^{-2}.

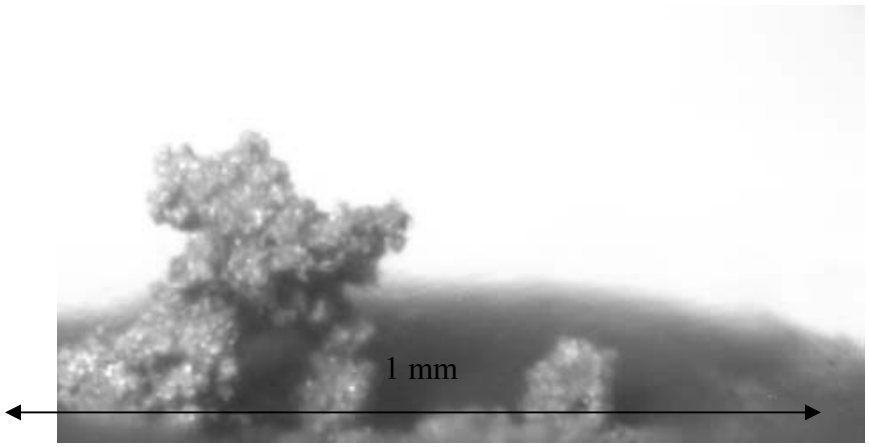


Figure 1. Side-view of Li deposition at a rate of 1.25 mA cm^{-2} from 1.2 M $LiPF_6$ in EC:EMC (3:7 by wt) after 30 minutes.

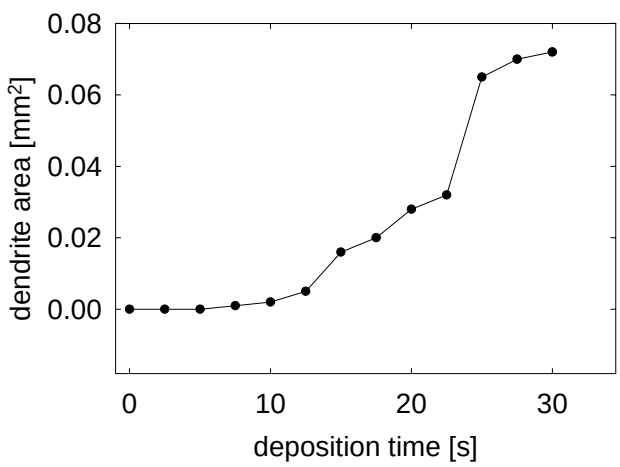


Figure 2. Area of dendrites as a function of deposition time for a Li deposition at a rate of 1.25 mA cm^{-2} from 1.2 M $LiPF_6$ in EC:EMC (3:7 by wt).

TASK 2.4 - PI, INSTITUTION: Prashant Kumta, University of Pittsburgh

TASK TITLE - PROJECT: Anodes - High Capacity Reversible Nanoscale Heterostructures: Novel Anodes for Lithium-ion Batteries

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

BARRIERS: Low energy, poor cycle life, large irreversible loss, poor rate capability, and calendar life.

OBJECTIVES: To identify new alternative anode materials to replace graphite that will provide higher gravimetric and volumetric energy density. The objective is to replace carbon with an inexpensive nanostructured anode material that will exhibit higher capacity in comparison to carbon while exhibiting similar irreversible loss and cyclability. The project addresses the need to improve the capacity, rate capability and cycle-life limitations of silicon-based electrodes as well as the irreversible loss.

GENERAL APPROACH: Our approach is to search for inexpensive silicon- and carbon-based composite electrodes (powders 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 700 mAh/g or greater (>1800 mAh/ml). We will focus on exploring novel low-cost approaches to generate nanoscale heterostructures comprising silicon and a variety of carbon forms derived from graphitic carbon as well as polymer derived carbons. Other electrochemically inactive matrices will also be explored. Promising electrodes will be evaluated in half cells against metallic Li and comparisons will be made to graphite. The rate capability, long- and short-term cyclability, as well as the origin and state of the SEI layers, also will be explored.

STATUS OCT. 1, 2007: This is a new project initiated September 1, 2007.

EXPECTED STATUS SEPT. 30, 2008: Progress will be made in synthesizing and evaluating nano-scale electrode powders comprising Si-graphitic carbon-polymer derived carbon, and related systems in half cells. Efforts will be made to generate nano-composite structures exhibiting capacities 700 mAh/g and even higher. Research will be conducted to study the synthesis and materials parameters, particularly the nano-scale microstructure affecting the rate capability; understand the origin of the irreversible loss; characterize the SEI layer composition; and outline methods to minimize the irreversible loss.

RELEVANT USABC GOALS: *Available energy*: 56 Wh/kg (10 mile) and 96 Wh/kg (40 mile); 10s discharge power: 750 W/kg (10 mile) and 316 W/kg (40 mile); *Cycle life*: 5000 cycles (10 mile) and 3000 cycles (40 mile); *Calendar life*: 15 years (at 40°C)

MILESTONES:
(a) Characterize the nano-scale heterostructures for structure and composition using high resolution electron microscopy (HRTEM/HRSEM). (Sep. 08) **On schedule**
(b) Achieve stable reversible capacity >700 mAh/g. (Sep. 08) **On schedule**
(c) Investigate the origin and characterize the SEI layers. (Sep. 08) **On schedule**
(d) Reduce irreversible loss to less than 20%. (Sep. 08) **On schedule**

PROGRESS TOWARD MILESTONES

The differential capacity plot (dQ/dV *vs.* V in Fig. 1) indicating the processes of alloying during 2nd discharge of the Si/C composite (see December report) shows the formation of the high Li content alloy of composition $Li_{3.5}Si$ at an onset potential ~0.07V with a peak potential ~0.048V. In order to study the effect of the formation of $Li_{3.5}Si$ on the stability of the Si/C composite, the as-prepared composite was discharged/charged for the 1st four cycles in the potential window 0.02-1.2V to activate the electrode, and then cycled in the potential window 0.07-1.2 V in order to generate amorphous Si and bypass the formation of $Li_{3.5}Si$ (Fig. 1). Figure 2 shows the electrochemical performance of the activated Si/C composite cycled in the potential window 0.07-1.2V at a discharge/charge rate of ~160mA/g. The Si/C composite, cycled in the potential window ~0.07-1.2V, shows a reversible capacity ~700mAh/g which is ~27% lower than the 1st charge capacity (~963mAh/g) obtained for pure Si/C composite cycled at 0.02-1.2V (Fig. 2). However, the capacity retention of the activated Si/C composite, cycled in the potential window 0.07-1.2V, has been improved to ~0.14% loss per cycle in comparison to ~0.34% loss per cycle of Si/C composite cycled in the potential window ~0.02-1.2V. The SEM micrographs (Fig. 3) of the activated Si/C composite electrode, cycled in the potential 0.07-1.2V for 30 cycles, shows better structural integrity than the Si/C composite electrode cycled at 0.02-1.2V for 30 cycles. This result clearly suggests that the formation of high Li content $Li_{3.5}Si$ at an onset potential ~0.07V is the main cause of structural failure of the Si/C composite during long term cycling. Therefore, the stability of the Si/C composite comprised of Si as a dispersoid on the graphite matrix is expected to be improved by designing a Si based alloy (*e.g.,* by doping with other materials or synthesis of structurally different morphologies of Si) which can bypass the formation of $Li_{3.5}Si$ during discharge up to 0.02V. Hence future work will be dedicated to synthesizing different structural morphologies of Si (*e.g.,* amorphous, nano-rods or nano-wires Si) and Si/C based composites comprised of the different structural morphologies of Si in order to bypass the formation of $Li_{3.5}Si$. This strategy is expected to yield structurally stable electrodes exhibiting excellent electrochemical performance.

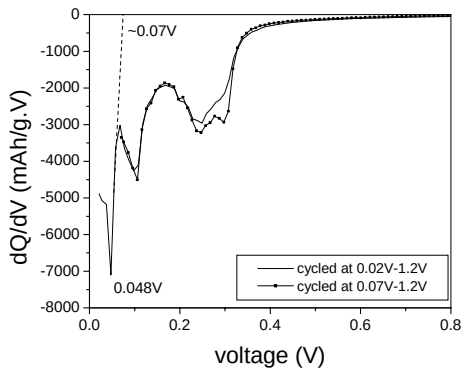


Figure 1. 2nd discharge differential capacity *vs.* cell potential curves for the Si/C composite electrodes.

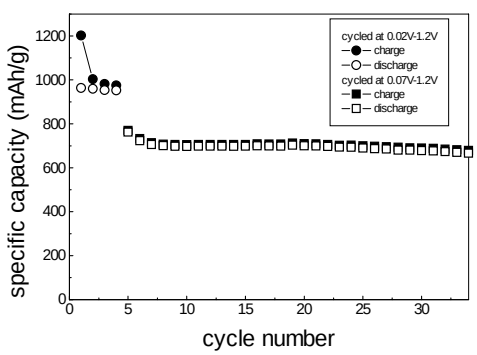


Figure 2. Specific capacity *vs.* cycle number of activated Si/C composite cycled in the potential window 0.07V-1.2V.

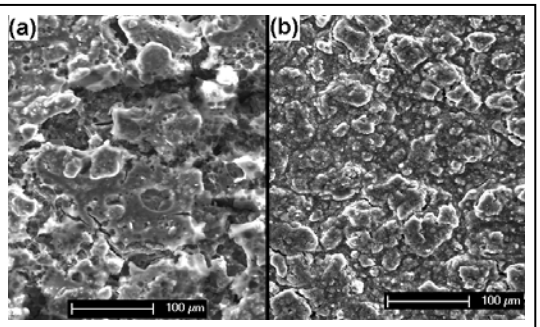


Figure 3. SEM micrograph of Si/C composite (a) cycled in the potential window 0.02V-1.2V for 30 cycles and (b) cycled in the potential window 0.07V-1.2V for 30 cycles.

BATT TASK 3
ELECTROLYTES

TASK STATUS REPORT

TASK 3.1 - PI, INSTITUTION: Nitash Balsara, Lawrence Berkeley National Laboratory

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

SYSTEMS: Nanostructured polymer electrolytes based on polystyrene-polyethyleneoxide (PS-PEO) block copolymers

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

OBJECTIVES: Study the stability of PS-PEO/LiTFSI electrolytes against Li electrodes. Synthesize PS-PEO diblock copolymers with varying molecular weights and compositions to obtain electrolytes with high ionic conductivity and shear modulus. Establish Li-metal deposition capability. Test the properties of PS-PEO electrolytes against Li-metal anodes and $LiFePO_4$ cathodes. Initiate a new program on the use of block copolymers to create mesoporous separators for conventional liquid electrolytes.

GENERAL APPROACH: Continue to synthesize and characterize robust PS-PEO dry polymer electrolytes with high conductivity and high shear modulus that resist dendrite growth during cell cycling. Salt/polymer mixtures will be characterized by AC-impedance spectroscopy and DC measurements with Li/polymer/Li cells. Methods to create efficient contact between the hard electrolyte and electrodes will be tested. Stability of the electrolyte against electrodes (Li metal and $LiFePO_4$) will be tested in collaboration with members of the BATT program. We will expand our program to include the synthesis of polymer separators. These materials will be prepared by synthesizing a block copolymer with a degradable block. The pores left behind by the degradable block will be filled with conventional electrolytes and will be used in Li cells.

STATUS OCT. 1, 2007: Synthesis of new PS-PEO block copolymers with varying compositions. AC-impedance and DC-cycling studies of block copolymer electrolytes in the newly-established polymer electrolyte characterization laboratory. Establishing methodologies for cathode preparation.

EXPECTED STATUS SEPT. 30, 2008: Continued testing of the stability of the PS-PEO samples against electrodes. Completing the synthesis of new PS-PEO polymers with higher molecular weights and larger volume fractions of polystyrene. A Li-deposition unit for anode preparation will be added to the existing glove box in the polymer electrolyte characterization laboratory. The effect of block copolymer molecular weight and composition on conductivity and dendrite prevention will be studied.

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. EV applications goals are specific energy 150 Wh/kg and specific power=300 W/kg.

MILESTONES:
(a) Establish Li-metal deposition system. (Dec. 07) **Complete**
(b) Complete synthesis of a new set of dry electrolytes. (Dec. 07) **Complete**
(c) Work on developing methodologies for making contact between cathode and electrolyte, and study cathode electrolyte interface. (Sep. 08) **On schedule**
(d) Decide on block copolymer that is ideally suited for making separator. Train student in synthesis and characterization of the block copolymer. (Sep. 08) **On schedule**

PROGRESS TOWARD MILESTONES

We have completed conductivity measurements on a series of cylindrical (70% styrene) and lamellar (50% styrene) samples. It is useful to construct a normalized conductivity parameter ($\sigma_{Normalized}$) to compare various samples. Ideally, conductivity in PS-PEO ($\sigma_{PS\text{-}PEO}$) can be predicted by assuming that the inherent conductivity of PEO is the same as the bulk (σ_{PEO}), and that deviations from the homopolymer conductivity will depend proportionally on the volume fraction of PEO (ϕ_{PEO}). Connectivity between randomly-oriented grains must also be considered. If one assumes no added transport resistance across grains, a constant morphology factor (MF) can be applied[i] to account for 1- or 2-dimensional conductivity in cylindrical (MF = 3) or lamellar (MF = 3/2) samples, according to the equation $\sigma_{Normalized} = \frac{\sigma_{PS-PEO}}{\sigma_{PEO}\phi_{PEO}} xMF$. If all assumptions hold about transport in PEO microdomains, the value of $\sigma_{Normalized}$ will be exactly 1 for all samples. Results for a variety of cylinder- and lamellae-forming polymers at fixed salt concentration and temperature show the validity of these assumptions varies widely with molecular weight (MW) and morphology (Fig. 1). Lamellar samples approach expected behavior as the MW of the PEO block increases, but the significant departures from ideality at low MWs and in cylindrical samples are under investigation. Understanding and correcting for the cause of these deviations would lead to significant improvements to electrolyte performance. Structural studies using small-angle X-ray scattering are underway and have provided insight on what structures are forming, how they are affected by salt, and what that means for electrochemical performance. For instance, we have found that structures exhibiting excellent long-range order with well-defined channels show no clear advantages in terms of conductivity.

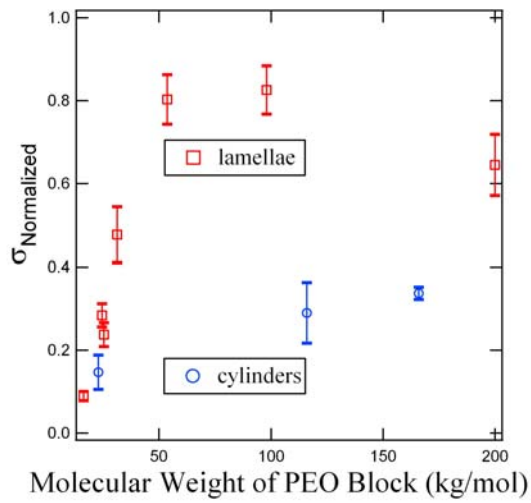


Figure 1. Normalized conductivities for lamellar and cylindrical samples show significant deviations from ideality at low molecular weight and in cylindrical samples. Salt concentration fixed at [Li]/[EO] = 0.085, T = 100°C.

We have further results on how the addition of salt affects the microstructure of these materials, and we have begun measuring diffusion coefficients as a function of salt concentration, temperature, morphology, and MW. Transference number measurements are also underway using the current interrupt method, and we are developing a new sample holder in order to make transference measurements using the concentration cell method developed by Newman and coworkers. The salt diffusion coefficient varies from 2 to 5 $x10^{-12}$ m^2/s and the Li^+ transference number varies between 0.15-0.35. Efforts towards interfacing $LiFePO_4$ cathodes to the SEO polymers and developing full batteries have started.

David Wong is in the process of synthesizing polystyrene-*block*-poly(L-lactic acid) in order to make battery separators. The PLA block will be depolymerized to leave behind well-defined pores.

[1.] Sax, J., Ottino, J.M. *Polym. Eng. and Sci.*, **1983**, *23*,3.

TASK 3.2 - PI, INSTITUTION: John Kerr, Lawrence Berkeley National Laboratory

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

SYSTEMS: High-voltage, high-energy: Gr/$LiPF_6$+EC:DEC/$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$
Low-voltage, high-stability: Gr/$LiPF_6$+EC:DEC/$LiFePO_4$
High-voltage, high-power: Gr/$LiPF_6$+EC:DEC/$LiMn_2O_4$

BARRIERS: Poor cycle and calendar life, low power and energy densities, particularly at low temperatures (-30°C) and high cost.

OBJECTIVES:
1. Investigate the feasibility of pre-forming SEI layers on both anodes and cathodes by use of electrolyte additives, chemical modification of the electrode particles and coating with single-ion conductor polymers.
2. Determine whether the interfacial impedance of single-ion conductors can be reduced to practical values (< 20 ohm.cm^2 at RT).
3. Evaluate the use of very high rate polymer electrodes and redox active binders.

GENERAL APPROACH: A physical organic chemistry approach is taken to electrolyte design, where the molecular structure is varied to provide insight into the various processes that may affect the performance of the battery. This involves model compounds as well as new synthesis of materials to test hypotheses which may explain battery behavior.

STATUS, OCT. 1, 2007: More detailed kinetics of the reaction of electrolyte components will have been completed. The effects of impurities, additives and cell components on the reaction kinetics will be established so that the kinetics can be used to provide time-dependent models of cell lifetime. For this detailed measurement of water content in cell components as well as electrolytes will be accomplished. Correlation of the reactivity of the electrolyte with the interfacial impedance of the electrodes will be established. The feasibility of the use of organic electrolytes with 5-volt cathodes will be determined.

EXPECTED STATUS, SEPT. 30, 2008: The effects of pre-coating electrodes with side-reaction products on the interfacial impedance will be evaluated as will chemical modification of the electrodes and coating with single-ion conductor polymers. These treatments should provide insight into some of the factors that control the charge transport across the interface as well as how to suppress side reactions. The practicality of the use of single-ion conductor polymer electrolytes will be assessed with respect to the interfacial impedance.

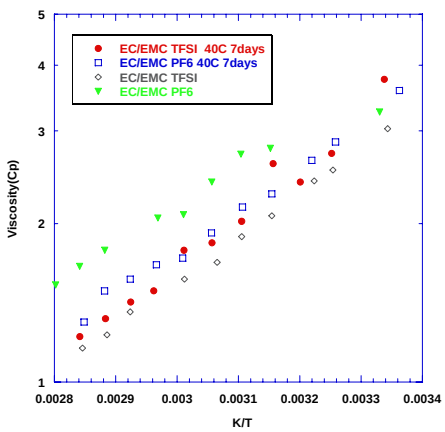
RELEVANT USABC GOALS: *Available energy*: 56 Wh/kg (10 mile) and 96 Wh/kg (40 mile); *10 s discharge power*: 750 W/kg (10 mile) and 316 W/kg (40 mile); *Cycle life*: 5000 cycles (10 mile) and 3000 cycles (40 mile); *Calendar life*: 15 years (at 40°C); cold cranking capability to -30°C; abuse tolerance.

MILESTONES:
(a) Determine the feasibility of pre-forming electrode SEI layers using additives, chemical modifications, and single-ion conductor polymer coatings. (Sep. 08) **On schedule**
(b) Complete the evaluation of the impedance characteristics of single-ion conductor electrolytes and binders at composite electrodes. (Sep. 08) **On schedule**

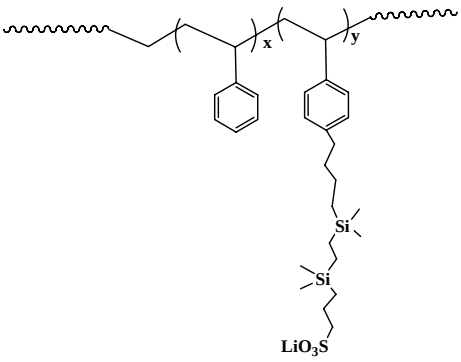
PROGRESS TOWARD MILESTONES

1. Modification of Electrode/Electrolyte Interfaces to Optimize Interfacial Impedance and Minimize Side Reactions. Work on this topic has been impeded by the unexpected absence of a staff member due to family affairs and visa issues. However, work has been possible due to the efforts of students funded by the DOE Science Undergraduate Laboratory Internship (SULI). A number of electrolyte mixtures have been prepared with varying amounts of water (8 ppm, 15ppm and 150ppm). Both $LiPF_6$ and LiTFSI electrolyte solutions have been prepared and subjected to heating at 40°C under sealed conditions in the glove boxes. Samples have been taken to follow the evolution of the water content, reaction of the electrolyte components and measurement of the electrolyte viscosity. Electrolyte samples have been analyzed by GC/MS and by GPC after 7 days at 40°C and the GPC clearly show the evolution of a small amount of product in the $LiPF_6$ electrolyte with an elevated molecular weight in the range of 5-10k. No such peak is observed with the TFSI control. Measurement of the solution viscosities were carried out before and after heating and the results are shown in Figure 1. The viscometer is set up in the glove box with a heating and cooling system built in to the box. Thus samples can be prepared, titrated by Karl–Fischer for water, measured for viscosity and incorporated into cells or other measuring devices without any exposure to atmosphere. The effect of heat on the viscosity of the 8-15ppm water content electrolytes is shown in Fig. 1. It can be seen that the effects are negligible for the conditions used and higher temperatures and higher water contents are under test. The effects of these treatments on the interfacial impedance behavior are being pursued but these more difficult tests require more experienced staff to perform

Figure 1. Viscosity of "dry" Electrolytes (1M Li salt concn.) as a function of salt and temperature.



2. Single-ion Polymer Electrolytes. Preparation of single-ion conductor materials is proceeding as described in the April report. A polyaryl sulfone material was prepared with alkyl sulfonate side chains. However, the polymerization reaction of this material proceeded inefficiently resulting in a material that has an indeterminate concentration of acid groups. Work is continuing on optimizing this chemistry. In the meantime, work in the DOE HFCIT Fuel Cell program has produced materials similar to that shown below which can be prepared with and without ether oxygen groups in the side chains. The addition of ethers limits the voltage that the materials can be used for (3.6V). The structure shows the method of attachment of the acid group and a similar method can be used for functionalization of carbon used in composite electrodes for the purpose of altering interfacial behavior. Work is proceeding on this aspect also.



Task 3.3 - PI, INSTITUTION: Darryl DesMarteau and Stephen Creager, Clemson University

TASK TITLE - PROJECT: Electrolytes – Lithiated Fluorosulfonimide Ionomers as Multifunctional Binders/Electrolytes in Battery Cathodes

SYSTEMS: High-voltage, high-energy: Gr/$LiPF_6$+EC:DEC/$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$

BARRIERS: Poor electrolyte transport, low-capacity, high-capacity fade, low power, short life, abuse tolerance.

OBJECTIVES: (1) Synthesize fluorosulfonimide ionomers of variable structure in lithiated form (LiFSI) as dispersions in solvent; (2) Fabricate high-voltage cathodes using the resulting LiFSI ionomers as binders and/or as integral electrolytes; (3) Characterize the resulting cathodes with respect to initial capacity, high-rate charging/discharging capability, and capacity fade.

GENERAL APPROACH: Ionomer synthesis will proceed using variants of methods developed at Clemson over the last 20 years, with recent focus on copolymerization of functionalized trifluorovinyl ether monomers with tetrafluoroethylene, and also homopolymerization of trifluorovinyl ether monomers. Ionomer characterization will utilize conventional approaches, *i.e.,* NMR, IR, calorimetry, titration. Electrode fabrication will follow known approaches utilizing mixtures of active materials ($LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$), conductive additives (graphite and/or carbon black), and binders (PVDF and LiFSI ionomers). Electrode characterization will be accomplished using galvanostatic polarization at variable current density using flooded three-electrode cells.

STATUS Oct. 1, 2007: Synthesis of new fluorosulfonate and fluorosulfonimide ionic liquids / melts, including imidazolium-based electrolytes and electrolytes from partially-fluorinated polyethers, will be completed. Characterization of these electrolytes, including conductivity, calorimetry, DC polarization, voltage stability, and cell cycle testing, will be almost completed, with full completion targeted for December 2007.

EXPECTED STATUS SEPT. 30, 2008: Synthesis of a range of lithiated fluorosulfonimide ionomers as dispersions in solvent will be complete. Conditions whereby high-voltage cathodes fabricated using first-generation LiFSI ionomers give improved performance (higher initial capacity, higher charging rates, diminished capacity fade) relative to electrodes fabricated without LiFSI ionomer will have been identified.

RELEVANT USABC GOALS: *10 s discharge power*: 750 W/kg (10 mile) and 316 W/kg (40 mile); *Cycle life*: 5000 cycles (10 mile) and 3000 cycles (40 mile); *Calendar life*: 15 years (at 40°C).

MILESTONES:
(a) Identify conditions where high-voltage cathodes fabricated with first-generation LiFSI ionomers give improved performance (higher initial capacity, higher charging rates, diminished capacity fade) relative to electrodes fabricated using other binders without LiFSI ionomer. (May 08) **Complete**
(b) Expand the range of variables considered for achieving optimal performance to include variations in monomer and ionomer structure and ionomer equivalent weight. (Sep. 08) **On schedule**

PROGRESS TOWARD MILESTONES

Much of the project work in the April-June 2008 quarter involved homopolymers prepared from the monomer shown in Fig. 1. The work focused on two areas: (1) single-ion conductor polymer electrolytes of the homopolymer in Li form; and (2) battery cathodes fabricated with the homopolymer as binder. In addition, progress on synthesis of new low-viscosity ionic liquid solvents is reported.

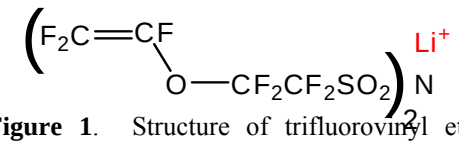


Figure 1. Structure of trifluorovinyl ether lithium fluorosulfonimide monomer used to make ionomers in membrane form and as binders in battery cathodes.

Figure 2 presents ionic conductivity data at variable temperature for a polymer electrolyte prepared by homopolymerization of the monomer shown in Fig. 1, and wetted by a 1:1 EC:DEC mixture. The polymer has a complex structure that is still being evaluated; however, even without definitive structural data it is clear from the preliminary conductivity data that the material is promising. Conductivities are above 0.3 mS/cm at all temperatures tested (ambient to 70°C), which is much higher than for similarly swelled Nafion in lithiated form. The high conductivity is thought to reflect a combination of the relatively high ion-exchange capacity of this polymer electrolyte (1.83 meq/g *vs.* 0.91 meq/g for Nafion 1100 EW), and its capacity to absorb large amounts of solvent (*i.e.,* it is a gel). Ongoing work will seek to prove that this material is in fact a single-ion conductor, and to test it as a battery separator.

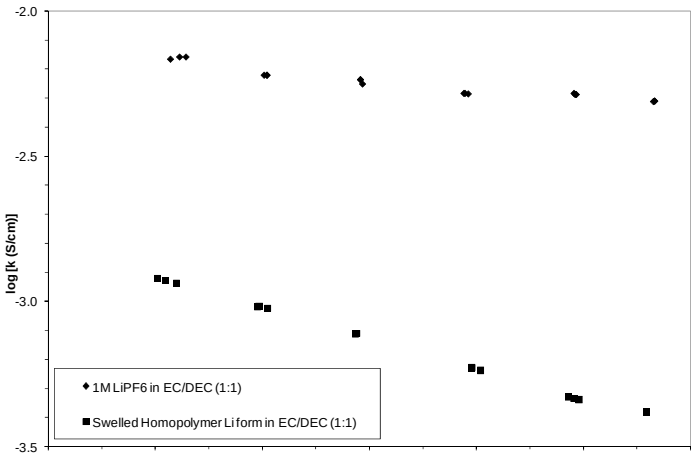


Figure 2. Ionic conductivity of lithiated polymer electrolyte from monomer in Fig. 1, wetted with a 1:1 EC:DEC mixture.

Battery cathodes were prepared using $LiCoO_2$ as active material with acetylene black additive, with and without ionomer present in the binder. Battery testing was performed on cells prepared using a lithium titanate anode (limiting capacity was the cathode) and lithium salts (LiTFSI and $LiPF_6$) in EC:DEC (1:1) solvent. Preliminary cycle testing shows that when salt concentration is low (*e.g.,* 0.1 M) the cells with the ionomer from Fig 1 in the cathode were much more easily charged than cells without ionomer in cathode. Ongoing work will explore more thoroughly the microstructure of cathodes containing ionomer, the effect of ionomer in the cathode on high-rate charging and discharging, and the capacity retention with $LiCoO_2$ and other cathodes.

We continue to pursue work on new low-viscosity ionic liquids for use as battery electrolyte solvents. We prepared a new series of liquids based on a phosphonium cation of structure $[(C_4H_9)_3PCH_2CH_2OCH_3]^+$, with three anions of the following structures: $[CF_3SO_2NSO_2CF_3]^-$ (TFSI); $[CF_3SO_2NSO_2C_4F_9]^-$; and $[(CN)_2N]^-$ (cyanamide). All three combinations are liquids at ambient temperature, and all three dissolve at least 20 percent by weight of LiTFSI salt. Ongoing work will focus on measurements of viscosity, ionic conductivity, and Li transference at ambient, elevated, and sub-ambient temperatures.

TASK 3.4 - PI, INSTITUTION: Grant Smith and Oleg Borodin, University of Utah

TASK TITLE - PROJECT: Electrolytes – Molecular Modeling of Electrolytes and Electrolyte/Electrode Interfaces

SYSTEMS: Li-ion

BARRIERS: Poor low-temperature operation. Poor transport through SEI layer and poor cycle life. High interfacial resistance at the electrolyte-cathode interface.

OBJECTIVES: Gain molecular level understanding of Li^+ cation transport mechanisms in ionic liquids, solid electrolyte interphase (SEI) layer components and the process of Li intercalation/deintercalation from/into graphite anode, and model cathode into/from liquid electrolyte. Provide guidance for design of novel electrolytes with improved Li transport, reduced interfacial resistance, and/or improved electrochemical stability allowing operation at higher voltages. Reduce electrolyte/anode charge transfer resistance *via* graphite surface modification.

GENERAL APPROACH: Extend a set of the previously developed and validated many-body polarizable force fields to allow accurate prediction of ion transport, structural and thermodynamic properties of novel ionic liquids, liquid electrolytes, and representative SEI components using molecular dynamics (MD) simulations. Calculate local resistance and a free energy barrier associated with the Li^+ cation intercalation from electrolyte into the SEI layer components, representative cathode material and modified graphite.

STATUS OCT. 1, 2007: Investigate the free energy barriers for Li^+ transfer from ethylene carbonate (EC) into outer part of the SEI layer and initiate investigations of Li^+ intercalation from EC into a representative cathode. Investigate improvements to Li^+ transport at low-temperature operation of ionic liquids by incorporation of siloxane groups in their structure. Investigate influence of the oligomer–Li^+ interactions on the ion transport for ionic liquids that do not exhibit concentration polarization.

EXPECTED STATUS SEPT. 30, 2008: Complete investigation of the local resistance to Li intercalation from EC into a model cathode material. Investigate dependence of the charge transfer resistance on anode side on the electrolyte composition for mixtures of EC and linear carbonates, and modification of the graphite anode. Predict Li transport in a number of ionic liquids. Predict structure and ion transport in the SEI phase formed by reduction of VC on the anode.

RELEVANT USABC GOALS: *10 s discharge power*: 750 W/kg (10 mile) and 316 W/kg (40 mile)

MILESTONES:
(a) Complete simulations aimed at understanding the influence of composition and chemistry of carbonate electrolytes on the charge transfer resistance at anode side. (Jun. 08) **Delayed – will be completed by Aug. 08**
(b) Parameterize potential and simulation cathode/electrolyte interface, predict local Li transport resistance. (Sep. 08) **On schedule**
(c) Parameterize ReaxFF and predict reduction products and possible SEI structure for EC and VC. (Sep. 08) **On schedule**

PROGRESS TOWARD MILESTONES

Simulations of Mixed Electrolytes: Molecular dynamics simulations have been performed on EC/DMC mixed electrolytes doped with $LiPF_6$ salt as a function of temperature. Excellent agreement between transport properties predicted from simulations and experiments has been found. For example, for EC/DMC (1/1 wt%) doped with 1 M salt, molecular dynamics (MD) simulations predicted conductivity 10.1 mS/cm, which is only 8% below published experimental data 10.9 mS/cm (*J. Power Sources* **2003,** *119*, 454). Intriguingly, analysis of the Li coordination shell reveals a substantial presence of DMC in addition to EC involved with complexation of Li cations. This result is unexpected because EC has a stronger Li salt solvating ability compared to DMC as observed in quantum chemistry calculations and MD simulations of EC/$LiPF_6$, DMC/$LiPF_6$, EC/LiTFSI and DMC/LiTFSI. Specifically, MD simulations performed at room temperature of 1 M $LiPF_6$ in EC yielded the fraction of Li solvent separated from PF_6 anion of 38% while this fraction was only 2.8% for DMC/$LiPF_6$. We are currently performing a detailed analysis of the simulated mixed carbonate electrolytes aimed at explaining the unexpected substantial presence of DMC in the Li first-coordination shell.

Interfacial Behavior of Liquid Electrolytes Next to Graphite: An interfacial resistance associated with Li desolvation from electrolytes and intercalation into electrodes presents significant problems at low temperature operation. Potential of mean force (PMF) and local diffusion coefficients are currently being calculated for carbonate electrolytes doped with $LiPF_6$ at room temperature with an emphasis of predicting interfacial impedance as a function of electrolyte composition next to graphite and $LiFePO_4$.

Ethylene and Vinylene Carbonate Decomposition Products

In this quarter we have conducted quantum chemistry investigations of reaction paths for gas phase vinylene carbonate (VC) decomposition in a presence of Li as well as the reaction of EC radical anion with VC. The former have been compared with similar calculations on EC+Li complexes. We find that that the barrier for ring opening in the presence of Li is much higher for VC than for EC molecule. The current version of the ReaxFF accurately captures this difference in the energy barriers and relative energy difference of reaction products predicted by quantum chemistry calculations for EC and VC compounds. Utilizing the developed ReaxFF we initiated investigation of EC and VC reduction mechanisms in condensed phases. Specifically, MD simulations of liquid EC and VC liquid phases containing various amounts of Li (neutral) have been initiated. Also simulations of EC/VC mixtures with Li have been initiated. Simulations with Li metal/electrolyte liquid interface are currently underway.

Stretched Polymeric Electrolytes

An additional analysis of the influence of stretching on salt dissociation and transport of poly(ethylene oxide) doped with LiTFSI has been performed in order to improve interpretation of the recent imaging experiments performed by Nitash Balsara's group.

Collaborations This Quarter

John Kerr (LBNL), Gerbrand Ceder (MIT), Nitash Balsara (Berkeley), Salvy Russo (R-MIT), Adri van Duin (Caltech)

BATT TASK 4
CATHODES

TASK STATUS REPORT

Task 4.1-PI, INSTITUTION: Michael Thackeray, Argonne National Laboratory

TASK TITLE: Cathodes - Novel Cathode Materials

SYSTEMS: High voltage, high energy: Gr/$LiPF_6$+EC:DEC/$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$
High voltage, high power: Gr/$LiPF_6$+EC:DEC/$LiMn_2O_4$

BARRIERS: Low energy, cost and abuse tolerance limitations of Li-ion batteries

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

GENERAL APPROACH: Our approach is to continue our search for, and to characterize and develop, low-cost manganese oxide cathodes for Li-ion cells. We will maintain the momentum we have developed in advancing the electrochemical properties and stability of high-capacity electrodes (>200 mAh/g) with composite structures such as 'layered-layered' $xLi_2M'O_3$•$(1-x)LiMO_2$ and 'layered-spinel' $xLi_2M'O_3$•$(1-x)LiM_2O_4$ electrodes in which M′ is predominantly Mn and M is selected predominantly from Mn, Ni and Co. A particular focus of the research will be to fabricate electrode surfaces that remain stable at high potentials (>4.4 V) over long-term cycling in the hope of suppressing oxygen evolution thereby mitigating the safety hazards of Li-depleted metal oxide cathodes at high states of charge.

STATUS OCT. 1, 2007: A greater understanding of the structural properties of 'layered-layered' xLi_2MnO_3•$(1-x)LiMn_{0.5}Ni_{0.5}O_2$ and xLi_2MnO_3•$(1-x)LiMn_{0.333}Ni_{0.333}Co_{0.333}O_2$ that account for their improved electrochemical behavior over conventional $LiMO_2$ (M=Mn, Ni, Co) was obtained. The anomalously high capacity that can be delivered by these types of electrodes, particularly during the first few cycles, was investigated. Work on stabilizing xLi_2MnO_3•$(1-x)LiMO_2$ electrodes by mild acid treatment was initiated. Theoretical studies of dissolution *vs.* H^+-Li^+ ion exchange reactions of $LiCoO_2$ were undertaken by first principles methods.

EXPECTED STATUS SEPT. 30, 2008: Improvements in the overall electrochemical performance (*i.e.,* capacity, power and cycling stability) of $xLi_2M'O_3$•$(1-x)LiMO_2$ electrodes and $xLi_2M'O_3$•$(1-x)LiM_2O_4$ will have been demonstrated. Progress in stabilizing electrode surfaces at high electrochemical potentials (>4.4 V) will have been made.

RELEVANT USABC GOALS: 200 Wh/kg (EV requirement); 96 Wh/kg, 316 W/kg, 3000 cycles (PHEV 40 mile requirement). Calendar life: 15 years. Improved abuse tolerance.

MILESTONES:
(a) Evaluate and optimize compositionally-modified 'layered-layered' $xLi_2M'O_3$•$(1-x)LiMO_2$ and 'layered-spinel' $xLi_2M'O_3$•$(1-x)LiM_2O_4$ electrodes with a high Mn content. (Sep. 08) **On schedule**
(b) Enhance surface stability of composite electrode structures at high potentials. (Sep. 08) **On schedule**
(c) Model dissolution *vs.* H^+-Li^+ ion-exchange phenomena of composite electrode structures and their components. (Sep. 08) **On schedule**

PROGRESS TOWARD MILESTONES

Collaborators: S.-H. Kang, J. Vaughey, C. Johnson (Argonne); C. Grey, J. Cabana (SUNY-Stony Brook), Primet Precision Materials Inc. (Ithaca, NY)
Milestone addressed: Optimize electrode structures - milestone (a)

We are continuing to exploit the concept of using integrated structures containing a Li_2MnO_3 component to stabilize layered $LiMO_2$ (M=Mn, Ni, Co) and spinel $Li[Mn_{2-x}M_x]O_4$ (M=Li, Ni) electrodes. We (and others) have already shown that integrated xLi_2MnO_3•$(1-x)LiMO_2$ ('layered-layered') and xLi_2MnO_3•$(1-x)LiMn_{2-x}Li_xO_4$ ('layered-spinel') electrodes can provide anomalously high capacities (240-250 mAh/g) when cycled between 5 and 2 V, albeit at relatively low current rates. Instead of using Li_2MnO_3 alone to stabilize $Li[Mn_{2-x}M_x]O_4$ spinel electrodes, we have turned our attention to using a three-component system, whereby a stabilized layered xLi_2MnO_3•$(1-x)LiMn_{0.5}Ni_{0.5}O_2$ component that delivers most of its capacity between 4.5 and 3 V is integrated with a $Li[Mn_{1.5}Ni_{0.5}]O_4$ spinel component that delivers its capacity over two voltage plateaus, one at 4.7 V and the other just below 3 V. For these studies, we selected the system $xLi[Mn_{1.5}Ni_{0.5}]O_4$•$(1-x)(Li_2MnO_3$•$Li[Mn_{0.5}Ni_{0.5}]O_2)$ ($0 \leq x \leq 1$) in which the Mn:Ni ratio of 3:1 remains invariant for all values of x. The end members of this system are simply the layered component, Li_2MnO_3•$Li[Mn_{0.5}Ni_{0.5}]O_2$ (x=0), and the spinel component, $Li[Mn_{1.5}Ni_{0.5}]O_4$ (x=1).

Representative charge/discharge profiles of three Li half cells for x=0, 0.5 and 1.0 in $Li/xLi[Mn_{1.5}Ni_{0.5}]O_4$•$(1-x)(Li_2MnO_3$•$Li[Mn_{0.5}Ni_{0.5}]O_2)$, obtained between 4.95 and 2.0 V, are shown in Fig. 1(a-c), respectively. The two end members provide the expected voltage response typical of the well-known layered and spinel electrodes. On the other hand, for x=0.5 (Fig. 1b), the profile appears to indicate an electrode structure that has significantly more layered character than expected for a 50:50 (layered:spinel) ratio, providing evidence that the integrated structure has highly complex atomic arrangements. ^{6}Li MAS NMR data have been collected at SUNY (Stony Brook) in an attempt to unravel the structural complexity of these electrodes, the analyses of which will be reported in due course.

Initial cycling data of $Li/xLi[Mn_{1.5}Ni_{0.5}]O_4$•$(1-x)(Li_2MnO_3$•$Li[Mn_{0.5}Ni_{0.5}]O_2)$ cells show that several break-in cycles are required to obtain the maximum capacity of 'layered-spinel' electrodes that can reach ~250 mAh/g after 30 cycles (Fig. 1b); the reason for the steadily increasing capacity with cycling is not yet understood. These high capacities are, however, obtained at a relatively low rate (0.1 mA/cm^2). Attempts are being made, in collaboration with Primet Precision Materials, Inc., to overcome the rate limitations of integrated electrode structures by reducing the particle size and, alternatively, by using physical blends of spinel and layered components instead of structurally-integrated materials.

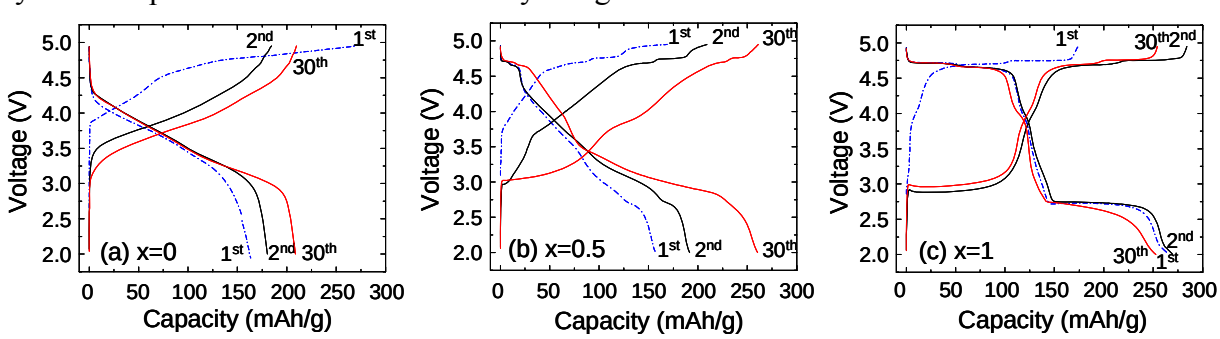


Figure 1. Electrochemical profiles of $Li/xLi[Mn_{1.5}Ni_{0.5}]O_4$•$(1-x)(Li_2MnO_3 \cdot Li[Mn_{0.5}Ni_{0.5}]O_2)$ cells for a) x=0 (layered) b) x=0.5 (layered-spinel), and c) x=1 (spinel).

TASK 4.2 - PI, INSTITUTION: M. Stanley Whittingham, SUNY at Binghamton

TASK TITLE - PROJECT: Cathodes - Materials: Novel Cathodes

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

BARRIERS: 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.

GENERAL 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 then characterized both structurally and for thermal and chemical stability. All will be evaluated electrochemically in a variety of cell configurations.

STATUS OCT. 1, 2007: 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. In the 1:1 Li/metal compounds, we have shown that the Mn content can be raised to 50% without deleterious effects. Magnetic studies have shown that there is always some Ni in the Li layer for Co-poor samples; these Ni ions, in low concentration, help stabilize the structure. We have completed an electrochemical and thermodynamic evaluation of $LiFePO_4$ as a base-case low-cost cathode, and have shown that we can synthesize it hydrothermally at ≤200°C, and that essentially any other divalent metal can be substituted for the iron.

- $LiFePO_4$: > 120 Ah/kg for 100 cycles at 1 mA/cm^2.
- Layered $Li_xCo_zNi_yMn_{1-y-z}O_2$: 160 Ah/kg 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, 2008: 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) Ni disorder, 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 also will have extended our studies beyond olivine-structured Li metal phosphate and evaluated some Mn containing iron phosphates, and explored some higher capacity next generation cathodes.

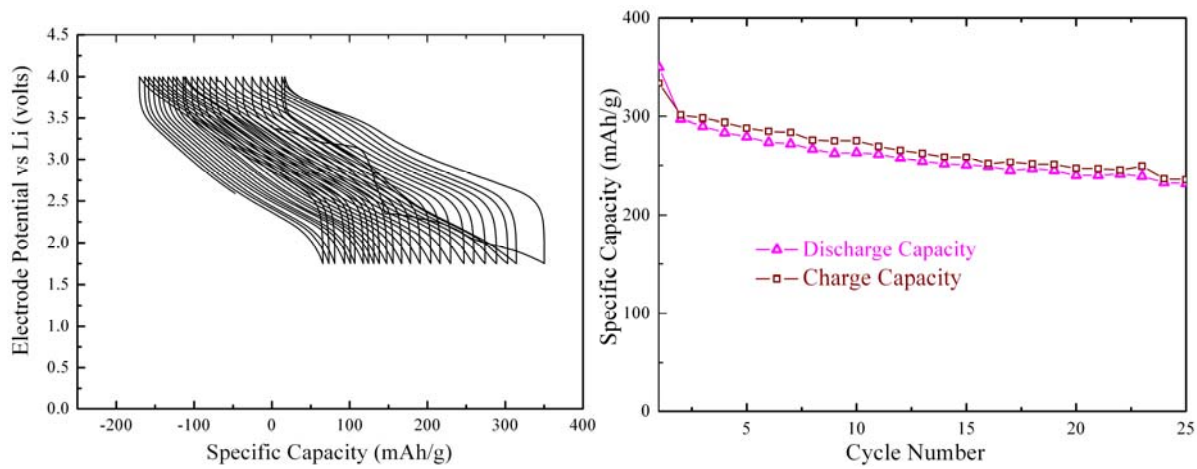
RELEVANT USABC GOALS: 300,000 shallow discharge cycles, and abuse tolerance to cell overcharge and short circuit

MILESTONES:
(a) 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 HEVs), to understand Ni disorder, and to compare the best samples with the base case cathodes. (Sep. 08) **On schedule**
(b) Improve the particle size of olivine $LiMPO_4$, and evaluate other phosphate structures containing Fe and Mn and compare them with high temperature $LiFePO_4$. (Sep. 08) **On schedule**

PROGRESS TOWARD MILESTONES

Substituted Metal Phosphates. This work continues the exploration of other phosphate structures that might have a higher capacity than the olivine $LiFePO_4$. Two structures being considered are those formed by substitution of all or part of the iron by manganese or vanadium. Earlier we showed that the vanadium phosphate, H_2VOPO_4, had a higher potential than the olivine structure and was capable of intercalating two Li ions per redox ion leading to a capacity approaching 250 mAh/g.

One structure being considered is $LiVPO_4OH$, which might be expected to be isostructural with $LiFePO_4OH$ and be easier to be synthesized than $LiVO_4F$. While attempting to synthesize pure specimens of this composition, we have been re-evaluating the parent vanadium pentoxide with an emphasis on nanoforms of the compound. We synthesized nanofibers of the delta form of $H_xV_4O_{10}\bullet nH_2O$ using the electrospinning technique we reported earlier for the nano manganese oxide anode. These nanofibers were then hydrothermally treated to remove the polymer precursors, and heated at 450°C to convert to the water-free, single-sheet V_2O_5 lattice. The cycling behavior is shown in Fig. 1(a) below. The first discharge shows the typical multi-step behavior. Subsequent discharges showed the typical single-phase behavior expected for V_2O_5. The capacity on cycling is shown in Fig. 1(b). The initial capacity exceeds 300 mAh/g, and around 250 mAh/g after 25 cycles. These are the values desired for a high-energy-density battery for PHEV or EV applications.



(a) (b)

Figure 1. (a) Cycling behavior, and (b) capacity retention of nano-sized fibers of vanadium pentoxide. An overcharge is observed on each cycle.

Publications and Presentations

(1) The Impact of Order and Disorder in Cathodes for Lithium Batteries, IMLB Tianjin, China, June 30, 2008. M. Stanley Whittingham.

(2) Influence of Manganese Content on Structure and Electrochemical Behavior of $Li_{(4-X)/3}Mn_{(2-0.5x)/3}(Ni_{0.4}Co_{0.1})_XO_2$ in Li Batteries, IMLB Tianjin, China, June 30, 2008. Jie Xiao, Natasha Chernova and M. Stanley Whittingham.

(3) The Electric Economy and Energy Storage: The Impact of Order and Disorder in Cathodes for Lithium Batteries, Wuhan University, China, July 5, 2008. Jie Xiao, Jiajun Chen, Natasha Chernova and M. Stanley Whittingham.

TASK 4.3 - PI, INSTITUTION: Marca Doeff, Lawrence Berkeley National Laboratory

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

SYSTEMS: Low and high voltage, high-stability (metal phosphates and silicates), high-voltage, high energy (mixed transition metal oxides), and high voltage, high energy (new materials).

BARRIERS: Cost, power and/or energy density, cycle life

OBJECTIVES: To develop low-cost benign cathode materials having electrochemical characteristics (*e.g.,* cycle life, energy and power densities) consistent with the goals of the USABC and/or FreedomCAR.

GENERAL APPROACH: Cathode materials are synthesized and characterized electrochemically. Relevant physical properties are measured in conjunction with the diagnostics teams. Emphasis is placed on reducing cost and improving electrochemical properties. Some work is directed towards surveying new materials with potential for increased energy density.

STATUS OCT. 1, 2007: Co-synthesis of carbon nanotubes and $LiFePO_4$ has been demonstrated using a combustion technique. The survey of tunnel manganese oxide compounds in Li metal cells with pyrolidinium-based ionic liquid electrolytes is complete. An electrochemically driven dissolution/precipitation mechanism causing failure of cells upon cycling can be stopped by partial Ti substitution. Rate limitations in cells with ionic liquids are traced to high interfacial impedance at the Li electrode; high viscosity, which interferes with wetting; and lower conductivity than $LiPF_6$ in carbonate solutions. A survey of the effect of partial substitution of Al, Fe or Ti for Co in mixed transition metal oxides (Ni, Mn, Co) is nearly complete.

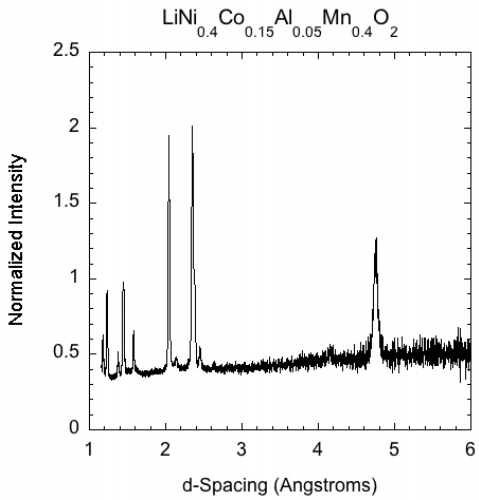
EXPECTED STATUS SEPT. 30, 2008: Co-synthesis techniques will be extended towards other phosphates of interest (*e.g.,* $LiMnPO_4$, mixed metal phosphates). A survey of fluorophosphates, oxyphosphates, silicates and other polyanionic compounds will be initiated. Thermal characterization of the best-performing substituted transition metal oxides will be underway.

RELEVANT USABC GOALS: High power, low cost (*HEV*). High energy, low cost, cycle life (*EV, PHEV*).

MILESTONES:
(a) Complete characterization of best-performing substituted transition metal oxides. (Sep. 08) **On schedule**
(b) Determine feasibility of synthesizing electrochemically active nano-$LiMnPO_4$ and/or $Li(Mn,Fe)PO_4$ and other polyanionic compounds for use in the BATT program. (Sep. 08) **On schedule**

PROGRESS TOWARD MILESTONES

4.3a.



Neutron powder diffraction experiments on selected $Li[Ni_{0.4}Co_{0.2-y}Al_yMn_{0.4}]O_2$ powders were carried out at the Manuel Lujan Jr. Neutron Scattering Center at Los Alamos National Laboratory in mid-June. Typical data is shown in Fig. 1 for the $Li[Ni_{0.4}Co_{0.15}Al_{0.05}Mn_{0.4}]O_2$ compound. Data from these experiments will be used in structural modeling (K. Persson), with a goal of understanding the origin of the rate enhancement observed with partial Al substitution of Co.

Figure 1. Neutron diffraction pattern of $Li[Ni_{0.4}Co_{0.15}Al_{0.05}Mn_{0.4}]O_2$.

4.3b. Citric acid:nitrate ratios were varied from 0.55:1 to 1:1 for the preparation of $LiMnPO_4$/C composites by combustion synthesis. Materials are either completely or partially amorphous after combustion, but become crystalline after calcination for one hour at 600-700°C. Carbon contents generally increase with increasing ratios, and H/C ratios decrease, suggesting more effective decomposition of the citric acid precursor due to a higher combustion temperature. Electrochemical characterization of these samples was carried out in Li coin cells. Best results at C/25 rates were obtained for materials made with fuel:nitrate ratios of 0.7-0.8, although utilization in all cases was much less than theoretical. Cells improved upon cycling (sometimes by as much as 50%), probably due to increased wetting of the carbon coatings by the electrolyte solution. For materials made with high fuel:nitrate ratios, the high carbon contents reduce the practical capacity in Li cells, but otherwise there does not seem to be any simple relationship between carbon content and performance. A composite containing $LiMg_{0.1}Mn_{0.9}PO_4$ was also prepared, using a 0.8:1 citric acid:nitrate ratio. This material showed better electrochemical behavior, although capacity was still low. The poor utilization is attributed to agglomeration of the nanoparticles and problems with sample homogeneity due to the method of solution delivery to the hot reaction vessel during combustion. Attempts to improve this are now being undertaken, by using an airbrush to spray solution more uniformly. An ultrasonic nozzle is also on order, which should allow a more controlled delivery and faster combustion of the precursor solution. This should result in better homogeneity and control over the characteristics of the sample.

Presentations and Publications

1. "Electrode Materials with the $Na_{0.44}MnO_2$ Structure: Effect of Titanium Substitution on Physical and Electrochemical Properties," J.A. Saint, J.D. Wilcox and M.M. Doeff, *Chem. Mater.,* **20,** 3404 (2008).
2. "Impact of Carbon Structure and Morphology on the Electrochemical Performance of $LiFePO_4$ Composites," M.M. Doeff, J.D. Wilcox, R. Yu, A. Aumentado, M. Marcinek, and R. Kostecki, *J. Solid State Electrochem.*, **12**, 995 (2008).

TASK 4.4 - PI, INSTITUTION: John Goodenough, The University of Texas at Austin

TASK TITLE – PROJECT: Cathodes – Novel Materials

SYSTEMS: Sulfochloride/$LiPF_6$ + EC:DEC/polymer + oxide

BARRIERS: Cost, energy density, safety, deep-discharge cycle life

OBJECTIVES: To evaluate alternative *cathode* and *anode* materials for a Li-ion battery.

GENERAL APPROACH: Goals: to identify and to develop (a) polymer/oxide composite cathodes to eliminate dead weight, (b) sulfochlorides as anode materials that are thermodynamically stable *vs.* the electrolyte so as to eliminate the SEI interface passivation layer, but having a smaller voltage *vs.* Li/Li^+ than $Li_4Ti_5O_{12}$. For task (a), we will compare and optimize electrodeposition and chemical polymerization of the polymer with an oxide (*e.g.*, carbon-coated C-$LiFePO_4$ and layered $Li(Ni_{0.5+\delta}Mn_{0.5-\delta})O_2$ and $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ with/without a SiO_2 coat). For task (b), we will explore layered sulfochlorides that operate on a Cr^{3+}/Cr^{2+} or a Ti^{3+}/Ti^{2+} redox couple.

STATUS OCT. 1, 2007: Significant improvement in capacity and rate capability has been obtained in C-$LiFePO_4$-based composite cathodes with polypyrrole (PPy) and polyaniline (PAn). The synthesis routes of simultaneous chemical polymerization and electrodeposition for these composites have been optimized. The technique for preparation of PAn nanowires, $LiFePO_4$ nanoparticles, layered $Li(Ni_{0.5+\delta}Mn_{0.5-\delta})O_2$, and $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ nanowires has been explored for the composite cathodes. Surface modification of layered $LiNi_{1-x}Mn_xO_2$ with SiO_2 has shown an improved cyclability and rate capability.

EXPECTED STATUS SEPT. 30, 2008:

- Enhancement in capacity and rate capability will be attained in the polymer-based (PPy and PAn) composite cathodes with $LiFePO_4$ and layered oxides. The fabrication technique will be completely developed.
- The technique for preparation of PAn nanowires, $LiFePO_4$ nanoparticles, layered $Li(Ni_{0.5+\delta}Mn_{0.5-\delta})O_2$, and $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ nanowires will be developed for the composite cathodes. The effects of particle size and morphology on the electrochemical properties will be investigated.
- An alternative sulfochloride anode that has a smaller voltage *vs.* Li/Li^+ than $Li_4Ti_5O_{12}$ will be developed.

RELEVANT USABC GOALS: *Available energy* > 80 Wh/kg, *10 s discharge rate*, 5000 deep-discharge cycles, 15-year *calendar life*.

MILESTONES:

(a) Complete investigation of electrochemical co-deposition of polyaniline (PAn) and C-$LiFePO_4$. (Dec. 07) **Complete**

(b) Prepare and test nanowires of PAn for chemical attachment to C-$LiFePO_4$. (Jun. 08) **Complete**

(c) Explore $LiCr_2S_3Cl$ and $LiTi_2S_3Cl$ as anode materials. (Jun. 08) **Complete**

(d) Develop novel soft-chemical routes of patterned composites containing nanoparticles and polymers. (Sep. 08) **Complete**

(e) Exploration of Ti^{3+}/Ti^{2+} and V^{3+}/V^{2+} redox couples in sulfides and sulfochlorides. (Jul. 08). **On schedule**

(f) Structural and electrochemical characterization of $Li_{1+x}VS_2$ nanoparticles without/with substitutions for V and S (Sept. 08). **On schedule**

PROGRESS TOWARD MILESTONES

In our exploration of insertion compounds operating on the Ti^{3+}/Ti^{2+} and V^{3+}/V^{2+} couples, we have found that where the Fermi energy, E_F, of the anode is less than 0.8 eV below that of Li, a LUMO in the electrolyte lying at 0.8 eV relative to Li is reduced with the formation of an SEI layer. The SEI layer on the surface of carbon is permeable to Li^+ ions, which makes reversible insertion of Li possible after the SEI formation. However, with the oxides, the SEI layer formed on the surface does not appear to be permeable to Li^+ ions, so formation of an SEI layer blocks insertion or extraction of Li. In the case of the layered sulfides $Li_{1+x}TiS_2$ and $Li_{1+x}VS_2$, an SEI layer forming on the surface of $LiTiS_2$ at 0.8 V *vs.* Li, Fig. 1-a, is followed by a reversible plateau at 0.5 V, which we believe corresponds to the Ti^{3+}/Ti^{2+} couple. We interpret this to mean that the SEI layer formed on the sulfide is permeable to Li^+ ions. In the case of $Li_{1+x}VS_2$, the V^{3+}/V^{2+} couple is seen to be at 1.0 V *vs.* Li in Fig. 1-b, which means that its E_F lies below the LUMO of the electrolyte. In this case, no SEI layer is formed, and this anode material can be cycled. However, there is some capacity fade, so we hope to prepare nanoparticles to minimize any problem of volume changes breaking electronic contact with the current collector.

Solutions for better anode materials appear to require either the development of an electrolyte with a higher LUMO energy or coating the particles with an amorphous carbon that provides a kinetic barrier to the formation of an SEI layer on the active particles. We intend to explore both alternatives in the future.

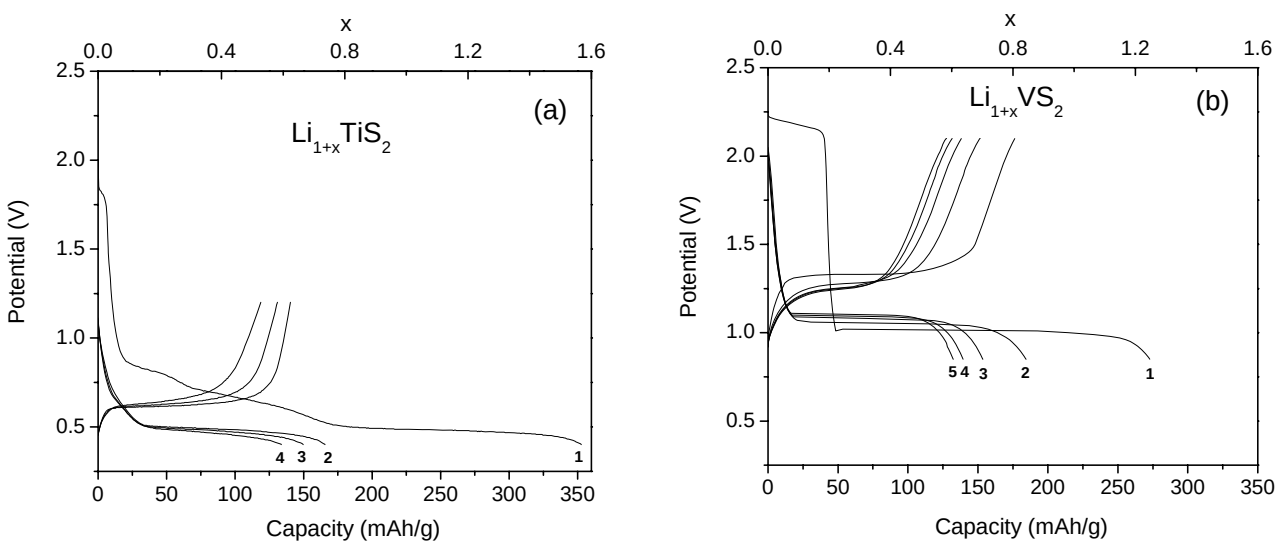


Figure 1. Discharge and charge curves for the (a) $LiTiS_2$ and (b) $LiVS_2$ for the first five cycles at rate of 0.1 mA/cm^2.

TASK 4.5 - PI, INSTITUTION: Arumugam Manthiram, University of Texas at Austin

TASK TITLE - PROJECT: Cathodes – High-Performance Cathode Materials

SYSTEMS: Spinel manganese oxides (high-power, high-stability, and low-cost) and layered oxides (high-capacity and low-cost)

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

OBJECTIVES: To develop (i) 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, (ii) low-cost layered oxide cathodes that can offer high capacity with low irreversible capacity loss, and (iii) low-cost spinel-layered oxide composite cathodes that can offer a combination of high-energy density and high rate.

GENERAL APPROACH: Our approach is to continue 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, cationic and anionic substitutions and surface modifications of both 4-V and 5-V spinel oxide cathodes as well as composites consisting of optimized high-power spinel oxides and high-energy density layered oxides to maximize the power and energy densities are being pursued. Conventional ceramic and solution-based synthesis, chemical and structural characterization, electrochemical evaluation of coin cells with Li and carbon anodes, and a fundamental understanding of their structure-property-performance relationships are being pursued.

STATUS OCT. 1, 2007: Evaluation of the optimized spinel oxyfluoride cathodes and composite cathodes consisting of optimized spinel and high-capacity layered oxides in Li-ion cells with carbon, $Li_4Ti_5O_{12}$, metal alloy, and graphite/metal alloy composite anodes and design and characterization of high-capacity layered oxide cathodes with low irreversible capacity loss.

EXPECTED STATUS SEPT. 30, 2008: Design and development of high-power 4-V spinel compositions, optimization of the 4-V spinel to layered oxide ratios and microstructures in spinel-layered oxide composite cathodes to maximize the energy and power densities, and optimization of the 5-V spinel cathodes and improvement of their chemical stability in contact with the electrolyte through surface modifications.

RELEVANT USABC GOALS: 300,000 shallow discharge cycles, 10-year life, <20 % capacity fade over a 10-year period

MILESTONES:
(a) Optimize 4-V spinel to layered oxide ratios and microstructures in the spinel-layered oxide composite cathodes. (Mar. 08) **Complete**
(b) Optimize and surface modify 5-V spinel cathodes based on $LiMn_{1.5}Ni_{0.5}O_4$. (Sep. 08) **On schedule**

PROGRESS TOWARD MILESTONES

Our previous work showed that the cyclability of the cation-substituted 5 V spinel ($LiMn_{1.5}Ni_{0.42}Zn_{0.08}O_4$ and $LiMn_{1.42}Ni_{0.42}Co_{0.16}O_4$) cathodes can be improved significantly by surface modification with oxides like Al_2O_3. The enhancement in capacity retention is due to the improved chemical stability of the 5 V cathode surface in contact with the electrolyte. One of the attractive features of the spinel cathodes is the ability of the 3-dimensional spinel lattice to support high rate capability, which is a critical parameter for HEV and PHEV applications. Although the bare 5 V cathodes $LiMn_{1.5}Ni_{0.42}Zn_{0.08}O_4$ and $LiMn_{1.42}Ni_{0.42}Co_{0.16}O_4$ were found to retain, respectively, 66 and 71% of their capacity on going from C/6 to 10C rate at 3rd cycle, the rate capability was found to decrease rapidly as the cycle number increases from 3 to 50. Interestingly, we find that the rate capability retention can be improved significantly by surface modification with other oxides as seen in Fig. 1. The rate capability retention in Fig. 1 was obtained by first calculating the percentage capacity retained on going from C/6 to various rates (up to 10C rate) at 3rd and 50th cycles separately and then dividing the latter by the former. For example, surface modification of $LiMn_{1.42}Ni_{0.42}Co_{0.16}O_4$ with Al_2O_3 leads to a rate capability retention of ~ 97 % in Fig. 1 on going from C/6 to 10C rate while the bare $LiMn_{1.42}Ni_{0.42}Co_{0.16}O_4$ has a rate capability retention of only ~55% under the same conditions. By carefully examining the discharge curves at various C rates, we find that the poor rate capability retention of the bare 5 V cathodes is due to the fast increase in polarization resistance R_P on cycling. Surface modification suppresses the increase in R_P during cycling and thereby improves the rate capability retention. EIS analysis indicates that the fast increase in R_P in the case of the bare 5 V spinel cathodes during cycling is due to a significant increase in both the SEI resistance and the electron transfer resistance, as seen in Fig. 2. Surface modification slows down the increase in both the SEI resistance and the electron transfer resistance (Fig. 2). The results suggest that surface modification is an effective way to improve the chemical stability of the 5 V spinel cathodes in contact with the electrolyte and improve their cyclability and rate capability during long-term cycling. XPS study reveals that the various coatings differ in their surface chemical stability during cycling, which leads to differences in electrochemical performances.

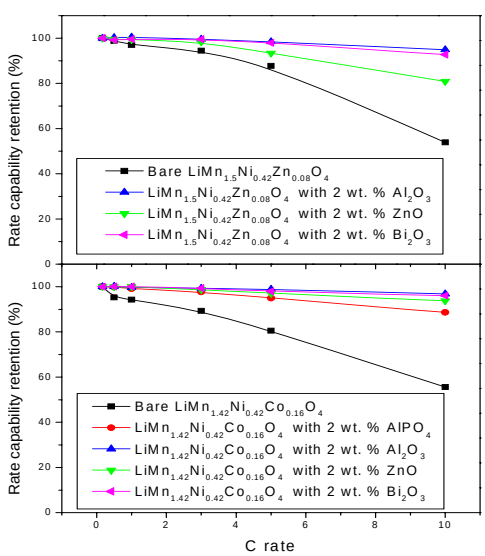


Figure 1. Rate capability retention of the bare and surface modified $LiMn_{1.5}Ni_{0.42}Zn_{0.08}O_4$ and $LiMn_{1.42}Ni_{0.42}Co_{0.16}O_4$ cathodes after 50 cycles.

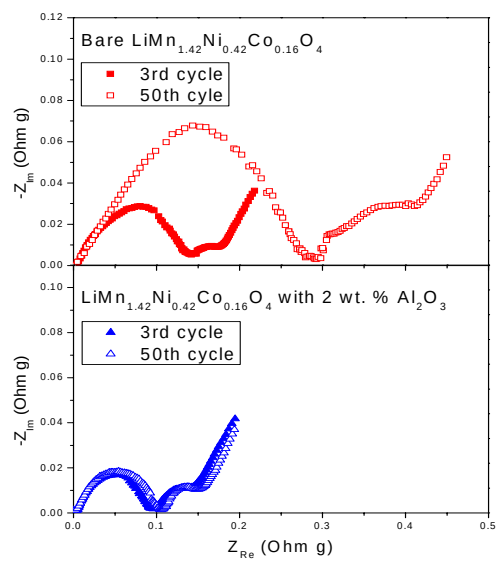


Figure 2. Comparison of the EIS data of the bare and Al_2O_3 modified $LiMn_{1.42}Ni_{0.42}Co_{0.16}O_4$ at 50% state of charge (SOC) after 3 or 50 cycles.

BATT TASK 5
DIAGNOSTICS

TASK STATUS REPORT

TASK 5.1 - PI, INSTITUTION: Robert Kostecki, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Diagnostics - Interfacial Processes: Diagnostics, Nanomaterials

SYSTEMS: High-voltage, high-energy: Gr/$LiPF_6$+EC:DEC/$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$

BARRIER: Low energy (related to cost), poor Li battery calendar/cycle lifetimes.

OBJECTIVES: (i) Design and manufacture nano-composite C/Sn thin-film electrodes with improved power and energy density, and extended cyclability, and (ii) establish direct correlations between BATT baseline electrodes surface chemistry, morphology, topology, interfacial phenomena, and cell power or capacity decline.

GENERAL APPROACH: Our approach is to (i) design, construct and apply an electrochemical cell of the Devanathan-Stachurski type to study the kinetics of Li intercalation and diffusion in graphite and its possible correlation with the formation and presence of the SEI layer, (ii) use one-step microwave plasma chemical vapor deposition (MPCVD) to synthesize nano-composite C/Sn-Me and C/Si thin-film anodes, (iii) apply *in situ* and *ex situ* Raman and FTIR spectroscopy and microscopy, scanning probe microscopy (SPM), spectroscopic ellipsometry, electron microscopy (SEM, HRTEM), and standard electrochemical techniques to detect and characterize surface processes in graphite anodes, and high-voltage (>4.3V) cathodes.

STATUS OCT. 1, 2007: We expect to gain insight into the mechanism of detrimental surface phenomena on pure Sn-foil anodes and evaluate their impact on the electrode electrochemical behavior during charge-discharge cycling. We anticipate optimizing the MPCVD process to synthesize thin-film C/Sn nano-composite anodes with a fine structure of electronically conductive carbon matrix loaded with uniformly distributed Sn nano-particles. We expect to evaluate and confirm improved high-rate performance, high energy density and extended cyclability of C/Sn nano-composite electrodes during prolonged charge-discharge cycling.

EXPECTED STATUS SEPT. 30, 2008: We plan to design and use an electrochemical cell of the Devanathan-Stachurski type to study mass and charge transfer mechanisms through the electrolyte/graphite interface and Li diffusion in graphite. We expect to develop a time-dependent mass transport model to validate the observed experimental behavior and determine Li^+ transport parameters in graphite. We also intend to determine correlations between the transport of Li through the electrolyte/HOPG interface and the formation of surface SEI films. We also expect to use MPCVD to synthesize C/Sn-Me and C/Si nano-composite anodes and evaluate their electrochemical performance.

RELEVANT USABC GOALS: *Cycle life*: 5000 cycles (10 mile) and 3000 cycles (40 mile). *Available energy*: 56 Wh/kg (10 mile) and 96 Wh/kg (40 mile).

MILESTONES:
(a) Report preliminary results of the Li^+ transport study in the Devanathan-Stachurski cell. (Apr. 08) **Complete**
(b) Evaluate surface phenomena on Sn anodes and their impact on the electrochemical behavior of the electrode. (Aug. 08) **On schedule**

PROGRESS TOWARD MILESTONES

In the third quarter of FY08 we developed an *in situ* AFM experimental protocol to detect and characterize early stages of the SEI layer formation and Li alloying on a Sn anode during the first potentiostatic charge. A tin foil (99.998% purity, d = 1.2 cm) was mechanically and electrochemically polished to surface roughness of <5 nm. The Sn electrode was investigated in an *in situ* AFM electrochemical cell equipped with two Li wire counter and reference electrodes and filled with 1 M $LiPF_6$, EC:DEC 1:2 w/w electrolyte. All measurements were performed under Ar atmosphere. The surface morphology of the tin electrode was monitored continuously during the potential scan.

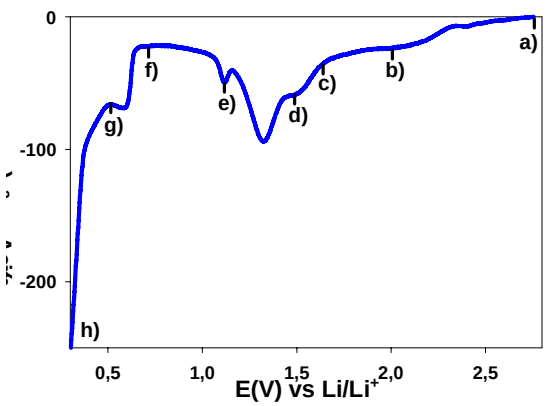


Figure 1. 1st voltammetric scan ($0.5 mVs^{-1}$) of a tin foil anode from OCP to 0.3 V *vs.* Li/Li^+ (*in situ* AFM cell under Ar atmosphere)

Figure 1 shows the current response during a potential scan ($0.5\ mVs^{-1}$) from the open circuit potential (2.8V *vs.* Li/Li^+) to 0.3 V, which corresponds to the early stage of Sn alloying with Li. The charge consumed in the process of SEI layer formation at E > 0.6V was determined ca. $0.12\ Ccm^{-2}$. A sequence of *in situ* AFM images of the Sn electrode recorded at different potentials (Fig. 2) shows significant changes in the surface morphology, which are associated entirely with the surface film formation. Interestingly, the SEI layer growth was highly non-uniform at different locations and produced a rough, multilayer deposit that consists of small <500 nm particles fused into large platelets in the order of several microns. The average roughness of the film reached ca. 200 nm at 0.33 V. *Ex situ* current-sensing AFM images of the Sn anode revealed no electronic conductivity across the SEI film. The formation of such a thick and insulating SEI layer is consistent with our earlier FTIR microscopy results and the literature data.

This task was done in collaboration with Stan Whittingham.

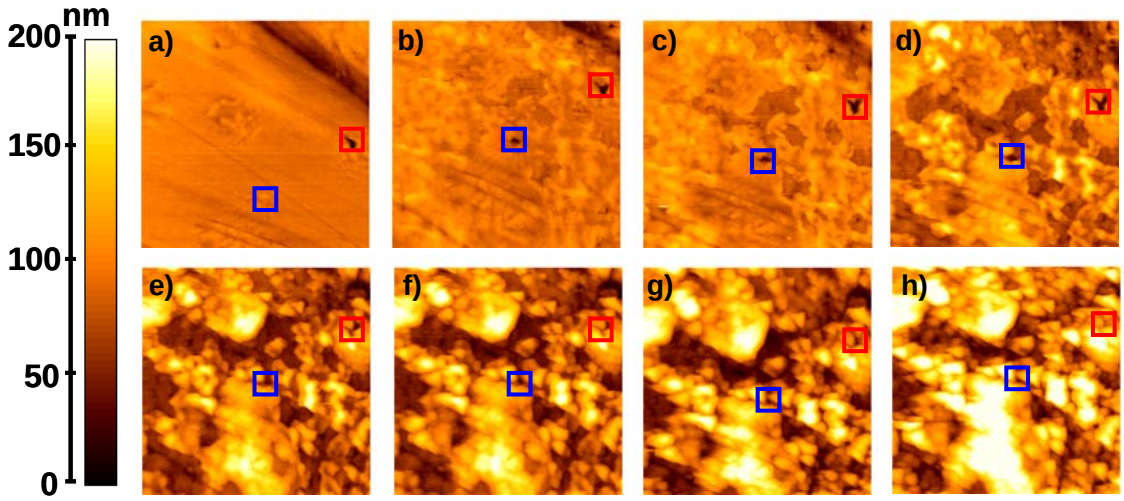


Figure 2. *In situ* 10 x10μm AFM pictures of Sn foil anode in 1M $LiPF_6$, EC:DEC 1:2 w/w recorded at a) 2.74, b) 2.00, c) 1.65, d) 1.44, e) 1.11, f) 0.72, g) 0.51, h) 0.33 V *vs.* Li/Li^+. The red and blue squares represent reference points at the surface of the electrode.

TASK 5.2 - PI, INSTITUTION: Won-Sub Yoon and Xiao-Qing Yang, Brookhaven National Laboratory

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

SYSTEMS: Gr/$LiPF_6$+EC:DEC/$LiFePO_4$(high-stability)
Gr/LiPF6+EC:DEC /$LiMn_2O_4$(high-power)
Gr/$LiPF_6$+EC:DEC/$LiCo_{1/3}Mn_{1/3}Ni_{1/3}O_2$(high-energy)

BARRIER: PHEV: energy density, cycle life; HEV: power density, abuse tolerance.

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

GENERAL APPROACH: Our approach is to use various 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. *In situ* X-ray diffraction (XRD) 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* XRD with position-sensitive detector (PSD) will be used to monitor the structural changes of the electrode materials during charge-discharge cycling at various C rates. These approaches developed at BNL will be available to other BATT members through extended collaboration.

STATUS OCT. 1, 2007: *In situ* XRD studies on the structural changes of the $Li_{1-x}FePO_4$ type of cathode materials used during electrochemically Li-ion deintercalation have been completed. These $Li_{1-x}FePO_4$ materials are obtained from various sources, with or without surface coating, with or without doping, cycled at various temperatures, especially at low and high temperatures. Soft X-ray XAS using partial electron yield and fluorescence yield detectors was applied to various cathode materials such as $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ and $LiFePO_4$ at the O, F, and P K edges and at the L_3 and L_2 edges of the 3d transition metals.

EXPECTED STATUS SEPT. 30, 2008: We expect to complete developing a new thermal *in situ* soft X-ray absorption spectroscopic technique, which will enable us to monitor structural changes both at the surface and in the bulk at thermal abuse conditions. We will continue our studies on the structural characteristics of the composite electrodes (layered-layered and layered-spinel) using various synchrotron X-ray techniques. We expect to complete the structural study on the layered, lithium-rich transition metal oxides containing manganese, nickel, and cobalt like $Li_{1+x}(Mn_{0.5}Ni_{0.5})_{1-x}O_2$ and $Li_{1+x}(Mn_{1/3}Ni_{1/3}Co_{1/3})_{1-x}O_2$ using *in situ* XRD.

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

MILESTONES:
(a) Complete *in situ* XRD studies of $Li_{1+x}(Mn_{0.5}Ni_{0.5})_{1-x}O_2$ type cathode materials during electrochemical cycling. (Apr. 08) **Complete**
(b) Identify oxidative processes in the cathode at high voltages. (Sep. 08) **On schedule**

PROGRESS TOWARD MILESTONES

We have been investigating the charge compensation mechanism of $Li_{1+x}M_{1-x}O_2$ system during electrochemical cycling. We are continuing *in situ* XAS study on $Li_{1+x}(Mn_{0.5}Ni_{0.5})_{1-x}O_2$ system during the charge/discharge process to elucidate the active role of Li_2MnO_3 or Li_2MnO_3-like phases in $Li_{1+x}(Mn_{0.5}Ni_{0.5})_{1-x}O_2$ system.

In collaboration with Dr. Kang at Argonne National Lab., we have carried out *in situ* Mn and Ni K-edge XAS for $Li_{1+x}(Mn_{0.5}Ni_{0.5})_{1-x}O_2$ electrodes during multiple charge/discharge cycling. Figure 1 (a) shows the *in situ* Ni K-edge XANES spectra of $Li_{1.0}(Mn_{0.5}Ni_{0.5})_{1.0}O_2$ and $Li_{1.2}(Mn_{0.5}Ni_{0.5})_{0.8}O_2$ electrodes during first charge/discharge. *In situ* Ni K-edge XANES spectra of the $Li_{1.0}(Mn_{0.5}Ni_{0.5})_{1.0}O_2$ electrode shows the completely reversible changes in the oxidation state from Ni^{2+} to Ni^{4+} and back to Ni^{2+} during first charge/discharge. On the other hand, the average oxidation state of Ni in $Li_{1.2}(Mn_{0.5}Ni_{0.5})_{0.8}O_2$ electrode changes from around Ni^{3+} to Ni^{4+} upon first charge, but reduces below the Ni^{3+} original state after first discharge. These results show that the charge compensation range at the Ni ions in the $Li_{1.2}(Mn_{0.5}Ni_{0.5})_{0.8}O_2$ system might progressively expands from the original Ni^{3+}/Ni^{4+} to the final Ni^{2+}/Ni^{4+} during the extended charge/discharge cycles.

The active role of Li_2MnO_3 or Li_2MnO_3-like phases in $Li_{1.2}(Mn_{0.5}Ni_{0.5})_{0.8}O_2$ electrode during first charge is also investigated using i*n situ* Mn K-edge EXAFS (Figs. 1 (b) and (c)). In contrast, not much changes in the local structure around Mn ions for $Li_{1.0}(Mn_{0.5}Ni_{0.5})_{1.0}O_2$ electrode. A clearly increased structural disorder around Mn ions, particularly in Mn-O bond, upon first charge is observed in the $Li_{1.2}(Mn_{0.5}Ni_{0.5})_{0.8}O_2$ electrode. Therefore, the abnormal capacity above 4.5V *vs.* Li^+/Li in $Li_{1.2}(Mn_{0.5}Ni_{0.5})_{0.8}O_2$ electrode during first charge could be attributed to the structural rearrangement of Li_2MnO_3 or Li_2MnO_3-like phases, due to certain processes such as the removal of Li_2O from the system.

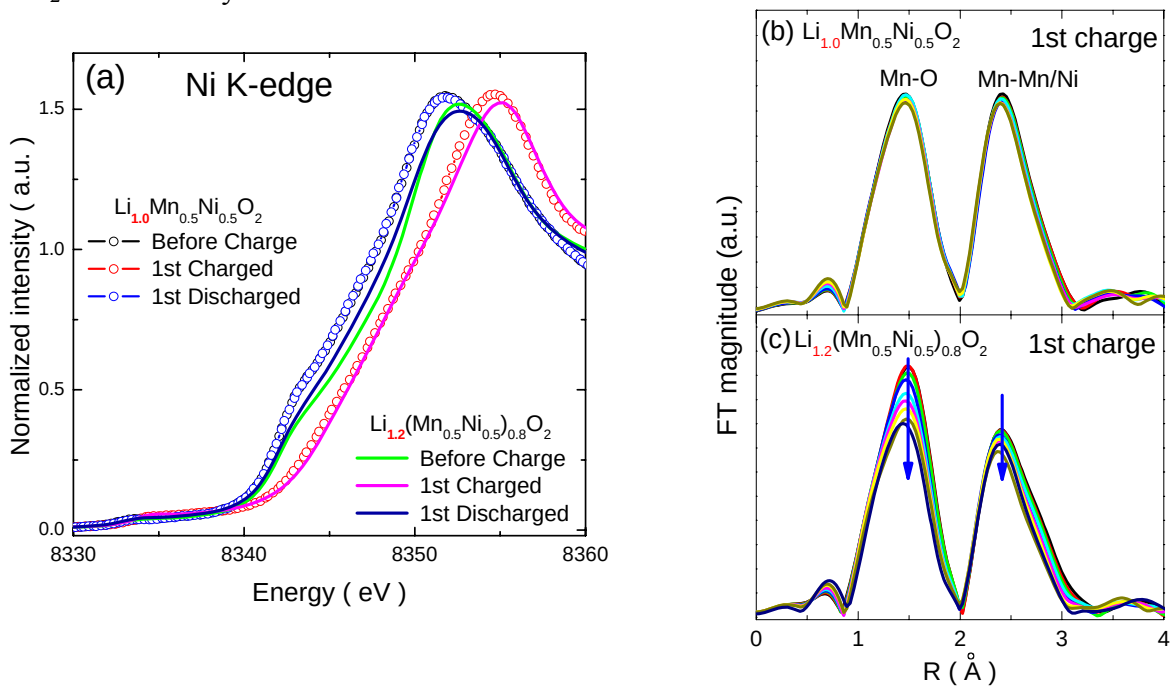


Figure 1. (a) *In situ* Ni K-edge XANES spectra of $Li_{1.0}(Mn_{0.5}Ni_{0.5})_{1.0}O_2$ and $Li_{1.2}(Mn_{0.5}Ni_{0.5})_{0.8}O_2$ during first charge/discharge process; *In situ* Mn K-edge EXAFS spectra of (b) $Li_{1.0}(Mn_{0.5}Ni_{0.5})_{1.0}O_2$ and (c) $Li_{1.2}(Mn_{0.5}Ni_{0.5})_{0.8}O_2$ during first charge.

TASK 5.3 - PI, INSTITUTION: Gerbrand Ceder, Massachusetts Institute of Technology, and Clare Grey, SUNY Stony Brook

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

SYSTEMS: Doped lithium nickel manganese oxides; lithium iron phosphates

BARRIERS: Low rate capabilities, high cost, poor stability, low energy density.

OBJECTIVES: Determine the effect of structure on stability of electrode materials. Explore rate limitations and relation to structure and particle size/morphology.

GENERAL APPROACH: Use NMR and diffraction to characterize structure as a function of particle size, sample preparation method, state of charge and number of charge cycles. Develop the use of *in situ* and *ex situ* NMR methods to identify structural changes and SEI formation. Use first principles calculations to identify redox-active metals, relative stability of different structures, the effect of structure on cell voltages, and promising cathode materials for BATT applications. Anticipate possible instabilities in materials at high states of charge by using calculations. Use calculations and NMR spectroscopy to identify low activation energy pathways for cation migration and to investigate electronic conductivity.

STATUS OCT. 1, 2007: $xLiCoO_2$-(1-x)$Li(NiMn)O_2$: The materials in this tie line will have been synthesized. NMR, XAS and Electron Spin Resonance (ESR) studies of these materials will be ongoing. Room temperature NMR studies of Li_xFePO_4 and the synthesis and characterization of $Li[Ni_{0.5}Mn_{0.5}]O_2$ *via* non-aqueous ion-exchange routes will be ongoing.

EXPECTED STATUS SEPT. 30, 2008: Investigation of structure and electrochemistry of $xLiCoO_2$-(1-x)$Li(NiMn)O_2$ will be complete. Static *in situ* NMR probe will be operational; applications of method to carbons and oxide systems will be demonstrated. NMR approaches to investigate SEI will have been demonstrated.

RELEVANT USABC GOALS: *Available energy*: 56 Wh/kg (10 mile) and 96 Wh/kg (40 mile); *10 s discharge power*: 750 W/kg (10 mile) and 316 W/kg (40 mile); *Cycle life*: 5000 cycles (10 mile) and 3000 cycles (40 mile); *Calendar life*: 15 years (at 40°C)

MILESTONES:
(a) Produce 1st design of the *in situ* NMR probe. (Nov. 07) **Complete**
(b) Initiate theoretical and experimental studies on metal nanoparticles. (Nov. 07) **Complete**
(c) Complete theoretical analysis of $LiFePO_4$ surfaces. (Nov. 07) **Complete**
(d) Generate initial results on thermal stability and decomposition of $LiFePO_4$. (Nov. 07) **Complete**
(e) Complete NMR analysis of charged $LiCoO_2$-$Li(NiMn)O_2$ samples; initiate diffraction experiments on key compositions. (Nov. 07) **Complete**
(f) Generate initial results on *in situ* and *ex situ* NMR experiments on oxide and metal nanoparticles and SEI formation. (May 08) **Complete**
(g) Generate computational results on lithiation of nanomaterials. (May 08) **Complete**
(h) Complete ion-exchange study of $Li(NiMn)_{0.5}O_2$. (May 08) **Complete**
(i) Complete variable temperature NMR analysis of partially charged lithium-iron phosphates. (May 08) **Complete**

PROGRESS TOWARD MILESTONES

We have now constructed and tested a simple set-up to allow *in situ* NMR studies of operating batteries. The design is based on that of Letellier and co-workers[1] and uses small plastic batteries (with electrodes with an area of approx. 0.35 x 0.9 cm^2) that can fit inside a 5 mm NMR coil in a static NMR probe. We have tested the set up with (bulk and nano-) $LiCoO_2$/Li and Si/Li cells to explore the information that can be extracted from the method. In the case of the Si system, we have directly observed the self-charge of the Si cells, which is extremely rapid at deep discharge. This completes Milestones (a) and (f).

Figure 1 shows the *in situ* NMR spectra of the Si/Li cell, and the corresponding electrochemical data. (Collaboration with J. –M. Tarascon and M. Morcrette, U. Picardie Jules Verne, France). The NMR spectra were compared with *ex situ* spectra of samples taken from batteries cycled to different states of charge, and from model compounds in the Li-Si phase diagram. Surprisingly, a new local environment was identified in the *in situ* NMR experiments at deep discharge (close to 0 V, *vs.* Li), which is associated with a negative chemical shift (of approx. -10 ppm). This local environment was not observed in the *ex situ* NMR experiments. We ascribe this new NMR signal to Li insertion into the crystalline phase, $Li_{15}Si_4$. The results suggesting that this phase, which has previously been shown to form at approx. 50 meV at the end of the discharge process,[2] is not a line-phase, but it can accommodate additional Li. Furthermore, the phase with additional Li is extremely reactive. The self-charge of the battery at deep discharge can be directly monitored in the *in situ* NMR set-up, the intensity of peak at –10 ppm, decreasing to zero over a period of 10 hours. We ascribe this to the oxidation of $Li_{15+\delta}Si_4$, and the accompanying reduction of the electrolyte. The effect of different binders/additives on this phenomenon is currently being explored.

On the modeling side we have started to set up a high-throughput computing environment in which a large number of potential electrode materials can be evaluated computationally. Equipment and automated job control and database integration are nearly completed at this point.

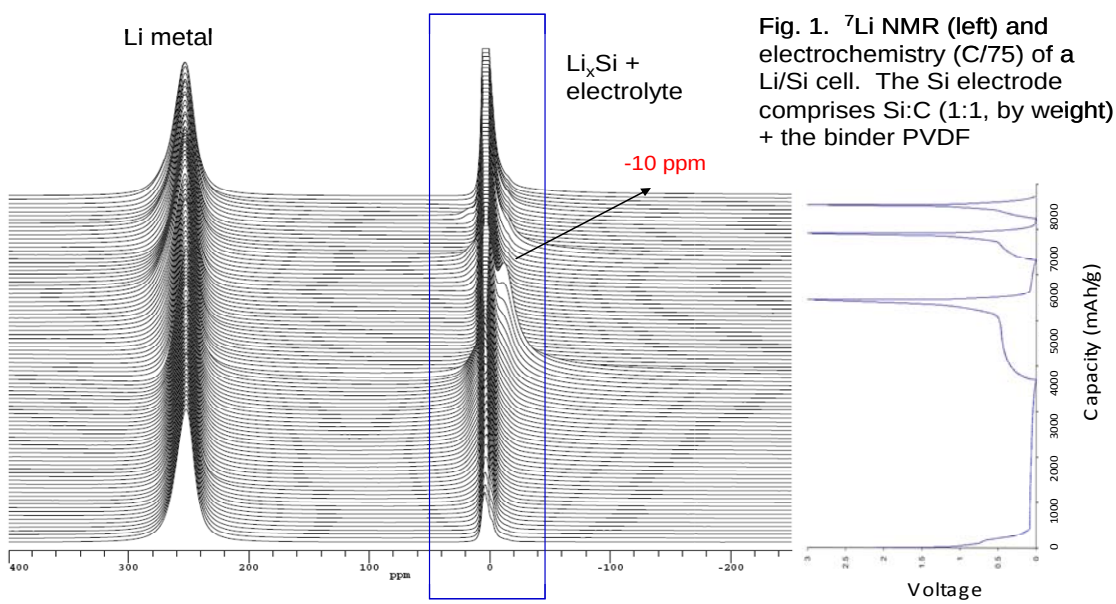


Fig. 1. ^{7}Li NMR (left) and electrochemistry (C/75) of a Li/Si cell. The Si electrode comprises Si:C (1:1, by weight) + the binder PVDF

Papers published during this quarter:

1. "Molten Salt Synthesis and High Rate Performance of the "Desert-Rose" form of $LiCoO_2$," H. Chen and C.P. Grey, *Adv. Mater.*, **20**, 2206-2210 (2008).

1. Letellier, M.; Chevallier, F.; Clinard, C.; Frackowiak, E.; Rouzaud, J. N.; Beguin, F.; Morcrette, M.; Tarascon, J. M.. *J. Chem. Phys.* **2003,** 118, 6038-6045.
2. Obrovac, M. N.; Christensen, L., *Electrochem. Solid St. Lett.* **2004,** 7, (5), A93-A96.

TASK 5.4-PI, INSTITUTION: Yang Shao-Horn, Massachusetts Institute of Technology

TASK TITLE - PROJECT: Diagnostics - Studies and Design of Chemically and Structurally Stable Surfaces of Lithium Storage 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/$LiMn_2O_4$ (high-power)

BARRIER: High cost, poor cycle and calendar life, and abuse tolerance

OBJECTIVES: Develop low-cost, high-energy, and high-power Mn-based cathodes.

GENERAL APPROACH: The surface chemistry and microstructure of oxide-electrolyte interface, with and without surface modification such as nanoparticle coating and how they change as a function of potential and cycle number, will be examined by scanning transmission electron microscopy (STEM and TEM) and X-ray photoemission spectroscopy (XPS). These surface features will be correlated to electrochemical impedance spectroscopy (EIS) of interfacial processes, cycling data and analysis of intrinsic thermal stability of oxides. This information is essential to design of stable interfaces between Li storage particles and electrolyte.

STATUS OCT. 1, 2007: The surface chemistry and microstructure of "$AlPO_4$" coating has been revealed and its implications on the cycling and thermal stability of positive electrode materials have been proposed. Studies to understand how the coating changes upon cycling to high voltages will be ongoing and preliminary EIS and XPS results of cycled electrodes will have been performed.

EXPECTED STATUS SEPT. 30, 2008: The changes in the surface chemistry and microstructure of surface-modified Mn-based Li storage materials such as $LiNi_{0.5}Mn_{0.5}O_2$ will be complete. Application of fundamental insights to design of new and stable interfaces for high-voltage systems will be ongoing.

RELEVANT USABC GOALS: *Specific energy* 56-96 Wh/kg, *Specific power* 316-750 W/kg, 15-year life (40°C), 3000-5000 cycles.

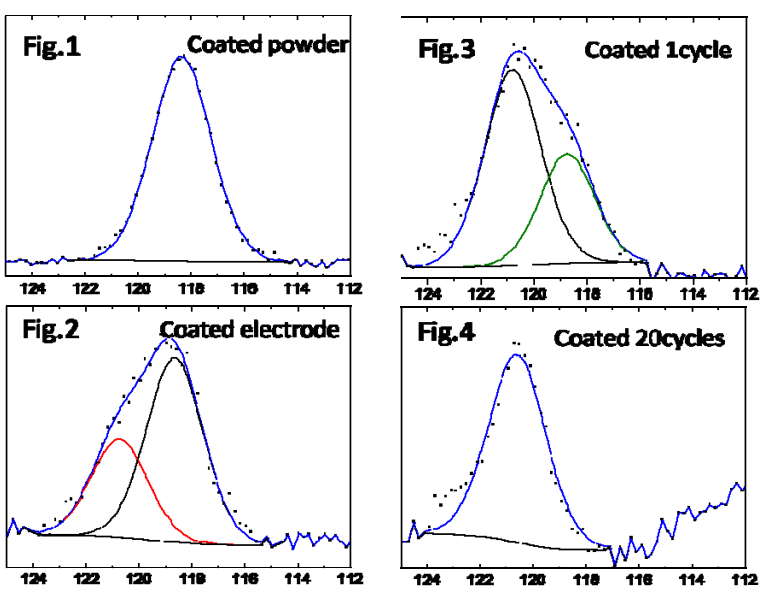
MILESTONES:
(a) Collect cycling and EIS data of $LiNi_{0.5}Mn_{0.5}O_2$ electrodes without surface modification upon cycling to high voltages and at different temperatures. (Dec. 07) **Complete**
(b) Collect XPS, TEM and STEM data of surface microstructure and chemistry of cycled electrodes without surface modification. (Mar. 08) **Delayed – will be complete by Sep. 08**
(c) Design and modify the surfaces of $LiNi_{0.5}Mn_{0.5}O_2$ and other Mn-based materials to improve cycling and thermal performance. (Mar. 08) **Delayed – will be complete by Sep. 08**
(d) Measure cycling and EIS data of surface modified electrodes to different upper voltage limits and at different temperatures. (Jun. 08) **Delayed – will be complete by Sep. 08**
(e) Collect XPS, TEM, and STEM data of surface microstructure and chemistry of cycled electrodes with surface modification. (Sep. 08) **On schedule**

Collaborations this quarter: We have continued our collaborations with Dr. A. Mansour at the NSWC in XPS measurements and analysis, and with C. Grey (SUNY SB) and G. Ceder (MIT) in understanding the structure and cation ordering of "$LiNi_{0.5}Mn_{0.5}O_2$" materials. We have begun collaborations with M. Thackeray and colleagues at ANL on high-resolution TEM and STEM studies of intergrowth compounds.

PROGRESS TOWARD MILESTONES

We have recently found that annealing of $LiNi_{0.5}Mn_{0.5}O_2$ provides high reversible capacity (~250mAh/g) upon cycling to 4.5V and very good rate capability at elevated temperatures. We are in the process of confirming this result and will report findings in the next quarterly report. Because of this, milestone b is being reevaluated and milestones c and d are being put back to later dates.

In this report, we discuss changes in the chemical nature of Al-containing surface species from XPS Al photoemission of electrode materials coated with "$AlPO_4$". The Al 2s photoemission spectra of a coated pristine powder sample and of an electrode are shown in Figs. 1 and 2 after subtracting the P 2p satellite contribution, which overlaps with the Al 2s region. The Al 2s region of the pristine coated electrode is different from the pristine powder sample and displays a highly asymmetric line, which was deconvoluted into two components. 1) One is at 118.6 eV, which is also found in the coated pristine sample and can be attributed to $LiAlO_2$ (118.67 eV in our reference materials). 2) The other peak is around 120.6 eV (and the Al 2p line is at ~76.6 eV), which indicates the evolution of a new Al chemistry. Such high binding energies (BE) of Al 2s and 2p lines indicate that a fraction of the Al is present in a highly ionic bonding environment such as in AlF_3. It cannot be attributed to the pure form of aluminum oxides or hydroxides. In fact, the Al 2s and Al 2p BEs for our AlF_3 reference of 121.6 and 76.5 eV, respectively, are close to the values measured for the pristine electrode. There are some possibilities that might be responsible for this high-BE peak. First, this may result from the more oxidized environment of Al atoms during the electrode making process. Other possible candidates might be attributed to Al atoms in a fluorine and oxygen environment (Al-O-F type bonds). This component might result from the small instability of PVDF, which is consistent with the fact that there is a small shoulder located at 685.0 eV in F1s for pristine coated electrodes. Figures 3 and 4 show the spectra of the coated cycled electrode for 1 cycle and 20 cycles. After one cycle, the intensity of the $LiAlO_2$ component decreased relative to the intensity of the high binding energy peak. After 20 cycles, the low-BE component is not resolved. This suggests that the surface film developed in the coated cycled sample contains Al-compounds in a relative high BE. It is speculated that Al present in the coating layer is reacting with surface species in the electrolyte, such as HF, and is consumed to form $Li_xAl_yO_zF_w$-type compounds on the surface, which give rise to the high-BE component at around 120.6 eV.



XPS spectra of Al 2s photoemission line for coated pristine powder (Fig.1), coated pristine electrode (Fig.2), coated 1 cycle electrode (Fig.3) and coated 20 cycles electrode (Fig.4). Cycle tests are in the voltage range of 2.5 and 4.7 V at C/5 rate, holding at 4.7 V for 4 hours between cycles.

BATT TASK 6
MODELING

TASK STATUS REPORT

TASK 6.1 - PI, INSTITUTION: John Newman, Lawrence Berkeley National Laboratory

TASK TITLE – PROJECT: Modeling - Improved Electrochemical Models

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

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.

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

STATUS OCT. 2, 2007: Optimization of lithium titanate spinel in various systems is complete. Characterization of transport in $LiPF_6$ electrolytes is ongoing. Incorporation of side reactions into dualfoil for Li-ion cells is complete. A study of side reactions in poly(3-butylthiophene) is complete. Modeling of capacity usage in HEVs and PHEVs is ongoing.

EXPECTED STATUS SEPT. 30, 2008: Characterization of transport in $LiPF_6$ electrolytes will be completed. Modeling of capacity usage in HEVs and PHEVs will be completed. A new project on experiments and modeling of the $Li_xTi_5O_{12}/Li_yMn_2O_4$ system will be ongoing. Another new project, possibly on aging mechanisms, will begin.

RELEVANT USABC GOALS: *Available energy*: 56 Wh/kg (10 mile) and 96 Wh/kg (40 mile); *10 s discharge power*: 750 W/kg (10 mile) and 316 W/kg (40 mile); *Cycle life*: 5000 cycles (10 mile) and 3000 cycles (40 mile); *Calendar life*: 15 years (at 40°C)

MILESTONES:
(a) Complete characterization of transport properties in $LiPF_6$ and modeling of the asymmetric hybrid supercapacitor system. (Nov. 07) **Complete**
(b) Complete study of capacity usage in HEVs and PHEVs. (Dec. 07) **Complete**
(c) Complete two-dimensional modeling of lithium deposition. (Aug. 08) **On schedule**

PROGRESS TOWARD MILESTONES

Quantifying Capacity Usage and Battery Size in HEVs and PHEVs

Two papers have been published in the Journal of Power Sources on capacity use and battery size in hybrid- and plug-in hybrid electric vehicles. We have also submitted a publication to the Electrochemical Society Transactions. We are now investigating experimentally one of the modeling results from that work, namely, whether a flat-potential system subjected to consecutive pulses will demonstrate a reduction in performance due to the persistence of solid-phase concentration gradients through the depth of a porous electrode. We have completed tests on a number of coin cells, but there have been some unusual features in the $FePO_4$ data. We have ongoing tests on pouch cells with $FePO_4$ *vs*. Li metal, and 18650 cells with $FePO_4$ *vs*. graphite. Preliminary results do show a history dependence of a constant-current discharge from 50% state-of-charge, when the cell is brought to that point at different rates from full charge.

Effects of Two-Dimensional Geometry on Lithium Deposition

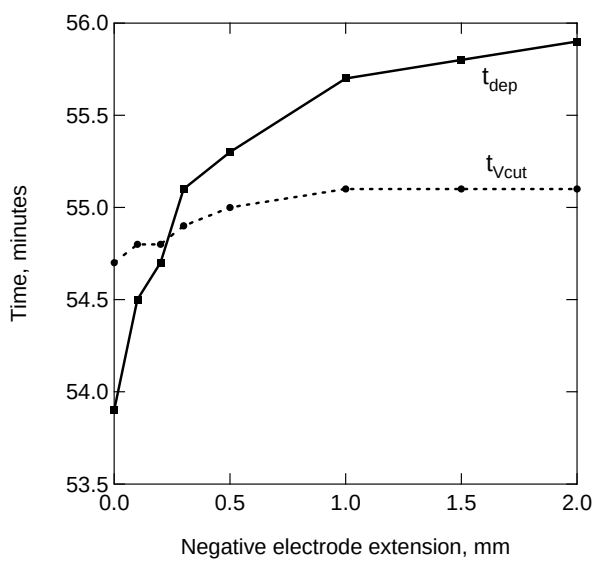


Figure 1. Time to reach conditions for lithium deposition (t_{dep}) and cell cutoff potential (t_{Vcut}) as excess capacity is added by extending the negative electrode beyond the positive. When $t_{dep} > t_{Vcut}$, cell charging will stop before deposition occurs.

A two-dimensional model of potential and current distributions during cell charging has been built. Simulations have been run in which the length of the negative electrode relative to the positive varied by 0 to 2 mm. Model results show that when electrode lengths are evenly matched the current distribution during cell charging yields a higher current at the edge of the negative electrode because of the edge's greater accessibility. This causes Li concentration to increase at the edge of the electrode faster than it does in the bulk, driving down the exchange current density and increasing the overpotential. An electrolyte-phase potential difference of 0.3 mV between the edge and bulk causes the potential drop at the edge of the electrode to reach 0 V. This favors Li plating at the edge, despite unused capacity in the bulk of the electrode. Extending the negative electrode beyond the edge of the positive provides excess capacity where it is needed and prevents deposition from occurring before the cutoff potential is reached. For electrodes where the negative is initially in excess by 10%, an extension of 0.5 mm is sufficient to postpone the onset of Li deposition until after the cutoff potential is reached (Fig. 1). The model is currently being adapted to include ion transport in the electrolyte and porous electrode theory; this will allow the simulation to more accurately predict the physical behavior of real systems.

TASK 6.2 - PI, INSTITUTION: Venkat Srinivasan**,** Lawrence Berkeley National Laboratory

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

SYSTEMS: High-voltage, high-energy: Gr/$LiPF_6$+EC:DEC/$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$
Low-voltage, high-stability: Gr/$LiPF_6$+EC:DEC/$LiFePO_4$

BARRIERS: High cost (or low energy)

OBJECTIVES:
1. Use models to optimize the performance of the Gr/$LiPF_6$+EC:DEC/$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ baseline.
2. Quantify the usefulness of alloy anodes for use in PHEVs.
3. Understand behavior and suggest means to enhance performance of high-energy phosphates (*e.g.,* $LiMnPO_4$).
4. Provide modeling support in the determination of diffusion coefficient in carbon anodes.

GENERAL APPROACH: Develop mathematical models for candidate Li-ion chemistries. Design experiments to test theoretical predictions and to estimate properties needed for the models. Use models to connect fundamental material properties to performance and provide guidance to material-synthesis and cell-development PIs and to quantify the ability of the candidate chemistry to meet DOE performance goals.

STATUS OCT. 1, 2007: A preliminary comparison of the BATT baseline chemistries under PHEV conditions would be complete. A silicon thin-films anode with excellent cycling capability will be identified for use in the modeling study.

EXPECTED STATUS SEPT. 30, 2008: The impact of poor kinetics of alloy anodes on PHEV performance will be quantified and a model developed to describe the phenomenon. A comparison of the use of alloy anodes compared to carbon anodes will be complete. A model for $LiMnPO_4$ will be under development.

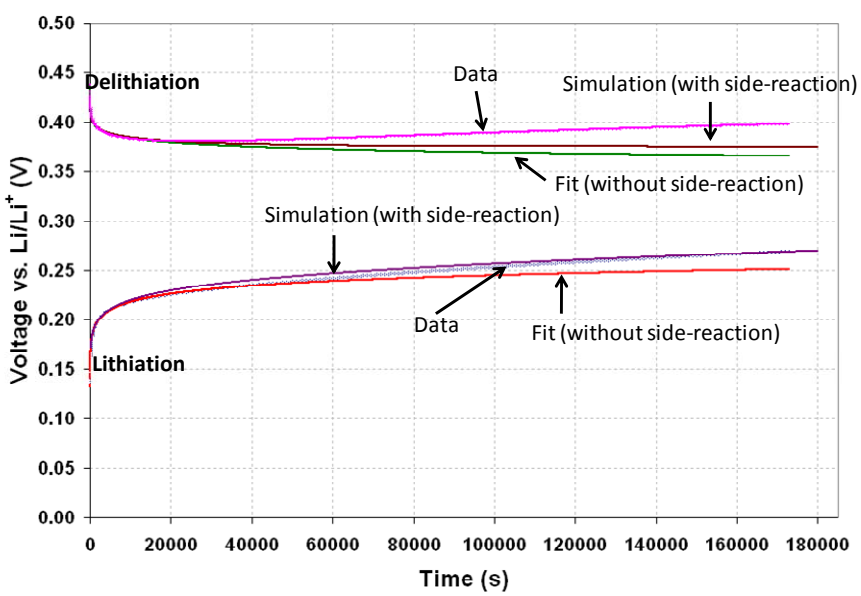
RELEVANT USABC GOALS: *Available energy*: 56 Wh/kg (10 mile) and 96 Wh/kg (40 mile); *10 s discharge power*: 750 W/kg (10 mile) and 316 W/kg (40 mile).

MILESTONES:
(a) Quantify experimentally the kinetic limitation in Si anodes including voltage drop and time constant for equilibration. (Dec. 07) **Complete**
(b) Develop a model that predicts polarization losses and time constants, and includes open-circuit potential, double-layer charging, and main and side reactions. (Mar. 08) **Complete**

PROGRESS TOWARD MILESTONES

The objective of this task is to understand the lithiation and delithiation phenomena in a silicon electrode. As reported in the last quarter, OCP relaxation data was obtained on thin films of silicon deposited using pulsed laser deposition. The data was fit to a model based on Tafel kinetics (main reaction) and double layer capacitance to estimate the apparent transfer coefficients (α_a, α_c) and the exchange current density to capacitance ratio (i_0/C_{dl}), all as a function of state-of-charge (SOC) for both lithiation and delithiation. The kinetic constants thus obtained were used to predict the charge/discharge behavior of the system.

Thus far, the side reactions were ignored during both the parameter estimation procedures based on the OCV relaxation data and the simulation of the charge/discharge behavior. In this quarter, we report the ongoing efforts towards understanding the kinetics of the side reactions in this system. The initial estimation of the exchange current density for the side reaction (i_0^{sr}) is based on the difference in the lithiation and delithiation capacities between the cutoff potentials (0.01 and 1.2 V). This difference in lithiation and delithiation capacities, with the former being always higher, is attributed to solvent reduction and SEI formation, and is a persistent problem with all silicon electrodes. Accordingly, we assumed an equilibrium potential for this side-reaction to be 0.8 V *vs*. Li/Li^+ and a transfer coefficient of 0.5. Only reduction reaction (*i.e.,* tafel kinetics) was taken into account. Using charge/discharge data (C/5), we estimated the exchange current density of the side reaction to be 4.2×10^{-12} mA cm^{-2}. The difference between lithiation and delithiation capacities between the cutoff potentials mentioned above was ~3%.



The open-circuit relaxation behavior at 50% SOC was then simulated using both the main reaction and the side reaction (assuming Tafel kinetics for both) and compared to data obtained at the same SOC (see fig.). The model predicts the open-circuit relaxation from the lithiation side is better than that from the delithiation side at longer time scales. Studies are underway to understand the difference.

This model, along with the parameters estimated, will be used with the OCP data to reevaluate the kinetic parameters of the main reaction to estimate the error induced due the presence of the side reaction. In addition, efforts are underway to control the side reaction rate by either using a different solvent or by depositing a single-ion (Li^+) conductor to isolate the silicon from the electrolyte.

Collaborations: Sam Mao (PLD Group, LBNL) and Keith Kepler (Farasis Energy Inc.).

TASK 6.3 - PI, INSTITUTION: Ann Marie Sastry, University of Michigan, Ann Arbor

TASK TITLE - PROJECT: Modeling - Multiscale Modeling and Validation of High-Performance and Long-Life PHEV Cells

SYSTEMS: High-voltage, high-energy: Gr/$LiPF_6$+EC:DEC/$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$
Low-voltage, high-stability: Gr/$LiPF_6$+EC:DEC/$LiFePO_4$
High-voltage, high-power: Gr/$LiPF_6$+EC:DEC/$LiMn_2O_4$

BARRIERS: Inadequate power and life systems for PHEVs

OBJECTIVES: Reduce the inactive mass fraction in baseline cathodes, using advanced simulation and experimentation. Determine optimal particle blends for high power and long lifetime for both energy- and power-dense systems. Predict failure mechanisms in baseline cells, considering coupled electrochemical and mechanical effects.

GENERAL APPROACH: Advanced finite element simulations, in collaboration with continuum modeling (V. Srinivasan, LBNL) will be used to eliminate unnecessary mass from cathodes, improving gravimetric properties. Coupled mechanical and electrochemical effects will be considered to develop optimal combinations of materials for high power and long lifetime. These will inform electrode design (V. Battaglia, LBNL). New atomistic simulation results will be used to provide first-principles-estimates of conductivity (Grey/Ceder). Shapes and type of materials will be considered, in collaboration with other BATT workers (M. Doeff, LBNL; K. Zaghib, Hydro-Québec).

STATUS OCT. 1, 2007: Experiments (LBNL and UM) and simulations on conduction and electrochemical performance in baseline anodes and cathodes, with correlations developed relating material composition, SEI layer formation and cell capacity losses will continue. 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.

EXPECTED STATUS SEPT. 30, 2008: Realistic mechanical loads and porosities (30-50%) will be used to specify composites with required conductive and mechanical properties. Elimination of unnecessary mass will be achieved, for high power systems.

RELEVANT USABC GOALS: *Available energy*: 56 Wh/kg (10 mile) and 96 Wh/kg (40 mile); *10 s discharge power*: 750 W/kg (10 mile) and 316 W/kg (40 mile); *Cycle life*: 5000 cycles (10 mile) and 3000 cycles (40 mile); *Calendar life*: 15 years (at 40°C)

MILESTONES:
(a) Implement 3D finite element (FE) model with coupled mechanical/electrochemical effects. (Feb. 08) **Complete**
(b) Identify specific blends for manufacture, which reduce unnecessary mass but maintain conductivity/capacity, in collaboration with Battaglia, Srinivasan and Doeff. (Mar. 08) **Complete**
(c) Use *ab initio* predictions of conductivities based on atomistic calculations (collaboration with Grey/Ceder) to perform large-scale FE modeling of lifetime. (Jul. 08) **Delayed – will be completed by Aug. 08**

PROGRESS TOWARD MILESTONES

Modeling—Optimization: During last quarter, we have been collaborating with Dr. Battaglia's group to identify specific blends for manufacturing high conductivity and capacity cathodes. Cathodes from Dr. Battaglia's group were comprised of active particle ($Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$), conductive additives (carbon black with graphite), and binder (Polyvinylidene Difluoride). The cathode had been compressed after casting on the current collector to various porosities by starting from 50% (uncompressed) to 40%, 30%, 20%, 10%, and 0%. To close the gap between numerical predictions and experimental results of conductivity in Q1 2008, we refined our computational models of microstructure via more intensive SEM. Subsequent results showed that distribution of PVDF/C became less uniform with reductions in porosity. Also, sedimentation of active material particles was observed, especially for cathodes with low porosity. Non-uniformities in cathode structures were shown to influence four-point-probe results [[i]]. We will continue to collaborate with Dr. Battaglia's group to identify possible origins of the observed nonuniformities.

In parallel, numerical estimations of ionic and electronic conductivities of cathodes were generated via our 3D mathematical approach [[ii]]. Conductivities were then used in executing a series of optimizations of cathode systems for battery performance, including 1D porous electrode models coupled with 2D spherical particle diffusion models. For the third milestone (c), this represents the last needed step for collaboration with groups in atomistic simulation, which will follow this work. With the results of the trade-off between ionic and electronic conductivity shown in Q2 2008 as the baseline, optimal schema for high specific energy will now be identified by considering the kinetic performance of the cathode *via* using a battery performance model. Current results allow mapping of specific energy as a function of electronic conductivity and ionic conductivity, respectively, for a specific cathode thickness. The specific energy drops from its maximum value with an increase or decrease in electronic or ionic conductivity around optimal points. We will further study the relationships among specific energy, cathode thickness, and volume fraction of active material with conductive additives. Ultimately, our results will include identification of optimal cathode compositions with high capacity, along with suggested guidelines for preparation of electrodes, for automotive applications.

References:

[i] C. -W. Wang, A. M. Sastry, K. A. Striebel, and K. Zaghib, Extraction of layerwise conductivities in carbon-enhanced, multilayered $LiFePO_4$ cathodes, *J. Electrochem. Soc.* **152** (5), A1001-A1010 (2005).

[ii] Y. H. Chen, C. W. Wang, G. Liu, X. Y. Song, V. S. Battaglia, and A. M. Sastry, Selection of conductive additives in Li-ion battery cathodes - A numerical study, *J. Electrochem. Soc.* **154**, (10), A978-A986 (2007).