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May 9, 2013

Mr. Tien Q. Duong
EE-2G/Forrestal Building
Office of Vehicle Technologies
U.S. Department of Energy
1000 Independence Avenue, S.W.
Washington D.C. 20585

Dear Tien,

Here is the second quarter FY 2013 report for the Batteries for Advanced Transportation Technologies (BATT) Program. This report and prior Program reports can be downloaded from <http://batt.lbl.gov/reports/quarterly-reports/>.

Sincerely,

A handwritten signature in black ink, appearing to be "Venkat Srinivasan".

Venkat Srinivasan
Acting Head
BATT Program

edited by: V. Battaglia
M. Foure
S. Lauer

cc: J. Barnes DOE/OVT
P. Davis DOE/OVT
D. Howell DOE/OVT
J. Muhlestein DOE-BSO

FEATURED HIGHLIGHTS

Anodes–

- ✦ Donghai Wang's group (Penn State) has developed a SiO/Fe₂O₃ composite material capable of 1700 mAh/g and good cyclability.

Diagnostics –

- ✦ Guoying Chen and Jordi Cabana (LBNL) each use *in situ* synchrotron XRD at SSRL to show the relationships between disorder, phase transformation, and performance of LiNi_xMn_{2-x}O₄.

Modeling –

- ✦ Venkat Srinivasan's group (LBNL) re-measures the diffusion coefficient of LiPF₆ in EC:DEC 1:1 at *ca.* 2×10^{-8} cm²/s, more than an order of magnitude greater than previously reported.

BATT TASK 1

ELECTRODE ARCHITECTURE

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

TASK TITLE: Electrode Architecture — Cell failure: electrochemical diagnostics

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Energy density of today's batteries is not high enough; cyclability is not high enough; calendar life is not long enough.

OBJECTIVE: To accurately assign the primary sources of energy and power fade of prominent chemistries and electrode designs that lead to advanced Li-ion technologies.

GENERAL APPROACH: Identify critical technology pathway to meet the USABC performance, life, and cost targets; and then identify cross-cutting failure modes of battery materials and electrodes that prevent the attainment of those goals. Design experiments and hardware that will provide fundamental insight into the problems. Materials from credible battery suppliers of a chemistry of particular interest to the BATT Program are procured. Electrochemical experiments are designed to draw out the identified problem. Additional hardware capable of extracting critical data is also designed, developed, and implemented.

STATUS OCT. 1, 2012: New project initiated October 1, 2012. The presently accepted mechanism, based on an acidic, aqueous solution is suspect in the aprotic solvents found in Li-ion cells. Preliminary experiments suggested that the loss of Mn may be driven by the oxidation of electrolyte decomposition products and not by reduction reactions driven by the presence of protons.

The three-electrode cell hardware can be modified such that the third electrode can be substituted with a tube. The present hardware is not showing satisfactory sensitivity. The source of an inductance loop in the ac-impedance is presently unknown.

EXPECTED STATUS SEP. 30, 2013: The loss of Mn from a commercial Mn-spinel cathode material, as a function of voltage, temperature, and time, will be measured. The loss of Mn in the presence of a LiPF₆-based electrolyte will be compared to the loss of a LiTFSI-based electrolyte. The gas-sensing hardware for a coin cell will be verified while cycling. The source of the inductance loop in a 3-electrode coin cell, as identified by the Modeling Group, will be validated.

RELEVANT USABC GOALS: 200 to 300 Wh/kg; 1000 to 5000 full cycles; 10- to 15-year calendar life

MILESTONES:

- (a) Make a modification to the three-electrode cell hardware based on guidance from Modeling Group and measure difference in response. (May 13) **On schedule**
- (b) Demonstrate gas-sensing apparatus for a coin cell on full cell. (Jun. 13) **On schedule**
- (c) Measure potential dependence of Mn loss from Mn-spinel. (Jun. 13) **On schedule**

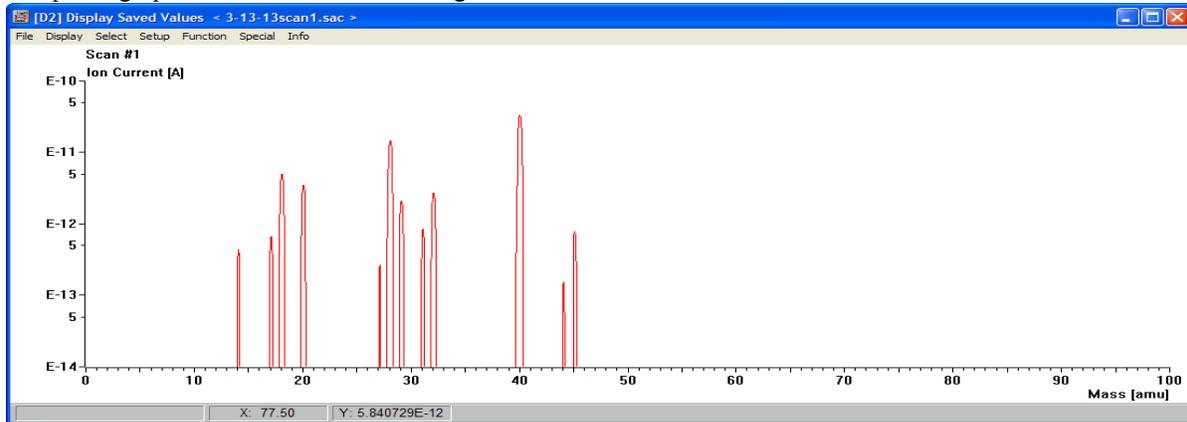
PROGRESS TOWARDS MILESTONES

All milestones are on schedule. **On schedule.**

1. Gas sensing apparatus for a coin cell demonstrated on full cell, June 2013.

This quarter, additional modifications were made to the apparatus shown last quarter that are being designed to sample gas from a coin cell. In this case, hardware was selected with minimal void volume. A half-cell of high-voltage Ni-spinel and Li metal was assembled. The cell was connected to the mass spec through a thin tube and a valve that entered the cell behind the cathode. The cell was charged at a 10-hour rate and after 2 hours of testing the valve was opened briefly and the mass spec pulled a small vacuum on the cell. Only a background gas was detected which was indicative of the vapor pressure of the carbonate electrolyte. Two hours later the valve was opened for a second time and this time hydrogen was detected, as indicated by the differences in the graphs provided in Fig. 1.

Mass spectrograph 2 hours into the first charge



Mass spectrograph 4 hours into the first charge

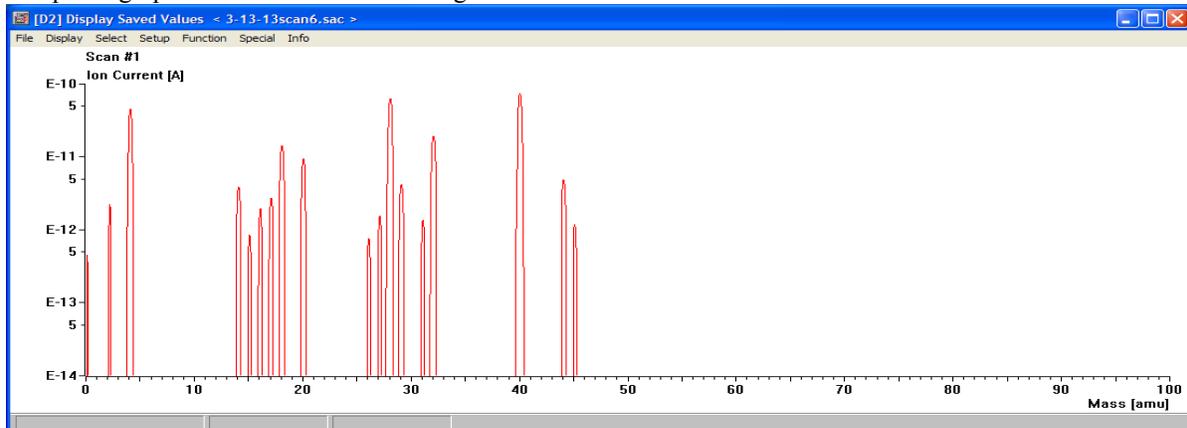


Figure 1. Mass spectrograph of the vapor in a coin cell 2 hours into a 10 hour charge (top) and 4 hours into the first charge (bottom). The spikes to the far left on the bottom graph suggest hydrogen.

This was somewhat unexpected and still needs to be confirmed. This work will be expanded to a full cell of graphite and Ni-spinel and to a pouch cell. If the result turns out to be significant, the source of the gas will be sought.

Task 1.2-PI, INSTITUTION: Karim Zaghbi, Hydro-Québec (IREQ)

TASK TITLE: Electrode Architecture — Assembly of Battery Materials and Electrodes

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC).

BARRIERS: Low energy and poor cycle/calendar life

OBJECTIVE: To develop high-capacity, low-cost electrodes with good cycle stability and rate capability to replace graphite in Li-ion batteries.

GENERAL APPROACH: To address and overcome the electrochemical capacity limitations (both gravimetric and volumetric) of conventional carbon anodes, proposal is to develop low-cost electrode architectures based on silicon that can tolerate its volumetric expansion and provide an acceptable cycle life with low capacity fade. Volume expansion, which is a common problem with Si-based electrode materials, will be addressed by: i) tortuosity/porosity optimization, and ii) improved current collector technology.

STATUS OCT. 1, 2012: This is a new project initiated April 1, 2013. In our recent study on the *in situ* analyses of SiO_x electrodes, it was shown that the bigger particles (*ca.* 13 μm) start to crack at around 0.1 V. During the charging process, all of the major cracks remained, while some fissures collapsed and others expanded. In general, it appeared that the smaller particles (<2 μm) did not crack. Furthermore, the *in situ* study revealed that delamination occurred at the particle/binder interface and the Cu current collector/electrode interface. These experiments provided a better understanding of the anode cycling mechanism and the failure mode associated with capacity fade. These results will help us to redesign the anode architecture.

EXPECTED STATUS SEP. 30, 2013: Complete the fabrication and testing of high-density Si-based electrodes with optimized tortuosity/porosity obtained by a dry-blended process. New current collector architecture will be used to coat the Si-based anode. *In-situ* SEM and TEM analyses will be utilized to monitor the real-time change to the structure undergoing volume expansion. These analyses will help to understand the failure mode and to guide further improvements.

RELEVANT USABC GOALS: High energy and low cost: 96 Wh/kg (PHEV, 40 miles). Cycle life, calendar life: 15 year life (at 40°C).

MILESTONES:

- (a) Identify an optimized dry-blended silicon-carbon powder composition. (Jun. 13) **On schedule**
- (b) Optimize the architecture of the Si-anode and LiMn_{1.5}Ni_{0.5}O₄ cathode. (Sep. 13) **On schedule**
- (c) Complete *in situ* SEM and TEM analyses of the optimized anodes. (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

The project was awarded under the 2012 RFP and will officially start on April 1, 2013.

In this quarter, work was directed at optimizing the Si-anode formulation. The source of Si is the powder distributed to multiple BATT PIs by Umicore. This material consists of 25 to 100 μm diameter secondary particles composed of agglomerated 20 to 150 nm diameter primary spherical particles. To minimize the stress in the anode, it is important to consider the anode architecture. An appropriate method for mixing the Si composite components was first considered. Different mixing methods were explored such as jar mill, ball mill (Spex), Thinky (planetary mixer), and their combination. Acetylene black and Alginate were selected as conductive additive and binder, respectively, and two fractions of Si considered. Two composition ratios (Si: binder: carbon black) were identified; (83%, 15%, 2%) and (50:25:25) (one with high-Si content and the other with a high carbon content.)

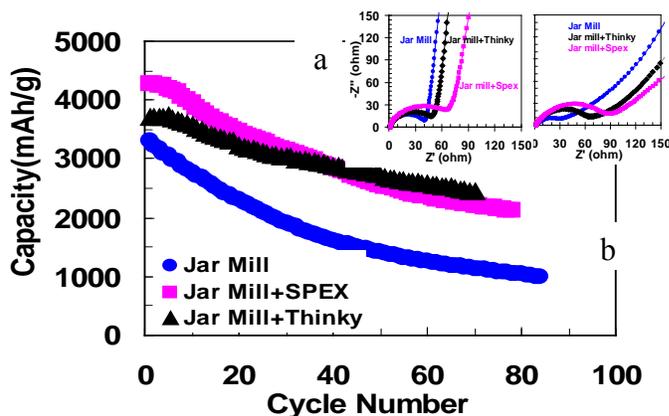


Figure 1. AC impedance before and after formation cycles (a), and cycling life of Li/EC-DEC-LiPF₆/Si cells.

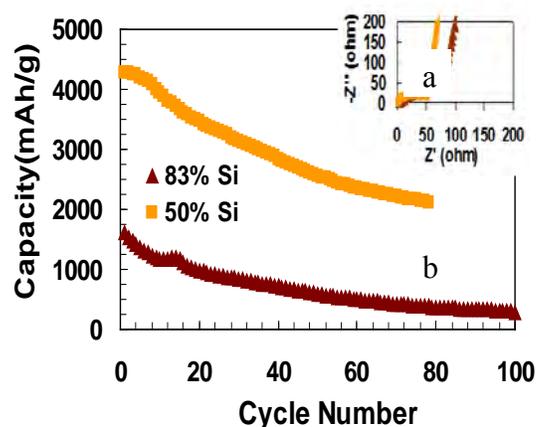


Figure 2. AC Impedance before cycling (a) and cycling life (b) of Li/EC-DEC-LiPF₆/Si cells.

The effect of different electrode composition and mixing methods is expected to improve our understanding of the electrode behavior and also identify the appropriate conditions for making a “good” Si-based anode. The cells were formed at C/24 with cut-off voltages of 5 mV and 1V. The reversible capacity after formation (Fig. 1) was 3500, 3810, and 4380 mAh/g, for the three mixing methods: Jar mill (JM), Jar mill + Thinky (JMT), and Jar mill + Spex (JMS), respectively. The 1st and 2nd cycle coulombic efficiencies of these cells were: (88, 97), (85, 97) and (88, 98), respectively. AC impedance spectroscopy was also used to compare the electrode preparation methods. Figure 1a shows the interface resistance (R_i) before and after formation cycles; higher R_i was found with JMS followed by JMT then JM, but this trend could not explain the capacity fade during cycling (Fig.1b). The highest capacity, at C/6, was obtained with JMS (4280 mAh/g), followed by JMT (3710 mAh/g) then JM (3300m Ah/g). The capacity fade after 70 cycles was 48, 34 and 65%, respectively. From this data, the conclusion is that JM alone is not effective as a mixing method. The effect of materials fractions was also investigated. As expected, R_i in Fig. 2a is low with high carbon and low Si content. It appears the high carbon content plays an important role in producing an appropriate anode structure and longer cycle life. The carbon facilitated improved electric contact between particles, hence high capacity was obtained and cycle life with 48% fading after 80 cycles compared to 72% for the low carbon loading.

HQ continues collaboration with LBNL researcher, V. Battaglia and R. Kosteki, in the BATT Program.

Task 1.3-PI, INSTITUTION: Yet-Ming Chiang, Massachusetts Institute of Technology

TASK TITLE - PROJECT: Electrode Architecture – Design and Scalable Assembly of High Density Low Tortuosity Electrodes

SYSTEMS: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC: DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Achieving sufficient electronic conductivity, achieving mechanical failure upon cycling, meeting automotive duty cycles, lowering cost.

OBJECTIVES: Develop scalable high density binder-free low-tortuosity electrode designs and fabrication processes to enable increased cell-level energy density compared to conventional Li-ion technology. Characterize electronic and ionic transport as a function of state-of-charge in relevant systems including Li(Ni,Co,Al)O₂ (NCA), Li₂MnO₃-LiMO₂ alloys and high-voltage spinels LiM_xMn_{2-x}O₄ and LiM_xMn_{2-x}O_{4-y}F_y.

GENERAL APPROACH: Fabricate high-density sintered cathodes with controlled pore volume fraction and pore topology. Test electrodes in laboratory half-cells and small Li-ion cells. Increase cell-level specific energy and energy density, and lower inactive materials cost, by maximizing area capacity (mAh/cm²) at C-rates or current densities commensurate with operating conditions for PHEV and EV. Measure electronic and ionic transport in pure single-phase sintered porous electrodes while electrochemically titrating the Li concentration.

STATUS OCT 1, 2012: This is a new project initiated April 1, 2013. Directional freeze-casting and sintering methodology were demonstrated for LiCoO₂, LiNi_{0.5}Mn_{1.5}O₄, and NMC. Measurement of electronic conductivity and ionic conductivity vs. Li concentration are substantially complete for LiNi_{0.5}Mn_{1.5}O₄ and Li₄Ti₅O₁₂ as a model “zero strain” system.

EXPECTED STATUS SEP. 30, 2013: Complete directional freeze-casting and sintering process development for NCA electrodes. Complete measurement of electronic conductivity and Li diffusivity vs. x in sintered NCA. Complete pulse-power characterization tests on sintered LCO electrodes as a model material.

RELEVANT USABC GOALS: EV: 200 Wh/kg; 1000 cycles (80% DOD).

MILESTONES:

- (a) Fabricate at least five NCA cathodes by directional freeze casting and sintering. (Apr. 13) **On schedule**
- (b) Complete electrochemical testing of cathodes in (a), and complete measurement of electronic conductivity and diffusivity vs. x in sintered NCA. (Jun. 13) **On schedule**
- (c) Complete measurement of electronic conductivity vs. x in sintered doped LiM_xMn_{2-x}O_{4-y}F_y. (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

The project was awarded under the 2012 RFP and will officially start on April 1, 2013.

Task 1.4-PI, INSTITUTION: Gao Liu, Lawrence Berkeley National Laboratory

TASK TITLE — PROJECT: Electrode Architecture – Hierarchical Assembly of Inorganic/Organic Hybrid Si Negative Electrodes

SYSTEMS: High-voltage, high-energy: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC).

BARRIERS: High-energy system: poor cycle life, high first-cycle irreversible capacity, low coulomb efficiency.

OBJECTIVES: Enable Si as a high capacity and long cycle-life material for negative electrode to address two of the barriers of lithium-ion chemistry for EV/PHEV application - insufficient energy density and poor cycle life performance.

GENERAL APPROACH: The volume change of Si during lithiation and delithiation disrupts the integrity of electrode and induces excessive side reactions, leading to fast capacity fade. This work will combine material synthesis and composite particle formation with electrode design and engineering to develop high capacity, long-life, and low-cost hierarchical Si-based electrode. The research and development activity will provide an in-depth understanding of the challenges associated with assembling large volume change materials into electrodes, and will develop a practical hierarchical assembly approach to enable Si materials as negative electrodes in Li-ion batteries.

STATUS OCT. 1, 2012: New project initiated October 1, 2012.

EXPECTED STATUS SEP. 30, 2013: Understand the function of polarity in the binder performance using the triethyleneoxide (TEO) side-chain conductive binders; design and synthesize a series of alkyl-substituted vinylene-carbonate (VC) additives. These additives form a compliance coating on Si surface during cycling. Study the impact of the compliance polymer coating on the coulombic efficiency of Si materials.

RELEVANT USABC GOALS: PHEV-40: 144 Wh/l, 4000 deep-discharge cycles.

MILESTONES:

- (a) Measure the adhesion of the triethyleneoxide (TEO)-containing conductive polymer binder, and characterize the electrode performance. (Mar. 13) **Complete**
- (b) Design and synthesize the alkyls-substituted VC additives. (Sep. 13) **On schedule**
- (c) Investigate the performance of Si electrode using the substituted VC additive electrolyte vs. baseline electrolyte. (Sep. 13) **On schedule**

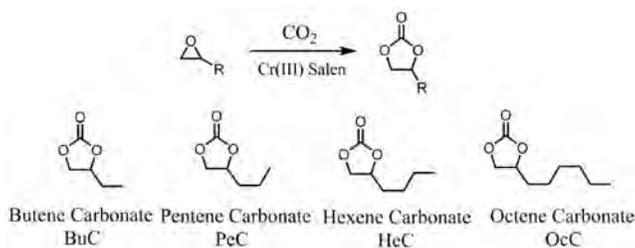
PROGRESS TOWARD MILESTONES

An alkyl moiety can be chemically grafted on ethylene carbonate (EC). The alkyl side-chain length can be controlled from 1 (propylene carbonate, PC) carbon to 10 (dodecene carbonate) carbons. The synthetic route to make this group of compounds is illustrated in Sch. 1. Five grams each of butene carbonate (BuC), pentene carbonate (PeC), hexene carbonate (HeC) and octene carbonate (OcC) was synthesized and purified according to Sch. 1.

BuC and PeC solvent-based LiPF_6 electrolytes cause graphite exfoliation during cycling, similar to PC-based electrolyte (Fig 1a). The graphite materials are able to cycle in HeC and OcC based electrolyte, which have longer alkyl substituents (Fig 1b). A proposed two-electron mechanism shows that after solvent co-intercalation into graphite layers, BuC and PeC decompose to 1-butene and 1-pentene, these gaseous products, under cycling conditions, cause graphite exfoliation. Decomposition products of HeC and OcC are 1-hexene and 1-octene, which are non-gaseous, thus graphite exfoliation does not occur.

A fundamental study of this series of cyclic carbonates using a graphite electrode improves the understanding of their basic properties. It is proposed that decomposition products from these cyclic carbonates with long alkyl chains could form a flexible and compliant coating during lithiation, and perhaps a stable SEI could be formed on high-volume-change alloy anode materials. Collaborations with diagnostic groups will be formed to help further understand the function of such an additive coating.

Collaborations: Collaborations are with BATT Program (Vince Battaglia, Venkat Srinivasan, Robert Kosteki, Phil Ross, and Xingcheng Xiao), DOE national user facility, ALS (Wanli Yang), and an industrial partner (GM).



Scheme 1. Synthetic route for alkyl substituted cyclic carbonates

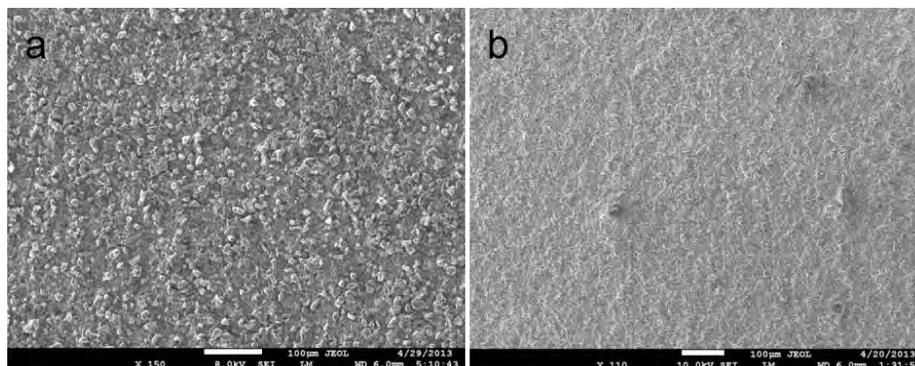


Figure 1. SEM surface images of the graphite electrodes with different electrolyte solvents after 10 cycles at a C/10 rate. a) With PC/ LiPF_6 electrolyte, the exfoliation of the graphite layers causes the graphite particles to separate from the laminate. b) With HeC/ LiPF_6 electrolyte, no graphite layer exfoliation or graphite particle separation is observed.

Task 1.5-PI, INSTITUTION: Vincent Battaglia, Lawrence Berkeley National Laboratory

TASK TITLE: Electrode Architecture – Electrode fabrication and materials benchmarking

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Energy density of today's batteries is not high enough; cyclability is not high enough; calendar life is not long enough.

OBJECTIVE: To develop a robust set of processes for fabricating electrodes and to understand the fundamental properties that underlie electrode performance. Then to use the set of processes to evaluate small quantities of BATT Program developed materials.

GENERAL APPROACH: Materials are identified through our own testing or testing performed in the Applied Battery Research Program to make up a baseline chemistry. Ultimately a set of processes for each electrode is developed that is robust enough so that when a small quantity of comparable BATT Program material arrives, the same processes will result in an equally good electrode. The Program material is then evaluated in a series of rate and cycling tests and the results are compared to the baseline material. Sources of cell failure are identified and communicated back to the originator of the material. Materials that look promising are considered for further scale-up and testing or as a possible focus area.

STATUS OCT. 1, 2012: New project initiated October 1, 2012. The group developed a fabrication manual over 5 years ago. The manual has been generally followed over the past two years. Many of the processes involved were developed based on a trial-and-error basis; although a methodical analysis of mixing order indicated that mixing the solids together before adding the polymer led to longer cycle life, and an analysis of carbon to polymer ratio indicated that this ratio should be kept between 1:5 and 4:5. It was recently determined that long mixing times can lead to a decline in viscosity.

EXPECTED STATUS SEP. 30, 2013: With regard to mixing, there are two steps: 1) mixing the solids together, 2) mixing the binder with the solids. By the end of the year the expectation is to know the most important of three variables: first, mixing time, speed of mixer; second, mixing time and optimum value of each of the three. Expectation is also to understand to what extent the drop in viscosity with mixing is a good thing or a bad result.

RELEVANT USABC GOALS: 200 to 300 Wh/kg; 1000 to 5000 full cycles; 10- to 15-year calendar life

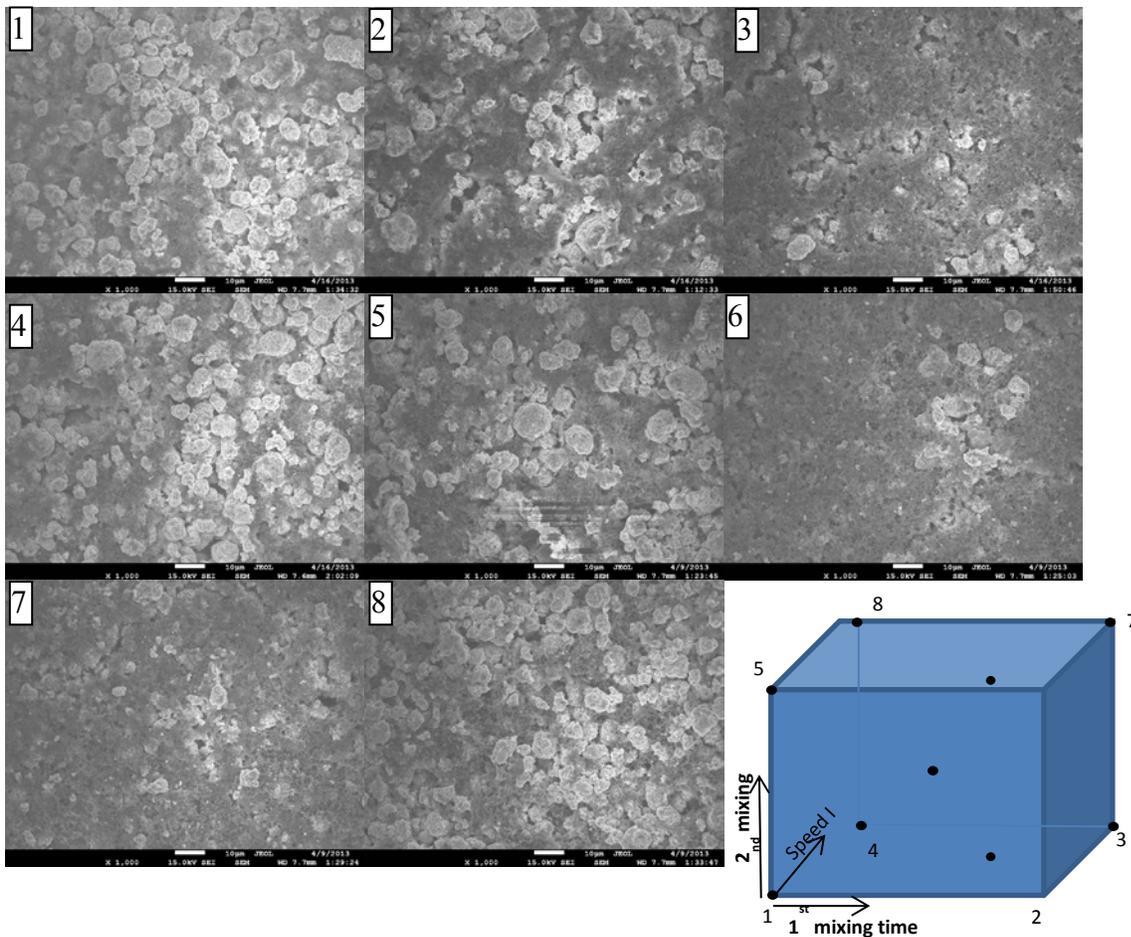
MILESTONES:

- (a) Measure the effect of mixing variables on electrode performance. (May 13) **On schedule**
- (b) Measure the viscosity with mixing time and the effect on performance. (Jun. 13) **On schedule**
- (c) Determine the optimum composition of an anode with high MW polymer. (Sep. 13) **On schedule**
- (d) Test three materials developed in the BATT Program. (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

- a. Measure the effect of mixing variables on electrode performance, May 2013. **On schedule.**

In the last quarterly, results were reported of a DOEx that included the mixing time of the first mixing step, the rate of mixing of the first mixing step, and the length of time of the second mixing step. This data indicated that the higher the mixing rate and the longer the total mixing time, the higher the conductivity of the laminate as measured by a four-point probe along its length. However, conductivity is just one measure of an electrode's performance and is typically of such a high value that it barely contributes to the overall impedance of the cell. With this in mind, to test the effect of mixing on cell performance, one actually has to build full cells and test their pulse power performance, overall rate performance, and long-term cyclability. Cells have been assembled and are ready to be put on test. Results will be reported in the next quarterly. In this quarter the SEM's of the different electrodes were examined. The SEMs of the laminates that resulted from the eight mixing conditions tabulated in the last quarterly are provided below.



Careful inspection of these 8 SEMs suggests that the laminate with the highest conductivity, #7, is also the laminate with the most uniform distribution of carbon black. Since the SEM only images the surface of an electrode, cross sections of electrodes will be made to determine if the distribution is the same through the electrode as it is across the electrode surface. Results will be reported in the next quarterly, which will complete this milestone on schedule.

BATT TASK 2

ANODES

Task 2.1-PI, INSTITUTION: Jack Vaughey, Argonne National Laboratory

TASK TITLE: Anodes — Novel Anode Materials

BASELINE SYSTEMS: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

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

OBJECTIVES: To overcome the electrochemical capacity limitations (both gravimetric and volumetric) of conventional carbon anodes by designing electrode architectures containing main group metal, metalloid or intermetallic components that can tolerate the volumetric expansion of the materials and provide an acceptable cycle life.

GENERAL APPROACH: To search for anode materials or formulations that provide an electrochemical potential a few hundred mV above the potential of metallic Li. Effort will be predominantly on Sn- and Si-based systems. A major thrust will be to design new electrode architectures in which an electrochemically active species is attached to the surface of a porous current collector providing a strong connection from the active species to the substrate. Such an approach minimizes the need for conductive additives and increases the power capabilities of these high energy anodes.

STATUS OCT. 1, 2012: Studies on the interfacial structure of Si-based electrodes bound to the substrate using metallic binders have been completed. Techniques have been determined and optimized to deposit electrochemically-active Si and Sn into porous substrates. Development of appropriate characterization tools to study active material/current collector interactions and their effect on cycle life and fade rate were optimized.

EXPECTED STATUS SEP. 30, 2013: A series of porous electrode structures with high loadings of active materials will be designed, created, and evaluated. Building on methodologies established earlier, diagnostic studies and *in situ* techniques will be employed to help refine required particle morphologies and other related issues associated with limited active material loadings and cycling.

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) Identify the thickness limits of Si film-based electrodes utilizing tools including tomography in a working electrode structure. (Mar. 13) **Complete**
- (b) Identify and demonstrate methodologies to incorporate higher levels. (>2 mAh/cm²) of active Si into three-dimensional electrode structures. (Sep. 13) **On schedule**
- (c) Demonstrate an *in situ* probe that can be used to correlate performance with sample preparation of an electrodeposited electrode. (Sep. 13) **On schedule**
- (d) Synthesize, characterize, and evaluate the role of polymeric film coatings in increasing the cycle life of Si-based electrodes. (Sep 13) **On schedule**

PROGRESS TOWARD MILESTONES

Team: Fulya Dogan

The team has been exploring the deposition of electrochemically active elements (elemental Si or Sn) into a foam structure and correlating the performance with its electrochemical and physical properties. Because a synthetic process based on electrochemical deposition is inherently complex, several variables were tested against the product formed and the electrochemical properties measured. Specifically, the most remarkable effect observed was the role of the counter-cation of the supporting electrolyte salt. In the past year a variety of electrolyte salts and solvents were evaluated for electrodepositing either Si or Sn metal onto various substrates. As a result of this effort, significant changes were noted in first cycle irreversible capacity and overall half-cell capacity with changes in the supporting salts.

Figure 1a highlights the performance Si deposited from a solution of SiCl_3 and tetraethyl ammonium chloride (TEACl) as the supporting salt. The cell showed >1200 mAh/g and $>99.7\%$ cycling efficiency over the first 125 cycles (Fig. 1a). The electrochemical voltage curves and powder X-Ray diffraction data are consistent with the deposition of an amorphous Si film (onto the Cu foam).

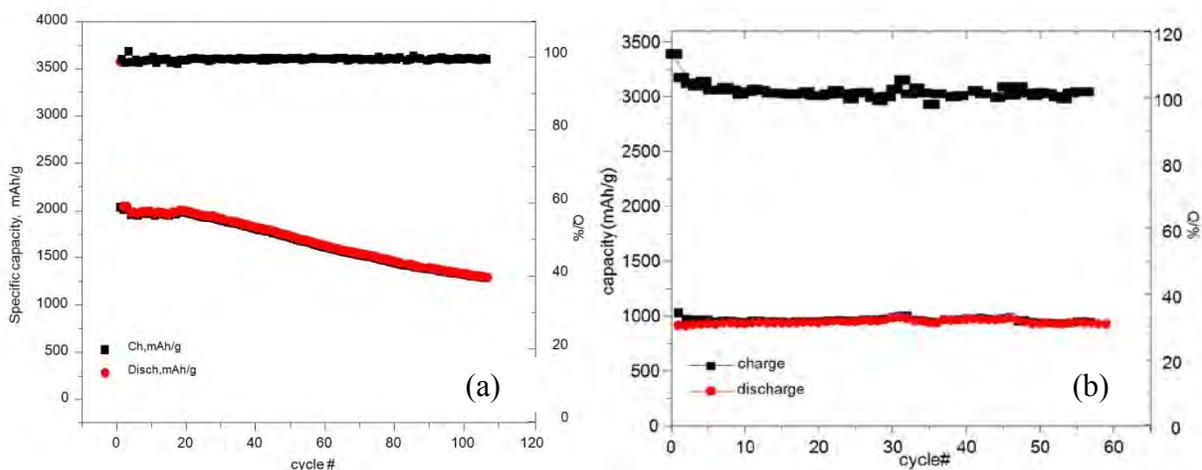


Figure 1. Cycling performance of a Si film on Cu using (a) TEACl as supporting electrolyte salt and (b) using TBACl as the supporting electrolyte salt.

Figure 1b shows the performance of a similar film in terms of quantity of Si deposited with tetrabutyl ammonium chloride (TBACl) as the supporting salt; immediate differences, including fade rate and overall capacity, are apparent. The electrochemical voltage curves and powder XRD data for this film are consistent with the deposition of a semi-crystalline Si film (onto the Cu foam).

A study of the surface and bulk composition differences between the two types of films has been initiated to better understand why the salt cation appears to play such an important role.

TASK 2.2 - PI, INSTITUTION: Stanley Whittingham, Binghamton University

TASK TITLE - PROJECT: Anodes – Metal-based High Capacity Li-ion Anodes

BASELINE SYSTEMS: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

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

OBJECTIVES: To replace the presently used carbon anodes with safer materials that have double the volumetric energy density, and will be compatible with low-cost layered oxide and phosphate cathodes and the associated electrolyte.

GENERAL APPROACH: Our anode approach is to 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 to have higher volumetric energy densities than carbon. Emphasis will be placed on simple metal alloys/composites at the nano-size. Initially, Sn will be emphasized, building on what has been learned from our studies of the tin-cobalt anode, the only commercial anode besides carbon. 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, 2012: It has been shown that amorphous nano-size Sn alloys have a high capacity and maintain it on deep or shallow cycling, when stabilized with elements like Co. In contrast, bulk crystalline metals have a high capacity, but their capacity fades rapidly after several deep cycles in carbonate-based electrolytes due to resistive continuous SEI formation. A nano-Sn material which shows electrochemical behavior comparable to that of the Sn-Co alloy, but where all the Co has been replaced by low-cost Fe, has been successfully formed by mechanical synthesis. This material has a higher volumetric capacity than Conoco Philips CPG-8 Graphite and has been formed by two different synthesis methods.

EXPECTED STATUS SEP. 30, 2013: The proposed work will result in the development of durable metal-based Li-ion battery anodes with volumetric energy densities that approach double those of the state-of-the art carbons. The reaction mechanism of the nano-Sn materials and the role of the carbon in their electrochemical activity will be understood. The major cause of the first-cycle excess charge capacity will be determined, and approaches to mitigate it will be proposed. Some clues as to how to control the SEI on such materials to optimize lifetime will be obtained.

RELEVANT USABC GOALS: 5000 deep and 300,000 shallow discharge cycles, abuse tolerance to cell overcharge and short circuit, and maximum system volume.

MILESTONES:

- (a) Determine the reaction mechanism of the nano-Sn-Fe-C system. (May 13) **On schedule**
- (b) Identify the cause of the first-cycle excess charge capacity; propose approaches to mitigate it. (Sep 13) **On schedule**
- (c) Identify an anode candidate having an energy density of 2 Ah/cc for at least 100 cycles. (Sep. 13) **On schedule**
- (d) Determine the electrochemistry of the leached nano-Si material, and compare to the standard Si. (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

The goal of this project is to synthesize new Sn- and Si-based anodes that have double the volumetric capacity of the present carbons, without diminishing the gravimetric capacity.

Milestone (c): In this quarter our work continued on nano-sized Sn-Fe-C anode materials mechanochemically synthesized by reducing SnO with reducing agents and carbon. It was found that Ti agents serve better than Al, and that hard iron balls work better than soft ones. Thus, Ti and hard iron balls were chosen as the optimum reductant and grinding media, respectively, to prepare the materials. Another important factor is the mechanochemical reaction time. The XRD patterns (Fig. 1a) show that as the reaction time increases, the Sn phase becomes Sn₂Fe; however if the reaction goes beyond a certain time when all the Sn is converted to Sn₂Fe, Fe metal is found. The electrochemical capacity and its retention (Fig. 1b) are closely related to the reaction time *e.g.*, 10-hour is better than 20-hour capacity retention. A study of the electrochemical performance of nano-Sn₅Fe material, provided by our collaborators at BNL, showed that an increase in Sn content in the deposit (Sn₅Fe *vs.* Sn₂Fe) resulted in the reduction of both the cyclability and rate capability (Figs. 2a and b).

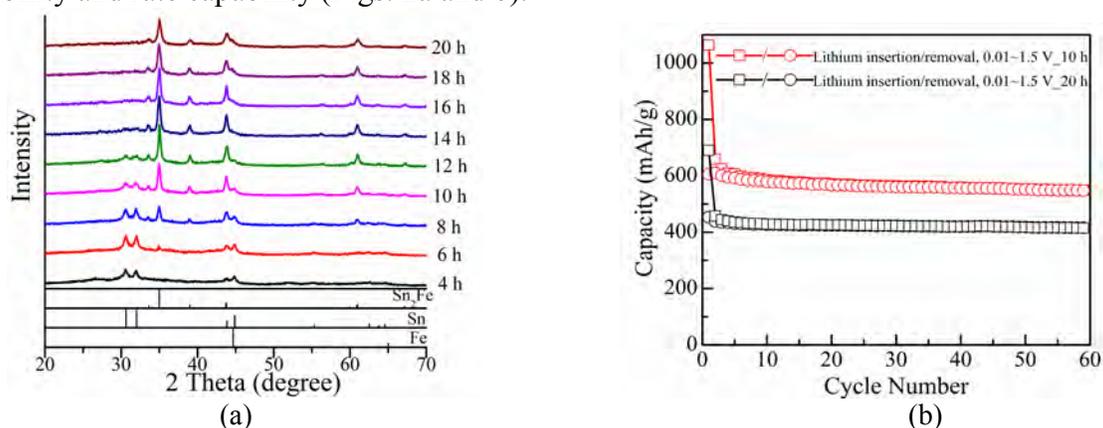


Figure 1. (a) XRD patterns and (b) cycling performances of nanosized Sn-Fe-C anode materials.

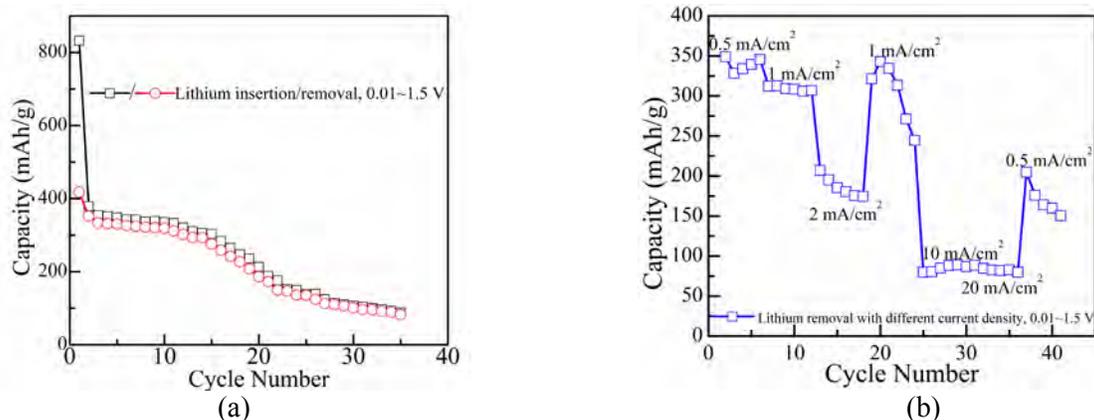


Figure 2. (a) Electrochemical cycling and (b) rate capability of nano-Sn₅Fe material

Further plans to meet or exceed milestones: None

Reason for changes from original milestones: None

Publication:

1. Wenchao Zhou, Tianchan Jiang, Yuxuan Wang, Jiye Fang and M. Stanley Whittingham, The Nanostructure of the Si-Al eutectic and its use in lithium batteries, *MRS Commun.*, in revision.

Task 2.3-PI, INSTITUTION: Prashant Kumta, University of Pittsburgh

TASK TITLE: Anodes – Nanoscale Heterostructures and Thermoplastic Resin Binders: Novel Li-ion Anode Systems

BASELINE SYSTEMS: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

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

OBJECTIVES: To identify new alternative nanostructured anode materials to replace graphite that will provide higher gravimetric and volumetric energy density. The goal is to replace carbon with an inexpensive nanostructured composite exhibiting higher capacity (1200 mAh/g) than carbon while exhibiting similar irreversible loss (<15%), coulombic efficiency (>99.9%), and cyclability. The project addresses the need to improve the capacity, specific energy, energy density, rate capability, cycle life, coulombic efficiency, and irreversible loss issues of Si anode.

GENERAL APPROACH: Our approach is to search for inexpensive silicon, carbon, and other inactive matrix-based composites (powders rather than thin films) that provide 1) an electrochemical potential a few hundred mV above the potential of Li, and 2) a capacity of 1200 mAh/g or greater (>2600 mAh/ml). The focus will be on exploring novel economical methods to generate nanoscale heterostructures of various Si nanostructures and different forms of C derived from graphitic carbon nanotubes (CNT) and new binders. Other electrochemically inactive matrices will also be explored. Promising electrodes will be tested in half cells against Li and compared to graphite as well as in full cells. Electrode structure, microstructure, rate capability, long- and short-term cyclability, coulombic efficiency, SEI origin and nature will also be studied.

STATUS OCT. 1, 2012: Nano-scale electrodes comprising Si-graphitic carbon-polymer derived C, and CNT related systems have been successfully synthesized and analyzed in half cells. The nano-composite Li-Si-C hetero-structures exhibit stable capacities of 700-3000 mAh/g with first cycle irreversible loss less than 15% and coulombic efficiency in the ~99.5-99.9% range.

EXPECTED STATUS SEP. 30, 2013: Efforts will continue to generate nano-composite ‘core-shell’, random, and aligned nanoscale Si, boron (B), and C exhibiting 1500 mAh/g and higher capacities. Research will be conducted to generate novel binders, explore novel synthesis and nano-scale microstructure affecting energy density, rate capability, first-cycle irreversible loss (FIR) and coulombic efficiency, characterize the SEI layer, and outline steps to yield stable capacity, reduce FIR, increase the coulombic efficiency and also improve the rate capability.

RELEVANT USABC GOALS: Available energy - CD Mode, 10 kW Rate: 3.4 kWh (10 mile) and 11.6 kWh (40 mile); Available Energy - CS Mode: 0.5 kWh (10 mile) and 0.3 kWh (40 mile); 10s peak pulse discharge power: 45 kW (10 mile) and 38 kW (40 mile); Peak Regen Pulse Power (10 sec): 30 kW (10 mile) and 25 kW (40 mile); Cold cranking power at -30°C, 2sec-3 Pulses: 7kW; Calendar life: 15 years (at 40°C); CS HEV Cycle Life, 50 Wh Profile: 300,000 Cycles

MILESTONES:

- (a) Identify binders and approaches to reach stable reversible capacity ≥ 1500 mAh/g (Mar. 13)
Delayed to Sep. 13
- (b) Identify strategies to achieve first cycle irreversible loss ($\leq 15\%$), efficiency ($\geq 99.95\%$), and rate capability matching carbon (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

Previously (2011, 2012), the electrochemical behavior of intra-type nanocomposites (INT) comprising microcrystalline, nanocrystalline, or amorphous silicon (a-Si) homogeneously dispersed in a carbon-based matrices such as graphite, K6-carbon, *etc.* was reported. The nanocomposite electrode, however, shows a capacity fade of *ca.* 0.01 to 0.03% per cycle when tested for long cycle life exceeding 100 cycles. The electrode is mainly fabricated by mixing 80 wt% active Si/C composite powder, 10 wt% commercial polyvinylidene fluoride (PVDF) binder, and 10 wt% conducting Super-P carbon black. The PVDF binds the fine active material particles together and is expected to maintain structural integrity during electrochemical cycling.

Currently, PVDF is the accepted commercial binder for anodes and cathodes. However, the large volume expansion of Si results in a significant stress field in the PVDF binder matrix leading to mechanical failure of the electrode. A high fracture-strength binder is hence necessary to accommodate the volume strain that arises due to the large related Si volume expansion. In 2012, preliminary data of few elastomeric binders developed by our group was reported for pure Si-based anode which showed improvement in long term cyclability of Si. In this quarter, further studies on the electrochemical properties of Si/C composite with our newly developed binder, named GG and MGG, will be presented.

Figure 1 shows the variation of specific capacity with voltage in the 1st cycle of Si/C nanocomposites comprised of microcrystalline Si dispersed homogeneously in a graphite matrix using the standard commercial PVDF binder. As shown in Fig. 1, the nanocomposite, cycled at a rate of *ca.* 50 mA/g (C/20) in the potential window 0.005 to 1.2 V, shows a 1st cycle discharge and charge capacity of *ca.* 1190 and 981 mAh/g, respectively, with an irreversible loss of *ca.* 17%. The Si/C nanocomposite with GG binder on the other hand, shows similar 1st cycle discharge (*ca.* 1179 mAh/g) and charge capacity (*ca.* 960 mAh/g) with an irreversible loss *ca.* 18% (Fig. 2), indicating that the newly-developed GG binder has no negative impact on the 1st cycle alloying/dealloying processes. The long-term cycling of Si/C composite cycled at 160 mA/g (C/6), Fig. 3, also shows that the GG binder exhibits better cycling stability (0.08% loss per cycle) in contrast to commercial PVDF (0.37% loss per cycle). However, significant chemical modification of the GG binder reflecting improvements in the mechanical strength is necessary for achieving excellent cycling stability (0.01% loss per cycle). A detailed report of the modified GG (MGG) will be presented in the next quarterly report.

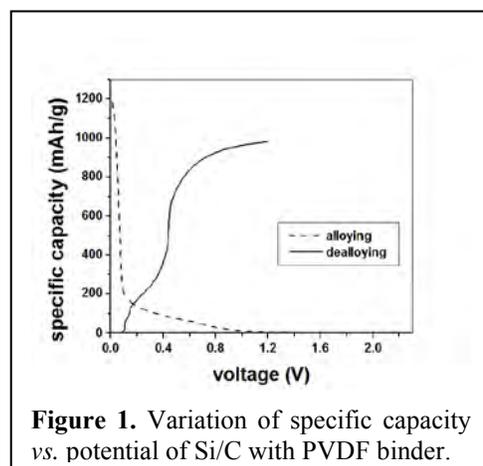


Figure 1. Variation of specific capacity vs. potential of Si/C with PVDF binder.

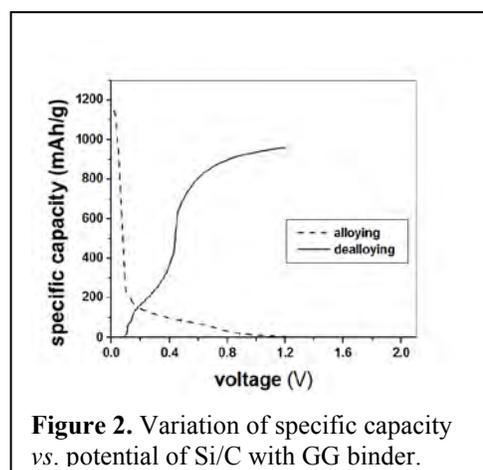


Figure 2. Variation of specific capacity vs. potential of Si/C with GG binder.

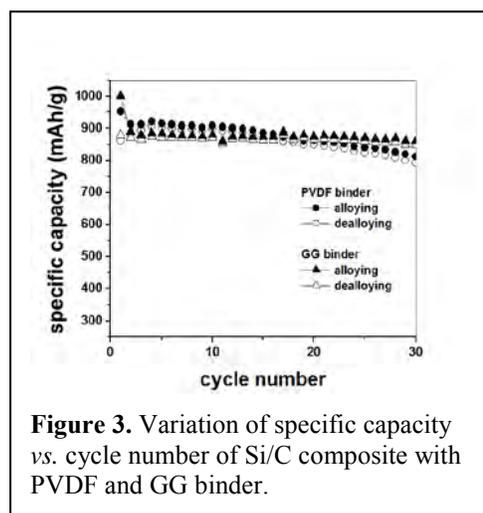


Figure 3. Variation of specific capacity vs. cycle number of Si/C composite with PVDF and GG binder.

TASK 2.4: PRINCIPAL INVESTIGATOR, INSTITUTION: Ji-Guang (Jason) Zhang and Jun Liu, Pacific Northwest National Laboratory

TASK TITLE – PROJECT: Anodes – Development of Silicon-based High Capacity Anodes

BASELINE SYSTEMS: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Low energy density, high cost, limited cycle life

OBJECTIVES: To develop high-capacity, low-cost electrodes with good cycle stability and rate capability to replace graphite in Li-ion batteries

GENERAL APPROACH: The main failure mechanism in Si-based anodes will be addressed using three approaches: improve the mechanical stability of Si-based anodes by manipulating the nano-structure of Si; improve electrical stability and conductivity of Si-based anodes by using conductive coating and binder; improve interface stability of Si-based anodes by choosing a stable electrolyte/binder with selective additives.

STATUS OCT. 1, 2012: Hollow core-shell structured porous Si-C nanocomposites with void space up to 30 nm between the Si core and the carbon shell have been designed and synthesized, and their electrochemical performance has been investigated. The porous core-shell structure of the Si-C composite helps to accommodate the large volume variations that occur during Li-insertion/extraction processes. In another effort, a conductive rigid skeleton-supported Si, such as B₄C/Si/C core-shell composite, was developed using the scalable ball-milling method. A high capacity of ~822 mAh/g (based on the full electrode) and capacity retention of ~94% over 100 cycles were obtained at a current density of ~0.63 A/g.

EXPECTED STATUS SEP. 30, 2013: The porous Si and the skeleton-supported core-shell structured composite (*e.g.*, B₄C/Si/C) will be further optimized. The optimized B₄C/Si/C material will be used as the baseline material for fundamental understanding of the failure mechanism. New binders, electrolyte, and electrolyte additives will be investigated to further improve the performance of Si-based anodes. New approaches will be developed to increase the capacity of thick Si-based anodes. An initial capacity of >800 mAh/g (based on the whole electrode) and ~80% capacity retention over 300 cycles will be obtained. Fundamental understanding of the formation and evolution of SEI layer, electrolyte additives, and the effect of electrode thickness will be investigated by *in situ* microscopic analysis.

RELEVANT USABC GOALS: >96 Wh/kg (for plug-in hybrid electric vehicles [PHEVs]), 5000 deep-discharge cycles, 15-year calendar life, improved abuse tolerance, and less than 20% capacity fade over a 10-year period.

MILESTONES:

- (a) Optimize the hollow core-shell structured porous Si and the rigid skeleton-supported Si composite for high capacity and stable cycling. (Mar. 13) **Complete**
- (b) Improve the performance of Si-based anodes with a capacity retention of >700 mAh/g over 250 cycles using new binders/electrolyte additives. (Sep. 13) **On schedule**
- (c) Develop new approaches to improve the cyclability of thick electrodes (>3 mAh/cm²). (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

The first cycle capacity loss of a porous Si-based anode was significantly improved by prelithiation of the porous Si particles using SLMP. The capacity and cycling stability of porous Si in the subsequent cycles were not affected by the prelithiation. Sodium carboxymethyl cellulose (CMC) binder and 1.0 M LiPF₆ in EC/DMC (1:2 vol) electrolyte with 10% FEC additive were used in the investigation. With a Si loading of *ca.* 51%, samples exhibited an initial capacity of *ca.* 700 mAh/g (based on the entire electrode weight including binder and conductive carbon) and demonstrated an excellent cycling stability (retained 96% of its capacity for over 200 cycles as shown in Fig. 1). The sample was initially cycled at 0.1 A/g for three cycles then tested at 1 A/g in subsequent cycles. The first-cycle capacity loss is *ca.* 8.1%. The capacity drop from the 3rd to 4th cycle shown in Fig. 1 is due to the change in discharge rate. In another effort, an optimized SBG (B₄C/Si/C) composite demonstrated good performance with high loading. The sample was initially cycled at 0.1 A/g for three cycles then tested at 1 A/g in the subsequent cycles. The first-cycle capacity loss is *ca.* 23.8%. It has a capacity of *ca.* 1.1 mAh/cm² and almost no capacity fade in 50 cycles at a current density of *ca.* 1A/g (Fig. 2). The battery was tested between 50 mV and 1.5V.

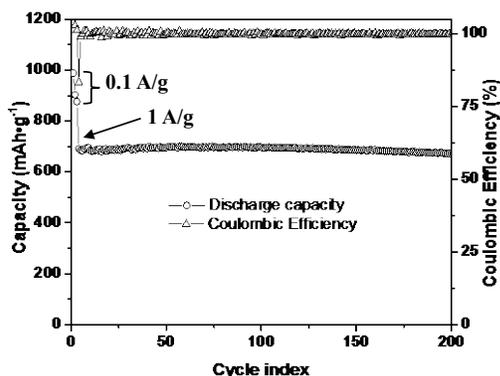


Figure 1. Cycling performance of prelithiated porous silicon with ~51% silicon in 1.0M LiPF₆ in EC/DMC (1:2 vol) electrolyte with 10% FEC additive.

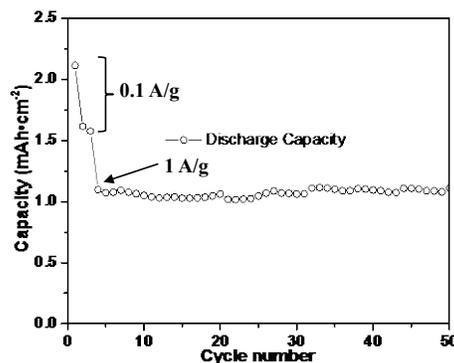


Figure 2. Cycling performance of the SBG composite in 1.0M LiPF₆ in EC/DMC (1:2 vol) electrolyte with 10% FEC as additive.

Prelithiation will be used to reduce the first-cycle loss of the SBG composite. The electrode thickness, structure, porosity, binders, and electrolyte additives will be further investigated. Fundamental understanding of the mechanism for capacity fade, especially the structure of the SEI layer with electrolyte additives, will be further investigated.

Collaborations: Michael J. Sailor of UCSD (porous Si preparation).

Publications:

1. Wang CM, X Li, Z Wang, W Xu, J Liu, F Gao, L Kovarik, J Zhang, J Howe, DJ Burton, Z Liu, X Xiao, S Thevuthasan, and DR Baer. 2012. "In Situ TEM Investigation of Congruent Phase Transition and Structural Evolution of Nanostructured Silicon/Carbon Anode for Lithium Ion Batteries." *Nano Letters* 12(3):1624–1632. doi:10.1021/nl204559u.
2. Gu M, Y Li, X Li, SY Hu, X Zhang, W Xu, S Thevuthasan, DR Baer, J Zhang, J Liu, and CM Wang. 2012. "In-Situ TEM Study of Lithiation Behavior of Silicon Nanoparticles Attached To and Embedded In a Carbon Matrix." *ACS Nano* 6(9):8439-8447. doi:10.1021/nn303312m.

TASK 2.5 - PI, INSTITUTION: Chunmei Ban, National Renewable Energy Laboratory; Co-PIs Steven M. George and Se-Hee Lee, University of Colorado (CU), Boulder

TASK TITLE - PROJECT: Anodes – Atomic Layer Deposition for Stabilization of Amorphous Silicon Anodes

BASELINE SYSTEMS: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Cost, low gravimetric and volumetric capacities, safety, rate capability, calendar and cycle life.

OBJECTIVES: To develop a low-cost, thick, and high-capacity Si anode with sustainable cycling performance. In FY13, our specific objectives are to develop a novel conductive and elastic scaffold by using Atomic Layer Deposition (ALD) and Molecular Layer Deposition (MLD), demonstrate the durable cycling by using our coating and electrode design, and investigate the effect of the atomic surface modification on the irreversible capacity loss.

GENERAL APPROACH: Chemical vapor deposition *via* silane decomposition on a hot filament has been used to synthesis the a-Si or nano-Si powders. Recently, a Nanocrystal RF Plasma Reactor was also utilized to synthesis Si/alloy nanocrystals with uniform size and shape. Size may be tuned from <10 to ~100 nm by varying the plasma conditions that will allow the study of how Si nanocrystal size affects the electrochemical performance. The conventional electrodes containing active material, conductive additive, and binder have been fabricated to evaluate the cycling properties. ALD is employed to coat both Si particles and Si electrodes in order to enhance the surface stability and electrode integrity.

STATUS OCT. 1, 2012: A Si anode coated with a unique copper/carbon composite was demonstrated to have a highly durable capacity at C/20 and C/10 with a coulombic efficiency of ~98%. ALD was employed on the thick Si anode to achieve the sustainable cycling performance. Recently, more durable cycling at higher rates (C/5 and C/3) has been achieved by using ALD-coated nano-Si anode. The thick Si electrodes (>15 μm) were recently sent to Dr. Vince Battaglia at LBNL for electrochemical testing.

EXPECTED STATUS SEP. 30, 2013: The optimal composition and structure of the ALD/MLD surface coatings will be established to improve the surface stability of Si particles as well as increase the integrity of Si electrodes. A thick Si anode with the appropriate ALD/MLD coatings will be demonstrated to have a high durable capacity as well as high rate capability. *In situ* characterization will be completed to better understand the structural evolution of the coated Si anodes during cycling.

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) Identify and characterize the MLD hybrid metal-organic coating on Si anode. (Dec. 12) **Complete**
- (b) Demonstrate durable cycling (>100 cycles) of the surface-engineered thick Si anodes (>15μm) at C/3. (Mar. 13) **Complete**
- (c) Characterize the effect of MLD metal alkoxide coatings on the cyclability of Si anodes, and demonstrate an MLD-coated Si anode with an irreversible capacity loss at 1st cycle less than 10%. (Jun. 13) **On schedule**
- (d) Supply the optimized thick electrodes (>20um) fabricated in the MLD flexible network to LBNL for verification. (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

In this quarter, Milestone (b) was successfully been completed. Details were provided in the previous report.

With regards to milestones (c) and (d), the growth of an aluminum alkoxide polymer (Alucone) on Si electrodes was demonstrated using molecular layer deposition (MLD). The Si electrodes were prepared with 60% Si nanoparticles (purchased from Aldrich without further treatments), 20% acetylene black, and 20% PVDF binder. Challenges are encountered during the MLD on high-surface-area Si electrode with a tortuous architecture. Two different reaction modes, static reactants exposure and viscous flow, were utilized during MLD to address the challenges in fabricating conformal coatings. The static reactants exposure allows the precursor gas to reach more surfaces of the electrode and enhance the completion of the self-limited reaction on the surface. Therefore, more conformal MLD Alucone coatings are achieved by using the static mode than the viscous flow mode.

Figure 1 shows the comparison of electrochemical cycling performance for the coated Si electrodes. Electrochemical cycling performance of the Alucone coated Si electrodes was investigated in coin-cells, with Li-metal as the counter electrode. All of cells were first cycled at 175 mA/g (C/20) for 10 cycles, and then cycled at 350 mA/g (C/10) in the voltage window between 0.05 and 1 V. The capacity obtained at a cycling rate of 0.1C stabilized for the static-coated Si electrode, while a slow fade in capacity was observed for the viscous flow-coated Si electrode. Besides, the static-coated Si electrode demonstrated a higher coulombic efficiency for the first cycle, which indicated a more conformal coating grown on the tortuous electrode structure.

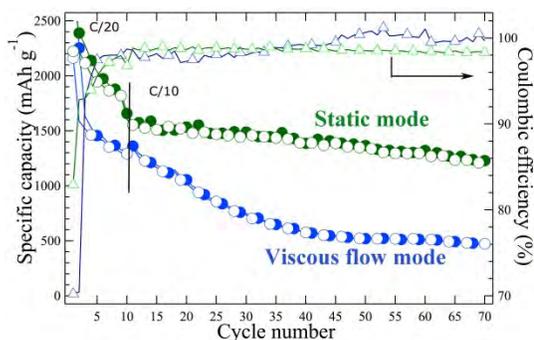


Figure 1. Cycling performance of Alucone coated Si anodes by using static mode and viscous flow mode.

Figure 2 displays the impact of different coating thicknesses on the cycling performance. The 3 nm, 10 nm, and 15 nm Alucone films were coated on the as-prepared Si electrode by using MLD at 100 to 120°C. The significantly improved cycling stability was achieved for Alucone MLD-coated Si electrodes compared to the bare Si anode. The highest capacity was obtained for both thicker MLD-coated Si anodes. The expectation is that the better conductivity in the conformal Alucone coatings may lead to higher capacity and better cycling performance than bare electrodes. Further characterization of the Alucone coatings will be conducted to identify the improved conductivity and the coating effect on the rate capability.

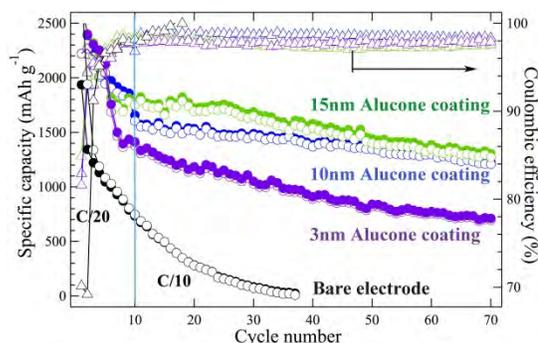


Figure 2. Cycling performance of bare and Alucone-coated Si anodes.

Publication and Presentation:

1. D.M. Piper, T.A. Yersak, S-B. Son, S.C. Kim, C.S. Kang, K.H. Oh, C. Ban, A.C. Dillon, and S.H. Lee, "Conformal Coatings of Cyclized-PAN for Mechanically Resilient Si nano-Composite Anodes," *Adv. Energy Mater.* 2013. doi: 10.1002/aenm.201200850.
2. Nanoscale Interface Engineering for Improved Li-ion Batteries (Invited talk), 2013 Spring MRS, San Francisco, CA, USA.

TASK 2.6 - PI, INSTITUTION: Yury Gogotsi and Michel Barsoum, Drexel University

TASK TITLE - PROJECT: Anodes – New Layered Nanolaminates for Use in Lithium Battery Anodes

BASELINE SYSTEMS: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Needs increased life, capacity and improved safety.

OBJECTIVES: Replace graphite with new solids: the layered binary carbides and nitrides known as MXenes, where the A-group element is selectively etched from the MAX phases – the latter ternary layered carbides and nitrides, may offer combined advantages of graphite and Si anodes with a higher capacity than graphite, less expansion, longer cycle life, and a lower cost than Si nanoparticles.

GENERAL APPROACH: Since, at this time the relationship between capacity and MXene phase chemistry is unknown, a rapid screening of as many MXene phases as possible is being carried out to determine the most promising chemistry by testing their performance in Li ion batteries. This work will also be guided by *ab initio* calculations.

STATUS OCT. 1, 2012: Fully exfoliate select MAX phases into two-dimensional layers of transition metal carbides or carbonitrides (MXenes) and test the different MXenes as anode materials in LIBs.

EXPECTED STATUS SEP. 30, 2013: Complete a study of the effect of different exfoliated MXenes chemistries and structures on SEI formation. Optimize the performance of MXenes anode materials in LIBs, by selecting the best carbon and binder additives for the MXenes.

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) Select the best carbon additive and binder that results in the highest Li uptake for select MXenes. (Dec. 12) **Complete**
- (b) Develop higher volumetric capacity anodes for LIBs than the commercial anodes. (Jun. 13) **On schedule**
- (c) Produce MXenes of new chemistries (such as Nb₂C, V₂C) that can achieve anode capacities of 400 mAhg⁻¹ at cycling rates of 1C or faster. (Sep. 13) **On schedule**
- (d) Produce MXene anodes with capability of delivering a stable performance at 10 C cycling rates. (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

The as-synthesized MXenes layers are stacked together. In order to separate the layers from each other, to achieve the highest accessibility for Li, and to make additives-free electrodes of MXenes, the chemical intercalation and delamination of MXenes was investigated.

Chemical Intercalation of MXene: The possibility of the intercalation of different molecules into the MXene structure was investigated. It was found that some compounds such as hydrazine monohydrate (HM), dimethylformamide (DMF), urea, dimethylsulfoxide (DMSO), can be inserted between Ti_3C_2 MXene sheets, resulting in the expansion of the MXene structure. Figure 1 shows the effect of the intercalation of Ti_3C_2 with hydrazine and co-intercalation with DMF on its XRD pattern. The shift of the major XRD peak to lower 2θ values confirmed its intercalation. After exposure to HM or HM in DMF at 80°C for 24 h and drying at room temperature, the c -lattice parameters (c -LPs) increased from 19.5 \AA to 25.48 \AA and 26.8 \AA , respectively. It also was shown that the intercalant molecules could be deintercalated by drying at higher temperatures (Fig. 1), indicating that the intercalation process is essentially reversible. It was shown that other MXenes, such as Ti_3CN and TiNbC , also can be intercalated with HM demonstrating that intercalation is a general phenomenon rather than the exclusive property of $f\text{-Ti}_3\text{C}_2$.

The possibility of intercalation of other compounds (acetone, ethyl alcohol, THF, chloroform, toluene, thiophene, and formaldehyde) was also studied; however, they did not show any shift of (000 l) XRD patterns.

Delamination of MXene: Intercalation of DMSO into Ti_3C_2 resulted in the increase of c -LP up to $44.8 \pm 0.1 \text{ \AA}$, which was the largest downshift of the (0002) peak position among all intercalated materials. Further sonication of a DMSO-intercalated material from an aqueous solution led to delamination of Ti_3C_2 single flakes. The schematic of the route of MXene delamination is shown in Fig. 2. The flakes can form binder-free films or “paper” by filtering the sonicated colloidal solution through a membrane (inset, Fig. 3). The “paper” showed a high volumetric capacity of $820 \text{ mAh}\cdot\text{cm}^{-3}$ at 1C cycling rate and $220 \text{ mAh}\cdot\text{cm}^{-3}$ at 36C (Fig. 3). Overall, the delaminated material increased the Li capacity by a factor of 4 over that of the as-synthesized MXene.

Mashtalir, O.; *et al.* Intercalation and Delamination of Layered Carbides and Carbonitrides, *Nature Communications*, 4, 1716, 2013, DOI: 10.1038/ncomms2664.

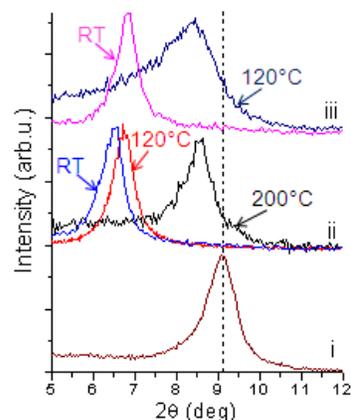


Figure 1. X-ray diffraction patterns of Ti_3C_2 : i) before any treatment, ii) after HM in DMF treatment, iii) after HM treatment, and dried at different conditions

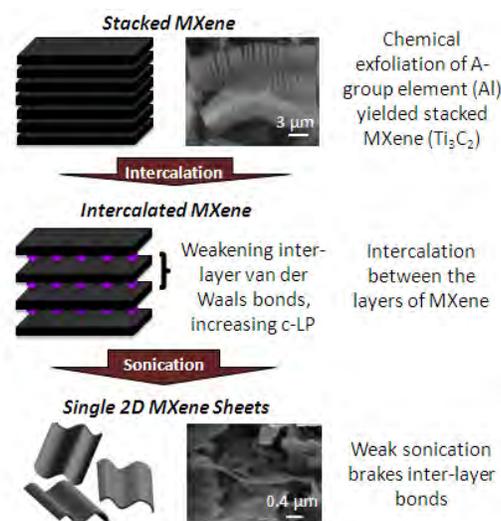


Figure 2. Schematic of delamination of MXene flakes.

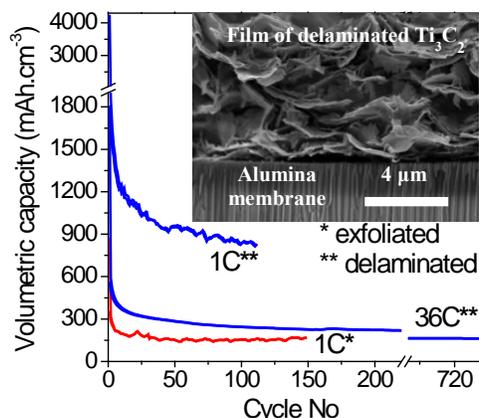


Figure 3. Comparison of the performance of exfoliated and delaminated Ti_3C_2 as anode material in Li-ion batteries. Inset shows SEM image of an additive-free film of delaminated Ti_3C_2 filtered through the membrane.

Task 2.7-PI, INSTITUTION: Donghai Wang and Michael Hickner, Pennsylvania State University

TASK TITLE - PROJECT: Anodes – Synthesis and Characterization of Structured Si/SiO_x-based Nanocomposite Anodes and Functional Polymer Binders

BASELINE SYSTEMS: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Low energy, poor capacity cycling, large initial irreversible capacity.

OBJECTIVES: Obtain high-performance Si anode materials by developing novel-structured Si/SiO_x-carbon nanocomposites and polymer binders to improve electrode kinetics and cycling life, and decrease initial irreversible capacity loss.

GENERAL APPROACH: Our approach is to synthesize Si/SiO_x-carbon nanocomposites with controlled nanostructures to improve kinetics and cycling stability upon lithiation/delithiation. New polymer binders will be developed with controlled mechanical properties by variation in crosslinking and SiO_x or carbon surface-binding functionality. These new binders are meant to help stabilize Si particles by providing a low-swelling polymer matrix with strong interactions with the anode particles and low electrolyte uptake.

STATUS OCT. 1, 2012: Silicon-carbon nanocomposites were developed with capacity above 800 mAh/g and capacity retention of 75% after 100 cycles. Evaluation of Si/SiO_x nanoparticles with stable capacity of 650 mAh/g after 500 cycles has been completed. New materials strategies for low electrolyte uptake sulfonated binders with variable crosslinking are reported with their performance evaluated against CMC-SBR and Na-CMC controls. Capacity degradation is still observed within 50 cycles and new binder formulations are being developed.

EXPECTED STATUS SEP. 30, 2013: Synthesis, characterization and electrochemical performance evaluation of Si/SiO_x-carbon nanocomposites will be completed to demonstrate optimized electrodes with stable cycle life and increased efficiency. Increased polymer binder performance with carboxylate-containing, cross-linked, mechanically stiff polymers will be demonstrated. Structure-property relationships for creating new, non-conductive binders that are soluble in benign solvents will be reported.

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 and characterize three types of Si/SiO_x-carbon nanocomposites. (Jan. 13) **Complete**
- (b) Demonstrate new crosslinking chemistry involving sulfonates, carboxylates, and azide chemistries for low-swelling polymer binders. (Jan. 13) **Complete**
- (c) Identify at least one Si/SiO_x-carbon nanocomposite anode with a reversible specific capacity of at least 1000 mAh/g over 200 cycles. (May 13) **On schedule**
- (d) Identify and optimize at least one polymer binder and processing solvent that shows better cycling performance than the reported binders with commercial Si nanoparticles. (May 13) **On schedule**
- (e) Supply laminates of the optimized electrodes with electrode capacity of 800 mAh/g that cycle 100 cycles to BATT PIs. (Aug. 13) **On schedule**

PROGRESS TOWARD MILESTONES

SiO-based anode materials: A SiO/Fe₂O₃ composite, composed of SiO coated with Fe₂O₃ nanoparticles, was synthesized by mechanical milling and characterized by XRD, SEM, TEM, and EDS. The TEM image and corresponding EDS maps showed that the SiO particles in the composite were coated uniformly with crystalline Fe₂O₃ nanoparticles (Fig. 1A). As shown in Fig. 1B, both SiO and milled SiO display very poor capacity retention. The SiO/Fe₂O₃ composite shows considerably better cyclability than either SiO sample, with 71% charge capacity retention (1335 mAh/g) with respect to the first charge capacity after 50 cycles. The rate capability of the SiO/Fe₂O₃ composite is also superior to that of SiO and milled SiO (Fig. 1C). The composite maintained a capacity of *ca.* 600 mAh/g at the high current density of 4.8 A/g, while the SiO only achieved a capacity of *ca.* 200 mAh/g at this current density. It's thought that metallic Fe forms during lithiation of the SiO/Fe₂O₃, increasing the conductivity of the composite and thereby improving its performance. Further investigations of the mechanism of the electrochemical performance are ongoing.

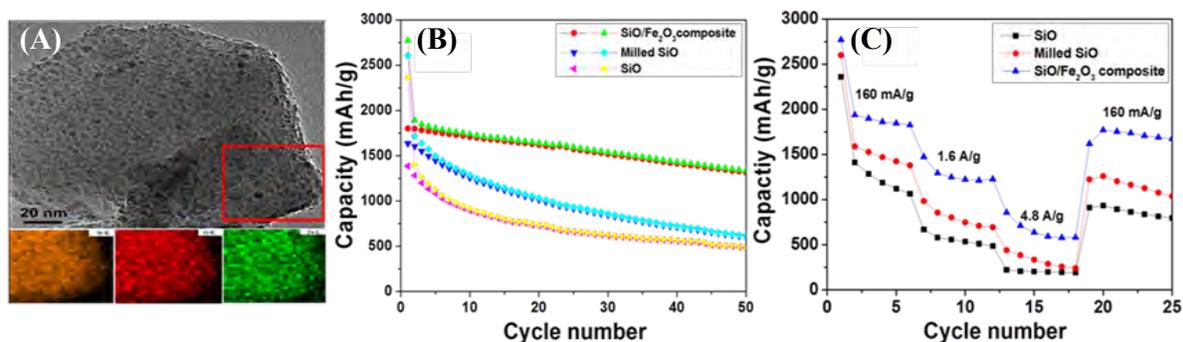


Figure 1. (A) TEM images and corresponding EDS elemental mappings of the SiO/Fe₂O₃ composite. (B) Cycling performance of SiO, milled SiO, and SiO/Fe₂O₃ composite in 50 cycles between 0.01-1.5V. (C) Galvanostatic rate capability of SiO, milled SiO, and SiO/Fe₂O₃ composite.

Polymer binders: Sulfonated poly(ether ether ketone) (SPEEK) binders have shown better rate capability than sulfonated poly(sulfone) (S-Radel) binder materials in Si-based anodes with commercial Si nanoparticles. The surface interactions of different binders with Si nanoparticles are being investigated using vibrational spectroscopy to gain fundamental information on their chemical interactions in the anode. Figure 2 shows no peak shifts in the aromatic C-C backbone region for S-Radel binders and only small shifts in the sulfonate bands. The peaks in the spectra do not shift with the weight % of binder in the composite, demonstrating little interaction between the binder and the Si nanoparticles. Current studies are investigating CMC and SPEEK binders in similar experiments, which have shown better performance in Si-based anodes.

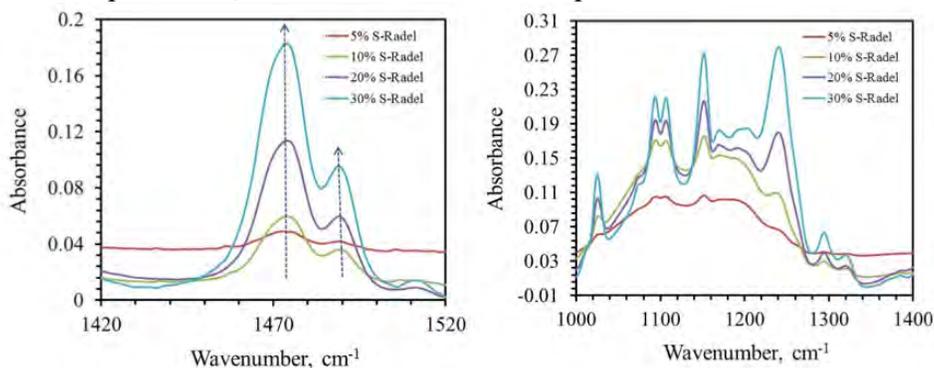


Figure 2. (left) No peak shifts for the C-C bonding in the backbone structure showing weak interactions between S-Radel and silicon surface and, (right) Asymmetric O=S=O bonds (1027 and 1080 cm⁻¹) and symmetric O=S=O bonds (1255 cm⁻¹) show peak shifts of < 1 cm⁻¹ and ~1-2 cm⁻¹, respectively.

TASK 2.8 - PI, INSTITUTION: Yi Cui, Stanford University

TASK TITLE - PROJECT: Anodes – Wiring up Silicon Nanoparticles for High Performance Lithium-ion Battery Anodes

BASELINE SYSTEMS: Conoco Phillips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Low energy density, low efficiency, short cycle life, and safety issues

OBJECTIVES: Overcome the charge capacity limitations of conventional carbon anodes by designing optimized nano-architected silicon electrodes as follows: 1) fabricate novel nanostructures that show improved cycle life, and 2) develop methods to study the lithiation/delithiation process to understand volume expansion for higher efficiency.

GENERAL APPROACH: This project explores 1) new types of nanostructured anodes, 2) methods for controlling SEI growth and electrode stability, and 3) the nature of volume changes in Si nanostructures. Over the course of the year, a variety of nanostructured electrodes will be developed, with particular emphasis placed on developing structures based on conductive frameworks and also making high performance electrodes with both nano- and micron-sized Si particles. In addition, hollow/porous nanostructures will be developed and optimized for SEI control in these electrode structures. Finally, separate efforts will be dedicated to understanding the fundamentals of volume expansion in Si nanostructures through *in situ* and *ex situ* single nanostructure observation; specifically, the fracture properties of Si with different crystallinity will be studied. This project was initiated January 1, 2011.

STATUS OCT. 1, 2012: A variety of conductive secondary additives (polymer, hydrogel, etc.) were developed. Nano- and micron-sized Si particle electrodes were fabricated with these additives. A variety of spherical, tubular, and porous Si nanostructures were fabricated and incorporated into Si anode architectures. Suitable amorphous and crystalline Si nanostructures with controlled sizes have been developed for study.

EXPECTED STATUS SEP. 30, 2013: Electrodes with cycle life >1000 cycles in a half cell and CE >99.5% will have been demonstrated from nano- and micron-sized Si particles. The critical size for fracture of amorphous nanostructures will have been found.

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) Develop conductive polymer additive/binder, incorporate into electrodes. (Jan 13) **On going, due Sep. 13**
- (b) Determine the effect of electrode additives, coatings, and porosity on SEI thickness and properties. (Apr. 13) **On schedule**
- (c) Optimize nano/micro particle electrodes for high capacity, >1000 cycles, >99.7% CE. (Jul. 13) **On schedule**
- (d) Use *in situ* TEM and *ex situ* SEM to test critical size and rate for fracture for crystalline, polycrystalline, and amorphous Si nanostructures. (Jul. 13) **Complete**

PROGRESS TOWARD MILESTONES

Si nanoparticles from abundant and cheap sources for Li battery anodes. Much effort has been directed towards designing Si-nanoparticle-based anodes with long cycle life, as detailed in previous progress reports and publications. A promising nanostructure design involves using a yolk-shell structure, in which Si nanoparticles are surrounded by carbon shells with empty space in between (Liu et al., *Nano Letters*, **12** (6) 3315, 2012). This allows for volume expansion of the Si while the outer carbon shell maintains dimensional stability, allowing for stable SEI growth. Although this design has yielded good cycle life, the starting Si nanoparticles are too expensive for mass production. Si is an abundant element in nature, but the electronic-grade Si that is commonly used to synthesize nanomaterials is quite expensive. Cheap methods to easily synthesize large quantities of lower-purity Si are needed.

To this end, a method has been developed to synthesize Si nanoparticles for Si batteries directly from agricultural waste products. Specifically, rice husks were used, which are extremely cheap (~\$18 per ton) and naturally contain up to 20 wt% SiO₂. First, the rice husks are converted to pure silica by burning in air and then the silica is reduced to Si. This results in an interconnected network of nanoparticles, as shown by the SEM and TEM images in Fig. 1. The particles are agglomerated and are physically interconnected, but the void space between the particles should allow for accommodation of volume expansion during lithiation. The synthesis process results in a 5 wt% yield of Si when considering the weight of the initial rice husks.

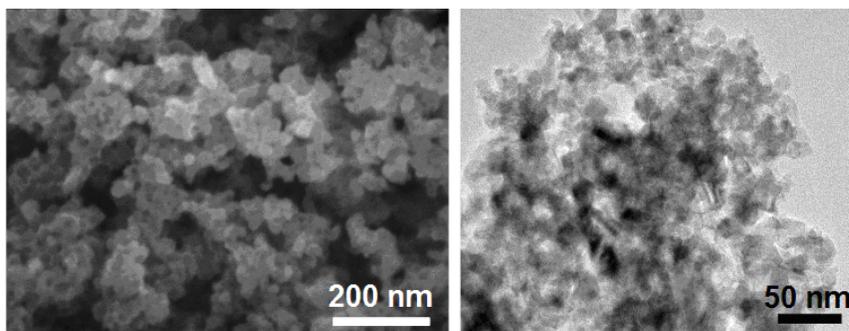


Figure 2. SEM (left) and TEM (right) images of the Si nanoparticles.

TASK 2.9 - PI, INSTITUTION: Kwai Chan and Michael Miller, Southwest Research Institute

TASK TITLE - PROJECT: Anodes – Synthesis and Characterization of Silicon Clathrates for Anode Applications in Lithium-ion Batteries

BASELINE SYSTEMS: Conoco Phillips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Low-energy density, low-power density, and short calendar and cycle lives

OBJECTIVES: The objectives are to synthesize and characterize silicon clathrate anodes designed to exhibit small volume expansion during lithiation, high specific energy density, while avoiding capacity fading and improving battery life and abuse tolerance.

GENERAL APPROACH: Our approach is to synthesize guest-free Type I silicon clathrate (Si₄₆, space group $Pm\bar{3}n$) using high-pressure and high-temperature experimental methods, including a newly-developed arc-melt technique. Concurrently, an investigational route for direct synthesis of guest-free clathrate is being explored, and *ab initio* and classical molecular dynamics (MD) computations will be performed to identify lithiation pathways. The silicon clathrates will be utilized to fabricate prototype silicon clathrate anodes. Electrochemical characterization will be performed to evaluate and improve, if necessary, anode performance including cyclic stability. The final year of the program will be directed at the design, assembly, and characterization of a complete (anode/cathode) small-scale, prototype battery suitable for concept demonstration.

STATUS OCT. 1, 2012: Possible reaction pathways for the formation of Si₄₆, Li_xSi₄₆, Li₁₅Si₄, and Li_xM_ySi_{46-y} have been identified using first-principles methods. Several hundred grams of Type I silicon clathrates and metal-silicon clathrate alloys have been fabricated by two different processing methods (arc-melting and direct solution-synthesis) and have been characterized for purity. Several half-cells of Si anodes have been constructed and characterized for electrochemical properties.

EXPECTED STATUS SEP. 30, 2013: Several half-cells of silicon clathrate anodes will have been fabricated using Year 2 materials, in combination with best-case additives and electrolyte formulations. The electrochemical properties of prototype anodes will have been characterized using a half-cell test apparatus. A suite of techniques will have been utilized to obtain a comprehensive understanding of the electrochemical behavior of such anodes under cyclic Li⁺ intercalation/de-intercalation conditions. An extensive post-mortem evaluation will be carried out to assess the structural and mechanical state of anode materials, and the experimental results will be compared against corresponding first-principles computations.

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) Construct and evaluate several electrochemical half cells using anode materials synthesized in Year 2, combined with best-case additives and electrolyte formulations. (Jan. 13) **Complete**
- (b) Characterize electrochemical properties of silicon clathrate anodes made from Year 2 materials. (Apr. 13) **On schedule**
- (c) Identify structural and mechanical states of silicon clathrate anodes during lithiation and delithiation processes and validate against theoretical calculations. (Jul. 13) **On schedule**
- (d) Achieve a reversible capacity of 400 mAh/g after 50 cycles at C/15 for either Si₄₆ or A₈M_ySi_{46-y} (A = Ba, Na; M = Al, Cu). (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

Task 1 – Synthesis of Type I Silicon Clathrates

Efforts to synthesize empty silicon clathrate *via* a low-temperature solution-based pathway continued this quarter by further refining the process steps leading to the formation of sodium silicide (NaSi) in high purity. Specifically, the formation of a reactive precursor of Zintl ions (Si_4^{4-}) essential for assembly of the clathrate structure in solution was the focus. Earlier attempts at converting a commercially-available fuel-grade form of sodium silicide ($\text{NaSi}_{1.5}$) to the Zintl phase were partially successful, leaving room for further improvement of phase purity. Presently, the conditions under which this phase transformation may occur were modified by judicious choice of excess NaH, elevated temperature, and soak time. XRD and Raman analyses are underway to determine the purity of the as-formed Zintl phase.

Task 2 – Molecular Modeling of Silicon Clathrates

The lithiation pathways for Na-stabilized Si_{46} have been completed and the results are compared against those of Ba-stabilized and empty Si_{46} clathrates. For all cases, insertion of Li causes expansion of the cage structure when the number of Li atoms inserted exceeds about 20 to 24, depending on the number of Na or Ba guest atoms residing within the cage structure but not on the number of Al substituted atoms on the framework.

Task 3 – Prototype Silicon Clathrate Anode Fabrication

Additional trials for experimenting with different additive and binder combinations in the fabrication of high performance silicon clathrate anodes were completed this quarter. Using the ball milling and particle sizing techniques previously optimized for the framework-substituted Type I clathrate alloy, $\text{Ba}_8\text{Al}_8\text{Si}_{38}$, the milled product was combined with the conductive additive Graphenol[®]: a colloidal solution consisting of edge-functionalized graphene particles suspended in toluene. The resulting slurry (0.2 to 4 wt% Graphenol[®] solids basis) was then used to cast thin-film anodes for electrochemical half-cell evaluation.

Task 4 – Half-Cell Electrochemical Characterization

Electrochemical studies aimed at evaluating the effects of conductive additives and additive concentration on anode performance were initiated this quarter. Electrochemical cycling measurements were made on the $\text{Ba}_8\text{Al}_8\text{Si}_{38}$ /Graphenol[®] anodes prepared in Task 3, and the performance was compared with previously-measured anode formulations containing amorphous carbon (Super P). At low concentrations of Graphenol[®] (0.2 wt%), less than half the theoretical capacity of the clathrate alloy (259 mA·h/g) was achieved during the first intercalation cycle at similar rates, as compared with the same micronized clathrate and 1 wt% (Super P) carbon additive (Fig. 1). These results indicate that the concentration of conductive additive plays as important of a role in clathrate anode performance as particle size. Additional electrochemical measurements are underway to examine the effects of Graphenol[®] over a range of concentrations and assess whether graphene-based additives provide any benefits in performance over more traditional carbon materials.

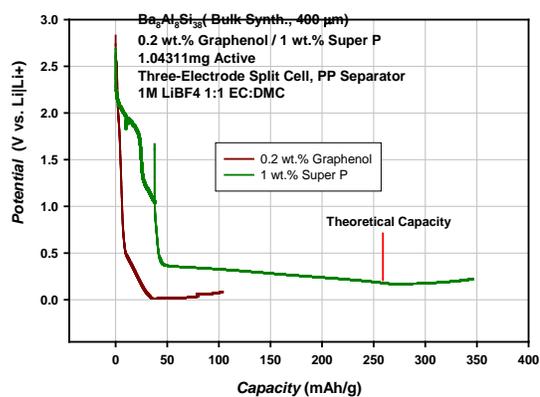


Figure 1. Comparison of the first intercalation cycle between Graphenol[®] (0.2 wt.%) and amorphous carbon (1 wt.% Super P)-containing clathrate anodes.

BATT TASK 3

ELECTROLYTES

TASK 3.1 - PI, INSTITUTION: John Kerr, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Electrolytes – Interfacial and Bulk Properties and Stability

BASELINE SYSTEMS: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

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

OBJECTIVES:

1. Determine the role of electrolyte structure upon bulk transport and intrinsic electrochemical kinetics and how it contributes to cell impedance (Energy/ power density).
2. Determine chemical and electrochemical stability of electrolyte materials to allow elucidation of the structure of and the design of passivating layers (*e.g.*, SEI).

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

STATUS, OCT. 1, 2012: Carbon nanotubes and other carbonaceous conducting elements have been further modified with a broader range of chemical groups (PEGs, imide and malonato-difluoroborate anions) and the effects on composite electrode performance determined. Combination of these modifications with variations of binder polymers were studied to determine how electrode ink formulation affects the electrode morphology and electrode performance, particularly for thick, high energy electrodes.

EXPECTED STATUS, SEP. 30, 2013: The demonstration of the advantages and drawbacks of single-ion conductor materials will be complete. The exploration of surface functionalization of conducting additives and the effect of interfacial impedance will be complete. Measurement of the composite electrode thickness increases made possible by use of single-ion conductor electrolytes will provide data to estimate the potential energy and power density increases. Initial estimates of calendar and cycle life will be complete. A completely solid state battery will be constructed with no solvent.

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) Complete construction and test of three different thicknesses of composite cathode electrode cells using gel electrolyte. (Apr. 13) **Delayed to Jun. 13**
- (b) Construct and test single-ion conductor solid-state cells with no free solvents and composite anodes and cathodes. (Sep. 12) **On schedule**

PROGRESS TOWARD MILESTONES

1) Surface Modification of Conducting Carbon Components in Composite Electrodes.

Preparation of the functional groups for fabrication of single-ion conductors and modified carbon components continued. These syntheses are proving to be a challenge. In the meantime it was discovered that the initial functionalization of the carbon imparts properties that are of considerable interest. The functionalized carbon nanotubes were found to assist in the nucleation of materials and lead to improved performance, particularly in poorly conducting materials such as LiFePO_4 , V_2O_5 , and TiO_2 . Recent results with the TiO_2 are shown.

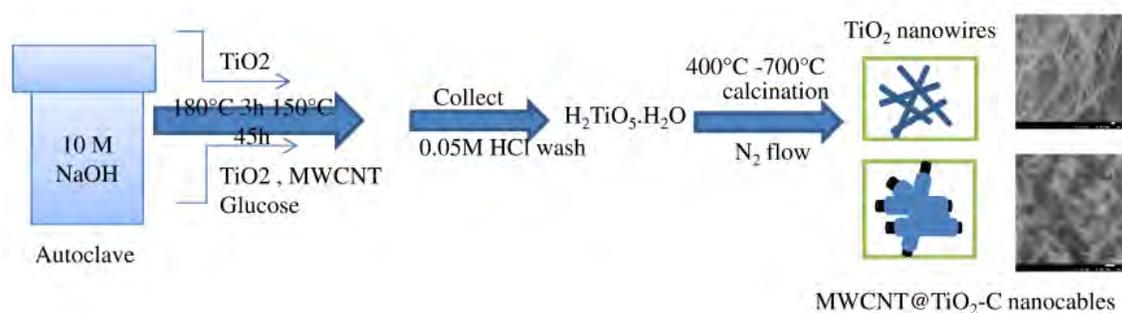


Figure 1. Synthesis of CNT@TiO_2 nanocables.

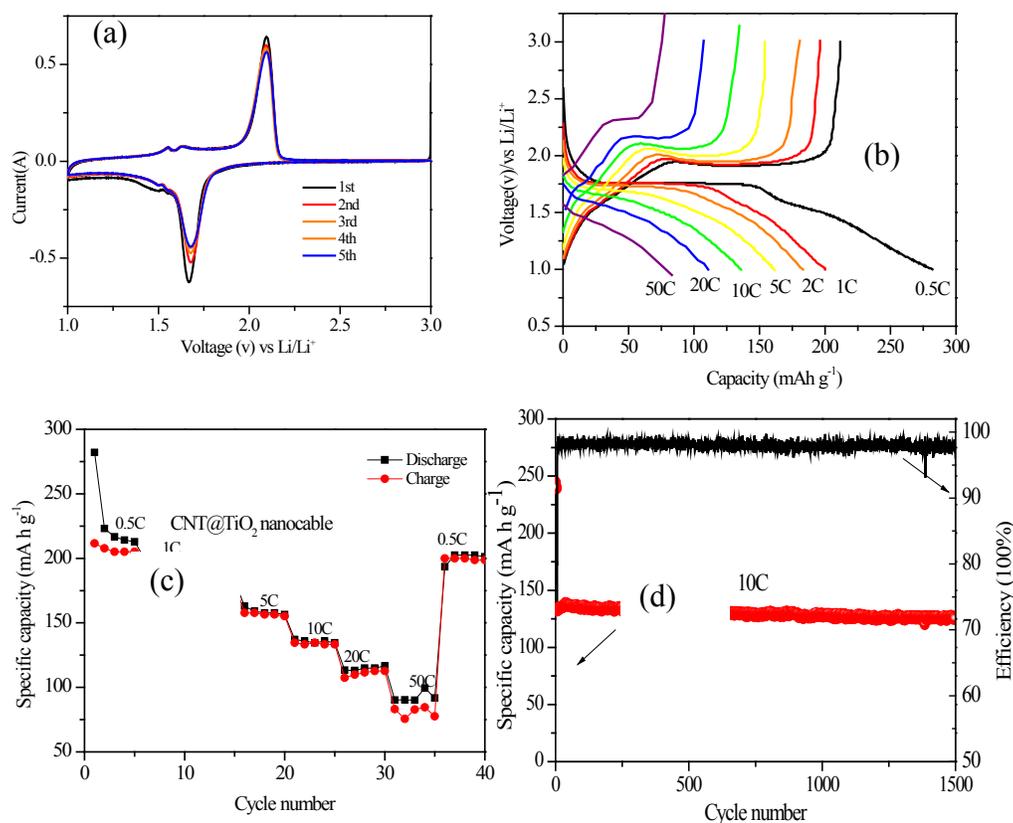


Figure 2. (a) Voltammograms of the $\text{CNT@TiO}_2\text{-C}$ nanocable electrode at a scan rate of 0.1 mV s^{-1} ; (b) The first charge-discharge voltage profiles at different current rates and (c) CNT@TiO_2 nanocable; (d) Cycling performance of the CNT@TiO_2 nanocable electrode at high current rate of 10 C.

TASK 3.2 - PI, INSTITUTION: Khalil Amine and Larry Curtiss, Argonne National Laboratory

TASK TITLE - PROJECT: Electrolytes — Advanced Electrolyte and Electrolyte Additives

BASELINE SYSTEMS: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Cycle/calendar life, abuse tolerance

OBJECTIVES: Develop advanced quantum chemical models to predict functional additives that form stable SEI on carbon anodes and cathodes and redox shuttles for overcharge protection. Synthesize suitable additives predicted by model, characterize, and perform extensive cycle and calendar life tests.

GENERAL APPROACH: Search for new electrolytic additives that react in a preferential manner to prevent detrimental decomposition of other cell components using experiment and theory. Use quantum chemical screening to predict oxidation and reduction potentials and decomposition pathways that form desirable coatings and prevent overcharge. Investigate SEI formation using a combination of computational and experimental techniques.

STATUS OCT. 1, 2012: Exploration of full decomposition pathways for selected additive candidates were carried out using advanced quantum chemical techniques. Experimental testing and characterization of the additives have been performed. Quantum chemical studies of the reaction energies for decomposition of shuttle candidates and experimental testing were carried out..

EXPECTED STATUS SEP. 30, 2013: Screening of redox shuttles based on tri- and quarterphenyls with various functional groups using advanced quantum chemical calculations of redox potentials, exploration of full decomposition pathways, and surface interactions. Experimental testing and characterization of the selected shuttles will be performed. Computational and experimental investigations of the SEI structure and properties from oxalate based additives.

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

MILESTONES:

- (a) Screening of redox potentials and oxidative stabilities of derivatived ter- and quaterphenyls R-C₆H₄(C₆H₄)_mC₆H₄-R (m=1,2), each with twelve different functional groups R, for use as redox shuttles for overcharge protection using advanced computational techniques. (Jan. 13) **Complete**
- (b) Synthesis of at least one ter- and quarterphenyl based shuttle from theoretical predictions. (Apr. 13) **On schedule**
- (c) Characterization of synthesized redox shuttles from experiment and computational studies of spectroscopic properties. (Jun. 13) **On schedule**
- (d) Demonstration of overcharge protection and cell balancing properties of selected redox candidates. (Sep 13) **On schedule**
- (e) Completion of modeling and characterization of polymeric SEI formed from an oxalate based additive on an anode surface. (Sep 13) **On schedule**

PROGRESS TOWARD MILESTONES

Our approach for the development of additives for SEI formation to prevent electrolysis of the electrolyte and increase battery cycle life involves screening of reduction and oxidation potentials through the use of accurate density functional methods followed by investigation of the mechanisms of decomposition through studies of reaction pathways. In addition, work continues on the development of redox shuttles for overcharge protection. The theoretical results are assessed by the performance of the additives in a Li-ion cell.

Density functional methods were used to examine the oxidation potential and decomposition reactions of a new, fused-ring shuttle, OFDDB. Ortho methoxy groups make the shuttle more polar. The calculated oxidation potential is 4.06 V vs. Li/Li⁺. Steric repulsion between methoxy groups causes a higher oxidation potential than DDB because one methoxy group is rotated out of the plane of the ring and cannot contribute electrons to the ring *via* resonance, whereas both methoxy groups are coplanar in DDB. The methoxy groups of both shuttles are coplanar with the ring in the cation radical.

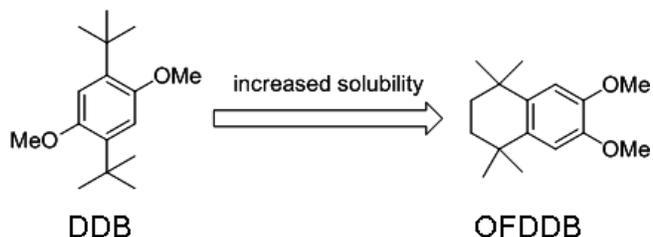


Figure 1. Illustration of the DDB redox shuttle and the new fused ring shuttle OFDDB.

Two decomposition pathways were also examined using density functional theory. In one case a methoxy group of the cation radical decomposes into formaldehyde and in the other case the fused ring decomposes into tetramethyl butadiene. While both decomposition pathways are thermodynamically favorable, OFDDB is likely to be stable with respect to decomposition because of high barriers to hydrogen transfer, which are required of these decompositions.

Experimentally, the redox potential of OFDDB is 4.06 V vs. Li/Li⁺ in agreement with theory. The negative voltage sweep does not show any significant peaks indicating good stability of the redox shuttle on the low voltage range. The fused ring structure and increased dipole moment significantly improve the solubility of the shuttle compounds to >0.4 M for OFDDB in EC/EMC solution (for DDB, solubility is less than 0.1 M). The sterically demanding fused alkyl ring structure also blocks undesired reaction at the ortho position (C-H bond) thus improving the stability of the shuttle molecule. The OFDDB can survive over 150 overcharge cycles (100% overcharge; more than 900 hours) as shown in Fig. 2 at a relatively high charge rate (C/2) for LiFePO₄-based cathode materials. The OFDDB can provide a promising new platform for a variety of new shuttles by simple molecular engineering. Replacement of the electron-rich methoxy groups with other electron-poor functional groups can tune the oxidation potential to create new shuttles for overcharge protection of high voltage cathode materials.

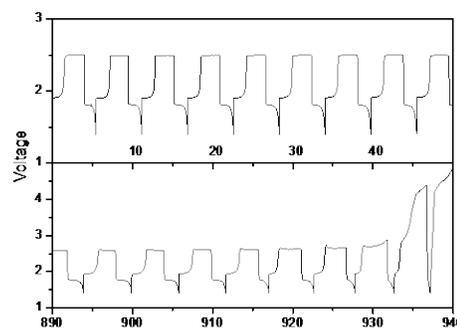


Figure 2. Voltage profile as a function of time (in hours) of a LiFePO₄/LTO cell at 100% overcharge (electrolyte contains 0.4 M OFDDB in the Gen2 electrolyte).

TASK 3.3 - PI, INSTITUTION: Brett Lucht, University of Rhode Island

TASK TITLE - PROJECT: Electrolytes — Development of Electrolytes for Lithium-ion Batteries

BASELINE SYSTEMS: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Cell performance, life, cost: Calendar life: 40°C, 15 yrs; Survival Temp Range: -46 to +66°C; Unassisted Operating & Charging Temperature Range, -30 to + 52°C.

OBJECTIVES: Develop novel electrolytes with superior performance to SOA (LiPF₆ in carbonates). Develop an understanding of the source of performance fade in graphite/LiNi_{0.5}Mn_{1.5}O₄ cells cycled to high voltage (4.8 V vs Li). Develop an electrolyte formulation that allows for superior performance of graphite/LiNi_{0.5}Mn_{1.5}O₄ cells. Synthesize and characterize novel non-fluorinated Li salts for Li battery electrolytes.

GENERAL APPROACH: Investigate the surface of cathodes and anodes cycled with novel electrolytes, with or without additives, to develop a mechanistic understanding of interface formation and degradation. Develop additives for high voltage (~4.8 V) cathode materials which inhibit performance fade *via* reduction of Mn dissolution or cathode surface passivation. Use novel synthetic methods to prepare non-fluorinated lithium salts for lithium ion battery electrolytes.

STATUS OCT. 1, 2012: LiPF₄(C₂O₄) electrolytes with optimized performance at low temperature after accelerated aging have been investigated. A better understanding of the role of electrolytes in the poor cycling efficiency and capacity fade of Li/LiNi_{0.5}Mn_{1.5}O₄ cells has been developed. Novel electrolyte formulations which optimize the performance of Li/LiNi_{0.5}Mn_{1.5}O₄ cells cycled to high voltage (4.8 V vs. Li) have been designed.

EXPECTED STATUS SEP. 30, 2013: A better understanding of the role of electrolyte in performance fade of graphite/LiNi_{0.5}Mn_{1.5}O₄ cells will have been developed. This understanding will be used to develop novel electrolyte formulations which improve the performance of graphite/LiNi_{0.5}Mn_{1.5}O₄ cells. One or more novel non-fluorinated salts will have been synthesized and the performance of the novel salt in electrolyte formulations in graphite/LiNi_xCo_{1-2x}Mn_xO₂ cells will be investigated.

RELEVANT USABC GOALS: Calendar life: 40°C, 15 yrs; Survival Temp Range: -46–52°C; Cold cranking power at -30°C; Cycle life; Peak Pulse Discharge Power, 10 sec.

MILESTONES:

- (a) Develop an understanding of the role of electrolyte in capacity fade for graphite/LiNi_{0.5}Mn_{1.5}O₄ full cells cycled at moderately elevated temperature (55°). (Mar. 13) **Complete**
- (b) Design electrolyte formulations to decrease cell inefficiency (50% of SOA) and decrease capacity fade (50% of SOA) for graphite/LiNi_{0.5}Mn_{1.5}O₄ full cells. (Jul. 13) **On schedule**
- (c) Synthesize and characterize novel non-fluorinated lithium salts and test novel electrolytes in graphite/LiNi_xCo_{1-2x}Mn_xO₂ cells. (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

With regards to milestone (a): The failure mechanism of graphite /LiNi_{0.5}Mn_{1.5}O₄ cells cycled at 25°C and 55°C have been analyzed by electrochemical methods and *ex situ* surface analysis of the electrodes. Graphite /LiNi_{0.5}Mn_{1.5}O₄ cells cycle well at 25°C, but show rapid capacity fade upon cycling at 55°C (Q1 Report). Independent electrochemical analysis of anodes and cathodes extracted from cells cycled at 55°C suggest that both electrodes have significant capacity loss, although the cathode capacity can be recovered with longer charging times. *Ex situ* surface analysis of the cathode with SEM reveals that the bulk cathode particles are retained. Analysis of the cathodes by XPS after cycling at 55°C reveal that the intensity of the Mn 2p peaks are decreased, consistent with Mn dissolution; but C 1s, O 1s, F 1s, and P 2p spectra are very similar (Fig. 1), consistent with small changes to the thin cathode surface film composed of the same electrolyte decomposition products including lithium alkyl carbonates, polyethylene carbonate, and lithium fluoride. Changes to the XPS spectra of the PVDF binder are also observed. The C1s peak at 290.4 eV is diminished and the F1s peak is shifted from 687.6 eV to a slightly lower binding energy (~687 eV), suggesting that the PVDF may be decomposing. Surface analysis of the anodes is consistent with the anode SEI becoming thicker after cycling at 55°C. Anodes, extracted from graphite/LiNi_{0.5}Mn_{1.5}O₄ cells cycled 55°C and analyzed by ICP-MS, contain 0.06 mg Mn, which is approximately 1% of the available Mn from the cathode, while fresh anodes and anodes cycled at 25°C contain two orders of magnitude lower concentrations of Mn. The deposited Mn may result in damage to the graphite SEI or anode laminate contributing to the capacity fade of the cell. The results suggest that both the anode and the cathode contribute to performance loss in graphite/LiNi_{0.5}Mn_{1.5}O₄ cells.

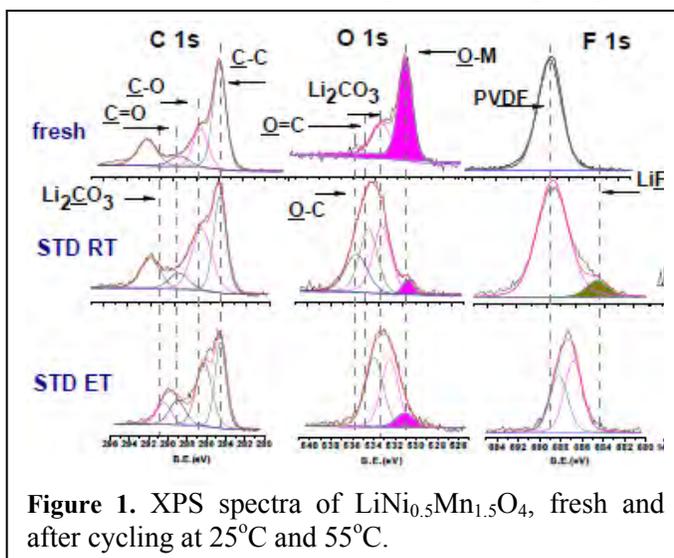


Figure 1. XPS spectra of LiNi_{0.5}Mn_{1.5}O₄, fresh and after cycling at 25°C and 55°C.

With regards to milestone (b): Novel additives were prepared which improve the performance of graphite/LiNi_{0.5}Mn_{1.5}O₄ cells cycled to 4.8 V (vs. Li) with LiPF₆ in EC/EMC at moderately elevated temperature (55°C). Additional details will be provided in our Q3 report.

With regards to milestone (c): Synthetic methods are being developed to prepare the novel salt.

Collaborations: D. Abraham (ANL), M. Smart (NASA-JPL), V. Battaglia, G. Chen, and J. Kerr (LBNL), A. Garsuch, M. Payne (BASF), and the High-Voltage Spinel Focus Group.

Publications and Presentation: “Performance of lithium tetrafluoroxyphosphate in methyl butyrate electrolytes,” *J. Appl. Electrochem.* 43, 497-505, 2013.

“Failure Mechanism of Graphite/LiNi_{0.5}Mn_{1.5}O₄ Cells at High Voltage and Elevated Temperature,” *J. Electrochem. Soc.* 160, A3138-A3143, 2013.

“Role of electrolyte in interface formation and cycling performance in Lithium ion batteries” *IBA meeting*, Barcelona, Spain, March 2013.

TASK 3.4 - PI, INSTITUTION: Daniel Scherson and John Protasiewicz, Case Western Reserve University

TASK TITLE - PROJECT: Electrolytes — Bifunctional Electrolytes for Lithium-ion Batteries

BASELINE SYSTEMS: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Abuse tolerance

OBJECTIVES: Design, synthesize, and characterize physical, electrochemical, and interfacial characteristics of functionalized Li-salt anions containing phosphorus moieties known to impart materials with flame retardant properties (Flame Retardant Ions or FRIONs) and additional functional redox active groups capable of providing overcharge protection. Develop and implement ATR-FTIR spectroscopic methods for monitoring *in situ* products generated at Li-ion battery anodes.

GENERAL APPROACH: Develop methods for the chemical functionalization of anions known to improve the performance of Li-ion batteries with covalently linked groups displaying flame retardant and/or overcharge protection attributes. Establish guidelines for the rational design and synthesis of optimized FRIONs and FROPs based on the analysis of results of testing in actual Li-ion batteries. Develop new *in situ* tactics for the application of attenuated total reflection Fourier transform infrared ATR-FTIR for the characterization of solution products generated at Li-ion battery anodes and solid electrolyte interfaces formed therein.

STATUS OCT. 1, 2012: Complete synthesis and purification of four cyclic triol borate (CTB) salts and determination of their flammability. Development of methods for the preparation of 100g of CTB-type compound for testing in actual batteries finished. Develop methods for depositing a thin layer of metal onto the diamond window for ATR measurements and thus avoid problems with electrolyte contributions due to migration effects of IRAS.

EXPECTED STATUS SEP. 30, 2013: Complete synthesis and characterization of new FRION materials based on diphosphonato-catecholate ligand (DPC) including flammability and electrochemical testing. Scale up synthesis of Li[B(DPC)₂] and Li[B(DPC)(oxalato)] salts for testing in cells. Establish structure-electrochemical performance relationships and comparisons with previously studied anion families. Systematic *in situ* ATR-FTIR spectroscopic and impedance studies involving selected solvent formulations incorporating Case FRIONs both as main salts and additives.

RELEVANT USABC GOALS: No fire or rapid disassembly of cells during abuse conditions.

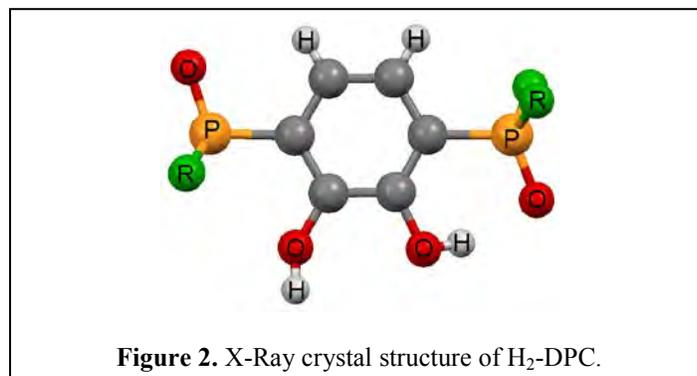
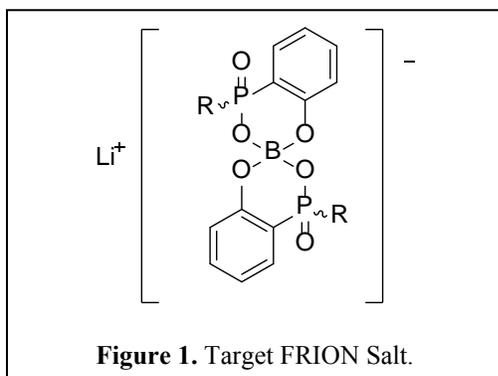
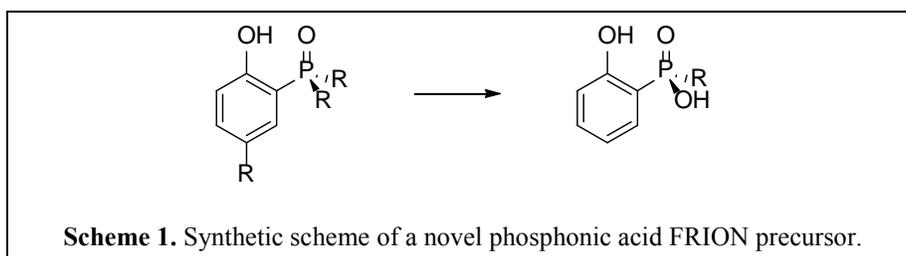
MILESTONES:

- (a) Prepare and fully characterize the electrochemical and flammability properties characteristics of Li[B(DPC)₂] and Li[B(DPC)(oxalato)] salts. (Oct. 12) **Complete**
- (b) Expand the Li[B(DPC)₂] and Li[B(DPC)(oxalato)] salts-type libraries of compounds (Mar. 12) **Delayed to Sep. 13**
- (c) Synthesize and characterize a Li[P(DPC)₃] FRION. (Sep. 13) **On schedule**
- (d) Complete characterization of the effect of Case additives by cyclic voltammetry and impedance measurements with the most promising materials as determined from milestone (e) below. (Sep 13) **On schedule**
- (e) Perform full testing of all Case salts as full fledge electrolytes and/or as additives in actual batteries at Novolyte (Oct 12), and LBNL and ANL. (Sep 13) **On schedule**
- (f) Improve cycling by at least 15% to reach the same decay/end of life vs. the control electrolyte.(Sep 13) **On schedule**
- (g) Construct and optimize cell for *in situ* ATR measurement with metal-coated diamond window. (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

Synthesis and characterization of FRIONS – Work in this quarter focused on the synthesis of new phosphonic acid based FRIONS (Fig. 1). A novel phosphonic acid FRION precursor has been prepared (Scheme 1) in high yield and in gram scale quantities. This FRION was designed to be lower in molecular weight and less symmetric than previous FRIONS, which generally leads to an increase in solubility. Synthesis of FRION salts containing this precursor were initiated, accompanied by spectroscopic evidence verifying these salts were made. Gram scale synthesis and full characterization is underway. Preliminary tests indicate this phosphonic acid FRION salt is more soluble than previous salts in organic solvents.

The precursor catechol phosphonate H₂-DPC from previous quarterly reports was structurally characterized using single-crystal XRD; the results are seen in Fig. 2. This confirms the precursor's predicted structure and, interestingly, the molecule processes both inter and intra-molecular hydrogen bonding.



TASK 3.5 - PI, INSTITUTION: Austen Angell, Arizona State University

TASK TITLE - PROJECT: Electrolytes – Sulfone Liquids and Sulfate/Triflate Solids for High Voltage Electrolytes

SYSTEMS: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Electrolyte needs increased oxidation resistance with decreased ionic resistance, and improved safety. Safety will follow increased ionic liquid or superionic solid content.

OBJECTIVES: To devise new electrolyte types (sulfone mixtures and superionic glasses or plastic solid derivatives) that will permit cell operation at high voltages without solvent oxidation and with adequate overcharge protection, and to provide optimized nanoporous supporting membranes for this electrolyte.

GENERAL APPROACH: The approach has been twofold: (i) A suite of electrolyte studies, beginning with cell-performance testing of additive protected sulfone electrolytes, extending to the design of novel Li⁺-conducting media is planned. The latter will retain the high oxidation resistance known for noncyclic sulfones, and conductivity of EC-DMC solutions, but will have Li⁺ transport number unity. Novel Li⁺-conducting silicon based solid-state conductors and rubbery polymers will be tested for compatibility with the chosen Li (Ni,Mn) spinel cathode. Finally, some novel ionic liquid electrolytes will be tested; and (ii) the further development of the “Maxwell slats” approach to synthesis of nanoporous supports. A hot water-soluble reversibly-self-assembling net has now been abandoned in favor of a successful stronger-bonded model that successfully self-assembles in hot ionic liquid and hydrogen bonding solvents.

STATUS OCT. 1, 2012: Half-cell and full-cell tests with the Li(NiMn) high voltage cathode using our newly developed graphite-compatible all-sulfone, and part sulfone electrolyte solvents, now completed, will begin examination. Progress towards understanding the nature of new Li conducting complex anion solid and liquid-state conductors will have been made. A range of different rigid and non-rigid struts for nano-porous nets (now called amorphous MOFs) will have been explored. Non-calorimetric strategies for determining softening temperatures will have been decided (by collaboration if preferable.)

EXPECTED STATUS SEP. 30, 2013. A go-no-go point will have been passed on sulfone-solvent-based high voltage cell development. An alternative solvent system of even higher voltage window and comparable conductivity, based on “ionic liquid” solvents, will have been tested for performance with the Li(Ni,Mn)O₄ cathode, and variants of the superionic glass and metastable crystal variety will have been examined. The best cases of the latter will have been tested with the Li(Ni,Mn)O₄ cathode and the expected absence of side reactions verified. The nanoporosity of aqueous self-assembling models of the Maxwell slat concept will have been assessed, and study of more practical (stronger-bonding) variants will have been commenced.

RELEVANT USABC GOALS: 1000 cycles (80% DoD); 10 year life. An electrolyte with electrochemical window 5.2 volts and conductivity 20 mS/cm.

MILESTONES:

- (a) Decide go-no-go on cathode half cells with sulfone electrolytes with HFiP additive. (Feb. 13)
Delayed to May 13
- (b) Produce new plastic Li-conducting phases of $\sigma(25^\circ\text{C}) > 10$ mS/cm. (Jun. 13) **On schedule**
- (c) Achievement of glassy or viscous liquid single-ion Li-conducting versions of (b). (Jun. 13)
On schedule
- (d) Production of new mixed 3 and 4-bonding covalent nanoporous nets (amorphous MOFs.) (Jun. 13) **On schedule**
- (e) Go-no-go development of mechanically robust nanoporous covalent networks for novel solution and plastic alkali-ion conductors. (Aug. 13) **On schedule**

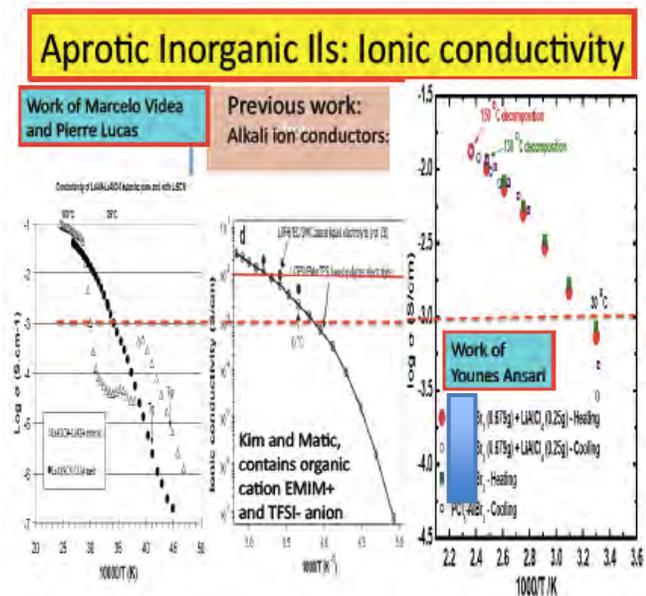
PROGRESS TOWARD MILESTONES

(a) **Go-no-go on cathode half cells with sulfone electrolytes with HFIP additive, Feb. 2013.** In previous Quarterlies it was reported that, although the sulfone solvents to be pursued were very satisfactory at graphite electrodes, their performance at the LMNO was unsatisfactory for reasons assumed to be due to their poor SEI formation. Studies using coin cells on a recently purchased battery tester had given reason for more optimism, but finally confirmed their weakness (originating in the low viscosity FMS component.) Further testing using some recommended additives LiBOB and HFIP are in progress, postponing the go/no-go to May 31.

(b) **Production of new plastic Li-conducting phases of $\sigma(25^\circ\text{C}) > 10 \text{ mS/cm}$, June 2013.**

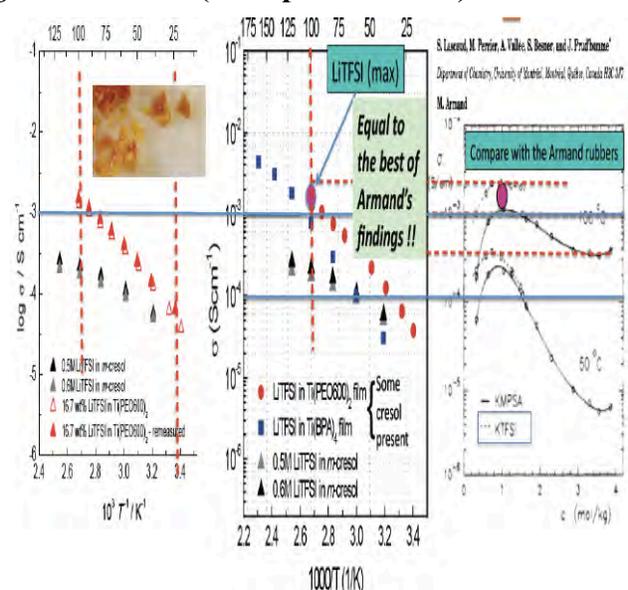
Refinements of the synthetic techniques have been made but their testing was put on hold while some new ideas on project (c) were tried out in preparation for an ionic liquids conference at which we launched the concept of "inorganic ambient temperature ionic liquids" (see Fig. 1).

(c) **Achievement of glassy or viscous liquid single-ion Li-conducting versions of (b), June 2013.** Highly promising cells using $\text{LiTFSI-EMIM}^+[\text{TFSI}]$ binary mixtures in gel form, have been reported by Kim *et al.* (*ElChem-Comm*, 2011, **13**, 1105). The group sought to emulate their success using only inorganic formulations. Some preliminary results for an inorganic equivalent of the EMIM-based ionic liquid and its solution containing LiAlCl_4 , are shown in Fig. 1, with comparison to the Kim work and to earlier chloroaluminate studies. The performance is promising proof of concept, but the conductivity is only superior at low temperatures; improvements are thought to be possible.



(d) **Production of new mixed 3 and 4-bonding covalent nets (amorphous MOFs)**

An interesting preparation reported earlier without full characterization of composition was repeated with essentially identical results. The corner linked PEO600 net is an orange rubbery material (see insert in Fig. 2) Conductivities during upscans and downscans are compared with earlier findings and the best polymer electrolyte conductivities reported in the literature (Armand *et al.*). Combination of rubbery properties with "chemical stretching" (first quarterly) is now being attempted.



(e) **Go-no-go development of mechanically robust nanoporous covalent networks for novel solution and plastic alkali-ion conductors, Aug. 2013.** On schedule see (d).

BATT TASK 4

CATHODES

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

TASK TITLE: Cathodes – Novel Cathode Materials and Processing Methods

SYSTEMS: Conoco Philips CPG-8 Graphite/1M LiPF₆+EC:DEC(1:2)/Toda NMC
Conoco Philips CPG-8 Graphite/High voltage electrolyte/Li-Ni-Mn-O spinel

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.

APPROACH: Li₂MnO₃-stabilized composite electrode structures, such as ‘layered-layered’ xLi₂MnO₃•(1-x)LiMO₂ (M=Mn, Ni, Co), ‘layered-spinel’ xLi₂MnO₃•(1-x)LiM₂O₄ and more complex ‘layered-layered-spinel’ y{xLi₂MnO₃•(1-x)LiMO₂}•(1-y)LiM₂O₄ systems are receiving international attention because they can provide rechargeable capacities between 200 and 250 mAh/g between 4.6 and 2.0 V vs. Li. These electrodes suffer from voltage decay and surface instability on cycling, thereby compromising the energy and power of the Li-ion cells and preventing their implementation in practical systems. A novel, simple, and versatile processing technique, using Li₂MnO₃ as a precursor, to synthesize composite electrode structures is advocated; it offers the possibility of tailoring composite electrode structures and enhancing their electrochemical properties to meet Li-ion battery performance targets for PHEVs and EVs.

STATUS OCT. 1, 2012: Significant progress in exploiting a new synthesis approach using Li₂MnO₃ as a precursor to fabricate high-capacity (200-250 mAh/g), structurally-integrated lithium-metal-oxide composite electrode materials, such as ‘layered-layered’, ‘layered-spinel’, ‘layered-rocksalt’ systems and more complex types, was made in FY 2012. The project focused predominantly on evaluating detailed structural, electrochemical, and surface properties of ‘layered-layered’ electrodes; the structural information was obtained from experiments conducted at Argonne’s Advanced Photon Source.

EXPECTED STATUS SEP. 30, 2013: Progress will be made in enhancing the electrochemical and structural stability of ‘layered-layered’ xLi₂M’O₃•(1-x)LiMO₂ electrodes at high potentials, with improvements in rate capability and cycle life.

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) Identify at least three promising, high-capacity (200-250 mAh/g) xLi₂M’O₃•(1-x)LiMO₂ compositions with a high Mn content using Li₂MnO₃ or LiMn_{0.5}Ni_{0.5}O₂ as a precursor, determine their structures, and evaluate their electrochemical properties. (Sep. 13) **On schedule**
- (b) Improve the surface stability of the electrode materials at high charging potentials by coating methodologies. (Sep. 13) **On schedule**
- (c) Model surface structures and interfacial phenomena of coated electrodes. (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

Collaborators: Jason Croy, Brandon Long, Mahalingam Balasubramanian, Kevin Gallagher

Milestone (a) addressed: Evaluate the electrochemical properties of $x\text{Li}_2\text{M}'\text{O}_3 \bullet (1-x)\text{LiMO}_2$ ('layered-layered') electrode structures with a high Mn content.

$x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{LiMO}_2$ ($M = \text{Mn, Ni, Co}$) composite electrodes are of interest because of the high capacity and stability that can be achieved with respect to various compositions and cycling conditions. Both of these desirable traits can be directly linked to the Li_2MnO_3 component and the initial concentration of Li present in the transition metal (TM) layers. Likewise, and also directly correlated to the Li_2MnO_3 component, is the voltage fade phenomenon. Recently, a systematic study of $x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ was initiated to better understand the role of Li_2MnO_3 in the degradation mechanisms of composite electrodes. Figure 1a shows the difference in cell voltage at 50% state of charge, between charge and discharge (2.0 to 4.7 V), of $\text{Li}/x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ cells as a function of x (*i.e.*, the hysteresis) measured on the second cycle after activation to 4.7 V. The data clearly show that hysteresis in this class of materials is directly correlated to the choice of x . Interestingly, it has been shown that hysteresis and voltage fade in composite electrodes are also directly correlated¹.

Figures 1b and 1c show Mn K and Ni K EXAFS data as a function of x in $x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ electrodes. Most notable from the Mn data (Fig. 1b) is the decrease in amplitude of the first-shell, Mn-Metal coordination at *ca.* 2.5 Å and the change in the peak at *ca.* 5.2 Å. Together, these observations reveal that excess Li and Mn, introduced with increasing x , readily order (*e.g.*, as LiMn_6) and that increasing Ni (decreasing x) alters the scattering associated with hexagonal TM units in the TM planes, likely *via* formation of NiMn_6 units (Fig. 1b inset). From the Ni K data (Fig. 1c), it is seen that the Ni environment becomes more layered with increasing x . Specifically, the Ni-O-Ni correlations at *ca.* 3.8 Å decrease with increasing x , revealing a decrease in Li/Ni exchange between the layers. These data have important implications for stabilizing MnNi-oxide cathodes, revealing the importance of TM ordering and the stabilizing effect of Ni-Mn interactions when correlated with previous cycling studies.

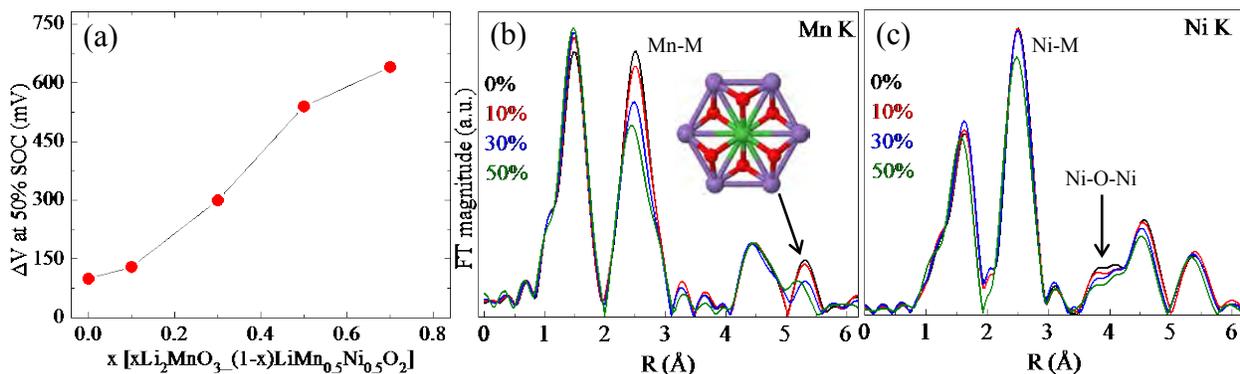


Figure 1. (a) Second-cycle hysteresis at 50% SOC in $x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ electrodes. (b) Mn and (c) Ni K EXAFS data of $x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ electrodes. The Li_2MnO_3 content is given as percent. Inset in (b) shows a NiMn_6 unit (red = O, green = Ni, purple = Mn).

Reference

1. K. Gallagher, J. Croy, M. Balasubramanian, M. Bettge, D. Abraham, A. Burrell, and M. Thackeray, *Electrochem. Comm.* Accepted (2013).

TASK 4.2 - PI, INSTITUTION: Marca Doeff, Lawrence Berkeley National Laboratory

TASK TITLE: Cathodes – Design of High Performance, High Energy Cathode Materials

SYSTEMS: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Cost, power and energy density, cycle life

OBJECTIVES: To develop high energy, high performance cathode materials including composites and coated powders, using spray pyrolysis and related synthesis techniques.

GENERAL APPROACH: High-energy cathode materials such as modified NMCs and LiNi_{0.5}Mn_{1.5}O₄ (LNMS) are synthesized *via* spray pyrolysis and related techniques, as well as composites containing these materials, and coated particles. For comparison, materials are also made by conventional techniques such as solid-state synthesis and the mixed hydroxide method. An array of physical and electrochemical techniques is used to characterize their behavior, in conjunction with members of the diagnostics team. Emphasis is placed on increasing energy density without sacrificing stability, safety, or cycle life.

STATUS OCT. 1, 2012: Phase-pure samples of LiNi_{0.5}Mn_{1.5}O₄ spinel (LNMS) have been produced by spray pyrolysis, and work on composite materials has begun. The survey of Li[Ni, Co, Ti, Mn]O₂ compounds was completed, allowing selection of the most promising compositions for further work to be carried out.

EXPECTED STATUS SEP. 30, 2013: Synthetic parameters for producing hollow LNMS particles (useful for making composites) and solid particles (for coated materials) will have been worked out. Work on NMCs will be directed towards understanding the mechanism of improvement in capacities and cycling behavior observed in some compounds when Ti is partially substituted for Co.

RELEVANT USABC GOALS: High energy, thermal stability, cycle life, cost (EV, PHEV).

MILESTONES:

- (a) Synthesize and electrochemically characterize composites consisting of spray-pyrolyzed LNMS hollow particles containing and coated with LiFePO₄ or a manganese oxide spinel. (Sep. 13) **On schedule**
- (b) Produce and electrochemically characterize thin-film electrodes of a high-energy Ti-substituted NMC suitable for synchrotron studies. (Sep. 13) **On schedule**. Milestone will be modified because thin films may not be needed for techniques currently being considered.

PROGRESS TOWARD MILESTONES

(1) A paper describing the results of a study on LNMS samples prepared by combustion synthesis is in preparation.

(2) Synthesis parameters for high capacity Ti-NMCs are currently under investigation for purposes of optimizing performance. Recently it was found that $\text{TiO}(\text{SO}_4)$ gave better control of the product stoichiometry than the unstable $\text{TiO}(\text{NO}_3)_2$ precursor used previously; however, sulfur is detected in the final products by EDS analysis when calcined for three hours at 900°C . Longer calcinations reduce the amount of sulfur and result in somewhat higher capacities and better cycling. The effect of Li source on the physical and electrochemical properties is also being investigated. NMCs made using LiOH have lower surface areas and larger primary particle sizes than those made with Li_2CO_3 . Ti-substituted NMCs also have somewhat higher surface areas than the unsubstituted variants. In spite of this, these materials appear to cycle better between 4.7 and 2.0V than the baseline materials.

Soft XAS experiments were performed on selected powders and electrodes harvested from cycled cells (collaboration with Dennis Nordlund and Tsu-Chien Weng at SSRL). A comparison of the Ti L-edges for two NMC442-2% Ti samples to an anatase reference shows unequivocally that Ti is incorporated into the NMC structure and not present as a separate phase. Ni L-edge experiments were also carried out on fresh, partially, and fully charged and discharged electrodes *ex situ*. Some of these results are shown in Fig. 1. The peak at about 855 eV corresponds to the Ni^{3+} oxidation state and the Auger electron yield (AEY), total electron yield (TEY), and fluorescence yield (FY) probe different sample depths from 1 to 2 nm (AEY) and 3 to 5 nm (TEY) to 50 nm (FY). The variation in the 855 eV peak intensities for both the half-charged electrode (top) and the electrode that was fully charged and then halfway discharged (bottom) indicates that there is a gradient in the Ni oxidation state. This suggests that a Ni^{2+} -containing species is concentrated at the surface, such as a rock salt $\text{Li}_x\text{Ni}_{1-x}\text{O}$ phase or an overlithiated NMC phase. More experiments are planned on the baseline material for comparison.

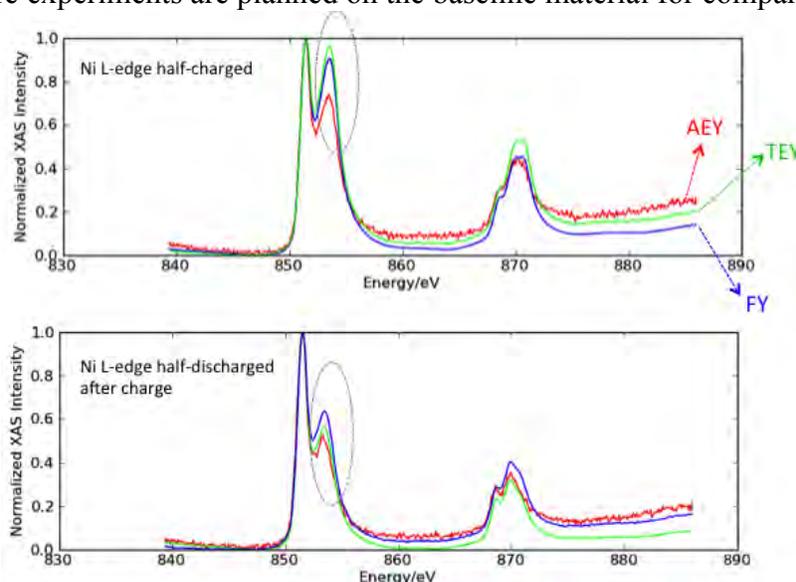


Figure 1. Ni L-edge soft XAS experiment on a halfway charged electrode (top) and a halfway discharged electrode (bottom).

TASK 4.3 - PI, INSTITUTION: Arumugam Manthiram, University of Texas at Austin

TASK TITLE - PROJECT: Cathodes – High-capacity, High-voltage Cathode Materials for Lithium-ion Batteries

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

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

OBJECTIVES: To develop (i) low-cost cathodes based on polyanions that can offer a combination of high energy and power with excellent thermal stability and safety, and (ii) low-cost, high-voltage spinel cathodes that can offer high power and energy along with long cycle life.

GENERAL APPROACH: Our focus is on the design and development of cathode materials based on polyanions that have the possibility for reversibly inserting/extracting more than one Li⁺ ion per transition metal ion, Mⁿ⁺, and/or operating above 4.3 V. Some example systems to be pursued are Li₂MSiO₄ and Li₂MP₂O₇ (M = Mn, Fe, Co, and Ni) and their solid solutions. However, there are technical challenges in achieving the theoretical energy densities of many of these cathode materials. Synthesis and processing conditions play a critical role in realizing the full capacities of these polyanion cathodes with more than one Li⁺ ion per Mⁿ⁺ ion. Novel solution-based synthesis approaches, such as microwave-assisted solvothermal methods that can offer controlled nanomorphologies, are pursued to maximize the electrochemical performance. The synthesized nanostructured polyanion cathodes are characterized by a variety of techniques including *ex situ* and *in situ* X-ray diffraction, electron microscopy (SEM, TEM, and STEM), X-ray photoelectron spectroscopy, time of flight–secondary ion mass spectroscopy, and in-depth electrochemical measurements. In addition, the role of cation doping, segregation of certain doped cations to the surface, cation ordering, morphology, and surface planes on the electrochemical properties of high-voltage spinel cathodes are investigated. Based on the characterization data gathered, a fundamental understanding of structure-composition-property-performance relationships is developed.

STATUS OCT. 1, 2012: Developed (i) novel synthesis approaches to obtain high-capacity, high-voltage polyanion (silicate and phosphate) cathodes with unique nanomorphologies, (ii) an understanding of the factors that control the performance of high-voltage (4.7 V) spinel oxide cathodes, and (iii) an understanding of their structure-composition-property-performance relationships.

EXPECTED STATUS SEP. 30, 2013: (i) Synthesis by novel solution-based synthesis approaches and characterization of Li₂MP₂O₇ (M = Fe, Mn, Co, and Ni) and their solid solutions, as well as Li₂MSiO₄ (M = Mn, Fe, Co, and Ni) and their solid solutions, and (ii) an understanding of the influence of morphology and crystal planes on the performance of high-voltage spinel cathodes.

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

MILESTONES:

- (a) Understand the influence of morphology and crystal planes on the electrochemical performance of high-voltage spinels. (Dec. 12) **Complete**
- (b) Synthesize and characterize Li₂MP₂O₇ (M = Fe, Mn, Co, and Ni) as well as their solid solutions. (Jun. 13) **On schedule**
- (c) Assess surface segregation in Li₂M_{1-x}Fe_xSiO₄ and Li₂M_{1-x}Fe_xP₂O₇ (M = Co, Mn, and Ni.) (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

Previous work on LiVOPO_4 has demonstrated the importance of having a smaller particle size in order to obtain good electrochemical performance, even at very slow rates. Our work on LiFePO_4 has shown that microwave-assisted solvothermal (MW-ST) processes can control the particle size and give unique morphologies. Accordingly, three polymorphs of LiVOPO_4 (α -triclinic; β -orthorhombic; α_1 -tetragonal) were synthesized by the MW-ST process, although both phase purity and the expected stoichiometry was only achieved for the α phase. The α phase was therefore selected for further optimization.

In order to reduce the particle size, the α phase was synthesized in various solvent mixtures of water and alcohols/glycols (Fig. 1). The ratio of water to alcohols/glycols (3:1) was crucial to eliminate impurities at a synthesis temperature of 230°C . A phase-pure sample was obtained with 100% water as the solvent, but the temperature had to be elevated to 240°C . The various solvent mixtures formed a micro-flower morphology as seen in Fig. 1, with the smallest particle size achieved with a mixture of water and glycols.

Figure 2 shows the electrochemical performance of each of the samples formed with the various solvent mixtures. Particles of various sizes achieved with various water/glycol mixtures show different capacities on the upper plateau (potential window of 3.0 to 4.5 V, dashed line in Fig. 2), where the highest capacities were achieved with the smallest particle sizes. This was also found to be of importance. For example, the water/glycol and butanol/water samples have similar particle sizes, but the former exhibits better performance in the 3.0 to 4.5 V range. Likewise, the pure water and alcohol/water samples have similar particle sizes, but the latter exhibits a higher capacity.

The typical voltage range to cycle LiVOPO_4 is between 3.0 and 4.5 V. Figure 2 also shows that by cycling down to 2.0 V instead of 3.0 V, more than one Li can be inserted/extracted by accessing the $\text{V}^{3+/4+}$ redox couple between 2.0 and 2.5 V. By increasing the voltage window, a discharge capacity of *ca.* 200 mAh g^{-1} was achieved.

Current work is on optimizing the synthesis conditions for the β and α_1 phases and assessing their electrochemical performance.

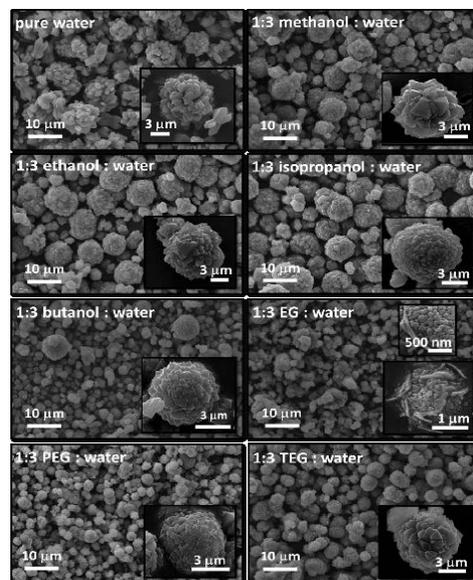


Figure 3. SEM of α - LiVOPO_4 prepared in various mixed solvents at 230°C except that in water, which was held at 240°C .

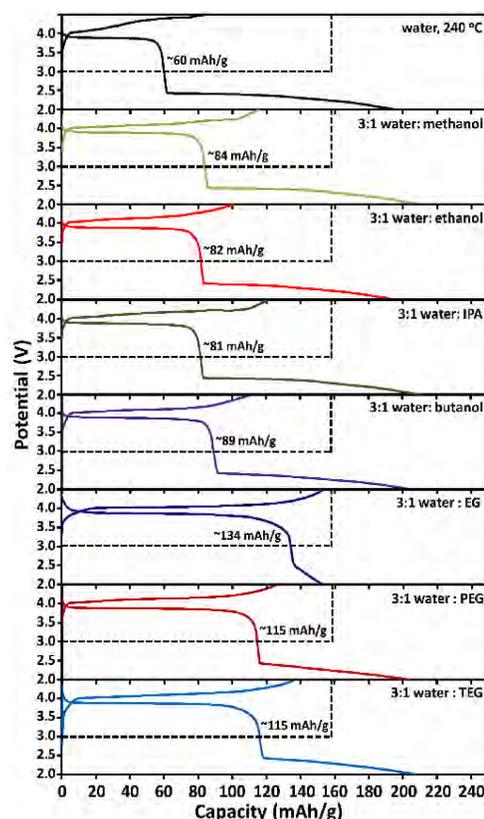


Figure 4. First charge-discharge profiles at a C/20 rate of α - LiVOPO_4 prepared in various mixed solvents at 230°C , except in water, which was held at 240°C .

TASK 4.4 – PI, INSTITUTION: Ji-Guang (Jason) Zhang and Jie Xiao, Pacific Northwest National Laboratory

TASK TITLE: Cathodes – Development of High Energy Cathode Materials

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Low energy density, high cost, limited cycle life

OBJECTIVES: To develop high-energy, low-cost, and long-life cathode materials.

GENERAL APPROACH: To develop high energy-density cathode materials through cost-effective methods. Appropriate doping, surface treatment, and appropriate electrolytes/additives will be used to improve the electrochemical performances of both high-voltage spinel LiNi_{0.5}Mn_{1.5}O₄ and Mn-based Li-rich layered composite. The fundamental reaction mechanisms of cathode materials during electrochemical processes will be systematically investigated to understand/address the challenges in these cathode materials.

STATUS OCT. 1, 2012: High-voltage LiNi_{0.5}Mn_{1.5}O₄ was synthesized by a facile approach, while the content of disordered phase in the spinel was precisely controlled through reheating, element substitution, or different cooling rates. Several other “inactive” components in the electrode, including cell cans, separators, and carbon additives, were also systematically re-examined for their stability in a high-voltage system. Using the optimized electrolyte and stable components, the high-voltage spinel cathode has achieved more than 500 cycles with less than 20% capacity fade (half cells.) Synthesis of the Li₂MnO₃ baseline has been completed. Surface treatment, doping, and electrolyte additives will be applied in the layered composite system coupled with advanced characterizations to understand/mitigate the degradation issues.

EXPECTED STATUS SEP. 30, 2013: High-energy cathodes for Li-ion battery applications will be further explored. Synthesis of xLi₂MnO₃•(1-x)LiMO₂ (M = Mn, Ni, Co; 0 ≤ x ≤ 1) will be optimized and their degradation mechanism will be investigated. Manganese dissolution issue in both layered composite and spinel will be studied and mitigated to improve the cell performance. Appropriate electrolyte additives will be identified in the layered composite system to improve the cycling stability. Safety, power rate, and cycling stability of these cathode materials will be improved to satisfy the need for HEV/EV applications.

RELEVANT USABC GOALS: >96 Wh/kg (for PHEVs), 5000 deep-discharge cycles, 15-year calendar life, improved abuse tolerance, and less than 20% capacity fade over a 10-year period.

MILESTONES:

- (a) Identify the key factors related to the oxygen release in layered composite xLi₂MnO₃•(1-x)LiMO₂ (M = Mn, Ni, Co; 0 ≤ x ≤ 1). (May 13) **On schedule**
- (b) Demonstrate the effects of different treatments (doping, coating, and electrolyte additive) on cathode and improve their cyclability by more than 20% as compared with untreated samples. (Sep. 13) **On schedule**
- (c) Identify electrolyte additives that can improve the cycling stability of layered composite to more than 200 mAh/g in 100 cycles at C/3 rate. (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

In order to identify key factors related with the layered-to-spinel transition for Li-Mn-rich cathode, aberration-corrected Scanning Transmission Electron Microscopy (S/TEM) combined with Electron Energy Loss Spectroscopy (EELS) were used to probe the structure evolutions of layered $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.2}\text{M}_{0.6}]\text{O}_2$ composite cathode during long-term cycling. The major findings are listed below:

- 1) Corrosion and fragmentation of cathode particles were identified on the cycled layered composite.
- 2) Mn^{2+} species and reduced Li content in the fragmented pieces were revealed by EELS, which correlated with capacity degradation.

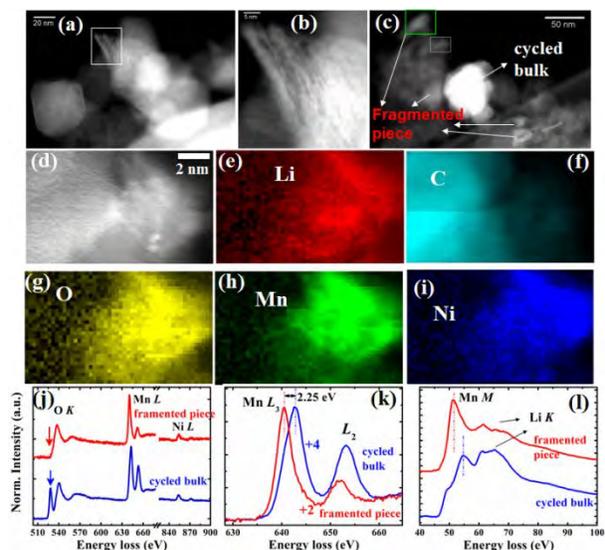


Figure 1. (a) Overview image showing the cathode nanoparticles after cycling; (b) magnified image of the region labeled by the white rectangle shown in (a); (c) Overview image of another region with fragmented pieces of cathode; (d) magnified image of the region labeled by the rectangle in (c); (e) Li map (58.25-65.5eV); (f) C map (282.25-314.75 eV); (g) O map (527.75-564eV); (h) Mn map (634.25-659eV); (i) comparison of O K, Mn L, and Ni L edges; (k) Mn L edges normalized to Mn L_3 peak; (l) Mn M, and Li K edge comparison of cycled bulk region and fragmented piece region.

Pristine $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.2}\text{M}_{0.6}]\text{O}_2$ is comprised of crystallized particles (*ca.* 200 nm) with a well-defined layered structure. However, after 300 cycles, sponge-like etched surfaces were clearly observed (Fig.1a, b) along with fragmented pieces (Fig.1c, d). Li, C, O, Mn, and Ni EELS maps (Fig.1e to i) were collected from selected regions of fragmented pieces, which suggested that the fragmented pieces, mixed with SEI components, likely originated from the bulk particles after repeated cycling. In addition, consistent with the oxygen-deficient environment (Fig.1j), Mn valence in the fragmented pieces was quantified to be 2^+ (Fig.1k), much lower than that in the bulk. In addition, Li K edge peak intensity in the fragmented particle was much lower than the cycled bulk region (Fig. 1), suggesting that the fragmentation probably initiated during the Li extraction/charge process. This was consistent with the large strain generated from extensive removal of Li^+ and oxygen release during charge. The etched surfaces, which may evolve into fragmented pieces after cycling are detrimental to the electrochemical properties of a Li-Mn-rich cathode due to the loss of intimate contact with the electrode and the accumulated cell impedance. Future work will investigate if surface modifications can prevent this and extend the stable cycling of Li-rich cathode materials.

Presentation:

Jason Zhang, Jie Xiao, and Chongmin Wang, “Factors Affecting the Structure and Performance of High Energy Cathodes.” Presented in 2013 US Drive meeting held in ANL, Chicago, Jan. 24, 2013

Task 4.5 - PI, INSTITUTION: Jordi Cabana, Lawrence Berkeley National Laboratory

TASK TITLE: Cathodes – Novel and Optimized Phases for High Energy Density Batteries

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Low-energy density, poor cycle life, safety

OBJECTIVE: Enable higher density Li-ion batteries through an increase in operation voltage and capacity of the cathode. Design electrode structures that maximize active material utilization and charge density. Understand the structure-composition-properties relationship for bulk and surface in electrodes. Identify new compounds containing non-oxide or polyanions in their crystal structure that are electrochemically active.

GENERAL APPROACH: Employ and develop a variety of synthetic methods to produce materials with controlled purity, crystal structure, and particle morphology. Use spectroscopic and diffraction techniques to monitor the reactions involved in battery electrodes. Explore chemical spaces in search for new phases that may provide performance improvements.

STATUS OCT. 1, 2012: A series of annealed LiNi_{1/2}Mn_{3/2}O₄ was produced, analyzed by spectroscopy and diffraction, and their performance was correlated with crystal-chemical parameters. The role of oxide additives on the extent of irreversible reactions has been assessed. A new project, focused on the discovery of new fluoride-containing phases as stable high voltage high capacity Li battery cathodes, was initiated.

EXPECTED STATUS SEP. 30, 2013: A systematic study of the interactions between LiNi_{1/2}Mn_{3/2}O₄ surfaces and the electrolyte will be performed. The correlation between crystal-chemistry in LiNi_{1/2}Mn_{3/2}O₄ and the phase transformation of the electrode will have been studied. Screening of Li-M-O-F (M=Mn, Fe, Cu) spaces in search for unreported phases will be performed through direct high temperature synthesis and low temperature fluorination.

RELEVANT USABC GOALS: 40-mile PHEV: Energy/Weight 96 Wh/kg; CD Cycle Life 5000 cycles; Calendar Life @ 40°C 15 years.

MILESTONES:

- (a) Complete *in operando* X-ray diffraction study of at least 4 samples of LiNi_{1/2}Mn_{3/2}O₄ with different degrees of order/disorder. (Mar. 13) **Complete**
- (b) Develop a synthetic protocol for the extensive fluorination of Li-M-O (M=Mn, Fe, Cu) using low temperature treatments. (Apr. 13) **On schedule**
- (c) Synthesize at least two new Li-M-O-F (M=Mn, Fe, Cu) using direct high-temperature methods. (Sep. 13) **On schedule**
- (d) Determine changes during cycling of the surface chemistry of LiNi_{1/2}Mn_{3/2}O₄ depending on coatings and doping, in coordination with the *Spinel Focus Group*. (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

Milestone (a) was completed during this quarter. *In operando* X-ray diffraction experiments were conducted at beamline 11-3 at the Stanford Synchrotron Radiation Lightsource (SSRL) on selected $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ samples representative of different degrees of cationic ordering. Figure 1 shows a summary of the data. It compares the electrochemical signatures on charge with the crystal phase evolution. The samples tested have decreasing degrees of crystallographic ordering, as probed by NMR, as follows: OO730 > OO700 > OO670 > A900. As is readily noticed, the difference in potential between the two faradaic electrochemical signatures smoothly traces ordering. A similar trend was observed during the phase transformation. All materials undergo two consecutive first-order phase transitions during Li deintercalation. However, the miscibility gap between the pristine and the first delithiated phase decreases with disorder, resulting in increasingly extended domains of solid solution. The size of the solid solution domain correlates very well with the rate performance of the materials (see reports in FY12), suggesting that the reason disordered samples outperform ordered ones lies not on carrier transport within the phases, but on the kinetics of the phase transformation.

Progress toward Milestones (b) and (c) was also made during this Quarter. The first oxide samples showing evidence of fluorination were produced. The extent of such fluorination is currently being evaluated and will be discussed in the 3rd Quarter report.

Collaborations: Prof. Grey (Cambridge), Dr. Casas-Cabanas (CIC Energigune, Spain).

Publications and Presentations this quarter:

- 3 oral presentations (1 invited) at the 2013 MRS Spring Meeting, April 1-5, 2013.
- 1 oral presentation (invited) at the 245th ACS National Meeting & Exposition. April 7-11, 2013.
- L. Xu *et al.*, *Nano Lett.*, 13 (2013), 1800–1805.
- C. Kim *et al.*, *Adv. Funct. Mater.*, 23 (2013), 1214-1222.

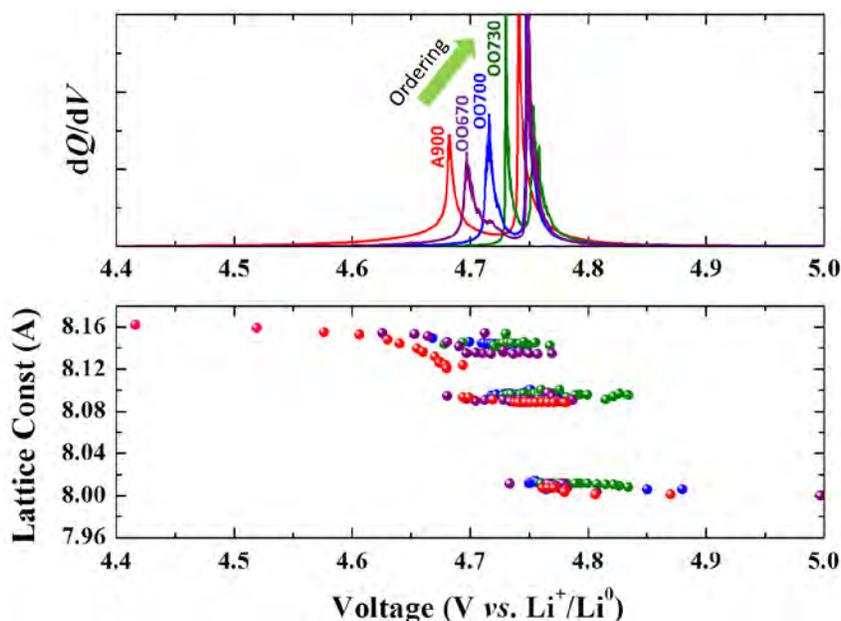


Figure 1: Summary of *in operando* XRD data collected upon Li deintercalation in a series of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ samples showing varying degrees of cationic ordering.

Task 4.6 - PI, INSTITUTION: Patrick Looney and Feng Wang, Brookhaven National Laboratory

TASK TITLE: Cathodes – *In situ* Solvothermal Synthesis of Novel High Capacity Cathodes

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Low energy density and cost

OBJECTIVE: Develop low-cost cathode materials that offer high energy density (>660 Wh/kg) and electrochemical properties (cycle life, power density, safety) consistent with USABC goals.

GENERAL APPROACH: Our approach is to develop and utilize a specialized *in situ* reactor designed to investigate synthesis reactions in real-time using synchrotron techniques. This capability will allow us to identify intermediate or transient phases and better control phase nucleation, reaction rates, and material properties. These new tools and insights will be used to prepare novel high energy density lithium cathode materials (≥ 660 Wh/kg).

STATUS OCT. 1, 2012: In FY12 work was initiated on the synthesis and electrochemical testing of the high capacity cathode Cu_{0.95}V₂O₅. By the end of FY12 a synthesis procedure for the preparation of pure, nano-scale Cu_{0.95}V₂O₅ was identified and electrochemical testing was performed. The development of an improved *in situ* synthesis reactor for synchrotron studies and a 2nd generation reactor is complete.

EXPECTED STATUS SEP. 30, 2013: In Year 2 investigation of Cu-V-O compounds will continue. By the end of FY13 multiple Cu-V-O compounds will have been synthesized. The optimal procedure for the synthesis of Cu_{0.95}V₂O₅ will be determined by evaluating a variety of precursors (Cu source, V source and reducing agents) and reaction conditions (temperature and time). Electrochemical studies (*in situ* and *ex situ*) along with material characterization (*e.g.*, particle size and morphology) will be determined to identify mechanism(s) of capacity fade. The feasibility of using ion exchange reactions will also be determined.

RELEVANT USABC GOALS: 200 Wh/kg (EV requirement); 96 Wh/kg, 3000 cycles (PHEV 40 mile requirement); lower cost batteries.

MILESTONES:

- (a) Determine optimal procedure for the synthesis of Cu_{0.95}V₂O₅. This will involve an evaluation of precursors, reducing agents and synthesis conditions. (Jan. 13) **Complete**
- (b) Identify mechanism(s) responsible for poor cycling in Cu_{0.95}V₂O₅ and identify a pathway for reducing capacity fade with cycling. (Mar. 13) **Complete**
- (c) Synthesize and electrochemically characterize at least one other Cu-V-O compound using hydrothermal/solvothermal and/or ion-exchange reactions. (May. 13) **On schedule**
- (d) Determine the feasibility of using hydrothermal and/or ion-exchange reactions to prepare polyanion cathodes. (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

Procedures were developed for synthesis of high-quality Cu-based vanadium oxides, ϵ - $\text{Cu}_{0.95}\text{V}_2\text{O}_5$ (ϵ -CVO), in the last quarter. The effort in this quarter was focused on identifying mechanisms responsible for poor cycling stability of ϵ -CVO and possible remedies. The electrochemical reaction process of ϵ -CVO cathodes during the 1st lithiation was investigated using *in situ* XRD (Fig. 1), indicating the loss of long-range ordering of ϵ -CVO with Cu extrusion, making it difficult to track structural changes with XRD.

A new simultaneous *in situ* XAS/XRD method was developed to track the correlated structural and chemical evolution of ϵ -CVO from the same working electrode. Detailed information on short-range ordering, redox of Cu, V, and Cu extrusion/insertion was obtained; some of the results are given in Fig. 2. Although ϵ -CVO electrodes undergo irreversible structural evolution during the 1st cycle, the newly-built structure seems to be stable in the subsequent cycles. Cu nanoparticles formed in the lithiated electrodes, despite their large size (~100 nm), move back to the structure upon delithiation. Cu and V were found on the anode, suggesting their loss from the cathode could be responsible for capacity decay. This may be alleviated by a surface-coated cathode.

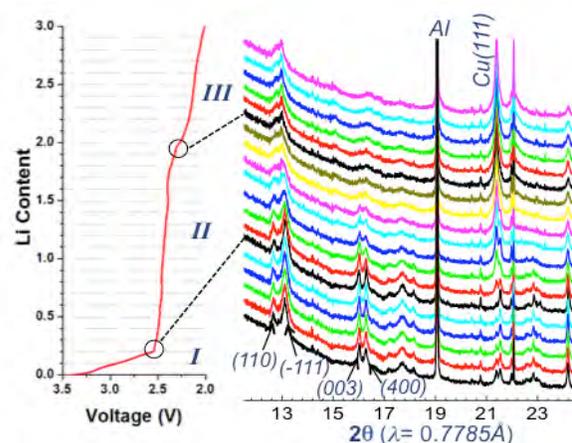


Figure 1. Time-resolved XRD patterns of ϵ -CVO electrode during the 1st discharge.

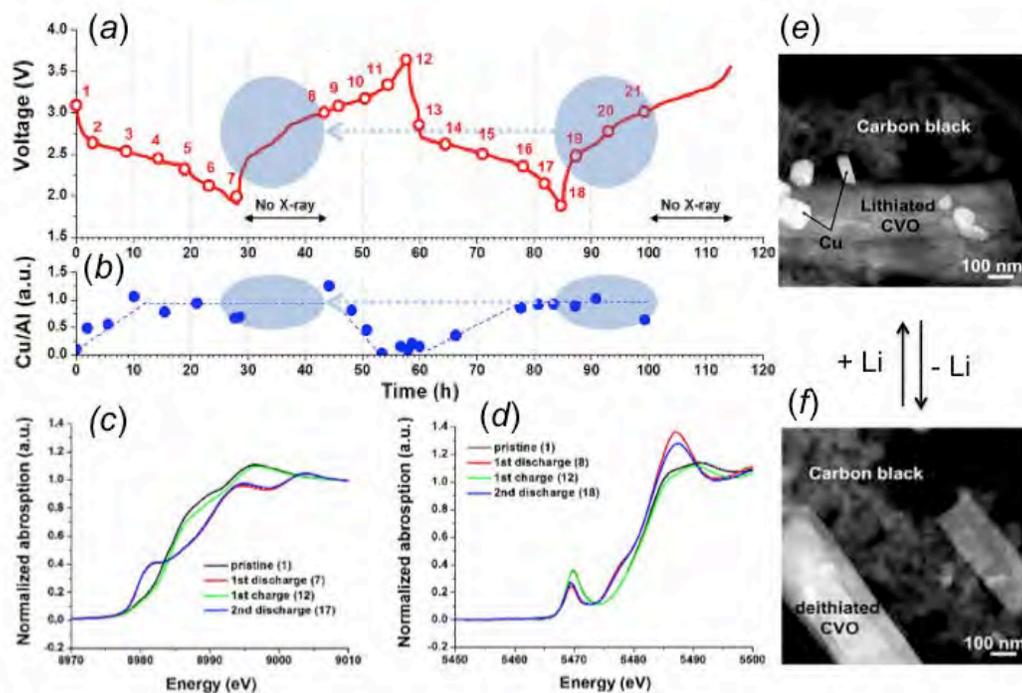


Figure 2. Simultaneous *in-situ* XAS/XRD of ϵ -CVO cathode upon cycling (a) voltage profile; (b) evolution of integrated Cu peak intensity (re-scaled to Al) (c, d) selected near-edge XAS spectra of Cu and V K-edges; (e, f) typical annual dark-field (z -contrast) images of the lithiated and delithiated samples.

Collaborations: Peter Khalifah (SBU) and Jordi Cabana (LBNL) on synthesis of new cathodes, Arumugam Manthiram (UT at Austin) on synchrotron X-ray characterization.

Task 4.7 - PI, INSTITUTION: Jim Kiggans and Andrew Kercher, Oak Ridge National Laboratory

TASK TITLE: Cathodes – Lithium-bearing Mixed Polyanion (LBMP) Glasses as Cathode Materials

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Cathodes for Li-ion batteries require lower cost materials and improved energy density, safety, and cycling stability.

OBJECTIVE: Develop lithium-bearing mixed polyanion (LBMP) glasses as potential cathode materials for Li-ion batteries with superior performance to lithium iron phosphate for use in electric vehicle applications. Modify compositions of LBMP glasses to provide higher electrical conductivities, higher redox potentials, and higher specific energies than similar crystalline polyanion framework materials. Test LBMP glasses for performance and cyclability. The final goal is to develop LBMP glass compositions with the potential to provide specific energies up to near 1000 mWh/g.

GENERAL APPROACH: The experimental approach combines: (1) structure and property modeling, (2) glass processing, (3) glass characterization, (4) conventional cathode production, and (5) electrical and electrochemical testing. Computer modeling will be used to suggest the most promising LBMP glass compositions in terms of electrochemical performance and glass processing capability. Classical heat-quench glass forming and sol gel processing will be used to make the LBMP glasses. Electrochemical performance will be demonstrated on coin cells with LBMP glass cathodes using cycle testing and variable discharge rate testing.

STATUS OCT. 1, 2012: An experimental test matrix for initial cathode glass compositions has been developed. Materials and equipment have been purchased for initial glass compositions. Initial work with TGA-DTA analyses of glass precursors is in progress.

EXPECTED STATUS SEP. 30, 2013: One or more promising glass compositions will be selected from an initial experimental screening. CALPHAD simulation will be developed and verified against initial experimental results. Optimization and examining the interrelation of properties, compositions, and synthesis methods will be underway.

RELEVANT USABC GOALS: Reduce the cost of electrochemical energy storage by developing Li-ion batteries and other advanced energy-storage technologies that afford higher energy densities without sacrificing safety and performance.

MILESTONES:

- (a) Setup CALPHAD database and perform initial simulation for one glass composition. (Jan. 13) **Complete**
- (b) Synthesize, characterize, and perform electrochemical testing on at least four different glass compositions. (Sep. 13) **On schedule**
- (c) Create CALPHAD thermodynamic database and verify results with comparison to initial experimental glass compositions and electrochemical performance. (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

The CALPHAD database development for the baseline glass materials, FePO_4 and $\text{Fe}_4(\text{P}_2\text{O}_7)_3$, has been completed by combining thermodynamic descriptions for their liquid and solid phases. The open circuit voltage of glass Li/FePO_4 has been predicted by calculating the chemical potential of Li (Fig. 1). In order to model the $\text{Li}_{1-x}\text{FePO}_4$ glass phase, different ratios between the liquid and solid phases of LiFePO_4 and FePO_4 (L:S) have been used, and ideal mixing between two end-members have been assumed. Thermodynamic modeling of Li/FeVO_4 has been initiated to incorporate additional polyanion species in the model. Once the thermodynamic modeling of $\text{Li}-\text{Fe}_2\text{O}_3-\text{V}_2\text{O}_5$ is completed, the cell voltage of $\text{Li}/\text{Fe}_4(0.5\text{P}_2\text{O}_7 \cdot 0.5\text{V}_2\text{O}_7)_4$ will be benchmarked against experimental measurements. Benchmarking against experimental measurements will be used to determine the proper ratio of liquid and solid Gibbs energies (L:S) for upcoming glass models.

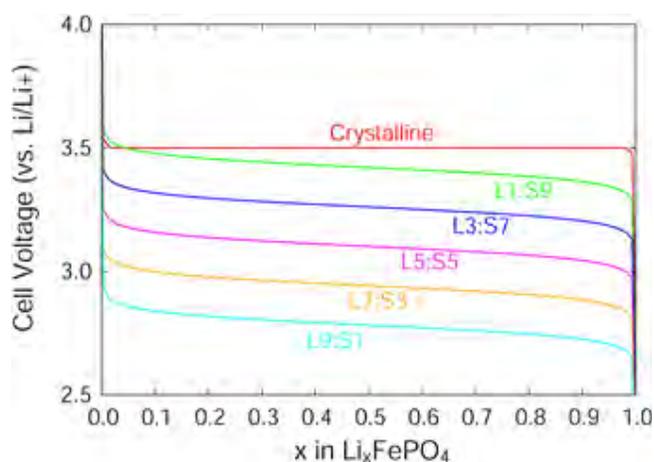


Figure 1. Thermodynamic discharge curves of crystalline and glassy lithium iron phosphate. Models for glass materials are based on mixing the Gibbs energies for liquid (L) and solid (S) phases.

The phosphate content of iron pyrophosphate glass ($\text{Fe}_4(\text{P}_2\text{O}_7)_3$) was partially substituted with vanadate to produce two mixed polyanion glass cathode materials. Splat quenching of iron phosphate/vanadate melts was used to produce 30% and 50% vanadate substituted glasses. XRD results on the two glasses showed no evidence of crystalline material.

In battery testing, the specific capacity and discharge rate performance of iron pyrophosphate glass cathodes have been shown to dramatically improve with the substitution of vanadate polyanions. Variable discharge testing down to 2 V has shown substantial changes in the percent theoretical capacity available at different discharge rates as a function of vanadate substitution (Fig. 2). Near full theoretical capacity was observed at C/5 and C/30 for 50% vanadate-substituted glass discharged down to 1.4V. The dramatic electrochemical improvement observed in iron pyrophosphate glass cathodes with vanadate substitution has provided proof-of-principle for the viability of the mixed polyanion glass cathode concept. Now that proof-of-principle has been established, research efforts will shift to making glass cathodes with higher voltages (containing Mn, Co, or Ni) and higher theoretical specific capacities.

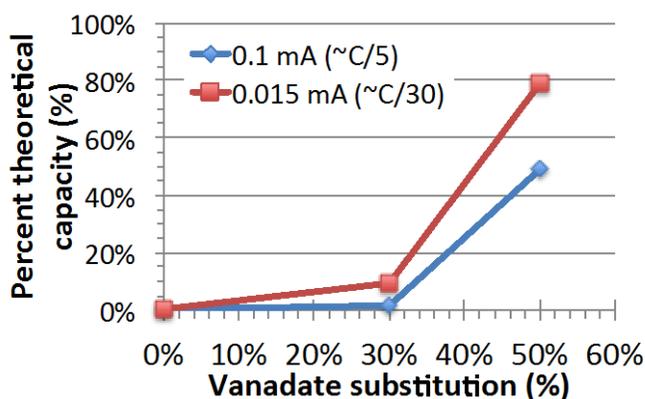


Figure 2. Vanadate substitution into iron pyrophosphate glass dramatically increased the specific capacity. Coin cells were discharged down to 2V.

BATT TASK 5 DIAGNOSTICS

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

TASK TITLE: Diagnostics – Interfacial Processes

BASELINE SYSTEMS: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

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

OBJECTIVES: (i) Establish direct correlations between electrochemical performance of high-energy Li-ion composite cathodes, and surface chemistry, morphology, topology and interfacial phenomena, (ii) improve the capacity and cycle life limitations of Li_xSi anodes

GENERAL APPROACH: Design and employ novel and sophisticated *in situ* analytical methods to address the key problems of the BATT baseline chemistries. Proposed experimental strategies combine imaging with spectroscopy aimed at probing electrodes at an atom, molecular, or nanoparticulate level to unveil structure and reactivity at hidden or buried interfaces and determine electrode performance and failure modes in baseline Li_xSi-anodes and high-voltage LMNO cathodes. The proposed methodologies, *in situ* and *ex situ* Raman, FTIR and LIBS far- and near-field spectroscopy/microscopy, SPM, spectroscopic ellipsometry, SEM, HRTEM, standard electrochemical techniques, and model single particle and/or monocrystal model electrodes will be used to probe and characterize bulk and surface processes in Si anodes and high-energy cathodes.

STATUS OCT. 1, 2012: This is a new project initiated October 1, 2012. Some insight into the mechanism of electrolyte decomposition at the surface of model anode and cathode materials has been gained and its impact on the electrode long-term electrochemical behavior evaluated. The composition and (re)formation dynamics of the surface layer on model monocrystal Sn and Si intermetallic anodes, and on model single particle and composite high-voltage cathodes, were determined using various complementary spectroscopy techniques. A unique strategy involving the use of *in situ* techniques (AFM, ellipsometry, Raman and fluorescence imaging, FTIR and AP-XPS) in conjunction with *ex situ* techniques (XAS, RBS and NRA) were applied to monitor and identify surface processes. Preliminary evaluation of near-field optical spectroscopy and imaging techniques for fundamental interfacial studies of Li-ion systems were carried out.

EXPECTED STATUS SEP. 30, 2013: Insight into the mechanism of surface phenomena on thin-film and monocrystal Sn and Si intermetallic anodes will be gained and their impact on the electrode long-term electrochemical behavior will be evaluated. Comprehensive fundamental study of the early stages of SEI layer formation on polycrystalline and single crystal face Sn and Si electrodes will be carried out. *In situ* and *ex situ* far- and near-field FTIR and Raman spectroscopy will be employed in conjunction with AFM surface imaging to detect and monitor surface phenomena at the intermetallic anodes. Similar experimental methodology will be used to detect and characterize surface and bulk processes in high-voltage (>4.3V) model and composite cathodes.

RELEVANT USABC GOALS: *Cycle life:* 5000 (deep) and 300,000 (shallow) cycles. *Available energy:* 200 Wh/kg. *Calendar life:* 15 years.

MILESTONES:

- (a) Resolve SEI layer chemistry of Si model single-crystal anodes (collaboration with the *BATT Anode Group*. (Jul. 13) **On schedule**
- (b) Incorporate an *in situ* electrochemical cell into existing ultrafast laser beam delivery/automated translation stage/spectrometer LIBS system. (Aug. 13) **On schedule**
- (c) Characterize interfacial phenomena in high-voltage composite cathodes (collaboration with the *BATT Cathode Group*. (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

In the second quarter of FY2013 work continued on fundamental fluorescence spectroscopy/imaging investigations of interfacial phenomena occurring at different crystal facets/orientations of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ single microcrystals. Model $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powder samples of different particle morphology were synthesized and provided by Guoying Chen, LBNL. SEM pictures of the pristine powders are shown in Fig. 1. Also shown is the fluorescence response obtained during cyclic voltammetry of carbon-

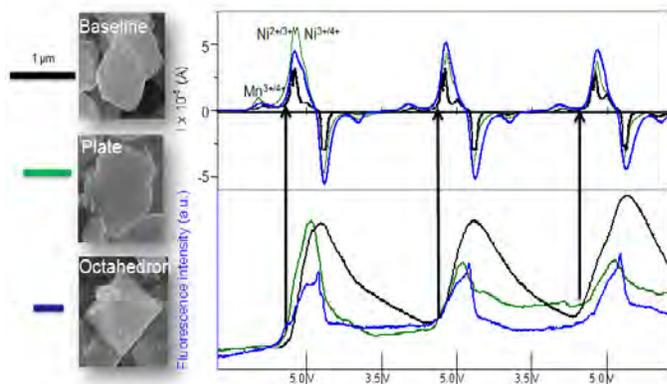


Figure 1. SEM images (left) (courtesy of Guoying Chen, LBNL), Electrochemical data (right-top), corresponding integrated fluorescence intensity (right-bottom) of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ baseline (black), platelet (green) and octahedron (blue) particles in EC:DEC 1:2 1M LiPF_6

and binder-free electrodes in EC:DEC 1:2, 1M LiPF_6 electrolyte cycled three times between 3.5 and 5.0 V vs. Li/Li^+ . The scan rate was 0.1 m V/s. The *in situ* spectro-electrochemical cell and the standard procedures were developed by our group in FY12.

The rate of electrolyte decomposition depends strongly on the crystalline orientation of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ surface and the electrode potential. Fluorescent electrolyte oxidation products dissolve in the electrolyte but some precipitate at the surface and form a thin layer. These

compounds, that formed on $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ octahedrons, tend to passivate the material better during the initial charge/discharge cycles. The rise in fluorescence correlates with the beginning of the Ni^{2+} oxidation, suggesting that Ni sites on $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ are responsible for the observed activity toward the electrolyte. Further investigations of the mechanism of these side phenomena and their impact on the electrochemical performance in Li-ion systems are underway (milestone “b”).

Preliminary *ex situ* near-field IR (NF-IR) imaging of the SEI layer on a Sn-foil model-electrode was successfully carried out. NF-IR images at different wavelengths taken of the Sn electrode (Fig. 2) cycled 5 times between 2.5 and 0.1 V display local spectral variance, which indicates non-uniform distribution of SEI layer basic building blocks at the nanometer level. These new results are consistent with earlier far-field spectroscopy observations. Additional near-field images of reference compounds to determine the local chemical composition in SEIs are on schedule in FY2013 (milestone “a”).

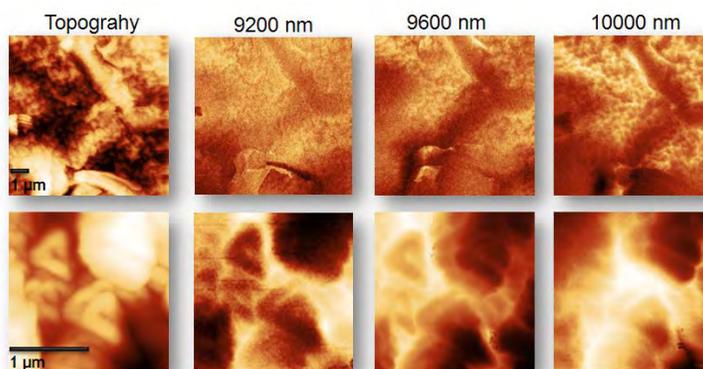


Figure 2. *Ex-situ* near-field IR and topography images of the SEI layer on Sn at 0.8V (top) and Li_xSn at 0.1V (bottom).

Task 5.2 - PI, INSTITUTION: Xiao-Qing Yang and Kyung-Wan Nam, Brookhaven National Laboratory

TASK TITLE: Diagnostics – Advanced *In situ* Diagnostic Techniques for Battery Materials

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: PHEV: Energy density, Cycle life; HEV: Power density, Abuse tolerance

OBJECTIVE: The primary objective is to determine the contributions of electrode materials changes, interfacial phenomena, and electrolyte decomposition to cell capacity and power decline in helping the development of high energy density Li battery with better safety characteristics and longer life.

GENERAL APPROACH: To use various synchrotron based X-ray techniques to characterize electrode materials and electrodes taken from baseline BATT Program cells. The following approaches will be used: *in situ* synchrotron XRD and hard XAS at transition metal K-edges during cycling; soft XAS on L-edges of Mn, Ni and Co and K-edges of C, O, and F using electron yield (surface) and fluorescence yield (bulk) detectors after cycle; high resolution transmission electron microscopy (HRTEM) coupled with electron energy loss spectroscopy (EELS) after cycle; *in situ* TR-XRD coupled with MS during heating of charged cathode materials (thermal stability study); *in situ* and *ex situ* Si K-edge XAS of Si based anode materials during cycling; *in situ* quick XAS of the cathode materials for dynamic study during cycling.

STATUS OCT. 1, 2012: This is a new project initiated October 1, 2012. Structural studies on the high energy density Li₂MnO₃-LiMO₂ (M = Ni, Mn, Co) layered materials have been carried out (in collaboration with ANL) and *in situ* XRD studies on different types of lithium iron phosphate cathode materials with mesoporous structure. *In situ* XRD and XAS diagnostic studies of high voltage LiMn_{2-x}M_xO₄ (M = Ni, Cu etc.,) have also been performed with spinel structure during cycling.

EXPECTED STATUS SEP. 30, 2013: Thermal stability studies of high-voltage LiMn_{2-x}Ni_xO₄ with ordered (*P4₃32*) and disordered (*Fd-3m*) spinel structure will have been carried out using time-resolved XRD coupled with MS and XAS during heating. The XAS studies on high energy density Si-based anode materials during cycles also will have been started.

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

MILESTONES:

- (a) Complete the *in situ* time-resolve XRD studies of LiMn_{2-x}Ni_xO₄ cathode material with ordered (*P4₃32*) spinel structure during heating. (Apr. 13) **Complete**
- (b) Complete the XAS studies of LiMn_{2-x}Ni_xO₄ cathode material with ordered (*P4₃32*) spinel structure during heating. (Apr. 13) **Complete**
- (c) Complete the *in situ* time-resolve XRD studies of LiMn_{2-x}Ni_xO₄ cathode material with disordered (*Fd-3m*) spinel structure during heating. (Sep. 13) **On schedule**
- (d) Complete the XAS studies of LiMn_{2-x}Ni_xO₄ cathode material with disordered (*Fd-3m*) spinel structure during heating. (Sep. 13) **On schedule**
- (e) Complete the *ex situ* Si K-edge XAS studies of Si-based high energy density anode materials after cycles. (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

In the 2nd quarter of FY2013, BNL focused on the thermal stability as related to structural changes of high-voltage $\text{LiMn}_{2-x}\text{Ni}_x\text{O}_4$ (LNMO) cathode materials with ordered ($P4_332$) and disordered ($Fd-3m$) spinel structures, consistent with milestones (b) and (d). The samples were heating while undergoing synchrotron-based time-resolved x-ray absorption.

Ni K-edge XANES data for charged, disordered LNMO and ordered LNMO during heating up to 420°C is shown in Fig. 1. The most notable change in the XANES spectra is the tremendous Ni edge shift, virtually causing a gap that separates the series of spectra into two parts. This edge jump happens at temperatures between 220°C and 270°C in the charged disordered case and somewhere between 270°C and 320°C in the charged ordered case. It is reasonable to associate this great edge shift with an oxygen release process and is in accordance with previous XRD and MS data. This indicates that charged ordered LNMO demonstrates better resistance to oxygen release than the charged disordered phase.

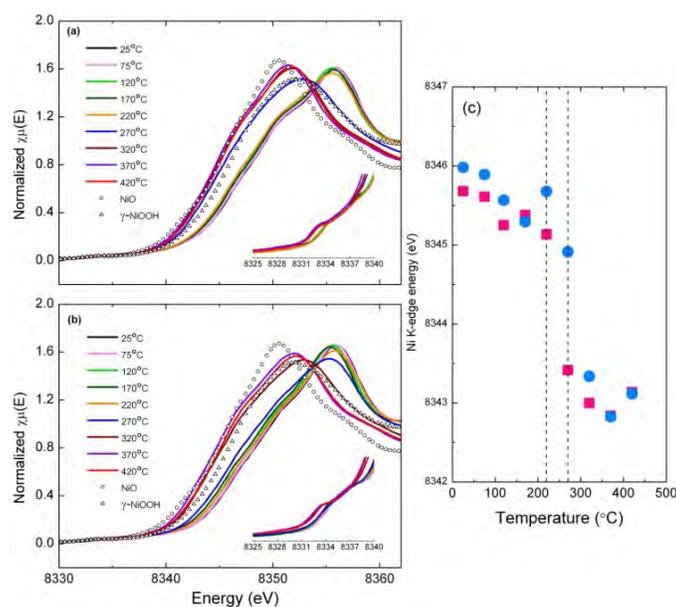


Figure 1. *In situ* Ni K-edge XANES spectra of fully charged a) disordered LNMO ($Fd-3m$) and b) ordered LNMO ($P4_332$) during heating up to 420°C . Insets show the detailed feature of pre-edge region. c) Variations of the Ni-K edge positions at half of the energy step (blue circle: ordered LNMO, purple square: disordered LNMO).

Task 5.3 - PI, INSTITUTION: Clare Grey, Cambridge University

TASK TITLE: Diagnostics – NMR and Pulse Field Gradient Studies of SEI and Electrode Structure

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Capacity fade due to significant SEI formation (focusing on Si); reduced rate performance due to SEI formation; high energy density; high power

OBJECTIVE: Identify major SEI components and their spatial proximity, and how this changes with cycling. Contrast SEI formation on Si vs. graphite and high voltage cathodes. Correlate Li⁺ diffusivity in particles and composite electrodes with rate. Investigate local structural changes of high voltage/high capacity electrodes on cycling.

GENERAL APPROACH: Multinuclear NMR of local structure; *in situ* NMR studies of Li⁺ transport. Pulse Field Gradient (PFG) measurements of electrolyte diffusivity and tortuosity; SIMS and XPS of SEI composition

STATUS OCT 1, 2012: This is a new project initiated April 1, 2013.

EXPECTED STATUS SEP. 30, 2013: The ¹³C NMR studies of the enriched carbonate electrodes will be ongoing, along with comparison studies with FEC and VC additives. Basic quantification studies of SEI formation vs. cycle number and depth of discharge will have been completed.

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

MILESTONES:

- (a) Identify major (NMR active) inorganic components (LiF, phosphates, carbonates) in Si SEI by NMR methods. (May 13) **On schedule**
- (b) Establish viability of TOF-SIMS measurements to identify SEI components on Si. (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

The project was awarded under the 2012 RFP and will officially start on April 1, 2013.

TASK 5.4 - PI, INSTITUTION: Nitash Balsara, University of California, Berkeley

TASK TITLE - PROJECT: Diagnostics – Simulations and X-ray Spectroscopy of Li-S Chemistry

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: (1) Elucidating the mechanism by which the redox reactions in a sulfur cathode proceed. (2) Development of unique diagnostic tools based on X-ray spectroscopy and molecular modeling.

OBJECTIVES: A mechanistic understanding of the redox reactions and diffusion of reaction intermediates in a model sulfur cathode based on experimentally-verified models that incorporate both statistical and quantum mechanics.

GENERAL APPROACH: (1) A model Li-S cell will be built with a simple cathode comprising a binder that conducts both electrons and ions on the 10 nm length scale and sulfur nanoparticles. (2) The cells will be fabricated in a manner that facilitates the use of soft and hard X-ray spectroscopy during charge-discharge cycles. (3) Detailed (first-principles or empirical force-field) molecular dynamics simulations will be used to sample molecular configurations at finite temperature, interpret associated X-ray spectra and obtain models of (electro-)chemical reaction pathways in the cells.

STATUS OCT. 1, 2012: New project initiated October 1, 2012. Begin measurements of X-ray spectra of polysulfides and electrolyte salts in polymer electrolytes. Begin simulations of polysulfides and electrolyte salts in polymer electrolytes that enable predicting X-ray spectra and simulate reference X-ray spectra for molecular and homogeneous condensed-phase components of interest.

EXPECTED STATUS SEP. 30, 2013: The synthesis procedure for PEDOT-PEO block copolymers that are predicted to serve as ion- and electron-conducting binders for sulfur cathodes will have been worked out. Definite spectral fingerprints of the lithiated compounds (polysulfides and salts) of interest near the absorption edges of interest (Li, O, S, C, etc.) will have been obtained.

RELEVANT USABC GOALS: Fundamental study to determine the factors that underlie limited cycle life of high energy couples such as Li-S cells.

MILESTONES:

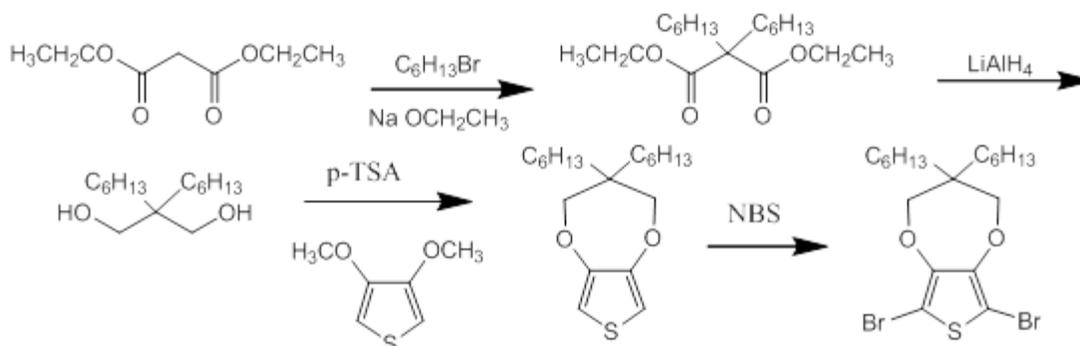
- (a) Obtain first-simulation results of molecular S₈, Li₂S_x, and Li salts in SEO PEO (or short-oligomer analogs) (Mar. 13) **Complete**
- (b) Make initial predictions of X-ray spectroscopy signatures of Li₂S_x and other components in the model Li-S cell. (Mar. 13) **Delayed to May 13**
- (c) Work out the synthesis procedure for poly(dihexylpropylenedioxythiophene)-polyethylene oxide, PEDOT-PEO, (ProDOT). (Mar. 13) **Delayed to Jun. 13**
- (d) Measure X-ray spectroscopy signatures of Li₂S_x and other components in the model Li-S cell (*e.g.*, salt) in SEO and PEDOT-SEO. (Sep. 13) **On schedule**
- (e) Design model Li-S cells appropriate for measurement of X-ray spectroscopy measurements as a function of state of charge of the cathode. (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

Milestone (a). Solvation thermodynamics for molecular simulations of polysulfide molecules in tetraglyme were examined. As seen in Fig. 1, Li_2S_4 and Li_2S_8 were revealed as the most soluble polysulfide species in tetraglyme.

Milestone (b). Work in conjunction with simulated spectra already obtained for Li_2S_x in oligomeric PEO is ongoing. Whereas previous spectra were obtained for single polysulfide molecules, current work is focused on obtaining spectra for solutions of polysulfide molecules.

Milestone (c). Work on the following synthesis is ongoing.



Milestone (d). Experimental x-ray absorption spectra for thin films of Li_2S_x ($x = 4, 6, 8$) dissolved in SEO have been obtained and can be seen in Fig. 2.

Features displayed by these spectra agree with predictions presented in our previous report: a pre-edge feature at 2471.0 eV attributable to the sulfur chain end, an uncharged sulfur peak at 2472.6 eV, and a broad higher energy peak spanning from 2476 to 2482 eV. As expected, the pre-edge peak is highest for Li_2S_4 , while the uncharged peak is highest for Li_2S_8 .

Milestone (e). Work to develop batteries appropriate for x-ray studies has not yet begun. Research has been focused on developing the library of XAS spectra needed for *in situ* experiments and on developing the ProDOT-PEO electrolyte.

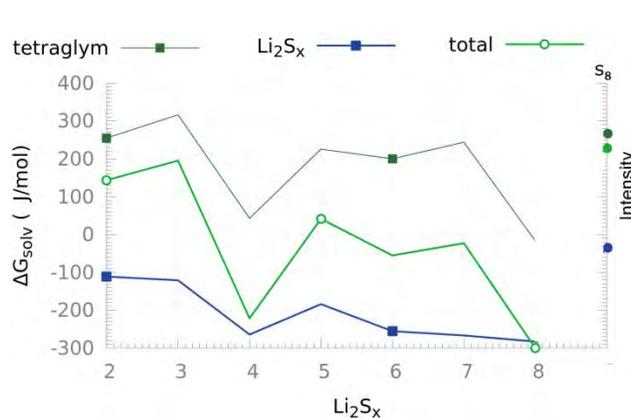


Figure 1.

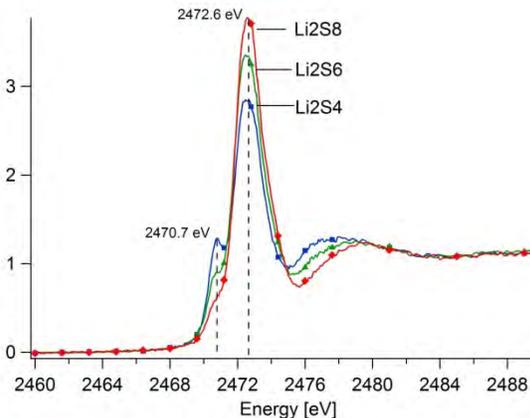


Figure 2.

Task 5.5 - PI, INSTITUTION: Jordi Cabana, Lawrence Berkeley National Laboratory

TASK TITLE: Diagnostics – Chemical and structural gradients in composite electrodes.

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Low energy density, poor cycle life

OBJECTIVE: Enable higher density Li-ion batteries by informing the design of optimized electrode architectures that maximize active material utilization and charge density. Establish correlations between inhomogeneities in local states of charge, pore structure and inactive component distribution in commercially relevant electrodes. Understand the role of phase transformations within active materials vis-à-vis utilization and durability.

GENERAL APPROACH: Use spectroscopic and diffraction techniques to monitor the reactions involved in battery electrodes. Use synchrotron-based spectromicroscopy tools to probe porous composite electrodes at high chemical and spatial resolution, in 2D and 3D. Develop methodologies that rely on less sophisticated techniques to probe inhomogeneities in battery electrodes. Correlate chemical and morphological information.

STATUS OCT. 1, 2012: New project initiated October 1, 2012. The validity of μ -X-ray absorption spectroscopy (XAS) to produce maps of local states of charge in battery electrodes has been established. Chemical tomography of particle agglomerates using full field transmission X-ray microscopy combined with XAS was established as previous work under different funding.

EXPECTED STATUS SEP. 30, 2013: *In operando* XRD will have been used to probe: i) bulk phase transformations in relevant materials and how they relate to utilization and durability, ii) the introduction of chemical gradients in NMC electrodes will have been validated. The first maps of local states of charge in commercially relevant materials will have been produced.

RELEVANT USABC GOALS: 40-mile PHEV: Energy/Weight 96 Wh/kg; CD Cycle Life 5000 cycles; Calendar Life @ 40°C 15 years.

MILESTONES:

- (a) Identify, source and gather baseline electrochemical data for relevant target systems. (Mar. 13) **Complete**
- (b) Determine changes during delithiation of new fluoride and oxyfluoride phases using *in operando* bulk XRD. (Sep. 13) **On schedule**
- (c) Establish the validity of using *in operando* bulk X-ray diffraction (XRD) to study the formation of chemical gradients in thick NMC composite electrodes (Sep. 13) **On schedule**
- (d) Produce the first collection of chemical maps of local states of charge in composite electrodes using μ -XAS. (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

The sourcing of a baseline cathode material was completed during the 2nd quarter of FY2013. The choice was $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NCM333, hereafter); electrodes of different thickness were provided. The electrochemical properties of these electrodes are being evaluated both experimentally and computationally by the Battaglia and Srinivasan groups.

The first sets of *in operando* XRD data for NCM333 electrodes have been acquired. The experiments were performed at beamline 11-3 at the Stanford Synchrotron Radiation Lightsource (SSRL), at SLAC National Accelerator Laboratory. Data were acquired after the X-ray beam was transmitted through the electrochemical cell, which consists of a standard coin cell with a very small window (*ca.* 1 mm diameter) that is covered with conductive tape. The small size of the window minimizes concerns over pressure gradients. Consequently, to a first approximation, the collected patterns represent an average of the composition of the composite cathode *in depth*. These data are, thus, amenable to comparison and fit using continuum models pioneered by the Newman group. In the case of a material undergoing a second-order phase transformation (*i.e.*, solid solution mechanism) such as NCM, a continuous shift of the XRD peaks, with no new reflections appearing, is expected.

Figure 1 shows the electrochemical profile of the *in operando* cell. After an initial charge to 4.3 V at 1C rate, the cell was relaxed for 100 min. XRD patterns were collected every 2 minutes during these processes (Fig. 2). As expected, a smooth shift of the peaks, indicative of a solid solution mechanism of Li deintercalation, was observed during charge. However, such shift was accompanied by a significant increase in peak width, indicative of the formation of compositional inhomogeneities in the electrode. This observation appears to be in contradiction with the fact that a homogeneous electrochemical potential is expected throughout the electrode when the reaction follows such a mechanism. More importantly, an evolution of the peak width and position was observed during cell rest, indicating that compositional relaxation was occurring in the electrodes. The data are currently under analysis.

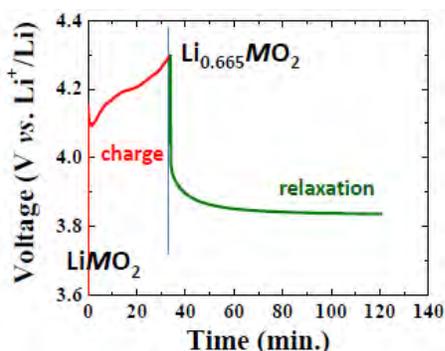


Figure 1: Voltage vs. time trace of an *in operando* XRD cell with Li metal and NCM333 electrodes.

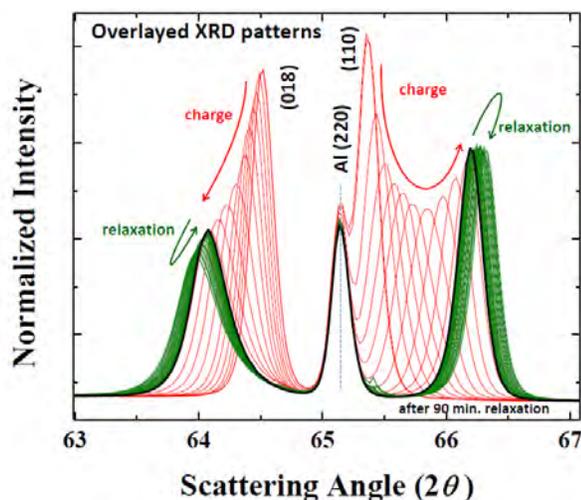


Figure 2: a) Selected *in operando* XRD patterns taken during operation of the cell in Figure 1.

Task 5.6 - PI, INSTITUTION: Guoying Chen, Lawrence Berkeley National Laboratory

TASK TITLE: Diagnostics – Design and Synthesis of Advanced High-Energy Cathode Materials

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Available energy (Goal: 11.6 kWh); Cycle life (Goal: 5,000 cycles/58 MWh).

OBJECTIVES: Obtain new insights into electrode materials by utilizing state-of-the-art analytical techniques. Gain fundamental understanding on structural, chemical and morphological instabilities during Li extraction/insertion and extended cycling. Establish and control the interfacial chemistry between the cathode and electrolyte at high operating potentials. Determine transport limitations at both material and electrode levels. Develop and synthesize next-generation electrode materials based on rational design as opposed to more conventional empirical approaches.

GENERAL APPROACH: Prepare single crystals of Li-rich layered composites and Ni/Mn spinels with well-defined physical attributes and perform advanced diagnostic and mechanistic studies at both bulk and single crystal levels. Global properties and performance of the samples will be established from the bulk analyses, while the single-crystal-based studies will utilize time and spatial-resolved analytical techniques to probe solid-state chemistry and solid-electrolyte interfacial processes at the crystallite level.

STATUS OCT. 1, 2012: This is a new project initiated October 1, 2012.

EXPECTED STATUS SEP. 30, 2013: A large collection of single-crystal samples with the layered Li_{1+x}M_{1-x}O₂ and spinel LiNi_xMn_{2-x}O₄ structures will have been synthesized. Structural, chemical, and morphological changes during first charge/discharge, particularly the activation process in the layered composites, and after extended cycling prompted deteriorated performance and stability will have been examined. Bulk and surface changes associated with metal dissolution in the active materials will have been evaluated and the dissolution mechanism examined. The impact of physical properties on these changes and subsequently the performance and stability of the oxide cathodes established. Approaches to characterize the side reaction products formed on the cathode crystal surface will have been developed.

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

MILESTONES:

- (a) Synthesize single-crystal samples of Li-excess layered composites and Ni/Mn spinels. (Apr. 13) **On going. Delayed due to the delay in postdoc hiring.**
- (b) Determine structural, chemical, and morphological changes resulting from initial Li extraction/insertion and extended cycling. Correlate these changes to crystal physical attributes. (Jul. 13) **On schedule**
- (c) Evaluate transition-metal dissolution in crystal samples and examine its mechanism. (Aug. 13) **On schedule**
- (d) Develop approaches to characterize the cathode-electrolyte interfacial layer. (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

Crystal synthesis: A collection of layered oxide crystals with compositions of $\text{Li}_{1+x}(\text{Ni}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33})_{1-x}\text{O}_2$ ($x=0$ and 0.14), $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}\text{O}_2$ and $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2$ were prepared in plates, needles, and polyhedrons of different sizes. Progress was also made in synthesizing large $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ crystals intended for single-particle measurements. The molten-salt method was modified to include an additional flux top layer that promoted crystal growth into the hundreds-of-micron size. Morphology was largely influenced by the choice of the flux and the ratio between the flux and precursors (denoted as R), as shown in Fig. 1. XRD characterization confirmed the formation of phase-pure spinel in each case.

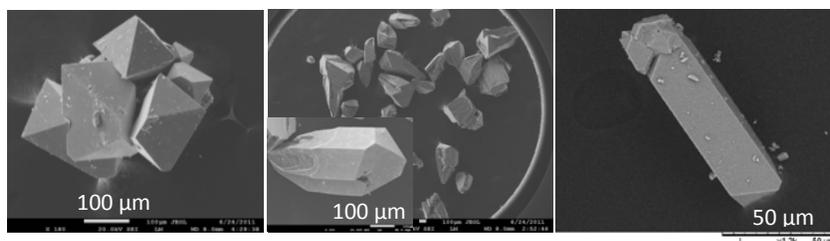


Figure 1. SEM images of Ni/Mn spinel crystals synthesized with chloride precursors in: a) LiCl and R=100, b) LiCl and R=50, and c) eutectic LiCl-KCl flux.

Structure and phase transformation in Ni/Mn spinels: Previous studies have shown the importance of Ni/Mn ordering in influencing structural evolution during charge and discharge, but direct correlation was not established due to the lack of consistency in experimental results. This study intends to illustrate the importance of Ni/Mn ratio and Mn^{3+} content that are likely the culprit of these inconsistencies found in the literature. To this end, controlled studies were performed on micron-sized $\text{LiNi}_x\text{Mn}_{2-x}\text{O}_4$ ($x=0.3$ and 0.5) octahedron crystals synthesized by a molten-salt method. An additional annealing process at 720°C for 1 min was performed on $x=0.5$ crystals to disorder the crystal structure, with both samples showing the signature disordered features on the FTIR spectra and the same peak separation of near 60 mV on the dq/dV profiles. Area integration of the broad peaks at 4.1 V estimated 5.8 and 19.3% Mn^{3+} for $x=0.3$ and 0.5 , respectively. Synchrotron *in situ* XRD experiments were performed at beamline 11-3 at SSRL to investigate structural changes in the crystal samples upon charge and discharge, with detailed phase composition at a given Li content obtained from structural refinement, shown in Fig. 2. While the crystal composite electrode with $x=0.5$ underwent two reversible two-phase transitions involving three cubic phases, an extensive solid-solution region with only two cubic phases was detected during the charge and discharge of $x=0.3$. The results demonstrate the intricacies in the relationship between the spinel structure and phase transformations.

Collaborations this quarter: Drs. J. Cabana, K. Persson, R. Kostecki, and M. Doeff, Profs. B. Lucht and Y.-M. Chiang, NCEM, SSRL, and ALS.

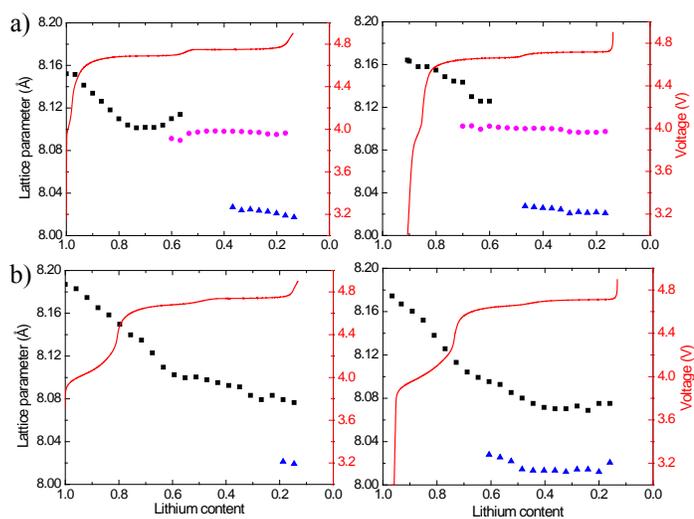


Figure 2. Phase transformation in $\text{LiNi}_x\text{Mn}_{2-x}\text{O}_4$ crystals: a) $x=0.5$ and b) $x=0.3$. (left) charge and (right) discharge.

Task 5.7 - PI, INSTITUTION: Shirley Meng, University of California, San Diego

TASK TITLE: Diagnostics – Optimization of Ion Transport in High-Energy Composite Cathodes

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: The Li-rich oxides offer considerably higher energy density than the baseline cathode materials, but they suffer severely from the lack of lithium mobility and unstable voltage discharge profiles upon cycling.

OBJECTIVE: The ultimate goal of the proposed diagnostic work is to control and optimize Li-ion transportation, TM migration, and oxygen activity in the high-energy Li rich composite cathodes so that their power performance and cycle life can be significantly improved.

GENERAL APPROACH: The approach uniquely combines atomic resolution scanning transmission electron microscopy (a-STEM) & Electron energy loss spectroscopy (EELS), X-ray photoelectron spectroscopy (XPS) and first-principles computation to elucidate the dynamic changes of the bulk and surface structural changes in the complex oxide materials during electrochemical cycling. A systematic study with powerful analytical tools is necessary to pin down the mechanisms of surface coating and determine the optimum surface characteristics for high rate and long life, and to help the synthesis efforts to produce the materials at large scale with consistently good performance.

STATUS OCT. 1, 2012: This is a new project initiated April 1, 2013.

EXPECTED STATUS SEP. 30, 2013: Establish the coherent interface between layer-layer phases and layer-spinel phases in first-principles modeling. Identify the key samples for in-depth diagnostic study by completing the electrochemical measurements. Due to the complexity of the problem, a suite of surface sensitive diagnostic tools will be applied.

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

MILESTONES:

- (a) Identify dynamic structure changes, quantify voltage stability upon cycling. Identify at least two best Li rich candidate materials as focused samples (among UCSD synthesized samples and other BATT teammate samples.) (Sep. 13) **On schedule**
- (b) Demonstrate the chemical sensitivity and special resolution of the suite of surface characterization tools, including STEM/EELS, XPS and first-principles computation models. (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

The project was awarded under the 2012 RFP and will officially start on April 1, 2013.

Task 5.8 - PI, INSTITUTION: Gabor Somorjai, UC Berkeley and Philip Ross, Lawrence Berkeley National Laboratory

TASK TITLE: Diagnostics – Analysis of film formation chemistry on silicon anodes by advanced *in situ* and *operando* vibrational spectroscopy

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: High energy density Si anodes have large irreversible capacity and are not able to cycle. These failures are due in part to loss of electrolyte by reduction and an SEI that is not stable on the surface with repeated cycling.

OBJECTIVE: To understand the composition, structure, and formation/degradation mechanisms of the SEI on the surfaces of Si during charge/discharge cycles and how the properties of the SEI contribute to failure of electrochemical systems for vehicular applications.

GENERAL APPROACH: Si anode materials including single crystals, e-beam deposited polycrystalline films, and nanostructures with baseline electrolyte and promising electrolyte variations will be studied. A combination of *in situ* and *operando* Fourier Transform Infrared (FTIR), Sum Frequency Generation (SFG), and UV-Raman vibrational spectroscopies will be used to directly monitor the composition and structure of electrolyte reduction compounds formed on the Si anodes. Pre-natal and post-mortem chemical composition is identified using X-ray photoelectron spectroscopy. The Si films and nanostructures are imaged using scanning and transmission electron microscopies.

STATUS OCT. 1, 2012: New project initiated October 1, 2012. A spectroelectrochemical FTIR cell was constructed for the Si anode system based on a previous design. The design phase of the SFG cell is on track. Control studies of SEI formation on Au films were performed using *operando* FTIR.

EXPECTED STATUS SEP. 30, 2013: Complementary *operando* FTIR and SFG studies of electrolyte reduction on Si(100) wafers and Si polycrystalline films, using the baseline electrolyte, are expected to have been conducted. At this time point Si nanostructures will have been prepared to complement the Si structures of larger dimensions.

RELEVANT USABC GOALS: EV: > 200 wH/kg with > 1000 cycles to 80 % DOD

MILESTONES:

- (a) Complete construction of SFG spectroelectrochemical cell. (Jan. 13) **Complete**
- (b) Perform *operando* FTIR and SFG analyses of electrolyte reduction products on doped and undoped 100-nm thick single crystalline Si using baseline electrolyte. (May 13) **On schedule**
- (c) Develop procedure to create Si thin films on current collector. (May 13) **On schedule**
- (d) Perform *operando* FTIR and SFG analyses of electrolyte reduction products on at least three Si film thicknesses (*e.g.*, 10 nm, 50 nm, and 100 nm) using baseline electrolyte. (Sep. 13) **On schedule**
- (e) Choose promising electrolyte additive(s) for further study to evaluate how it (they) impact the surface chemistry. (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

In the second quarter, *ex situ* FTIR and *in situ* SFG were used to monitor the chemistry of the electrolyte at the surface of a p-type Si(100) single crystal (doped). Using FTIR, the vibrational spectra of the Si surface was measured following Li cycling to identify electrolyte reduction products. While changes were seen in the surface chemistry following electrochemical cycling of the anode, the experimental results were difficult to repeat and the results were inconclusive.

In situ SFG was performed to monitor the surface of the Si anode in the presence of baseline electrolyte during Li cycling. Figure 1 shows SFG spectra in the C-H vibrational stretching region monitored at open circuit following cell assembly (a), after Li insertion at 50 mV (b), and after Li extraction at 2 V (c). The spectra following Li insertion exhibits a greater intensity and lineshape in comparison to the spectra before Li insertion. After Li extraction, the spectrum nearly returns to the lineshape observed before Li insertion, but with greater intensity. These results suggest that Li insertion impacts the surface chemistry on the Si anode; however, the experiment will be repeated and the vibrational regions that reflect C-C and C-O bond vibrations will be studied to make definitive conclusions.

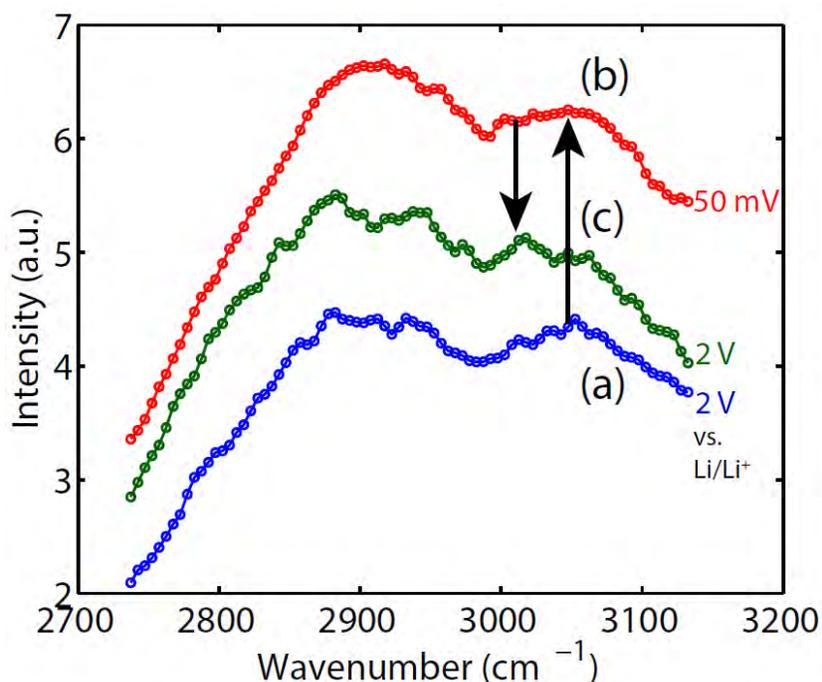


Figure 1. *In situ* sum frequency generation vibrational spectra of the C-H stretching region in the presence of baseline electrolyte (a) following assembly of the cell (at 2 V vs. Li/Li⁺), (b) Li insertion at 50 mV vs. Li/Li⁺, and (c) Li extraction at 2 V vs. Li/Li⁺. The change in intensity of the features and lineshape reflect changes in the Si surface that occurs during Li cycling.

BATT TASK 6

MODELING

Task 6.1 - PI, INSTITUTION: Venkat Srinivasan, Lawrence Berkeley National Laboratory

TASK TITLE – PROJECT: Modeling – Model-Experimental Studies on Next-generation Li-ion Battery Materials

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Low calendar/cycle life; Low energy, High cost

OBJECTIVES: (1) Quantify power limitations in porous cathodes and its relationship to design; (2) Measure concentration dependent transport properties of the baseline electrolyte of the BATT Program [LiPF₆ in EC:DEC (1:1)]; (3) Quantify polarization losses at single ion conductor (ceramic) / liquid electrolyte interface; (4) Develop a model to predict the onset of mechanical damage to particle-binder interfaces in porous electrodes.

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 degradation modes and provide guidance to material-synthesis and cell-development PIs. Use models to quantify the ability of the candidate chemistry to meet DOE performance goals.

STATUS OCT. 1, 2012: New project initiated October 1, 2012. A mathematical model that accounts for the concentration and reaction distributions in the porous electrode will be developed. A simulation of a spherical particle, surrounded by a binder layer and undergoing large volume changes when charging and discharging, will be complete, and a modified kinetic expression incorporating the influence of deformation will be obtained.

EXPECTED STATUS SEP. 30, 2013: The porous-electrode model that predicts the performance of NMC cathode will be completed and compared with the experiments. Measurement of concentration dependent transport properties for the baseline electrolyte of the BATT Program [LiPF₆ in EC:DEC (1:1)] will be complete. Polarization losses at the single ion conductor (ceramic)/liquid electrolyte interface will be quantified. Stress calculations in 2D domains, simulating multiple interacting particles embedded in binder, will be complete.

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) Measure concentration dependent transport properties (diffusion coefficient, conductivity, transference number) of LiPF₆ in EC: DEC (1:1 by weight); Quantify polarization losses at the single ion conductor (ceramic) / liquid electrolyte interface; Construct a simple two-dimensional system consisting of a region of active material in contact with a region of binder. Using a large-deformation intercalation model to describe the active material behavior during charge and discharge, calculate stresses at the interface between the two regions. (May 13) **On schedule**
- (b) Find out baseline parameters for the porous-electrode model and compare the model results with experimental data to understand solution-phase limitation; Quantify the rate of side reactions for NMC cathodes and extract kinetic parameters; Use the large-deformation model to approximately represent a system of particles dispersed in a binder matrix, calculating stresses throughout the system. (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

Ion Transport in Liquid Electrolytes: To better understand and model limitations in the electrolyte phase, reasonable estimates of transport properties of the electrolyte become imperative. Concentration dependent transport properties for the baseline electrolyte for the BATT Program, LiPF_6 in EC: DEC (1:1 by weight), are largely unknown. A custom diffusion cell has been designed for this purpose. Figure 1 shows experimentally determined diffusion coefficient (D) values obtained using restricted diffusion. These numbers are higher by one to two orders of magnitude when compared to data available in the literature. To crosscheck the D values obtained, reference electrode experiments were performed. Progression of concentration wave and the time it takes for it to reach the reference electrodes depends on the D values. Modeling the concentration profiles confirmed that results obtained by the reference electrode experiments were consistent with restricted diffusion experiments. Limiting current experiments were also performed to validate the numbers obtained by restricted diffusion. In a limiting current experiment, a cell was run at constant current and in the process Li^+ concentration rises at one electrode and drops at the other. If current density is high and there is mass transfer limitation (low D values), concentration of Li^+ on one electrode drops to zero and overall cell potential rises too steeply. These experiments further validated the D values measured by restricted diffusion were consistent.

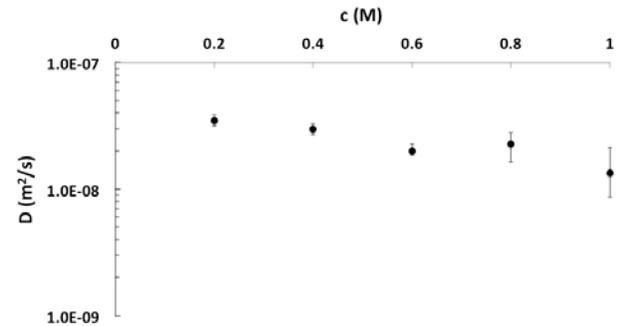
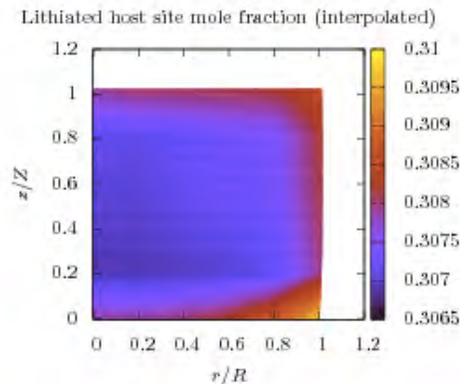
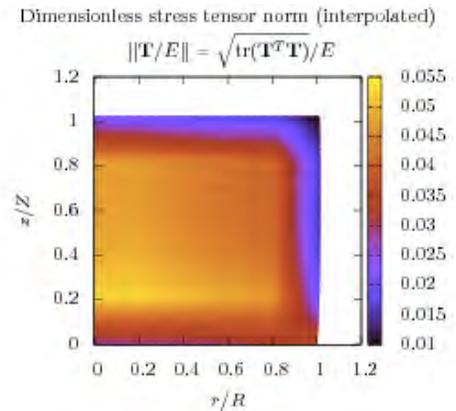


Figure 1 : Diffusion coefficient measurements using restricted diffusion for LiPF_6 in EC:DEC (1:1)

Understanding Mechanical Degradation: The large-deformation model of intercalation material presented by Christensen and Newman (2006) was used to model an axially-symmetric cylindrical particle. The equations used for numerical calculations for a cylinder of finite length involve two spatial dimensions. Available simulation packages did not appear to be entirely suitable, so a new numerical library was developed. As an initial test, numerical solutions were obtained on a graphite cylinder with a stationary base. The figures show results at 30% SOC over a normalized cross section. Stresses are lowest on the exposed surfaces (top and right), which have more freedom to move, relieving stress. Although Li enters only through the exposed surfaces, the distribution of Li within the particle is fairly even because of competition between the two driving forces for diffusion, the gradients of mole fraction and thermodynamic pressure. In order to reach the May milestone, a region of binder/conductive material composite in contact with the active material will be incorporated.



Task 6.2 - PI, INSTITUTION: Kristin Persson, Lawrence Berkeley National Laboratory

TASK TITLE – PROJECT: Modeling – Predicting and Understanding Novel Electrode Materials From First-Principles

SYSTEMS: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: High cost, low energy, low rate, poor cyclability.

OBJECTIVES: 1) Understand the atomistic mechanisms underlying the behavior and performance of the Li-excess as well as related composite cathode materials underlying, and 2) make recommendations for modifications to mitigate voltage and capacity fade.

GENERAL APPROACH: First-principles atomistic simulations and statistical mechanics approaches will be used to study the thermodynamic and kinetic processes that govern the electrochemical behavior of the lithium excess and related composite layered-layered or layered-spinel materials. Phase stability, defect formations in the Li, oxygen and cation lattices will be studied, as well as the migration paths for the mobile species.

STATUS OCT. 1, 2012: New project initiated October 1, 2012. First-principles calculations utilized to map out the layered Li₂MnO₃ (LMR), layered LiMnO₂ and LiMn₂O₄ phase diagrams, and structures including defect cation compositions to yield the possible stable and metastable delithiation and lithiation paths from the first charge and onwards. This will yield an understanding of the thermodynamically accessible phase space as a function of the oxygen release and possible cation rearrangements.

EXPECTED STATUS SEP. 30, 2013: Comprehensive phase diagrams as function of Li, O, Mn and defect (vacancies) in layered and spinel (defect) structures to inform on the stability as a function of SOC.

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

MILESTONES:

- (a) Map phase diagram including relevant bulk Li, O and Mn and defect phases in layered Li₂MnO₃. (Jun. 13) **On schedule**
- (b) Map phase diagram including relevant bulk Li, O and Mn and defect phases in layered LiMnO₂ (Sep. 13) **On schedule**
- (c) Map phase diagram including relevant bulk Li, O and Mn and defect phases in spinel LiMn₂O₄ (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

Collaborations: Gerbrand Ceder (MIT), Clare Grey (U Cambridge, UK). Mike Thackeray (ANL), Guoying Chen (LBNL).

The layered Li_2MnO_3 structure is a key material to explain the high capacity in layered-layered or layered-spinel composite electrode materials. Layered Li_2MnO_3 has been assumed to be largely electrochemically inactive due to the high oxidation state of Mn ($4+$ in the discharged state). Additions of Li_2MnO_3 to other spinel and/or layered materials have been used to increase the structural stability of the composite materials and allow more Li extraction than for the layered or spinel only materials. However, many recent experimental works have shown that the Li_2MnO_3 component is actually electrochemically active, which demands a re-examination of the conventional belief on the structural and chemical behavior of Li_2MnO_3 and the existing explanation of the origin of the high capacity in the composite materials.

A cluster expansion model of the ionic interactions in Li_xMnO_3 ($0 \leq x \leq 2$) is being developed and will predict the ground state as a function of Li. Density-functional theory is being used within the GGA+U formalism to describe the electronic state of the layered material. Hundreds of Li/Mn arrangements within the Li_2MnO_3 structure are being computed and used to fit the cluster expansion to arrive at a converged model of the coupled ionic interactions. Once converged, the model yields the corresponding voltage profile as a function of the Li content and chemical/structural evolution of the material. Stability against oxygen release is also being examined.

In experiments, layered Li_2MnO_3 shows a large ‘activation’ capacity (about 350 mAh/g) for the first charge, but then for the first discharge and later charge/discharge cycles it exhibits much lower capacity. It is believed to be due to the phase transformation to the spinel structure. In combination with the cluster expansion, possible phase transformations in the Li_2MnO_3 structure and their driving mechanisms are being computationally investigated, from first principles.

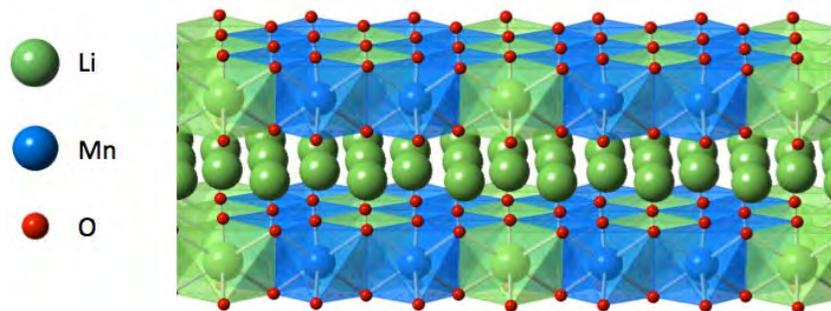


Figure 1. The crystal structure of Li_2MnO_3 where the Li layer is shown without local coordination spheres but the combined Li/Mn layer shows the blue octahedrally coordinated Mn and the green octahedrally coordinated Li ions.

Task 6.3 - PI, INSTITUTION: Gerbrand Ceder, Massachusetts Institute of Technology

TASK TITLE: Modeling — First Principles Calculations of Existing and Novel Electrode Materials

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Low rate capabilities; high cost; poor stability; low energy-density

OBJECTIVE: Develop more stable high capacity Li-excess layered cathodes. Develop high-capacity, high-rate Na-intercalation electrodes. Generate insight into the behavior of alkali-intercalating electrode materials.

GENERAL APPROACH: Use first-principles calculations (density functional theory) to identify redox-active metals, relative stability of different structures, mobility of Li- and transition-metal ions, and the effect of structure on rate capability. Anticipate possible instabilities in materials at high states of charge by using calculations.

STATUS OCT. 1, 2012: This is a new project initiated April 1, 2013.

EXPECTED STATUS SEP. 30, 2013: Models for Li transport in partially disordered Li-excess NMC materials will have been initiated. The phase diagram calculation of this material will have been started by studying the ground states of the Li-Ni-Mn-O and Li-Co-Mn-O system. An understanding of what determines the structure selection of Na_xMO₂ materials and its effect on rate will be reached.

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

MILESTONES:

- (a) Obtain relative stability of Na_xMO₂ materials in different structures: P2, P3, O3, O2 for M = single metal (Jun. 13) **On schedule**
- (b) Obtain ground state structures in the Li-Co-Mn-O and Li-Ni-Mn-O system covering layered, spinel, and the known ternary compounds in this space. (Sep. 13) **On schedule**
- (c) Initiate model study to understand Li transport in overcharged Li-excess materials. (Sep. 13) **On schedule**
- (d) Understand Na mobility difference between P2 and O3 structures (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

The project was awarded under the 2012 RFP and will officially start on April 1, 2013.

Task 6.4 - PI, INSTITUTION: Perla Balbuena, Texas A&M University

TASK TITLE: Modeling — First-principles Modeling of SEI Formation on Bare and Surface/additive Modified Silicon Anode

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Modeling different surface terminations; characterization of electron transfer through the SEI layer; description of SEI structure and evolution.

OBJECTIVE: Develop fundamental understanding of the molecular processes that lead to the formation of a SEI layer due to electrolyte decomposition on Si anodes, and use such new knowledge for a rational selection of additives and/or coatings.

GENERAL APPROACH: Focus is placed SEI layer formation and evolution during cycling and subsequent effects on capacity fade using two models: 1) SEI layers on bare Si surfaces, and 2) SEI layers on coated surfaces. Reduction reactions will be investigated with quantum chemistry (cluster-based) calculations on simplified models of electrodes; static ultra-high vacuum type DFT calculations of model electrodes with one electrolyte solvent/salt molecule; ab initio molecular dynamics simulations of the liquid-solid interface; and ab initio-Green's function theories to evaluate rates of electron transfer.

STATUS OCT. 1, 2012: This is a new project initiated on April 1, 2013. Preliminary DFT evaluations of Li_xSi_y surfaces will be initiated. A large pool of data has been obtained through literature search regarding current knowledge of Li_xSi_y cluster structures evaluated with quantum chemistry methods.

EXPECTED STATUS SEP. 30, 2013: Most stable Li_xSi_y surfaces will have been identified and adsorption of most common solvents characterized. Adhesion of common surface oxides (*i.e.*, SiO₂, Li₄SiO₄) on Li_xSi_y surfaces and reactivity of the composite surface will be evaluated. Assessment of electron transfer through simple models of SEI layers on model electrodes; surface effects on reduction reactions of EC, VC, FEC, including solvation effects characterized through cluster models, will be carried out.

RELEVANT USABC GOALS: Additives/coatings for improved SEI layers in Si anodes

MILESTONES:

- (a) Identify most favorable surfaces of bare Li_xSi_y periodic structures and characterize their reactivity. (Jun. 13) **On schedule**
- (b) Characterize geometric, electronic, and Li⁺ transport properties of surfaces coated with thin layers of SiO₂ and Li₄SiO₄ oxides. (Sep. 13) **On schedule**
- (c) Estimate maximum SEI layer thickness for electron transfer in model SEI films. (Jun. 13) **On schedule**
- (d) Characterize surface effects on EC, VC, FEC decomposition using cluster models of bare Li_xSi_y structures. (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

The project was awarded under the 2012 RFP and will officially start on April 1, 2013.

Task 6.5 - PI, INSTITUTION: Yue Qi, General Motors

TASK TITLE: Modeling — A Combined Experimental and Modeling Approach for the Design of High Current Efficiency Si Electrodes

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Low calendar and cycle life; low current efficiency, high cost

OBJECTIVE: Combine modeling and experimental approaches to understand, design, and make stabilized nanostructured Si anode with high capacity and high coulombic efficiency.

GENERAL APPROACH: In this project, four coherent steps will be taken: a) Develop a multi-scale model to predict the stress/strain in the SEI layer (including artificial SEI) on Si and establish a correlation between the capacity loss (or current efficiency) and mechanical degradation of SEI on Si; b) Use atomic simulations combined with experiments to provide critical material properties used in the continuum modeling; c) Investigate the impact of the SEI formation on the stress/strain evolution, combined with modeling to quantify the current efficiency related to a variety artificial SEI layers using *in situ* electrochemical experiments; d) Use the validated model to guide surface-coating design and Si size/geometry optimizations that mitigate mechanical degradation to both SEI and Si.

STATUS OCT. 1, 2012: This is a new project initiated on May 1, 2013. Collaboration between all CoPIs: Yue Qi (GM), Xingcheng Xiao (GM), Huajian Gao, (Brown U), Brian W. Sheldon (Brown U), and Yang-Tse Cheng (U. of Kentucky) has been established.

EXPECTED STATUS SEP. 30, 2013: In phase one of this project some key mechanical and electrochemical properties of non-coated and coated Si thin-film electrode will be determined.

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) Determine the elastic properties of artificial SEI on Si (including Li_xCO₃, AlO_x, SiO_x) *via* both atomic modeling and laser acoustic wave measurements. (May 13) **On schedule**
- (b) Correlate the interfacial charge-transfer kinetics and coating thickness on Si film electrode. (Jun. 13) **On schedule**
- (c) Evaluate the chemical composition of the initial SEI formed on uncoated Si thin-film electrodes. (Aug. 13) **On schedule**
- (d) Evaluate the evolution of stress and surface roughness of the Si electrode during SEI formation and growth in *in situ* cells to inform the continuum stress model. (Sep 13) **On schedule**
- (e) Formulate a theoretical framework to connect mechanical degradation and coulombic efficiency. (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

The project was awarded under the 2012 RFP and will officially start on May1, 2013.

Task 6.6 - PI, INSTITUTION: Dean Wheeler and Brian Mazzeo, Brigham Young University

TASK TITLE: Modeling — Predicting Microstructure and Performance for Optimal Cell Fabrication

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Cell performance, life, cost

OBJECTIVES: Develop rapid, reliable, and standardized methods for measuring electronic and ionic conductivities in porous electrodes. Determine and predict microstructures for porous electrodes. Understand tradeoffs and relationships between fabrication parameters and electrode performance.

GENERAL APPROACH: Use particle-based microstructural modeling, coupled with extensive experimental validation and diagnostics, to understand relationships between fabrication processes, microstructure, and corresponding electron and ion transport in composite electrodes. Assess electronic and ionic conductivities of porous electrodes attached to current collectors, including local heterogeneities and anisotropic effects, through the use of newly-designed instrumentation. Validate and parameterize the particle model using experimental microstructural and macroscopic properties. Use modeling and diagnostic tools to suggest processing conditions that will improve cell performance.

STATUS OCT 1, 2012: This is a new project initiated on April 1, 2013. Plans to accomplish the above objectives over a 4-year period are in place.

EXPECTED STATUS SEP. 30, 2013: Micro-four-line probe will have been fabricated and the utility of the measurement technique will have been demonstrated on laboratory-prepared and commercial films.

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

MILESTONES:

- (a) Fabricate first-generation micro-four-line probe to determine bulk electronic conductivity in non-delaminated battery films. (Sep. 13) **On schedule**
- (b) Develop mathematical-model inversion technique to determine current collector contact resistance from film measurements. (Sep.13) **On schedule**

PROGRESS TOWARD MILESTONES

The project was awarded under the 2012 RFP and will officially start on April 1, 2013.