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December 13, 2012

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 fourth quarter FY 2012 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,

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

SIX FEATURED HIGHLIGHTS

Anodes–

- ✦ Liu and Zhang's Group develops a B₄C-supported Si electrode capable of 3500 mA/g and good cycling stability.
- ✦ Cui's Group uses *in situ* TEM to measure the rate of penetration of Li into a Si particle, demonstrating that it is dependent on the stress at the Si/Li-Si interface.

Electrolytes –

- ✦ Henderson's Group shows that the more viscous oxalate-anion-based electrolytes are more conductive than the less viscous tert-fluoroborate-anion-based electrolyte presumably due to higher levels of solvation of the oxalates.

Cathodes–

- ✦ Manthiram's Group demonstrates that the rate capability and cyclability of high-voltage Ni-spinel depends on which facets are predominantly in contact with the electrolyte.

Diagnostics –

- ✦ Grey's Group demonstrates the capability of *in situ* electrochemical synchrotron XRF imaging in resolving the mechanism of insertion/displacement materials *vs.* time.

Modeling–

- ✦ Newman's Group discovers that at a high open-circuit-potential, the SEI film on the anode becomes more porous with time.

BATT TASK 1

CELL ANALYSIS

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

TASK TITLE – PROJECT: Cell Analysis - Electrode Fabrication and Failure Analysis

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

BARRIERS: High energy systems: low energy; moderate cycle life; moderate calendar life

OBJECTIVES: There are six overarching objectives associated with this task. 1) To bring fundamental understanding to the electrode fabrication process. 2) To make “good” electrodes and “good” cells. Good electrodes means electrodes that help identify chemical and physical limitations of a material, be it an active or inactive component. Good cells mean that the material is being evaluated in an environment consistent with what is found in a large size, industrially produced cell. 3) Determine the source or sources of electrode and cell failure and provide samples from used cells for diagnostics. 4) Provide a means for testing electrochemical models. 5) Provide a resource for others in the BATT program for making their own cells.

GENERAL APPROACH: These objectives are accomplished through methodically changing different aspects of the electrode fabrication process and examining the results of the changes *via* electrochemical, physical, and chemical characterization techniques. They are also carried out through close collaboration with other BATT PIs, publishing and speaking about all of our findings, and the willingness to share our resources and produce electrodes and cells as requested.

STATUS OCT. 1, 2011: Powders of LiNi_{1/2}Mn_{3/2}O₄ from NEI were distributed to interested PIs as well as an electrolyte of 1 M LiPF₆ in EC:DEC 1:2 from Daikin, America. After a large initial capacity loss in a full cell, the NEI high-voltage spinel material shows good cyclability. VC has a higher reduction potential than EC but with slower kinetics. Slow formation processes of cells with and without VC do not show significant differences in the rate of the side reactions.

FY 2012 AOP EXPECTED STATUS SEP. 30, 2012: Differences in performance of a baseline electrolyte *versus* a “high-voltage” electrolyte against LiNi_{1/2}Mn_{3/2}O₄ will be elucidated. The effects of mixing time on electrode uniformity and performance will have been studied. The dissolution of spinel materials will be measured at 55°C.

RELEVANT USABC GOALS: PHEV-40: 207 Wh/l; 5000 deep-discharge cycles; 15 years.

MILESTONES:

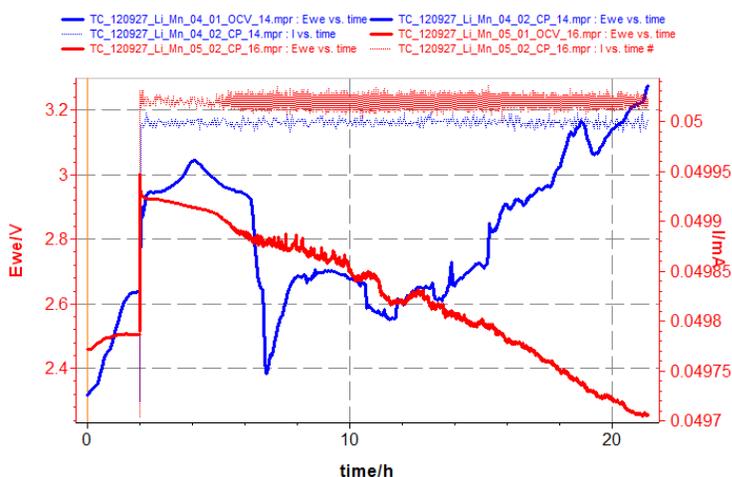
- (a) Measure the difference in performance of our baseline electrolyte when compared to a high voltage electrolyte from industry. (Dec. 11) **Complete**
- (b) Evaluate the effects of mixing time on cell performance. (Apr. 12) **Complete**
- (c) Compare the rate of side reaction and capacity fade of Gr./NCM* with and without VC. (Apr. 12) **Complete**
- (d) Measure the rate of dissolution of a spinel material containing Mn. (Sep. 12) **Complete**

PROGRESS TOWARD MILESTONES

- Measure the difference in performance of our baseline electrolyte when compared to a high voltage electrolyte from industry. Dec. 2011 **Complete** (Reported in 1st Quarterly).
- Evaluate the effects of mixing time on cell performance; April 2012 **Complete** (Reported in 3rd Quarterly.)
- Compare the rate of side reaction and capacity fade of Gr/NCM with and without VC. April 2011 **Complete** (Reported in 2nd Quarterly)
- Measure the rate of dissolution of a spinel material containing Mn; Sept 2012 **Complete**.

If the US hopes to see more EVs on the road, the batteries will have to be less expensive and last 10 years or more. Since Mn-based cathodes are generally less expensive than Co- and Ni-based cathodes, many cell manufacturers look to include Mn in their cathode formulations. It is well known that cathodes that contain Mn typically lose Mn in the electrolyte and that the loss of Mn from the cathode in a week's time is typically less than 1%, while the loss of cycleable capacity of the full cell is much greater. It is understood that this loss in cycleable capacity is due to a loss of cycleable Li, as the Mn in the electrolyte leads to degradation of the SEI on the anode that requires cycleable Li to repair it.

Because Mn is so important with regard to developing low-cost batteries, it is important to understand the mechanism for its loss from the cathode, as limiting the dissolution is the most straight forward way to curtail its negative impacts. By knowing the electrochemical potential of the species involved in a dissolution process, one can calculate the driving force for Mn dissolution. In water, Mn is known to oxidize to Mn^{2+} at 1.86 V vs. a Li/Li⁺ electrode in water. This quarter, our group tried to make this measurement for Mn in EC:DEC 1:2 with 1 M LiPF₆. The graph shows the results for two cells. Electrodes were made from Mn metal chips that were sanded in a glovebox to remove Mn oxidation products. The chips were assembled into coin cells against Li counter electrodes and left at open circuit (OC) for two hours, then a small current was passed through the cells (50 μA).



The data shows that the cell voltage leveled off at around 2.5 V after the two hour OC and then jumped to 2.8 V once the small oxidizing current was initiated. This test was repeated using a LiMn_2O_4 electrode as the counter electrode. Again, the Mn electrode went to 2.8 V vs. a Li/Li⁺ reference electrode in EC:DEC once the small current was initiated.

This data indicates that the combination of activities of Mn^{2+} and Li⁺ in EC:DEC electrolyte is much less than in water, which suggests that the driving force for dissolution should also be less.

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

TASK TITLE - PROJECT: Cell Analysis - Cell and Component Diagnostics

BASELINE SYSTEMS: 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: 5,000cycles/58 MWh).

OBJECTIVES: Investigate the relationship of structure, morphology and performance of cathode and anode materials. Explore kinetic barriers, and utilize the knowledge gained to design and develop cells with improved energy density, rate performance and stability.

GENERAL APPROACH: Employ XRD, visible and electron microscopy, vibrational spectroscopies, and electro-analytical techniques to determine their applicability to BATT goals. Characterize known and modified electrode materials and establish correlations between performance and factors such as crystal structures, morphologies, and surface chemistry. Provide guidelines for materials synthesis and electrode fabrication processes.

STATUS OCT. 1, 2011: To have developed new techniques for visualizing the distributions of both materials and charge in lithium battery electrodes. These have been applied to LFP cathodes.

FY 2012 AOP EXPECTED STATUS SEP. 30, 2012: Additional methods will have been demonstrated for diagnosis and evaluation of cell components. Charge distribution diagnostics will have been applied to electrodes harvested from commercial cells.

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 charge distribution assessments of harvested cathodes. (Mar. 12) **Complete**
- (b) Develop new optical microscopy methods for *in situ* and *ex situ* diagnosis of electrode and separator chemistries. (Aug. 12) **Complete – improvements/tests ongoing**

PROGRESS TOWARD MILESTONES

A new technique (LIBS) has been developed. Some further improvements in sampling conditions and standardization are needed before it can be used routinely.

Charge distribution: A 1.1 Ah A123 Racing Nanophosphate cell was discharged at 30 A to 50% state of charge (SOC). The cell was disassembled and the charge distribution in the cathode (Fig. 1) was determined by conventional XRD with a sample area of about 2 mm x 5 mm.

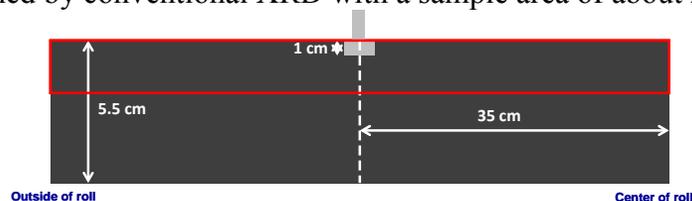


Figure 1. Cathode harvested from 1100 mAh 18650 nanophosphate cell.

Both anode and cathode had a single tab at the center of one edge. The cathode surface (Fig. 2.a) was fractured and non-uniform, most likely due to calendaring. The interior, however, was quite uniform, with 50 μm particles and a bimodal distribution of 100 nm and 1 μm pores (Fig. 2.b, c).

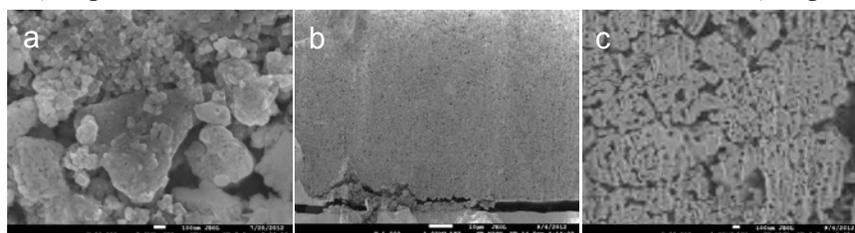


Figure 2. SEM images of a) surface and b, c) ion-milled cross section of A123 cathode at different magnifications.

The SOC along the lower edge of the rectangle in Fig. 1 was found to vary with distance from the tab. The overall SOC was much lower than expected, indicating that the cell may have been shorted during disassembly, though no evidence for this was observed at the time. The extent of discharge was significantly greater in the cathode area that was near the center of the jelly roll. It may be that the components were more intimately compressed there than near the outside of the roll; that the interior of the roll was wetted by the electrolyte more effectively; or that the substantial heat generated during discharge resulted in a higher temperature in the center.

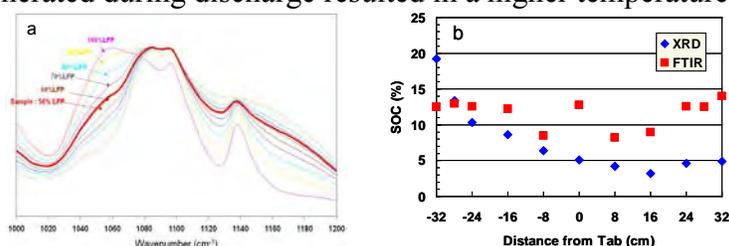


Figure 3. a) Transmission FTIR spectra of LFP/FP mixtures; b) cathode SOC from XRD and FTIR.

SOC was also determined from transmission FTIR spectra (Fig. 3.a) of samples scraped from the electrode at the same locations and diluted in KBr. These results (Fig. 3.b) were inconsistent with the XRD data, possibly due to poor dispersion of the active material which is strongly bound to the carbon black and binder.

In situ diagnostics: Correlations of concentrations of polysulfide species with distance between the electrodes in transparent Li-S cells have been thwarted due to the emergence of the highly complex time dependence in their distributions even under steady-state current conditions.

Collaborations: Guoying Chen, Vassilia Zorba, Jordi Cabana, National Center for Electron Microscopy, Advanced Light Source, and Stanford Synchrotron Radiation Laboratory.

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

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

BASELINE SYSTEMS: 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

OBJECTIVES: Synthesis and evaluation of high voltage cathode (spinel Mn-Ni) with improved electrochemical stability. Reduce the oxidation of the cathode composition, electrolyte, and separator. Find the appropriate alternative anode material composition that meets the requirement for low cost and high energy. Continue the development of binders for the cathode and alternative anode to understand and improve the properties of the SEI layer.

GENERAL APPROACH: Our approach is to develop an appropriate method to stabilize the interface reaction of the high voltage oxide (Mn-Ni based like LiMn_{1.5}Ni_{0.5}O₄) by surface coating with more stable material like olivine. The emphasis is to improve electrochemical performance at high voltage. Binder type, electrolyte composition, separator will be investigated at this level of voltage. Going with high capacity anode; Si based anode composition will be optimized in terms of particle size (micro vs. nano), graphite and SiO_x content.

STATUS OCT. 1, 2011: Effort is oriented to silicon based anode alloys; LiMn_{1.5}Ni_{0.5}O₄ based cathode and SEI study and its stabilization. Work will start on these items in August by exploring an appropriate composition of anode material based on carbon coated nano-silicon, SiO_x and graphite. More work on high voltage cathode will be addressed by reducing its oxidation problem with electrolyte.

FY 2012 AOP EXPECTED STATUS SEP. 30, 2012: Due to its low cost and high capacity, the development of silicon-oxide anodes material will continue to achieve the DOE objectives, research will be conducted to find a suitable composition of the Si-based high capacity anode. Different anode composition; pure Si and its mixing with SiO_x and graphite will be investigated. For the cathode side, as recommended by the DOE, high voltage cathode based on Mn-Ni spinel oxide will be used in this work. In order to reduce the oxidation of the electrolyte at high voltage, some items will be considered; more stable binder, different electrolyte composition, carbon additives and surface coating of this high voltage cathode. With the scope of the work tendency, the investigation of SEI layer on both sides of the anode and cathode is essential. Many parameters will affect this SEI layer; binder type, electrolyte composition, the cathode and anode composition.

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 a candidate of a silicon based composition as anode material. (Mar. 12) **Complete**
- (b) Demonstrate stabilized high-voltage LiMn_{1.5}Ni_{0.5}O₄ spinel cathode material with surface-coated of ceramic and oxides material. (Sep. 12) **Complete**
- (c) Complete the development the *in situ* SEM analysis of the Si-based anode. (Sep. 12) **Complete**

PROGRESS TOWARD MILESTONES

In this quarter, the post-mortem analysis of a Si-based anode was completed by addressing the effect of cycling. The electrode was prepared using a PEO-LiTFSI-based polymer binder and then cycled in an SEM at 80°C. A large increase in the primary particle size was observed. Before cycling, the particles' size ranged between 72 and 180 nm, but after cycling the particles' size increased from 110 to 640 nm. A very large Si expansion, in the absence of particle cracking, was observed at around 0.045 V during the 2nd discharge (Fig.1). It appears that "electrochemical sintering" is occurring between the particles. In addition, some polymer was present between the sintered particles. This morphology was not seen in the initial state before cycling. More effort is needed to resolve the challenges surrounding this material.

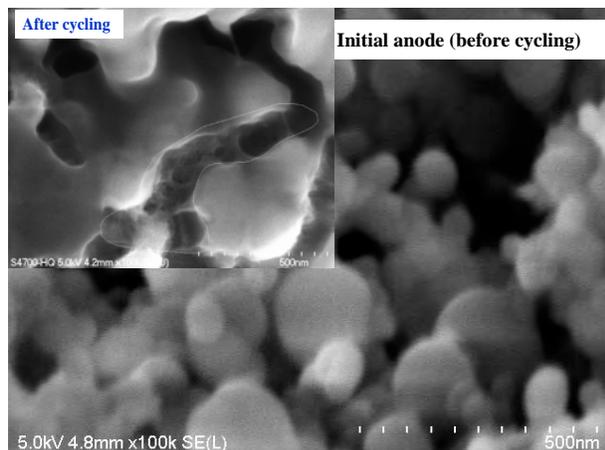


Figure 1. SEM photos of Si-nano-polymer anode, before and after cycling in SEM.

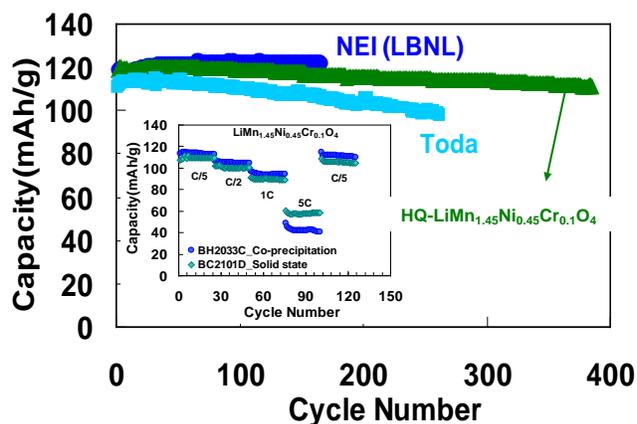


Figure 2. Cycling of HQ-LiMn_{1.45}Cr_{0.1}Ni_{0.45}O₄ compared to commercial materials vs. Li in EC-DEC-LiPF₆.

For the high-voltage cathode, the effort on doped LiMn_{1.5}Ni_{0.5}O₄ was completed by producing materials by co-precipitation (CP) and by a solid state (SS) method. It was found that a post-annealing step at lower temperature is beneficial towards modifying the oxygen deficiency while maintaining a disordered structure. Cr³⁺ doping was selected due to its electrochemical activity at *ca.* 4.8 V. A small amount of Cr was used to substitute equal amounts of Ni²⁺ and Mn⁴⁺ to keep the Mn⁴⁺ oxidation state unchanged ($2\text{Cr}^{3+} = \text{Ni}^{2+} + \text{Mn}^{4+}$) and to improve the cycling. It was found that with the Cr substitution, the impurity phase (Li_xNi_{1-x}O) was eliminated after the re-annealing step. The cycle life at 1C of the CP material when compared to the commercial material showed good cyclability, achieving 390 cycles. The materials obtained from the two techniques, CP and SS, were also compared. Cycling of these materials at 25°C at different rates shows comparable capacities at low rates (Fig. 2 inset). At high rates (5C), the reversible capacity was 58 mAh/g and 42 mAh/g for the SS and CP methods, respectively. This result confirms the attractive quality of material synthesized *via* the SS method. HQ has the facilities to scale-up the spinel cathode materials for evaluation by other BATT researchers upon request.

HQ is continuing its collaboration with LBNL researchers Vince Battaglia and Robert Kostecki in the BATT program. 10 g of LiFSI, produced by HQ, was sent to Vince Battaglia for evaluation.

TASK 1.4 - PI, INSTITUTION: Yet-Ming Chiang, Massachusetts Institute of Technology

TASK TITLE - PROJECT: Cell Analysis – New Electrode Design for Ultrahigh Energy Density

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

BARRIERS: High energy system: low energy, poor cycle life

OBJECTIVES: Develop a scalable high density binder-free low-tortuosity electrode design and fabrication process to enable increased cell-level energy density compared to conventional Li-ion technology for a range of electrode-active materials. Characterize transport properties in high voltage Ni-Mn spinel.

GENERAL APPROACH: Fabricate high density sintered cathodes and anodes with controlled pore volume fraction and pore topology. Electrochemically test electrodes in laboratory half-cells and small lithium ion cells (<100 mAh), and model electrode response. Aim to increase cell-level specific energy and energy density by maximizing electrode density and thickness, under operating conditions commensurate with USABC targets for PHEV and EV. Titrate Li content in pure single phase sintered porous electrodes while measuring electronic and ionic transport.

STATUS OCT. 1, 2011: 1) Fabrication and testing of at least two cathode materials in the proposed high density low tortuosity electrode approach; 2) Development of methodology for measurement of electronic conductivity vs. Li concentration in porous sintered electrodes.

FY 2012 AOP EXPECTED STATUS SEP. 30, 2012: 1) Conclude electrode fabrication and electrochemical testing in at least one targeted cathode compound; 2) Fabrication and testing of high density low tortuosity electrodes of at least one anode compound; 3) Conclude measurement of electronic conductivity vs. x in sintered undoped Li _{x} Ni_{0.5}Mn_{1.5}O₄

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

MILESTONES:

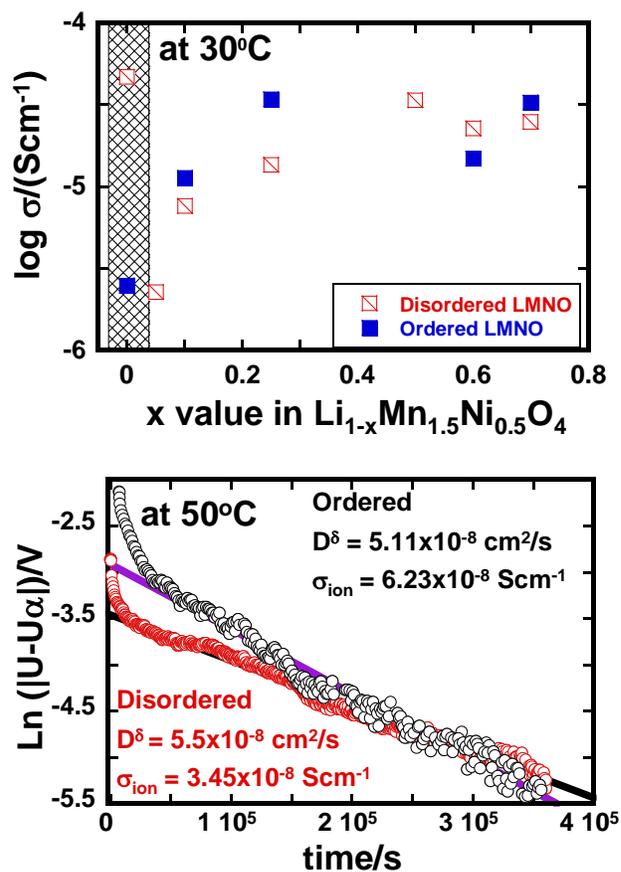
- (a) Demonstrate >80% capacity retention at 2C rate in additive-free low tortuosity LiCoO₂ electrode of >50 vol% density and >200 μ m thickness. (Oct. 11) **Complete**
- (b) Complete measurement of electronic conductivity vs. x in sintered undoped Li _{x} Ni_{0.5}Mn_{1.5}O₄. (Jan. 12) **Complete**
- (c) Complete measurement of electronic conductivity vs. x in sintered Li₄Ti₅O₁₂ anode. (Jan. 12) **Complete**
- (d) Develop tortuosity measurement for freeze-cast/sintered cathodes. (Mar. 12) **Complete**
- (e) Complete process development study for directionally freeze-cast and sintered LiNi_{0.5}Mn_{1.5}O₄ cathodes. (Jun. 12) **Complete**

PROGRESS TOWARD MILESTONES

Collaborator: Antoni P. Tomsia (LBNL)

Accomplishments: During the present reporting period, further progress was made in measuring the electronic and ionic transport in $\text{Li}_{1-x}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LMNO) as a function of temperature and Li content. Measurements were performed on additive-free, sintered LMNO, and, therefore, reflect purely on the spinel phase conductivity. Samples were fired at 900 or 1000°C, followed by a 48 h hold at 650°C where the ordered phase was desired. Electrochemical delithiation was conducted to obtain a range of x values. Silver paste electrodes were used as ion-blocking electrodes for the measurement of electronic conductivity (Ag/LMNO/Ag), while PEO-based solid polymer electrolyte was used as ion-conducting/electron-blocking electrodes (Li/PEO/LMNO/PEO/Li) for the measurement of ionic conductivity. The latter measurements were conducted at *ca.* 50°C to ensure sufficient ionic conductivity in the electrodes. Representative results are shown below. The electronic conductivity of fully-lithiated, *disordered* spinel is one and a half orders of magnitude higher than that of fully-lithiated, *ordered* spinel. In the ordered samples, the electronic conductivity increased monotonically with increasing x , while in the disordered LMNO, the higher initial conductivity first dropped, to about the same value as in the ordered LMNO, before increasing monotonically with increasing x . Both ordered and disordered LMNO exhibit semiconducting behavior at all Li concentrations, wherein the electronic conductivity increases with temperature.

The ionic conductivity of fully-lithiated samples of both ordered and disordered spinel was measured using the dc-polarization method (example shown) as well as by ac-impedance spectroscopy. Good agreement was obtained between the two methods, with the ionic conductivity measuring 5×10^{-8} S/cm at *ca.* 50°C, about 10^3 lower than the electronic conductivity at the same temperature. The chemical diffusion coefficient at the same temperature is 5×10^{-8} to 10^{-7} cm^2/s . The results clearly show that the chemical diffusion is limited by ionic rather than electronic transport. Within experimental variability, no significant difference was found in ionic transport between the ordered and disordered spinel. Preliminary results of partially-delithiated, ordered spinel ($x = 0.1$) indicates that the ionic conductivity decreases with delithiation.



TASK 1.5 - PI, INSTITUTION: Gao Liu, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Cell Analysis - Advanced Binder for Electrode Materials

BASELINE SYSTEMS: 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: Develop new conductive polymer binder materials to enable large volume change lithium storage materials to be used in lithium-ion electrode.

GENERAL APPROACH: Use functional polymer design and synthesis to develop new conductive polymers with proper electronic properties, strong adhesion and improved flexibility to provide electric pathways in the electrode, and to accommodate large volume/phase change of the active material during lithium insertion and removal.

STATUS OCT. 1, 2011: Gained fundamental understanding of the Si particle surface properties to the electrode performance characteristics; developed HF etching process to clean off SiO₂ surface layer for improved initial performance; demonstrated change of porosity of the cycled Si/conductive polymer electrode as a main issue to prevent high loading electrode from stable cycling, demonstrated over 600 cycles of the Si/conductive polymer composite electrode between 0.01-1V vs. Li/Li⁺ with less than 15% capacity loss, and demonstrated initial cycling performance of the Sn/conductive binder electrode.

FY 2012 AOP EXPECTED STATUS SEP. 30, 2012: Investigate conductive binder properties to Si electrode performance in various electrode compositions and configurations; explore electrolyte and additives to increase coulomb efficiency; and explore the conductive binders in other high capacity material systems.

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

MILESTONES:

- (a) Continue to optimize the Sn/conductive binder electrode system to achieve 600 mAh/g-Sn specific capacity cycling. (Mar.12) **Complete**
- (b) Study conductive binder properties to Si electrode performance in various electrode compositions and configurations, aim to achieve 3.5 mAh/cm² loading electrode. (Sep. 12) **Complete**
- (c) Develop one type of electrolyte additives and select Si materials to minimize side reactions, and increase coulombic efficiency to 99.5%. (Sep. 12) **Complete**

PROGRESS TOWARD MILESTONES

It is a challenge to fabricate Si-particle-based electrodes at high area-specific loadings of at least 3 mAh/cm² as the Si material volume expansion during lithiation disrupts the integrity of the composite electrode. A secondary particle Si/PFFOMB[1] composite approach was developed in order to stabilize the primary particle level volume expansion (Fig. 1 inset). The composite particles have three components: Si nanoparticles, electrically conducting polymer, and open porosity. During lithiation, the primary particles' volume expands into the conductive polymer and open porosity, while the composite of particles maintains its shape and volume. Thus, the overall electrode structure is not interrupted during cycling. This approach has shown promising cycling results for an electrode loading at 3.5 mAh/cm² (Fig. 1).

The coulombic efficiency (CE) is another important parameter for Si-based electrodes - the CE is a measure of the side reactions in the electrode. Due to the volume change, Si has an ever changing exposed surface area; this results in a low, persistent CE and fast fading of full cells. Electrolyte additives have routinely been used to improve the cycling stability of graphite-based Li-ion batteries, including the use of VC. VC was added to a cell with a Si/PFFPMB-based electrode. Increasing the amount of VC in the electrolyte significantly enhanced the CE of the Si electrode and stabilized the cycling capacity (Fig. 2). At 10% of VC in the electrolyte, the CE reached 99.5% after 90 cycles.

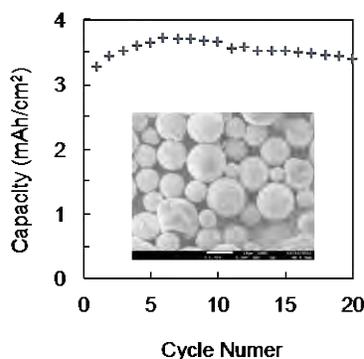


Figure 1. Si/PFFOMB conductive polymer electrode over 3.5 mAh/cm² area specific capacity. The in-set SEM image is of the composite Si/PFFOMB particles (scale bar is 10 μm).

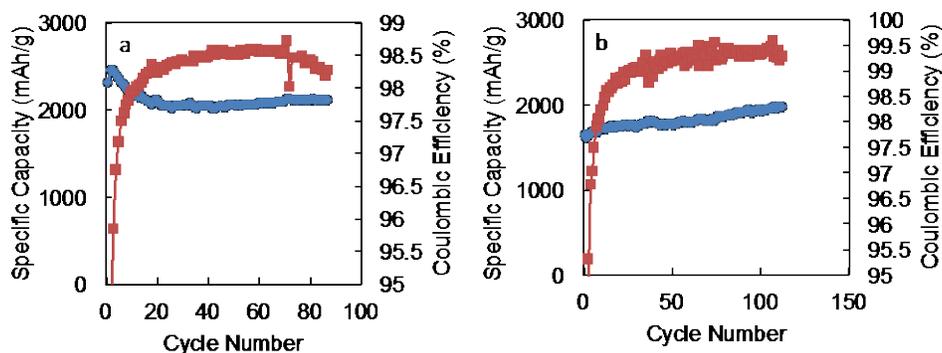


Figure 2. Cycling stability and coulombic efficiency of the Si/PFFOMB electrode at (a) 2% VC and (b) 10% VC in the electrolyte.

[1] PFFOMB stands for poly(9,9-dioctylfluorene-co-fluorenone-co-methylbenzoic ester).

TASK 1.6 - PI, INSTITUTION: Guoying Chen, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Cell Analysis - High-Energy Cathodes - Improving Performance, Safety, and Cycle Life through Structure and Morphology Design

BASELINE SYSTEMS: 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: Identify phase transition mechanisms and kinetic barriers of high voltage and high capacity cathode materials. Establish direct correlations between crystal structure, composition, morphology, performance and stability. Provide guidelines to design and fabricate cathode materials with improved energy density, rate capability and safety, especially with regard to thermal stability.

GENERAL APPROACH: Prepare well-formed crystals with various structure, composition, size and morphology using wet synthesis routes, such as solvothermal and molten salt methods. Characterize their physical properties and investigate their solid state chemistry using advanced spectroscopic, spectromicroscopic, scanning calorimetry and electron microscopic techniques.

STATUS OCT. 1, 2011: Overlithiation in Li_{1+x}(Ni_{0.33}Mn_{0.33}Co_{0.33})_{1-x}O₂ (NMC333) was found to increase extractable Li in the structure and energy density of the cathode. Increasing Mn content in the overlithiated NMC333 improves rate capability but decreases the stability of the initial O3 phase, which transforms to P3 structure upon deep Li extraction. The irreversible charging plateau observed at high voltage was attributed to overlithiation in Li_{1+x}M_{1-x}O₂. LiNi_{0.5}Mn_{1.5}O₄ single crystals were synthesized in a variety of sizes and shapes, with the best performance achieved with the octahedral micron-sized crystals. Large crystals with a range of Mn³⁺ content were prepared by varying the Ni/Mn ratio in LiNi_xMn_{2-x}O₄. Synthesis precursors were found to influence the transition-metal ordering in the prepared spinel.

FY 2012 AOP EXPECTED STATUS SEP. 30, 2012: The effect of structural, composition and morphological changes during Li extraction and insertion in Li_{1+x}M_{1-x}O₂ will have been further evaluated. Oxygen evolution mechanism and kinetics will have been investigated. The effect of particle size and morphology on oxide activation process and electrode stability will have been revealed. The impact of Mn³⁺ content on property and performance of LiNi_xMn_{2-x}O₄ cathode will have been established, and the kinetics of structural disordering in the spinel examined.

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

MILESTONES:

- (a) Investigate the kinetics of order/disorder transitions in LiNi_xMn_{2-x}O₄. (Mar. 12) **Complete**
- (b) Determine the effect of Mn³⁺ content on property and performance of the spinels. (Jun. 12) **Complete**
- (c) Investigate the mechanism and kinetics of delithiation/relithiation on oxide crystals. (Aug. 12) **Complete**
- (d) Synthesize at least four oxide crystal samples with different physical characteristics. (Sep. 12) **Complete**

PROGRESS TOWARD MILESTONES

Li-excess Layered Oxides: Phase-pure $\text{Li}_{1.2}\text{Mn}_{0.13}\text{Ni}_{0.54}\text{Co}_{0.13}\text{O}_2$ (alternatively $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiMn}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{O}_2$) crystals with four different morphologies were synthesized by the molten-salt method. Synthesis temperature, time, precursors, and flux were found to largely control the size and shape of the crystals. For example, in the temperature range of 750 to 900°C, micron-sized hexagonal-shaped crystal plates were obtained when nitrate precursors and CsCl flux (m.p.= 645°C) were used. Synthesis at 850°C for 16 h produced crystals with the best uniformity in size and morphology, as shown in the SEM image in Fig. 1a. Replacing CsCl flux with KCl (m.p.= 770°C) led to the formation of needle-shaped crystals in 2 μm length and 100 nm diameter (Fig. 1b). Regardless of the flux, cuboctahedral-shaped crystals were obtained when oxide precursors were used, with micron-sized crystals (Fig. 1c) synthesized in CsCl and much smaller crystals of 100 to 200 nm (Fig. 1d) made in NaCl flux (m.p.= 801°C).

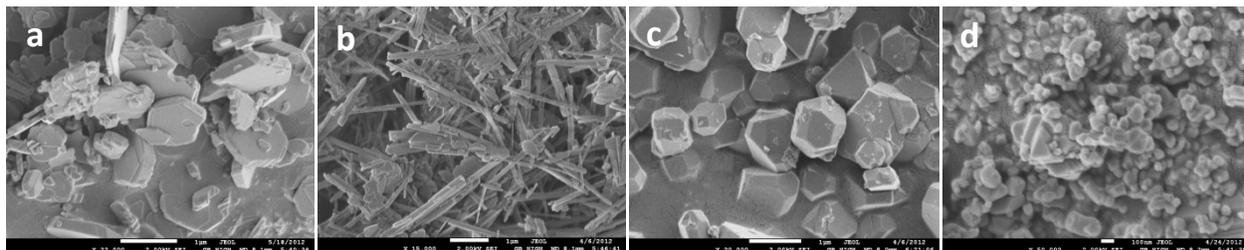


Figure 1. SEM images of $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}\text{O}_2$ crystals synthesized from: a) nitrate precursors in a CsCl flux, b) nitrate precursors in a KCl flux, c) oxide precursors in a CsCl flux, and d) oxide precursors in a NaCl flux.

Electrochemical performance of the crystal samples were evaluated by half-cell cycling of the composite electrodes consisting of the oxide crystals (80 wt%), a carbon additive (10 wt%), and PVdF binder (10 wt%). Figure 2 (top) compares the first-cycle voltage profiles of the $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}\text{O}_2$ cells when charged and discharged at a current density of 10 mA/g. All cells showed an activation plateau at around 4.5 V, but higher polarization and a much shorter plateau length were observed in the cell with the micron-sized cuboctahedrons. While both the plate- and needle-shaped crystals delivered large capacities close to the theoretical value, the cuboctahedron samples had lower capacities that are directly proportional to their level of first-charge activation. The effects of particle size and morphology were further demonstrated in a rate capability comparison, as shown in Fig. 2 (bottom). The plates consistently delivered the highest capacity at all rates, while the large cuboctahedrons yielded the lowest capacities among the tested samples. This report completes the work toward milestones (c) and (d) in FY12.

Collaborations this quarter: Richardson, Grey, Cabana, Kostecki, Doeff, Chiang, Lucht, SSRL, and NCEM.

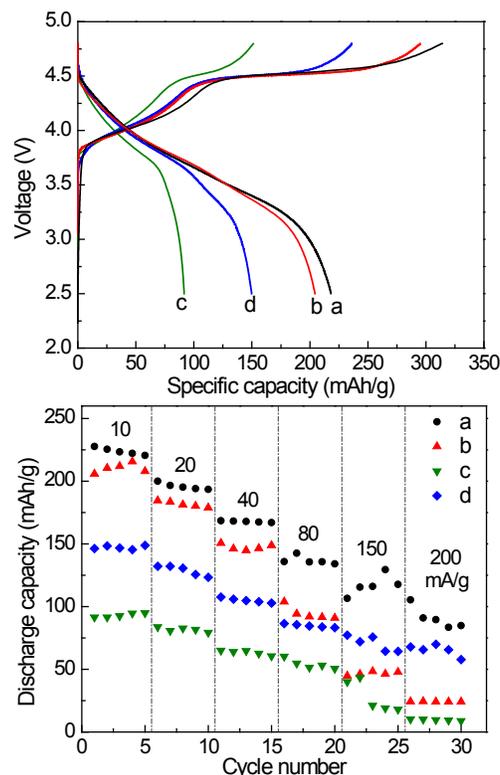


Figure 2. Top: First-cycle charge and discharge voltage profiles and Bottom: rate capability comparison of the $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}\text{O}_2$ crystals.

BATT TASK 2

ANODES

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

TASK TITLE - PROJECT: 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 address and 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: Our approach is 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, 2011: A series of new electrode structures will have been synthesized and evaluated that use elemental silicon and tin as the active material. The energy and power advantages of three-dimensional electrode architectures when compared to two dimensional anode structures will be quantified. Electrodes that utilize metallic copper as both the binder and conductive additive will have been evaluated. Methods to create the three dimensional copper current collector around the active materials, notably silicon, will have been developed.

FY 2012 AOP EXPECTED STATUS SEP. 30, 2012: The interfacial structure of silicon-based electrodes bound to the substrate using metallic binders will have been determined. Studies will have been initiated on the deposition of silicon and tin into porous substrates and developed characterization tools to study active material/current collector interactions and their effect on cycle life and fade rate.

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) Complete characterization of the interfacial region in Cu-Si metallic electrodes. (Mar. 12) **Complete**
- (b) Characterize the phases formed and extent of electrode homogeneity for a series of electrodeposited Sn-based electrodes. (Sep. 12) **Complete**
- (c) Assess the role of electrolytes and irreversible capacity and SEI formation in three-dimensional electrode structures. (Sep. 12) **Delayed, due Mar. 13**
- (d) Demonstrate the benefit of polymeric surface coatings on the cycle life of three-dimensional electrode structures. (Sep. 12) **Delayed, due Sep. 13**

PROGRESS TOWARD MILESTONES

Team: Fulya Dogan, Lynn Trahey, Duminda Sanjeeva, Jack Vaughey

In alignment with BATT goals our task has been to explore the amount of Si that can be electrodeposited within a foam structure and correlating the performance with the electrochemical and physical properties. Two different foam structures have been chosen to compare – both made from Cu metal – that represent different levels of porosity. The purpose of the support foam is two-fold: 1) to act as a platform for the Si electrodeposition and maintain porosity of the active electrode, and 2) to act as a substrate that provides constant volume to the anode while providing a high capacity. At the present time the BATT-Anode goal is approximately 6 mg/cm^2 of active Si. Our concurrent metallic binder studies, still under study, have met the loading goals but not performance lifetime. The electrodeposition studies to date have a much better cycling lifetime but have lower loadings ($\sim 1 \text{ mg/cm}^2$).

In this report, the electrodeposition technique (constant potential or constant current) was assessed based on the morphology and thickness of the films produced and their electrochemical performance. Figure 1 highlights the differences in morphology and appearance of two representative films.

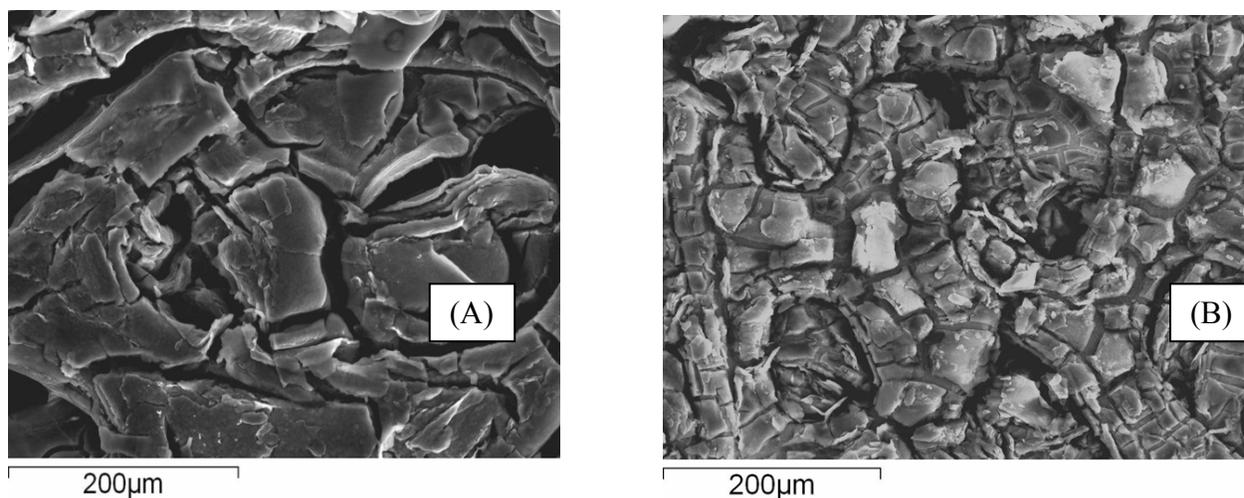


Figure 1. Post 1st cycle SEM of two films deposited over a 2-hr period and cycled vs Li in the range of 0.1-2 V in Gen2 electrolyte. Film (A) was fabricated under constant potential (-3.3V), and Film (B) under constant current (-50 mA).

Using the method recently published by Kumta, *et al.*, (*Mat Sci Eng B*, 2012) it was estimated that the amount of active material of Film (A) is 1.9 mg/cm^2 and of Film (B) is 2.4 mg/cm^2 . Based on preliminary data, the rougher film produced under constant current conditions had superior capacity retention than the initially smoother film from constant potential. In both cases the first-cycle irreversible capacity was 60 to 70%, in agreement with literature values. This value is high *versus* dense Si films (*ca.* 40 to 50%) but comparable to nanoparticles of Si and laminates derived from SiO (*ca.* 70%). The difference when compared to dense Si films and the similarity to Si nanoparticles may arise from the similarly high surface areas (SEI formation) and from the inclusion of secondary phases within the electrode structure, *e.g.*, Li₂O, LiCl (from SiCl₄ - the source of Si for the electrodeposition), that are generated during formation.

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 lithium (to minimize risk of Li plating and thus enhance safety) and have higher volumetric energy densities than carbon. Emphasis will be placed on simple metal alloys/composites at the nano-size. Tin will initially be emphasized, building on what was learnt 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, 2011: It has been shown that bulk crystalline metals have a high capacity, react readily with lithium but that their capacity faded rapidly after several deep cycles in carbonate-based electrolytes; their behavior was no better under shallow cycling. In contrast, it has been shown that amorphous nano-size tin alloys, unlike pure tin, have a high capacity and maintain it on deep or shallow cycling, when stabilized with elements like cobalt. A nano-tin material that shows electrochemical behavior comparable to that of the Sn-Co alloy but without the need for cobalt was successfully formed by mechanochemical synthesis. It has also been shown that small amounts of silicon enhance the cyclability of aluminum.

FY 2012 AOP EXPECTED STATUS SEP. 30, 2012: Our 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. Nano-tin materials will have been synthesized by at least two different approaches and then characterized, to determine their morphology and electrochemical behavior. Clues as to how to control the SEI on such materials to optimize lifetime will have been gathered.

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) Synthesize a nano-size Sn material by a second method. (Dec. 11) **Complete**
- (b) Have the nano-size Sn meet the gravimetric capacity of the Sn-Co-C electrode and exceed the volumetric capacity of the Conoco Philips CPG-8 Graphite. (Mar. 12) **Complete**
- (c) Determine the limitations to the electrochemical behavior of the mechanochemical Sn; characterize these materials and determine their electrochemical behavior. (Sep. 12) **Complete**
- (d) Determine the electrochemistry of a new synthetic nano-Si material. (Sep. 12) **Complete**

PROGRESS TOWARD MILESTONES

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

Milestone (d): This quarter reports a synthesis of a new synthetic nano-Si material and the initial electrochemical measurements performed on it. A low-cost Al-Si engine-block alloy was used as the starting material. The powder was etched in aqueous HCl acid, resulting in the selective dissolution of the Al. The XRD pattern showed just peaks from the Si phase. The nanostructured porous Si sphere was retained after the etching as indicated in Fig. 1 (left). Overnight etching with vigorous stirring caused these spheres to break. The average crystallite size of the Si in both the initial Al-Si powder and the etched sample is around 20 nm, as determined using the Scherrer Equation, and hence showing no change in size during Al removal.

The electrochemical behavior of this porous Si material is shown in Fig. 1 (right). On Li insertion, 2.8 Ah of Li were inserted per gram of Si spheres and 2.1 Ah of the Li was removed in the first cycle. The capacity dropped to 1.5 Ah/g in the first 3 cycles, but then stabilized. After more than 60 cycles, the capacity was still 1.15 Ah/g. The coulombic efficiency of the broken Si, as indicated in the figure, was 76.5% in the first cycle and rose to 99% after 10 cycles.

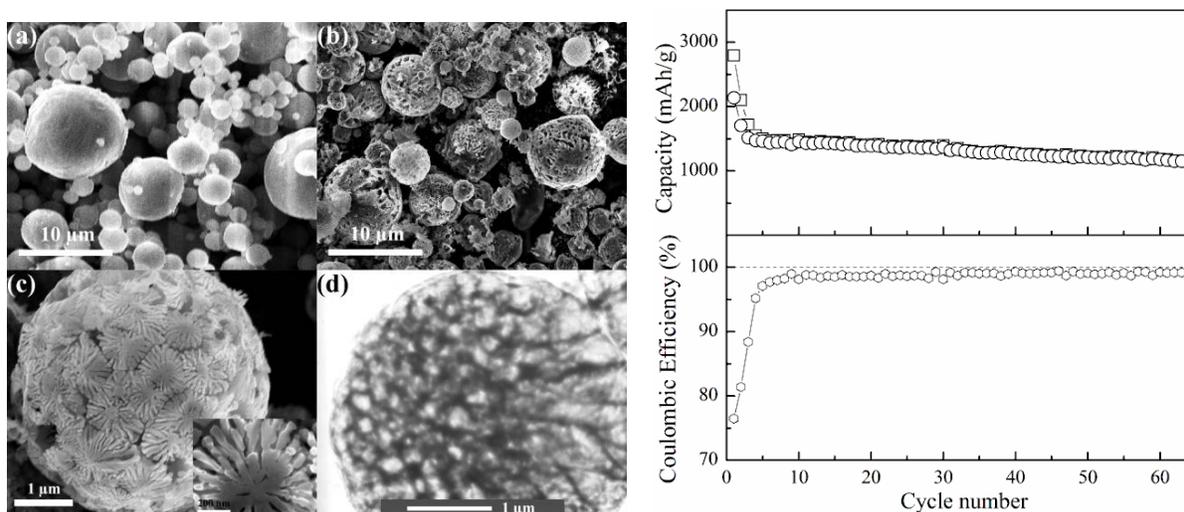


Figure 1. (left) SEM of (a) initial Al-Si, and of (b) and (c) porous Si spheres; (d) TEM of the Si spheres; (right) Electrochemical cycling of the porous Si spheres material at 0.5 mA/cm² between 0.01 V and 1.5 V. First cycle current density was 0.3 mA/cm². The electrodes were made of Si, carbon black additive, and binder in a weight ratio of 70:20:10. Capacities were calculated based on the weight of Si (2 to 3 mg/cm²).

Further plans to meet or exceed milestones: None

Reason for changes from original milestones: None

Publications and Presentations:

1. Wenchao. Zhou, Ruigang Zhang, Shailesh Upreti, and M. Stanley Whittingham, “Sn-Fe Nano-Materials as Anodes for Li-Ion Batteries,” Materials Research Society, San Francisco, April 2012.

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

TASK TITLE - PROJECT: 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 objective 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 limitations of silicon based electrodes.

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). Research will be focused 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, 2011: 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.

FY 2012 AOP EXPECTED STATUS SEP. 30, 2012: Efforts will continue to generate nano-composite ‘core-shell’, random, and aligned structures of varying nanoscale Si morphologies, boron (B), and C nanotubes exhibiting 1500 mAh/g and higher capacities. Research will be conducted to generate novel binders, study the synthesis conditions, nano-scale microstructure affecting the energy density, rate capability, first cycle irreversible loss and coulombic efficiency, characterize the SEI layer, and outline steps to yield stable capacity, reduce irreversible loss and increase coulombic efficiency.

RELEVANT USABC GOALS: Available energy for CD Mode, 10 kW Rate: 3.4 kWh (10 mile) and 11.6 kWh (40 mile); Available Energy for 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

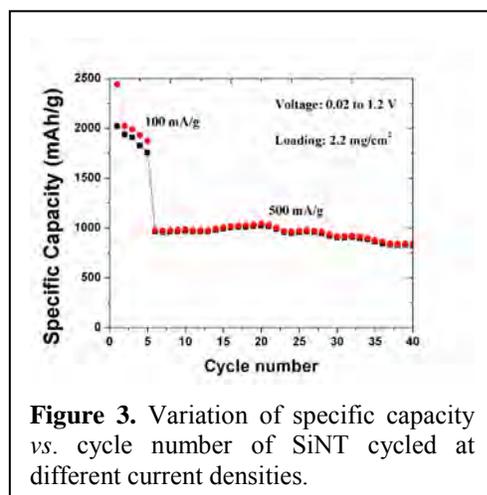
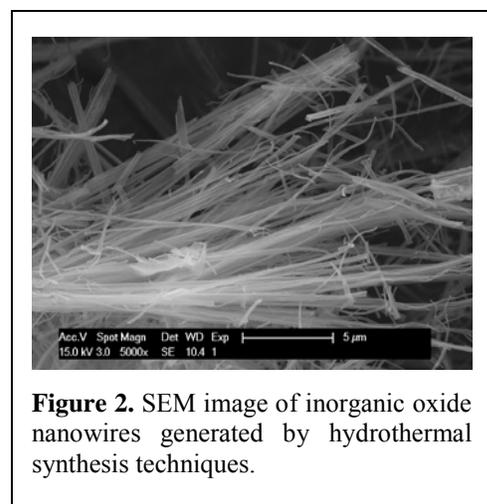
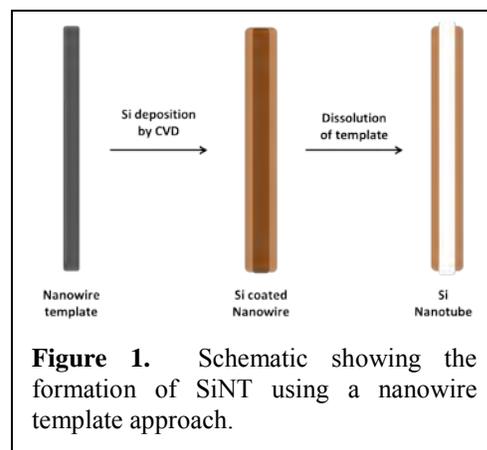
MILESTONES:

- (a) Achieve stable reversible capacity of 1500 mAh/g or higher (Mar. 12). **Complete**
- (b) Achieve irreversible loss ($\leq 15\%$) and efficiency ($\geq 99.95\%$) to match carbon (Sep. 12). **Complete**

PROGRESS TOWARD MILESTONES

Our previous studies have shown that one dimensional (1D) structures comprising nanocrystalline/amorphous forms of Si have exhibited excellent electrochemical performance in terms of specific capacity, long term cyclability, and rate capability when compared to bulk forms of Si. Heterostructures of nanocrystalline/amorphous Si coated on vertically-aligned carbon nanotubes were developed and reported on in our earlier quarterlies (Q-2, Q-3 2012) displayed capacities > 2800 mAh/g with very low irreversible loss ($< 15\%$) and high coulombic efficiency ($\geq 99.5\%$). In this report, a novel and simple technique has been developed to generate large quantities of Si nanotubes using a template-based approach (**Fig.1**). First, large quantities of inorganic-oxide-based nanowires were synthesized by a hydrothermal process inside a microwave reactor. Figure 2 shows the SEM image exhibiting the inorganic oxide-based nanowires developed by this method. These nanowires have a smooth rod-like morphology and are 5 to 10 μm in length with diameters varying between 10 to 50 nm. These inorganic oxide nanowires were then used as a template on which a thin film of amorphous Si was coated by thermal decomposition of Silane (SiH_4) gas at 500°C inside a chemical vapor deposition (CVD) reactor. The Si-coated inorganic oxide nanowire was then dispersed in mineral acids to dissolve the nanowire template. Following the dissolution, hollow Si nanotubes (SiNTs) are generated. The current method is a simple, convenient, and facile technique to generate large quantities of Si nanotubes involving inexpensive processing techniques and precursors.

The obtained SiNTs were mixed with binder and conductive additive to form a slurry that was coated on Cu foil resulting in a mass loading of 2 to 3 mg/cm². The obtained electrodes were tested in a half-cell configuration with Li foil as counter electrode and cycled within the voltage range of *ca.* 0.02 to 1.2 V vs. Li^+/Li . Figure 3 shows the electrochemical cycling behavior and stability of SiNTs cycled at current densities of *ca.* 100 mA/g and 500 mA/g, consecutively. The SiNTs exhibited a high first-discharge capacity of *ca.* 2450 mAh/g and a low first-cycle irreversible loss (FIR) of 18%. These SiNTs when cycled at higher current densities of *ca.* 500 mA/g (C/2 rate) resulted in capacities of *ca.* 1000 mAh/g with very good cyclability and a coulombic efficiency exceeding 99.5%. An initial fade rate less than 0.5%/cycle is obtained with a capacity retention of *ca.* 80% at the end of 35 cycles. Currently efforts are on-going to optimize the morphology of the inorganic nanowires and Si to further improve the cyclability and rate capability of the SiNTs.



TASK 2.4 - PI, 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: Our approach is to manipulate the nano-structure and conductivity of silicon (Si)-based anodes to improve their mechanical and electrical stability. Si-based nanostructures, including micro-sized Si particles with nano-pore structures and core-shell Si composite materials will be investigated. Interactions between Si-based anode and binders also will be investigated. PNNL's capabilities in *in situ* characterization (including *in situ* TEM and NMR) and modeling will be leveraged to investigate the fundamental fading mechanism in Si-based anodes.

STATUS OCT. 1, 2011: Porous Si with micrometer particle sizes and different nano-pore sizes have been investigated for anode applications. The electrochemical performances of micro-sized Si particles with larger nano-pores have demonstrated improved performance. The porous Si powders have been coated with a thin layer (~6% in weight) of carbon by chemical vapor deposition (CVD) to increase their electrical conductivities. The porous structure of Si helps to accommodate the large volume variations that occur during Li-insertion/extraction processes. An initial capacity of ~1200 mAh/g (based on the full electrode) and capacity retention of ~800 mAh/g over 30 cycles were obtained at a 0.1C rate. In another effort, a SiC/SiO/C core-shell composite was developed. An initial capacity of ~1000 mAh/g (based on the full electrode) and capacity retention of ~600 mAh/g over 100 cycles were obtained.

FY 2012 AOP EXPECTED STATUS SEP. 30, 2012: Micro-sized Si particles with large nano-pores will be prepared. An initial capacity of >1000 mAh/g (based on electrode) and capacity retention of ~700 mAh/g over 100 cycles will be obtained. A SiC/Si/C (or SiC/SiO/C) core-shell composite will be investigated further to improve its performance with a targeted initial capacity of >1200 mAh/g (based on the full electrode) and capacity retention of ~700 mAh/g over 100 cycles. The initial capacity loss of the electrodes will be minimized, and their coulomb efficiency during cycling will be increased further by selection of electrolytes and additives. The structure and evolution of the solid electrolyte interface (SEI) will be investigated by *in situ* microscopic analysis.

RELEVANT USABC GOALS: > 96 Wh/kg (plug-in hybrid electric vehicles [PHEV]), 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 main failure mechanisms of the Si-based anode. (Mar. 12) **Complete**
- (b) Improve the performance of Si based anode with a capacity-retention of >700 mAh/g over 150 cycles. (Sep. 12) **Complete**
- (c) Select binders and electrolyte additive to improve the coulombic efficiency of Si-based anodes to more than 99%. (Sep. 12) **Complete**

PROGRESS TOWARD MILESTONES

All of the milestones in FY12 have been completed. For a B₄C supported silicon anode (Si:B₄C:graphite = 4:3), several binders and electrolyte additives were investigated to further improve the cyclability and coulombic efficiency. The samples using sodium carboxymethyl cellulose (CMC) binder and 10% FEC additive in the electrolyte [1 M LiPF₆ in ethylene carbonate and dimethyl carbonate (1:2 ratio in volume)] demonstrated the best performance. After 150 cycles, a specific capacity of 859 mAh·g⁻¹ (based on the whole electrode weight, including binder and conductive carbon) and a coulombic efficiency of > 99% was obtained (Fig. 1).

The electrospin method was used to further improve the cycling stability and rate performance of the composite fiber of rigid skeleton supported Si. The annealing temperature of the fiber was found to have great effect on the cycling stability. The composite fiber annealed at 900°C shows improved cycling stability. CVD treatment also helps to improve the specific capacity. The CVD treated 900°C annealed sample demonstrated a stable cycling behavior with a specific capacity of *ca.* 3500 mAh·g⁻¹ (based on the Si), close to the theoretical capacity, for over 50 cycles (Fig. 2). An *in situ* TEM study and *ex situ* NMR and SEM studies were performed on the rigid skeleton-supported Si composite to investigate its volume change under charge/discharge and its SEI layer evolution. The *in situ* TEM study indicates a mechanically stable electrode with <8% volume change for the composite. The *ex situ* NMR and SEM studies show that the SEI thickness increases with prolonged cycling. It also reveals that the thickness of the SEI layer decreases significantly after adding FEC to the electrolyte. One main reason for the capacity fading of our composite may be due to the continuous consumption of electrolyte.

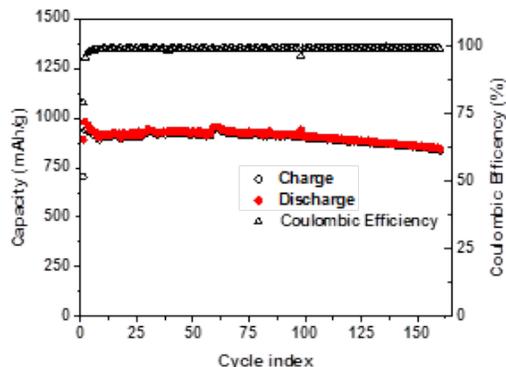


Figure 1. Cycling performance of the rigid skeleton supported Si composite (SBG).

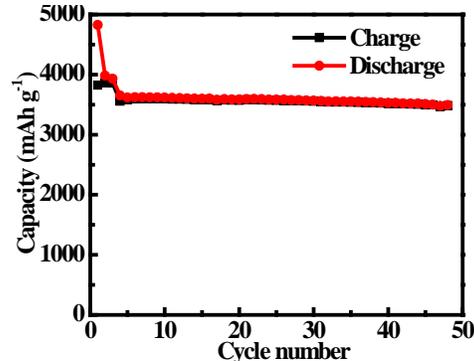


Figure 2. Stable cycling of the electrospun fibers of the rigid skeleton supported Si composite after CVD treatment.

Further optimization of the composite fiber will be performed to improve the cycling stability. The electrode thickness, structure, porosity, and novel binders and electrolyte additives will be further investigated. Fundamental understanding of the mechanism behind the capacity fade, especially the structure of the SEI layer with electrolyte additives, will be systematically investigated.

Publication:

“Conductive Rigid Skeleton Supported Silicon as High-performance Li-ion Battery Anodes,” Xilin Chen, Xiaolin Li, Fei Ding, Wu Xu, Jie Xiao, Yuliang Cao, Praveen Meduri, Jun Liu, Gordon L. Graff, and Ji-Guang Zhang, *Nano Lett.*, **12**, 4124-4130 (2012).

TASK 2.5 - PI, INSTITUTION: Chunmei Ban (Acting Lead), National Renewable Energy Laboratory

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)

BARRIER: Cost, low gravimetric and volumetric capacities, safety

OBJECTIVES: In this work, an inexpensive and scalable hot wire chemical vapor deposition (HWCVD) technique for the production of either amorphous silicon (a-Si) or nano-Si powders and/or doped a-Si or nano-Si will continue to be used. Novel atomic layer deposition (ALD) coatings that will enable durable cycling to be achieved for the high volume expansion Si materials (~ 400 %) will also be developed. Coatings and electrode design may also be demonstrated with commercially available crystalline nano-Si particles.

GENERAL APPROACH: The a-Si or nano-Si powders will be fabricated with HWCVD *via* silane decomposition on a hot filament. Growth parameters will be explored to optimize yield as well as incorporate dopants to produce more conductive a-Si as well as additives to improve cycling stability. Conventional electrodes containing active material, conductive additive and binder will be fabricated and subsequently coated *via* ALD that will serve as an artificial solid electrolyte interphase (SEI) and will importantly help minimize degradation upon volume expansion.

STATUS OCT. 1, 2011: This award was initiated at NREL in FY11. The University of Colorado was funded as of January 1, 2011. Collaborations with both Prof. M. Stanley Binghamton and Prof. Arumugam Manthiram, as well as with General Motors and LG Chem, are in place. Samples were sent to Prof. Clare Grey to perform *in situ* NMR studies to provide mechanistic information about our ALD coatings.

FY 2012 AOP EXPECTED STATUS SEP. 30, 2012: A thick Si anode with an ALD coating will be demonstrated to have a high durable capacity as well as high rate capability. Both gravimetric and volumetric capacities will be optimized.

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) Demonstrate mechanistic information about ALD coatings *via in situ* techniques including Raman spectroscopy, nuclear magnetic resonance and/or Time of Flight Secondary Ion Mass Spectrometry. (Jan. 12) **Complete**
- (b) Send an optimized thick electrode ($\geq 15 \mu\text{m}$) with a reversible capacity of at least 2000 mAh/g at C/20 to Dr. Vince Battaglia at LBNL for verification. (May 12) **Complete**
- (c) Demonstrate an ALD coating with rate performance of $\geq C/5$ for a thick Si anode. (Jul. 12) **Complete**
- (d) Demonstrate at least 50 cycles at a minimum of C/3 rate. (Sep. 12) **Complete**

PROGRESS TOWARD MILESTONES

Greatly improved cycling performance has been achieved by using a Si-cyclized polyacrylonitrile (PAN) hybrid material as a Li-ion anode. The stable cycling of this anode was demonstrated at a rate of C/3, which will be included in the next Milestone report. In this quarter, the structure and mechanical properties of the Si-cyclized PAN hybrid material have been studied by using nano-indentation and Raman spectroscopy. The formation of the sp^2 bonding in the Si-PAN hybrid material has been confirmed through Raman spectroscopy. Figure 1 presents the Raman spectra for the pristine PAN, Si-PAN cyclized at 300°C, and Si-PAN cyclized at 500°C. The two Raman shifts at 1600 cm^{-1} and 1360 cm^{-1} were observed in both cyclized Si-PAN materials, and are attributed to the G and D bands from the graphite-like structure. However, these two peaks are absent in the Raman spectrum of the pristine PAN. The observation of both the D and G bands attests to the existence of graphite-like domains with varying degrees of crystallinity. The peaks in the cyclized PAN were fitted with a Gaussian-Lorentzian function in order to compare the relative intensity of the G band (crystalline graphite-like structure) and D bands (disordered graphite-like structures). As indicated in Fig.1(b and c), a stronger relative G band for the sample treated at 500°C indicates a graphite-like structure with a higher degree of order than that for the sample treated at 300°C. The evolution of a cyclized pyridine-ring structure occurs at a low temperature of *ca.* 300°C. These cyclized pyridine rings have sp^2 bonding with delocalized π bonding that enables good electronic conductivity.

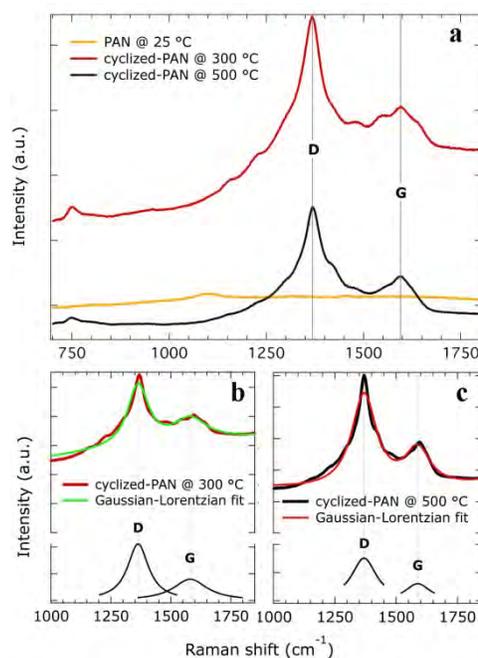


Figure 1. Raman spectrum of pristine PAN and cyclized PAN.

Elastic modulus (E_r) of the cyclized-PAN has been calculated by using nano-indentation. The constant E_r below 500°C was observed to confirm that the low-temperature cyclized-PAN maintains similar mechanical properties as the pristine polymer, but an abrupt increase in hardness was found at temperatures $\geq 300^\circ C$. This sudden increase in hardness is due to the cyclization of PAN at *ca.* 300°C, consistent with the results from the Raman spectrum. The development of the cyclic (ring) polymeric molecular structure at low temperatures enhances the conductivity and maintains the favorable mechanical properties of the polymer. The half-cells with Li metal as counter electrode have been cycled at C/20, followed by 20 cycles at C/10, and then finally cycled at C/3. The cycling performance is shown in Fig. 2. The Si-cyclized PAN has a reversible capacity of 800 mAh/g after 100 cycles, and maintains a reversible capacity of 600 mAh/g after 300 cycles. Moreover, coulombic efficiency of the Si/cyclized-PAN composite anodes approaches 100% after 150 cycles. The greatly improved cycling performance at a rate of C/3 is believed to be due to the enhanced electronic and mechanical properties of the Si-cyclized PAN composite material. Collaborations this quarter: Vince Battaglia (LBNL), Kang Xu (Army Research Lab); Hong Li (Institute of Physics, Chinese Academy of Science), Dow Corning Corporation.

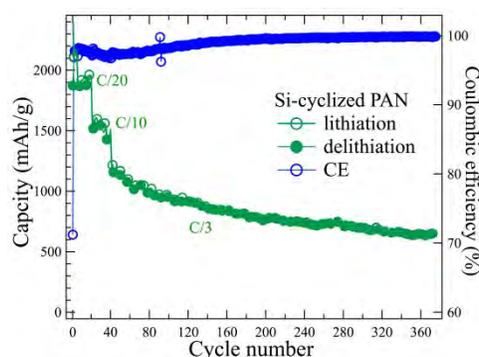


Figure 2. Cycling performance of Si-cyclized PAN.

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 a new material. Layered ternary carbides and nitrides known as MAX phases - may offer combined advantages of graphite and Si anodes with a higher capacity than graphite, lesser expansion, longer cycle life and potentially, a lower cost than Si nanoparticles.

GENERAL APPROACH: Since at this time the relationship between capacity and MAX phase chemistry is unknown; a rapid screening of as many MAX phases as possible will be carried out to determine the most promising chemistry, by testing their performance in lithium ion batteries. This will be guided by *ab initio* calculations. Reducing particle size, selective etching of an A element out from the MAX structure, and exfoliation of these layered structure will also be investigated to increase the Li⁺ uptake by these structures and improve the Faradaic efficiency.

STATUS OCT. 1, 2011: Based on the selection of the most promising MAX phases from the 60-phase family (guided by *ab initio* calculations) perform the testing of the binder-less material as Li-ion battery anodes. Reduce the particle size to < 1 μm and evaluate the effect of the particle size. Exfoliate MAX phases into nanolayers and conduct preliminary electrochemical studies using coin and swagelok-type cells.

FY 2012 AOP EXPECTED STATUS SEP. 30, 2012: MAX-phase based anode formulation providing an optimum performance (capacity and cyclability) in a coin cell configuration.

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) Reduce the particle size of MAX phase to submicrometer level and demonstrate a correlation between the particle size and the Li uptake capacity. (Mar. 12) **Canceled due to change in research direction**
- (b) Partially/and or fully remove the A-group layer from the MAX phase (fully removing “A” layer resulted in exfoliation of MAX phases into graphene-like 2-D structure which were labeled "MXene") and study its effect on electrochemical behavior as anodes Li-ion batteries. (Sep. 12) **Complete**
- (c) Produce anodes from MAX and/or MXene with the capacity of about 80% of the commercial graphite anodes. (Sep. 12) **Complete**
- (d) Investigate the effect of different carbon additives on the performance of MXene anodes and define the best additive conditions (Sep. 12) **Complete**

PROGRESS TOWARD MILESTONE

During this quarter (Q4 FY-2012), all milestones were accomplished and a higher capacity than targeted in milestone (c) was achieved. A summary of the most notable results is given below.

The effect of various carbon additives in different forms (carbon black, carbon onions, carbon nanotubes, carbide-derived carbon) on the performance of MXene anodes was studied. Also, different binders were tested. Ti_3C_2 was used as the active material representative for all other MXenes. Figure 1a shows the effect of selected additives on the performance of Ti_3C_2 . Among the different binders, alginate (10 wt%) showed the best electrochemical performance without carbon additives. 10 wt% of carbon onions (6 to 7 nm in size) resulted in the best performance for Ti_3C_2 (240 mAh/g). The capacity increase can be explained by the enhancement of the conductivity, which resulted in activating new Li sites in MXene. This is suggested by the emergence of new lithiation and delithiation peaks in the CV curves (not shown) when adding alginate or carbon onions.

Recently, full delamination of Ti_3C_2 was successfully achieved. Additive-free anodes of Ti_3C_2 (see inset of Fig. 1b) were made by filtering a dispersion of delaminated flakes in water. The new anodes showed a capacity of 410 mAh/g at a 1C cycling rate, which is higher than graphite. Also, a good capacity (110 mAh/g) was obtained at the very high cycling rate of 36 C. Such a rate is significantly faster than what graphite can handle. This will lead to improved abuse tolerance. It is important to note that the results shown in Fig. 1b were obtained on *additive free* – no binders or other additive – electrodes. This feature should prove useful commercially in simplifying LIB design and in containing costs. In short, we are making excellent progress towards the project goals.

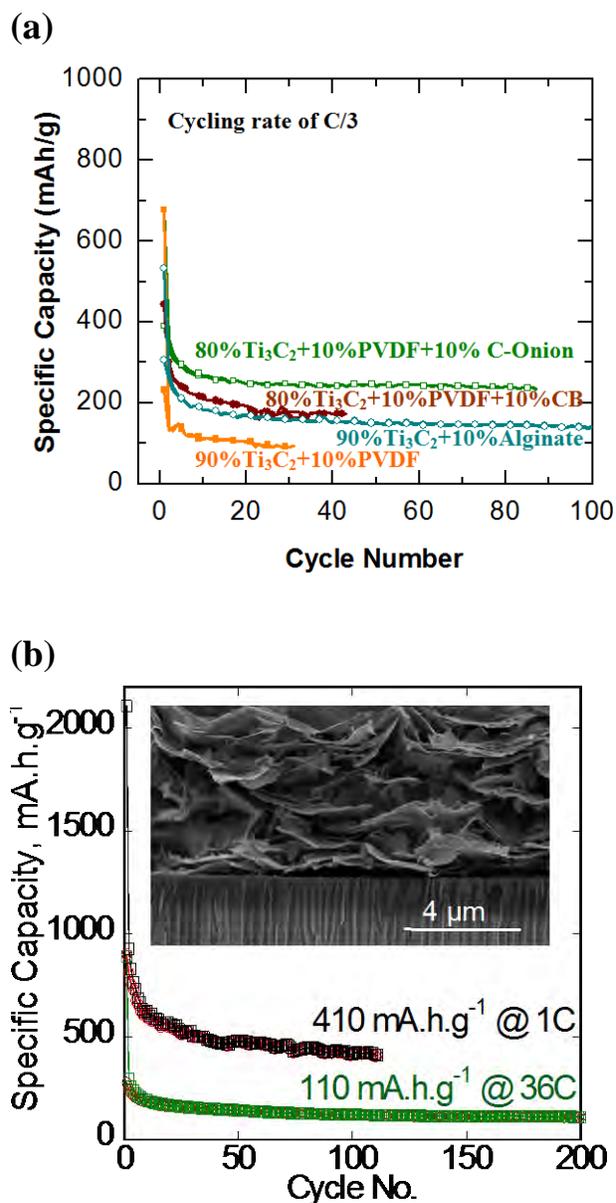


Figure 1. a) Specific capacities (per mass of active material) vs. cycle number, for Ti_3C_2 with different binders and different carbon additives. b) Specific capacities for additive-free delaminated Ti_3C_2 . Inset shows SEM image of an *additive-free* Ti_3C_2 film used in the half-cell experiment.

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

TASK TITLE - PROJECT: Anodes – Synthesis and Characterization of Polymer-coated Layered SiO_x-graphene Nanocomposite Anodes

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: To seek mitigation of the electrochemical limitations of SiO_x anodes during charge/discharge by designing novel SiO_x-graphene nanocomposite and polymer binders to tolerate volume change, improve electrode kinetics, and decrease initial irreversible capacity loss. The new materials proposed and optimized fabrication strategies will improve the performance of SiO_x-based anodes.

GENERAL APPROACH: Our approach is to synthesize SiO_x-graphene nanocomposites to tolerate volume change upon lithiation/delithiation while maintaining Li-ion conductivity. Novel polymer binders will be developed with controlled elastic properties, ion-conductive moieties, and SiO_x surface binding functionality, in order to stabilize and bridge SiO_x particles. To improve the initial coulombic efficiency, SiO_x-graphene nanocomposites to compensate for Li consumption upon irreversible conversion of SiO_x into Li₂O and Li silicates will be prelithiated.

STATUS OCT. 1, 2011: Si nanoparticles with controlled particle sizes and Si-graphene nanocomposites have been successfully synthesized via a solution approach. Several types of polymer binders with controlled SiO_x binding groups and Li-conducting blocks have been synthesized. Processing parameters that control Si nanoparticle size and polymer functionality will be determined. Formation of SiO_x/Si nanoparticles by coating SiO_x layer onto Si nanoparticles and the corresponding SiO_x-graphene nanocomposites will be also demonstrated.

FY 2012 AOP EXPECTED STATUS SEP. 30, 2012: Evaluation of electrochemical performance of Si nanoparticles and Si-graphene nanocomposites will be completed. Processing parameters that control SiO_x coating on Si nanoparticles and polymer functionality will be determined. The electrochemical properties of SiO_x/Si nanoparticles and the novel polymer binders will be optimized, and their compositions and cycling protocols will be evaluated at LBNL BATT partner labs to confirm the initial results.

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) Demonstrate Si nanoparticles and Si-graphene nanocomposites that can achieve a reversible capacity of at least 1200 mAh/g and a cycle life of at least 50 cycles. (Dec. 11) **Complete**
- (b) Synthesize and characterize SiO_x/Si nanoparticles, SiO_x/Si-graphene nanocomposites, and binders with multiple functionalities. (May 12) **Complete**
- (c) Demonstrate SiO_x/Si-graphene nanocomposite anode coated with novel binder with a reversible capacity of at least 1500 mAh/g within 100 cycles. (Sep. 12) **Complete**

PROGRESS TOWARD MILESTONES

Si-based anode materials:

A variety of Si-based anode materials and novel polymer binders were developed and characterized. The materials will be ready for evaluation by LBNL BATT partners bringing the project to the expected status.

A series of novel micron-sized porous Si/C material with controlled pore structures (labeled as PSiC-1, 2 and 3) were synthesized. XRD patterns of the porous Si/C materials clearly showed phases of crystalline Si (Fig. 1A). The electrochemical performance of the porous Si/C materials as anodes was tested. The first cycle discharge of all three Si/C materials were 2303, 1709, and 2557 mAh/g (Fig. 1B). The coulombic efficiencies of the first cycle (>60%) of all three materials were much improved compared to the SiO_x material (*ca.* 30%) provided in the previous report. After the initial cycles (3 cycles at a current density of 0.4 A/g), the electrodes showed capacity retention (>90%) after 50 cycles at a current density of 1 A/g. The charge capacity after 100 cycles of PSiC-1 and 3 were still above 1000 mAh/g at a current density of 1 A/g. The PSiC-2 showed an excellent rate performance (> 400 mAh/g) at high current density (12.8 A/g) (Fig. 1C). Further investigations on the effect of pore size are ongoing.

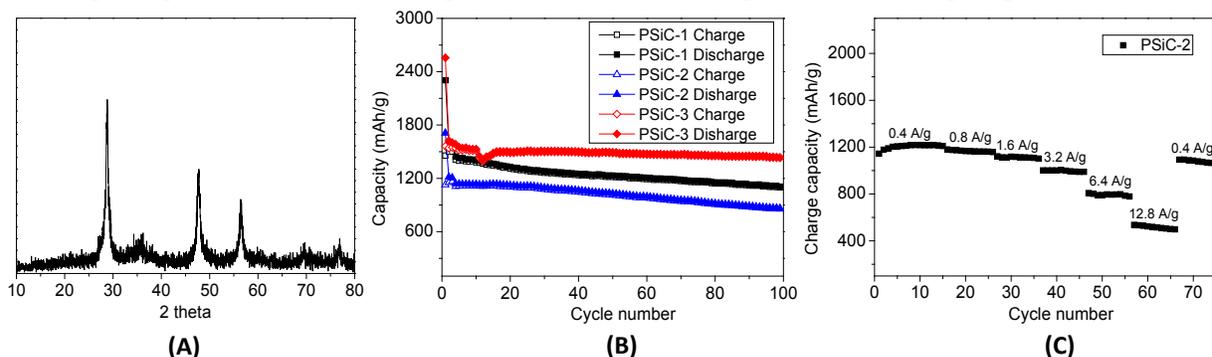


Figure 1. (A) Typical XRD pattern of the porous Si materials. (B) Charge and discharge capacities of all three porous Si/C materials in 100 cycles between 0.01-1.5V. (C) Rate performances of the PSiC-2 material.

Polymer binders: New binders containing ketone and sulfonate groups, SPEEK or sulfonated poly(etheretherketone), were synthesized, Fig. 2. These binders are meant to have ketone groups that mimic NaCMC and also uptake some electrolyte *via* the sulfonate groups to promote ion conductivity in the binder. The cycling performance of cells with commercial Si powder anodes and added fluoroethylene carbonate (FEC) is shown in Fig. 2.

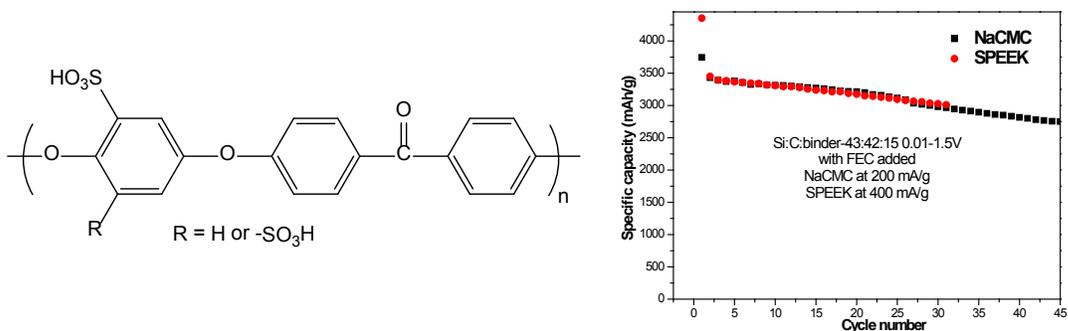


Figure 2. Chemical structure of SPEEK and cycling performance compared to NaCMC.

The SPEEK binder showed nearly equivalent cycling to the NaCMC when FEC was added to the electrolyte. This promising result helps us to clarify the needed functional groups in the polymer binder. A series of ketone/carboxylate/sulfonate-containing binders are being designed for parametric tests of binder composition and cycling performance.

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: To overcome the charge capacity limitations of conventional carbon anodes by designing optimized nano-architected silicon electrodes 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 new types of Si nanostructures to be used as lithium ion battery anodes. Specifically, a variety of hollow and porous nanostructures will be fabricated, and their performance will be compared with other nanostructures such as nanowires. These hollow/porous nanostructures could act to minimize external volume expansion and produce stable SEI layers that will lead to more efficient long-term cycling. In addition, separate efforts will be dedicated to understanding the fundamentals of volume expansion in Si nanostructures through single nanostructure observation. This project was initiated January 1, 2011.

STATUS OCT. 1, 2011: A variety of spherical, one-dimensional, tubular, and porous Si nanostructures will have been fabricated and incorporated into Si anode architectures. Critical size for fracture of various nanostructure geometries during lithiation/delithiation will be established.

FY 2012 AOP EXPECTED STATUS SEP. 30, 2012: Anode cycle life, Coulombic efficiency, first cycle irreversible capacity loss, specific capacity, and mass loading will be optimized by varying synthesis conditions. Effect of hollow/porous structure on volume expansion and Coulombic efficiency will be identified. A detailed understanding of how volume expansion depends on nanostructure geometry will be advanced.

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) Fabricate hollow/porous nanostructured anode with high reversible capacity and high Coulombic efficiency. (Jan. 12) **Complete**
- (b) Determine effect of hollow structure on volume expansion, compare to non-hollow nanostructures. (Apr. 12) **Complete**
- (c) Optimize nanostructure design for high mass loading and long cycle life (>1000 cycles). (Jul. 12) **Complete**
- (d) Develop fundamental understanding of the features that control volume expansion/contraction in Si nanostructures (*i.e.*, Li diffusivity, Si mechanical properties). (Sep. 12) **Complete**

PROGRESS TOWARD MILESTONES

To better design Si-based anodes for Li-ion batteries, it is important to understand both the phase transformations and the details of the Li-Si reaction. Recently, the first lithiation of crystalline Si is suggested to be kinetically controlled by the two-phase reaction at the Si/Li_xSi interface instead of by diffusion of Li through the amorphous phase [1,2]. However, the nanoscale details of the reaction are still largely unknown, hence, *in situ* experiments to determine the details of the reaction are highly desired.

Here, *in situ* TEM experiments are reported in which Si nanoparticles of different sizes were observed in real-time during lithiation (Fig. 2). At 148 sec (d), the particles have been lithiated and are expanded compared to the pristine particles (b). To analyze the reaction kinetics, the diameter of the crystalline Si core and the total particle diameter were measured as a function of time for dozens of individual nanoparticles (Fig. 2). It is evident from this data that the reaction front velocity slows significantly as the lithiation reaction progresses.

This is rather surprising. If the kinetics were only controlled by short-range interactions at the reaction front (as previously suggested), the velocity of the reaction front should be constant.

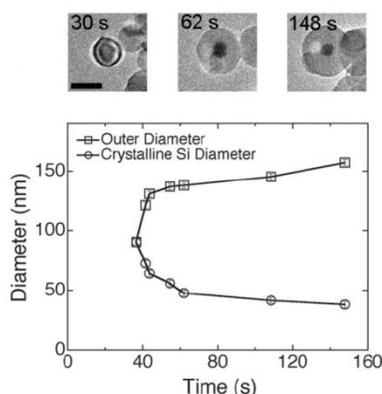


Figure 2. Outer diameter and crystalline core diameter as a function of time for a single nanoparticle during lithiation.

Based on analysis of the reaction front trajectories and analytical models of the mechanical stress evolution during the lithiation of Si [2], the reaction front slowing behavior is attributed to the effect of mechanical stress on the reaction. As a spherical particle is lithiated, significant hydrostatic pressures develop on either side of the reaction front, and the stress becomes more compressive with the degree of lithiation. This hydrostatic stress affects the driving force of the reaction, and if the reaction rate is assumed to depend exponentially on the driving force, this would explain the slowing reaction front. This conclusion is supported by the data in Fig. 3, which shows the lithiated thickness of various particles as a function of time. This graph shows that particles of all sizes show a slowing reaction front on a similar time scale, which suggests that this phenomenon is not diffusion-controlled.

Overall, these findings have implications for the rate behavior of actual Si-based anodes. In addition, this study shows that stress can significantly affect the reaction in addition to causing physical changes such as fracture.

[1] S. W. Lee, M.T. McDowell, J.W. Choi, Y. Cui, *Nano Letters* **2011** (11) 7, 3034.

[2] K. Zhao et al, *J. Electrochem. Soc.* **2012** (159) 3, A238.

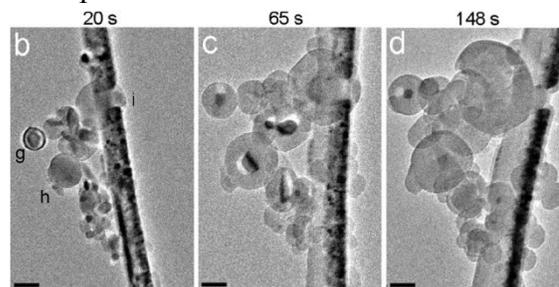


Figure 1. Group of nanoparticles being lithiated. The nanoparticles are attached to a Si nanowire. The darker crystalline cores can be seen in the middle of some of the particles in (c). Scale bar = 100nm.

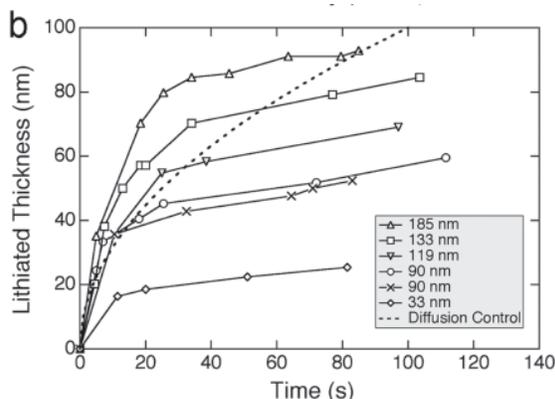


Figure 3. Lithiated thickness as a function of time for particles of different sizes.

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 will be explored, and *ab initio* and classical molecular dynamics (MD) computations to identify lithiation pathways will be performed. 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, 2011: Batch quantities (1-2 grams) of Type I silicon clathrates will have been fabricated by down-selecting and adopting at least two synthetic approaches. Furthermore, computational results will have been obtained using first principles and classical theories to identify possible reaction pathways for the formation of clathrates, Li_xSi₄₆, and Li₁₅Si₄. Several half cells of clathrate anodes will have been fabricated.

FY 2012 AOP EXPECTED STATUS SEP. 30, 2012: The most viable method of synthesizing Type I silicon clathrate will have been selected and optimized in terms of yield and purity. Scale-up of synthesis from small quantities (1-2 grams) to hundreds of grams *via* one or two methods will have been completed. Three different approaches to fabricating clathrate anodes on suitable substrates would have been explored and one selected for laboratory-scale measurements. The intrinsic electrochemical properties of these anodes will have been characterized using a half-cell test apparatus. Classical and *ab initio* computations will have continued with the aim of assessing the effects of metal alloying on Li⁺ occupancy and lattice expansion, while identifying possible reaction pathways for intercalation and deintercalation of Li.

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 one synthetic pathway. (Dec. 11). **Complete**
- (b) Predict the Li⁺ occupancy and lattice expansion potential of Type I metal-silicon clathrate alloys using classical and *ab initio* calculations. (Mar. 12) **Complete**
- (c) Identify possible reaction pathways for the formation of empty clathrates □Si₄₆, Li_xSi₄₆, Li₁₅Si₄, and Li_xM_ySi_{46-y}. (Jun. 12) **Complete**
- (d) Synthesize hundreds of grams of Type I silicon clathrates and/or metal-silicon Type I clathrate alloys with complementary determination of structural purity. (Sep. 12) **Complete**

PROGRESS TOWARD MILESTONES

Task 1 – Synthesis of Type I Silicon Clathrates

The framework-substituted Type I clathrate alloy, $\text{Ba}_8\text{Al}_8\text{Si}_{38}$, was successfully synthesized in bulk (200 g) using a large-volume vacuum arc-melting technique, thus achieving, in part, milestone (d) of the program goals. By making adjustments to the starting materials, process conditions, and hardware, an improved degree of crystallographic purity was achieved as compared with previously-obtained (and evaluated) product (Fig. 1). Earlier and on-going electrochemical measurements are showing that Li^+ can be intercalated reversibly in this clathrate slightly beyond the theoretical limit with negligible lattice expansion despite the presence of Ba guest atoms. Additionally, further progress has been made toward the solution-based synthesis of empty Type I silicon clathrate (Si_{46}). Process methods were devised to enable the phase transformation of fuel-grade NaSi to the required Zintl phase ($\text{Na}_{4.5}\text{Si}_9$) under mild conditions. The more reactive precursor sodium silicide will be used in place of BaSi_2 in the solution synthesis of empty Si_{46} .

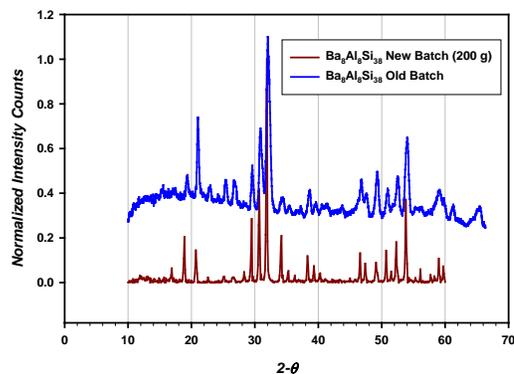


Figure 1. Powder XRD patterns for Type I clathrate alloys as formed from a revised (200 g) and old vacuum arc-melting process.

Task 2 – Molecular Modeling of Silicon Clathrates

The possible use of Na guest atoms to stabilize the empty Si_{46} structure was evaluated by computing the energy of formation of $\text{Na}_x\text{Li}_y\text{Si}_{46}$ as a function of the lattice constant using the first-principles code CPMD. These results, summarized in Fig. 2, indicate that Na guest atoms stabilize the Si_{46} structure by producing a slightly negative energy of formation. Insertion of up to 6 Li atoms into the $\text{Na}_2\text{Si}_{46}$ structure reduces the energy of formation without a volume expansion. The energy of formation becomes positive and the unit cell expands by 8% when the number of Li inserted is increased to 22 (Fig. 2). The results suggest that Li insertion into Na-stabilized Si_{46} may be easier compared to Ba-stabilized Si_{46} .

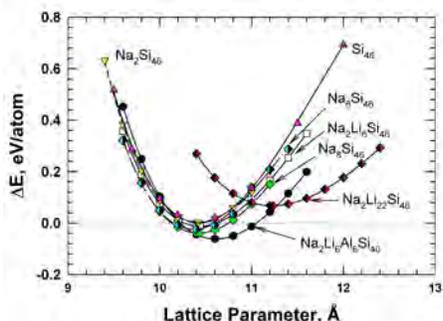


Figure 2. Computed energy change of $\text{Na}_x\text{Li}_y\text{Si}_{46}$ as a function of lattice constant.

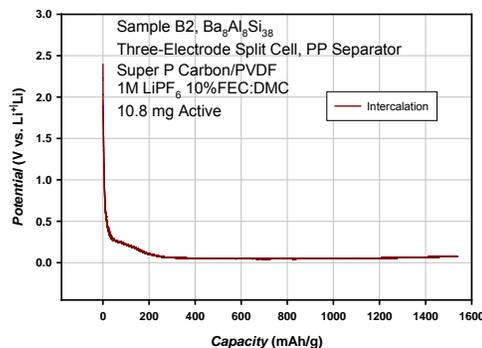


Figure 3. Electrochemical intercalation of Li^+ into thin-film $\text{Ba}_8\text{Al}_8\text{Si}_{38}$ anode composition using FEC-based electrolyte.

Task 4 – Half-Cell Electrochemical Characterization

Electrochemical cycling measurements were made on anodes formed by casting slurries composed of $\text{Ba}_8\text{Al}_8\text{Si}_{38}$, carbon additive, and binder into thin layers. To overcome the instability of the SEI previously observed in similar anode formulations, leading to capacity losses, the half-cells containing the thin-cast anodes were combined with a fluoroethylene carbonate (FEC)-based electrolyte. These changes resulted in marked improvements in the anode material's capacity: 1500 mAh/g based on 10.8 mg of active material (Fig. 3).

BATT TASK 3 **ELECTROLYTES**

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

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

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

BARRIERS: Needs improved cycle life, energy density and safety.

OBJECTIVES: Characterize PS-PEO electrolytes with LiTFSI against Li-metal anodes in symmetric cells, sulfur, and air cathodes. Use block copolymers to create mesoporous battery separators for conventional liquid electrolytes.

GENERAL APPROACH: Synthesize and characterize dry PS-PEO (and PS-PEO-PS) polymer electrolytes. Continue to characterize salt/polymer mixtures by AC impedance spectroscopy, and make DC measurements with Li|polymer electrolyte|Li cells to obtain Li transference numbers. Collaborate with members of the BATT Program to test stability of the electrolyte against electrodes (Li metal, sulfur, and air). Synthesize and characterize porous PS-PE polymer separators by synthesizing a block copolymer, blending with a homopolymer, and washing out the homopolymer to yield a porous block copolymer.

STATUS OCT. 1, 2011: Complete study of morphology on solubility of Li₂S_x in PS-PEO copolymers. Use membrane casting device to create Li|SEO| air cells. Identify ideal molecular weight of homopolymer for creating block copolymer-based separators. Cycle cells with an electronically and ionically conducting polymer binder in the cathode. Obtain conductivity-morphology relationships in block copolymer-based separators with well-defined pores.

FY 2012 AOP EXPECTED STATUS SEP. 30, 2012: Complete study of effect of morphology on transference number in PS-PEO copolymers. Quantify dendrite resistance of SEO electrolytes in symmetric and full cells. Study polysulfide dissolution in Li|SEO/LiTFSI|S cells. Cycle Li|SEO|air cells. Optimize conductivity-morphology relationships in block copolymer-based separators with well-defined pores. Obtain conductivity-morphology relationships in block copolymer-based separators with well-defined pores. Build Li/SEO/FePO₄ cells with an electronically and ionically conducting polymer binder in the cathode with active loading greater than 50 wt%.

RELEVANT USABC GOALS: EV applications goals are a specific energy of 200 Wh/kg and a specific pulse power of 400 W/kg.

MILESTONES:

- (a) Complete transference number measurement as a function of morphology of SEO. (Dec. 11) **Complete**
- (b) Quantify improvement in dendrite resistance due to nanostructuring. (Mar. 12) **Complete**
- (c) Report on improving cathode loading in Li/SEO/FePO₄ cells with electronically and ionically conducting binder. Target active material loading: 65 wt%. (Jun. 12) **Complete**
- (d) Report cycling characteristics of Li/SEO/S and Li/SEO/air cells. (Sep. 12) **Complete**
- (e) Report on conductivity and morphology of second generation porous block copolymer separators and demonstrate performance comparable to Celgard. Target conductivity: 0.4 mS/cm. (Sep. 12) **Complete**

PROGRESS TOWARD MILESTONES

Milestone 3.1 (a) was completed December 2011.

Milestone 3.1 (b) has been completed. A manuscript is currently in preparation.

Completion of milestone 3.1 (c) is delayed to September 2012. Figure 1 shows the cycling data for ten cells with 70 wt% loading of LiFePO_4 active material. Average cell capacities for the first 10 cycles approach the theoretical value for LiFePO_4 , indicating good contact/conductivity between the particles and the polymer matrix. Further analysis of data obtained from varied C rates is necessary to determine the cathode's stability at higher currents.

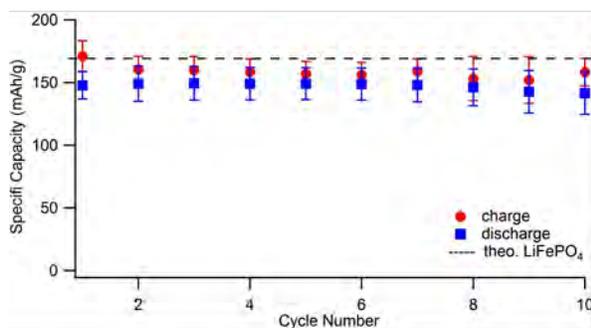


Figure 1. Cycling data for lithium battery with 70 wt% LiFePO_4 .

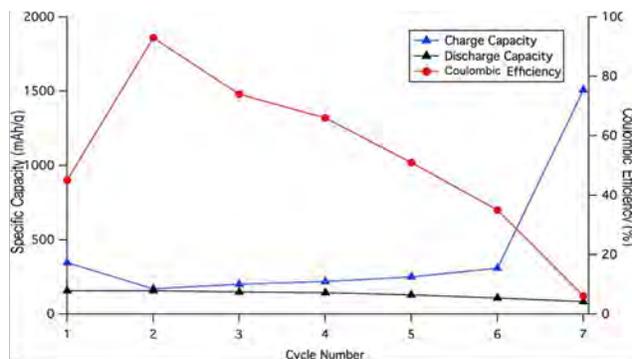


Figure 2. Cycling data for Li/SEO/S battery at 25 wt% sulfur.

For milestone 3.1 (d), preliminary data for Li/SEO/S cells with over 25 wt% sulfur in the cathode show evidence of significant polysulfide diffusion into the SEO electrolyte (Fig.2). When cycled at $40 \mu\text{A}$, low values are observed for coulombic efficiency, yet no significant decrease in the cell capacity. This indicates a high rate of self-discharge that could be due to the polysulfide shuttle mechanism. Future work will be on cells cycled at higher currents, which may reduce the influence of the polysulfide shuttle on the data. Li/SEO/air battery studies remain on schedule. Cell designs are being developed to determine the cathode reaction(s) using XPS and IR.

Work toward milestone 3.1 (e) is ongoing and on schedule. A manuscript discussing the characterization of the morphology of the SES battery separators using Resonant Soft X-Ray Scattering (RSoXS) is under preparation. Separators with the highest conductivity from each synthesized block copolymer are being tested in coin cells. These data will be compared to tensile strength tests to demonstrate the decoupling of the mechanical properties from the conductivity.

Publications:

1. Simultaneous Conduction of Electronic Charge and Lithium Ions in Block Copolymers. Patel, S.N.; Javier, A.E.; Stone, G.M.; Mullin, S.A.; Balsara, N.P. *ACS Nano*, **6** (2), 1589–1600 (2012).
2. Relationship between Morphology and Conductivity of Block-Copolymer Based Battery Separators. Wong, D.T.; Mullin, S.A.; Battaglia, V.S.; Balsara, N.P. *J. Membrane Science*, **394-395**, 175-183 (2012).

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

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

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:

- Determine the role of electrolyte structure upon bulk transport and intrinsic electro-chemical kinetics and how it contributes to cell impedance (Energy/ power density).
- 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, 2011: Initial studies on composite electrodes using single-ion conductor binders will be complete with the focus area materials: High voltage Ni-Mn Spinel cathodes and Conoco Philips CPG-8 Graphite anodes. Experiments will be complete on the use of modified multiwalled carbon nanotubes and carbon blacks for preparation of improved composite electrodes. The TGA/GC/MS system will be used to identify SEI components. Work on high volume expanding anodes with single-ion conducting binders and modified conducting additives will be extended to Si-based alloys. Dry polymer systems will be tested with LiFePO₄ and non-lithium metal anodes.

FY 2012 AOP EXPECTED STATUS SEP. 30, 2012: Carbon nanotubes and other carbonaceous conducting elements will be 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 will be studied to determine how electrode ink formulation affects the electrode morphology and electrode performance particularly for thick, high energy electrodes.

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

MILESTONES:

- (a) Determine the benefits of conducting element modifications on electrode performance. (Apr. 12). **Complete**
- (b) Determine the role of electrode ink properties (*e.g.*, viscosity, stability, *etc.*) on electrode coating morphology and effects on electrode performance. (Sep. 12). **Delayed to Jan. 13**

PROGRESS TOWARD MILESTONES

Preparation of larger samples of the components of single-ion conductor materials has continued. Setbacks occurred due to irreversible cross-linking of the polymer which lead to an intractable material. This was caused by attempts to accelerate the functionalization process at higher temperatures. The yields of the expensive fluoroalkylsulfonyl imide group have also been low, which is disappointing. In addition to preparation of polymers, new methods of surface functionalization have been developed, as shown in Fig. 1.

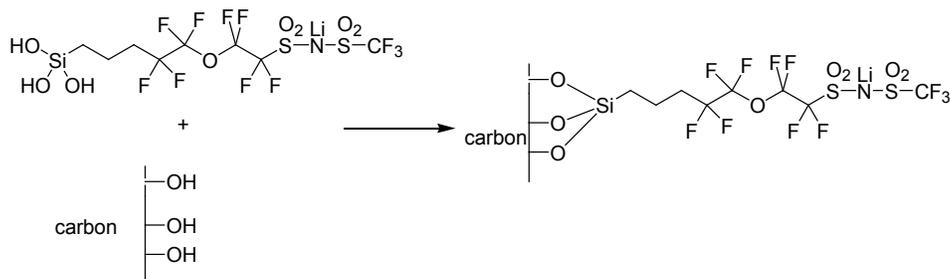


Figure 1. Functionalization of carbon surfaces with imides (Harmer et al, *JCS Chem. Commun.*, 1997 1803).

The functionalized carbons will be used to prepare electrode inks for coating electrodes using unfunctionalized binders and single-ion conductor binders. Preparation of the inks is guided by measurements of the ink rheological properties. The methods for this have been developed for fuel cell electrodes but issues due to atmospheric contamination have delayed the accomplishment of the milestone above.

Further experiments with the use of functionalized multiwalled carbon nanotubes (MWCNT) have shown impressive improvement in rate capabilities for other cathode materials such as V_2O_5 , which have often exhibited poor behavior due to poor conductivity. Comparison of the effect of the MWCNT nanocable materials is shown in Fig. 2.

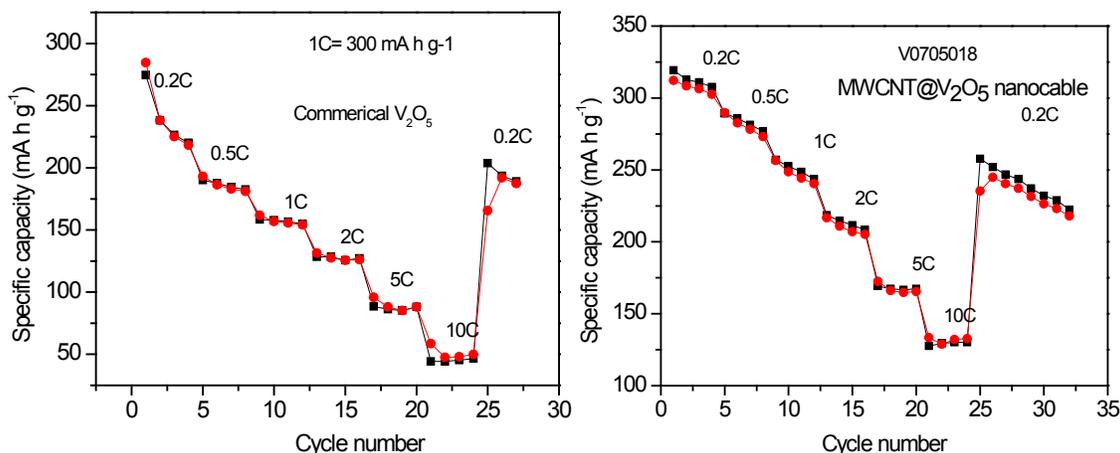


Figure 2. Half-cell testing of V_2O_5 cathodes with MWCNT carbon supports.

TASK 3.3 - PI, INSTITUTION: Dmitry Bedrov, Feng Liu, University of Utah, and Oleg Borodin, Army Research Laboratory

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

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

BARRIERS: Poor low temperature operation, transport through SEI layer and cycle life. High interfacial resistance. Low energy and power density.

OBJECTIVES: Prediction of low energy surface structures and electrolyte reactivity for high voltage cathodes. Prediction and understanding of properties of novel high voltage electrolytes and additives including oxidative stability and degradation products on the cathode. Improved understanding of electric double layer structure, capacitance and transport as a function of electrode potential and temperature for high voltage cathode. Prediction and investigation of structure and formation of the SEI at high voltage cathodes using reactive molecular dynamics (MD) simulations.

GENERAL APPROACH: Utilize DFT methodologies to investigate low energy surfaces of high voltage cathodes, investigate electrolyte reactions at cathode surfaces and investigate oxidative stability of electrolyte components. Develop reactive and non-reactive MD force fields and simulation methods to simulate high voltage novel electrolytes. Utilize reactive force field (ReaxFF) methods to study oxidation reactions and SEI formation at model cathodes with emphasis on additives and electrolyte oxidation at model cathodes.

STATUS OCT. 1, 2011: Investigation of electric double layer structure and charge transfer resistance as a function of electrode potential for model electrodes, investigation of conductivity of novel high voltage electrolytes, investigation study of SEI formation and role of additives for model anodes completed.

FY 2012 AOP EXPECTED STATUS SEP. 30, 2012: Prediction of low energy surface structures and electrolyte reactivity for high voltage cathodes will be completed. Prediction and understanding of properties of novel high voltage electrolytes and additives including oxidative stability and degradation products on the cathode will be completed for initial electrolytes and additives and compared with experiment. Prediction and investigation of structure and formation of the SEI at high voltage cathodes using reactive MD simulations will be completed for initial electrolyte compounds.

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

MILESTONES:

- (a) Predict low energy surface structures and electrolyte reactivity for high voltage cathodes. (Jan. 12) **Complete**
- (b) Predict and understand properties of novel high voltage electrolytes and additives including oxidative stability and degradation products on the cathode. (Mar. 12) **Complete**
- (c) Perform MD simulations of electric double-layer structure, capacitance and transport as a function of electrode potential and temperature for high voltage cathode. (Jun 12) **Complete**
- (d) Predict and investigate structure and formation of the SEI at high-voltage cathodes using reactive MD simulations. (Sep 12) **Terminated**

PROGRESS TOWARD MILESTONES

During the 4th quarter of FY2012 the following tasks were performed:

DFT studies of EC interactions with the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ surface were performed for the 100 and 111 crystallographic surfaces. Our preliminary analysis indicates that due to strong interaction of the EC carbonate group with Li^+ , it can be relatively easy to pull Li^+ from the top layer of the surface. None of the investigated orientations of EC near the surface resulted in spontaneous reaction between EC and the spinel surface. Potential reaction pathways are currently investigated to determine the barrier for possible reactions.

Oxidation-induced decomposition of bis(oxalate) borate (BOB) anion was investigated using DFT calculations to assist in understanding the formation of the cathode passivation layer found on the high voltage spinel cathode in contact with electrolytes containing LiBOB additive studied by B. Lucht's group (URI) in the BATT Program. DFT calculations yielded an oxidative potential of the BOB anion, which is lower than that of PF_6^- , in accord with experimental evidence. The oxidized BOB geometry is asymmetric due to a C-C bond extension as shown in Fig. 2. The most probable initial BOB⁻ oxidation induced decomposition reaction resulted in CO_2 evolution and had a low barrier of only 20 kJ/mol.

A mechanism for improvement of DMC oxidation stability by mixing it with TMS was suggested in a recently completed MD simulation study. The study focused on the double layer structure of a tetramethyl sulfone TMS:DMC/ LiPF_6 electrolyte next to a carbon electrode as a function of applied potential (Xing, Vatamanu, Borodin, Smith, Bedrov, *J. Phys. Chem. C* dx.doi.org/10.1021/jp3054179). This study was complemented by DFT calculations exploring the influence of BF_4^- on TMS oxidation stability and its decomposition reactions. The presence of BF_4^- next to TMS during oxidation significantly reduced the barrier for the TMS ring opening reaction to 0.17 eV. This result should be contrasted with the barrierless H-transfer reaction observed upon oxidation of EC_2 , EC_4 , and EC/BF_4^- clusters (Xing, L.; Borodin, O. *Phys. Chem. Chem. Phys.* **2012**, *14*, 12838-12843). The most probable reaction observed in DFT calculations of the oxidized TMS/ BF_4^- complex involved F-transfer from BF_4^- anion to TMS, highlighting the role of the anion on the oxidation of electrolytes.

Investigation of the oxidative decomposition of electrolyte on model cathode surfaces using ReaxFF showed that the application range of the current ReaxFF method is somewhat limited. The lack of electron localization in ReaxFF in the current model means that at this stage, it does not properly describe oxidative events. For example, during the oxidation it would not localize the electron loss on a particular atom site. However, ReaxFF developers have shown that it is possible to mimic the necessary electron loss/gain and its local chemical effects by a change in atom type. At this point, systematic modifications to ReaxFF are considered in order to implement an automatic atom type change on the fly to account for the electron loss/gain. After the new methodology is available, the oxidation decomposition chemistry of electrolyte at the cathode surface using ReaxFF will be continued.

Collaborators: B. Lucht (URI), W. Henderson (NCSSU), Adri van Duin (Penn State).

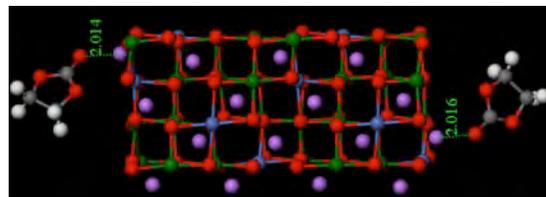


Figure 1. Snapshot from GGA+U calculations on EC/spinel surface interaction.

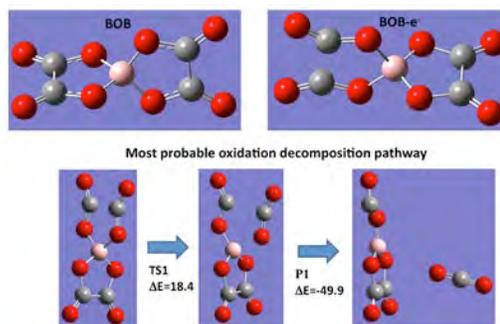


Figure 2. Molecular structure of BOB, oxidized BOB anion as well as most probable decomposition pathway.

TASK 3.4 - 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 for testing by experiment, Use density functional studies of graphite surface reactions to determine mechanisms for protective film formation from additives.

STATUS OCT. 1, 2011: Promising additive candidates obtained from our reduction potential screening will have been further investigated computationally for the initial decomposition step in formation of the SEI. Experimental testing and characterization of selected additives will be performed. Oxidation potentials for potential redox shuttles will have been calculated.

FY 2012 AOP EXPECTED STATUS SEP. 30, 2012: Exploration of full decomposition pathways for selected additive candidates will be carried out using advanced quantum chemical techniques. Experimental testing and characterization of the additives will be performed. Quantum chemical studies of the reaction energies for decomposition of shuttle candidates and experimentally testing.

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

MILESTONES:

- (a) Use quantum chemical predictions of reaction energies for decomposition of redox shuttle candidates selected based on calculated oxidation potentials (Feb. 12) **Complete**
- (b) Explore full decomposition pathways to formation of SEI for additive candidates based on salts, anhydrides, and carbonates will be carried out using advanced quantum chemical techniques. (Apr. 12) **Complete**
- (c) Perform experimental testing of carbonate based additive candidates predicted from our computational model (May 12) **Complete**
- (d) Perform experimental synthesis and testing of redox shuttles for overcharge protection. (Jul. 12). **Delayed, due Feb. 13**
- (e) Synthesize, characterize, and test selected carbonate-based additives from theoretical prediction. Identify at least one additive that significantly improves the cycle and calendar life. (Sep. 12). **Complete**

PROGRESS TOWARD MILESTONES

Our approach for the development of additives for SEI formation and overcharge protection involves screening of reduction and oxidation potentials through the use of accurate density functional methods followed by investigation of the mechanism of decomposition through an investigation of reaction pathways. The screening of over 400 additive candidates for SEI formation has been completed. Selected materials have been examined for performance in cells. The decomposition pathways of various functionalized benzene shuttles have been predicted.

Density functional calculations were used to investigate how 3-oxabicyclohexane-2,4-dione shown in Fig.1 can form a SEI before EC can. The calculations show that the ring form of 3-oxabicyclohexane-2,4-dione has a reduction potential of 0.66 V and an open form reduction potential of 1.04 V, compared to a calculated reduction potential of 1.43 V (Expt. 1.36 V) for the open form of EC. In order for a new SEI film to form before EC is reduced, the reduction potential of an additive must be significantly larger than that of EC. If the ring anion of 3-oxabicyclohexane-2,4-dione breaks various CC bonds followed by a hydrogen transfer, then the resulting species will have a much larger reduction potential. Several isomers were investigated. The results showed that citraconic anhydride anion gives the highest reduction potential relative to 3-oxabicyclohexane-2,4-dione (2.75 V). This suggests that a larger reduction potential of an additive can be achieved by using a high energy isomer (3-oxabicyclohexane-2,4-dione) that can rearrange to the anion radical of a lower energy isomer (citraconic anhydride). The resulting citraconic anhydride anion radical can then polymerize with either 3-oxabicyclohexane-2,4-dione or EC to form the new and potentially improved SEI compared to EC, consistent with experimental studies showing improved performance when a small amount is added to the electrolyte.

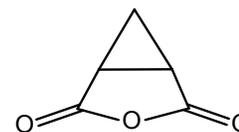


Figure 1. Structure of 3-oxabicyclohexane-2,4-dione.

Our density functional investigation of potential redox shuttles has focused on p-quaterphenyls, shown in Fig. 2. Three p-quaterphenyl structures were examined including one with alternating dihedral angle signs between benzene rings, helical (all dihedrals have same sign), and one with three helical benzene rings and the fourth dihedral with the opposite sign. The oxidation potentials of the three structures are similar. Then, the oxidation potentials of mono-substituted F, CN, and CH₃O p-quaterphenyls were calculated. The CN group is strongly electron withdrawing, the methoxy group is electron releasing, and the F group is electron withdrawing by inductance, but electron releasing by resonance. The F and CN groups have the most effect on the oxidation potential (relative to the unsubstituted p-quaterphenyl) in the 3' position. The electron releasing methoxy group has the most effect on the 4 position. Then our group looked at di-substituted species in which the substituents were placed at the positions in which the corresponding monosubstituted species had the maximum effect on the oxidation potential. Over 70 different possible substituted p-quaterphenyls were investigated. It was found that substituent effects are approximately additive and allow the oxidation potential to be tailored for a range of oxidation potentials for this class of potential redox shuttles.

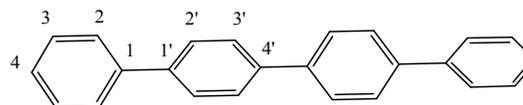


Figure 2. Illustration of possible substituent sites on p-quaterphenyl.

TASK 3.5 - 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 and understanding of the source of performance fade in LiNi_{1.5}Mn_{0.5}O₄ cathodes cycled to high voltage (4.9 V vs. Li). Develop an electrolyte formulation that allows for superior performance of LiNi_{0.5}Mn_{1.5}O₄ cathodes.

GENERAL APPROACH: Optimize properties of LiPF₄C₂O₄/carbonate electrolytes in small Li-ion cells at low temperature (-30°C) after accelerated aging. Investigate electrode surface films for cells cycled with LiPF₄(C₂O₄) to determine source of performance differences. Investigate cathode film forming additives for high voltage (> 4.5 V) cathode materials. 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.

STATUS OCT. 1, 2011: Additional cathode film forming additives was developed for high voltage cathodes. An understanding of the source poor first efficiency for LiPF₄(C₂O₄) electrolytes on graphite anodes was developed. The low-temperature performance of LiPF₄(C₂O₄)/PC electrolytes after accelerated aging was investigated. Novel electrolytes to improve performance of Si-based alloy anodes were investigated.

FY 2012 AOP EXPECTED STATUS SEP. 30, 2012: An LiPF₄(C₂O₄) electrolyte with optimized performance at low temperature after accelerated aging will have been developed. A better understanding of the role of electrolytes in the poor cycling efficiency and capacity fade of LiNi_{0.5}Mn_{1.5}O₄ cathodes will have been developed. Novel electrolyte formulations which optimize the performance of LiNi_{0.5}Mn_{1.5}O₄ cathodes cycled to high voltage (4.9 V vs. Li) will have been designed.

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 electrolytes in capacity fade and poor cycling efficiency of LiNi_{0.5}Mn_{1.5}O₄ cathodes. (Mar. 12) **Complete**
- (b) Design electrolyte formulations to improve performance of high voltage Ni-Mn spinel cathode materials. (Jul. 12) **Complete**
- (c) Optimize a LiPF₄(C₂O₄) electrolyte for graphite/LiNi_xCo_{1-2x}Mn_xO₂ cells for high and low temperature performance. (Sep. 12) **Complete**

PROGRESS TOWARD MILESTONES

With regards to milestone (a): Was completed in our Q3 report, preparation of a manuscript is in progress.

With regards to milestone (b): Was completed in our Q3 report, a manuscript has been accepted for publication.

With regards to milestone (c): Li-ion coin cells were constructed with 1.2 M LiPF₆ in 3:7 EC/EMC, 1.2 M LiPF₆ in 2:2:6 EC/EMC/MB (Methyl Butyrate) and 1.2 M LiFOP in 2:2:6 EC/EMC/MB with natural graphite/LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ electrodes. The first cycle efficiency and cycling performance at room temperature of cells with methyl butyrate (LiPF₆/MB and LiFOP/MB) are similar to the cells with baseline electrolyte (LiPF₆ in EC/EMC). The cycling performance of electrolytes containing MB are superior to the baseline electrolyte at low temperature (-10°C), but the LiFOP/MB electrolyte does not perform well at -30°C, especially after accelerated aging experiments. Electrochemical impedance spectroscopy suggests that both the film resistance and the charge-transfer resistance of the cells containing the LiFOP/MB electrolyte are much larger than the LiPF₆ electrolytes. The IR spectrum of the natural graphite anode after accelerated aging with LiFOP/MB electrolyte is quite different from that of the natural graphite anode after accelerated aging with LiPF₆ electrolytes (Fig. 1). The presence of lithium oxalate is supported by peaks at *ca.* 1640 cm⁻¹ and 1323 cm⁻¹, and poly(ethylenecarbonate) is supported by a peak at 1760 cm⁻¹. The IR results are consistent with the XPS data of anodes cycled with LiFOP/MB electrolyte and suggest that the surface film is thicker for cells cycled with LiFOP/MB electrolyte and have high concentrations of lithium oxalate. The increased impedance and poor cycling performance at -30°C for cells with LiFOP/MB electrolyte is likely due to the thicker surface films on the anode.

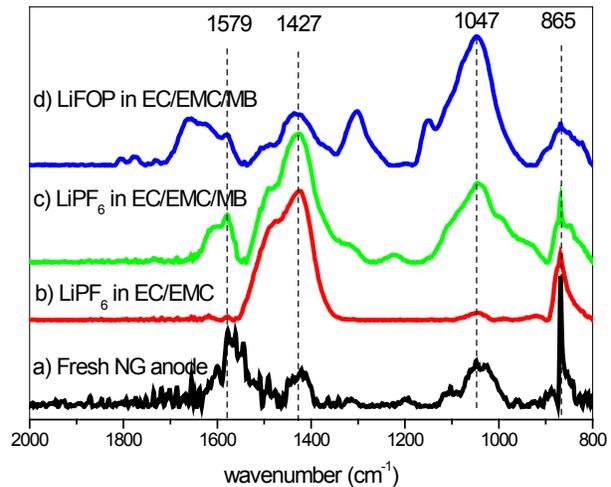


Figure 1. FT-IR spectra of natural graphite anode cycled with LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ cathode, fresh and after accelerated aging.

Collaborations: M. Smart (NASA-JPL), V. Battaglia and G. Chen (LBNL), O. Borodin (ARL), W. Li (S. China Univ. Tech.), A. Garsuch (BASF), and Spinel Focus Group.

Publications:

“The Effect of Additives upon the Performance of MCMB/ LiNi_xCo_{1-x}O₂ Li-Ion Cells Containing Methyl Butyrate-Based Wide Operating Temperature Range Electrolytes,” M.C. Smart, B.L. Lucht, S. Dalavi, F.C. Krause, and B.V. Ratnakumar, *J. Electrochem. Soc.*, **159**, A739-A751 (2012).

“Improved Performance of LiNi_{0.5}Mn_{1.5}O₄ Cathodes with Electrolytes Containing Dimethylmethylphosphonate (DMMP),” M. Xu, D. Lu, A. Garsuch, and B.L. Lucht, *J. Electrochem. Soc.*, In Press.

“Performance of lithium tetrafluoroxyalato-phosphate in methyl butyrate electrolyte,” L. Zhou, M. Xu, B.L. Lucht, *J. Power Sources*, submitted.

TASK 3.6 - 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* the nature of products generated at Li-ion battery anodes under highly controlled conditions.

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, 2011: Synthesis and purification of three cyclic triol borate (CTB) and one bicyclic borate phosphine oxide (CBPO) salts and determination of their flammability. Develop methods for the preparation of 100g of CTB-type compound for testing in actual batteries. Collect data using the *in situ* IRAS-FTIR cell for monitoring *in situ* the composition of the electrolyte and surface films on ultrapure Li metal in selected alkyl carbonate-salt formulations.

FY 2012 AOP EXPECTED STATUS SEP. 30, 2012: Complete synthesis and characterization of three additional CTB-type and CBPO-type materials including flammability and electrochemical testing. Establish structure-electrochemical performance relationships within the CTB and CBPO anion families. Explore monocyclic FRION frameworks. Explore other synthetic routes towards Li BOBPHO-R (R = Ph), especially those involving larger scale methods. Systematic *in situ* ATR-FTIR spectroscopic studies involving selected solvent formulations incorporating Case FRIONs both as main salts and additives.

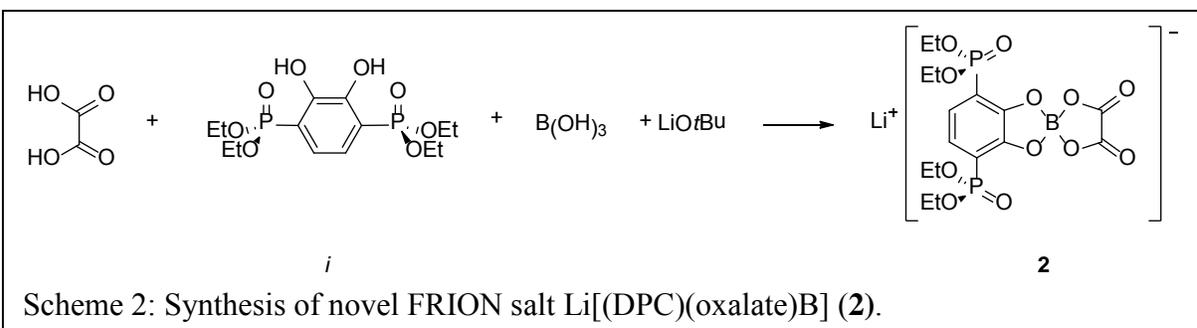
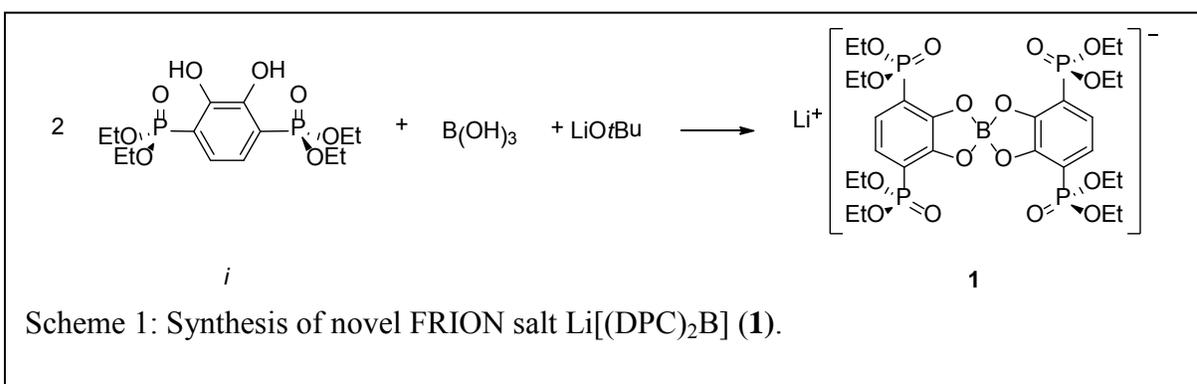
ELEVANT USABC GOALS: No fire or rapid disassembly of cells during abuse conditions.

MILESTONES:

- (a) Prepare and fully characterize the electrochemical and flammability properties characteristics of three CTB-type compounds and one CBPO-type compound. (Oct. 11) **Complete**
- (b) Expand the CTB-type and CBPO-type libraries of compounds. (Mar. 12) **Complete**
- (c) Synthesize and characterize a monocyclic FRION. (Sep. 12) **Complete**
- (d) Complete design, construction and testing of cell for *in situ* new infrared reflection absorption (IRAS) spectroscopy and impedance measurements with first (Oct. 11) **Delayed, due Mar. 13;** and two additional Case electrolytes. (Sep. 12) **Delayed, due Jul. 13**
- (e) Perform full testing of three Case salts as full fledge electrolytes and as additives in actual batteries at Novolyte (Oct 11), and LBNL and ANL. (Sep 12) **Complete; on-going to Mar. 13**
- (f) Improve cycling by at least 15% to reach the same decay/end of life *vs.* the control electrolyte. (Sep 12) **Complete; on-going to Mar. 13**

PROGRESS TOWARD MILESTONES

Synthesis and characterization of FRIONS – The two novel FRION salts featuring a diphosphinate catecholate (DPC) ligand reported in the previous quarterly were prepared on a scale large enough for full characterization, and electrochemical and flame retardant testing (>1g). Li[(DPC)₂B] (**1**) was prepared using two equivalents of a diphosphorylated catechol intermediate (*i*), boric acid and lithium t-butoxide (Scheme 1). For Li[(DPC)(oxalato)B] (**2**), one equivalent of oxalic acid replaced one equivalent of *i* (Scheme 2) to make a lower molecular weight oxalato borate salt. Initially there was some difficulty preparing pure, large scale quantities of *i*, as the preparation method from the literature for this compound contains known impurities.¹ Those issues have been resolved by optimizing the reaction conditions. Large scale (> 5g) synthesis has been performed.



(1) Dhawan, B.; Redmore, D. *The Journal of Organic Chemistry* **1984**, *49*, 4018.

TASK 3.7 - PI, INSTITUTION: Wesley Henderson, North Carolina State University

TASK TITLE - PROJECT: Electrolytes - Inexpensive, Nonfluorinated (or Partially Fluorinated) Anions for Lithium Salts and Ionic Liquids for Lithium Battery Electrolytes

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

BARRIERS: Low cost cell materials, abuse tolerance, low temperature performance

OBJECTIVES: Develop new anions as replacements for PF₆⁻ or as additives for electrolytes

GENERAL APPROACH: Synthesize and fully characterize two classes of nonfluorinated (or partially fluorinated) anions: 1) chelated and non-chelated organoborate anions (related to bis(oxalato)borate (BOB⁻)), and 2) Hückle-type anions in which the charge is stabilized on a 5-member azole ring and noncyclic cyanocarbanions. Characterize the physical properties of these new anions, incorporated in both Li salts and ionic liquids, by examining the thermal phase behavior (phase diagrams); thermal, chemical and electrochemical stability; transport properties; interfacial properties; molecular interactions and cell performance. These salts will be compared with widely used salts such as LiPF₆ and LiBOB and ionic liquids based upon the bis(trifluoromethanesulfonyl)imide anion.

STATUS OCT. 1, 2011: Several synthesis procedures for new lithium salts have been developed. The characterization of the salts is in progress. Ionic liquids (ILs) have been prepared with *N*-alkyl-*N*-methylpyrrolidinium cations and the difluoro(oxalato)borate (DFOB⁻) anion. These ILs have been characterized as additives to electrolyte formulations.

FY 2012 AOP EXPECTED STATUS SEP. 30, 2012: Extensive characterization of solvent-LiFSI and -LiDFOB mixtures will be completed. Several new lithium salts will be reported along with a comparison of their properties with conventional salts such as LiBF₄ and LiPF₆. ILs will have been prepared from these anions and tested in IL-LiX and IL-LiX-solvent mixtures, as well as for use as additives to conventional electrolyte formulations.

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 35°C); cold cranking capability to -30°C; abuse tolerance.

MILESTONES:

- (a) Determine the phase behavior/properties of solvent-LiPF₆ mixtures. (Apr. 12) **Complete**
- (b) Determine the phase behavior/properties of solvent-LiFSI and -DFOB mixtures. (Sep. 12) **Delayed to Mar. 13**
- (c) Prepare/characterize lithium salts with partially fluorinated cyanocarbanions and dianions. Conduct half/full-cell electrochemical testing (graphite and NMC electrodes) using the salts as replacements for LiPF₆ or as additives, in parallel with the control electrolyte with LiPF₆, to demonstrate improved cycling behavior performance over 200+ cycles. (Sep. 12) **Delayed to Mar. 13**
- (d) Prepare/characterize ILs with DFOB⁻ and partially fluorinated cyanocarbanions. Conduct half/full-cell electrochemical testing (graphite and NMC electrodes) using the salts as replacements for aprotic solvents or as additives, in parallel with the control electrolyte with LiPF₆, to demonstrate improved cycling performance over 200+ cycles. (Sep. 12) **Delayed to Mar. 13**

PROGRESS TOWARD MILESTONES

Characterization of Solvent-LiDFOB and -LiFSI Mixtures: The properties of (solvent)_n-lithium difluoro(oxalato)borate (LiDFOB) mixtures (with EC, PC, GBL and GVL) have been compared to similar mixtures with -LiBF₄ and -LiBOB. For some of the mixtures, the solutions with LiDFOB and LiBOB are found to have a significantly higher conductivity than those with LiBF₄ (Fig. 1). Perhaps contrary to expectations, the viscosity of the LiDFOB and LiBOB mixtures is higher than that for the corresponding LiBF₄ mixtures (Fig. 2). A spectroscopic characterization of the mixtures indicated that the electrolytes with LiDFOB and LiBOB are more solvated—and thus more dissociated—than those with LiBF₄ (for a given solvent).

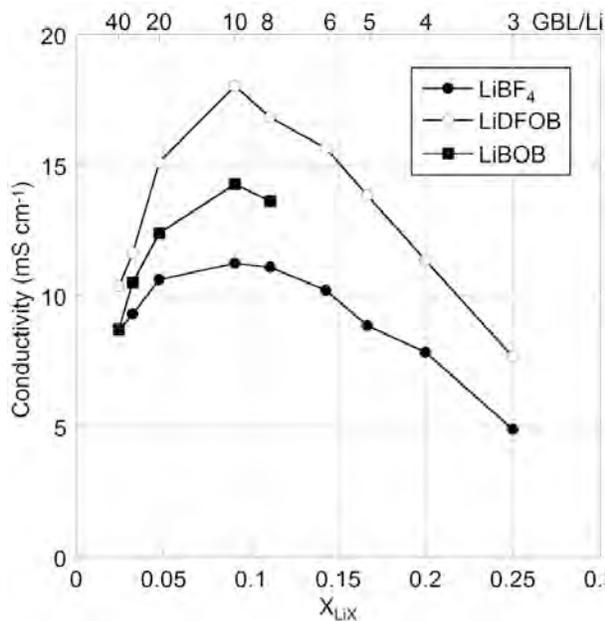


Figure 1. Ionic conductivity of (GBL)_n-LiX mixtures at 60°C.

To aid in the analysis of (solvent)_n-LiFSI mixtures (to better understand their properties), a crystalline solvate structure has been determined with tetraglyme—(G4)₁:LiFSI in which the FSI anions are uncoordinated (Fig. 3). This is the first solvate structure reported with this salt.

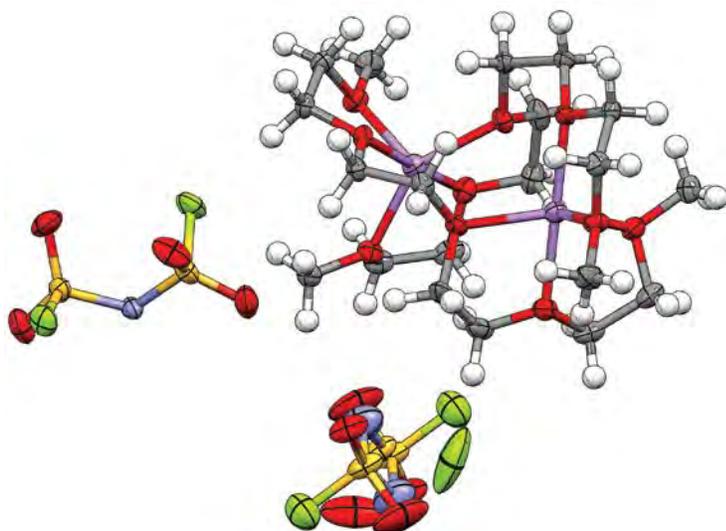


Figure 3. Ion coordination in the crystal structure of the (G4)₁:LiFSI solvate (Li-purple, O-red, N-blue, S-yellow, F-green)—one anion is disordered.

GBL-LiBF ₄	GBL-LiDFOB	GBL-LiBOB
● 4	● 4	
● 5	● 5	
● 6	● 6	● 8
● 8	● 8	● 10
● 10	● 10	
● 20	● 20	● 20
● 40	● 40	● 40
	● 30	● 30

Figure 2. Viscosity of (GBL)_n-LiX mixtures at 60°C (GBL/Li concentrations shown).

Collaborations:

Oleg Borodin and Richard Jow
(Army Research Laboratory).

TASK 3.8 - PI, INSTITUTION: Austen Angell, Arizona State University

TASK TITLE - PROJECT: Electrolytes – Sulfones with Additives as Electrolytes

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

BARRIERS: Increased oxidation resistance, decreased ionic resistance, and improved safety.

OBJECTIVES: 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 provide optimized nanoporous supporting membranes.

GENERAL APPROACH: Twofold: (i) A suite of electrolyte studies, beginning with cell-performance testing of recently developed sulfone electrolytes and extending to the design of novel Li⁺-conducting media, are 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 thiophosphate solids (known $\sigma > 10$ S/cm) and rubbery polymers (developing) will be tested for compatibility with the chosen Li(Ni,Mn) spinel cathode. Some ionic liquid electrolytes will be tested. (ii) Further development of the “Maxwell slats” approach to synthesis of nanoporous supports. A hot water-soluble reversibly-self-assembling net has already been developed as model, and a stronger-bonded model that self-assembles in hot ionic liquid solvents, is the next target.

STATUS OCT. 1, 2011: 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, were completed, and relative merits assessed. Tests of fluorinated sulfone FPMS, with DMC co-solvent in similar half-cell and full cell modes were done. The crystal structures of one of our self-assembling open-network structures (and its pore space fraction) is known, and XRD of its nearest glass-forming analog is available for comparison. Studies to expand the glassy range and mechanical properties are in progress.

FY 2012 AOP EXPECTED STATUS SEP. 30, 2012: 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 be 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) Complete full evaluation of sulfone solvent-based high voltage cells. (Dec. 11) **Complete**
- (b) Complete development of water-soluble self-assembling models of “Maxwell slat” porous solids for creation of self-supporting nanoporous membranes. (Dec. 11) **Complete**
- (c) Complete evaluation of ionic liquid-based, and hybrid, solvent electrolytes. (Apr. 12) **Delayed to Jan. 13**
- (d) Test and compare Li(Ni,Mn) spinel cells using ionic liquid-based electrolyte. (May 12) **Complete**
- (e) Test and compare glass and glass-stuffed polymer electrolyte types in cells. (Jun. 12) **Complete**
- (f) Develop covalent-bonded equivalents of the self-assembling nets. (Jul. 12) **Complete**,
publication pending

PROGRESS TOWARD MILESTONES

(b) Complete evaluation of ionic liquid-based, and hybrid, solvent electrolytes (Mar. 2012)

The investigation of novel, inorganic salts with high alkali cation mobilities is now reaching a mature stage. The one remaining problem of retaining the high conducting state over long periods of time seems to have been solved by a method used previously for stabilizing the plastic crystal state of molecular crystals, namely, by making homogeneous solutions of one crystal in the other. In our case, the high conducting state of the preparation designated Li3 in Fig. 1, which previously decayed with time as shown in Fig. 2, is now stable with time (Fig. 2, dashed lines) after homogeneous mixing with Li2. Thus, a Li-conducting solid electrolyte (provisional patent applied for) with conductivity equal to that of the best electrolytes on record is now in hand. It is all-inorganic, non-toxic, inexpensive, and (preliminary data only) retains conductivity at low temperature, just as the $\text{Li}_{12}\text{GeP}_2\text{S}_{12}$ material included in Fig. 1. Cell tests using this electrolyte are being made.

(c) Test and compare Li(Ni,Mn) spinel cells using ionic liquid-based electrolyte. This part of the program is being conducted in collaboration with Vince Battaglia at LBNL. The project is on hold while a replacement for the post-doc who performed our initial work on sulfone electrolytes and cells (in press JPC) is found.

(d) No reports (e) Completed

(f) Develop covalent-bonded equivalents of the self-assembling nets.

New amorphous MOFs with pore sizes up to 25\AA , having stoichiometries of A_2X_3 and ABX_2 , close to the ideal strain-free glasses of constraint theory ($\langle r \rangle = 2.4$ (Fig. 3), have now been produced and are being converted into continuous films for gas and solvent permeability tests. The nets are being solvent-cast onto Celgard membranes for electrolyte tests. Figure 4 shows XRD patterns and their real space transforms, the latter indicating the pore size distribution. This is especially sharply defined for the stoichiometry ABX_2 which should be a zeolite analog. The possibility that these may be useful supports for catalysts is being evaluated. Mechanical properties may be controlled by the inclusion of flexible and rigid strut materials in a single film.

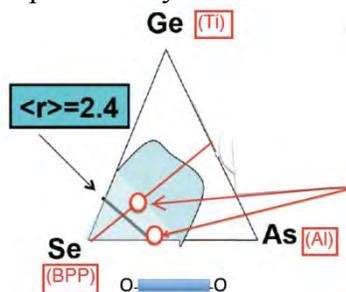


Figure 3.

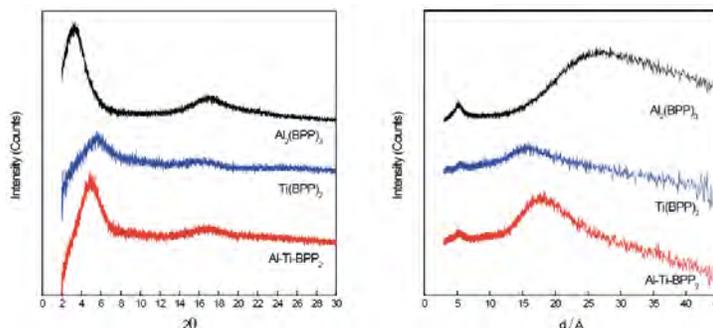


Figure 4.

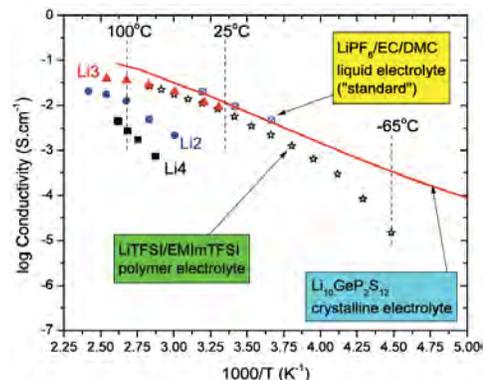


Figure 1. Conductivities

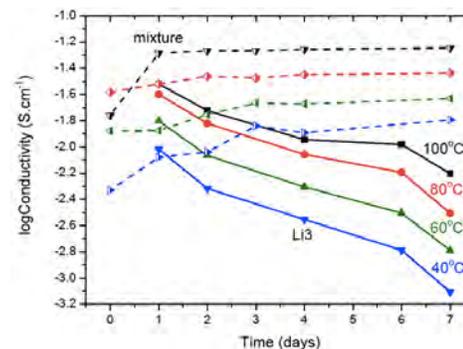


Figure 2. Conductivity vs. time.

Collaborations: Vince Battaglia, LBL.

BATT TASK 4 **CATHODES**

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

TASK TITLE - PROJECT: Cathodes – Novel Cathode Materials and Processing Methods

BASELINE 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.

GENERAL 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. lithium. These electrodes suffer from voltage decay and surface instability on cycling, thereby compromising the energy and power of the lithium-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, 2011: This is a new project. During the last six months of FY2011, progress was made in exploiting a new synthesis approach in which Li₂MnO₃ was used as a precursor to fabricate structurally-integrated lithium-metal-oxide composite electrode materials, including ‘layered-layered’, ‘layered-spinel’, ‘layered-rocksalt’ and more complex types. This technique showed promise for stabilizing high capacity (250 mAh/g) lithium-metal-oxide cathodes to cycling over a wide voltage window and, in particular, for combating voltage decay phenomena.

FY 2012 AOP EXPECTED STATUS SEP. 30, 2012: Progress will have been 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) Evaluate a new processing route to fabricate stabilized xLi₂M’O₃•(1-x)LiMO₂ (‘layered-layered’) electrode structures with a high Mn content using Li₂MnO₃ as a precursor (Sep. 12) **Complete**
- (b) Use atomic layer deposition and other methods to stabilize the surface of electrode particles at high charging potentials. (Sep. 12) **Complete**
- (c) Model surface structures and interfacial phenomena of coated electrodes. (Sep. 12) **Complete**

PROGRESS TOWARD MILESTONES

Milestone (b) addressed: Use atomic layer deposition and other methods to stabilize the surface of electrode particles at high charging potentials

Electrode materials with ‘layered-layered’ composite structures, $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ ($M = \text{Ni}, \text{Mn}, \text{and Co}$), having capacities of *ca.* 250 mAh/g, are leading candidates for the next generation of high energy density Li batteries to power EV and PHEV vehicles. However, the high-voltage (*ca.* 4.6 V), electrochemical-activation processes necessary to access these remarkable capacities can lead to oxygen loss, electrolyte decomposition, transition metal dissolution, and irreversible surface damage. The damaged surfaces of electrode particles adversely affect the rate of Li diffusion, attenuating the power (rate) capability of cells. In addition, this damage may influence the voltage fade process. Therefore, effective particle-surface protection must be sought if both high capacity and a high rate capability are to be realized in this class of cathode materials.

Figure 1(a) shows a schematic of a sonochemical approach being explored for coating electrode particle surfaces. In this process, desired precursors such as $\text{TiOSO}_4 \cdot x\text{H}_2\text{O}$ are decomposed by acoustic cavitation in a sonic bath into hydroxide species, which precipitate on the surface of particles. A subsequent, low-temperature annealing serves to further decompose and congeal the hydroxide species into a uniform oxide TiO_2 coating (Fig. 1a). ‘Layered-layered’ $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ electrodes, fabricated from a newly-developed synthesis technique using Li_2MnO_3 as a layered, lithium-manganese-oxide ‘template’, were coated with Al_2O_3 using the sonochemical method. Figure 1(b) shows that these electrodes have a first-cycle efficiency (FCE) of *ca.* 85% and deliver a capacity of 250 mAh/g when cycled at 15 mA/g; they deliver *ca.* 210 mAh/g when cycled at 10 times that rate. By comparison, untreated electrodes have a 79% FCE and deliver *ca.* 195 mAh/g at 150 mA/g. In addition, coated samples showed slightly superior cycling behavior, providing *ca.* 230 mAh/g above 3 V after the initial 12 high-voltage cycles, compared to *ca.* 210 mAh/g for uncoated particles (Fig. 1c). However, the coating does not significantly impact voltage fade, consistent with data in the January report. These latest results suggest that this method of coating holds promise for improving the surface stability and rate of these high-capacity cathodes. Other candidate metal oxides, as well as phosphates and fluorides, are currently being investigated as surface stabilizing agents using sonochemical deposition.

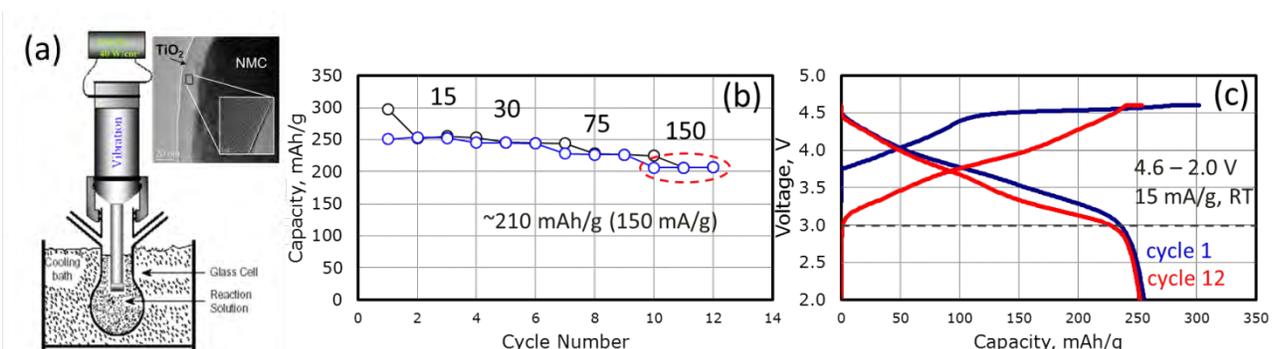


Figure 1. (a) Sonochemical reactor and images of a uniform coating of TiO_2 on NMC; (b) Capacity of $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ electrodes as a function of rate; (c) Voltage profiles of the sample in (b) showing *ca.* 230 mAh/g above 3.0 V, after 12 cycles to 4.6 V.

Three publications on this Task were published during FY 2012.

Collaborators: J.R. Croy, V. Pol

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

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

BASELINE 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 cathodes such as modified NMCs and LiNi_{0.5}Mn_{1.5}O₄ (LNMS) are synthesized via spray pyrolysis, as well as composites containing these materials, and coated particles. An array of physical and electrochemical techniques are used to characterize their behavior, in conjunction with members of the diagnostics team. Emphasis is placed on increasing energy density without sacrificing stability and cycle life.

STATUS OCT. 1, 2011: Phase-pure samples of LiNi_{0.5}Mn_{1.5}O₄ spinel (LNMS) have been produced by spray pyrolysis. Structural characterization of cycled Li[Ni_{0.45}Co_{0.1-y}Al_yMn_{0.45}]O₂; y=0, 0.05 electrodes was completed. Structural and electrochemical characterization of high capacity Li[Ni, Co, Ti, Mn]O₂ compounds will continue.

FY 2012 AOP EXPECTED STATUS SEP. 30, 2012: Hierarchically structured LNMS with differing primary and secondary particle sizes will be produced by spray pyrolysis, and optionally provided to interested members of the high voltage spinel discussion group. 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) Complete electrochemical characterization of hierarchically structured LNMS made by spray pyrolysis and compare to results obtained on conventional samples and simple particles made by spray pyrolysis. (Sep. 12). **Complete/on-going to Sep. 13**
- (b) Make a go/no go decision on Ti-substitution in NMCs as an approach for increasing energy density and improving cycle life. (Sep. 12). **On-going to Sep. 13**

PROGRESS TOWARD MILESTONES

1) *In situ* XRD experiments on cells containing disordered LNMS were subjected to charge and discharge at SSRL to understand the phase behavior. Plans for performing a similar experiment on the ordered LNMS sample with no Mn^{3+} are underway and should be completed by the end of the calendar year (with J. Cabana and G. Chen, LBNL). Experiments to determine the best heat treatments for $LiFePO_4@LNMS$ samples are underway. For this process, solutions of $LiFePO_4$ precursors are infiltrated into hollow LNMS spheres made by spray pyrolysis. $LiFePO_4$ also forms a protective coating on the outside of the spheres. Cross sectioning of particles (Fig. 1) indicate that there is relatively little $LiFePO_4$ inside the infiltrated particles and contact between the $LiFePO_4$ and LNMS occurs only in a small area. Nevertheless, heat treatment from 500 to 600°C for one hour in an inert atmosphere led to changes in the structure of the LNMS, suggesting that a reaction between the two phases occurs. A lower temperature hydrothermal treatment of an infiltrated sample led to Li loss in the LNMS phase. These results suggest that lower heat treatments are needed to form the $LiFePO_4$ phase without adversely affecting the LNMS, at least initially. This can be followed by a very brief higher temperature treatment to improve crystallinity of the phosphate phase without causing deterioration of the spinel phase.

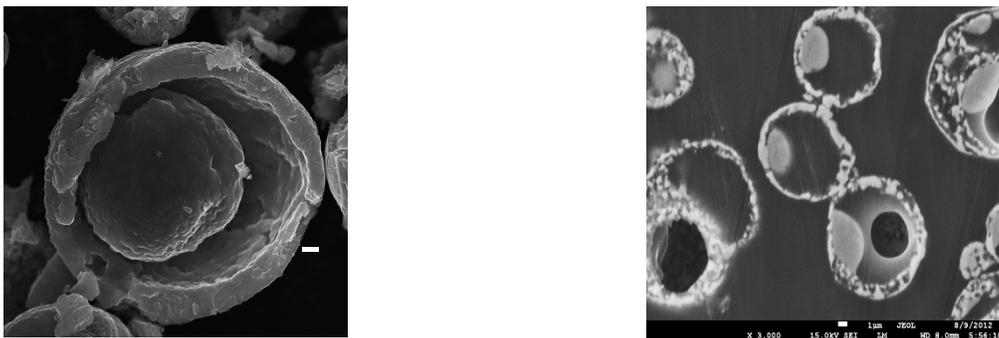


Figure 1. SEM image of a broken $LiFePO_4@LNMS$ particle (left) and particles that have been cross-sectioned (right).

2) Scale-up to 20g batches of several promising compositions of high capacity Ti-substituted NMCs and baseline materials for comparison is underway. These samples will be provided to Vince Battaglia and Guoying Chen, LBNL, for full cell testing (VB) and thermal characterization (GC). Based on results, further action will be taken to improve materials and understand their behavior, with the help of additional members of the BATT Program.

Publications:

- 1) “XAFS Investigations of $LiNi_{0.45}Mn_{0.45}Co_{0.1-y}Al_yO_2$ Positive Electrode Materials” Thomas E. Conry, Apurva Mehta, Jordi Cabana, and Marca M. Doeff, *J. Electrochem. Soc.* **159**, A1562 (2012).
- 2) “Electrochemical and Physical Properties of Ti-substituted Layered Nickel Manganese Cobalt Oxide (NMC) Cathode Materials” Kinson C. Kam, Apurva Mehta, John T. Heron, and Marca M. Doeff, *J. Electrochem. Soc.* **159**, A1383 (2012).
- 3) “Structural Underpinnings of the Enhanced Cycling Stability upon Al-Substitution in $LiNi_{0.45}Mn_{0.45}Co_{0.1-y}Al_yO_2$ Positive Electrode Materials for Li-Ion Batteries,” Thomas E. Conry, Apurva Mehta, Jordi Cabana, and Marca M. Doeff, *Chem. Mater.*, **24**, 3307 (2012).

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 SYSTEMS: 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: 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). 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 performances. The synthesized nanostructured polyanion cathodes are characterized by a variety of techniques including *ex situ* and *in situ* XRD, electron microscopy (SEM, TEM, and STEM), X-ray photoelectron spectroscopy (XPS), time of flight – secondary ion mass spectroscopy (ToF-SIMS), and in-depth electrochemical measurements. In addition, the role of cation doping, segregation of certain doped cations to the surface, cation ordering, and morphology on the electrochemical properties of 4.7 V spinel cathodes will be investigated. Based on the characterization data gathered, a fundamental understanding of structure-composition-property-performance relationships will be developed.

STATUS OCT. 1, 2011: Understanding of the self-surface segregation of cations during the synthesis process of high-voltage (4.7 V) spinel oxide cathodes through advanced characterization methodologies, development of novel solution-based synthesis approaches to obtain high-capacity nanostructured polyanion (silicate and phosphate) cathodes, and an investigation of their structure-composition-property-performance relationships.

FY 2012 AOP EXPECTED STATUS SEP. 30, 2012: Development of (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.

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

MILESTONES:

- (a) Understand the role of cation doping, surface modification, and morphology on the electrochemical properties of 4.7 V spinel cathodes. (Dec.11) **Complete**
- (b) Perform surface characterization of LiFe_{1-x}Co_xPO₄ with various x by XPS and ToF-SIMS. (Jun. 12) **Complete**
- (c) Perform novel synthesis and characterization of Li₂MSiO₄ and their solid solutions. (Sep. 12) **Complete**

PROGRESS TOWARD MILESTONES

With an aim to increase capacity while keeping the safety advantages associated with polyanion cathodes, the focus this quarter was on synthesizing Li_2MSiO_4 cathodes with unique morphologies by novel synthesis approaches. The Li_2MSiO_4 cathodes offer the potential to reversibly extract/insert two Li ions per transition-metal ion and thereby to increase the capacity by a factor of two compared to the LiMPO_4 phosphate analogs. Accordingly, $\text{Li}_2\text{FeSiO}_4$ was prepared by microwave-assisted hydrothermal (MW-HT) and solvothermal (MW-ST) synthesis approaches at $<300^\circ\text{C}$ for a short reaction time of <30 min, followed by heat treatment with sucrose at 650°C in an Ar atmosphere. Figure 1 compares the morphologies of samples obtained by the MW-HT and MW-ST methods. While the MW-HT method offers walnut-shaped particles with a large particle size (1.5 to 2 μm) as seen in Fig. 1a, the MW-ST method offers much smaller particles (20 to 50 nm) that are fused together into larger clusters as seen in Fig. 1b. Both the MW-HT (C/50 rate) and MW-ST (C/20 rate) samples show low discharge capacities even at much slower C rates (Fig. 1c); the lower rate capability of the MW-HT sample is due to the larger particle size. In order to improve the capacity, the MW-ST sample was prepared by incorporating graphene into the reaction medium. The MW-ST sample with graphene shows *ca.* 70 mAh/g higher capacity than the pristine MW-ST sample (Fig. 1c) due to the improvement in electronic conductivity. The synthesis approach is now extended to other Li_2MSiO_4 ($\text{M} = \text{Mn}, \text{Co}, \text{and Ni}$) cathodes and the $\text{Li}_2\text{Fe}_{1-x}\text{M}_x\text{SiO}_4$ solid solutions.

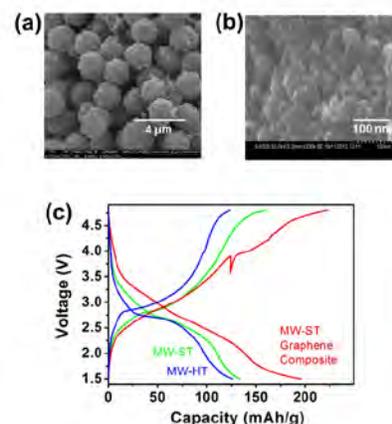


Figure 1. Morphologies of the (a) MW-HT and (b) MW-ST $\text{Li}_2\text{FeSiO}_4$ samples, and (c) electrochemical performances of the MW-HT, MW-ST, and MW-ST-Graphene samples.

During this quarter, with an aim of developing a better understanding of factors that lead to variations in the electrochemical performance of undoped $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ spinel cathodes, the project has focused on examining the orientation of the crystal planes facing the electrolyte and how these planes influence the cyclability and rate capability. By comparing two samples made by different wet-chemical routes but having identical undoped $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ composition, it was determined that the Poly 1 sample, (prepared with a tank reactor) with octahedral crystals in which the $\{111\}$ family of planes are exposed to the electrolyte (Fig. 2a), gives better rate capability and cyclability (Fig. 2b) than the Poly 2 sample, (prepared by traditional coprecipitation) with truncated octahedral crystals in which the $\{100\}$ family of planes are exposed to the electrolyte. The results illustrate that the surface planes and SEI play a dominant role in controlling the performance of undoped $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$.

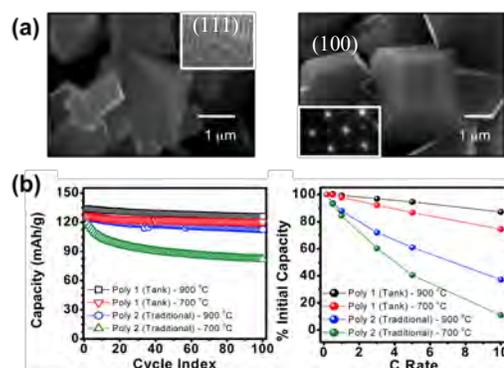


Figure 2. (a) Morphology and crystal planes of undoped $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ spinel cathodes prepared by two different methods and (b) electrochemical performances of the samples fired at 900°C and annealed at 700°C .

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

TASK TITLE - PROJECT: Cathodes – Development of High Energy Cathode Materials

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-energy, low-cost, and long-life cathode materials.

GENERAL APPROACH: Our approach is to develop high-energy cathode materials through a cost effective synthesis process. Appropriate doping, surface treatment and the identification of the electrolytes/additives will be used to improve the electrochemical performance of high voltage LiNi_{0.5}Mn_{1.5}O₄ based cathode. This high voltage cathode will be further combined with layer cathode to form a composite electrode with ‘layered-spinel’ structure. The experience and technologies developed in the high-capacity composite cathode will be used to further improve the capacity and stability of composite cathode.

STATUS OCT. 1, 2011: High-voltage LiNi_{0.5}Mn_{1.5}O₄ doped with Cr has been synthesized by a facile approach suitable for mass production. The reversible capacity is around 130mAh/g from the doped spinel, which exhibits a stable cycling for more than 100 cycles in half cells. The thermal stability investigation for electrochemically cycled LiMnPO₄ electrodes has been completed. The MnPO₄ reduction to Mn₂P₂O₇ with oxygen evolution was observed only at a temperature higher than 490°C, while the charged MnPO₄ undergoes structure distortion at above 180°C, possibly because of the Jahn-Teller effect accompanied by the decomposition of the passivation film formed on the cathode surface. Investigation of the electrochemical performance of non-stoichiometric LiMnPO₄ will be completed.

FY 2012 AOP EXPECTED STATUS SEP. 30, 2012: High-energy cathodes for Li-ion battery applications will be further explored. Using rheological phase reactions that involve only milling and heating processes and are suitable for scale up, layered composite cathodes based on xLi₂MnO₃•

(1-x)LiMO₂ (M=Mn, Ni, Co, x = 0.3-0.5) will be synthesized and their degradation mechanism will be investigated. The performance of high-voltage spinel LiNi_{0.45}Cr_{0.05}Mn_{1.5}O₄ will also be further improved. Safety, power rate, and cycling stability of these cathode materials will be improved to satisfy the need for HEV/EVs applications.

RELEVANT USABC GOALS: >96 Wh/kg (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) Synthesize and electrochemically evaluate Li₂MnO₃ as a baseline. (Mar. 12) **Complete**
- (b) Utilize rheological phase synthesis of layered composite cathode with 200 mAh/g capacity and stable cycling performance. (Sep. 12) **Complete**
- (c) Optimize the synthesis approach and inactive components for the high-voltage spinel and composite cathode. (Sep. 12) **Complete**

PROGRESS TOWARD MILESTONES

Milestones b) and c) for FY12 have been completed in Q4 of FY12:

- 1) Completed the evaluation of “inactive” components at high voltages, which are useful for both spinel and layered composite cathodes. The electrochemical behaviors of carbon additives were reported here, while cell cans and separator effects have already been published earlier this year.
- 2) Finished synthesis of Li-rich Mn-based layered composite and the preliminary data were compared with cathode materials supplied by ANL.

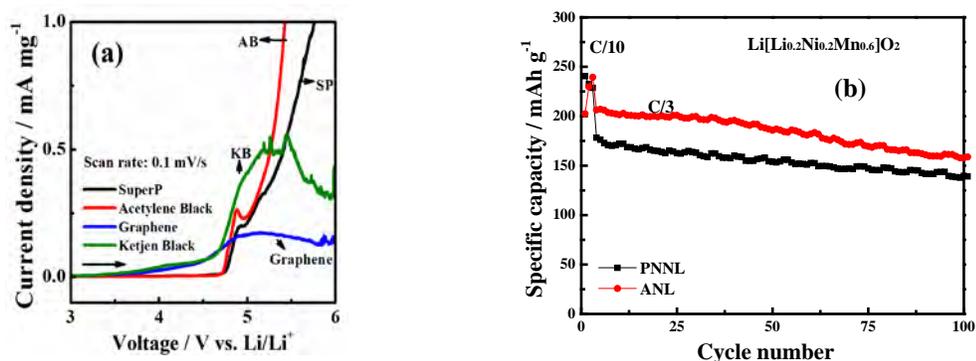


Figure 1. (a) Linear scanning voltage curves of different carbons in Li|C cells at a scan rate of 0.1 mV s⁻¹; (b) Comparison of Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O₂ supplied by ANL and synthesized at PNNL prior to optimization.

Carbon additives were found to behave differently at high voltages (Fig.1a), which greatly affects the coulombic efficiency and thus the cycling stability of the cells (data not shown here). High surface area carbons not only accelerated electrolyte decomposition, but also lowered the coulombic efficiency of the cathode due to continuous oxidation of functional groups. Even for the low surface area carbon, the intercalation of PF₆⁻ into the carbon structure is identified. Therefore, a carbon additive with minimal electrochemical activity is required for high voltage operation.

Figure 1b compares the layered composites with the same formula of Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O₂ prepared at ANL and PNNL. At a C/10 rate, both cathodes exhibited more than 200 mAh/g capacity. However, when the current density was increased to C/3 after the first three cycles, the ANL cathode demonstrated higher capacity retention at high rate, although relatively fast capacity decay was observed, compared with the PNNL material. Optimization of PNNL layered composite is underway and will be further investigated along with the ANL material to unravel the fundamental mechanisms that limit the electrochemical performance of this layered composite.

Collaborations: Drs. K. Amine and I. Belharouak at ANL for supplying layered composite cathode. Dr. Xiao-Qing Yang at BNL for XRD characterizations. Dr. Karim Zaghib for material milling. Dr. Kang Xu at Army Research Lab for new electrolyte. Prof. Whittingham at SUNY Binghamton for characterization.

Publications:

“Enhanced Li⁺ ion transport in LiNi_{0.5}Mn_{1.5}O₄ through control of site disorder,” J. Zheng, J. Xiao, X. Yu, L. Kovarik, M. Gu, F. Omenya, X. Chen, X.-Q. Yang, J. Liu, G.L. Graff, M.S. Whittingham, and J.-G. Zhang, *Phys.Chem.Chem.Phys.*, **14**, 13515–13521 (2012).

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

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

BASELINE SYSTEMS: 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

OBJECTIVES: 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 and controlled materials to get a complete picture of the different reactions involved in battery electrodes. Explore chemical spaces in search for new phases that may provide performance improvements. Establish the importance of the extended electrode structure on electrochemical performance.

STATUS OCT. 1, 2011: Samples of LiNi_{1/2}Mn_{3/2}O₄ with morphology decoupled from the crystal chemistry (Mn³⁺ content, Ni-Mn ordering) were successfully synthesized. Annealing of the samples provided control of these parameters. Analysis of their electrochemical properties as battery electrodes revealed that seemingly small variations among samples produce significant effects on electrochemical performance.

FY 2012 AOP EXPECTED STATUS SEP. 30, 2012: The composition and crystal structure of the annealed samples of LiNi_{1/2}Mn_{3/2}O₄ will have been analyzed by coupling spectroscopic tools with diffraction. The role of oxide additives on the performance of spinel electrodes will have been assessed. The first set of new fluoride-containing phases will have been prepared and their applicability as Li battery cathodes will have been established.

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 the crystal-chemical characterization of annealed LiNi_{1/2}Mn_{3/2}O₄ and identify its role on electrochemical performance. (Mar. 12) **Complete**
- (b) Synthesize and physico-chemically characterize at least two different new phases showing an oxyfluoride network, containing lithium and a light transition metal. (Sep. 12) **Delayed to FY 2013**
- (c) Identify the influence of oxide additives on the extent of electrolyte-electrode side reactions in spinel electrodes. (Sep. 12) **Complete**

PROGRESS TOWARD MILESTONES

Milestone (a): The study of the structure-composition-property relationships in $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ was completed during Q2. The data analysis is now complete and ready to be submitted for publication. It is concluded that transition metal ordering is much more correlated to electrochemical performance than the Mn^{3+} content, which is generated during annealing through preferential segregation of Ni into a rock-salt secondary phase. The correlations between morphology and performance were explored in a separate study by Dr. Guoying Chen (see corresponding reports).

Milestone (b): This milestone was only partially complete, and delayed to FY13, due to a

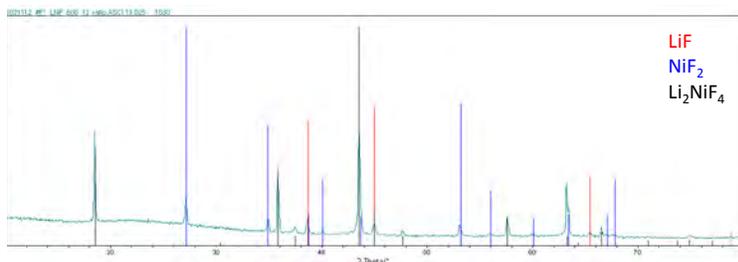


Figure 1. XRD of the product of $\text{LiF}+\text{NiF}_2$ at 600°C .

corresponding delay in personnel hiring. Nonetheless, exploration of phase diagrams of a number of transition metal (oxy)fluorides has begun. During Q4, Li_2NiF_4 was successfully synthesized using conventional solid state methods under a pure N_2 atmosphere. Only small impurities of LiF and NiF_2

remained after heating at 600°C (Fig. 1). Attempts at electrochemically extracting Li were made by ball milling the material with as much as 30% carbon. No activity was found when tested in Li half-cells in any case. This observation is consistent with computational predictions that the potential of extraction is well above 5.0 V. The addition of oxygen is viewed as a strategy to introduce covalence in the compound that lowers the electrochemical potential as well as increases its electronic conductivity. The first reactions with oxygen in the reagent mixture have been initiated.

Milestone (c): This milestone is complete. Results were extensively reported in Q3; follow-up experiments confirmed the same trends. During Q4, our knowledge of the surface of $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ during Li removal using XAS developed during Q1 was combined with the study of modified materials. An example is shown in Fig. 2. Fe $L_{\text{II,III}}$ edge XAS was performed on $\text{LiFe}_{0.08}\text{Ni}_{0.42}\text{Mn}_{1.5}\text{O}_4$ (provided by Prof. Manthiram) in its pristine state and after full Li removal. The data was collected with a total electron yield detector, which is sensitive only to the first 5 to 10 nm of material; therefore, changes correspond to the surface of the powder. The spectra of the two samples show noticeable differences in lineshape, especially at the Fe L_{III} edge (705 to 710 eV). They are indicative of a change in electronic structure of Fe and point to the electroactivity of this ion during electrochemical charging.

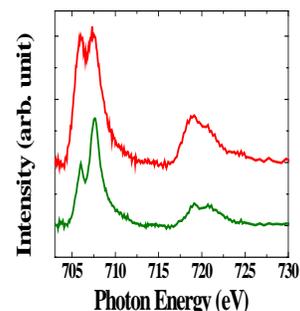


Figure 2. Fe $L_{\text{II,III}}$ edge XAS of $\text{LiFe}_{0.08}\text{Ni}_{0.42}\text{Mn}_{1.5}\text{O}_4$ before (bottom) and after (top) a full charge.

Collaborations this quarter: Prof. Grey (Cambridge), Prof. Manthiram (UT-Austin), Drs. Persson, Doeff, Chen, (LBNL), Dr. Chernova, Prof. Whittingham (SUNY Binghamton).

Publications and Presentations this quarter:

1. T.E. Conry, A. Mehta, J. Cabana and M.M. Doeff; *Chem. Mater.*, **24**, 3307 (2012).
2. J. Cabana, M. Casas-Cabanas, F.O. Omenya, N.A. Chernova, D. Zeng, M.S. Whittingham, and C.P. Grey; *Chem. Mater.*, **24**, 2952 (2012).

Task 4.6 - PI, INSTITUTION: Jason Graetz, Brookhaven National Laboratory

TASK TITLE - PROJECT: Cathodes – Novel Materials

BASELINE SYSTEMS: 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 specialized *in situ* reactors designed to investigate solvothermal synthesis reactions in real-time using synchrotron techniques. This unique 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, 2011: This project is a new start. All equipment and plans are in place for the initial project tasks.

FY 2012 AOP EXPECTED STATUS SEP. 30, 2012: In Year 1 the existing quartz capillary reactor will be modified to accommodate higher pressures and temperatures. A procedure for the synthesis of LiMBO₃ (M = Mn and/or Fe) will be developed and complete preliminary electrochemical measurements.

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

MILESTONES:

- (a) Complete design and order necessary components for second-generation capillary reactor capable of accommodating higher pressures and temperatures. (Apr. 12) **Complete**
- (b) Develop a procedure for the synthesis of LiMBO₃ (M = Mn and/or Fe). (Sep. 12) **Complete**
- (c) Complete preliminary characterization of synthesis reaction(s) using the *in situ* capillary reactor. (Sep. 12) **Complete**

PROGRESS TOWARD MILESTONES

Efforts in the fourth quarter of FY12 were focused on the *in situ* synthesis of $\text{Cu}_{0.95}\text{V}_2\text{O}_5$. The conventional hydrothermal reaction was performed in deionized water at 180°C for *ca.* 17 hours:



Figure 1 shows the phase transformations that occurred during the conventional hydrothermal synthesis of $\text{Cu}_x\text{V}_2\text{O}_5$ (reaction 1). At the onset of the reaction the primary peaks are associated with the V_2O_5 phase. As the temperature was raised to 180°C the V_2O_5 diffraction peaks disappeared and weak peaks from the $\text{Cu}_x\text{V}_2\text{O}_5$ phase emerged indicating a dissolution-recrystallization reaction. There was no evidence of an intermediate phase in this reaction, but intermediate phases were observed with different precursors and under different reaction conditions. The $\text{Cu}_x\text{V}_2\text{O}_5$ phase grew steadily with time until the reaction was stopped after approximately 17 hours. The final product consisted of a Cu deficient phase of $\text{Cu}_{0.36}\text{V}_2\text{O}_5$, which is isostructural with V_2O_5 . Scanning transmission electron microscopy (STEM) and energy dispersive spectroscopy (EDA) analysis of the product (Fig. 1c) revealed a rod-shaped morphology, indicative of preferential growth along a specific direction, along with a homogeneous distribution of Cu.

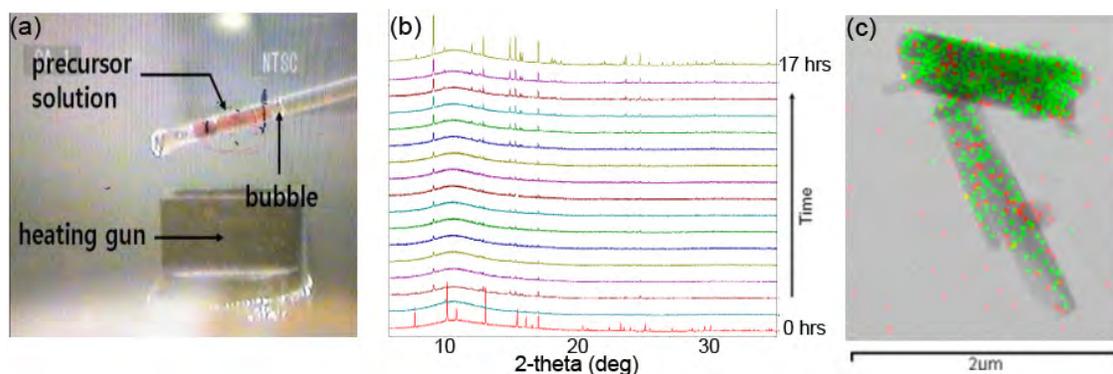
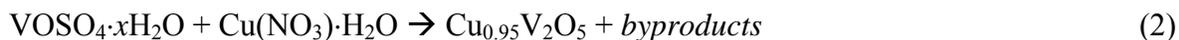


Figure 1. (a) *In situ* capillary reactor used for hydrothermal synthesis. (b) Time-resolved XRD patterns of the hydrothermal synthesis of $\text{Cu}_x\text{V}_2\text{O}_5$ at 180°C . (c) Bright-field STEM and EDS of the as-synthesized $\text{Cu}_x\text{V}_2\text{O}_5$ ($x \approx 0.36$) showing rod-like morphology and Cu distribution (green).

A number of variations on the hydrothermal synthesis were explored, including the following hydrothermal reaction at 140°C for 24 hrs:



However, this reaction was unsuccessful, no $\text{Cu}_{0.95}\text{V}_2\text{O}_5$ was formed. Another attempt utilized different precursors that react quickly to form an intermediate phase followed by $\text{Cu}_{0.95}\text{V}_2\text{O}_5$:



All Milestones for FY12 have been completed and the progress for this project has exceeded the Expected Status for this year.

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

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

BASELINE SYSTEMS: 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: Lithium-bearing mixed polyanion (LBMP) glasses are herein proposed as potential cathode materials for lithium ion batteries with superior performance to lithium iron phosphate for use in electric vehicle applications. The composition of LBMP glasses can be tailored to provide higher electrical conductivities, higher redox potentials, and higher specific energies than similar crystalline polyanion framework materials. The disordered covalently bonded structures of LBMP glasses could provide excellent cyclability and safety performance. In addition, LBMP glass compositions may enable cyclable multi-valent changes in the transition metal cations of the cathode material, which has 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 JUL. 1, 2012: This project was initiated June 22, 2012.

FY 2012 AOP EXPECTED STATUS SEP. 30, 2012: Initial glass compositions will serve as a baseline for electrochemical properties as well as means to develop our materials synthesis capability and electrode fabrication techniques. Similarly CALPHAD modeling will build from baseline preliminary work on the iron phosphate system. Both efforts will be ready to move to more complex and promising compositions in the following year.

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

MILESTONES:

- (a) Synthesize, characterize, and perform electrochemical testing on two of baseline glass cathode compositions. (Sep. 12) **Delayed to Dec. 2012 due to funding delay**
- (b) Create CALPHAD thermodynamic database for the baseline system. (Sep. 12) **Delayed to Dec. 2012 due to funding delay**
- (c) Synthesize and characterize one of baseline glass cathode composition. (Sep. 12) **Complete**

PROGRESS TOWARD MILESTONES

In order to provide a proof-of-principle for the potential benefits of producing cathodes from mixed polyanion glass, phosphate glass cathode materials were chosen for the initial study. Iron phosphate glasses of similar compositions as crystalline iron phosphates were chosen for baseline glasses. Iron phosphate glass containing vanadate or molybdate will be produced this calendar year and directly compared to the pure iron phosphate glasses.

Simultaneous differential thermal analysis and thermogravimetric analysis (SDT) was performed on the phosphate glass precursors and precursor mixtures to provide fundamental insights into precursor reactions that occur during thermal processing of phosphate glasses. SDT analysis has assisted glass processing development to obtain compositional accuracy, minimization of volatile phosphate loss, and control of anionic valence.

Glass processing of iron phosphate materials was performed in a high temperature muffle furnace in air using a quench in both a graphite mold and copper plates. The two target glass compositions were: FePO_4 and $\text{Fe}_4(\text{P}_2\text{O}_7)_3$. X-ray diffraction of the FePO_4 material revealed a glass material with a small fraction of FePO_4 crystallites. Based on previous experience and literature references, a higher quench rate or a slight compositional change is anticipated to produce a pure glass material. X-ray diffraction of $\text{Fe}_4(\text{P}_2\text{O}_7)_3$ quenched by a graphite mold was consistent with a pure glass material.



Figure 1. A baseline glass cathode material (above) has been produced with a composition of $\text{Fe}_4(\text{P}_2\text{O}_7)_3$.

The $\text{Fe}_4(\text{P}_2\text{O}_7)_3$ glass was characterized by XRD, inductively coupled plasma atomic emission spectroscopy (ICP-AES), and XPS. Elemental analysis of the glass by ICP-AES showed that the iron / phosphorous ratio was near the exact target ratio (0.82 measured; 0.83 target) and that a small percentage (0.85 wt%) of Al was present, presumably from the alumina crucible. X-ray photoelectron spectroscopy of the material found a mixture of iron valences (*ca.* 2/3 Fe^{3+} / *ca.* 1/3 Fe^{2+}). Glass processing parameters are being adjusted to obtain an improved baseline glass with a minimized Fe^{2+} content.

The FY2012 milestones were adjusted for the funding delay (project started in late June). A baseline glass cathode composition was synthesized and characterized, as scheduled. The two milestones that were delayed to December 2012 are on schedule. Two baseline phosphate glasses are on schedule to be synthesized, characterized, and electrochemically tested. Thermodynamic modeling of the crystalline Li/ FePO_4 system has been obtained from the phase diagram data in the literature and thermodynamic model parameters of constituent binary oxides.

BATT TASK 5 **DIAGNOSTICS**

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

TASK TITLE - PROJECT: 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-alloy anodes

GENERAL APPROACH: Our approach is to (i) apply *in situ* and *ex situ* Raman and FTIR far field and near field spectroscopy/microscopy, scanning probe microscopy (SPM), spectroscopic ellipsometry, electron microscopy (SEM, HRTEM), and standard electrochemical techniques to detect and characterize bulk and surface processes in intermetallic anodes, and high-energy cathodes, (ii) design and apply a new model electrochemical experimental setup to study the kinetics of Li alloying and diffusion in intermetallic anodes, and possible correlations with the formation and long-term stability of the SEI layer.

STATUS OCT. 1, 2011: Insight into the mechanism of surface phenomena on thin-film and monocrystal Sn and Si intermetallic anodes is expected to have been gained and their impact on the electrode long-term electrochemical behavior is expected to have been 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 will be applied 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.

FY 2012 AOP EXPECTED STATUS SEP. 30, 2012: The mechanism of electrolyte decomposition at the surface of model anode and cathode materials is expected to be fully understood 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 as well as on model single particle and composite high-voltage cathodes will be 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) will be 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 will be carried out.

RELEVANT USABC GOALS: *Cycle life:* 5000 (deep) and 300,000 (shallow) cycles. *Available energy:* 96 Wh/kg. *Calendar life:* 15 years.

MILESTONES:

- (a) Resolve SEI layer chemistry of Si and Sn model anodes - collaboration with the BATT Anode Group. (Jul. 12) **Complete**
- (b) Characterize surface phenomena and bulk phenomena in high-voltage composite cathodes - collaboration with the BATT Cathode Group. (Sep. 12) **Complete**
- (c) Use near-field IR and Raman spectroscopy to characterize battery materials. (Sep. 12).

Complete

PROGRESS TOWARD MILESTONES

In the fourth quarter, main efforts towards milestone “b” focused on fluorescence spectroscopy measurements of surface phenomena at the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ composite cathode. The previously reported studies of electrochemical activity of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ were supplemented with *in situ* fluorescence spectroscopy of the conductive additive carbon black, which constitutes the majority of the composite cathode surface area. Figure 1 shows *in situ* fluorescence intensity variations during voltammetry scans of a carbon black/PVdF composite electrode between 3.5 and 5.0 V at a $v = 0.1$ mV/s. The fluorescence signal started to rise abruptly at 4.25 V and continued to increase up to 4.75 V, and then began to decrease at 4.75 V during the cathodic scan. Interestingly, the fluorescence signal decreased slightly around the 5 V potential limit, and the intensity of the residual fluorescence was higher at the end of the cycle. This pattern was repeated during the following cycles, indicating that electrolyte oxidation on CB additives also contributes to the interfacial side-reaction of the composite cathodes. This study completes efforts toward milestone “b”.

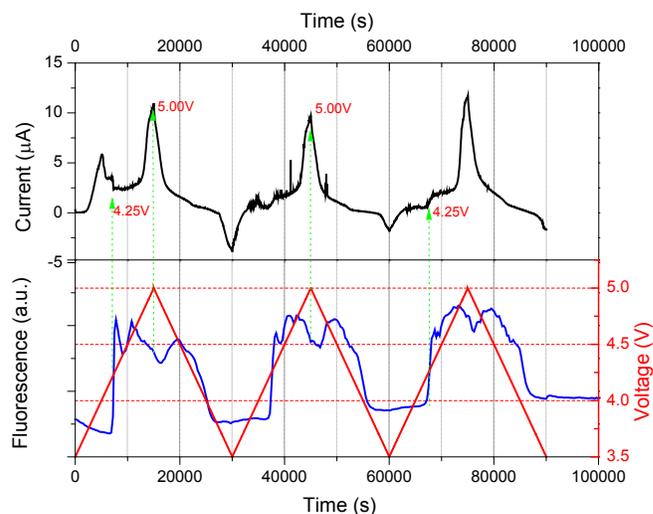


Figure 1. Fluorescence spectroscopy of CB electrode.

The combined research thrusts toward milestones “a” and “c” resulted in a pioneering *ex situ* near-field IR imaging of the SEI formed on polycrystalline Sn electrodes. The images were collected at three different wavelengths, *i.e.*, 9.6, 10.0, and 10.4 μm for a Sn electrode that was cycled potentiostatically 5 times between 2.5 and 0.8 V. The images shown in Fig. 2 displayed strong variations in signal intensity and contrast as the function of the IR light energy. The image recorded at 10.4 μm showed an inverted IR contrast, which is indicative of a complex composition and/or non-uniform distribution of the layer building components. Additional IR spectroscopic investigations of reference compounds such as LiF, Li_2CO_3 , lithium oxalate, *etc.*, will enable determination of the local chemical composition of the SEI with one simple mapping step. These results complete our efforts toward milestones “a” and “c”.

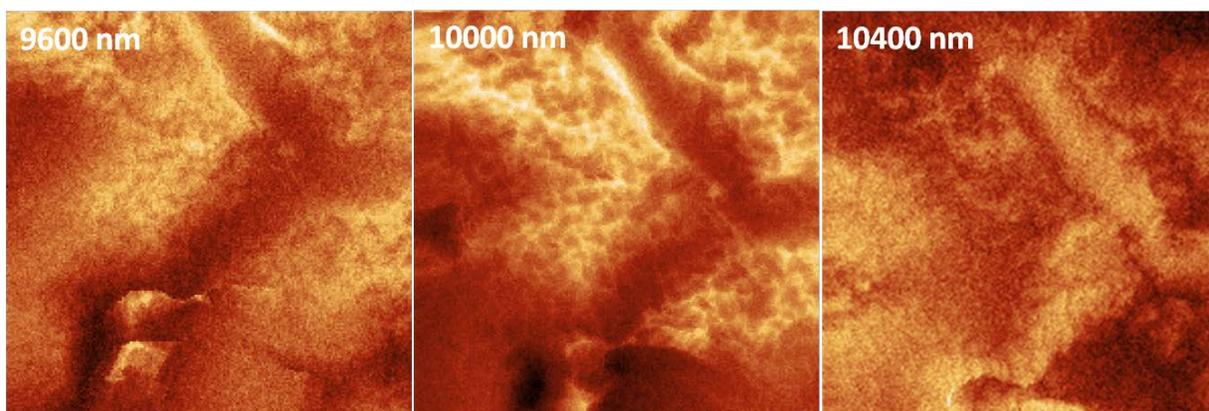


Figure 2. *Ex situ* near-field IR images of the SEI layer on Sn electrode.

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

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

BASELINE SYSTEMS: 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

OBJECTIVES: 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 lithium 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. *Ex situ* soft XAS will be used to distinguish the structural differences between surface and bulk of electrodes. Time resolved X-ray diffraction (TRXRD) technique will be used to understand the reactions that occur in charged cathodes at elevated temperatures.

STATUS OCT. 1, 2011: Studies on high energy Li_{1.2}Ni_{0.2}Mn_{0.6}O₂ cathode materials during charge-discharge cycling using combined *in situ* hard XAS and *ex situ* soft XAS will be completed. Important information about the roles of Mn cations will be obtained. The *in situ* XAS and XRD studies on mesoporous LiFe_{1-y}Mn_yPO₄ (0.0≤y≤0.8) cathode materials during charge-discharge cycling will be completed. The effects of particle size and morphology on the phase transition behavior and performance of Li-ion cells will be obtained.

FY 2012 AOP EXPECTED STATUS SEP. 30, 2012: Structural studies on the high energy density Li₂MnO₃-LiMO₂ (M = Ni, Mn, Co) layered materials (in collaboration with ANL) and *in situ* XRD studies on different types of lithium iron phosphate cathode materials with mesoporous structure will be carried out. The diagnostic studies of high voltage LiMn_{2-x}M_xO₄ (M= Ni, Cu etc.) with spinel structure will be completed. Diagnostic studies on high energy density anode materials, such as Si, Sn and alloys will also be conducted.

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

MILESTONES:

- (a) Complete *in situ* XRD studies of LiMn_{0.4}Fe_{0.6}PO₄ cathode material with different particle size and morphology during electrochemical delithiation. (Apr. 12) **Complete**
- (b) Complete *in situ* XRD studies of Li₂CO₃ during electrochemical decomposition and the potential application of this process. (Apr. 12) **Complete**
- (c) Complete *in situ* XAS studies of high voltage LiMn_{2-x}M_xO₄ (M= Ni, Cu etc.) with spinel structure cathode materials during electrochemical cycling. (Sep. 12) **Complete**

PROGRESS TOWARD MILESTONES

In the 4th quarter of FY2012, milestone (c) was successfully completed. The diagnostic studies of high voltage spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode material were completed and the diagnostic studies of high energy density Si based anode materials were initiated.

The studies of structural changes of high voltage spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode materials with ordered structure ($P4_332$ space group) have been carried out. To confirm the ordered structure of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ samples, Rietveld refinements were performed using synchrotron XRD data, the results are shown in Fig.1. The XRD patterns (inset in Fig. 1) revealed the existence of weak super lattice peaks arising from Ni/Mn ordering. The XRD diffraction peaks matched with space group $P4_332$ very well, confirming the ordered spinel structure of our $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ sample. Unlike the disordered spinel phase with the existence of a relatively high amount of impurity phase (*ca.* 2.9%), it was found that the amount (*ca.* 0.5%) of impurity phase (*i.e.*, cubic rock salt Ni_6MnO_8) in this ordered spinel is very small.

In situ XAS at Ni and Mn K-edges were then performed on this ordered sample to study the local electronic and structure changes during 1st charge and discharge as shown in Fig. 2 (only first discharge data shown due to the limited space). The first discharge curve in Fig. 2(a) showed no detectable 4.0V plateau, which is well in agreement with previous results for the ordered spinel $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$. As shown in Figs 2(b) and (c), unlike the Ni K-edge XANES spectra, which show clearly the edge shift to lower energy, the Mn spectra do not show rigid edge shift, suggesting that most of the high-voltage capacity around 4.7V is associated with the redox reaction from Ni^{4+} to Ni^{2+} while the Mn did not contribute much to the capacity during the 1st discharge. One interesting feature observed in the Mn K-edge XANES spectra is the disappearance of two shoulder peaks located at the edge rising region (marked by asterisk) in Fig. 2(b) during discharge. The appearance of these shoulder peaks is due to the ligand-to-metal charge transfer (LMCT), which suggests that oxygen donates some electrons to metal 3d orbitals in a covalent bond manner. Appearance of strong two-shoulder peaks at highly-charged states (spectrum A) may suggest some contribution to the charge compensation reaction at high voltages from oxygen atoms bonded with Mn atoms. Disappearance of these two peaks during discharge reveals decreased oxygen contribution to the charge compensation reaction as the voltage decreased.

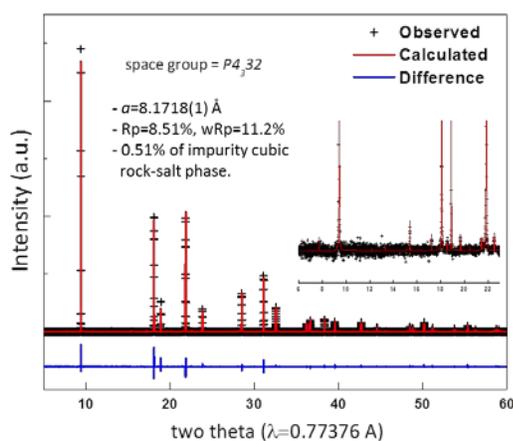


Figure 1. Rietveld refinement of the synchrotron x-ray diffraction for the ordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel cathode.

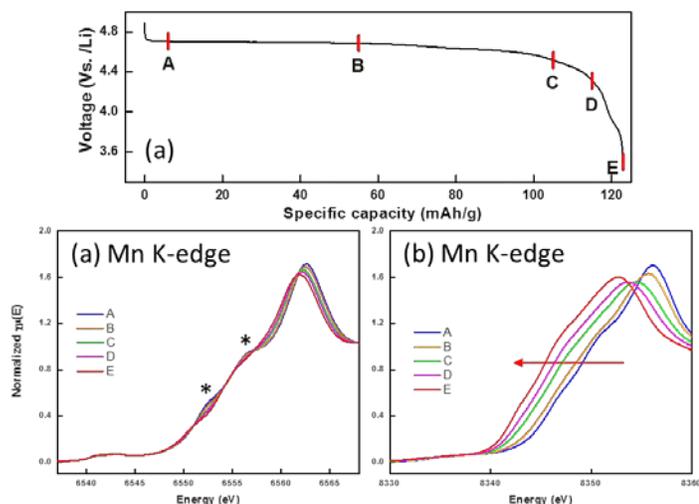


Figure 2. (a) 1st discharge profile of the ordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode during *in situ* XAS, and corresponding *in situ* (b) Mn and (c) Ni K-edges XANES spectra.

TASK 5.3 - PI, INSTITUTION: Gerbrand Ceder, Massachusetts Institute of Technology, and Clare Grey, Cambridge University

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

BASELINE SYSTEMS: 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

OBJECTIVES: Determine the effect of structure on stability and rate capability of cathodes and anodes. Explore relationship between electrochemistry and particle size and shape. Develop new, stable, cathode materials with high energy-density.

GENERAL APPROACH: Use solid state NMR and diffraction/TEM to characterize local and long-range structure as a function of particle size, sample preparation method, state of charge and number of charge cycles (cathodes). Use electrochemistry to correlate particle size with rate performance. Continue to develop the use of *in situ* NMR methods to identify structural changes and reactivity in oxides and intermetallics and to examine Li dendrite formation. Use first principles calculations (density functional theory) to identify redox-active metals, relative stability of different structures, the effect of structure and particle size on cell voltages and rate capability. Use high-throughput computing to identify promising cathode materials for BATT applications. Anticipate possible instabilities in materials at high states of charge by using calculations. Use calculations and NMR to identify low activation energy pathways for cation migration and to investigate electronic conductivity. Extend to Na systems.

STATUS OCT. 1, 2011: *In situ* NMR of silicon and lithium metal anodes, new phosphocarbonates and high voltage cathodes will be ongoing. Several compounds from computational search under experimental investigation.

FY 2012 AOP EXPECTED STATUS SEP. 30, 2012: Completed ²⁹Si studies of lithium silicides and phosphocarbonates. Insights into viability of several Na cathodes.

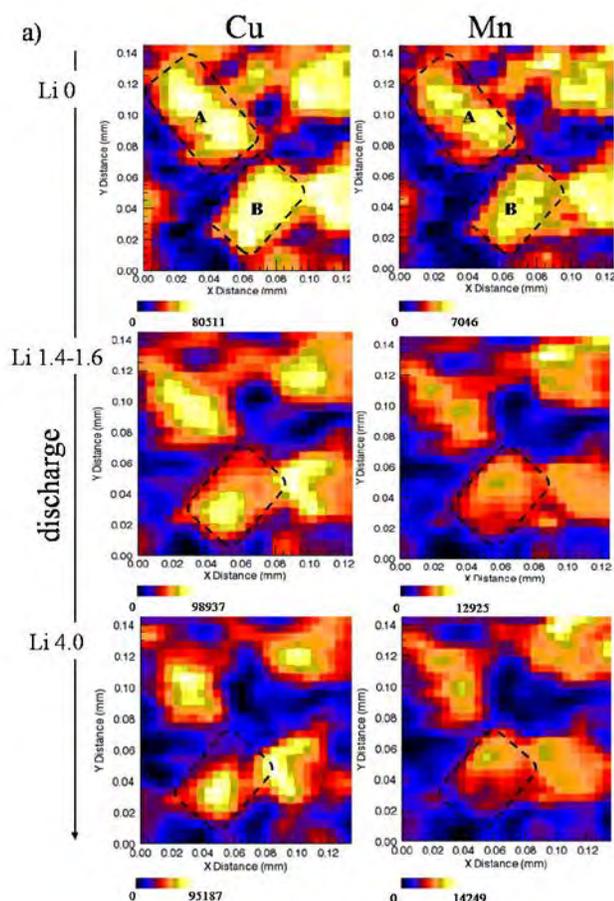
RELEVANT USABC GOALS: Specific power 300 W/kg, 10 year life, <20% capacity fade

MILESTONES:

- (a) Complete ²⁹Si NMR experiments on crystalline lithium silicides. (Mar. 12) **Complete**
- (b) Complete electrochemical testing of sidorenkites for Li and Na batteries. (Mar. 12) **Complete**
- (c) Complete NMR studies of metal doping of LiMnPO₄. (Mar. 12) **Complete**
- (d) Complete work on novel intercalation cathode. (Mar. 12) **Complete**
- (e) Complete ²⁹Si NMR of amorphous lithium silicide electrodes. (Sep. 12) **Complete**
- (f) Initiate *in situ* NMR studies of SEI formation on silicon anodes; complete lithium dendrite study. (Sep. 12) **On schedule**
- (g) Suggest at least one new Na intercalation compounds. (Sep. 12) **Complete**
- (h) Provide computed data on pyrophosphates to Whittingham (Sep. 12) **Complete**

PROGRESS TOWARD MILESTONES

Ex situ and *in situ* micro-focused synchrotron X-ray fluorescence imaging (μ XRF) coupled with selective micro-focused X-ray absorption near edge spectroscopy (μ XANES) and micro-focused X-ray diffraction methods (μ XRD) were investigated as methods to image the elemental components within a battery electrode and to follow the metal oxidation states and phase distributions. The techniques were applied to investigate $\text{Sr}_2\text{MnO}_2\text{Cu}_{3.5}\text{S}_3$, a cathode material that operates by a combined insertion/displacement mechanism. After 2 moles of Li intercalation, Cu metal extrusion is observed by μ XRD, which also reveals the formation of the $\text{Sr}_2\text{MnO}_2\text{Cu}_{3.5-x}\text{Li}_x\text{S}_3$ phase. *Ex situ* μ XRF images of the electrode after 4 mol of Li intercalation show a segregation between the Cu metal particles, while *in situ* μ XRF imaging experiments reveal that the Cu and Mn elemental distribution maps are highly correlated with the particle orientation giving different results when the particle is oriented perpendicular or parallel to the incident beam (Fig. 1). *In situ* electrochemical synchrotron XRF imaging has the advantage over the *ex situ* mode of resolving the mechanism of single particles *vs.* time. *In situ* μ XRF imaging data suggest that the microstructure of the $\text{Sr}_2\text{MnO}_2\text{Cu}_{3.5-x}\text{Li}_x\text{S}_3$ electrode, on a micron-scale level, is not affected during the reaction process.



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Figure 1. *In-situ* X-ray fluorescence imaging maps at the Cu^+ energy (8981 eV) for Cu $K\alpha$ and Mn $K\alpha$ of an *in situ* $\text{Sr}_2\text{MnO}_2\text{Cu}_{3.5}\text{S}_3|\text{Li}$ cell at different stages of discharge, (from up to down): Li0, Li1.4-1.6 and Li4.0 (fully discharged) maps. The Li contents, denoted by x in Li_x , indicate the amount of Li inserted in the $\text{Sr}_2\text{MnO}_2\text{Cu}_{3.5-x}\text{Li}_x\text{S}_3$ structure. The maps were collected at the same region on the electrode film of an area ($120/130\mu\text{m} \times 140\mu\text{m}$) at $5\mu\text{m}/\text{step}$ with dwell time of $2\text{s}/\text{pixel}$.¹

In a second method development, *in situ* ^7Li and ^6Li -NMR studies of working batteries have been performed to investigate paramagnetic cathode materials. Our initial approach was modified to solve some of the challenges that result from the paramagnetism. Initial studies have focused on $\text{Li}_{1.08}\text{Mn}_{1.92}\text{O}_4$ and it was shown that the method can be used to detect changes of Li transport within the electrode, *in situ*. *Ex situ* Li studies have been performed to determine the limits of Li substitution in this material.

1. R. Robert, D. Zeng, A. Lanzirrotti, P. Adamson, S.J. Clarke, and C.P. Grey, *Chem. Mat.*, **24**, 684-2691, (2012).

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

TASK TITLE - PROJECT: Diagnostics - Studies and Design of Chemically and Structurally Stable Surfaces and Structures of Lithium Storage Materials

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

BARRIERS: Inadequate energy, and abuse tolerance of Li-ion batteries

OBJECTIVES: To develop high-energy and long-cycle-life cathodes.

GENERAL APPROACH: Efforts will be focused on exploring the use of lithium peroxides and oxides in the positive electrodes to provide significant enhancement in gravimetric energy relative to conventional lithium interaction compounds. Of particular interest is to examine the influence of catalysts on the charging voltage of such high-energy electrodes. The surface chemistry, microstructure of oxide-electrolyte interface, and oxide crystal structure of high-energy positive electrodes will be examined by a range of techniques such as transmission electron microscopy, synchrotron X-ray diffraction, Raman spectroscopy and X-ray adsorption spectroscopy, and X-ray photoelectron spectroscopy. These surface and structural features and their changes during electrochemical measurements would provide insights into developing strategies in the design of high-energy and long-cycle-life cathodes.

STATUS OCT. 1, 2011: Select (Li₂O_x)_yMO_z electrodes will be prepared and tested in two-electrode and three-electrode cells having lithium as the negative electrode, where the activity of MO_z such as MnO₂ and Co₃O₄ for Li₂O_x oxidation will be compared with that of the state-of-art precious metal catalysts such as Pt/C.

FY 2012 AOP STATUS SEP. 30, 2012: The influence of some metal oxide catalysts on the charging voltage of such high-energy electrodes has been established and compared with Pt/C. Changes in the microstructure and crystal structure of select (Li₂O_x)_yMO_z electrodes have been identified by scanning or transmission electron microscopy and X-ray diffraction. Application of fundamental insights to design of new and stable surfaces for high-energy cathodes will be ongoing.

RELEVANT USABC GOALS: High Energy/Power Ratio Battery, energy density (>100 Wh/kg), power density (>400 W/kg), 15-year calendar life and cycle life (5,000 cycles).

MILESTONES:

- (a) Complete XPS analysis of the surface chemistry changes of LiNi_{0.5}Mn_{1.5}O₄ cycled to two voltages and compare with the surface chemistry changes of Li_xCoO₂ and LiNi_{0.5}Mn_{0.5}O₂. (Jun. 12). **Complete**
- (b) Demonstrate the oxide catalyst influence on the capacities, discharge/charge voltages or cycle life of (Li₂O₂)_x(MO₂)_y (where M = Mn, Co, Ni, etc.) in lithium cells. (Jun. 12) **Complete**
- (c) Supply XPS and TEM data demonstrating the surface chemistry and morphological changes of (Li₂O₂)_x(MO₂)_y during charge and discharge. (Sep. 12) **Delayed to Dec. 12**

PROGRESS TOWARD MILESTONES

The influence of select metal oxides on the oxidation kinetics of Li_2O_2 has been studied and *in situ* electrochemical XPS studies of Li_2O_2 formation/oxidation on the $\text{Li}_x\text{V}_2\text{O}_5$ surface were completed. The surface chemistry and morphological changes from microscopy studies are ongoing and will be completed by Dec. 2012. This milestone is delayed due to implementation of a new method, the potentiostatic intermittent titration test (PITT), to study the electrochemical oxidation kinetics of Li_2O_2 . PITT is a quasi-equilibrium technique that gives access to the kinetic information for each redox process, and will be used to study the Li-O₂ charge kinetics.

The lack of mechanistic understanding of the oxygen evolution reaction (OER) in Li^+ -containing nonaqueous media has strongly impeded further advances of Li/air (Li-O₂) batteries. To investigate the electrochemical processes during charging, PITT was applied. Figure 1a shows the PITT measurement performed in the potential windows of 2.8 to 3.8V vs. Li^+/Li (V_{Li}) with 10 mV potential steps. The zoom-in of the PITT results for the first 25% of charge capacity is shown in Fig. 1b. A maximum current at the start of each potential increment was observed, followed by monotonic decay. The characteristic monotonic decay is indicative of the diffusion-dominated process as well as the absence of a significant reaction barrier. The PITT current response for the middle 50% of the charge capacity is shown in Fig. 1c. Interestingly, a completely different response was noted in which the current rises slowly to reach its local maximum, then decays gradually thereafter. This kinetic response cannot be modeled by the regular diffusional process and suggests a phase transformation barrier that is gradually overcome at constant potential as the reaction proceeds. In addition, this current response can be qualitatively described by a nucleation and growth process where the rising current segment

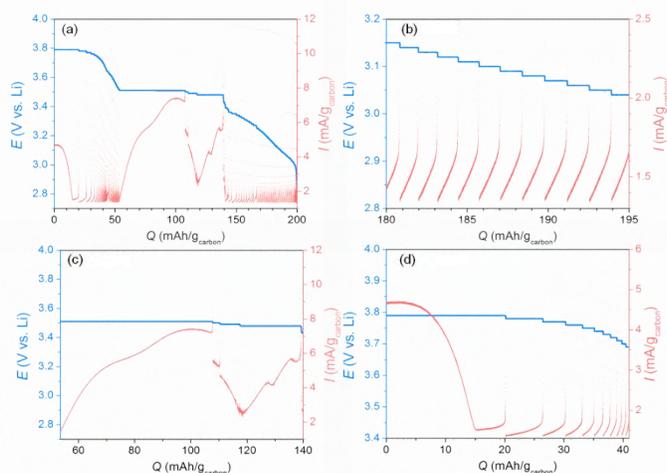


Figure 1. (a) Potential steps (blue) and corresponding current response (red) during PITT measurements (10 mV steps, 1.3 mA/g_c current cut-off or 50 hrs durations) on charging an electrode that was discharged to 200 mAh/g at 100 mA/g. (b) The zoom-in of (a) for the first 25% charge capacity. (c) The zoom-in of (a) for the middle 50% charge capacity. (d) The zoom-in of (a) for the last 20% charge capacity.

reflects the increase in electroactive area (e.g., each independent nucleus grows in size and/or the number of nuclei increases). The current then falls, after the local maximum, as a result of a decrease in the driving force for nucleation and/or a decrease in the available reactant (Li_2O_2). This behavior is consistent with the electro-oxidation of the chemically-synthesized Li_2O_2 reported recently. (Harding and Shao-Horn et al., *Phys. Chem. Chem. Phys.*, 2012). Lastly, the PITT current response of the last 25% charge capacity (Fig. 1d) shows monotonic decays at each potential step. The current increases as the potential step increases (so does the time before current cut-off) as a result of increasing driving force for electrolyte decomposition. At a potential of ca. 3.8 V_{Li} , the current increases sharply and reaches a steady-state at ca. 4.6 mA/g_c, with accumulated charge capacity larger than the total discharge capacity (200 mAh/g_c), indicating that the governing reaction here is likely to involve electrolyte decomposition and/or decomposition of byproducts such as Li_2CO_3 . This is consistent with a recent study reporting that CO_2 is evolved at the end of the Li-O₂ recharge due to decomposing electrolyte- and carbonate-type species (McCloskey et al., *J. Phys. Chem. Lett.*, 2012).

Collaborations: A. Mansour, NSWC, for XPS and XAS measurements; M. Thackeray, ANL, TEM and XPS.

BATT TASK 6
MODELING

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

TASK TITLE – PROJECT: Modeling - Improved Electrochemical Models

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

BARRIERS: Poor transport properties, capacity and power fade

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

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

STATUS OCT. 1, 2011: Experiments measuring the kinetics of ferrocene reduction through a passivating film on glassy carbon will be complete. Characterization of the SEI on highly-oriented-pyrolytic graphite (HOPG) will be ongoing. Comparison of ferrocene kinetics in the presence and absence of additives will be ongoing.

FY 2012 AOP EXPECTED STATUS SEP. 30, 2012: Characterization of the SEI on HOPG will be complete. Comparison of ferrocene kinetics in the presence and absence of additives will be complete. A model for the formation of the SEI will be complete.

RELEVANT USABC GOALS:
300,000 shallow discharge cycles
15 year calendar life

MILESTONES:

- (a) Obtain AFM and ferrocene kinetic measurements of SEI on HOPG. (Dec. 11).
Complete/canceled
- (b) Compare through-film ferrocene kinetics for SEI formed in presence of VC and FEC.
(Apr. 12) **Canceled due to change in research direction**
- (c) Develop model to explain current-time curves for film formation. (Aug. 12) **Complete**

PROGRESS TOWARD MILESTONES

In the previous quarterly, a ferrocene characterization method was used to determine that the SEI products formed at lower potential are inherently more passivating than those formed at higher potential. Both the through-film limiting current ($i_{lim,f}$) and effective rate constant (k_{eff}) are smaller for the same amount of formation charge as the formation potential is decreased. Previous work in our group has suggested that a decrease in the film porosity is responsible for a similar trend of transport and kinetics. In this quarter, the study continued and a manuscript submitted to the Journal of the Electrochemical Society. It is currently under review. A BATT seminar on the subject was also given on June 11.

Figure 1 shows the porosity of the SEI calculated using either the value of $i_{lim,f}$ or k_{eff} . Only data at 0.45 V formation are shown. The two methods both yield reasonable values, but do not agree exactly. Although adjusting the assumed thickness can improve the agreement slightly, the difference between the calculated values increases at greater amounts of formation charge. The same trends apply for data at different formation potentials (not pictured). While this disagreement may seem to contradict the explanation of decreasing porosity, the disagreement could also point to the existence of a porosity gradient through the SEI. If the porosity is smaller at the compact/porous layer interface than it is at the porous layer/electrolyte interface, the accessible area for charge-transfer reaction will be smaller than the area limiting transport through the SEI.

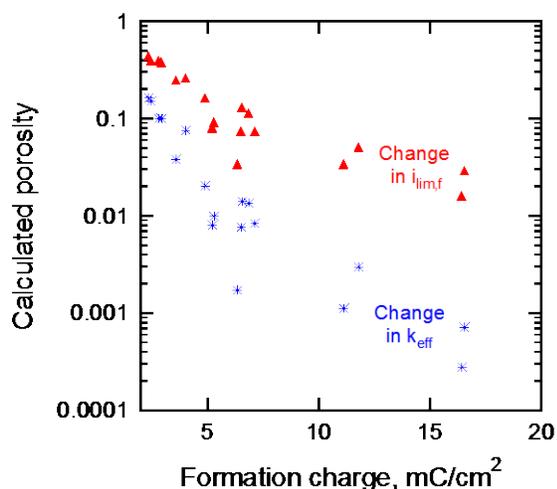


Figure 1. Calculated porosity of 0.45 V formation.

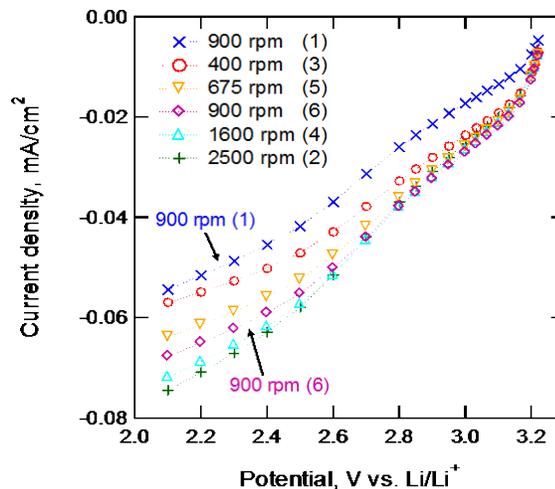


Figure 2. Instability of SEI formed at 0.1 V.

Figure 2 shows another result that suggests that porosity is indeed the limiting phenomenon for through-film ferrocenium reduction. The data shown are for through-film reduction after 10 seconds of formation at 0.1 V. The order of measurement is shown in parentheses. Figure 2 shows that current increases with order of measurement (parentheses) and rotation speed; thus, the film is unstable. However, the open circuit potential does not change, and from fitting the curves (not pictured), both $i_{lim,f}$ and i_0 increase with time. Thus, either the thickness and the rate constant decrease simultaneously at open-circuit conditions, or the porosity increases, possibly because intermediates diffuse away and open up void space in the film.

More details on this work can be found in the submitted manuscript, which completes milestone c) It was initially planned to experiment with additives instead of varying the formation potential; therefore, milestone b) is cancelled due to the change in research direction.

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

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

BASELINE SYSTEMS: 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. Develop a model to account for porosity in electrode secondary particles and quantify effect on performance
3. Develop a model for mechanical degradation of electrodes with consideration of particles and binder.

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, 2011: A preliminary model that quantifies the importance of incorporating binder effects in predicting failure of particles will be complete. The impact on low volume change systems like graphite and high volume change systems like silicon will be examined. The rate capability of NCM cathodes on a particle scale will be quantified and the relevant transport properties measured.

FY 2012 AOP EXPECTED STATUS SEP. 30, 2012: The performance models for Si anode with the NMC cathode will be complete and comparison made with the baseline. The degradation of graphite and candidate alloy anodes that takes into account the interaction of the active material and the binder will be complete. A model that accounts for the reaction distribution across the electrode will be developed and compared to experimental data.

MILESTONES:

- (a) Construct a silicon anode particle model that incorporates a coupling between kinetics and stress during lithiation and delithiation. (Feb. 12) **Complete**
- (b) Compare the porous electrode model with experimental data of NCM cathode and quantify effect of porosity and conductive aids on performance. (Mar. 12) **Complete**
- (c) Develop a model for porous particles applying to Ni/Mn spinel oxides and report on the effects of secondary particle porosity on battery performance. (Sep. 12) **Complete**
- (d) Couple the particle model with a model of the surrounding binder material to quantify the effect of binder properties on damage to the binder and binder-particle interface. (Sep. 12) **Complete**

PROGRESS TOWARD MILESTONES

Modeling Porous Ni/Mn Spinel Particle: This milestone has been refocused to look at limitations in the porous electrode rather than the particle. This is because the Ni/Mn spinel is a high rate material at the particle level and, therefore, no limitations are expected on that scale.

Modeling NMC Cathode: Over the last year, models of the layered NiCoMn cathode system have been developed with the aim of predicting the performance at high rates. While these models show the ability to predict data to a rate of 2C, higher currents lead to significant deviation from experimental data. A series of experiments on laminates of varying thicknesses with similar porosity and of varying porosity with similar thicknesses were performed in order to understand the cause for the deviation.

Figure 1a shows the utilization of electrodes for three different thicknesses as a function of current density based on the interfacial area of NMC particles. When the applied current was small, all the electrodes showed gradual decreases in electrode utilization with increasing current, which was previously shown to be caused by the decrease in the diffusion coefficient of Li in the solid cathode particles toward the end of discharge. As the current density was increased further the thicker electrodes showed a rapid loss in capacity. This suggests a change in electrode limitation as thickness increases. However, as the total current changes in all the electrodes, it is not clear where this limitation occurs. Comparison of the model to this data suggests that the current densities on these cells could lead to large concentration buildup on the Li anode, possibly inducing saturation of salt, which could be the cause of the utilization drop.

Replotting Fig. 1a as electrode utilization *versus* current density based on the cross-sectional area of the porous electrode (Fig. 1b) helps elucidate the cause of the limitation. Here the deviation of the thick cell at the same current density is apparent, suggesting that the limitation occurs on the electrolyte phase within the porous electrode, rather than the Li-metal electrode. Further comparisons of the model to the experiments suggest that the model's inability to predict the data is due to a lack of knowledge of the electrolyte transport properties. This will be the focus of the efforts in the next quarter.

Understanding Mechanical Degradation in Silicon Anodes: Electrical isolation of active material as a consequence of mechanical degradation is an important source of capacity fade in Si anodes. As described last quarter, a coupled particle-binder model was implemented to understand particle-level damage in electrodes. This fulfills the September milestone. This model is built on the work of Christensen/Newman (2006), which describes a spherical, isotropic particle undergoing large deformation due to Li insertion and removal. The present model allows for a binder layer of user-specified thickness on the surface of the electrode particle, and includes the composition-dependence of the Young's modulus and Poisson's ratio as obtained by Shenoy/Johari/Qi (2010). Using this model, one can simulate the evolution of stress throughout the particle-binder system and use the material yield-stress as a threshold for damage. However, insight gained through this investigation has suggested that a new mathematical model be developed specifically for materials in which the inserted species plays a role in supporting anisotropic stress and strain. This category includes alloying materials such as Si. Thermodynamic relationships underpinning this new model have been obtained, and new descriptions of dynamic behavior such as diffusion, reaction kinetics, and inelasticity will be built on this foundation.

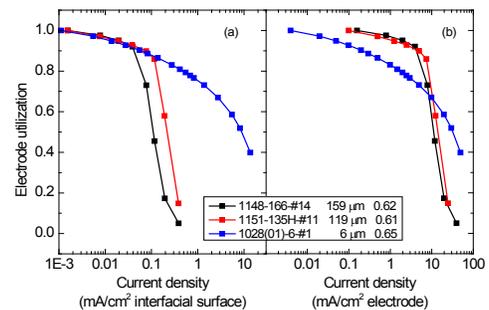


Figure 1. Experimental capacity of NMC electrode as a function of discharge current density based on (a) the interfacial area of active material, and (b) the cross-sectional area of the porous electrode.

TASK 6.3 - PI, INSTITUTION: Jonghyun Park, University of Michigan

TASK TITLE - PROJECT: Modeling – Thermo-electrochemistry, Capacity Degradation, and Mechanics with SEI Layer

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

BARRIERS: Prediction of capacity and power degradation, and excessive additive materials which penalize energy and power density and increase cost.

OBJECTIVES: (i) multiscale FE modeling considering phase transition and the mismatch between active material and SEI layer, (ii) simulation in Li-ion batteries including microscale features, (iii) measurement of mechanical properties (*i.e.*, Young's modulus and thickness) of the SEI layer

GENERAL APPROACH: Parallel numerical and experimental approaches to study the interrelationships of the solid electrolyte interphase and lithium manganese oxide will be used. The numerical approach will rely upon voxelation of real particle geometries and the finite element technique to solve the complex multiphysics problem of the electrochemical, mechanical and thermal aspects of the SEI layer. Experimentally, the composition, morphology, and physical and electrochemical properties of the SEI using ATR-FTIR, TEM, and AFM, as well as electrochemical techniques to measure the diffusivity and conductivity of the SEI layer will be measured.

STATUS OCT. 1, 2011: A multiscale FE model considering particle aggregation, its effect on cathode structure, and the effect in turn on cathode dissolution has been established. An SEI layer formation model and parametric studies for different electrochemical systems have also been established. Finally, experimental techniques (*ex-situ* and/or *in-situ*) will be applied to validate the SEI layer formation model. With these three objectives completed, capacity degradation of Li-ion batteries can be correlated to the properties of SEI layers and particle microstructures.

FY 2012 AOP STATUS SEP. 30, 2012: To have (1) applied finite element methods to the phase change/intercalation interrelationship to graphitic anodes, (2) applied numerical techniques to the modeling of the SEI layer on complex electrode geometries, and (3) verified the model using experimental data collected on the physical properties of the SEI layer.

RELEVANT USABC GOALS: *Available energy for CD mode:* 3.4 kWh (10 miles) and 11.6 kWh (40 miles); *Cycle life:* 5000 cycles (10 miles) and 300,000 cycles (40 miles); *10- s discharge power:* 45 kW (10 miles) and 38 kW (40 miles); *Calendar life:* 15 years (40°C).

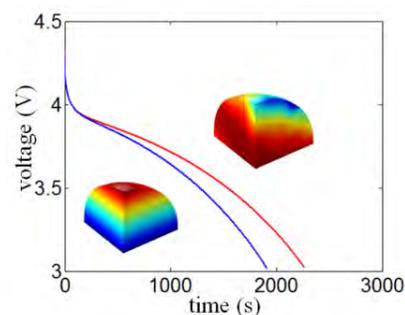
MILESTONES:

- (a) Implement multiscale modeling for stresses in active material considering SEI layer. (Mar. 12) **Complete**
- (b) Couple the 1D electrochemical model with a previously developed micro scale model. (May 12) **Complete**
- (c) Quantify variation in the mechanical properties of the SEI layer as a function of cycle number. (Aug. 12) **Complete; additive effect; on-going; mechanical properties**

PROGRESS TOWARD MILESTONES

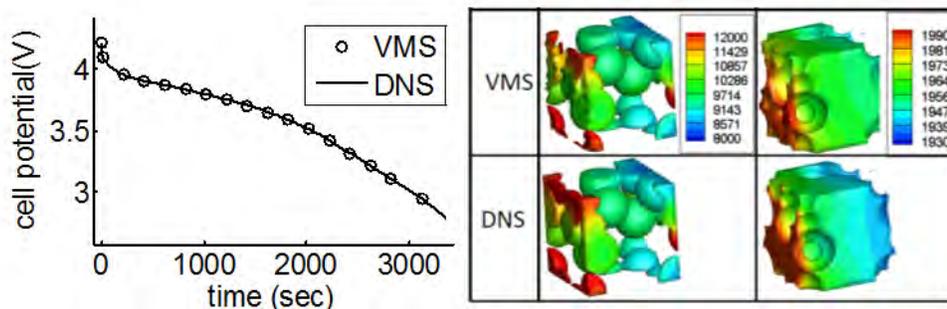
1) Intercalation- and Misfit-Induced Stress in the Graphite Electrodes

The effect of the anisotropic features of a graphite electrode on cell performance was examined *via* cell-scale electrochemical modeling including local grain boundaries of the active materials. The orientation of each grain was selected randomly for multiple grain particles. The right figure shows the voltage profile during 1C cell discharge. As shown in the figure, the case of the single-grain particle results in lower capacity compared to the case of the multiple-grain particles. This is due to usage limitations of the particle in local regions: Li-ions cannot intercalate effectively through the basal plane of the graphite.



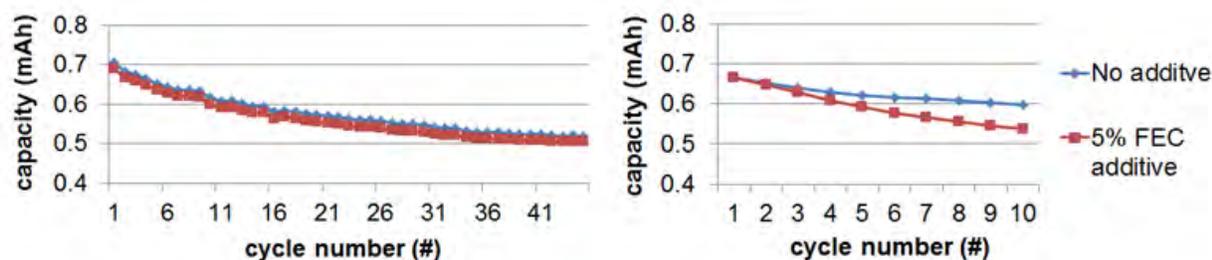
2) Multiscale modeling with self-assembly and dissolution

A variational, multi-scale, simulation (VMS) model for Li-ion batteries was validated by comparison with a direct numerical simulation (DNS) model. One particle-cluster in each electrode was modeled to reduce the computational cost. The cell was discharged at a rate of 1C. As shown in the figures below, cell potential (left) and the concentration profile in the particles and electrolyte (right) are almost identical.



3) Characterization of SEI layers

The effect of the additive-derived surface layer on Mn dissolution was examined. FEC additive (5%) was added to the 1M LiPF₆ EC/DMC(1:1 v/v) solution. The cells were cycled 45 times at room temperature, then cycled 10 more times at 50°C. The additive FEC had little influence on capacity fade at room temperature (see left figure below). At high temperatures, however, the added FEC clearly affected capacity fade (see right figure below). Based on the previous ICP results, the additive FEC resulted in the acceleration of Mn dissolution. The combined results imply that the FEC additive is advantageous for generating a stable SEI layer on the anode at high temperatures. However, it can also result in aggravated Mn dissolution on the cathode at high temperatures.



TASK 6.4 - PI, INSTITUTION: Kristin Persson, Lawrence Berkeley National Laboratory

TASK TITLE – PROJECT: Modeling – Predicting and Understanding New Li-ion Materials Using *Ab Initio* Atomistic Computational Methods

BASELINE 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) Predict new chemistries and crystal structures for improved electrodes as defined by the goals of USABC. 2) Understand diffusion-limiting behavior in current and novel electrode materials in order to suggest chemical or morphological improvements. 3) Understand surface interactions in electrode materials to optimize stability and kinetics.

GENERAL APPROACH: Use computational *ab initio* atomistic modeling methods to understand current Li-ion battery electrode materials and use this knowledge to suggest improvements as well as new electrode materials. Use statistical mechanics models to understand Li diffusion in bulk and on surfaces. Combine and make efficient access to all relevant calculated knowledge in a searchable database, facilitating computational materials design.

STATUS OCT. 1, 2011: Evaluation of Al substitution effect on LiNi_{1/3}Mn_{1/3}Co_{1/3-x}Al_xO₂ in terms of Li mobility and electronic conductivity has been concluded. The study of Li absorption on graphene and multi-layer graphene surfaces will be underway. The Li and cation interactions in LiNi_{1/2}Mn_{3/2}O₂ will be understood as a function of Li content. The materials genome web site is launched from LBNL.

FY 2012 AOP EXPECTED STATUS SEP. 30, 2012: Li kinetics on graphene and multi-layer graphite is concluded. Electronic structure studies of surface facet stability of electrode materials (LiMnO₂ and LiFePO₄) will be underway. Phase diagram of LiNi_{1/2}Mn_{3/2}O₂ will be concluded. The study of Li kinetics and electronic structure of Li_xNi_{1/2}Mn_{3/2}O₂ as a function of Li content will be underway.

RELEVANT USABC GOALS: PHEV: 96 Wh/kg, 5000 cycles; Operating charging temperature: -30 to 52 °C

MILESTONES:

- (a) Go online with the Materials Genome database from LBNL. (Oct. 11) **Complete**
- (b) Map the electronic structure of Li_xNi_{1/2}Mn_{3/2}O₂ as a function of Li content. (Oct. 11) **Complete**
- (c) Calculate the band structures of LiMnO₂ surfaces. (Dec. 11) **Complete**
- (d) Predict the stable phases of the Li-graphene and Li-multi-graphene. (Feb. 12) **Complete**
- (e) Complete the phase diagram of Li_xNi_{1/2}Mn_{3/2}O₂. (Mar. 12) **Complete**
- (f) Calculate the surface DOS of LiFePO₄ with different absorbents. (May 12) **Canceled due to change in research direction**
- (g) Complete the kinetics of Li-graphene. (Sep. 12) **Canceled due to change in research direction**

PROGRESS TOWARD MILESTONES

Collaborations: Prof. Gerbrand Ceder (MIT), Dr. Jordi Cabana (LBNL), Dr. Robert Kostecki (LBNL), Dr. Phil Ross (LBNL).

The high voltage spinel work is concluded. The cation-ordering influence has been investigated on the stable ground state, the electrochemical profile, the Li/Vacancy phase diagram and the Li diffusivity in $\text{Li}_x(\text{Ni}_{0.5}\text{Mn}_{1.5})\text{O}_4$ as a function of Li content. Over 250 different Ni/Mn and Li/Vacancy arrangements were calculated and a coupled cluster expansion technique was applied to divulge the underlying cation interactions in the system and the preferred ground state arrangements. This cluster expansion was employed to derive the Li/Vacancy phase diagram as a function of cation ordering and temperature and to obtain the chemical diffusivity as a function of Li content.

It was found that perfectly ordered high-voltage spinel transforms through a two-phase reaction (Fig. 1) between the end states $x_{\text{Li}} = 0$ and $x_{\text{Li}} = 1$ and resists solid solution until very high temperatures. However, deviations from perfect ordering dramatically increase the stability of the solid solution, even at room temperature for high Li content. This is important, as solid solution reactions are associated with less strain and higher cyclability of the material. A ‘uniformly’ disordered material (highest entropy) shows that the Li/Vacancy ordered state remains at room temperature but that the solid solution reaction is much more accessible than for the ordered material, throughout the Li composition range, even for low Li contents.

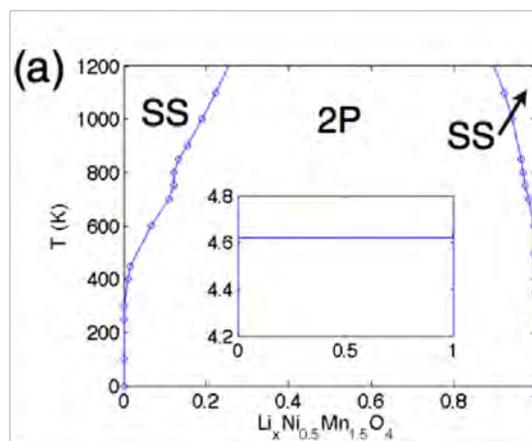


Figure 1. Li/Vacancy phase diagram for the ordered high-voltage spinel and voltage profile at RT (see inset).

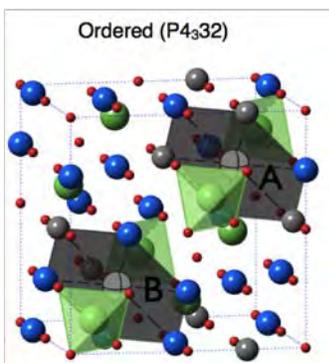


Figure 2. The ordered high-voltage spinel exhibits two different diffusion paths – indicated in the figure by ‘A’ and ‘B’.

The intrinsic bulk Li diffusivities in both the ordered as well as the disordered material were found to be very high which indicates that difference in rate capability between the two materials originate from other factors. The value of the Li activation barrier was correlated to the cation decoration of the hexagonal plane through which the Li diffuses which is exemplified in Fig. 2.