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August 30, 2013

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

Dear Tien,

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

Sincerely,

Venkat Srinivasan
Acting Head
BATT Program

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

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

FEATURED HIGHLIGHTS

Electrode Architecture

- ✦ Battaglia's and Srinivasan's Groups demonstrate, through experiments and modeling, that the impedance data for each electrode vs. a reference electrode results in contributions from both electrodes in both sets of data.

Cathodes

- ✦ Cabana's Group demonstrates that a MgO-coating on LNMS leads to a surface that is more stable against reduction when in the presence of a typical Li-ion electrolyte.

Diagnostics –

- ✦ Chen's Group demonstrates the use of XAS in the TEY mode as a means of detecting structural changes as a result of cycling.
- ✦ Chen's Group also shows that layered $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}\text{O}_2$ crystals in the form of platelets demonstrate the highest rate capability.
- ✦ With a new *in situ* ATR-FTIR designed cell, Samorjai and Ross' Group detect a soluble and an insoluble electrolyte reduction product and propose a mechanism for their formation.

Modeling

- ✦ Srinivasan's Group measures the resistance at the electrolyte solid oxide conductor interface at $0.398 \pm 0.0199 \text{ kohm cm}^2$.

BATT TASK 1

ELECTRODE ARCHITECTURE

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

TASK TITLE: Electrode Architecture — Cell failure: electrochemical diagnostics

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

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

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

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

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

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

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

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

MILESTONES:

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

PROGRESS TOWARDS MILESTONES

(b) Gas sensing apparatus for a coin cell demonstrated on full cell, June 2013. **Completed**
Please see the first two quarterly reports of 2013 for details.

(c) Potential dependence of Mn loss from Mn-spinel measured, June 2013. **Completed.**
Will be reported on in the next quarterly.

(a) Make a modification to the three electrode cell hardware based on guidance from Modeling Group and measure difference in response, May 2013. **Completed.**

Srinivasan's Group used Comsol to see if the inductance loops seen experimentally in three-electrode cells could be simulated. Instead of the 2-D geometry in cylindrical coordinates, the problem was solved in the 2-D Cartesian coordinates. Laplace's equation for the potential distribution with linear kinetics at electrode boundaries was solved and mass transfer effects ignored. In so doing, the inductance loops could be reproduced. Now, the impedance data for a full cell looks like what most others find when they perform ac-impedance on 2-electrode cells and that the impedance data from the electrodes to the reference can be added together to give the 2-electrode cell data. It appears that the source of the odd loops in the individual cell data comes from geometries where the reference electrode is placed close to a region where the anode and cathode are not perfectly aligned. An investigation of different electrode alignments and reference electrode placements indicates that, short of expecting to perfectly align the electrodes, one can not use the reference electrode impedance data to distinguish the contributions from the anode and the cathode separately. Below is an example of 2-electrode data, on the left; 3-electrode data of the ref/cathode and ref/anode cells, middle; and the sum of the ref/anode and ref/cathode data, right. [In this case, the reference is under the cathode and a small hole has been punched through the cathode.] One can see that the 2-electrode data is indistinguishable from the sum of the data from each electrode *vs.* the reference. According to the modeling, impedance associated with the cathode is being captured by the impedance data measured on the ref/anode couple. This would clearly lead to a false interpretation of what is happening in the cell.

In the next quarter, this experiment will be repeated but with two electrode geometries to demonstrate that the impedance data for each electrode can be unequivocally identified and the rate of impedance growth appropriately measured and assessed.

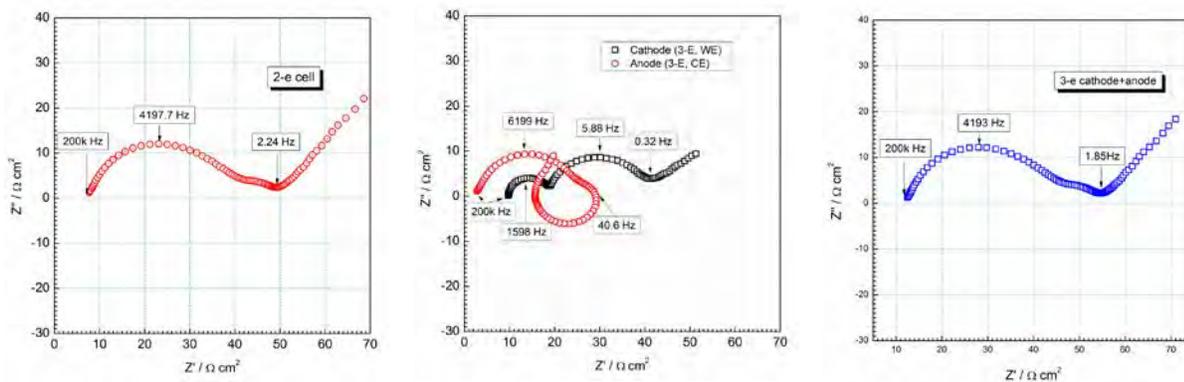


Figure 1. EIS data from a three electrode cell. Left, 2-electrode cell data; middle, ref./anode and ref./cathode; right, sum of impedance from ref./anode and ref./cathode.

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

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

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

BARRIERS: Low energy and poor cycle/calendar life

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

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

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

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

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

MILESTONES:

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

PROGRESS TOWARD MILESTONES

In this quarter, the focus was on optimizing the Si-anode formulation and electrode architecture with the reference material recommended by the BATT Program, Si (Umicore). The studies identified the best anode composition and the appropriate method for mixing the Si composite. The best ratio of Si:binder:carbon black is 50%:25%:25% for the electrode composition, and the appropriate mixing method is jar-mill followed by planetary mixing. The porosity of the electrode, which is strongly influenced by the electrode composition, is a major parameter affecting the electrode performance. A high carbon content and low Si ratio in the anode composition yielded significantly better performance. The electrode with the composition 50%:25%:25% was evaluated at C/6 and 1C to determine the effect of stress on the particles as a result of long-term cycling. Figure 1 shows the capacity fade profile with the two rates. The capacity fade is more pronounced when the rate is higher. The Si particle suffers more at high rate (1C), which induces a fade of 85% of the initial capacity compared to 56% at C/6.

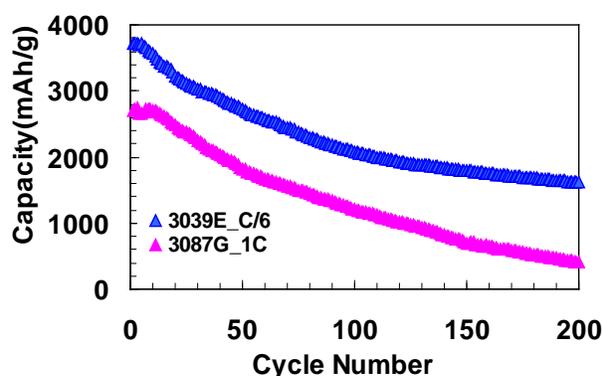


Figure 1. Cycle life of Li/EC-DEC-LiPF₆/Si cells at 1C and C/6.

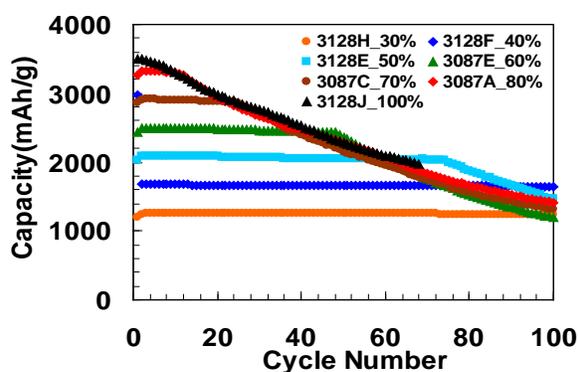


Figure 2. Cycle life at C/6 of Li/EC-DEC-LiPF₆/Si cells at different DoD.

Analyzing the stress on the Si particles involved a systematic study of the depth of discharge (DoD) and its effect on the cycling performance. The stress level was controlled by varying DoD. At low DoD, the Si particles in the anode will experience minimum stress. Figure 2 shows clearly the effect of DoD on the cycling stability at C/6. Capacity fade is severe when Si is cycled at high DoD - the particles suffer from high stress that induces cracks. At DoDs higher than 50% (2000 mA/g capacity), the cells show capacity that degrade in the same manner. At 40% DoD, an acceptable reversible capacity of 1670 mAh/g with good stability after 100 cycles is obtained. The results of the *in situ* analysis and cycling studies on the Si (Umicore) anode material indicate that controlling the rated capacity by limiting DoD is beneficial to reduce stress and to maintain the mechanical integrity of the particles. Sacrificing some of the capacity is an acceptable compromise to obtain a useful Li-ion cell with long cycle life.

HQ continues collaboration with LBNL researchers V. Battaglia and G. Liu in the BATT Program.

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

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

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

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

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

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

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

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

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

MILESTONES:

- (a) Fabricate at least five NCA cathodes by directional freeze casting and sintering. (Apr. 13)
Complete
- (b) Complete electrochemical testing of cathodes in (a), and complete measurement of electronic conductivity and diffusivity vs. x in sintered NCA. (Jun. 13) **On-going, due Sep. 13**
- (c) Complete measurement of electronic conductivity vs. x in sintered doped LiM_xMn_{2-x}O_{4-y}F_y. (Sep. 13) **Composition revised to LiMn_{1.5}Ni_{0.5-x5}Fe_xO₄ based on preliminary results.**

PROGRESS TOWARD MILESTONES

Collaborator: Antoni P. Tomsia (LBNL)

Accomplishments: During the present reporting period, progress was made in measuring the ionic conductivity and diffusivity on sintered, dense $\text{Li}_1\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (NCA) as a function of temperature. Measurements were performed on additive-free, sintered NCA, and therefore reflect pure-phase conductivity and diffusivity. Samples were fired at 850°C for 12h and cooled at $5^\circ/\text{min}$, resulting in samples of 96% density. A thin sheet of polyethylene oxide (PEO) with 1% lithium iodide salt was used as an electron blocking electrode for the measurement of ionic conductivity and diffusivity, with the layer sequence being: Li/PEO/NCA/PEO/Li. The Li-metal sheet functions as a source and sink of Li ions as well as the current collector. The DC polarization technique, as well as the AC impedance measurements, were performed to obtain the ionic conductivity and diffusivity. Representative results are shown below.

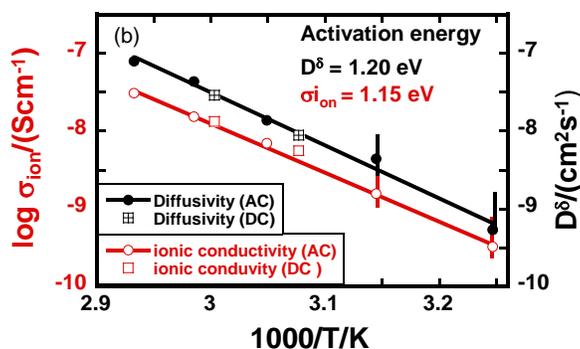


Figure 1. AC impedance spectra obtained from an electron-blocking cell at 58°C and fitted with an equivalent circuit (a), lithium ionic conductivity and diffusivity as a function of temperature (b).

The lithium ion conductivity and diffusivity agreed well between DC and AC measurements (Fig.1b). The values of activation energy calculated using an Arrhenius law are almost the same for ionic conductivity (1.15 eV) and diffusivity (1.20 eV) (within ± 0.20 eV error) as shown in Fig. 1b. Despite the extensive commercial use of NCA and its long research history, this is, to our knowledge, the first report of such data.

The Li-ion diffusivity in NCA was also measured as a function of Li concentration, x , using GITT and depolarization techniques. The diffusivity was found to vary strongly with x , being nearly 10^2 times lower for $x < 0.5$ than for $x > 0.5$, as will be reported in detail in the future. While the Li concentration dependence is complex, the absolute value of diffusivity is high enough that it can be concluded that for micron-scale particles and practical C-rates, bulk transport in NCA is not rate-limiting in Li-ion cells.

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

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

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

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

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

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

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

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

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

MILESTONES:

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

PROGRESS TOWARD MILESTONES

High Li-ion transport is critical for achieving the full capacity of the high-capacity materials used to form battery electrodes. The binder employed coats the surface of the active material and may impede the Li-ion diffusion. Although ion mobility in a doped conductive polymer system has been demonstrated, strategies to further improve the ion mobility are still necessary. In our polymer system, this issue is addressed by improving the electrolyte uptake through the incorporation of polar ethyleneoxide side chains.

The enhanced polarity of a PEFM¹ polymer resulted in a three-fold uptake of electrolyte (Fig. 1). The enhanced swelling is due to an overall increase in polarity of the polymer, which is indicated by water contact angle measurements (Fig 1a). The static contact angle is 90.9° for PEFM with the E group, vs. 101.0° for PFM². The ether side chains distribute uniformly in the polymer because they are chemically attached to the backbone. The uniform distribution of the ether moieties is essential to improving the overall electrolyte uptake. Although PFM also swells in electrolyte solution, the total electrolyte uptake is only 10% of its final weight. In swelled PEFM films, the electrolyte uptake is tripled, accounting for 30% of the final swelling weight (Fig. 1b). This number is similar to the amount of swelling of non-conductive PVDF in electrolyte. As explained above, the enhanced electrolyte uptake is important for allowing facile Li-ion transportation through the polymer binder to the surface of the active material.

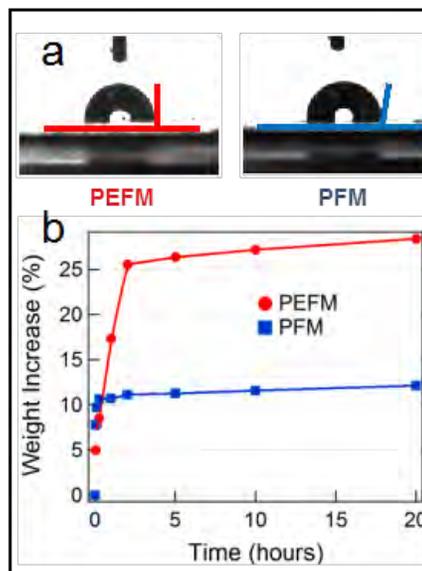


Figure 1. (a) Water contact angles on surfaces of PEFM and PFM films. (b) The swelling tests of PEFM and PFM polymer films in 1M LiPF₆ EC/DEC (1:1) electrolyte.

Collaborations: LBNL: V. Battaglia, V. Srinivasan, R. Kostecki, P. Ross, W. Yang (ALS), A. Minor (NCEM); GM: X. Xiao.

Publications:

1. Shidi Xun, Bin Xiang, Andrew Minor, Vince Battaglia, and Gao Liu, “Conductive Polymer and Silicon Composite Secondary Particles for a High Area-Loading Negative Electrode,” *Journal of The Electrochemical Society*, 160 (9) A1380-A1383 (2013).
2. Mingyan Wu, Xingcheng Xiao, Nenad Vukmirovic, Shidi Xun, Prodip K. Das, Xiangyun Song, Paul Olalde-Velasco, Dongdong Wang, Adam Z. Weber, Lin-Wang Wang, Vincent S. Battaglia, Wanli Yang, and Gao Liu, “Toward an Ideal Polymer Binder Design for High-Capacity Battery Anodes,” *Journal of the American Chemical Society* doi: 10.1021/ja4054465, 2013.

PEFM = Poly(2,7-9,9-dioctylfluorene-co-2,7-9,9-(di(oxy-2,5,8-trioxadecane))fluorene-co-2,7-fluorenone-co-2,5-1-methylbenzoate ester)

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

TASK TITLE: Electrode Architecture – Electrode fabrication and materials benchmarking

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

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

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

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

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

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

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

MILESTONES:

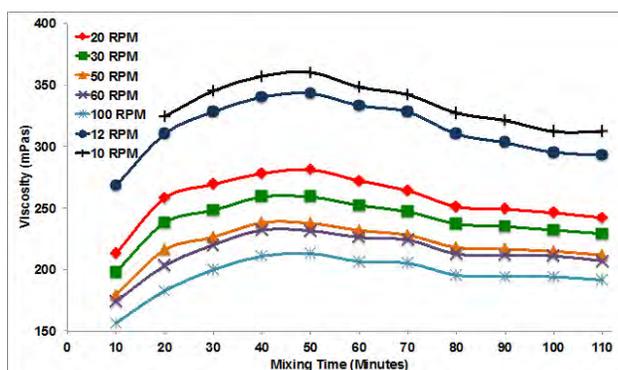
- (a) Measure the effect of mixing variables on electrode performance. (May 13) **On going, due Sep. 13**
- (b) Measure the viscosity with mixing time and the effect on performance. (Jun. 13) **On going, due Sep. 13**
- (c) Determine the optimum composition of an anode with high MW polymer. (Sep. 13)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

PROGRESS TOWARD MILESTONES

1. Measure the effect of mixing variables on electrode performance, May 2013. **On going.**
The rate performance of electrodes constructed under different conditions is similar; the cycling performance is on-going and will be reported in the next Quarterly.

2. Measure the viscosity with mixing time and the effect on performance, June 2013. **On-going.**
This quarter, an investigation of mixing time on slurry properties continued. The object of this study is to understand the effects of the mixing process on cell performance, where performance includes reversible capacity, rate capability, and long-term cyclability. Earlier work reported this year was on the effects of selected limits of mixing time and mixing speed on slurry morphology and electrode performance. This quarter a more refined analysis was undertaken to investigate the effect of the second mixing step on slurry properties, specifically, viscosity.

Our present mixing process consists of two stages. In the previously reported effort, the effect of varying the first mixing speed, mixing time, and the second mixing time were each investigated *via* a full design of experiments where each parameter was varied between two extremes. In this quarter, a more in-depth analysis of the second mixing step was conducted. NCM (Umicore MX6) and carbon black (Super P) were combined at a ratio of 94:2 in NMP at a ratio of 5:4 solids to liquids. The materials were mixed with a homogenizer at 10,000 rpm for 20 mins. This was followed by the addition of PVDF 1100 at twice the concentration as that of the carbon additive and mixed for nearly 2 hrs. with the same homogenizer set at 2500 rpm. The viscosity was measured every 10 mins. at different shear rates; the results are presented in the figure. As expected, the slurry is shear thinning, thus, at higher shear rates, the proportionality constant between shear rate and shear force, *i.e.* the viscosity, is lower. It is also evident from the figure that there is a maximum in the viscosity at around 50 mins. into the mixing. It is



believed that the first 50 mins. is a reflection of the macro mixing of the solids mix with the polymer. Once the two materials are uniformly distributed, the mixture of solids, and in particular, the high-surface area carbon additive, which starts out highly aggregated, starts to breakdown and the solution shows a lower viscosity. After 80 mins., the viscosity of the solution begins to level off with time. In the next stage of this experiment, electrodes and cells will be fabricated from the 80-min. and the 2-hr. limit to determine if

the time after 80 mins. shows any performance improvements. Also, extended mixing will be performed to see how long this constant velocity interval remains that way. There is a presumption in the electrode fabrication community that a slurry can be over mixed. The goal is to try to reach such a point and to understand what occurs in the slurry beyond this point.

3. Determine the optimum composition of an anode with High MW polymer, September 2013. **On-schedule.**

4. Test three materials developed in the BATT Program, September 2013. **On-schedule.**

BATT TASK 2

ANODES

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

TASK TITLE: Anodes — Novel Anode Materials

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

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

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

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

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

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

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

MILESTONES:

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

PROGRESS TOWARD MILESTONES

Team: Fulya Dogan

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

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

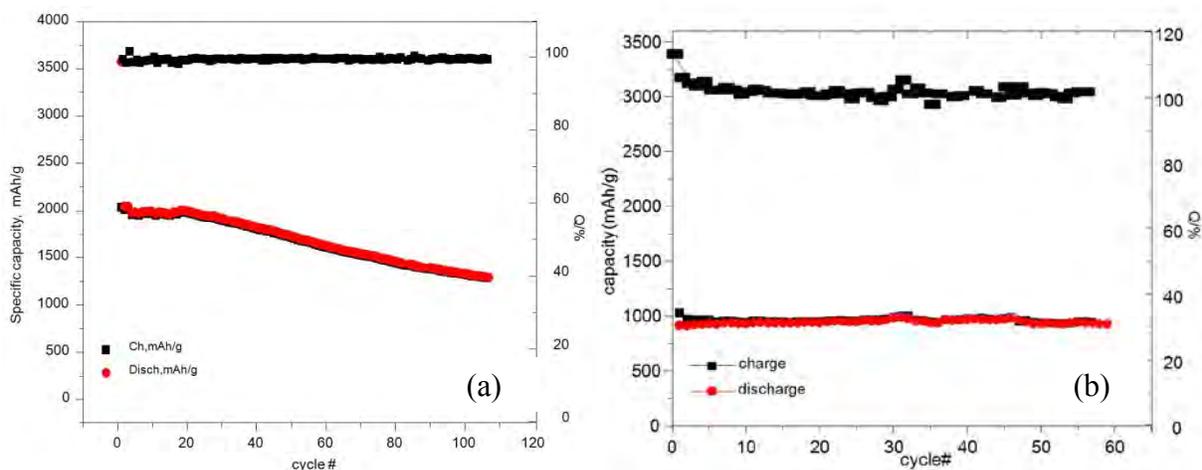


Figure 1. Cycling performance of a Si film on Cu using (a) TEACl as supporting electrolyte salt and (b) using TBACl as the supporting electrolyte salt.

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

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

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

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

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

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

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

GENERAL APPROACH: Our anode approach is to synthesize, characterize and develop inexpensive materials that have a potential around 500 mV above that of pure Li (to minimize risk of Li plating and thus enhance safety), and to have higher volumetric energy densities than carbon. Emphasis will be placed on simple metal alloys/composites at the nano-size. Initially, Sn will be emphasized, building on what has been learned from our studies of the tin-cobalt anode, the only commercial anode besides carbon. All materials will be evaluated electrochemically in a variety of cell configurations, and for thermal, kinetic and structural stability to gain an understanding of their behavior.

STATUS OCT. 1, 2012: It has been shown that amorphous nano-size Sn alloys have a high capacity and maintain it on deep or shallow cycling, when stabilized with elements like Co. In contrast, bulk crystalline metals have a high capacity, but their capacity fades rapidly after several deep cycles in carbonate-based electrolytes due to resistive continuous SEI formation. A nano-Sn material which shows electrochemical behavior comparable to that of the Sn-Co alloy, but where all the Co has been replaced by low-cost Fe, has been successfully formed by mechanical synthesis. This material has a higher volumetric capacity than Conoco Philips CPG-8 Graphite and has been formed by two different synthesis methods.

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

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

MILESTONES:

- (a) Determine the reaction mechanism of the nano-Sn-Fe-C system. (May 13) **Delayed until Sep. 2013**
- (b) Identify the cause of the first-cycle excess charge capacity; propose approaches to mitigate it. (Sep 13) **On schedule**
- (c) Identify an anode candidate having an energy density of 2 Ah/cc for at least 100 cycles. (Sep. 13) **On schedule**
- (d) Determine the electrochemistry of the leached nano-Si material, and compare to the standard Si. (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

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

Milestones (a): In this quarter the reaction mechanism of nano-sized Sn-Fe-C anode materials was studied *via* X-ray absorption spectroscopy (XAS). Samples prepared at different lithiation and delithiation states were evaluated *ex situ*. As shown in Figs. 1(a) and 1(b), an obvious absorption edge energy shift can be found in the Sn K-edge of the X-ray absorption near edge structures (XANES), which means the oxidation state of Sn undergoes a substantial change during the lithiation/delithiation processes. The XAS study of pure Sn during the lithiation/delithiation processes is underway in order to compare and get further information of this structural evolution.

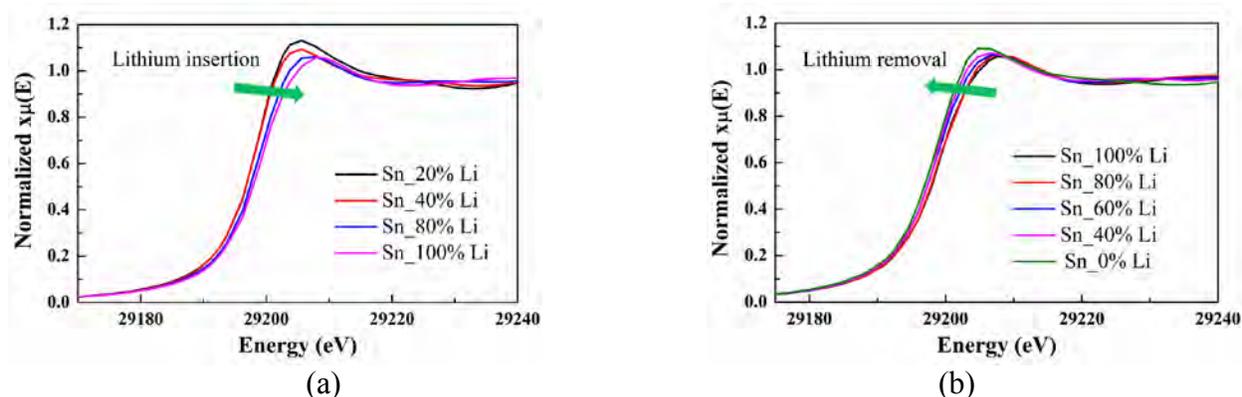


Figure 1. Sn K-edge XANES for different (a) lithiation states and (b) delithiation states of nano-sized Sn-Fe-C.

Milestones (c): In this quarter the group continued its investigation of improving the electrochemical performance of Sn₂Fe materials synthesized by the solvothermal method. When the initial molar ratio of Sn:Fe is increased (*e.g.*, from 2:1 to 10:1), the final product becomes a mixture of Sn/Sn₂Fe instead of pure Sn₁₀Fe. The cyclability decreases dramatically with the increase in Sn.

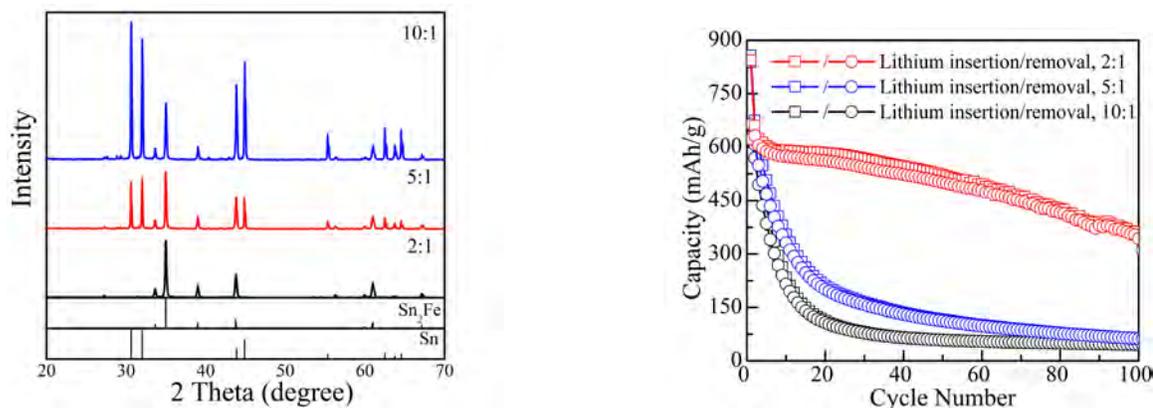


Figure 2. (a) XRD patterns and (b) electrochemical performance of Sn₂Fe materials synthesized by the solvothermal method with different initial molar ratios of Sn:Fe.

Further plans to meet or exceed milestones: None

Reason for changes from original milestones: Milestone (a) is slipping until Sep 2013 to allow completion of experiments at Brookhaven as described above.

Presentations: Presentations at the DOE Merit Review and the BATT Anode work group in May 2013 in Washington.

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

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

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

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

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

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

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

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

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

MILESTONES:

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

PROGRESS TOWARD MILESTONES

In our 2013 Q1 report, the synthesis of hollow Si nanostructures and the accompanying electrochemical performance were demonstrated. Continuing further along this approach, a method was optimized to obtain consistent and smooth inorganic matrix nanowires (IMNW) that serve as a sacrificial template for developing the hollow Si structures, Si nanotubes (SiNTs). In this report, the IMNWs were synthesized in an autoclave using hydrothermal conditions and the heating rate of the calcination process was optimized to generate smooth IMNW without failure. The length of the IMNWs varied from 5 to 100 μm while the diameters were in the range of 0.6 to 1 μm . *a*-Si was coated uniformly by thermal cracking of silane (SiH_4) at 500°C in a CVD reactor. The *a*-Si/IMNW core-shell structure was later dispersed in a mineral acid to remove the IMNW template and generate hollow SiNTs as shown in Fig. 1. The wall thickness of the SiNTs was estimated to be in the range of 60 to 100 nm. Raman spectra of the SiNTs showed a broad peak around 480 cm^{-1} which indicates that the Si formed is amorphous. Figure 2 is the TEM image showing the open-ended hollow structures of SiNTs.

Slurries of SiNTs were prepared using an organic binder (40 wt%), Super-P as the conductive additive (10 wt%), and the active material (SiNTs). The electrolyte used for the electrochemical characterization was 1M LiPF_6 dissolved in EC:DEC:FEC (45:45:10) solvent. A medium current density of 300 mA/g was employed for the first cycle to generate a quality solid electrolyte interface (SEI) and a high current of 2A/g was applied for subsequent cycles to determine the cycleability. All tests were conducted between the voltage limits of 0.01 and 1 V vs. Li^+/Li . Figure 3 shows the plot of specific capacity vs. cycle number obtained from the above testing conditions. Specific capacities of 2615 and 1960 mAh/g were obtained for the first-cycle discharge and charge capacity, respectively. A first-cycle irreversible loss of *ca.* 25% was observed for these SiNTs, which may be due to the SEI layer formation on the surface of the SiNTs. At 2A/g, the SiNTs show excellent cycling stability over hundreds of cycles. Specific capacities in excess of 1000 mAh/g were obtained after 400 cycles corresponding to a fade rate of 0.067% loss/cycle (for 400 cycles) and a coulombic efficiency in the range of 99.9%. The loading of the electrode was 0.7 mg/cm^2 , which is significantly higher than that reported for Si nanotubes synthesized by other methods such as chemical infiltration, electrospinning, *etc.*

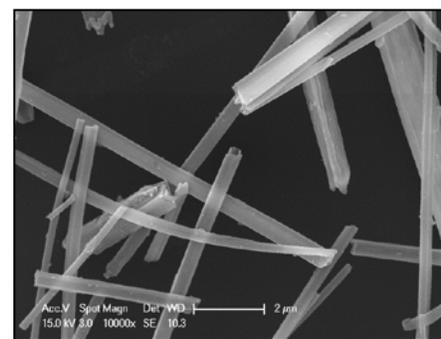


Figure 1. SEM image of SiNTs obtained after removal of the IMNW template in a mineral acid.

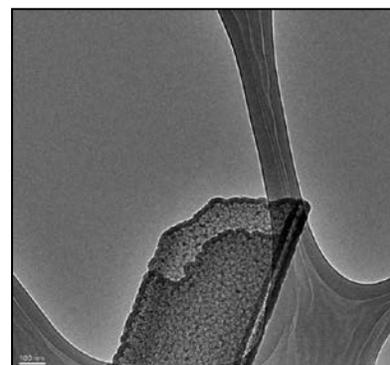


Figure 2. TEM image of the SiNTs.

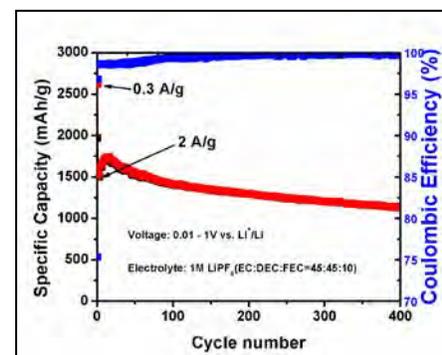


Figure 3. Variation of specific capacity vs. cycle number of SiNT cycled at 300 mA/g (1st cycle) and 2 A/g (subsequent cycles).

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

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

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

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

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

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

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

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

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

MILESTONES:

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

PROGRESS TOWARD MILESTONES

A porous Si-based anode, after prelithiation treatment using SLMP, shows good cycling stability. With a Si loading of *ca.* 51%, samples exhibit an initial capacity of *ca.* 700 mAh/g (based on the whole electrode weight including binder and conductive carbon) and demonstrate an excellent cycling stability (retaining 90% capacity over 300 cycles as shown in Fig. 1). The sample was initially cycled at a current density of 0.1 A/g for three cycles, then tested at 1 A/g current density in subsequent cycles. The first-cycle capacity loss is 8.1%. In another effort, optimized SBG ($B_4C/Si/C$) composites demonstrated good performance with high loading. The electrolyte was 1.0 M $LiPF_6$ in EC/DMC/FEC (0.45:0.45:0.1) by weight. The voltage range was set between 0.005 and 1 V. The sample was initially cycled at 0.06 mA/cm² for 3 cycles and then charged (delithiated) at 0.75 mA/cm² and discharged (lithiated) at 0.5 mA/cm². It has an initial capacity of 1.5 mAh/cm² and >80% capacity retention after 50 cycles at a current density of *ca.* 0.5 mA/cm² (see Fig. 2).

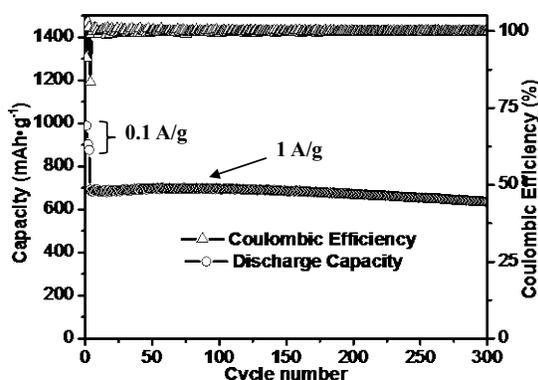


Figure 1. Cycling performance of prelithiated porous silicon with ~51% silicon in 1.0M $LiPF_6$ in EC/DMC (1:2 vol) electrolyte with 10% FEC additive.

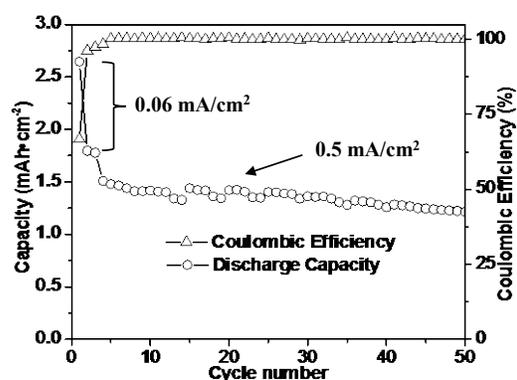


Figure 2. Cycling performance of the SBG composite in 1.0M $LiPF_6$ in EC/DMC (1:2 vol) electrolyte with 10% FEC as additive.

The fundamental mechanism of the effect of FEC as an electrolyte additive was investigated by ⁶Li Nuclear Magnetic Resonance and an X-ray Photoelectron Scanning study. It was found that the high tensile strength of the FEC-derived lithium poly (vinyl carbonate) enhanced the stability of the SEI film and subsequently led to significantly improved cycling stability of the Si-based anodes. More detailed analysis on NMR data will be performed in the next quarter. New electrode structures, novel binders, and electrolyte additives will be further investigated to improve the cycling stability of thicker electrodes. Fundamental understanding of the capacity fading mechanism, especially the structure of the SEI layer formed in the presence of different electrolyte additives, will also be investigated.

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

Publications:

1. Li XL, Gu M, Kennard R, Hu SY, Chen XL, Wang CM, Sailor MJ, Liu J, and Zhang JG. "Porous Structured Silicon-based Nanocomposites as High Performance Li-ion Battery Anodes." MRS Spring Meeting, April 1-5, 2013, San Francisco, CA.

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

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

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

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

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

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

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

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

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

MILESTONES

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

PROGRESS TOWARD MILESTONES

Improving electrochemical performance by Alucone MLD coating: The aluminum alkoxide polymer (Alucone) coating synthesized by molecular-layer-deposition (MLD) has been used to improve the cycling performance of Si anodes. To better accommodate the volume expansion of lithiated Si anodes, nanoscale conformal coatings were grown on the Si anodes using static-precursor exposure during the MLD process. Figure 1 compares the cycling behaviors of the Alucone coated and uncoated Si anodes. Fast capacity decay was observed for the bare Si electrode, but the Alucone-coated Si anodes exhibited sustainable cycling over hundreds of cycles with a coulombic efficiency (CE) in excess of 99%. The specific charge capacity of 900 mAh g^{-1} at the 150th cycle corresponds to an electrode volumetric capacity of 569 mAh cm^{-3} , based on an initial electrode thickness of $12.74 \mu\text{m}$. Such good cycle life and CE for these thick electrodes is evidence that the Alucone MLD coating provides favorable mechanical properties, accommodating the volumetric changes of the Si electrode and preserving the structural integrity of the electrode network throughout deep cycling.

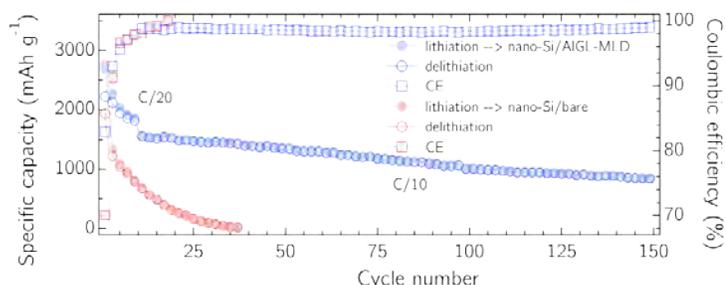


Figure 1. Cycling performance of the bare and Alucone MLD coated electrodes. The Si electrodes were prepared with 60% Si nanoparticles, 20% acetylene black and 20% PVDF binder.

TEM characterizing the resilience of the Alucone MLD coating: Figure 2 exhibits cross-section SEM images before and after the first lithiation, and then after the 20th delithiation. Figures 2a and 2d show the cross-sections of the fresh bare- and Alucone-coated electrodes with an initial thickness of 12.15 and $12.74 \mu\text{m}$, respectively. Figures 2b and 2e correspond to the first lithiation of the bare and coated electrode with the thickness of 20.34 and $23.06 \mu\text{m}$. Volume expansion in the thickness direction was observed for both bare and coated electrodes. Similar volume expansion on the coated electrodes indicates that the Alucone coating allows volume expansion in the coated electrodes to full lithiation. The cross-sections after the 20th delithiation, Figs. 2c and 2f, show that the bare and coated electrodes have a thickness of 18.13 and $14.97 \mu\text{m}$, respectively. A near full recovery from the massive volumetric expansion was observed for the Alucone-coated electrodes. To the contrary, the bare electrode remains almost fully expanded after the 20th delithiation. Therefore, the bare electrode loses electrical contact and structural integrity, resulting in rapid capacity degradation. The findings imply that the good resilience of the Alucone coatings provides sufficient mechanical support to accommodate the major volumetric changes experienced by Si anodes, and to aid in the recovery and preservation of the whole composite network upon delithiation.

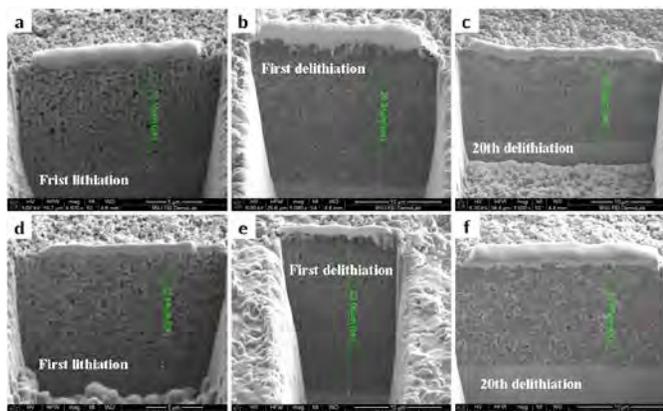


Figure 2. SEM images showing the cross-sections of the bare electrodes (a,b,c) and Alucone coated electrodes (d,e,f).

Publication: D.M. Piper, J.J. Travis, M. Young, S-B. Son, S.C. Kim, K.H. Oh, S.M. George, C. Ban, S-H. Lee, “Reversible High Capacity Si Nanocomposite Anodes enabled by Molecular Layer Deposition,” submitted to *Adv. Mater.* 2013.

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

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

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

BARRIERS: Needs increased life, capacity and improved safety.

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

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

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

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

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

MILESTONES:

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

PROGRESS TOWARD MILESTONES

In the previous quarter, synthesis of an additives-free electrode of delaminated Ti_3C_2 was reported. Those electrodes showed reversible volumetric capacities of $820 \text{ mAh}\cdot\text{cm}^{-3}$ at 1C, and $220 \text{ mAh}\cdot\text{cm}^{-3}$ at 36C, values that cannot be achieved with commercial graphite anodes.

In principle, M_2X MXenes should have 50% higher Li^+ uptake as compared to their M_3X_2 counterpart. For this reason Nb_2C and V_2C were synthesized by etching Al from Nb_2AlC and V_2AlC , respectively, and tested as electrodes for LIBs.

The voltage profile for Nb_2C at a 1 C cycling rate (Fig. 1a) yields a first-cycle capacity of *ca.* $422 \text{ mAh}\cdot\text{g}^{-1}$. The second-cycle capacity was about $250 \text{ mAh}\cdot\text{g}^{-1}$. Reasons for the first-cycle irreversibility include SEI formation or irreversible reactions of Li with the surface groups and water molecules in the as-synthesized MXenes. After 100 cycles, a reversible capacity of $170 \text{ mAh}\cdot\text{g}^{-1}$ was obtained. The irreversibility could be minimized by controlling the surface MXene chemistry or by prelithiating the electrode material as reported for other systems. Figure 1b shows the voltage profile at 1 C for V_2C . The first-cycle capacity was found to be *ca.* $380 \text{ mAh}\cdot\text{g}^{-1}$; the reversible capacity was *ca.* $210 \text{ mAh}\cdot\text{g}^{-1}$.

Intriguingly, the V_2C , produced by etching attrition-milled V_2AlC , showed >30% enhancement in Li uptake (Fig. 1c) compared to V_2C produced from un-milled V_2AlC . This can be explained by the decreased particle size, facilitating Li diffusion between the layers. A reversible capacity of $280 \text{ mAh}\cdot\text{g}^{-1}$ was obtained instead of $210 \text{ mAh}\cdot\text{g}^{-1}$ at the same cycling rate of 1 C. Note that >2/3 of the reversible lithiation capacity for Nb_2C is below 1 V. Conversely, in the case of V_2C , less than 1/2 of the reversible lithiation capacity is below 1 V and more than 2/3 of the delithiation capacity of V_2C is at voltages higher than 1.5 V. This is an important finding since it shows that each MXene has its own active voltage window. With the variety of possible MXene chemistries, selection of an optimum MXene for a required voltage window can in principle be achieved. Said otherwise, some MXenes could function better as anodes, while others could, in principle, be used as cathode materials for LIBs. Figure 1c further shows that at 10 C, capacities of $110 \text{ mAh}\cdot\text{g}^{-1}$ for Nb_2C and $125 \text{ mAh}\cdot\text{g}^{-1}$ for V_2C were obtained after 150 cycles. These values are approximately 50 % higher than what was reported previously for Ti_2C at the same rate and closer to the capacities obtained at 1 C. The coulombic efficiency was about 99.6% for Nb_2C at 10 C. For V_2C it varied between 98 and 100%.

It is worth noting that all the results reported here for Nb_2C and V_2C are for as-produced powders that were not delaminated. By delaminating them, much higher capacities are expected, similar to what was reported for Ti_3C_2 (a 4 times increase in the capacity was obtained after delamination). The challenge at this point is to delaminate the Nb_2C and V_2C from their substrates.

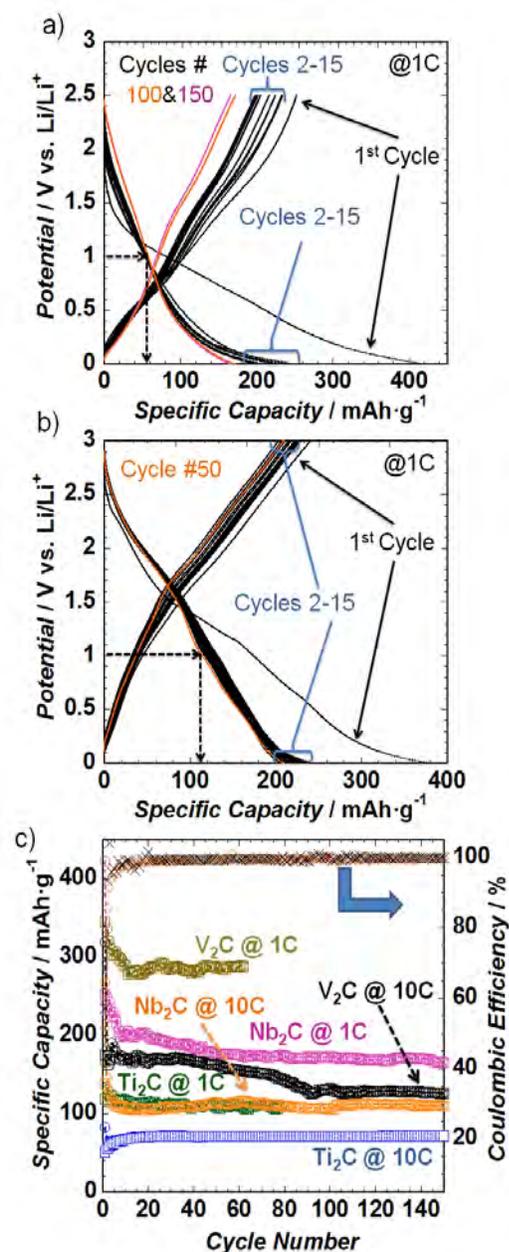


Figure 1. Electrochemical performance of Nb_2C and V_2C as electrodes in LIB. (a) Voltage profile of f- Nb_2C between 0 and 2.5 V vs. Li/Li^+ . (b) Voltage profile of V_2C (produced by HF treatment of V_2AlC at RT for 90 h) between 0 and 3 V vs. Li/Li^+ . (c) Specific lithiation (circles) and delithiation (squares) capacities (per mass of active material) vs. cycle number at different rates for Nb_2C and V_2C (produced by HF treatment of attrition milled V_2AlC) compared to what was reported previously for Ti_2C .

Publication:

Naguib, M.; et al. New Two-Dimensional Niobium and Vanadium Carbides as Promising Materials for Li-ion Batteries, *Under Review* 2013.

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

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

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

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

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

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

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

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

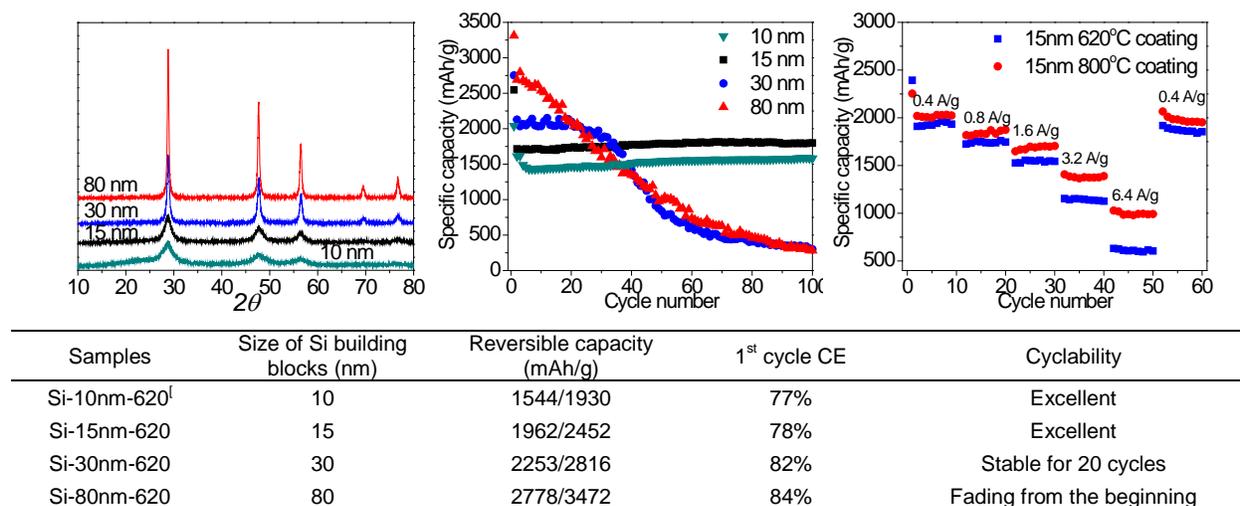
RELEVANT USABC GOALS: 200 Wh/kg (EV requirement); 96 Wh/kg, 316 W/kg, 3000 cycles (PHEV 40 mile requirement). Calendar life: 15 years. Improved abuse tolerance.

MILESTONES:

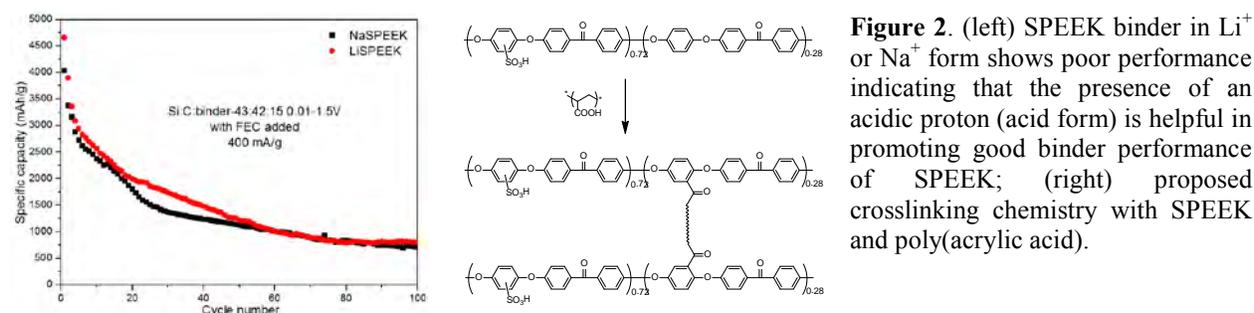
- (a) Synthesize and characterize three types of Si/SiO_x-carbon nanocomposites. (Jan. 13) **Complete**
- (b) Demonstrate new crosslinking chemistry involving sulfonates, carboxylates, and azide chemistries for low-swelling polymer binders. (Jan. 13) **In progress - delayed to Sep. 13**
- (c) Identify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

PROGRESS TOWARD MILESTONES

SiO-based anode materials: The influence of nanoscale building-block-size and carbon coating on the electrochemical performance of the micron-sized Si-C composites reported in FY13 Q1 was investigated. Four primary Si building sizes (10 nm, 15 nm, 30 nm, and 50 nm) were obtained by adjusting the heat treatment temperature. It was found that the critical Si building block size was 15 nm, which enabled a high capacity without compromising the cycling stability (see Table below). It was also confirmed that carbon coating at higher temperature improves the first cycle coulombic efficiency (CE) and the rate capability. At elevated temperature, the carbon gas source helps reduce the surface oxides, which was confirmed by Raman and XPS spectroscopy. A more graphitic carbon layer was also achieved at higher temperature. An optimized coating temperature of 800°C was identified through experimental testing.



Polymer binders: Sulfonated poly(ether ether ketone) (SPEEK) binders have shown similar performance to NaCMC binder, but with higher rate capability (see previous reports). The group is currently investigating the key factors that contribute to SPEEK's good performance including interactions between the binder and the Si NPs. Figure 2 (left) shows that the metal neutralized form of SPEEK with Li⁺ or Na⁺ counterions does not perform as well as the SPEEK binder with the acid-form sulfonate groups. The hypothesis is that both the ketone and acidic groups of the SPEEK are helping bond the polymer to the commercial Si NPs. Measurement of this bonding interaction with FTIR continues.



Crosslinking binder studies are underway, Fig. 2 (right). Results have been delayed by a slower than planned synthesis of the binders and the attachment of crosslinkable groups. Azide functional polymers were attempted but were unsuccessful. Battery testing on crosslinkable binders is currently being conducted and will be reported next quarter before the end of the FY.

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

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

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

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

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

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

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

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

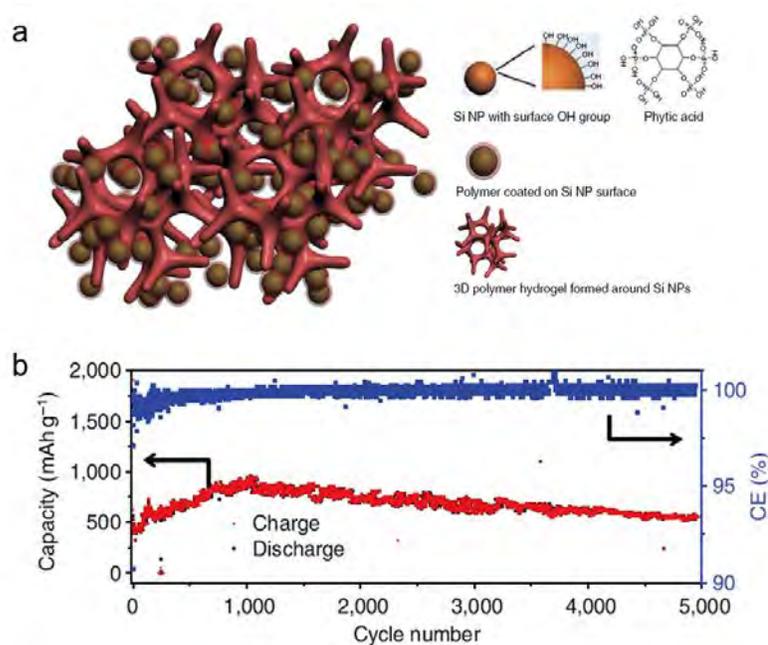
RELEVANT USABC GOALS: 200 Wh/kg (EV requirement); 96 Wh/kg, 316 W/kg, 3000 cycles (PHEV 40 mile requirement). Calendar life: 15 years. Improved abuse tolerance.

MILESTONES:

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

PROGRESS TOWARD MILESTONES

Incorporation of conducting hydrogel into Si nanoparticle anodes. This quarter the group has developed a facile and scalable solution process to fabricate high-performance Li-ion battery anodes by encapsulating Si nanoparticles in a 3D, porous, conductive-polymer, hydrogel framework. Si nanoparticles are mixed with monomer and crosslinker in the solution first, and then initiator is added to start the polymerization. This unique *in situ* polymerization fabrication technique results in a well-connected 3D network structure consisting of Si nanoparticles conformally coated by the conducting polymer (Fig. 1a). Such hierarchical hydrogel framework combines multiple, advantageous features. First, the continuous, porous, electrically-conductive PANi-network provides fast electronic and ionic transfer channels. Second, strong interactions are introduced between the Si nanoparticles and the PANi hydrogel to make the framework more stable. Third, the porous hydrogel network provides enough free space for Si volume change during the lithiation/delithiation processes. With this anode, high capacity and extremely stable electrochemical cycling was successfully achieved. The electrode demonstrates a cycle life of 5,000 cycles with over 90% capacity retention at a current density of 6.0 A/g (Fig. 1b).



The solution synthesis and electrode fabrication process are highly scalable and compatible with existing slurry-coating battery manufacturing technology. This will potentially allow for high-performance composite electrodes to be scaled up for manufacturing for the next generation of high-energy Li-ion batteries.

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

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

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

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

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

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

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

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

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

MILESTONES:

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

PROGRESS TOWARD MILESTONES

Task 1 – Synthesis of Type I Silicon Clathrates

During the present quarter, the conditions for the phase transformation of fuel-grade silicide were optimized to yield the highest purity of Zintl phase possible. This was achieved by varying excess additions of NaH to the silicide. XRD analyses of the thermal transformation products (Fig. 1) have shown that new reflections emerge at or near the positions theoretically computed for the Zintl phase. Similar relative intensities when 10% excess NaH is combined with the silicide during thermal processing were also achieved. Higher additions of NaH did not result in the required XRD reflections for the Zintl phase. Using these process conditions, scale-up synthesis of Na_4Si_4 (~10 g) is underway for subsequent use in the batch synthesis of Si_{146} .

Task 3 – Prototype Silicon Clathrate Anode Fabrication Long-term cycling tests on the $\text{Ba}_8\text{Al}_8\text{Si}_{38}$ anode material combined with Super-P carbon (10 wt%) and FEC electrolyte are ongoing. The overall capacity fade and coulombic efficiency will be determined from these measurements.

Task 4 – Half-Cell Electrochemical Characterization

As the best-case formulation and fabrication methods are established in Task 3, a suite of *ex situ* techniques were employed to map the structural and mechanical state of the clathrate anodes as a function of lithiation/delithiation cycles. Structural and compositional analysis of $\text{Ba}_8\text{Al}_8\text{Si}_{38}$ was performed using high-resolution magic angle spinning nuclear magnetic resonance (MAS-NMR) and neutron diffraction measurements (facilitated through ORNL). In the case of NMR, the chemical shift environments of ^{29}Si and ^{27}Al along with that of the ^6Li and ^7Li isotopes were probed to study the effects of Li intercalation on structural parameters and local interactions. Both ^{29}Si - and ^{27}Al -NMR spectra show two distinct magnetic environments, possibly associated with the 6d and 2a framework cages of the Type I clathrate structure. Additionally, neutron diffraction measurements (Fig. 2) were used to verify the first principles computations that the lattice constants for the clathrate alloy ($\text{Ba}_8\text{M}_y\text{Si}_{146-y}$) do not change as a function of Li intercalation up to the theoretical capacity. Additional diffraction measurements are needed to determine the extent to which the clathrate framework can be lithiated reversibly beyond its theoretical capacity.

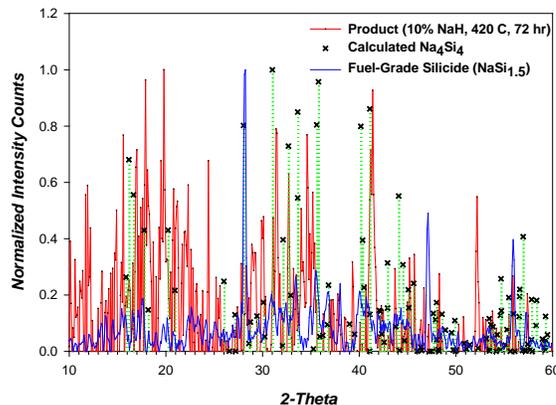


Figure 1. Overlay of powder XRD patterns for the fuel-grade silicide and the transformation product, compared with the calculated reflections for the Zintl phase (Na_4Si_4).

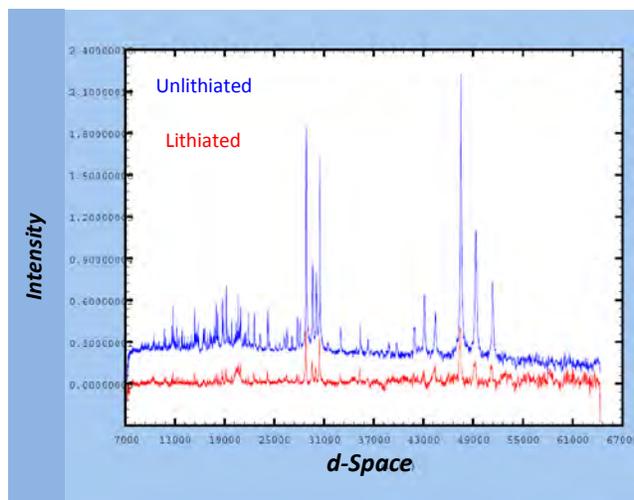


Figure 2. Neutron diffraction patterns obtained for $\text{Ba}_8\text{Al}_8\text{Si}_{38}$ before (blue) and after lithiation (red), providing evidence that the clathrate framework remains structurally intact up to its theoretical capacity.

BATT TASK 3

ELECTROLYTES

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

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

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

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

OBJECTIVES:

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

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

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

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

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

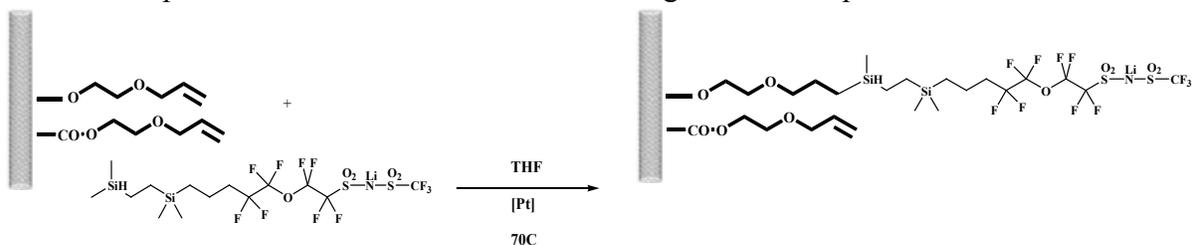
MILESTONES:

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

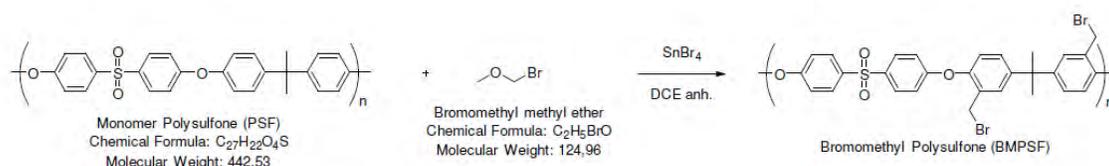
PROGRESS TOWARD MILESTONES

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

Preparation of the functional groups for the fabrication of single-ion conductors and modified carbon components continued. The imide anion fragments are in process for attachment.

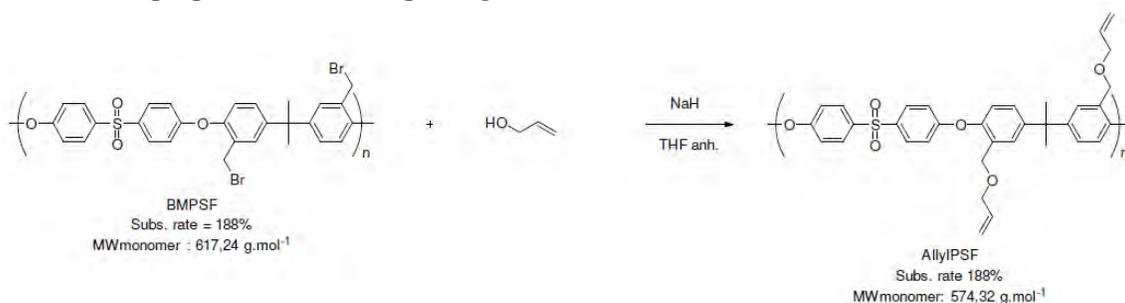


In addition to the preparation of modified, conducting components, good progress has been made on the optimization of the synthesis of the single-ion conductor polyelectrolytes. Previously, difficulty had been found with the functionalization of the polysulfone backbone. This has been successfully overcome; high substitution has been achieved while avoiding cross-linking. The synthesis has been scaled up to 20 gram per batch.

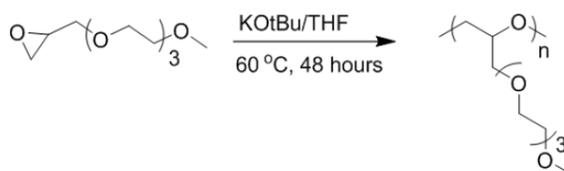


PSF	Bromomethyl methyl ether	Tin(IV) Bromide	1,2-Dichloroethane anhydrous
20 g	20.0 ml	6.0 ml	250 ml
45.19 mmol	220.5 mmol (4.9 eq)	45.19 mmol (1 eq)	50°C 24h

The next stage has also been successfully completed on a 14 gram scale. Attachment of the imide fragment still needs to be performed and more imide is in preparation. These large scale syntheses are in preparation for completing milestone 1.



Preparation of comb-branch polyepoxide polyethers for fabrication of solvent-free solid state electrolytes is also progressing. This is in preparation for completing milestone 2.



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

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

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

BARRIERS: Cycle/calendar life, abuse tolerance

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

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

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

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

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

MILESTONES:

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

PROGRESS TOWARD MILESTONES

Our approach for the development of additives for SEI and redox shuttles for overcharge protection involves screening of reduction and oxidation potentials through the use of accurate density functional methods (DFT) followed by investigation of the mechanism of decomposition through investigation of reaction pathways. The theoretical results are related to the performance of the additives and shuttles in a cell.

Density functional methods were used to examine the oxidation potential and other properties of a potential redox shuttle 1-(2,2,2-trifluoroethoxy)-4-methoxy-2,5-di-*tert*-butylbenzene (F3-DDB) shown in Fig. 1. This molecule has less symmetry compared to previously studied shuttles, DDB (1,4-di-*tert*-butyl-2,5-dimethoxybenzene) and F6-DDB (bis-(2,2,2-trifluoroethoxy)-2,5-di-*tert*-butylbenzene), also shown in Fig. 1. The calculated oxidation potential of F3-DDB of 4.02 V is in good agreement with the experimental value of 4.09 V from the work described below. This is smaller than that of F6-DDB (4.23 V, expt. 4.25 V), but larger than that of DDB (3.82 V, expt. 3.92 V). Calculated spin densities suggest that the less symmetric F3-DDB is slightly more prone to radical attack than the symmetric DDB and F6-DDB. Calculated ethyl radical binding energies $E_b(\text{ER})$ show that while F3-DDB has a slightly higher $E_b(\text{ER})$, all three redox shuttles should be stable from this probe radical. Decomposition pathways were also examined. F3-DDB has three exergonic side arm reactions, F6-DDB has two, and the parent DDB has one. All proposed decomposition reactions have large activation barriers so they are unlikely to decompose; however, decomposition could be catalyzed by transition metal sites on the electrode surface.

The F3-DDB compound was synthesized for testing as a redox shuttle. This was done using commercially available precursors. The introduction of $-\text{OCH}_2\text{CF}_3$ groups increases the oxidation potential compared to DDB. The compound was characterized using NMR. The F3-DDB compound displays a reversible redox potential at 4.09 V vs. Li/Li^+ in carbonate-based electrolytes. F3-DDB also showed improved solubility in the carbonate-based electrolytes due to the introduction of the fluorinated alkoxy group. Up to a 0.2 M solution of F3-DDB in 1.2 M LiPF_6 in 3:7 EC/EMC can be prepared.

The overcharge effect was investigated in a $\text{LiFePO}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$ cell containing 0.1 M F3-DDB. In this cell configuration, the F3-DDB shuttle can survive for 73 cycles (>48 days) at C/5 rate with 100% overcharge.

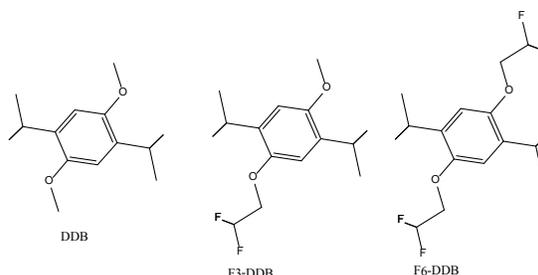


Figure 1. DDB and modified DDB redox shuttles.

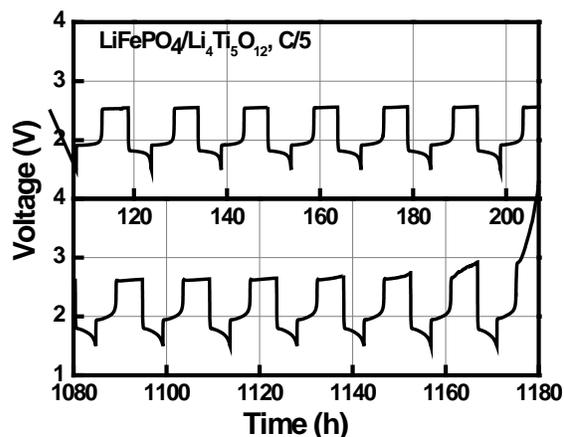


Figure 2. Voltage vs. time profile of $\text{LiFePO}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$ cell containing 0.1 M F3-DDB during the overcharge test (C/5 charging rate, 100% overcharge).

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

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

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

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

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

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

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

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

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

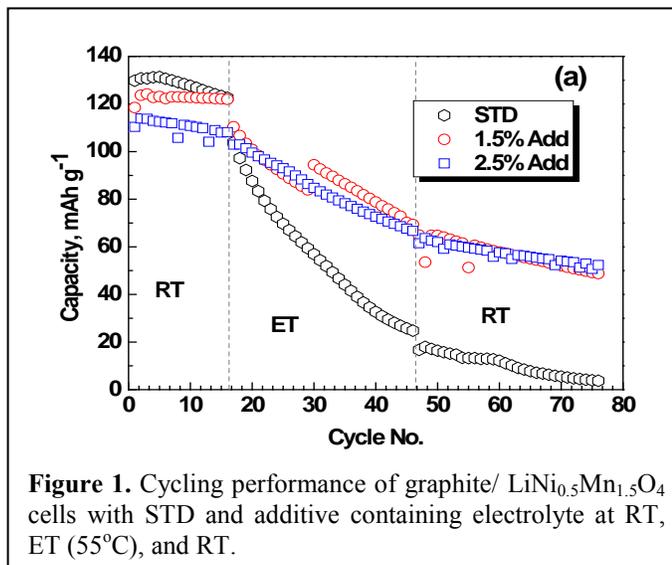
MILESTONES:

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

PROGRESS TOWARD MILESTONES

With regard to milestone (a): The failure mechanism of graphite/LiNi_{0.5}Mn_{1.5}O₄ cells cycled at 25 and 55°C have been analyzed by electrochemical methods and *ex situ* surface analysis of the electrodes. A manuscript detailing these results was published in the *Journal of the Electrochemical Society*.

With regard to milestone (b): Novel additives have been prepared that improve the performance of graphite/LiNi_{0.5}Mn_{1.5}O₄ cells cycled to 4.8 V (*vs.* Li) with LiPF₆ in EC/EMC at moderately elevated temperature (55°C). Figure 1 shows the cycling performance of the graphite/LiNi_{0.5}Mn_{1.5}O₄ cells with baseline electrolyte and electrolyte containing the additive at RT, ET (55°C), and RT, again. The initial discharge capacity of the cells with 1.5 and 2.5% additive are slightly lower than the cells with baseline electrolyte at RT. This difference is ascribed to the irreversible



decomposition of the additive on the electrode surface. However, after 30 cycles at 55°C, the cell with baseline electrolyte suffered significant capacity loss, only delivering 24% of the original capacity. The cells with 1.5 and 2.5% additive showed excellent cycling stability upon cycling at 55°C: 63 and 69% capacity retention, respectively. After cycling at 55°C the cells were cycled at RT. The cell with baseline electrolyte had continued capacity fade, while the cells with additive exhibited much better cycling stability. In addition to the improved capacity retention, the cells containing the additive have better columbic efficiency while cycling at 55°C.

Ex situ surface analysis of both the anode and the cathode extracted from graphite/LiNi_{0.5}Mn_{1.5}O₄ cells was conducted *via* a combination of XPS, SEM, TEM with EDX, and ICP-MS to develop a better understanding of the role of the additive in capacity retention upon cycling at elevated temperature. Incorporation of the additive results in the generation of a thin cathode surface film. The cathode surface film inhibits the deposition of poly(ethylene carbonate) and dissolution of Mn and Ni at the cathode surface during cycling at 55°C. The additive also inhibits damage to the anode surface. The presence of the additive results in less Mn and Ni deposition on the anode surface and less damage to the anode SEI. Incorporation of the novel additives to graphite/LiNi_{0.5}Mn_{1.5}O₄ cells cycled to 4.8 V (*vs.* Li) results in improved capacity retention and efficiency. The improved cycling performance can be attributed to the inhibition of electrolyte decomposition at the electrode surfaces and inhibition of Mn and Ni dissolution from the cathode and deposition on the anode. A manuscript is in preparation for submission to the *Journal of the Electrochemistry* and a patent application is in progress.

With regards to milestone (c): Synthetic methods are being developed to prepare novel salts. Two different novel salts are being targeted and more details will be provided in our Q4 report.

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

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

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

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

BARRIERS: Abuse tolerance

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

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

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

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

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

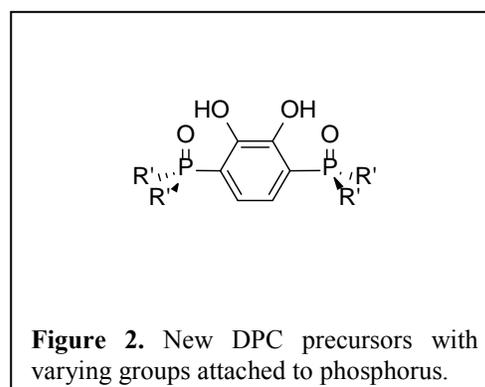
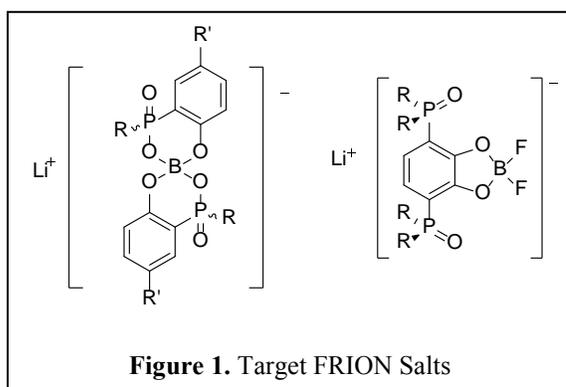
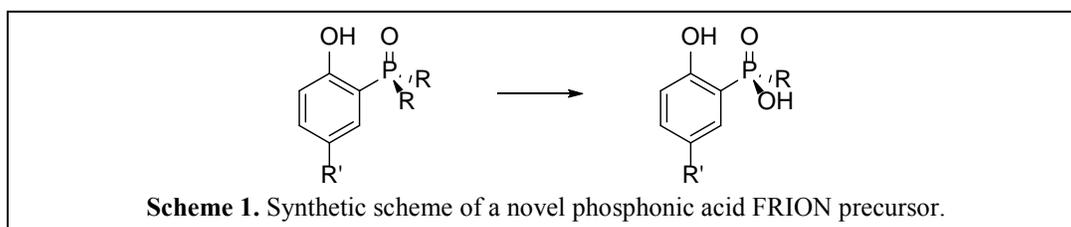
MILESTONES:

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

PROGRESS TOWARD MILESTONES

Synthesis and characterization of FRIONS – Work in this quarter has involved the synthesis of new phosphonic-acid-based FRIONS (Fig. 1, left). Novel phosphonic-acid FRION precursors have been prepared (Scheme 1) in high yield and in gram scale quantities. These categories of FRION were designed to disrupt pi stacking of the final salt and reduce the symmetry of previous FRIONS, which generally leads to an increase in solubility. Synthesis of FRION salts containing this precursor, and precursors listed in previous reports, have been initiated and supported by spectroscopic evidence showing these salts have been made. Gram scale synthesis and full characterization is underway.

The library of $\text{Li}[\text{B}(\text{DPC})_2]$ and $\text{Li}[\text{B}(\text{DPC})(\text{oxalato})]$ salts is being expanded. One approach to new FRION salts is to vary the R' groups attached to phosphorus (Fig. 2). This substitution will provide insight into the solubility of the Li salts and will give direction regarding the best substitutions to increase the solubility of the Li salt in EC/EMC solvent. A second approach to increasing the library of FRION salts is the synthesis of the novel salt $\text{Li}[(\text{DPC})\text{F}_2\text{B}]$ (Fig. 1, right). Small quantities have been prepared, supported by spectroscopic evidence that the target compound has been made. Gram scale synthesis as well as full characterization and testing is underway.



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

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

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

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

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

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

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

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

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

MILESTONES:

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

PROGRESS TOWARD MILESTONES

(a) **Go-no-go on cathode half cells with sulfone electrolytes with HFIP additive - postponed to Sep. 31.** Studies using coin cells on a recently purchased battery tester had initially given reason for more optimism about all-sulfone electrolytes, but finally confirmed the weakness as originating in the low-viscosity fluoromethylsulfone (FMS) component. Before abandoning our search for undoped sulfone-based solvent for use with the high voltage LMNO cathodes, further tests were carried out replacing the source of problems, *i.e.* FMS, with a carbonate co-solvent, the dimethyl carbonate used in the standard carbonate electrolytes. This was deemed worthwhile in view of the findings that ethylmethyl sulfone has superior fire and overcharge resistance in Li-ion batteries. Indeed the EMS-DMC proves very nearly as good as EC-DMC in half-cell tests with a Li counter electrode. Some data are shown in Fig. 1. Although the half-cell tests with graphite anodes for this electrolyte were not as satisfactory as the high performance EMS-FMS electrolyte reported earlier, the performance using LTO cathodes (which are the choice being made in different parts of the world for high-safety Li-ion cells using LMNO cathodes) might well prove a very favorable one.

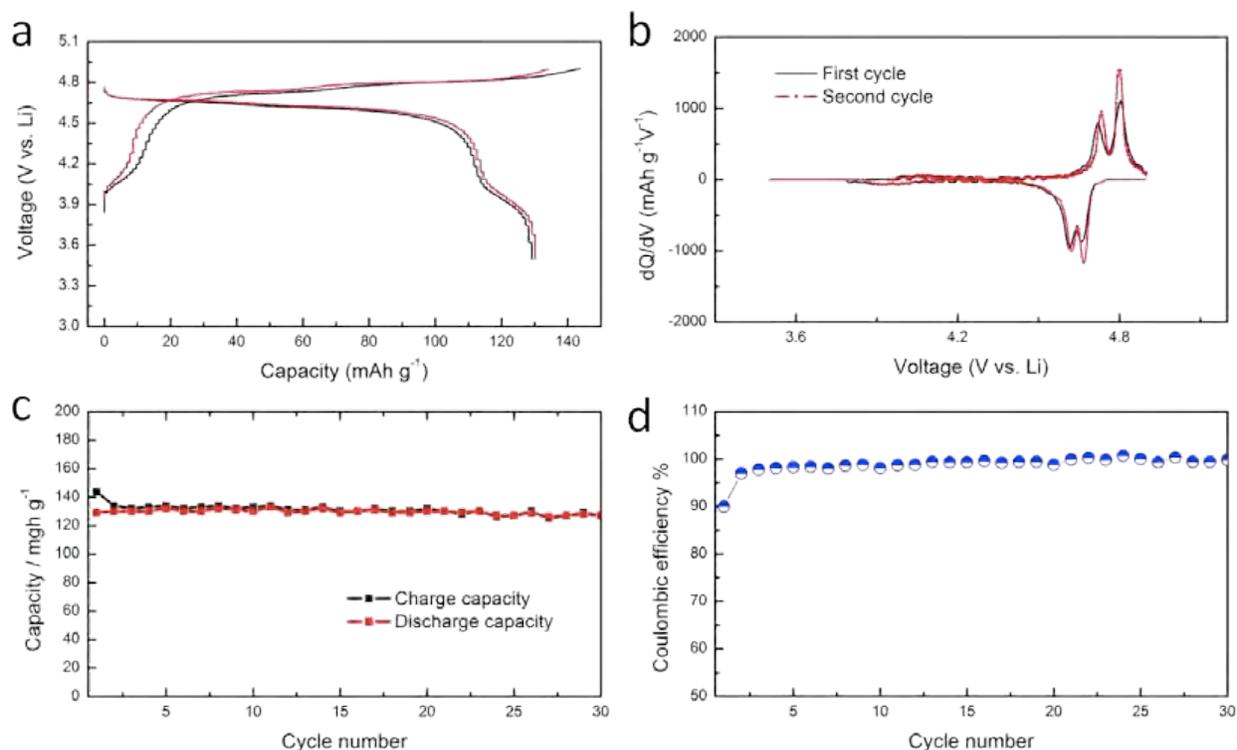


Figure 1. Performance of the LNMO electrode with EMS/DMC electrolyte in a lithium half cell. (a) illustrates the voltage profiles of the LNMO electrode cycled at 0.2C. It clearly shows that the LNMO electrode operates with two consecutive plateaus, corresponding to the two redox processes of nickel, that is Ni²⁺/Ni³⁺ and Ni³⁺/Ni⁴⁺, at 4.6 and 4.7 V vs. Li, respectively. The two steps are likewise evidenced in the corresponding derivative, dQ/dV, response shown in (b). The excellent cycling stability (c) and high-coulombic efficiency (d) indicates the electrolyte works well with LNMO at high voltage, free of decomposition. (Results at room temperature).

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

Refinements of the synthetic techniques have greatly clarified the compositions of novel silicosulfate solid acids. The higher purity of their Li salts has however had a negative effect on their plasticity; studies continue to try to understand and restore the plasticity.

(c) (d) (e) are on schedule without breakthroughs. Strategies for polymer incorporation to strengthen covalent nets during desolvation are under study.

BATT TASK 4

CATHODES

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

TASK TITLE: Cathodes – Novel Cathode Materials and Processing Methods

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

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

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

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

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

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

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

MILESTONES:

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

PROGRESS TOWARD MILESTONES

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

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

Previous reports have highlighted the electrochemical connection between the value of x in $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ ($M = \text{Mn, Ni, Co}$) composite electrode structures and the phenomena of voltage fade and hysteresis. A series of studies focused on synthesis, as well as the value of x , is being pursued to understand the structure-property relationships of these complex materials.

Figure 1a shows first-cycle dQ/dV data of two $\text{Li}/0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ cells between 4.7 and 2.0 V. These samples were prepared by co-precipitation, followed by annealing at 850°C for 12 hours (black) and 96 hours (red). There are differences in the 4.6 V activation peak as well as in the 3.3 V discharge peak, which can be related to the Li_2MnO_3 component and x value. Figure 1b shows the second-cycle dQ/dV data for the same samples between 4.1 and 2.0 V. Significant differences are visible in the 3.8 V charging peak as well as the region below 3.5 V. The 3.8 V peak does not appear until after activation and contributes to hysteresis. The region below 3.5 V reflects the onset of the voltage fade phenomenon following activation and cycling. Figure 1c shows the Mn K-edge EXAFS spectrum of $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ samples synthesized from a Li_2MnO_3 precursor. All samples were annealed at 950°C for 6 hours, followed by either: 1) slow cooling, 2) intermediate cooling, or 3) quenching. All three data sets overlap and reveal that the local Mn environments are identical and similar to that found in pure Li_2MnO_3 . Similar results were found for the Ni K-edge data (not shown) revealing more layered, but identical environments, for all samples. These data imply that charge ordering, particularly Li-Mn ordering, is the dominant driving force that dictates the initial localized configurations and structures in these electrode materials.

This study reveals unequivocally the existence and importance of Li_2MnO_3 -like domains. Furthermore, the EXAFS data show that charge ordering in these materials drives the domain microstructure. As such, connections between LiM_6 (e.g., LiMn_6 , LiMn_5Ni) units in the transition metal layers, which occur in all Li- and Mn-rich composite structures, play a key role in the voltage fade phenomenon. These results serve as an important guide for our future research in understanding and improving the electrochemical properties of these materials.

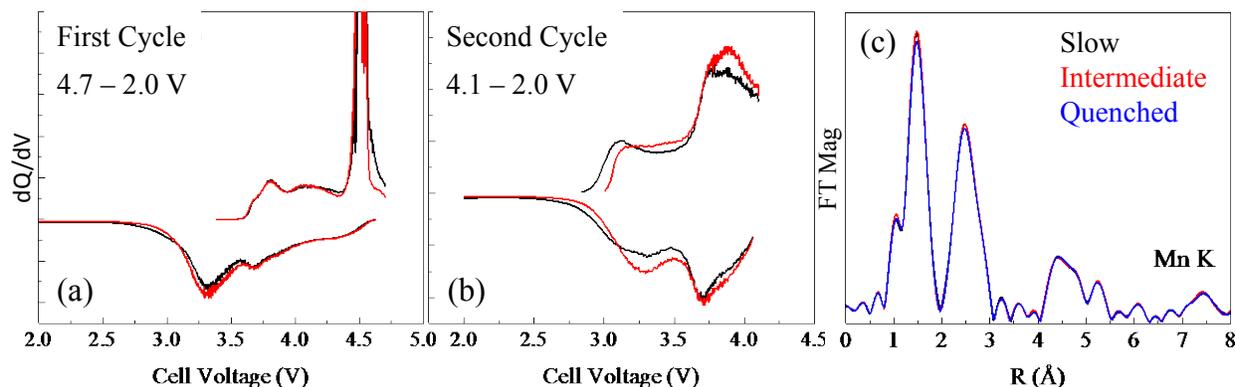


Figure 1. (a) 1st cycle dQ/dV of samples annealed for 12 hours (black) and 96 hours (red). (b) 2nd cycle data of samples in (a). (c) Mn K-edge EXAFS after various cooling rates.

Reference. J. R. Croy, K. Gallagher, M. Balasubramanian, B. Long, and M. Thackeray, *Hysteresis and Voltage Fade as a Function of Li_2MnO_3 Content in $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$* , in preparation (2013).

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

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

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

BARRIERS: Cost, power and energy density, cycle life

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

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

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

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

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

MILESTONES:

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

PROGRESS TOWARD MILESTONES

(1) Various synthetic and annealing conditions were examined for the preparation of LNMS to maximize yields using spray pyrolysis. Optimal conditions are being developed to limit Li-Ni ion-mixing and cubic impurities. Preliminary electrochemical data is being collected and analyzed. Experimental details have been formalized to achieve compatible composite cathode materials based on LNMS.

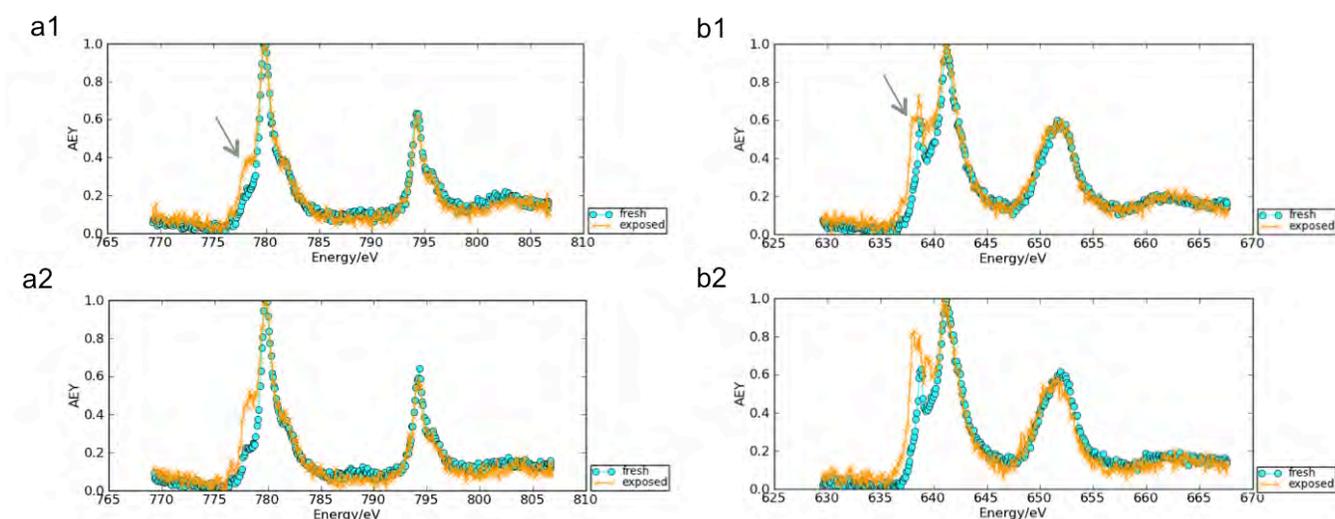


Figure 1. Soft XAS spectra (AEY mode) of fresh electrodes (cyan) and electrodes with 7-day electrolyte exposure using normal coin-cell configuration (orange): (a1) Co L-edge of NMC442, (a2) Co L-edge of Ti-substituted NMC442, (b1) Mn L-edge of NMC442, and (b2) Mn L-edge of Ti-substituted NMC442.

(2) The surface chemistry of NMC442 and Ti-substituted NMC442 is currently under investigation. Both materials undergo reaction upon electrolyte exposure (LiPF_6 in EC/DMC 1/1) prior to cycling. Figure 1 shows the soft XAS (AEY mode, surface sensitive) results for the electrodes after 7-day electrolyte exposure using normal coin-cell configurations. Co and Mn ions were both reduced at the material surface, which is indicated by the build-up of lower energy shoulders (arrows), shifting of the absolute energy scale, and increased L_3/L_2 ratio. Interestingly, the Ti-substituted NMC442 exhibited a stronger signal for reduced species. This could be due to its higher specific surface area. Electrochemical cycling imposes additional effects on the reduction of Mn and Co. The effects of this are currently being examined using a STEM-EELS technique and will be reported. The soft XAS experiments were conducted in collaboration with Dennis Nordlund and Tsu-Chien Weng at SSRL; STEM/EELS experiments were conducted in collaboration with Haimei Zheng and Huolin Xin at LBNL.

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

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

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

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

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

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

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

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

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

MILESTONES:

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

PROGRESS TOWARD MILESTONES

Our previous report presented the synthesis of α -LiVOPO₄ (triclinic) by the microwave-assisted solvothermal (MW-ST) process and the optimization of its electrochemical performance. Reducing its particle size was possible by employing various solvent mixtures of water and alcohols/glycols. The water to alcohol/glycol ratio of 3:1 was found to be crucial to eliminate impurities at a synthesis temperature of 230°C. The various solvent mixtures led to the formation of micro-flower morphologies with the smallest particle size achieved with a mixture of water and glycols.

The focus this quarter was on optimizing the particle size further by controlling the reaction time and reactant concentrations, as well as by adding cetyl trimethylammonium bromide (CTAB) to the precursor solution as shown in Fig. 1. Higher initial capacities were generally realized with smaller particle size when the cells were cycled in the typical potential window (3.0 to 4.5 V, shown by the dashed box), as seen in Fig. 2 for the samples shown in Fig. 1. For instance, the initial capacity for the material with a 10 min. reaction hold time (0.067 M in V, 0 mL CTAB) was *ca.* 115 mAh/g, while that for the material with a 45 min. hold time was *ca.* 72 mAh/g. The addition of CTAB helped to prevent particle growth and agglomeration and reduced particle size as seen in Fig. 1. The electrochemical performance was improved with the addition of an optimum amount of CTAB. For example, the first discharge capacity increased from 82 mAh/g to 124 mAh/g on going from 0 to 0.5 mL of CTAB, but decreased to 90 mAh/g with further addition of CTAB (1 mL). The cycling performance was also improved by coating the particles with the conductive PEDOT:PSS.

Li₂MP₂O₇ (M = Fe, Mn, and Co) cathodes offer the potential to extract two Li ions per transition metal and high operating voltages. Accordingly, Li₂MnP₂O₇ and Li₂CoP₂O₇ were synthesized by the MW-ST process, but their capacities were 90–100 mAh/g with the extraction of only 0.8 to 0.9 Li due to a larger particle size (3 to 5 μ m). Further work is focused on reducing the particle size.

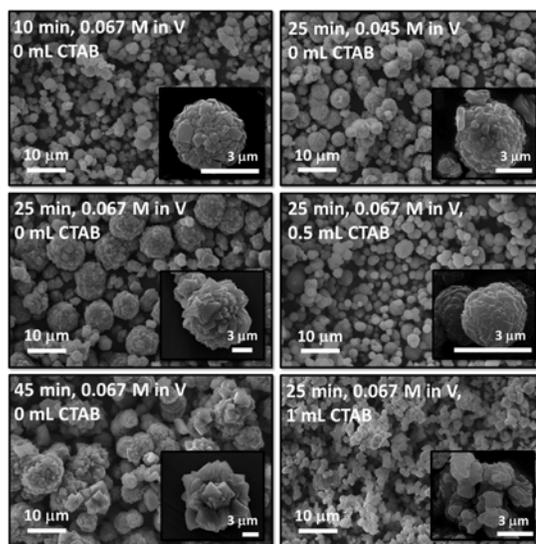


Figure 1. SEM of α -LiVOPO₄ prepared with a water:ethanol ratio of 3:1 for the various indicated reaction hold times at 230°C (not including ~25 min. ramp time to 230°C), V concentrations, and amounts of CTAB solution substituted for water.

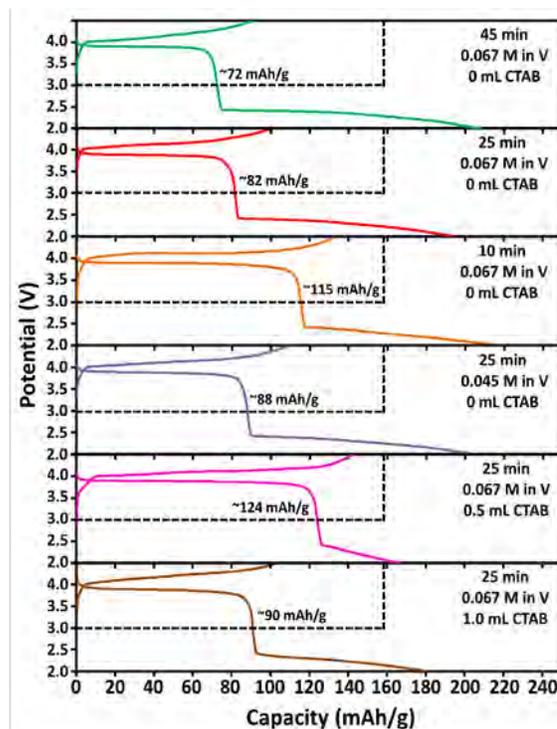


Figure 2. First charge-discharge curves at C/20 rate of α -LiVOPO₄ prepared with water:ethanol = 3:1 for various reaction hold times at 230°C, V concentrations, and amounts of CTAB solution substituted for water.

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

TASK TITLE: Cathodes – Development of High Energy Cathode Materials

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

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

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

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

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

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

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

MILESTONES:

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

PROGRESS TOWARD MILESTONES

The key factors related to oxygen release in the Li-Mn-rich (LMR) layered composite were identified in the last quarter. Corrosion and fragmentation of LMR particles observed after cycling were correlated to the large stress generated from extensive removal of Li^+ and release of oxygen during charge. Mn^{2+} species and reduced Li content in the fragmented pieces are directly related to the capacity degradation mechanism in LMR. In this quarter, the electrochemical kinetics of the layered $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ and Li_2MnO_3 components in LMR were further investigated during the electrochemical charge-discharge processes. The major findings are:

- 1) The transformed Li_2MnO_3 phase exhibited good charge rate capability but poor discharge capability.
- 2) The Li^+ diffusion rate in LMR materials is mainly dictated by the Li_2MnO_3 and the phase to which it transforms.

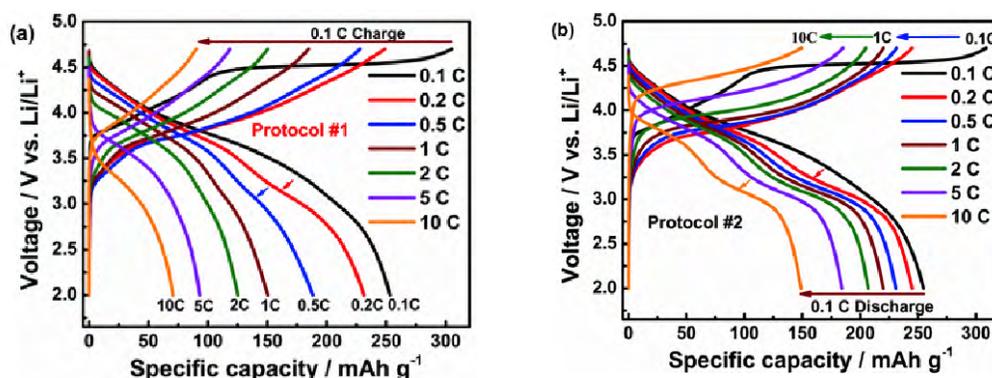


Figure 1. Voltage profiles of $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6}]\text{O}_2$ (a) Charged at a constant rate of 0.1 C ($1\text{C} = 250 \text{ mA/g}$) and discharged at different rates during succeeding cycles. (b) Charged at different rates and discharged at a constant rate of 0.1 C during succeeding cycles.

In Fig. 1(a), a slow rate of 0.1C was used for all charges and different rates were applied during discharge. The voltage fading corresponding to the onset of a spinel-phase transition was only observable at relatively slow discharge rates ($\leq 2\text{C}$) and completely disappeared at rates above 2C. This points to the ramifications of the slow discharge rate capability of the Li_2MnO_3 component. In other words, discharge capacity delivered at the 10C rate was dominated by the layered $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ component. When different charge rates are applied on the LMR cathode, followed by a constant discharging rate of 0.1C (Fig. 1b), the capacity retention is largely improved compared with Fig. 1a. In this case, the voltage fading is evident during discharge even after charging at 10C, which further supports the notion that Li_2MnO_3 -derived spinel phase has fast charge capability. It is suggested that slow discharge should be used to effectively capture and understand the voltage-fading phenomenon in LMR. The diffusion of Li^+ ions within the lattice structure of the Li_2MnO_3 -derived phase needs to be enhanced in order to improve the rate performances of LMR.

Publications:

1. J. Zheng, M.Gu, J.Xiao, P. Zuo, C. Wang and J.-G. Zhang, "Corrosion/Fragmentation of Layered Composite Cathode and Related Capacity/Voltage Fading during Cycling Process" *Nano Lett.*, DOI: 10.1021/nl401849t.
2. J. Xiao, X. Yu, J. Zheng, Y. Zhou, F.Gao, X. Chen, J.Bai, X.-Q. Yang, J.-G. Zhang, "Interplay between two-phase and solid solution reactions in high voltage spinel cathode material for lithium ion batteries" *J. Power Sources*, **2013**, 242, 736-741.
3. J. Zheng, Jie Xiao, Z. Nie, and J.-G. Zhang, "Lattice Mn^{3+} Behaviors in $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ Full Cells" *J. Electrochem. Soc.*, **2013**, 160, A1264-A1268.

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

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

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

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

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

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

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

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

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

MILESTONES:

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

PROGRESS TOWARD MILESTONES

Milestone (a): Heating Li transition metal oxides in the presence of transition metal fluorides at temperatures as low as 250°C is sufficient to incorporate significant amounts of fluorine into the oxide lattice - up to 40 mol% fluorination has been observed in certain cases. In collaboration with the Wang group at BNL, also in the BATT Program, the thermal stability of these oxyfluorides was evaluated by collecting XRD patterns during heating. It was found that these phases are metastable and decompose to binary phases above 500°C. Therefore, it appears that these types of phases cannot be obtained at high temperature. As a result, this *in situ* XRD work with temperature provides a no-go conclusion to **Milestone (b)**. Instead, focus is now placed on low temperature fluorination, which resulted in a collection of phases (four were identified as pure so far) to be electrochemically tested in the near future.

Milestone (d): XAS was collected at the O *K* edge for MgO-coated samples of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Spectra were acquired in the pristine and fully delithiated state, using total fluorescence and total electron yield (TFY and TEY) detectors, simultaneously. The TEY detector provides XPS-like, surface-sensitive insight, whereas experimental conditions were designed such that TFY signals are representative of the bulk of the material. A comparison between a bare sample and the coated materials each treated at 500 and 800°C was established (Fig. 1). The existence of broad, low-energy shoulders in the pre-edge peak at 531 eV is indicative of the formation of $\text{Ni}^{4+}\text{-O}^{2-}$ species during Li deintercalation. Their absence in the TEY data for the bare material is taken as evidence that the surface of the electrode is more reduced than the bulk (see FY12 Q1 report). In contrast, the coated samples show pronounced shoulders in the bulk and on the surface. It is hypothesized that Mg^{2+} ions pin the charges of the O^{2-} ions so that they cannot be polarized by the Ni^{4+} ions and become electrophilic. The result is a more stable surface against electrolyte oxidation for coated *versus* bare samples, and provides the rationale for the performance trends established for the two materials (see FY12 Q3 report).

Collaborations: Dr. Wang (BATT-BNL), Dr. Nordlund (SSRL-SLAC).

Publications this quarter:

- C. Kim *et al.*, *Adv. Energy Mater.*, 2013, doi: 10.1002/aenm.201300264.

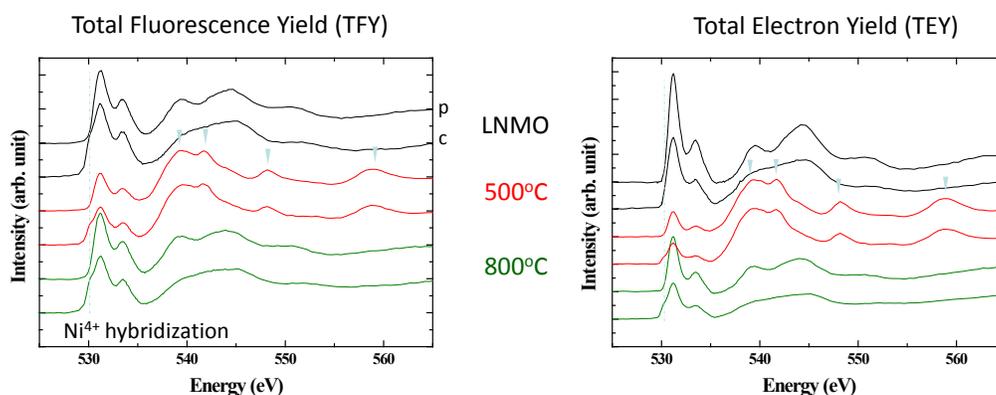


Figure 1: O *K* edge XAS of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (black), coated with MgO and treated at 500 (red) and 800°C (green), before (p) and after (c) complete lithium removal. TEY data is substantially more surface sensitive than TFY.

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

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

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

BARRIERS: Low energy density and cost

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

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

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

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

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

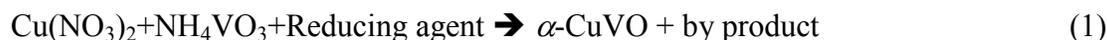
MILESTONES:

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

PROGRESS TOWARD MILESTONES

There are large variations in the phases and crystal structures of Cu-based vanadium oxides (Cu-V-O). By exploring the synthesis process and possible reaction pathways using specialized *in-situ* reactors, our group has been able to synthesize several different Cu-V-O compounds, and some of them are promising for use as cathode materials, including ϵ -Cu_xV₂O₅ that has been thoroughly investigated in previous quarters. The effort in this quarter was focused on the synthesis of a new α -phase (α -CuVO). In addition, structural and preliminary electrochemical characterization of the material was carried out.

For synthesis of this new α -CuVO compound, procedures using hydrothermal (HT) reaction were developed, typically *via* the route:



The synthesis reaction at certain conditions, *i.e.*, Cu/V ratio, pH value, and concentration of reducing agent, led to the formation of an intermediate phase at low temperatures, and the final product of α -CuVO phase at about 200°C. According to our structural analysis, this α -phase is promising for use as a cathode due to its unique structure, with 3D V-O framework and open channels for Cu-ion and Li-ion transport.¹ The as-synthesized powder is composed of μm -sized particles, with uniform Cu, V elemental distribution across individual particles (Fig. 1). Solid-state reaction (SSR) was also used to obtain this α -phase, with similar crystal structure but much larger particle size. Typical voltage profiles from electrochemical tests of the synthesized powders (by HT and SSR) are provided in Fig. 2. The long single plateau observed at about 2.5 V in the discharging curves suggests that a Cu displacement reaction should be dominant, but the reaction during charging appears to be asymmetric, as indicated by the two plateaus. In the preliminary electrochemical tests, a capacity of *ca.* 185 mAh/g was measured at a moderate rate (C/20) for the material obtained by HT, much larger than that by SSR (Fig. 2). Improvement in the electrochemical performance is expected as a result of particle-size reduction. The study so far shows the feasibility of using the hydrothermal method to synthesize this new α -CuVO phase. Optimization of synthesis and electrochemical performance of the material is under way and will be reported in the future.

Collaboration: Peter Khalifah (Stony Brook University).

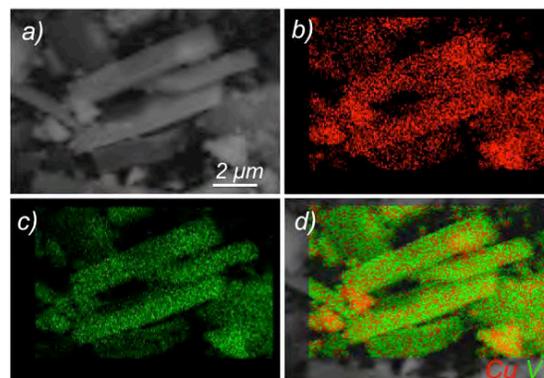


Figure 1. Morphological and chemical studies of the synthesized Cu-V-O materials by hydrothermal method, using scanning electron microscopy (SEM) imaging (a), and EDX mapping for Cu (b), V (c), and composite (d; Cu: red, V: green).

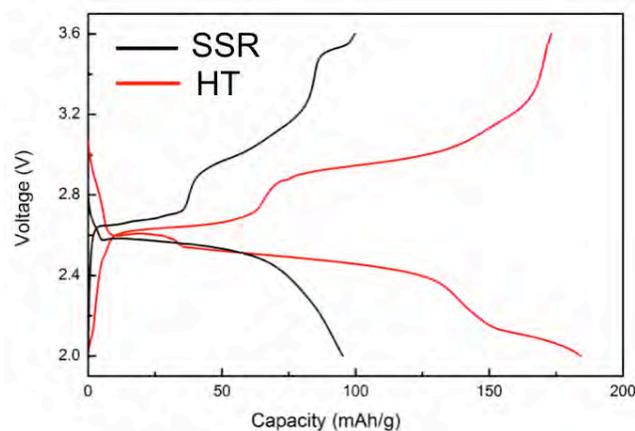


Figure 2. Electrochemical measurements of the Cu-V-O powders synthesized by hydrothermal (HT) and solid state reaction (SSR), by galvanostatic cycling at a rate of C/20 between 3.6-2.0 V.

¹ Details on the synthesis and structural analysis will be reported after the disclosure of invention is filed.

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

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

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

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

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

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

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

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

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

MILESTONES:

- (a) Setup CALPHAD database and perform initial simulation for one glass composition. (Jan. 13) **Complete**
- (b) Synthesize, characterize, and perform electrochemical testing on at least four different glass compositions. (Sep. 13) **Complete**
- (c) Create CALPHAD thermodynamic database and verify results with comparison to initial experimental glass compositions and electrochemical performance. (Sep. 13) **On schedule – 75% complete**

PROGRESS TOWARD MILESTONES

Room temperature cycle testing of three coin cells containing 50% vanadate substituted iron pyrophosphate glass cathodes is underway. The discharge and charge rates are C/10 between 2 and 4 V. The initial cycles showed some variation. However, after the first cycles, the coin cells have shown good capacity retention for over 30 cycles (Figure 1).

Polyanion glasses have been observed to undergo a low voltage (≤ 1.5 V), high capacity cathode reaction (Figure 2). Interestingly, this high capacity cathode reaction has been observed in all polyanion glasses produced. Initial results suggest at least substantial reversibility. For iron and manganese pyrophosphate glasses with vanadate substitution, the voltage of this high capacity reaction has been too low to be practically useful in automotive applications. However, once the reaction mechanism is understood, perhaps glasses can be designed to undergo this high capacity cathode reaction at higher voltages. Character-ization is underway to determine the cathode reaction mechanism.

A computational thermodynamic model of 50% vanadate-substituted iron pyrophosphate glass has been created and used to predict its electrochemical performance. Thermodynamic descriptions for both pure iron pyrophosphate and vanadate have been obtained from a self-consistent, model-parameters-evaluation process to reproduce their phase stabilities in the equilibrium phase diagrams. The formation energetics of lithiated phases of iron pyrophosphate and vanadate were obtained by reproducing their experimental voltages. By comparing the modeled discharge curves with experimentally-measured discharge curves, this initial model is being refined to improve agreement with experimental results. This may require introduction of interaction parameters to describe non-ideal mixing extrapolated from the constituents. This refined, computational-thermodynamic modeling approach will be used to predict the electrochemical performance of future mixed polyanion glasses; correspondingly, future experimental results will be used to iteratively refine the model.

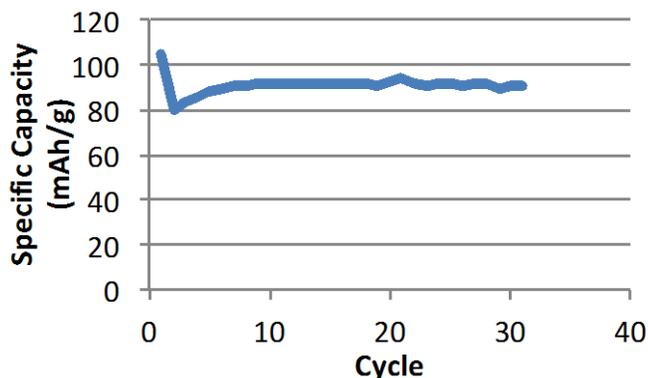


Figure 1. C/10 cycling results for 50% vanadate substituted iron pyrophosphate glass.

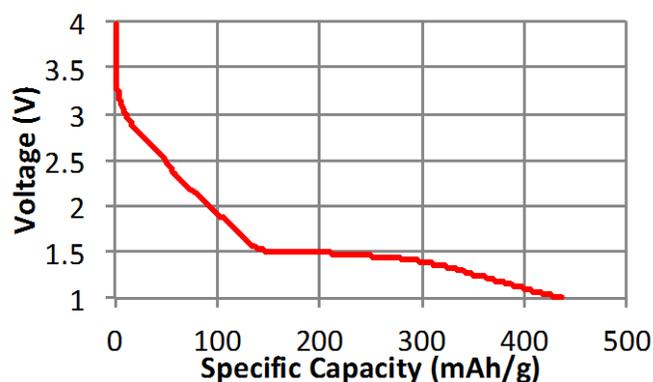


Figure 2. Discharge curve (50 mA, 2.6 mg active powder) for 50% vanadate substituted iron pyrophosphate glass showing a low voltage, high capacity cathode reaction below ~ 1.5 V.

BATT TASK 5 DIAGNOSTICS

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

TASK TITLE: Diagnostics – Interfacial Processes

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

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

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

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

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

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

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

MILESTONES:

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

PROGRESS TOWARD MILESTONES

In the third quarter of FY2013, the main efforts toward milestone (a) focused on identification of the interfacial phenomena occurring on Si single-crystal electrodes in organic electrolytes and their impact on electrochemical behavior. Figure 1 depicts cycling behavior of Si single crystals with (100), (110) and (111) orientations in 1M LiPF₆ EC:DEC [3:7] in three electrode cell configurations controlled electrochemically during the first lithium intercalation from 2.5 V vs.

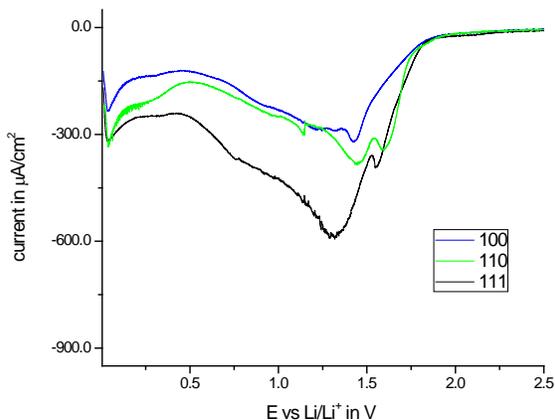


Figure 1. SEM images (left) (courtesy of Guoying Chen, LBNL), Electrochemical data (right-top), corresponding integrated fluorescence intensity (right-bottom) of LiNi_{0.5}Mn_{1.5}O₄ baseline (black), platelet (green) and octahedron (blue) particles in EC:DEC 1:2 1M LiPF₆

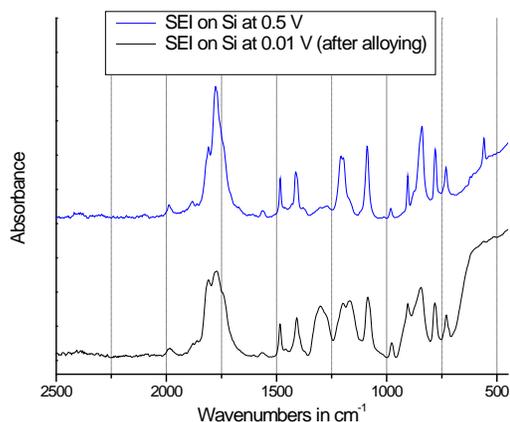


Figure 2. FTIR spectra of the SEI layer on the Si (111) electrode at 0.5 and 0.01 V. *i.e.*, before and after alloying with lithium in 1M LiPF₆ EC:DEC [3:7].

Li/Li⁺ to 0.5 and 0.01 V. Between 1.8 and 0.6 V, decomposition of electrolyte leads to SEI layer formation on the Si surface. Electrochemical response upon polarization depends on the surface crystal orientation of the Si. The (111) crystal facet displays the highest current density and lowest decomposition potential.

Figure 2 displays the different FTIR spectra of the SEI on the (111) Si electrode at 0.5 and 0.01 V. At potentials > 0.5 V, partially-lithiated surfaces remain in the original orientation. Chemical composition of the SEI layer varied strongly on the different crystal orientations of Si and included LiPF₆ salt and EC and DEC solvent decomposition products. On (100) facets, the SEI contains more carbonate and salt decomposition products and appears to be less stable.

At potentials below 0.5 V, the SEI undergoes reformation due to Si cracking and structural transition from crystalline to amorphous Si upon alloying with Li. This results in similar SEI chemical composition for the three different crystal orientations. A lower potential induces an increase in decomposition products, *e.g.*, LiF, P-O-C, and P-F.

A clear correlation between surface activity, SEI composition, stability, and crystal facets has been highlighted. These results point out the critical role of the Si crystal orientation in achieving longer Li battery lifetime and its impact on electrochemical performance.

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

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

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

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

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

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

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

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

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

MILESTONES:

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

PROGRESS TOWARD MILESTONES

In Q3, BNL studied the thermal stability and gas evolution behavior of high voltage $\text{LiMn}_{2-x}\text{Ni}_x\text{O}_4$ ($x=0.5$, LNMO) cathode materials with disordered ($Fd-3m$) spinel structure. During heating, synchrotron-based time-resolved XRD (TR-XRD) combined with mass spectroscopy (MS) were used to detect crystallographic changes. Milestone (c) is complete.

The investigation of the thermal stability, which could greatly impact safety behavior of LIBs with high voltage $\text{LiMn}_{2-x}\text{Ni}_x\text{O}_4$ cathode material with either ordered ($P4_332$) or disordered ($Fd-3m$) structure as a result of heating, is one of our important milestones for FY13.

The *in situ* TR-XRD pattern combined with the simultaneously measured MS data that traces oxygen gas release for a fully-charged, disordered LNMO (*d*-LNMO) are shown in Fig. 1(a). In general, the XRD patterns shift toward low angles as the temperature increases, indicating the expansion of the lattice parameter. Significant growth of the (220) and (422) peaks were also observed, which is clear evidence of transition metal migration to tetrahedral sites in the spinel structure. The charged *d*-LNMO started to release oxygen at a temperature as low as 210°C , accompanying the abrupt change of the XRD pattern from previous patterns at this temperature. This can be seen from the great broadening of peaks and evolution of new peaks, indicating the destruction of well-crystallized structures and phase transitions to new phases. The new phases, which emerged after the onset of the oxygen release, were identified as ilmenite NiMnO_3 , $\alpha\text{-Mn}_2\text{O}_3$, and spinel NiMn_2O_4 .

To have a better idea of the thermal degradation pathways, the evolution of each phase upon heating, which was calculated by integrating intensities of characteristic peaks of each phase, is plotted in Fig. 1(b). It was observed that both NiMnO_3 and $\alpha\text{-Mn}_2\text{O}_3$ showed intermediate phase behavior once the thermal degradation and oxygen release commenced. Because of this, the NiMn_2O_4 -type spinel phase first grew slowly and then rapidly at the expense of the NiMnO_3 and $\alpha\text{-Mn}_2\text{O}_3$ phases. Upon oxygen release, Ni^{4+} in the charged samples was rapidly reduced to close to Ni^{2+} , and Mn^{4+} reduced to Mn^{3+} in a more mild way, giving rise to the formation of NiMnO_3 ilmenite and $\alpha\text{-Mn}_2\text{O}_3$ intermediate phase, respectively. The creation of abundant Mn^{3+} due to reduction leads to the favorable disproportionation reaction, generating Mn^{2+} that has strong preference for tetrahedral sites in spinel. Such large scale Mn^{2+} migration to tetrahedral sites yields the NiMn_2O_4 -type spinel phase at the latter stages of thermal degradation of fully charged *d*-LNMO. In summary, features like Mn oxidation state, oxygen deficiency, amount of impurity phase, and Ni/Mn ordering, identified as key factors for the electrochemical performance of LNMO material, also play decisive roles in the material's thermal stability.

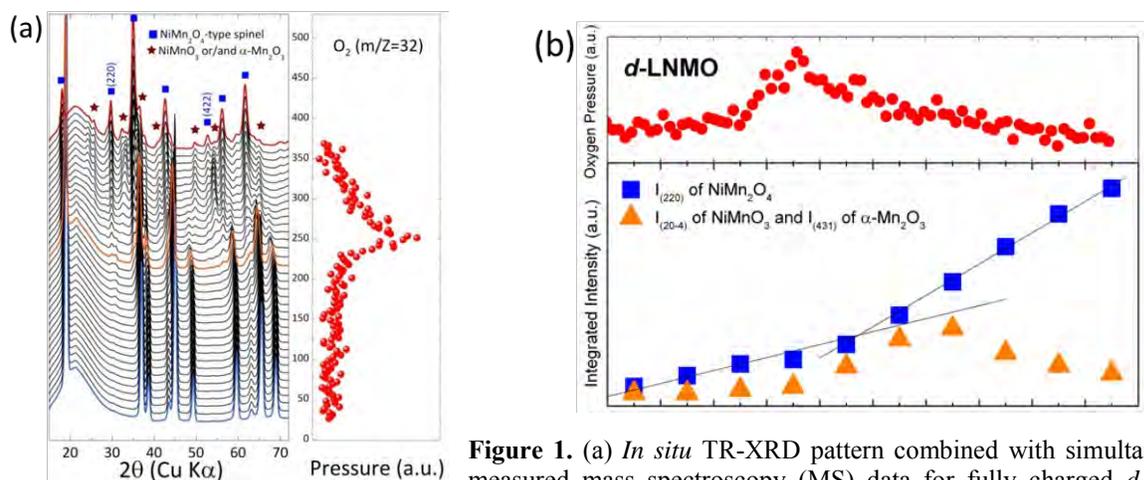


Figure 1. (a) *In situ* TR-XRD pattern combined with simultaneously measured mass spectroscopy (MS) data for fully charged *d*-LNMO upon heating; (b) evolution of characteristic peaks of different phases (e.g., ilmenite NiMnO_3 , $\alpha\text{-Mn}_2\text{O}_3$ and spinel NiMn_2O_4) upon heating. Corresponding oxygen release profiles are plotted for comparison.

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

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

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

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

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

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

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

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

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

MILESTONES:

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

PROGRESS TOWARD MILESTONES

1. Ordering in layered $\text{Na}_x\text{Ni}_{x/2}\text{Mn}_{1-x/2}\text{O}_2$ ($2/3 \leq x \leq 1$): A series of layered cathode materials within the $\text{Na}_x\text{Ni}_{x/2}\text{Mn}_{1-x/2}\text{O}_2$ ($2/3 \leq x \leq 1$) system were synthesized by solid-state methods and their long and short-range structures were investigated by combining XRD and NMR spectroscopy. A transition from P2 to O3 stacking was observed at $x > 0.8$ when samples were made at 900°C , which was accompanied by disordering of ions in the transition metal layer. This cation order/disorder could be clearly observed *via* the ^{23}Na NMR spectra of these materials (Fig. 1) - a very broad ^{23}Na signal being observed for the O3 materials.

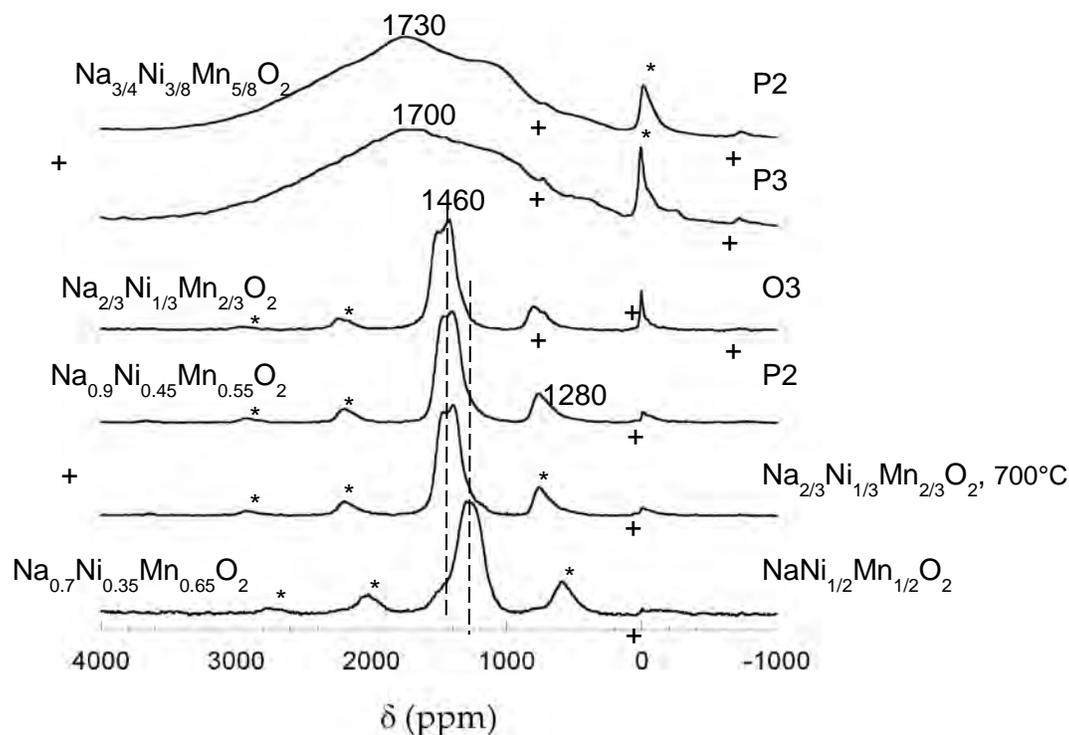


Figure 1. ^{23}Na MAS NMR spectra of the $\text{Na}_x\text{Ni}_{x/2}\text{Mn}_{1-x/2}\text{O}_2$ series. All the samples were prepared at 900°C unless noted.

At $x=2/3$, both the P2 and P3 structures were observed, depending on the synthesis temperature. Na/Li exchange led to structures with octahedral or tetrahedral coordination of the alkali metal. The transition from alkali metal prismatic coordination to octahedral/tetrahedral involves $[\text{TMO}_6]_\infty$ layer shearing that induces structural disorder through the formation of stacking faults. These results help our understanding of how these materials operate as Na and Li-ion batteries. This project was performed in collaboration with J. Cabana and M.S. Whittingham,¹ and now with the additional BATT PI, Y.S. Meng.

2. Silicon and its SEI: Work in this quarter has focused on the development of a new approach to allow *in situ* NMR spectroscopy of Si nanomaterials to be performed. The approach allowed multiple cycles to be performed, which had not been possible in our previous work. This allowed the processes that occur in the second cycle to be explored. The second focus was to develop a robust NMR methodology with which to monitor SEI formation. Finally, pulse field gradient (PFG) methods have been performed to study tortuosity, with initial experiments focusing on porous carbons since they provide an ideal model system with which to develop a new methodology.

Publication: J. Cabana, N.A. Chernova, K.A. Aldi, J. Xiao, M. Roppolo, M.S. Whittingham, and C.P. Grey, *Inorg. Chem.*, in press (2013).

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

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

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

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

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

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

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

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

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

MILESTONES:

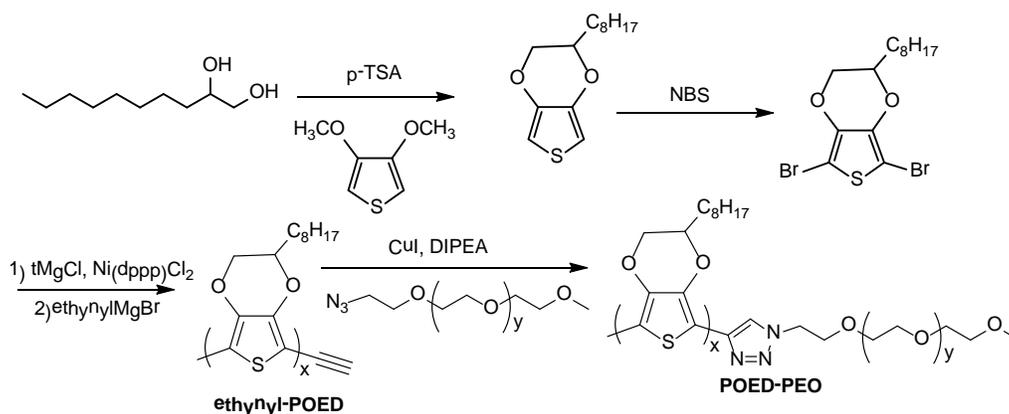
- (a) Obtain first-simulation results of molecular S₈, Li₂S_x, and Li salts in SEO PEO (or short-oligomer analogs) (Mar. 13) **Complete**
- (b) Make initial predictions of X-ray spectroscopy signatures of Li₂S_x and other components in the model Li-S cell. (Mar. 13) **Complete**
- (c) Work out the synthesis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

PROGRESS TOWARD MILESTONES

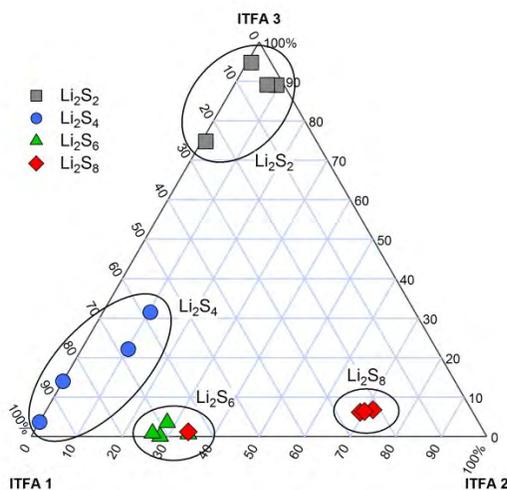
Milestone (a). Molecular dynamic simulations of Li_2S_x molecules dissolved in tetraglyme have shown that lithium polysulfide molecules elect to form nano-crystals/clumps in solution. Work to further understand this phenomenon is on-going.

Milestone (b). Spectroscopic signatures have been obtained for both single polysulfide molecules in tetraglyme and polysulfide molecules that have formed nano-crystals in simulation.

Milestone (c). The group just succeeded in synthesizing PEDOT-containing block copolymers following the synthetic scheme below. The cyclic voltammograms of the material show promise for conducting ions and electrons to active particles in electrodes.



Milestone (d). Sulfur K-edge spectra was obtained for Li_2S_x ($x=2, 4, 6, 8$) dissolved in both PEO and SEO, and at two different overall sulfur concentrations. By performing a principal component analysis, the system of obtained spectra were found to be represented by three primary components. Then, using a target factor analysis, three hypothetical spectra were developed, which, through linear combinations, could represent the whole system of spectra. The weightings of these three hypothetical spectra in each experiment are shown in the ternary diagram below, which suggests that speciation at the sulfur K-edge may be possible:



Milestone (e). The design of Li-S cells are now ready for *in situ* x-ray experiments. This work is on-going.

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

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

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

BARRIERS: Low energy density, poor cycle life

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

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

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

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

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

MILESTONES:

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

PROGRESS TOWARD MILESTONES

Milestone (c): Our *in operando* XRD study of 150 μm thick NCM333 ($\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$) electrodes was complemented by comparing the data collected during a charge to 4.3 V at 1C followed by relaxation (see Q2 Report) with a different set of data collected at C/10. While a continuous evolution of the XRD peaks was observed during relaxation after the 1C charge, the peaks remained unchanged during relaxation after a charge at C/10. This observation provides further support to the conclusion that a fast charge in such thick composite electrodes results in the buildup of *in depth* chemical gradients due to kinetic limitations imposed by inhomogeneous carrier transport. This work completes this milestone.

Milestone (d): Figure 1, top, shows an *ex situ* chemical map of the cross section of a NMC333 electrode harvested after a charge to 4.3 V at 3C. The current collector is located at the bottom in the image. This map was produced by collecting $\mu\text{-XAS}$ at the Ni K edge. In such an experiment, the X-ray beam is focused down to 2 μm and rastered across a sample of interest. The energy of the beam was set at a discrete number of energies in the vicinity of the edge, at values where the spectroscopic difference between pristine and oxidized material is largest. The intensity at these points was normalized by collecting maps above and below the edge. The intensity at these points was normalized by collecting maps above and below the edge. Separately, full spectra were collected at selected points (Fig. 1, bottom) to confirm the trends in the map. The results indicate the existence of areas in the electrode that did not charge (*i.e.* oxidize, red) as effectively as the rest. Contrary to what would be expected, based on porous electrode theory of materials reacting through solid solutions, such as NMC333, there is no homogenization of the composition when the electrochemical potential is removed. This effect could be an indication of poor electrical connection of the domains, an early sign of a possible source of failure upon extended cycling.

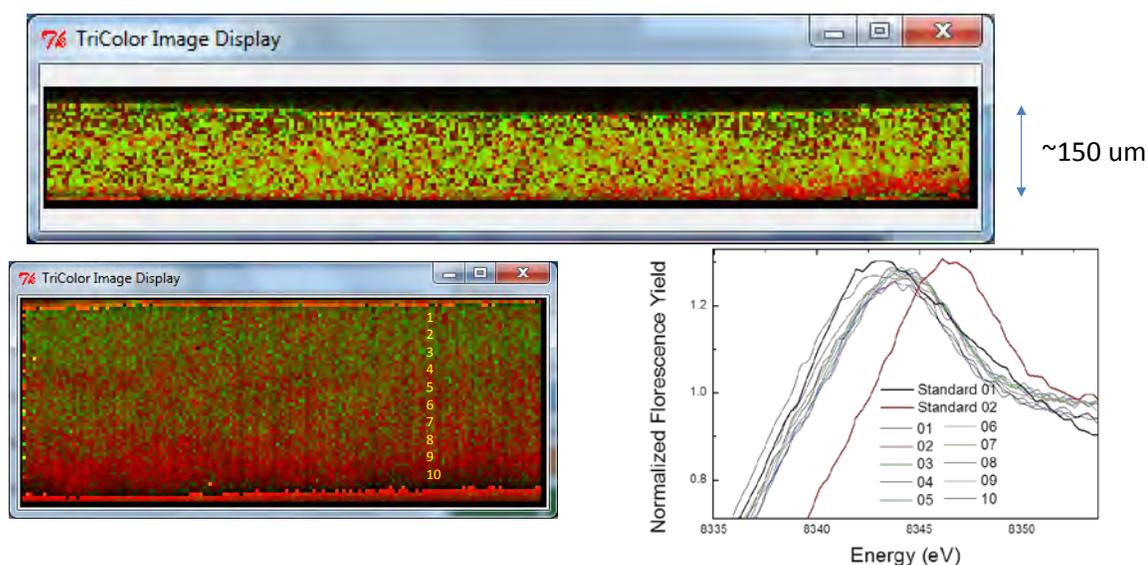


Figure 1: (Top) Ni K edge $\mu\text{-XAS}$ of the cross-section of a NMC333 electrode charged to 4.3 V at 3C. (Bottom) Magnification of the top image, indicating the points where individual full spectra were collected (right).

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

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

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

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

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

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

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

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

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

MILESTONES:

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

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

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

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

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

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

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

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

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

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

MILESTONES:

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

PROGRESS TOWARD MILESTONES

Chemical synthesis and materials characterization. Solid state and soft chemistry (sol-gel and co-precipitation) methods have been well established to produce phase pure oxide samples in both the micron and nano size ranges. It has been shown, through controlled experiments, that the Li excess layered-layered composites $\text{Li}[\text{Li}_{1/6}\text{Ni}_{1/4}\text{Mn}_{7/12}]\text{O}_2$ and $\text{Li}[\text{Li}_{1/5}\text{Ni}_{1/5}\text{Mn}_{3/5}]\text{O}_2$ can be successfully synthesized by sol-gel, double hydroxide co-precipitation, and carbonate co-precipitation methods. Different secondary particle morphologies and surface characteristics are obtained and subsequently different electrochemical performances are observed (see Fig. 1). The conclusion is that the double hydroxide method would be most suitable to consistently synthesize high quality samples for subsequent diagnostic efforts.

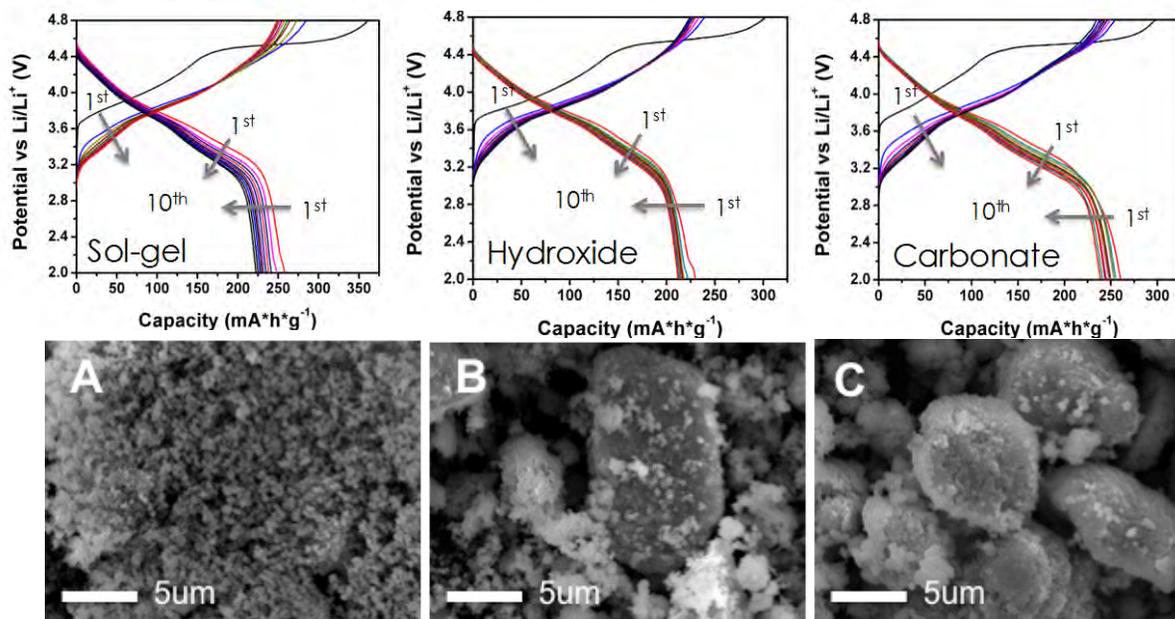


Figure 1. Electrochemical performance and scanning electron microscopy images of sol-gel product (A), hydroxide co-precipitation product (B), and carbonate co-precipitation product (C).

STEM/EELS and First principles modeling diagnosis. Surface structure change can be clearly visualized by high resolution STEM: transition metal (TM) ions migrate to the Li layer forming a defect spinel phase upon cycling. Chemical differences can be identified from the EELS spectra: the surface layer after cycling exhibits no oxygen pre-peak when compared to other spectra. This strongly suggests that the change in the TM coordination environment can be rationalized by a TM valence change, TM-O bond length change, O vacancy formation, *etc.*

First principles calculations were carried out in the spin-polarized GGA+U framework of density functional theory (DFT) in VASP code. A computational model was built to calculate the surface and interface properties in Li-excess materials. Thermodynamically, the spinel phase stabilizes the layered surface. In other words, after adding a spinel phase on to the surface of the layered phase, the calculated energy decreased. The TM-O bond increases in the surface layer as compared to the bulk, while the Mn at the interface gives a smaller band gap. The results from calculations help explain the EELS spectra of the surface after cycling. In addition, our oxygen vacancy calculations indicate that TMs tend to migrate with the presence of oxygen vacancies, and the oxygen vacancies may be responsible for voltage depression.

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

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

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

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

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

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

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

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

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

MILESTONES:

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

PROGRESS TOWARD MILESTONES

In Q3, a new design for an *in situ* ATR-FTIR cell was developed to analyze the chemistry of the electrolyte reduction at the surface of a *p*-type Si(100) single crystal (doped) *in operando*. With this new design, the group was able to vary the penetration depth of the IR radiation and analyze both near-surface (<1 μm) and boundary layer (>10 μm) regions, thus analyzing for both precipitated and dissolved products. This cell was used to compare the chemistry of reduction on Si *vs.* Au and Sn surfaces obtained earlier by conventional *in situ* reflection absorption infrared spectroscopy (RAIRS) and *ex situ* ATR-FTIR. Analysis of the reaction products was aided significantly by synthesis of reference compounds provided by Hui Zhao, a member of Gao Liu's group at LBNL. Publications are in preparation.

Figure 1 shows the *in situ* spectra from the near surface region and the change when the potential is applied to the electrode. Two strong peaks appear above the electrolyte features which could be attributed to diethyl 2,5 dioxohexane dicarboxylate (DEDOHC) by comparison to the spectrum of the pure compound synthesized for this work. The spectrum of DEDOHC is very similar to that of the co-solvent DEC, diethylcarbonate, but the effect of solvation with the Li ion (or ion-pair) shifts the frequency of DEC enough for resolution of the two. The relative intensities of the vibrations are also significantly different to resolve the two molecules. The amount of DEDOHC was time-potential-depth dependent. Briefly, it appears that the DEDOHC appears over a large potential window beginning at around 1.5 V *vs.* Li/Li⁺, but not increased by stepping to lower potentials. The DEDOHC diffuses away from the surface quickly and the concentration in the bulk is very low. The reaction appeared to be self-limiting, possibly due to a parallel reaction forming an insoluble product, *i.e.*, passivation. The passivating product appeared to be lithium propionate, seen only *ex situ*. There were also experiments that indicated the reaction to form DEDOHC is a surface reaction with oxide on the surface of the Si. Similar results were observed with Sn.

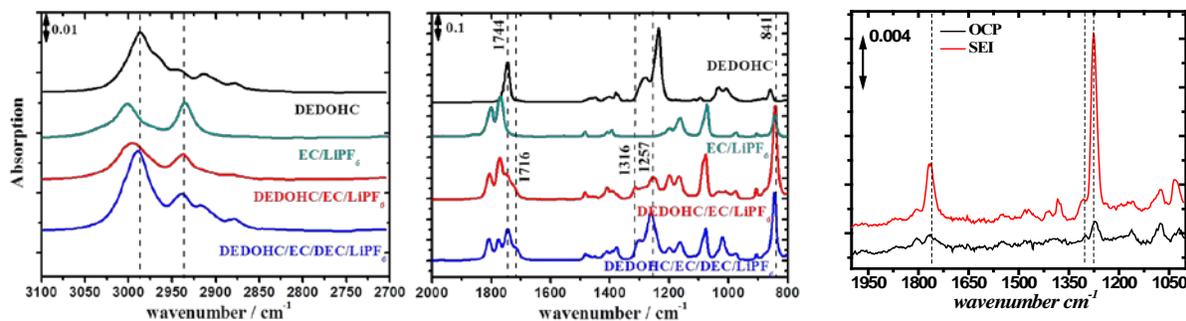


Figure 1. Comparison of *in situ* ATR-FTIR spectra after stepping potential below 1.5 V *vs.* Li/Li⁺ with spectra of electrolyte and pure DEDOHC.

A reaction scheme that would reconcile these results can be constructed from reactions previously proposed in the literature, *e.g.*, by Ogumi's group. The electrochemical reduction of DEC produces simultaneously ethyl radicals and ethoxide radical anions. The ethoxide radical anions react with EC to produce DEDOHC. This reaction is not self-limiting if there are no other reactions consuming ethoxide radical anions. The ethyl radicals react with the carboxyl radical fragment and ethoxide radical anion to form lithium propionate, which has low solubility in the electrolyte and precipitates on the surface, passivating it for further reduction. These are the same reactions that produce transesterification reactions with EMC in Li-ion cells. In comparison with other electrode materials, *e.g.*, Au, these reactions may be catalyzed by the oxide functional groups found on Si and Sn electrodes. How much Li is consumed by these reactions would depend on a delicate balance of the relative kinetics of reactions forming insoluble *vs.* soluble products. Experiments are in progress to determine the effect of the surface termination of Si, *e.g.*, H-terminated *vs.* O-terminated, on the reactivity.

BATT TASK 6

MODELING

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

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

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

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

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

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

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

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

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

MILESTONES:

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

PROGRESS TOWARD MILESTONES

Understanding solution-phase limitations in NMC electrodes: NMC electrode experimental results with different thickness have shown that system limitations come from the solution phase within the porous electrode. In this quarter, experiments were performed on electrodes with the same thickness but different electrolyte concentrations. As seen in Fig. 1, electrode capacity increases with increasing electrolyte concentration; however, the cell voltage is lower at higher concentration. This is because the conductivity of the electrolyte (LiPF_6 in 1:1 EC:DEC) at 1.5 M is lower than that at 1.0 M and 0.5 M, resulting in a larger ohmic drop in the solution phase and hence a smaller cell potential. Experimental results confirm the influence of electrolyte phase on electrode behavior, especially at rates $>1\text{C}$. Further work will focus on porous electrode model improvements using effective electrolyte properties to better predict the electrode behavior at different rates.

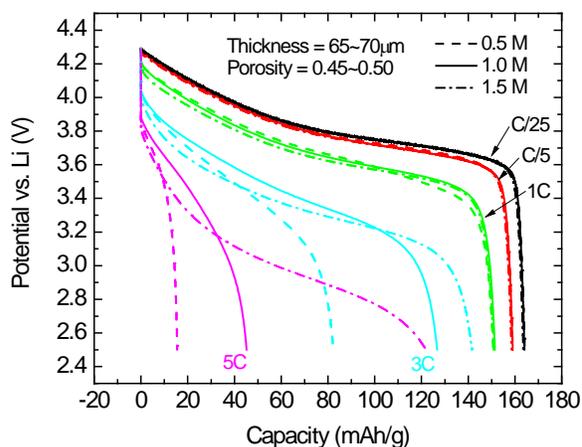


Figure 1. Experimental discharge potentials on NMC electrode using different concentrations of LiPF_6 in EC:DEC (1:1).

Electrolyte transport and interfacial polarization: In the previous quarter, experimental measurements of diffusion coefficient and activity coefficient were described (which satisfy the May milestone). In this quarter, these values were used in a model to extract the polarization across a liquid/single-ion conductor interface. Such interfaces are of great importance in Li-S and Li-air batteries. The model provides a consistent methodology to extract the interfacial resistance. The resistance was measured to be $0.398 \pm 0.0199 \text{ kohm cm}^2$ for 1M LiPF_6 in EC:DEC (1:1) satisfying the May milestone.

Stress calculations for particle-binder interactions: A modified form of Christensen and Newman's (2006) large-deformation model of Li insertion has been used in conjunction with a newly-developed software package to simulate an axially-symmetric cylinder of active material sandwiched between binder/conductive material regions. Consistency of displacements and stresses on adjacent faces is enforced. Stresses and strains are computed throughout the simulation domain. Figure 2 shows volume expansion ratios in a PVdF-on-silicon system. This fulfills the May milestone. To meet the September milestone, the model equations will be rewritten and discretized in Cartesian coordinates, and periodic boundary conditions will be introduced to create a simple model mimicking the arrangement of particles within a porous electrode.

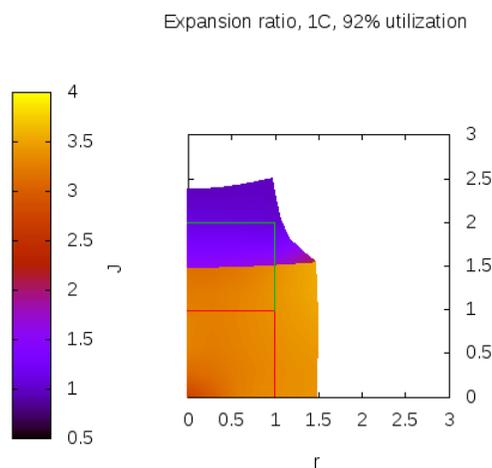


Figure 2. Quadrant of cross-section, showing expansion ratio (relative to initial volume) for PVdF/conductive additive composite on top of silicon. Red outline shows original extent of silicon cylinder, green outline shows original extent of the composite cylinder.

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

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

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

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

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

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

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

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

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

MILESTONES:

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

PROGRESS TOWARD MILESTONES

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

A cluster expansion model of the ionic interactions in Li_xMnO_3 ($0 \leq x \leq 2$) is being developed to predict the ground states as a function of Li. DFT is being used within the GGA+U formalism to describe the electronic state of the layered material. Hundreds of Li/Mn arrangements within the Li_2MnO_3 structure are being computed and used to fit the cluster expansion to arrive at a converged model of the coupled ionic interactions.

In experiments, layered Li_2MnO_3 shows a large ‘activation’ capacity (about 350 mAh/g) for the first charge, but then for the first discharge and later charge/discharge cycles it exhibits lower capacity. It is believed to be due to a phase transformation to the spinel structure. In combination with the cluster expansion, the group is computationally investigating, from first principles, possible phase transformations in the Li_2MnO_3 structure and their driving mechanisms. Figure 1 shows the formation energies (‘stability’) of a large number of Li_xMnO_3 structures, including a large number of Mn/Li defect phases. The blue points signify compounds that retain the overall Li_2MnO_3 structure; the red points correspond to compounds that exhibit large structural deformations from the parent Li_2MnO_3 compound. As can be seen from the figure, the structural deviations significantly increase with the amount of Li extracted from the compound, especially at $x_{\text{Li}} < 1$. Analyzing the chemical and structural arrangements of the defect structures (red points) provides evidence of the thermodynamic stable states and the driving force towards structural transformations in the Li_2MnO_3 compound.

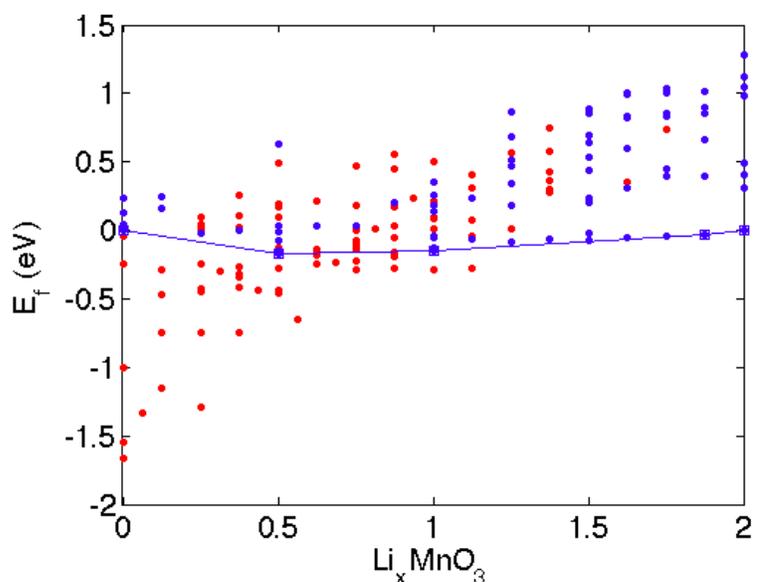


Figure 1. Calculated formation energies of Li_xMnO_3 structures with Li/vacancy defects spanning both the Mn as well as the Li layer. The blue points signify structures that retain the overall Li_2MnO_3 structure but the red points correspond to structures with a large deformation compared to the parent structure.

As can be seen from the figure, the structural deviations significantly increase with the amount of Li extracted from the compound, especially at $x_{\text{Li}} < 1$. Analyzing the chemical and structural arrangements of the defect structures (red points) provides evidence of the thermodynamic stable states and the driving force towards structural transformations in the Li_2MnO_3 compound.

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

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

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

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

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

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

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

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

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

MILESTONES:

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

PROGRESS TOWARD MILESTONES

As this is a newly initiated program, our current progress is mainly on the algorithm side, with limited technical results to report.

Algorithms have been constructed to enumerate the possible atomic arrangements for layered and spinel structures in the Li-Co-Mn-O system. These structures will be queued up and computed over the next two quarters in order to give us information on the phase diagram of this system. Once a reliable set of ground states is obtained, the phase diagram construction will be initiated.

Work was initiated to understand the effect of Li-excess on Li diffusion in Li-excess materials. As these materials become partially disordered after overcharge, work is on estimating the effect of this disorder on the rate capability.

Work has begun on Na-ion intercalating layered-oxides with aims to design high energy density Na-ion battery cathodes and understand the effects of structure (P2 or O3) on their functional properties. Our first principles work has included the calculation of voltage curves for both structure types (Fig. 2), and the determination of the Na-ion diffusion mechanisms for the O3 and P2 versions of these structures.

Ab initio molecular dynamics work has been initiated to calculate the diffusion mechanisms in both the O3 and P2 type structures to examine how they differ (Fig. 1). These calculations have so far determined that the di-vacancy diffusion mechanism present in O3 type structures is absent in P2 type structures. Work is continuing on how these contribute to Na-ion mobility and diffusion rates.

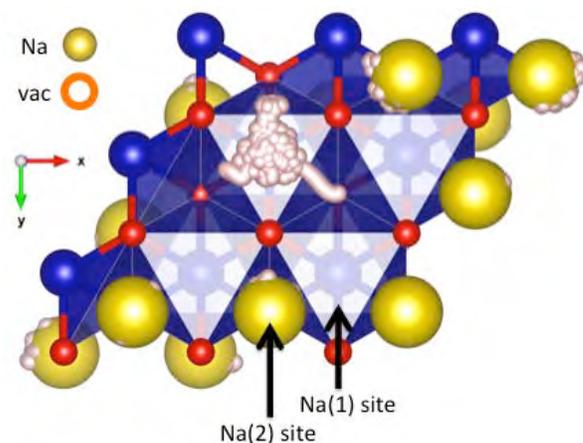


Figure 1. Sodium trajectory as calculated by AIMD simulation.

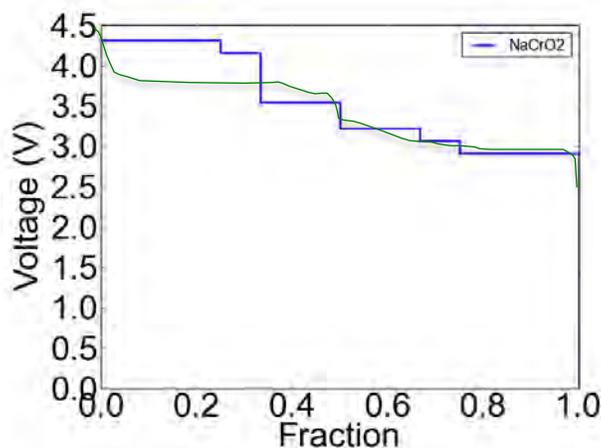


Figure 2. Computed voltage curve (blue) compared to experimental voltage curve (green). Komaba, S., *et al.* *ECS Transactions*, **16**, 42 (2009), 43-55.

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

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

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

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

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

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

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

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

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

MILESTONES:

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

PROGRESS TOWARD MILESTONES

a) Identify most favorable surfaces of bare Li_xSi_y periodic structures and characterize their reactivity. Structures of the $\text{Li}_{13}\text{Si}_4$ and LiSi phases were evaluated using the PBE functional. These phases are representative of high- and intermediate-Li content alloys. Si-Si bonds are absent in $\text{Li}_{13}\text{Si}_4$ but are present in LiSi . The (100) surface is predicted to be the most stable, low-index surface of the LiSi phase, with a surface energy of $0.0387 \text{ eV}/\text{\AA}^2$. For $\text{Li}_{13}\text{Si}_4$, the two most stable low-index surfaces are (100) and (010), which exhibit surface energies of 0.356 and $0.371 \text{ eV}/\text{\AA}^2$, respectively. *Ab initio* molecular dynamics (AIMD) of liquid EC on H, O, and OH terminated (100) and (101) LiSi surfaces yielded a majority of two-electron EC reductions yielding $\text{O}(\text{C}_2\text{H}_4)\text{OCO}^{2-}$, and much less frequently one e^- reductions, followed by a 2nd e^- transfer to the formed radical anion yielding CO_3^- and C_2H_4 . AIMD simulations of liquid FEC and VC on $\text{Li}_{13}\text{Si}_4$ (010) surfaces also yielded two-electron reduction events for FEC and VC. A strong correlation is found between the surface structure and its reactivity, but the mechanism is less dependent on the type of surface functional groups. VC decomposes to $\text{CO} + \text{C}_2\text{H}_2\text{O}_2^{2-}$, while FEC generally degrades into $\text{CO} + \text{C}_2\text{H}_3\text{FO}_2^{2-}$. The $\text{C}_2\text{H}_3\text{FO}_2^{2-}$ fragments *always* subsequently lose an F^- ion each, and one of them even loses another proton to form $\text{C}_2\text{H}_2\text{O}_2^{2-}$.

(b) Characterize geometric, electronic, and Li^+ transport properties of surfaces coated with thin layers of SiO_2 and Li_4SiO_4 oxides. The thermodynamics and Li vacancy diffusion kinetics of Li_4SiO_4 and $\text{Li}_2\text{Si}_2\text{O}_5$ phases have been evaluated (synergistic with work on a DOE-EFRC program in which one of the team members is involved). These results will be used in future studies of SEI formation on an oxide-coated Si anode surface. DFT/PBE calculations were used to predict voltages at which various lithium silicate and SiO_2 phases exist. Transitions between SiO_2 , $\text{Li}_2\text{Si}_2\text{O}_5$, and Li_4SiO_4 are predicted to occur at 1.37 and $1.01 \text{ V vs. Li}^+/\text{Li(s)}$, respectively. This suggests that these lithium silicate phases are more relevant than SiO_2 . Results indicate that Li transport is reasonably fast in both types of oxide films. However, Li_4SiO_4 may contain Li that are kinetically difficult to remove. This may be related to the published observation of crystalline Li_4SiO_4 domains in TEM measurements even after the Si anode has been polarized to $3 \text{ V vs. Li}^+/\text{Li(s)}$.

(c) Estimate maximum SEI layer thickness for electron transfer in model SEI films. An existent electron transfer algorithm and program have been modified and calculations have been made evaluating a model interfacial system. Decay of electron transfer through a model interface has been obtained based on first principles calculations.

(d) Characterize surface effects on EC, VC, FEC decomposition using cluster models of bare Li_xSi_y structures. Extensive EC reduction and decomposition studies on $\text{LiSi}_{15}\text{H}_{16}$ clusters representing Si (100) surfaces reveal one and two-electron reduction steps and decomposition products. Two of the six pathways yield C_2H_4 which is not observed in solution. Most of the surface reactions are more exothermic than in solution. A *hybrid* DFT model, surrounded by a dielectric continuum, optimization of an FEC molecule on the surface of a Li cluster illustrated the two-electron reduction event found with AIMD. For a one electron reduction, cluster models of FEC^-/Li^+ surrounded by a dielectric continuum indicate that the elimination of F^- from FEC^- is exothermic by over 1 eV . FEC^- decomposes spontaneously in the gas phase, suggesting that this additive molecule is fragile under battery charging conditions. The 1st and 2nd reduction potentials of FEC are found to be substantially larger than for EC. Invariably an F^- ion is lost, which may explain why FEC-based SEI films do not contain C-F signatures. Multiple FEC breaking modes were identified; the most favorable involve Si-O and Si-C formation. However, elimination of HF molecules is not observed, which has been proposed in the literature.

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

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

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

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

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

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

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

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

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

MILESTONES:

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

PROGRESS TOWARD MILESTONES

The project was awarded under the 2012 RFP and officially started in May 2013. All milestones are on schedule. The main achievements during this quarter are:

1) **Correlate the interfacial charge-transfer kinetics and coating thickness.** (Accomplished in July). The kinetics of Si thin-film electrodes coated with Al_2O_3 by ALD was studied using a model thin-film system that provides the intrinsic properties of electrodes. Using a modified PITT measurement, the overall interfacial resistance of Al_2O_3 -coated Si electrodes by ALD was quantified by means of a fit of an exchange current density. Three physicochemical parameters were extracted, including the Li diffusion coefficient within Si, the interfacial exchange current density, and the reaction rate constant.

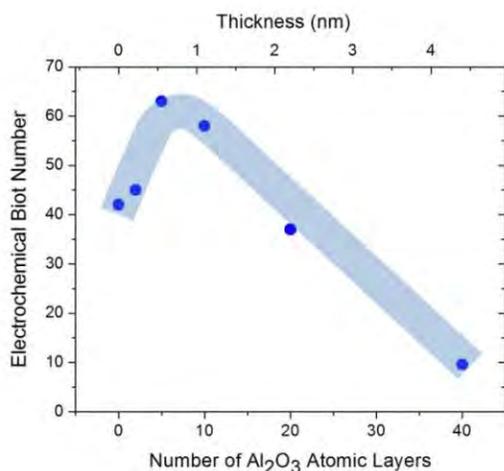


Figure 1. Electrochemical Biot number B obtained from PITT measurements. The light blue curve is provided to portray the trend in the data. The data shows the optimum surface coating thickness was identified as *ca.* 0.7 nm. Thus, with five to ten atomic layers of an alumina ALD coating, the silicon electrode can deliver 2600 mAh g^{-1} capacity within 3 seconds.

2) **Correlated the Young's modulus (E) of amorphous Al_2O_3 coatings with its density (which can be controlled by ALD deposition conditions and cycles), using molecular dynamics (MD) and ReaxFF.** (Initial results, more in progress). To capture the main characters of the ALD- Al_2O_3 coating, the atomic structures were designed to be disordered within the film in-plane directions but to have an average layer distance of 1.1 Å along the film growth direction. The predicted Young's modulus compared well with limited experimental measurements.^[1] Since the optimized film thickness is less than 1 nm, laser acoustic wave measurement of its modulus becomes extremely difficult. Thus, MD simulations will be performed on a range of film thicknesses to bridge the experimental gap and extrapolate the modulus to ALD coatings with a few atomic layers.

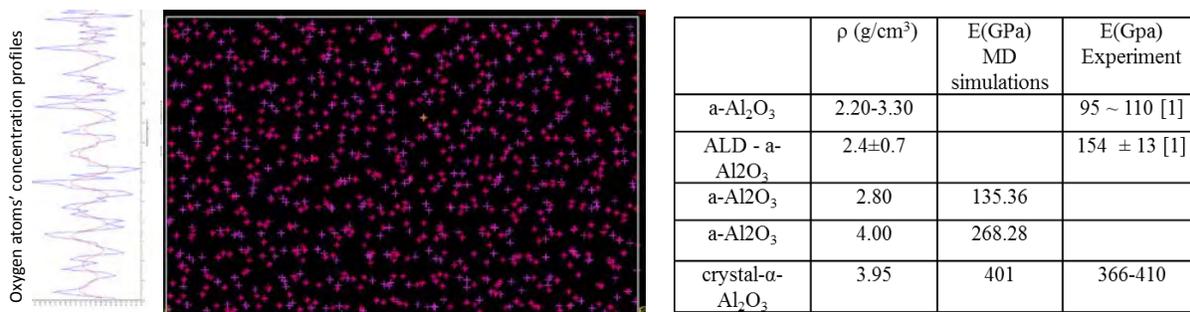


Figure 2. The atomic structure of amorphous ALD- Al_2O_3 , the concentration profile of O atoms shows 1.1Å periodicity, and the computed modulus scales with film density.

Reference: [1] Wang, L., et al., Nano Lett., 2012, 12, 3706].

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

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

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

BARRIERS: Cell performance, life, cost

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

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

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

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

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

MILESTONES:

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

PROGRESS TOWARD MILESTONES

Milestone (a)

The micro four-line-probe is a means of measuring the effective electronic conductivity of intact battery electrodes. The probe is made using semiconductor fabrication techniques such as photolithography, metal and oxide depositions, and etching. Our preliminary device was based on using aluminum on a silicon substrate. Subsequent design revisions have included other metals such as nickel, copper, and gold. The probe geometry was also redesigned to improve the passage of current through the device and decrease contact resistance with the sample. Devices are currently being tested on a series of electrode films obtained from Argonne National Lab and A123. These films are also being tested using a previously-developed method in order to validate the accuracy of the new probe.

A procedure and apparatus to regulate pressure for repeatable film measurements using the probe is being established. This includes development of a computer-controlled testing protocol to make repeated measurements while minimizing heat dissipation in the sample. Figure 1 shows the apparatus, in which a power supply and multiple voltage meters are used.

Milestone (b)

A numerical, finite-element model of probe electrodes and cathode structure were developed to correlate with the data that will be obtained from probe measurements of battery films. The model allows us to decouple or invert nearly simultaneous electrical measurements to obtain bulk effective electronic conductivity of the film as well as contact resistance between the electrode film and the current collector.

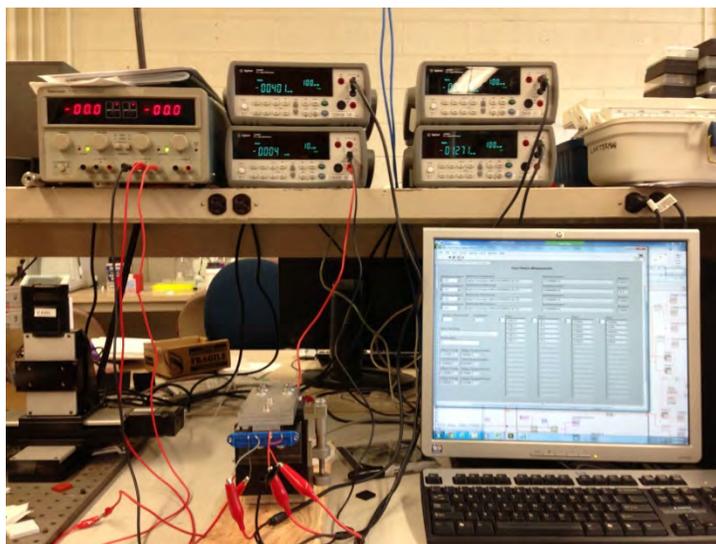


Figure 1. Micro-four-line probe with battery film sample (middle bottom) and associated multimeters and current source (top).