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

Here is the second quarter FY 2012 report for the Batteries for Advanced Transportation Technologies (BATT) Program. This report and prior Program reports can be downloaded from http://batt.lbl.gov/reports/quarterly-reports/.  

Sincerely,  

[Signature]  
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

Cell Analysis–

Richardson’s Group uses laser-induced breakdown spectroscopy to deduce the state of charge of the active material through the cross section of the electrode.

Liu’s Group demonstrates cycleability of Sn powder with the use of an electronically conductive binder.

Anodes–

Cui’s Group demonstrates 6000 cycles with hollow nanotubes of Si encapsulated in SiOx.

Cathodes–

Cabana’s Group demonstrates that the discharge rate of LiNi1/2−xMn3/2+xO4 is higher for disordered materials and independent of x.

Diagnostics–

Grey’s Group demonstrates that NMR can accurately detect the level of order/disorder between the Ni and Mn in LiNi1/2Mn3/2O4 materials.

Modeling–

Newman’s Group demonstrates that an SEI formed on graphite at lower voltages is inherently more passivating than an SEI formed at higher voltages.
BATT TASK 1

CELL ANALYSIS

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

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

BASELINE SYSTEMS: Conoco Philips CPG-8 Graphite/1 M LiPF<sub>6</sub>+EC:DEC (1:2)/Toda high-energy layered (NMC)

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

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

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

STATUS OCT. 1, 2011: Powders of LiNi<sub>1/2</sub>Mn<sub>3/2</sub>O<sub>4</sub> from NEI were distributed to interested PIs as well as an electrolyte of 1 M LiPF<sub>6</sub> in EC:DEC 1:2 from Daikin, America. After a large initial capacity loss in a full cell, the NEI high-voltage spinel material shows good cyclability. VC has a higher reduction potential than EC but with slower kinetics. Slow formation processes of cells with and without VC do not show significant differences in the rate of the side reactions.

EXPECTED STATUS SEP. 30, 2012: Differences in performance of a baseline electrolyte versus a “high-voltage” electrolyte against LiNi<sub>1/2</sub>Mn<sub>3/2</sub>O<sub>4</sub> will be elucidated. The effects of mixing time on electrode uniformity and performance will have been studied. The dissolution of spinel materials will be measured at 55°C.

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

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

a) Measure the difference in performance of our baseline electrolyte when compared to a high voltage electrolyte from industry. Dec. 2011 **Complete** (Reported on last quarter).

b) Evaluate the effects of mixing time on cell performance; April 2012 **On schedule**

Positive electrode laminates were prepared with 92.8% NCM, 3.2% acetylene black, and 4% PVDF binder. Varying mixing times of 15, 25, 35, and 45 mins were used to in the preparation of the slurries for casting. All electrodes, upon completion of the casting and initial drying step, were calendered to the same porosity. Coin cells were prepared and rate tests and cycling tests are being performed to understand the difference in the behavior of these electrodes. No substantial results have been observed to date.

c) Compare the rate of side reaction and capacity fade of Gr./NCM with and without VC. April 2011 **Complete**

Full cells with 1% VC and no VC in the baseline electrolyte of 1 M LiPF₆ in EC:DEC 1:2 are under test. The first test performed on the cells upon assembly is C/10 charge/discharge cycles to 4.1 V. This was repeated seven times and then the upper voltage cutoff was increased 100 mV to 4.2 V and another seven cycles performed. This continued to 4.6 V. The cells with 1% VC show less side reaction at every cutoff potential (consistent with Jeff Dahn’s recently published results), although the side reaction increases more for the VC cells as the cutoff voltage approached 4.6 V, see Fig.

The Dahn Group claims that cells with less side reaction necessarily last longer than cells with more side reaction; our group is evaluating this hypothesis.

d) Measure the rate of dissolution of a spinel material containing Mn; Sept. 2012 **On schedule**
TASK 1.2 - PI, INSTITUTION: Thomas Richardson, Lawrence Berkeley National Laboratory

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

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

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

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

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

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

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

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

MILESTONES:
(a) Complete charge distribution assessments of harvested cathodes. (Mar. 12) Delayed to Jul. 12 due to late arrival of new postdoc.
(b) Develop new optical microscopy methods for in situ and ex situ diagnosis of electrode and separator chemistries. (Aug. 12) On schedule
PROGRESS TOWARD MILESTONES

**Charge distribution:** In collaboration with Dr. Vassilia Zorba of LBNL, a technique is being developed to analyze and map charge distribution in electrodes is being developed using ultrafast laser induced breakdown spectroscopy (LIBS). This technique offers elemental analysis with high spatial resolution, and is ideal for depth profiling because it does not require sample preparation such as mounting and slicing to expose the cross section. A coin-cell electrode charged at 18C to 40% SOC that was previously mapped by micro-XRD was subjected to LIBS depth profiling by obtaining plasma-emission spectra during repeated laser pulses directed at a single spot. The Li-to-Fe gradient measured by LIBS (Fig. 1a) was reproduced at three different spots across the electrode. The LIBS data compares well with the gradient obtained by XRD (Fig. 1b) except that the latter technique failed to access the top portion of the electrode, possibly due to loss of composite material during sectioning and polishing. When the data are offset to correct for this, the agreement is excellent.

![Figure 1](image1.png)

**Optical microscopy:** Insoluble redox active materials in Li-S and Li/air batteries can become isolated from the electrodes. In order to participate in cycling, they must be solubilized through some intermediate species formed at the electrode surface. To identify these agents and their origin, cells are developed in which the gap between the electrode and an insoluble, solid reactant is visible. An example is the dissolution of LiOH by a species generated at high potential. In a transparent cell, (Fig. 2), anodic polarization of an adjacent non-contacting electrode in PC on a LiOH•H$_2$O crystal cluster produces an agent that breaks it up by dissolving the matrix surrounding the component crystals.

![Figure 2](image2.png)

Collaborations: Robert Kostecki, Guoying Chen, Marca Doeff, Vassilia Zorba, Jordi Cabana, Vince Battaglia, the Molecular Foundry, National Center for Electron Microscopy, Advanced Light Source and Stanford Synchrotron Radiation Laboratory.
TASK 1.3 - PI, INSTITUTION: K. arim Zaghib, Hydro-Québec (IREQ)

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

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

BARRIERS: Low energy and poor cycle/calendar life

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

GENERAL APPROACH: Our approach is to develop an appropriate method to stabilize the interface reaction of the high voltage oxide (Mn-Ni based like LiMn₁.₅Ni₀.₅O₄) by surface coating with more stable material like olivine. The emphasis is to improve electrochemical performance at high voltage. Binder type, electrolyte composition, separator will be investigated at this level of voltage. Going with high capacity anode; Si based anode composition will be optimized in terms of particle size (micro vs. nano), graphite and SiOₓ content.

STATUS OCT. 1, 2011: Effort is oriented to silicon-based anode alloys; LiMn₁.₅Ni₀.₅O₄ based cathode and SEI study and its stabilization. Work will start on these items in August by exploring an appropriate composition of anode material based on carbon coated nano-silicon, SiOₓ and graphite. More work on high voltage cathode will be addressed by reducing its oxidation problem with electrolyte.

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


MILESTONES:
(a) Identify a candidate of a silicon-based composition as anode material (Mar. 12). Complete
(b) Demonstrate stabilized high-voltage LiMn₁.₅Ni₀.₅O₄ spinel cathode material with surface-coated of ceramic and oxides material (Sep. 12). On schedule
(c) Complete the in situ SEM analysis of the Si-based anode (Sep. 12). On schedule
PROGRESS TOWARD MILESTONES

During the past quarter, the focus was on C-SiO<sub>x</sub> electrodes that did not include a graphite additive. The SiO<sub>x</sub> electrodes were prepared by using just a polyimide binder. The effect of the cut-off voltage and the floating step were investigated. The cycling evaluation was performed in Li cells with EC-DEC-1M LiPF<sub>6</sub> at C/6 with a lower cut-off voltage of 5 or 50 mV with or without a floating step. The cycling results in Fig. 1 shows dendrites are formed in cells cycled to a cut-off voltage of 5 mV, with or without a the floating step. When a cell was cycled to 50-mV, the use of a floating step resulted in a dendrite. On the other hand, when no floating step was added at this cut-off voltage, no dendrite was observed. The lower cut-off voltage and floating step gave a higher capacity (1000-1400 mAh/g) but a shorter cycle life. These data indicate that the cut-off voltage should be higher than 50 mV to avoid dendrites, if the float step is considered necessary in Li-ion cells.

![Figure 1. Li/EC-DEC-1M LiPF<sub>6</sub>/C-SiO<sub>x</sub> cells cycled at C/6 at 5 and 50 mV cut-off voltages with and without(WO) floating](image1)

![Figure 2. Cycling and rate capability of LiMn<sub>1.45</sub>Cr<sub>0.1</sub>Ni<sub>0.45</sub>O<sub>4</sub> /Li in EC-DEC-LiPF<sub>6</sub>](image2)

For the high-voltage cathode focus area, more effort was put toward a doped LiMn<sub>1.5</sub>Ni<sub>0.5</sub>O<sub>4</sub>. Spinel LiMn<sub>1.45</sub>Cr<sub>0.1</sub>Ni<sub>0.45</sub>O<sub>4</sub> (LMCrNO) was successfully synthesized by a post-annealing method at 600°C using oxalic acid. A small amount of Cr<sup>3+</sup> substitution for Ni<sup>2+</sup> and Mn<sup>4+</sup> appeared to keep the Mn<sup>4+</sup> oxidation state unchanged (2Cr<sup>3+</sup> = Ni<sup>2+</sup> + Mn<sup>4+</sup>) and to improve the cycling. XRD refinement showed that the final material could be indexed in the space group of Fd<sub>3</sub>m (disordered) and was without impurities. Two two-phase reactions at ca. 4.7 V also proved the presence of the disordered structure; in addition, no Mn<sup>4+</sup>/Mn<sup>3+</sup> redox couple was observed in the charge/discharge cycling. The reversible capacity was 128 mAh/g at C/12 with coulombic efficiencies of 78 and 92% for the first and second cycles, respectively. Measurements of the high-rate capability of LMCrNO indicated higher capacity and more stability at each rate compared to undoped LMNO. The cathode can deliver 88 and 68% of the capacity at 2 and 5C, respectively. After 230 cycles, less than a 5% capacity loss was observed at 0.2 C cycling (Fig. 2). Further analyses will be conducted to understand the effect of VC on the LMNO’s performance.

HQ is continuing its collaborations with LBNL researchers Vince Battaglia and Robert Kostecki.
TASK 1.4 - PI, INSTITUTION: Yet-Ming Chiang, Massachusetts Institute of Technology

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

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

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

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

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

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

EXPECTED STATUS SEP. 30, 2012: 1) Conclude electrode fabrication and electrochemical testing in at least one targeted cathode compound; 2) Fabricate and test high-density, low-tortuosity electrodes of at least one anode compound; 3) Conclude measurement of electronic conductivity vs. x in sintered undoped Li$_x$Ni$_{0.5}$Mn$_{1.5}$O$_4$.

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

MILESTONES:
(a) Demonstrate >80% capacity retention at 2C rate in additive-free low tortuosity LiCoO$_2$ electrode of >50 vol% density and >200 μm thickness. (Oct. 11) Complete
(b) Complete measurement of electronic conductivity vs. x in sintered undoped Li$_x$Ni$_{0.5}$Mn$_{1.5}$O$_4$. (Jan. 12) Complete
(c) Complete measurement of electronic conductivity vs. x in sintered Li$_4$Ti$_2$O$_12$ anode. (Jan. 12) Complete
(d) Develop tortuosity measurement for freeze-cast/sintered cathodes. (Mar. 12) Complete
(e) Complete process development study for directionally freeze-cast and sintered LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cathodes. (Jun. 12) Complete
PROGRESS TOWARD MILESTONES

Collaborator: Antoni P. Tomsia (LBNL)

Accomplishments: Following achievement of Milestone (a) in the LiCoO₂ system, attention has been turned to applying the directional freeze-casting approach to additional systems. Slurry formulations and freeze-casting procedures were developed for LiNi₀.₅Mn₁.₅O₄, allowing Milestone (c) to be accomplished ahead of schedule. However, while electrodes of low-tortuosity, high-density structures were obtained, its electronic conductivity, measured in Milestone (b), was found to have a relatively low value of ca. 10⁻⁴ S/cm at room temperature. This results in excessive polarization upon electrochemical cycling of ca. 200 µm thick electrodes at C-rates of interest. That is, electronic conductivity is the rate-limiting transport step for transport across macroscopic thicknesses of sintered, additive-free LiNi₀.₅Mn₁.₅O₄ electrodes. Accordingly, alternative systems with varying levels of electronic conductivity are being tested to determine the specific relationship to macroscopic transport in the electrode structures of interest. One system of interest has electronic conductivity in between that of LiCoO₂ and LiNi₀.₅Mn₁.₅O₄ is Li(Ni,Co,Al)O₂ (NCA). During the present reporting period, systematic experiments led to the development of slurry formulations that could be successfully freeze-cast to obtain highly-oriented porosity in structures with ca. 50 vol% open porosity, as shown in the Fig. It has also been found that domains of millimeter scale are produced in the freeze-cast samples, the size of which can be influenced by process variables. These electrode structures will now be tested in electrochemical cells (Li half-cells).

In other work, sintered additive-free Li₄₊ₓTi₅O₁₂ samples have been used to measure in situ electronic conducitivity vs. x, using dc and ac measurements of electrochemical cells across the entire state-of-charge range. The results are now being corroborated by ex situ 4 point van der Pauw measurements. This system is of interest as a model spinel that shares many features with the high voltage manganate spinels, including having a broad SOC range over which two cubic spinel phases co-exist, but has the advantage of having zero transformation strain between co-existing phases. One question being addressed is how electronic conductivity varies in the spinels when two cubic spinel phases of widely differing electronic conductivity co-exist, a situation that may exist in LiNi₀.₅Mn₁.₅O₄ as well as other high-voltage spinels. In other work under the high-voltage spinel focus group, the temperature dependence of electronic conductivity and the ionic conductivity in LiNi₀.₅Mn₁.₅O₄ are being measured, the latter using nonblocking electrode techniques.
TASK 1.5 - PI, INSTITUTION: Gao Liu, Lawrence Berkeley National Laboratory

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

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

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

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

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

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

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

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

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

Progress in the use of electronic conductive PFFOMB [1] and inert PVDF binders for Sn nanoparticles was reported in the last quarter. Acetylene black (AB) conductive additive was used in both cases to improve the electronic conductivity of the composites. Both electrodes can be cycled stably for the first few cycles but the capacity of electrodes made of PVDF fades in subsequent cycles. PFFOMB tends to provide higher specific capacities in the range of 600 mAh/g range and improved cycling stability.

Since an electronic conductive binder can provide molecular level electronic connection between the Sn particles and an electric-conducting medium at the interface, and provide inter-particle electronic connection, the usage of PFFOMB alone may be sufficient for the Sn electrode design. This changes the electrode to a two-composition system between Sn and PFFOMB. A limited optimization of the composition between Sn and PFFOMB was conducted. To optimize the composition of the electrode, the binder content was changed from 2 to 10% by weight. The testing results in Fig. 1 show that electrode performance is sensitive to the binder content. With 5% polymer binder, the electrode can retain over 500 mAh/g of reversible capacity after 38 cycles. On the contrary, the electrodes with 2 and 10% polymer binder fade dramatically. Overall, the PFFOMB provides mechanical stability to the electrode and electric conduction. The balance between these two functions is responsible for the optimum in performance of this electrode. This work has demonstrated that the conductive polymer binder can successfully stabilize the pure Sn-based anode for extended cycling.

![Figure 1](image-url)

**Figure 1.** Cycling performance Sn electrodes with different amounts of PFFOMB binder without the addition of carbon conductive additives.

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

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

BASELINE SYSTEMS: Conoco Philips CPG-8 Graphite/1 M LiPF$_6$+EC:DEC (1:2)/Toda high-energy layered (NMC)

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

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

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

STATUS OCT. 1, 2011: Overlithiation in Li$_{1+x}$(Ni$_{0.33}$Mn$_{0.33}$Co$_{0.33}$)$_{1-x}$O$_2$ (NMC333) was found to increase extractable Li in the structure and energy density of the cathode. Increasing Mn content in the overlithiated NMC333 improves rate capability but decreases the stability of the initial O3 phase, which transforms to P3 structure upon deep Li extraction. The irreversible charging plateau observed at high voltage was attributed to overlithiation in Li$_{1+x}$_M$_{1-x}$O$_2$. LiNi$_{0.5}$Mn$_{1.5}$O$_4$ single crystals were synthesized in a variety of sizes and shapes, with the best performance achieved with the octahedral micron-sized crystals. Large crystals with a range of Mn$^{3+}$ content were prepared by varying the Ni/Mn ratio in LiNi$_x$Mn$_{2-x}$O$_4$. Synthesis precursors were found to influence the transition-metal ordering in the prepared spinel.

EXPECTED STATUS SEP. 30, 2012: The effect of structural, composition and morphological changes during Li extraction and insertion in Li$_{1+x}$M$_{1-x}$O$_2$ will have been further evaluated. Oxygen evolution mechanism and kinetics will have been investigated. The effect of particle size and morphology on oxide activation process and electrode stability will have been revealed. The impact of Mn$^{3+}$ content on property and performance of LiNi$_x$Mn$_{2-x}$O$_4$ cathode will have been established, and the kinetics of structural disordering in the spinel examined.

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

MILESTONES:
(a) Investigate the kinetics of order/disorder transitions in LiNi$_x$Mn$_{2-x}$O$_4$. (Mar. 12) Complete
(b) Determine the effect of Mn$^{3+}$ content on property and performance of the spinels. (Jun. 12) On schedule
(c) Investigate the mechanism and kinetics of delithiation/reliothiation on oxide crystals. (Aug. 12) On schedule
(d) Synthesize at least four oxide crystal samples with different physical characteristics. (Sep. 12) On schedule
PROGRESS TOWARD MILESTONES

Ni/Mn Spinels: The synthesis of micron-sized LiMn$_{1.5}$Ni$_{0.5}$O$_4$ single crystals in plate and octahedral shapes was reported previously. The main surface facets on the plates were determined to be (112) crystal planes, while the octahedrons were predominantly enclosed by the (111) crystal planes and had a slightly more ordered structure. In this quarter, the transport properties of the crystal samples with different morphologies were compared by employing the Potentiostatic Intermittent Titration Technique (PITT) on composite electrodes composed of 80 wt% crystals, 10 wt% PVdF binder, 5 wt% graphite, and 5 wt% acetylene carbon. The experiments were performed between 3.5 and 4.9 V at a step size of 10 mV. The potential was stepped to the next level when the current dropped to 10 $\mu$A, equivalent to C/150. The Li chemical diffusion coefficient, D, was then calculated from the slope of the linear region in a ln($I$) vs. $t$ plot, as defined in Equation (1):

$$D = -\frac{d\ln(I)}{dt} \frac{4L^2}{\pi^2}$$

Figure 1a compares the measured chemical diffusion coefficients during charge and discharge. Lithium diffusion exhibited concentration dependent behavior in both crystal samples, which ranged from 1.9x10^{-16} to 1.2x10^{-14} cm$^2$/s in the plates and 2.4x10^{-14} to 1.6x10^{-11} cm$^2$/s in the octahedrons. Despite the more ordered crystal structure, diffusion in the octahedrons with (111) facets is at least two orders of magnitude higher than that in the plates with the (112) facets. The results demonstrate the importance of spinel particle-morphology design for maximum Li transport.

The incremental capacities and chemical diffusion coefficients obtained during the charge and discharge of the plate-shaped crystals are superimposed in Fig. 1b. Two diffusion minima were observed at 4.73 and 4.77 V on charge and 4.74 and 4.71 V on discharge, respectively, which correlated well with the capacity maxima. Similar behavior was also observed on the octahedral-shaped crystals (Fig. 1c), where two minima were seen at 4.73 and 4.76 V on charge and 4.73 and 4.70 V on discharge. To our knowledge, the appearance of a diffusion minimum at the occurrence of the first-order phase transition has not been previously reported in the spinel system, although it has been observed in several other electrode materials. The study suggests that Li transport in the Ni/Mn spinel is likely limited by the movement of phase boundaries.

Work toward milestone (a) was completed and reported in the FY12 Q1 report.

Collaborations this quarter: Richardson, Grey, Angell, Cabana, Kostecki, Doeff, Chiang, SSRL, NCEM.
BATT TASK 2
ANODES

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

TASK TITLE: Anodes: Novel Anode Materials

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

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

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

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

ANTICIPATED STATUS OCT 1, 2011: Synthesized and evaluated a series of new electrode structures that use elemental silicon and tin as the active material. Quantified the energy and power advantages of three-dimensional electrode architectures when compared to two-dimensional anode structures. Evaluated electrodes that utilize metallic copper as both the binder and conductive additive. Developed methods to create the three-dimensional copper current collector around the active materials, notably silicon.

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

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

MILESTONES:
(a) Completed characterization of the interfacial region in Cu-Si metallic electrodes Completed
(b) Characterized the phases formed and extent of electrode homogeneity for a series of electrodeposited Sn-based electrodes (Sep 2012) – On schedule
(c) Assessed the role of electrolytes and irreversible capacity and SEI formation in three-dimensional electrode structures (Sep 2012) – On schedule
(d) Demonstrated the benefit of polymeric surface coatings on the cycle life of three-dimensional electrode structures. (Sep 2012) – On schedule
PROGRESS TOWARD MILESTONES

Team: Fikile Brushett, Fulya Dogan, Lynn Trahey, Jack Vaughey (ANL)

In an effort to improve diagnostic capabilities pertaining to Li-ion battery anodes, the use of synchrotron tomography at ANL’s Advanced Photon Source is being explored. Unlike SEM and TEM, tomography can shed light on material behavior in sub-surface locations of an electrode being cycled in realistic battery environments. This will be extremely useful in diagnosing electrode failure mechanisms. This report will highlight work performed at sector 2-BM, which has an incident X-ray energy of 50 keV and capable of a full-field view of the anode during each tomographic scan (little motor use or lag time required). Our current in situ cell configuration is shown in Fig. 1. The electrode pieces are located within a Torlon® tube and flattened stainless steel screws provide cell stacking pressure.

The electrodes analyzed initially were commercial Cu foams of roughly 100 μm thick, electrolessly coated with Sn. Electroless plating was chosen for its conformal nature. Three-dimensional architectures for Li-ion anodes are being explored because they act to constrain the volume expansion of anodes of Si and Sn, and they offer better integration between the current collector and the active material. These carbon- and binder-free Sn on Cu anodes last ca. 30 cycles in coin cells before a dramatic loss of capacity (see last Quarterly). Through the use of tomography, the suspected surface area to volume ratio variations, as a function of electrode depth (distance from counter electrode), can be analyzed to determine the effects of unequal Li⁺ diffusion throughout the electrode. Initial results indicate that 1 μm resolution can be achieved within the electrode and that the SA:V increases with cycling. More rigorous treatment of the data is underway. Figure 2 shows tomographic reconstructions of one section of electrode and highlights the type of surface features that can be tracked and evaluated.

This technique will be used for all anodes that BATT deems relevant. To this end, an effort has begun to study Si laminates made with 70% active material. The Si is 325 mesh particles from Alfa Aesar. This particle size ranges from nanometers to 40 microns. All particles greater than 1 micron in diameter can be resolved. The first and second cycle capacity of our Si laminates is extremely high, and then falls off rapidly, as is known and expected for electrodes of large particles and wide size distribution. The changes that lead to capacity fade should be evident through tomographic investigation. Current efforts are toward ensuring that the in situ cycling accurately mimics laboratory coin-cell cycling, and qualifying any changes to the electrolyte caused by beam damage.
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 LiPF_{6}+EC:DEC (1:2)/Toda high-energy layered (NMC)

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

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

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

STATUS OCT. 1, 2011: It has been shown that bulk crystalline metals have a high capacity, react readily with lithium but that their capacity faded rapidly after several deep cycles in carbonate-based electrolytes; their behavior was no better under shallow cycling. In contrast, it has been shown that amorphous nano-size tin alloys, unlike pure tin, have a high capacity and maintain it on deep or shallow cycling, when stabilized with elements like cobalt. A nano-tin material that shows electrochemical behavior comparable to that of the Sn-Co alloy but without the need for cobalt was successfully formed by mechanochemical synthesis. It has also been shown that small amounts of silicon enhance the cyclability of aluminum.

EXPECTED STATUS SEP. 30, 2012: Our proposed work will result in the development of durable metal-based Li-ion battery anodes with volumetric energy densities that approach double those of the state-of-the art carbons. Nano-tin materials will have been synthesized by at least two different approaches and then characterized, to determine their morphology and electrochemical behavior. Clues as to how to control the SEI on such materials to optimize lifetime will have been gathered.

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

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

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

Milestone (b) nano-tin anodes, has been met with the gravimetric energy density exceeding 500 Ah/kg compared with a value of 350 Ah/kg for carbon. The calculated volumetric energy is 2.2 Ah/cm^3, compared with less than 1.0 Ah/cm^3 for carbon. Figure 1 (left) shows the capacity as a function of the Li removal rate relative to the capacity at low rates: the rate when used as the anode in a charged cell. The capacity retention is slightly higher when the anode is charged to 1.5 volts vs. 1.2 volts. At all rates, the capacity retention is superior to that of the SONY SnCoC anode. Figure 1 (right) shows the capacity as a function of the Li insertion rate (comparable to the charging of an anode). Here again the capacity retention is higher when the electrode is charged to 1.5 volts vs. Li. The capacity is superior to that of the SONY SnCoC without the presence of any expensive Co.

Figure 1. (left) Rate capability of Li removal from the nano-tin anode, and (right) rate capability of Li insertion into the nano-Sn anode relative to the SONY SnCoC anode.

The challenge remains to minimize the first-cycle loss capacity and, in a future study, the impact of reducing the amount of carbon present on this first-cycle loss will be investigated.

Further plans to meet or exceed milestones: None
Reason for changes from original milestones: See above

Publication and Presentation:
**Task 2.3-PI, INSTITUTION:** Prashant N. 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 objective is to replace carbon with an inexpensive nanostructured composite exhibiting higher capacity (1200 mAh/g) than carbon while exhibiting similar irreversible loss (<15%), coulombic efficiency (>99.9%), and cyclability. The project addresses the need to improve the capacity, specific energy, energy density, rate capability, cycle life, coulombic efficiency, and irreversible loss limitations of silicon based electrodes.

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

**STATUS OCT. 1, 2011:** Nano-scale electrodes comprising Si-graphitic carbon-polymer derived C, and CNT related systems have been successfully synthesized and analyzed in half cells. The nano-composite Li-Si-C hetero-structures exhibit stable capacities of 700-3000 mAh/g.

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

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

**MILESTONES:**
(a) Achieve stable reversible capacity of 1500 mAh/g or higher (Mar. 12). **Partially complete, due Sep. 12**
(b) Achieve irreversible loss (≤15%) and efficiency (≥99.95%) to match carbon (Sep. 12). **On schedule**
PROGRESS TOWARD MILESTONES

In earlier reports, heterostructures of Si deposited on vertically aligned carbon nanotubes (VACNTs) formed by a simple 2-step chemical vapor deposition (CVD) approach were described. The Si/VACNT structures exhibit very high specific capacities (>2800 mAh/g) with a very low 1st cycle irreversible loss of <15%. However, the Si/VACNT displayed continuous capacity fading especially in the case of Si film morphologies deposited directly on VACNT. These structures yielded a capacity of less than 1500 mAh/g at the end of 25 cycles when cycled with a current density of ca. 100 mA/g. The capacity fade response of the Si/VACNT is attributed to the weak interface between Si and VACNTs, leading to delamination or clustering of the Si films over long-term cycling. In order to improve the interfacial strength of the Si/VACNT interface, an interface control agent (ICA) was investigated.

In this report, the VACNTs were grown on a quartz substrate using a ferrocene-based floating catalyst approach. Then, a thin layer (ca. 10 nm thick) of an ICA was electron-beam deposited on the VACNTs at a growth rate of 0.2 Å/s. This was followed by Si deposition through the thermal cracking of silane (SiH₄). Silicon was deposited as a thick film over the ICA layer as shown in Fig. 1. The electrode, when cycled at a current density of ca. 300 mA/g in the voltage range 0.01 to 1.2 V vs. Li⁺/Li, shows a first discharge capacity of ca. 2300 mAh/g (Fig. 2). It also displayed a modest irreversible loss of 14%. These results were similar to those obtained with the same heterostructures without the use of an interface control agent. After 25 cycles, a capacity of ca. 1600 mAh/g was retained with a fade in capacity of 0.4% loss/cycle. Studies are currently on-going to ascertain the effect of the ICA upon the cycling behavior, coulombic efficiency, and adhesion of Si films to the VACNTs.

To exploit a binder-free approach, the Si/VACNT heterostructures were directly grown on Inconel 600 alloy metallic substrates by a combined chemical vapor deposition and pulsed laser deposition (CVD-PLD) method. First, VACNTs were grown using the CVD approach reported above and followed by Si deposition by PLD. A 248-nm KrF excimer laser irradiation pulsed at 25 ns FWHM in a high vacuum chamber with a base pressure of 10⁻⁶ Torr was used with a fluence of 8.3 to 9.6 J/cm². The laser pulse frequency was maintained at 10 Hz and the deposition rate was approximately 2.3 Å/s, determined as a mean value. A 30-min deposition yielded Si films approximately 15 to 20 nm thick (Fig. 3) that comprised of nanocrystalline and amorphous Si. Electrodes of these heterostructures showed a low irreversible loss of <15 % with a first-discharge capacity ca. 2800 mAh/g (Fig. 4) when cycled at ca. 100 mA/g between the voltage range 0.02 to 1.2V vs. Li⁺/Li. A stable reversible capacity >1600 mAh/g was obtained for 50 cycles resulting in a capacity fade of 0.24% loss/cycle. More research is currently in progress to ascertain the effect of ICA on the Si-CNT interface, and the combined use of CVD and PLD to obtain Si/VACNT heterostructures with the desired attributes of low first-cycle irreversible loss, stable reversible capacity, and excellent coulombic efficiency.
**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 LiPF$_6$+EC:DEC (1:2)/Toda high-energy layered (NMC)

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

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

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

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

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

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

**MILESTONES:**
(a) Identify the main failure mechanisms of the Si-based anode. (Mar. 12) Complete
(b) Improve the performance of Si based anode with a capacity-retention of >700 mAh/g over 150 cycles. (Sep. 12) On schedule
(c) Select binders and electrolyte additive to improve the coulumbic efficiency of Si-based anodes to more than 99%. (Sep. 12) On schedule
PROGRESS TOWARD MILESTONES

A core/shell/shell structured Si was designed to provide high efficiency, exceptional rate performance, and long-term stability to Si. Milling materials with high Mohs hardness serve not only as micro-/nano-millers in the ball-milling process to break down micron-sized Si but also as the conductive rigid skeleton to support the in situ-formed sub-10 nm core/shell particles. These are small enough to alleviate cracking as a result of the volume change during charge/discharge. Graphite is coated on the B4C/Si composite to further improve the conductivity and stability of the composite and the formation of a stable SEI. An excellent stable cycling with a specific capacity of 822 mAh/g (based on the whole electrode weight, including binder and conductive carbon) and 94% capacity retention over 100 cycles was obtained (Fig. 1). The capacity retention after 200 cycles was 78%. The coin cell was tested between 0.05 and 1.5 V at a current density of 0.63 A/g (the first three formation cycles are run at a current density of 100 mA/g). These structures also demonstrated exceptional rate performance (Fig. 1). The average capacity based on the electrode weight, including binder and conductive carbon, was 900.1 mAh/g at 0.31 A/g, 822.5 mAh/g at 0.63 A/g, 723.6 mAh/g at 1.25 A/g, and 601.2 mAh/g at 2.50 A/g.

The uniformity of the electrode was further optimized by changing the synthesis parameters such as the ball-milling time. Electrolyte additives will be investigated to further improve the cycle stability. Fundamental understanding of the structure of the SEI layer in the presence of electrolyte additives will be systematically investigated.

Collaborations: I.A. Aksay, Princeton University, and Vorbeck Inc. have provided the graphene for this work.

Publication/Presentation
2. “Silicon composite anodes with three-dimension rigid structures for lithium ion batteries,” Xilin Chen, Xiaolin Li, Fei Ding, Wu Xu, Jie Xiao, Yuliang Cao, Praveen Meduri, Jun Liu, Gordon L Graff, Ji-Guang Zhang, Materials Research Society, San Francisco, Spring Meeting, April 9–12, 2012.
TASK 2.5 - PI, INSTITUTION: Anne Dillon, National Renewable Energy Laboratory

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

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

BARRIER: Cost, low gravimetric and volumetric capacities, safety

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

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

STATUS OCT. 1, 2012: This award was initiated at NREL in FY11. However, the University of Colorado was funded as of January 1, 2011. Collaborations with both Prof. M. Stanley Binghamton and Prof. Arumugam Manthiram, as well as with General Motors and LG Chem, are already in place. Samples will be sent to Prof. Clare Grey and she will perform in-situ NMR studies to provide mechanistic information about our ALD coatings.

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

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

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

(a) Demonstrate an ALD coating with rate performance of ≥ C/5 for a thick Si anode. (July 2012)

Early Completion (with new structure and no ALD coating)

The early completion of the July 2012 milestone to “demonstrate an ALD coating with rate performance of ≥ C/5 for a thick Si anode” is presented. The milestone has been achieved by fabricating unique core shell structures comprised of “commercial” Aldrich Si and a carbon shell fashioned by a method that is currently being patented. Figure 1a displays a low-resolution transmission electron microscope image of the Si-particles that have a non-uniform diameter distribution (ca. 10 to 70 nm), but are surrounded and interconnected by a carbon shell. Figure 1b displays a high-resolution image of one of the Si/C core shell structures, with electron diffraction of the carbon shell in the inset for the area denoted in red showing that the ca. 10 nm carbon shell is comprised of amorphous material. The initial Si core structures are comprised of crystalline silicon with the small spot electron diffraction not shown.

Complete electrodes of the Si/C core shell structures ≥8 µm in thickness were fashioned. The electrodes were prepared by a conventional method and contained ca. 70:30 Si:C. The mass ratio is of the core shell structures as well as the entire electrode. Importantly, the shell served as both the conductive additive and the binder. The mass loading of the high-capacity, thick Si electrode is ca. 1 mg/cm². Figure 1c displays cycling data and coulombic efficiency for the thick Si/C electrodes cycled at both C/10 and C/5. The electrodes were cycled in a half-cell configuration between 1.0 and 0.05 V vs. Li/Li⁺. Capacity retention above 2500 mAh/g is observed at C/5 for over 50 cycles, representing early completion of the July 2012 milestone. More importantly, the coulombic efficiency of both the electrodes cycled at C/5 and C/10 is ≥99.99 % (Fig. 1c). However, Fig. 1c also depicts a gradual capacity fade over 200 cycles. Since the coulombic efficiency remains high throughout cycling, the capacity fade is most likely attributed to mechanical degradation of the high volume expansion Si and physical separation from the electrode. Preliminary data of ALD coated Si/C core shell structures suggest that capacity fade due to mechanical degradation can be overcome.

Figure 1. TEM images of a) Si/C core shell structures: low resolution b) individual Si / C core shell structure: high resolution, with electron diffraction and c) cycling performance of thick electrodes composed of the Si/C core shell structures: 70:30 Si:C, mass loading ca. 1 mg/cm².
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 LiPF$_6$+EC:DEC (1:2)/Toda high-energy layered (NMC)

BARRIERS: Needs increased life, capacity and improved safety.

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

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

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

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

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

MILESTONES:
(a) Reduce the particle size of MAX phase to submicrometer level and demonstrate a correlation between the particle size and the Li uptake capacity. (Mar. 12) Canceled - due to change in research direction to concentrate on MXenes (exfoliated MAX phases) instead of pristine MAX phases.
(b) Fully remove the A-group layers from the MAX phases to produce graphene-like 2-D structure which we labeled "MXene" and study its effect on electrochemical behavior as anodes Li-ion batteries. (Sep. 12) On schedule
(c) Produce anodes from MAX and/or MXene with the capacity of about 80% of the commercial graphite anodes. (Sep. 12) On schedule
(d) Investigate the effect of different carbon additives on the performance of MXene anodes and define the best additive conditions (Sep. 12) On schedule
PROGRESS TOWARD MILESTONES

In our previous quarterly report, performance of the MXene Ti\textsubscript{2}C as an anode material in LIBs was reported. Since Ti\textsubscript{2}C is a new material, its lithiation and delithiation mechanisms are not well understood. \textit{In situ} XRD is one of the more powerful techniques to understand the lithiation and delithiation mechanisms.

The XRD diffraction patterns of Ti\textsubscript{2}C as a function of lithiation and delithiation are shown in Fig. 1a. The latter were obtained during a relaxation period of every 0.2 Li\textsuperscript{+} ions per unit formula of Ti\textsubscript{2}C, as shown in Fig. 1b. Before cycling, the diffractograms show peaks associated mainly, with Ti\textsubscript{2}C, Ti\textsubscript{3}C\textsubscript{2}, and un-reacted Ti\textsubscript{2}AlC and Ti\textsubscript{3}AlC\textsubscript{2}. Note that even though the latter two are electrochemically inactive, their presence was quite useful since they acted as internal references for the other peak positions. No new peaks appeared during lithiation, but a progressive downshift of the 002 peaks was observed from 2\textdegree = 11.4 to 9.4\textdegree. This corresponded to an increase of the \textit{c} lattice parameter from 15.46 to 18.72 Å. After delithiation (Fig. 1c), the \textit{c} parameter decreased from 18.72 to 17.96 Å. In other words, after delithiation the \textit{c} lattice parameter was ca. 16\% higher than its value before any cycling. This result can partially explain the large irreversibility observed during the 1\textsuperscript{st} cycle, as Li\textsuperscript{+} ions are trapped between the layers of MXene in addition to the SEI layer. No increase of the \textit{c} parameter was observed at \textit{x} values below 0.6 (Fig. 2c), which is consistent with: i) an irreversible faradic reaction taking place at the surface of the particles, such as SEI layer formation, and possibly, ii) a fast Li\textsuperscript{+}-ion intercalation in the bulk of the Ti\textsubscript{2}C particles that does not involve any lattice volume expansion. Based on the XRD results it is reasonable to conclude that the charge storage in Ti\textsubscript{2}C and by extension all other MXenes, is due to Li\textsuperscript{+}-ion intercalation between the Ti\textsubscript{2}C layers and not due to a conversion reaction. This important conclusion supports the wisdom of changing research directions to focus on MXenes instead of MAXs. Research is ongoing to understand the lithiation and delithiation mechanisms.

A detailed study of how the morphology of the added C-additives affects the electrochemical behavior is being conducted; Li is also being intercalated into other MXenes.
Task 2.7-PI, INSTITUTION: Donghai Wang and Michael Hickner, Pennsylvania State University

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

BASELINE SYSTEMS: Conoco Philips CPG-8 Graphite/1 M LiPF$_6$+EC:DEC (1:2)/Toda high-energy layered (NMC)

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

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

GENERAL APPROACH: Our approach is to synthesize SiO$_x$-graphene nanocomposites to tolerate volume change upon lithiation/delithiation while maintaining Li-ion conductivity. Novel polymer binders will be developed with controlled elastic properties, ion-conductive moieties, and SiO$_x$ surface binding functionality, in order to stabilize and bridge SiO$_x$ particles. To improve the initial coulombic efficiency, SiO$_x$–graphene nanocomposites to compensate for Li consumption upon irreversible conversion of SiO$_x$ into Li$_2$O and Li silicates will be prelithiated.

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

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

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

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

Si-based anode materials:
A new series of nanocomposites composed of commercial Si nanoparticles and hollow carbon spheres (Si@HC) were developed to accommodate the volume changes during lithiation for high-performance Li-ion battery anodes. The TEM image of the Si@HC (Fig. 1a) clearly shows that the Si nanoparticles are covered with a hollow carbon shell with void space. In such structures, Si nanoparticles can expand/shrink freely during the discharge/charge processes, however, various void sizes result in different performances. Too small of a void volume may lead to the pulverization of the C while too large of a void volume may lead to loss of electric contact between the carbon and Si nanoparticles. In order to optimize the void/Si volumetric ratio, three different Si@HC nanocomposites with volumetric ratios of 1.5:1, 3:1, and 6:1 were synthesized and investigated. The Si@HC material with the void/Si = 1.5/1 shows the highest first-cycle discharge capacity of around 4050 mAh/g Si (at the equivalent C/10 rate). The material with void/Si = 3/1 showed the best capacity after 80 cycles of ca. 2000 mAh/g Si. The Si@HC with void/Si = 6:1 yields the lowest first-cycle discharge capacity of ca. 2900 mAh/g and after 10 cycles, it shows a discharge capacity of only ca. 750 mAh/g. Therefore, the Si@HC material with void/Si = 3:1 showed both promising first-cycle discharge capacity and good cycling stability.

![Image](a) (b) (c)

Figure 1. (a) Si@HC, scale bar: 1000 nm (b) Si@HC structure; (c) comparison of three void/Si ratios (black line 1.5:1; red line 3:1; blue line 6:1).

Polymer binders: The swelling of new binders in EC:DMC solvent has been measured (Fig. 2). It has been observed that binders that reach their equilibrium swelling quickly tend to cycle better in cell-performance tests. Binders that swell slowly over 100s to hours tend not to cycle well. This swelling experiment gives us a method to screen new binders for Si-based anodes. Currently, surface changes of electrodes (example micrograph shown in Fig. 2) are being observed and new crosslinked polymers having low swelling in EC:DMC are being designed.

![Image](d) (e) (f)

Figure 2. Swelling and surface visualization of Si-based anodes with novel binders.
TASK 2.8 - PI, INSTITUTION: Yi Cui, Stanford University

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

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

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

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

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

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

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

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

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

**Electrochemical Results from Electrospun Hollow Nanofibers.** Promising results were recently acquired from electrodes based on a hollow Si nanofiber geometry. This structure is designed for SEI control: the surface region of the thin (ca. 40 nm) tube wall is oxidized and this oxide layer acts as a constraint, promoting inward expansion of the Si material during lithiation. In this way, outward expansion of Si and repeated SEI fracture and electrolyte exposure is avoided. Thus, SEI formation is expected to be limited and less severe than in traditional geometries; this is demonstrated by the SEM images in Fig. 1. The top image shows that a relatively extensive SEI film grows on tubes without the external oxide constraining layer after 200 cycles. The bottom image shows a much more compact and uniform film for grows on the tubes with the oxide layer after 2000 cycles. This leads to better coulomb efficiency and lower overpotential in the cell. This geometry also leads to remarkable cycling behavior. Fig. 2 shows the good capacity retention for 6000 cycles at a rate of 5C.

![SEM image of SEI on Si Nanotubes](image1)

**Figure 1.** Top, SEM image of SEI on Si Nanotubes after 200 cycles. Bottom, Similar image of SEI on nanotubes with oxide constraint.

![Graph of Capacity with cycling at a rate of 5C.](image2)

**Figure 2.** Capacity with cycling at a rate of 5C.

**The effect of crystallinity on volume changes.** To study the effects of crystallinity on volume change, bilayer structures were fabricated by depositing thin Cu layers onto single sidewalls of Si nanowires. During lithiation/delithiation, the Si NWs deform but the Cu layer acts as a constraint that causes bending deformation. By monitoring the curvature of the bent bilayer structure after lithiation and partial delithiation, using an *ex situ* TEM technique, the intrinsic deformation mechanisms in Si nanowires that were initially single crystalline, polycrystalline, or amorphous could be studied. Through this method, it was discovered that single crystalline wires show an axial length decrease after delithiation, amorphous wires show a length increase, and polycrystalline wires fall somewhere in between. This is due to the anisotropic expansion during lithiation of crystalline Si, whereas the amorphous wires were found to undergo a more isotropic volume change.

![Axial dimensional changes after lithiation and partial delithiation for Si nanowires with different crystallinity.](image3)

**Figure 3.** Axial dimensional changes after lithiation and partial delithiation for Si nanowires with different crystallinity.
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 Pm₃m) using high-pressure and high-temperature experimental methods, including a newly-developed arc-melt technique. Concurrently, an investigational route for direct synthesis of guest-free clathrate will be explored, and ab initio and classical molecular dynamics (MD) computations to identify lithiation pathways will be performed. The silicon clathrates will be utilized to fabricate prototype silicon clathrate anodes. Electrochemical characterization will be performed to evaluate and improve, if necessary, anode performance including cyclic stability. The final year of the program will be directed at the design, assembly, and characterization of a complete (anode/cathode) small-scale, prototype battery suitable for concept demonstration.

STATUS OCT. 1, 2011: Batch quantities (1-2 grams) of Type I silicon clathrates will have been fabricated by down-selecting and adopting at least two synthetic approaches. Furthermore, computational results will have been obtained using first principles and classical theories to identify possible reaction pathways for the formation of clathrates, LiₓSi₄₆, and Li₁₅Si₄. Several half cells of clathrate anodes will have been fabricated.

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

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

MILESTONES:
(a) Select one synthetic pathway. (Dec. 11). Complete
(b) Predict the Li⁺ occupancy and lattice expansion potential of Type I metal-silicon clathrate alloys using classical and ab initio calculations. (Mar. 12) Complete
(c) Continue identifying possible reaction pathways for the formation of empty clathrates \( \square \)Si₄₆, LiₓSi₄₆, Li₁₅Si₄, and Li₁₅MₓSi₄₆₋ₓ. (Jun. 12) On schedule
(d) Synthesize hundreds of grams of Type I silicon clathrates and/or metal-silicon Type I clathrate alloys with complementary determination of structural purity. (Sep. 12) On schedule
Task 2.9 - K. Chan/M. Miller (SwRI)

PROGRESS TOWARD MILESTONES

Task 1 – Synthesis of Guest-Free Type I Silicon Clathrate

**Batch Synthesis via Soft Oxidation of NaSi.** During the previous reporting period, gram quantities of a Type I silicon clathrate (Si\textsubscript{46}) were successfully synthesized under relatively mild conditions (ca. 300°C) from BaSi\textsubscript{2} using a solution-based batch process (Hoffman-type elimination and soft oxidation reaction) in a liquid-eutectic ionic salt (IL), dodecyltrimethylammonium bis(trifluoromethylsulfonyl)imide (DTMAC-BTFSI). To further improve the yield and structural purity of the Si\textsubscript{46} product, and thus afford additional electrochemical measurements of Li capacity to be made, efforts during the next quarter will be focused on establishing a revised synthetic procedure in which the much more reactive NaSi (Zintl phase) will be employed. Although there are no known domestic sources of fine chemical-grade NaSi, SwRI has established an exclusive agreement with a domestic producer of a packaged form of NaSi and has obtained fuel-grade bulk material for evaluation. Trials are currently underway to examine product yield from this material using the established conditions for synthesis.

Task 2 – Molecular Modeling of Silicon Clathrates

Electrochemical (EC) cycling measurements made on the metal-substituted Type I silicon clathrate, Ba\textsubscript{8}Al\textsubscript{6}Si\textsubscript{40}, previously synthesized using a vacuum arc-melting technique, indicated that 300 to 350 Li atoms can be intercalated into the Ba-occupied clathrate lattices, equivalent to a specific capacity in excess of 4000 mAh/g. EC experiments further indicated that Ba atoms cannot be extracted (deintercalated) from as-prepared Ba\textsubscript{8}Al\textsubscript{6}Si\textsubscript{40} even at large over potentials. In order to gain a fundamental understanding of the thermodynamic stability of these compositions when intercalated with Li atoms, first-principles molecular dynamics computations based on the Carr-Parrinello theory were performed over a range of lattice parameters for each composition. As shown in Fig. 1, the results indicate that certain compositions already containing Ba as guest atoms are further stabilized by the presence of Li guest atoms, up to six, with little change in the lattice parameter. Large changes in both the thermodynamic stability and lattice parameters occur as the clathrate framework is occupied by a larger number (14 to 18) of Li atoms, suggesting that the large specific capacities measured experimentally would be far from the lattice equilibrium of Ba\textsubscript{8}Al\textsubscript{6}Si\textsubscript{40} and would render the bulk anode material structurally metastable. The results of these computations will be compared with the cyclic capacity losses measured electrochemically.

Task 4 – Half-Cell Electrochemical Characterization

Using Ba\textsubscript{8}Al\textsubscript{6}Si\textsubscript{40} as the basis for an anode material, experimental efforts during this quarter were directed at optimizing techniques used in electrode formation and examining the effects that binder and conductive additives (graphite and SWNTs) have on SEI formation and the Li capacity of the electrode material. Accordingly, several electrodes were made and cycled in three-electrode half-cells under charge/discharge conditions (vs. Li||Li\textsuperscript{+}) using various combinations of binder and conductive additive. The results are being analyzed and correlated.
BATT TASK 3
ELECTROLYTES

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

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

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

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

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

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

STATUS OCT. 1, 2011: Complete study of morphology on solubility of Li₂Sₓ in PS-PEO copolymers. Use membrane casting device to create Li|SEO| air cells. Identify ideal molecular weight of homopolymer for creating block copolymer-based separators. Cycle cells with an electronically and ionically conducting polymer binder in the cathode. Obtain conductivity-morphology relationships in block copolymer-based separators with well-defined pores.

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

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

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

Milestone 3.1a was completed in December 2011.

Regarding milestone 3.1b, our results show that the nanostructured polymer electrolyte can resist failures due to dendrites for 1 order of magnitude longer as compared to unstructured polymer electrolytes.\(^1\) Figure 1 shows that LiFePO\(_4\)-SEO-Li batteries resist dendrite formation 3 times longer than Li-SEO-Li symmetric cells. Our hypothesis is that the porous LiFePO\(_4\) cathode allows for better current density distribution leading to a more even plating of Li. The nanostructured electrolyte may have a similar effect on the current density distribution, such that thicker electrolytes lead to a more homogeneous current density distribution causing the Li dendrites to take longer to link the two electrodes.

Work on milestone 3.1c is on schedule. The effect of increased C rates on the polymer binder stability is currently under investigation.

For milestone 3.1d, the preliminary cycling tests of Li/SEO/S and Li/SEO/air cells are ongoing. Capacities greater than 500 mAh/g sulfur have been obtained at a rate of 40 µA for 10 cycles and a sulfur loading of 10%. For air batteries, a cell consisting of Ni-SEO-Li\(_2\)O\(_2\) was assembled. The open circuit voltage of this cell is approximately 0, and upon charging (which plates Li on the Ni), the voltage should increase to about 3 V. Preliminary results show that charging increases the open circuit cell voltage to 2.7 V.

Work towards milestone 3.1 (e) is ongoing and on schedule. In Fig. 2, the conductivity (\(\sigma\)) of three different porous SES block copolymers is shown. The SES copolymers all have the same PS length, but the length of the middle PE block is different. As the PE length increases, the optimal normalized chain length (\(\alpha\)) value decreases, while the \(\sigma\) at the optimal \(\alpha\) value stays roughly the same. This is due to the decreased miscibility of the homopolymer PS in the PE phase of the block copolymer. The most conductive separators for each block copolymer are being tested as separators in coin cell batteries.

\[\text{Figure 1. Battery and symmetric cell lifetime as a function of electrolyte thickness.}\]

\[\text{Figure 2. Conductivity for different SES block copolymers with fixed PS length. The molecular weights of each block are shown in kg/mol.}\]

Publication

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

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

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

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

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

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

STATUS OCT. 1, 2011: Initial studies on composite electrodes using single-ion conductor binders will be complete with the focus area materials: High voltage Ni-Mn Spinel cathodes and Conoco Philips CPG-8 Graphite anodes. Experiments will be complete on the use of modified multiwalled carbon nanotubes and carbon blacks for preparation of improved composite electrodes. The TGA/GC/MS system will be used to identify SEI components. Work on high volume expanding anodes with single-ion conducting binders and modified conducting additives will be extended to Si–based alloys. Dry polymer systems will be tested with LiFePO₄ and non-lithium metal anodes.

EXPECTED STATUS SEP. 30, 2012: Carbon nanotubes and other carbonaceous conducting elements will be further modified with a broader range of chemical groups (PEGs, imide and malonato-difluoroborate anions) and the effects on composite electrode performance determined. Combination of these modifications with variations of binder polymers will be studied to determine how electrode ink formulation affects the electrode morphology and electrode performance particularly for thick, high energy electrodes.

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

MILESTONES:
(a) Determine the benefits of conducting element modifications on electrode performance. (Apr. 12). On schedule
(b) Determine the role of electrode ink properties (e.g., viscosity, stability, etc.) on electrode coating morphology and effects on electrode performance. (Sep. 12). On schedule
PROGRESS TOWARD MILESTONES

Following the encouraging results of functionalized multiwalled carbon nanotubes (MWCNT) as conductive additives, a number of other systems were examined using similar approaches. A commercial form of TiO was tested and found to be less conductive than carbon black and attempts to prepare NiO on the nanotubes were unsuccessful. However, functionalized MWCNT additives were found to have interesting performance in various anode materials such as TiO$_2$ and SnO$_2$. The SnO$_2$ materials are most interesting due to the volume change during charge and discharge and the SnO$_2$ is incorporated into the surface films on the tubes:

The cycling behavior during the first two cycles is shown below as well as the rate behavior of these materials compared to other forms of SnO$_2$. Once again, the surface modified materials give better performance, which appears to be due to the morphology of the electrode.
TASK 3.3 - PI, INSTITUTION:  Dmitry Bedrov, Feng Liu, University of Utah, and Oleg Borodin, Army Research Laboratory

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

BASELINE SYSTEMS:  Conoco Philips CPG-8 Graphite/1 M LiPF$_6$+EC:DEC (1:2)/Toda high-energy layered (NMC)

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

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

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

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

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

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

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

During this quarter, DFT studies of LiNi_{0.5}Mn_{1.5}O_{4} spinel surface energies, transport properties of Li_{2}DBC (Li(O_{2}COCH_{2}CH_{2})_{2}) SEI component in the crystalline and amorphous states as a function of temperature, and transport and structural properties of the interface of Li_{2}DBC || EC:DMC(3:7)/LiPF_{6} continued. An extensive molecular dynamics (MD) simulation study of the double layer structure of tetramethylene sulfone (TMS)$_{x}$:DMC$_{y}$ electrolytes (x:y=1:2, 1:1, 2:1) doped with 1 M LiPF$_{6}$ as a function of electrode potential are discussed in detail in this report.

The double layer structure of (TMS)$_{x}$:DMC$_{y}$/LiPF$_{6}$ electrolytes was investigated in order to obtain molecular insight into experimental observations. The observations indicate that the addition of oxidatively stable TMS solvent noticeably increases the oxidative stability of electrolyte (Ethyl acetate:TMS doped with Bu$_{4}$NBF$_{4}$ on Pt, (J. Power Sources, 179, 770-779, 2008). Our MD simulation study explored how the addition of low viscosity thinning solvents such as DMC influences the interfacial structure of the higher voltage TMS-based electrolyte was studied. By investigating three solvent compositions TMS:2DMC, TMS:DMC, and 2TMS:DMC, a link was established between bulk and interfacial compositions as well as the composition of the interfacial Li solvation shell. These properties were then compared with EC-based electrolytes. MD simulations revealed that despite the relative similarity of TMS and EC dipole moments, a significant difference in electrolyte double-layer composition is observed for TMS- and EC-based electrolytes, depending on the direction of polarization. Analysis of the solvent molecule composition in the interfacial layer as a function of electrode potential (Fig. 1a) showed that on the anode the fraction of polar TMS or EC increases as the magnitude of electrode potential increases. On the cathode, however, the TMS:DMC ratio either remained the same as in the bulk or was reduced, indicating a partitioning of DMC to the interface, which was contrary to the EC-based electrolytes. There the preference for EC at the interface was observed with increasing cathode potential.

A more detailed analysis of atomic distributions showed that while the overall concentration of TMS in the interface might be similar to the bulk, TMS could still potentially provide oxidative protection to DMC in the electrolyte. Even in the DMC-rich TMS:2DMC/LiPF$_{6}$ electrolyte, it was found that oxygens of TMS preferentially adsorbed on the positive electrode and largely displaced carbonyl oxygens of DMC. The oxygens of the DMC moved from the inner Helmholtz layer to the outer layer located around 5 Å from the electrode (Fig. 1b). This atomic repartitioning should allow DMC carbonate groups located in the outer interfacial layer to be subjected to a lower potential compared to the TMS solvent in the inner interfacial layer. In the EC:DMC(3:7)/LiPF$_{6}$ electrolyte, carbonyl oxygens of EC also preferentially adsorbed on the positive electrode (Fig. 1c) but not to the extent as observed for TMS:2DMC/LiPF$_{6}$ electrolyte.

**Figure 1.** a) Ratios of TMS/EC and DMC molecules in the electrode interfaceal layer defined as within 6 Å from the surface. Bulk compositions shown by horizontal bars. Density profiles of oxygen atoms TMS or EC (solid black line) and DMC (red line) in TMS:DMC(1:2)/LiPF$_{6}$ (b) and in EC:DMC(3:7)/LiPF$_{6}$ (c) electrolytes at 2.4 V vs. bulk. Zero on x-axis is the position of the electrode surface.

The observed Li$^{+}$ enrichment on the anode and PF$_{6}^{-}$ enrichment on the cathode in TMS:DMC/LiPF$_{6}$ electrolytes were similar to those found in EC:DMC(3:7)/LiPF$_{6}$ electrolytes.
TASK 3.4 - PI, INSTITUTION: Khalil Amine and Larry Curtiss, Argonne National Laboratory

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

BASELINE SYSTEMS: Conoco Philips CPG-8 Graphite/1 M LiPF<sub>6</sub>+EC:DEC (1:2)/Toda high-energy layered (NMC)

BARRIERS: Cycle/calendar life, abuse tolerance

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

GENERAL APPROACH: Search for new electrolytic additives that react in a preferential manner to prevent detrimental decomposition of other cell components using experiment and theory. Use quantum chemical screening to predict oxidation and reduction potentials and decomposition pathways that form desirable coatings for testing by experiment. Use density functional studies of graphite surface reactions to determine mechanisms for protective film formation from additives.

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

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

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

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

Our approach for the development of new electrolyte additives for SEI formation and overcharge protection involves screening of properties through the use of accurate density functional methods followed by investigation of the mechanism of decomposition and experimental testing. Our database of additives has increased to over 380 species.

2,4,6-Tris(2-propen-1-yloxy)-1,3,5-triazine (TPYT) has been shown to be a promising SEI additive. A good SEI prevents further electrolysis of the electrolyte and increases battery cycle life. Density functional theory (DFT) has been used to investigate the molecule TPYT as SEI additive for Li-ion batteries. The DFT calculations using B3LYP and a continuum model for the surrounding electrolyte showed that when this molecule is reduced, an allyl radical detaches via an apparent charge-spin segregation mechanism as shown in Fig. 1. DFT calculations show that upon reduction an allyl radical can separate with a small energy barrier. This allyl radical can initiate free radical polymerization by attacking C=C bonds of TPYT species in solution to form an effective SEI. The pores of this SEI layer are likely to be large enough to allow uninterrupted Li⁺ transport. Thus, our calculations indicate that allyl groups are promising substituents for the design of SEI additives for Li-ion batteries.

In order to unravel the complex chemistry of the SEI for Li-ion batteries, the reactivity of reduced EC is being studied. Several new pathways have been explored for parameterization in MD simulations. It is well accepted that EC can become reduced at the anode and degrade during the first discharge to form the SEI layer. Recent attempts at modeling this process using the ReaxFF force field have produced products that have not been considered to be major constituents of the SEI layer. In order to test the efficacy of ReaxFF, the formation of these products using accurate density functional theory calculations were performed. Optimization of several of these minima resulted in structures already considered in other quantum chemical calculations or in high-energy structures. However, the ester-carbonate species predicted by ReaxFF is a minimum on the DFT potential energy surface. The barrier of formation for this species, seen in Fig. 2, was found to be less than other reactions known to occur in the electrolyte (i.e., EC ring-opening after reduction) and the calculated reaction energy was similar to other species believed to exist in the SEI layer. Therefore, this is a product that will be given consideration as part of the simulations of the SEI layer in Li-ion batteries in collaboration with D. Bedrov (Utah).
TASK 3.5 - PI, INSTITUTION: Brett Lucht, University of Rhode Island

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

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

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

OBJECTIVES: Develop novel electrolytes with superior performance to SOA (LiPF₆ in carbonates). Develop and understanding of the source of performance fade in LiNi₁.₅Mn₀.₅O₄ cathodes cycled to high voltage (4.9 V vs. Li). Develop an electrolyte formulation that allows for superior performance of LiNi₀.₅Mn₁.₅O₄ cathodes.

APPROACH: Optimize properties of LiPF₄C₂O₄/carbonate electrolytes in small Li-ion cells at low temperature (-30°C) after accelerated aging. Investigate electrode surface films for cells cycled with LiPF₄(C₂O₄) to determine source of performance differences. Investigate cathode film forming additives for high voltage (>4.5 V) cathode materials. Investigate the surface of cathodes and anodes cycled with novel electrolytes, with or without additives, to develop a mechanistic understanding of interface formation and degradation.

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

EXPECTED STATUS SEP. 30, 2012: An LiPF₄(C₂O₄) electrolyte with optimized performance at low temperature after accelerated aging will have been developed. A better understanding of the role of electrolytes in the poor cycling efficiency and capacity fade of LiNi₀.₅Mn₁.₅O₄ cathodes will have been developed. Novel electrolyte formulations which optimize the performance of LiNi₀.₅Mn₁.₅O₄ cathodes cycled to high voltage (4.9 V vs. Li) will have been designed.

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

MILESTONES:
(a) Develop an understanding of the role of electrolytes in capacity fade and poor cycling efficiency of LiNi₀.₅Mn₁.₅O₄ cathodes. (Mar. 12) Complete
(b) Design electrolyte formulations to improve performance of high voltage Ni-Mn spinel cathode materials. (Jul. 12) On schedule
(c) Optimize a LiPF₄(C₂O₄) electrolyte for graphite/LiNiₓCo₁₋₂ₓMnₓO₂ cells for high and low temperature performance. (Sep. 12) On schedule
PROGRESS TOWARD MILESTONES

With regards to milestone (a): A detailed analysis of the role of electrolytes in capacity fade and poor cycling efficiency of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cathodes cycled to high voltage was conducted. As previously reported, there are two primary sources of performance loss. First, decomposition of the LiPF$_6$ salt leads to the generation of Lewis-acid species that corrode the cathode surface and dissolve transition metals (Mn and Ni). Second, the high oxidation potentials of the cathode result in the oxidation of carbonate solvents to generate polyethylene carbonate. Our experiments suggest that Mn dissolution is the primary problem, but that Mn dissolution is worse at high voltage and that electrolyte oxidation is a secondary contributor. A new collaboration was initiated with G. Chen (LBNL) to investigate the structural dependence of the LiNi$_{0.5}$Mn$_{1.5}$O$_4$ particles (crystal structure and Mn$^{3+}$ content) on Mn dissolution has been initiated.

With regards to milestone (b): Electrolyte formulations are being designed to optimize the performance of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cathodes cycled to 4.9 V (vs. Li) were initiated. Two primary types of additives are under investigation. First, Lewis-base species that inhibit the thermal decomposition of LiPF$_6$ are being identified. Preliminary investigations suggest that incorporation of Lewis-base additives inhibits Mn dissolution and improves cycling performance at high voltage. The second type of additive that is being considered are cathode film forming additives. Cathode film forming additives are preferentially oxidized on the cathode surface to generate a passivation layer which inhibits electrolyte oxidation. Novel cathode film forming additives have been incorporated into Li/LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cells. The incorporation of the additive resulted in a significant reduction in the capacity loss during the first 55 cycles. The standard electrolyte resulted in the lost 28% of the capacity while the electrolyte with additive lost only 13%, a 54% reduction in capacity loss. In addition, the efficiencies were improved from 98.2 to 99.3%. Ex situ surface analysis of the electrode after cycling suggests that incorporation of the novel additive reduced the thickness of the cathode surface film and reduced the detrimental reactions of the electrolyte with the cathode surface. Further investigation on the optimization of electrolyte additives is in progress.

With regards to milestone (c): lithium tetrafluorooxalatophosphate (LiPF$_4$(C$_2$O$_4$)) electrolyte formulations are being investigated for good low temperature performance are being investigated. The research focuses on the incorporation of methyl butyrate (MB) as a co-solvent.

**Figure 1.** Cycling capacity and efficiency of Li/LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cells with and without additive.

**Collaborations:** M. Smart (NASA-JPL), V. Battaglia and G. Chen (LBNL), O. Borodin (ARL), W. Li (S. China Univ. Tech.), A. Garsuch (BASF), and Spinel Focus Group.
TASK 3.6 - PI, INSTITUTION: Daniel Scherson and John Protasiewicz, Case Western Reserve University

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

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

BARRIERS: Abuse tolerance

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

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

STATUS OCT. 1, 2011: Synthesis and purification of three cyclic triol borate (CTB) and one bicyclic borate phosphine oxide (CBPO) salts and determination of their flammability. Develop methods for the preparation of 100g of CTB-type compound for testing in actual batteries. Collect data using the in situ IRAS-FTIR cell for monitoring in situ the composition of the electrolyte and surface films on ultrapure Li metal in selected alkyl carbonate-salt formulations.

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

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

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

a. Synthesis and characterization of FRIONS – In the synthesis on a new FRION, preliminary data suggests the formation of a phosphorylated borate diester intermediate (Scheme 1). The $^{31}$P{H} NMR spectrum shows three peaks at 48.4, 42.5, and 35.4 (Fig. 1) Solvent free synthesis of the cyclic triol borate intermediate has been performed (Scheme 2). This synthetic method allows for rapid preparation of analytically pure material on a large scale (>10 g). Organometallic lithium reagents for the preparation of LiC$_r$B$_r$ salts have been investigated as a means of optimizing the synthesis of Li salts. Lithium diisopropyl amine (LDA) (Scheme 4) has emerged as an attractive Li source, because the reaction avoids a water byproduct and has a high yield. Product formed via this route has also shown higher initial solubility in organic solvents, perhaps due to coordination of diisopropylamine to the Li cation.

\[
\begin{align*}
\text{Scheme 1} & \\
\text{Scheme 2} & \\
\text{Scheme 3} & \\
\text{Scheme 4} & \\
\end{align*}
\]

b. Coin-Cell Measurements – The improved performance obtained with the Case additive described in an earlier report was confirmed with several samples prepared independently. This is illustrated in Fig. 2, which compares the results obtained with three such specimens (data in the upper three traces) with that of the background electrolyte without the Case additive (symbols in the lower trace). Larger quantities of the additive are being prepared for testing in prismatic type cells.
TASK 3.7 - PI, INSTITUTION: Wesley Henderson, North Carolina State University

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

BASELINE SYSTEMS: Conoco Philips CPG-8 Graphite/1 M LiPF$_6$+EC:DEC (1:2)/Toda high-energy layered (NMC)

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

OBJECTIVES: Develop new anions as replacements for PF$_6^-$ or as additives for electrolytes

GENERAL APPROACH: Synthesize and fully characterize two classes of nonfluorinated (or partially fluorinated) anions: 1) chelated and non-chelated organoborate anions (related to bis(oxalate)borate (BOB’)), and 2) Hückle-type anions in which the charge is stabilized on a 5-member azole ring and noncyclic cyanocarbanions. Characterize the physical properties of these new anions, incorporated in both Li salts and ionic liquids, by examining the thermal phase behavior (phase diagrams); thermal, chemical and electrochemical stability; transport properties; interfacial properties; molecular interactions and cell performance. These salts will be compared with widely used salts such as LiPF$_6$ and LiBOB and ionic liquids based upon the bis(trifluoromethanesulfonyl)imid anion.

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

EXPECTED STATUS SEP. 30, 2012: Extensive characterization of solvent-LiFSI and -LiDFOB mixtures will be completed. Several new lithium salts will be reported along with a comparison of their properties with conventional salts such as LiBF$_4$ and LiPF$_6$. ILs will have been prepared from these anions and tested in IL-LiX and IL-LiX-solvent mixtures, as well as for use as additives to conventional electrolyte formulations.

RELEVANT USABC GOALS: Available energy: 56 Wh/kg (10 mile) and 96 Wh/kg (40 mile); 10-s discharge power: 750 W/kg (10 mile) and 316 W/kg (40 mile); cycle life: 5000 cycles (10 mile) and 3000 cycles (40 mile); calendar life: 15 years (at 35°C); cold cranking capability to -30°C; abuse tolerance.

MILESTONES:
(a) Determine the phase behavior/properties of solvent-LiPF$_6$ mixtures. (Apr. 12) On schedule
(b) Determine the phase behavior/properties of solvent-LiFSI and -DFOB mixtures. (Sep. 12) On schedule
(c) Prepare/characterize lithium salts with partially fluorinated cyanocarbanions and dianions. Conduct half/full-cell electrochemical testing (graphite and NMC electrodes) using the salts as replacements for LiPF$_6$ or as additives, in parallel with the control electrolyte with LiPF$_6$, to demonstrate improved cycling behavior performance over 200+ cycles. (Sep. 12) On schedule
(d) Prepare/characterize ILs with DFOB’ and partially fluorinated cyanocarbanions. Conduct half/full-cell electrochemical testing (graphite and NMC electrodes) using the salts as replacements for aprotic solvents or as additives, in parallel with the control electrolyte with LiPF$_6$, to demonstrate improved cycling performance over 200+ cycles. (Sep. 12) On schedule


**PROGRESS TOWARD MILESTONES**

**Phase Behavior/Properties of Solvent-LiX Mixtures:** The phase behavior and transport properties of (solvent)$_n$-LiPF$_6$ mixtures with EC, PC, GBL, and GVL have been completed. This is being compared with the phase behavior and properties of LiBF$_4$, LiDFOB, LiBOB, and LiFSI mixtures. Interestingly, the solvent coordination numbers suggest that LiDFOB is as solvated or more solvated than LiBF$_4$. Numerous solvate structures have been determined for LiDFOB (i.e., (G1)$_2$:LiDFOB with monoglyme - Fig. 1) to examine how this anion coordinates Li$^+$ cations and to correlate this with the Raman bands for the DFOB$^-$ anion. Using the anion Raman bands, the characterization of (AN)$_n$-LiDFOB solutions suggests that this salt is less associated than the corresponding LiBF$_4$ solutions, in agreement with the solvent coordination numbers. Further, the conductivity (Fig. 2) and viscosity data for the mixtures also supports this surprising conclusion. From the information gleaned from the phase diagrams, concentrated electrolytes have been selected for characterization. The solvent-LiX mixtures contain little to no uncoordinated solvent. The properties of these mixtures differ markedly from those of more dilute mixtures.

**Anion Synthesis:** The synthesis of lithium 4,5-dicyano-2-(trifluoromethyl)imidazolide (LiTDI) has been scaled up to facilitate the full characterization of this salt. Modifications to the synthesis procedure have been made in attempts to improve the purity and yield. Solvates have been prepared to examine the manner in which the TDI$^-$ anion coordinates Li$^+$ cations. Aggregate solvates (i.e., (AN)$_2$:LiTDI with acetonitrile - Fig. 3) indicate that the anion utilizes both the ring and nitrile nitrogens to coordinate the cations.

**Collaborations:** Oleg Borodin/Richard Jow (Army Research Laboratory), Stefano Passerini (Münster Electrochemical Energy Technology group, University of Münster), and Yuri Andreev/Peter Bruce (St. Andrews University, Scotland).

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Figures:

1. **Figure 1.** Li$^+$ cation coordination in the crystal structure of the (G1)$_2$:LiDFOB solvate (Li-purple, O-red, B-tan, F-green).

2. **Figure 2.** Molar conductivity of (AN)$_n$-LiX solutions at 60°C.

3. **Figure 3.** Li$^+$ cation coordination in the crystal structure of the (AN)$_2$:LiDFOB solvate (Li-purple, N-blue, F-green).
TASK 3.8 - PI, INSTITUTION:  Austen Angell, Arizona State University

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

SYSTEMS:  Conoco Philips CPG-8 Graphite/1 M LiPF$_6$+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 is twofold: (i) A suite of electrolyte studies, beginning with cell-performance testing of recently developed sulfone electrolytes and extending to the design of novel Li$^+$-conducting media, are planned. The latter will retain the high oxidation resistance known for noncyclic sulfones, and conductivity of EC-DMC solutions, but will have Li$^+$ transport number unity. Novel Li$^+$-conducting thiophosphate solids (known $\sigma >10$ S/cm) and rubbery polymers (developing) will be tested for compatibility with the chosen Li(Ni,Mn) spinel cathode. Finally, some ionic liquid electrolytes will be tested. (ii) The second is the further development of the “Maxwell slats” approach to synthesis of nanoporous supports. A hot water-soluble reversibly-self-assembling net has already been developed as model, and a stronger-bonded model that self-assembles in hot ionic liquid solvents, is the next target.

STATUS OCT. 1, 2011:  Half-cell and full-cell tests with the Li(NiMn) high voltage cathode using our newly developed graphite-compatible all-sulfone, and part sulfone electrolyte solvents, will have been completed, and relative merits assessed. Tests of fluorinated sulfone FPMS, with DMC co-solvent in similar half-cell and full cell modes will be done. The crystal structures of one of our self-assembling open-network structures (and its pore space fraction) will be known, and the XRD of its nearest glass-forming analog will be available for comparison. Studies to expand the glassy range and mechanical properties will be in progress.

EXPECTED STATUS SEP. 30, 2012:  A go-no-go point will have been passed on sulfone-solvent-based high voltage cell development. An alternative solvent system of even higher voltage window and comparable conductivity, based on “ionic liquid” solvents, will have been tested for performance with the Li(Ni,Mn)O$_4$ 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)O$_4$ cathode and the expected absence of side reactions verified. The nanoporosity of aqueous self-assembling models of the Maxwell slat concept will have been assessed, and study of more practical (stronger-bonding) variants will have been commenced.

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

MILESTONES:
(a) Complete full evaluation of sulfone solvent-based high voltage cells. (Dec. 11) Complete
(b) Complete development of water-soluble self-assembling models of “Maxwell slat” porous solids for creation of self-supporting nanoporous membranes. (Dec. 11) Complete
(c) Complete evaluation of ionic liquid-based, and hybrid, solvent electrolytes. (Apr. 12) On schedule
(d) Test and compare Li(Ni,Mn) spinel cells using ionic liquid-based electrolyte. (May 12) On schedule
(e) Test and compare glass and glass-stuffed polymer electrolyte types in cells. (Jun. 12) Complete
(f) Develop covalent-bonded equivalents of the self-assembling nets. (Jul. 12) On schedule

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PROGRESS TOWARD MILESTONES

(a) Complete

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

Investigation of novel inorganic salts that favor de-trapping of the Li cation from its anion environment to maximize Li mobility has continued. Conductivity data for a series of the new systems both in liquid and conducting solid states are shown in Fig. 1. They are compared with data for special Nasicon ceramic, the recent germanosulfide crystal, and LiPF₆ in EC-PC liquid electrolytes. The new systems should have Li transport numbers of unity and very wide electrochemical stability windows. Since the melting points of our new salts are near 100 °C it can be seen that there already are cheap, nontoxic, Li-conducting solids with conductivities within a factor of 10 of the best available are already at hand.

(c) and (d) No reports; (e) Complete

(f) Develop covalent-bonded equivalents of the self-assembling nets by July 2012.

This work has continued successfully. Networks with a density as low as 0.18 g/ml have been prepared and characterized by RD. Some pore size results are shown in Fig. 2 (by inversion of low angle XRD patterns) for the very low density net made with long slats, for nets made with a combination of stiff and flexible slats to reduce the brittleness of the films, and for a rubbery net made with all flexible slats (600MW PEO)... The average nanopore dimension in the low density membrane and with 50% stiff strut is 1.5 to 2nm according to Fig. 2, while the net with all flexible struts has very small pores. Such rubbery nets containing LiTFSI have shown conductivities equal to the best reported for "dry" polymer electrolytes with LiTFSI. Note that our rubbers self-assemble from solution. Our emphasis is on the nanoporous films with liquid electrolytes in the pores. Preparation of films that can be filled "post-preparation" has moved slowly. New casting molds and filling techniques need further development. Results will be available for the next quarterly report. Characterization of the membrane mechanical properties has been attempted by glass-temperature measurements during formation from casting solutions, but glass temperatures become undetectable before all of the casting solvent has been removed, see Fig. 3. The loss of thermal manifestation of softening (calorimetric Tg) seems to be characteristic of true 3D amorphous structures.
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. lithium. These electrodes suffer from voltage decay and surface instability on cycling, thereby compromising the energy and power of the lithium-ion cells and preventing their implementation in practical systems. A novel, simple and versatile processing technique, using Li2MnO3 as a precursor, to synthesize composite electrode structures is advocated; it offers the possibility of tailoring composite electrode structures and enhancing their electrochemical properties to meet Li-ion battery performance targets for PHEVs and EVs.

STATUS OCT. 1, 2011: This is a new project. During the last six months of FY2011, progress was made in exploiting a new synthesis approach in which Li2MnO3 was used as a precursor to fabricate structurally-integrated lithium-metal-oxide composite electrode materials, including ‘layered-layered’, ‘layered-spinel’, ‘layered-rocksalt’ and more complex types. This technique showed promise for stabilizing high capacity (250 mAh/g) lithium-metal-oxide cathodes to cycling over a wide voltage window and, in particular, for combating voltage decay phenomena.

EXPECTED STATUS SEP. 30, 2012: Progress will have been made in enhancing the electrochemical and structural stability of ‘layered-layered’ xLi2M'O3•(1-x)LiMO2 electrodes at high potentials, with improvements in rate capability and cycle life.

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

MILESTONES:
(a) Evaluate a new processing route to fabricate stabilized xLi2M'O3•(1-x)LiMO2 (‘layered-layered’) electrode structures with a high Mn content using Li2MnO3 as a precursor (Sep. 12) On schedule
(b) Use atomic layer deposition and other methods to stabilize the surface of electrode particles at high charging potentials. (Sep. 12) On schedule
(c) Model surface structures and interfacial phenomena of coated electrodes. (Sep. 12) On schedule
PROGRESS TOWARD MILESTONES

Collaborators: J. R. Croy, M. Balasubramanian, S.-H. Kang, Yang Ren

Milestone (b) addressed: Evaluate a new processing route to fabricate stabilized xLi$_2$MnO$_3$•(1-x)LiMO$_2$ electrode structures with a high Mn content using Li$_2$MnO$_3$ as a precursor

Despite the growing attention received by xLi$_2$MnO$_3$•(1-x)LiMO$_2$ (M = Ni, Mn, and Co) composite electrode materials, the ability to utilize their exceptionally high capacities (ca. 250 mAh/g) in practical applications is hindered largely because of a voltage decay phenomenon during cycling. Electrochemical ‘activation’ above ca. 4.4 V alters the structure of these electrode materials and sets in motion a gradual phase transformation that lowers the discharge voltage of the cells, thereby lowering their energy and power output. In an attempt to combat this voltage decay, a new synthesis technique to fabricate xLi$_2$MnO$_3$•(1-x)LiMO$_2$ electrode materials with greater resilience to internal phase transformations is being explored.

Specifically, the unique behavior of layered Li$_2$MnO$_3$ (alternatively Li[Li$_{1/3}$Mn$_{2/3}$]O$_2$) when used as a precursor in an ion-exchange process is being explored. Namely, when treated in acid (e.g., 2 M HNO$_3$), Li$_2$MnO$_3$ undergoes proton exchange with Lithium, which is accompanied by a shift of the oxygen layers from O3 to P2 stacking to form H[Li$_{1/3}$Mn$_{2/3}$]O$_2$. On drying and annealing, (i.e., retaining all ions in the solution), the original Li$_2$MnO$_3$ structure can be completely reconstituted. If this process is carried out in the presence of suitable metal cations, such as Ni$^{2+}$, the metal ions can be driven into the Li layers of the Li$_2$MnO$_3$ template and subsequently integrated within the Li$_2$MnO$_3$ structure, the extent of which is controlled by the temperature and time of the annealing step. This technique can produce complex composite structures including ‘layered-layered,’ ‘layered-spinel,’ and ‘layered-rocksalt’ xLi$_2$MnO$_3$•(1-x)MO materials (e.g., M=Co, Ni). Figures 1a and 1b show the differences in the electrochemical behavior of Li half cells with a cathode with a targeted composition of 0.5Li$_2$MnO$_3$•0.5LiNi$_{0.5}$Mn$_{0.5}$O$_2$, fabricated at 850 and 450ºC, respectively. The composite electrode prepared at 450ºC contains a NiO component that, on heating, is gradually absorbed by the Li$_2$MnO$_3$ template to ultimately form 0.5Li$_2$MnO$_3$•0.5LiNi$_{0.5}$Mn$_{0.5}$O$_2$, as shown by the XRD patterns obtained in situ during the heating process (Fig. 1c). The NiO-containing materials require break-in cycles but show indications of enhanced stability (Fig. 1b).

![Figure 1](image-url)
TASK 4.2 - PI, INSTITUTION: Stanley Whittingham, Binghamton University

TASK TITLE - PROJECT: Cathodes - Materials: Novel Cathodes

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF_6+EC:DEC (1:2)/Toda high-energy layered (NMC)

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

OBJECTIVES: The primary objectives are to find (a) lower-cost and higher-capacity cathodes, exceeding 200 Ah/kg (700-800 Wh/kg), and (b) moderate-rate PHEV compatible cathodes, both of which are based on environmentally benign materials.

GENERAL APPROACH: Our cathode approach is to place emphasis on low cost oxides and phosphates, both pure and modified with other transition metals, using a range of practical synthesis approaches. These materials will be synthesized, and characterized both structurally and for thermal and chemical stability. All will be evaluated electrochemically in a variety of cell configurations.

STATUS OCT. 1, 2011: For the LiFePO_4 olivine, we have determined that the rate capability can be improved by substituting in around 5% of another ion, because the nucleation energy for formation of the second phase is reduced. Such substitution also substantially enhances the volumetric capacity, by minimizing the amount of carbon conductor. For the layered metal dioxides, we have determined that no more than 20% cobalt is required to achieve optimum capacity at rates exceeding 2C, and that charging potentials in excess of 4.3 V are required to achieve discharge capacities exceeding 200 Wh/kg. We will have identified a candidate material, lithium iron pyrophosphate that may allow for more than one electron reduction per transition metal if a suitable electrolyte can be identified.

• LiFePO_4: > 120 Ah/kg for 100 cycles at 1 mA/cm^2 (1C rate).
• Layered Li_xCo_yNi_zMn_1-x-y-O_2: 160 Ah/kg and 150 Ah/kg for 60 cycles at 1 and 2 mA/cm^2 respectively.

EXPECTED STATUS MAY. 31, 2012: For low-cost Li-Ion cells, we expect to have completed the synthesis and evaluation of lithium iron phosphate, Li_2FeP_2O_7, and its solid solution with manganese, cobalt and other transition metal elements. We will also have explored some higher capacity next generation cathodes, including some based on vanadium including VOPO_4.

RELEVANT USABC GOALS: 5000 deep and 300,000 shallow discharge cycles, and lower cost batteries.

MILESTONES:
(a) Complete the characterization of the lithium iron pyrophosphate (May 12) On schedule
(b) Synthesize a vanadyl phosphate that has an energy density of 700 Wh/kg. (May 12) On schedule
PROGRESS TOWARD MILESTONES

Milestone (a) – Lithium iron pyrophosphates
In order to achieve 800 Wh/kg in phosphates it is necessary to extract the 2\textsuperscript{nd} Li, for example in the compound Li\textsubscript{2}MP\textsubscript{2}O\textsubscript{7}. Four different electrolytes were tried: sulfone, carbonate electrolyte with additive, ionic liquid, and nitrile through collaborations with PNNL, ARL, CSIRO/Monash, and Rutgers. None of these electrolytes was found to be sufficiently stable to allow potentials to be attained above 5 volts without significant side-reactions occurring. Even when apparent capacities above that for one Li were attained, the studies described below suggest that the extra capacity is associated with side-reactions.

The charge and discharge process was characterized by \textit{ex situ} and \textit{in situ} techniques. Fig. 1(a) shows slight changes in the x-ray pattern on cycling. Above 4.0 volts a new peak is found at around 13\(^\circ\), the peaks at around 26.5\(^\circ\) and 31\(^\circ\), disappeared, and the two peaks at around 33\(^\circ\) split into four peaks. These changes are reversible and consistent with solid solution phases being formed at the beginning and end of the reaction, with a small, two-phase region in between. The redox process was followed \textit{in situ} and \textit{ex situ} using XANES. Figures 1(a) and 1(b) show, respectively, the spectra on charge and discharge up to 4.8 volts. There was no evidence for charged states of Fe above 3+, suggesting that the capacity exceeding Fe\textsuperscript{3+} is related to side-reactions either of the electrolyte or of the carbon in the cathode.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{(a) \textit{in situ} XRD patterns during the charge and discharge and \textit{in situ} XANES during (b) the charge and (c) the discharge process for C-coated Li\textsubscript{2}FeP\textsubscript{2}O\textsubscript{7} samples. FeC\textsubscript{2}O\textsubscript{4}\cdot2H\textsubscript{2}O and Fe(NO\textsubscript{3})\textsubscript{3} are selected as divalent and trivalent references, respectively, for the XANES.}
\end{figure}

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

Presentation
1. H. Zhou, S. Upreti, N. A. Chernova, A. Lal, G. Hautier, G. Ceder and M.S. Whittingham, “Is it possible to reversibly cycle the 2\textsuperscript{nd} Li in Li\textsubscript{2}MP\textsubscript{2}O\textsubscript{7}?” \textit{Materials Research Society}, Spring Meeting, San Francisco, April 9–12, 2012.
TASK 4.3: 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 cathodes such as modified NMCs and LiNi0.5Mn1.5O4 (LNMS) are synthesized via spray pyrolysis, as well as composites containing these materials, and coated particles. An array of physical and electrochemical techniques are used to characterize their behavior, in conjunction with members of the diagnostics team. Emphasis is placed on increasing energy density without sacrificing stability and cycle life.

STATUS OCT. 1, 2011: Phase-pure samples of LiNi0.5Mn1.5O4 spinel (LNMS) have been produced by spray pyrolysis. Structural characterization of cycled Li[Ni0.45Co0.1-yAl0.05Mn0.45]O2; y=0, 0.05 electrodes was completed. Structural and electrochemical characterization of high capacity Li[Ni, Co, Ti, Mn]O2 compounds will continue.

EXPECTED STATUS SEP. 30, 2012: Hierarchically structured LNMS with differing primary and secondary particle sizes will be produced by spray pyrolysis, and optionally provided to interested members of the high voltage spinel discussion group. Work on NMCs will be directed towards understanding the mechanism of improvement in capacities and cycling behavior observed in some compounds when Ti is partially substituted for Co.

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

MILESTONES:
(a) Complete electrochemical characterization of hierarchically structured LNMS made by spray pyrolysis and compare to results obtained on conventional samples and simple particles made by spray pyrolysis. (Sep. 12). On schedule
(b) Make a go/no go decision on Ti-substitution in NMCs as an approach for increasing energy density and improving cycle life. (Sep. 12). On schedule
PROGRESS TOWARD MILESTONES

1) Composite powders consisting of hollow particles of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ infiltrated and coated with LiFePO$_4$ were cross-sectioned using an Argon ion-beam technique and imaged. Figure 1 shows SEM and EDS mapping on several of these cross-sectioned particles.

![Figure 1. SEM image of cross-sectioned LiFePO$_4$@LiNi$_{0.5}$Mn$_{1.5}$O$_4$ particles and EDS elemental mapping.](image)

The images show that the shell (LiNi$_{0.5}$Mn$_{1.5}$O$_4$) thickness is quite variable (e.g., the large particle on the right originally had little void space) and that the LiFePO$_4$ does not completely fill the shells, although it infiltrates all of the particles, including the ones with little void space. For optimum energy densities, particles should be as close to solid as possible. This should be possible to achieve by adjusting the concentration of infiltrant (LiFePO$_4$ precursor solution) during the filling process. Our work next quarter will be directed towards optimizing these composite particles as well as attempting to make solid particles of LiNi$_{0.5}$Mn$_{1.5}$O$_4$.

(Collaborations with Jordi Cabana, Guoying Chen, and members of the high voltage spinel group).

2) A paper on Ti-substitution in NMC materials has just been submitted to the Journal of the Electrochemical Society. Analysis of the data indicates that the solid solution limit for Ti in NMCs is about 4 to 7%, depending on synthesis method (glycine-nitrate combustion or co-precipitation) and global composition. Improvements in capacities and cycling retention were universally seen for all materials with Ti-contents below 4%, compared to the baseline materials. The improvements were most noticeable for cells charged to 4.7 V (rather than the customary 4.3 V). Although some capacity fading was still evident for the Ti-substituted materials cycled under these conditions, it was significantly less than that seen for the baseline materials. The best cycling results, in terms of capacity retention, were found for materials made by co-precipitation. Further work will be directed towards improving the cycling behavior of high-capacity, Ti-substituted NMCs by coating powders and other strategies, as well as optimization of the synthesis by either spray pyrolysis or spray drying techniques. (Collaboration with A. Mehta of the Stanford Synchrotron Radiation Lab).

Presentations
**TASK 4.4 - 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:** Focus is on the design and development of cathode materials based on polyanions that have the possibility for reversibly inserting/extracting more than one Li⁺ ion per transition metal ion Mⁿ⁺ and/or operating above 4.3 V. Some example systems to be pursued are Li₂MSiO₄ and Li₂MP₂O₇ (M = Mn, Fe, Co, and Ni). However, there are technical challenges in achieving the theoretical energy densities of many of these cathode materials. Synthesis and processing conditions play a critical role in realizing the full capacities of these polyanion cathodes with more than one Li⁺ ion per Mⁿ⁺ ion. Novel solution-based synthesis approaches such as microwave-assisted solvothermal methods that can offer controlled nanomorphologies are pursued to maximize the electrochemical performances. The synthesized nanostructured polyanion cathodes are characterized by a variety of techniques including ex situ and in situ XRD, electron microscopy (SEM, TEM, and STEM), X-ray photoelectron spectroscopy (XPS), time of flight – secondary ion mass spectroscopy (ToF-SIMS), and in-depth electrochemical measurements. In addition, the role of cation doping, segregation of certain doped cations to the surface, cation ordering, and morphology on the electrochemical properties of 4.7 V spinel cathodes will be investigated. Based on the characterization data gathered, a fundamental understanding of structure-composition-property-performance relationships will be developed.

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

**EXPECTED STATUS SEP. 30, 2012:** Development of (i) novel synthesis approaches to obtain high-capacity, high-voltage polyanion (silicate and phosphate) cathodes with unique nanomorphologies, (ii) an understanding of the factors that control the performance of high-voltage (4.7 V) spinel oxide cathodes, and (iii) an understanding of their structure-composition-property-performance relationships.

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

**MILESTONES:**
(a) Understand the role of cation doping, surface modification, and morphology on the electrochemical properties of 4.7 V spinel cathodes. (Dec.11) Complete
(b) Perform surface characterization of LiFe₁₋ₓCoₓPO₄ with various x by XPS and ToF-SIMS. (Jun. 12) On schedule
(c) Perform novel synthesis and characterization of Li₂MSiO₄ and their solid solutions. (Sep. 12) On schedule
PROGRESS TOWARD MILESTONES

Previous efforts focused on how the cation ordering between Mn$^{4+}$ and Ni$^{2+}$ in the octahedral sites of the undoped and doped high-voltage LiMn$_{1.5}$Ni$_{0.5}$O$_4$ spinels influenced the cycle performance. A more detailed analysis of the electrochemical behavior was carried out using the dQ/dV plots (Q and V refer to specific capacity and voltage) of a highly-ordered undoped LiMn$_{1.5}$Ni$_{0.5}$O$_4$ spinel and a highly-disordered doped LiMn$_{1.5}$Ni$_{0.42}$Fe$_{0.08}$O$_4$ spinel (Fig 1a-b). The wider voltage gap between the oxidation and reduction dQ/dV peaks at ca. 4.7 V for the ordered spinel indicated higher polarization due to lower electronic and/or Li-ion conductivity. Moreover, the voltage gap between the oxidation and reduction peaks of the ordered LiMn$_{1.3}$Ni$_{0.5}$O$_4$ increases during the first 50 charge-discharge cycles, indicating a continuous increase in polarization. This is reflected in an increase in the charge transfer resistance during cycling (Fig. 1c). In contrast, the disordered LiMn$_{1.5}$Ni$_{0.42}$Fe$_{0.08}$O$_4$ spinel exhibited lower polarization without much of an increase in polarization or charge transfer resistance during cycling.

Additionally, the dQ/dV peaks in the 4.0 V region of the ordered, undoped LiMn$_{1.5}$Ni$_{0.5}$O$_4$ spinel exhibited an asymmetry in its intensity: The reduction peak area was larger than the oxidation peak area, and the ratio of the reduction peak area to the oxidation peak area increased on cycling. It appears that a certain amount of Mn$^{4+}$ ions in the ordered spinel is reduced to Mn$^{3+}$ during discharge; then a fraction of the generated Mn$^{3+}$ ions leaches out prior to the subsequent oxidation cycle. The net result is capacity fade. In contrast, for the disordered, doped LiMn$_{1.5}$Ni$_{0.42}$Fe$_{0.08}$O$_4$, the ratio of the reduction peak area to the oxidation peak area is almost constant during cycling, resulting in excellent capacity retention.

The thermal stability of undoped LiMn$_{1.5}$Ni$_{0.5}$O$_4$ with different morphologies by DSC and the results were correlated to surface area and Mn$^{3+}$ content (Fig. 2). The thermal stability deteriorates, as indicated by the increase in enthalpy and decrease in onset temperature, with increasing surface area. It is believed that the larger surface area induces more extensive SEI reaction, resulting in poorer thermal stability. The data also indicate an increase in thermal stability with increasing Mn$^{3+}$ content, which could be related to the decrease in Ni content in the samples as indicated by the ICP analysis as the Ni$^{4+}$/Ni$^{3+}$ redox couple on the surface is known to cause the oxidation of electrolyte.

Future work will focus on the surface properties of the undoped and Cr-, Fe-, and Ga-doped spinels with differing degrees of cation ordering and surface segregation that can sensitively influence the reaction of the cathode surface with the electrolyte.
TASK 4.5 – 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: Our approach is to develop high-energy cathode materials through a cost effective synthesis process. Appropriate doping, surface treatment and the identification of the electrolytes/additives will be used to improve the electrochemical performance of high voltage LiNi₀.₅Mn₁.₅O₄ based cathode. This high voltage cathode will be further combined with layer cathode to form a composite electrode with ‘layered-spinel’ structure. The experience and technologies developed in the high-capacity composite cathode will be used to further improve the capacity and stability of composite cathode.

STATUS OCT. 1, 2011: High-voltage LiNi₀.₅Mn₁.₅O₄ doped with Cr has been synthesized by a facile approach suitable for mass production. The reversible capacity is around 130mAh/g from the doped spinel, which exhibits a stable cycling for more than 100 cycles in half cells. The thermal stability investigation for electrochemically cycled LiMnPO₄ electrodes has been completed. The MnPO₄ reduction to Mn₂P₂O₇ with oxygen evolution was observed only at a temperature higher than 490°C, while the charged MnPO₄ undergoes structure distortion at above 180°C, possibly because of the Jahn-Teller effect accompanied by the decomposition of the passivation film formed on the cathode surface. Investigation of the electrochemical performance of non-stoichiometric LiMnPO₄ will be completed.

EXPECTED STATUS SEP. 30, 2012: High-energy cathodes for Li-ion battery applications will be further explored. Using rheological phase reactions that involve only milling and heating processes and are suitable for scale up, layered composite cathodes based on xLi₂MnO₃•(1-x)LiMO₂ (M=Mn, Ni, Co, x = 0.3-0.5) will be synthesized and their degradation mechanism will be investigated. The performance of high-voltage spinel LiNi₀.₄₅Cr₀.₅Co₁.₅O₄ will also be further improved. Safety, power rate, and cycling stability of these cathode materials will be improved to satisfy the need for HEV/EVs applications.

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

MILESTONES:
(a) Synthesize and electrochemically evaluate Li₂MnO₃•x as a baseline. (Mar. 12) Complete
(b) Utilize rheological phase synthesis of layered composite cathode with 200 mAh/g capacity and stable cycling performance. (Sep. 12) On schedule
(c) Optimize the synthesis approach and inactive components for the high-voltage spinel and composite cathode. (Sep. 12) On schedule
PROGRESS TOWARD MILESTONES

Li$_2$MnO$_3$ has been synthesized and evaluated by various approaches during this quarter. These investigations have set up a baseline to further understand the evolution of Li$_2$MnO$_3$ in the layered composites. The effects of PVDF coating on Celgard 2500 monolayer polypropylene (PP) separator for high voltage cathode materials were also investigated.

Baseline Li$_2$MnO$_3$ was synthesized from Li$_2$CO$_3$ and MnCO$_3$ in a molar ratio of 1:1. After heat treatment at different temperatures, a pure phase of Li$_2$MnO$_3$ was formed as indicated by the XRD in Fig. 1a. However, the reversible capacities of Li$_2$MnO$_3$ varied significantly among samples calcined at different temperatures, as shown in Fig. 1b. Li$_2$MnO$_3$ heated at 700°C delivered the highest reversible capacity of 175 mAh/g along with a relatively stable cycling for the first 35 cycles. Large gaps were observed between charge and discharge in the first few cycles for all three samples shown in Fig. 1b. The low coulombic efficiency in the beginning was closely related to the release of oxygen, which is also the reason for the oxygen generation in the layered composite. Investigation of the Li$_2$MnO$_3$ component simplifies the system and provided informative clues to address the challenges of the composite material.

In the last quarter the PVDF coating on a Celgard 2500 separator was reported to largely improve the stability of a PP-based membrane at high voltage. SEM images in Fig. 2 show that a PVDF coating does not completely cover the Celgard 2500 surface; therefore phosphorus elements in the form of P-O and P-F bonding originating from the decomposition of LiPF$_6$ were detected by FTIR before and after the PVDF coating. However, the main disadvantage of the PP-based separator is that PP itself was oxidized at high voltage and reacted with the electrolyte components, such as LiPF$_6$, leading to an increased impedance of the cell (as indicated by HOMO energy calculations and experimental observations). After applying a PVDF coating on Celgard 2500, direct contact between PP and LiPF$_6$ was largely reduced, and thus the electrochemical behavior was greatly improved.

**Collaborations:** Dr. Xiao-Qing Yang at BNL for XRD characterizations. Dr. Kang Xu at Army Research Lab for new electrolyte. Prof. Whittingham at SUNY Binghamton for magnetic measurements.

**Publication:**
Task 4.7- PI, INSTITUTION: Jordi Cabana, Lawrence Berkeley National Laboratory


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

STATUS OCT. 1, 2011: Samples of LiNi₁/₂Mn₃/₂O₄ with morphology decoupled from the crystal chemistry (Mn³⁺ content, Ni-Mn ordering) were successfully synthesized. Annealing of the samples provided control of these parameters. Analysis of their electrochemical properties as battery electrodes revealed that seemingly small variations among samples produce significant effects on electrochemical performance.

EXPECTED STATUS SEP. 30, 2012: The composition and crystal structure of the annealed samples of LiNi₁/₂Mn₃/₂O₄ will have been analyzed by coupling spectroscopic tools with diffraction. The role of oxide additives on the performance of spinel electrodes will have been assessed. The first set of new fluoride-containing phases will have been prepared and their applicability as Li battery cathodes will have been established.

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

MILESTONES:
(a) Complete the crystal-chemical characterization of annealed LiNi₁/₂Mn₃/₂O₄ and identify its role on electrochemical performance. (Mar. 12) Complete
(b) Synthesize and physico-chemically characterize at least two different new phases showing an oxyfluoride network, containing lithium and a light transition metal. (Sep. 12) On schedule
(c) Identify the influence of oxide additives on the extent of electrolyte-electrode side reactions in spinel electrodes. (Sep. 12) On schedule
PROGRESS TOWARD MILESTONES

During the second quarter of FY12, the characterization of LiNi$_{1/2}$Mn$_{3/2}$O$_4$ annealed at different temperatures, from 500 to 900°C, in air or O$_2$ for 12 h, after an initial synthesis step at 900°C for 1 h was completed. The result is a collection of samples with the same microstructure and surface area. As expected, differences were observed in the Mn$^{3+}$, as determined from the capacity obtained at 4 V during charge, meaning the samples are better defined as LiNi$_{1/2-x}$Mn$_{3/2+x}$O$_4$, based on our previous work. Differences were also observed in the degree of Ni/Mn disorder, which is also supported by our previous knowledge of an order/disorder transition at 700°C. Such differences were probed by $^6$Li MAS NMR and found to be in agreement with the separation between the two high voltage plateaus typically observed during Li (de)intercalation: higher $\Delta V$ was found for the more disordered samples.

The rate capability of these 11 samples was tested. A clear divide between disordered and ordered samples was found (Fig. 1). In contrast, the Mn$^{3+}$ varied notably in the case of the disordered samples, and almost did not change for the ordered ones. These results hinted at the fact that, contrary to what is commonly believed in the field, the presence of this ion does not critically determine rate capability. Further evidence was provided when cycling the same sample using two different discharge cutoff voltages, 3.5 and 4.4 V. The first enables the Mn$^{3+}$/Mn$^{4+}$ redox activity, whereas the second does not. Therefore, in the second case, Mn$^{3+}$ was not regenerated during cycling. The results at different rates showed very similar capacity retention. This work was done in coordination within the BATT Ni/Mn Spinel Focus Group.

Collaborations: Prof. Grey (SUNY Stony Brook), Prof. Manthiram (UT-Austin), Drs. Persson, Dong, Doeff, Richardson, Chen, Guo, Yang, Kostecki (LBNL), Dr. Casas-Cabanas (CIC Energigune, Spain), Dr. Chernova, Prof. Whittingham (SUNY Binghamton), Drs. Barenco, Bloom (ANL).

Presentations:
Task 4.8 - PI, INSTITUTION: Jason Graetz, Brookhaven National Laboratory

TASK TITLE: Cathodes – Novel Materials

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF$_6$+EC:DEC (1:2)/Toda high-energy layered (NMC)

BARRIERS: Low energy density and cost

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

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

STATUS OCT. 1, 2011: This project is a new start. All equipment and plans are in place for the initial project tasks.

EXPECTED STATUS SEP. 30, 2012: In Year 1 the existing quartz capillary reactor will be modified to accommodate higher pressures and temperatures. A procedure for the synthesis of LiMBO$_3$ (M = Mn and/or Fe) will be developed and complete preliminary electrochemical measurements.

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

MILESTONES:
(a) Complete design and order necessary components for second-generation capillary reactor capable of accommodating higher pressures and temperatures. (Apr. 12) On schedule
(b) Develop a procedure for the synthesis of LiMBO$_3$ (M = Mn and/or Fe). (Sep. 12) On schedule
(c) Complete preliminary characterization of synthesis reaction(s) using the in situ capillary reactor. (Sep. 12) On schedule
PROGRESS TOWARD MILESTONES

This project is expected to start in April 2012. Efforts in the second quarter of FY12 were focused on recruiting and training a new graduate student (Stony Brook University) who will begin working on this project. Preliminary studies will focus on developing and optimizing a hydrothermal synthesis procedure for CuV$_2$O$_5$ via in situ synchrotron diffraction studies. The preliminary chemicals and equipment needed for the project were procured and seven days of synchrotron XRD beam-time was allocated for this project in April.
BATT TASK 5
DIAGNOSTICS

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

TASK TITLE - PROJECT: Diagnostics – Interfacial Processes

BASELINE SYSTEMS: Conoco Philips CPG-8 Graphite/1 M LiPF$_6$+EC:DEC (1:2)/Toda high-energy layered (NMC)

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

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

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

STATUS OCT. 1, 2011: Insight into the mechanism of surface phenomena on thin-film and monocrystal Sn and Si intermetallic anodes is expected to have been gained and their impact on the electrode long-term electrochemical behavior is expected to have been evaluated. Comprehensive fundamental study of the early stages of SEI layer formation on polycrystalline and single crystal face Sn and Si electrodes will be carried out. In situ and ex situ far- and near-field FTIR and Raman spectroscopy will be employed in conjunction with AFM surface imaging will be applied to detect and monitor surface phenomena at the intermetallic anodes. Similar experimental methodology will be used to detect and characterize surface and bulk processes in high-voltage (>4.3V) model and composite cathodes.

EXPECTED STATUS SEP. 30, 2012: The mechanism of electrolyte decomposition at the surface of model anode and cathode materials is expected to be fully understood and its impact on the electrode long-term electrochemical behavior evaluated. The composition and (re)formation dynamics of the surface layer on model monocrystal Sn and Si intermetallic anodes as well as on model single particle and composite high-voltage cathodes will be determined using various complementary spectroscopy techniques. A unique strategy involving the use of in situ techniques (AFM, ellipsometry, Raman and fluorescence imaging, FTIR and AP-XPS) in conjunction with ex situ techniques (XAS, RBS and NRA) will be applied to monitor and identify surface processes. Preliminary evaluation of near-field optical spectroscopy and imaging techniques for fundamental interfacial studies of Li-ion systems will be carried out.

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

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

In the 2nd quarter of FY12, studies continued to address surface phenomena of high-voltage cathode LiNi_{0.5}Mn_{1.5}O_4 spinel (LMNO) using in situ spectro-electrochemical techniques as part of work toward milestone (b). In situ fluorescence spectroscopy, an indicator of electrolyte decomposition, was applied to both LiMn_2O_4 (LMO) spinel particles and a carbon black electrode with the purpose of identifying the components involved in the formation of fluorescent species in composite cathodes with 1 M LiPF_6:EC:DEC (1:2 w/w) electrolyte.

**In situ** fluorescence data was collected from a LMO aggregate pressed on Al as it was cycled three times between 3.5 and 4.6 V (Fig. 1-blue). The twin peaks observed during the anodic sweeps at 4.07 and 4.17 V correspond to the Mn^{3+/4+} oxidation reaction. The fluorescence does not show any significant changes during cycling, in contrast to the 70 times increase in fluorescence that was previously observed on LMNO particles cycled to 5 V, or a five times increase as measured on LMNO at 4.6 V (Fig. 1-red). This indicates that Ni and Mn exhibit dramatically different electrocatalytic behaviors toward electrolyte decomposition, despite residing in the same spinel lattice, even at equivalent potentials.

Fluorescence measurements recorded during cycling between 3.5 and 5 V of a 90% carbon black/10% PVdF electrode (Fig. 2) show a large jump in fluorescence intensity with a rise in current at ca. 4.1 V, highlighting the contribution to the fluorescence of non-active components in a composite electrode. Similar jumps in fluorescence following rises in anodic current during the 2nd and 3rd cycles confirm the close relationship between the electrochemical side reactions and the generation of fluorescent species.

Interestingly, on the 2nd and 3rd cycles, the cumulative irreversible capacity drops to 44 and 3.6%, respectively, relative to the 1st cycle. This indicates that passivation of the carbon surface may be limiting the extent of electrolyte decomposition. This is supported by the smaller maximum jumps in fluorescence intensity on the 2nd and 3rd cycle of 40 and 36% relative to the 1st cycle. In contrast, the fluorescence intensity of the 2nd and 3rd cycles from LMNO rose to 81 and 96% of the 1st cycle, respectively. These results suggest the important role that carbon may play in reducing catalytic decomposition of electrolyte on an active material like LMNO. Progress toward milestones (a) and (c) are on schedule.

**Figure 1.** Electrochemical data (top) and corresponding integrated fluorescence intensity (bottom) collected during three CV cycles between 3.5 and 4.6 V for LMO (blue) and during the first linear sweep to 5.0 V for LMNO (red).

**Figure 2.** Electrochemical data (top) and corresponding integrated fluorescence intensity (bottom) collected during three CV cycles between 3.5 and 5.0 V for a 90% Denka Black/10% PVDF electrode.
TASK 5.2 - PI, INSTITUTION: Xiao-Qing Yang and Kyung-Wan Nam, Brookhaven National Laboratory

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

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

BARRIERS: PHEV: Energy density, cycle life; HEV: power density, abuse tolerance

OBJECTIVES: To determine the contributions of electrode materials changes, interfacial phenomena, and electrolyte decomposition to cell capacity and power decline in helping the development of high energy density lithium battery with better safety characteristics and longer life.

GENERAL APPROACH: To use various synchrotron based X-ray techniques to characterize electrode materials and electrodes taken from baseline BATT Program cells. *Ex situ* soft XAS will be used to distinguish the structural differences between surface and bulk of electrodes. Time resolved X-ray diffraction (TRXRD) technique will be used to understand the reactions that occur in charged cathodes at elevated temperatures.

STATUS OCT. 1, 2011: Studies on high energy Li₁₂Ni₀₂Mn₀₆O₂ cathode materials during charge-discharge cycling using combined *in situ* hard XAS and *ex situ* soft XAS will be completed. Important information about the roles of Mn cations will be obtained. The in situ XAS and XRD studies on mesoporous LiFe₁₋₊ₙMnₙPO₄ (0.0≤ₙ≤0.8) cathode materials during charge-discharge cycling will be completed. The effects of particle size and morphology on the phase transition behavior and performance of Li-ion cells will be obtained.

EXPECTED STATUS SEP. 30, 2012: Structural studies on the high energy density Li₂MnO₃-LiMO₂ (M = Ni, Mn, Co) layered materials (in collaboration with ANL) and *in situ* XRD studies on different types of lithium iron phosphate cathode materials with mesoporous structure will be carried out. The diagnostic studies of high voltage LiMn₂₋ₓMₓO₄ (M= Ni, Cu etc.) with spinel structure will be completed. Diagnostic studies on high energy density anode materials, such as Si, Sn and alloys will also be conducted.

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

MILESTONES:
(a) Complete *in situ* XRD studies of LiMn₀.₄Fe₀.₆PO₄ cathode material with different particle size and morphology during electrochemical delithiation. (Apr. 12) **Complete**
(b) Complete *in situ* XRD studies of Li₂CO₃ during electrochemical decomposition and the potential application of this process. (Apr. 12) **Complete**
(c) Complete *in situ* XAS studies of high voltage LiMn₂₋ₓMₓO₄ (M= Ni, Cu etc.) with spinel structure cathode materials during electrochemical cycling. (Sep. 12) **On schedule**
PROGRESS TOWARD MILESTONES

In the 2nd quarter of FY2012, research at BNL was focused on a comparative study of the structural changes during electrochemical charge-discharge cycling of two LiMn_{0.4}Fe_{0.6}PO_4 cathode materials with different particle size and morphology. Milestones (a) and (b) have been completed. In collaboration with Prof. Hong Li and his research group at the Institute of Physics (IOP), Chinese Academy of Sciences (CAS), in situ and ex situ XRD studies on LiMn_{0.4}Fe_{0.6}PO_4 samples with mesoporous structure (Meso-46) and without mesoporous structure (Bulk-46) were carried out. The phase transformation behaviour is quite different. The ex situ XRD results for Bulk-46 and Meso-46 are plotted in Fig. 1. Different cells were charged to different Li contents at a constant C/25 rate and then relaxed for about 24 hours. Six charge states A’, B’, C’, D’, E’, and F’ are marked on the corresponding charge curve in Fig. 1-a1 and the corresponding ex situ XRD patterns are plotted in Fig. 1-b1. The peaks of the original, intermediate, and final phases are plotted with black, red, and blue colors, respectively. XRD patterns show two two-phase transformation features with clear peak separations between the original and the intermediate phase (as well as between the intermediate and the final phase). Therefore, for the Bulk-46 sample, the original phase has no detectable solid-solution region and the 2-phase reaction takes place in the first plateau and the solid solution of the intermediate phase covers a wide range on the charge curve including both plateaus. In the second plateau to the end of the charge curve, the 2-phase reaction between the intermediate phase and the final phase takes place followed by the single phase region of the final phase. In contrast, the ex situ XRD results for Meso-46 sample shown in Fig. 1-b2 are quite different. Significant shifts of the Bragg peaks to higher two-theta angles are observed. It should be noted that significant peak width broadening and intensity reduction occurred at charge state B. At charge state C, a single phase is observed at this transition region between the two plateaus. The results in the second plateau at charge state D are similar to those at state B in the first plateau, showing reduced intensity and a broadened peak width. From charge state D to state E and F at the end of charge, the system exhibits a single phase behavior with continued peak position shifting. The reduced intensity and broadened peak width at charge state B and D are right at the middle of the first and second plateaus, giving hints about the possible unresolved peaks for two phases. More detailed studies with slower charge rates and more data collected near these points to further clarify the present interpretation.

Figure 1 Ex situ XRD results for bulk and mesoporous LiMn_{0.4}Fe_{0.6}PO_4 at different charged states.
**TASK 5.3 - PI, INSTITUTION:** Gerbrand Ceder, Massachusetts Institute of Technology, and Clare Grey, Cambridge University

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

**BASELINE SYSTEMS:** Conoco Philips CPG-8 Graphite/1 M LiPF$_6$+EC:DEC (1:2)/Toda high-energy layered (NMC)

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

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

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

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

**EXPECTED STATUS SEP. 30, 2012:** Completed $^{29}$Si studies of lithium silicides and phosphocarbonates. Insights into viability of several Na cathodes.

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

**MILESTONES:**
(a) Complete $^{29}$Si NMR experiments on crystalline lithium silicides. (Mar. 12) Complete
(b) Complete electrochemical testing of sidorenkites for Li and Na batteries. (Mar. 12) Complete
(c) Complete NMR studies of metal doping of LiMnPO$_4$ (Mar. 12) Complete
(d) Complete work on novel intercalation of LiMnPO$_4$ (Mar. 12) Complete
(e) Complete $^{29}$Si NMR of amorphous lithium silicide electrodes. (Sep. 12) On schedule
(f) Initiate *in situ* NMR studies of SEI formation on silicon anodes; complete lithium dendrite study. (Sep. 12) On schedule
(g) Suggest at least one new Na intercalation compounds. (Sep. 12) On schedule
(h) Provide computed data on pyrophosphates to Whittingham (Sep. 12) Complete
High voltage spinels. In collaboration with Jordi Cabana (LBNL) and Stan Whittingham (Binghamton), $^6$Li and $^7$Li MAS NMR spectroscopy were used to characterize a series of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ samples synthesized by Jordi. The results clearly show that NMR is very sensitive to the degree of ordering. Samples prepared at low temperatures (500ºC) show broad NMR resonances presumably due to kinetic limitations associated with the formation of an ordered phase. The signals sharpen and fewer resonances are observed as the calcination temperature approaches the order-disorder temperature (700ºC). The spectra just before this temperature can be modeled by assuming Ni-Mn ordering, resulting in the structure with the P4$_3$32 space group but allowing for some disorder between the two transition-metal sites of this structure. The results are consistent with the diffraction results (neutron diffraction studies performed by M. Casas-Cabanas). The spectra become broader and contain multiple peaks above 700ºC as the disorder increases. A shift to lower frequencies is observed which is consistent with increased Mn$^{3+}$ in the sample and also the formation of a rock salt phase (seen by XRD and electron microscopy). The NMR spectroscopy of these and a wider series of samples are being correlated with the electrochemical properties to understand the role that local structure plays in controlling performance.

NMR Studies of Coatings. A study of layered Li[Li$_{1/3}$Ni$_{1/3}$Mn$_{5/3}$]O$_2$ positive electrodes nominally coated with aluminum fluoride was completed. Coatings were prepared by using aluminum fluoride aqueous solutions with 0.25 to 10.0 mol% AlF$_3$ and compared with samples treated under similar conditions but with aqueous HCl solutions. Samples were investigated following heat treatment at 120 and 400ºC XRD, TEM, and both $^6$Li and $^{27}$Al magic angle spinning (MAS) NMR spectroscopy. The TEM/EDS and $^{27}$Al NMR data provide support for an Al-rich amorphous coating that, following drying at 120ºC, comprises six coordinated, partially-hydrated Al environments containing no more than one or two fluoride ions in the Al local coordination sphere. Heat treatment at 400ºC results in a phase that resembles partially-fluorinated $\gamma$- or $\gamma'$ Al$_2$O$_3$, at least locally. An Al:F elemental ratio of 2:1 is obtained in stark contrast to the ratio used in the original solution (1:3). The acidic coating procedures result in significant structural rearrangements of the bulk. The results highlight the need to distinguish between, the effect of the coating itself and the structural (bulk) effects induced by the coating method, on the resulting electrochemical performance.

Figure 1. $^6$Li MAS NMR spectra of “LiNi$_{0.5}$Mn$_{1.5}$O$_4$” samples as a function of calcination.

Figure 2. $^{27}$Al MAS NMR (isotropic resonance) of coated samples and comparison with crystalline AlF$_3$.
Task 5.4 - PI, INSTITUTION: Yang Shao-Horn, Massachusetts Institute of Technology

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

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

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

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

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

STATUS OCT. 1, 2011: Select (Li₂Oₓ)ₓMO₂ electrodes will be prepared and tested in two-electrode and three-electrode cells having lithium as the negative electrode, where the activity of MO₂ such as MnO₂ and Co₃O₄ for Li₂Oₓ oxidation will be compared with that of the state-of-art precious metal catalysts such as Pt/C.

EXPECTED STATUS SEP. 30, 2012: The influence of some metal oxide catalysts on the charging voltage of such high-energy electrodes has been established and compared with Pt/C. Changes in the microstructure and crystal structure of select (Li₂Oₓ)ₓMO₂ electrodes have been identified by scanning or transmission electron microscopy and X-ray diffraction. Application of fundamental insights to design of new and stable surfaces for high-energy cathodes will be ongoing.

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

MILESTONES:
(a) Complete XPS analysis of the surface chemistry changes of LiNi₀.₅Mn₁.₅O₄ cycled to two voltages and compare with the surface chemistry changes of LiₓCoO₂ and LiNi₀.₅Mn₀.₅O₂. (Jun. 12) On schedule
(b) Demonstrate the oxide catalyst influence on the capacities, discharge/charge voltages or cycle life of (Li₂O₂)ₓ(MO₂)ₘ (where M = Mn, Co, Ni, etc.) in lithium cells. (Jun. 12) On schedule
(c) Supply XPS and TEM data demonstrating the surface chemistry and morphological changes of (Li₂O₂)ₓ(MO₂)ₘ during charge and discharge. (Sep. 12) On schedule
PROGRESS TOWARD MILESTONES

The high overpotential required to charge Li/O2 cells remains an important impediment to the development of Li/air batteries. In addition, variability in the discharge behavior and composition of Li/O2 cells adds further uncertainty in determining the intrinsic charging activity of the catalysts. Separating the effects of changes in discharge product from changes in electrode composition requires a greater understanding of the discharge process than is currently available. Vulcan XC72 carbon-based electrodes (VC) were developed in which commercially available Li2O2 particles were introduced into the electrode during fabrication. In this study, the electrochemical oxidative activity of Li/Li2O2 cells with unmodified VC and VC decorated with Au nanoparticles were compared.

All electrodes consisted of a VC or 40 wt% Au on VC (Au/C) carbon structure containing lithiated Nafion® as a binder and mixed with Li2O2 under Argon before casting it on Al. For both catalysts, electrodes were prepared with Li2O2 (denoted by “+Li2O2”, e.g., Au/C+Li2O2) and without Li2O2, which was used to quantify the background current.

The electrodes were charged potentiostatically at voltages between 4.0 and 4.4 V vs. Li (V Li) in 0.1 M LiClO4 in DME. For both electrodes containing Li2O2 and at each voltage, the net current was calculated by subtracting the background current due to reactions not involving Li2O2. Integrating the net current with respect to time gave the capacity of the electrode associated with Li2O2 oxidation.

VC was found to become active in catalyzing the oxidation of Li2O2 at 4.0 V Li and higher. The net oxidation current obtained from VC+Li2O2 was found to significantly increase with increasing applied potentials, as shown in Fig. 1a. A maximum current of 20 mA/gcarbon was reached at 4.0 V Li while 1000 mA/gcarbon was obtained at 4.4 V Li. Au/C was found to be no more active in catalyzing the oxidation of Li2O2 than VC. The net oxidation current densities obtained from Au/C+Li2O2 electrodes at select applied potentials are shown in Fig. 1b.

XRD and SEM analyses show that Li2O2 could be removed completely upon charging, which confirms that the measured oxidation currents in Fig. 1 are associated with oxidation of Li2O2.

Collaborations: Collaborations with A. Mansour at the NSWC for XPS and XAS measurements through a subcontract with MIT will be continued. Collaborations will continue with M. Thackeray (ANL) using TEM and XPS to study the atomic structure and surface chemistry, respectively, of layered LiₙNiₓMnₙO₂ materials.
BATT TASK 6
MODELING

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

TASK TITLE – PROJECT: Modeling - Improved Electrochemical Models

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

BARRIERS: Poor transport properties, capacity and power fade


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

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

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

MILESTONES:
(a) Obtain AFM and ferrocene kinetic measurements of SEI on HOPG. (Dec. 11). Complete/canceled
(b) Compare through-film ferrocene kinetics for SEI formed in presence of VC and FEC. (Apr. 12) On schedule
(c) Develop model to explain current-time curves for film formation. (Aug. 12) On schedule
PROGRESS TOWARD MILESTONES

Efforts continued to expand our method of SEI characterization to study the effect of formation voltage on the ability of the SEI to passivate against ferrocene. Our previous work studied the SEI formed on glassy carbon at 0.6 V vs. Li/Li⁺. By varying the formation voltage, the conditions found in an actual Li-ion battery were expanded, and more was learned about the nature of the SEI formation reactions.

Figure 1 shows the formation charge vs. time (Q-t) at different formation potentials. As the formation potential decreases from 0.9 to 0.3 V, the SEI formation current increases at all times. Close overlap between data points measured for the same time shows good reproducibility between experiments. Previously, problems with irreproducible Q-t curves, especially at lower potentials, were observed. In Q2, it was found that a combination of oxidizing the surface at high voltage and allowing the electrode to equilibrate before beginning SEI formation allowed for the successful acquisition of reproducible Q-t formation curves. Figure 2 shows the rate constant for through-film ferrocene reduction vs. the formation charge on a log scale. The different series of data correspond to different formation potentials. As potential decreases, the SEI becomes more passivating even after accounting for the amount of charge passed; e.g., forming the SEI for 60 min at 0.6 V and 30 min at 0.45 V will produce approximately 10 mC/cm² of product; however, the product of reaction at 0.45 V will block the electrode to ferrocene much more effectively. Figure 2 clearly indicates that SEI reaction products differ strongly with voltage, and that the products formed at higher voltage do not contribute greatly to passivation. In the next quarter, the plan is to expand the data series to 0.1 V, close to the operating potential of graphite, and to formalize and publish our arguments about the nature of passivation.

Figure 1: SEI formation charge increases at lower potential, as expected. Reproducibility between trials is very good.

Figure 2: Rate constant for through-film ferrocene reaction decreases with increased formation charge for all formation potentials, but products formed at lower potentials passivate the electrode much more strongly.
TASK 6.2 - PI, INSTITUTION: Venkat Srinivasan, Lawrence Berkeley National Laboratory

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

BASELINE SYSTEMS: Conoco Philips CPG-8 Graphite/1 M LiPF$_6$+EC:DEC (1:2)/Toda high-energy layered (NMC)

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

OBJECTIVES:
1. Quantify power limitations in porous cathodes and its relationship to design.
2. Develop a model to account for porosity in electrode secondary particles and quantify effect on performance
3. Develop a model for mechanical degradation of electrodes with consideration of particles and binder.

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

STATUS OCT. 1, 2011: A preliminary model that quantifies the importance of incorporating binder effects in predicting failure of particles will be complete. The impact on low volume change systems like graphite and high volume change systems like silicon will be examined. The rate capability of NCM cathodes on a particle scale will be quantified and the relevant transport properties measured.

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

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

**Modeling NMC Cathode:** In the last quarter, the rate limitations in NMC electrodes were studied on the porous-particle scale. The Bruggeman relation, which relates the porosity ($\varepsilon$) and tortuosity ($\tau$) of the electrode, was examined to explore the diffusion limitation in the solution phase. It was found that a value of 5.5 for the Bruggeman exponent (as opposed to the exponent of 1.5 often used in the literature) is needed in order to fit the experiment at a rate up to 5C. The result suggested that the effective conductivity and ionic diffusion coefficient are smaller than that predicted by the Bruggeman equation.

In this quarter, a generalized Bruggeman equation, $\tau = \gamma \varepsilon^{1-\alpha}$, was used to correlate the electrode tortuosity with porosity. The scaling factor $\gamma$ and the exponent $\alpha$ were adjusted to estimate the tortuosity, and further, the effective electrolyte properties in the porous electrode model. Note that as long as the ratio of porosity to tortuosity ($\varepsilon/\tau$) is fixed, the discharge curves will be the same. A smaller $\varepsilon/\tau$ leads to a smaller effective conductivity and ionic diffusion coefficient, which resulted in model fits that were comparable to experiment at a rate up to 5C. However, the model was still unable to fit the potential at 10C.

Further, simulation results suggest that the pore distribution in the electrode determines the transport of Li ions in the solution phase. Therefore, future work will focus on understanding the pore structure and the homogeneity of the electrode through the use of X-ray tomography and the investigation of the transport of Li ions in the tortuous pores will continue.

**Understanding Mechanical Degradation in Silicon Anodes:** Mechanical degradation in electrodes is an important source of capacity fade, especially in silicon anodes. We are developing a simulation to investigate damage at the level of the electrode particles used in silicon anodes. We have re-implemented the model of Christensen and Newman (2006), which describes a spherical, isotropic electrode particle undergoing large deformation due to lithium insertion and removal. In this model, we have assumed that electrode particles consist of amorphous silicon. Our choice of an alternative coordinate system has facilitated the extension of this model with a binder layer of user-specified thickness on the surface of the electrode particle, with continuity of displacement and stress enforced at the interface between particle and binder. This implementation also includes the influence of composition on the Young’s modulus and Poisson’s ratio of the lithiated silicon, as obtained by Shenoy, Johari, and Qi (2010).

With the stress fields throughout the particle-binder system now available, we are currently investigating options for describing the accumulation of mechanical damage. One may use yield stress as a threshold for damage or integrate the more detailed models of damage mechanics or fracture mechanics. Due to variations among particles, ensembles of single-particle simulations should then be considered in order to draw inferences about the contribution of mechanical damage to capacity loss at the electrode scale. Also, the composition of the electrodes can change significantly within a single charge or discharge, so the use of a constant diffusion coefficient might introduce significant error. There is substantial disagreement in the literature about diffusion coefficient values, and results showing the influence of composition do not seem to be available for amorphous silicon at typical operating temperatures. Experimental work may be needed in order to address these concerns.
TASK 6.3 - PI, INSTITUTION: Ann Marie Sastry, University of Michigan

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

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

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

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

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

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

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

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

MILESTONES:
(a) Implement multiscale modeling for stresses in active material considering SEI layer. (Mar. 12) Complete
(b) Couple the 1D electrochemical model with a previously developed micro scale model. (May 12) On schedule
(c) Quantify variation in the mechanical properties of the SEI layer as a function of cycle number. (Aug. 12) On schedule
PROGRESS TOWARD MILESTONES

1) Intercalation- and Misfit-Induced Stress in the Graphite Electrodes
Anisotropic features in a graphite electrode were examined via electrochemical-mechanical modeling of a particle with multiple grains during a galvanostatic condition. The orientation of each grain was controlled with a fixed number of grains in the particle. Figure 1a shows the misorientation distribution for 5 different cases and the Li concentration distribution for case 1 and case 5, with the single grain case as the reference. Each misorientation distribution for each case was averaged with 5 different random generations. As the mean misorientation angle was increased, the concentration distribution became more irregular. As a result, the relative maximum principal stress was increased as the misorientation angle increased Fig. 1b.

2) Multiscale modeling with self-assembly and dissolution. Li-ion battery cell performance with different microstructures was explored using the macro/micro-coupled variational multiscale simulation. The volume fractions of the active material varied from 0.368 to 0.379, and, consequently, the corresponding interfacial area between solid and electrolyte phases changed. Figure 2a shows the voltage response at a 1C rate. Battery performance increased as volume fraction increased (DOD was increased by 3.16% when 3.14 V was set as the cut off). The performance improvement was closely related to the specific area: a higher specific area resulted in improved performance Fig. 2b.

3) Characterization of SEI layers.
The effect of the cathode surface layer on Mn dissolution was investigated via ICP-OES measurement. Surface layers were formed in the electrolyte with different additives (5 wt% FEC and 5 wt% VEC) during five days. The amount of the Mn dissolution was then observed as a function of time at different temperatures. Figure 3 shows Mn dissolution increased as both the temperature and the storage time increased. Also, the FEC-derived surface layer clearly resulted in relatively large Mn dissolution compared to the normal (without additive) surface layer. However, the VEC-derived surface layer showed a comparable effect on the Mn dissolution as compared to the normal surface layer.
TASK 6.4 - PI, INSTITUTION: Kristin Persson, Lawrence Berkeley National Laboratory

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

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

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

OBJECTIVES: 1) Predict new chemistries and crystal structures for improved electrodes as defined by the goals of USABC. 2) Understand diffusion-limiting behavior in current and novel electrode materials in order to suggest chemical or morphological improvements. 3) Understand surface interactions in electrode materials to optimize stability and kinetics.

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

STATUS OCT. 1, 2011: Evaluation of Al substitution effect on LiNi₀.₃Mn₀.₃Co₀.₃₄AlₓO₂ in terms of Li mobility and electronic conductivity has been concluded. The study of Li absorption on graphene and multi-layer graphene surfaces will be underway. The Li and cation interactions in LiNi₀.₃Mn₀.₃₂O₂ will be understood as a function of Li content. The materials genome web site is launched from LBNL.

EXPECTED STATUS SEP. 30, 2012: Li kinetics on graphene and multi-layer graphite is concluded. Electronic structure studies of surface facet stability of electrode materials (LiMnO₂ and LiFePO₄) will be underway. Phase diagram of LiNi₀.₃Mn₀.₃₂O₂ will be concluded. The study of Li kinetics and electronic structure of LiₓNi₀.₃Mn₀.₃₂O₂ as a function of Li content will be underway.

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

MILESTONES:
(a) Go online with the Materials Genome database from LBNL. (Oct. 11) Complete
(b) Map the electronic structure of LiₓNi₁/₂Mn₃/₂O₂ as a function of Li content. (Oct. 11) Complete
(c) Calculate the band structures of LiMnO₂ surfaces. (Dec. 11) Delayed to May 12
(d) Predict the stable phases of the Li-graphene and Li-multi-graphene. (Feb. 12) Complete
(e) Complete the phase diagram of LiₓNi₁/₂Mn₃/₂O₂. (Mar. 12) Delayed to Jun. 12
(f) Calculate the surface DOS of LiFePO₄ with different absorbents. (May 12) On schedule
(g) Complete the kinetics of Li-graphene. (Sep. 12) On schedule
PROGRESS TOWARD MILESTONES

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

Using the cluster expansion method and density functional theory calculations, a thorough investigation was performed of the stability of Li absorbed on a single-layer graphene vs. the two-phase separation into a single-layer graphene and metallic Li. Li interactions – both absorption and intercalation – also were examined with few-layer graphene to study how the Li-graphene system evolves from Li-graphene to Li-graphite. A semi-empirical potential is calibrated to account for the van der Waals interaction, which has a significant effect on the interactions between carbon atoms in the neighboring graphene layers.

For single-layer graphene, the cluster expansion method is used to systemically search the lowest energy ionic configuration as a function of absorbed Li content. In the calculations, a supercell consisting of a single-layer graphene with 4 by 4 primitive cells and 15 Å vacuum space in perpendicular to the graphene. The iteration of fitting-predicting converged after 87 DFT calculations with a resulting CV score of 8 meV/C and a root-mean-square error of 7 meV/C. For few-layer graphene, standard density-functional theory methods were combined with a semi-empirical potential to include the effect of van der Waals interactions. The Li absorption in few-layer graphene was compared with that of bulk graphite with interesting differences in the Li-C phases formed in the move from single-layer graphene, through multi-layer graphene, to graphite.

The large public database structure contained in the Materials Project (www.materialsproject.org) continues to be developed and expanded. Currently it is displaying over 200 Li intercalation paths with multiple voltage profiles, energy density, capacity, oxygen release, and crystal structure information; also presented is over 4000 Li conversion energy storage materials. Since its launch in October 2011, The Materials Project has over 2000 registered users, whereof approximately 25% are industry affiliated.

Figure 1. (a) Top view of single layer graphene and possible absorption sites indicated. (b) Side view of bulk graphite in stage II Li intercalation stage.