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November 19, 2014

Mr. Tien Q. Duong
3V/Forrestal Building
Office of Vehicle Technologies
U.S. Department of Energy
1000 Independence Avenue, S.W.
Washington D.C. 20585

Dear Tien,

Here is the fourth quarter FY 2014 report for the Batteries for Advanced Transportation Technologies (BATT) Program. This report and prior Program reports can be downloaded from <http://batt.lbl.gov/reports/quarterly-reports/>.

Sincerely,

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

Venkat Srinivasan
Acting Head
BATT Program

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Featured Highlights

Anodes

- ✦ Kumta (U. Pittsburgh) achieved excellent cyclability at over 1000 mAh/g from Si nanotubes modified with a carbon coating.
- ✦ Cui (Stanford) demonstrated a high loading, very cyclable Si-anode that consists of porous Si nanoparticles which aggregate to form microparticles coated with carbon.

Cathodes

- ✦ Zhang and Xiao (PNNL) used a hydrothermal-assisted solid synthesis to produce a Mn-rich material with uniform Ni content that results in very low voltage fade.

Diagnostics

- ✦ Grey (Cambridge) used NMR to show that Li_2S is formed early on in the discharge of a Li/S cell.

Modeling

- ✦ Persson (LBNL) showed through first principles calculations that Mn preferentially migrates to Li sites in Li_xMnO_3 when delithiated past $x < 1$ and is accompanied by a drop in voltage. She also showed that the O loses stability as lithium is removed but can not migrate in the bulk, and could leave the structure at the interface.
- ✦ Wheeler and Mazzeo (BYU) confirmed the electric conductivity measurements of their micro-four-line-probe and demonstrated that it has less variability in its measurement as compared to the spacial variability of the electrode.

Electrode Failure Benchmarking Analysis

PROJECT OBJECTIVE: This project is to support the BATT Focus Groups. The emphasis of this work will be on the High-Voltage Cathode Project and the Si Anode Project. If the difference in cycleability of NMO and NCM can be understood through identification of a difference in reaction products, then perhaps the cycleability of NCM at higher voltages can be improved. If differences between the side reactions on graphite and Si can be measured, then perhaps the Si surface can be modified to allow for long-term full cell cycleability comparable to that of cells containing graphite.

PROJECT IMPACT: Success with understanding and improving the stability of NCM in the presence of electrolyte at voltages greater than 4.3 V vs. Li/Li⁺ will translate to an increase in capacity and voltage and hence a compounding improvement in energy density. Improvement in the passivating effects of SEI on Si that allows for long term cycleability, would result in larger fractions of Si in the anode and improved energy density of high-capacity cathode cells.

OUT-YEAR GOALS: The goal of this project is to support the High-Voltage Focus Group, which is to understand the limits of cycleability of NCM as the voltage is increased. This project will provide electrochemical and chemical data to support that effort. The other goal of the project is to support the Si Anode Focus Group, which is to effectively use Si in a battery. This project will provide electrochemical and chemical data to support that effort.

COLLABORATIONS: None this quarter.

Milestones

- 1) Make a pouch cell with the same cycling behavior as a coin cell. (Dec. 13) **Complete.**
- 2) Go/No-Go: Generate measurable levels of soluble reaction products. Criteria: Evaluate one of the proposed experimental test set-ups for its ability to generate measurable levels of soluble reaction products. (Mar. 14) **Go**
- 3) Demonstrate a 3-electrode cell where the impedance data of the individual electrodes can be directly assigned to the full cell data. (Jun. 14) **Complete**
- 4) Measure the gas composition of a high voltage cell. (Sep. 14) **Ongoing**
- 5) Measure the gas composition of a Si-anode cell. (Sep. 14) **Ongoing**

Progress Report

Milestones 4 and 5. In the first quarter, the ability to produce pouch cells that cycle as well as coin cells was demonstrated. In the second quarter, the ability to capture a significant quantity of gas for analysis was shown. Since then, several attempts have been made to reliably extract the gas from the pouches without contamination, but with limited success. This will be pursued into the next quarter until complete. It is believed that the gas composition may change as the voltage of a cell exceeds 4.3 V, thus, capturing and analyzing the gas from a functional cell may play a critical role in understanding cell behavior above 4.3 V.

With regard to improving the ability to assess failure mechanisms of cells, the rate of side reactions on Si and the rate of material isolation were determined. If the charge and discharge endpoints of a half-cell are plotted with respect to time, then these points will describe a line with a slope equivalent to the rate of side reactions +/- (the rate of particle isolation plus rate of capacity decline as a result of resistance rise). When the rates are added together, the result is two times the rate of side reactions. When the rates are subtracted from each other, the result is two times the rate of particle isolation plus the loss of capacity as a result of resistance rise. To determine if there is resistance rise in a cell, the average charge and discharge voltage are plotted and one measures the difference in voltage between the two lines with cycle number. If this does not change, than resistance is not contributing significantly to capacity fade.

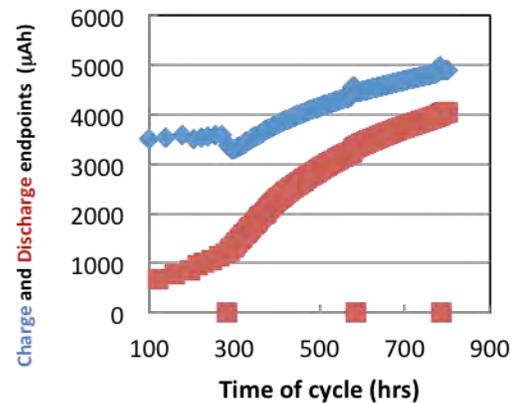


Figure 1. The charge and discharge endpoints of a Li/Si cell cycled at different rates plotted versus time of cycling.

The charge and discharge endpoints *vs.* time of a Li/Si cell are provided in Fig. 1. One can fit second order polynomials to the data. The derivatives of the equations yield the rate of change of the curves *vs.* time. These curves can then be added and subtracted to obtain the rate of side reactions and particle isolation. The results produce the following equations for times after 380 hours:

$$\dot{S}R = 8.7 - 0.0086t_D \text{ [}\mu\text{Ah/h]}$$

$$\dot{P}I = 2.8 - 0.0032t_D \text{ [}\mu\text{Ah/h]}$$

If it is preferred to view particle isolation (*PI*) as a capacity loss per completed cycle, then a fit of the time the discharge ends versus the cycle number is required. For the data in Fig 1, the equation is:

$$t_D = 273 + 3.0861N - 0.0035N^2 \text{ [h] \{starting at cycle 38\}}$$

Combining these equations gives a rate of particle isolation per cycle of:

$$PI = 5.941 - 0.044N + 0.0010N^2 - 7.8E(-8)N^3 \text{ [}\mu\text{Ah/cycle] \{starting from cycle 38\}}$$

Further details are provided in the 2014 Annual Progress Report.

Assembly of Battery Materials and Electrodes

PROJECT OBJECTIVE: To develop high-capacity, low-cost electrodes with good cycle stability and rate capability to replace graphite in Li-ion batteries. The *in situ* analyses of Si based electrodes showed that the bigger particles (ca. 13 μm) start to crack at around 0.1 V. During the charging process, all of the major cracks remained, while some fissures collapsed and others expanded, but the smaller particles (< 2 μm) did not crack. Furthermore, the *in situ* study revealed that delamination occurred at the interfaces of the particle/binder and the Cu current collector/electrode. These experiments provided a better understanding of the anode cycling mechanism and the failure mode associated with capacity fade. The results will be helpful to redesign the anode architecture. This study will also be beneficial to design the architecture of the high-voltage cathode (LMNO).

PROJECT IMPACT: This project will have a major impact on the wide spread adoption of EVs by (i) demonstrating scale-up production of nano-Si powders (to kilogram levels) for advanced EV batteries, and (ii) improving electrode performance by the understanding gained from *in situ* SEM and TEM studies. The success of the project will contribute to the advancement of EV battery technology by developing batteries with increased energy density and improved cycle life, leading to EVs with longer driving range.

OUT-YEAR GOALS: Complete the *in situ* SEM and TEM studies of the Si-anode material during electrochemical cycling and real-time monitoring of structure changes. These analyses will help to understand the failure mode and to guide further improvements in the electrode architecture. These studies will also help to investigate the high-voltage passivation layer to identify the appropriate electrolyte and electrode compositions. The results of this effort will help to identify an alternative supplier of Si powder material as a baseline for the BATT Program. As a final goal, the optimized Si-anode and LiMnNiO-doped Cr cathode will be evaluated in a laminate 20 Ah Li-ion cell.

COLLABORATIONS: V. Battaglia and G. Liu (LBNL) and J. Goodenough (UT Austin.)

Milestones

- 1) Identify Si-based anode materials that can achieve a capacity of 1200 mAh/g. (Dec. 13) **Complete**
- 2) Supply Si powder (1 Kg) from an alternative supplier as a baseline material for BATT PIs. (Mar. 14) **Complete**
- 3) Go/No-Go: Terminate production of Si powder in anode tests that show more than 20% capacity fade in the initial 100 cycles. Criteria: Supply laminated Si-based electrodes to BATT PIs. (Jun. 14) **Complete**
- 4) Supply a 20-Ah Li-ion flat cell based on Si and LiMNO materials to BATT PIs. (Sep. 14) **Complete**

Progress Report

This quarter's effort addressed the assembly of large format prismatic cells (21Ah) using the HQ automatic assembly line. The cell is based on the high-voltage LMNO cathode and a Si-nano anode, as defined by DOE. Large films of anode and cathode were produced by the pilot coating machine at HQ. It was noted that during anode film preparation a gas was generated due to side reactions on the large surface area nano-Si anode. The material has a high surface energy which makes it extremely reactive with water. Thus, some precautions must be considered during slurry preparation and film coating of this material (Fig. 1). It was found that the Si-slurry must stand for a minimum of 8 hours to fully exhaust the generation of gas bubbles. Based on the previous cycling result of the anode, stable cycling was obtained at 40% DoD with a capacity of 1600mAh/g. This criterion was adopted to prepare the large cell. The parameters such as loading and electrode density were studied in half-cells before assembling the full Li-ion cells. This study identified the optimum critical parameters such as anode and cathode loading. The high capacity of the Si-anode involves thin films having a thickness of about 10 μm per side, which makes the lamination step of the anode more sensitive. In addition, this high anode capacity requires a high cathode loading. The cathode thickness used in this cell configuration was about 4x that of the anode. Figures 1c and d show the SEM photos of the cross-section of the double-sided coating of the cathode and anode current collectors, respectively.

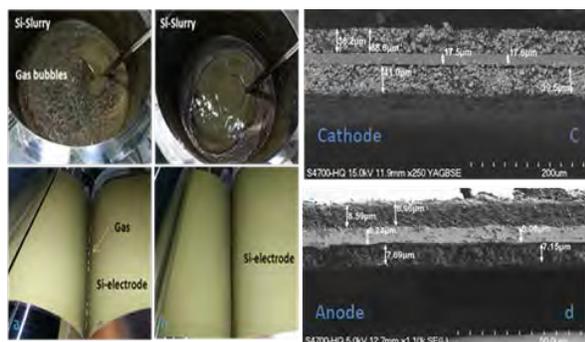


Figure 1. Slurry and electrode of Si-nano anode; a) after mixing, b) after 8 hours of relaxing for degassing. SEM cross-section of the cathode (c), and the anode (d) used in the 21Ah stacking cell.

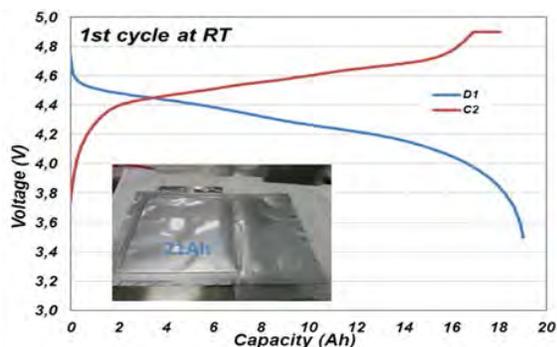


Figure 2. Charge/discharge curves of Si-nano/EC-DEC-FEC $\text{LiPF}_6/\text{LMNO}$ stacking cell (21Ah), between 4.9 V and 3.5 V at RT.

Since a new technology is being explored, many parameters were investigated, including formation protocols. Cells with a capacity of 21 Ah were successfully assembled (electrolyte composition EC/DEC-1MLiPF₆-10%FEC) using the pilot stacking line machine at HQ. To achieve this capacity with the given area, 35 anode and 34 cathode films were required. Different formation protocols were used to maximize the reversible capacity, such as cut-off voltage, temperature and degassing steps. Figure 2 shows the charge/discharge curves of the cell from 3.5 V to 4.9 V at RT. The highest reversible capacity obtained with different formation protocols is 19Ah compared to the installed capacity of 21Ah (90.5%). One of the challenging problems is gas generation. It was observed that the gas was generated continuously with cycling up through the first seven cycles, even after 3 degassing steps. This problem was not previously identified due to the use of small coin-type cells utilized during previous testing. A significant effort is still required to optimize these large pouch cells. It is thought that the use of aqueous media and the exposure of fresh Si surface during cycling are the main factors responsible for the gas evolution. With this in mind, the binder and the formation protocols will be re-evaluated to limit the gas generation. Further work is necessary to understand the interaction of the Si particle surface and binder, and how to stabilize their surfaces.

HQ supplied two large format prismatic cells (21Ah, Si-nano/LiMNO) to LBNL and electrodes (Si and LMNO) to BYU (Dean Wheeler.)

Design and Scalable Assembly of High Density Low Tortuosity Electrodes

PROJECT OBJECTIVE: 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. Characterize and optimize the electronic and ionic transport properties of controlled porosity and tortuosity electrodes as well as densely-sintered reference materials in $\text{Li}(\text{Ni},\text{Co},\text{Al})\text{O}_2$ (NCA), high capacity Li_2MnO_3 - LiMO_2 and high voltage $\text{LiM}_{1-x}\text{Mn}_2\text{O}_4$ and $\text{LiM}_{1-x}\text{Mn}_2\text{O}_4\text{-yFy}$ spinels in order to elucidate rate limiting steps.

PROJECT IMPACT: The high cost (\$/kWh) and low energy density of current automotive Li-ion technology is in part due to the need for thin electrodes and associated high inactive materials content. If successful this project will enable use of electrodes based on known families of cathode and anode actives but with at least 3 times the areal capacity (mAh/cm^2) of current technology while satisfying the duty cycles of vehicle applications. This will be accomplished via new electrode architectures fabricated by scalable methods with higher active materials density and reduced inactive content, and will in turn enable higher energy density and lower-cost EV cells and packs.

OUT-YEAR GOALS: After downselection of cathodes, identify an anode approach that therefore allows full cells in which both electrodes have high area capacity under EV operating conditions. Anode approach will include identifying compounds amenable to same fabrication approach as cathode, or use of very high capacity anodes such as stabilized Li or Si-alloys that in conventional form can capacity-match the cathodes. Use data from best performing electrochemical couple in techno-economic modeling of EV cell and pack performance parameters.

COLLABORATIONS: Within BATT, this project collaborates with Antoni P. Tomsia (LBNL) in fabrication of low-tortuosity, high-density electrodes by directional freeze-casting and sintering, and with Gao Liu (LBNL) in the Si Anode Focus Group on acoustic emission-based characterization of electrochemically-induced microfracture of Si anodes. Outside of BATT, the project collaborates with Randall Erb (Northeastern U.) on magnetic-alignment based fabrication of low tortuosity electrodes.

Milestones

- 1) Measure electronic and ionic conductivities and diffusivity in sintered dense $\text{Li}(\text{Ni},\text{Co},\text{Al})\text{O}_2$ (NCA) and Fe-doped high voltage spinel $\text{Li}_{1-x}\text{Mn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ spinel. Fabricate first freeze-cast samples of at least one cathode composition (Dec. 13) **Complete**
- 2) Go/No-Go: Downselect one cathode composition for follow-on work. Criteria: Based on transport measurements and cycling tests of freeze cast and sintered electrodes. (Mar. 14) **Go for downselecting one cathode composition for follow-on work**
- 3) Demonstrate at least $5 \text{ mAh}/\text{cm}^2$ capacity per unit area at 1C continuous cycling rate for a freeze-cast cathode (Jun. 14) **Complete**
- 4) Demonstrate at least $10 \text{ mAh}/\text{cm}^2$ capacity per unit area for a 2C 30 sec pulse for a freeze-cast cathode. (Sep. 14) **Complete**

Progress Report

During this quarter, freeze-cast and sintered- $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (NCA) electrodes having aligned porosity and high areal capacity (mAh/cm^2) were tested in Li half-cells according to hybrid pulse power characterization (HPPC) protocols. The electrodes displayed capabilities of delivering $>10 \text{ mAh}/\text{cm}^2$ area capacity at reasonable rates. Key results are shown in Fig. 1. The NCA electrode tested has a very high area capacity of $16 \text{ mAh}/\text{cm}^2$ when measured at C/10 (compared to 3 to 4 mAh/cm^2 for conventional Li-ion cathodes) and has a thickness of $300 \mu\text{m}$. The HPPC test was initiated with galvanostatic charging at C/5 to the cutoff voltage followed by an open circuit hold for 1h. A 10s charge/10s discharge pulse at 2C current was then applied, followed by a galvanostatic discharge at 1C to 10% of the cell's capacity (i.e., 6 min). This sequence was repeated for every 10% depth of discharge. Figure 1a shows the voltage profile of the cell during the HPPC test; note that the cell remains within the specified voltage limits throughout the 10s, 2C charge/discharge pulses. Figure 1b shows the voltage vs. cumulative area capacity during the test, where it is seen that the cumulative capacity reaches *ca.* $12 \text{ mAh}/\text{cm}^2$. In the previous quarter, a similar electrode exhibited *ca.* $5 \text{ mAh}/\text{cm}^2$ capacity under continuous 1C discharge. The current results show that a much higher area capacity can be obtained from these novel electrodes under tests which more closely resemble HEV testing. The discharge power during the 2C, 10s pulses is shown in Fig. 1c, plotted as area-specific power against depth of discharge. The values range from $150 \text{ mW}/\text{cm}^2$ at low DoD to $95 \text{ mW}/\text{cm}^2$ at high DoD, which is more than 2x and 4x higher, respectively, than reference data for a conventional NCA composite electrode (tested under 3.75C pulses, J. Shim and K. A. Striebel, *Journal of Power Sources*, **122** (2003), 188–194). The 3 to 4x greater area capacity of the present electrodes would correspond to lower electrode area for the same cell capacity, thus the higher area-specific power is promising and necessary to meet power requirements for vehicle applications.

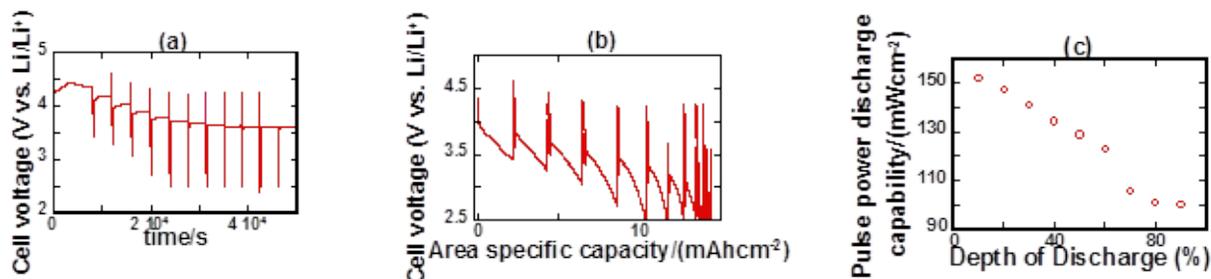


Figure 1. (a) Voltage vs. time for the hybrid pulse power characterization (HPPC) test; (b) voltage vs. cumulative area-specific discharge capacity; and (c) area-specific discharge pulse power vs. depth of discharge for a freeze-cast, sintered, NCA electrode of $300 \mu\text{m}$ thickness.

Hierarchical Assembly of Inorganic/Organic Hybrid Si Negative Electrodes

PROJECT OBJECTIVE: This proposed work aims to enable Si as a high-capacity and long cycle-life material for negative electrode to address two of the barriers of Li-ion chemistry for EV/PHEV application: insufficient energy density and poor cycle life performance. The proposed work will combine material synthesis and composite particle formation with electrode design and engineering to develop high-capacity, long-life, and low cost hierarchical Si-based electrode. State of the art Li-ion negative electrodes employ graphitic active materials with theoretical capacities of 372 mAh/g. Silicon, a naturally abundant material, possesses the highest capacity of all Li-ion anode materials. It has a theoretical capacity of 4200 mAh/g for full lithiation to the $\text{Li}_{12}\text{Si}_5$ phase. However, Si volume change disrupts the integrity of electrode and induces excessive side reactions, leading to fast capacity fade.

PROJECT IMPACT: This work addresses the adverse effects of Si volume change and minimizes the side reactions to significantly improve capacity and lifetime to develop negative electrode with Li-ion storage capacity over 2000 mAh/g (electrode level capacity) and significantly improve the coulombic efficiency to over 99.9%. The research and development activity will provide an in-depth understanding of the challenges associated with assembling large volume change materials into electrodes and will develop a practical hierarchical assembly approach to enable Si materials as negative electrodes in Li-ion batteries.

OUT-YEAR GOALS: There are three aspects of this proposed work - bulk assembly, surface stabilization and Li enrichment, which are formulated into 10 tasks in a four-year period. 1) Develop hierarchical electrode structure to maintain electrode mechanical stability and electrical conductivity. (Bulk assembly). 2) Form *in situ* compliant coating on Si and electrode surface to minimize Si surface reaction (surface stabilization). 3) Use prelithiation to compensate first cycle loss of the Si electrode. (Li enrichment) In the end of the 4th year, the goal is to achieve a Si based electrode at higher mass loading of Si, and can be extensively cycled cycles with minimum capacity loss at high coulombic efficiency to qualified for vehicle application.

COLLABORATIONS: Vince Battaglia and Venkat Srinivasan (LBNL), Xingcheng Xiao (GM), Jason Zhang (PNNL), Chongming Wang (PNNL), Yi Cui (Stanford), and the Si-Anode Focus Group.

Milestones

- 1) Design and synthesize 3 more PEFM polymers with different EO content to study the adhesion and swelling properties of binder to the Si electrode performance. (Dec. 13) **Complete**
- 2) Go/No-Go: Down select Si vs. Si alloy particles and particle sizes (nano vs. micro.) Criteria: Down select based on cycling results. (Mar. 14) **Complete**
- 3) Prepare one type of Si/conductive polymer composite particles and test its electrochemical performance. (Jun. 14) **Complete**
- 4) Design and synthesize one type of vinylene carbonate (VC) derivative that is targeted to protect Si surface and test it with Si-based electrode. (Sep. 14) **Complete**

Progress Report

Si and its alloys have specific capacities which are approximately ten times greater than that of graphitic anodes, however, the drastic volume change inherent in Si's use causes formidable challenges toward achieving stable cycling performance. Large quantities of binder and conductive additive are typically required to maintain good cell performance. In this report, an electrode of 2% (by weight) functional conductive polymer binder without any conductive additive was successfully utilized with a micron-size SiO anode material, demonstrating stable and high gravimetric capacity (>1000 mAh/g) for *ca.* 500 cycles and more than 90% capacity retention. Prelithiation of this anode using stabilized Li metal powder (SLMP) improves the first cycle coulombic efficiency of a SiO/NMC full cell from 48 to *ca.* 90%. The combination enables good capacity retention of more than 80% after 100 cycles at C/3 in a Li-ion full cell.

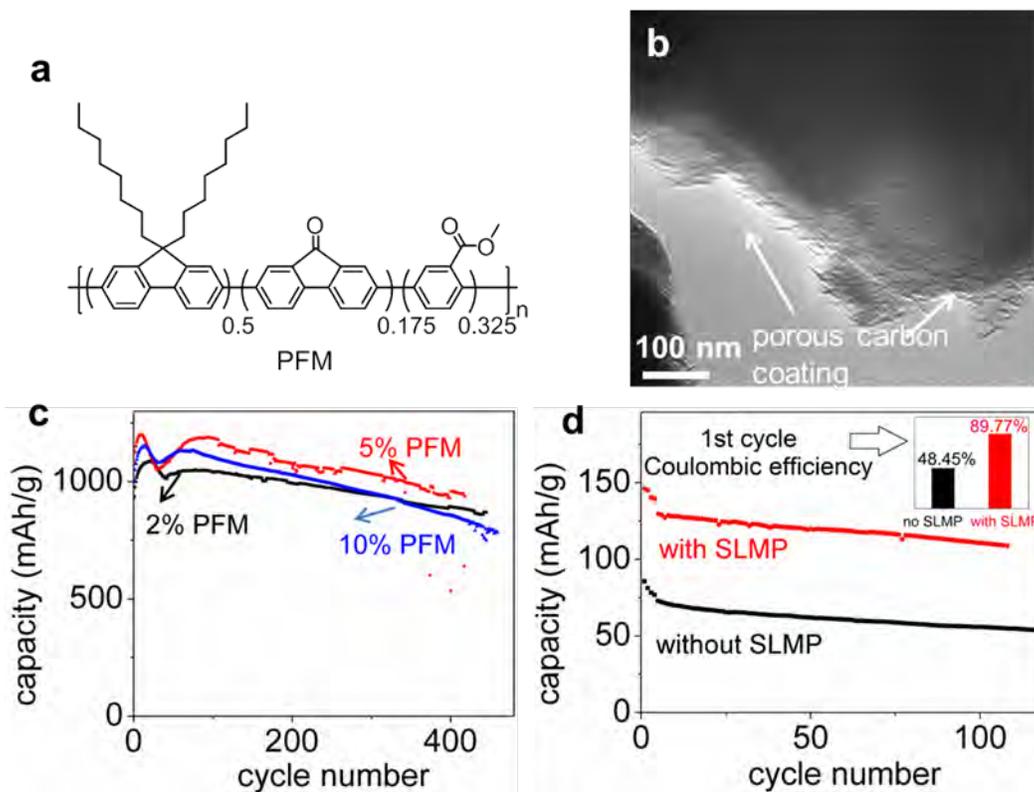


Figure 1. (a) Chemical structure of PFM conductive polymer binder; (b) HRTEM of the carbon-coated SiO pristine particles; (c) cycling performance of the PFM/SiO half-cells at C/5 (200 mA/g); (d) cycling performance of the NMC/SiO full-cells with and without prelithiation by SLMP: C/20 for 2 cycles, C/10 for 2 cycles, followed by C/3.

Figures 1a and b show the chemical structure of the PFM conductive polymer binder and morphology of the SiO anode, respectively. Long-term stable cycling performance is shown in Fig. 1c for the half-cell. Only 2% PFM is necessary to achieve satisfactory performance. To eliminate the large, first-cycle, irreversible capacity, SLMP is used in the NMC/SiO full-cell and the first cycle capacity improves from 48.5 to 89.8%. A very stable full-cell performance was achieved by the combined strategies of a small fraction of conductive polymer and prelithiation with SLMP.

Task 1.5 - Vincent Battaglia (Lawrence Berkeley National Laboratory)

Electrode Fabrication and Materials Benchmarking

PROJECT OBJECTIVE: The objective of this task is to bring together a large fraction of the BATT community together to work on a single chemistry. Thus, the best combination of materials will be provided to multiple researchers in the BATT Program for the Focus Groups. The Liu Group will be supplying the Si anodes and this group will develop matching cathodes of LiFePO_4 that will be used to benchmark the effect of side reactions at the anode on cell capacity fade. For the High Voltage Focus group, the group will benchmark (i.e. measure reversible capacity, rate performance, cycle efficiency.) the latest NMO material from NEI and an NCM material for comparative testing. This project also serves as a hub for testing new materials developed in the BATT program.

PROJECT IMPACT: This project supports two focus groups. For the Si Focus Group, it is critical that the effect of the side reactions in a full cell are quantified as the side reaction on the Si is considered a major flaw of the material. For the High-Voltage Focus group, it is important to source good materials and to make good cells in order to compare the effects of side reactions on the performance of the active materials that address critical questions for the BATT Program. This project is the key to demonstrating progress within the program against industry standards.

OUT-YEAR GOALS: The long-term goal of this project is to support focus groups and identify and provide quality materials, electrodes, and cell performance data. This effort supplies a benchmark for the rest of the BATT Program to build upon. Advancing Li-ion chemistry through proper analysis of state-of-the-art materials.

COLLABORATIONS: Gao Liu (LBNL)

Milestones

- 1) Go/No-Go: Decide if the newest NMO material from NEI should be the baseline material or not.
Criteria: Benchmark the newest NMO material from NEI. (Dec. 13) **Go to use NMO.**
- 2) Identify the NCM baseline material. (Sep. 14) **Ongoing**
- 3) Demonstrate a cyclable LiFePO_4 electrode. (Jun. 14) **Complete**
- 4) Measure the difference in side reactions of graphite and Si when cycled against LiFePO_4 . (Sep. 14) **Complete**

Progress Report

Measure the difference in side reactions of graphite and Si when cycled against LiFePO_4 . When this milestone was originally established, some of the coulombic efficiencies and cyclabilities of the Si-based anodes being reported on in the BATT Program were approaching the values typically reported for graphite: 99.8% coulombic efficiency and negligible capacity fade. It was the group's intention to compare these electrodes against the same cathode to see if the full cells operated similarly. However, as of today, the Si electrodes made from the baseline Si material are showing high capacity fade. Nevertheless, the comparison was performed.

Over the last two quarters, the group learned to make LiFePO_4 (LFP) cathodes with negligible capacity fade and a very high coulombic efficiency: 99.95%. Full cells were assembled with the LFP cathodes and of Si anodes prepared by the Liu Group and graphite anodes prepared by the Battaglia Group. The graphite is from Superior Graphite as recommended by ANL. Half-cells were also prepared and tested for all three electrodes. All cells were cathode-limited except the Si/LFP cells. Below is a report of the comparison.

The graphite electrodes cycled in a half-cell showed very good capacity retention (over 98% after 150 cycles) and a coulombic efficiency of 99.9%. However, the full cell lost around 30% of its capacity after 180 cycles. This is consistent with a coulombic efficiency of 99.8% and 0.2% capacity loss per cycle. The amount of capacity fade in the Gr./LFP cell was surprising since the literature reports very good cyclability for this chemistry. This cyclability could be improved by 2.5 times simply by increasing the cycling rate to C/1. Further improvements may come from the addition of VC.

The Si electrodes showed poor cycle performance in a half-cell. After 200 cycles, the cells lost over 70% of their capacity as compared to the first discharge capacity. Fourteen percent of this loss could be attributed to a shift in current from C/20 to C/3, but the rest was a result of a loss of cyclable sites in the Si electrode. The coulombic efficiency was around 99% at cycle 200, but it took 50 cycles to exceed 98%. The Si/LFP full cells fared slightly less well. These cells lost nearly 80% of their capacity after 200 cycles. These cells would have performed much worse if they had been cathode-limited and would have likely lost all of their capacity by the 120th cycle. Since they were not cathode-limited, the coulombic efficiency had little impact on the capacity fade and a majority of the fade is attributed to the loss of active sites for Li interaction (either sites for Li become too small in the Si or material is lost through particle/electrode fracture and isolation).

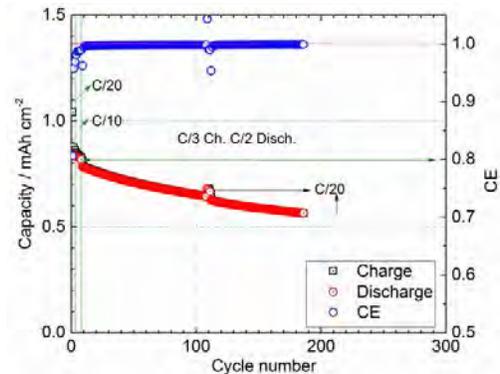


Figure 1. The charge and discharge capacities and coulombic efficiency of a Gr./LFP cell cycled at different rates.

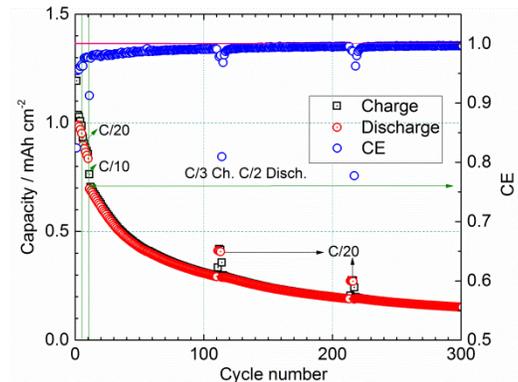


Figure 2. The charge and discharge capacities and coulombic efficiency of a Si/LFP cell cycled at different rates.

Novel Anode Materials

PROJECT OBJECTIVE: The project seeks to understand how the cycling of elemental Si in a lithium-ion cell configuration affects the local electrode structure and relate the information garnered to counter cell failure mechanisms. By using various types of electrode formulations and diagnostic spectroscopies, probing from the surface of the Si to the final complex laminate electrode can take place. Initial work included creation of an all-inorganic electrode that allowed the effects of cycling on the Si to be examined as the electrolyte was the only source of carbon in the cell. This work extended to developing thin film deposition techniques that allow tailoring of the surface chemistry of the Si that influence how the binder and Si interact. In addition to normal cycling, imaging, and impedance spectroscopies, tomography studies of conventional electrodes were initiated to examine how electrode porosity and particle size influenced the isolation of Si particles on cycling, a major cause of capacity fade.

PROJECT IMPACT: The project utilizes a combination of synthesis and characterization to discern how the cycling of elemental Si in a lithium-ion cell affects the surrounding electrode structure and how this can be modified to increase cycle life and stability. Results from these studies will be of interest to cell builders and end-users as degradation of the electrode structure can often be traced as the root cause of inconsistent results and premature cell failure. These goals are in line with EERE and OVT goals of furthering development of novel electrode materials and energy storage systems.

OUT-YEAR GOALS:

- Design and formulate Si-based electrodes using the new BATT standard Si source that allow for volume expansion in a less rigid environment than a porous copper substrate.
- Design and evaluate alternative structures that integrate the role of the current collector with the conductive additive requirement of the electrode to reduce materials requirements

COLLABORATIONS: Fikile Brushett (MIT), Lynn Trahey (ANL), Fulya Dogan (ANL)

Milestones

- 1) Synthesize and evaluate a Si-based electrode that utilizes a multilayer structure to stabilize the active Si. (Dec. 13) **Complete**
- 2) Synthesis and evaluation of at least three alternative electrode structures based on non-copper porous substrates. (Mar. 14) **Complete**
- 3) Utilize surface sensitive techniques to develop a model of the Si - substrate interface in the alternative electrodes created. (Jun. 14) **Complete**
- 4) Evaluate optimized electrode structure against BATT standard Si electrode for rate capability and stability on cycling. Make recommendations to improve BATT standard electrode. (Sep. 14) **Complete**

Progress Report

The stability of Si surfaces has significant effects on the cycling properties of Si anodes in Li-ion batteries. Previous studies identified surface functional groups that interact with the electrolyte, and these groups were also used by binder designers to make stronger contact between the active particle and current collectors. As part of the effort examining surface stability on electrochemical properties, studies continued on the Si/SiO₂ interface and the role of FEC electrolyte additives.

In an EQCM experiment, as noted in the Q2 report, a thin film Si or Si/SiO₂ electrode is cycled in an electrochemical cell while the weight of the electrode is monitored. Weight losses (*e.g.* dissolution) or gains (*e.g.* SEI formation) were quantified and compared to the number of electrons passed to help separate electrochemical from chemical degradation. In Gen2, the presence of the SiO₂ layer should stop the electrolyte at the surface of the electrode from reaching a sufficiently low potential to cause electrolyte reduction. However, the mass increase observed is even less than the mass of the Li that was transported to the electrode, as calculated from the charge transferred during the voltage sweep from OCP to 0.01V. This indicated that the dissolution of some species from the surface of the Si/SiO₂ electrode occurred upon lithiation. With the BATT-standard, FEC-containing electrolyte, there are several important differences between the two surfaces. Figure 1 shows the applied potential as well as frequency and dissipation changes for $n=3, 5,$ and 7 for Si and Si/SiO₂ electrodes in the FEC-containing electrolyte. Both the mass of the SEI formed and the dissipation changes are reduced in the FEC-containing electrolyte by factors of approximately 3 and 10, respectively, implying that less SEI forms and what forms is more rigid than in the case of Gen2 electrolyte (not shown). In addition, the magnitude of the harmonics in both frequency and dissipation are much less variable than in the case of Gen2, implying that what forms is more uniform and consistent with previous TEM work. This also indicates that FEC produces a smoother SEI film when used with a Si-based electrode.

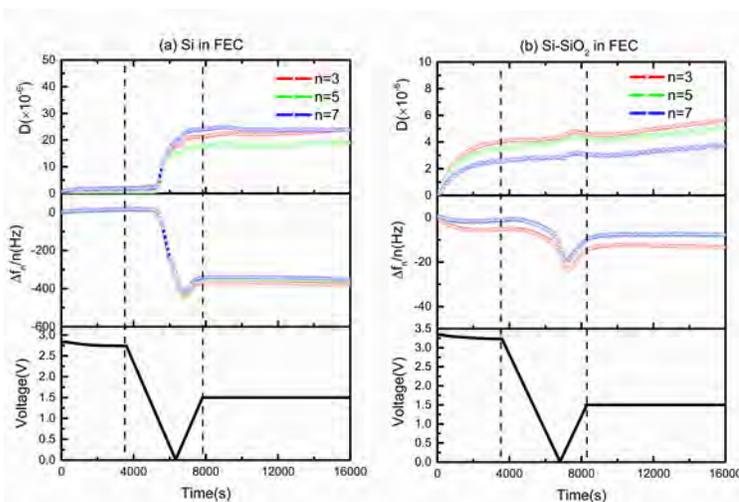


Figure 1. EQCM data comparing the weight gain and film density of a Si thin film electrode *vs.* the same electrode passivated with SiO₂. Data collected using BATT standard EC:DEC:FEC (45:45:10) electrolyte.

Mass loss on Si/SiO₂ electrodes during lithiation was seen in both Gen2 and FEC-containing electrolytes. NMR measurements (noted in Q3 report) performed on Li₄SiO₄ powders that were soaked in EC:EMC solvents confirmed that Li₂O will dissolve from the silicate, which suggested that the most likely cause of mass loss on lithiation of oxide-coated electrodes is due to Li₂O dissolution.

Task 2.2 - Stanley Whittingham (SUNY Binghamton)

Metal-Based High Capacity Li-Ion Anodes

PROJECT OBJECTIVE: 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.

Specifically, the primary objectives are to:

- Increase the volumetric capacity of the anode by a factor of two over today’s carbons
 - 1.6 Ah/cc
- Increase the gravimetric capacity of the anode
 - ≥ 500 Ah/kg
- Lower the cost of materials and approaches

PROJECT IMPACT: The volumetric energy density of today’s Li-ion batteries is limited primarily by the low volumetric capacity of the carbon anode. If the volume of the anode could be cut in half, then the cell energy density can be increased by over 50% to approach 1 kWh/liter (actual cell). In addition, alloys with higher Li diffusivity than carbon would minimize the possible formation of cell-shortening dendritic Li under high charging rates or low temperature conditions. Moreover, smaller cells using lower cost manufacturing will lower the cost of tomorrow’s batteries.

OUT-YEAR GOALS: The long-term goal of this project is to replace the present carbon used in Li-ion batteries with lower cost anodes that have double the volumetric energy density of carbon. This will be accomplished by using tin and/or silicon based materials. By the end of this project it is anticipated that a new tin anode will be available that can exceed the charging and discharging rates of carbon thereby making it safer, that will have minimal excess capacity on the first cycle, and that can be cycled at greater than 99% efficiency over 200 cycles.

COLLABORATIONS: National Synchrotron Light Source (BNL) and Advanced Photon Source (ANL)

Milestones

- 1) Identify the two most promising approaches for nano-silicon. (Dec. 13) **Complete**
- 2) Reduce the first cycle excess capacity to less than 20% for nano-tin. (Sep. 14) **Partially completed - reduced to 35%**
- 3) Go/No-Go: Decision on solvothermal approach for nano-tin. Criteria: Identify the optimum synthesis approach for nano-tin anode material. (Jun. 14) **Complete – No-Go on solvothermal**
- 4) Achieve more than 200 cycles on nano-tin at double the capacity of carbon at the 1C rate. (Sep. 14) **Partially completed – failure of Li anode restricts cycling at the 1C rate.**

Progress Report

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

Milestone 2. As shown in Fig. 1, the first cycle excess capacity (*i.e.*, the first cycle capacity loss, defined by the equation below*) is reduced from 68 to 36% when the upper voltage limit is increased from 1.5 to 2.0 V, but at the cost of capacity fade. Efforts will continue to reduce this excess capacity.

$$* 1^{st} \text{ cycle excess capacity} = \frac{1^{st} \text{ lithiation capacity} - 1^{st} \text{ delithiation capacity}}{1^{st} \text{ delithiation capacity}} \times 100\%$$

The first cycle excess capacity is due to SEI formed on reactive interfaces, formation of lithium titanium oxides (Li not recovered within the voltage window), and some irreversible Li-carbons. At the same time, part of the reversible capacity is due to the formation of LiC_2 . Effort will be placed to better understand the ve+ and ve- roles of LiC_2 in the next and final quarter.

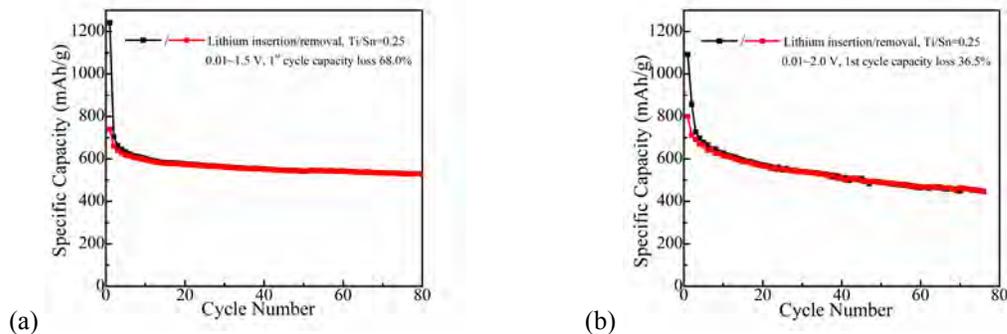


Figure 1. Optimized Sn-Fe-C composite cycled within different voltage windows (a) 0.01 to 1.5V, (b) 0.01 to 2.0 V

Milestone 4. As shown in Fig. 2a, the optimized Sn-Fe-C composite doubles the volumetric capacity of standard graphite for up to 140 cycles under 1C rate. However, the coin cells usually die after long cycling (>150 cycles). This cell failure is associated with failure of the Li anode since the capacity can be partially recovered when the Li anode is replaced. A new cell design will be used in the new BATT project to assure that more cycles can be achieved.

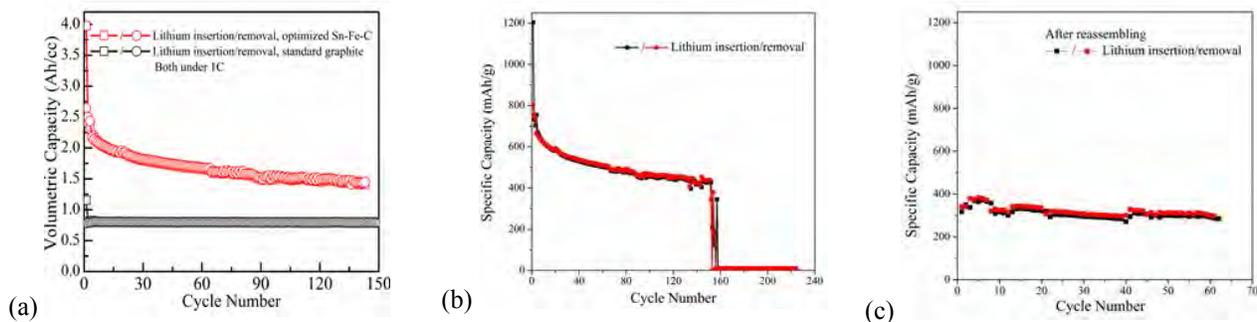


Figure 2. (a) Volumetric capacity comparison of the optimized Sn-Fe-C composite with standard graphite cycled under 1C rate (1C corresponding to a current density of 600 mA/g for Sn-Fe-C, 372 mA/g for standard graphite). The cycling curves of optimized Sn-Fe-C composite: (b) before and (c) after replacing Li anode in the coin cell.

Nanoscale Composite Hetero-structures and Thermoplastic Resin Binders: Novel Li-ion Anode Systems

PROJECT OBJECTIVE: The objective is to identify novel materials and configurations, improved polymeric binders and cost effective scalable strategies to generate these systems to overcome the Si anode limitations. The goals of the present project are to identify an inexpensive nanoscale composites, new class of polymeric binders and electrode configurations displaying higher capacity (>1200 mAh/g) than carbon while exhibiting similar first cycle irreversible loss ($<15\%$), higher coulombic efficiency ($>99.9\%$), and excellent cyclability to replace graphite.

PROJECT IMPACT: Identification of new Si based systems displaying higher gravimetric and volumetric energy densities than graphite will likely result in new commercial battery systems that are more robust, capable of delivering better energy and power densities and will be more lightweight than current Li-ion battery packs utilizing graphite anodes for identical performance specifications. New Si anode based strategies and configurations will also lead to more compact battery designs for the same energy and power density specifications as current Li-ion systems. Commercialization of these new Si anode based Li-ion battery packs will represent fundamentally, a major hallmark contribution of the BATT Program and the BATT community.

OUT-YEAR GOALS: This is a multi-year project comprising of four major phases to be successfully completed in four years. Phase 1: Development of cost effective high energy mechanical milling (HEMM) and direct mechano-chemical reduction (DMCR) approaches to generate nanocrystalline and amorphous Si, and $\text{Li}_x\text{Si}(x>3.5)$ alloys exhibiting capacities in the ~ 1600 mAh/g range and higher. This phase was completed in year 1. Phase 2: Use of chemical vapor deposition (CVD) to generate amorphous and nanocrystalline Si on vertically aligned carbon nanotubes (VACNT) based nano-scale heterostructures exhibiting specific capacity in the ~ 2000 - 2500 mAh/g range. This phase was completed in Year 2. Phase 3: Identify interface control agents (ICA) and surface electron conducting additives (SECA) to lower the first cycle irreversible (FIR) loss ($<15\%$) and improve the coulombic efficiency (CE) ($>99.9\%$). This phase was completed in Year 3. Phase 4: Develop elastic and high strength polymeric binders, to be completed in Year 4.

COLLABORATIONS: Ayyakkannu Manivannan (NETL), Spandan Maiti (University of Pittsburgh), Shawn Lister and Amit Acharya (Carnegie Mellon University)

Milestones

- 1) Go/No-Go: Stop microwave approach if it fails to generate nanoscale electrochemically-active architectures of Si and C resulting in capacities greater than or equal to 1200 mAh/g. (Dec. 13) **Discontinued**
- 2) Demonstrate generation of α -Si hollow nanotubes using cost effective ($< \$65/\text{kg}$) chemical approaches. (Dec. 13) **Complete**
- 3) Develop interface control agents (ICA) to reduce the first cycle irreversible loss to $<15\%$. (Mar. 14) **Complete**
- 4) Develop surface electron conducting additives (SECA) to improve the coulombic efficiency to $>99.9\%$. (Sep. 14) **Ongoing – delayed to Dec. 14**
- 5) Develop multilayered α -Si/M (M = Matrix) composite films to lower the first-cycle irreversible loss ($<15\%$) and improve the active mass loadings ($2\text{-}3\text{mg}/\text{cm}^2$). (Sep. 14) **Ongoing – delayed to Dec. 14**

Progress Report

In the previous report, the SEM analysis of hollow Si nanotubes (h-SiNTs) synthesized by a novel template method showed mechanical integrity of the Si nanostructures both in their lithiated and unlithiated stages, which was directly correlatable to a highly stable specific capacity (1500 mAh/g at 2A/g) and very good rate capability. Hydrocarbon gas at atmospheric pressure was decomposed in a tube furnace containing these hollow SiNTs at 700°C for 10 min to obtain a coating of carbon directly on the h-SiNTs. In a subsequent step, the carbon-coated h-SiNTs were dispersed, vacuum filtered, and washed.

Slurries of carbon-coated and carbon-coated and solution-washed h-SiNTs were prepared with an organic binder (40 wt%) and Super-P as the conductive additive (10 wt%). The slurries were cast on Cu foils and dried to prepare the electrodes. 1M LiPF₆ dissolved in EC:DEC:FEC (45:45:10) (EC: ethylene carbonate, DEC: diethyl carbonate, FEC: fluoroethylene carbonate) solvent was used as the electrolyte for electrochemical characterization in the 0.01 to 1.2 V vs Li/Li⁺ voltage window. A medium current density of 300 mA/g was employed for the first three cycles to generate a good-quality solid-electrolyte-interface (SEI) and a high current of 1 A/g was applied for subsequent cycles to determine the cycling and long-term stability.

The first cycle discharge capacity and charge capacity at initial current rates of 300 mA/g for carbon coated h-SiNTs were 1780 and 1520 mAh/g, respectively (Fig. 1), while for the solution-washed material, the capacities were accordingly, 1800 and 1565 mAh/g (Fig. 2). Both materials showed stable long-term cycling, exhibiting charge capacities of 975 mAh/g for carbon-coated h-SiNTs and 1100 mAh/g for solution-washed active material at the end of 100 cycles at 1A/g. The first cycle irreversible (FIR) loss in the carbon-coated h-SiNTs was 14.5%, while the solution-treated material exhibited a lower FIR loss (13%). This may be due to a reduction in unwanted phases. A similar reason could be attributed to the slight increase in charge capacity of the solution-treated, carbon-coated h-SiNTs.

The loading density in the electrode was approximately 0.8 to 1.1 mg/cm² of active material leading to a first cycle areal charge capacity greater than 1.5 mAh/cm² for both of the materials at a modest current rate of 300 mA/g. The carbon content in the active material was approximately 25 to 30 wt% as determined by EDAX analysis taken during an SEM, which explains the decrease in the specific capacity as compared to the uncoated h-SiNTs reported in Q3-2013, but with a drastic reduction (*ca.* 50%) in FIR loss.

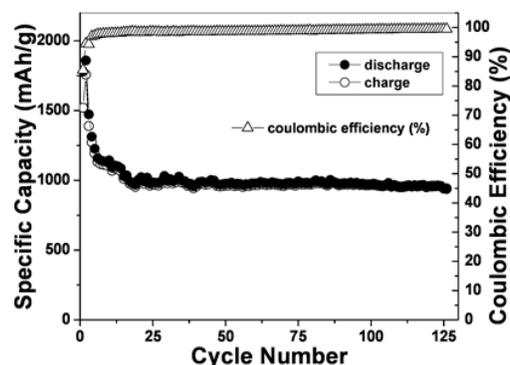


Figure 1. Specific charge/discharge capacity and coulombic efficiency vs. charge/discharge cycles of carbon-coated h-SiNTs electrodes in a Li/Li⁺ battery.

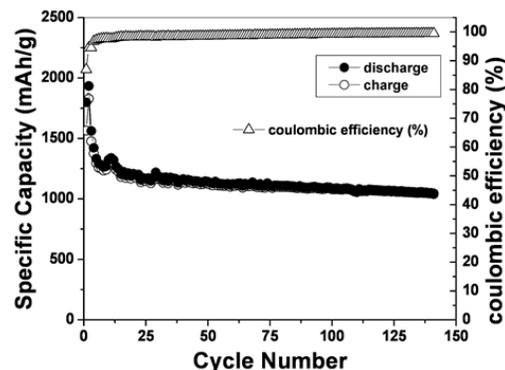


Figure 2. Specific charge/discharge capacity and coulombic efficiency vs. charge/discharge cycles of solution-treated, carbon-coated h-SiNTs electrodes in a Li/Li⁺ battery.

Development of Silicon-Based High Capacity Anodes

PROJECT OBJECTIVE: The objective of this project is to develop high-capacity, low-cost electrodes with good cycle stability and rate capability to replace graphite in Li-ion batteries. The porous Si and the rigid-skeleton supported Si/C composite anode (B₄C/Si/C) will be further optimized. The optimized B₄C/Si/C material will be used as the baseline material for both thick electrode fabrication and studies to advance the fundamental understanding of the degradation mechanism in Si based anode. New electrolyte additives, binders, and artificial SEI layers will be investigated to further improve the performance of anodes. New approaches will be developed to prelithiate Si-based and other Li-alloy anodes to minimize their first-cycle losses. Fundamental understanding on the formation and evolution of SEI layer, the effect of electrolyte additives and electrode thickness will be investigated by *in situ* microscopic analysis.

PROJECT IMPACT: Si-based anodes have much larger specific capacities compared with conventional graphite anodes. However, the cyclability of Si-based anodes is limited because of the large volume expansion that is characteristic of these anodes. This work will develop a low-cost approach to extend the cycle life of high-capacity, Si-based anodes. The success of this work will further increase the energy density of Li-ion batteries and accelerate market acceptance of electrical vehicles (EV), especially for plug-in hybrid electrical vehicles (PHEV) required by the EV Everywhere Grand Challenge proposed by DOE/EERE.

OUT-YEAR GOALS: The main goal of the proposed work is to enable Li-ion batteries with a specific energy of >96 Wh/kg (for PHEVs), 5000 deep-discharge cycles, 15-year calendar life, improved abuse tolerance, and less than 20% capacity fade over a 10-year period

COLLABORATIONS:

Collaboration on anode development will continue with the following battery groups:

- Michael Sailor (UCSD): Preparation of porous Si.
- Gao Liu (LBNL): Binders.
- Yi Cui (Stanford): Failure mechanism study.
- M.V. Yakovleva (FMC Corp): SLMP
- Chunmei Ben (NREL): Surface protection and failure mechanism study.
- David Ji (Oregon State University): Preparation of porous Si by thermite reactions.

Milestones

- 1) Identify the fading mechanism in the thick Si electrode vs. thin electrode. (Dec. 13). **Complete**
- 2) Achieve Coulombic charge efficiency of the electrode >90% during the first cycle, through application of SLPMs and sacrificial Li electrode to PNNL's B₄C/Si/C anode. (Mar. 14) **Complete**
- 3) Achieve high loading Si-based anode capacity retention of >1.2 mAh/cm² over 150 cycles using new binders/electrolyte additives. (Jun. 14) **Complete**
- 4) Achieve improved cycling stability of thick electrodes (> 3 mAh/cm²). (Sep. 14) **Complete**
- 5) Achieve a specific energy greater than 30 Wh/kg and the specific power greater than 5 kW/kg, and cycle life greater than 30,000 cycles for Li ion capacitors. (Sep. 14) **Complete**

Progress Report

Porous Si electrodes have demonstrated good cycling stability at high mass loading. Recently, it was found that ether-based electrolytes (such as 1M LiFSI in DME) can largely improve the cycling stability of Li metal electrodes. This electrolyte was used to test Si-based anodes in an effort to improve their high rate cyclability. The Si electrodes were tested in 1M LiFSI in DME with 10 wt% FEC and 1 wt% VC. Figure 1 shows the long-term cycling of a porous Si electrode with a loading of *ca.* 3.1 mg/cm². It was cycled at a low-current density of 0.06 mA/cm² for 3 cycles and then charged at 0.75 mA/cm² and discharged at 0.5 mA/cm². It exhibits a capacity of *ca.* 3.5 mAh/cm² (*ca.* 1150 mAh/g) at low-current density and a capacity of *ca.* 2.9 mAh/cm² (*ca.* 930 mAh/g) at a higher current density. Its capacity retention is *ca.* 79% over 100 cycles. This work showed that the electrolyte composition has a significant impact on the cycling stability of Si anodes.

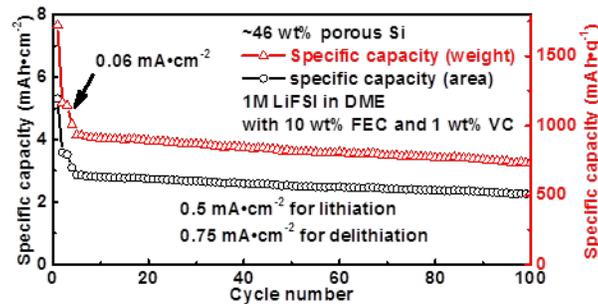


Figure 1. Cycling stability of a porous Si electrode in 1M LiFSI in DME with 10 wt% FEC and 1 wt% VC.

In another effort, effects of cycling range on a Si-based anode were investigated. A Si/B₄C/graphite composite anode was further optimized to improve the cycling stability at high loading; they were cycled in BATT electrolytes at a low-current density of 0.06 mA/cm² for 3 cycles and then charged at 0.75 mA/cm² and discharged at 0.5 mA/cm². Figure 2a shows the cycling stability of a Si/B₄C/graphite composite anode (2.4 mg/cm²) between 0.005 and 1 V. It has a capacity of *ca.* 2.25 mAh/cm² (*ca.* 950 mAh/g) at the low-current density and a capacity of *ca.* 1.85 mAh/cm² (*ca.* 780 mAh/g) at the higher rate. Figure 2b shows the cycling stability of Si/B₄C/graphite composite anode (2.8 mg/cm²) between 0.005 and 0.6 V. It has a capacity of *ca.* 2.1 mAh/cm² (*ca.* 770 mAh/g). Its capacity retention is *ca.* 85% over 100 cycles. By lowering the charge voltage from 1V to 0.6V, the capacity retention of Si/B₄C/graphite composite anodes of similar loadings can be improved by 20% at the expense of a *ca.* 20% overall reduction in capacity.

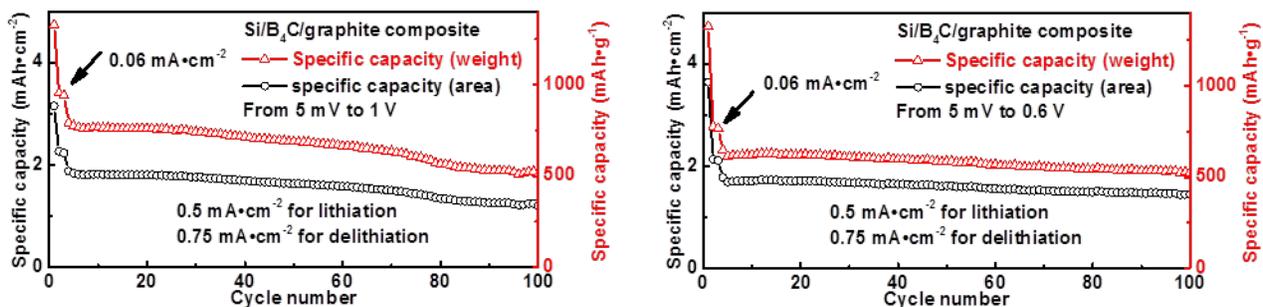


Figure 2. (a) Cycling stability of a Si/B₄C/graphite composite anode of *ca.* 2.4 mg/cm² between 0.005 to 1 V. (b) Cycling stability of a Si/B₄C/graphite composite anode of *ca.* 2.8 mg/cm² between 0.005 and 0.6 V.

Atomic Layer Deposition for Stabilization of Amorphous Silicon Anodes

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

PROJECT IMPACT: Due to its high theoretical capacity and natural abundance, silicon has attracted much attention as a promising Li-ion anode material. However, progress towards a commercially-viable Si anode has been impeded by the rapid capacity fade of silicon caused by large volumetric expansion. In this project, new ALD/MLD conformal nanoscale coatings with desirable elastic properties and good conductivity are developed to accommodate the volumetric expansion and to protect the surface from reactive electrolytes, as well as to ensure the electronic paths through the composite electrodes. Successful completion of this project will enable the coated Si anodes to have high coulombic efficiency, as well as durable high-rate capability. This project supports the goals of the DOE EV Everywhere Grand Challenge and EERE's Vehicle Technologies Office to develop high-energy batteries for wider adoption of electric vehicles to reduce consumption of imported oil and generation of gaseous pollutants.

OUT-YEAR GOALS:

- Demonstrate durable cycling performance of thick Si anodes (>15 μ m) by using new ALD/MLD coatings and electrode designs
- Explore the importance and mechanism of various coatings via the BATT coating group
- Collaborate within the BATT program with the aim of developing high-rate plug-in hybrid electric (PHEV)-compatible electrodes (both anodes and cathodes)

COLLABORATIONS: J. Zhang (PNNL), C. Wang (PNNL), P. Ross (LBNL), G. Liu (LBNL), R. Kostecki (LBNL), Y. Qi (MSU), X. Xiao (GM), P. Balbuena (Texas A&M) and Kevin Leung (SNL).

Milestones

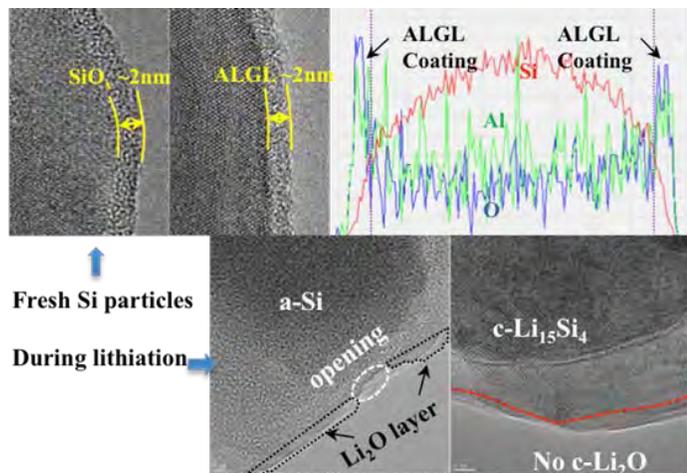
- 1) Identify the impact of Alucone MLD coating on the structure and morphology of Si anodes during cycling. (Dec. 13) **Complete**
- 2) Develop Al₂O₃/carbon composite coatings by pyrolysis of Alucone MLD film. (Mar. 14) **Complete**
- 3) Go/No Go: Test coated electrodes in coin cells. Criteria: Stop the development of Al₂O₃/carbon composite coatings if the coating cannot help the performance of Si anodes. (Jun. 14) **Complete**
- 4) Synthesize and characterize novel AlF₃/Alucone hybrid coating by using ALD and MLD. (Sep. 14) **Complete**

Progress Report

Hybrid inorganic-organic coatings have been developed *via* Molecular Layer Deposition (MLD) techniques. Different from Atomic Layer Deposition (ALD), MLD can integrate various organic groups into the inorganic structure, such as that of Al_2O_3 . Work in the past quarters focused on developing aluminum alkoxide (alucone) with two different organic precursors: glycerol and hydroquinone. Electrochemical analysis has been applied to demonstrate the impact of these two alucone coatings on the Si anodes. Improved cycling performance and a greatly reduced irreversible capacity have been achieved in both of the MLD-coated anodes.

The research performed this quarter was an investigation of the morphology and chemical evolution of uncoated and coated Si particles, during lithiation and delithiation. Specially designed *in situ* TEM was used to monitor the morphology of the Si particles upon cyclic lithiation/delithiation. Electron diffraction equipped with *in situ* TEM was applied to identify the structure. During initial lithiation, the native oxide layer converts to crystalline Li_2O islands, which essentially increases the impedance on the particle, resulting in ineffective lithiation/delithiation, and, therefore, low coulombic efficiency. In contrast, the alucone MLD-coated particles show extremely fast, thorough, and highly reversible lithiation behavior, which appears to be associated with the mechanical flexibility and fast Li^+/e^- conductivity of the alucone coating. Surprisingly, the alucone MLD coating process chemically changes the Si surface, essentially removing the native oxide layer and thus mitigates the side reactions and other detrimental effects of the native oxide. This study provides a vivid picture of how the MLD coating works to enhance the coulombic efficiency and preserve capacity and clarifies the role of the native oxide on Si nanoparticles during cyclic lithiation and delithiation. Most broadly, this work also demonstrated that the effect of the subtle chemical modification of the surface during the coating process might be of equal importance as the coating layer itself.

In addition, ALD has been utilized to fabricate an AlF_3 coating. The sequential and self-limiting reactions between trimethylaluminum and hydrogen fluoride-pyridine precursors have been confirmed. *In situ* quartz crystal microbalance and *ex situ* X-ray reflectivity have been applied to monitor the mass gain and film thickness, as a function of ALD cycles. The results show that the ALD AlF_3 process exhibits a growth rate of $1.0 \text{ \AA}/\text{cycle}$ and a density of 2.9 g/cm^3 . The use of Rutherford backscattering spectrum was used to identify composition and impurities of the AlF_3 ALD film. It shows that the atomic ratio of Al:F is constant at 1:2.85 with low-oxygen contamination.



The coating has been applied to Si anodes to evaluate the effect of an AlF_3 coating on the electrochemical performance of Si anodes. Although the AlF_3 -coated Si anode exhibits better cycling performance than the uncoated Si anode, the capacity fades slowly. It is believed that the AlF_3 coating failed to withstand the high-volume-change of the Si particles. Among all of the coated Si anodes, the MLD alucone-coated anode shows the best cycling performance. To address mechanical issues in ALD-coated electrodes, a hybrid ALD-MLD coating has been developed for Si anodes; however, the hybrid ALD-MLD coating showed negligible improvement in electrochemical performance compared with the alucone-coated electrodes.

New Layered Nanolaminates for Use in Lithium Battery Anodes

PROJECT OBJECTIVE: Replace graphite with a new material selected from a group of layered (two-dimensional) binary carbides and nitrides known as MXenes, which may offer combined advantages of graphite and Si anodes with a higher capacity than graphite, less expansion, longer cycle life and a lower cost than Si nanoparticles.

PROJECT IMPACT: As a result of this project, a new family of 2D materials (MXenes) was discovered. Using MXenes as anode materials in LIB could lead to higher capacities than graphite with the ability to handle higher cycling rates than graphite anodes. Since each MXene has its own voltage window, considering their rich chemistry and the possibility of solid solutions, MXene compositions can be selected and tuned for certain voltages to produce high-performance batteries with improved safety.

OUT-YEAR-GOALS: The project's long term goal is to produce new anode materials (MXenes) that may replace graphite in anodes of Li-ion batteries.

FY2014 - Improvement of the cycle-life of the anodes. Optimization and modification of the material manufacturing processes to enable large-volume, low-cost production.

COLLABORATIONS:

- Xiao-Qing Yang and Kyung-Wan Nam, BNL
- Yu Xie and Paul Kent, ORNL
- Jun Lu, Lars Hultman and Per Eklund, Linkoping University, Sweden.
- Yohan Dall'Agnese and Patrice Simon, Université Paul Sabatier, Toulouse, France

Milestones

- 1) (a) Produce MXene anodes with capability of delivering a stable performance at 10 C cycling rates (Dec. 13). **Complete**
(b) Complete *in situ* and *ex situ* studies of the lithiation and delithiation of MXenes and determine the most promising materials (Jun. 14). **Complete**
- 2) Maximize capacity of MXenes and test newly discovered MXenes that have shown the highest capacity so far (Mo₂C) (Jun. 14). **Complete**
- 3) Predict the theoretical capacity and Li insertion potential of MXenes, and synthesize and test MXenes that are expected to have the largest Li uptake (>600 mAh/g theoretical capacity) and a lithiation/delithiation potential below 1 V (Sep. 14). **Complete**
- 4) Demonstrate improved charge/discharge behavior by controlling particle size and surface chemistry of MXenes (Sep. 14). **Complete**

Progress Report

With the goal of exploring MXenes expected to have the largest Li uptake, a new Mo containing MXene, Mo_2TiC_2 , was synthesized and tested as an anode. Cyclic voltammetry curves, at a rate of 2 mVs^{-1} , for the Mo_2TiC_2 anode with conductive carbon black additive and polyvinylidene fluoride (PVDF) binder in a 70:20:10 ratio (Fig. 1a) show that the majority of lithiation and delithiation capacity is at voltages below 2.5 V. Also, contrary to other MXene materials, a clear lithiation peak was observed at voltages lower than *ca.* 0.5 V. The discharge curves at 0.3C rate show a voltage plateau for potentials lower than 0.5 V (first MXene demonstrating a clear plateau!) and a capacity of *ca.* 120 mAhg^{-1} (Fig. 1b). These experiments were performed using one of the first produced batches of Mo_2TiC_2 and a higher gravimetric capacity is expected once the processing conditions are optimized and non-reacted MAX and other impurities are eliminated. Also, more experiments are under way to study the performance of this anode at higher C rates and determine its cycle life.

Following the previously demonstrated increase in capacity and rate performance through delamination and the use of carbon nanotubes (CNTs) to form composite electrodes, the same was applied to Nb_2C . It was delaminated into single flakes by intercalation with isopropylamine followed by sonication in water for 1 hr. d- Nb_2C /CNT nanocomposite paper was prepared by filtering a mixture of d- Nb_2C colloidal solution and 10 wt.% CNT dispersion (see inset in Fig. 2b). At 0.5 C, the capacity yielded by the d- Nb_2C /CNT paper (*ca.* 430 mAhg^{-1} over 100 cycles) was almost double that for d- Ti_3C_2 /CNT paper at the same current density (Fig. 2a). It should be noted that the capacities for both kinds of electrodes increased after tens of cycles due to the enlarged d-spacing of the MXene flakes with increased number of cycles and improved access of Li-ions to the interlayer spaces in MXene. This result is encouraging since it clearly implies that further improvement through optimization of the electrode architecture is possible.

Figure 2b shows the rate performance of the d- Nb_2C /CNT paper. A highly reversible capacitance of *ca.* 600 mAhg^{-1} was achieved at 0.1 C, even higher than the theoretical value for d- Nb_2CO_2 (466 mAhg^{-1}) for 2 Li layers on the surface. This suggests formation of more than 2 Li layers on each d- Nb_2C flake or the presence of additional storage mechanisms in the composite paper. At 10 C, the capacitance was stable at *ca.* 270 mAhg^{-1} , greatly exceeding the performance of any commercial electrodes at that rate. A capacitance of *ca.* 150 mAhg^{-1} can still be preserved at a high current density of 20 C, which means that the charge and discharge process can be finished within 3 min, indicating the outstanding high-rate performance of the d- Nb_2C /CNT paper.

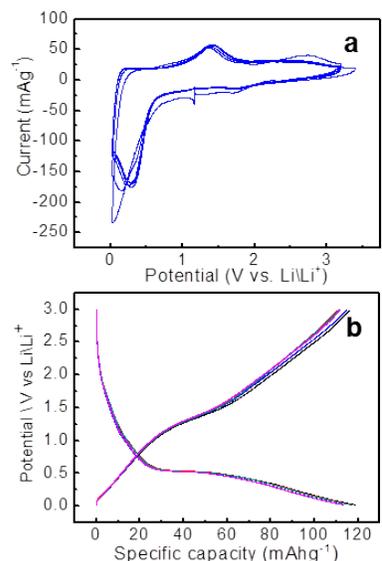


Figure 1. (a) Cyclic voltammetry (CV) curves of Mo_2TiC_2 recorded at 2 mVs^{-1} . (b) The galvanostatic charge-discharge curves (5 cycles) at a 0.3C rate recorded after CV measurements.

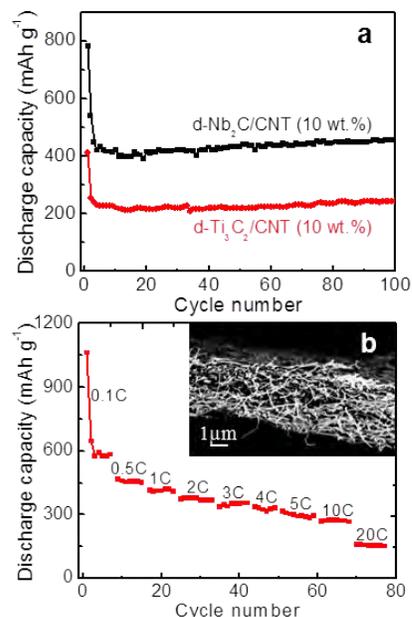


Figure 2. Electrochemical performance of d- Nb_2C /CNT nanocomposite paper: (a) Cycling performance compared to d- Ti_3C_2 /CNT paper at 0.5 C; (b) Rate performance - inset shows a cross-sectional SEM image of the d- Nb_2C /CNT paper.

Synthesis and Characterization of Si/SiO_x-Graphene Nanocomposite Anodes and Polymer Binders

PROJECT OBJECTIVE: Novel structured Si/SiO_x-carbon nanocomposites and polymer binders will be designed and synthesized to improve Si-based anode electrode kinetics and cycling life, and decrease initial irreversible capacity loss in high capacity Li-ion batteries. By combining the new Si-based anode materials and new polymer binders and investigating their structure-performance relationships, a high performance Si anode can be achieved.

1. Synthesis and characterization of Si/SiO_x-based nanocomposite Li-ion battery anodes.
2. Identify and evaluate the electrochemical performance of the Si/SiO_x-based nanocomposite and the polymer binder.
3. Develop understanding of long-lifetime Si anodes for Li-ion batteries by considering both the Si active phase and the polymer binder and surface interactions between the electrode components.

PROJECT IMPACT: The proposed collaborative effort closely integrates synthesis of Si-based composite anodes with controlled structure and composition, development of novel functional polymer binders, and materials characterization and electrochemical evaluation. The resulting optimized Si anode electrode will provide electrochemical performances which are essential to achieving higher energy densities in plug-in hybrid vehicle (PHEV) and electrical vehicle (EV) applications.

OUT-YEAR GOALS: According to the accomplishments of the project, several types of Si-based composite with promising electrochemical performance will be developed and demonstrated. New functional polymer binders will be developed. The mechanical and chemical influences of the structure, chemical composition and surface modification on electrochemical performance of those materials will be identified and demonstrated, thus to provide systematic fundamental understanding to guide the Si-based anode material design. The Si-based electrode design, including the selection of materials and polymer binders, will be demonstrated in cell testing at Penn State and with BATT project partners.

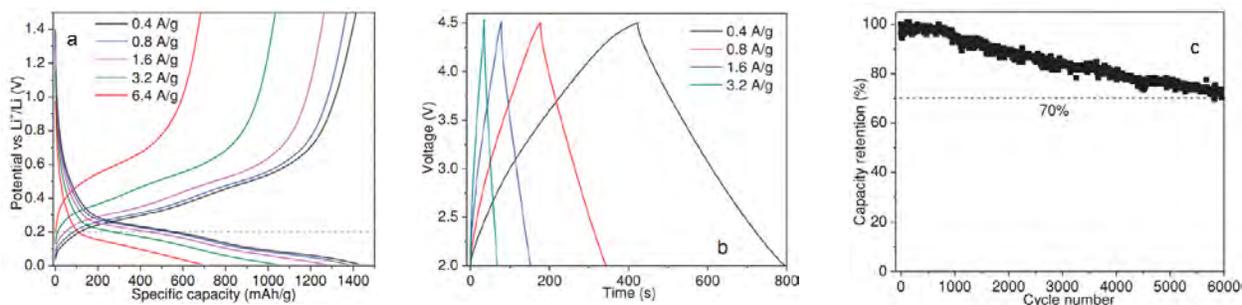
COLLABORATIONS: Gao Liu (LBNL), Chunmei Ban (NREL), Nissan R&D center.

Milestones

- 1) Go/No-Go: Stop the metal composites coating approach and focus on carbon coating approach if the capacities are less than 1500 mAh/g. Criteria: Synthesize, characterize and evaluate Si-based composite with novel coating (e.g. non-oxidic metal composites). (Dec. 13) **Go for carbon coating**
- 2) Identify and demonstrate the optimized composition, structure and surface modification of micro-sized Si/C and porous Si/C composites. (Mar. 14) **Complete**
- 3) Synthesize acidic/semiconducting polymer binders using grafting approach. (Jun. 14) **Complete**
- 4) Go/No-Go: Determine if semiconducting polymer approach can generally be applied to Si anodes. Criteria: Synthesis and electrochemical evaluation of Si/Si alloy composites. Fully characterize acidic/semiconducting polymer binders. Supply laminates of the optimized Si/Si alloy electrodes with electrode capacity of 800 mAh/g that cycle 100 cycles to BATT PIs. (Sep. 14) **Ongoing evaluation of new binders is continuing to end of project.**

Progress Report

Si-based anode materials: A Si-based anode material with controlled electrochemical prelithiation and superior high-rate performance by element doping has been demonstrated as an anode in a Li-ion hybrid supercapacitor to enable high energy and power densities. Benefiting from high capacity and good rate performance, a large portion of capacity is reserved even under lower voltage, for example, 0.2 V, as marked by the dashed line in the left figure. A Li-ion hybrid supercapacitor was constructed by coupling the prelithiated Si-based anode with a porous carbon cathode in conventional Li-ion electrolyte. The middle figure shows the voltage profiles of the Li-ion hybrid supercapacitor at different current densities. The curves show little deviation from the linear slope of an ideal supercapacitor, which is due to the relatively flat charge/discharge plateau of the Si-based anode. The energy and power densities of the hybrid supercapacitor were calculated based on these curves. A high energy density of 128 Wh/kg can be achieved at a power density of 1,229 W/kg. Even at an ultra-high power density of 9,704 W/kg, which is on par with conventional supercapacitors, the hybrid supercapacitor can still deliver 89 Wh/kg. The right figure shows the cycling performance of the hybrid supercapacitor at 1.6 A/g. The capacity retention is 70% after 6,000 cycles. This work demonstrates that incorporating high-performance Si-based anodes is an effective approach to boost the energy and power densities of Li-ion hybrid supercapacitors.



Binders: SPEEK binders synthesized in previous quarters were tested by BATT researchers Gao Liu and Hui Zhao (LBNL). An electrode composition of 25% SPEEK, 25% Super C-65, and 50% Umicore Si was prepared in a slurry with NMP, and then low (0.15 mg Si/cm^2), medium (0.51 mg Si/cm^2) and high-loaded electrodes (1.06 mg Si/cm^2) were tested. The capacity fade in these tested samples was severe after only 20 cycles and far below the CMC baseline. These results are in contrast to those reported earlier with SPEEK and Alfa Aesar commercial Si nanoparticles tested at Penn State. Attempts to troubleshoot the poor recent performance of the SPEEK binders and to understand the binder-Si interactions that lead to the observed cycling fade are ongoing. New ionic binders are being synthesized with the goal of final testing before the end of Q4 2014. Also, optimization of the single-phase Suzuki coupling synthesis of new binder structures and post-modification of these polymers for attachment of ionic groups continues in order to achieve similar results to those previously reported for SPEEK.

Wiring up Silicon Nanoparticles for High Performance Lithium Ion Battery Anodes

PROJECT OBJECTIVE: The charge capacity limitations of conventional carbon anodes are overcome by designing optimized nano-architected silicon electrodes.

This study pursues two main directions:

- 1) fabricating novel nanostructures that show improved cycle life, and
- 2) developing methods to study the lithiation/delithiation process to understand volume expansion for higher efficiency.

PROJECT IMPACT: The Li ion storage capacity, as well as the cycling stability of Si anodes, will be dramatically increased. This project's success will make Si the high performance Li-ion battery anode material toward high energy batteries to power vehicles.

OUT-YEAR GOALS: Mass loading, cycling life and first cycle Coulombic efficiency (1st CE) will be improved and optimized (over 1 mg/cm² and >85%) by varying material synthesis and electrode assembly. Fundamentals of volume expansion as well as SEI formation in Si nanostructures will be identified. A detailed study of inter-particle interactions during electrochemical reaction will be performed by *in situ* and *ex situ* microscopy.

COLLABORATIONS:

- BATT Program PIs
- SLAC: *In situ* X-ray
- Stanford: Prof. Nix, mechanics; Prof. Bao, materials.

Milestones

- 1) Utilize Si particles as an anode with capacity > 1000 mAh/g, mass loading of 1mAh/cm² and cycle life >100 cycles (Dec. 13) **Complete**
- 2) Go/No-Go: Try other conducting coating materials. Criteria: If the first cycle coulombic efficiency cannot go >80%. (Mar. 14) **Go**
- 3) Complete *in situ* TEM and *ex situ* tu SEM studies of two or multiple Si nanostructures during lithiation/delithiation to understand how neighboring particles affect each other and volume changes. (Oct. 14) **Complete**
- 4) Increase mass loading of Si material to achieve 2 mAh/cm² and first cycle coulombic efficiency (>85%) and cycle life >300 cycles (Sep. 14) **Complete**

Progress Report

A carbon-coated porous Si microparticle (nC-pSiMP) was designed. In this structure, porous Si microparticles (pSiMPs) consist of many interconnected primary Si nanoparticles; only the outer surface of the pSiMPs was coated with the carbon, leaving the interior pore structures unfilled (Fig. 1). Such design offers multiple attractive features for large-volume-change anode materials. 1) A commercially available SiO micro-particle source and a simple synthesis procedure make the process highly cost-effective and scalable. 2) The interconnected Si primary nanoparticles

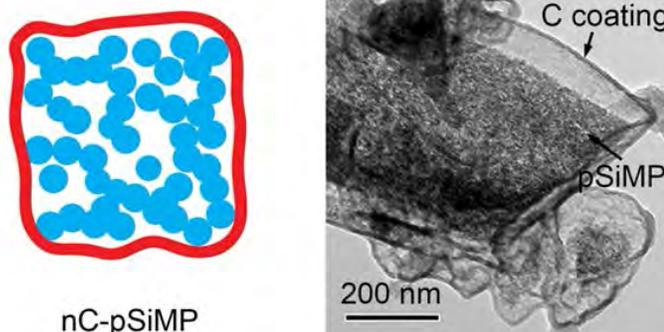


Figure 1. Schematic and TEM image of nC-pSiMP.

formed by thermal disproportionation of SiO microparticles ensures the size of the primary Si building blocks is less than 10 nm, which is below the critical fracture size. Thermal disproportionation also results in densely packed primary Si nanoparticles, which allow for good electronic conductivity among neighboring particles. 3) Carbon coats the exterior surface of the Si microparticles, prevents electrolyte diffusion into the interior pore space and restricts SEI formation to the outer surface. 4) Non-filling coating retains enough internal void space to accommodate the volume expansion of the Si nanoparticles, and keeps the carbon shell intact during electrochemical cycling. 5) The non-filling coating introduces less carbon to the composites, which not only increases specific capacity, but also increases the initial coulombic efficiency by reducing the amount of Li trapping in the carbon.

As a result, the nC-pSiMP composite demonstrates excellent cycling stability with high reversible specific capacity (*ca.* 1500 mAhg⁻¹, 1000 cycles) at the rate of C/4, shown in Fig. 2a. The anodes were also tested with different areal mass loadings up to 2.01 mg cm⁻² (Fig. 2b). A reversible areal capacity of 3.22 mAh cm⁻² is achieved at first cycle with a current density of 0.05 mA cm⁻², corresponding to a specific capacity of 1602 mAhg⁻¹ based on the total mass of the Si/C composites. The capacity remains stable during the subsequent 4th to 100th cycles at the higher rate of 0.25 mA cm⁻², and the areal capacity maintains 2.84 mAh cm⁻² after 100 cycles, which is close to the capacity of a commercial Li-ion battery cell. Little decrease of specific capacity is found as the areal mass loading increased. Moreover, the production of nC-pSiMP is simple and scalable using the low-cost starting material of SiO microparticle. Thus nC-pSiMP shows great promise for future mass production as a high-performance composite anode.

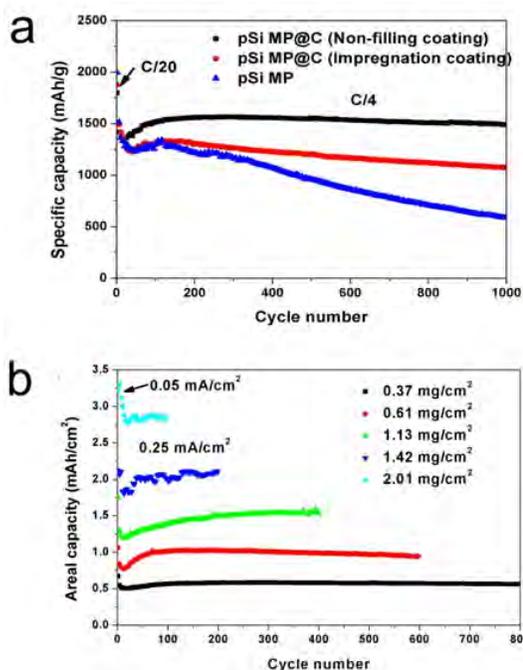


Figure 2. (a) Reversible delithiation capacity for the first 1000 galvanostatic cycles of the pSiMPs with different coatings. (c) High areal mass loading test (Up to 2.0 mg cm⁻² active material) of nC-pSiMPs. All electrodes were cycled at 0.5 mA cm⁻² for the initial three cycles and 0.25 mA cm⁻² afterward.

Fluorinated Electrolyte for 5-V Li-ion Chemistry

PROJECT OBJECTIVE: The objective of this project is to develop a new advanced electrolyte system with outstanding stability at high voltage and high temperature and improved safety characteristic for an electrochemical couple consisting of the high voltage $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) cathode and graphite anode. The specific objectives of this proposal are the design, synthesis and evaluation of (1) non-flammable high voltage solvents to render intrinsic voltage and thermal stability in the entire electrochemical window of the high-voltage cathode materials, and (2) electrolyte additives to enhance the formation of a compact and robust solid electrolyte interphase (SEI) on the surface of the high voltage cathode. A third objective is to gain fundamental understanding of the interaction between electrolyte and high voltage electrode materials, the dependence of SEI functionality on electrolyte composition, and the effect of high temperature on the full Li-ion cells using the advanced electrolyte system.

PROJECT IMPACT: This innovative fluorinated electrolyte is intrinsically more stable in electrochemical oxidation due to the fluorine substitution; therefore it would be also applicable to cathode chemistries based on TM oxides other than LNMO. The results of this project can be further applied to a wide spectrum of high-energy battery systems oriented for PHEVs that operate at high potentials, such as LiMPO_4 (M=Co, Ni, Mn), or battery systems that require a high-voltage activation process, such as the high-capacity Li-Mn-rich $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{Li}[\text{Ni}_x\text{Mn}_y\text{Co}_z]\text{O}_2$. This electrolyte innovation will push the U.S. supply base of batteries and battery materials past the technological and cost advantages of foreign competitors, thereby increasing economic value to the USA. ANL's new fluorinated electrolyte material will enable the demand for more PHEVs and EVs, which directly transforms to much less gasoline consumption and less pollutant emissions.

OUT-YEAR-GOALS: The goal of this project is to deliver a new fluorinated electrolyte system with outstanding stability at high voltage and high temperature with improved safety characteristic for an electrochemical couple consisting of 5-V Ni-Mn spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) cathode and graphite anode. The specific objectives of this proposal are the design, synthesis, and evaluation of (1) non-flammable high voltage fluorinated solvents to attain intrinsic voltage stability in the entire electrochemical window of the high-voltage cathode material and (2) effective electrolyte additives that form a compact and robust solid-electrolyte interphase (SEI) on the surfaces of the high voltage cathode and graphitic anode.

COLLABORATIONS: Kang Xu, U.S. Army Research Laboratory; Xiao-Qing Yang, Brookhaven National Laboratory; Brett Lucht, University of Rhode Island; Andrew Jansen and Dr. Gregory Krumdick, Argonne National Laboratory.

Milestones

- 1) Complete theoretical calculation of electrolyte solvents (fluorinated carbonate, fluorinated ether) and additives (fluorinated phosphate, fluorinated phosphazene); Validate the electrochemical properties of the available fluorinated solvents by CV and leakage current experiment. (Dec. 13) **Complete.**
- 2) Synthesize and characterize the Gen-1 electrolyte (3 linear/cyclic F-carbonate solvents + 1 additive) by NMR, FT-IR, GC-MS, DSC. (Mar. 14) **Complete.**
- 3) Evaluate the LNMO/graphite cell performance of Gen-1 electrolyte [Solvent(s) + Additive(s)]. (Jun. 14) **Complete.**
- 4) Optimize the Gen-1 high voltage F-electrolyte; (Sep. 14) **Complete**; Deliver 10 baseline pouch cells. (Sep. 14) **Ongoing.**

Progress Report

Based on the floating test results reported in Q3, a number of new formulations of fluorinated electrolytes were made and their electrochemical performance in LNMO/A12 graphite cells was examined. One formulation employed a more fluorinated solvent trifluoropropylene carbonate (TFPC) than those used in the HVE1 formulation (1.0 M LiPF₆ in FEC/F-EMC/F-EPE=3/5/2 with 1% LiDFOB). This new formulation exhibited stable cycling performance in a LNMO/A12 cell as shown in Fig. 1a, indicating the intrinsic stability of TFPC towards oxidation. However, this electrolyte is not quite compatible with the graphite anode (Fig. 1b). Other electrolyte formulations employing non-fluorinated solvents were also investigated. Figure 1c showed the cycling stability of a LNMO/A12 cell with 1.2M LiPF₆ FEC/DMC = 1/1 at room temperature.

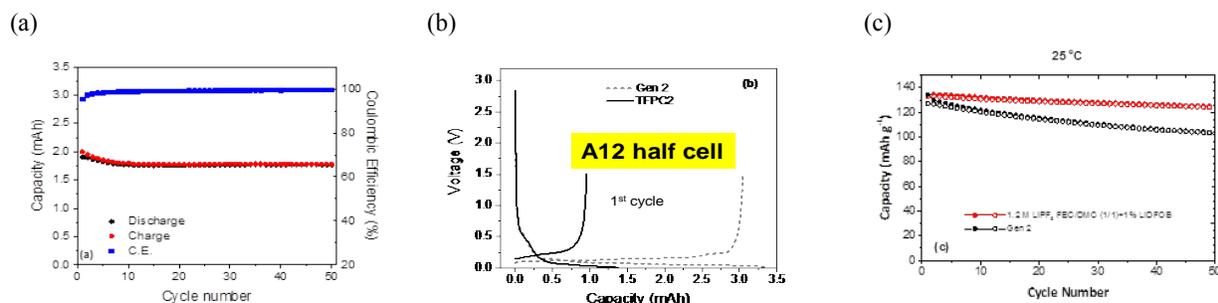


Figure 1. (a) Cycling performance of LNMO/A12 cells with electrolyte 1.0 M TFPC/F-EMC/F-EPE=3/5/2 at RT, (b) A12/Li half-cell voltage profiles with 1.0 M TFPC/F-EMC/F-EPE = 3/5/2 at RT and (c) Cycling performance of LNMO/A12 cell with 1.2 M LiPF₆ FEC/DMC =1/1 at RT.

Both formulations showed improved performance in the high voltage cell over Gen2; however, TFPC-electrolyte suffered from low initial capacity due to inferior SEI formation on the anode (Fig. 1b) and its lower ionic conductivity. Both issues can be solved by a hybrid FEC/DMC formulation, as evidenced by the data in Fig. 1c; however, the HT performance is compromised (data not shown) indicating the non-fluorinated DMC is not intrinsically stable toward oxidation. Research focus will be shifted to the development of new SEI additives to enable the fluorinated cyclic carbonates for LNMO/A12 cells.

The mechanistic study of the HVE1 electrolyte revealed new details to account for the improvement over Gen2. The LNMO cathode harvested from Gen2, HVE1 and HVE1+1% LiDFOB electrolyte cells was examined by high resolution TEM. LNMO from the Gen 2 cells showed significant degradation of the active material particles with edge loosing and cracking (Fig. 2a), while smooth and intact surfaces were observed for the electrodes cycled with fluorinated electrolytes HVE1 (Fig. 2b) and HVE1+1% LiDFOB (Fig. 2c). This result is in good agreement with the ICP-MS results reported in Q3 suggesting the Mn/Ni dissolution and the cathode material degradation are closely related.

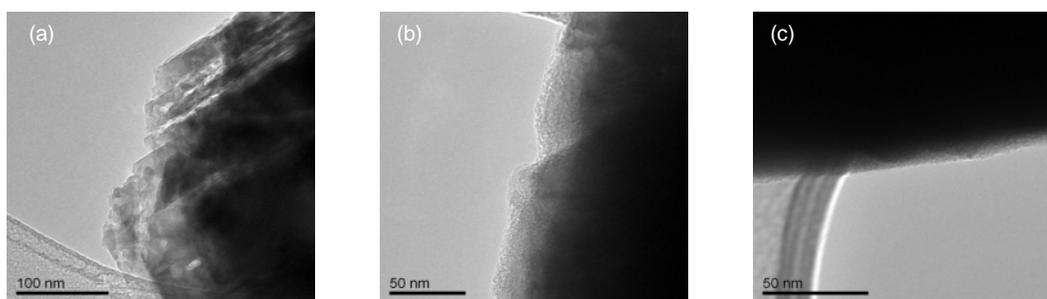


Figure 2. TEM image of harvested LNMO cathode cycled at 55°C for 20 cycles with (a) Gen 2 electrolyte, (b) HVE1 electrolyte without additive and (c) HVE1 electrolyte with 1% LiDFOB.

The oxidation and reduction potentials of new fluorinated sulfones were calculated by DFT and the organic synthesis has started. These results will be reported in the first quarter of the next fiscal year.

Task 3.2 – Joe Sunstrom and Hitomi Miyawaki (Daikin America, Inc.)

Daikin America High Voltage Electrolyte

PROJECT OBJECTIVE: Development of a stable (300 – 1000 cycles), high-voltage (at 4.6 volts), and safe (self-extinguishing) formulated electrolyte.

Exploratory Development (Budget Period #1 – October 1, 2013 to January 31, 2015)

- Identify promising electrolyte compositions for high-voltage (4.6 v) electrolytes via the initial experimental screening and testing of selected compositions

Advanced Development (Budget Period #2 – February 1, 2015 to September 31, 2015)

- Detailed studies and testing of the selected high-voltage electrolyte formulations and the fabrication of final demonstration cells

PROJECT IMPACT: Fluorinated small molecules offer the advantage of low viscosity along with high chemical stability due to the strength of the C-F bond. Due to this bond strength, Daikin fluorochemical materials are among the most electrochemical stable materials that still have the needed performance attributes for a practical electrolyte. Such an electrolyte will allow routine operating voltages to be increased to 4.6 volts. This technological advance would allow significant cost reduction by reducing the number of cells needed in a particular application and/or allow for greater driving range in PHEV applications.

OUT-YEAR-GOALS: This project has a clearly defined goals for both temperature and voltage performance which are consistent with the deliverables of this proposal. Those goals are to deliver an electrolyte capable of 300 - 1000 cycles at 3.2 - 4.6 V at nominal rate with stable performance. An additional goal is to have improved high temperature (> 60°C) performance. An additional safety goal is to have this electrolyte be self-extinguishing.

COLLABORATIONS: At present, the team is collaborating with and receiving great advice from Vince Battaglia's group at LBNL. In addition, there are plans to collaborate with another group (TBD) for electrode surface analysis.

Milestones

Budget Period #1 – Oct. 1, 2013 to Jan. 31, 2015

- 1) Complete identification of promising electrolyte formulations. Experimental design completed with consistent data sufficient to build models. Promising electrolyte formulations are identified which are suitable for high-voltage battery testing. **Ongoing**
- 2) Successful fabrication of 10 interim cells and delivery of cells to DOE laboratory to be specified. **Ongoing**
- 3) Electrochemical and battery cycle tests are completed and promising results are obtained which demonstrate stable performance at 4.6 volts. **Ongoing**

Progress Report

No report received this quarter.

Novel Non-Carbonate Based Electrolytes for Silicon Anodes

PROJECT OBJECTIVE: The objective of this project is to develop non-carbonate electrolytes that form a stable solid electrolyte interphase (SEI) on silicon alloy anodes, enabling substantial improvements in energy density and cost relative to current lithium ion batteries (LIBs). These improvements are vital for mass market adoption of electric vehicles. At present, commercial vehicle batteries employ cells based on LiMO_2 ($M = \text{Mn, Ni, Co}$), LiMn_2O_4 , and/or LiFePO_4 coupled with graphite anodes. Next generation cathode candidates include materials with higher specific capacity or higher operating voltage, with a goal of improving overall cell energy density. However, to achieve substantial increases in cell energy density, a higher energy density anode material is also required. Silicon anodes demonstrate very high specific capacities, with a theoretical limit of 4200 mAh/g and state-of-the-art electrodes exhibiting capacities greater than 1000 mAh/g. While these types of anodes can help achieve target energy densities, their current cycle life is inadequate for automotive applications. In graphite anodes, carbonate electrolyte formulations reductively decompose during the first cycle lithiation, forming a passivation layer that allows lithium transport, yet is electrically insulating to prevent further reduction of bulk electrolyte. However, the volumetric changes in silicon upon cycling are substantially larger than graphite, requiring a much more mechanically robust SEI film.

PROJECT IMPACT: Silicon alloy anodes enable substantial improvements in energy density and cost relative to current lithium ion batteries. These improvements are vital for mass market adoption of electric vehicles, which would significantly reduce CO_2 emissions as well as eliminate the US dependence on energy imports.

OUT-YEAR-GOALS:

Development of non-carbonate electrolyte formulations that

- form stable SEIs on 3M silicon alloy anode, enabling coulombic efficiency > 99.9% and cycle life > 500 cycles (80% capacity) with NMC cathodes;
- have comparable ionic conductivity to carbonate formulations, enabling high power at room temperature and low temperature;
- are oxidatively stable to 4.6V, enabling the use of high energy NMC cathodes in the future; and
- do not increase cell costs over today's carbonate formulations.

COLLABORATIONS: Wildcat is working with 3M on this project. To date, 3M is supplying the silicon alloy anode films and NMC cathode films for use in Wildcat cells.

Milestones

- 1) Assemble materials, establish baseline performance with 3M materials (Dec. 13) **Complete**
- 2) Develop initial additive package using non-SEI forming solvent. (Mar. 14) **Complete**
- 3) Screen initial solvents with initial additive package. (Jun. 14) **Complete**
- 4) Design/build interim cells for DOE (Sep. 14) **Ongoing - ship by end of 2014**

Progress Report

The fourth quarter of this project includes two main efforts. First, primary electrochemical screening of non-carbonate solvents was completed using several of the promising additives identified in Q3. Approximately 30 high dielectric constant solvents and 30 low viscosity solvents were selected based on criteria such as: 1) aprotic; 2) low-melting point; 3) high-boiling point; 4) appropriate dielectric constant or viscosity; 5) commercial availability. These solvent candidates were evaluated as follows. Each of the low-viscosity solvents were blended with ethylene carbonate (EC) at two ratios. Each of the high dielectric constant solvents were blended with ethylmethyl carbonate (EMC) at two ratios. Each solution was then screened to determine if 1M LiPF₆ was completely soluble. For those that met the solubility criteria, both the cathode and anode films were soaked in the solvent blends overnight to ensure the stability of the films in the electrolyte. Finally, full cells (NMC/Si) were prepared with electrolyte solutions that met both the solubility and the electrolyte stability criteria. The electrolyte solutions were prepared with five of the most promising additives identified in Q3.

The results of the high-dielectric-constant solvent/EMC blends are shown below, where the dashed lines represent the mean value for the control and the gray bands are +/- one standard deviation about the mean.

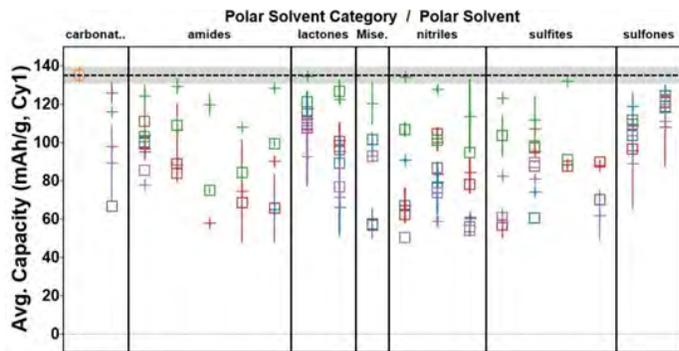


Figure 1. Cycle 1 capacity of polar solvent/EMC formulations (color: additive type, shape: additive concentration).

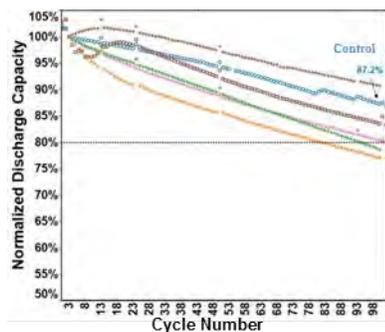


Figure 2. Capacity retention of best polar solvent/EMC formulations

The most promising high-dielectric-constant (polar) solvents were then blended with various low-viscosity solvents, and formulated with additives identified in Q3. Results are shown below.

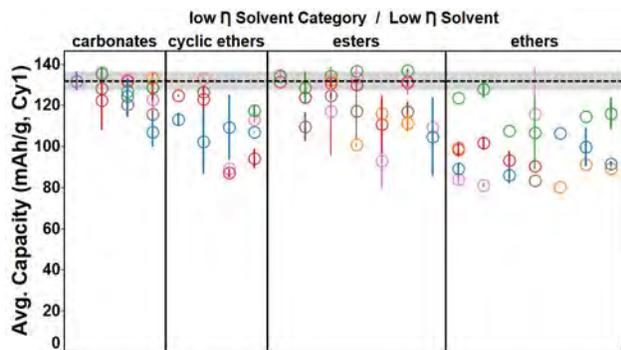


Figure 3. Cycle 1 capacity of best polar solvent/low-viscosity formulations (color: polar solvent type)

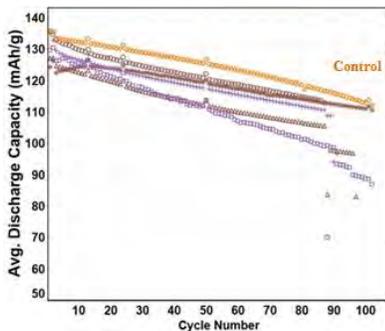


Figure 4. Capacity retention of best non-carbonate formulations

Task 4.1 – Michael M. Thackeray (Argonne National Laboratory)

Novel Cathode Materials and Processing Methods.

PROJECT OBJECTIVE: The end-goal of this project is the development of low-cost, high-energy and high-power, Mn-oxide-based cathodes for PHEV and EV vehicles. Improvement of design, composition and performance of advanced electrodes with stable architectures, facilitated by an atomic-scale understanding of electrochemical and degradation processes, is a key objective of this work. New processing routes as well as Argonne National Laboratory's comprehensive characterization facilities will be used to explore novel, surface and bulk structures both *in situ* and *ex situ* in the pursuit of advancing lithium-ion battery cathode materials.

PROJECT IMPACT: Standard Li-ion technologies are currently unable to meet the demands of next-generation PHEV and EV vehicles. Battery developers and scientists alike will take advantage of the knowledge, both applied and fundamental, generated from this project to further advance the field. In particular, it is expected that this knowledge will significantly enable progress towards meeting the DOE goals for 40-mile, all-electric range, PHEVs.

OUT-YEAR-GOALS:

- Identify composite electrode structures that mitigate or eliminate voltage fade.
- Identify and characterize surface chemistries and architectures that allow fast Li-ion transport, are stable to ~5 V, and mitigate or eliminate transition-metal dissolution.
- Scale-up, evaluate and verify promising cathode materials using Argonne National Laboratory's Scale-up and Cell Fabrication facilities.
- Take advantage of Argonne National Laboratory's user facilities (e.g., the Advanced Photon Source (APS), the Center for Nanoscale Materials (CNM), the Electron Microscopy Center (EMC) and the Argonne Leadership Computing Facility (ALCF) to build on the fundamental knowledge gained to promote and implement the rational design of new electrode materials.
- Use complementary theoretical approaches to further the understanding of electrode structures and electrochemical processes to accelerate the progress of materials development.

COLLABORATIONS: Brandon R. Long, Joong Sun Park.

Milestones

- 1) Evaluate the stabilization and performance of near end-member, Li_2MnO_3 -containing composite electrodes. Specifically, high and low Li_2MnO_3 -content electrodes. (Dec. 13) **Ongoing**
- 2) Evaluate new synthetic routes using layered LiMO_2 (M = Mn, Ni, Co) precursors to prepare composite electrode materials. (Mar. 14) **Complete**
- 3) Synthesize and characterize unique surface architectures that enable >200 mAh/g at a $>1\text{C}$ rate with complementary theoretical studies of surface structures. (Jun. 14) **Ongoing** (see text).
- 4) Identify structures and compositions, including surface and bulk, that can deliver ~ 230 mAh/g at an average discharge voltage of ~ 3.5 V on extended cycling. (Sep. 14) **Ongoing**

Note: This project is broad in scope and although several projects have been completed and papers submitted and accepted for publication during FY14, the overall theme of the project will be continued in FY15. For this reason, most of the milestones are labelled 'Ongoing'.

Progress Report

Recent reports indicate that high capacities (*ca.* 200 mAh/g) and good stability can be obtained from “layered-layered” (LL) $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ ($M=\text{Mn, Ni, Co}$) cathodes for x values less than *ca.* 0.3. Lowering the Li_2MnO_3 content serves to mitigate structural instabilities brought about by the activation and utilization of excess Li residing in the transition metal layers of as-prepared electrodes. Likewise, enhanced stabilization of LL cathode structures at high capacities can be achieved through the integration of a spinel component. These complex, “layered-layered-spinel” (LLS) structures, represented by the general formula $y[x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2] \cdot (1-y)\text{LiM}_2\text{O}_4$, have also shown promise for improving first-cycle efficiencies (FCE) as well as the rate performance of LL cathodes. A challenge that remains is defining the relevant, large compositional space made available when considering both elemental and structural contributions to the final chemistries. For example, optimization of both LL and spinel components, as well as the integration of the two, is complex. The performance of both the LL and spinel components is dependent on factors such as the ratios of transition metals (Mn:Ni:Co), Li_2MnO_3 content, and synthesis conditions. Similarly, the electrochemical properties of integrated LLS electrode structures are dependent on the same parameters. Furthermore, the contribution of Co is particularly sensitive as it can serve to enhance electrode performance (e.g., conductivity and layering); however, Co must be limited in terms of content due to practical considerations, such as cost and safety. In order to fully exploit the concept of LLS electrodes, systematic studies are being undertaken to determine the key properties of the individual components (LL and spinel) and synthesis procedures associated with their integration.

Figure 1a shows the first-cycle capacities of a series of LL $0.05\text{Li}_2\text{MnO}_3 \cdot 0.95\text{LiMn}_{0.5-y}\text{Ni}_{0.5+y/2}\text{Co}_{y/2}\text{O}_2$ electrodes (in Li half-cells) in which $0 \leq y \leq 0.3$. The Co content is a critical parameter relative to the Mn and Ni concentrations; an optimum value is found at $y=0.1$. It appears that the overall Co content can be kept low (*ca.* 5%) for selected Mn:Ni ratios, which is in line with the strategy to design a highly layered electrode that is rich in Mn and low in Co. Figure 1b reveals that, for $y=0.1$, the electrode can provide a cell energy density of approximately 750 Wh/kg of oxide with a 6% energy loss over 50 cycles. These compositions are being explored as precursor templates for synthesizing stabilized LLS structures. Because of the layered and composite nature of these materials, it is envisioned that selected cations can be inserted into the Li layers with some degree of control, as has already been demonstrated in fabricating LL structures from a Li_2MnO_3 precursor. The ability to control the occupation of Li-layer sites by transition metal cations is consistent with the strategy of embedding spinel domains into structurally compatible LL electrode materials. This approach provides new possibilities for tuning not only the stability of high-capacity LL cathodes, but also the voltage profiles of the cells.

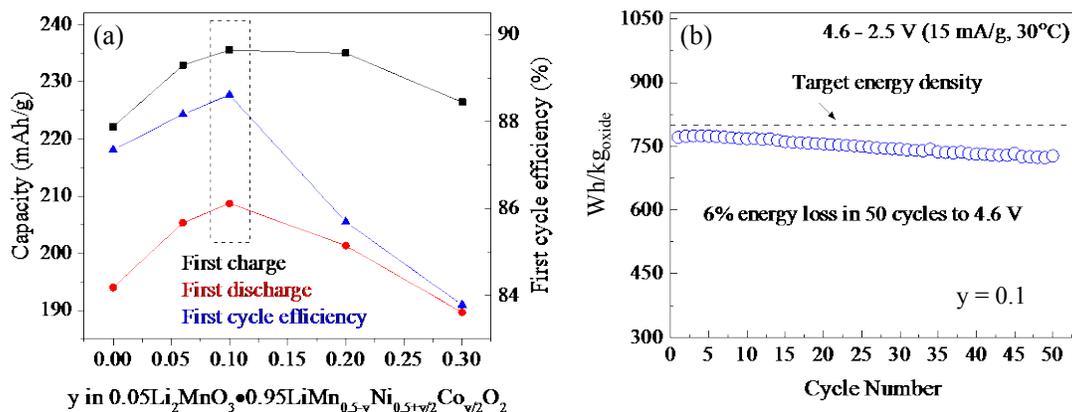


Figure 1. (a) First cycle capacities and the associated FCE's of a series of $0.05\text{Li}_2\text{MnO}_3 \cdot 0.95\text{LiMn}_{0.5-y}\text{Ni}_{0.5+y/2}\text{Co}_{y/2}\text{O}_2$ electrodes for $0 \leq y \leq 0.3$. (b) Specific energy density of a Li half-cell (cathode composition: $y=0.1$) for 50 cycles between 4.6 and 2.5 V (30°C, 15 mA/g).

Design of High Performance, High Energy Cathode Materials

PROJECT OBJECTIVE: To develop high-energy, high-performance cathode materials including composites and coated powders, using spray pyrolysis and other synthesis techniques. The emphasis is on two systems; modified NMC materials and the high voltage spinel, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO). Partial substitution of Ti for Co in NMCs results in higher discharge capacities (up to 225 mAh/g) without the need for a formation reaction and without risk of structural change during cycling. Experiments are directed towards optimizing the synthesis, improving cycle life, and understanding the effect of Ti substitution. For LNMO, particle size and morphology are controlled during spray pyrolysis synthesis by varying residence time, temperature, precursors and other synthetic parameters. By exploiting differences in precursor reactivity, coated materials can be produced, and composites can be prepared by post-processing techniques such as infiltration. These approaches are expected to improve cycling due to reduced side reactions with electrolytes.

PROJECT IMPACT: To increase the energy density of Li ion batteries, cathode materials with higher voltages and/or higher capacities are required, but safety and cycle life cannot be compromised. In the short term, the most promising materials are based on high voltage spinels or modified NMCs that do not require formation cycles or undergo structural transformations during cycling. Ti-substituted NMCs exhibit increased discharge capacity, due to improved first cycle efficiencies and are not expected to undergo structural changes or voltage decay during cycling. Optimizing LNMO particle morphologies, utilizing coatings and composites are expected to improve coulombic efficiencies and safety as well as cycle life.

OUT-YEAR GOALS: Two high-energy cathode systems will have been optimized for this work; LNMO and high capacity Ti-substituted NMC cathodes, which do not require activation via charge to high potentials. Materials will be synthesized by a simple, low cost spray pyrolysis method, which has potential for commercialization. This technique produces phase-pure, unagglomerated powders and allows for excellent control over particle morphologies, sizes and distributions. Coated materials will also be produced in either one or two simple steps by exploiting differing precursor reactivities during the spray pyrolysis procedure, or by first preparing hollow spheres of an electroactive material, infiltrating the spheres with precursors of the high voltage cathodes, and subsequent thermal treatment. The final result is expected to be a high energy density cathode material with good safety and cycling characteristics suitable for use in vehicular applications, which can be made by a low-cost process that is easily scalable.

COLLABORATIONS: Huolin Xin (BNL), Dennis Norlund, Tsu-Chien Weng and Dimosthenis Sokaras (SLAC), Mark Asta (U.C. Berkeley) and Chunmei Ban (NREL)

Milestones

- 1) Complete optimization of Ti-NMC synthesis with TiOSO_4 precursor (Dec. 13) **Discontinued. This effort has been transferred to the ABR program**
- 2) Go/No-Go: Decision on infiltration of LiFePO_4 into LNMO. Criteria: A “no go” decision will be made if attempts to prevent reaction of LiFePO_4 with LNMO during processing fail (Mar. 14) **No go. Effort will be redirected towards composites with spray pyrolyzed NMCs.**
- 3) Complete soft XA7S experiments on Ti-NMCs (Jun.14) **Complete**
- 4) Go/No-Go: Decision on spray pyrolysis of NMCs. Criteria: A “no go” decision will be made if the electrochemical performance of the spray-pyrolyzed material does not equal that of the material made by co-precipitation. (Sep. 14). **Go decision, performance is better than that of conventionally made materials.**

Progress Report

Spray pyrolysis synthesis of cathode materials continued this quarter with more syntheses, electrochemical measurements, and characterizations. STEM characterization was performed to investigate the particle-particle interfaces between the primary NMC particles (Figs. 1a-c). It was found that multiple types of interfaces were formed and the dominant types are shown in Figs. 1b and c. Two adjacent particles show different crystal orientations, which potentially leads to structural disorder thus allowing for Li diffusion along the interfaces (computational efforts will follow). Aliovalent substitution was applied to NMC materials during spray pyrolysis. To date, Ru and Ti substitution on the cobalt site was performed. The first cycle coulombic inefficiency remained as low as 10% in all these materials between 2.0 and 4.7 V vs. Li^+/Li (intrinsic benefit of spray pyrolysis and small primary particle size). Figure 1d shows the discharge capacity retention behaviors for the pristine NMC442 and the 2%Ti-substituted NMC442. Ti substitution significantly reduces the initial discharge capacity, but the capacity was remarkably stable within the measured 20 cycles (2.0 to 4.7 V vs. Li^+/Li). Furthermore, the voltage profile was also very stable (data not shown). Further improvement on Ti-substituted NMCs is being performed. ALD coating was also applied to spray pyrolysis produced NMC materials. The preliminary results showed that the 1 nm Al_2O_3 coating on the electrode surface did impact cycling performance. The coating behaves like a passivation layer and reduces the practical capacity. The electrode underwent an activation period and then slowly degraded (black curve in Fig. 1e). More efforts on the coating protection are being implemented and an improvement on the cycling stability is still possible.

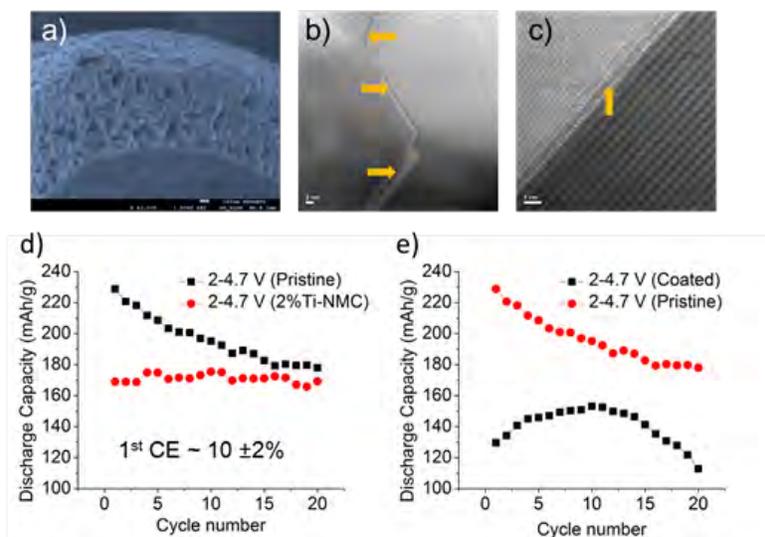


Figure 1. (a-c) Interface study of NMC materials characterized by SEM and STEM, where the orange arrows indicate particle-particle interfaces; (c) comparison of discharge capacity retention between NMC442 and 2%Ti-substituted NMC (cobalt site); and (d) comparison of discharge capacity retention between NMC 442 electrode and ALD-coated NMC442 electrode.

TEM has also been used this quarter to characterize NMC materials, work done in collaboration with Huolin Xin (BNL). Synchrotron and computational efforts are continued in collaboration with Mark Asta (UCB), Dennis Nordlund (SSRL), Dr. Tsu-Chien Weng (SSRL) and Dimosthenis Sokaras (SSRL). Atomic layer deposition was performed in collaboration with Chunmei Ban (NREL).

High-capacity, High-voltage Cathode Materials for Lithium-ion Batteries

PROJECT OBJECTIVE: A significant increase in capacity and/or operating voltage is needed to make the Li-ion technology viable for vehicle applications. This project addresses this issue by focusing on the design and development of cathode materials based on polyanions that have the possibility for reversibly inserting/extracting more than one lithium ion per transition-metal ion and/or operating above 4.3 V. Specifically, high-capacity and/or high-voltage Li transition-metal phosphate, silicate, and carbonophosphate cathodes are investigated. The major issue with the phosphate and silicate cathodes is the poor electronic and ionic transport, which limits the practical capacity, energy density, and power density. To overcome these difficulties, novel microwave-assisted solvothermal, microwave-assisted hydrothermal, and template-assisted synthesis approaches are pursued to realize controlled morphology with smaller particle size and to integrate conductive additives like graphene in a single synthesis step.

PROJECT IMPACT: The critical requirements for the widespread adoption of Li-ion batteries for vehicle applications are high energy, high power, long cycle life, low cost, and acceptable safety. The currently available cathode materials do not adequately fulfill these requirements. The polyanion cathodes with the novel synthesis approaches pursued in this project have the potential to significantly increase the energy and power. More importantly, the covalently bonded polyanion groups can offer excellent thermal stability and enhanced safety. The microwave-assisted synthesis approaches pursued also lower the manufacturing cost of the cathodes through a significant reduction in reaction time and temperature.

OUT-YEAR GOALS: The overall goal is to enhance the electrochemical performances of high-capacity, high-voltage polyanion cathode systems and to develop a fundamental understanding of their structure-composition-performance relationships. Specifically, the project is focused on enhancing the electrochemical performance of systems such as LiMPO_4 , $\text{Li}_2\text{MP}_2\text{O}_7$, Li_2MSiO_4 , $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, $\text{Li}_9\text{V}_3(\text{P}_2\text{O}_7)_3(\text{PO}_4)_2$, $\text{Li}_3\text{M}(\text{CO}_3)(\text{PO}_4)$, and their solid solutions with $\text{M} = \text{Mn, Fe, Co, Ni, and VO}$. Advanced structural, chemical, surface, and electrochemical characterizations of the materials synthesized by novel approaches are anticipated to provide in-depth understanding of the factors that control the electrochemical properties of the polyanion cathodes. For example, the possible segregation of certain cations to the surface in solid solution cathodes consisting of multiple transition-metal ions and the role of conductive graphene integrated into the polyanion cathodes can help design better-performing cathodes.

COLLABORATIONS: None this quarter.

Milestones

- 1) Establish whether or not LiMnPO_4 can be aliovalently doped with V^{3+} and determine its effect on electrochemical performance. (Dec. 13) **Complete**
- 2) Demonstrate > 200 mAh/g capacity with LiVOPO_4 prepared by novel synthesis approaches. (Mar. 14) **Complete**
- 3) Establish whether or not LiCoPO_4 can be aliovalently doped with V^{3+} and determine its effect on electrochemical performance. (Jun. 14) **Complete**
- 4) Go/No-Go: Stop the microwave-assisted synthesis if capacities are < 150 mAh/g. Criteria: demonstrate > 150 mAh/g capacity with $\text{Li}_3\text{M}(\text{CO}_3)(\text{PO}_4)$ prepared by microwave-assisted synthesis. (Sep. 14) **Complete. A No-Go decision has been made with the carbonophosphates.**

Progress Report

This quarter's focus was on microwave-assisted hydrothermal (MW-HT) and solvothermal (MW-ST) syntheses of the carbonophosphates, $\text{Li}_3\text{MCO}_3\text{PO}_4$ ($\text{M} = \text{Mn, Co, Ni, and Cu}$). Previously, the synthesis of $\text{Na}_3\text{MCO}_3\text{PO}_4$ has been reported in the literature with a hydrothermal method. In this work, $\text{Na}_3\text{MCO}_3\text{PO}_4$ with $\text{M} = \text{Mn, Co, Ni, and Cu}$ were successfully synthesized by the MW-HT method at 220°C (Fig. 1). Additionally, the synthesis of $\text{Na}_3\text{CoCO}_3\text{PO}_4$ by the MW-ST method with tetraethylene glycol (TEG) as a solvent offered a favorable sub-micrometer platelet morphology (Fig. 2). The advantage of the MW-HT and MW-ST methods is that they produce the products faster in two hours compared to 48 hours with the hydrothermal method. Unfortunately, attempts to directly synthesize the Li analogs $\text{Li}_3\text{MCO}_3\text{PO}_4$ were unsuccessful. Cells were assembled with the Na forms ($\text{Na}_3\text{MCO}_3\text{PO}_4$) as cathodes and both Li and Na as anodes. The highest first cycle capacity achieved with $\text{Na}_3\text{MnCO}_3\text{PO}_4$ was 117 and 42 mAh/g with the Na and Li anodes, respectively, with a coulombic efficiency $< 30\%$ in both cases, suggesting a severe side reaction with the electrolyte. To overcome this problem, various combinations of the following electrolytes were tried: ethylene carbonate, ethylmethyl carbonate, diethylmethyl carbonate, propylene carbonate, dimethylsulfoxide, 15-crown-5 ether, 1-methyl-3-pentylimidazolium, and bis(trifluoromethanesulfonyl)imide. Unfortunately, none of the electrolytes increased the electrochemical performance, and the goal of capacity values > 150 mAh/g could not be achieved.

In addition to the carbonophosphate work, research continued on the electrochemical and chemical lithiation of the α_1 - LiVOPO_4 /graphene nanocomposite in order to understand the phase evolution. The α_1 - LiVOPO_4 /graphene nanocomposite was prepared by the MW-ST approach as reported before, which has a grey-green color. After chemical lithiation with n-butyllithium, the color of the samples gradually changed to brown with increasing amount of Li inserted into the lattice. This finding is consistent with what was observed before with α - and β - LiVOPO_4 after a similar lithiation process. The *ex situ* X-ray diffraction (XRD) patterns of the α_1 - LiVOPO_4 /graphene electrodes at various depths of discharge show the phase evolution (Fig. 3). For example, the intensity of the (001) peak is significantly reduced below 2.5 V, along with the growth of a new peak on the right side of the (001) peak. Similarly, the (020) peak is progressively replaced by another peak located on its left side upon discharge to 1.7 V. These results suggest a two-phase reaction of the electrochemical lithiation process. Additionally, the chemically-lithiated α_1 - Li_2VOPO_4 displays an XRD pattern similar to the sample discharged to 1.5 V, indicating the consistency between the electrochemical and chemical lithiation processes. Future work will focus on the understanding of the detailed structure of the new lithiated α_1 - Li_2VOPO_4 phase.

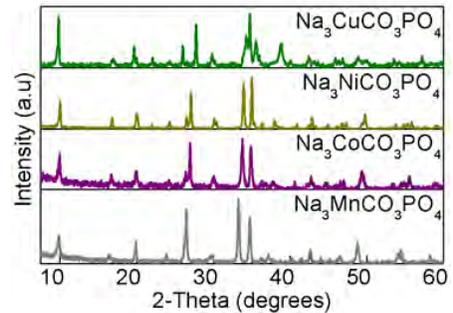


Figure 1. XRD patterns of $\text{Na}_3\text{MCO}_3\text{PO}_4$.

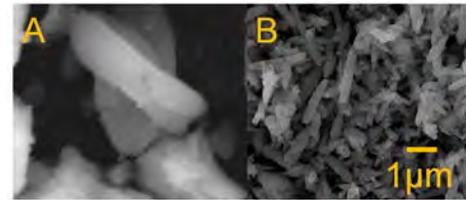


Figure 2. SEM micrographs of $\text{Na}_3\text{CoCO}_3\text{PO}_4$ synthesized by the (A) MW-HT and (B) MW-ST methods.

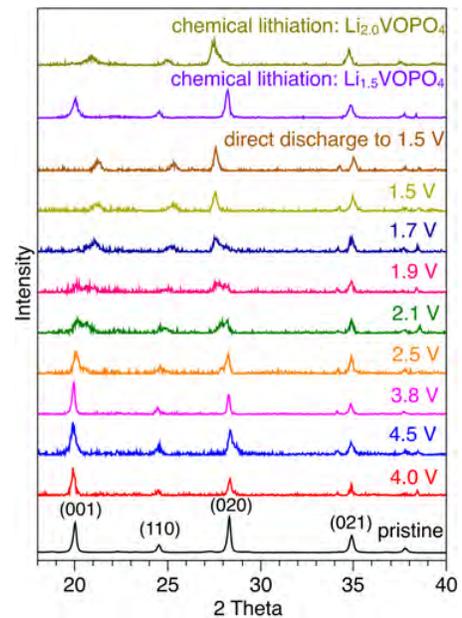


Figure 3. XRD patterns of the α_1 - LiVOPO_4 /graphene nanocomposite after various depths of electrochemical discharge and chemical lithiation with n-butyllithium.

Development of High Energy Cathode Materials

PROJECT OBJECTIVE: The objective of this project is to develop high-energy, low-cost, and long-life cathode materials. Synthesis of Li-Mn-rich (LMR) layered composite cathodes will be further optimized by using the novel approaches developed for high-voltage spinel in FY 2013. The working mechanism of the identified electrolyte additive will be systematically explored to reveal key factors that enable stable cycling of the LMR cathode. Advanced characterization techniques will be combined with electrochemical measurements to understand and mitigate the challenges in the LMR cathode.

PROJECT IMPACT: Although state-of-the-art cathode materials such as LMR layered composites have very high energy densities, their voltage fade and long-term cycling stability still need to be further improved. In this work, the fundamental fading mechanism of LMR cathodes will be investigated and develop new approaches to reduce the energy loss of these high-energy cathode materials. The success of this work will increase the energy density of Li-ion batteries and accelerate market acceptant of electrical vehicles (EV), especially for plug-in hybrid electrical vehicles (PHEV) required by the EV Everywhere Grand Challenge proposed by DOE/EERE.

OUT-YEAR GOALS: The long-term goal of the proposed work is to enable Li-ion batteries with a specific energy of >96 Wh/kg (for PHEVs), 5000 deep-discharge cycles, 15 year calendar life, improved abuse tolerance, and less than 20% capacity fade over a 10-year period.

COLLABORATIONS:

- Bryant Polzin (ANL): LMR electrode supply
- X.Q. Yang (LBNL): *in situ* XRD characterization during cycling
- Karim Zaghib (Hydro-Québec): material synthesis
- Kang Xu (ARL): new electrolyte

Milestones

- 1) Preparatory work on stable cycling of 80% capacity retention after 150 cycles high energy cathode based on $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ ($M = \text{Mn, Ni, Co}$; $0 \leq x \leq 1$) (Dec. 13). **Complete**
- 2) Obtain stable cycling of 80% capacity retention after 150 cycles from high energy cathode based on $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ ($M = \text{Mn, Ni, Co}$; $0 \leq x \leq 1$). (Mar. 14) **Complete**
- 3) Identify the fundamental mechanism responsible for electrolyte-additive-induced performance improvement of LMR cathode. (Jun. 14) **Complete**
- 4) Demonstrate the effects of elemental doping to improve the cycling stability of >200 cycles. (Sep. 14) **Complete**

Progress Report

The relationship between voltage fading and the uniform elemental distribution in the starting materials was investigated. Different methods including traditional co-precipitation; sol-gel method; and hydrothermal-assisted, solid-state synthesis were adopted to prepare Li-Mn-rich (LMR) cathode materials with the same stoichiometry of $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6}]\text{O}_2$. LMR derived from these three different approaches were compared in detail in terms of their elemental distribution in the bulk and on the surface and their electrochemical properties as shown in Fig. 1.

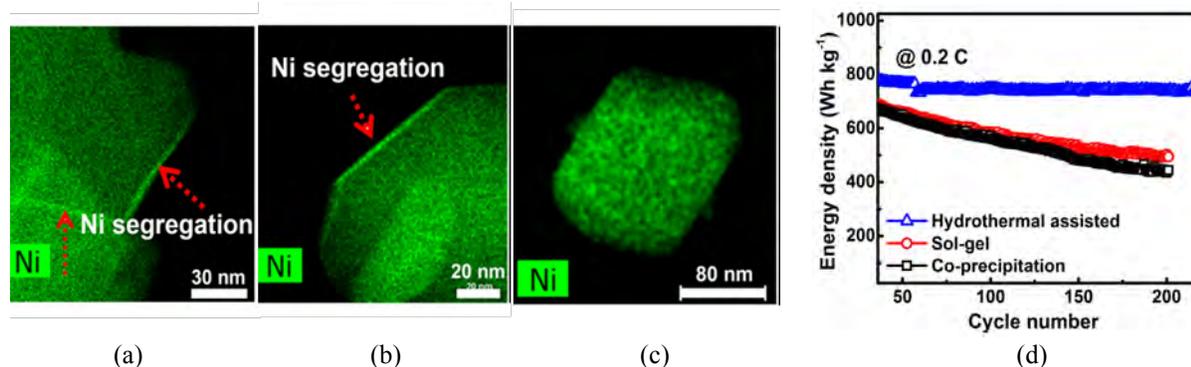


Figure 1. XEDS mapping and electrochemical performance of LMR cathodes prepared by different methods: (a) co-precipitation-derived, (b) sol-gel method-derived and (c) hydrothermal-assisted, method-derived LMR materials; (d) specific energy of different LMR cathodes as a function of cycle number.

A new four-detector system was used in TEM to determine the local chemical species, both in the bulk and at the surface, and quantitatively map the Mn, Ni, and O in these LMR particles. Both Mn and O elements were uniformly distributed in all LMR, which were prepared differently. However, the distribution of Ni (green) was not homogeneous in those prepared from co-precipitation (Fig. 1a) and sol-gel methods (Fig. 1b). The surface regions of LMR particles in Figs. 1a and b have enhanced contrast for Ni, implying a higher concentration of Ni on the surface. For LMR cathode prepared from hydrothermal-assisted solid synthesis, Ni element showed much more uniform distribution without obvious aggregation on the particles' surfaces as shown in Fig. 1c. A comparison of the electrochemical behaviors of these three LMR cathodes revealed that the voltage fading issue was also mitigated (Fig. 1d) by using hydrothermal treatment on the precursors before high temperature calcination. The specific energy of LMR cathode prepared by the hydrothermal-assisted method retained more than 95% over 250 cycles which is much better than those prepared by other synthesis methods. These results indicate that voltage fade and energy degradation can be mitigated by modifying the synthesis method and improving the uniformity of chemical species at the atomic level as an alternative approach for elemental doping.

In-situ Solvothermal Synthesis of Novel High Capacity Cathodes

PROJECT 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.

PROJECT IMPACT: Present-day Li-ion batteries are incapable of meeting the 40-mile all-electric-range within the weight and volume constraints established for PHEVs by DOE and the USABC. Higher energy density cathodes are needed for Li-ion batteries to be widely commercialized for PHEV applications. This effort will focus on increasing energy density (while maintaining the other performance characteristics of current cathodes) using synthesis methods that have the potential to lower cost. The primary deliverable for this project is a reversible cathode with an energy density of about 660 Wh/kg or higher.

OUT-YEAR GOALS: In FY14, work on Cu-V-O cathodes will be concluded, and efforts will be directed to the synthesis and electrochemical characterization of V-based (fluoro)phosphates. Hydrothermal-based synthesis techniques for preparing ternary and/or quaternary Li-V-PO₄(-X) type cathodes will be explored, either *via* direct chemical reaction or through ion exchange. By the end of FY14, structural and electrochemical characterization of two different types of Cu-V-O compounds will be completed, as well as the preparation of multiple Li-V-PO₄(-X) cathodes. *In-situ* x-ray analysis will be used to determine the precursors and reaction conditions for optimal synthesis procedures. Electrochemical testing, along with material characterization (*in-situ* and *ex-situ*), will be used to identify lithium reaction mechanisms and limitations to cycling stability of synthesized cathodes.

COLLABORATIONS: Jianming Bai, Lijun Wu, and Yimei Zhu (Brookhaven Nat. Lab), Arumugam Manthiram (U. Texas at Austin), Brett Lucht (U. Rhode Island), Karim Zaghib (Hydro-Québec), Jason Graetz (HRL), Peter Khalifha (StonyBrook U.), Kirsuk Kang (Seoul Nat. U., Korea).

Milestones

- 1) Complete the structural and electrochemical characterization of ϵ -Cu_xV₂O₅ cathodes. (Dec. 13) **Complete**
- 2) Develop synthesis procedures to prepare Li-V-PO₄ cathodes. (Mar. 14) **Complete**
- 3) Optimize the synthesis and characterize the structural and electrochemical properties of 2nd class of Cu-V-O cathode. (Jun. 14) **Complete**
- 4) Develop synthesis procedures to prepare Li-V- PO₄-X cathodes, and electrochemically characterize at least one Li-V-PO₄-X compound. (Sep. 14) **Complete**

Progress Report

A large number and variety of polyanion-type cathodes exist, and among them V-based phosphates are particularly interesting given the potential for high-energy density enabled by high voltage induced by phosphate groups and accessible multiple redox states of V, as well as the open, while potentially stable, framework. In previous reports the synthesis of phase-pure vanadium phosphates, $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (LVP) and $\text{Li}(\text{Na})_{1+x}\text{VOPO}_4\text{F}_x$ (LVPOF), were reported. This quarter, extensive electrochemical characterization was performed on LVP and LVOPF. The results demonstrate that desirable electrochemical properties, such as long-term cyclability and high rate capability are enabled *via* synthetic control of morphology and stoichiometry.

Monoclinic LVP was prepared using a solvothermal-assisted procedure (reported previously.) The synthesized LVP particles are about 50 nm, single-crystalline, and coated with a thin layer of amorphous carbon (Fig. 1a.) Galvanostatic cycling measurements were performed on the LVP electrodes at a rate of C/10 in two different voltage windows, 3.0 to 4.8 and 3.0 to 4.3 V (Fig. 1b.) A capacity as high as $190 \text{ mAh}\cdot\text{g}^{-1}$ was obtained during initial charge to 4.8 V, but the capacity fades quickly with cycling (top panel.) With a restriction of the window to 3.0 to 4.3 V, while the capacity was reduced to $120 \text{ mAh}\cdot\text{g}^{-1}$ (bottom panel), an extraordinary capacity retention of 95% was obtained after 200 cycles. The LVP electrodes also exhibit an excellent rate capability of $88 \text{ mAh}\cdot\text{g}^{-1}$ measured at 10C, in stark contrast to the low capacity and large polarization obtained from the LVP synthesized *via* the solid state reaction (Fig. 1c). Although the ionic conductivity of LVP is intrinsically high due to the 3D Li diffusion pathways across the NASICON structure, it appears that carbon coating and particle size reduction achieved *via* synthetic control is essential to achieving high rate capability.

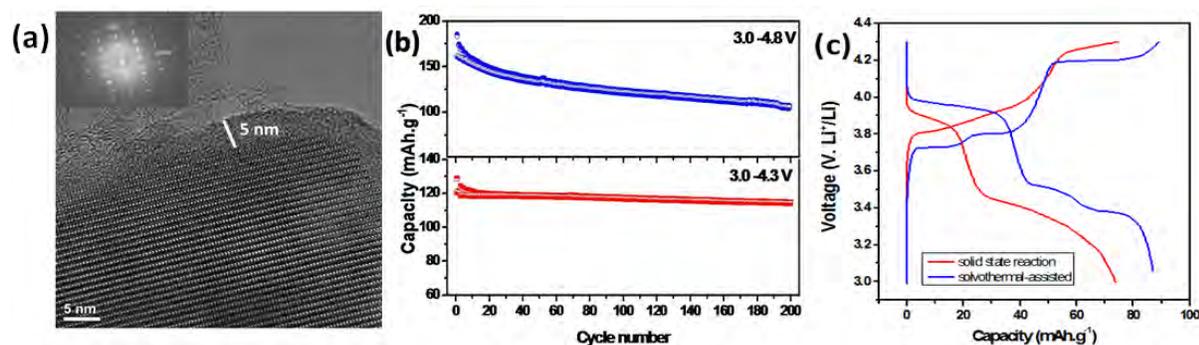


Figure 1. Structural and electrochemical properties of LVP particles, shown by (a) TEM image (inset: FFT), (b) galvanostatic cycling performance at C/10 in the voltage windows of 3.0 to 4.8 V (top) and 3.0 to 4.3 V (bottom), (c) typical voltage profiles of LVP synthesized *via* two different routes.

Micron-sized $\text{Li}_x\text{Na}_{1.5-x}\text{VOPO}_4\text{F}_{0.5}$ (LVOPF) with pseudo-layered structure was synthesized *via* hydrothermal ion-exchange from the Na counterpart ($\text{Na}_{1.5-x}\text{VPO}_5\text{F}_{0.5}$). The exchange process is complicated, involving a multiple-step phase transformation (reported previously), and so *in situ* ion-exchange synthesis was used to systematically evaluate synthesis parameters, including the concentration of LiBr solution, reaction temperature, Li/Na ratio and heating rate. With the determined optimum exchange conditions, a series of LVOPF of different stoichiometry and structures were obtained. The preliminary electrochemical tests indicate the strong dependence of their electrochemical properties on the extent of Li^+ replacement. High capacity was achieved in the LVOPF with high Li content and, interestingly, maximizing Li-ion exchange appears to also be essential to the long-term cyclability. This is likely due to the enhancement of structural stability with a close-to-complete replacement of Na^+ by Li^+ .

Lithium-bearing Mixed Polyanion (LBMP) Glasses as Cathode Materials

PROJECT OBJECTIVE: Develop mixed polyanion glasses as potential cathode materials for Li-ion batteries with superior performance to lithium iron phosphate for use in electric vehicle applications. Modify compositions of mixed polyanion glasses to provide higher electrical conductivities, specific capacities, and specific energies than similar crystalline polyanionic materials. Test mixed polyanion glasses in coin cells for electrochemical performance and cycleability. The final goal is to develop mixed polyanion glass compositions for cathodes with specific energies up to near 1,000 Wh/kg.

PROJECT IMPACT: The projected performance of glass cathode materials addresses the Vehicle Technology Multi-Year Plan goals of higher energy densities, excellent cycle life, and low cost. Mixed polyanion glasses offer the potential of exceptional cathode energy density up to 1,000 Wh/kg, excellent cycle life from a rigid polyanionic framework, and low cost conventional glass processing.

OUT-YEAR GOALS: The composition of successful mixed polyanion glasses with multivalent transitions will be used as the basis to model, produce, and electrochemically test glasses from multiple polyanion systems (ex. phosphates, borates, silicates), polyanion substitutions (ex. vanadate, molybdate), and transition metal contents. The electrochemical performance of these compositionally varied glasses will be used to develop optimized glass compositions to obtain maximum specific energy within a desirable voltage window. Cathode processing of the most promising mixed polyanion glasses will be refined to obtain desired cycling and rate performance. Complex mixed polyanion glasses will be modeled, and those glasses with excellent predicted properties will be produced and tested. In-depth electrochemical testing will be performed on the most successful mixed polyanion glasses. The predicted and experimentally verified electrochemical performances from computational thermodynamic models for different glass systems will be used to develop a summary perspective on the design of mixed polyanion glasses for use as cathodes.

COLLABORATIONS: Worked with Kyler Carroll (MIT) to analyze XAS data taken at the National Synchrotron Light Source at Brookhaven National Laboratory in order to measure the valence states of transition metal cations in *ex situ* glass cathodes.

Milestones

- 1) Synthesize, characterize, and perform electrochemically testing on a mixed polyanion glass that is theoretically capable of a multi-valent transition. (Dec. 13) **Complete**
- 2) Demonstrate the effect of submicron particle size on the electrochemical performance of mixed polyanion glass cathodes. (Mar. 14) **Complete**
- 3) Measure the electrical conductivities of a series of mixed polyanion glasses as a function of polyanionic substitution. (Jun. 14) **Complete**
- 4) Synthesize, characterize, and perform electrical testing on at least four different glass cathode compositions with theoretical specific energies exceeding lithium iron phosphate. (Sep. 14) **Complete**

Progress Report

In collaboration with Kyler Carroll (MIT), X-ray absorption spectroscopy (XAS) was performed *ex situ* on glass cathodes to determine the valence states of transition metal cations at key states of charge. XAS work was performed at the National Synchrotron Light Source at BNL. Evidence of glass-state conversion reactions was found in XAS of a nickel metaphosphate/vanadate (NMP50V) glass and a copper metaphosphate/vanadate glass. In NMP50V glass, XAS at the Ni-K edge (Fig. 1) showed a reversible Ni valence change from Ni^{2+} in the original material (orig.) to Ni metal after discharge to 1V (dis. 1V) to Ni^{2+} upon recharge to 4V (rech. 4V), but XAS at the V-K edge (Fig. 2) showed a mostly irreversible vanadium valence change occurring in a first-cycle intercalation reaction. To date, XAS has been used to confirm glass-state conversion reactions in Fe-, Ni-, and Cu-based glass cathodes.

Introducing Fe cations was theorized to increase the electrical conductivity and to enable an intercalation reaction in non-Fe-based glass cathodes. Two mixed cation/mixed polyanion (MC/MP) glasses with 50% Fe cation content were produced to test this theory: a copper/iron phosphate/vanadate glass and a manganese/iron phosphate/vanadate glass. Unfortunately, neither MC/MP glass exhibited a significant intercalation reaction. Interestingly, the Cu-Fe MC/MP glass did not exhibit a noticeable glass-state conversion reaction, even though similar Fe-based and Cu-based glasses exhibit glass-state conversion reactions with full theoretical capacity. While the MC/MP approach was not successful, other compositional variations are being actively pursued to improve the key properties and resulting electrochemical performances of glass cathodes.

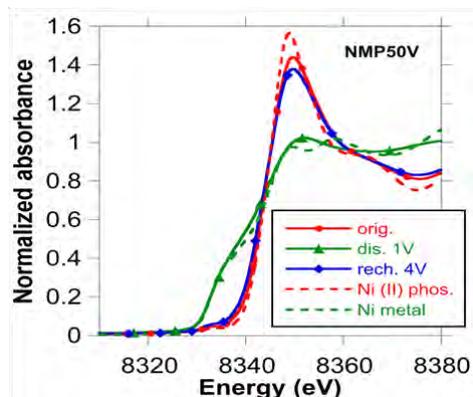


Figure 1. XAS analysis at the Ni-K edge showed evidence of a glass-state conversion in a nickel metaphosphate glass with 50% vanadate substitution (NMP50V).

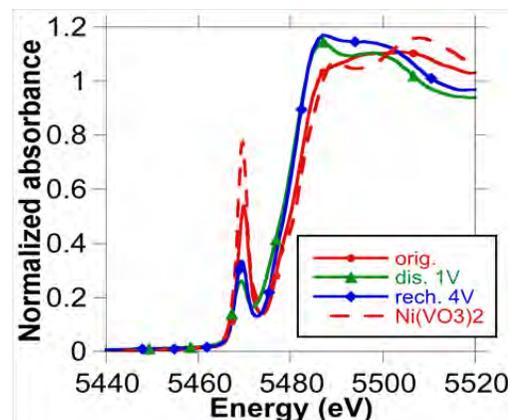


Figure 2. X-ray absorption spectroscopy analysis at the V-K edge revealed that an irreversible vanadium intercalation reaction caused the first-cycle irreversible capacity loss in NMP50V.

Lithium Batteries of Higher Capacity and Voltage

PROJECT OBJECTIVE: To develop a solid Li^+ electrolyte that (1) can block dendrites from a Li^0 anode, (2) has a Li^+ conductivity $\sigma_{\text{Li}} > 10^{-4} \text{ S cm}^{-1}$, (3) is stable in different liquid electrolytes at anode and cathode, (4) has a low impedance for Li^+ transfer across a solid/liquid electrolyte interface, (5) is capable of low-cost fabrication as a thin, mechanically robust film.

PROJECT IMPACT: A solid Li^+ -electrolyte separator would permit use of a Li^0 anode, thus maximizing energy density for a given cathode, and liquid flow-through and air cathodes of high capacity as well as high-voltage solid cathodes given two liquid electrolytes having different windows.

OUT-YEAR-GOALS: Prepare an oxide/polymer composite Li^+ electrolyte having a $\sigma_{\text{Li}} > 10^{-4} \text{ S cm}^{-1}$ that can be fabricated at low cost as a mechanically robust membrane and can demonstrate a viable performance of a test cell with a Li^0 anode and a variety of solid, liquid, and air cathodes. Prepare dense garnet membranes with $\sigma_{\text{Li}} \approx 5 \times 10^{-4} \text{ S cm}^{-1}$ that have a reduced impedance for Li^+ transfer across the oxide interface with a liquid electrolyte.

COLLABORATIONS: Li/S cell with A. Manthiram (UT Austin), and membrane characterization with K. Zaghib, (Hydro-Québec.)

Milestones

- 1) Go-No/Go: Polymer composite membrane project will stop if demonstration of a liquid cathode without crossover of the redox molecule and blocking of Li dendrites with a PEO/ Al_2O_3 membrane fails. Criteria: Suppression of drying of anolyte with an Al_2O_3 /PEO membrane. Elimination of redox-molecule crossover to anolyte. Demonstration that Li dendrites are blocked. (Dec. 13) **Go**
- 2) Determine TEM garnet surface structure in contact with a liquid electrolyte. Design of a surface coat of a garnet membrane to minimize impedance of Li^+ transfer across garnet surface. (Sep. 14) **Discontinued - Stopped garnet work as the garnet is unstable in water**
- 3) Prepare dense Li^+ -electrolyte alternative to garnet and test impedance of Li^+ transfer across it. (Jun. 14) **Discontinued - Stopped work on a Li^+ solid electrolyte stable in water and identified instead a Na^+ solid electrolyte for testing in a Na-ion battery. In an ARPA-E project, it was shown that dry $\text{Na}_x\text{MnFe}(\text{CN})_6$ is a suitable rechargeable cathode for a Na-ion battery and for use with the Na^+ polymer separator.**
- 4) Construct and test a Li/S cell with a solid Li^+ -electrolyte separator. (Sep. 14) **Complete**

Progress Report

The purpose of a solid Li^+ electrolyte stable in water was to act as a separator in a Li-air battery that has an aprotic liquid anolyte and aqueous catholyte. A Li^+ solid electrolyte stable in water was not ascertained, so a Na^+ solid electrolyte for a Na-air cell was identified and tested.

Two Li-S cells with the same Li_2S_6 cathode trapped in porous carbon with one using a Li^+ polymer-electrolyte separator and a second with a carbon-fiber paper for capturing mobile Li_xS soluble species. The membranes were made by a thiolene chemistry which enabled fabrication of mesh-type polymer chain structures. Here, tetrathiol crosslinker was used in all batches since fewer thiol units (e.g. trithiol crosslinker) and less crosslink density brought more polysulfide crossover. The monomers in each membrane used are mainly composed of (1) tri(ethylene glycol), (2) double vinyl ester, (3) perfluorohexane, and (4) double vinyl sulfones. Monomers for the (2 to 4) cases were chosen to have less chemical and electrochemical interactions with Li^+ in the liquid electrolyte. The perfluorohexane-tetrathiol membrane showed severe rolling after soaking in liquid electrolyte, probably owing to the hydrophobic-hydrophilic combination of chain units, which made the cell test impossible. The double vinyl sulfones-tetrathiol membrane was notably stiff and did not absorb the liquid electrolyte, which prevented Li^+ transport through the membrane.

The other two membranes with ethylene glycol and ester absorbed an ether-based liquid electrolyte, and coin cell tests were conducted. The tests showed a little crossover to the anode side, but an osmosis problem prevented good performance. Lithium nitrate was not added to the electrolyte to see if the crosslinked mesh structure in the membrane could block the polysulfide crossover. There was not endless charging in the voltage curves, however, a large polarization was observed. It was identified that the interface between Li metal and the membranes dried out after cycling, which suggested a possible osmosis issue in this case. Indeed, the catholyte contained concentrated Li_2S_6 while the anolyte did not have any polysulfide molecules, which brought a strong driving force for the osmosis across the membrane. The data demonstrated that a separator which blocks dendrites was not sufficient for a practical metallic-Li anode. An interface layer between the polymer and a Li^0 anode that provides a stable polymer- Li^0 contact on repeated cycling needs to be developed. The solution to this problem will be pursued.

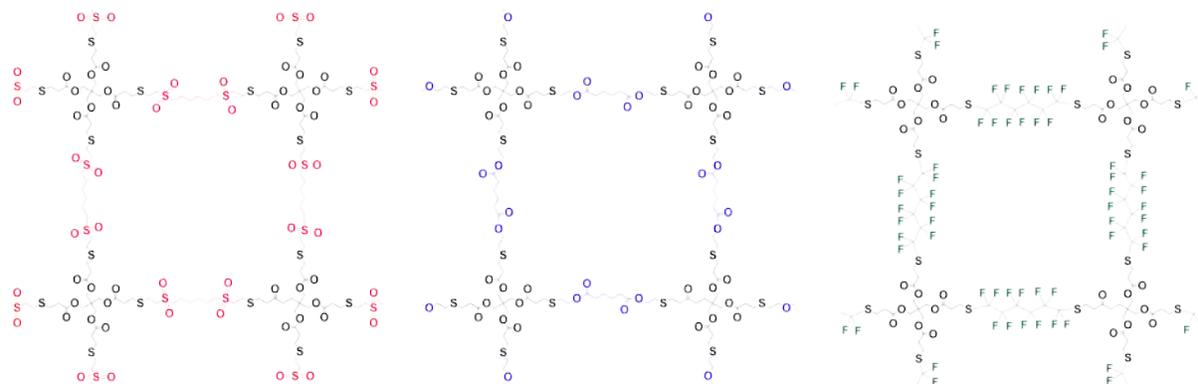


Figure. 1 Crosslinked polymer membranes with double vinyl sulfones, double vinyl ester, and perfluorohexane units (from the left).

Interfacial Processes - Diagnostics

PROJECT OBJECTIVE: The main objective of this task is to obtain detailed insight into the dynamic behavior of molecules, atoms, and electrons at electrode/electrolyte interfaces of intermetallic anodes (Si) and high voltage Ni/Mn-based materials at a spatial resolution that corresponds to the size of basic chemical or structural building blocks. The aim of these studies is to unveil the structure and reactivity at hidden or buried interfaces and interphases that determine battery performance and failure modes. To accomplish these goals novel far- and near-field optical multifunctional probes must be developed and deployed *in situ*. The proposed work constitutes an integral part of the concerted effort within the BATT Program and it attempts to establish clear connections between diagnostics, theory/modelling, materials synthesis, and cell development efforts.

PROJECT IMPACT: This project provides a better understanding of the underlying principles that govern the function and operation of battery materials, interfaces and interphases, which is inextricably linked with successful implementation of high energy density materials such as Si and high voltage cathodes in Li-ion cells for PHEVs and EVs. This task also involves the development and application of novel innovative experimental methodologies to study and understand the basic function and mechanism of operation of materials, composite electrodes, and Li-ion battery systems for PHEV and EV applications.

OUT-YEAR GOALS: Design and employ novel and sophisticated *in situ* analytical methods to address the key problems of the BATT baseline chemistries. The proposed experimental strategies combine imaging with spectroscopy aimed at probing electrodes at an atom, molecular, or nanoparticulate level to unveil structure and reactivity at hidden or buried interfaces and determine electrode performance and failure modes in baseline Li_xSi -anodes and high-voltage LMNO cathodes. The main goal is to gain insight into the mechanism of surface phenomena on thin-film and monocrystal Sn and Si intermetallic anodes and evaluate their impact on the electrode long-term electrochemical behavior. 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 scanning probe spectroscopy will be employed to detect and monitor surface phenomena at the intermetallic anodes high-voltage (>4.3V) model and composite cathodes.

COLLABORATIONS: None this quarter.

Milestones

- 1) Determine the origin of fluorescent species that are produced at high-energy Li-ion cathodes. (Dec. 13) **Complete**
- 2) Resolve SEI layer chemistry of Si model single crystal anodes (collaboration with the BATT Anode Group. (Mar. 14) **Complete**
- 3) Characterize interfacial phenomena in high-voltage composite cathodes (collaboration with the BATT Cathode Group. (Jun. 14) **Complete**
- 4) Go/No-Go: Stop development of *in situ* near-field techniques, if the preliminary experiments fail to deliver adequate surface-bulk selectivity. Criteria: Demonstrate feasibility of *in situ* near-field techniques to study interfacial phenomena at Li-battery electrodes. (Sep. 14) **Complete**

Progress Report

This quarter, *in situ* Laser Induced Breakdown Spectroscopy (LIBS) was continued to be developed. Double-femtosecond (fs) pulse LIBS in a collinear configuration was used to improve the sensitivity of LIBS analysis of interfacial layers on Si(100) and SEI formed on Si(100) electrodes submerged in liquid electrolytes (Fig. 1a). Initial experiments were aimed towards improvement of excitation parameters for optimization of emission intensities. Significant emission signal enhancements were observed in the double- vs. the single-pulse LIBS of Si (100) in 1M LiPF₆ in EC/DEC (Fig. 1b). These data were obtained in an *in situ* cell without the application of an electrochemical potential. The emission of specific lines (Li and C₂) of Si(100) and SEI grown on Si(100) was also compared in preliminary experiments in 1M LiPF₆ in EC/DEC, demonstrating emission intensity differences between the two electrodes associated with elemental and molecular concentration variations at two solid/liquid interfaces (Fig. 1c).

The development of *in situ* techniques in near-field characterization of electrochemical interfaces was also pursued. Although the initial strategy was development of a liquid cell similar to those available in some commercial atomic force microscopes, the engineering complications associated with retrofitting the near-field microscope proved this approach infeasible. The approach was altered to using graphene as a thin model electrode, shown in Fig. 2a. It was shown previously that graphene can be used as a Li-ion electrode, whereas the monatomic thickness of the graphene layer will allow the optical probe near-field to interact with the dielectric properties of the surface layer on the observed side. As a proof of principle, observation of the domain structure of a block copolymer spin-coated on graphene without cycling is proposed, and if this experiment yields positive results, then the *in situ* configuration described above will be continued. Figure 2b shows successful near-field imaging of the SEO block copolymer domain structure over 1 x 1 μm. This measurement was carried out in a continuous-flow nitrogen enclosure, thus also demonstrating near-field imaging in an inert atmosphere, an essential component of *in situ* imaging and spectroscopy.

A cell may be constructed with the graphene working electrode at the top, a counter electrode beneath, and a semi-rigid block copolymer electrolyte (e.g. SEO/LiTFSI) serving both as an ion conductor and a structural element. This cell will be cycled and the formation of the SEI layer observed in the near-field. The group is confident this approach will be effective and propose the end of FY2015 Q2 as a date to demonstrate that it is feasible. This completes Milestone 4. However, the intention is to carry this effort into FY15 and link it with the Q4 milestone “Demonstrate feasibility of *in situ* LIBS/NF to study interfacial phenomena at Li-battery electrodes.”

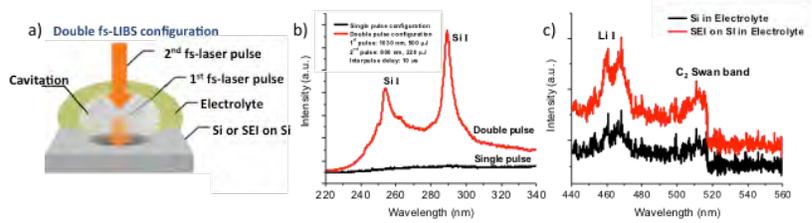


Figure 1. a) Double fs-pulse LIBS scheme used for analysis of SEI layers in liquid electrolytes. b) Signal enhancement of Si (100) in 1M LiPF₆ EC/DEC electrolyte with the double-pulse configuration. c) Comparison of double fs-pulse LIBS signals of Si and SEI on Si in the same electrolyte.

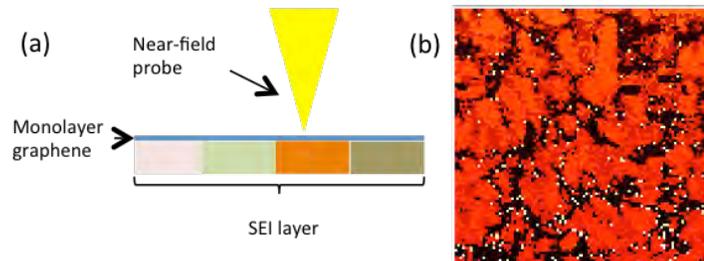


Figure 2. (a) Proposed near-field measurement with graphene electrode window. (b) Near-field phase distribution over 1 x 1 μm, showing domain structure of polystyrene/poly(ethylene oxide) block copolymer (SEO).

Advanced *In-situ* Diagnostic Techniques for Battery Materials

PROJECT OBJECTIVE: The primary objective of this proposed project is to develop new advanced in situ material characterization techniques and to apply these techniques to support the development of new cathode and anode materials for the next generation of lithium-ion batteries (LIBs) for plug-in hybrid electric vehicles (PHEV). In order to meet the challenges of powering the PHEV, LIBs with high energy and power density, low cost, good abuse tolerance, and long calendar and cycle life must be developed.

PROJECT IMPACT: In the Multi Year Program Plan (MYPP) of Vehicle Technology Program (VTP), the goals for battery were described as: “Specifically, lower-cost, abuse-tolerant batteries with higher energy density, higher power, better low-temperature operation, and longer lifetimes are needed for the development of the next-generation of HEVs, PHEVs, and EVs.” If this project is successfully carried out, the knowledge learned from diagnostic studies and collaborations with US industries and international research institutions through this project will help US industries to develop new materials and processes for new generation of lithium-ion batteries in their efforts to reach these VTP goals.

OUT-YEAR GOALS: For the Si-based anode materials, the capacity fading needs to be resolved, which is caused by the pulverization of the Si particles during cycling. In order to overcome these barriers, fundamental understanding of the physical and chemical changes of the cathode and anode materials in the bulk and at the surface are critical. This project will focus on applying integrated advanced in situ diagnostic characterization techniques to investigate these issues, through collaborative efforts with synthesis groups and industrial end users.

COLLABORATIONS: The BNL team will work closely with material synthesis groups at ANL (Drs. Thackeray and Amine) for the high energy composite; at UT Austin (Prof. Manthiram) for the high voltage spinel; and at PNNL (Drs. Liu and Zhang) for the Si-based anode materials. Such interaction between the diagnostic team at BNL and synthesis groups of these other BATT members will catalyze innovative design and synthesis of advanced cathode and anode materials. The team will also collaborate with industrial partners at General Motors (Dr. Wu), Duracell (Dr. Bae), and Johnson Controls (Drs. Cho and Bonhomme) to obtain feedback information as battery end users.

Milestones

- 1) Complete the studies of the kinetic properties of $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Co}_{0.1}\text{Mn}_{0.55}\text{O}_2$ [$0.5\text{Li}(\text{Ni}_{0.375}\text{Co}_{0.25}\text{Mn}_{0.375})\text{O}_2 \bullet 0.5\text{Li}_2\text{MnO}_3$] high energy density cathode materials during constant current charge using X-ray absorption spectroscopy. (Dec. 13) **Complete**
- 2) Complete the development of using quick X-ray absorption spectroscopy technique to study the kinetic properties of $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Co}_{0.1}\text{Mn}_{0.55}\text{O}_2$ [$0.5\text{Li}(\text{Ni}_{0.375}\text{Co}_{0.25}\text{Mn}_{0.375})\text{O}_2 \bullet 0.5\text{Li}_2\text{MnO}_3$] high energy density cathode materials during constant voltage charge. (Mar. 14) **Complete**
- 3) Complete the *in situ* X-ray diffraction studies of Fe substituted high voltage spinel during charge-discharge cycling. (Jun. 14) **Complete**
- 4) Complete the *in situ* X-ray absorption studies of Fe substituted high voltage spinel during heating. (Sep. 14) **Complete**

Progress Report

In the 4th quarter of FY2014, all milestones for FY2014 had been completed. BNL has been focused on studying the *in situ* x-ray absorption studies of Fe-substituted, high-voltage spinel during heating, towards Milestone 4 for FY2014. This milestone was completed successfully.

The results of *in situ* XAS spectra for Fe-substituted $\text{LiNi}_{1/3}\text{Fe}_{1/3}\text{Mn}_{4/3}\text{O}_4$ sample during heating at Fe-K-edge, Mn K-edge, and Ni K-edge are shown in Fig. 1 together with the schematic of the migration of Fe to the tetrahedral sites. The stabilizing role of Fe is further confirmed by the *in situ* XANES study of the charged $\text{LiNi}_{1/3}\text{Fe}_{1/3}\text{Mn}_{4/3}\text{O}_4$ sample as shown in Fig. 1. By examining the changes of the pre-edge spectra during the heating process, it is clear that the pre-edge of Fe increases significantly as temperature is increased. In contrast, pre-edges for Mn and Ni are almost invariant during the entire process. Since the intensity of the pre-edge is very sensitive to the local environment of transition metals, such great intensity increase implies Fe migrates from an octahedral site to a tetrahedral site. This process is illustrated in Fig. 1d. It should be noted that the absence of an oxygen release peak in these experiments does not rule out the possibility of a small amount of oxygen release. In fact, it is very likely that a trace amount of oxygen is released during the heating, spread over the entire profile, making it undetectable under the experimental conditions. This can be seen from the XANES spectra of Ni shown in Fig. 1c.

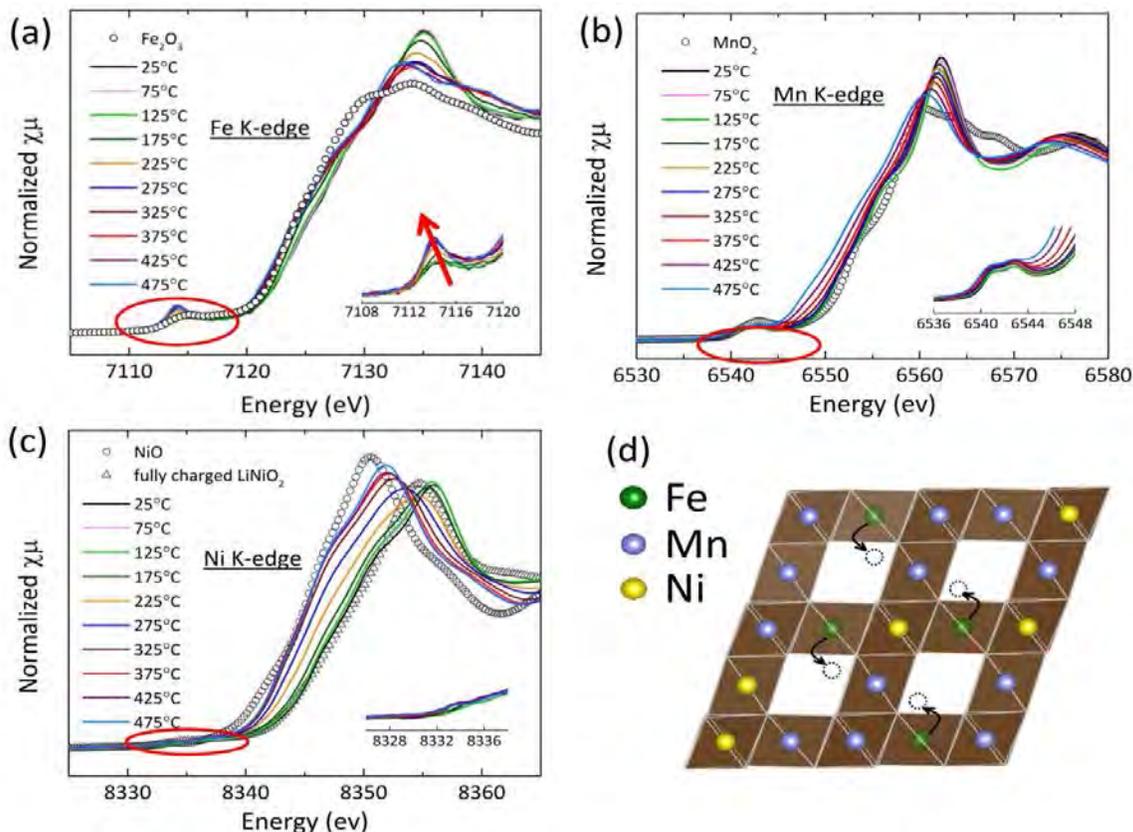


Figure 1. *In situ* (a) Fe (b) Mn and (c) Ni K-edge XANES spectra of fully charged $\text{LiNi}_{1/3}\text{Mn}_{4/3}\text{Fe}_{1/3}\text{O}_4$ during heating up to 475°C, (d) migration of Fe to a tetrahedral site.

NMR and Pulse Field Gradient Studies of SEI and Electrode Structure

PROJECT OBJECTIVE: The formation of a stable surface electrode interphase (SEI) is critical to the long-term performance of a battery, since the continued growth of the SEI on cycling/aging results in capacity fade (due to Li consumption) and reduced rate performance due to increased interfacial resistance. Although arguably a (largely) solved problem with graphitic anodes/lower voltage cathodes, this is not the case for newer, much higher capacity anodes such as silicon, which suffer from large volume expansions on lithiation, and for cathodes operating above 4.3 V. Thus it is essential to identify how to design a stable SEI. The objectives are to identify major SEI components, and their spatial proximity, and how they change with cycling. SEI formation on Si vs. graphite and high voltage cathodes will be contrasted. Li⁺ diffusivity in particles and composite electrodes will be correlated with rate. The SEI study will be complemented by investigations of local structural changes of high voltage/high capacity electrodes on cycling.

PROJECT IMPACT: The first impact of this project will be an improved, molecular based understanding of the surface passivation (SEI) layers that form on electrode materials, which are critical to the operation of the battery. Second, direct evidence will be provided on how additives to the electrolyte modify the SEI. Third, insight will be provided to guide and optimize the design of more stable SEIs on electrodes beyond LiCoO₂/graphite.

OUT-YEAR GOALS: The goals of this project are to identify the major components of the SEI as a function of state of charge and cycle number different forms of silicon. It will be determined how the surface oxide coating affects the SEI structure and established how the SEI on Si differs from that on graphite and high voltage cathodes. It will be determined how the additives that have been shown to improve SEI stability affect the SEI structure and explore the effect of different additives that react directly with exposed fresh silicon surfaces on SEI structure. Via this program, new NMR based methods will be developed to identify different components in the SEI and their spatial proximities within the SEI, which will be broadly applicable to the study SEI formation on a much wider range of electrodes. These studies will be complemented by studies of electrode bulk and surface structure to develop a fuller model with which to describe how these electrodes function.

COLLABORATIONS: Ram Seshadri and Anton van der Ven (UCSB), Brett Lucht (Rhode Island), Kristin Persson (LBNL), Jordi Cabana (UICC), M. S. Whittingham (Binghamton), Shirley Meng, (UCSD), Stephan Hoffman and Andrew Morris (Cambridge)

Milestones

- 1) Identify major components (LiF, phosphates, carbonates and organics) in Si SEI by NMR methods. (Dec. 13). **Complete**
- 2) Correlate presence of SEI components with cycle number and depth of discharge of Si. Complete preliminary TOF-SIMS measurements to establish viability of approach. (Mar. 14) **Studies on first cycle complete (NMR). Difficulties encountered with sample reproducibility and Si cracking (TOF-SIMS).**
- 3) Identify SEI components in the presence of FEC and VC in Si and determine how they differ from those present in the absence of additives. (Jun. 14) **Delayed to Dec. 14 - Studies on reduced VC and FEC model compounds complete.**
- 4) Go/No-Go: Stop Li⁺ PFG diffusivity measurements of electrodes. Criteria: If experiments do not yield correlation with electrochemical performance. (Sep. 14) **Go criterion met.**

Progress Report

The *in situ* NMR method was used to investigate the different components in a Li-S cell in collaboration with R. Seshadri (UCSB.) The Li-S phase diagram was first explored using computational techniques. Both the computational and experimental studies are consistent with the suggestion that the only solid product formed in the cell is Li_2S . No Li_2S_2 was observed. *In situ* NMR spectroscopy also allows the direct observation of both soluble Li^+ -species and solids (Li_2S) during cell discharge. It is suggested that during the first discharge plateau, sulfur is reduced to soluble polysulfide species concurrently with the formation of a solid component (Li_2S): Li_2S was found to form near the beginning of the first plateau in the cell configuration studied here. The NMR data suggests that the second plateau is defined by the reduction of the residual soluble species to solid product (Li_2S). A ternary phase diagram was developed which helps explain why Li_2S formation is seen initially in this study, but is only seen on the second plateau in some other studies.

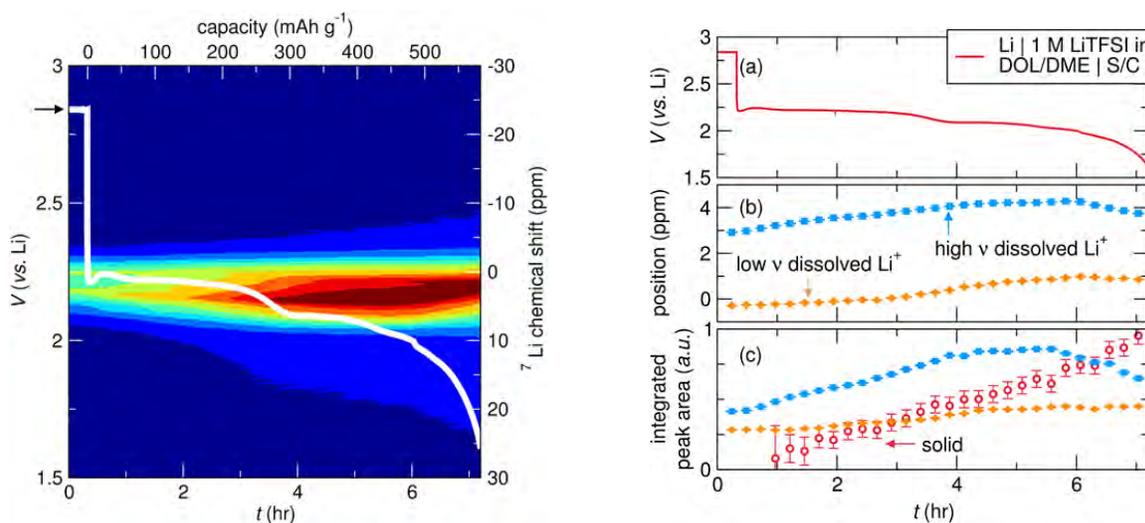


Figure 1. Left: The *in situ* ^7Li NMR signal overlaid on the electrochemical discharge curve for a Li-S bag cell discharged galvanostatically at a rate corresponding to $C/20$, using a 1 M LiTFSI in DOL/DME electrolyte. A spectrum is recorded every 14.6 min. The cell is held at open circuit for 15 min before discharge. The Li metal resonance at approximately +250 ppm is not shown. Right: (a) The discharge profile of the same Li-S bag cell. The spectra were fit using three components (two liquid (high and low frequency) and one solid) to extract the changes in (b) chemical shift and (c) integrated intensities as a function of discharge.

SEI studies in this quarter have focused on a comparison between graphite and Si. Currently, the use of graphene nanoflakelets is being explored, in order to increase the amount of SEI formation and enable NMR studies.

Simulations and X-ray Spectroscopy of Li-S Chemistry

PROJECT OBJECTIVE: Li-S cells are attractive targets for energy storage applications as their theoretical specific energy of 2600 Wh/kg is much greater than the theoretical specific energy of current lithium-ion batteries. Unfortunately, the cycle-life of Li-S cells is limited due to migration of species generated at the sulfur cathode. These species, collectively known as polysulfides, can transform spontaneously, depending on the environment, and it has thus proven difficult to determine the nature of redox reactions that occur at the sulfur electrode. The objective of this project is to use X-ray spectroscopy to track species formation and consumption during charge-discharge reactions in a Li-S cell. Molecular simulations will be used to obtain X-ray spectroscopy signatures of different polysulfide species, and to determine reaction pathways and diffusion in the sulfur cathode. The long-term objective of this project is to use the mechanistic information to build high specific energy Li-S cells.

PROJECT IMPACT: Enabling rechargeable Li-S cells has the potential to change the landscape of rechargeable batteries for large-scale applications beyond personal electronics due to: (1) high specific energy, (2) simplicity and low cost of cathode (the most expensive component of current Li-ion batteries), and (3) earth abundance of sulfur. The proposed diagnostic approach also has significant potential impact as it represents a new path for determining the species that form during charge-discharge reactions in a battery electrode.

OUT-YEAR GOALS: Year 1 Goals: Simulations of sulfur and polysulfides (PSL) in oligomeric polyethylene oxide (PEO) solvent. Prediction of X-ray spectroscopy signatures of PSL/PEO mixtures. Measurement of X-ray spectroscopy signatures PSL/PEO mixtures. Year 2 Goals: Use comparisons between theory and experiment to refine simulation parameters. Determine speciation in PSL/PEO mixtures without resorting to adhoc assumptions. Year 3 Goals: Build an all-solid Li-S cell that enables measurement of X-ray spectra *in situ*. Conduct simulations of reduction of sulfur cathode. Year 4 Goals: Use comparisons between theory and experiment to determine the mechanism of sulfur reduction and Li₂S oxidation in all-solid Li-S cell. Use this information to build Li-S cells with improved life-time.

COLLABORATIONS: Tsu-Chien Weng, Dimosthenis Sokaras and Dennis Nordlund (SLAC)

Milestones

- 1) Complete simulations of PSL/PEO mixtures including calculation of solvation free energy and X-ray spectra; compare spectra with experimental measurements. (Dec. 13) **Complete**
- 2) Go/No-Go: Viability of the use of X-ray spectroscopy to study speciation of lithium sulfides in Li-S cells. Criteria: Determine speciation using X-ray spectra. (Mar. 14) **Complete**
- 3) Build *in situ* cell for generating polysulfides by electrochemically driven redox reactions and measuring X-ray spectra. (Jun. 14) **Complete**
- 4) Synthesize an electron- and ion-conducting polymer binder for the sulfur cathode. (Sep. 14) **Complete**

Progress Report

Milestone 1. The first ever theoretical calculation of the Sulfur K-edge XAS of isolated Li_2S_x species solvated in tetraglyme was determined. Additionally, the XAS of radical polysulfides in tetraglyme was calculated and a unique feature was identified which can be used to find these species in solution.

Milestone 2. It was previously determined and shown using principal component analysis that XAS is capable of speciating Li polysulfide molecules. Calculations indicate that the ratio of the main-/pre-edge peak area, and not the peak intensities, can be used to differentiate dissolved Li polysulfides.

Milestone 3. Solid-state Li-S pouch cells have been modified to allow soft X-rays to probe both electrodes. The modified cell is shown in Fig. 1. The corresponding first discharge curve for the battery is shown in Fig. 2. The X-ray transparency of the Mylar window was tested and was determined to be acceptable. *In situ* XAS experiments will be performed during the next APS cycle.



Figure 1. Solid state Li-S pouch cells

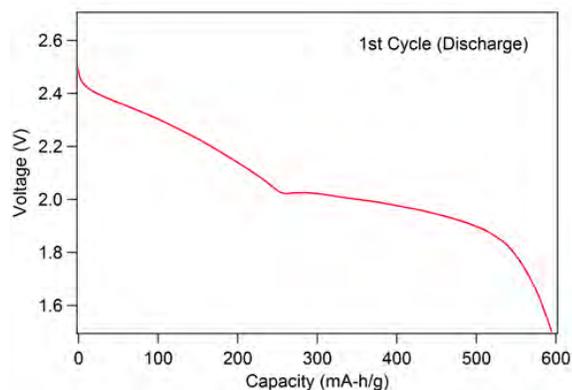


Figure 2. First discharge curve of the solid-state Li-S pouch cells

Milestone 4. The group has synthesized and demonstrated a new concept for confining S and providing pathways for electron and ion conduction to the S. An electronically conducting nanosphere is covalently linked to a single-ion-conducting polymer and the S is contained within the nanosphere. A TEM of the electronically-conducting carbon is shown below (Fig. 3.) Initial cycling data from cathodes comprising the particles described above appear promising.

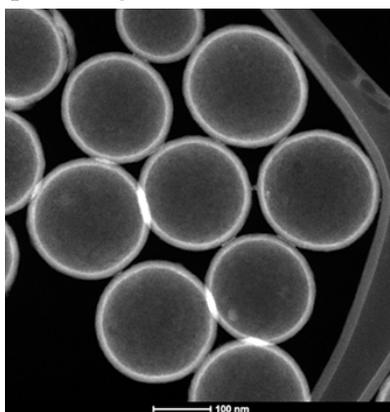


Figure 3. TEM image of electron-conducting nanospheres.

Design and Synthesis of Advanced High-Energy Cathode Materials

PROJECT OBJECTIVE: The successful development of next-generation electrode materials requires particle-level knowledge of the relationships between materials' specific physical properties and reaction mechanisms to their performance and stability. This single-crystal-based project was developed specifically for this purpose and it has the following objectives: 1) obtain new insights into electrode materials by utilizing state-of-the-art analytical techniques that are mostly inapplicable on conventional, aggregated secondary particles, 2) gain fundamental understanding on structural, chemical and morphological instabilities during Li extraction/insertion and prolonged cycling, 3) establish and control the interfacial chemistry between the cathode and electrolyte at high operating voltages, 4) determine transport limitations at both particle and electrode levels, and 5) develop next-generation electrode materials based on rational design as opposed to more conventional empirical approaches.

PROJECT IMPACT: This project will reveal performance-limiting physical properties, phase-transition mechanisms, parasitic reactions, and transport processes based on the advanced diagnostic studies on well-formed single crystals. The findings will establish rational, non-empirical design methods that will improve the commercial viability of next-generation $\text{Li}_{1-x}\text{M}_{1-x}\text{O}_2$ (M=Mn, Ni and Co) and spinel $\text{LiNi}_x\text{Mn}_{2-x}\text{O}_4$ cathode materials.

OUT-YEAR GOALS:

- Synthesize single-crystal samples of lithium transition-metal oxide cathode materials.
- Characterize structural and morphological changes and establish their correlation to rate performance and cycling stability.
- Determine crystal-plane specific reactivity between cathode particles and the electrolyte.
- Measure lithium-concentration dependent transport and kinetic properties.
- Define performance-limiting fundamental properties and mechanisms and outline mitigating approaches. Design, synthesize, and evaluate the improved electrode materials.

COLLABORATIONS: R. Kostecki, M. Doeff, K. Persson, V. Zorba, T. Tyliszczak and Z. Liu (LBNL), C. Grey (Cambridge), B. Lucht (URI), and Y.-M. Chiang (MIT).

Milestones

- 1) Synthesize at least five new cathode crystal samples with at least two new morphologies. (Dec. 13) **Complete**
- 2) Characterize the interface between the high-voltage cathode and the electrolyte. Identify the role of particle surface planes in interfacial reactivity (Mar. 14) **Complete**
- 3) Complete the studies on structural evolution during initial Li extraction/insertion and extended cycling. Illustrate the impact of structural changes and phase transformation on rate capability and stability. (Jun. 14) **Complete**
- 4) Go/No-Go: Continue low-temperature based solvothermal synthesis. Criteria: If the crystal samples show similar quality and performance to those made at high temperatures. (Sep. 14) **No-go. Effort will be redirected towards synthesis at high temperatures.**

Progress Report

Solid solution in the Ni/Mn spinel system. In the intercalation materials, single-phase transformation is considered kinetically advantageous over a two-phase process but the characteristics of solid solutions are largely unknown. In the ordered $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ (LMNO), *in situ* XRD studies revealed a solid solution process at low states of charge (estimated Li content of $0.59 < x < 1$, Fig. 1a), but isolating the single phases was unsuccessful. As shown in the *ex situ* XRD patterns collected on the cathodes recovered from partially charged cells, two-phase mixtures instead of single phase were obtained in $\text{Li}_x\text{Mn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ (Li_xMNO) with a Li content of $0.7 < x < 1$ (Fig. 1b). Nearly identical mixtures were obtained when Li was removed either by electrochemical or chemical methods (Fig. 1c), suggesting that the solid solutions appearing during the *in situ* electrochemical charge and discharge are metastable transient intermediates that bear kinetic significance but are thermodynamically unstable.

Efforts were directed toward the preparation of solid solutions through thermal treatment, a technique that was successfully used in synthesizing Li_xFePO_4 single phases at elevated temperatures. This quarter, a phase diagram revealing the structural evolution of Li_xMNO as functions of both temperature and Li content was constructed (Fig. 2). At room temperature, the samples with a Li content between 0.71 and 1 were composed of Phase I and II while those with a low Li content between 0 and 0.25 consisted of Phase II and III, with Phase III dominating in the mixture. The samples with an intermediate Li content between 0.25 and 0.71 were mixtures of all three cubic phases. At high temperatures ($>150^\circ\text{C}$), Li_xMNO single phases formed in Li-rich samples ($0.71 < x < 1$) as the miscibility gap between Phase I and II was reduced. The solid solutions remained phase pure after cooling to room temperature which rendered the isolation of Li_xMNO phases for the first time. A new spinel-type impurity was detected in samples with $x < 0.71$, which was attributed to the thermal decomposition of Phase III. The decomposition process releases oxygen from the spinel lattice and triggers Ni reduction to a lower oxidation state as a compensation mechanism.

Crystal synthesis by the solvothermal method. A low-temperature solvothermal method was explored to prepare oxide crystals with preferred metastable crystal habits, complementing cathode materials prepared at high temperatures. Micron-sized and phase-pure spinel LMNO with a variety of morphologies were successfully obtained (Fig. 3). Electrochemical evaluation, however, showed the presence of a large Mn^{3+} content in all samples, suggesting potential TM off-stoichiometry. The rate capability test also indicated much poorer performance compared to those synthesized by the molten-salt method (Fig. 3d). The effort in exploring low temperature crystal synthesis will not continue.

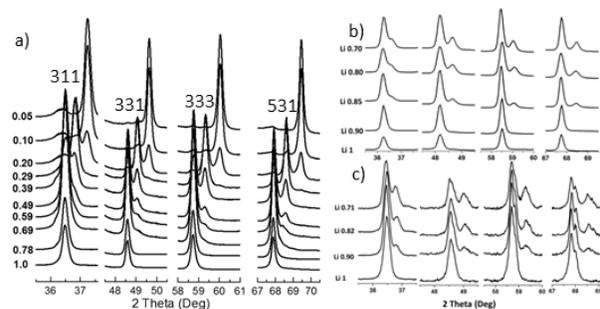


Figure 1. XRD patterns collected during: a) *in situ* electrochemical, b) *ex situ* electrochemical and c) chemical delithiation of LMNO.

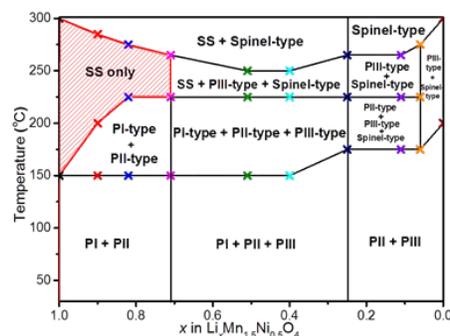


Figure 2. Phase diagram of Li_xMNO .

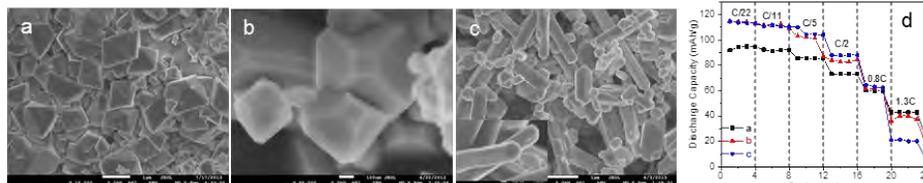


Figure 3. SEM images of solvothermal synthesized LMNO crystals: a) octahedrons, b) truncated-octahedrons and c) rods; d) rate capability of the crystal samples.

Optimization of Ion Transport in High-Energy Composite Cathodes

PROJECT OBJECTIVE: This project aims to probe and control the atomic-level kinetic processes that govern the performance limitations (rate capability and voltage stability) in a class of high energy composite electrodes. A systematic study with powerful suite of analytical tools (including atomic resolution scanning transmission electron microscopy (a-STEM) & Electron energy loss spectroscopy (EELS), X-ray photoelectron spectroscopy (XPS) and first principles (FP) computation) will be used to pin down the mechanism and determine the optimum bulk compositions and surface characteristics for high rate and long life, and to help the synthesis efforts to produce the materials at large scale with consistently good performance. It is also aimed to extend the suite of surface-sensitive tools to diagnose the silicon type of anodes.

PROJECT IMPACT: If successful, this research will provide a major breakthrough in commercial applications of the class of high energy density cathode material for lithium ion batteries. Additionally, it will provide in-depth understanding of the role of surface modifications and bulk substitution in the high voltage composite materials. The diagnostic tools developed here can also be leveraged to study a wide variety of cathode and anode materials for rechargeable batteries.

OUT-YEAR GOALS: Careful engineering of the surface (coating) and bulk compositions (substitution) of the high energy composite cathode materials can lead to significant improvement on ion transport and voltage stability. The goals are to establish the STEM/EELS and XPS as quantitative diagnostic tools for surface and interface characterization and to enable quick identification of causes of surface instability (or stability) in various types of cathode materials. It is also planned to identify ways to extend the techniques for anode materials, such as silicon anode.

COLLABORATIONS:

- Robert Kostecki and Gao Liu (LBNL): on cathode electrolyte interface diagnosis and anode SEI diagnosis
- Se-Hee Lee (U. of Colorado, Boulder): on surface coating of cathode materials.
- Michael Sailor (UCSD): porous Si and carbonization of Si-based anodes.
- Keith Stevenson (UT Austin): XPS and TOP-SIMS
- Nancy Dudney and Juchuan Li (ORNL): Si thin film fabrication

Milestones

- 1) Establish the initial suite of surface and interface characterization tools, including STEM/EELS, XPS and FP computation (Dec. 13) **Complete**
- 2) Identify the surface coated materials (AlF_3 and Li_3PO_4) electrochemical performance matrices, including first cycle irreversible capacity, discharge energy density, voltage stability upon cycling and rate capabilities. (Mar. 14) **Complete/Initiated morphological control**
- 3) Go/No-Go: Stop and change the coating materials if the improvements for rate capability and voltage stability are not significant. Criteria: Characterize coated samples - coating thickness, compositions and morphology before, during and after cycling. (Jun. 14) **Complete**
- 4) Identify ways to extend the STEM/EELS and XPS techniques for anode materials, such as silicon anode. (Sep. 14) **XPS completed, STEM/EELS delayed due to instrument downtime**

Progress Report

Effect of FEC additive on the interface stability of sputtered *a*-Si thin film electrodes. It has been shown that a sputtered *a*-Si thin film electrode is mechanically stable during its formative cycles if it has a thickness < 150 nm. Using 50 nm thick *a*-Si electrodes, it is proposed that chemical irreversibilities can be isolated from mechanical irreversibilities. In this way, electrolyte additives and Si surface treatments can be properly investigated as strategies to improve the chemical stability of Si electrode surfaces.

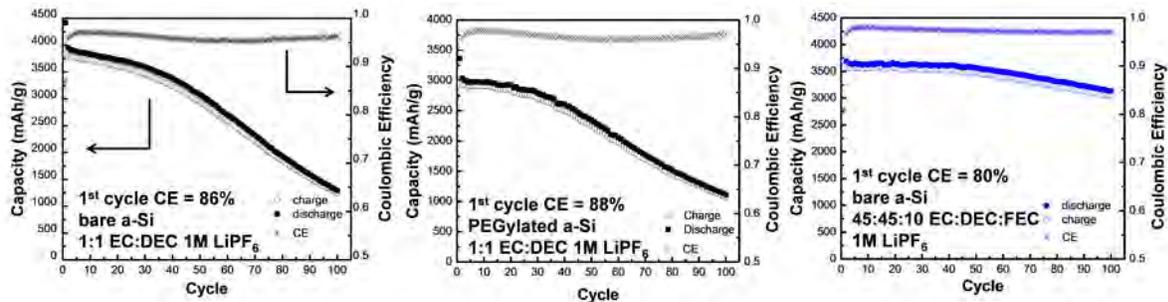


Figure 1. Cyclic capacity and coulombic efficiency for the control electrode, the PEGylated electrode, and the electrode cycled in electrolyte with the FEC additive.

Figure 1 presents the electrochemical data for bare *a*-Si in 1:1 EC:DEC electrolyte (control), PEGylated *a*-Si in 1:1 EC:DEC 1M LiPF₆ electrolyte, and bare Si in 45:45:10 EC:DEC:FEC 1M LiPF₆ electrolyte. PEG was chosen for its similarity to polymeric electrolyte decomposition products previously identified in Si's SEI. Previously presented work confirms the proper functionalization of *a*-Si. Without any surface treatments or electrolyte additives, the first cycle CE is 86%. PEGylation of *a*-Si improves the first cycle CE to 88% as well as the CE on subsequent cycles. The results presented here are improved from previously presented data through better cell construction. It is accepted by the battery research community that FEC preferentially decomposes during the first cycle to form inorganic LiF. The preferential decomposition of FEC should decrease first cycle CE not increase first cycle CE. In agreement with this notion, when 50 nm thick *a*-Si thin films are cycled with FEC, the first cycle CE decreases to 80% and a dramatic improvement in cyclic capacity retention is observed.

XPS data supporting a particular decomposition mechanism for FEC. Two early studies suggest that FEC reduces to VC, which then self-polymerizes to form either polycarbonates or a poly(alkene). The Balbuena *et al.* computation study shows that the most probable decomposition mechanism for FEC occurs *via* a ring opening reaction to form F⁻, CO₂²⁻ and CHOCH₂. These reduction products can then react further to form LiF, RCOLi, and Li₂CO₃. Figure 2 presents the XPS spectra of an *a*-Si surface after 1 full cycle in electrolyte with and without an FEC additive. The F(1s) spectra suggest that the surface of the SEI contains more LiF in the presence of FEC. The C(1s) spectra provides evidence for the preferential formation of RCOLi, PEO, and Li₂CO₃ in the presence of FEC. It is noted that polyethylene (C=C) may be convoluted with the C-C peak at 285 eV. Finally, polycarbonates are not observed in the O(1s) FEC spectrum at 534.5 eV. The XPS results presented here correlate best with Balbuena *et al.*'s FEC decomposition mechanism.

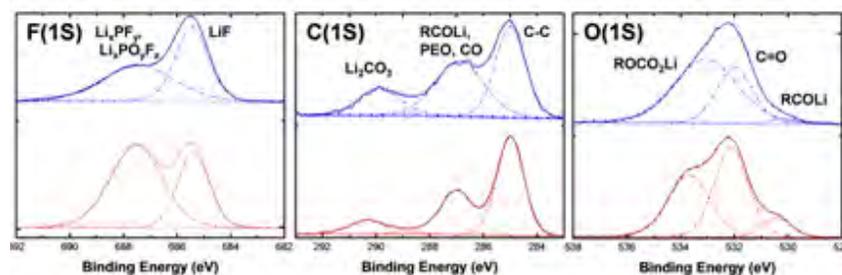


Figure 2. XPS spectra of *a*-Si surface after 1 full cycle in 1:1 EC:DEC 1M LiPF₆ electrolyte (red) and 45:45:10 EC:DEC:FEC 1M LiPF₆ electrolyte (blue).

Analysis of Film Formation Chemistry on Silicon Anodes by Advanced *In Situ* and *Operando* Vibrational Spectroscopy

PROJECT OBJECTIVE: Understand the composition, structure, and formation/degradation mechanisms of the solid electrolyte interface (SEI) on the surfaces of Si anodes during charge/discharge cycles by applying advanced *in-situ* vibrational spectroscopies. Determine how the properties of the SEI contribute to failure of Si anodes in Li-ion batteries in vehicular applications. Use this understanding to develop electrolyte additives and/or surface modification methods to improve Si anode capacity loss and cycling behavior.

PROJECT IMPACT: A high capacity alternative to graphitic carbon anodes is Si, which stores 3.75 Li per Si versus 1 Li per 6 C yielding a theoretical capacity of 4008 mAh/g versus 372 mAh/g for C. But Si anodes suffer from large first cycle irreversible capacity loss and continued parasitic capacity loss upon cycling leading to battery failure. Electrolyte additives and/or surface modification developed from new understanding of failure modes will be applied to reduce irreversible capacity loss, improve long term stability and cyclability of Si anodes for vehicular applications.

OUT-YEAR GOALS: Extend the study of interfacial processes with advanced vibrational spectroscopies to high voltage oxide cathode materials. The particular oxide to study will be chosen based on materials of interest at that time and availability of the material in a form suitable for these studies, e.g. sufficiently large crystals or sufficiently smooth/reflective thin films. The effect of electrolyte composition, electrolyte additives, and surface coatings will be determined and new strategies for improving cycle life developed.

COLLABORATIONS:

Chunmei Ban (NREL) Functionalization of Si by Atomic Layer Deposition (ALD): Effect of functionalization on electrolyte reduction

Gao Liu (LBNL) Surface electrochemistry of electrolyte additives on model Si electrodes

Milestones

- 1) Develop method to attach Si nanostructures to the electrode substrate used in the spectroelectrochemical cell. (Sep. 14) **Complete**
- 2) Determine the oxidation and reduction potentials and products of at least one electrolyte additive provided by Gao Liu's group. (Mar. 14) **Complete**
- 3) Determine role of the Si nanostructure on the SEI formation structure and properties (Sep. 14) **Complete**
- 4) Go/No-Go: Feasibility of surface functionalization to improve SEI structure and properties. Criteria: Functionalize a model Si anode surface and determine how SEI formation is changed. (Sep. 14) **Delayed to Oct. 14**

Progress Report

In Q4, a method to attach Si nanostructures to the electrode substrate used in a spectroelectrochemical cell was developed. A top-down strategy (lithography method) was used to generate a binder-free Si microstructure on a Si wafer substrate. Two patterns (square pillar and line grating) with two sizes (3, 10 μm) were synthesized on Si (100) wafer. All the galvanostatic tests were done with EC/DEC/LiPF₆ electrolyte (v/v=1:2) at a 5 μAcm^{-1} charging rate.

As shown in Fig. 1, an *in situ* FTIR spectroelectrochemical cell accompanied with a lithography Si microstructure on Si wafer was developed to investigate SEI dependence on Si micro/nano structures. The IR beam comes from the backside of the prism and patterned Si wafer, and the chemical species signal from the Si micro/nano structure surface is collected from the front. Utilizing this method, good electrochemical and FTIR signals on a well-controlled Si surface with no surfactant or binder contamination can be obtained. Furthermore, by adjusting the photolithography mask alignment direction, selective crystal planes of the sidewalls are preferentially exposed (e.g. Si (100), (110)). Thus, investigation of SEI formation dependence on Si crystal orientation of micro/nanostructures is available as well.

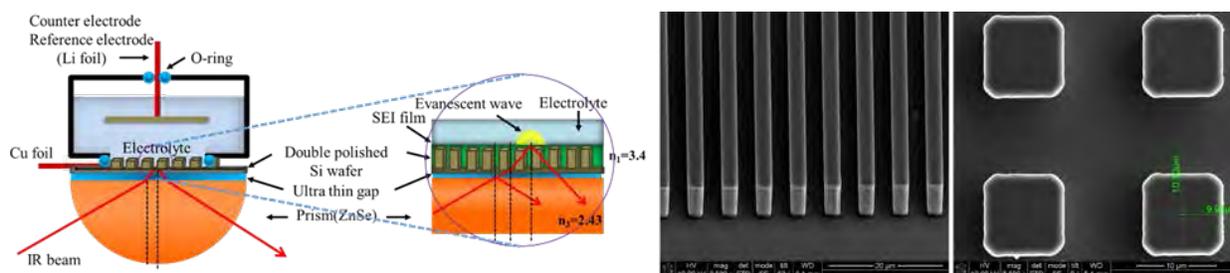


Figure 1. Schematic of *in situ* FTIR cell with lithographed Si microstructures (10 μm line grating and square pillar patterns).

The first cycle galvanostatic curves in Fig. 2 show that the patterned Si sample has much larger irreversible capacity, which indicates much more electrolyte reduction from the surface of Si microstructure electrodes during the first discharge. The main reasons for the irreversible capacity are: the catalytic activity of the etched Si walls for the initial reduction to dissolved species at $E > 1$ V, and the space between those microstructures allow for more dissolved product to accumulate locally before precipitation occurs, passivating the surface. The *ex situ* FTIR results shows SEI component signals of the same chemical species on both surfaces.

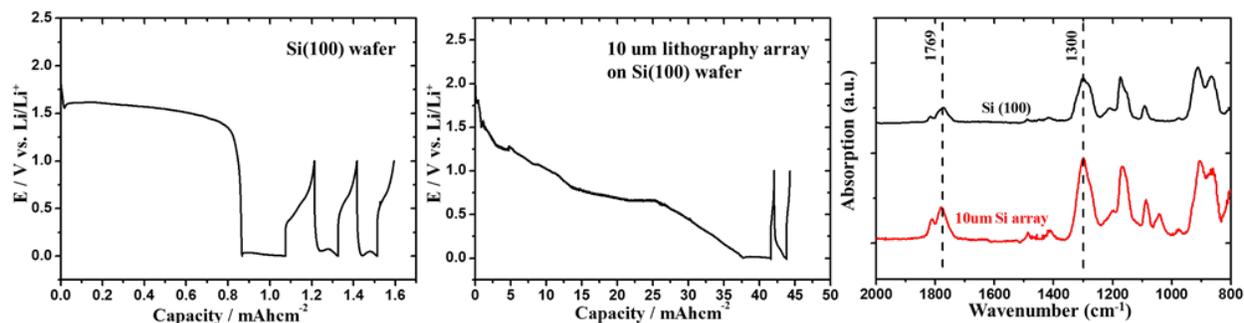


Figure 2. First cycle galvanostatic curve comparison between Si (100) wafer (left) and a 10 μm array on Si (100) wafer (center). (Right) *ex situ* ATR spectra of Si (100) wafer and 10 μm array samples after 5 cycles with a 5 μAcm^{-2} charging rate.

Electrode Materials Design and Failure Prediction

PROJECT OBJECTIVE: The goal of this project is to use continuum-level mathematical models along with controlled experiments on model cells to (i) understand the performance and failure models associated with next-generation battery materials, (ii) design battery materials and electrodes to alleviate these challenges. The focus of the research will be on two systems, silicon-based anodes and Li-S cells. In silicon anodes, the challenges associated with the large volume change and the associated stress effects will be studied. In the Li-S system, the focus will be on the concept of using ceramic single-ion conducting glass layers for lithium protection, along with quantification of the losses associated with such a design and its impact on the performance of the chemistry. A theoretical study of the impact of polarization losses on the energy density will be conducted.

PROJECT IMPACT: Si-anode-based Li-ion cells and Li-S cells promise to increase the energy density and decrease the cost of batteries compared to the state-of-the-art. If the performance and cycling challenges can be alleviated, these systems hold the promise for meeting the EV-Everywhere targets.

OUT-YEAR-GOALS: At the end of this project, a mathematical model will be developed that can address the power and cycling performance of next-generation battery systems. The initial focus will be on silicon anodes and Li-S cells, although the project will adapt to newer systems, if appropriate. The models will serve as a guide for better design of materials, including mechanical properties to reduce stress in silicon anodes, and the kinetics and solubility needed to decrease the morphological changes in sulfur cells and increase the power performance.

COLLABORATIONS: None this quarter.

Milestones

- 1) Go/No-Go: Stop materials testing. Criteria: Stop materials testing if unsuccessful at obtaining reproducible results for mechanical property values of binder and conductive material composites saturated in electrolyte. (Dec. 13) **Go**
- 2) Incorporate material property values and behavior measured for binders saturated with electrolyte into simulations of model systems. (Feb. 14) **Complete**
- 3) Quantify polarization losses at liquid/SIC interface for different electrolytes. (Mar. 14) **Complete**
- 4) Determine possible reasons for dynamic nature of polarization loss in liquid/SIC interface (e.g., interfacial vs. bulk.) (Jun. 14) **Complete**
- 5) Quantify the impact of the interfacial polarization loss between the liquid/SIC by estimating the energy density of a Li-S cell for a given power to energy ratio. (Sep. 14) **Complete**

Progress Report

In previous quarters, the liquid electrolyte/single ion conductor (SIC) junction polarization losses in three different solvents and at different concentrations of LiPF_6 were measured to be between 0.35 and $0.5 \text{ K}\Omega\text{-cm}^2$. Comparison with the charge transfer resistance of a porous NMC electrode suggested that the unavailability of high-surface area for ion transfer at a planar SIC may explain the high polarization losses observed in these experiments.

This quarter, the impact of polarization losses on the energy density of Li-S batteries was investigated. Figure 1 shows the specific energy of batteries at different C-rates (ranging from C/50 to C/2) with different battery designs: (1) batteries without a SIC and with an electrode loading of 0.5 mg/cm^2 of sulfur, (2) batteries with a SIC and the same 0.5 mg/cm^2 sulfur loading, and (3) batteries with a SIC and a loading of 3 mg/cm^2 . The specific energy was calculated based on the mass of active material only and was assumed that the rate performance is not dependent on the degree of S loading.

The results plotted in Fig. 1 suggest that the presence of an SIC makes little difference to the specific energy of a battery when the sulfur loading is low (0.5 mg/cm^2). This is because the applied current density is correspondingly small. However, the low-energy densities of these batteries make such a design impractical. If the sulfur loading is increased to 3 mg/cm^2 , the specific energy at the highest C-rate is a small fraction of that obtained in the low-loading cases. The higher loading is associated with a larger applied current density, which in turn is associated with a large liquid electrolyte/SIC junction polarization loss. This huge loss of energy would limit the usefulness of Li-S batteries containing this SIC. Although incorporation of a SIC improves Li-S battery stability, polarization losses at the liquid/SIC interface must be reduced in order to make such a battery practical. These findings complete Milestone 5.

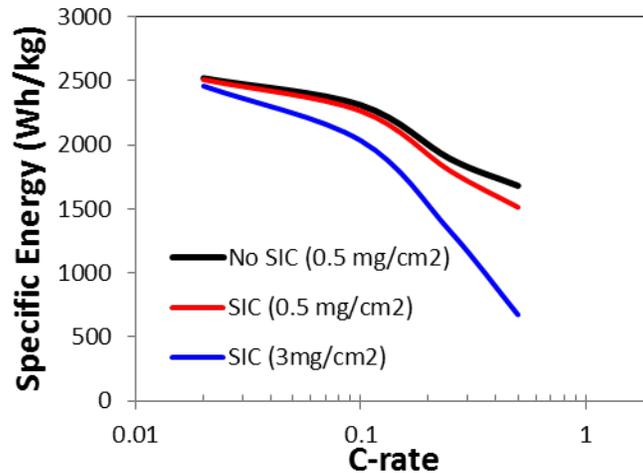


Figure 1. Specific energy densities of Li-S batteries with different designs, at a range of C-rates: 0.5 mg/cm^2 sulfur loading in batteries without a SIC, 0.5 mg/cm^2 loading in batteries with a SIC, and 3 mg/cm^2 loading of batteries with a SIC.

Predicting and Understanding Novel Electrode Materials from First-Principles

PROJECT OBJECTIVE: The aim of the Project is model and predict novel electrode materials from first-principles focusing on 1) understanding the atomistic interactions behind the behavior and performance of the high-capacity lithium excess and related composite cathode materials and 2) predict new materials using the recently developed Materials Project high-throughput computational capabilities at LBNL. More materials and new capabilities will be added to the Materials Project Lithium Battery Explorer App (www.materialsproject.org/apps/battery_explorer/).

PROJECT IMPACT: The project will result in a profound understanding of the atomistic mechanisms underlying the behavior and performance of the Li-excess as well as related composite cathode materials. The models of the composite materials will result in prediction of voltage profiles and structural stability – the ultimate goal being to suggest improvements based on the fundamental understanding that will increase the life and safety of these materials. The Materials Project aspect of the work will result in improved data and electrode properties being calculated to aid predictions of new materials for target chemistries relevant for ongoing BATT experimental research.

OUT-YEAR GOALS: During year 1-2, the bulk phase diagram will be established – including bulk defect phases in layered Li_2MnO_3 , layered LiMO_2 ($M = \text{Co}, \text{Ni}, \text{and Mn}$) and LiMn_2O_4 spinel to map out the stable defect intermediate phases as a function of possible transition metal rearrangements. Modeling of defect materials (mainly Li_2MnO_3) under stress/strain will be undertaken to simulate effect of composite nano-domains. The composite voltage profiles as function of structural change and Li content will be obtained. In year 2-4, the project will focus on obtaining Li activation barriers for the most favorable TM migration paths as a function of Li content as well as electronic DOS as a function of Li content for the most stable defect structures identified in year 1-2. Furthermore, stable crystal facets of the layered and spinel phases will be explored, as a function of O_2 release from surface and oxygen chemical potential. Within the Materials Project, hundreds of novel Li intercalation materials will be calculated and made available.

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

Milestones

- 1) Finalize low T phase diagram including relevant bulk Li, O and Mn and defect phases in layered Li_xMnO_2 , spinel Li_xMnO_3 and spinel $\text{Li}_x\text{Mn}_2\text{O}_4$ (Dec. 13) **Complete**
- 2) Over-charge mechanism processes: oxygen migration paths and activation barriers obtained in lowest energy defect structures; oxygen redox potentials obtained (Mar. 14) **Complete**
- 3) Go/No-Go: On over-charge mechanism. Criteria: Oxygen release, migration or oxygen redox process; process down select based on data. (Jun. 14) **Complete**
- 4) Composite voltage profiles as function of structural change and Li content obtained (Sep. 14) **Complete**

Progress Report

A first-principles investigation was completed on the redox reaction mechanism and associated chemical and structural instability in Li_2MnO_3 , as a function of state of charge. In the low Li content region ($x < 1$), it is noted that all low-energy structures are defect-layered (red dots in Fig. 1), supporting experimental evidence that Li_2MnO_3 and related materials are far from equilibrium when activated. In all defect-layered structures, a fraction of Mn ions are displaced to the Li-layer, which implies a strong tendency towards Mn migration into the Li layer. At charge beyond $x=1$, clearly, the layered structure experiences a frustration and thermodynamic driving force towards cation migration.

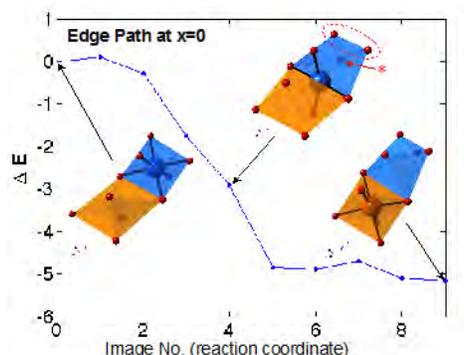


Figure 1. Migration barrier for Mn^{4+} through the edge path at $x=0$ indicating an almost mechanical instability of the material. x represents the amount of Li in Li_xMnO_3 .

The Mn^{4+} ion is predicted to move rapidly to the Li layer, if Li is depleted (even locally) through a local cooperative displacement of the oxygen environment. Two paths were examined, as a function of state-of-charge: the dumbbell path and a direct transition through an oxygen edge. While the dumbbell path exhibits sluggish but feasible migration energetics for $x=1$, the edge path becomes almost mechanically unstable for an almost depleted Li region (even locally). This indicates a severe instability of the material as Li is extracted at high charge.

Furthermore, while Li_xMnO_3 exhibits a thermodynamic instability towards oxygen release for $x < 1$, the oxygen migration barriers (even for the O^{1-} species at high charge) are found to be too high for facile oxygen diffusion in the bulk. However, oxygen release in the surface region of the particles is deemed likely, where local under-coordination and strain may also facilitate the diffusion. Finally, the voltage profile for the first charge of the pristine material and a subsequent discharge were compared, where it was assumed that the structure has transformed to a structure with Mn defects in the Li layer. The change in voltage is pronounced, almost 1 V, which qualitatively agrees with experiments. The results suggest that a significant voltage fade can manifest as a result of local Mn migration into the Li layer, effectively creating a defect structure that is more stable when the Li contents are low.

First Principles Calculations of Existing and Novel Electrode Materials

PROJECT OBJECTIVE: Identify the structure of layered cathodes that leads to high capacity. Clarify the role of the initial structure as well as structural changes upon first charge and discharge. Give insight into the factors that control the capacity and rate of Na-intercalation electrodes, and make suggestions for novel Na-intercalation cathode materials. Generate insight into the behavior of alkali-intercalating electrode materials.

PROJECT IMPACT: The project will lead to insight in how Li excess materials work and ultimately to higher capacity cathode materials for Li-ion batteries. The project will also lead to definite conclusions as to whether Na-ion batteries can exceed Li-ion batteries in energy density.

OUT-YEAR GOALS: Higher capacity Li-ion cathode materials, and novel chemistries for higher energy density storage devices.

COLLABORATIONS: K. Persson (LBNL), C. Grey (Cambridge U).

Milestones

- 1) Identify at least three ordered states in Na_xMO_2 compounds that can be verified with experiments. (Dec. 13) **Complete**
- 2) Obtain computed voltage curve of Li_2MO_3 compound where $\text{M} = \text{Mn}$ or other metal. (Mar. 14) **Complete**
- 3) Go/No-Go: If voltage curves of Na compounds with less than 0.5V error cannot be modeled. Criteria: Obtain voltage curves for all the O_3 Na_xMO_2 compounds where M is at least five distinct 3d metals. (Jun. 14) **Complete**
- 4) Complete ground state study in Li-Ni-Mn-O and Li-Co-Mn-O system. (Sep. 14) **Complete**

Progress Report

Previously, work was reported on Na-ion intercalating layered oxides for use as materials for high-energy density Na-ion battery cathodes. These materials are distinctive in that they exhibit multiple reversible first order phase transformations, which appear as steps in the electrochemical cycling voltage curves. One such material examined in this work, Na_xMnO_2 , shows multiple reversible phase transformation steps as it is cycled [1].

The ground state hull for Na_xMnO_2 was computed (Fig. 1) and in doing so, confirmed a newly characterized superstructure at $x=0.625$. This superstructure provides direct visualization of a cooperative Jahn-Teller effect *via* a correlated distortion of atoms in the layered structure, seen both in extensive experimental characterization and in the density functional theory (DFT) model [2]. Figure 2 shows the Na and Na-vacancy ordering in one layer of this structure, as well as the ordering of transition metal charge and ferrimagnetic and AF stripe orderings. The structure is particularly unusual because it shows Na⁺ ions as being displaced from their original octahedral environments.

The convex energy hull is constructed by several computational means. Enumeration algorithms calculate possible atomic arrangements for Na ions within the Na layer and their formation energies are calculated by DFT. This set of calculated structural energies can then be used to formulate parameters for a cluster expansion, which will be applied through Grand Canonical Monte Carlo methods to calculate a full voltage curve.

As well as providing the opportunity to confirm observed ground state phases, these methods can be used predictively to explore the nature of the voltage curve and all phases formed during the electrochemical cycling of a potential battery cathode material.

[1] X. Ma, H. Chen, and G. Ceder. *Journal of the Electrochemical Society* **158** (2011) A1307-A1312

[2] X. Li et al. *Nature Materials* **13** (2014) 586-592.

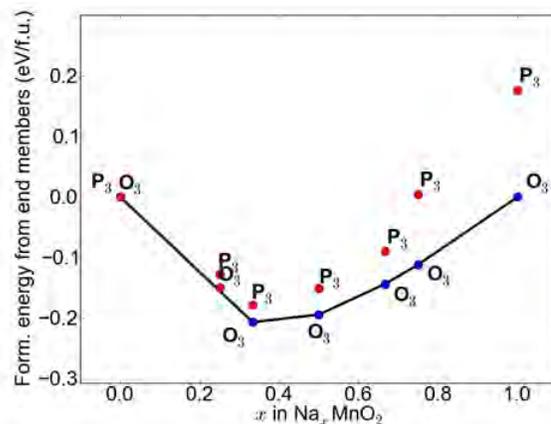


Figure 1. Calculated ground state hull for Na_xMnO_2 , including predicted superstructure at $x=0.625$.

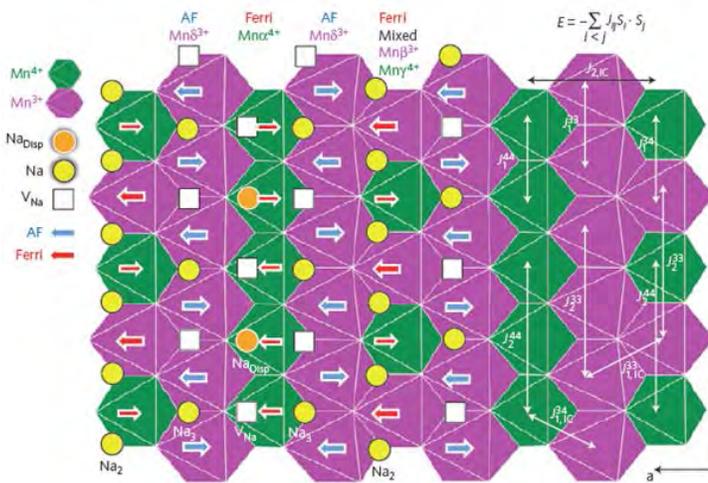


Figure 2. $\text{Na}_{5/8}\text{MnO}_2$ superstructure with vacancy (V_{Na}) ordering, Mn charge, and magnetic stripe orderings.

First Principles Modeling of SEI Formation on Bare and Surface/Additive Modified Silicon Anode

PROJECT OBJECTIVE: This project aims to develop fundamental understanding of the molecular processes that lead to the formation of a solid electrolyte interphase (SEI) layer due to electrolyte decomposition on Si anodes, and to use such new knowledge in a rational selection of additives and/or coatings. The focus is on SEI layer formation and evolution during cycling and subsequent effects on capacity fade through two concatenated problems: 1) SEI layers formed on lithiated Si surfaces, and 2) SEI layers formed on coated surfaces. Key issues that this project addresses include the dynamic evolution of the system and electron transfer through solid-liquid interfaces.

PROJECT IMPACT: Finding the correspondence between electrolyte molecular properties and SEI formation mechanism, structure, and properties will allow the identification of new/improved additives. Studies of SEI layer formation on modified surfaces will allow the identification of effective coatings able to overcome the intrinsic deficiencies of SEI layers on bare surfaces.

OUT-YEAR GOALS: Investigating the SEI layer formed on modified Si surfaces involves analysis of the interfacial structure and properties of specific coating(s) deposited over the Si anode surface, characterization of the corresponding surface properties before and after lithiation, especially how such modified surfaces may interact with electrolyte systems (solvent/salt/additive), and what SEI layer structure, composition, and properties may result from such interaction. This study will allow identification of effective additives and coatings able to overcome the intrinsic deficiencies of SEI layers on bare surfaces. Once the SEI layer is formed on bare or modified surfaces, it is exposed to cycling effects that influence its overall structure (including the anode), chemical, and mechanical stability. Elucidating such effects using a molecular level approach will help establish their relationship with capacity fading, which will lead to revisiting additive and/or coating design.

COLLABORATIONS: Work with Chunmei Ban, (NREL) consists in modelling the deposition-reaction of trimethylaluminum and glycerol on Si surfaces and their reactivity. Work with B. Lucht (URI) relates to finding the best additives for optimum SEI formation on Si anodes. Reduction of solvents and additives on Si surfaces were studied in collaboration with K. Leung and S. Rempe, from Sandia National Labs. Work with Partha Mukherjee (TAMU) in the development of a multi-scale model to describe the SEI growth on Si anodes.

Milestones

- 1) Identify reaction pathways and activation energies for electrolyte reduction on lithiated Si surfaces, both clean and covered with surface oxides and/or with selected SEI products. (Dec. 13) **Complete**
- 2) Quantify electron transfer from a lithiated Si surface covered by a model SEI layer to the electrolyte; develop theory/algorithms accounting for voltage effect on electrolyte reduction reactions. (Mar. 14) **Electron transfer studies completed; voltage effect delayed (Sandia's part of the project started in Aug 14).**
- 3) Characterize reactivity of additives; identify reaction pathways and interactions of reaction products with electrolyte components; assess aggregation effects. (Jun. 14) **Complete**
- 4) Go/No-Go: Development of a coarse-grained Kinetic Monte-Carlo approach for assessing long-time evolution (order of days) of SEI films. Criteria: Continuation will be based on the demonstrated effectiveness of the technique. (Sep. 14) **Complete**

Progress Report

Mesoscopic model. Work shown in the 2nd and 3rd quarterly reports indicated a rapid decay of electron transfer within the first nanometer of SEI thickness through various SEI blocks. This suggests that a different electron transfer mechanism must be prevalent for the SEI to grow to thicknesses of the order of hundreds of nanometers. Thus, a new model has been formulated to describe the SEI layer nucleation and growth behavior within realistic time and length scales; the schematic (Fig. 1) illustrates the main concepts.

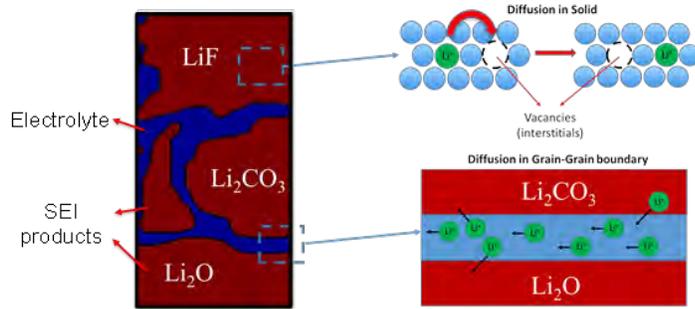
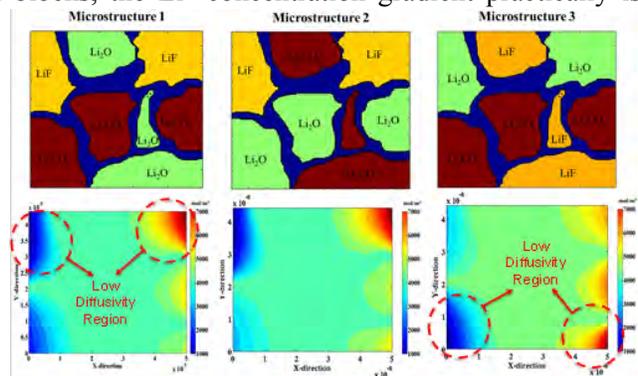


Figure 1. The SEI is assumed to be composed of blocks that may interface with each other as separate entities, separated by channels of variable thicknesses. Cationic and anionic transport may have two different transport mechanisms: through the blocks or through the ion channels that separate the blocks. Anions that result from electrolyte decomposition may travel these channels allowing the reaction to continue. Only when these channels become blocked would the SEI growth stop.

Describing the interfaces between blocks and between the blocks and the anode surface is carried out at two different levels: a) *Ab initio* molecular dynamics (AIMD) simulations; and b) Classical molecular dynamics (CMD) simulations. The AIMD simulations provide information about mixing of the various SEI species at the molecular level. If the species do not mix, it provides information about the geometry and atomic constitution of the channel walls. The CMD simulations provide similar insights at higher length and time scales. For example, nucleation involves longer times that cannot be detected *via* AIMD but it can be detected *via* CMD. Further, diffusion coefficients of Li^+ and anions through the channels are also obtained from CMD. The transport information is then fed to a mesoscopic model (collaboration with Partha Mukherjee, TAMU) where the formation of cracks and other long time phenomena will be investigated. The analysis so far yielded the following conclusions: 1) if the diffusion through the channels is much higher than that inside the SEI blocks, the Li^+ concentration gradient practically is established at the boundaries; 2) the concentration profile of Li ions in the SEI structure is dependent on the ionic conductivity of the blocks and the structure and nature of the channels; 3) the ionic diffusion may lead to microcrack formation; and 4) the SEI microstructure (arrangement of blocks) affects the propagation of microcracks and therefore the subsequent SEI growth.

Voltage effects. AIMD simulations of the anode potential in a simulation cell with explicit $\text{Li}_{26}\text{Si}_8$ /liquid EC interfaces are examined for investigation of voltage effects of the SEI reactions. A prerequisite of a successful potential determination is that no redox reaction occurs during the trajectory, which allows equilibrium sampling. But even when four PF_6^- anions added to the liquid electrolyte region make the surface positively charged and the voltage to rise, EC decomposition occurred in ps time scales, which prevented voltage determination. This suggested that (1) the voltage associated with the anode surface remained low despite its positive charge; or (2) the surface is "catalytic" and reacted chemically rather than electrochemically. To proceed further, the (lithiated) Si surface was coated with a monolayer of LiF so that no Si remains exposed to the liquid. LiF force fields are being fitted for pre-equilibration simulations and AIMD potential calculations will resume afterwards.



A Combined Experimental and Modeling Approach for the Design of High Current Efficiency Si Electrodes

PROJECT OBJECTIVE: The use of high capacity Si based electrode has been hampered by its mechanical degradation due to the large volume expansion/contraction during cycling. Nanostructured Si can effectively avoid Si cracking/fracture. Unfortunately, the high surface to volume ratio in nanostructures leads to unacceptable amount of solid-electrolyte interphase (SEI) formation and growth, thereby low current/coulombic efficiency and short life. Based on mechanics models it is demonstrated that the artificial SEI coating can be mechanically stable despite the volume change in Si, if the material properties, thickness of the SEI, and the size/shape of Si are optimized. Therefore, the objective of this project is to develop an integrated modeling and experimental approach to understand, design, and make coated Si anode structures with high current efficiency and stability.

PROJECT IMPACT: The validated model will ultimately be used to guide the synthesis of surface coatings and the optimization of Si size/geometry that can mitigate SEI breakdown. The optimized structures will eventually enable a negative electrode with a 10x improvement in capacity (compared to graphite) while providing a >99.99% coulombic efficiency, which could significantly improve the energy/power density of current LIB.

OUT-YEAR GOALS: The out year goal is to develop a well validated mechanics model that directly import material properties either measured from experiments or computed from atomic simulations. The predicted SEI induced stress evolution and other critical phenomena will be validated against in-situ experiments in a simplified thin-film system. This comparison will also allow fundamental understanding of the mechanical and chemical stability of artificial SEI in electrochemical environments and the correlation between the coulombic efficiency and the dynamic process of SEI evolution. Thus the size and geometry of coated Si nanostructures can be optimized in order to mitigate SEI breakdown, thus provide high current efficiency.

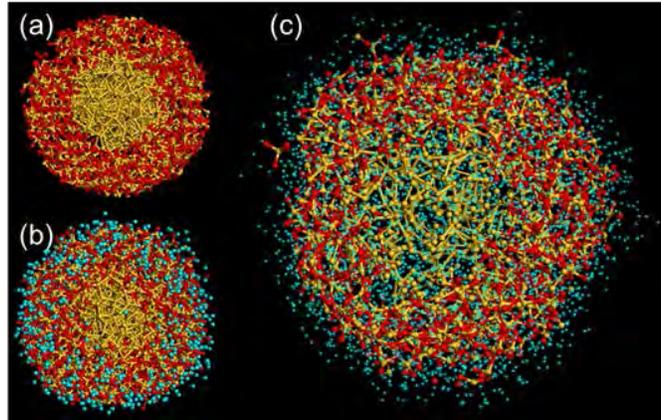
COLLABORATIONS: LBNL, PNNL.

Milestones

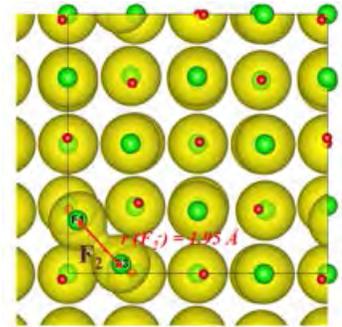
- 1) Compare the basic elastic properties of ALD coatings (e.g., Al₂O₃) computed from MD simulations with ReaxFF and measured by AFM and acoustic wave for method validation. (Dec. 13) **Complete**
- 2) Predict the interface strength of given coatings on Si substrate from QM calculations and compare with nanoindentation and scratch tests. (Sep. 14) **Completed calculations and experiments to be completed in Jan 2015 (due to the delay of installation of nanoindenter)**
- 3) Develop a continuum frame work to model SEI deformation and stability on Si film and compare with *in situ* MOSS measurement. (Jun. 14) **Complete**
- 4) Go/No-Go: Stop hard coating core-shell structure design. Criteria: If no mechanically stabled coating can be identified after searching in ALD coating property design space using the continuum model. (Sep. 14) **Go**

Progress Report

1) **Atomic simulation of Si-core/SiO₂-shell nanowires revealed a mechanically stable coating thickness.** Reactive molecular dynamics simulations of the lithiation of Si-core/SiO₂-shell nanowires were performed. The coating structural integrity and stability vs. its thickness were investigated. Upon lithiation, the SiO₂ shell was immediately lithiated without volume expansion, followed by the lithiation of the Si core. When the thickness of the SiO₂ is comparable to the size of the Si, the lithiated coating remained intact. For thinner coatings, the SiO₂ coating is spread out and loses its structural integrity. These results indicate the existence of an optimal coating thickness to tolerate the volume expansion of a Si anode.

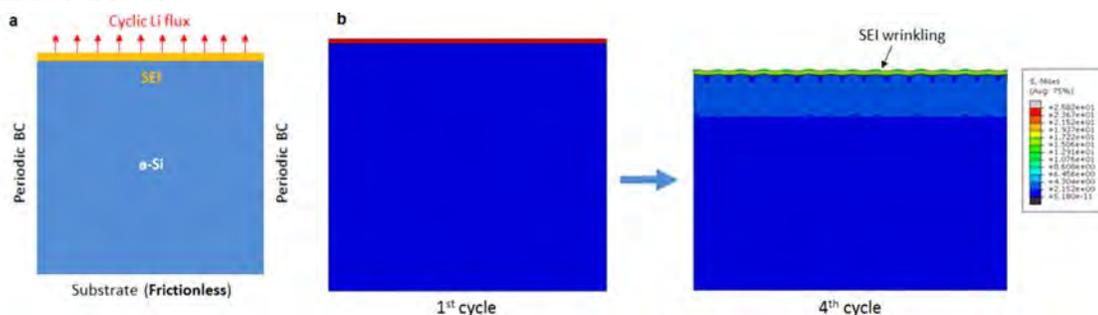


2) **Desirable SEI composition and properties designed by the combination of atomic simulation and experimental validation.** The main possible pathways for electron leakage from LiF are *via*: 1) movements of ionic defects and 2) polaron migration. First principle calculations predicted the ionic defects carrying electrons have negligible concentration, thus the electron leakage through ionic defects is unlikely in LiF coated on an anode surface. Comparing the performance of various synthesized surface coatings of natural SEI components suggested that the desirable SEI should have a high LiF concentration, uniform SEI morphology, high Young's modulus, and low impedance. The properties of an artificial SEI layer are still being optimized.



F₂ molecular ion lies in (101) plane

3) **SEI fracture induced by plastic ratcheting on *a*-Si anode.** The finite element simulations have suggested a potentially new and important failure mode of SEI layer as a result of plastic ratcheting in the *a*-Si electrode. In the model, SEI is considered as a nanoscale thin layer attached on the *a*-Si anode and cyclic Li flux is applied on the top surface to simulate the lithiation/delithiation half cycles (see figure below, a). During cycling, a ratcheting mechanism of accumulative plastic deformation in the *a*-Si is observed, leading to the gradual wrinkling and delamination of SEI (see figure below, b), which may result in battery degeneration. An analytical approach and molecular dynamics simulation will be conducted in the near future to confirm and interpret the simulation results.



Predicting Microstructure and Performance for Optimal Cell Fabrication

PROJECT OBJECTIVE: This work uses microstructural modeling coupled with extensive experimental validation and diagnostics to understand and optimize fabrication processes for composite particle-based electrodes. The first main outcome will be revolutionary methods to assess electronic and ionic conductivities of porous electrodes attached to current collectors, including heterogeneities and anisotropic effects. The second main outcome is a particle-dynamics model parameterized with fundamental physical properties that can predict electrode morphology and transport pathways resulting from particular fabrication steps. These two outcomes will enable the third, which is an understanding of the effects of processing conditions on microscopic and macroscopic properties of electrodes.

PROJECT IMPACT: This work will result in new diagnostic tools for rapidly and conveniently interrogating electronic and ionic pathways in porous electrodes. A new mesoscale 3D microstructure prediction model, validated by experimental structures and electrode-performance metrics, will be developed. The model will enable virtual exploration of process improvements that currently can only be explored empirically.

OUT-YEAR GOALS: This project was initiated April 2013 and concludes March 2017. Goals by fiscal year are as follows.

1. Fabricate first-generation micro-four-line probe and complete associated computer model.
2. Assess conductivity variability in electrodes; characterize microstructures of multiple electrodes.
3. Fabricate four-line ionic conductivity probe; complete first-gen dynamic particle packing (DPP) model.
4. Fabricate N-line probe for anisotropic film conductivity; validate DPP model; assess effect of processing variables.
5. Use conductivity predictions in full electrochemical model; evaluate effect of innovative processing conditions.

COLLABORATIONS: Karen Thomas-Alyea of A123 and Andrew Jansen (ANL) both provided battery materials. Transfer of technology to A123 to improve their electrode production process is in progress. A modeling collaboration with Simon Thiele of University of Freiburg was continued.

Milestones

- 1) Measure variability and average electronic conductivity for five candidate electrode compositions using four-line probe. (Dec. 13) **Complete**
- 2) Measure microstructure of three candidate electrodes using SEM/FIB. (Mar. 14) **Complete**
- 3) Determine appropriate set of descriptors or metrics that effectively characterize previously observed microstructures. (Jun. 14) **Complete**
- 4) Go/No-Go: Discontinue current four-line probe geometry. Criteria: If measurement variability is not significantly less than sample-to-sample variability. (Sep. 14) **Complete – Go criterion met**

Progress Report

Completion of Milestone 4. As described in the report for the first quarter of FY2014, a prototype micro four-line probe (μ 4LP) measurement apparatus for accurate and repeatable measurements of local electronic conduction properties of thin-film battery electrodes was completed. The apparatus included an XYZ stage controlled by a LabView program that enables full automation of measurements. To ensure accurate force application on the electrode, a force sensor with feedback loop was used to measure and control the applied pressure. Multiple digital multimeters measured current and potentials. A computer program inverted the results to compute bulk electronic conductivity and contact resistance with the current collector.

Since that time, bulk electronic conductivity measurements from the μ 4LP apparatus have been validated *via* comparison to three other methods, including the van der Pauw technique, a traditional four-point probe, and a macro four-line probe. In addition, contact resistance measurements from the μ 4LP apparatus were validated by a direct method based on sandwiching a film between Cu plates. A conductive film composed of carbon black and silicone (Parker Chomerics) was used, which simulated the conductive properties of a typical Li-ion electrode. Examples of the validation results are below, which includes 95% confidence intervals.

Method	Bulk Electronic Conductivity (mS/cm)
Van der Pauw	265.4 ± 1.1
Four-Line-Probe	276.5 ± 16.4

Method	Current Collector contact R ($\Omega \text{ cm}^2$)
Direct	0.134 ± 0.028
Four-Line-Probe	0.146 ± 0.008

The criterion for the Go/No-Go Decision was whether the apparatus could reduce measurement error to a level below that of the innate spatial variability of conductivity of the sample. This was accomplished for multiple samples including the one shown in Fig. 1. This demonstrates that the basic design of the μ 4LP is effective, though ongoing improvements will continue to be made.

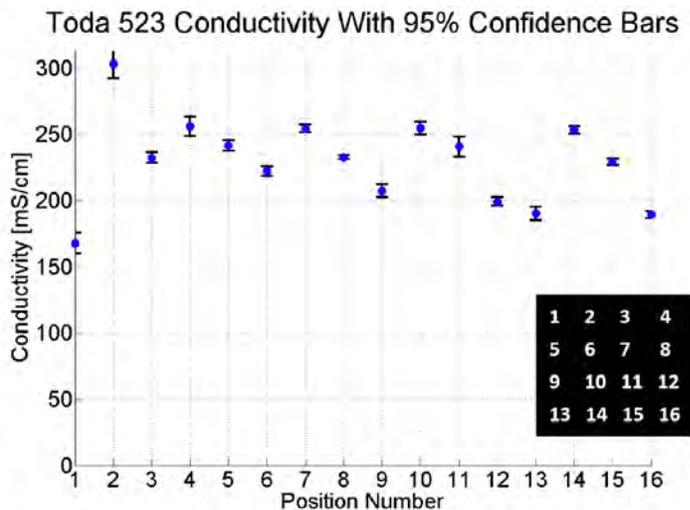


Figure 1. Spatial variability of conductivity for a sample cathode, produced by repeated measurements on a series of locations on a 1mm grid (inset location map). Error bars at each location (95% confidence interval) are significantly smaller than spatial variability, showing that the method is capable of producing highly accurate conductivity maps across the electrode.