

Integrated Lab/Industry Research Project

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Argonne National Laboratory

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Project ID:
ES103

Overview

Timeline

- Start date: August, 2010
- End date: September, 2014
- Percent complete:
 - < 10% complete

Budget

- Total project funding
 - 100% DOE
- FY11: \$1000K

Barriers

- Developing higher energy density electrodes
- Improving cycle life
- Increasing lithium battery safety

Partners

- Jordi Cabana, Marca Doeff, Lily Zhang, Tom Richardson , R. Kostecki, G. Liu (LBNL)
- Dave Schroeder (Northern Illinois)
- Susanna Neuhold, C. Grogger (TU Graz)
- Collaborations
 - Russell Cook (Electron Microscopy Center)
 - David Gosztola, Nancy Dietz-Rago (Center for Nanoscale Materials)



Objectives - Relevance

To overcome the well known problems with the metallic lithium electrode -stability, safety, and cycling efficiency - that continue to block its implementation into advanced lithium batteries for PHEVs and next generation technologies (Li/Air, Li/Sulfur).

Project Areas:

- Develop tools to gain a better understanding of how lithium interacts within an electrochemical cell and identify methodologies that extend cycle life.
- Search for ceramic phases with high Li^+ conductivity that are stable against the lithium metal electrode to enable next generation technologies.
- Understand the ion transfer processes that occur at the liquid/solid electrolyte and solid electrolyte/lithium metal interfaces to increase safety and performance of lithium-based cells.
- Identify, design, and characterize polymeric and organic materials that produce interfacial coatings stable to lithium metal in a liquid electrolyte environment in order to increase the safety and stability of lithium-based batteries.



Milestones

April 2011

- Prototype new cell fixtures for electrochemical cell testing using ceramic electrolytes.
- Prototype in-situ cell design for CNM and APS User facilities
- Synthesize, design and characterize films deposited on the surface of a lithium electrode.

September 2011

- Investigate new types of surface coatings with better surface adhesion
- Evaluate stability of lithium-ion conducting ceramics in relevant electrochemical systems.
- Synthesize and scale up a variety of established Li-ion conducting ceramics and develop methods to produce as thin ceramic plates.



Approach/Strategy

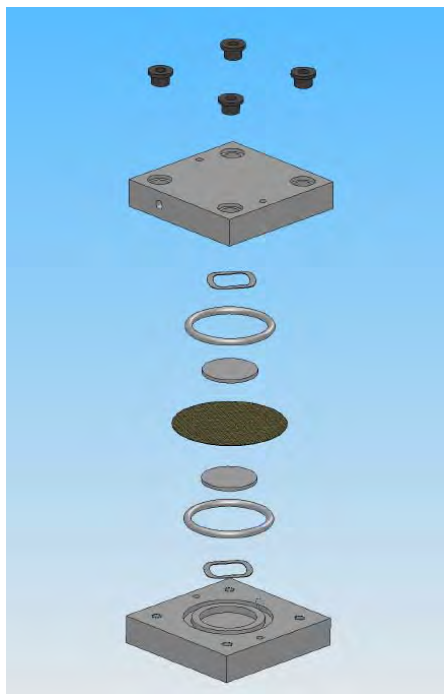
Leverage expertise at LBNL and ANL to study fundamental processes with critical impact on industrial development of Lithium metal based cells.

- Establish a stable, dense, and uniform lithium/electrolyte interface exhibiting good electrochemical performance.
 - Develop and characterize organic coatings that are ionically conducting and stable to lithium metal potentials.
 - Study and analyze the failure mechanism of various Li-metal electrode coatings. Develop and characterize conformal stable monolayer coatings.
- Develop spectroscopic tools and methodologies to examine the lithium metal /electrolyte and lithium metal / ceramic interfaces.
 - Electrode surface and bulk analysis
- Develop general approaches to synthesizing and evaluating established and emerging solid state lithium ion conductors.
 - Source commercial samples where available, develop methods to synthesize a variety of materials in appropriate forms.



Technical accomplishments:

Progress toward diagnostics cell development



Ceramic plate
electrochemical test
fixture.

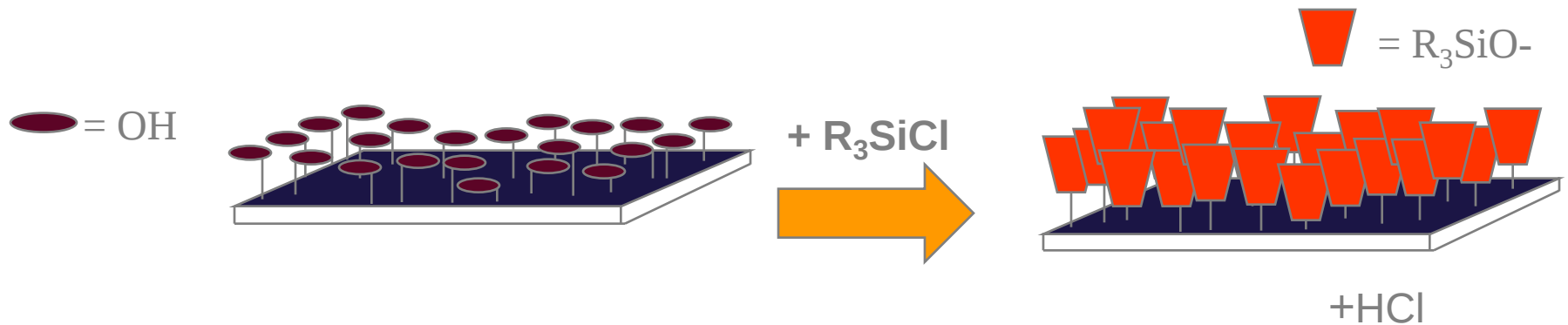
Raman Spectroscopy fixture
designed to interface with
CNM equipment



- Designed and prototyped an electrochemical test fixture for ceramic plates and a Raman Spectroscopy fixture designed to interface with CNM equipment (*met milestone*).
- Initiated evaluation of the surface coatings (natural and synthetic) on lithium metal anodes as a function of cycle number. Preliminary results and progress discussed with Robert Kostecki (LBNL) at ILIRP Diagnostics Meeting in February. (*met milestone*)

Technical accomplishments:

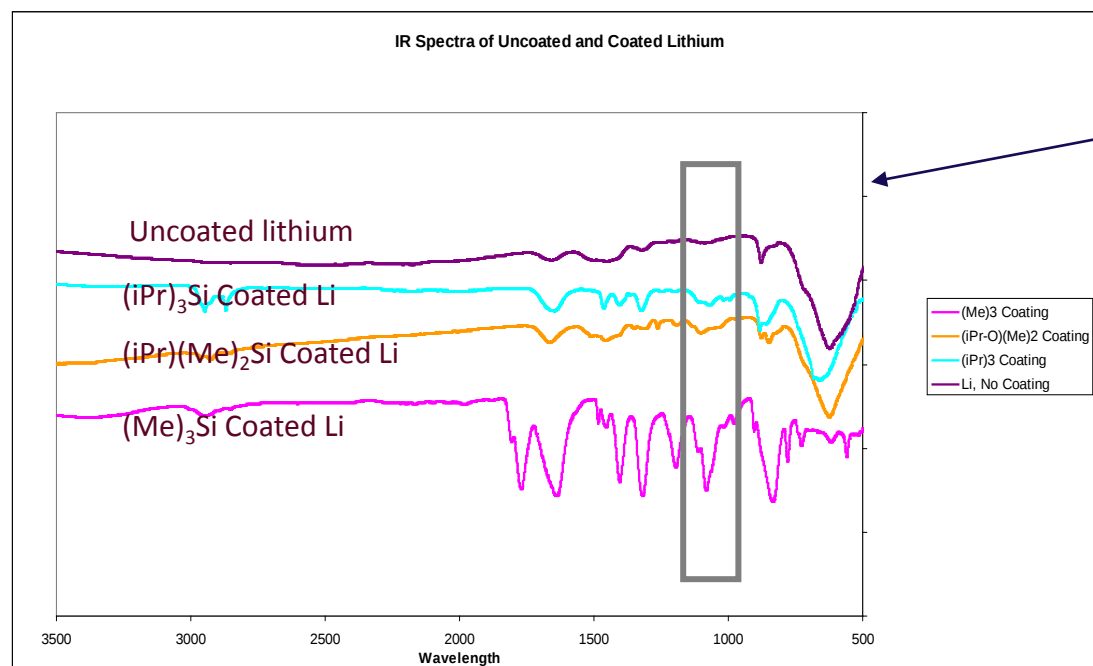
Stabilizing the lithium- liquid electrolyte interface



- We've been exploring the coatings formed by the attachment of organosilanes to the surface layer of the naturally hydroxy-terminated lithium metal.
- Previous work had shown that that the layer formed is self-terminating and stable in the electrolyte.
- We've initiated studies on a variety of R-groups (to vary surface coverage) and number of chloro-groups (to vary surface density and binding strength).

Technical accomplishments:

Stabilizing the lithium- liquid electrolyte interface



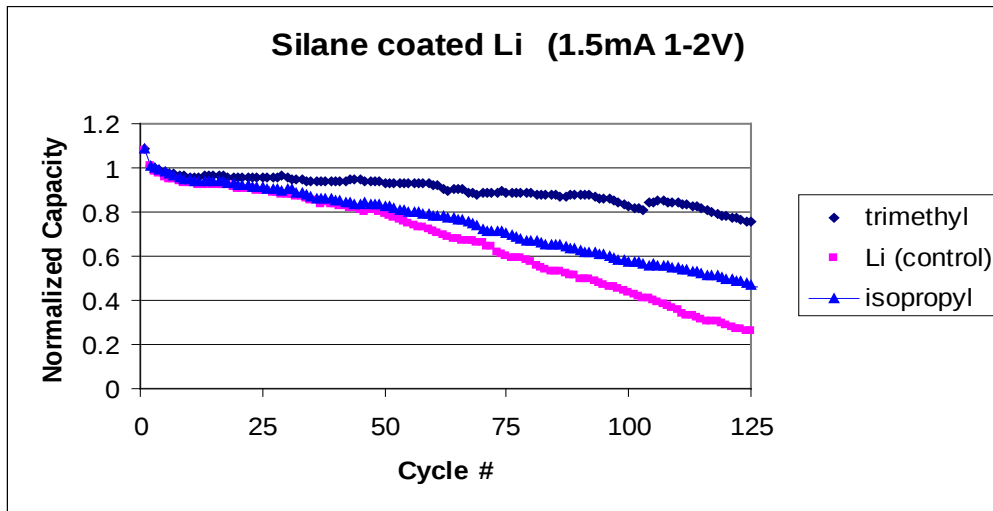
IR Region of Si-O peak
(~ 1050 cm^{-1}).

Higher peak intensity for the $(Me)_3Si$ coated sample indicates more surface coverage compared to larger $(iPr)_3Si$ samples.

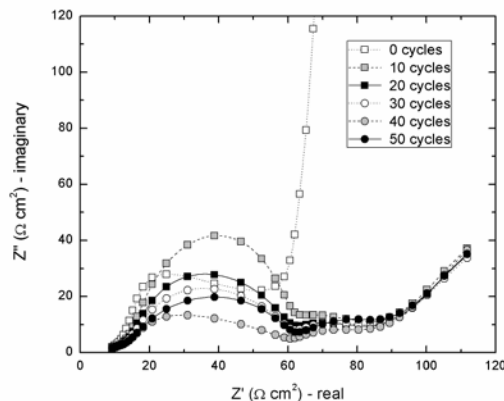
FTIR studies on coated vs uncoated Li indicated that (1) the R_3Si-O bond was formed on exposure to the chloro-organosilanes, and (2) **the size of the R-group (cone angle) has some influence on the extent of the surface reaction**

Technical accomplishments:

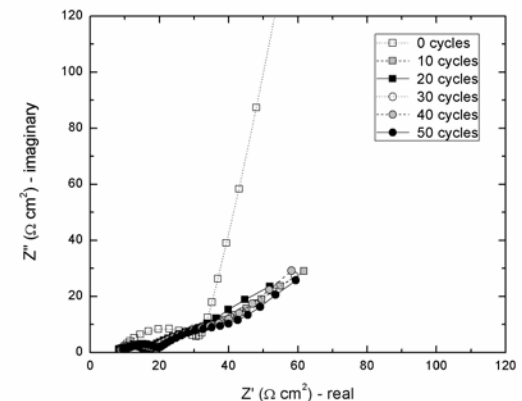
Stabilizing the lithium- liquid electrolyte interface



Coated samples have much more stable cycling (usage: 6-9% Li / cycle)



Coated samples show much lower and stable impedance on cycling. Drop in impedance on cycling associated with an increase in active surface area -formation of mossy and dendritic Li.



Uncoated Li

TMS-coated Li



Technical accomplishments:

Stabilizing the Lithium-Electrolyte Interface

Coatings appear to stabilize interface with electrolyte – denser packed coatings seem to have longer cycle life and lower impedance than uncoated controls.

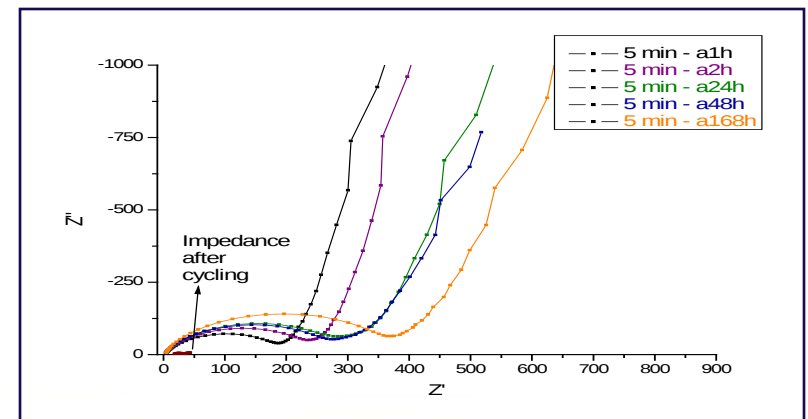
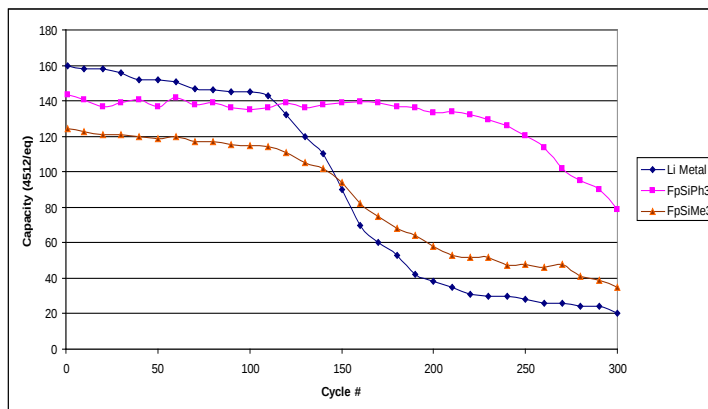
- **Coating thickness –**
 - XPS data on coated samples and related spectroscopy's gives a range between 1-5 nm on surface coating thickness.
 - Small changes in impedance on cycling indicate that, at least up to 100 cycles, only a small change in surface area is observed when compared to metallic uncoated lithium
 - Thickness of film appears to be independent of the exposure to time to the precursor and the method of application – indicating stable monolayer formation.
- **Stability –**
 - After coating sample surface was stable to vacuum indicating presence of bound Si moieties from reaction. (TMSCl, hexamethyl disiloxane dimer, HCl are all volatile).
 - Samples show enhanced visual stability to air and under nitrogen.
- **Surface Coverage -**
 - Collaboration with CEES (EFRC) researchers to use LERIX beamline at APS to determine Si/O coverage as a function of R-group size (*on-going*).



Technical accomplishments:

Interfacial Coatings to increase SEI Li-ion Conductivity

- Studied use of soluble silanes, e.g. FpSiMe_3 , as a source of Si for the SEI layer
 - $\text{Fp} = \text{Fe}(\text{Cp})(\text{CO})_2$
- Typical Reaction $\rightarrow \text{FpSiR}_3 + \sim 8 \text{ Li} \rightarrow \text{Fe(s)} + \text{Li}_x\text{Si} (+ 3 \text{ LiR} + \text{LiCp})$
- Incorporating nanoscale Si and Fe into the SEI layer increases Li-ion conductivity (via Li_{3+x}Si formation) and extends the electronic conductivity of the Li surface interface into the bottom of the SEI.** Experimentally varying the initial layer thickness (time) can be correlated with capacity fade and cell capacity.
- Bulky substituent's perform better than smaller ones; layer appears to grow with exposure to precursor. **On charging - impedance drops by an order of magnitude to levels well below uncoated Li control and remains stable on cycling.**

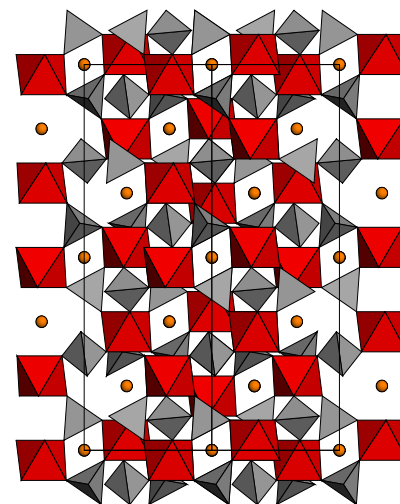
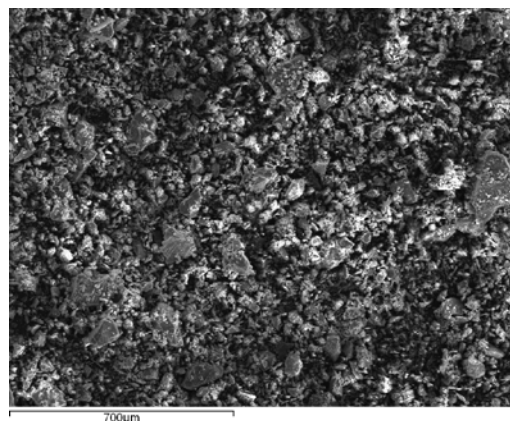


Technical accomplishments:

Low Temperature Synthesis of Lithium-Ion Conducting Ceramics

In conjunction with LBNL, we have studied and evaluated a series of lithium-ion conducting ceramics for inclusion in next generation Lithium cells.

- Initial Focus on $\text{Li}_{1+x}(\text{Ti},\text{Al})_2(\text{PO}_4)_3$ (LATP) and $(\text{Li}, \text{La})_{1-x}\text{TiO}_3$ (LLTO)
- Scaled up LATP (30% Al)
 - Ionic conductivity of sample determined by L. Zhang and J. Cabana (LBNL)
 - Assessing glass method for larger samples suggested by Marca Doeffer (LBNL)
- Determined loss of lithia at the temperature required to generate a single phase was effecting sample quality.
 - Incorporated water soluble titania source that lowered synthesis temperature by 150 °C.

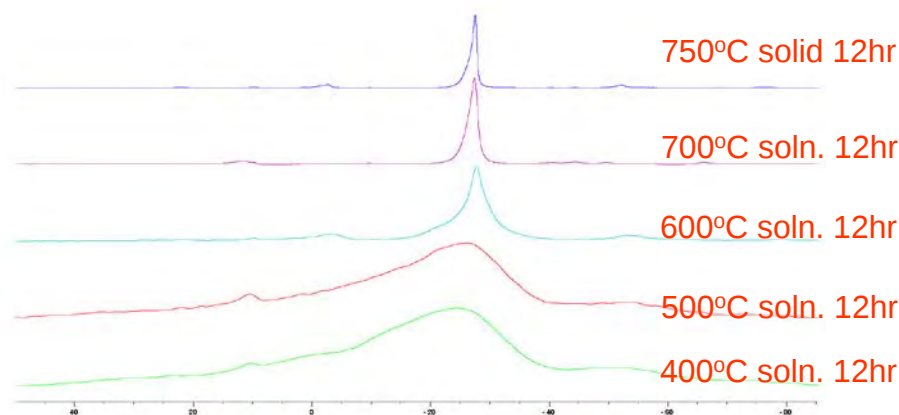


Technical accomplishments:

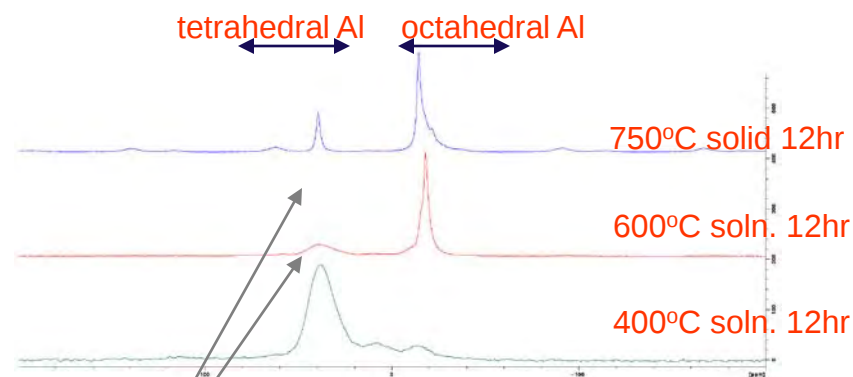
Evaluating Lithium-Ion Conducting Ceramics

- Solid State MAS NMR Studies of the formation of LATP Ceramics

^{31}P MAS NMR



^{27}Al MAS NMR



- Octahedral Al indicates substitution of Al into LATP
- Tetrahedral Al indicates presence of AlPO_4 tridymite
- Al substitution occurs into LATP between 600-400 °C to complete formation of LATP
- Phosphate ordering of LATP structure observed above 500°C. Below 500°C, P still resembles free PO_4

Technical accomplishments:

Evaluating Lithium-Ion Conducting Ceramics

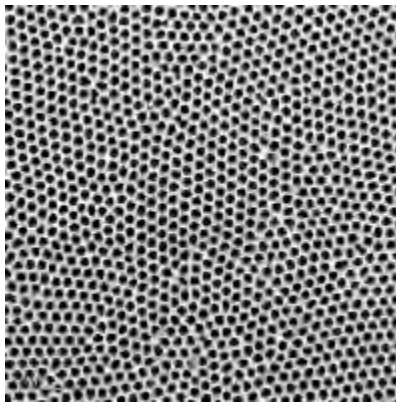
- Observations
 - Lower temperature synthesis allows us to examine the crystallization of the LATP from its constituent binaries.
 - MAS NMR indicates **after** formation of LATP (by XRD), an amorphous AlPO_4 phase still is present probably at the grain boundaries.
 - Sample is probably slightly Al deficient to the loaded composition
 - Literature studies indicate that
 - The ionic conductivity of the crystallites is not that dependant on the Li/Al substitution (Aono, Chem Rev, 1994) – GB effect.
 - Excess Al is probably in the form of a glassy AlPO_4 (Forsythe, et al, Sol St Ion 1999)
 - $\text{Ti}(\text{P}_2\text{O}_7)$, TiO_2 , and an amorphous (5-coordinate) AlPO_4 phase at GB from a Li_2O deficient synthesis do not enhance GB conductivity (Best, et al., Sol St Ion 2000).
 - **A 4-coordinate Al phase ($\sim \text{AlPO}_4$) appears at the GB in a narrow temperature window and is associated with enhanced ionic conductivity. At higher temperatures the peak sharpens (more ordered environment) and the phase is visible in XRD patterns.**



Technical accomplishments:

Evaluating Lithium-Ion Conducting Ceramics

- Progress towards ceramic plate synthesis
 - Should be able to supply ceramic plates with variable compositions to ILIRP researchers. Joint group meetings with LBNL helps define material goals.
 - With Brian Ingram (ANL) and Dave Schroeder (NIU) evaluating variables to develop a general recipe for making ceramic plates to evaluate.
 - Working with Jordi Cabana (LBNL) on CVD, PVD, and sputter coatings to evaluate buffer layer compositions.
 - In contact with OHara Corporation (Japan) and they have supplied some commercial LATP plates.
- Set up to supply LBNL with variety of porous substrates



AAO-substrate (L. Trahey – ANL)



Ceramic plate test fixture

Collaboration and Coordination with Other Institutions

Partners

- Ceramics - Baris Key, David Schroeder (NIU), Brian Ingram, Jordi Cabana (LBNL), Marca Doeff (LBNL), Tom Richardson (LBNL), Lily Zhang (LBNL)
 - Collaborating to develop lithium ion conducting ceramics, characterizational tools, and processing techniques.
- Polymers / Coatings - Susanna Neuhold (TUGraz/ANL), John Zhang, J. J. Woo, John Kerr (LBNL), C. Grogger (TUGraz)
 - Collaborating to develop new coating strategies, diagnostic techniques, and polymeric materials stable to the lithium-electrolyte interface
- Diagnostics – Chris Johnson, Wenquan Lu, Dan Abraham, Robert Kostecki (LBNL)
 - Collaborating to develop and utilize diagnostic tools that we can use to better understand the failure mechanisms and electrochemistry of lithium metal anode cells. Work closely with User Facilities around the US.
- Electrochemistry / Modeling – Dennis Dees, Gao Liu (LBNL), Venkat Srinivasan (LBNL)
 - Collaborate to develop a baseline cell and determine the variables important to extending cycle life.
- User Facilities: Russell Cook (Electron Microscopy Center), David Gosztola (Center for Nanoscale Materials, CNM), Nancy Dietz-Rago (CNM), John Muntean (CSE-NMR Center), NIU Fabrication Design Lab
- **Technology Transfer**
 - Information generated in the ILIRP program is shared with colleagues in the US Battery industry through presentations, articles, reports, and workshops.



Future Work

- Investigate the chemistry of the surface layer created on the lithium surface by silane coupling reactions and interfacial additives.
 - Collaborate with ILIRP Diagnostic and Polymer teams to study artificial SEI layers as function of depth and cycling.
 - Work with ILIRP Diagnostic and Polymer teams to evaluate stability of coatings and additives to extend cycle life. Develop diagnostic tools that help define coating limitations.
- Study the stability of ceramic lithium ion conductor in the electrochemical cell environment.
 - Work with ILIRP Ceramic and Diagnostic teams to determine how the electrolyte composition changes over time evaluate the stability of the ceramic.
 - Work with ILIRP Electrochemistry and Ceramics team to construct buffer-solid electrolyte structures and evaluate stability of the system under various cycling routines to enhance performance.
 - Collaborate with ILIRP Ceramics and Diagnostics teams to investigate the interactions between buffer layer and ceramic layer that cause long term capacity fade.
- Help define and characterize a baseline system for modeling effort



Summary

- **The objective of these studies is to identify materials, factors, and system variables that limit the commercialization of lithium-metal based electrochemical cells in conjunction with LBNL scientists and engineers.**
- We have initiated a multi-pronged approach to evaluating highly conductive solid state Li-ion conductors with the ceramic materials group at LBNL that includes regularly scheduled joint group meetings and joint projects.
 - We have identified several synthetic variables that contribute to achieving high conductivity LATP and developed a new low temperature synthetic process.
 - We have examined the relationship between Al-doping, GB phase separation, and performance to better focus the processing variables.
- We have started evaluating the stability and electrochemical properties of conformal silane coatings.
 - We've identified and studied the coupling reaction of an organosilane to the surface of lithium metal and characterized its thickness, stability, and impact on cycling.
 - A joint program with LBNL studying siloxane and PEO-derived coatings has been initiated.
- Several diagnostic tools to help in materials design and characterization have been developed including a ceramic plate test fixture, a Raman Spectroscopy cell, an in-situ Raman cell (Kostecki), and an in-situ IR cell (Kostecki).

