Integrated Lab/Industry Research Project

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Chemical Sciences and Engineering Division
Argonne National Laboratory

DOE Vehicle Technologies Program Annual Merit Review
Washington, D.C.
May 14-18, 2012

Project ID:
ES155

This presentation does not contain any proprietary or confidential information.

Overview

Timeline

- Start date: August, 2010
- End date: September, 2014
- Percent complete:
  - 33% complete

Budget

- Total project funding
  - 100% DOE
- FY12: $1000K

Barriers

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

Partners

- Jordi Cabana, Marca Doeff, Tom Richardson, R. Kostecki, G. Liu, John Kerr (LBNL)
- NIU Fabrication Design Lab
- Jun Lu (UU/ANL), University of Utah Metallurgical Engineering Dept.
- Collaborations
  - Russell Cook (Electron Microscopy Center)
  - John Muntean (CSE-NMR Center)
  - APS Beamline 11-BM – High resolution powder X-Ray diffraction.

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:

- Identify and study 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.
- Develop diagnostic techniques to track phase formation and identify synthetic variables that are limiting commercialization.
- 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 2012

- Demonstrate feasibility of making and evaluating dense LATP sintered plates *(12/11 – refocused effort on LLZ).*
- Determine feasibility of using porous AAO supports combined with glassy or ceramic lithium-ion conducting phases in a lithium-based battery *(04/12 – thickness required for diagnostic test cell does not have required stability; initiated studies of more durable porous substrates).*

September 2012

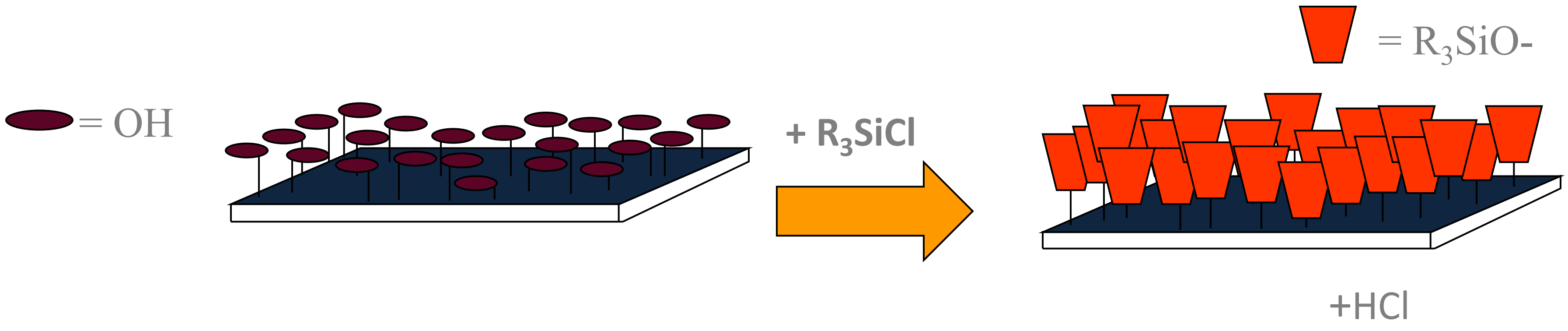
- Develop techniques to better understand silane organic coating layers to stabilize the surface of a lithium metal electrode. Evaluate effect of coating materials on cycling efficiency and cycle life.
- Develop spectroscopic techniques to help ANL and LBNL ceramics groups better understand the formation processes of ceramic membranes – from material formation to sintered plate or supported glass electrolyte.
- Identify and apply coating layers to stabilize the side of the sintered plate that is in contact with lithium metal. Evaluate effect of coating materials on cycling and cycle life.

Approach/Strategy

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

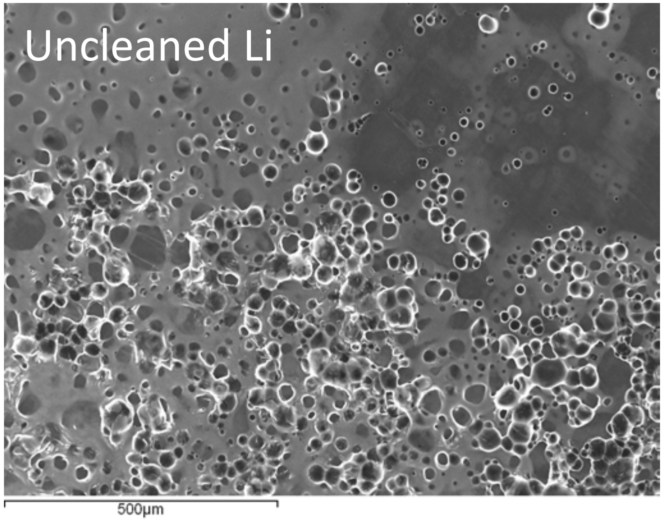
- Establish a stable, dense, and uniform lithium/electrolyte interface exhibiting good electrochemical performance.
    - Develop and characterize organic coatings that are ionically conducting and stable to lithium metal potentials.
    - Study and analyze the failure mechanism of various Li-metal electrode coatings. Develop and characterize conformal stable monolayer coatings.
- Develop models and spectroscopic tools to better understand the lithium metal /electrolyte and lithium metal / ceramic interfaces.
    - Electrode surface and bulk analysis
    - Systems modeling
- 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.

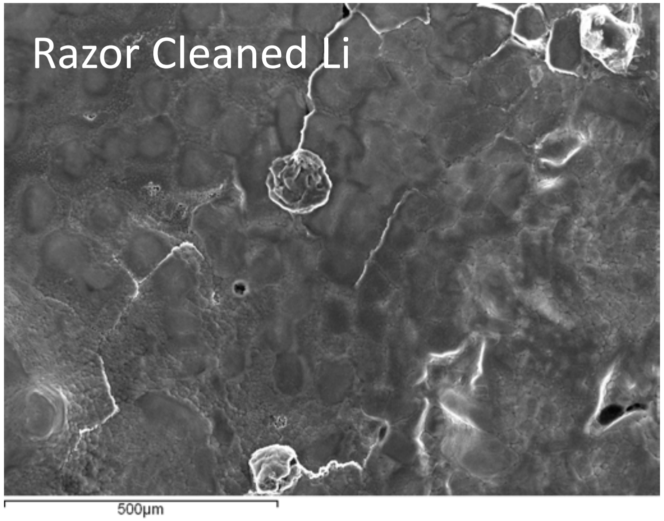
Technical accomplishments:
Stabilizing the lithium- liquid electrolyte interface

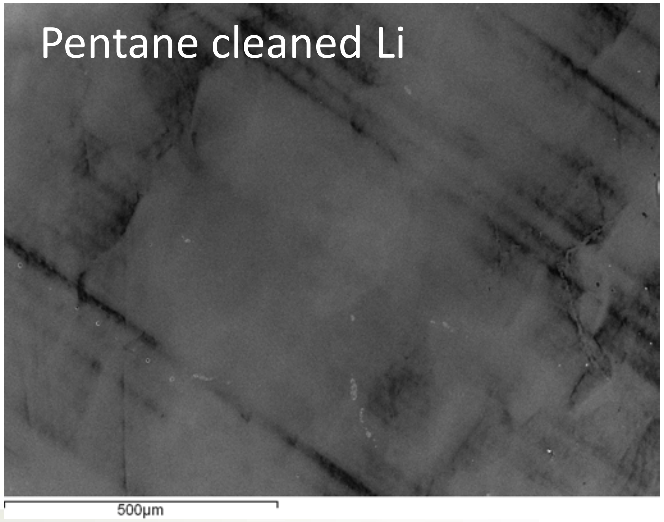


- We've been exploring the coatings formed by the attachment of organosilanes to the surface layer of the naturally hydroxy-terminated lithium metal.
- Previous we've shown that that the layer formed is self-terminating and stable in the electrolyte, and close to a monolayer in thickness.
- Synthetic and electrochemical studies on a variety of R-groups (to vary surface coverage) indicated a second protective mechanism.

Technical accomplishments:
Stabilizing the lithium- liquid electrolyte interface



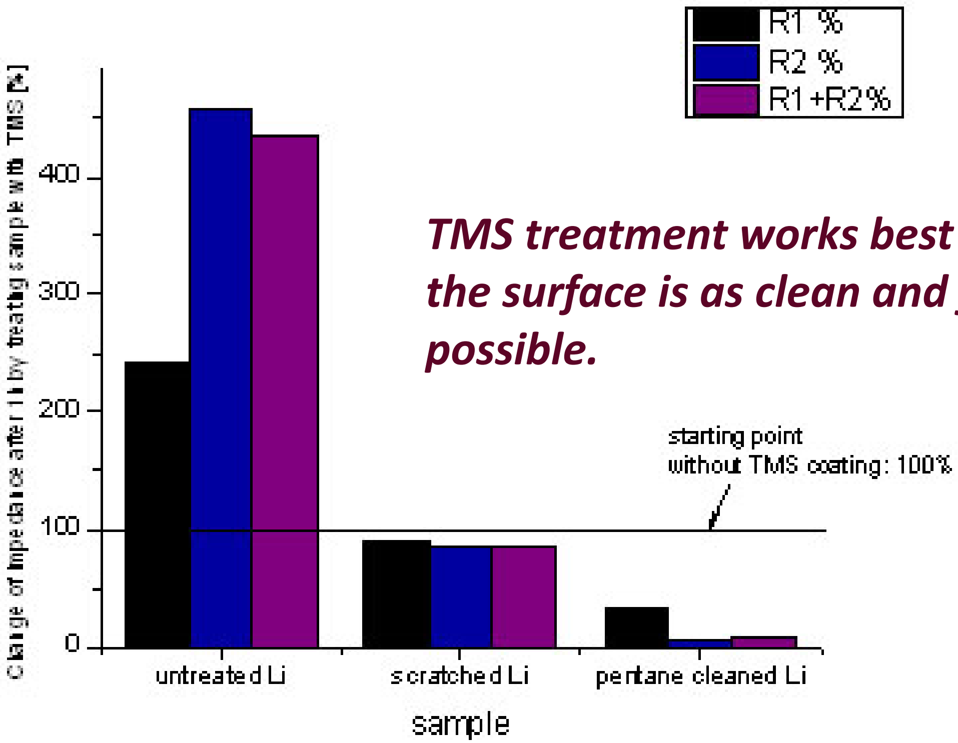




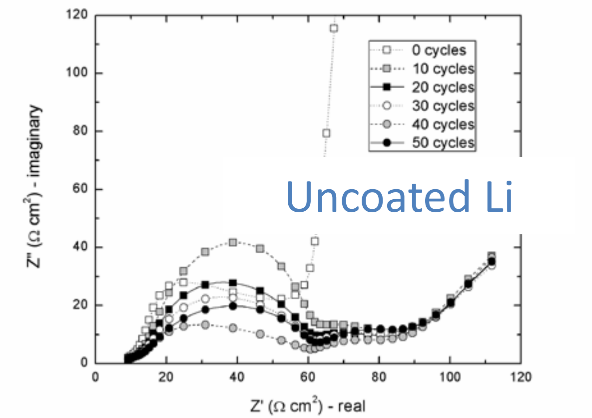
Cleaning the lithium surface: Surface was prepped three different ways, coated with trimethylsilane, then exposed for 45 min to commercial battery electrolyte (1.2M $LiPF_6$, EC/EMC).

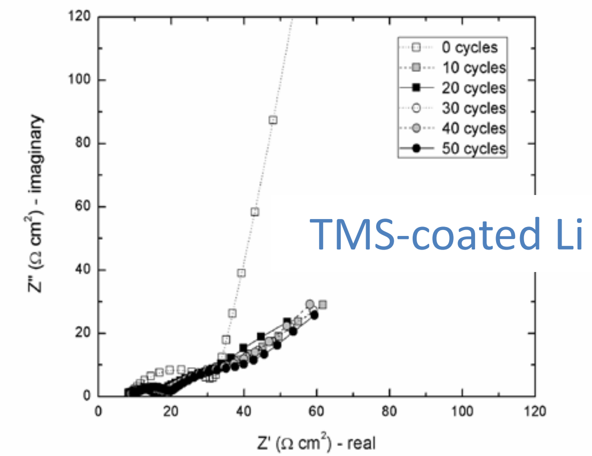
- **Proper cleaning dramatically increases effectiveness of protective coating**

Technical accomplishments:
Stabilizing the lithium- liquid electrolyte interface



TMS treatment works best when the surface is as clean and flat as possible.





Relative changes in impedance for lithium foil treated three different ways. Sample Preparation: Clean sample (as described), TMS-coat samples, Wait 1 hr, EIS measurement.

Technical accomplishments:
Stabilizing the Lithium-Electrolyte Interface

XPS Characterization of Silane Coatings

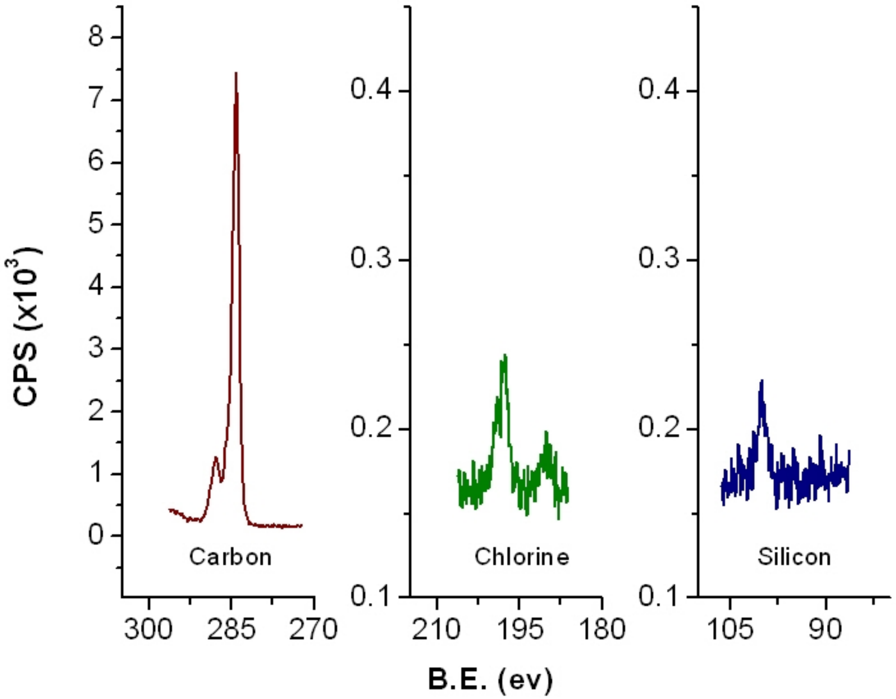
•After coating samples were placed under vacuum (10^{-9} torr), which should also remove volatiles.

• Samples all showed thin surface layers on top of the sample most likely from incomplete cleaning

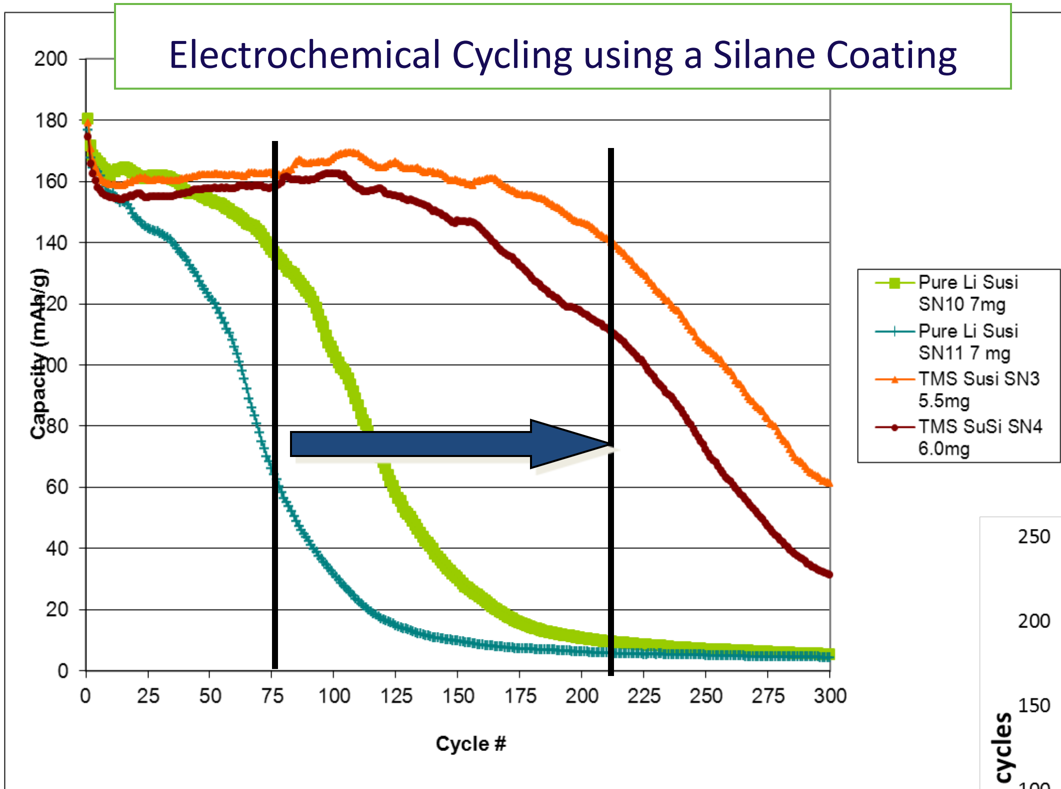
• Si signal was small but always present in coated samples, absent in uncoated samples.

• Collaborating with Kostecki Group at LBNL to use ellipsometry to characterize the silane layer.

Combination of signal strength and coating characteristics puts coating Si thickness below 1 nm

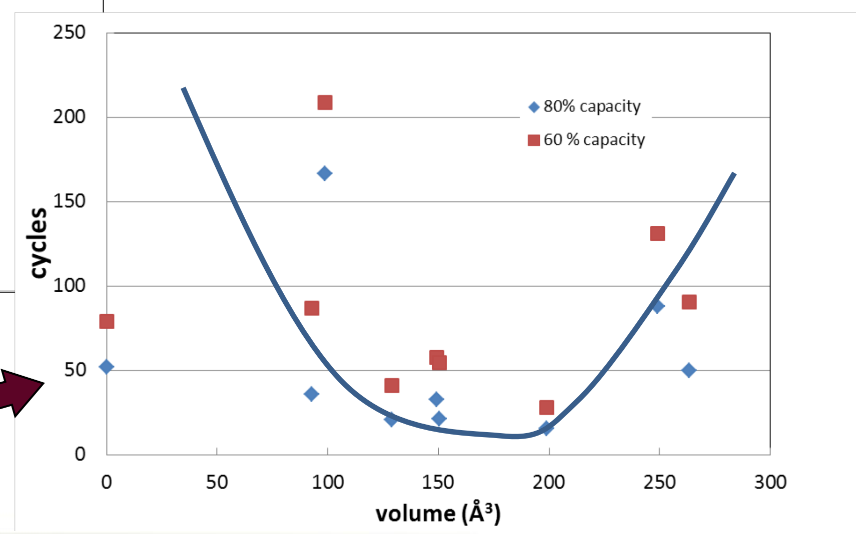


Technical accomplishments:
Stabilizing the lithium- liquid electrolyte interface



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

Test cell uses $Li_4Ti_5O_{12}$ as the counter electrode.

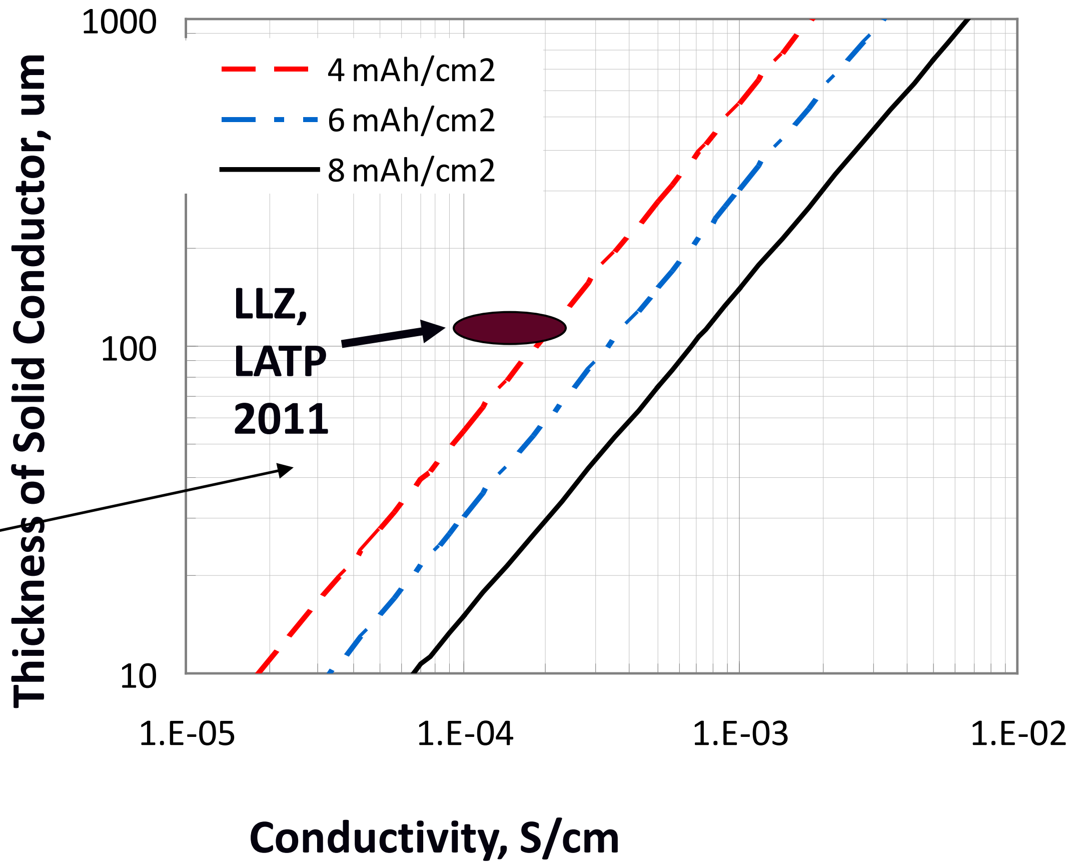


Small R-groups inhibit solvent attack via packing density whereas larger R-groups may offer more steric hindrance.

Model Performance - Thin Film Ceramic Electrolytes

- Consumer electronics batteries - 4 mAh/cm^2,
- PHEVs - 2 mAh/cm^2.
- Successful Li-air and Li-S research could reach > 8 mAh/cm^2.

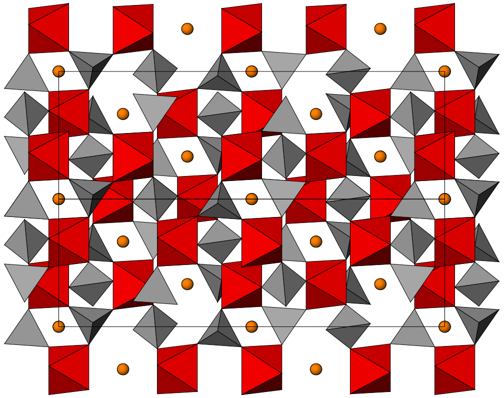
Oval approximates reported bulk values for the two most common solid electrolytes

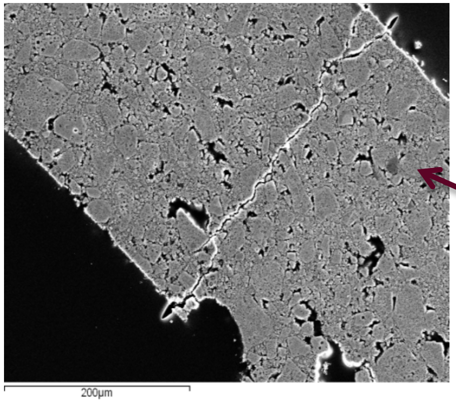


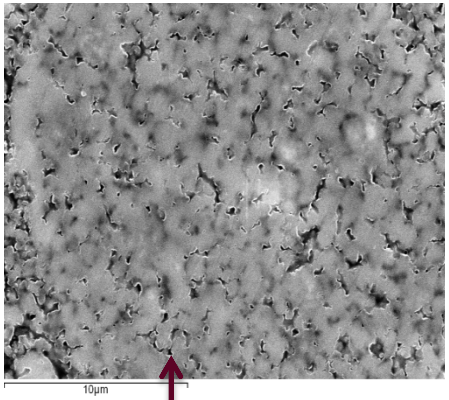
Modeling indicates two strategies to reach PHEV goals: 1) develop thin film approach to solid electrolytes, 2) identify higher conductivity materials.

Technical accomplishments:
Low Temperature Synthesis of Lithium-Ion Conducting Ceramics

- $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ (LATP) was our starting point for ceramic Li-ion conductors
  - commercial interest
  - commercial availability
  - high RT conductivity
- Synthesis & Characterization
  - solid state and aqueous synthetic routes developed
  - combined low temperature synthetic process with advanced characterization to better understand a high temperature de-sintering process
  - identified a new phase transition around 650 C related to Li/Al cation ordering





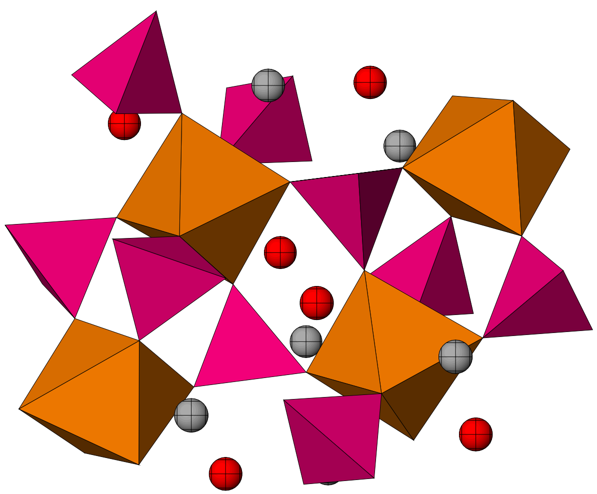


Desintering observed at temperatures necessary for densification locally

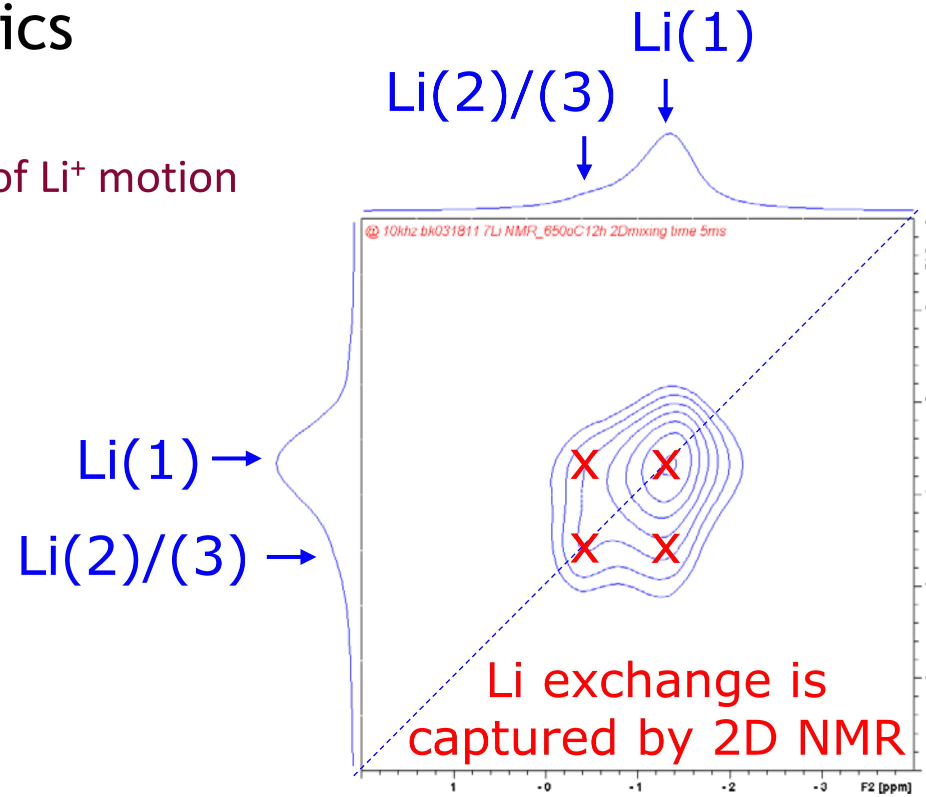
Technical accomplishments:

Lithium-Ion Conducting Ceramics

- ^{7}Li MAS NMR – Evidence and analysis of Li^+ motion
- All of the Li is in the LATP structure



LATP – Lithium Coordination (Red = Li2, Gray = Li1)



Calculated lithium diffusion between crystallographic sites is close to the values reported by other methods - D_{Li} = 7x10^{-3} S/cm

Technical accomplishments:

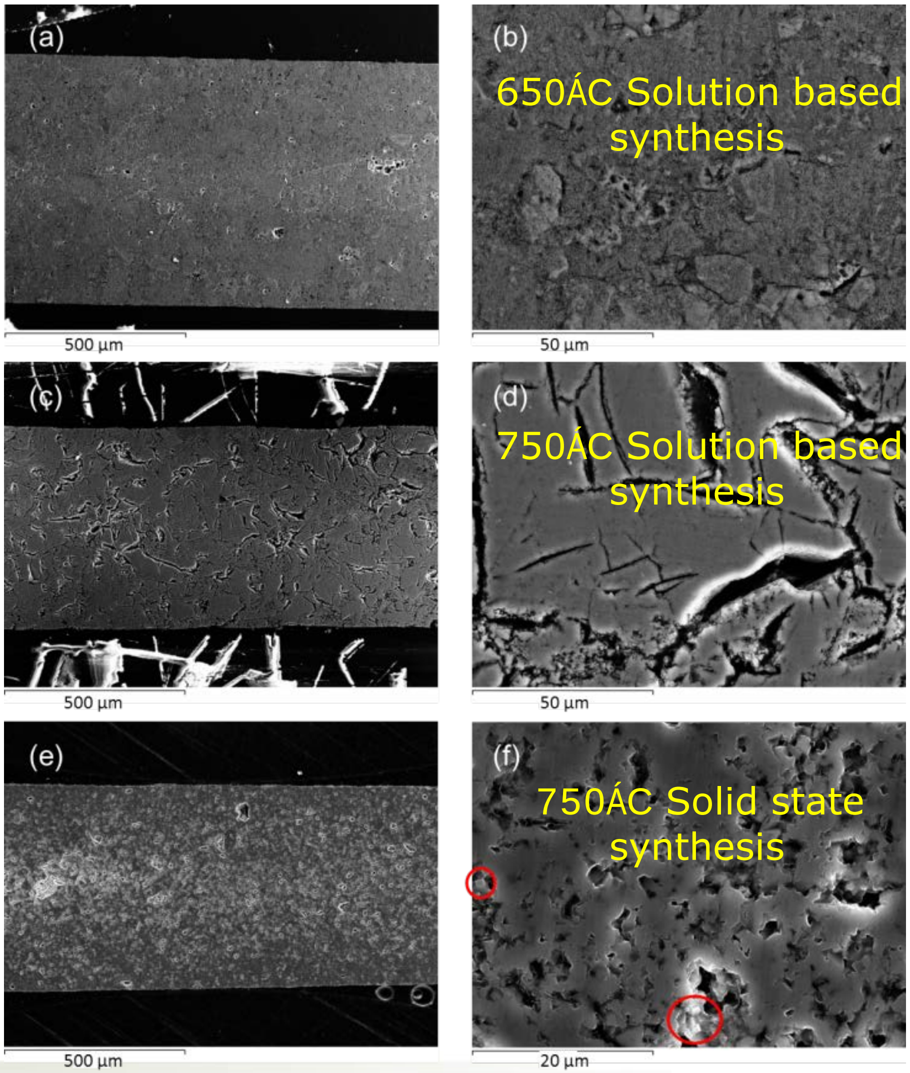
Lithium-Ion Conducting Ceramics: Synthesis & Sinterability

$Li_{1.3}Al_{0.29}Ti_{1.7}(PO_4)_{2.99}$ +
0.01 $AlPO_4$ (amorphous)

Sinterability and ionic conductivity are directly correlated with the composition (Al content analyzed by ^{27}Al MAS NMR)

$Li_{1.3}Al_{0.225}Ti_{1.7}(PO_4)_{2.925}$ +
0.075 $AlPO_4$ (amorphous)

$Li_{1.3-y}Al_{0.2}Ti_{1.7-z}(PO_4)_{2.9-2z}$ +
0.1 $AlPO_4$ + TiP_2O_7 + TiO_2



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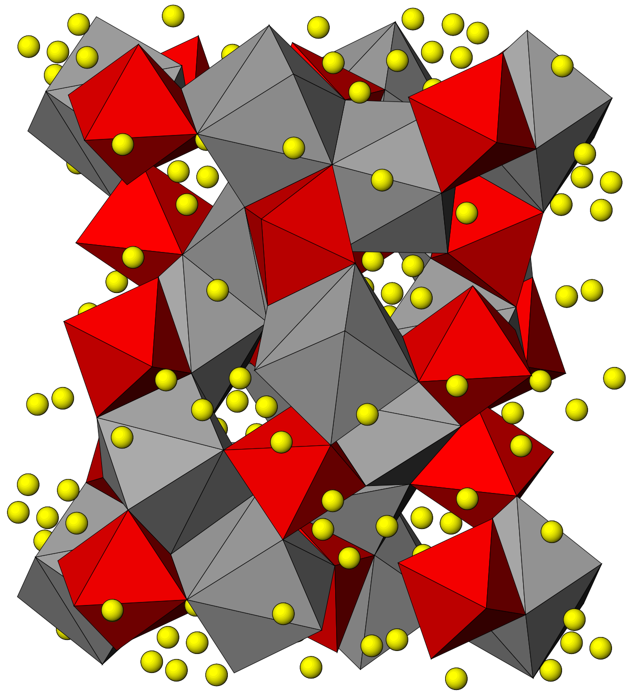
Technical accomplishments:
Evaluating Lithium-Ion Conducting Ceramics

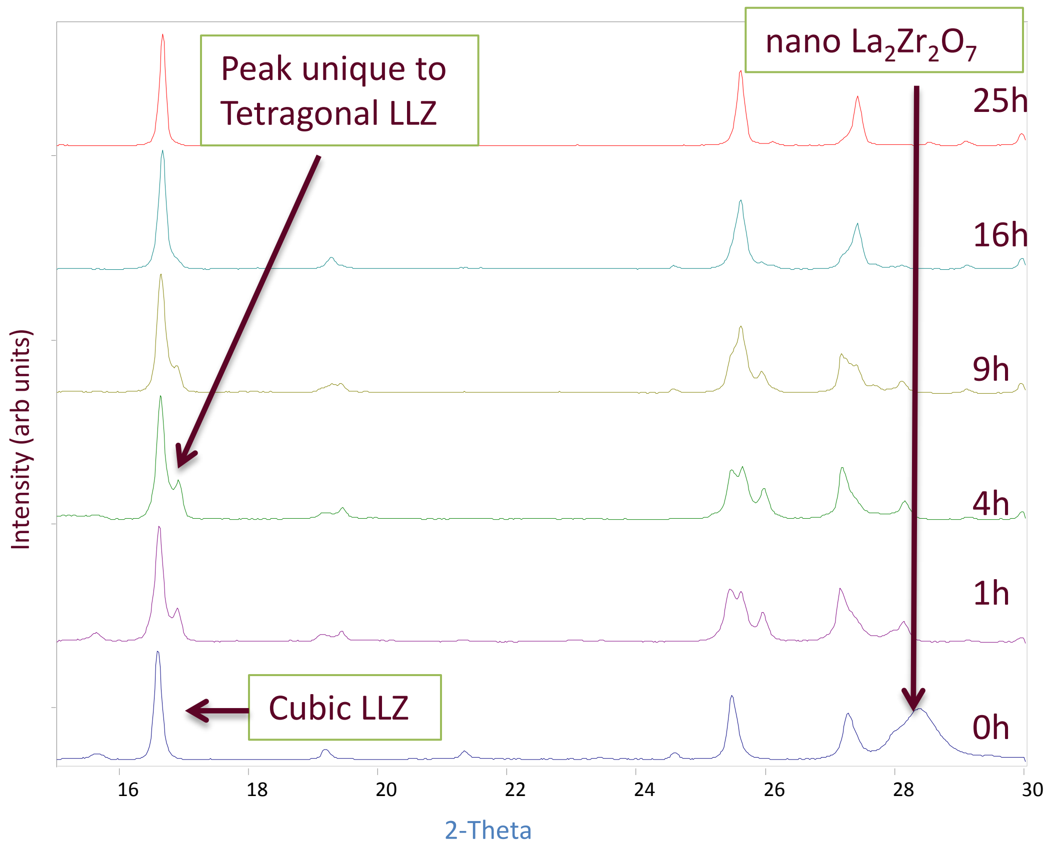
$Li_7La_3Zr_2O_{12}$ (LLZ)

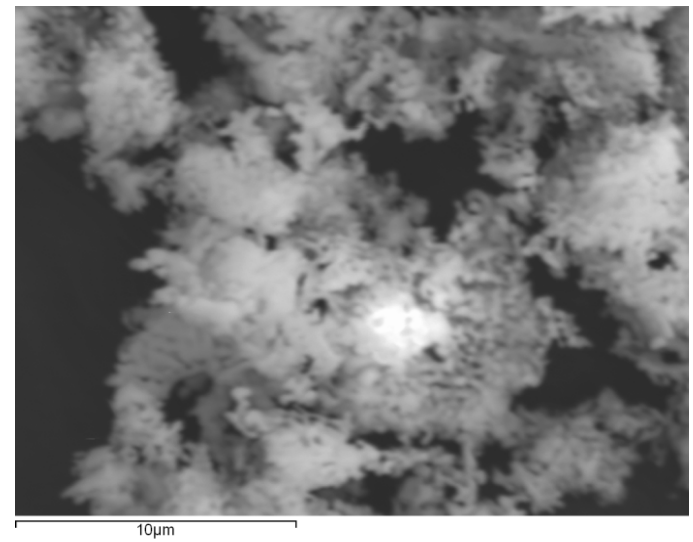
- Garnet $Li_7La_3Zr_2O_{12}$ (LLZ) exhibits high Li-ion conductivity (σ_{TOT} = 5x10^{-4} S cm^{-1} at 25°C) and good stability in contact with Li metal
- LLZ has 2 symmetries: tetragonal and cubic
  - Long sintering >1200°C reported for forming cubic phase
  - Tetragonal phase has lower conductivity
- Recently it has been reported that addition of Al_2O_3 to LLZ stabilizes the cubic phase at lower temperature
  - Possibly acts to relieve strain
  - Suppresses the formation of $La_2Zr_2O_7$

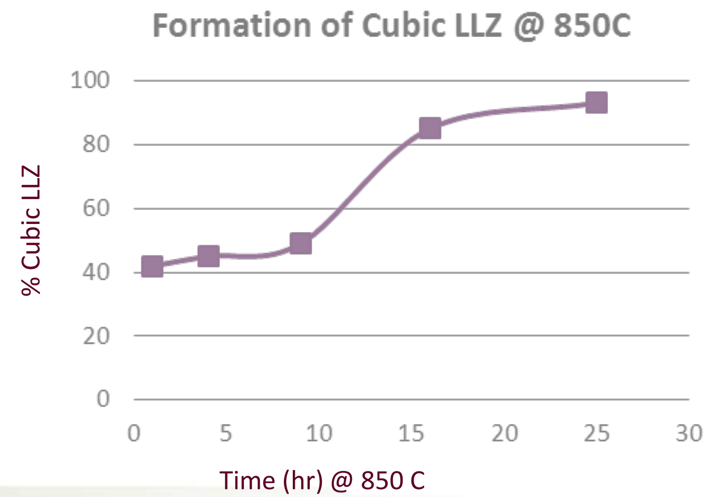


Red – $[ZrO_6]$ octahedron,
Gray - $[LaO_8]$ polyhedron,
Yellow – lithium cations.

Technical accomplishments:
Evaluating Lithium-Ion Conducting Ceramics





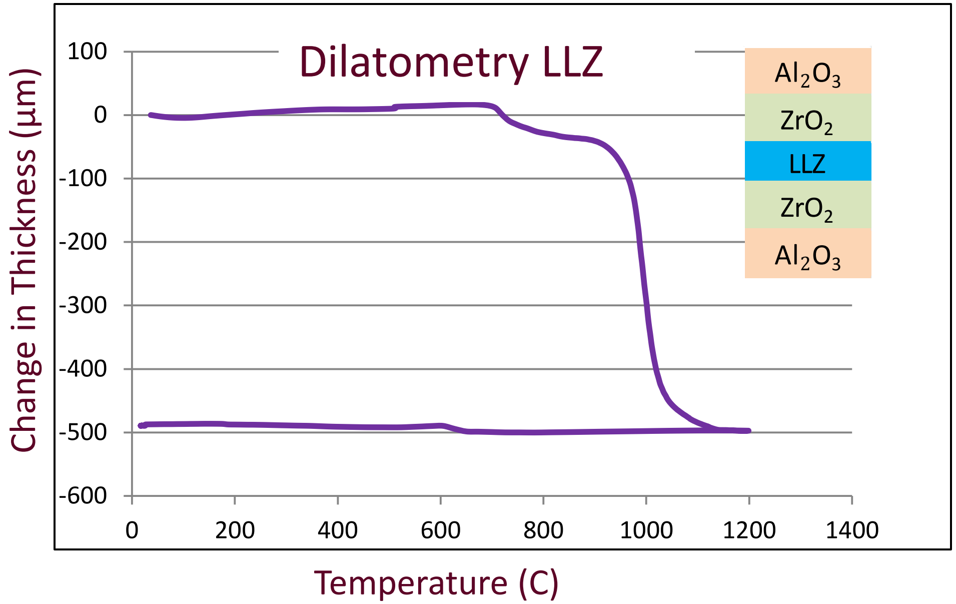


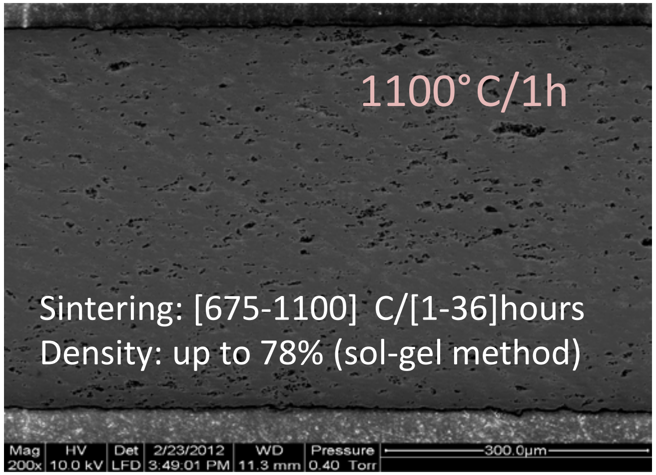
Sample Precursors preheated at 700 C for 12h;

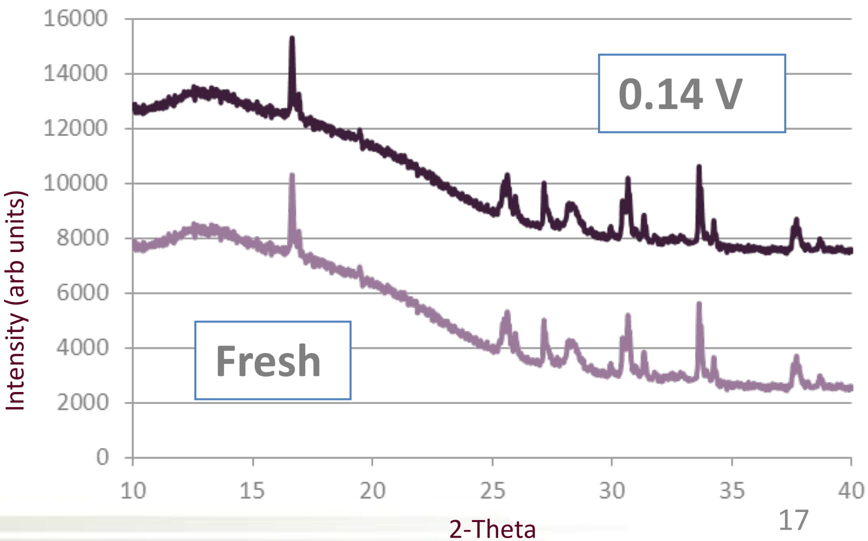
Formation Reaction @850°C:

$La_2Zr_2O_7 + Li_2O \rightarrow$ LLZ-tetr ($+Al_2O_3$) $\rightarrow$ LLZ-cubic

Technical accomplishments:
Evaluating Lithium-Ion Conducting Ceramics







Effect of low voltage: Laminates were made using 50% LLZ (tetr) and equilibrated in a coin cell at 0.14V. **No significant structural changes were observed compared to the starting material.**

Collaboration and Coordination with Other Institutions

Partners

- Ceramics
  - Collaborating to develop lithium ion conducting ceramics, characterization tools, and processing techniques.
- Polymers / Coatings
  - Collaborating to develop new coating strategies, diagnostic techniques, and polymeric materials stable to the lithium-electrolyte interface
- Diagnostics
  - 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
  - Develop a baseline cell and determine the variables important to extending cycle life.
- Companies – discussions with several companies on coatings and protective strategies.

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.
- Study the stability of ceramic lithium ion conductor in the electrochemical cell environment.
  - Work with ILIRP Ceramic and Diagnostic teams to determine how the LLZ solid electrolyte composition changes over time in a lithium metal cell configuration.
  - Collaborate with ILIRP Ceramics and Diagnostics teams to investigate the interactions between buffer layer and ceramic layer that cause long term capacity fade.
  - Utilize solid state NMR to quantify the role of aluminum in stabilizing the cubic form of LLZ.
- Models/Baseline
  - Build a model of a Li_3N buffer layer in contact with a solid electrolyte.
  - Utilize thin film synthetic techniques to make model cells for evaluation.

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 are using a multi-pronged approach to evaluate 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 completed a combined synthesis, characterization, and sintering study of LATP and identified several factors that control sintered plate porosity. Materials to LBNL.
  - We have extended our methodologies to the promising material $Li_7La_3Zr_2O_{12}$ (LLZ) and have initiated sintering studies and supplied materials to LBNL.
- We have started evaluating the stability and electrochemical properties of conformal silane coatings.
  - The connection between surface preparation and cycling stability has been identified.
  - The coupling reaction of an organosilane to the surface of lithium metal has been characterized in terms of thickness, stability, and impact on cycling.
  - A second mechanism of performance enhancement has been identified with larger alkyl-groups.
  - An ellipsometry study with LBNL was initiated (2011).
- A new modeling effort has started (Oct 2011) and identified the several synthetic goals for the ceramics effort.