Composite Electrolyte to Stabilize Metallic Lithium Anodes
(Integrated Laboratory Industry Research Program)

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“This presentation does not contain any proprietary, confidential, or otherwise restricted information”
Overview

- **Timeline**
  - Start October, 2011

- **Technical barriers**
  - Energy density (500-700 Wh/kg)
  - Cycle life, 3000 to 5000 deep discharge cycles
  - Safety

- **Budget**
  - $300k FY12

- **Partners**
  - Oak Ridge National Laboratory (lead)
  - Center for Nanophase Materials Sciences, ORNL
  - University of Tennessee
  - SHaRE user facility, ORNL
  - Companies and collaborators for electrolyte materials
Objectives and relevance

Lithium anodes must be completely isolated from the electrolyte to prevent dendrites, side reactions and to stabilize the structure. Composites of multiple electrolytes may provide the needed combination of properties.

- **Objectives:**
  - Understand Li$^+$ transport at interface between two dissimilar solid electrolytes, e.g. ceramic/polymer
  - Develop composites of electrolyte materials with requisite electrochemical and mechanical properties
  - Fabricate thin membranes to provide good power performance and long cycle life

- **Relevance:**
  - Enables implementation of Li metal anodes for high energy density chemistries (e.g. Li-air, Li-S)
  - USABC has targeted a 5X improvement in energy density
## Milestones

<table>
<thead>
<tr>
<th>Milestones</th>
<th>Target:</th>
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<tbody>
<tr>
<td>1. A composite electrolyte membrane &lt;1mm thick where the internal interfaces do not significantly impede the Li ion transport.</td>
<td>October 2012</td>
</tr>
<tr>
<td>2. Simulation to estimate the ion conduction of an optimized composite structure.</td>
<td>October 2012</td>
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<tr>
<td>3. Evaluate composite membrane with a lithium metal electrode for cycling stability and dc transport properties.</td>
<td>October 2012</td>
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Approach

1. Develop methodologies to characterize both electrochemical and mechanical properties including impedance spectroscopy and nanoindentation of thin films.

2. Characterize barriers to charge transport in laminated electrolyte structures, e.g. interfacial resistances, poor adhesion.

3. Demonstrate improved properties in composite electrolyte.

4. Simulate the optimal composite design.

5. Fabricate optimized, thin composite membranes with a lithium metal electrode to evaluate cycling stability and DC transport properties.
Approach- Many electrolyte materials have been evaluated.

<table>
<thead>
<tr>
<th>Polymer Electrolytes</th>
<th>Notable Features</th>
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<tbody>
<tr>
<td><strong>PEO&lt;sub&gt;10&lt;/sub&gt;:LiTFSI</strong></td>
<td>• High conductivity (( \sigma_{25^\circ C} = 2 \times 10^{-6} \text{ S cm}^{-1} ))</td>
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<tr>
<td><strong>PEO&lt;sub&gt;16&lt;/sub&gt;:LiCF&lt;sub&gt;3&lt;/sub&gt;SO&lt;sub&gt;3&lt;/sub&gt;</strong></td>
<td>• T&lt;sub&gt;melt&lt;/sub&gt; ( \approx 35 \degree \text{C} )</td>
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<tr>
<td><strong>PEO&lt;sub&gt;6&lt;/sub&gt;:LiAsF&lt;sub&gt;6&lt;/sub&gt;</strong></td>
<td>• Slower crystallization kinetics</td>
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<td>- Sample from P. Bruce at University of St. Andrews (Scotland)</td>
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<table>
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<tr>
<th>Ceramic and Glass Electrolytes</th>
<th>• Lower conductivity than PEO&lt;sub&gt;10&lt;/sub&gt;:LiTFSI</th>
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<tbody>
<tr>
<td>Lithium phosphate oxynitride (Lipon)</td>
<td>• Faster crystallization kinetics</td>
</tr>
<tr>
<td><strong>Li&lt;sub&gt;1.3&lt;/sub&gt;Ti&lt;sub&gt;1.7&lt;/sub&gt;Al&lt;sub&gt;0.3&lt;/sub&gt;(PO&lt;sub&gt;4&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;</strong> (LTAP)</td>
<td>• 100% crystalline</td>
</tr>
<tr>
<td>Sample from nGimat</td>
<td>• Crystalline phase is conductive</td>
</tr>
<tr>
<td><strong>Ohara Nasicon-type</strong> (protected composition; crystal structure is similar to LTAP’s)</td>
<td>• Unity transference number</td>
</tr>
<tr>
<td></td>
<td>• Fabricated as thin film</td>
</tr>
<tr>
<td></td>
<td>• Chemically compatible with Li</td>
</tr>
<tr>
<td></td>
<td>• High conductivity</td>
</tr>
<tr>
<td></td>
<td>• Chemically incompatible with Li</td>
</tr>
<tr>
<td></td>
<td>• Commercially available</td>
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</table>
Ionic conductivity is measured by impedance spectroscopy with blocking electrodes.

Characteristic time scales of $\text{PEO}_{10}:\text{LiTFSI}$ and $\text{PEO}_{16}:\text{LiCF}_3\text{SO}_3$ are very different → enables a useful comparison of the interfacial impedances with Ohara ceramic.
Conductivities of individual phases vary over several orders of magnitude

Melting Temperatures
PEO_{10}:LiTFSI = 35 °C
PEO_{16}:LiCF_{3}SO_{3} = 60 °C

Controlling reproducibility of polymer electrolytes is a challenge → error bars.
Using laminated bilayer samples to characterize interfacial resistances between two dissimilar solid electrolytes

Laminated structures provided a well-defined interfacial area which enables quantitative characterization of interfacial impedances.

Previous results from similar systems show that interfacial impedance is dominant.

The interfacial resistance must be minimized for conductivity enhancements in polymer–ceramic composites.
Interfacial resistance is not observed in bilayers of Ohara glass ceramic and PEO$_{16}$:LiCF$_3$SO$_3$

Here, the experimental impedance of the bilayer is compared with that predicted from the individual materials in series.

Double layer capacitances of the blocking electrodes at low frequencies were not modeled in the predicted spectra above.
Interfacial Impedance in Ohara\PEO_{16}:LiCF_3SO_3

Unlike previous studies, the interfacial resistance between Ohara and PEO_{16}:LiCF_3SO_3 is small and not statistically different from zero for most temperatures.

\[
R_{\text{interface}} = R_{\text{composite}, \text{exp}} - \left( R_{\text{Ohara}} + R_{\text{polymer}} \right)_{\text{predicted}}
\]

Interfacial resistance is dominant at all temperatures.

\[
R_{\text{interface}} > R_{\text{Lipon}} + R_{\text{polymer}}
\]

Approach: Novel nanoindentation technique is used to characterize the mechanical properties of electrolytes

- Enables the direct observation of the nanoindentation process
- Allows the measurement of air/moisture sensitive materials, e.g. polymer electrolytes, lithium, etc.

Nanoindentation was done in conjunction with our collaborators at the University of Tennessee, George Pharr and Erik Herbert.
Initial nanoindentation characterizations were performed on crystalline PEO samples from Peter Bruce (PEO$_6$:LiAsF$_6$)

<table>
<thead>
<tr>
<th>ID</th>
<th>Composition</th>
<th>Average Elastic Modulus, E (GPa)</th>
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<tbody>
<tr>
<td>A</td>
<td>PEO$_6$:LiAsF$_6$</td>
<td>0.96</td>
</tr>
<tr>
<td>B</td>
<td>PEO$_6$:(95% LiAsF$_6$-5% LiTFSI)</td>
<td>1.5</td>
</tr>
</tbody>
</table>
Future Work

- Continue characterizing interfacial impedances between polymers and newly developed ceramic electrolytes through partnerships
- Fabricate polymer composite electrolytes with particulate phase composed of conductive ceramics
  - Characterize transport and mechanical properties
- Develop models to elucidate composite architectures with optimal properties
- Electrochemical and DC transport measurements for composite electrolytes with Li electrodes

Collaborations

- Ceramic electrolytes supplied by: Ohara Corp. and nGimat
- Lab samples of ceramic electrolytes from: Jeff Sakamoto (Michigan State University)
- Lab samples of polymers from: Peter Bruce (University of St. Andrews, Scotland)
Summary

- **Relevance:** Polymer composite electrolytes with Li\(^+\)-conductive ceramic fillers will enable the implementation of Li metal anodes for high energy density cells.

- **Approach**
  - A variety of polymeric and inorganic solid electrolytes are characterized
  - A unique nanoindentation technique is used to characterize the mechanical properties of air and moisture sensitive materials
  - Simplified bilayer studies are performed to quantify interfacial resistances between two solid electrolytes

- **Accomplishments and progress**
  - Showed that crystalline PEO has a relatively high elastic modulus (around 1 GPa), which is several orders of magnitude higher than conventional amorphous polymer electrolytes
  - Demonstrated negligible interfacial impedance across planar interfaces of Ohara (ceramic) and PEO-based electrolytes

- **Future work**
  - Develop polymer composites with both phases conducting Li cations, characterize electrical and mechanical properties. Develop models to reveal optimal architectures.
  - Characterize stability and cycleability of polymer nanocomposites with Li metal electrodes