Composite Electrolyte to Stabilize Metallic Lithium Anodes

(Integrated Laboratory Industry Research Program)

Project ID: ES157

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Vehicle Technologies Program Annual Merit
Review and Peer Evaluation Meeting

May 2012

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

Milestones:	**Target:**
1. A composite electrolyte membrane <1mm thick where the internal interfaces do not significantly impede the Li ion transport.	October 2012
2. Simulation to estimate the ion conduction of an optimized composite structure.	October 2012
3. Evaluate composite membrane with a lithium metal electrode for cycling stability and dc transport properties.	October 2012

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**

Individual electrolytes

Bilayer composites

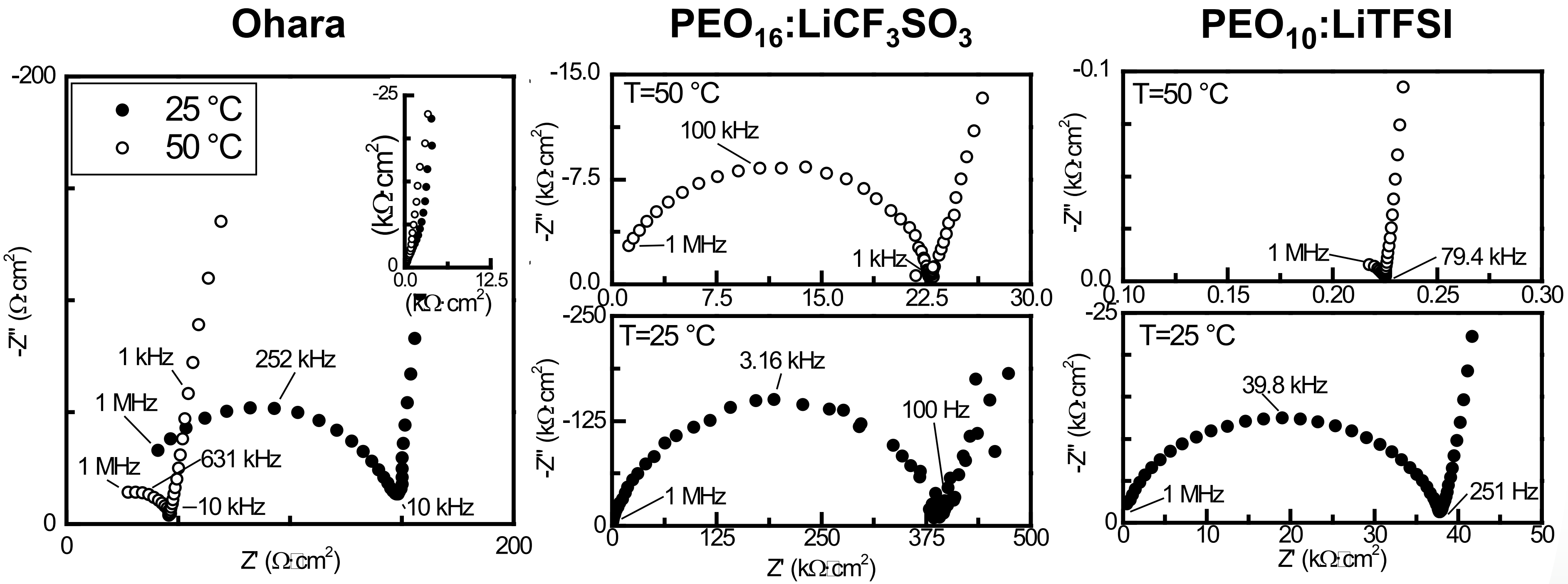
Dispersed composites

Optimized composites

Approach- Many electrolyte materials have been evaluated.

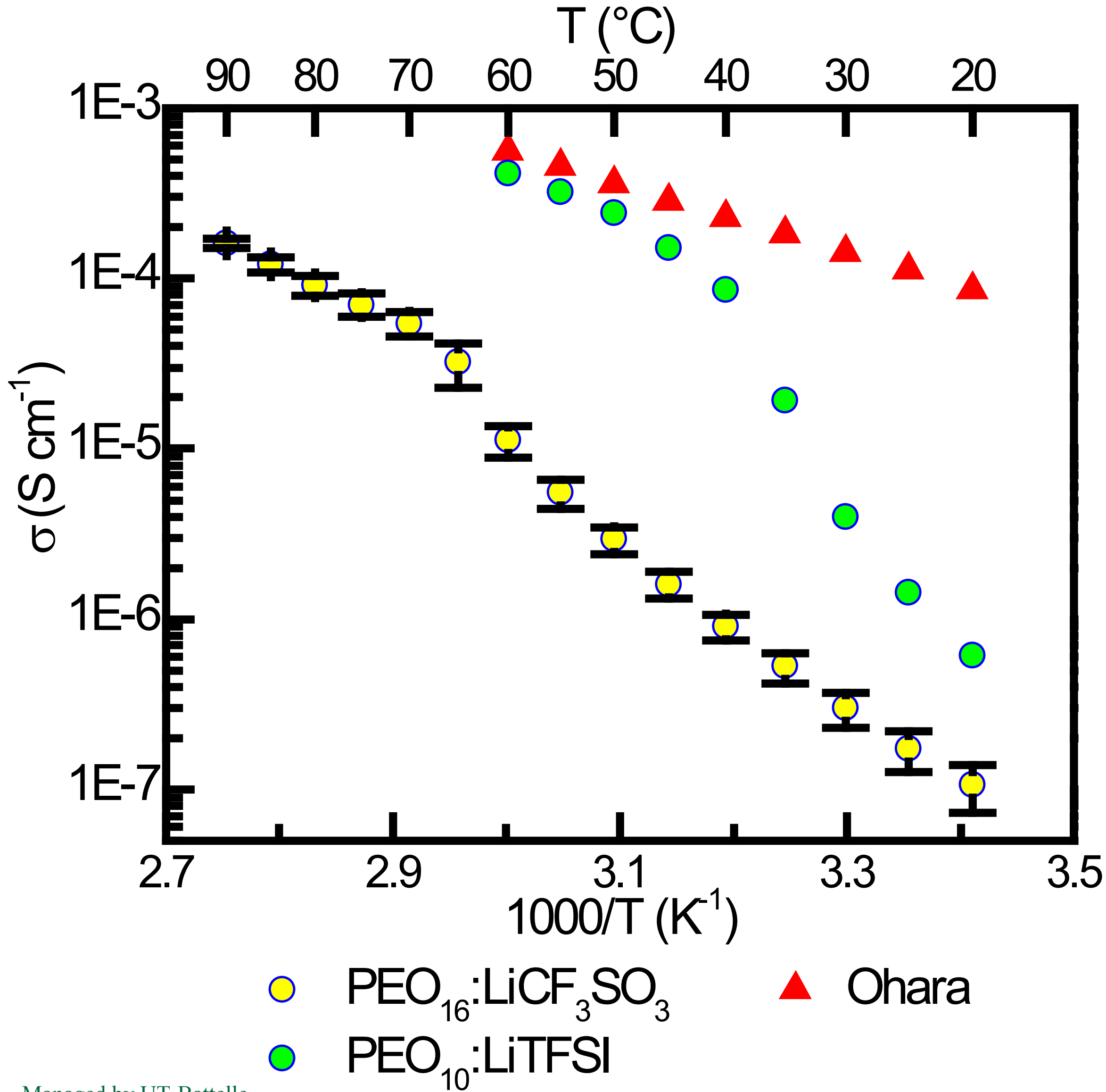
Polymer Electrolytes	***Notable Features***
PEO$_{10}$:LiTFSI	• High conductivity ($\sigma_{25°C} = 2\text{x}10^{-6}$ S cm^{-1}) • T$_{melt}$ ≈ 35 °C • Slow crystallization kinetics
PEO$_{16}$:LiCF$_3$SO$_3$	• Lower conductivity than PEO$_{10}$:LiTFSI • Faster crystallization kinetics
PEO$_6$:LiAsF$_6$ -Sample from P. Bruce at University of St. Andrews (Scotland)	• 100% crystalline • Crystalline phase is conductive • Unity transference number
Ceramic and Glass Electrolytes	
Lithium phosphate oxynitride (Lipon)	• Fabricated as thin film • Chemically compatible with Li
Li$_{1.3}$Ti$_{1.7}$Al$_{0.3}$(PO$_4$)$_3$ (LTAP) Sample from nGimat	• High conductivity • Chemically incompatible with Li
Ohara Nasicon-type (protected composition; crystal structure is similar to LTAP's)	• High conductivity • Chemically incompatible with Li • Commercially available

Ionic conductivity is measured by impedance spectroscopy with blocking electrodes



Characteristic time scales of PEO$_{10}$:LiTFSI and PEO$_{16}$:LiCF$_3$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

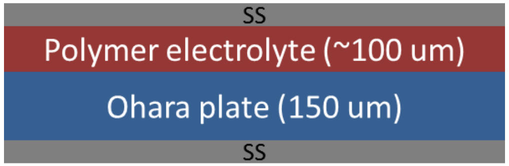


Melting Temperatures
$PEO_{10}:LiTFSI$ = 35 °C
$PEO_{16}:LiCF_3SO_3$ = 60 °C

Controlling reproducibility of polymer electrolytes is a challenge → error bars.

Using laminated bilayer samples to characterize interfacial resistances between two dissimilar solid electrolytes

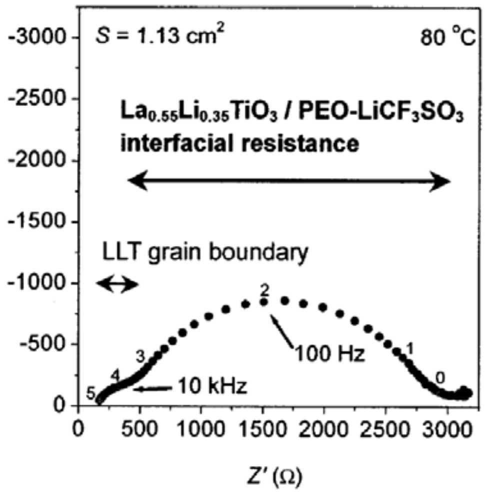
Laminated structures provided a well-defined interfacial area which enables quantitative characterization of interfacial impedances



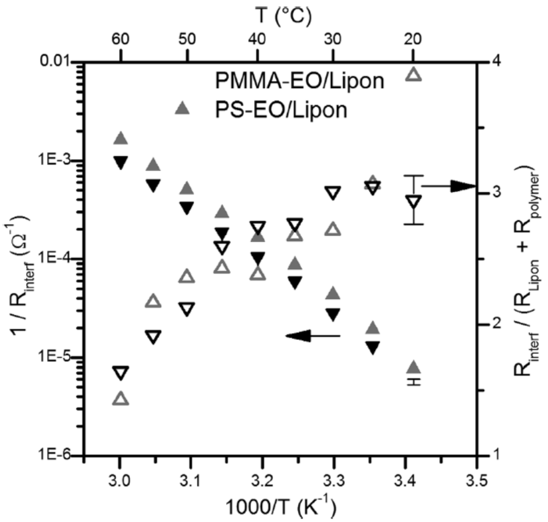
Characterizing Li^+ transport normal to the interface

Previous results from similar systems show that interfacial impedance is dominant

Abe cast polymer over polished and sintered LLT pellet.



Abe, T. et al. *J Electrochem Soc.* 2004.
**Note: different ceramic*

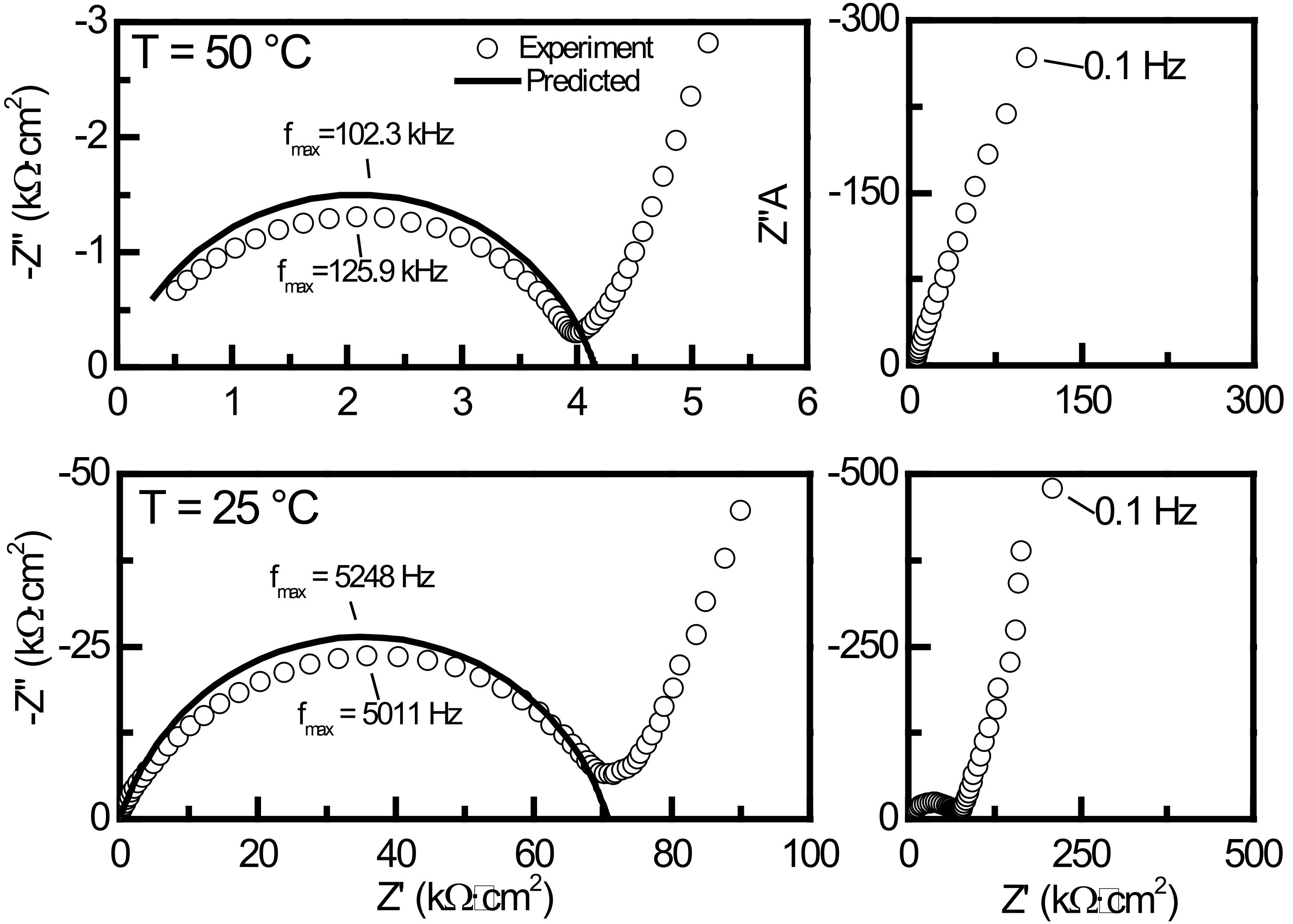


Tenhaeff, W.E. et al. *J Electrochem Soc.* 2011.
**Note: different inorganic, polymer*

Here polymer was solvent cast over Lipon glass. Interface adds resistance.

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}:$LiCF_3SO_3$

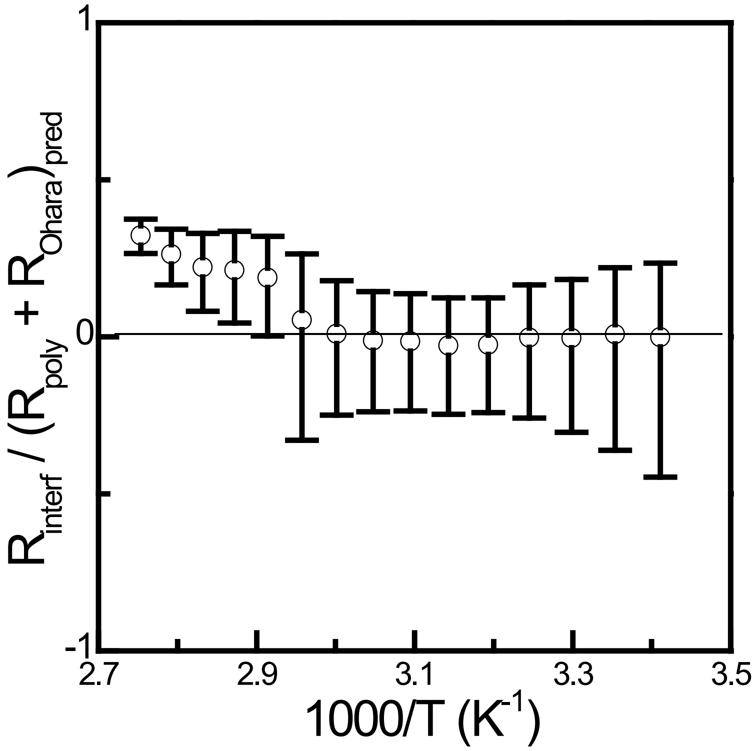


Here, the experimental impedance of the bilayer is compared with that predicted from the individual materials in series.

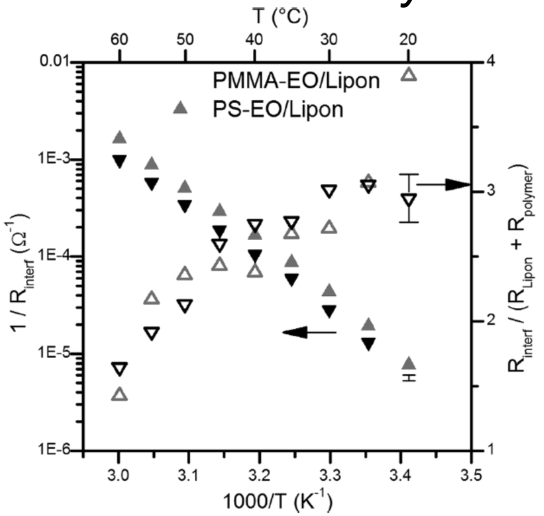
Double layer capacitances of the blocking electrodes at low frequencies were not modeled in the predicted spectra above.

Interfacial Impedance in Ohara\PEO$_{16}$:LiCF$_3$SO$_3$

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



Previous study



Tenhaeff, W.E. et al. *J Electrochem Soc.* 2011.

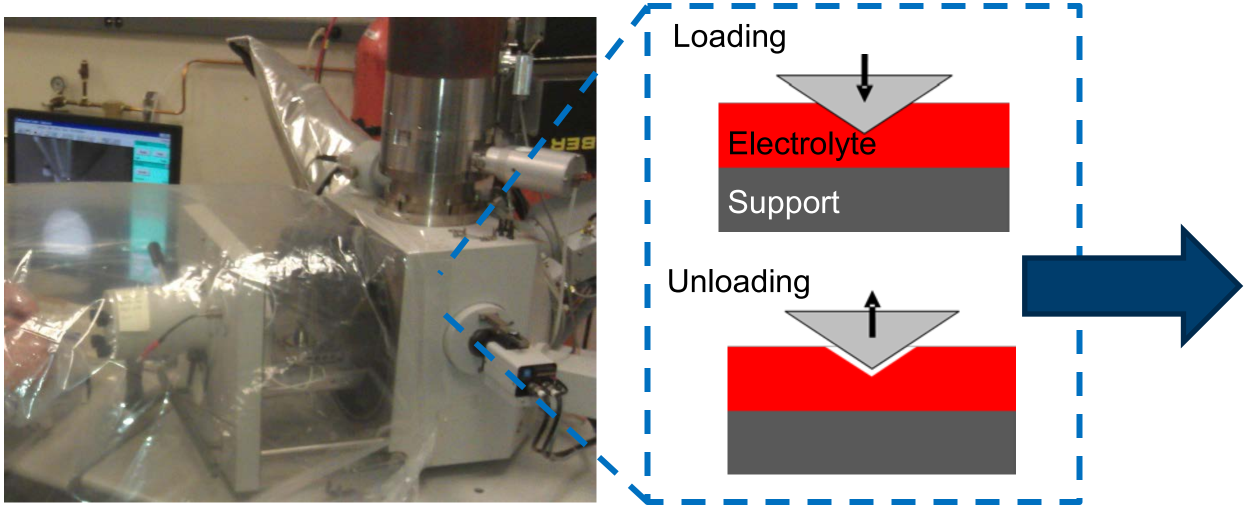
Interfacial resistance is dominant at all temperatures.

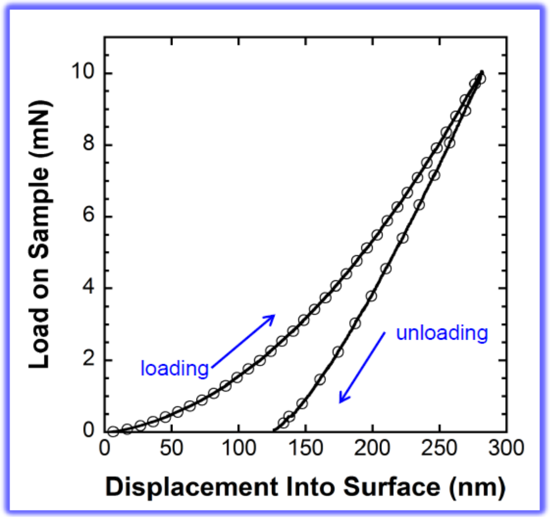
$$R_{interface} > R_{Lipon} + R_{polymer}$$

Unlike previous studies, the interfacial resistance between Ohara and PEO$_{16}$:LiCF$_3$SO$_3$ is small and not statistically different from zero for most temperatures.

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

Nanoindentation
inside the SEM:



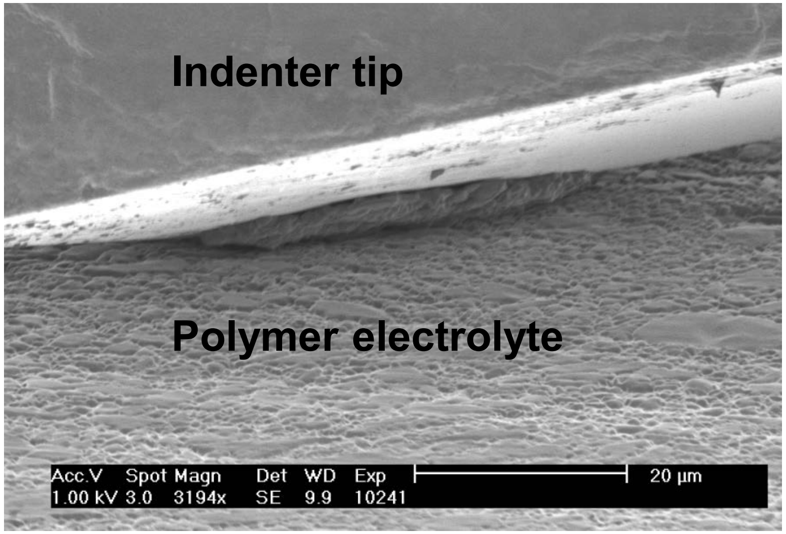


Nanoindentation was done in conjunction with our collaborators at the University of Tennessee, George Pharr and Erik Herbert.

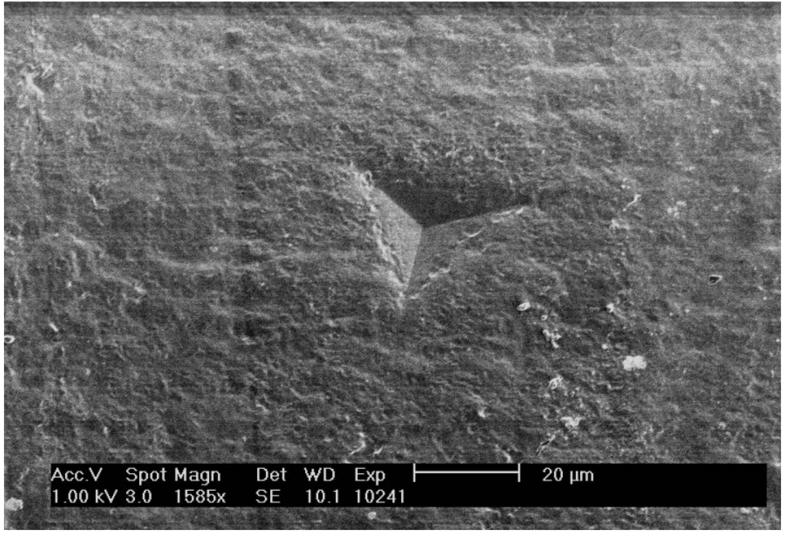
- **Enables the direct observation of the nanoindentation process**
- **Allows the measurement of air/moisture sensitive materials, e.g. polymer electrolytes, lithium, etc.**

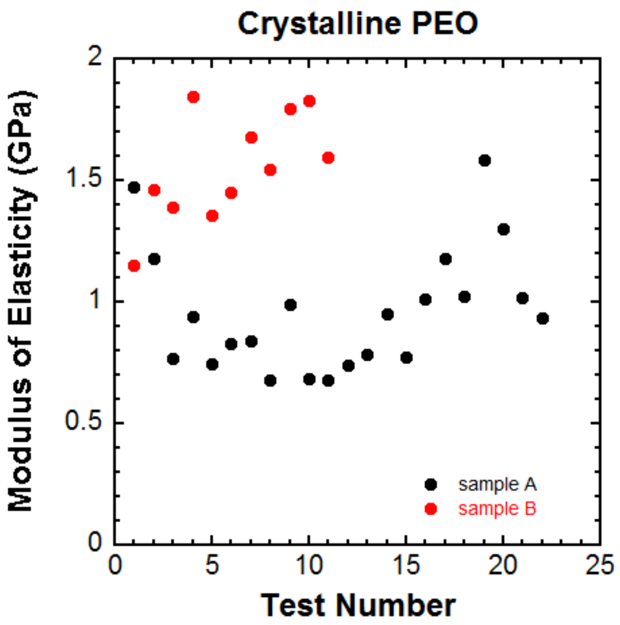
Initial nanoindentation characterizations were performed on crystalline PEO samples from Peter Bruce (PEO_6:$LiAsF_6$)

Indenter at Peak Load



Residual Impression





ID	Composition	Average Elastic Modulus, E (GPa)
A	PEO_6:LiA_SF_6	0.96
B	PEO_6:(95% $LiAsF_6$-5% LiTFSI)	1.5

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