

Composite Electrolyte to Stabilize Metallic Lithium Anodes

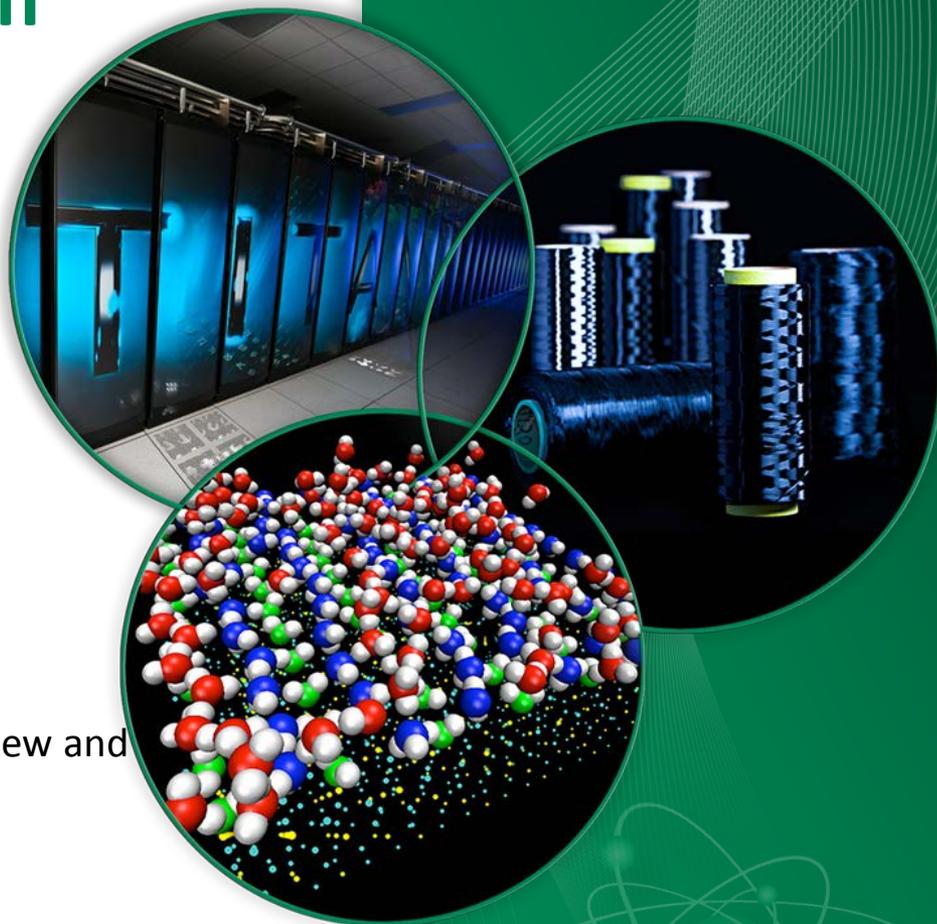
Project ID: ES182

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Oak Ridge National Laboratory

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Peer Evaluation Meeting

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**“This presentation does not contain any proprietary,
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Overview

- **Timeline**

- Start October, 2011

- **Technical barriers**

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

- **Budget**

- \$300k FY11,
- \$300k FY12,
- \$335k FY13

- **Partners and collaborators**

- Oak Ridge National Laboratory (lead)
- Center for Nanophase Materials Sciences, ORNL
- SHaRE user facility, ORNL
- Collaborators:
 - Jeff Sakamoto, Michigan State University
 - Nitash Balsara, UC Berkeley
 - nGimat, GA
 - Ohara Corporation, CA

Relevance – Our strategy

Premise: To ensure stable and efficient use of high energy dense lithium metal anode requires a protective and robust solid electrolyte. The combination of two or more solid electrolytes is more likely to meet the many materials and manufacturing requirements than any single material.

What single solid has:
adequate Li^+ conductivity AND
robust mechanical properties AND
thin sheet processing AND
no pathways for dendrites AND
chemical stability with Li ?



composite of
solid
electrolytes

Relevance and Objectives

- **Objectives:**

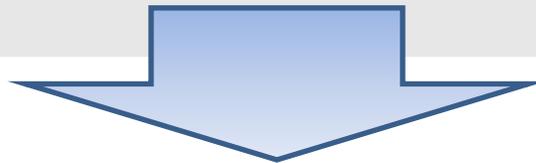
- Understand Li⁺ transport at interface between two dissimilar solid electrolytes, e.g. ceramic/polymer
- Develop composites of electrolyte materials with requisite electrochemical and mechanical properties as guided by simulation
- Fabricate thin membranes to use with a thin metallic lithium anode providing good power performance and long cycle life

- **Relevance to technical barriers:**

- Multi-year program plan identifies the Li metal anode and its poor cycling as the fundamental problem for very high energy Li batteries. Hence, research takes the approach of completely isolating the anode from the electrolyte.
- Success of our composite electrolyte will:
 - Enable very High Energy Li-S Battery (500 Wh/kg) by 2020 and Li-Air Battery (700 Wh/kg) by 2030
 - Fully protect lithium anode for long cycle life (3000 to 5000 deep discharge cycles)
 - Ensure lithium remains dense and free of dendrites (Safety)
 - Improve energy density lithium batteries (USABC has targeted a 5X improvement)

Milestones

Milestones:	Target:	Status:
1. An electrolyte composite where the internal interface does not significantly impede the Li ion transport.	Oct. 2012	✓ for bilayer
2. Simulation the ion conduction of an optimized composite structure.	Oct. 2012	✓
3. Evaluate composite membrane with a lithium metal electrode for cycling stability and dc transport properties.	Oct. 2012	✓ in FY13
4. Demonstrate functionalized surface of solid electrolyte powders	Feb. 2013	✓
5. Measure conductivity of composites to determine role of surface functionalization on interfacial resistance	June 2013	on schedule
6. Quantify the Li cycling efficiency and the effect of stack pressure	Oct. 2013	on schedule

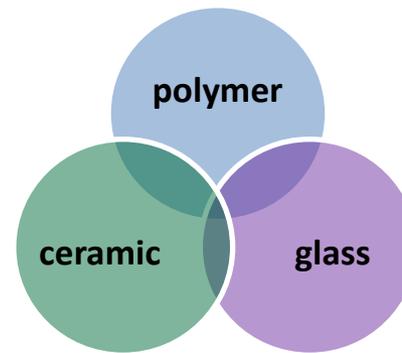


Proof of principle - Composite electrolyte to stabilize/protect Li metal anode

Approach

1. Utilize known solid electrolytes.

(Our goal is to investigate *combinations* of electrolytes, not to discover new electrolytes.)



2. Determine interfacial properties (transport and mechanics) of pairs of dissimilar electrolytes** and how it can be modified.

What are reasonable expectations?

3. Use simulation to explore mechanical stability and transport in different composite structures and composition. *What are design targets?*

4. Fabricate composites using practical processing methods. *Are new strategies needed?*

5. Evaluate stability with lithium metal** upon cycling.

**** Key to success - fundamental understanding and control of these interfaces.**

One of the unique aspects of program – We address mechanical properties, as well as ion transport.

Choose electrolytes

Assess & modify interface

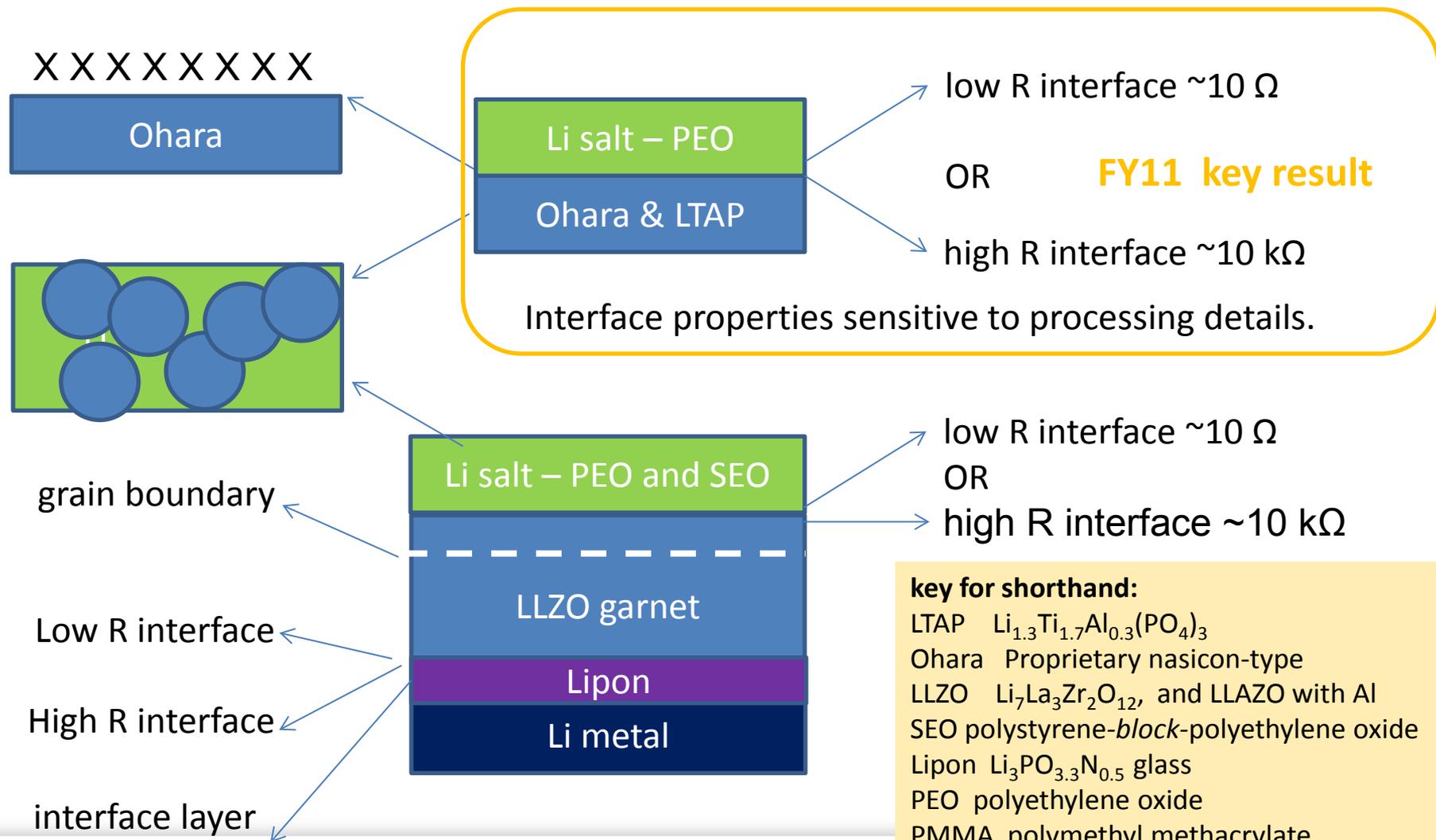
Simulate composites

Prepare composites

Cycle lithium metal

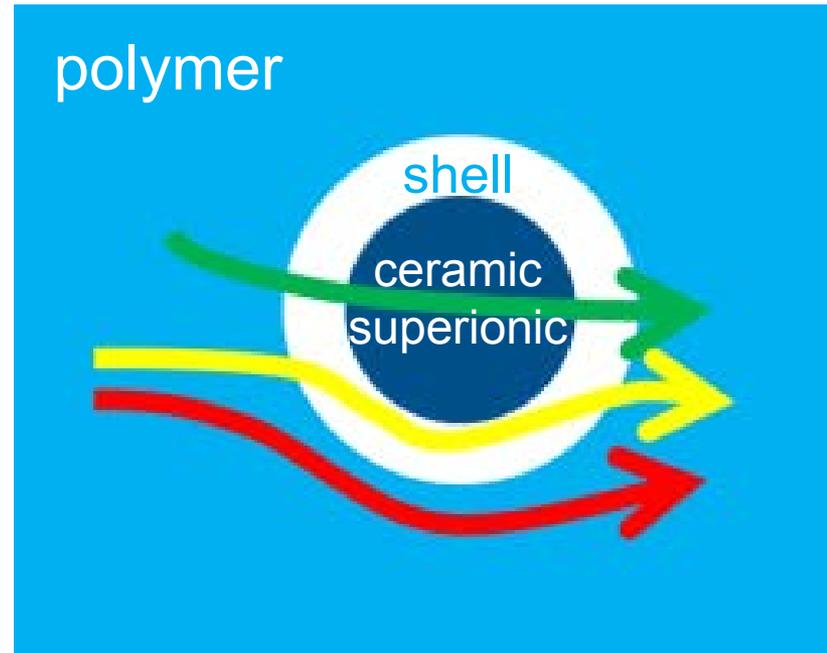
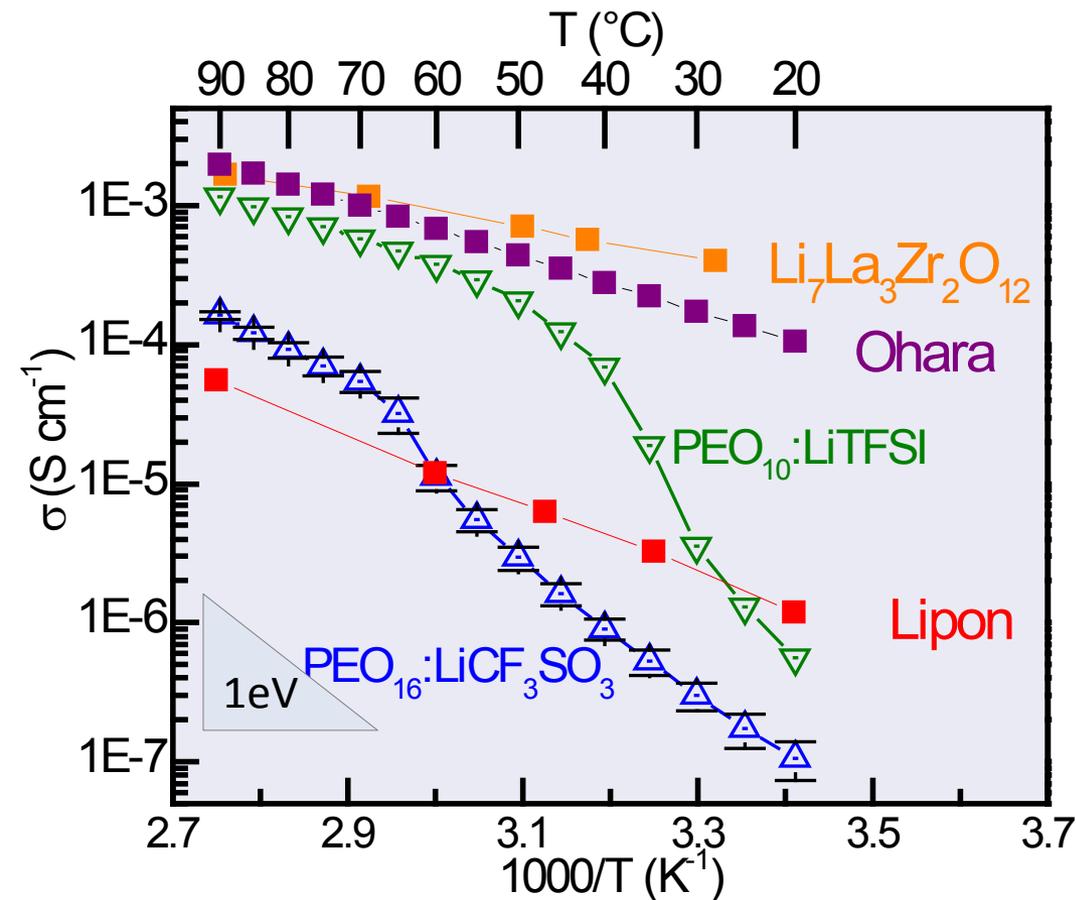
Progress overview: Greatly expanded study of interfaces and effects of alternative fabrication routes.

- Key is learning to control the interface properties



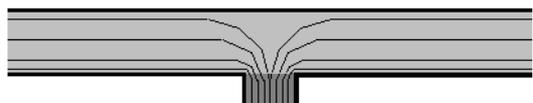
Background information: Composites combine “superionic” ceramic materials with dry polymer electrolytes.

- Need facile Li^+ transport across interface to access ceramic phase
- Ceramic has highest conductivity. Shell conductivity may be enhanced or suppressed relative to polymer matrix.

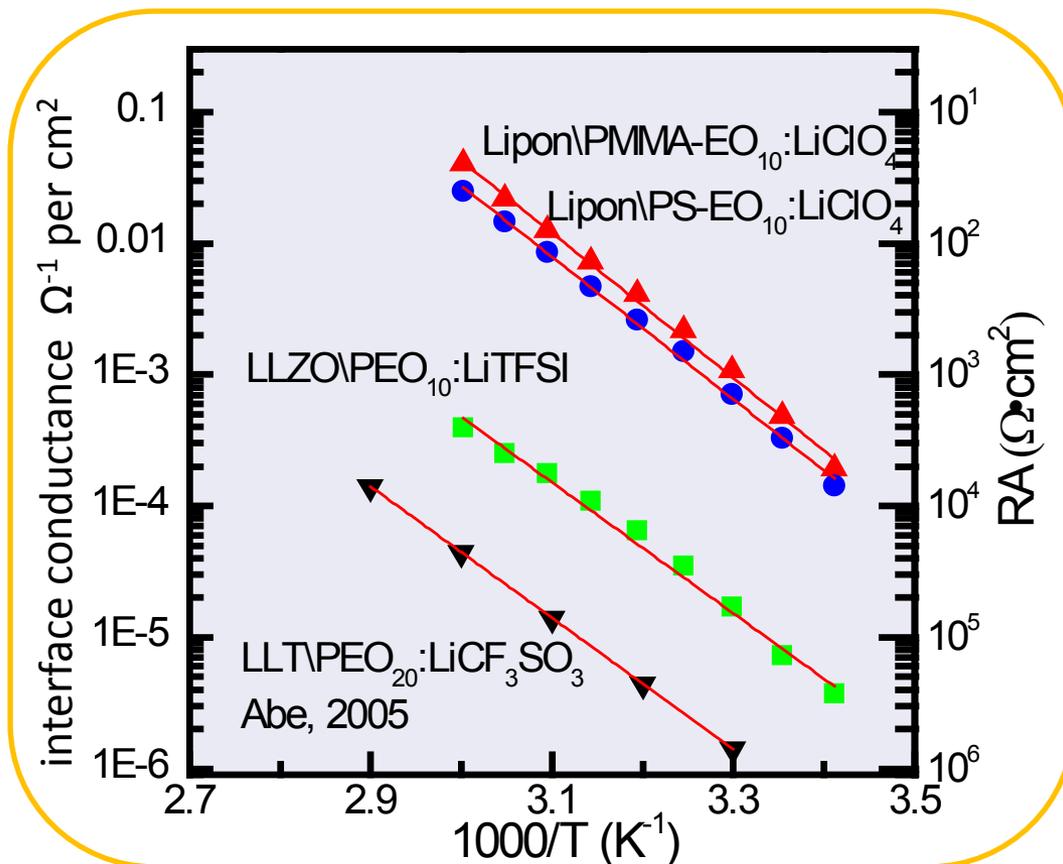


Discovered, in fy13, the strong similarity of many polymer-ceramic bilayers. Interface conductance is low; activation energy is high.

- **Typical fabrication as films by**
 - solvent cast polymers or
 - laminated sheets
- **E_a surprisingly consistent for different materials**
 - all ≈ 100 kJ/mol, similar to crystalline polymer
 - common source of resistance
- **Possible causes of high resistance:**
 - barrier or impurity layer
 - conformation of polymer chains
 - polarization



current flow at point contact from thin film

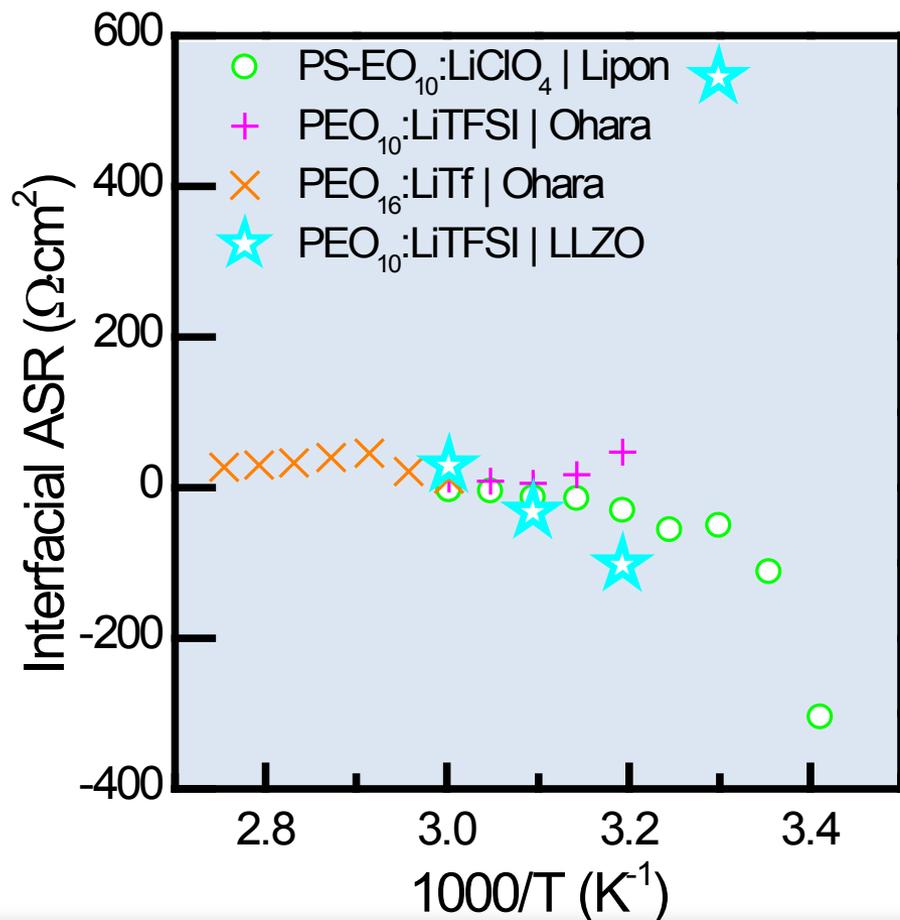


Lipon\PMMA-EO ₁₀ :LiClO ₄	(E _a = 106 kJ/mol)
Lipon\PS-EO ₁₀ :LiClO ₄	(E _a = 104 kJ/mol)
LLZO\PEO ₁₀ :LiTFSI (laminated film)	(E _a = 95 kJ/mol)
LLT\PEO ₂₀ :LiCF ₃ SO ₃ **	(E _a = 96 kJ/mol)

** Abe, et.al JECs, 2005

Good news - interfaces of polymer with ceramic or glass can be much more conductive! (with the right processing).

- Difficult to measure accurately, as $R_{\text{interface}} \approx 0$. Hence scatter, even negative.
- Small resistance, but probably not zero, even with improved interface fabrication.
- Temperature dependence not clear.



Conductive interfaces:

- Lipon sputtered on PS- EO_{10} : LiClO_4
- Ohara / PEO_{10} : LiTFSI
- Ohara / PEO_{16} : LiCF_3SO_3

Not shown here, **but low interfacial ASRs** for Lipon sputtered onto

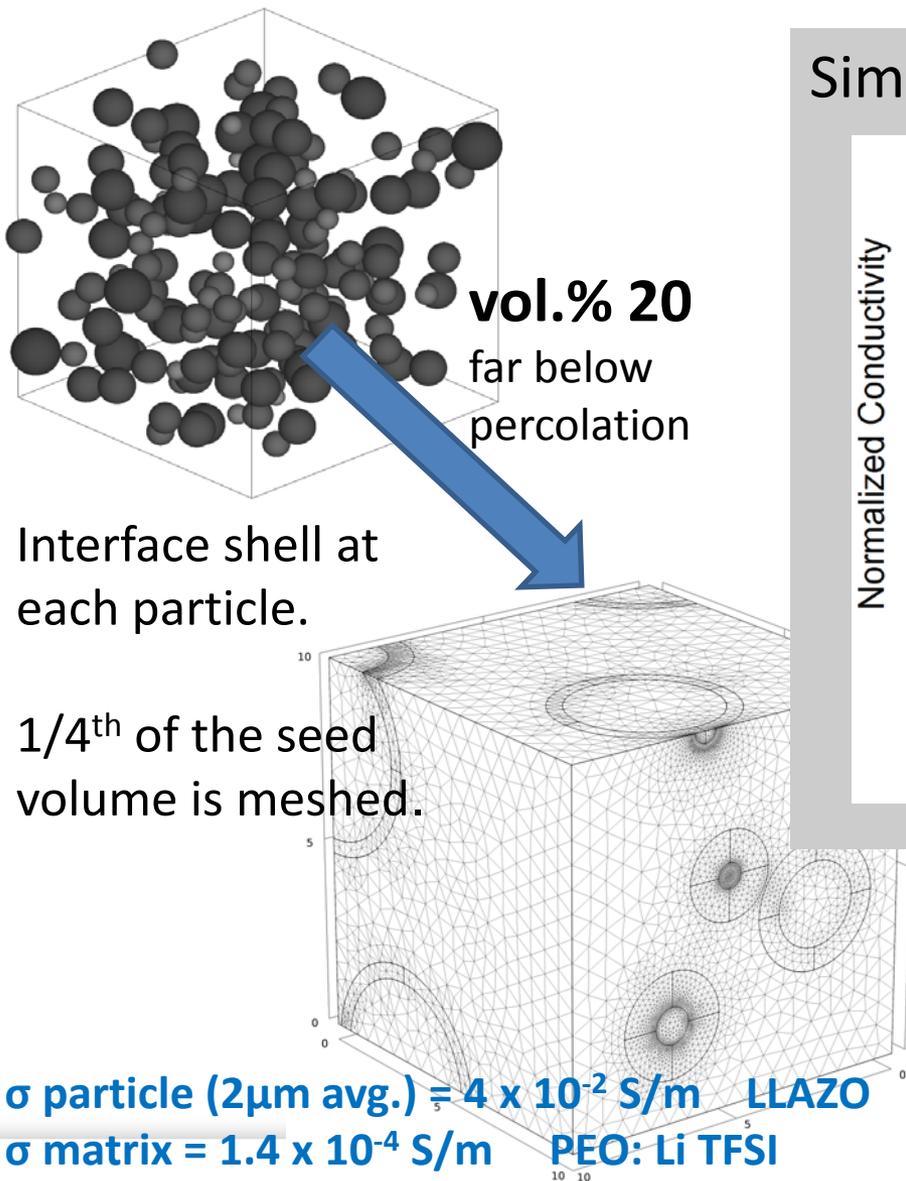
- Polymer electrolyte membranes
- Ceramic electrolytes (LLZO & Ohara)



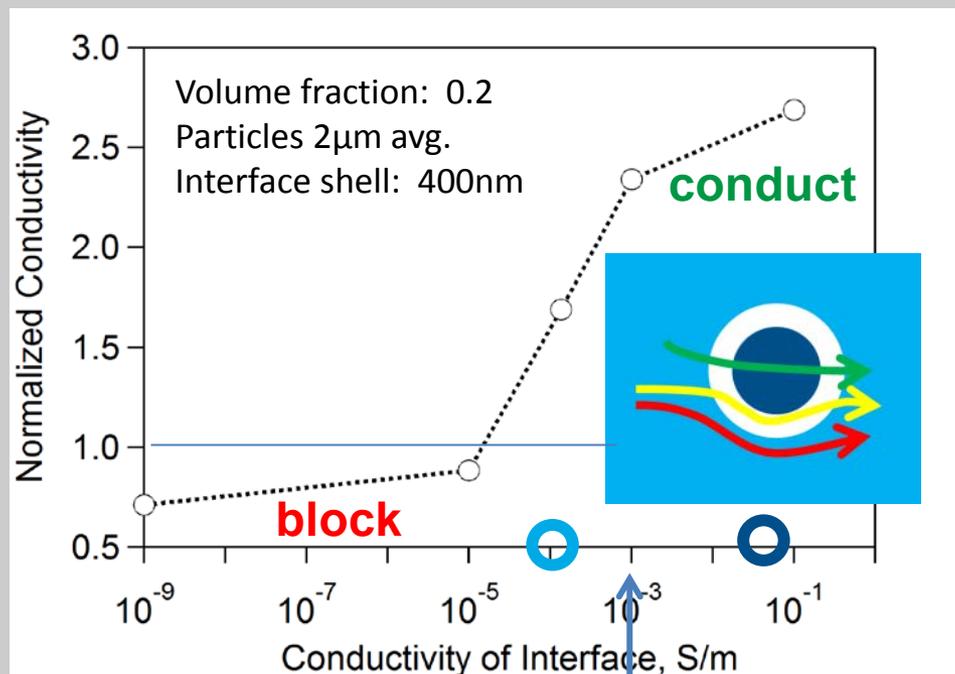
Resistance adds up if many interfaces in the composite



Simulation can take a different view, posing a new question for fy13: *How conductive does the interface need to be?*



Simulations with superionic powders



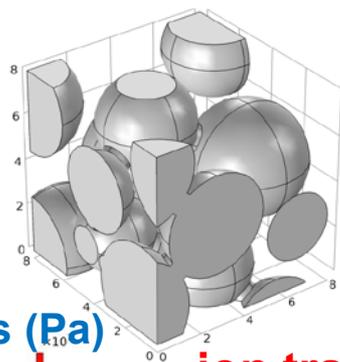
ASR of 4 Ω

Answer:
Interface resistance must be small, but comparable to our best bilayers.

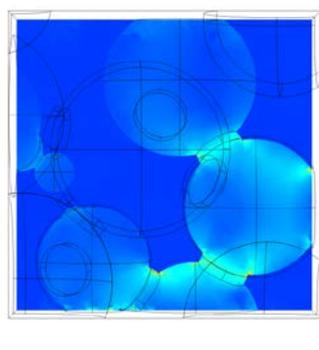
For mechanical stability, a high loading or 3D network of the hard (LLZO) phase is needed. New modeling for fy13 added necks.

- **Simulation predicts mechanical stability at**
 - 57 vol.% dispersed particles OR $\approx 52\%$ if necks formed between particles
- **Simulation with neck formation predicts Li transport that**
 - does not depend on matrix conductivity and increases with the neck radius
 - Concern: Li at anode will be very non-uniform if confined to one phase

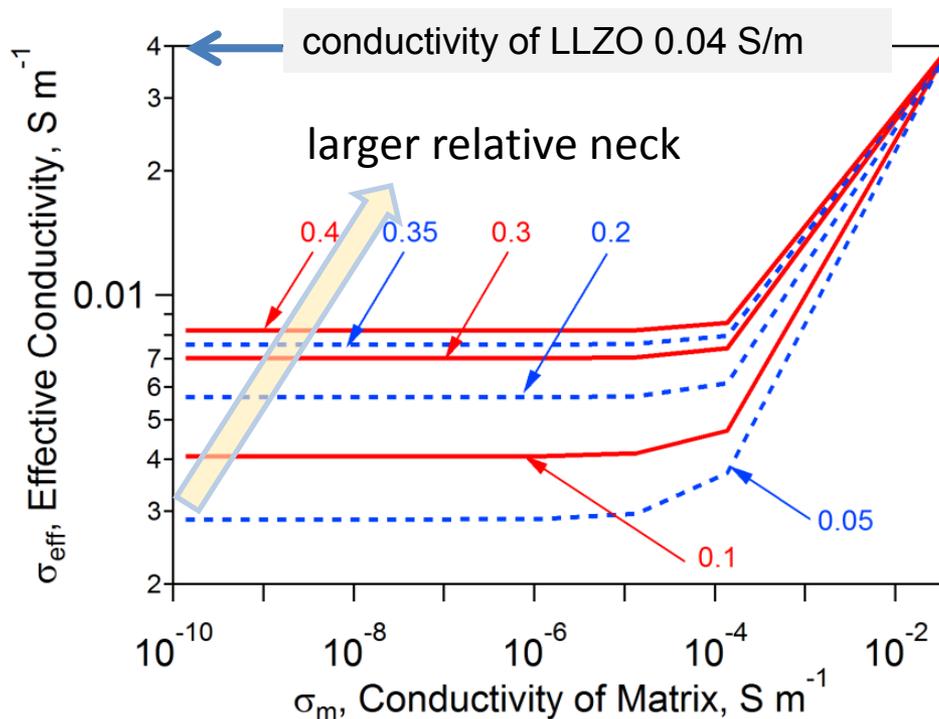
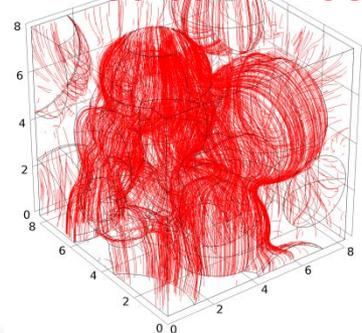
Superionic particles connected by necks



Von Mises stress (Pa)



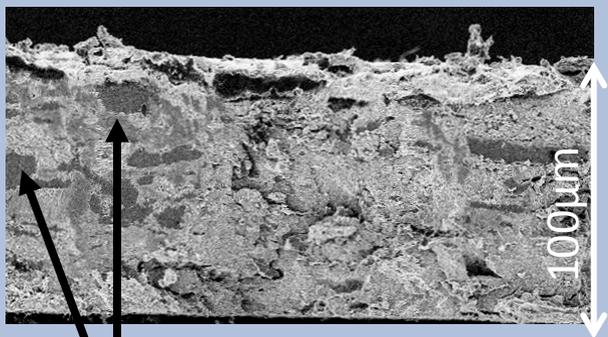
ion transport streamlines



Continuing work with evaluate three promising approaches to forming composites with high loading of ceramic electrolyte

- Achieved high ceramic loading with reasonable dispersion.
- Processing methods developed with salt-free PEO

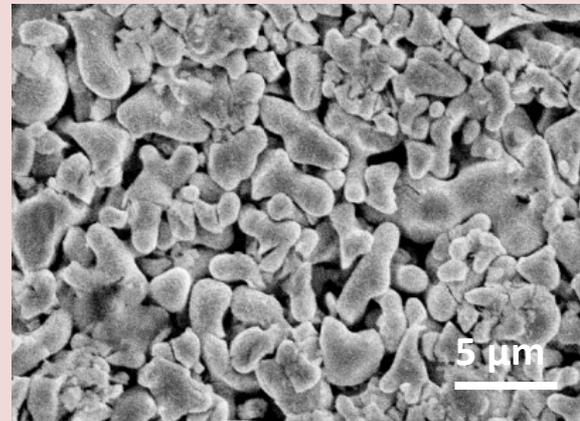
Melt + press method to 60 vol.%



PEO-enriched phase

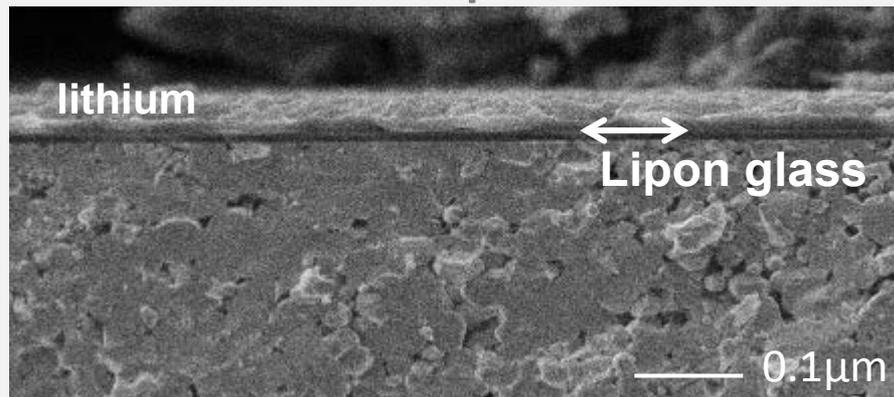
Cryo fracture edge, Ohara powder in PEO.
Practical for manufacturing.

Partial sintering to form necks



garnet powder compact, later PEO

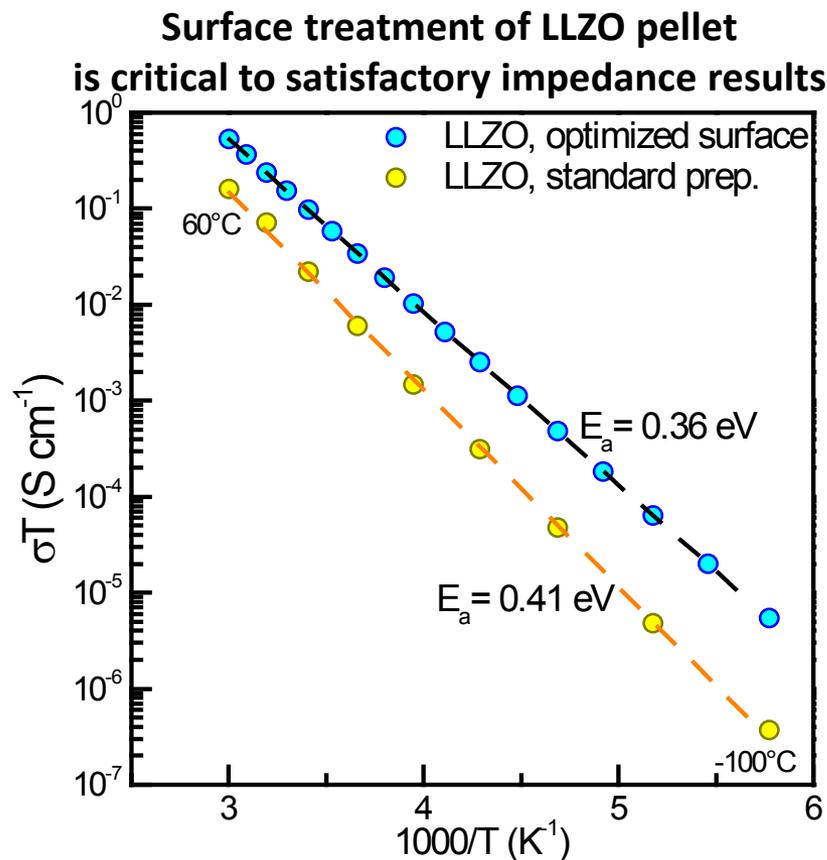
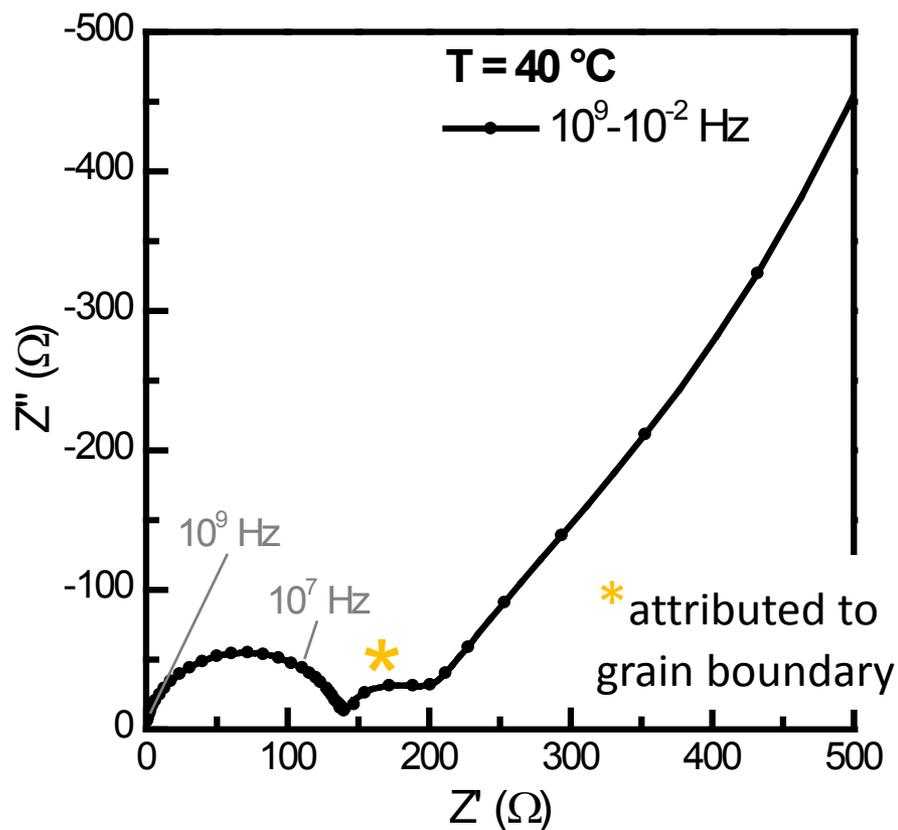
Surface coating (glass or polymer) for uniform lithium transport at electrode



Lipon on garnet pellet, little added resistance

Progress shows that: Grain boundary of LLZO garnet impedes Li^+ transport, but only slightly. (sample from J. Sakamoto)

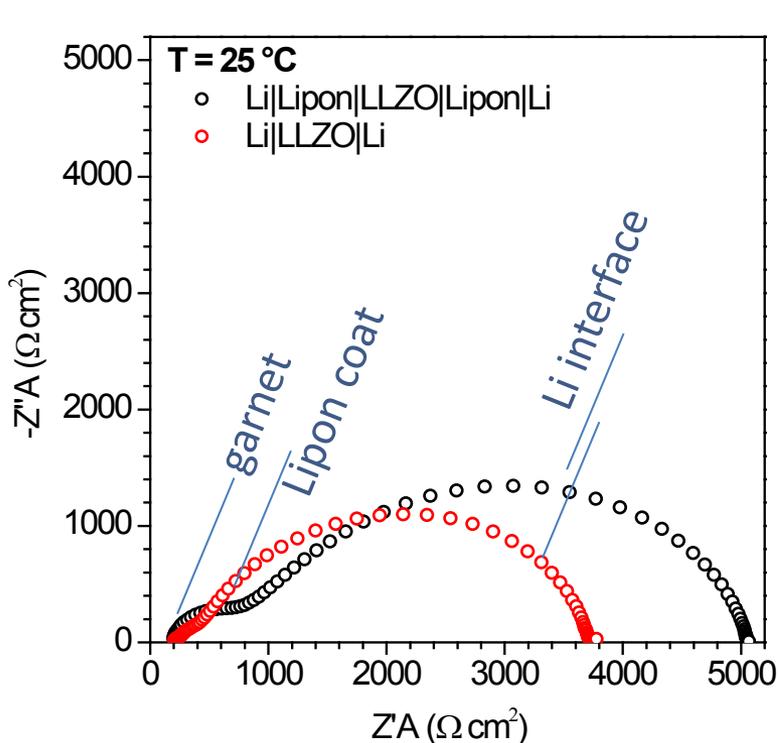
- Grain boundary resistance is surprisingly small, hard to distinguish from total and surface effects.
- Total impedance is highly dependent upon surface preparation.



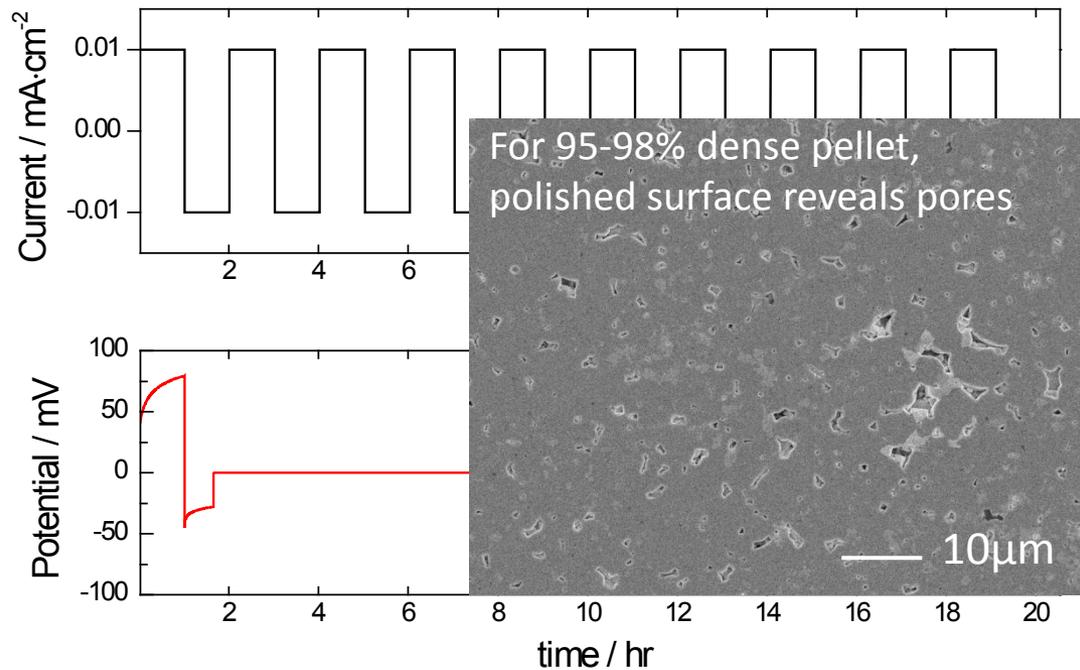
Advancing the understanding of Li conduction in polycrystalline $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ garnet electrolytes using impedance spectroscopy. W.E. Tenhaeff, E. Rangasamy, et.al., in preparation.

Progress shows: Advantage of using evaporated Li films electrodes is a less resistive interface. Disadvantage is premature short.

- Using rolled Li sheet – Sakamoto shows interface resistance decreasing with cycling, pressure, heating.
- Using vapor deposited Li film – reduces interface resistance.



Lithium, even when vapor deposited, dominates the impedance.



Rapid shorting during DC cycling when using evaporated Li (not observed with Li foils)

Future Work

- **Remainder of FY13**

- Quantify interfacial impedances between polymers & functionalized ceramics
- Compare performance of highly loaded dispersed particulate composites and sintered neck garnet frameworks filled with polymer electrolyte
- Characterization of DC transport and Li cycling efficiencies of composites

- **FY14**

- Develop technologies to remedy flaws or heterogeneities (e.g. porosity) of solid electrolyte surfaces to maintain uniform current densities
- Develop strategies to maintain dense Li through extended cycling

- **Beyond**

- Fully package protected lithium with electrolyte and seals
- Characterize electrochemical performance, coulomb efficiency and cycling stability of full cells

Collaborations and coordination

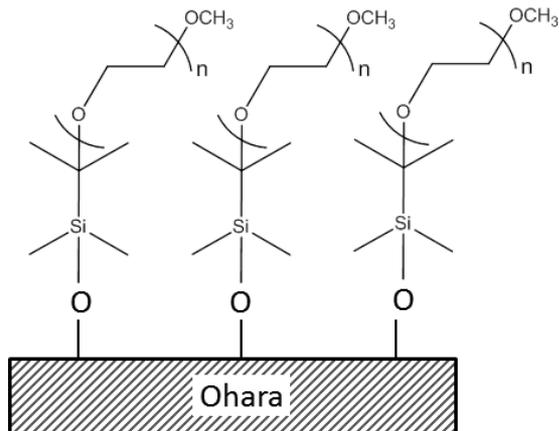
- Collaborations which include coordinated sample preparation, sample exchange for analysis. We anticipate joint publications; several are in preparation.
 - Jeff Sakamoto (Michigan State University) outside of VT program
 - Nitash Balsara (UC Berkeley) inside VT program
- Ceramic electrolytes supplied by: Ohara Corp. and nGimat and Jeff Sakamoto
- Polymer electrolytes contributed by: Nitash Balsara and Peter Bruce
- Coordination with team members of ILIRP (Integrated Laboratory Industry Research Program)
- Collaboration with companies and researchers developing new solid electrolytes is actively sought, being consistent with program strategy of incorporating known solid electrolytes into composites.

Summary

- **Relevance** Success of our composite electrolyte will completely isolate the anode from any liquid electrolyte, enabling very high energy Li-S and Li-air batteries, with thousands of deep cycles, negligible consumption of lithium and good safety.
- **Approach** Premise: the combination of two or more solid electrolytes is more likely to meet the many materials and manufacturing requirements than any single material.
 - Investigate combinations of different electrolytes, particularly to control interface properties.
 - Use simulation to guide optimization for good transport and mechanically robust structure.
 - Evaluate interface to lithium metal, and stability with cycling.
- **Accomplishments and progress - new understanding that will address technical barriers**
 - Many polymer-ceramic interfaces have similar behavior, possibly related to PEO conformation.
 - Even small interface resistance will alter Li⁺ path through a composite.
 - Large volume fraction of ceramic particles has been dispersed into a polymer for higher modulus.
 - Sintered necks between ceramic particles is predicted to enhance conduction and stiffness.
 - Vapor deposited lithium anode may cause premature failure of ceramic electrolytes.
- **Future work**
 - Quantify interfacial impedances between polymers & functionalized ceramics
 - Compare performance of highly loaded dispersed particulate composites and sintered neck garnet frameworks filled with polymer electrolyte
 - Characterization of DC transport and Li cycling efficiencies of composites
- **Collaborations and coordination** – Sakamoto, Balsara, ILIRP team, Ohara and nGimat

Technical backup slides

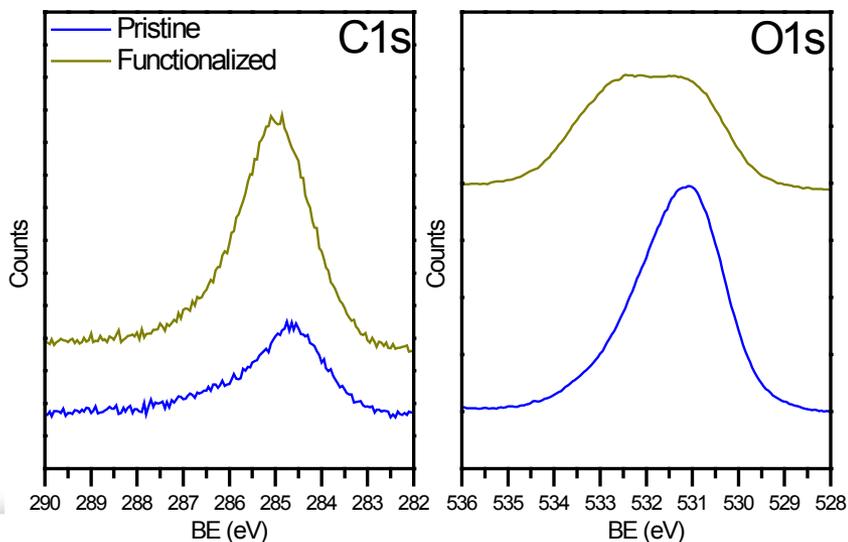
Surface functionalization chemistry has been developed showing exceptional coverage on Ohara plate, but so far without Li salt.



Requirements for surface functionality

- Solvates Li^+ ions
- Improves ceramic wettability \rightarrow greater adhesion
- Ultrathin (few nanometers)

XPS confirms surface functionalization



Impedance characterization confirms presence of the surface layer

