

Composite Electrolyte to Stabilize Metallic Lithium Anodes

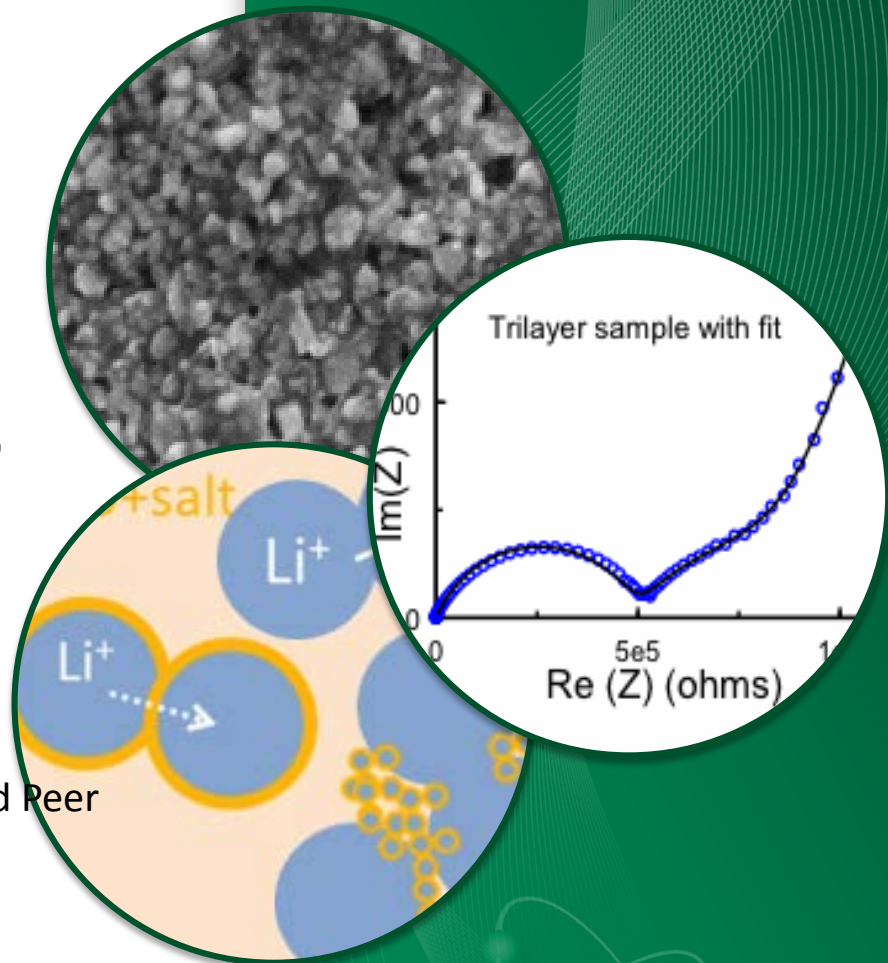
Project ID: ES273

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Evaluation Meeting

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Overview – Composite Electrolytes to Stabilize Li Metal Anode

- **Timeline**

- Start: October 2014
- End: September 2017

- **Budget**

- \$400k FY15
- \$400k FY16

- **Technical barriers**

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

- **Partners and collaborators**

- Oak Ridge National Laboratory (lead)
- Center for Nanophase Materials Sciences, ORNL
- Collaborators:
 - Jeff Sakamoto, Michigan State University
 - Ohara Corporation, CA

To match Li-ion cathodes,	Li cycling must achieve:
20-40 μm Li per cycle	no loss to reaction
10-20 nm/sec, pulse	no loss to physical isolation
3000 cycles	no roughening or dendrites

**For high energy density, there can be no excess lithium in battery.
Cycling of lithium must be stabilized by the solid electrolyte.**

To match Li-ion cathodes and meet EV goals:

20⁺ μm Li per cycle

10-20 nm/sec, pulse

3000 cycles

10-15 mA/cm², pulse

99.99% coul. efficiency

no Li roughening

no Li lost to physical isolation

no Li lost to reaction

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

Can polymer-ceramic composite electrolytes protect the Li?




- **Objectives:**

- 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
- Identify design rules that can be generally applied to composites of other solid electrolyte materials
- Understand Li^+ transport at interface between two dissimilar solid electrolytes, e.g. ceramic/polymer

- **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)

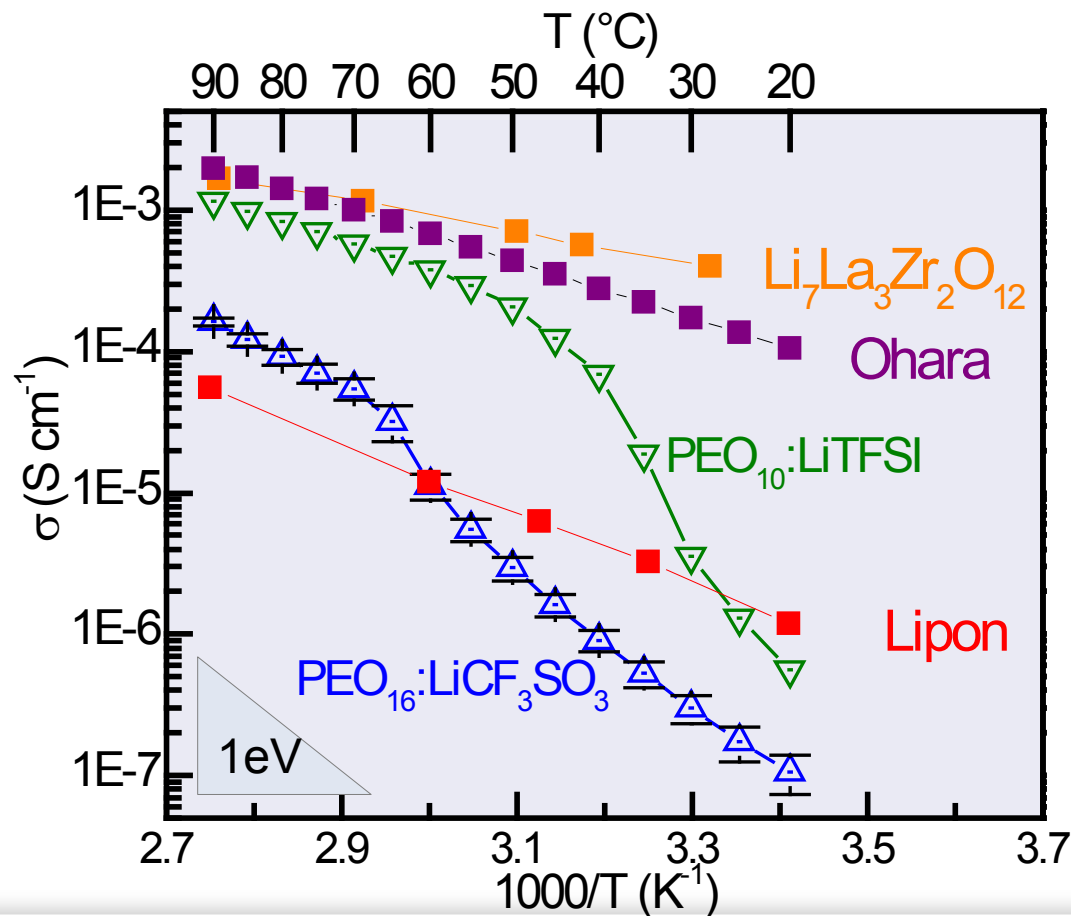
Milestones

Milestones: FY15-FY16	Target:	Status:
Generate a database with at least 5 compositions, determine if the presence of trace solvent molecules that enhance the ionic conductivity are also detrimental to the stability and cycleability of a lithium metal electrode.	Q3 FY15	 See below
Demonstrate a practical processing route to a thin, dense membrane 100μm x 50cm ²	Q4 FY15	 Exceed goal
Measure the removal of solvent molecules introduced via solution synthesis or gas absorption from ceramic-polymer composite sheets under vacuum and heating conditions	Q1 FY16	
Prepare ceramic-polymer electrolyte sheets with a coating and map the uniformity with nanoindentation and by profile the Li plating.	Q3 FY16	On schedule

Different trace solvents	DMC	18 mm Hg (21°C)	Highest conductivity, Li reacts	
	H ₂ O	22 mm Hg (21°C)	Inc. conductivity, Li reacts	
	TEGDME	< 0.01 mm Hg (21°C)	Inc. conductivity, poss. more stable	
	EC+DMC+LiPF ₆		uncertain	
	THF	143 mm Hg (21°C)	No change, not adsorbed by PEO	

Background for approach: composite that is largely ceramic, with just enough polymer –

- Being more conductive and stiff, a high volume loading of ceramic is needed for best mechanical and transport properties of the composite.
- Most results here are for **Ohara powder (submicron)** in **PEO₁₆:LiTf**

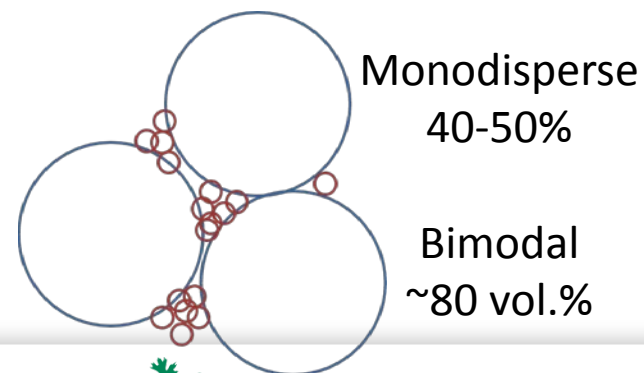


Target (this work):

- 40-50 volume % of ceramic in polymer matrix.

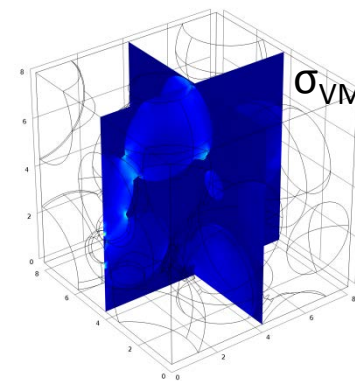
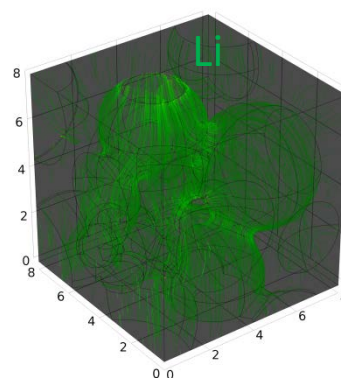
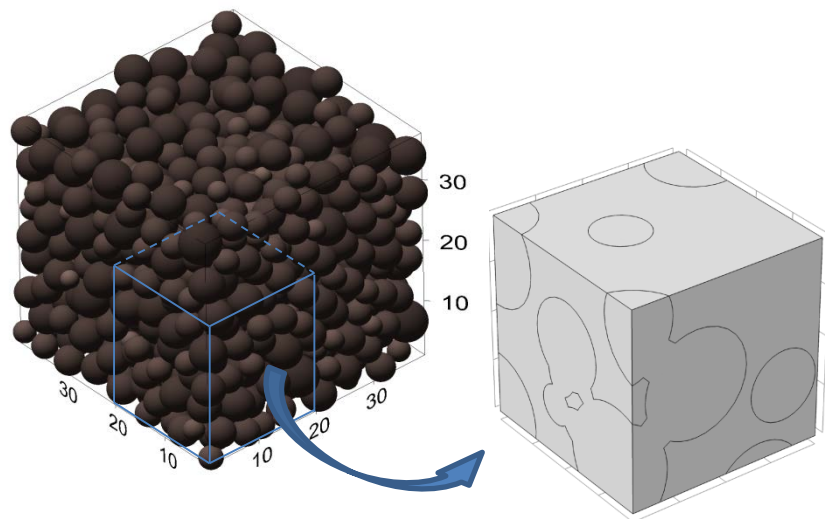
Ultimate target:

- ~ 80 volume % total ceramic by using bimodal particle size



Background for approach: composite that is largely ceramic, with just enough polymer –

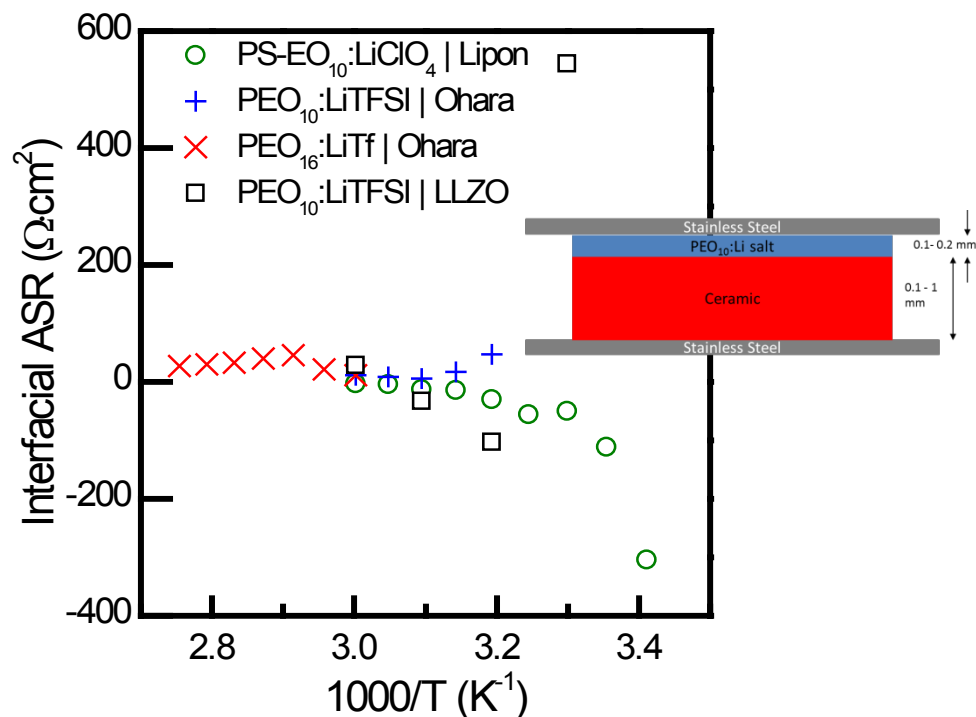
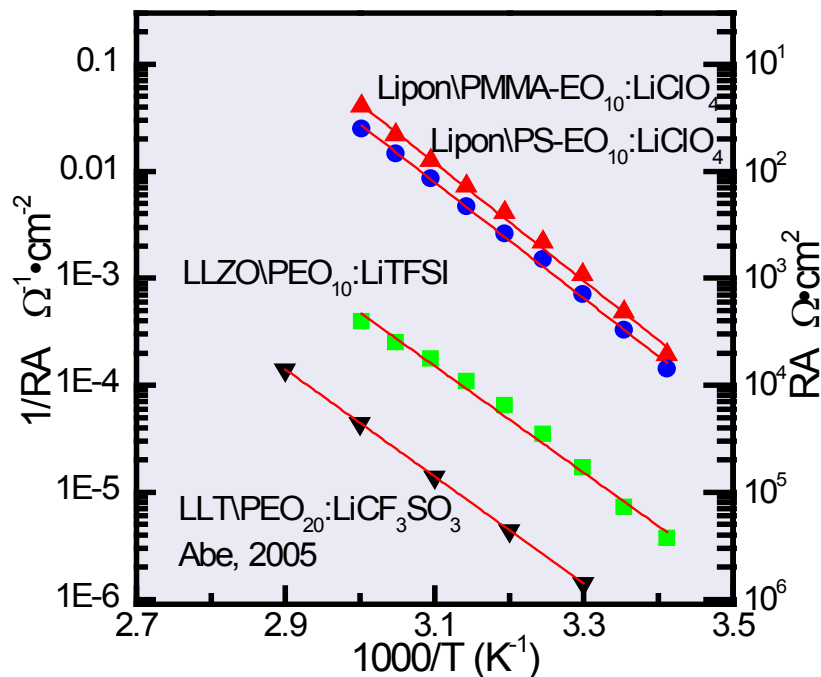
- Earlier models of modulus and conductivity of composites provided guidance for composition and structure goals (Kalnaus, this program)
 - High ceramic loading needed for high modulus in dispersed system.
 - Polymer-ceramic interface resistance is critical in dispersed composite.
 - Partial sintering so that necks connect ceramic particles eliminates need for highly conductive polymer electrolyte
- Yet polymer electrolyte will facilitate manufacturing and handling



- Li transport through ceramics percolation network
- High stiffness with polymer providing additional cohesion

Ceramic-polymer interface resistance depends on processing; warrants further study of fundamental effects.

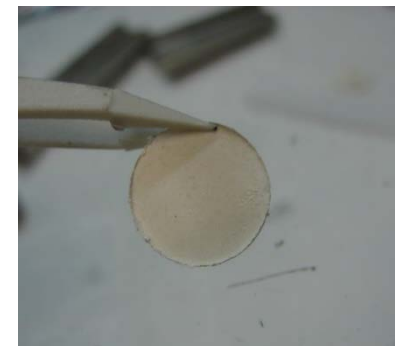
APPROACH



Intrinsic interface effects	Extrinsic effects
available sites	reaction layer
space charge	impurity molecules
Li ⁺ solvation	voids, pores
polymer structure, density	salt segregation

Initially melt-pressing was used for fabrication and control of ceramic – polymer composites (small pellets of dispersed particle composites)

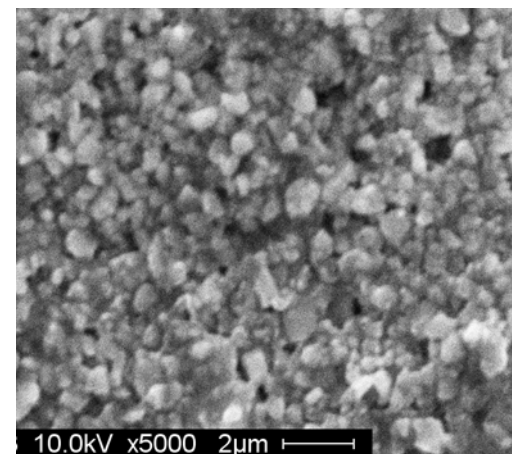
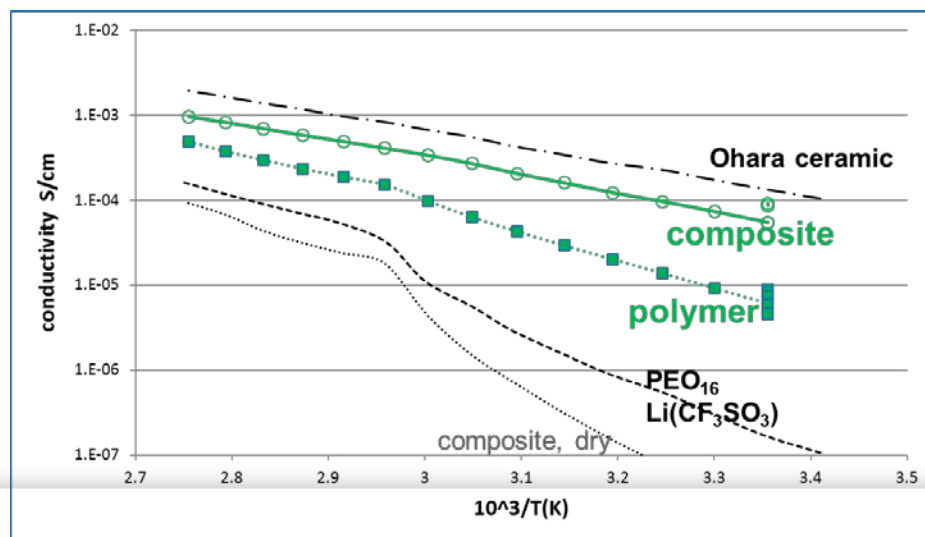
- Earlier work: composites are resistive unless the polymer is plasticized with DMC vapor.
- Composite is stiff because high vol.% ceramic



*dose by
vapor*

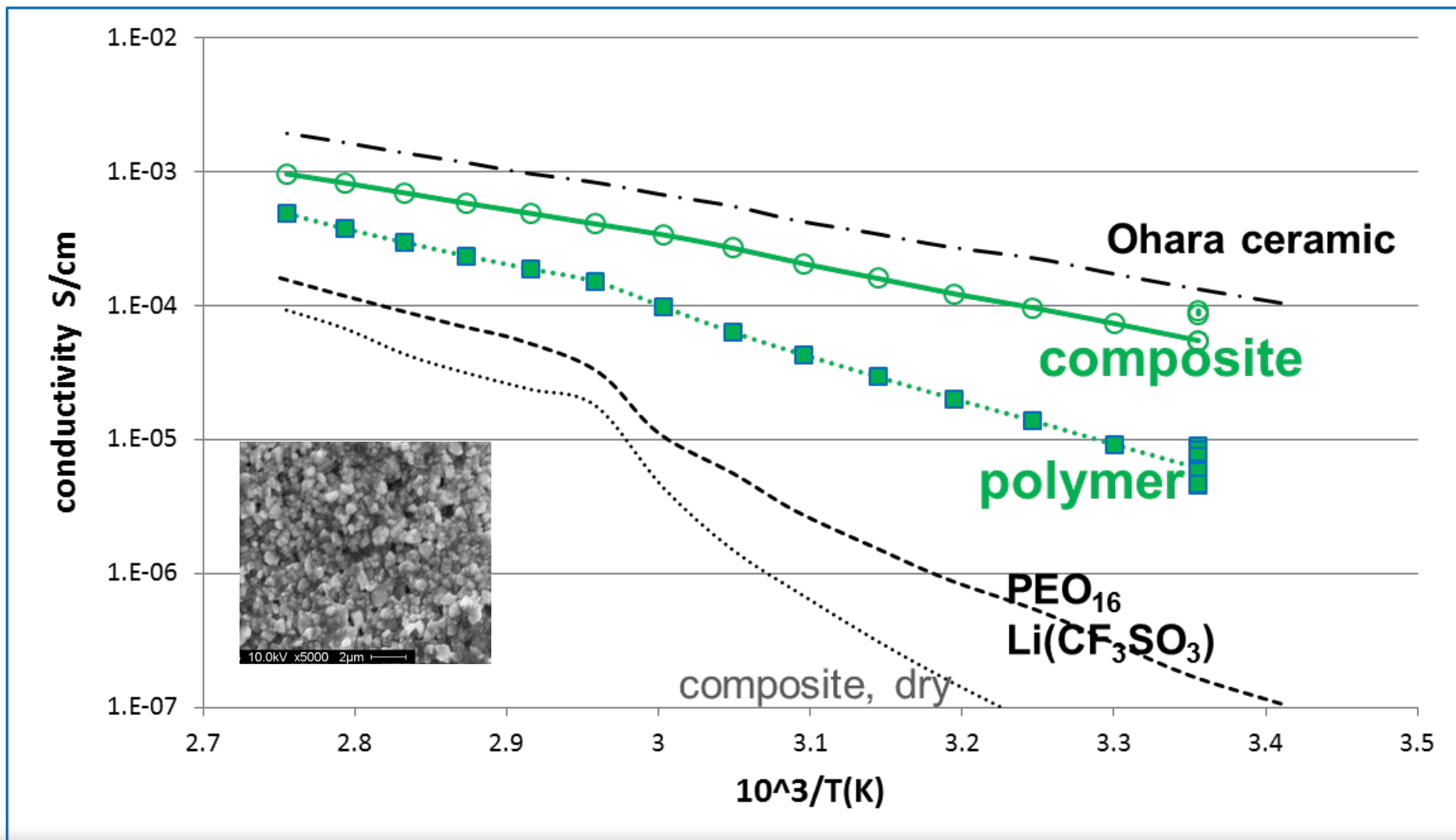
Dry mill and
melt form

Plasticized composite
40-50 vol% ceramic



Key technical accomplishment from last year:

- Composite of PEO + LiTf + 50 v% Ohara is conductive *if* DMC added.
- Composite is stiff because of high vol.% ceramic (*Response to reviewer*)



Now slurry coating replaces the melt-pressing of the composite membrane

- Problems with melt-pressing, so abandon
 - Small samples, difficult to scale to uniform, very thin membranes.
 - DMC reacts in direct contact to Li metal.



- First efforts from slurries, doctor blade coating of aqueous and acetonitrile slurries
- Replace DMC, with more stable

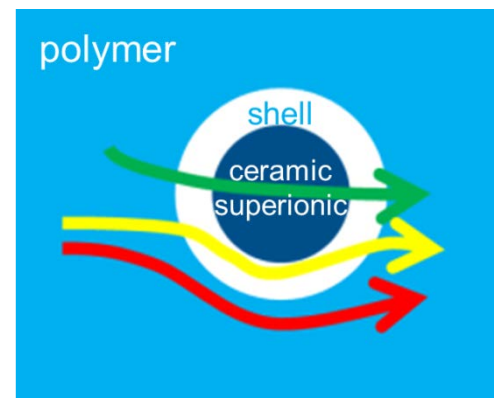
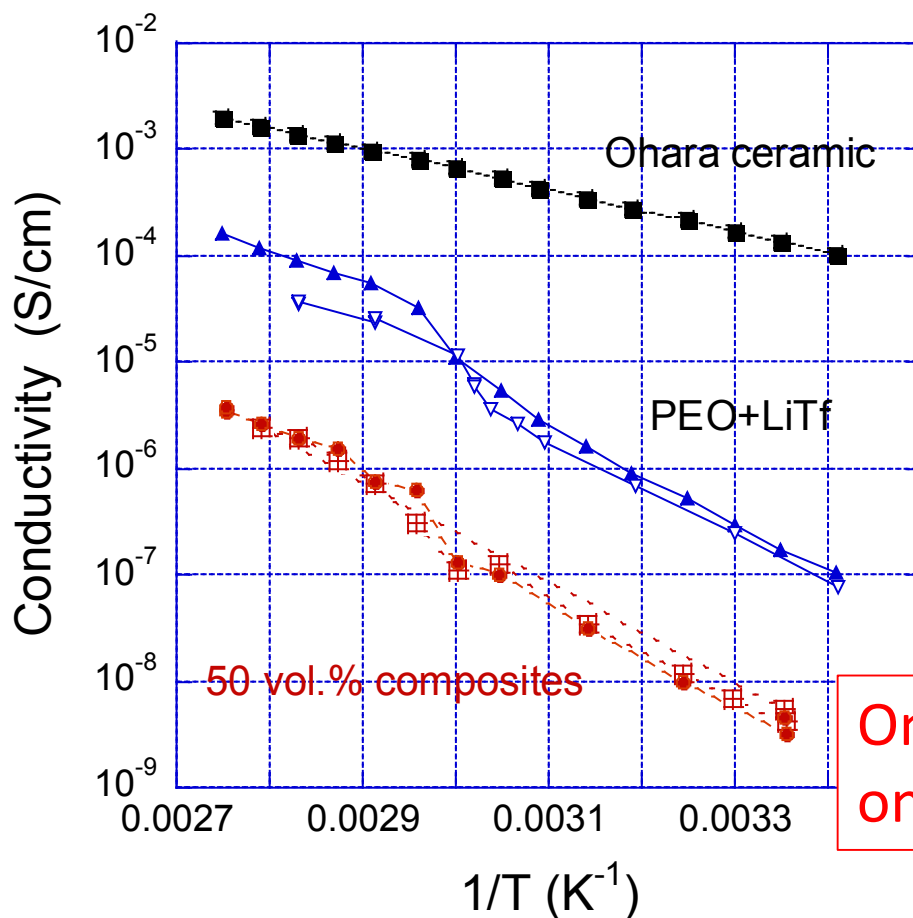
“dry” composite



Solution and
slurry cast

Composites (50 vol.% Ohara ceramic) cast by doctor blade are similar to melt-pressed.

- Achieved stable slurries, using both aqueous and acetonitrile carrier
- Doctor blade to coat; heat to dry
- Result - conductivity very low, \approx melt cast before DMC treatment.



Li⁺ ions likely going around the ceramic particles

One aqueous,
one acetonitrile.

Several methods to form and coat slurries with high ceramic loading have been demonstrated

- Processing using doctor blade was slow process and gave low conductivity and poor uniformity.
- Subsequently, large area thin membranes by spraying slurry using (manual) air brush was better. Technique is still being improved.



“Dry” composite

dry by heating

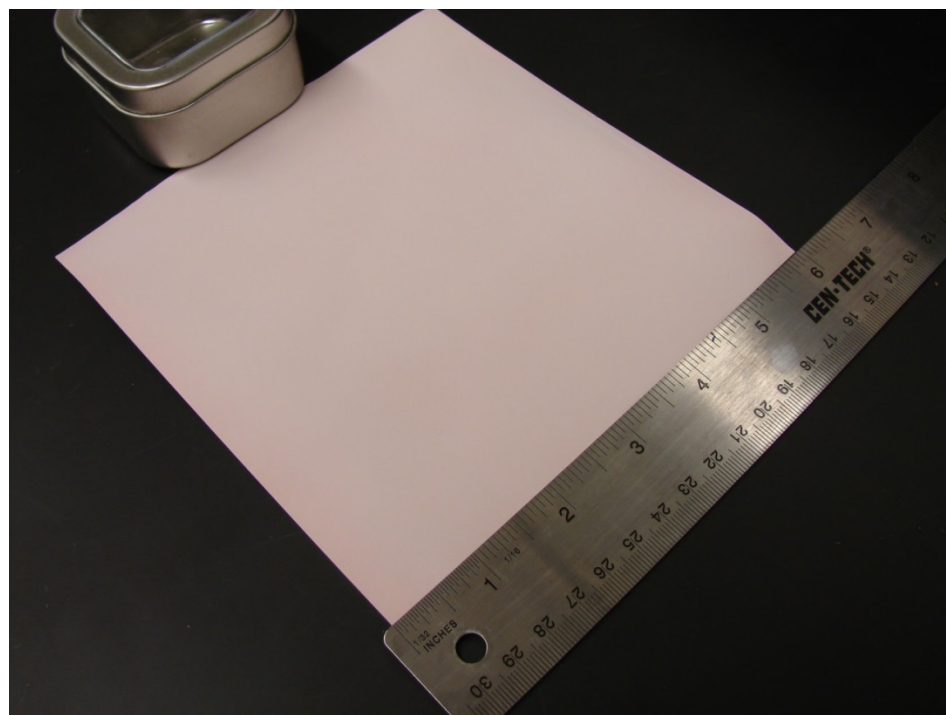
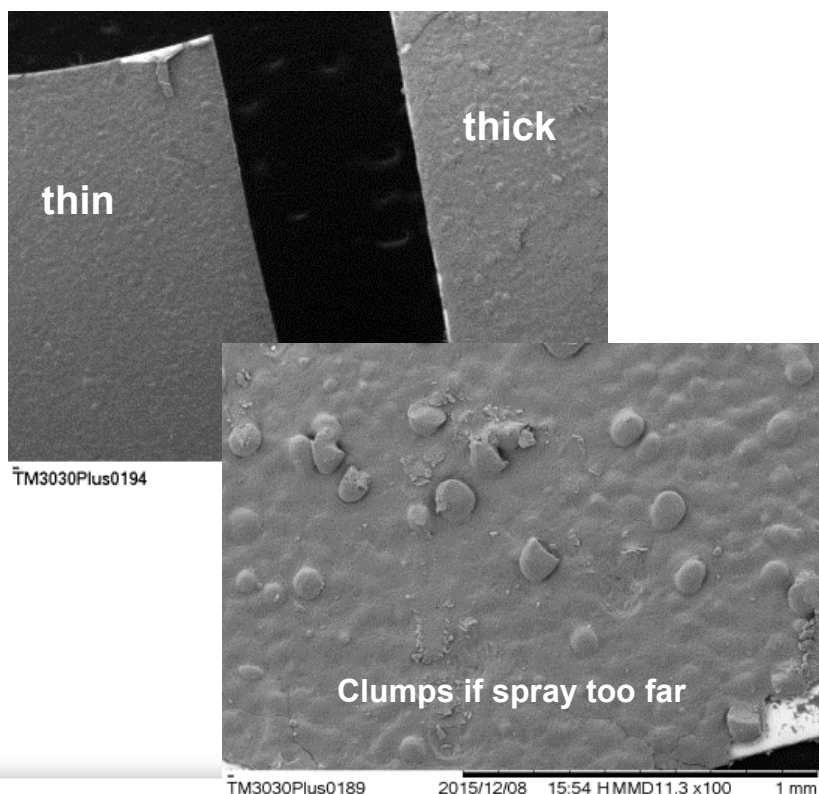
Slurry of PEO + salt + Ohara power + additives

- Aqueous solution
- Sonicated for dispersion
- Low viscosity for sprayer

Solution and slurry cast

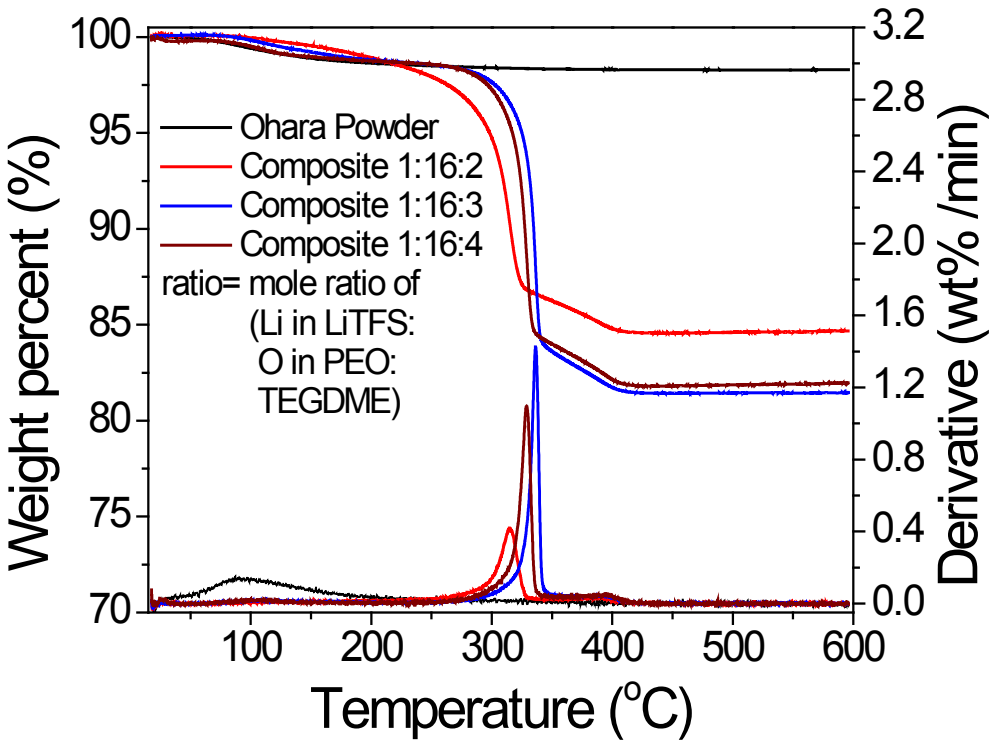
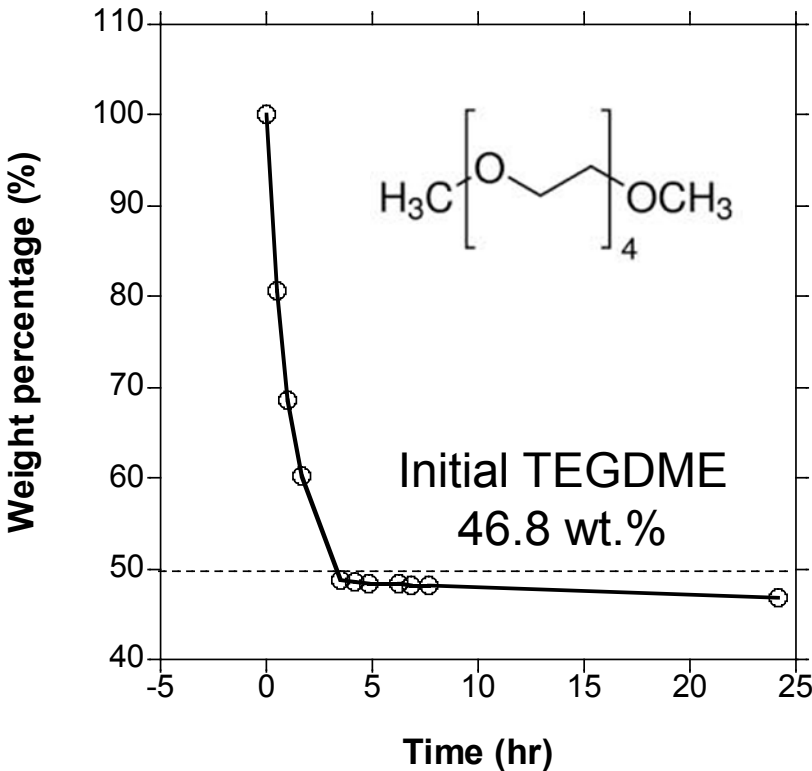
Good quality composites (50 vol.% Ohara ceramic) were formed by spray coating

- Faster than doctor blade. Air brush good at low viscosity slurry, infinitely scalable.
- On copper, C-coated aluminum, and stainless foils.
- Wetting, uniformity improved with TEGDME. Approx. 30-50 μm before pressing.
- Composition 16:1:4 (EO:Li:TEGDME) to be consistent with earlier melt-pressed.
- Techniques for spray and slurry dispersion are important for quality.



TEGDME added to the slurry remains in the coating, but water is removed with careful drying.

- TEGDME is mixed with H₂O solvent in slurry; TEGDME should remain.
- Gravimetric test (left) with liquid mix at 80°C shows all the water lost in 5 hrs.
- From TGA under N₂ (right), TEGDME may be as stable as the PEO.

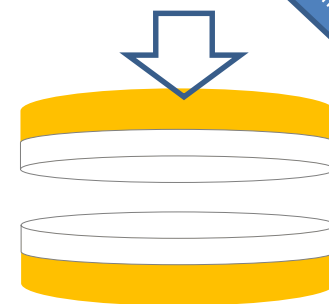


TEGDME: 222=MW, 275°C=bp, 1.009 g/cc, <0.01 mmHg(@20°C)

TEGDME and physical pressing increase conductivity of the composite membrane

- Samples formed of two disks, coatings facing,
- Pressed, 3-7 tons/cm², to increase composite density
- Then assembled in coin cells, and heated before EIS.

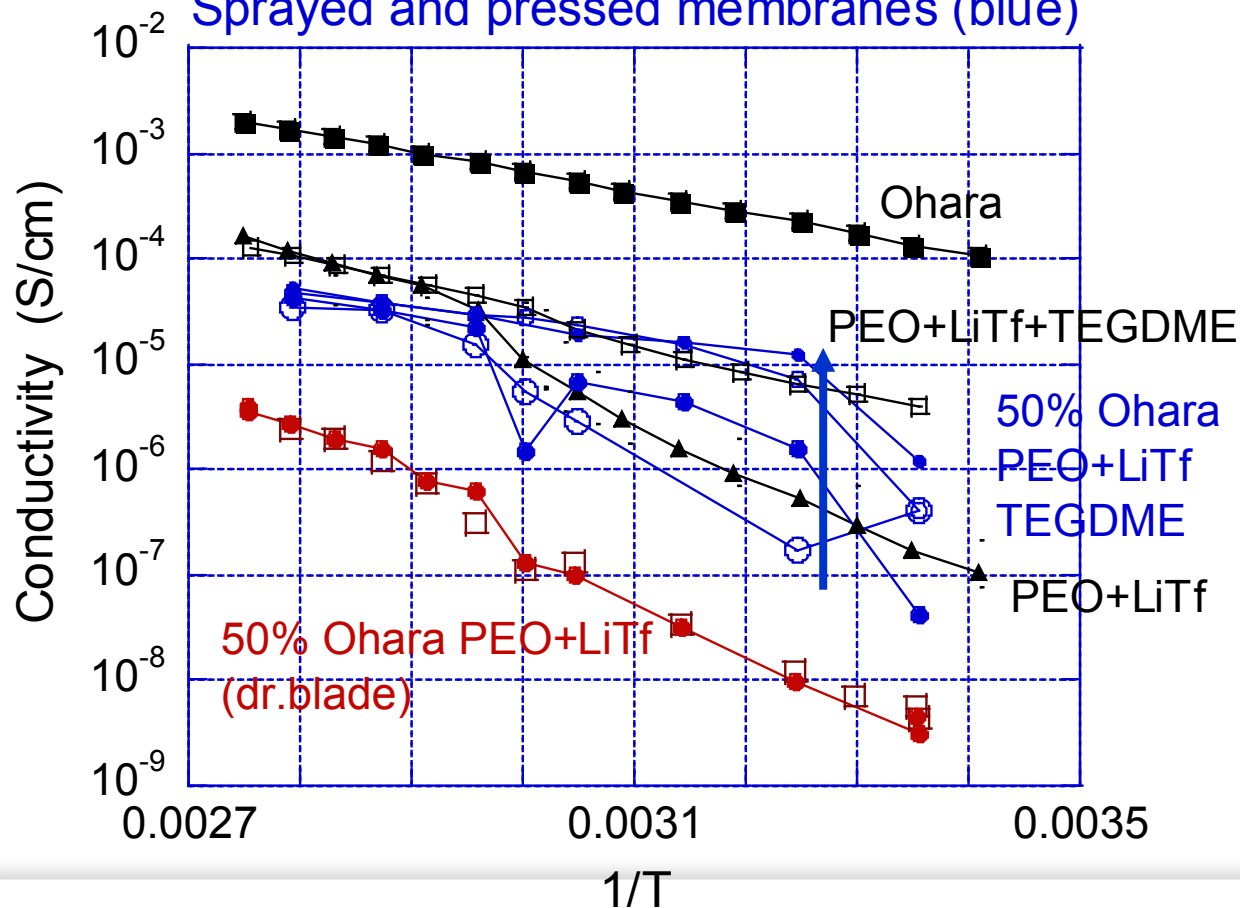
ACCOMPLISHMENT



Coated Cu disks



Sprayed and pressed membranes (blue)

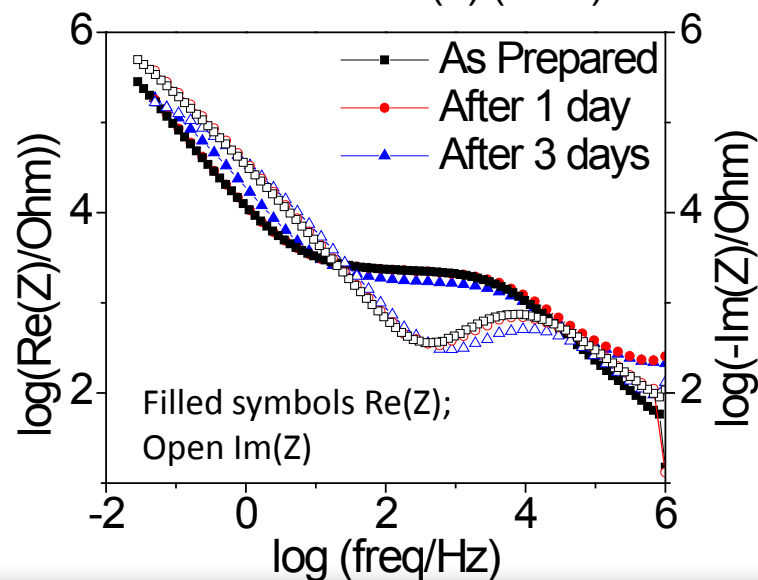
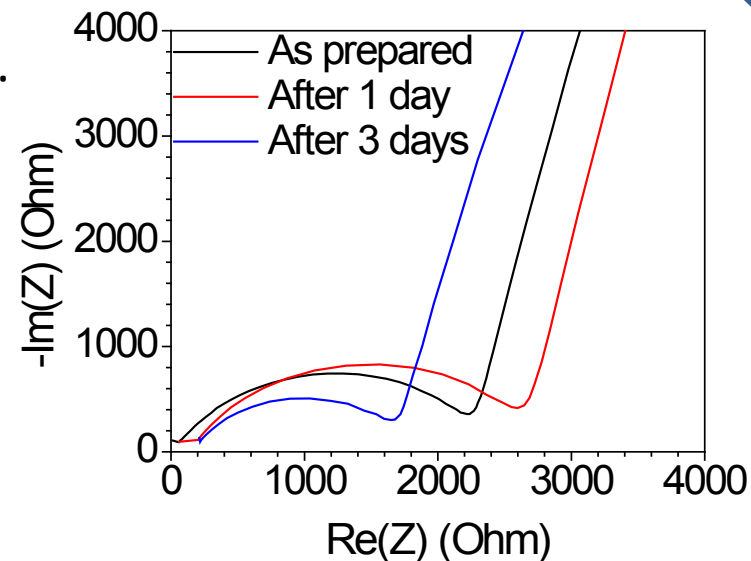
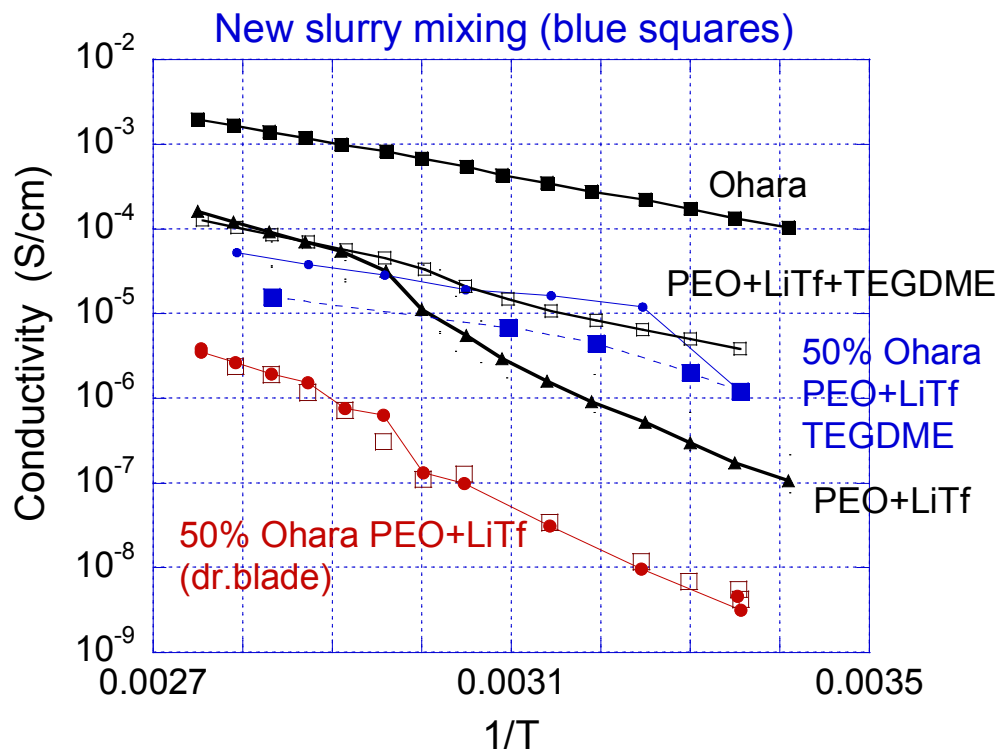


- Some scatter in data, so trends are not clear
- Activation energy is similar to melt pressed pellets treated with TEGDME.

↑ Indicates higher pressure (smaller symbols) applied to membrane

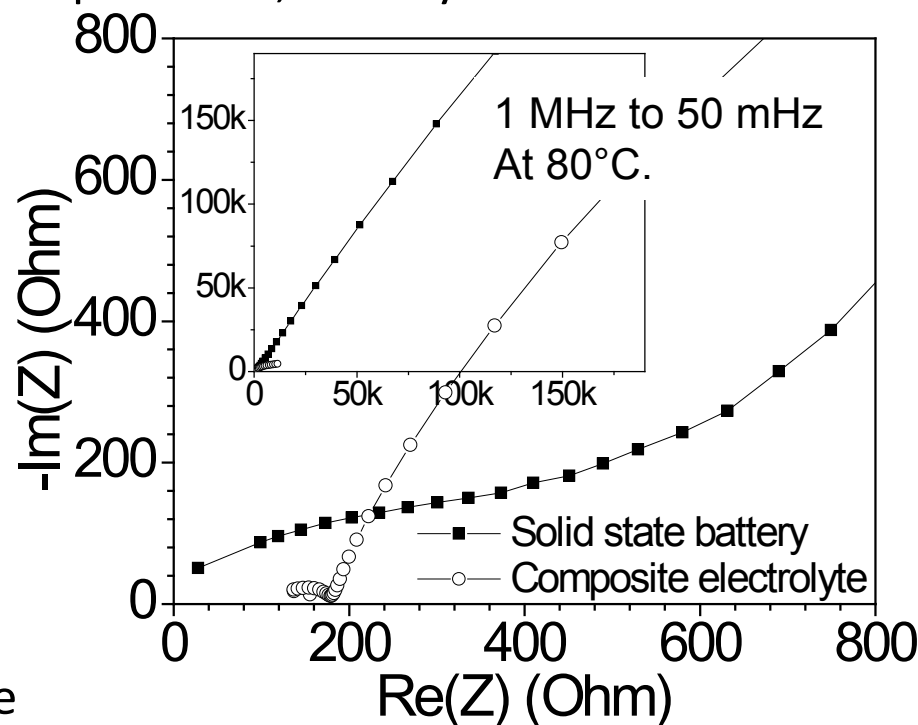
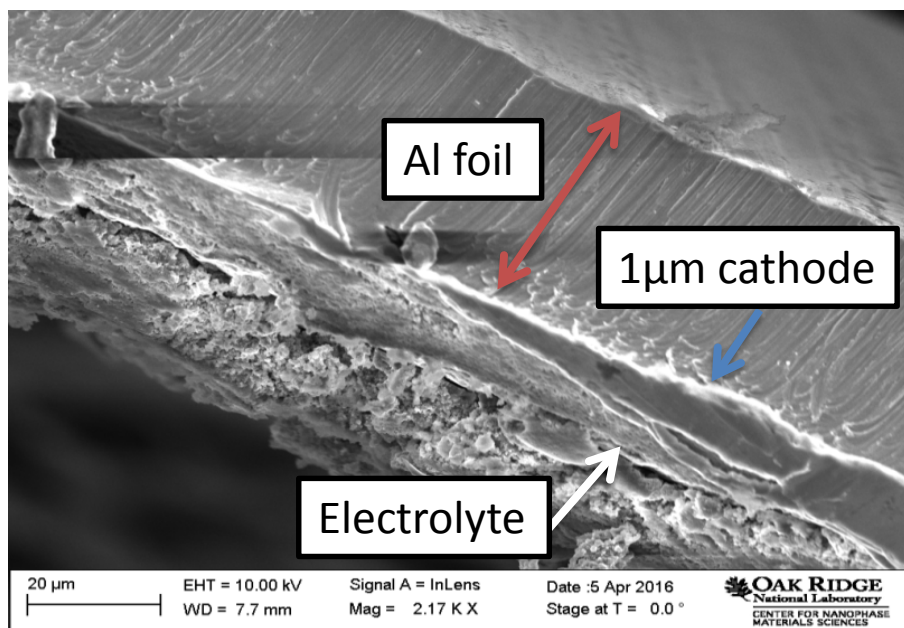
Latest membranes are better behaved, which is attributed to improved slurry preparation.

- Components added sequentially with sonication.
- Again spray coated and dried at 80 °C as before.
- EIS has expected behavior with blocking contacts.



Initial attempts to form battery are promising. Li may passivate with TEGDME.

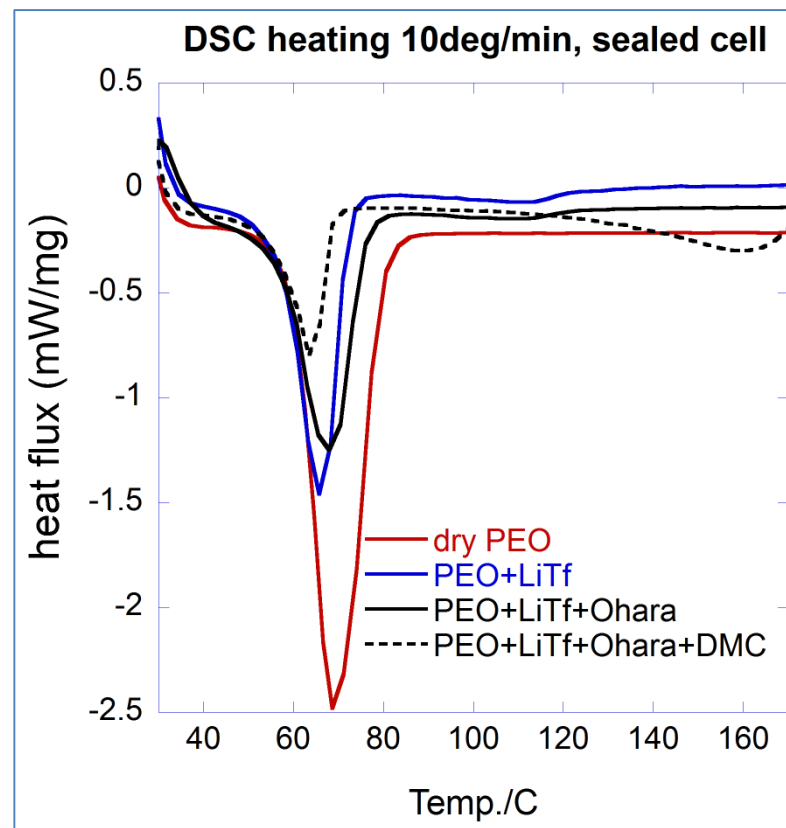
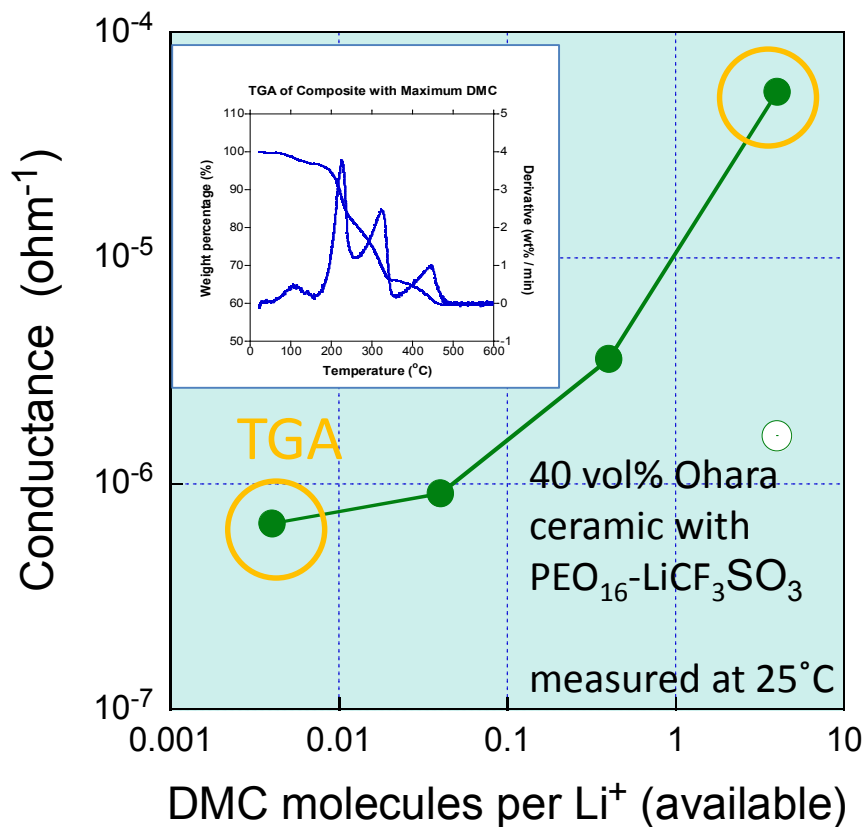
- Composite was sprayed over thin film ($\sim 1 \mu\text{m}$) cathode on Al foil, dried, pressed.
- Pressing Li sheet to surface caused shorts. (Li disk is too thick, electrolyte is very thin.)
- Vacuum vapor depositing Li anode resulted in reaction at interface, but this may passivate. Result was stable, although compromised, battery 1.7V at RT.



- With only 1 μm Li, the Li appeared to be reacted. No metallic contact possible.
- With 20 μm , Li looks ok – cell alive.

Water, DMC, and TEGDME incorporation into composites has been evaluated by TGA, DSC, FTIR to quantify effects.

- Only examples shown here.
- Tests quantify the amount and stability of the molecular additives, and their effect on PEO crystallization.



Future Work

- **Remainder of FY16**

- Continue tests of spray composite electrolyte with TEGDME to establish Li stability.
 - Temporarily reducing ceramic loading may facilitate this, although maximizing the ceramic loading is key to optimizing mechanical and transport properties.
 - Test stability between Li and a cathode, rather than symmetric Li-Li cell for correct potential gradient and view toward practical battery fabrication.
- Identify suitable barrier treatment or coating to passivate the Li for extended cycling. Practical coating from solution, as well as vapor depositions, will be evaluated.
- Evaluate TEGDME effect on Ohara/PEO+LiTf polymer interface by EIS of trilayer samples.
 - This will be compared to effects of DMC on interface versus bulk polymer transport.
- Open up the polymer composition to investigate alternative Li salts and concentrations

- **FY17**

- Improve composites, substitute LLZO garnet powders for Ohara particles.
 - The LLZO electrolyte offers stability with Li, but is more reactive in air, forming Li_2CO_3 .
- Explore bimodal size distribution for higher ceramic loading and control of processing and mechanical properties.
 - This may identify tradeoff between jamming particles together for high stiffness while providing for effective densification during processing.

Challenges and mitigation

- TEGDME is stable to near Li/Li⁺ potentials, yet this may not passivate the Li interface; and it does not greatly enhance the conductivity, as does DMC. A practical substitute for TEGDME is not apparent
- A barrier layer between the thin composite electrolyte and Li metal will likely be needed for uniform Li plating as well as passivation.
- Having a high ceramic loading is critical to high modulus and high conductivity, but makes processing of very dense membranes more difficult due to particle jamming effects. Modifying the composite with bimodal particle sizes may provide an additional means to tailor the processing while increasing the ceramic component.

Collaborations and coordination

- Collaboration with Jeff Sakamoto and his team investigating the stability of Li with the LLZO garnet ceramics. This includes coordinated sample preparation with Li deposited at ORNL and LLZO from Michigan. We have joint publications; several are in preparation.
- Coordination with a BES program at ORNL is growing; both programs focus on solid electrolytes, particularly the bulk and interfacial ion transport.
- Ceramic electrolytes supplied by: Ohara Corp. and Jeff Sakamoto

Summary

- **Relevance** Success of our composite electrolyte will isolate the anode from any liquid electrolyte, enabling very high energy 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. Interface is critical.
 - New approach this year to demonstrate slurry-based approach to making composite membranes.
 - Membranes evaluated for conductivity and stability with thin layers of vapor deposited Li metal.
 - Having a high ceramic loading is critical to high modulus and high conductivity, but makes processing more difficult.
- **Technical accomplishments** Good quality composites (50 vol.% Ohara ceramic) were formed by spray coating (by hand) from aqueous slurry. Membranes are ~25 μ m thick x large area ~6x6 inch.
 - Water and acetonitrile can be dried from the sprayed or drawn coatings; conductivities match earlier results from melt-pressed composites. TEGDME added to the slurry does not evaporate.
 - TEGDME and physical pressing increase density and conductivity of the composite membrane. Details of slurry preparation also influence uniformity.
 - Initial attempts to form battery are promising. Li may passivate with TEGDME.
- **Future work**
 - Continue evaluation of thin spray coated composite electrolyte membranes for stability with Li and in Li metal battery. Test barrier coatings as needed.
 - Move toward alternate materials and particle size distribution control.
 - As time permits, continue fundamental investigation of the polymer-ceramic electrolyte interface.
- **Collaborations and coordination** – key collaborations Sakamoto and Ohara

Response to previous reviewer comments - A mixed response from reviewers, depending upon their focus on application or understanding the materials and interfaces.

Reviewer comments last AMR (June 2015)	Response
“The promise of a solid electrolyte for Li batteries is high ... but this technical plan got waylaid. ... intention to scale up.”	In this and other review comments there is disagreement about effort to understand the interface, or show progress toward technical goals. A difficult balance – see reviewer only slide.
“the work does not appear to be reproducible in another lab or even after the glove box was changed for maintenance”	I almost did not mention the contamination in high quality glove boxes to avoid this concern. But, there are two important points: 1. Caution that some reports in literature might have missed this effect, 2. There may be a way to enhance transport across the interface without adding plasticizing molecules.
“use theory and simulation to explore mechanical stability has apparently been postponed ... it may be helpful to know whether these impurities would also cause problems with mechanical properties...”.	In earlier years, the theory built the foundation for the program. Also, the reviewer may have missed the important point that at high ceramic loading, the packing of the ceramic particles against themselves provide mechanical stiffness. The polymer could in fact be fluid.