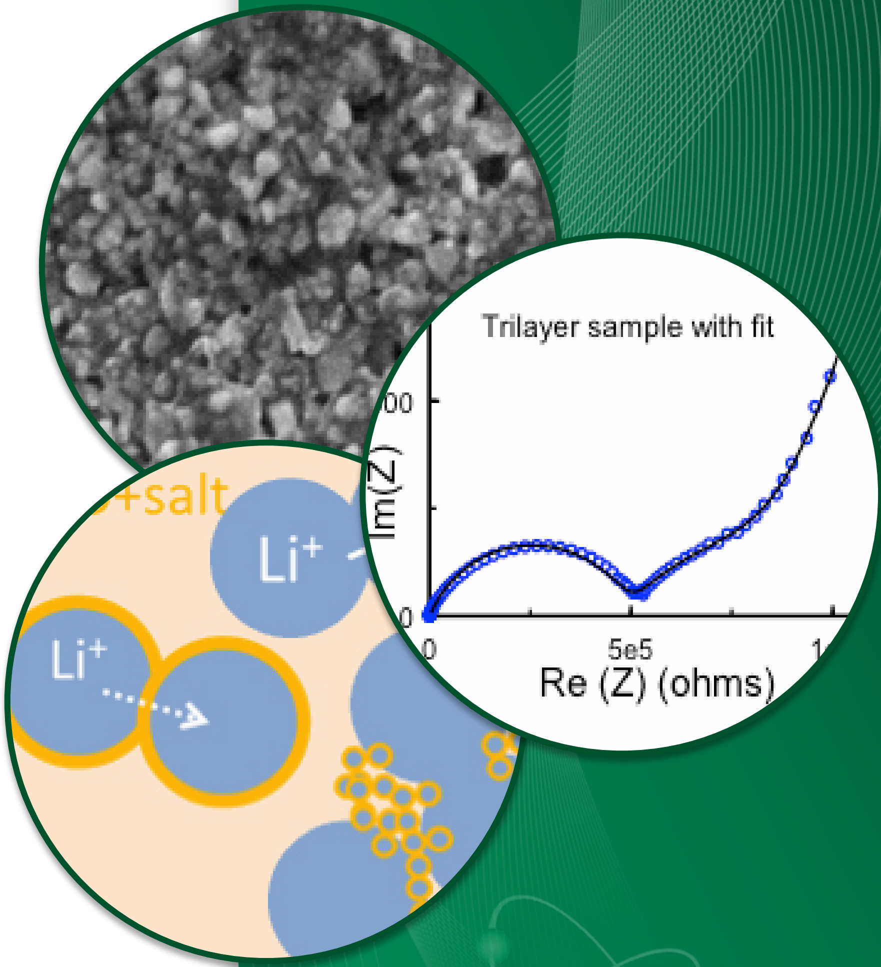
Composite Electrolyte to Stabilize Metallic Lithium Anodes

Project ID: ES182



Nancy Dudney and Sergiy Kalnaus

Oak Ridge National Laboratory

Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting

June 2015

Overview – Composite Electrolytes to Stabilize Li Metal Anode

- **Timeline**
  - Start October, 2011
  - End September, 2016
- **Technical barriers**
  - Energy density (500-700 Wh/kg)
  - Cycle life, 3000 to 5000 deep discharge cycles
  - Safety
- **Budget**
  - $335k FY13
  - $400k FY14

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

Overview – Composite Electrolytes to Stabilize Li Metal Anode

- Timeline
  - Start October, 2011
  - End September, 2016

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

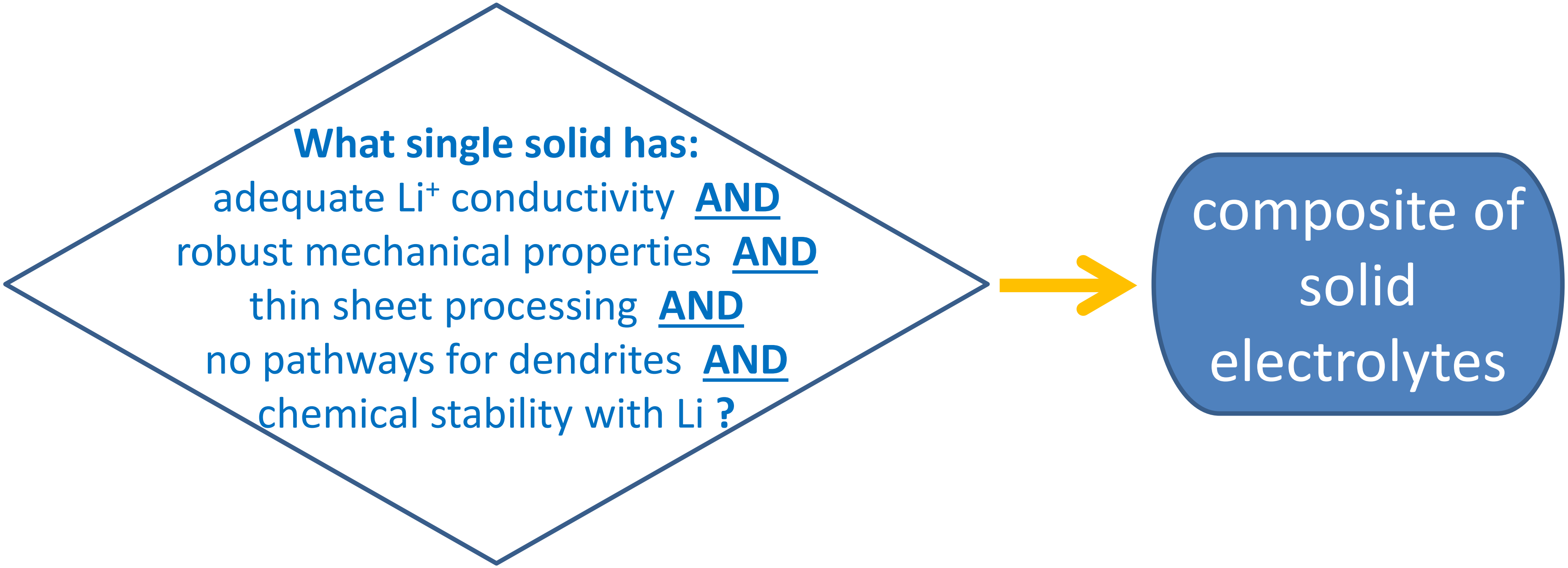
- Budget
  - $335k FY13
  - $400k FY14

- Partners and collaborators
  - Oak Ridge National Laboratory (lead)
  - Center for Nanophase Materials Sciences, ORNL
  - Collaborators:
    - Jeff Sakamoto, Michigan State University
    - Nitash Balsara, UC Berkeley
    - nGimat, GA
    - 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

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

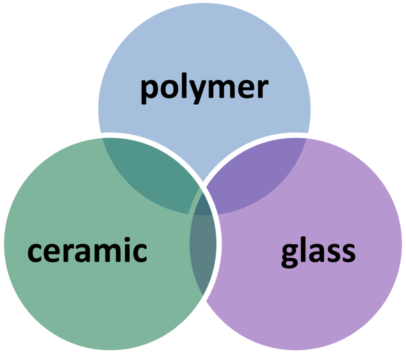
Relevance and Objectives

- **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
  - Identify design rules that can be generally applied to composites of other solid electrolyte materials
- **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)

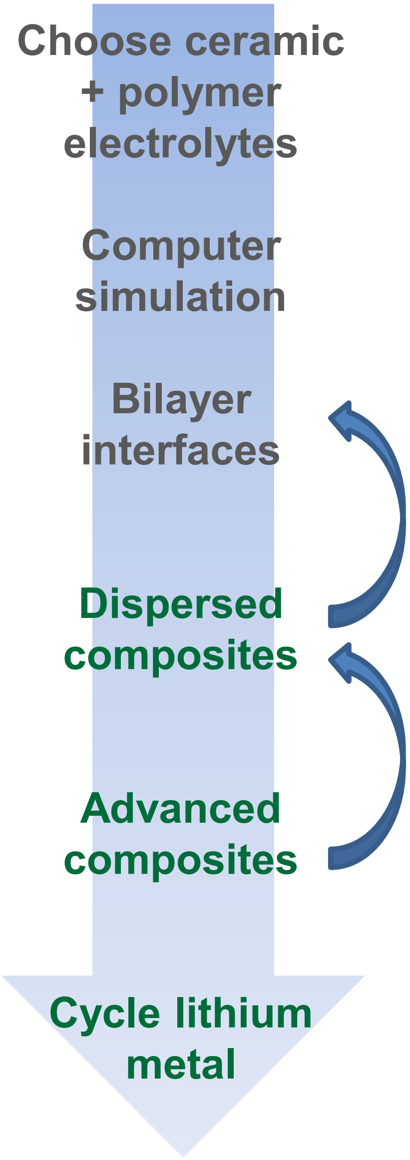
Milestones

Milestones: FY14-FY15	**Target:**	**Status:**
1. Fabricate ceramic-polymer composite sheets with **20-60 vol% ceramic** to determine the composition dependence of the conductivity as the structure approaches mechanical stability	Q1 FY14	✓
2. Demonstrate, with at least two **ceramic-polymer composites**, how the Li conductivity is impacted by either the connectivity or **dimensions of the component phases**	Q2	✓
3. Cycle the most promising composite electrolyte membranes with a thin **lithium metal electrod**e and quantify interface **resistance** and coulombic **efficiency**.	Q3	impedance, limited cycling ✓
4. Probe whether homogeneity of the composite electrolyte contacting the **Li electrode** is important to the interface stability in order to assess whether an **interface coating** is needed	Q4	lithium reacts ✓
1. Compare the **vapor absorption** (rate and equilibrium) of small molecules in a single phase polymer and a corresponding ceramic/polymer composite electrolyte.	Q1 FY15	✓
2. By generating a database with at least 5 compositions, determine if the presence of **trace solvent molecules** that enhance the ionic conductivity is also detrimental to the stability and cycleability of a lithium metal electrode, and if the effect can be altered by adding an intermediate films. (SMART)	Q3	on schedule

Approach -



1. Utilize known solid electrolytes.
2. Determine properties of interfaces joining different solid electrolytes
3. Use theory and simulation to explore mechanical stability and ion transport
4. Fabricate simple composites with high loading of dispersed particles and no solvents
5. Fabricate refined composites and develop practical processing methods.
6. Evaluate stability with lithium metal upon cycling.



Choose ceramic + polymer electrolytes

Computer simulation

Bilayer interfaces

Dispersed composites

Advanced composites

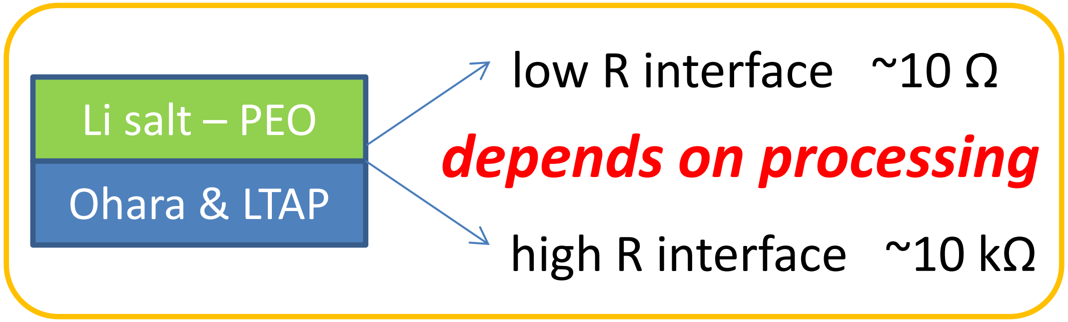
Cycle lithium metal

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.

Background: About a year ago, paths to low resistance polymer - ceramic interfaces and high conductivity composites were at hand.

- Processing was important, but why?



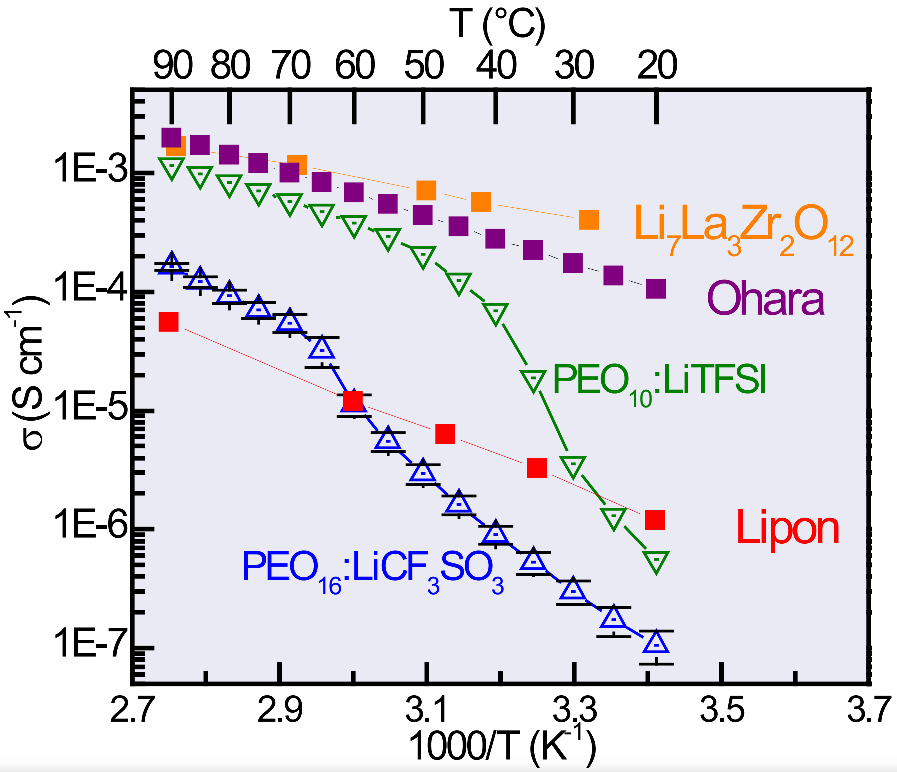
Li salt – PEO

Ohara & LTAP

low R interface ~10 Ω

depends on processing

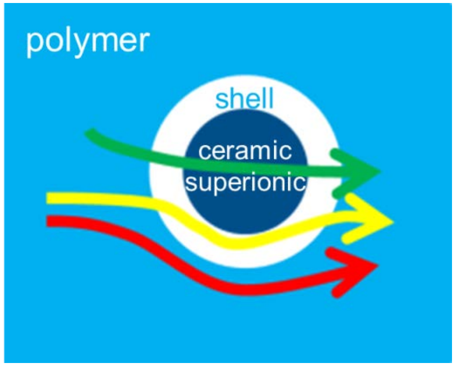
high R interface ~10 kΩ

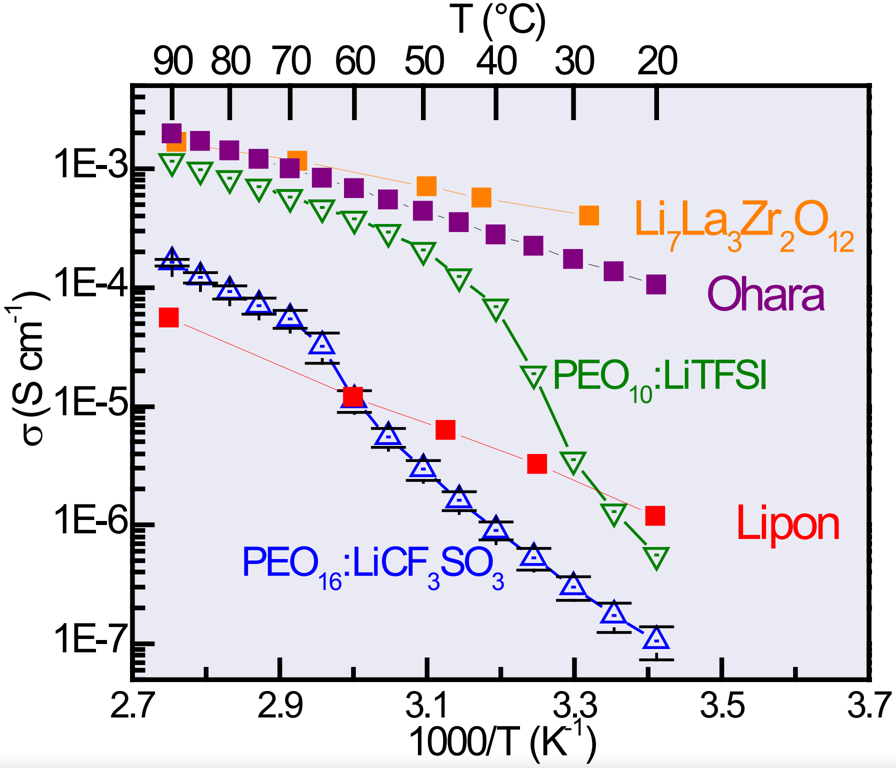


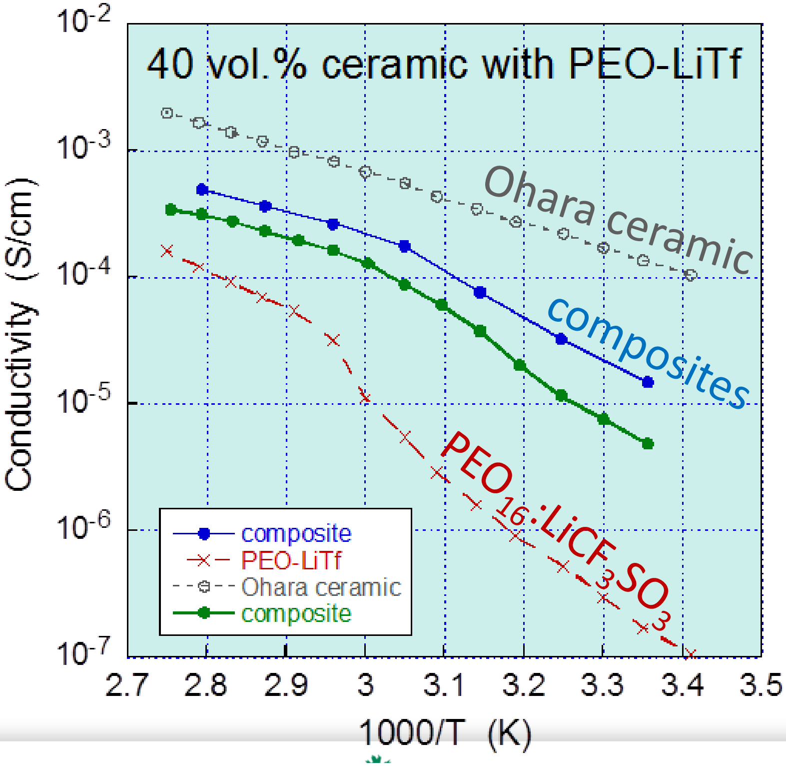
Ion transport across interfaces	
intrinsic	**extrinsic**
available lattice sites	reaction layer
space charge	impurity molecules
Li^+ solvation	voids, pores
polymer anchors	salt segregation

Background: About a year ago, paths to low resistance polymer - ceramic interfaces and high conductivity composites were at hand.

- Processing was important, but why?
- Need evidence that Li^+ ions cross interface in composite.

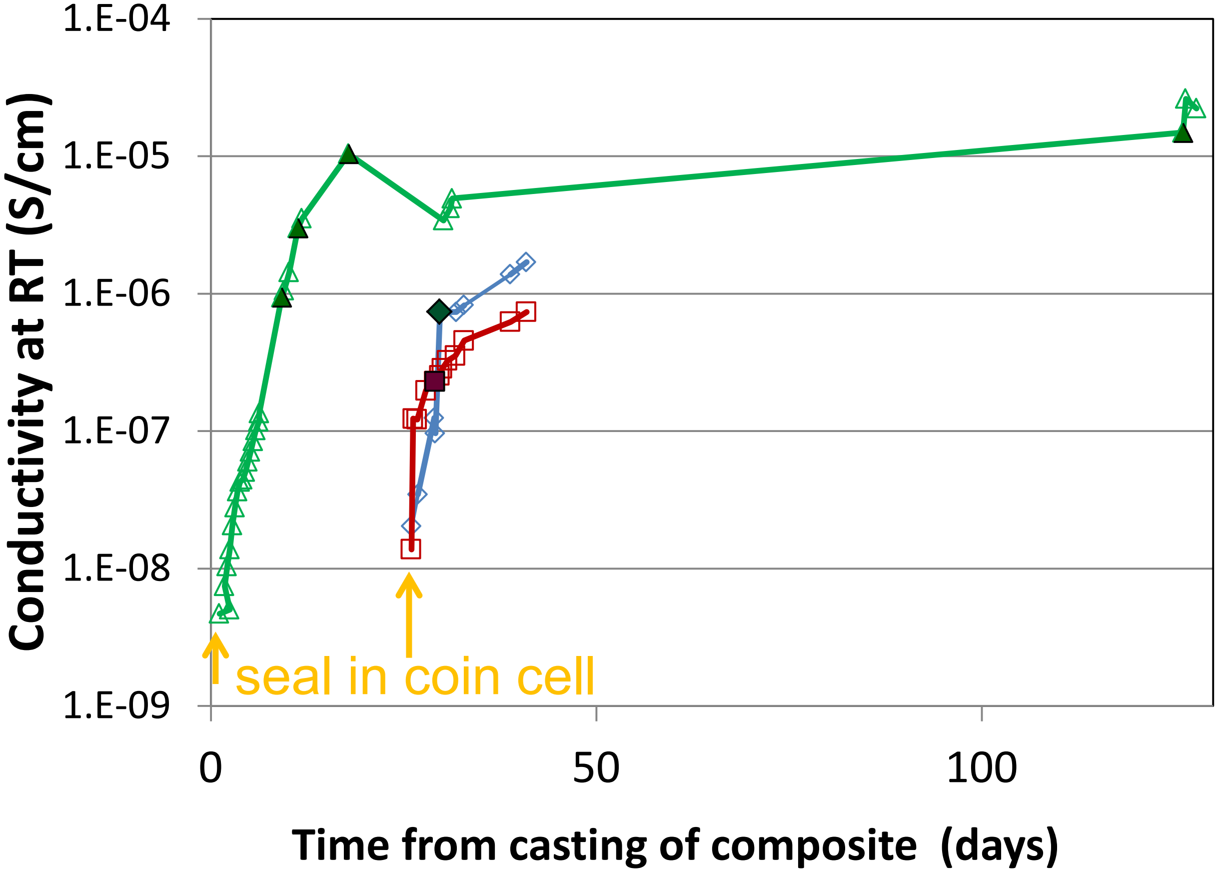






Technical progress: Several loose ends raise doubt about basis for highly conductive composite.

- Why is conductivity increasing and why so slowly?
- Why is increase initiated by crimping and not accelerated by heating?

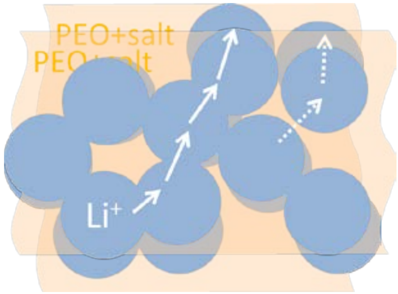


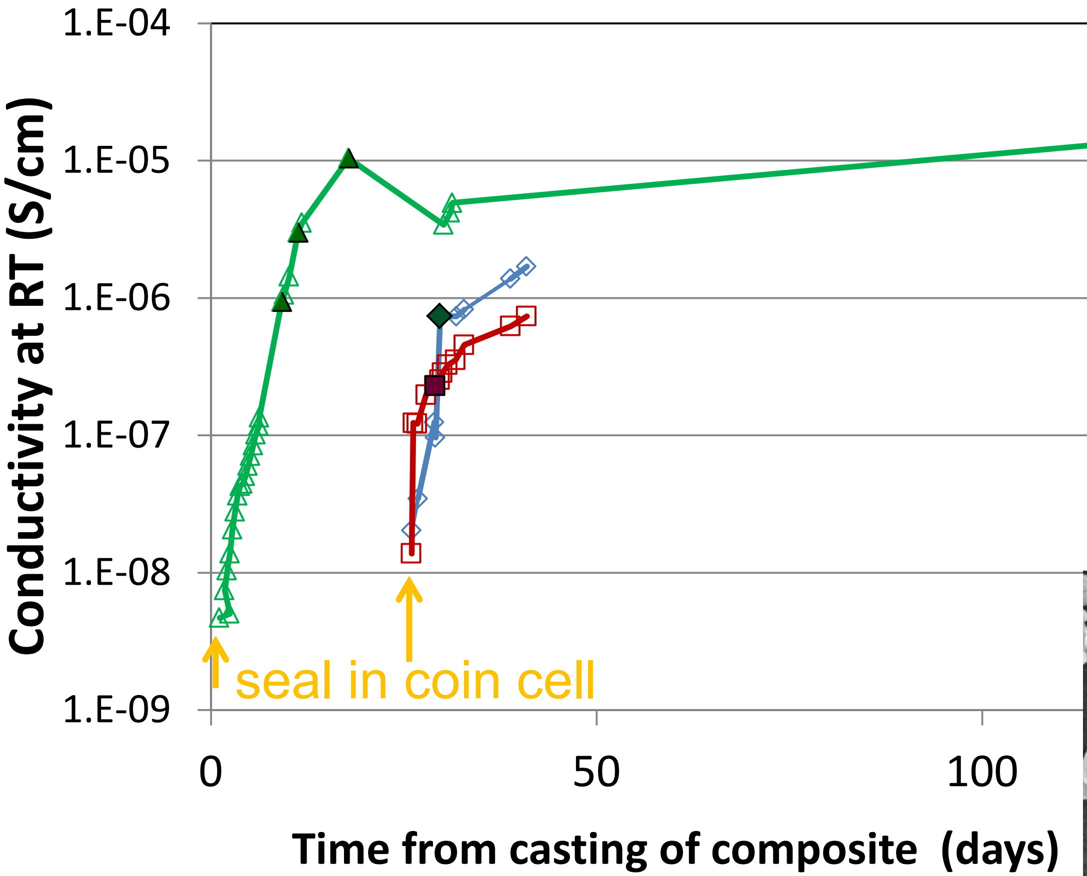
40-50 vol% ceramic
MW_{PEO} is 100k or 1M
LiTf salt

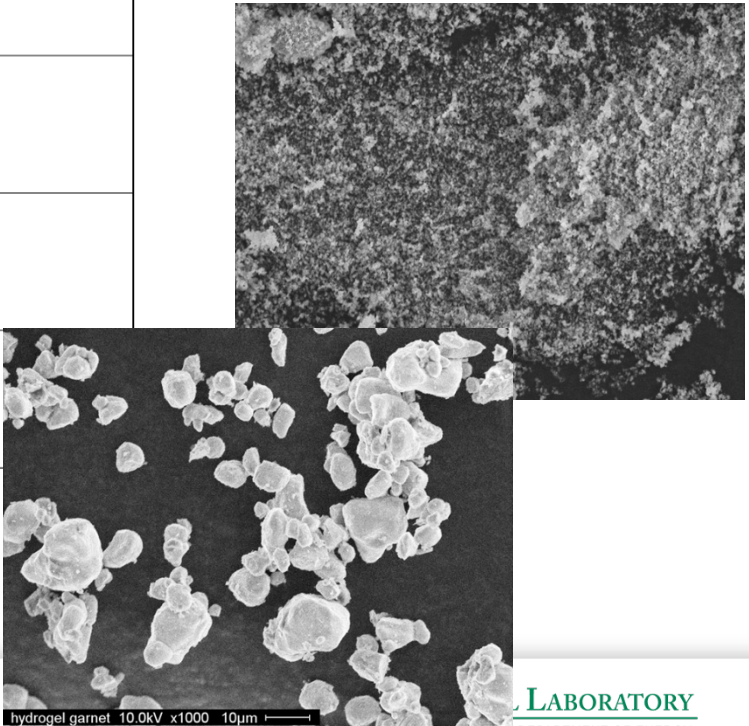
Darker symbols at RT
following scans to 90˚C

Technical progress: Several loose ends raise doubt about basis for highly conductive composite. (milestone)

- Why is conductivity increasing and why so slowly?
- Why is increase initiated by crimping and not accelerated by heating?
- Why does this change with coarser ceramic particles?

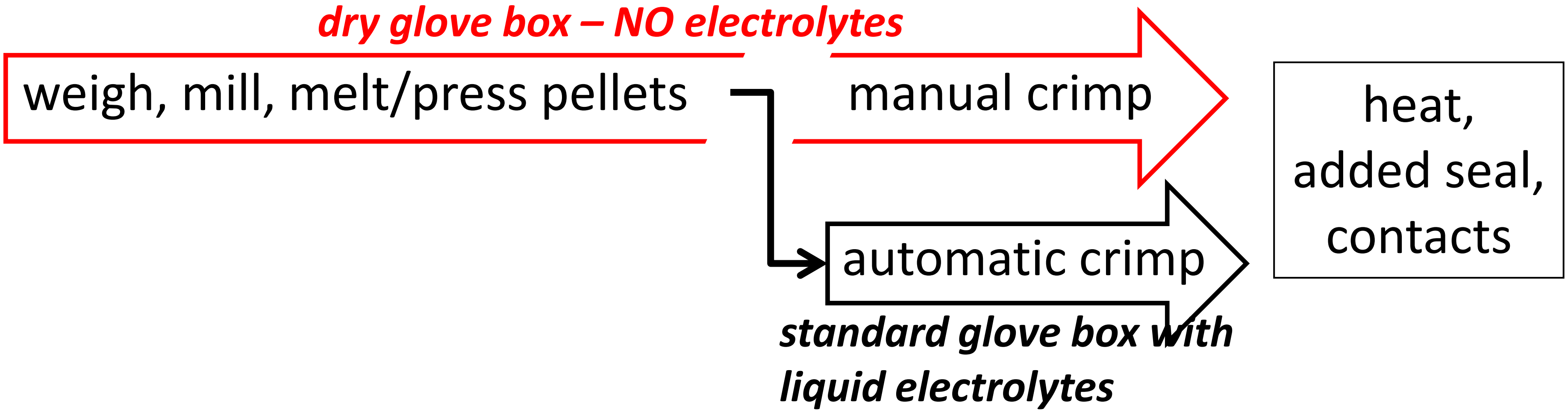






Technical progress: Further analysis showed effect of glove box.

- Alternative explanations
  - Crimping into coin cells → composite percolated conductive path
  - Exposure to standard glove box for crimping



dry glove box – NO electrolytes

weigh, mill, melt/press pellets

manual crimp

automatic crimp

standard glove box with liquid electrolytes

heat, added seal, contacts

Technical progress: Further analysis showed effect of glove box.

- Alternative explanations
  - Crimping into coin cells → composite percolated conductive path
  - Exposure to standard glove box for crimping

dry glove box – NO electrolytes

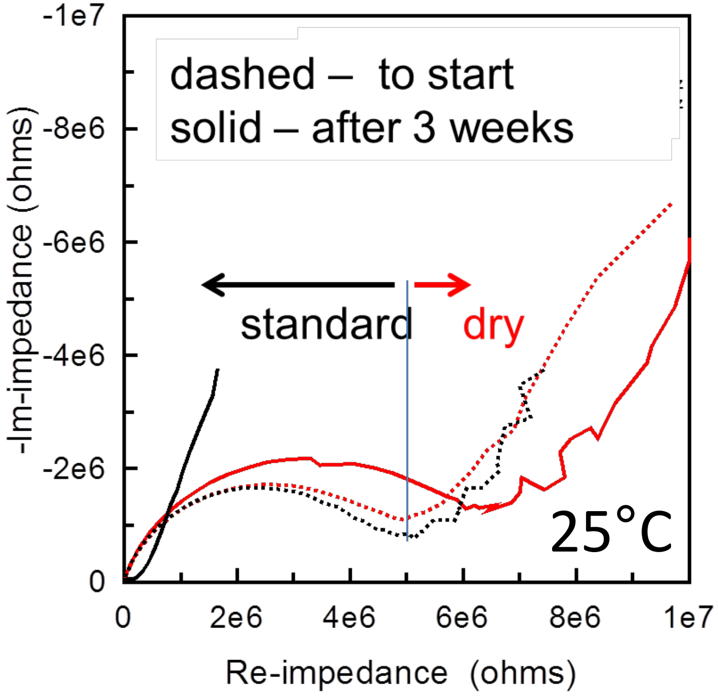
weigh, mill, melt/press pellets

manual crimp

automatic crimp

standard glove box with liquid electrolytes

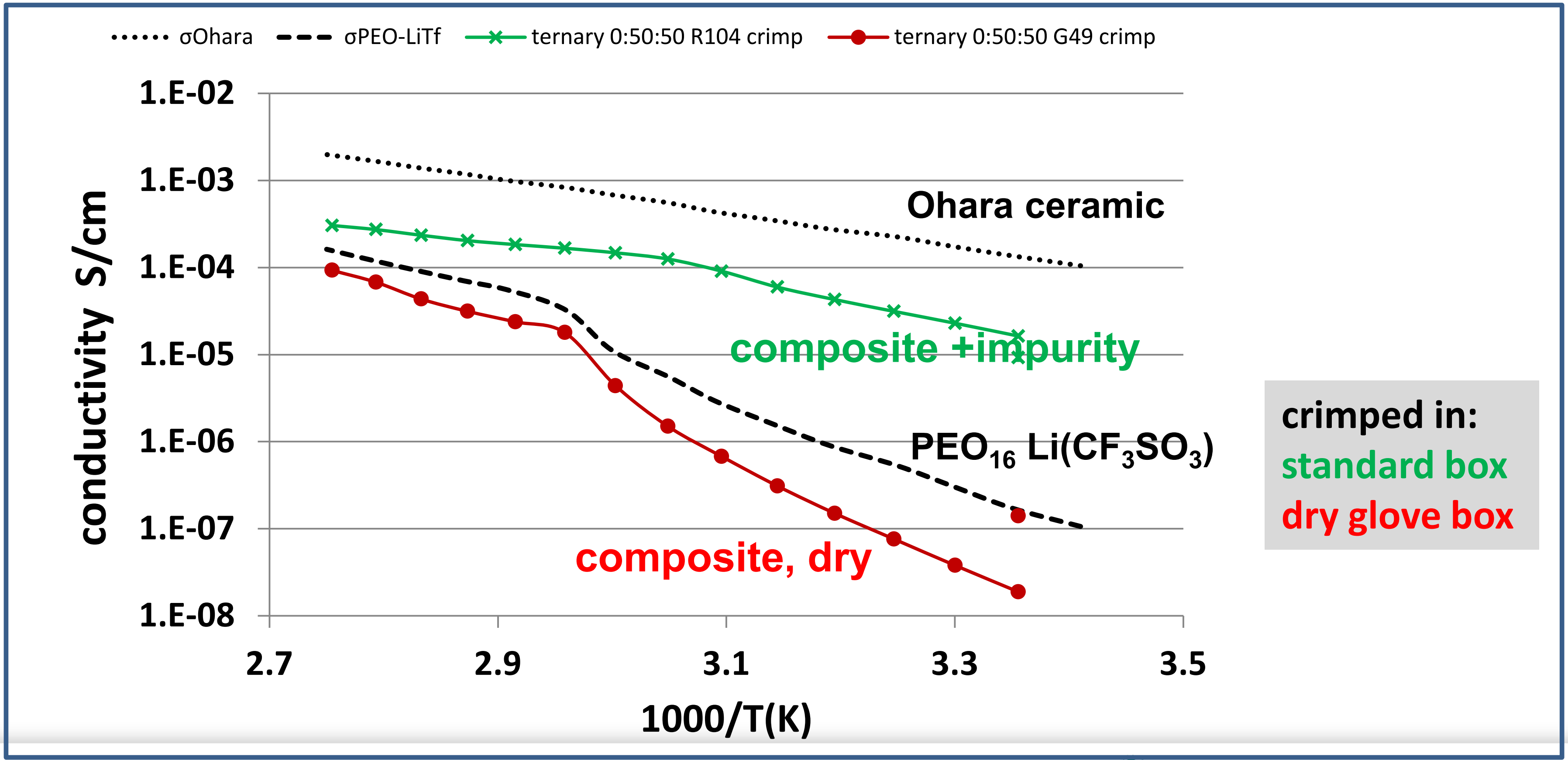
heat,
added seal,
contacts



- Reproduced with several side by side sets

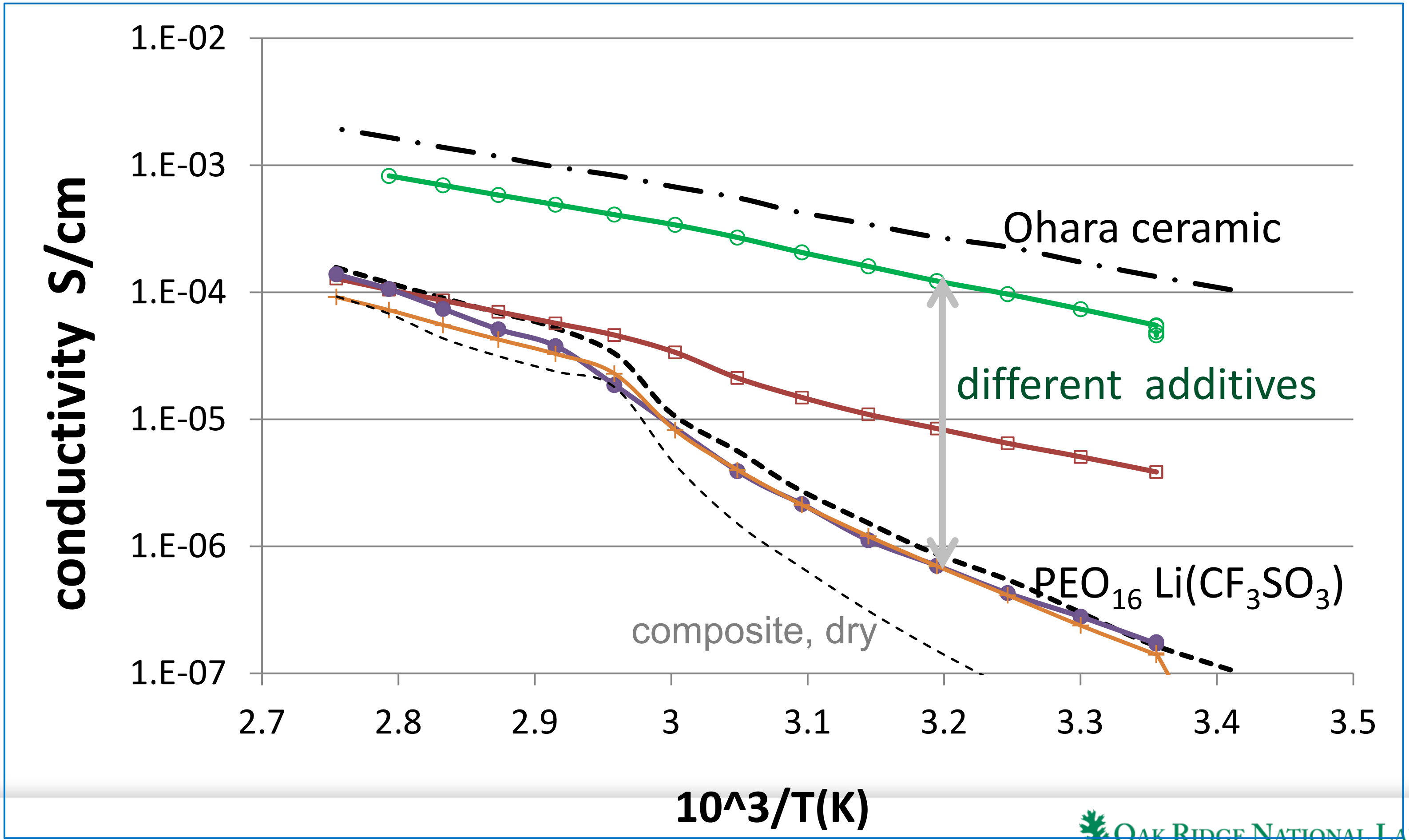
Technical progress: ~ 15 minutes in a standard glove box makes a huge difference in the ionic conductivity. Due to contamination?

- New investigation (milestones FY15)
  - Treat composite and polymer electrolytes with selected vapors
  - Revisit planar interface studies



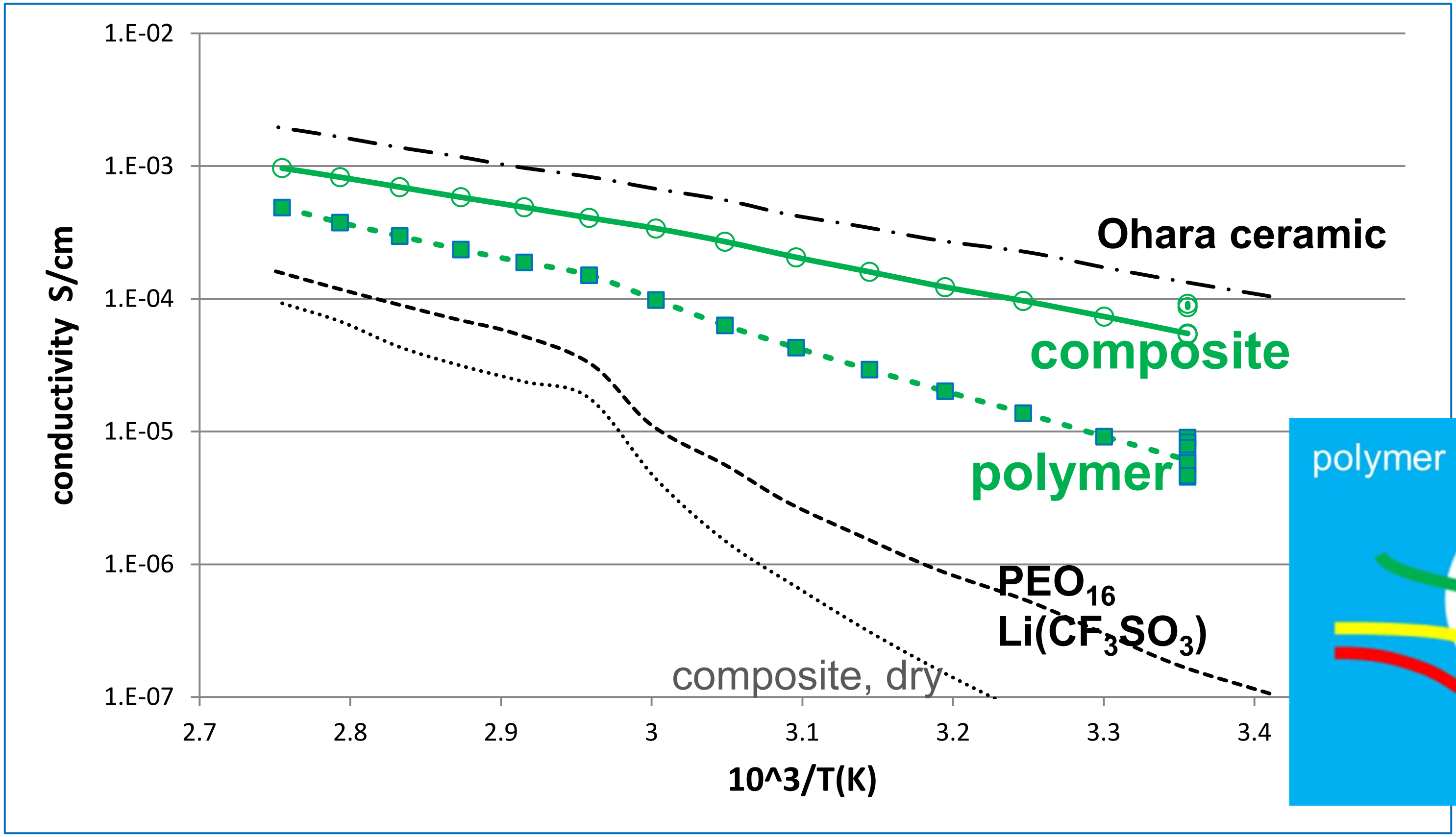
Technical progress: Intentional exposure to likely vapor phase ‘contaminants’ or additives give little to large enhancement

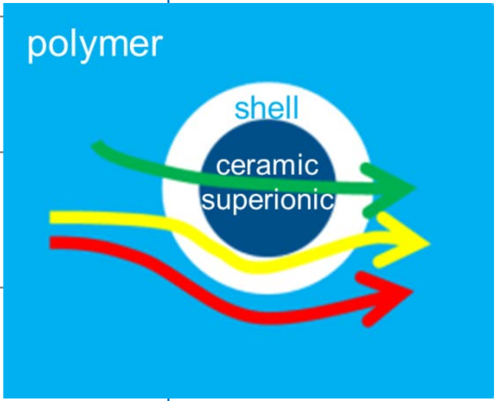
- Some additives inhibit polymer crystallization, others no effect.
- Others provide enhanced conduction



Technical progress: DMC and water vapor treatments have large effects for polymer-alone and composite

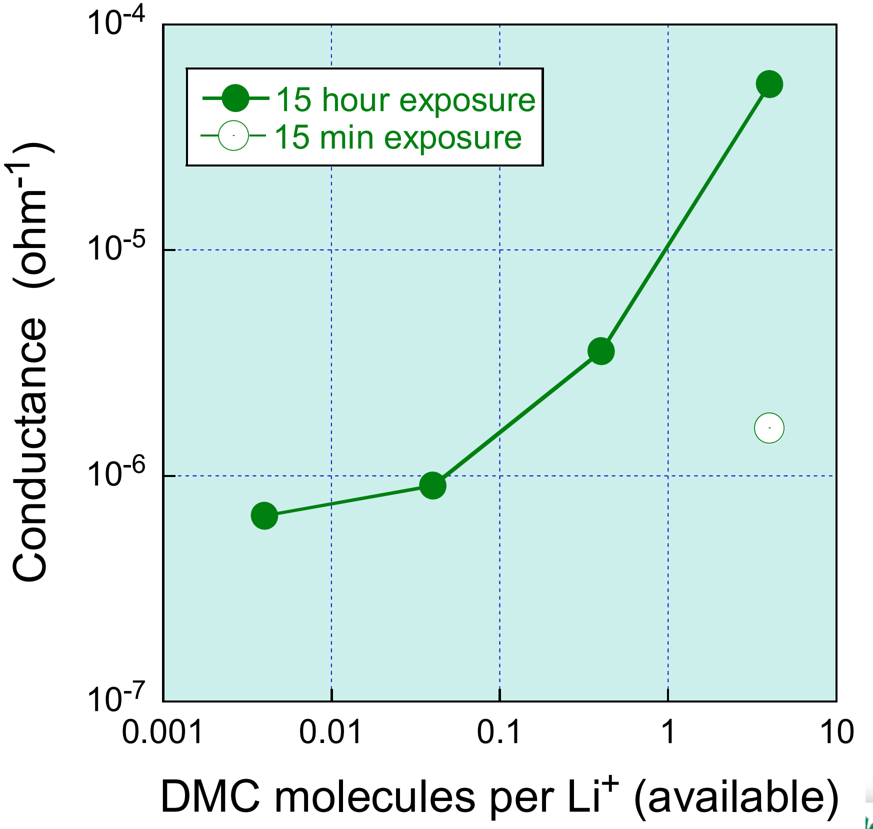
- Treatment in DMC saturated Argon → enhanced conductivity
- Higher conductivity for composite, but ion path still uncertain





Technical progress: Controlled dose of DMC indicate that DMC is readily adsorbed, but trace quantities have small effect. (milestone)

- Plot assumes all available DMC is adsorbed.
- Conductivity does not change with time, differing from previous observation
- *Short 15 minute* treatment with DMC → slight increase

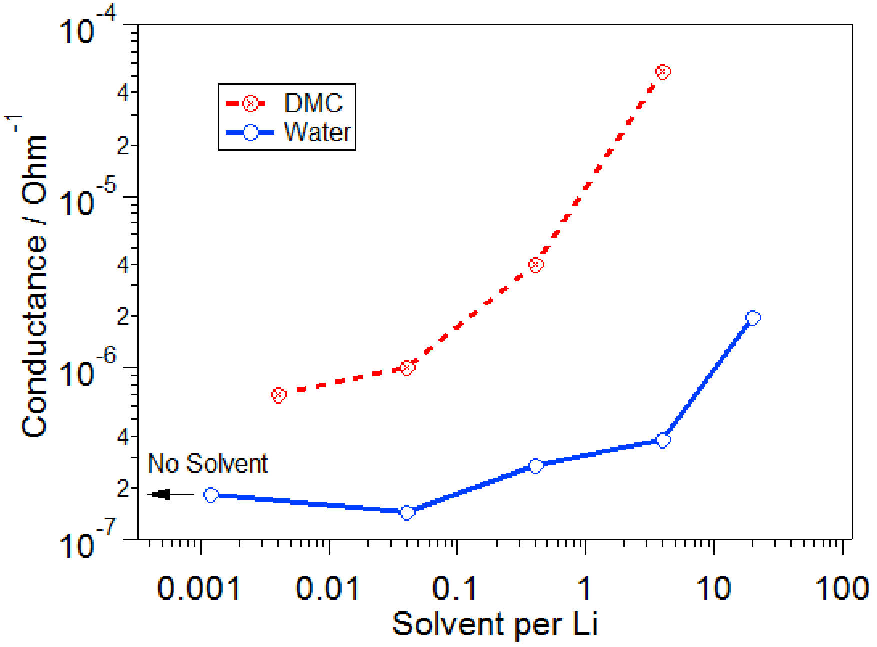


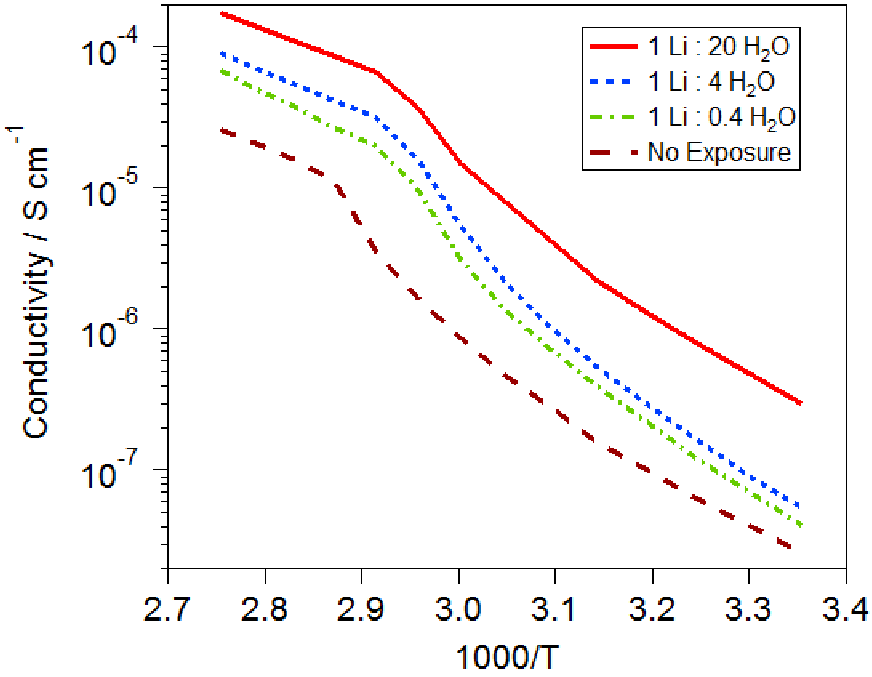
40 vol% Ohara ceramic with PEO_{16}-$LiCF_3SO_3$

measured at 25˚C

Technical progress: Less dramatic results for water exposure of composite samples. Extending to other vapors. (milestone)

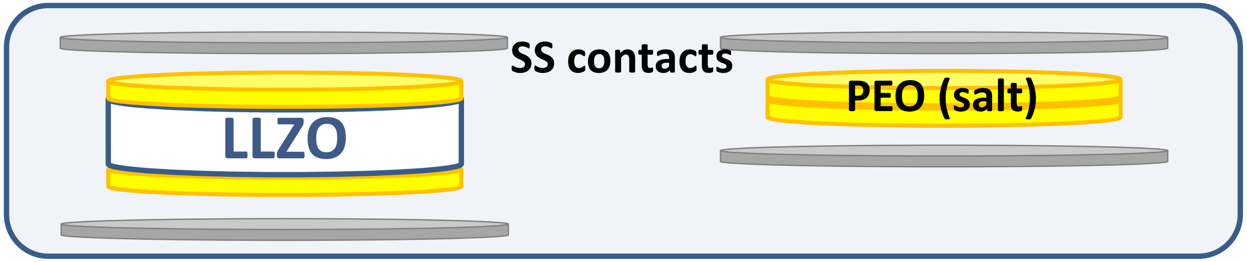
- In response to reviewer comment, and also because water would be likely effect of a poor seal.
- Need to separate dissolution from adsorption kinetics
  - DMC & H_2O similar vapor pressure, different Hansen distances

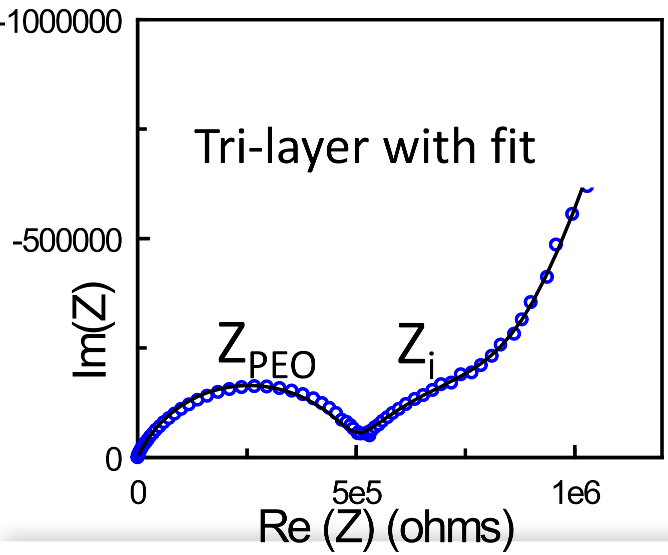


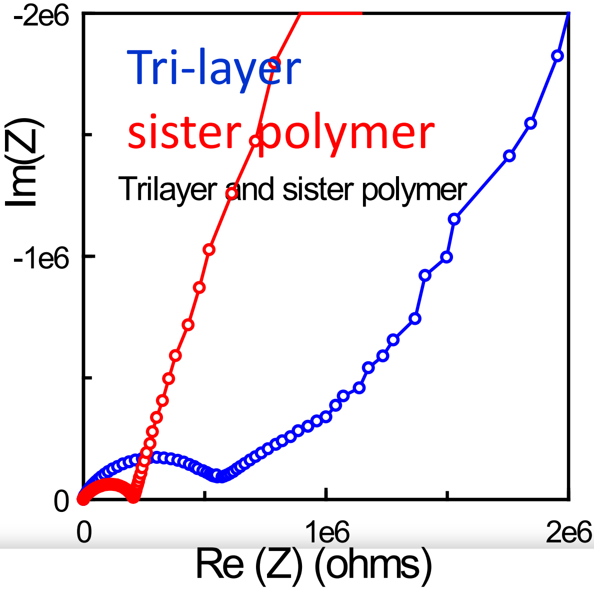


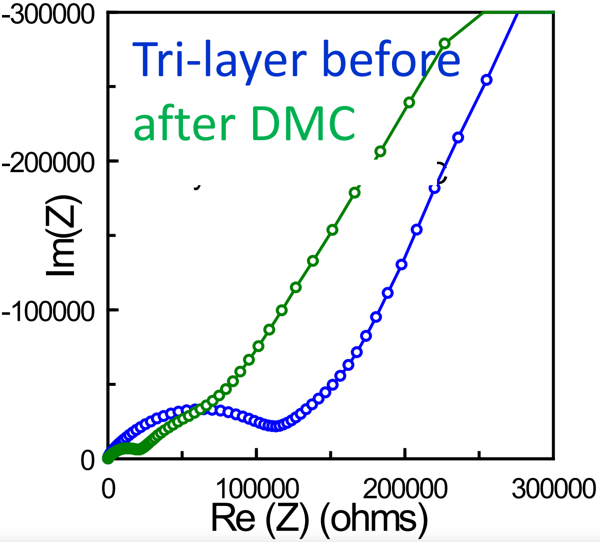
Technical progress: Trilayer samples have significant interface resistance, reduced by DMC exposure

- Tri-layer of PEO(salt) – sintered LLZO disk – PEO(salt), compared to PEO(salt) of same thickness
  - LLZO only adds ~300 ohms, outside frequency window at 25˚C
  - Interface impedance ≈ polymer layer impedance
  - Both interface and polymer impedance reduced with DMC exposure



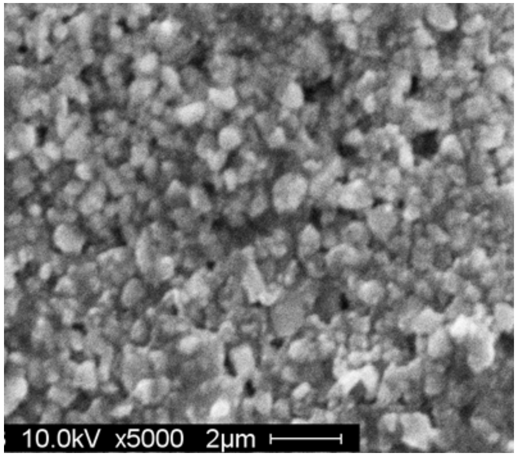






Technical progress: For composite with high ceramic loading, cycling with Li proved unstable. (milestone)

- Composites studied after Li foil pressed to one face
  - High and increasing interface resistance
  - Failed when Li plated to SS contact

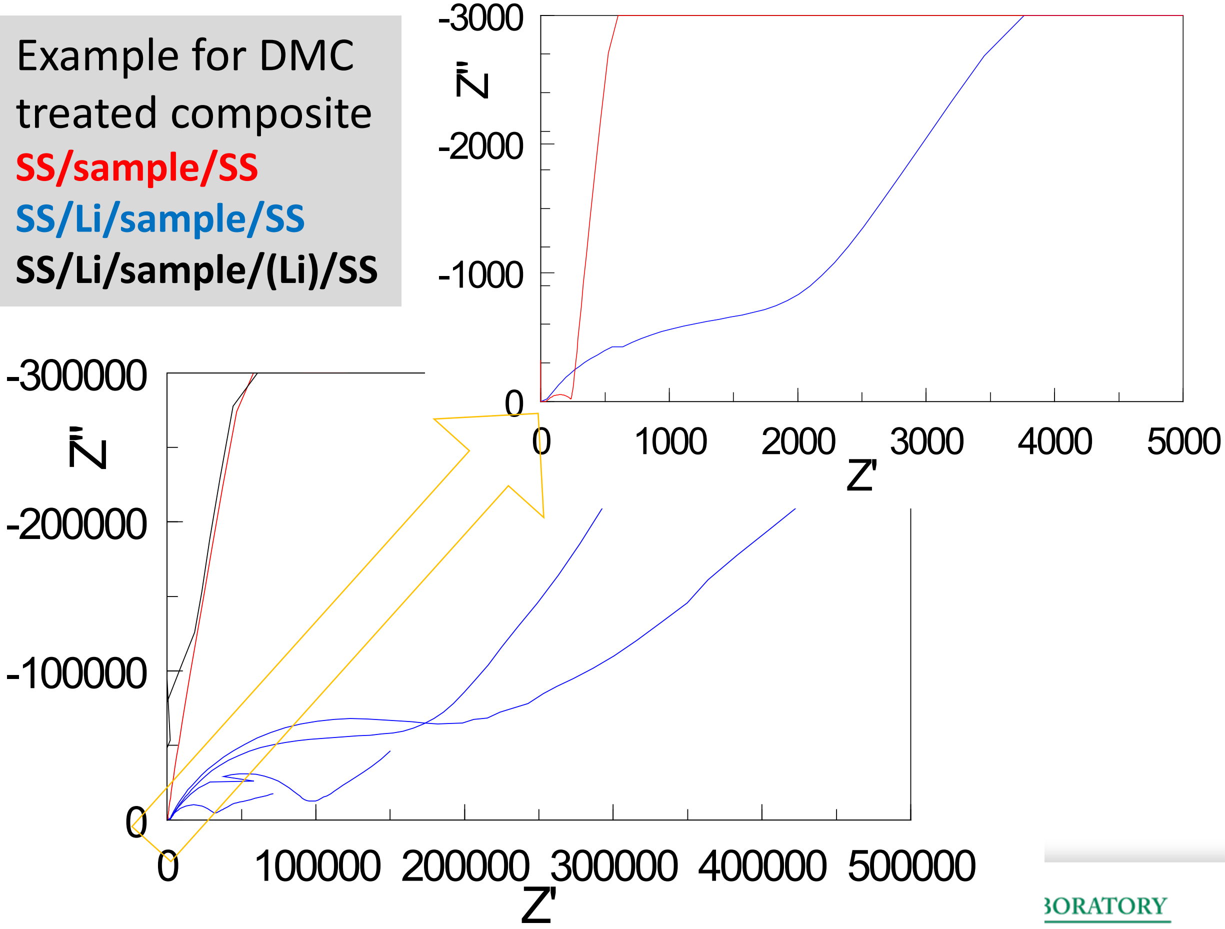


Example for DMC treated composite

SS/sample/SS

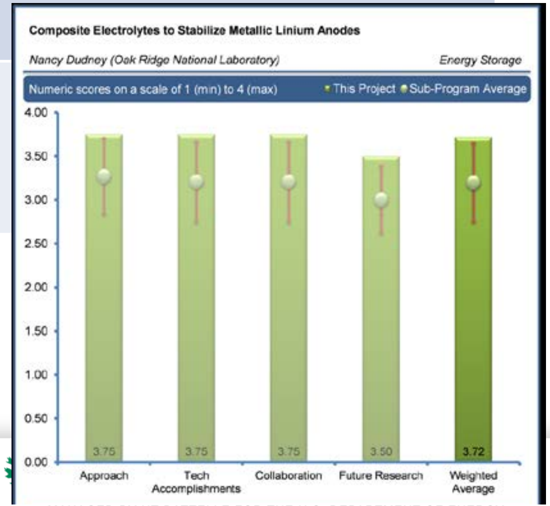
SS/Li/sample/SS

SS/Li/sample/(Li)/SS



Response to previous reviewer comments - Many positive comments, but a few concerns addressed here.

Reviewer comments last AMR (June 2013) and US DRIVE tech team (Sept 2014)	Response
"… the technical accomplishments have shown the need for low interfacial impedances. Effort is now needed to lower these interfacial impedance values."	Small additives may be key to lowering the interface impedance. More investigation is needed.
"… developing a dense and thin electrolyte will be challenging."	This is true , but expect composite to be easier to form and use than ceramic plates. Others will assist.
"Water contamination may be an issue, better experimental set up to account for outside influences and better preplanning and experimental design "	Following this recommendation, water treatment was specifically investigated.
"The critical path to meeting project goal was not very clear. Risks and mitigation strategies are unclear."	Next slide.



Challenges, Barriers and Future Work

- **Challenges, Risks and Mitigation**
  - Subtle differences in composite processing have large impact on the bulk conductivity. Risk - we may not identify root causes of this effect.
  - Mitigation - provide additives that overwhelm the variable processing effects without compromising the mechanical properties and Li reactivity.
  - With better understanding, this may indicate path to form stable, conductive composite.

- **Remainder of FY15**
  - Publish DMC/H_2O treatment results of composite
  - Complete and publish trilayer with LLZO. Vary thickness of PEO layers.
  - For Li tests, reduce ceramic loading for full density. Test barrier coating & DMC effects.
  - Identify vapor species that prove to be most beneficial additive.

- **FY16**
  - Improve composites, substitute LLZO for LATP particles. Bimodal size distribution.

Collaborations and coordination

- Collaborations which include coordinated sample preparation, sample exchange for analysis. We have joint publications; several are in preparation.
  - Jeff Sakamoto (University of Michigan) inside VT
- 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 nGimat and Jeff Sakamoto
- Industrial communications, outside VT.
  - Corning Corp., Paul Johnson & K P Reddy, tapped for discussion regarding ceramic electrolytes
  - A similar contact regarding polymer electrolytes would be helpful.

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.
  - Use model structures to simplify evaluation of the ceramic –polymer interface.
  - Following simulation, fabricate composites with maximum ceramic loading.
  - Evaluate interface to lithium metal with and without barrier coating. Cathode is not considered.
- **Accomplishments and progress - new understanding that will address technical barriers**
  - A subtle variation in processing conditions for composite electrolytes can profoundly alter the ionic conductivity of ceramic-polymer composites. This may well have been overlooked.
  - Adsorption of some organic vapors and water can enhance Li^+ ion transport in ceramic-polymer dispersed composites, multi-layers, and polymer electrolytes.
  - Enhancement has been quantified for different molecules, including dimethyl carbonate and water. Controlled exposure may be a new path to improve properties of composites.
  - Contact and cycling with Li metal led to reaction with DMC and/or LATP ceramic particles.
- **Future work**
  - Publish DMC/H_2O treatment results of composites and trilayer samples.
  - For Li tests, reduce ceramic loading for full density. Test barrier coating & DMC effects.
  - Identify vapor species that prove to be most beneficial additive.
  - Improve composites; substitute LLZO for LATP; increase ceramic loading with bimodal size.
- **Collaborations and coordination** – key for past year are: Sakamoto and Ohara

Technical backup slides

Technical progress: Analysis of standard versus dry (no volatile) glove box reveals only small differences

- Mass spec and FTIR of gas samples – nothing obvious
- XPS of high surface area carbon – possible F surface contamination
- G49 is dry glove box; R103 is standard glove box.