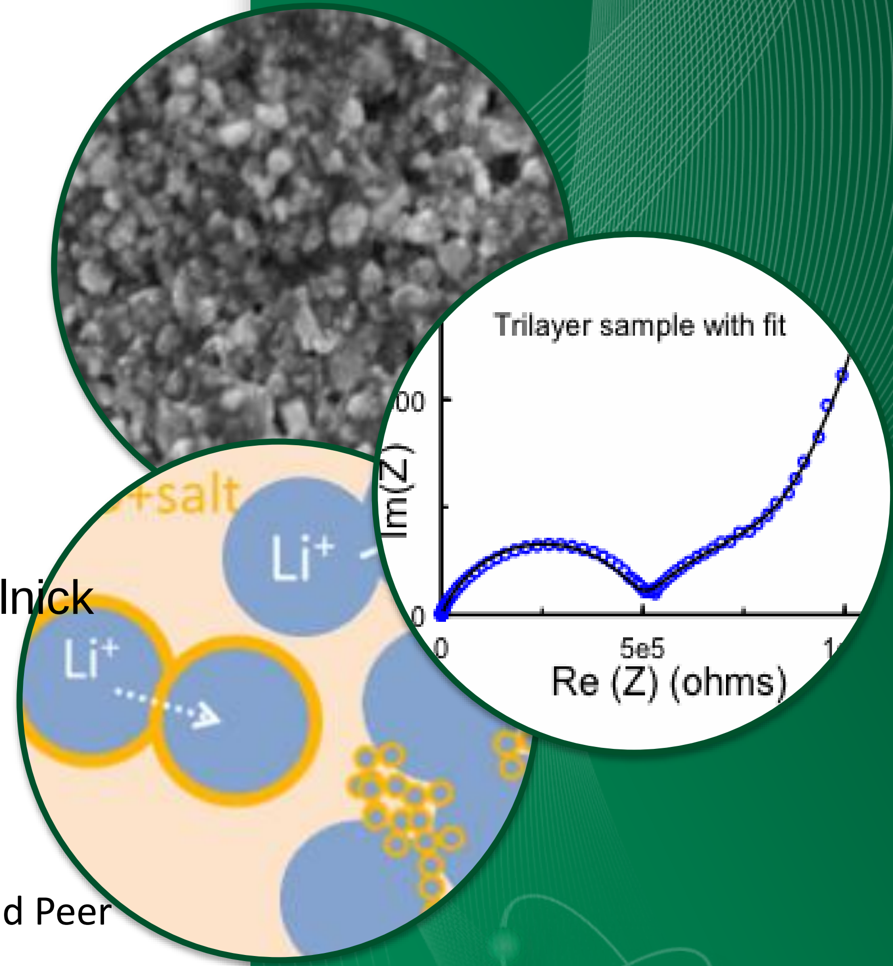
Composite Electrolyte to Stabilize Metallic Lithium Anodes



Project ID: bat273

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Oak Ridge National Laboratory
Materials Science and Technology Division

Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting

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Overview – Composite Electrolytes to Stabilize Li Metal Anode

- **Timeline**
  - Start: October 2014
- **Budget**
  - $400k FY16
  - $400k FY17
- **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		no Li roughening
10-20 nm/sec, pulse	10-15 mA/cm^2, pulse	no Li lost to physical isolation
3000 cycles	99.99% coul. efficiency	no Li lost to reaction

Polymer Electrolytes

- Thin sheet processing
- Chemical stability with Li
- Low shear modulus
- Low Li$^+$ conductivity

Ceramic Electrolytes

- Adequate Li$^+$ conductivity
- High shear modulus
- Processability
- Chemical stability with Li

→

composite solid electrolytes

Need > 50 vol% ceramic to satisfy conductivity and modulus requirements

Nancy J Dudney, William C West, Jagjit Nanda, *Handbook of Solid State Batteries*, World Scientific Publishing; 2 edition, **2015**
S. Kalnaus, A.S. Sabau, W.E. Tenhaeff, N.J. Dudney, C. Daniel, *J. Power Sources* **2012**, 201, 280–287

Can polymer-ceramic composite electrolytes protect the Li?

- **Objectives:**
  - Identify model polymer and ceramic electrolyte that are compatible to complement each other and deliver reasonable properties for working in a battery.
  - Identify a method for producing highly reproducible composite electrolyte.
  - Introduce a barrier layer between composite and lithium and understand the interface through different layers.
  - Fabricate a working battery to demonstrate the composite electrolyte.
  - Extend the design rules obtained to next generation of ceramic and polymer electrolytes.
- **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. Using a solid electrolyte to isolate lithium from all liquid components is the best route to safety and efficiency.
  - Success of our composite electrolyte will:
    - Enable Li-S Battery (500 Wh/kg) by 2020 and Li-Air (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).

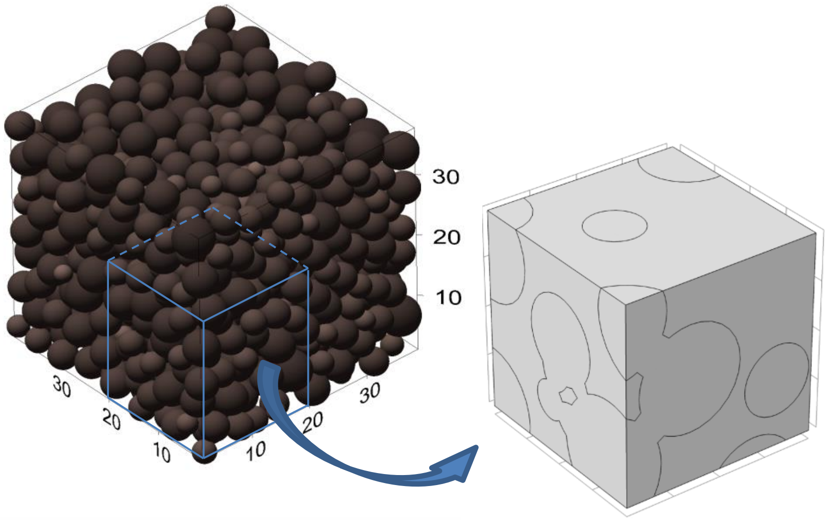
Milestones

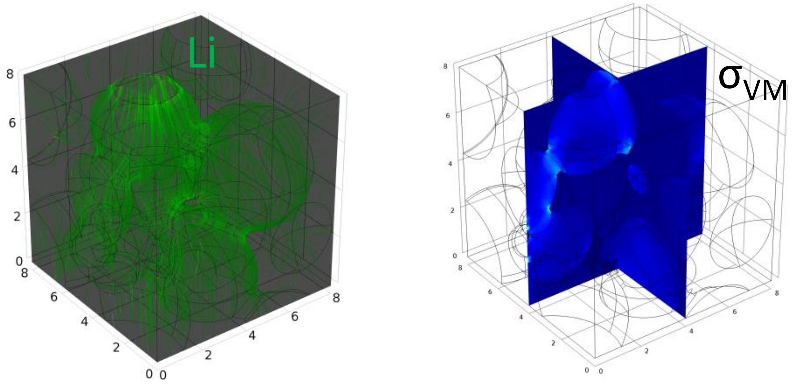
Milestones: FY17-FY18	Target:	Status:
Assess the Li/solid electrolyte interface resistance. Adjust the composition and/or add a coating to reduce the ASR and passivate the interface.	Q3 FY17	✓
Fabricate a full battery using aqueous spray coating for both the composite electrolyte and cathode incorporating a protected Li metal anode. Demonstrate Li cycleability. (stretch goal)	Q4 FY17	Done. Cell optimization ongoing.
Accurately determine the polymer/ceramic electrolyte interface resistance for PEO and Ohara based materials using bi- and tri-layer samples. Minimize the interface ASR by chemical and mechanical treatment with a goal of < 100 ohm.	Q1 FY18	Interfacial resistance quantified.
Revisit our earlier investigation to confirm the effect of DMC plasticizer on polymer structure, Li ion mobility, ion solvation, transference number and interface resistance.	Q2 FY18	On schedule

APPROACH

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.

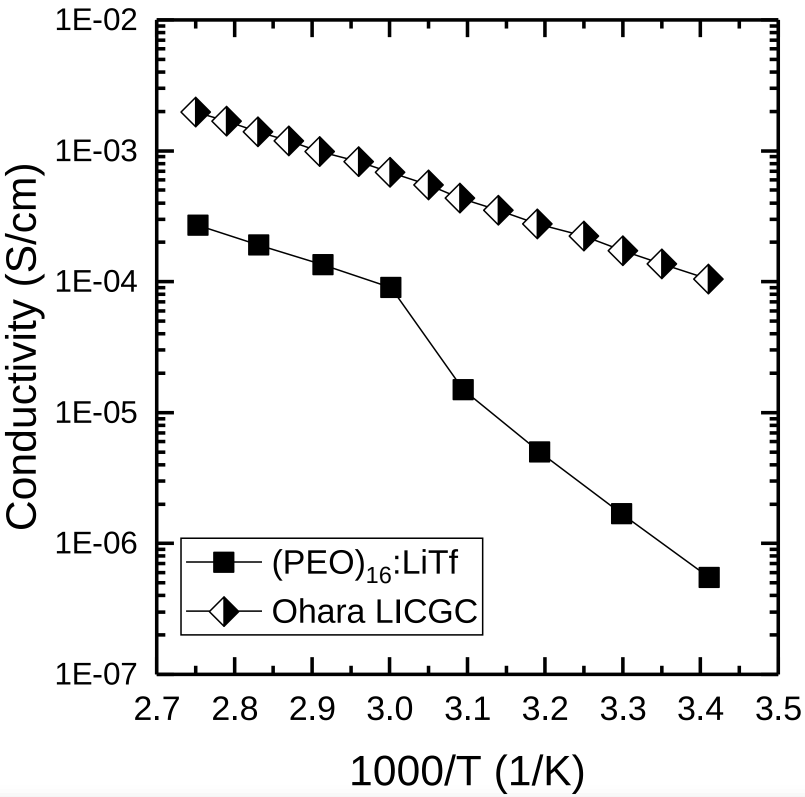




- Li transport through ceramics percolation network
- High stiffness with polymer providing additional cohesion

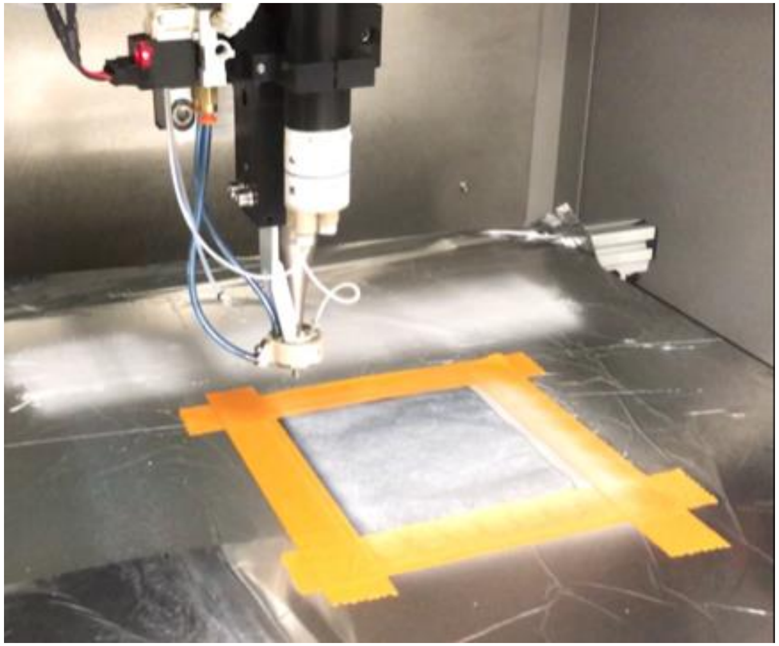
Use model electrolyte materials to develop processing

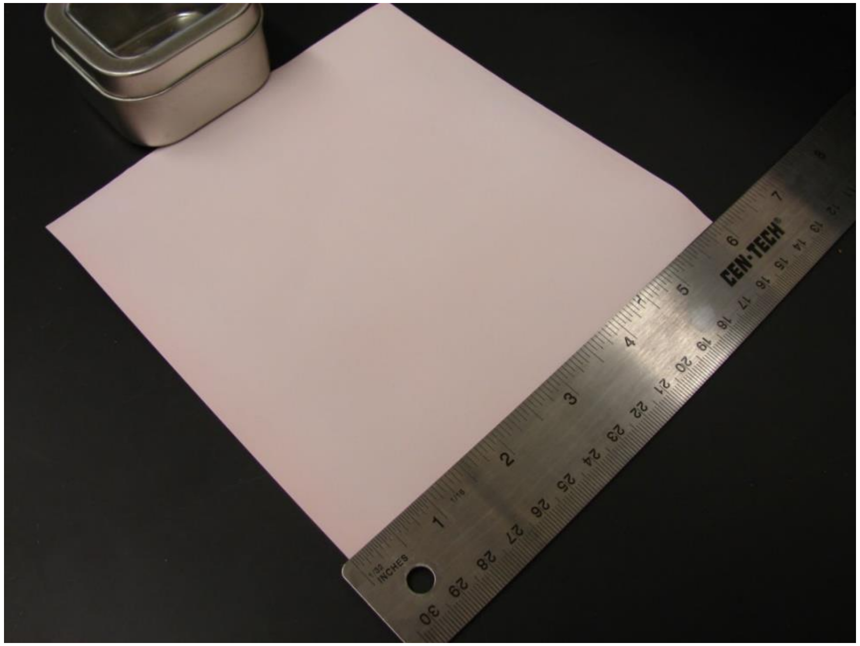
- Model materials used for study, which are already well understood, but maybe not the final choice:
  - PEO polymer with LiTriflate salt. Stable with Li; fast crystallization kinetics.
  - Ohara LATP based ceramic powders. Reproducible batch to batch, submicron powders. Air stable, but expected to reduce with Li contact.
- Processing for uniform, dense composite.
  - Target is much higher ceramic loading than other programs to produce mechanically strong membrane.
- Characterization - electrochemical and mechanical
  - Compare dispersed composite electrolytes with laminated polymer/ceramic samples.
- Outcome – Design rules that can be applied to alternative composite electrolyte materials and architectures.



Key earlier technical accomplishment: good quality composites (55 vol.% Ohara ceramic) were formed by spray coating

EARLIER RESULT

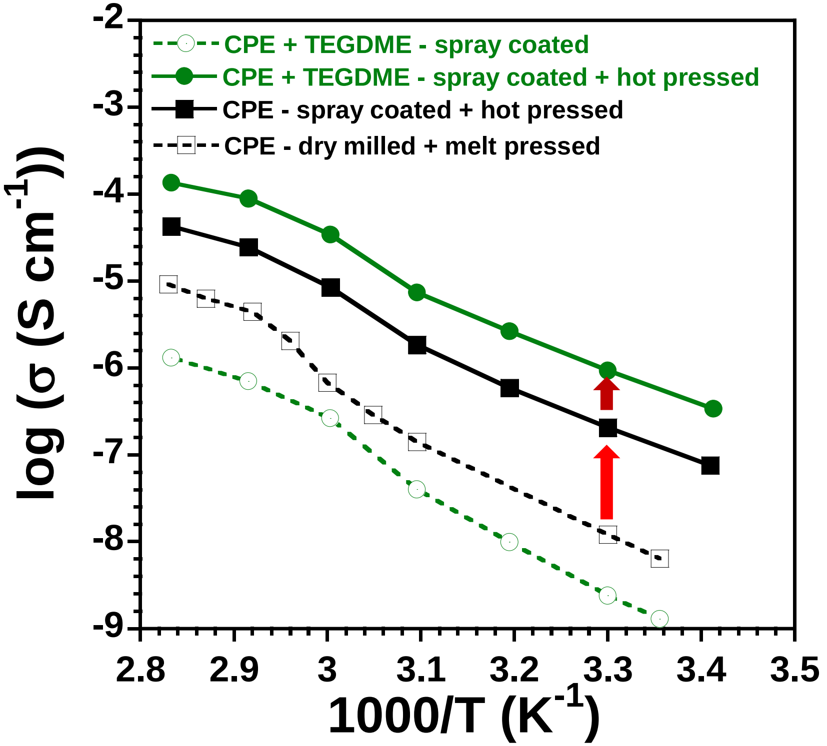


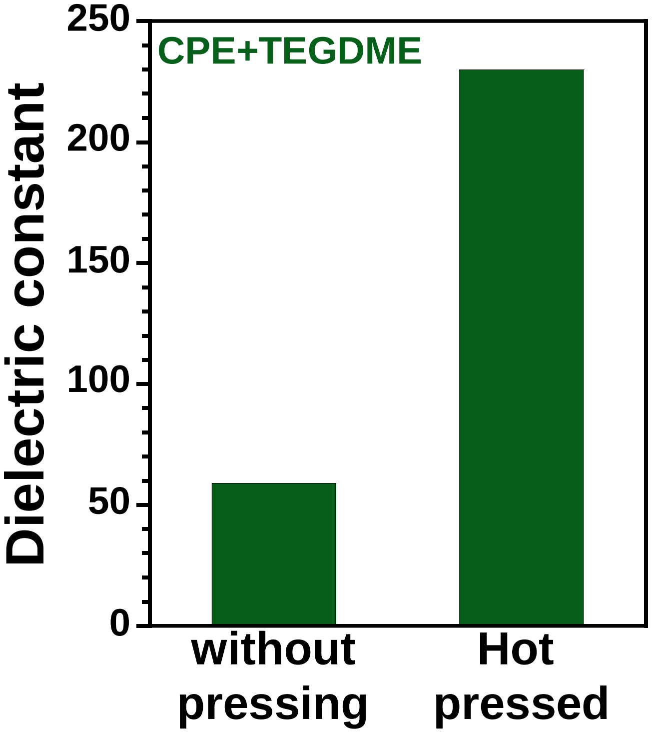


- Faster than doctor blade. Sonicated spray head good at low viscosity slurry, infinitely scalable.
- On copper, C-coated aluminum, and stainless foils.
- Wetting, uniformity improved with TEGDME. Approx. 30-50 µm before pressing.
- Composition 16:1:2 (EO:Li:TEGDME) to be consistent with earlier melt-pressed.
- Techniques for spray and slurry dispersion are important for quality.

Comparison of processing methods: spray coat + hot press + plasticizer produced membrane with maximum ceramic loading and ionic conductivity

EARLIER RESULT



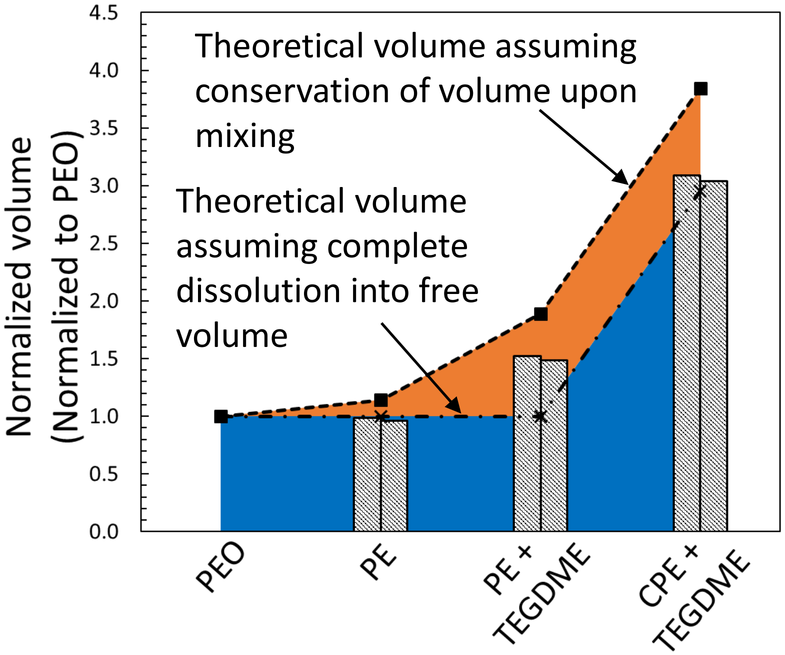


- After spray coating and rigorous drying steps, hot pressing is needed to achieve high conductivity of the composite polymer electrolyte (CPE).
- Conductivity of spray coat + hot pressed membrane is 1 order of magnitude higher than dry mill + melt pressed. Solution casting did not resolve in usable membranes.
- Introduction of plasticizer TEGDME further improves conductivity of CPE.
- CPE + TEGDME room temperature conductivity: 10^{-5} S/cm.

Spray coat + hot pressed membranes: extremely dense with actual volume fraction much higher than the target 50 vol%

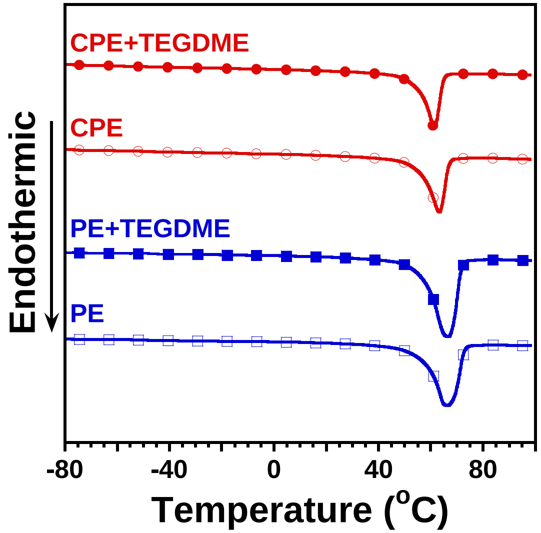
Sample	#	Measured density (g cm^{-3})	Expected density (g cm^{-3})	Expected density range (g cm^{-3})
PE	1	1.4848	1.286	1.286 – 1.466
	2	1.5268		
PE+TEGDME	1	1.4588	1.290	1.176 – 2.222
	2	1.4979		
CPE	1	2.5520	2.386	2.222 – 2.358
	2	2.5901		
CPE+TEGDME	1	2.6498	2.367	2.129 – 2.770
	2	2.6913		

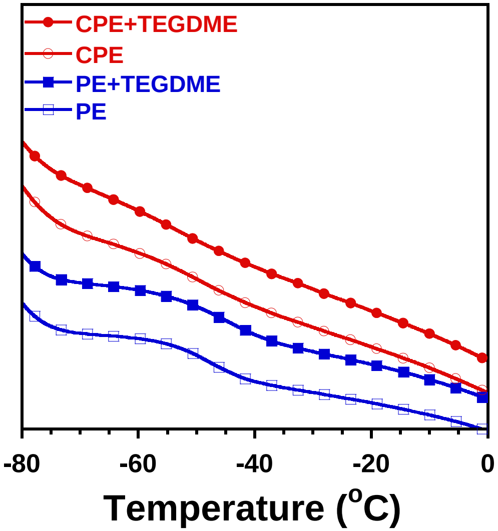
PE: polymer electrolyte; CPE: composite electrolyte



- Measured density > expected density indicates negative volume of mixing between PEO and Li triflate salt, TEGDME and Ohara ceramic.
- Li triflate completed dissolved into the free volume of PEO and does not swell PEO.
- TEGDME partly dissolved into the free volume of PEO.
- CPE + TEGDME: close to lowest theoretical volume – extremely dense.
- **Actual volume fraction of ceramic in CPE is calculated to be 61% and that in CPE+TEGDME to be 64%. This is much higher loading than our target 50%.**

Thermal properties revealed the plasticizing effect of Ohara ceramic on PEO chains.

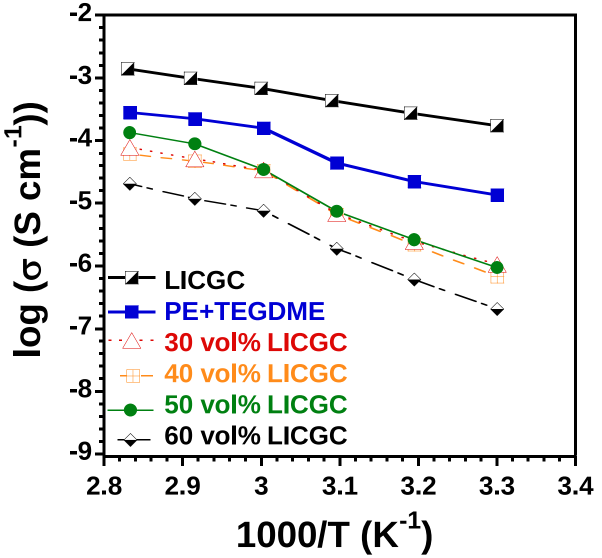


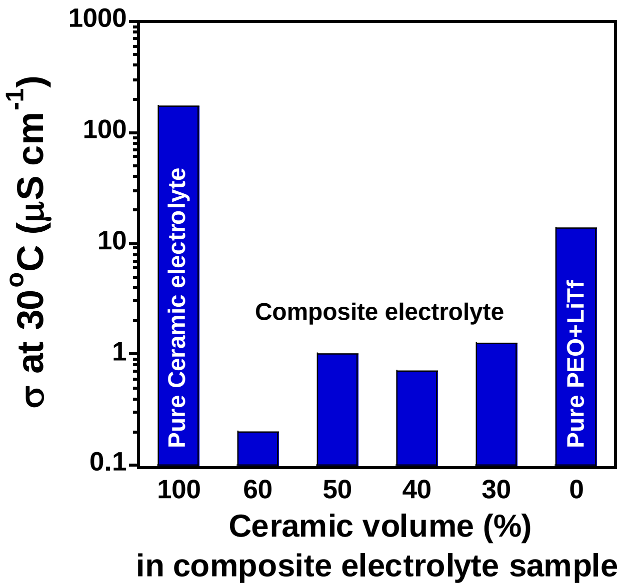


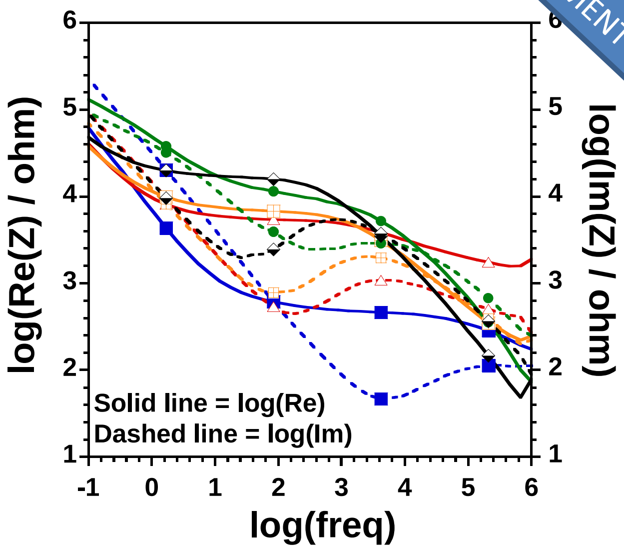
Sample	T_c (°C)	T_g (°C)	T_m (°C)	Heat of Fusion (J per g of polymer electrolyte)
PE	47.8	-47.9	66.2	88.3
PE+TEGDME	46.2	-46.0	66.5	83.3
CPE	47.0	-50.4	63.2	84.1
CPE+TEGDME	45.3	-52.4	61.3	63.7

- Effect of TEGDME: decreased the degree of crystallinity of PEO (promotes conductivity), but caused slight increase in T_g (decreases conductivity).
- CPE: decreased the degree of crystallinity of PEO, also decreased T_g, both having positive effects on conductivity.

Conductivity: effect of ceramic loading



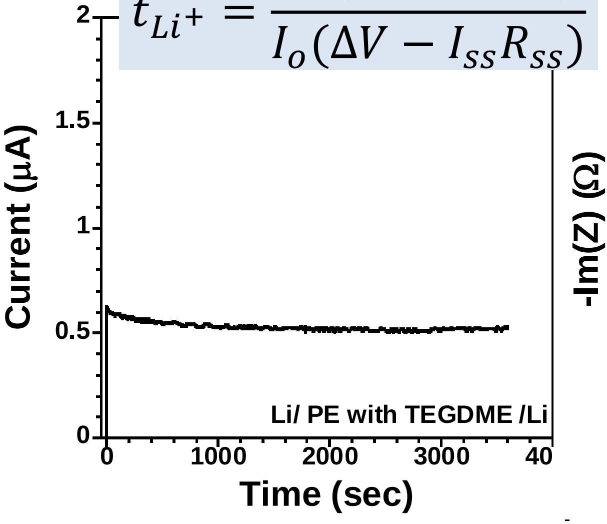


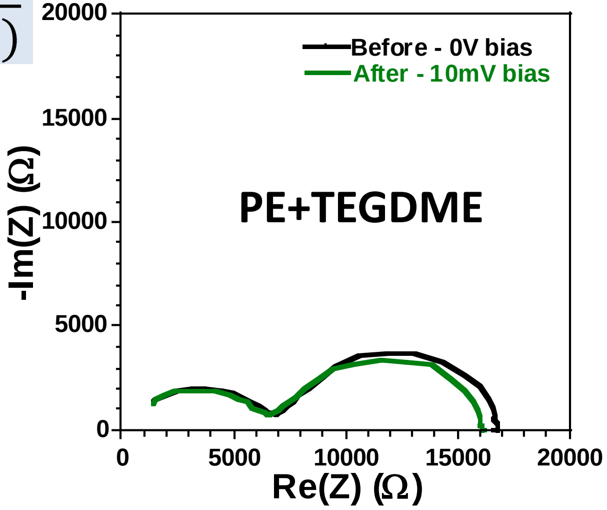


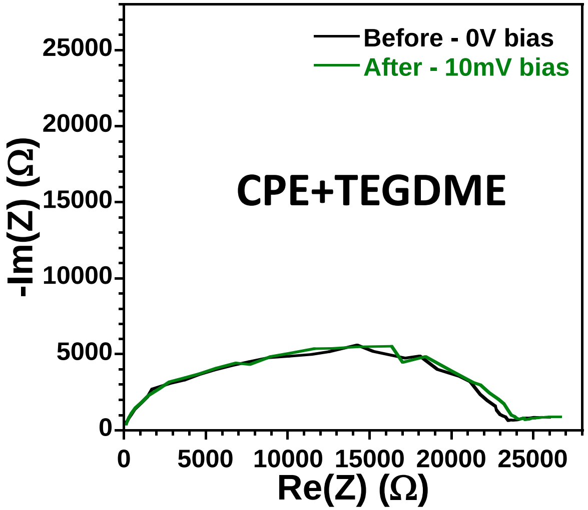
- 30 – 50 vol% ceramic: 1 order of magnitude decrease in conductivity – this indicates large interfacial resistance between polymer and ceramic electrolytes
- 30 – 50 vol% ceramic: conductivity doesn't change much - multiple factors (increased resistive area, decreased degree of crystallinity, etc.) offset each other.
- 60 vol% ceramic: significant decrease in conductivity caused by inefficient packing of ceramic particles.
- Note that the volume fraction used here are nominal volume fractions; the actual volume fractions of the ceramic are higher according to our density measurements.
- Single transient in Bode plot: one transport mechanism – ion conduction likely only through polymer electrolyte.

Li$^+$ transference number of PE+TEGDME is 0.69 and that of CPE+TEGDME is 0.79

$$t_{Li^+} = \frac{I_{ss}(\Delta V - I_o R_o)}{I_o(\Delta V - I_{ss} R_{ss})}$$

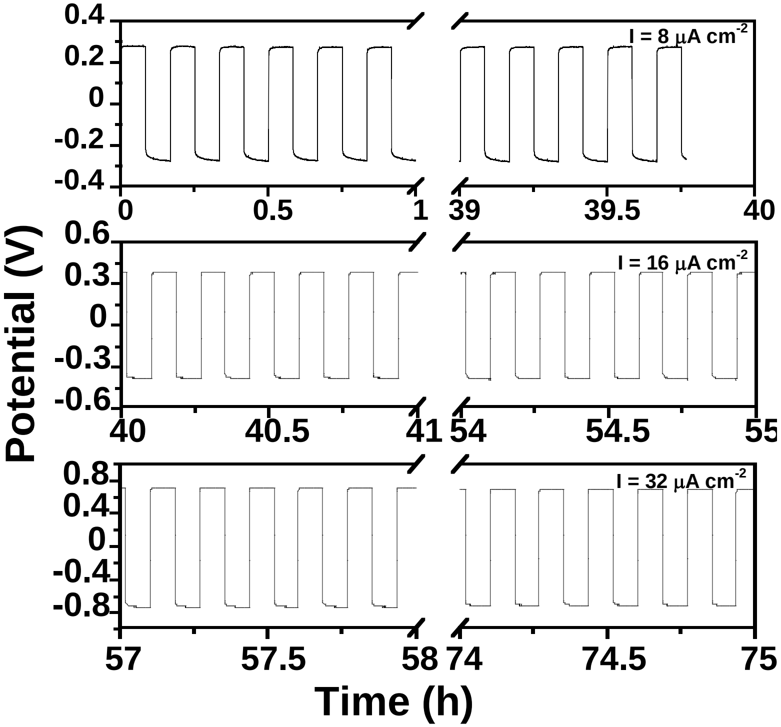


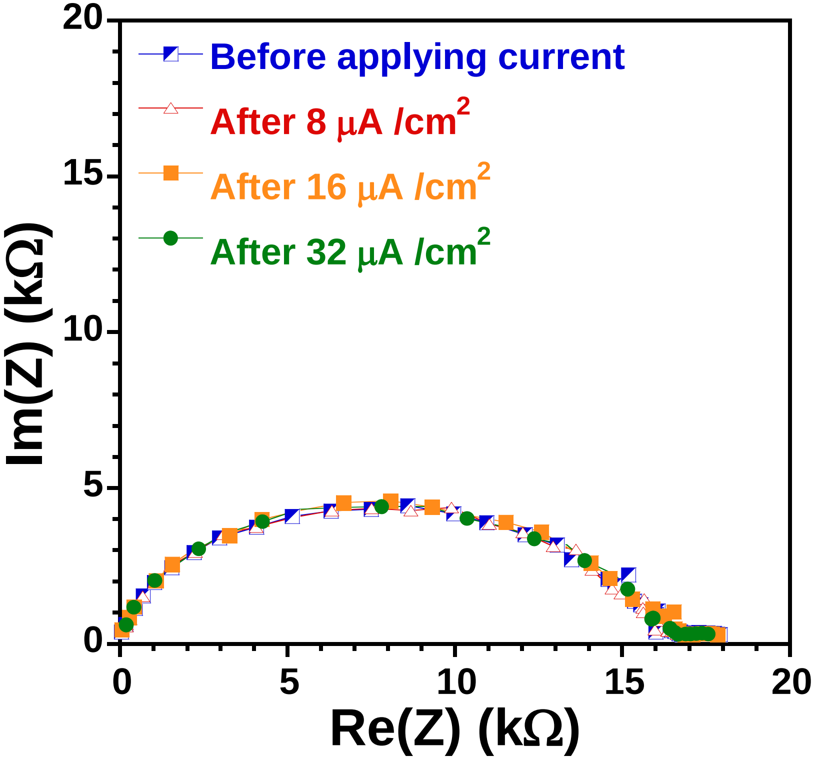




- A symmetrical cell of configuration Li//Li was constructed, and the Li$^+$ transference number was obtained by applying a small potential of 10 mV and monitoring the current decay over time.
- PE + TEGDME: transference number for Li$^+$ is 0.69 while for that of PE was reported to be between 0.47 and 0.57
- CPE + TEGDME: transference number for Li$^+$ is a remarkable 0.79.

Composite electrolyte: improved stability with Li compared to pure Ohara ceramic.

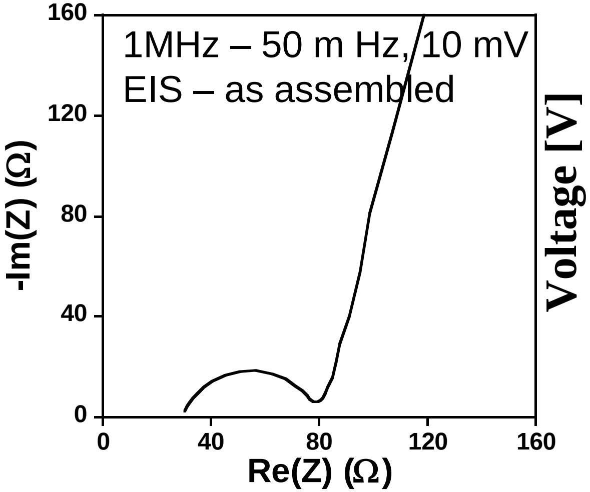


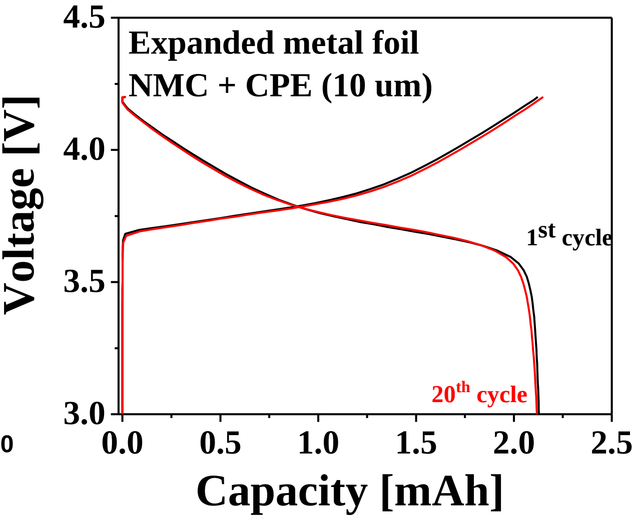


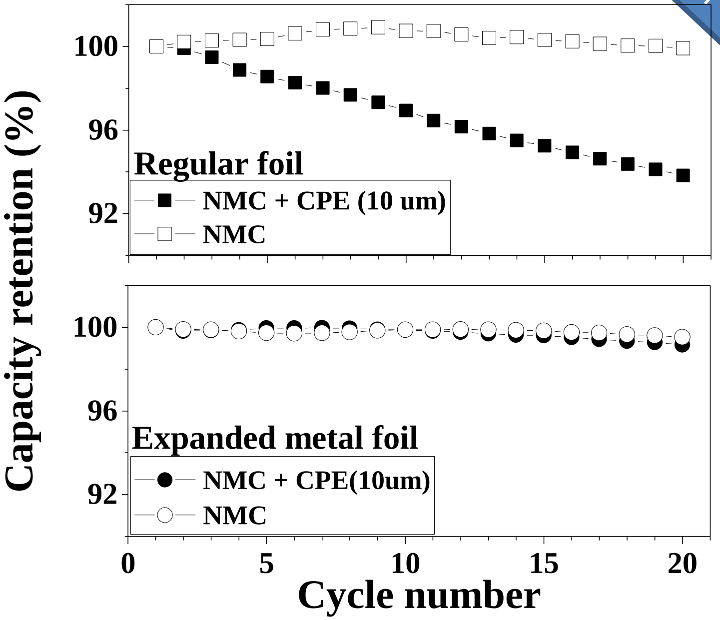
- Cycling data for Li|CPE+TEGDME|Li at 8, 16 and 32 μA cm^{-2} for extended hours - no change in impedance after 75 h.
- Postmortem diagnosis showed signs of Ohara degradation. Compared to pure Ohara ceramic that reacts with Li within seconds, the cyclability of CPE is drastically improved.
- Polymer mitigates the reaction and help protect Li while LICGC provides mechanical strength.

ACCOMPLISHMENT

Full battery fabricated by spray coating the cathode followed by the composite electrolyte



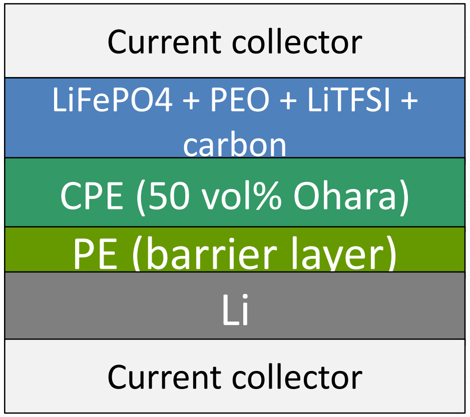




- Full batteries were fabricated by spray coating a thick NMC (5:3:2) cathode with carbon and binder on expanded aluminum foil, followed by a spray coating of the composite electrolyte.
- The spray-coated cathode cycled well in a flooded cell with a liquid electrolyte (LE), EC-DMC-$LiPF_6$(1.2M).
- However, when limiting the catholyte to a minimum amount (0 to 12 µL), the cells had poor cyclability. This could be due to catholyte drying, poor contact between layers, delamination and too high of a cycling voltage for composite electrolyte.

ACCOMPLISHMENT

All-solid full battery demonstrated dramatically improved cyclability



Current collector

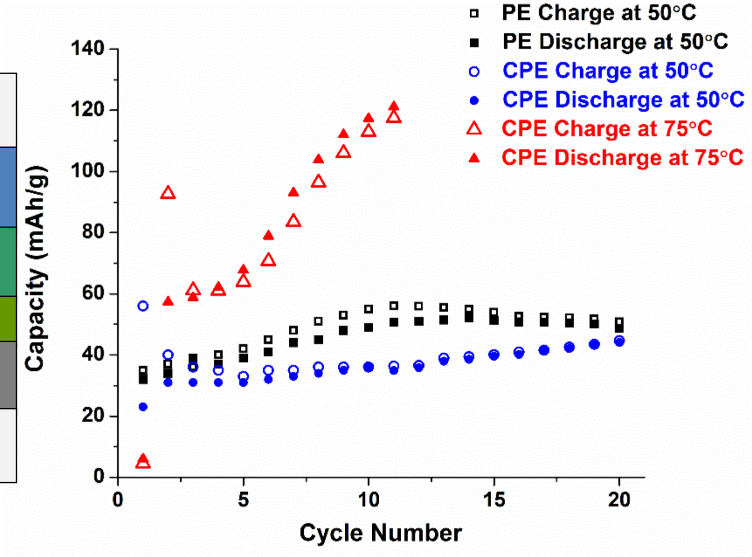
LiFePO4 + PEO + LiTFSI + carbon

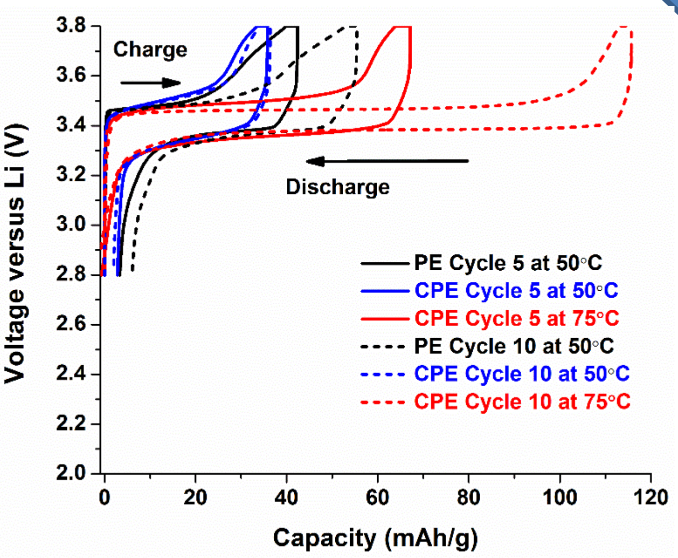
CPE (50 vol% Ohara)

PE (barrier layer)

Li

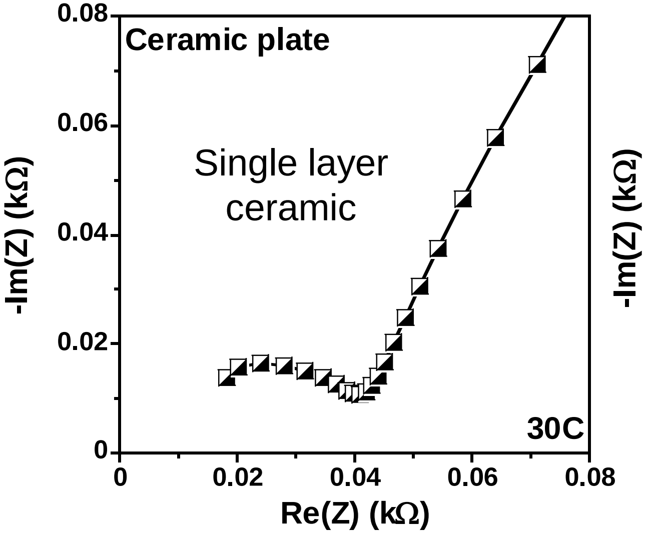
Current collector

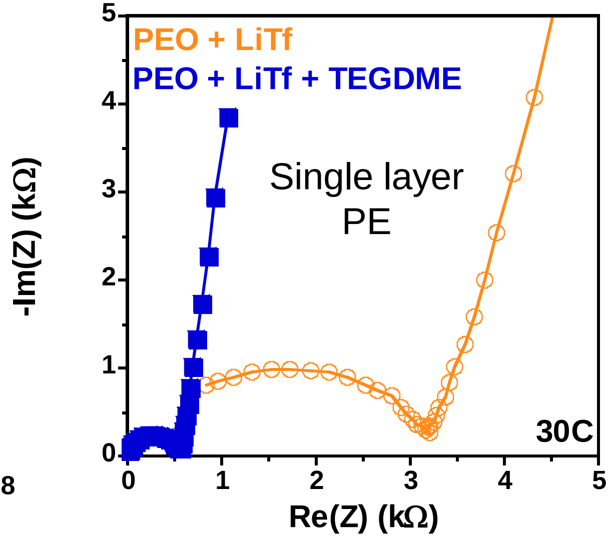


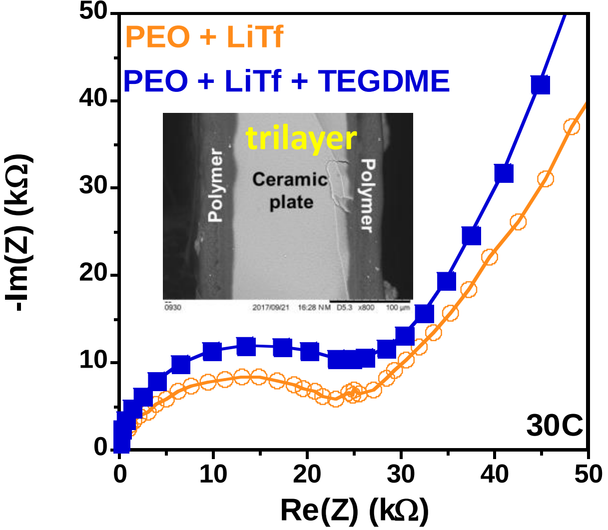


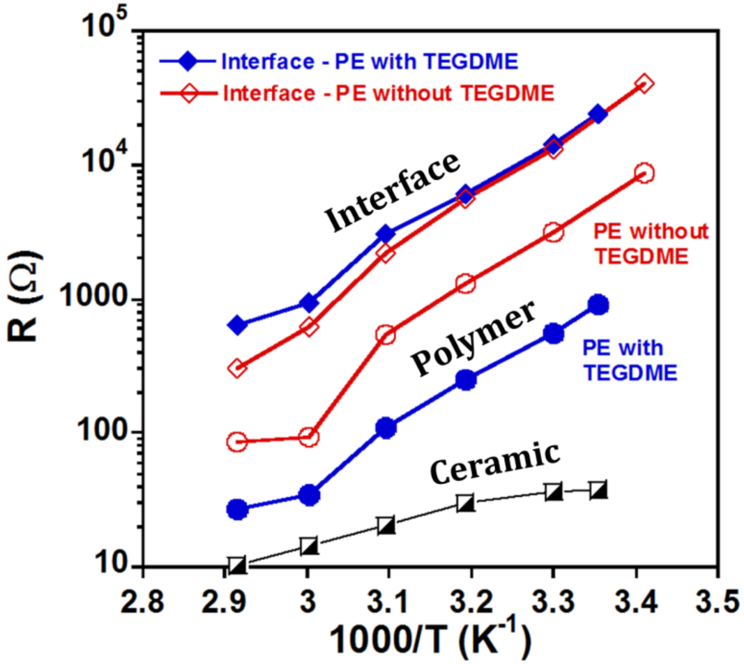
- To eliminate catholyte drying problem, we replaced liquid catholyte with solid polymer catholyte (PEO + LiTFSI).
- Bilayer electrolyte CPE + PE was used to construct full cell to enhance adhesion of the solid electrolyte and prevent deleterious reactions between Ohara ceramic and lithium.
- Dramatically improved cycling performance was achieved compared to cells using limited amounts of liquid catholyte.

PE-Ceramic interface is evaluated using a trilayer cell



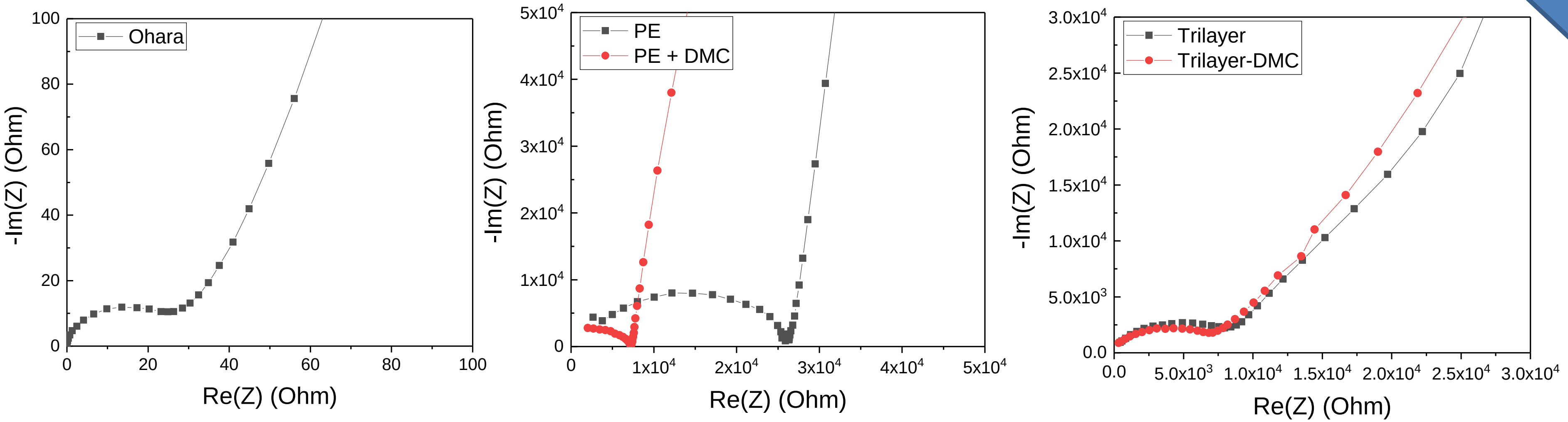


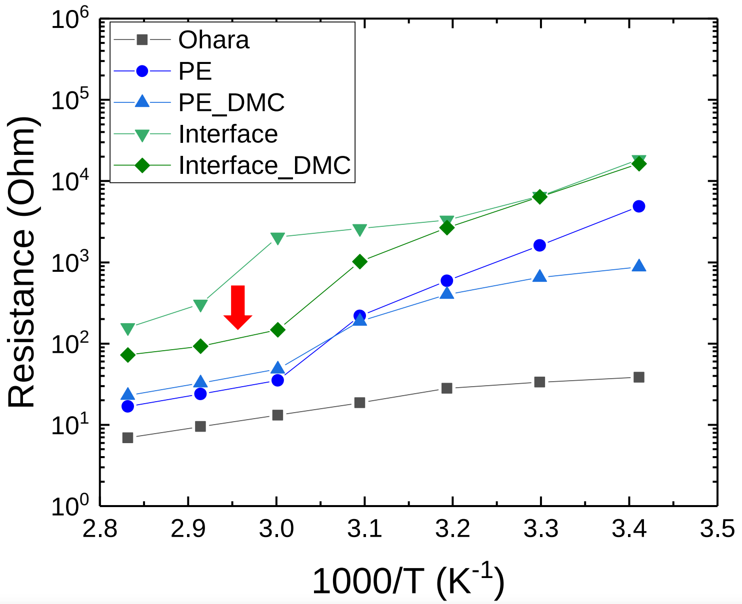




- Trilayer cell was constructed by spray coating thin polymer electrolyte onto sintered Ohara plate.
- At 30 °C, the interfacial resistance between PE and Ohara plate for ion transport is **~10000 Ohm**.
- TEGDME, while enhances the ionic conductivity of the polymer electrolyte, does not facilitate ion transport across the polymer-ceramic interface

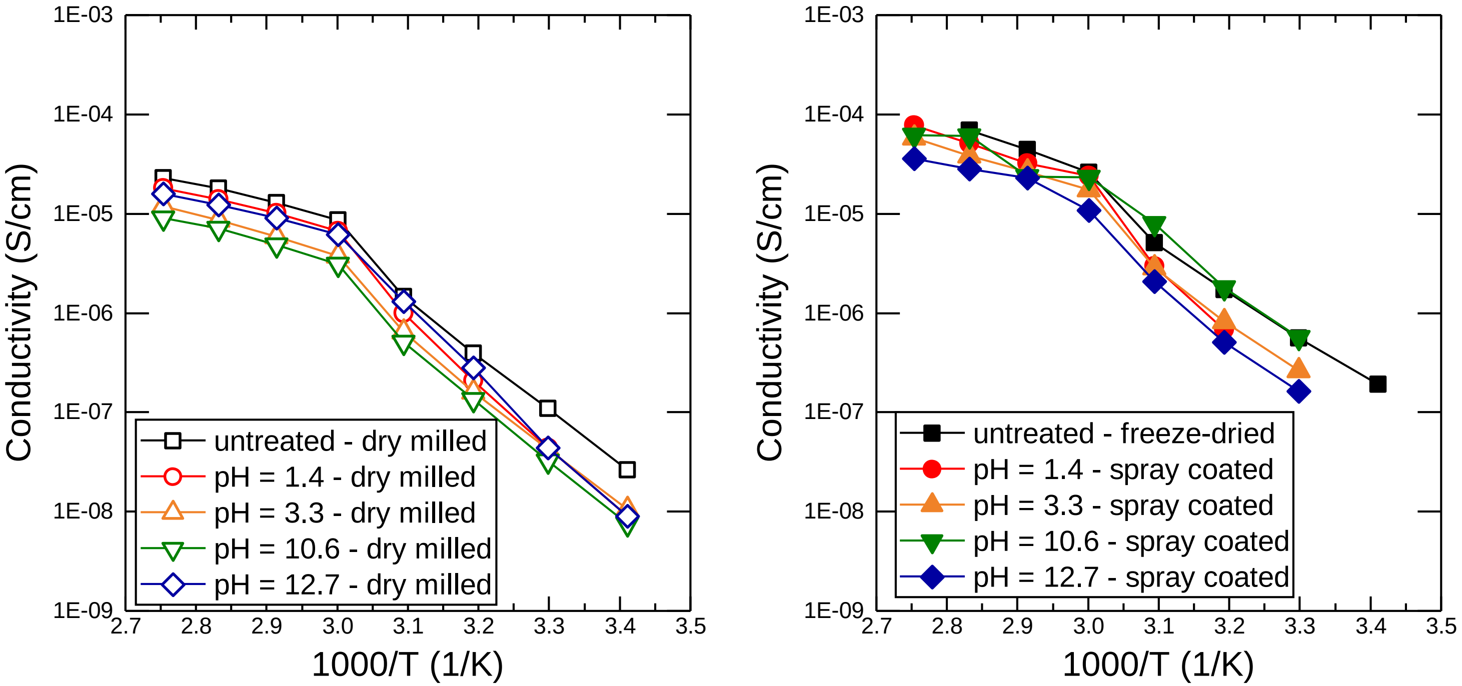
Dimethyl carbonate (DMC) reduced the interfacial resistance between PE and Ohara Ceramic, but not enough





- Trilayer cell was constructed by spray coating thin polymer electrolyte onto Ohara plate using acetonitrile as the carrier solvent.
- The trilayer cell was sealed in a vial with DMC vapor ([DMC]:[Li^+] = 10:1). The impedance of DMC infused trilayer was measured.
- DMC decreased the interfacial resistance at high temperature, but it’s still too high compared to bulk PE and Ohara.

Acid/base treatment of the Ohara ceramic: limited effect on interfacial resistance between PE and Ohara Ceramic



- Previous studies* have shown moderate change in the ion conductivity of PEO-LiX-alumina composites by using alumina with acidic, neutral and basic surfaces.
- We treated Ohara ceramic powder with HNO_3 and NaOH aqueous solutions with 4 pH values, 1.4, 3.3, 10.6 and 12.7.
- The treated powders were mixed with PEO and Li triflate salt (50 vol% ceramic) using two methods: spray coating from aqueous solution and dry milling.
- The effect of acid/base treatment was limited.

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*Croce, F., et al., Electrochimica Acta, 2001. **46**(16), p. 2457-2461.

Future Work

Remainder of FY18

- Ion transport in composite polymer electrolyte.
  - Minimize interface ASR by chemical and mechanical treatment with a goal of < 100 ohm.
  - Move beyond model materials like Ohara and PEO, to include polymer gels.
- Li interface with composite electrolyte.
  - Study the barrier layer (Lipon) over CPE to stabilize the plasticizer and provide for low interface impedance from vapor or melt deposited lithium.
- Full battery by spray coating – fabricate and cycle at or above room temperature.
  - Optimize cell design such as thickness of CPE|PE bilayer electrolyte, adding plasticizer and replacing PE with Lipon as the barrier layer.
  - Assess the feasibility of slurry spray coating to form the thin membrane of new materials.

Beginning in FY19

- Thoroughly evaluate ion transport, thermal and structural properties of new polymer ceramic composite systems.
- Push to higher ceramic loading with bimodal particle sizes. Evaluate mechanical properties.

“Any proposed future work is subject to change based on funding levels.”

Challenges and mitigation

- Plasticizers such as TEGDME and DMC improved the conductivity, but did not effectively reduce the interfacial resistance between PEO and Ohara ceramic. At least not the way we introduced them into the system. New chemical and mechanical treatment methods need to be discovered to effectively decrease the interfacial resistance.
- We need to move beyond model materials like Ohara and PEO and identify alternative promising polymer ceramic systems with interfacial ASR less than 10 ohm.
- 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. Bimodal particle size distribution and sintering before infusing polymer electrolyte are additional ways to process the composite.

Collaborations and coordination

- Jihua Chen and Bradley S. Lokitz in Soft Materials Program of CNMS, ORNL helped in TEM imaging and obtaining thermal properties using DSC.
- Sakamoto (es277) provides LLZO materials and guidance for air/water reactions.
- Nanda (es106) collaborates on interpretation of Raman characterization.
- Coordination with a BES program at ORNL is synergistic towards understanding synthesis challenges of related solid electrolytes.
- Ceramic electrolytes are supplied by Ohara Corp.

Response to reviewer comments

- **Approach, technical accomplishments and progress**
  - *Reviewer 1: …reviewer worried that composites will lead to current focusing and result in issues with dendrites*
    - A thin polymer electrolyte layer was used between the composite electrolyte and Li anode for uniform Li plating as well as passivation.
  - *Reviewer 3: …a LiPON coating. This adds yet another interface with a relatively poor conducting solid, and the reviewer said it seems unlikely to work out.*
    - Our preliminary study showed promising results that Lipon was effective at addressing instability between Ohara ceramic and Li.
    - Alternatively, using a thin polymer electrolyte as the protecting layer does not add extra interface and will result in uniform Li plating.
  - *Reviewer 4, Reviewer 1 and 2*: *…addressing interfacial resistance between two phases, remains a grand challenge for all the people working on this area…. Room temperature conductivity of composite is too low.*
    - We developed a spray-on polymer-ceramic-polymer (trilayer) method to accurately assess the interfacial resistance between the polymer and ceramic electrolyte. We are currently trying different approaches to minimize the interfacial resistance.
- **Future plans**
  - *Reviewer 1: Using some improved polymer is the key to improve the ionic conductivity of the membrane.*
  - In FY 18 we will move beyond model polymer electrolyte like PEO + Li triflate, to include polymer gels.

Summary

Relevance Success of composite electrolyte will isolate the anode from liquid electrolyte, enabling high energy, thousands of cycles, negligible consumption of lithium, and safety.

Approach

- New approach uses slurry with inexpensive solvent and spray coating to obtain large area of uniform composite films with high ceramic loading.
- Develop a spray-on polymer-ceramic-polymer (trilayer) method to accurately determine the interfacial resistance between the polymer and ceramic electrolyte.

Technical accomplishments

- Densities of membranes formed by aqueous spray coating + hot pressing was confirmed to matched the highest theoretical values by gas pycnometer.
- A Li^+ transference number of 0.79 of TEGDME-plasticized composite electrolyte was determined, compared to that of polymer electrolyte, 0.47 – 0.57.
- Full battery was fabricated by spray coating the cathode followed by the composite electrolyte and good cyclability was demonstrated.
- Polymer-ceramic-polymer (trilayer) cell was constructed to quantify the interfacial resistance between the polymer and ceramic electrolyte. A very large interfacial resistance for ion transport (10000 Ohms at room temperature) was identified.

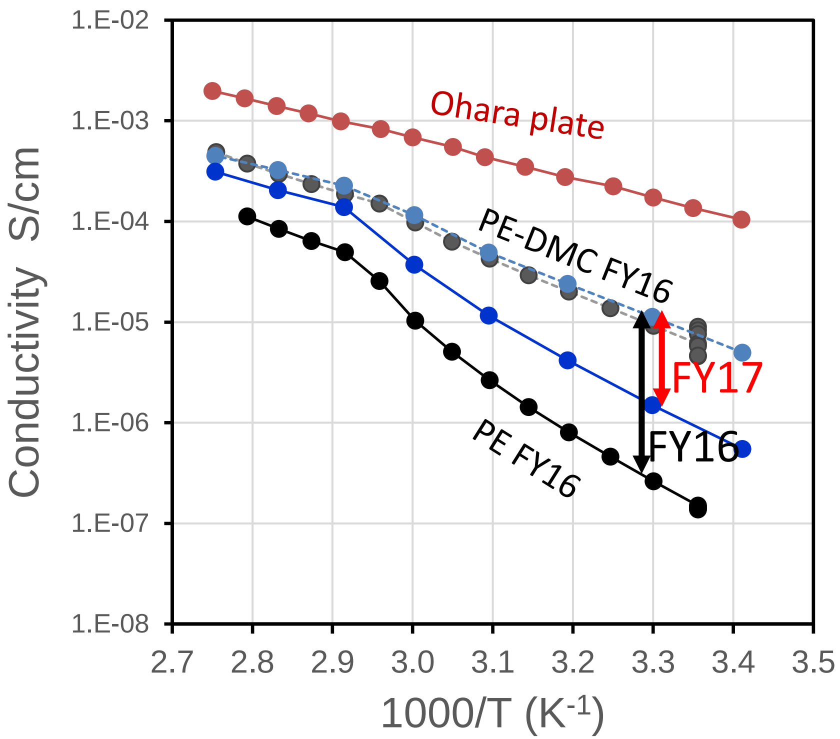
Future work

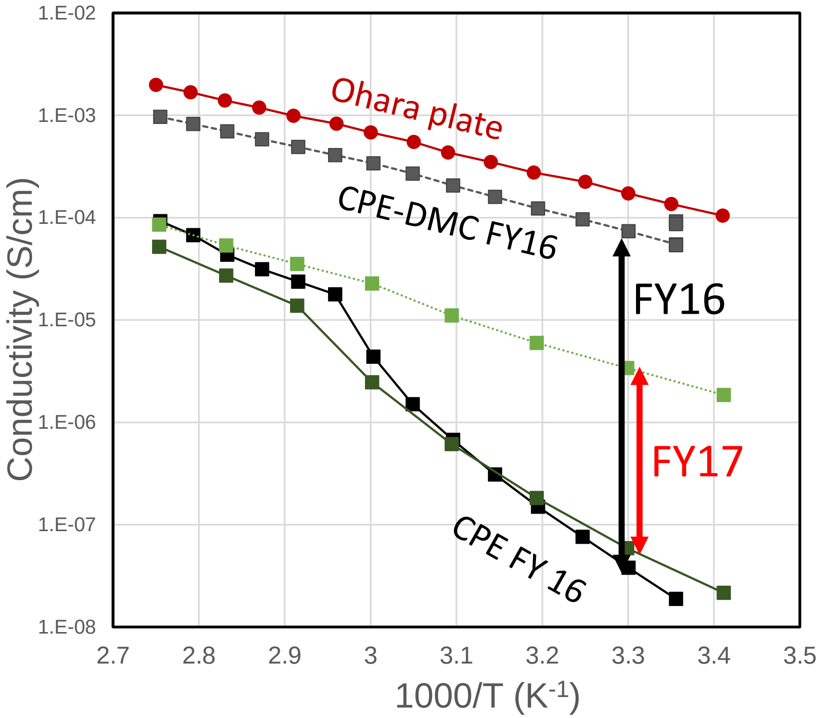
- Minimize interfacial ASR by chemical and mechanical treatments.
- Move beyond model materials like Ohara and PEO, to include polymer gels.
- Optimize cell design such as thickness of CPE|PE bilayer electrolyte, adding plasticizer and replacing PE with Lipon as the barrier layer.

Collaborations and coordination – key Sakamoto, Ohara, polymer researchers at ORNL.

Technical backup slides

Revisit DMC, comparison of effect of DMC with earlier results





- In FY16, we achieved extraordinary conductivity of DMC plasticized CPE. In FY17, due to change of PEO source and sample preparation method, the amount of DMC that can be infused into PE and CPE decreased – leading to decreased conductivity in both DMC plasticized PE and CPE.
- We will search for more reliable methods to plasticize polymer electrolyte.