Polymers For Advanced Lithium Batteries

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Project ID # ES088

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Overview

- **Timeline for projects A and B:**
- Project start date: October 2008
- Project end date: September 2012
- Percent complete: 80%

- **Budget:**
- Total project funding
  - –DOE share (100%)
  - –Contractor share (0%)
- Funding received in FY11 $550K
- Funding for FY12 $700K

- **Barriers:**
  - –(1) Energy density
  - –(2) Safety
  - –(3) Low cycle fife.
- **Partners:** ANL, ALS (at LBNL) and NCEM (at LBNL)

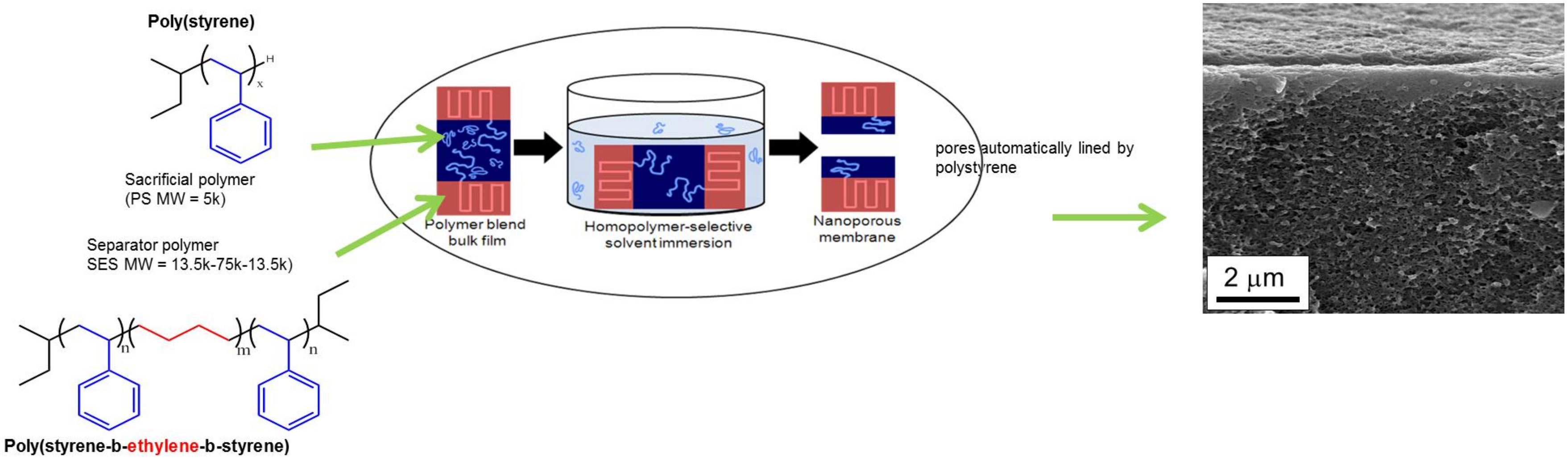
Objectives

- A) Develop cost-effective method for creating nanoporous separators.
- B) Study the effect of electrolyte nanostructuring on dendrite formation in symmetric cells.
- C) Study the effect of electrolyte nanostructuring on dendrite formation in full cells.
- D) Study the efficacy of SEO copolymers in cycling of cells with conversion reactions (e.g. Li-SEO-S cells).
- E) Develop a binder that conducts ions and electrons
- F) Develop ceramic/polymer composite electrolyte in collaboration with ANL.

Milestones

- A) Quantify the relationship between morphology and conductivity of separators (Sept 2011). *Completed.*
- B) Quantify improvement in dendrite resistance due to nanostructuring in symmetric cells (Mar 2012). *Completed.*
- C) Quantify improvement in dendrite resistance due to nanostructuring in full cells (Mar 2012). *Completed.*
- D) Report on the cycling characteristics of Li/SEO/S and Li/SEO/air cells (Sept 2012). *Thus far, reasonable progress on Li/SEO/S cells only.*
- E) Improve on loading of cathodes with conducting binder to 65 wt.%. *On target for completion.*
- F) Demonstrate feasibility making and using LATP/polymer composites (Sept. 2012). *On target for completion.*

Approach: Nanoporous Separators (A)



Create blends of SES triblock copolymers and PS homopolymers, dissolve the PS homopolymer in THF to obtain nanoporous separator. Correlate pore structure of the separators with conductivity of separators when they are filled with a liquid electrolyte.

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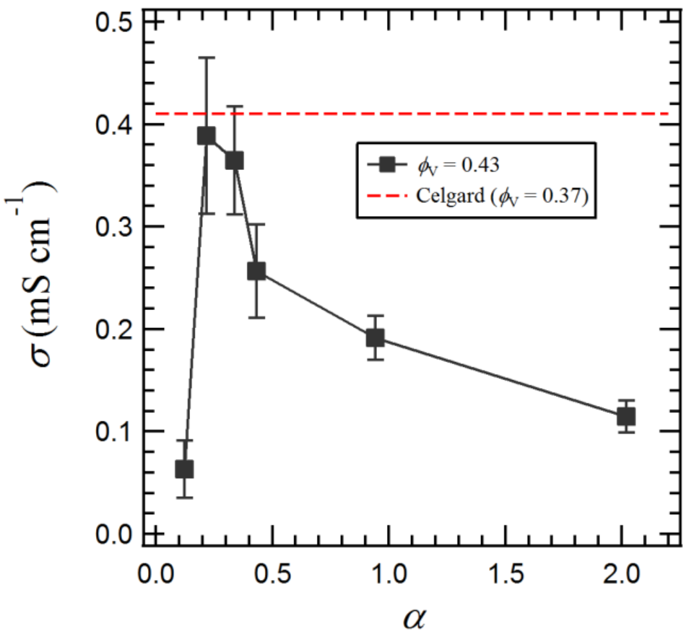
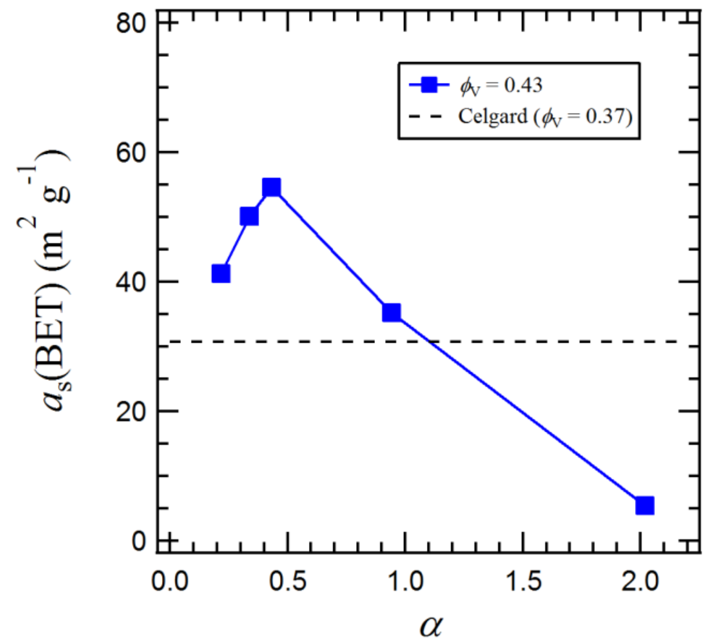
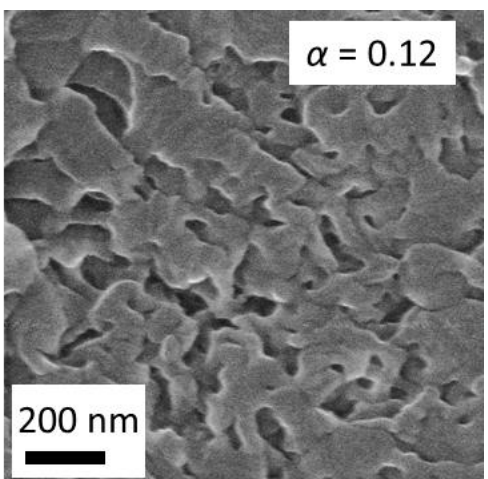
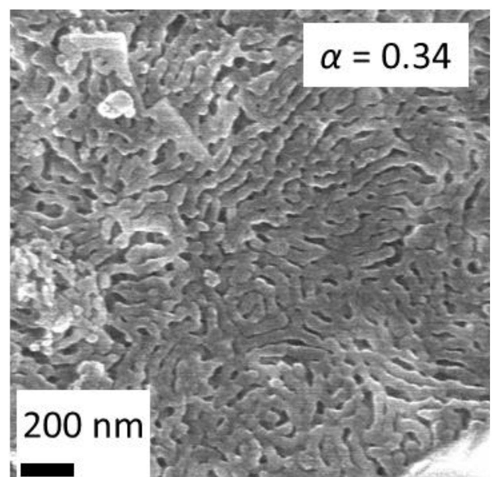
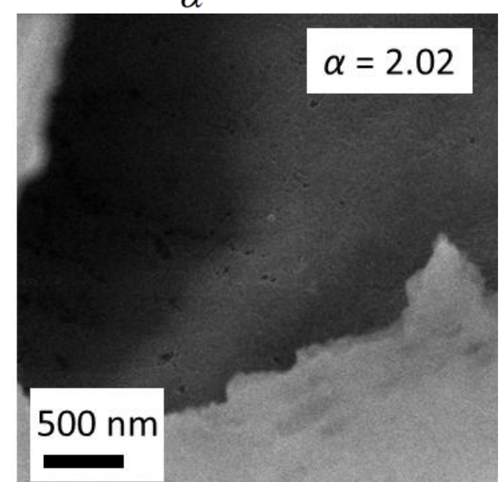
Accomplishment: Low Cost nanoporous separators with uniform pore structures (A)











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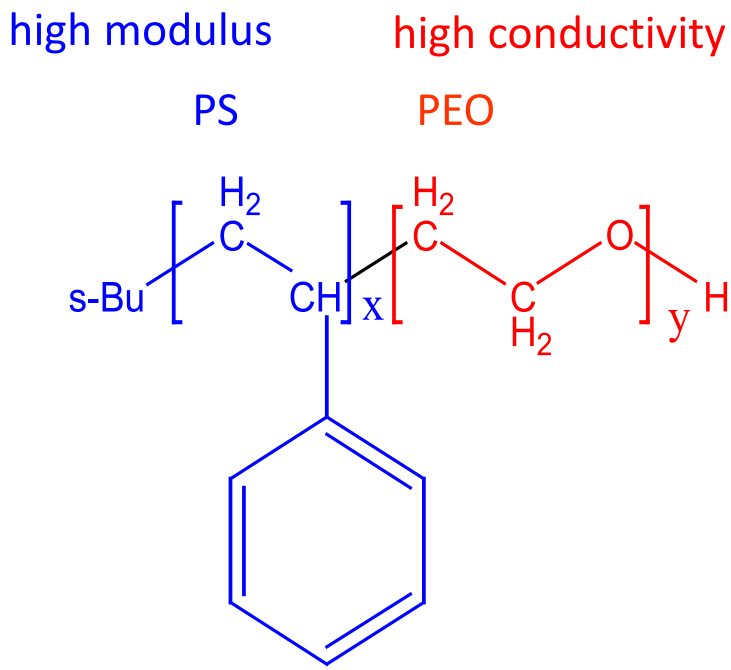
Future work: nanoporous separators (A)

Optimize the pore morphology by tuning the composition of the polymers and quantify the efficacy of the separators by cycling full cells.

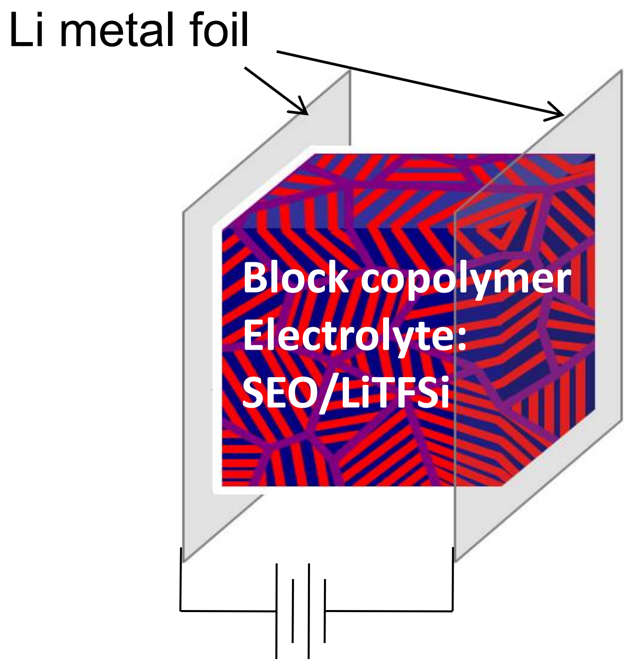
Overall Approach (B-F): Nanostructured block copolymer electrolytes

We use a solid block copolymer electrolyte SEO to prevent the formation of Li dendrites. The high modulus of the PS block resists dendrite formation and enables the use of lithium metal as an anode.

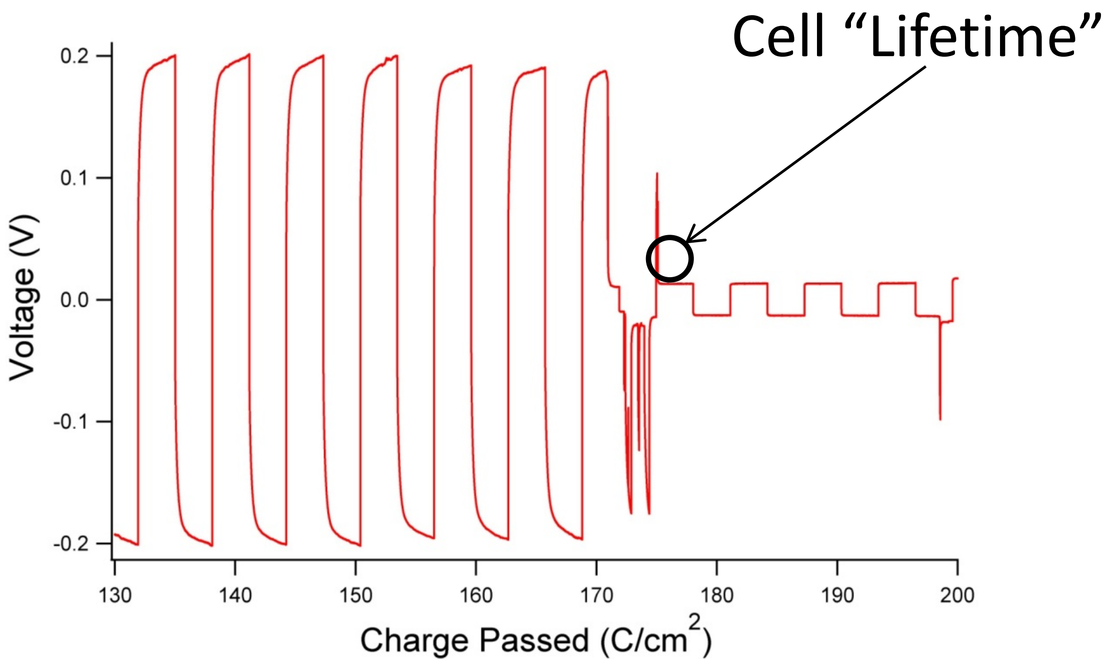


SEO(x,y) block copolymer

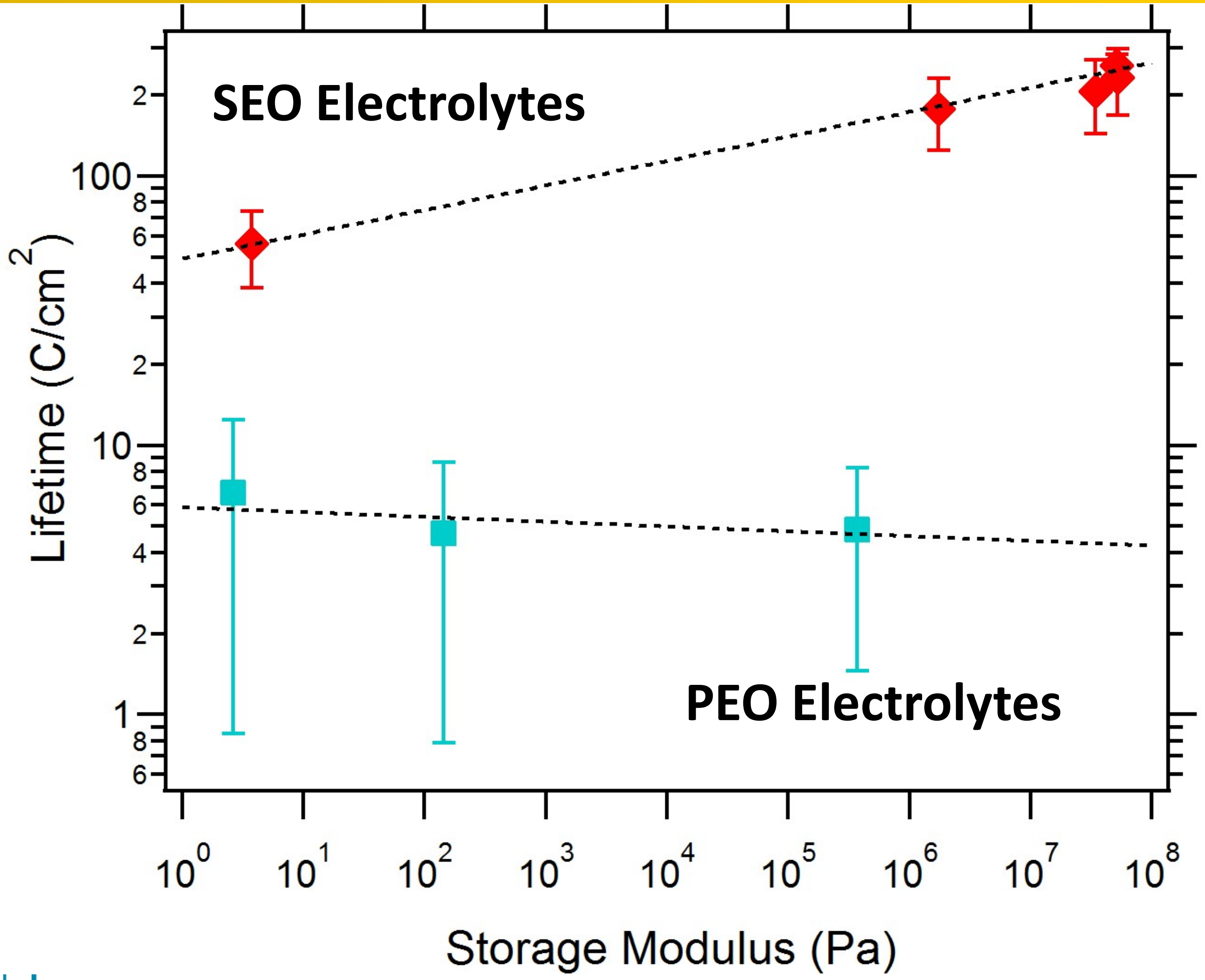
Approach: Cycle Li/SEO/Li batteries until they short to test SEO efficacy (B)



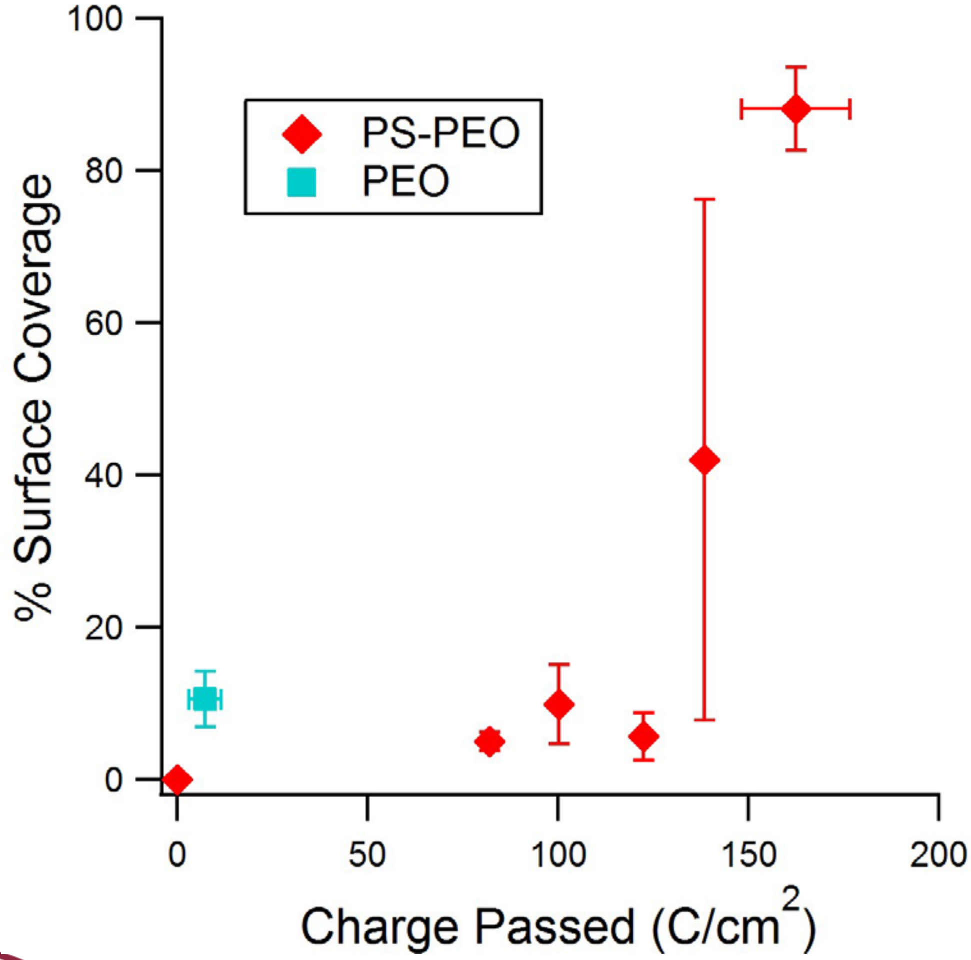
SEO (16 – 16) Electrolyte

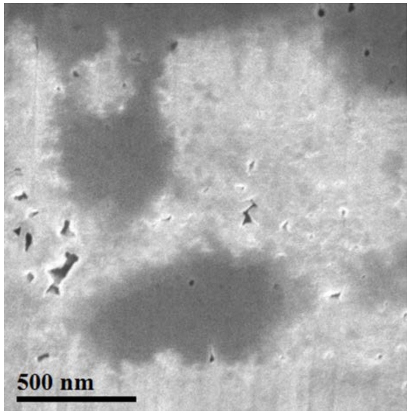


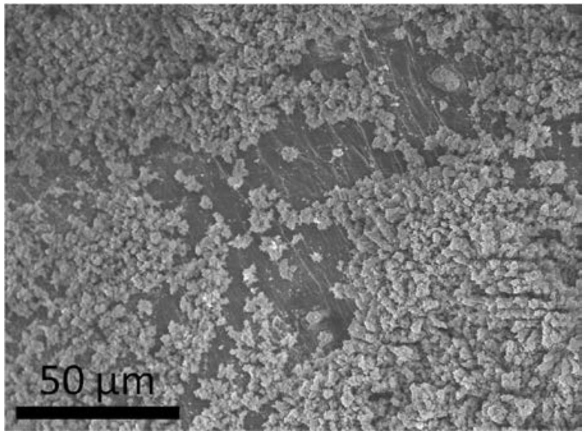
Accomplishments: Nanostructured SEO electrolytes increase anode lifetime as high as 20 times relative to PEO (B)



Accomplishments: Quantified roughening of Li electrodes when cycled with SEO and PEO electrolytes (B)







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Future work: Li/SEO/Li symmetric cell cycling (B)

Efficacy of SEO electrolytes for preventing dendrite formation in full cells will be quantified.

Approach: Quantify lifetime of Li/SEO/$LiFePO_4$ battery (C)

Discharge Reactions

Cathode

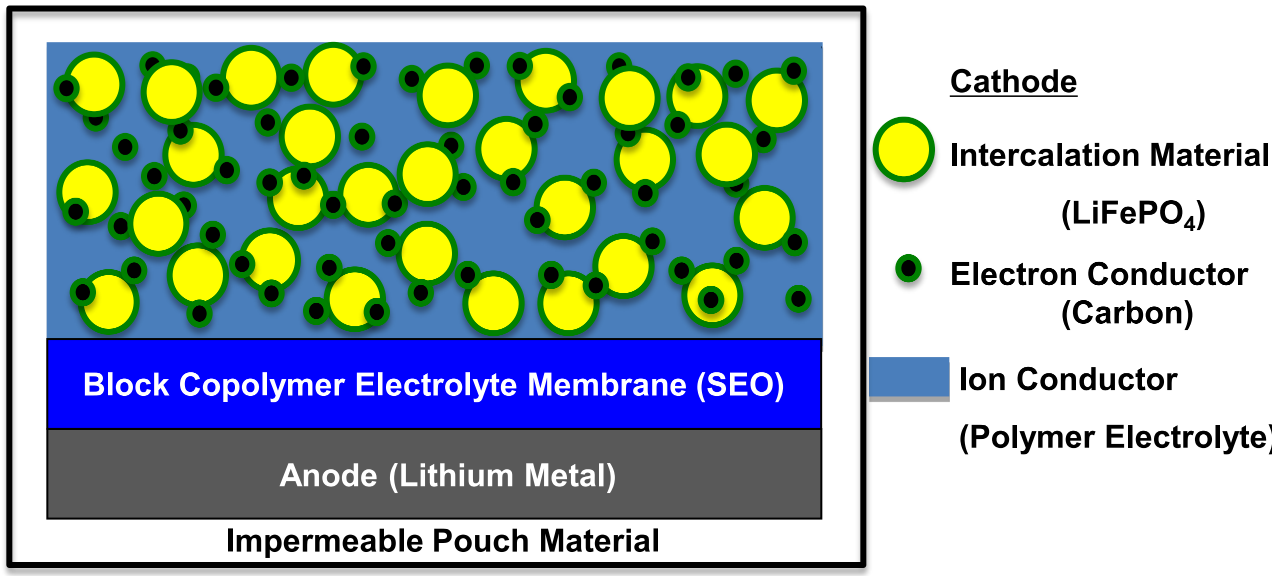
$$\underset{}{Li^+} + e^- + \underset{\text{(Solid)}}{FePO_4} \longrightarrow \underset{\text{(Solid)}}{LiFePO_4}$$

170 mAh/g

Lithium Metal Anode

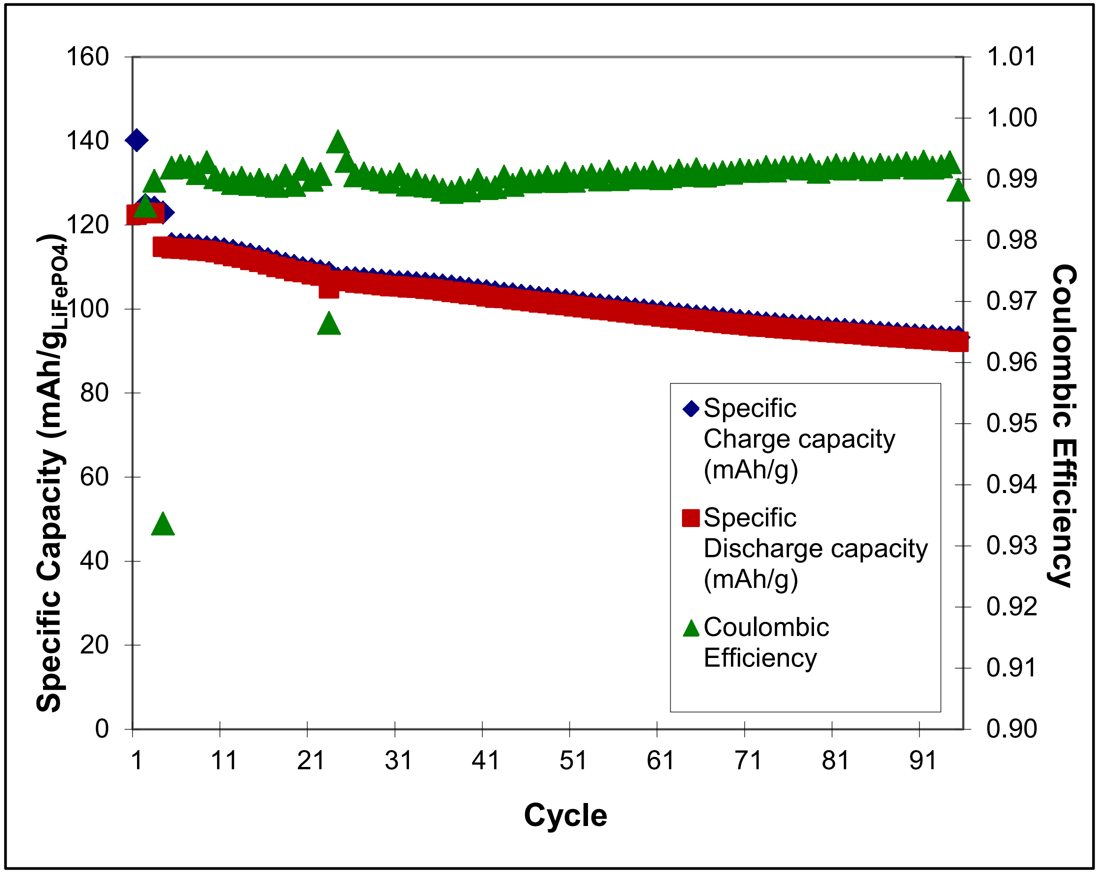
$$Li \longrightarrow Li^+ + e^-$$

3860 mAh/g

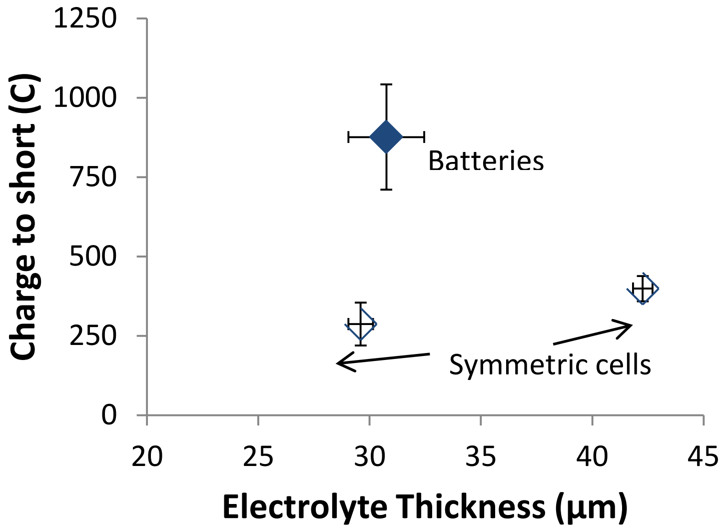


- **Block Copolymer Electrolyte replaces inert binder, separator and liquid electrolyte.**

Accomplishments: Battery capacity of Li/SEO/$LiFePO_4$ (C)



Charge passed to dendrite failure in $LiFePO_4$/SEO/Li batteries is a factor of about 2.5 higher than that of symmetric Li/SEO/Li cells.



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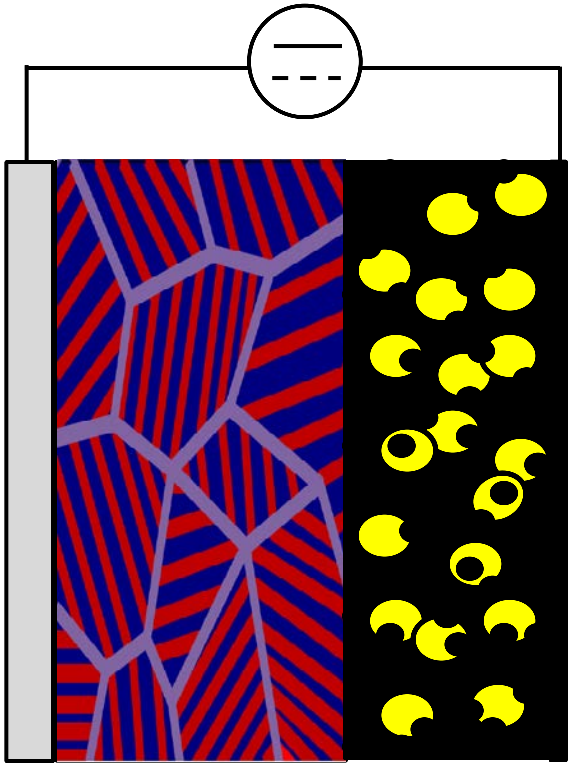
Future work: Li/SEO/$LiFePO_4$ batteries (C)

The task of synthesis and characterization of SEO cells will be terminated when this cycling study is completed.

Approach: Control polysulfide dissolution and enable good cycle life in Li-S cells by nanoconfinement (D)



Series of redox reactions

$S_{8(s)} + 2Li^+ + 2e^- \rightarrow Li_2S_8$

$\frac{1}{2}Li_2S_8 + Li^+ + e^- \leftrightarrow Li_2S_4$

$\frac{1}{2}Li_2S_4 + Li^+ + e^- \leftrightarrow Li_2S_2$

$\frac{1}{2}Li_2S_2 + Li^+ + e^- \leftrightarrow Li_2S_{(s)}$

Very Soluble

Not Soluble

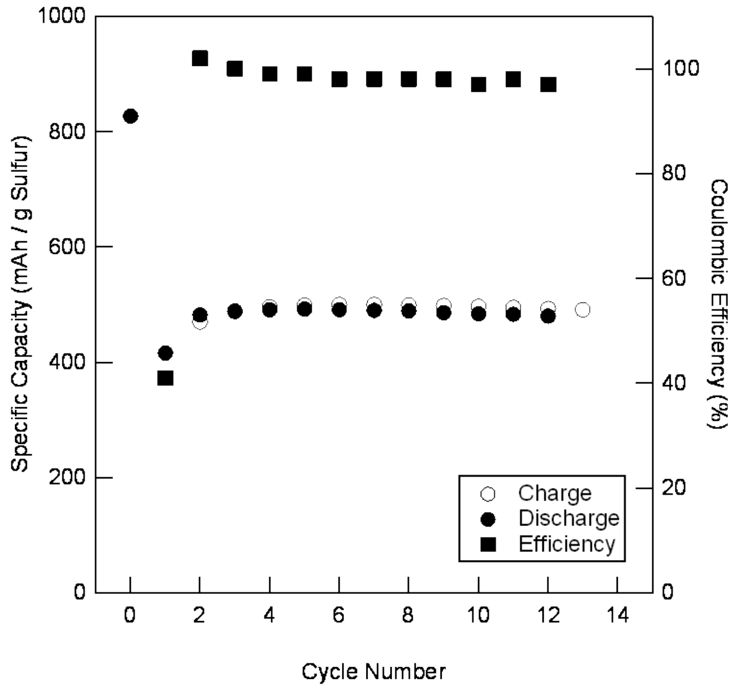
Overall Reaction:

$S_8 + 16Li^+ + 16e^- \rightarrow 8Li_2S$

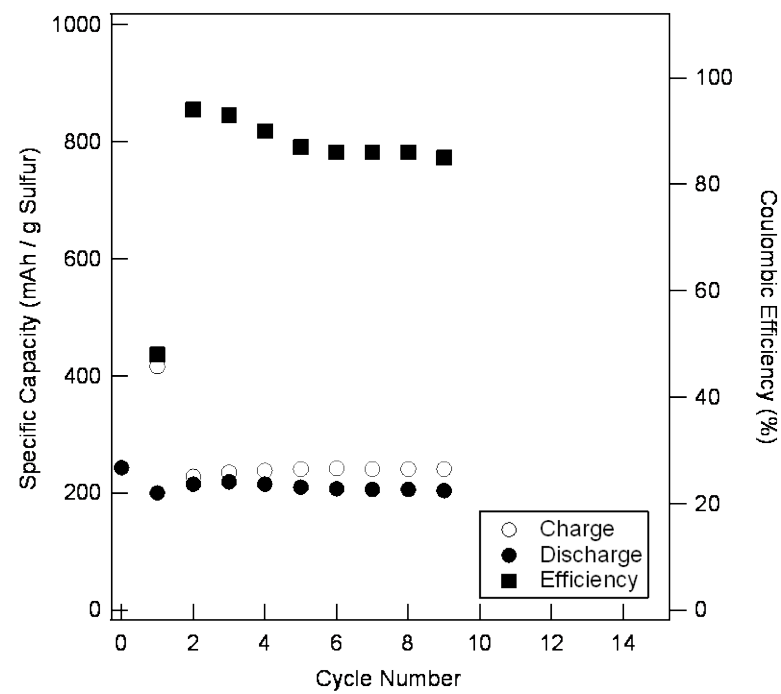
Li metal | SEO + LiTFSI | SEO + LiTFSI + S + C

Accomplishments: Li/SEO/S batteries assembled and preliminary cycling data are promising (D)

- 10% Sulfur
- 45% SEO/LiTFSI
- 45% Carbon



- 40% Sulfur
- 30% SEO/LiTFSI
- 30% Carbon



Lower sulfur loading give better specific capacity.

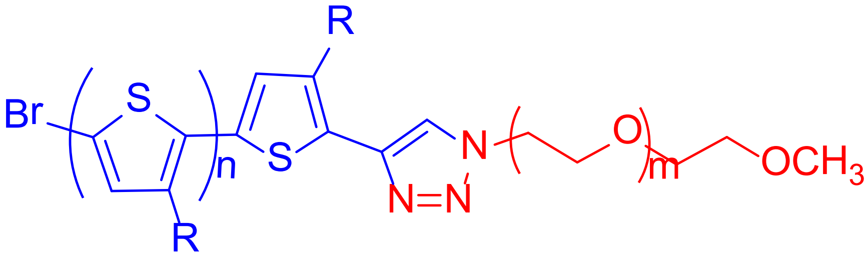
Future work: Li/SEO/S batteries (D)

Quantify the effect of SEO morphology on cell cycling. Since the domain size of SEO copolymers can be varied systematically, we will obtain a systematic understanding of the role of nanoconfinement of cell performance.

Approach: Synthesize ion and electron conducting binder (E)

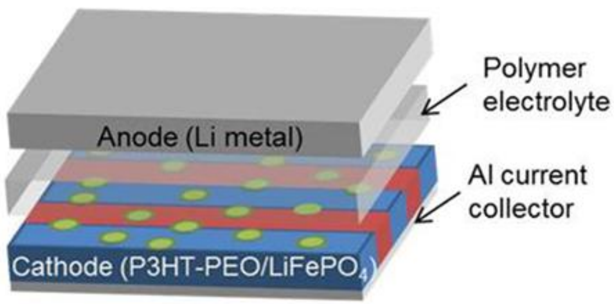
Redox reactions in battery electrodes require transport of both ions and electrons to active centers. We have developed a novel binder (P3HT-PEO) to provide both ionic and electronic transport to the redox centers.

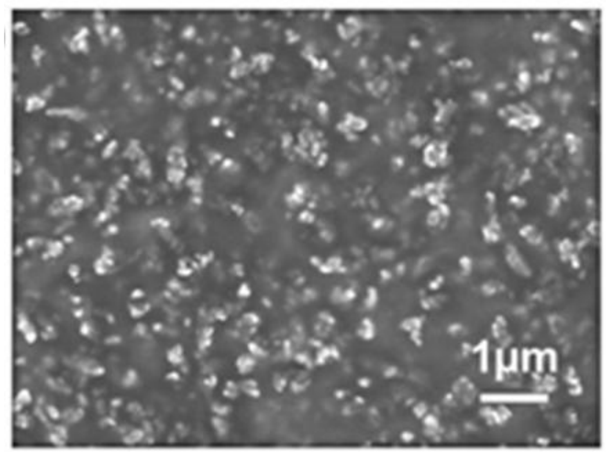
Use one material to provide both ionic and electronic transport.



Poly(3-hexylthiophene)-*b*-poly(ethylene oxide) (P3HT-PEO)

Accomplishment: Synthesized PSHT-PEO, first polymer to exhibit both electronic and ionic conductivity (E)



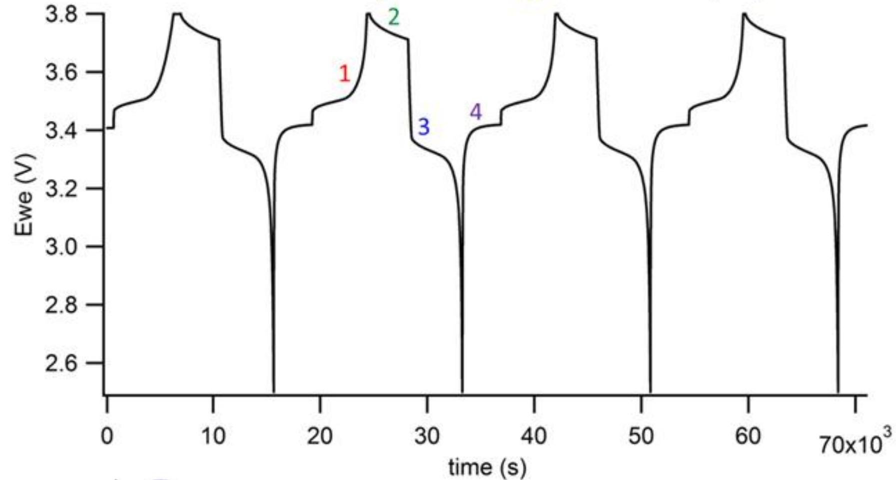


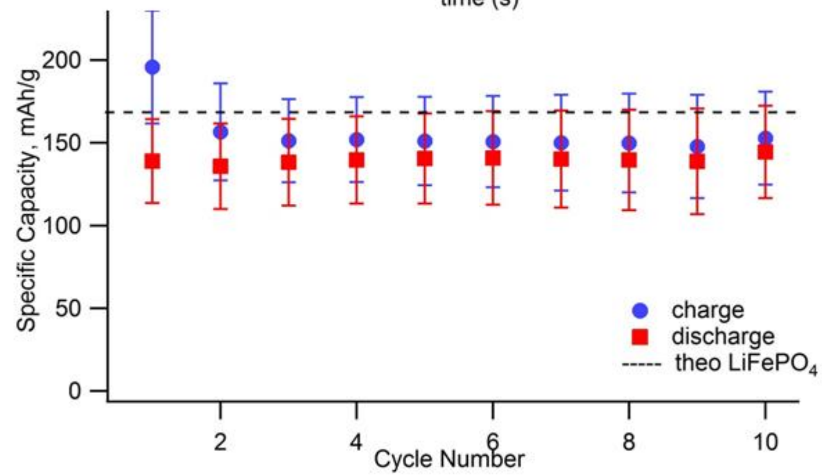
Cathode SEM

- 50 wt% $LiFePO_4$
- Electrolyte and cathode both contain LiTFSI, r=0.085
- Approaches theoretical limit

Current density: 0.02 mA/cm^2 (T = 90^{O}C)

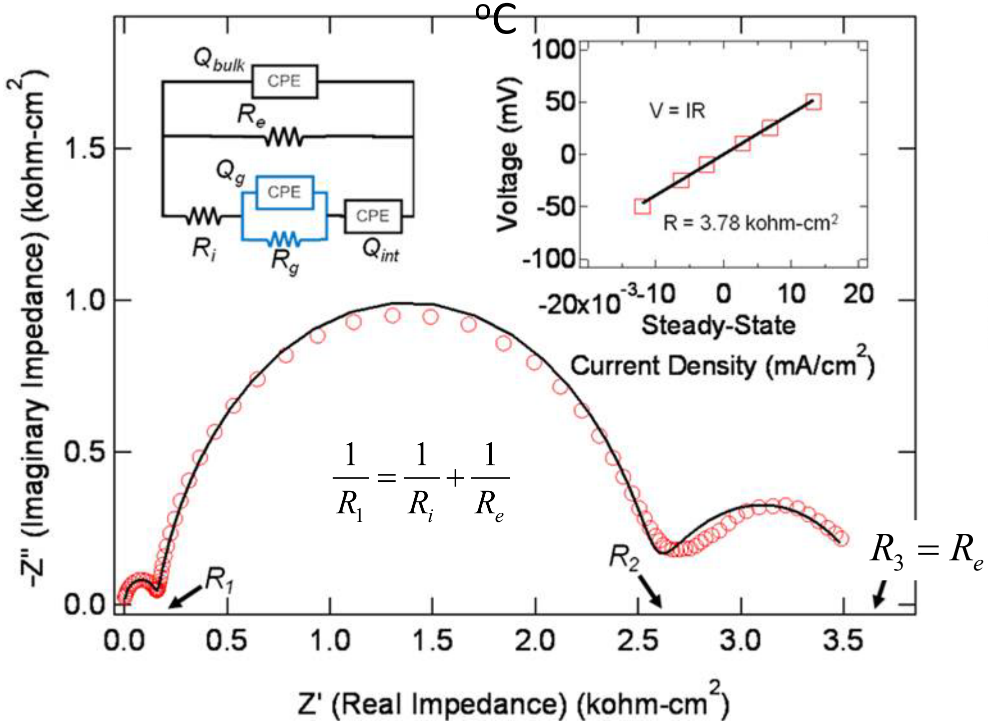
1 cycle = 4 steps: 1) Charged to 3.8V; 2) 1hr rest; 3) discharged to 2.5V; 4) 1hr rest



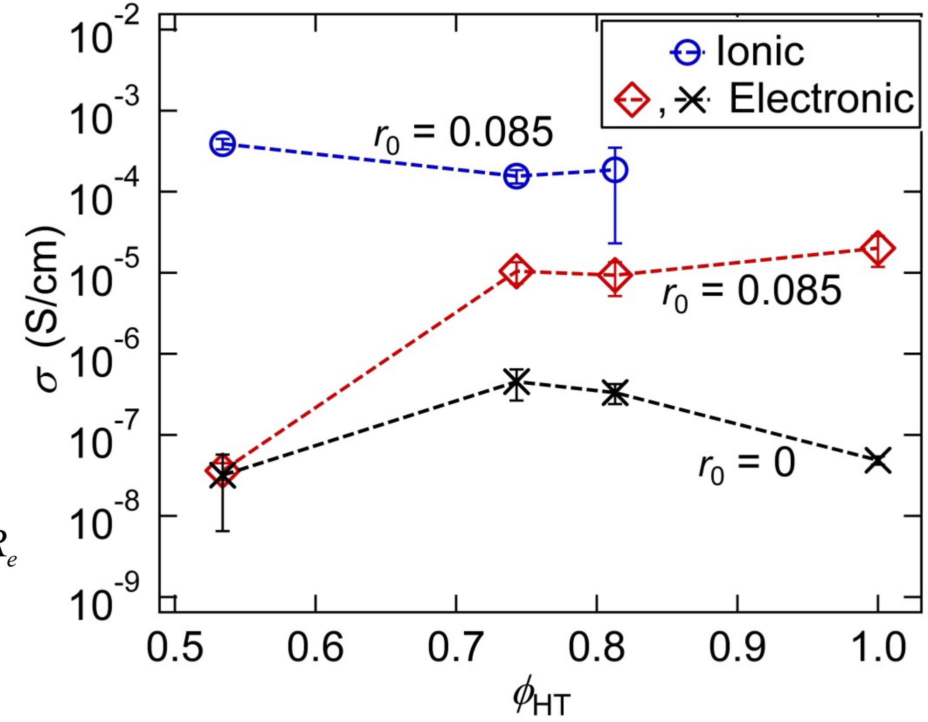


Accomplishments: Determined electronic and ionic conductivity of P3HT-PEO by a combination of AC and DC experiments (E)

Nyquist Plot of
P3HT-PEO-6-2 with LiTFSI at 90 °C



Electronic and Ionic
Conductivity at 90 °C

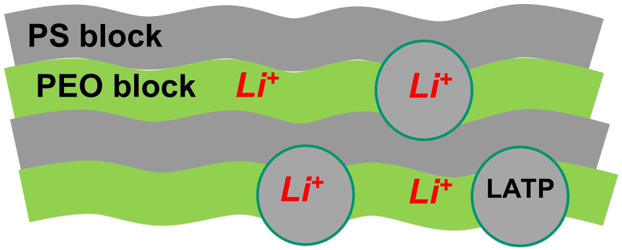


Future work: P3HT-PEO binders (E)

Study the effect of increasing the active material loading in the cathode and determine the upper limit of loading.
Develop ion- and electron-conducting polymers for the sulfur cathode.

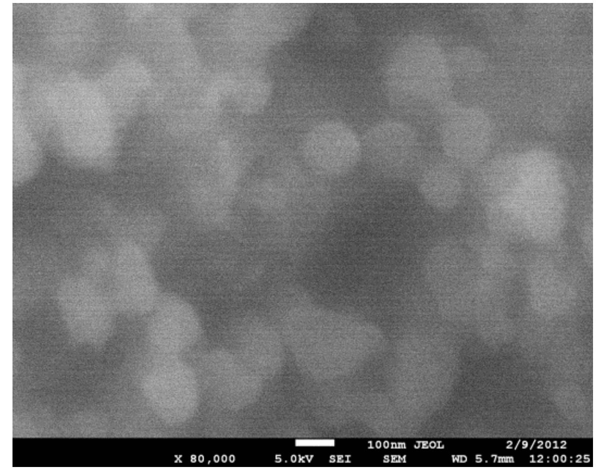
Approach: Add Lithium Aluminum Titanium Phosphate (LATP) to SEO to increase conductivity (F)

- LATP is a ceramic lithium-ion conductor that has a higher room temperature conductivity that all known polymer electrolytes. However it is brittle and thus prevents use of this material as a stand-alone electrolyte. In this task LATP particles obtained from ANL are dispersed in SEO copolymer electrolytes and study the properties of these composite electrolytes.

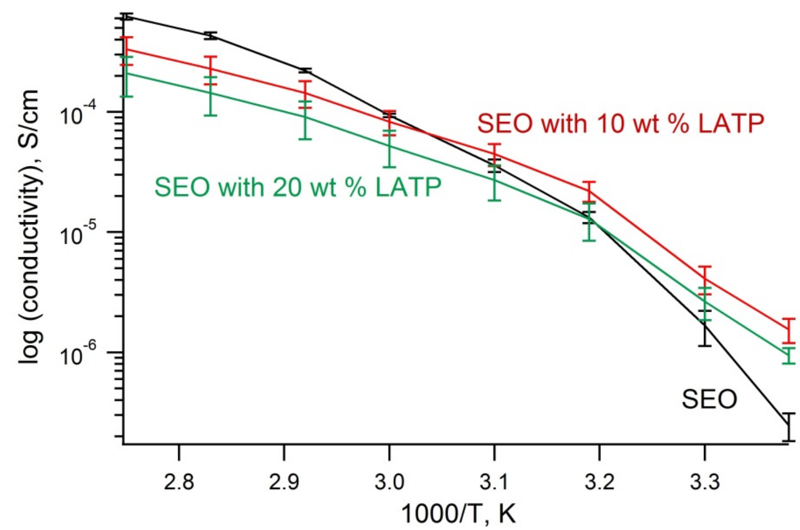


Accomplishments: Synthesized and measured conductivity of LATP particles in SEO (F)

By incorporating LATP nanoparticles in SEO, room temperature conductivity of SEO/LiTFSi systems can be increased slightly.

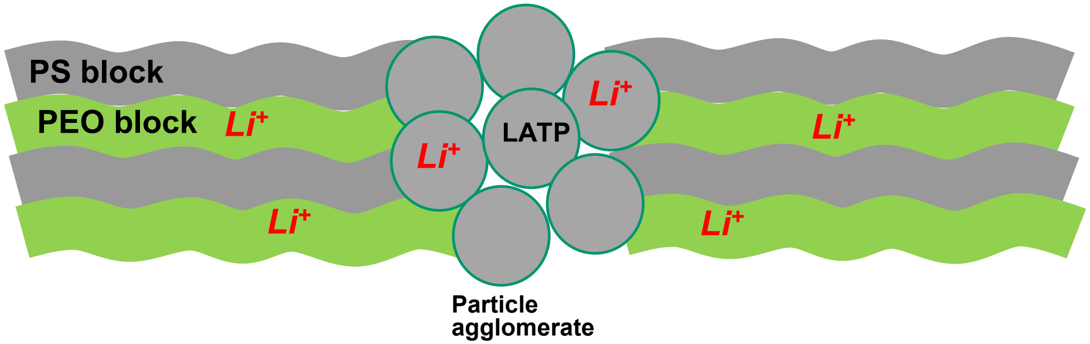


LATP with diameter 50 nm to 100 nm



Future work: LATP/SEO dispersions (F)

We will study morphology of the dispersion by TEM and correlate dispersion with conductivity. Promising composites will be used to cycle cells to test the ability of these composites to resist dendrite formation from Li metal anodes.



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Collaboration and Coordination with Other Institutions

- Partners:
  - –Jack Vaughey (ANL, VT Program) and Jordi Cabana (LBNL, VT program: prime on production of Li-conducting ceramics
  - –Alex Hexemer (LBNL, outside VT Program): Synchrotron X-ray scattering at ALS
  - –Andrew Minor (LBNL, outside VT Program): Electron microscopy at NCEM
- Coordination:
  - –Binder team leader, responsible for coordinating binder effort of VT program [Kumta (Univ. Pittsburgh), Hickner (Penn. State), and Liu (LBNL)]
- Technology Transfer:
  - –Cofounded Seeo, a battery start-up, in 2007 to commercialize solid-state battery. Company has moved into pilot production in 2011-12

Summary

Established a comprehensive program to study the potential role of nanostructured block copolymers in lithium batteries.

- (A) Established a low-cost approach for creating reliable nanoporous separators.
- (B) Quantified the efficacy of SEO copolymers as electrolytes for the prevention of lithium dendrites in symmetric Li-polymer-Li cells.
- (C) Efforts to quantify dendrite resistance in full cells are underway.
- (D) Efficacy of confinement of polysulfides in SEO block copolymers and the effect of this on cycling of Li-S cells is being studied.
- (E) An active binder that conducts both ions and electrons has been developed, characterized and incorporated into cells.
- (F) Conductivity of composite ceramic/SEO electrolytes have been made.