Polymers For Advanced Lithium Batteries

Nitash P. Balsara

Lawrence Berkeley National Lab

May 12, 2011

Project ID #
ES088

This presentation does not contain any proprietary, confidential, or otherwise restricted information

BERKELEY LAB

Overview

Timeline

- FY08
- FY11
- 65%

Barriers

- Energy density
- Safety
- Low cycle life

Budget

- FY10 funding: 390 K
- FY 11 funding: 550 K
- No contractors

Partners

- Lead: LBNL

Milestones

Month-Year	Milestone
Mar-11	Electrochemical characterization of block copolymer electrolytes. Partially accomplished.
June-11	Synthesis of a binder that conducts electrons and ions. Accomplished
Sept-11	Synthesis of nanoporous block copolymer separators. Accomplished.

All *go* decisions.
No show stoppers.

Objective

Current lithium batteries use a polymeric binder (**inactive** glue in cathode) and a polymeric separator (**expensive inactive** polyolefin with pores) .

Objective: Comprehensive overhaul of the way polymers are used in lithium batteries

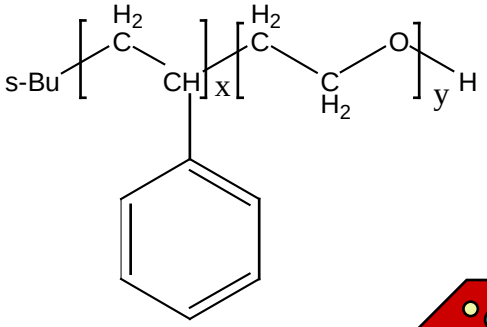
Specific Objectives:

1. Characterization of dry nanostructured polymeric separators for stabilizing the lithium metal anode (95% complete).
2. Synthesis and characterization of a polymeric binder that conducts both ions and electrons (50% complete).
3. Synthesis and characterization of templated nanoporous separators (50% complete).

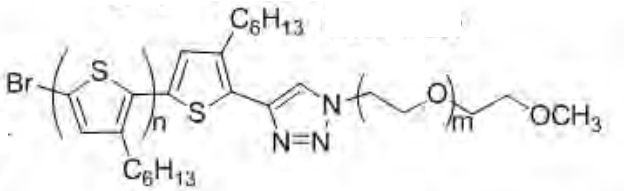
Approach

- Synthesize block copolymers
- Study morphology and ion and electron transport
- Build and test full cells

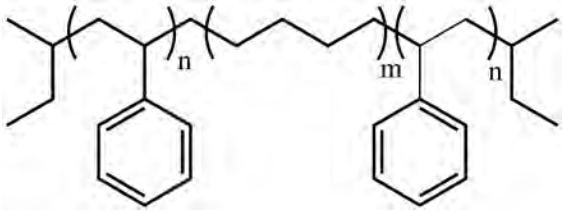
Nanostructured solid electrolyte

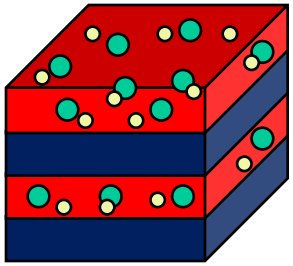


Electron- and ion-conducting binder

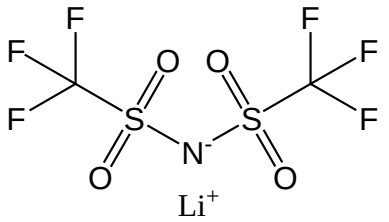


Nanoporous separator





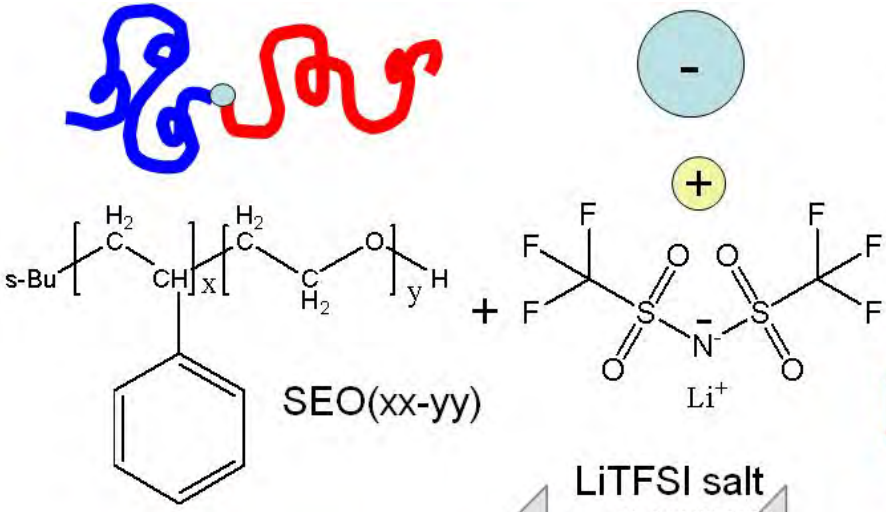
Salt, LiTFSI

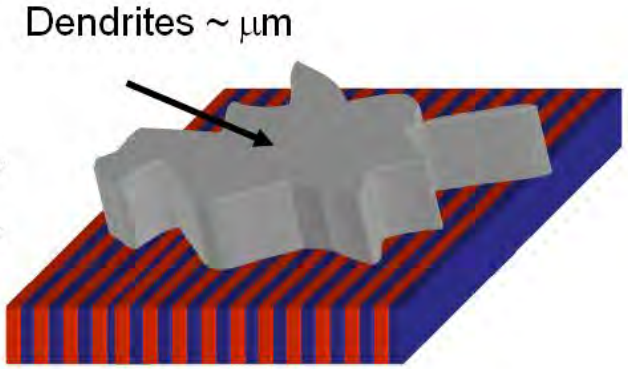


BERKELEY LAB

Technical Accomplishments

Nanostructured solid electrolyte

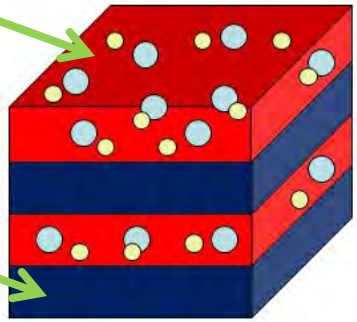




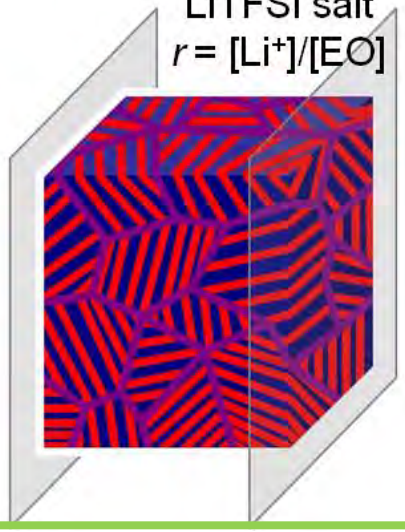
Nanostructured conductor ~ 10 nm

soft phase conducts ions

hard phase prevents dendrite formation



LiTFSI salt
$r = [Li^+]/[EO]$



No effort to control alignment

Symmetric lithium-polymer-lithium cell experiments

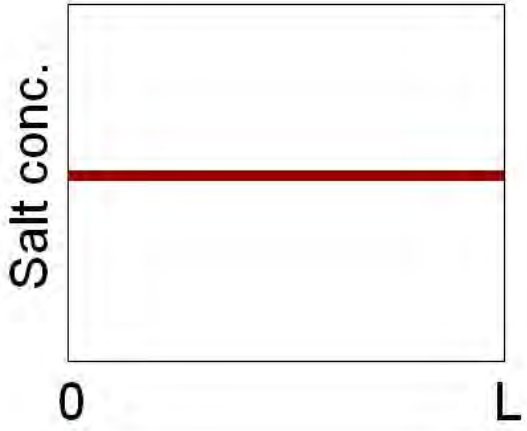
Technical Accomplishments

Nanostructured solid electrolyte

Measurement of diffusion coefficient by restricted diffusion.

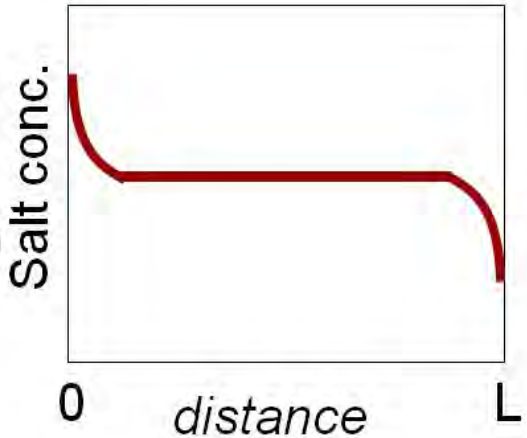
Step 1:

relax cell



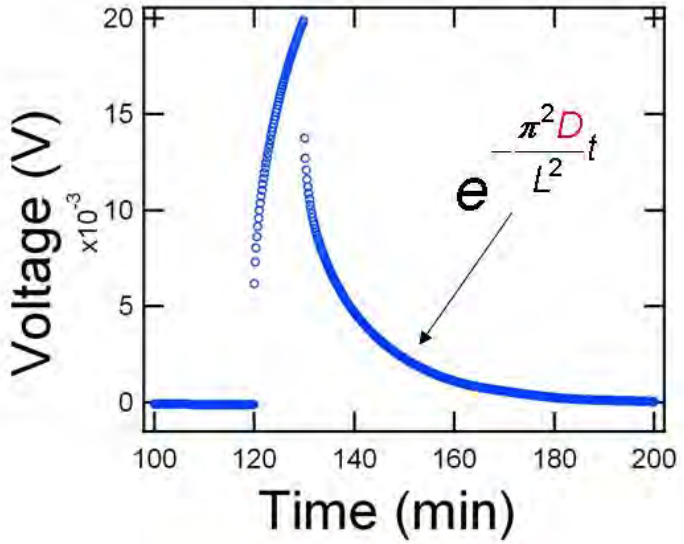
Step 2:

polarize cell (dc charging)



Step 3: watch voltage decay

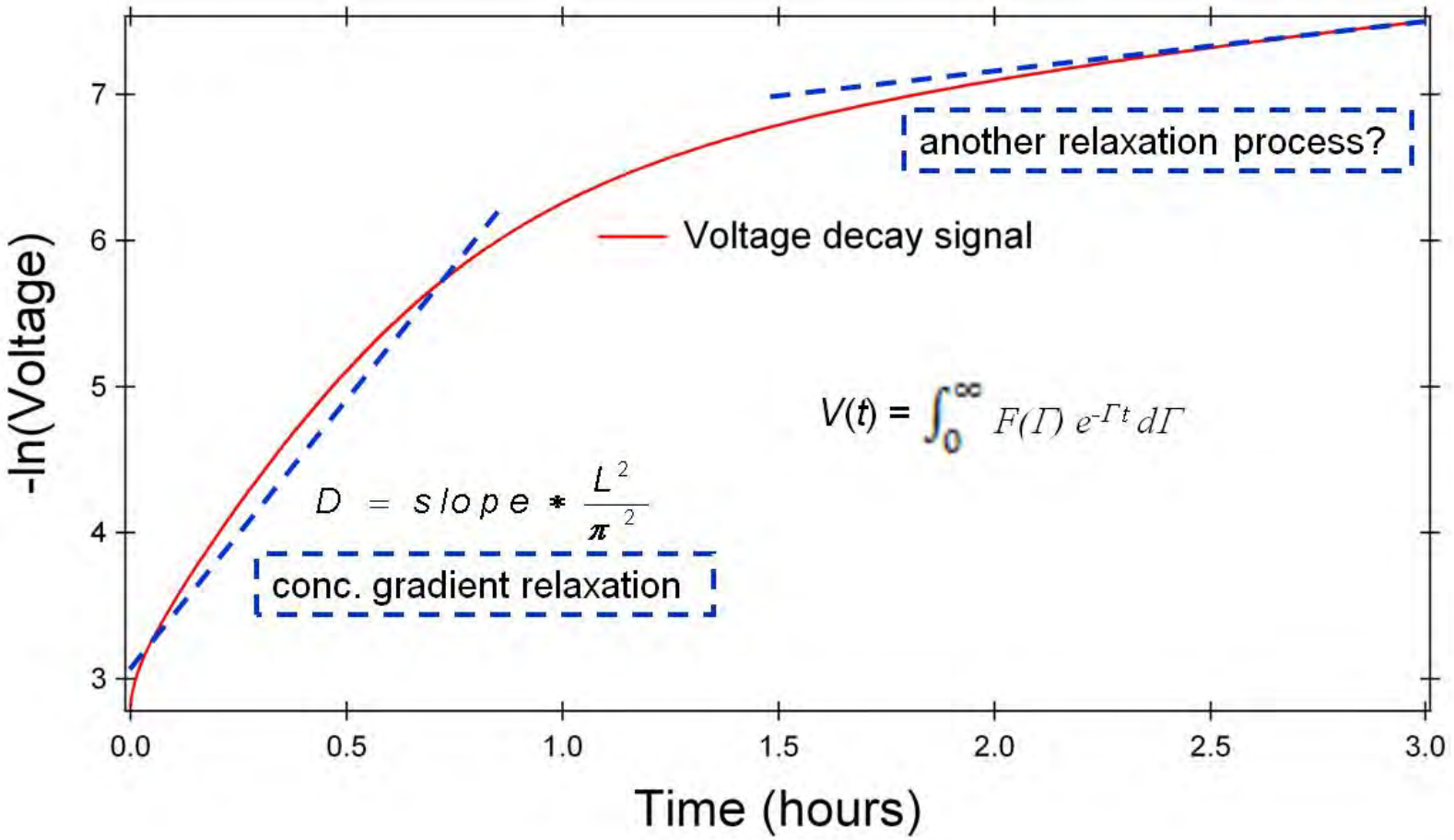
cell voltage with time



Get *D* from slope of –ln(Voltage) vs time

Technical Accomplishments

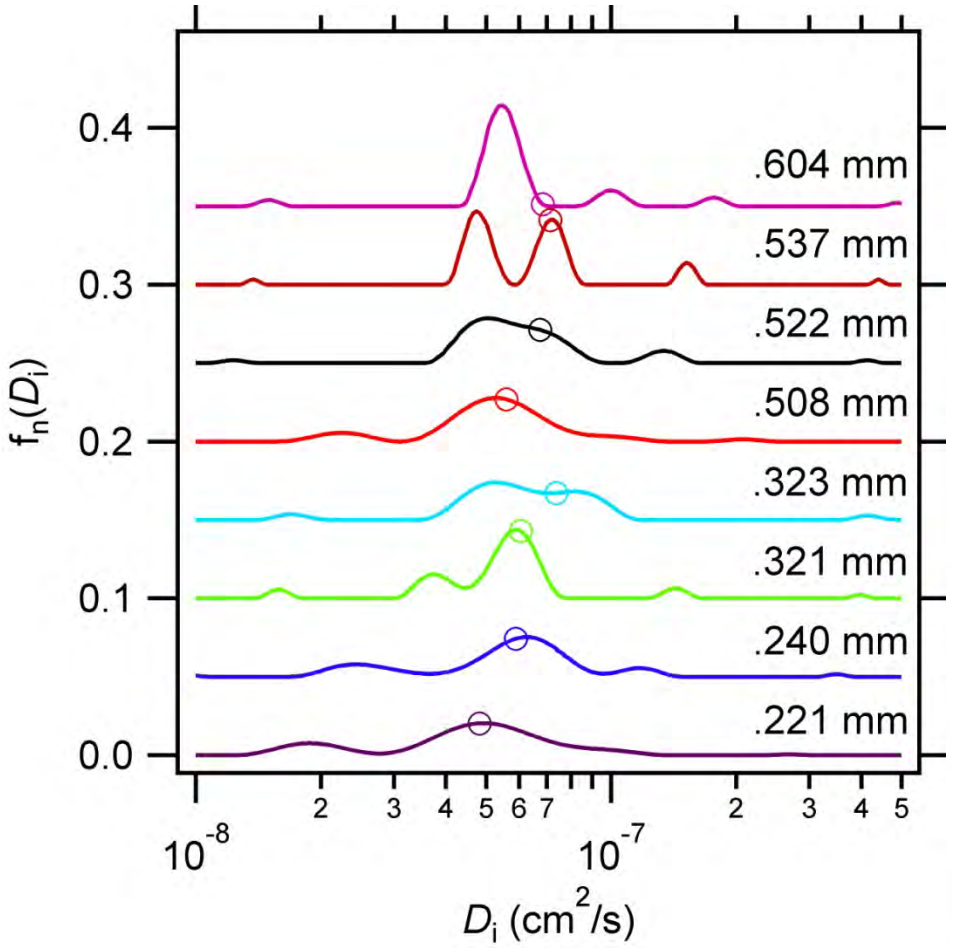
Nanostructured solid electrolyte



Signal resolved over orders of magnitude.

Technical Accomplishments

Nanostructured solid electrolyte



Varying sample thickness

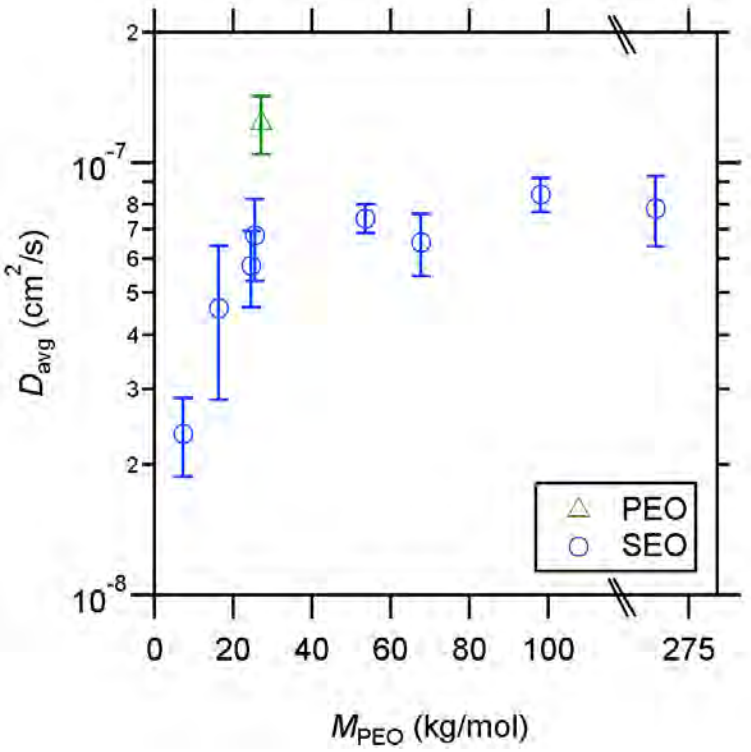
Average diffusion coefficient and widths of diffusion coefficient distribution functions are determined.

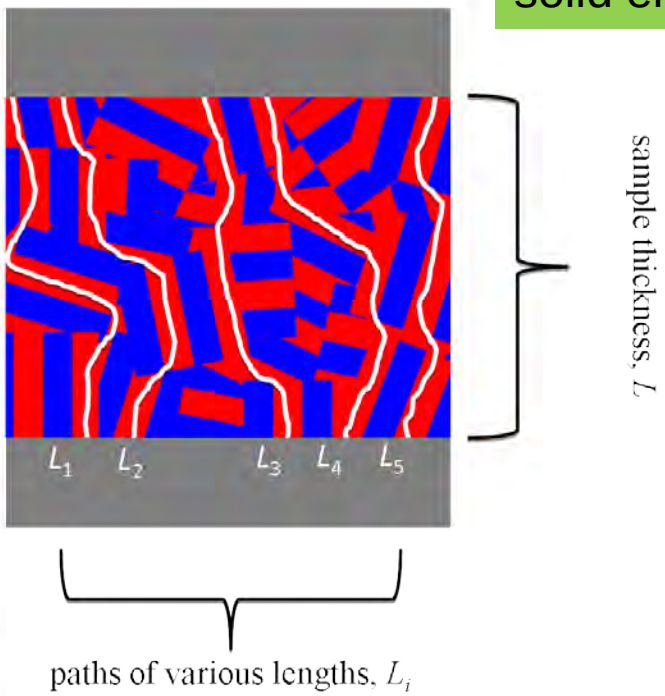
Table II. Average diffusion coefficient, D_{avg}, and $PDI_{diffusion}$ of the relaxation distribution functions for the polymers used in this study. All listed values are at 90°C and $r = 0.085$.

Polymer	D_{avg} (cm^2/s)	Average $PDI_{diffusion}$
PEO(27)	$(1.23 \pm 0.12) \times 10^{-7}$	1.16 ± 0.13
SEO(6–7)	$(2.36 \pm 0.49) \times 10^{-8}$	1.67 ± 0.32
SEO(16–16)	$(4.62 \pm 0.18) \times 10^{-8}$	1.59 ± 0.26
SEO(36–24)	$(5.79 \pm 1.2) \times 10^{-8}$	1.41 ± 0.18
SEO(37–25)	$(6.80 \pm 1.5) \times 10^{-8}$	1.64 ± 0.35
SEO(40–54)	$(7.44 \pm 0.6) \times 10^{-8}$	1.31 ± 0.15
SEO(53–68)	$(6.54 \pm 1.1) \times 10^{-8}$	1.36 ± 0.27
SEO(74–98)	$(8.45 \pm 0.8) \times 10^{-8}$	1.38 ± 0.21
SEO(240–269)	$(7.83 \pm 1.5) \times 10^{-8}$	1.35 ± 0.26

Technical Accomplishments

Nanostructured solid electrolyte





- System characterized by a range of diffusion coefficients.
- Probably true for all heterogeneous transport processes.
- Resolved due to sophistication of electrochemical instrumentation.

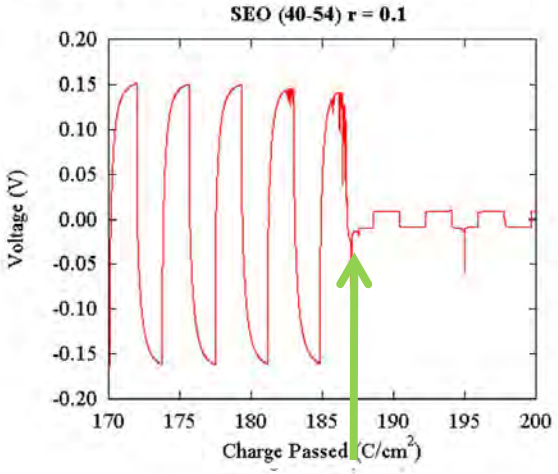
Mullin, et al., J. Electrochem. Soc, ***2011****.*

BERKELEY LAB

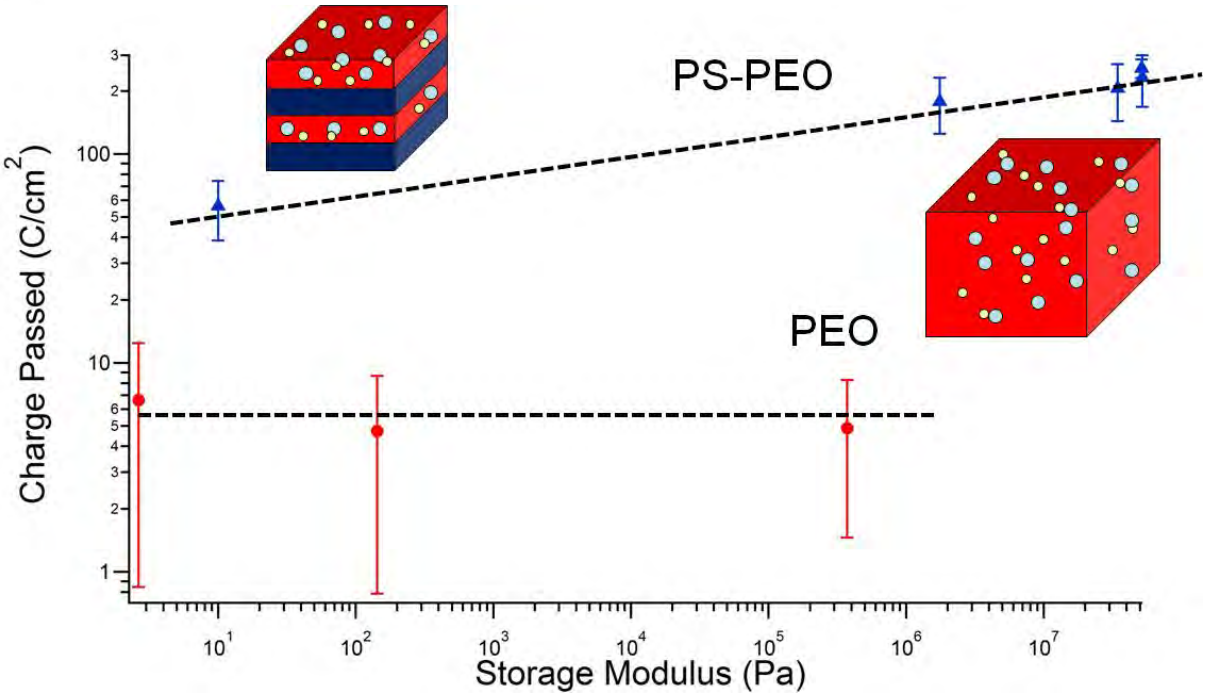
Technical Accomplishments

Nanostructured solid electrolyte

- Constant current (0.17 mA/cm^2), T=90 °C



Measurement of charge passed to obtain a dendrite short.

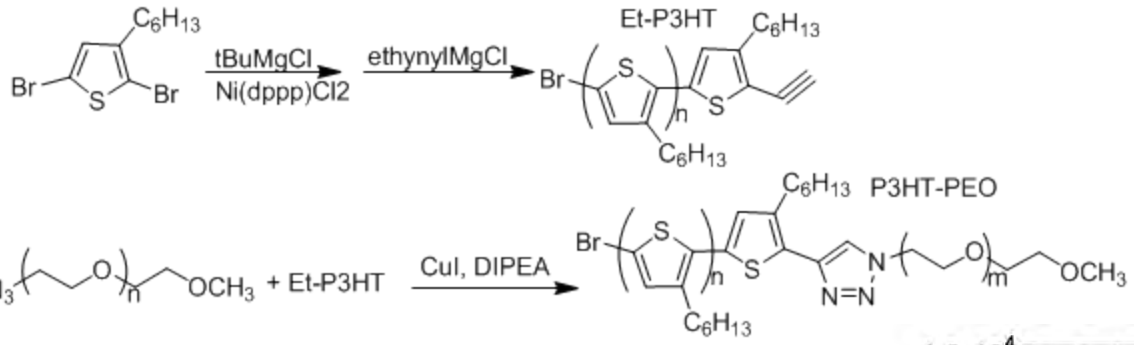


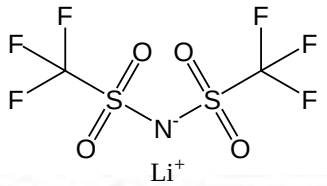
High molecular weight block copolymers are a factor of 30 better than homopolymer of identical modulus.

Stone, et al., manuscript under review.

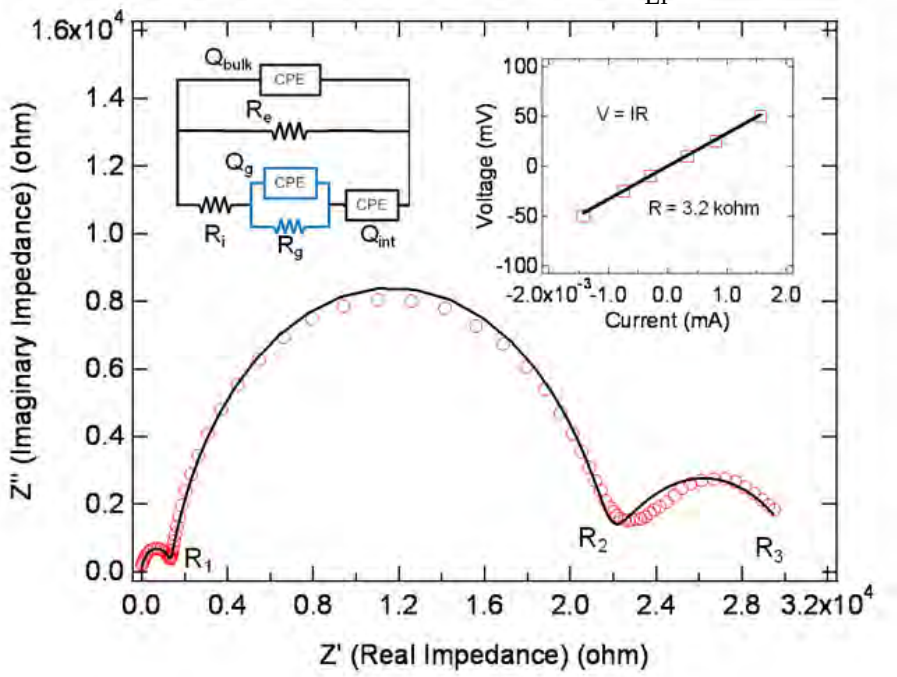
Technical Accomplishments

Electron- and ion-conducting binder





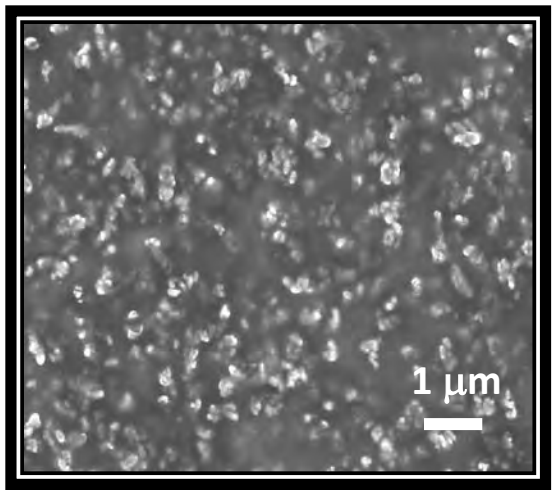
First impedance spectrum of a polymer that conducts both ions and electrons. Unambiguous determination of electronic and ionic conductivity.



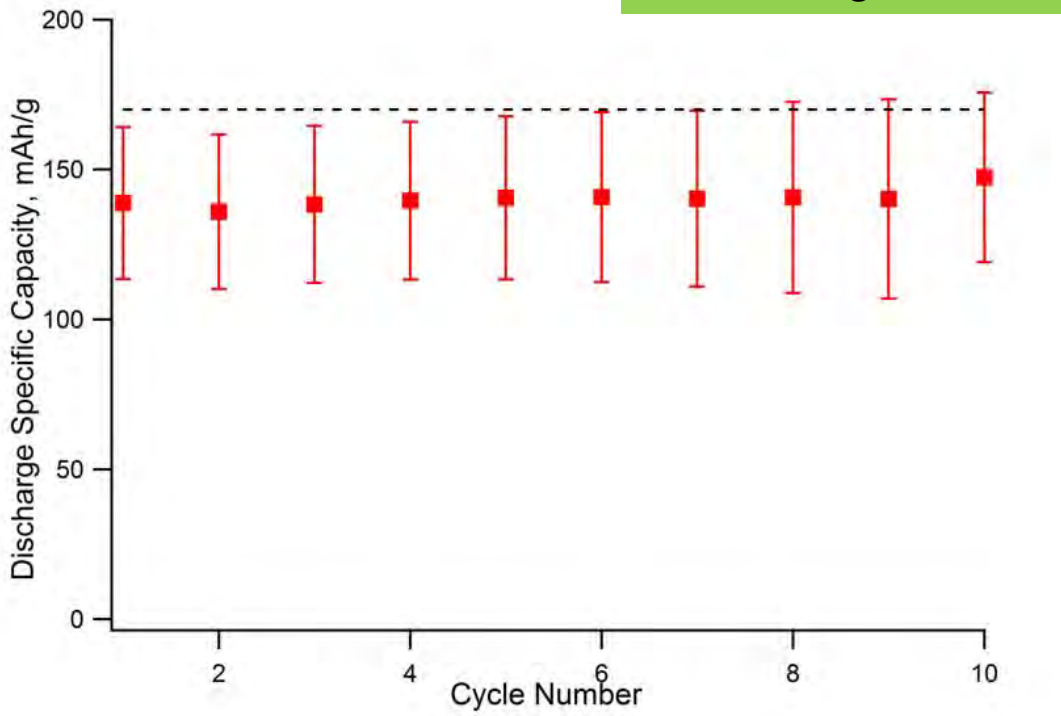
AC impedance and steady-state DC current

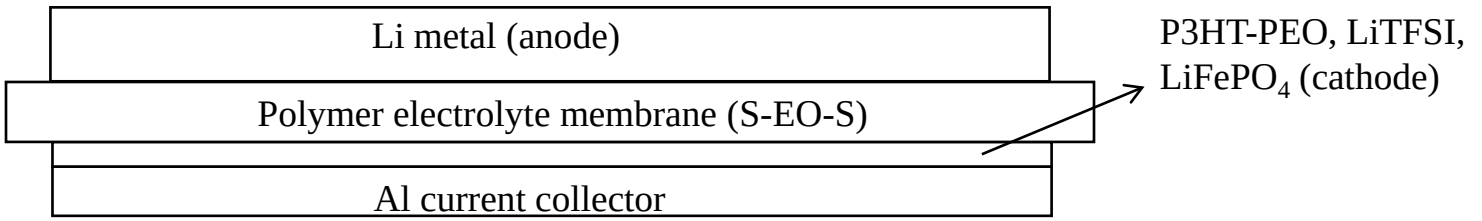
Technical Accomplishments

Electron- and ion-conducting binder



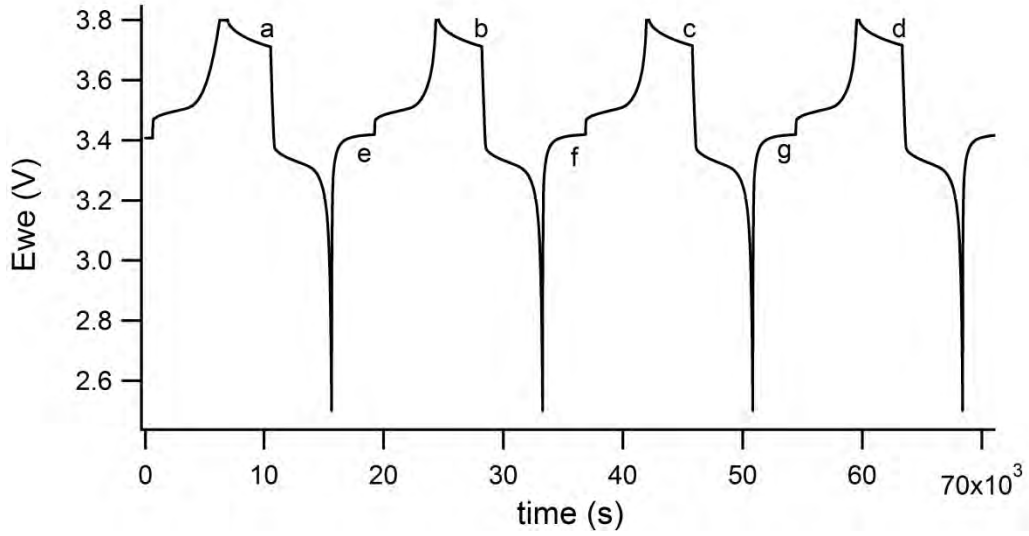
SEM of cathode
$LiFePO_4$+Binder (50/50)
Nothing else, no optimization

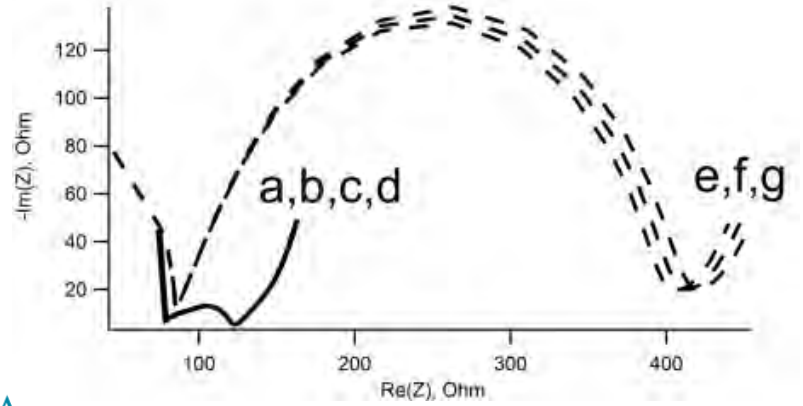




Technical Accomplishments

Electron- and ion-conducting binder



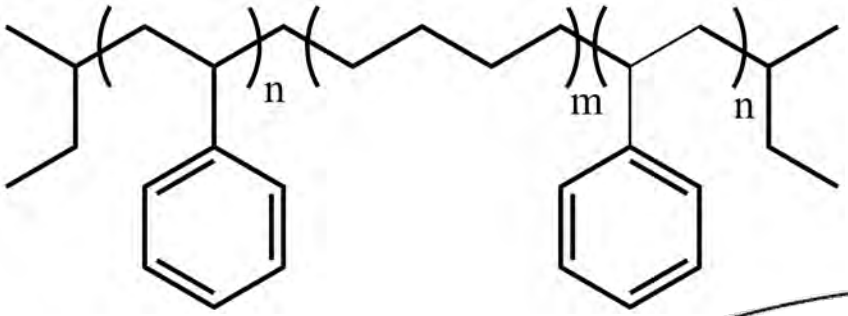


- Cathode with only active binder provides access to nearly all active sites.
- Semi-conducting nature of conducting binder gives unprecedented control over battery performance.

Javier, Patel, Hallinan, et al., manuscript under preparation.

Technical Accomplishments

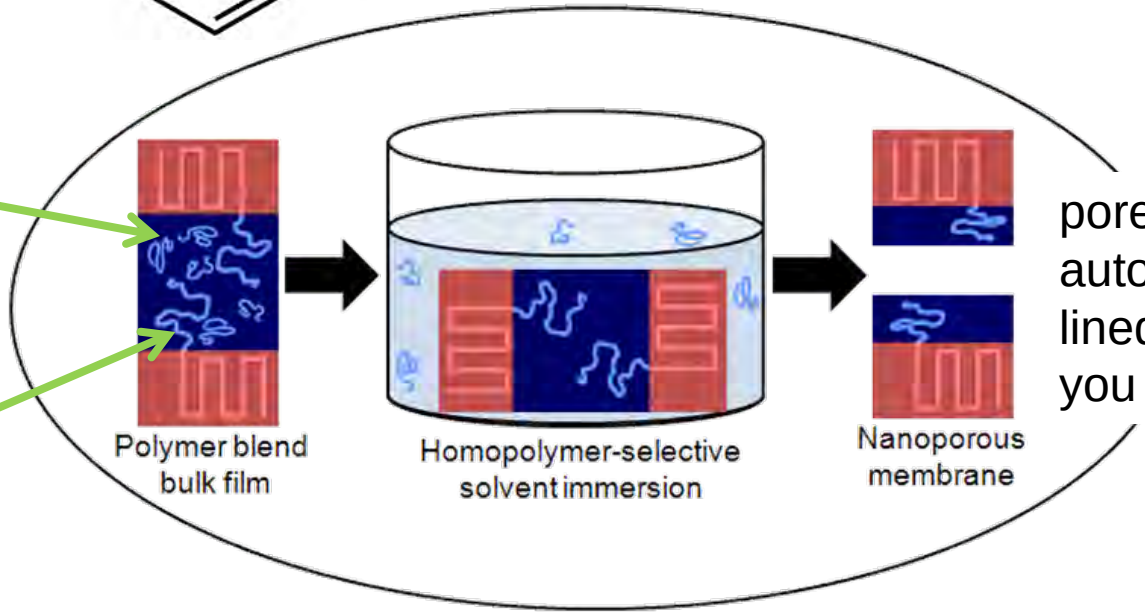
Nanoporous separator



Add PS homopolymer and then wash it out with THF.

sacrificial polymer

separator polymer

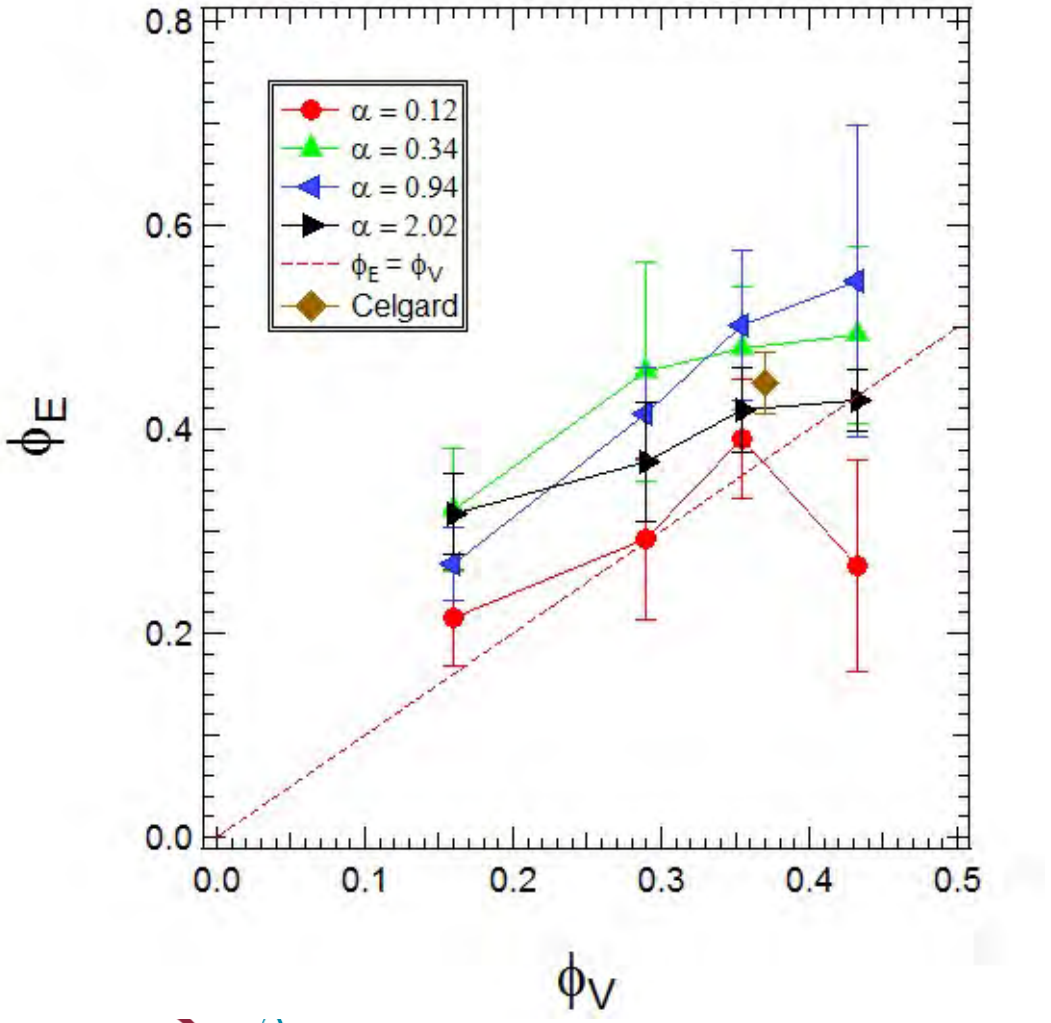


pores automatically lined by polymer you choose

Next generation membranes will be made with a water wash.

Technical Accomplishments

Nanoporous separator



α is the chain length of the sacrificial PS homopolymer normalized by PS block

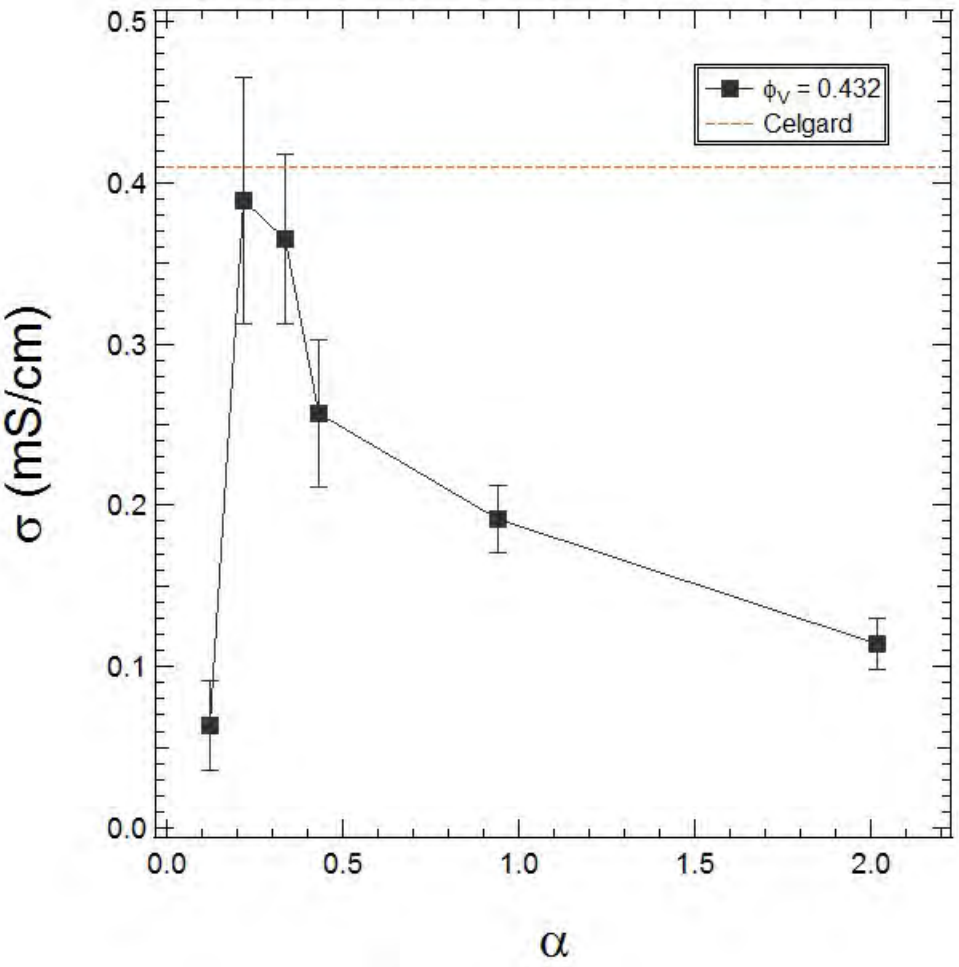
ϕ_V is the void fraction (fraction of holes in film)

ϕ_E is the electrolyte fraction (fraction of electrolyte soaked by film)

Electrolyte:
1M $LiPF_6$ in ethylene carbonate/diethyl carbonate (1:1 v/v, Novolyte)

Technical Accomplishments

Nanoporous separator

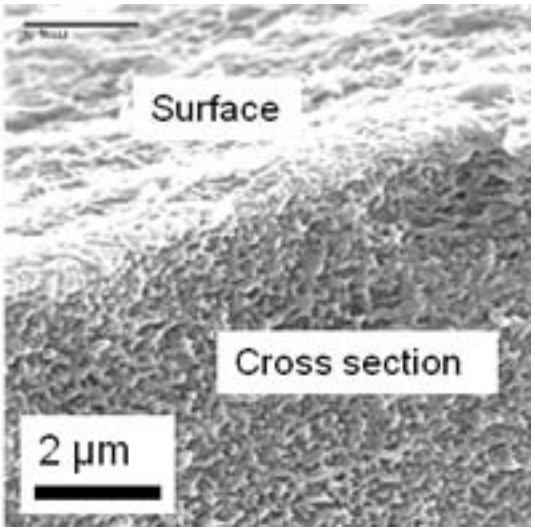


Length of the polymer that is **not there** matters.

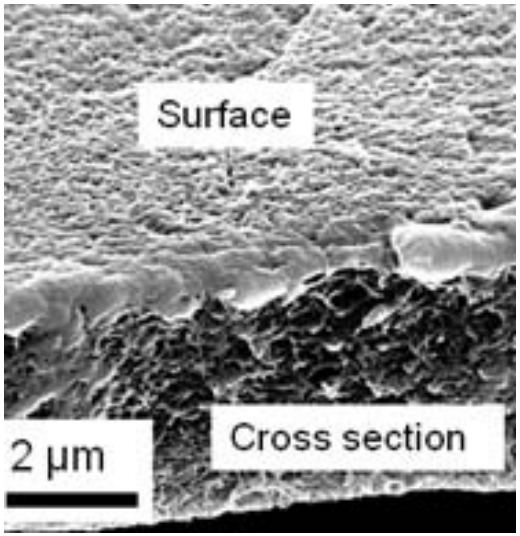
α is the chain length of the sacrificial PS homopolymer normalized by PS block

Technical Accomplishments

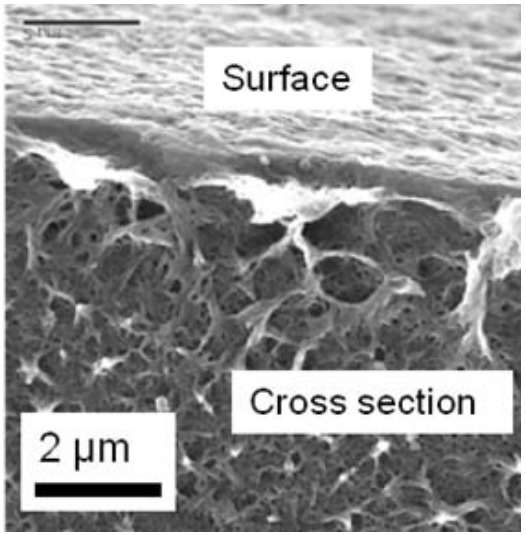
Nanoporous separator



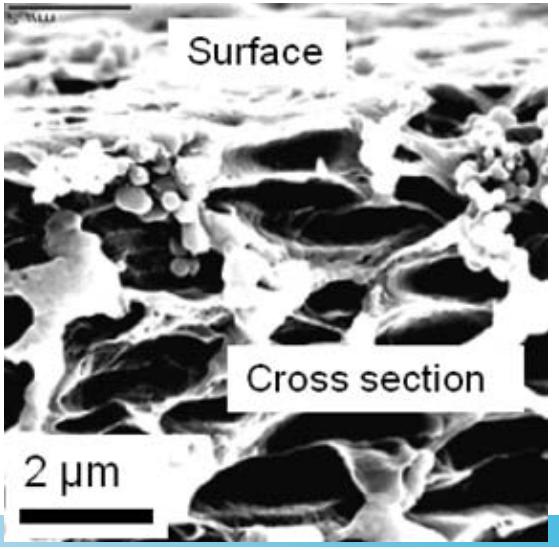
α =0.12



α =0.22



α =0.34



α =2.02

- Optimum sacrificial polymer length has nanopores with no micropores.
- Both α=0.12 and 2.02 have identical conductivities but for entirely different reasons.

Wong, et al., manuscript under preparation.

Future Work

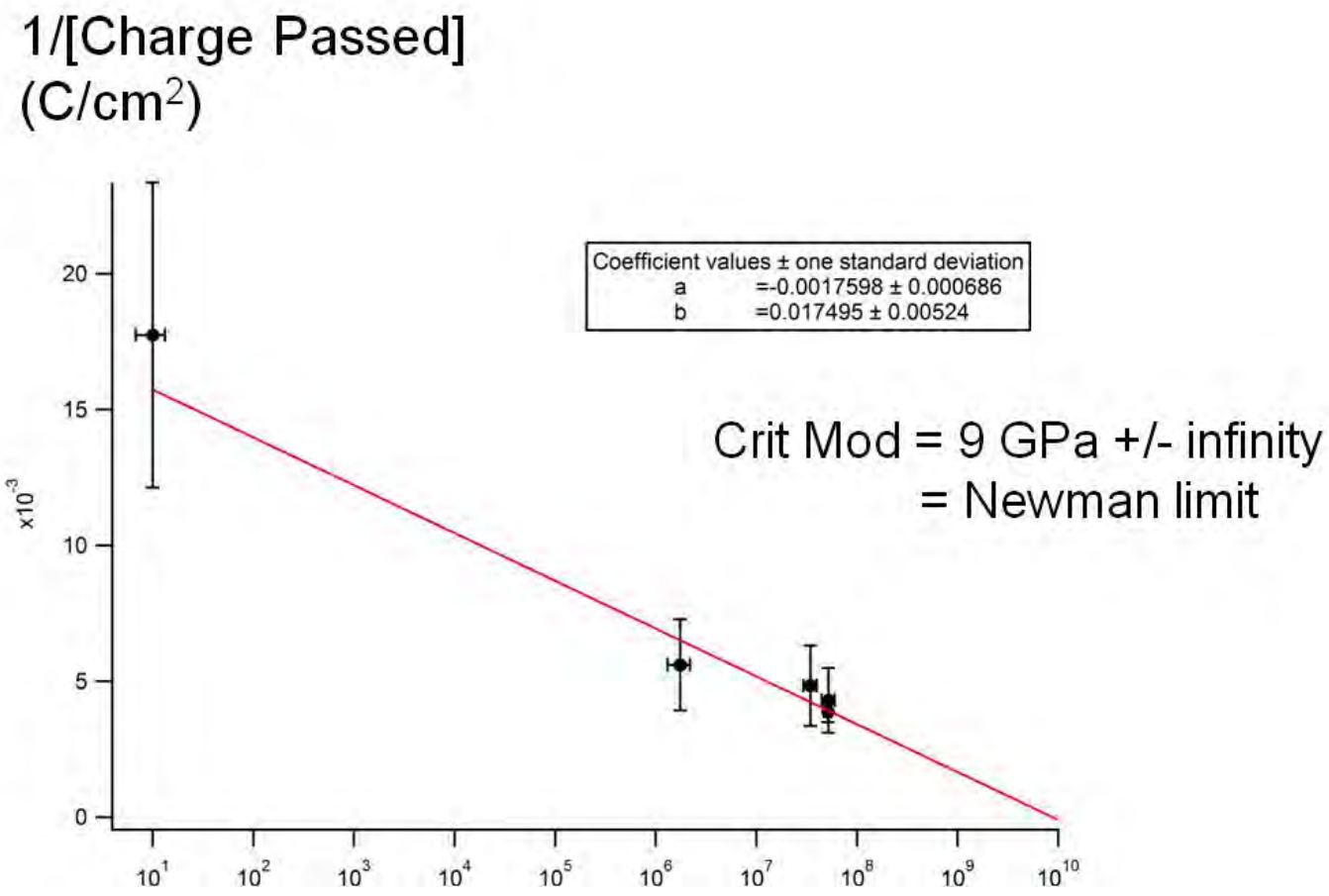
- Complete electrochemical characterization (transference number and activity coefficients) measurements of block copolymer electrolytes.
- Optimize of electron- and ion-conducting binder. (Can we make a cathode with 95% loading?)
- Can block copolymer electrolytes and binders be used to stabilize other chemistries (Sn-$LiFePO_4$, Li-S, Li-air)?
- Study the effect of block copolymer morphology on performance of nanoporous separators and move to water-soluble sacrificial polymers.

Summary

• Determined the dependence of **diffusion** on morphology of block copolymer electrolytes (Mullin et al., *J. Elect. Soc.*, in press).
• Demonstrated that nanostructuring increases **dendrite resistance** by a factor of 30 (Stone et al., under review).
• Synthesized a **binder** can carry both **ion** and **electrons** (Javier et al., in preparation).
• Incorporated a **semiconductor** into a battery **electrode**.
• Synthesized **nanoporous separators** templated by block copolymers (Wong et al., in preparation).
• **Technology transfer to Seeo, Inc.** (2007) polymer-based batteries for vehicles and stationary energy storage.
• Established **collaborations** with V. Battaglia to study nanporous separators, N. Dudney to cycle thin film electrodes with block copolymer electrolytes, J. Cabana on cycling Sn nanoparticles, with T. Richardson and G. Chen to improve electronic conduction in binders.

Technical Back-up Slides

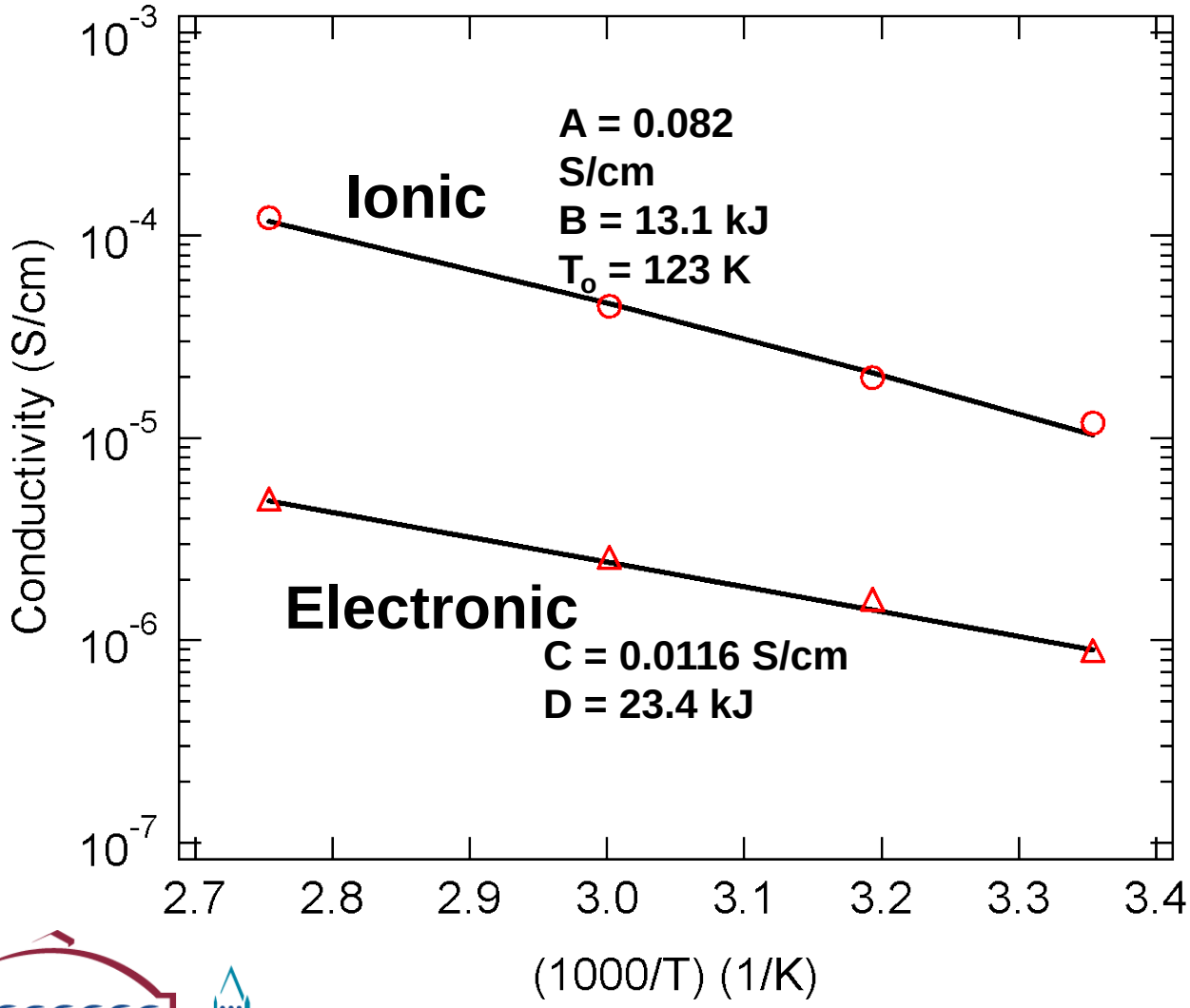
Technical Accomplishments



Crit Mod = 9 GPa +/- infinity
= Newman limit

Technical Accomplishments

Electron- and ion-conducting binder



Vogel-Tamman-Fulcher

$$\sigma(T) = A \exp\left\{\frac{-B}{R(T - T_0)}\right\}$$

Arrhenius Equation

$$\sigma(T) = C \exp\left\{\frac{-D}{RT}\right\}$$

Electronic conductivity is potential /dopant dependent.

BERKELEY LAB