Polymer Electrolytes for Advanced Lithium Batteries

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Project ID: es_38_balsara

Overview

Timeline

- FY04
- FY10
- 80%

Barriers

- Poor ion transport in electrolyte (conductivity, diffusion coefficient, and transference number)
- Low power
- Low cycle life

Budget

- Total project funding: 1300K
- Funding received in FY08 and FY09: 700K

Partners

- Lead: LBNL
- Technology licensed to Seeo, Inc.

(Practical aspects of barriers are being addressed there.)

Milestones

Month-Year	Milestone
Dec-08	Complete conductivity measurements on dry nanostructured electrolytes. Accomplished.
Mar-09	Measure transference numbers and diffusion coefficients of dry nanostructured electrolytes. Accomplished
July-09	Improve cathode utilization in dry full cells. Accomplished by technology transfer to Seeo, Inc.

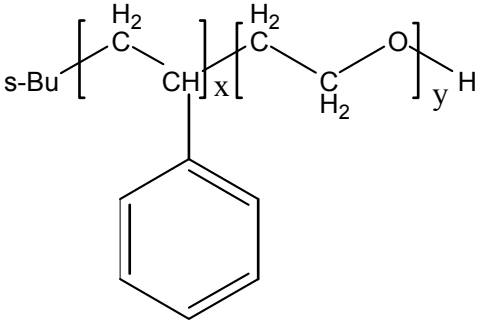
Objectives

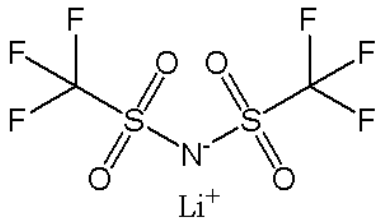
Structural and electrochemical characterization of nanostructured electrolytes.

- Synthesis of dry block copolymer electrolytes for lithium metal batteries.
- Measurement of conductivity, transference number and diffusion coefficient of electrolytes.
- Unexpected thermodynamic effects lead to improved safety of solid-state Li batteries.
- Established synthesis methodology for nanostructured porous separators (new project).

Approach

- Synthesize block copolymers
- Create novel electrolytes by self-assembly of block copolymer/salt mixtures
- Study the relationship between morphology, thermodynamics, and transport (conductivity, diffusion coefficient, transference number, salt activity).
- Understand the thermodynamics of system.
- Predict the behavior of full cells.
- Build full cells and test predictions.

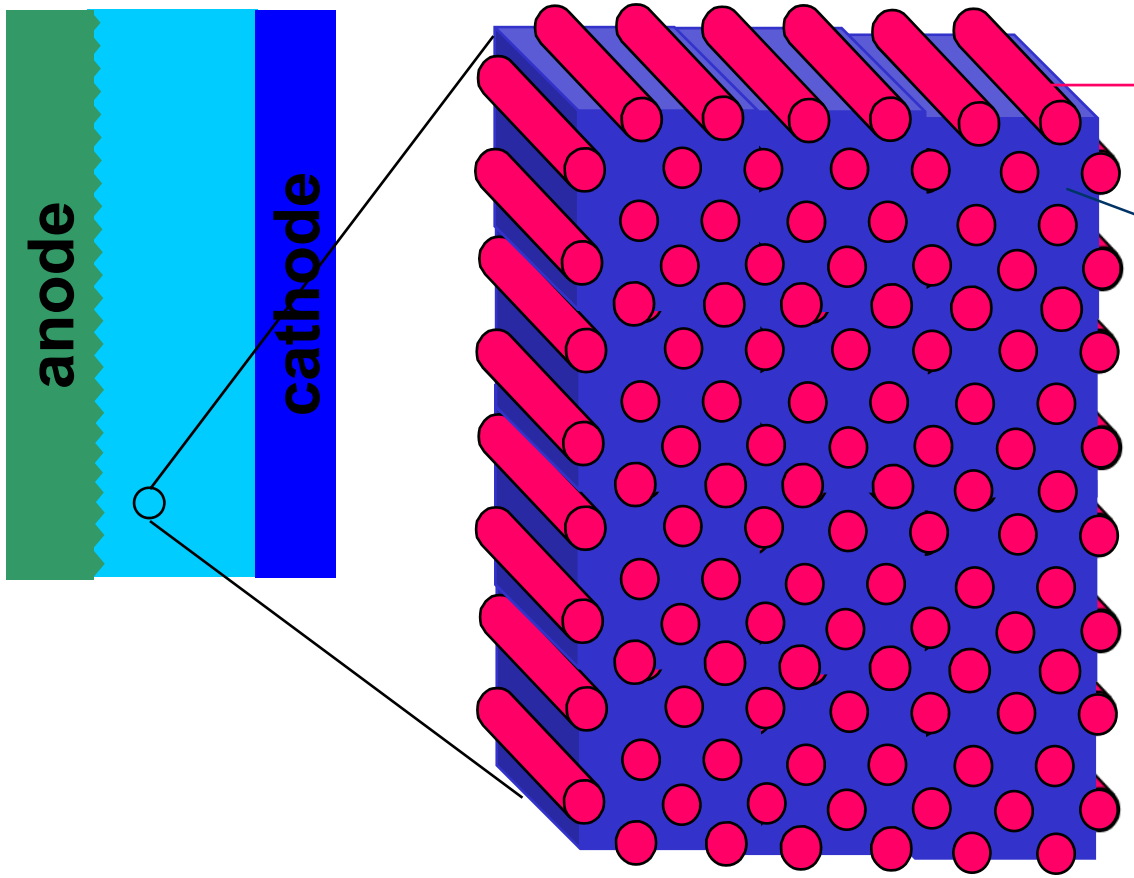




LiTFSI salt

r = [Li^+]/[EO]

Approach

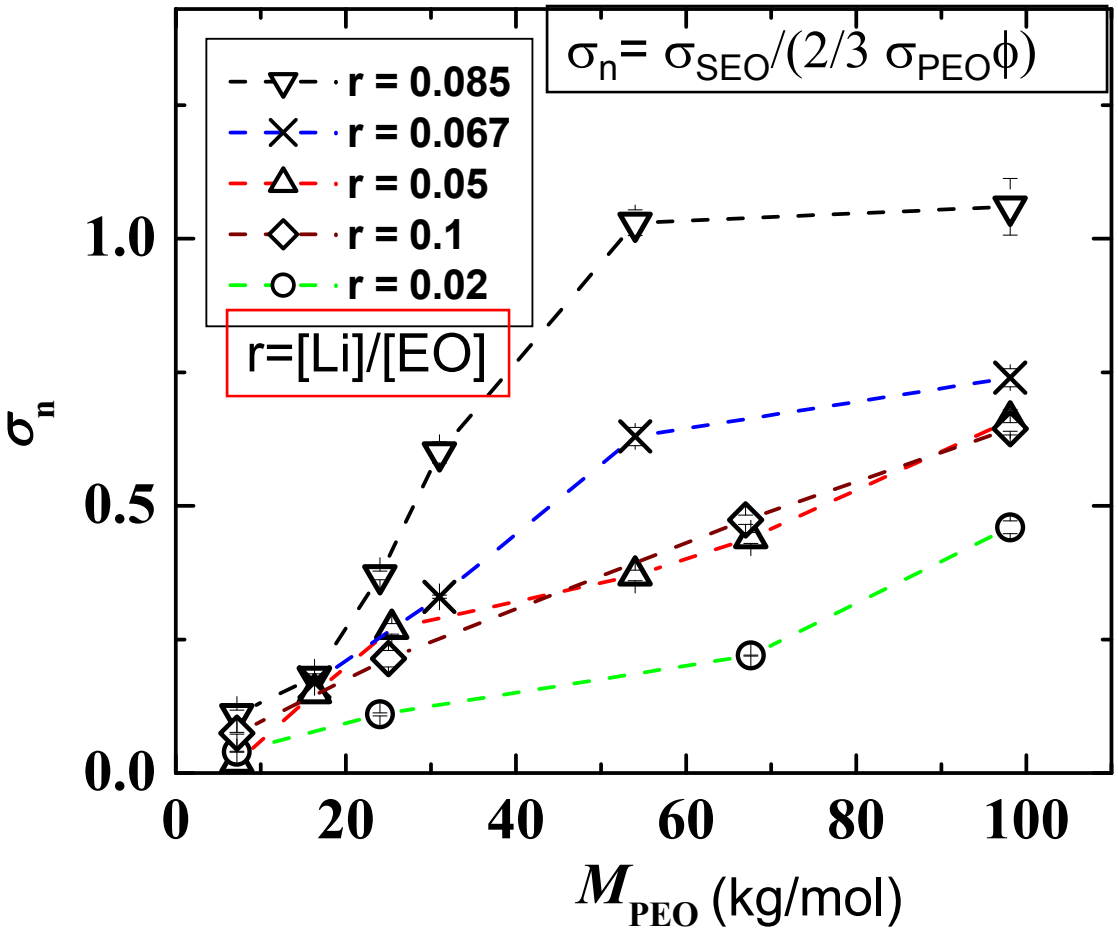


2008

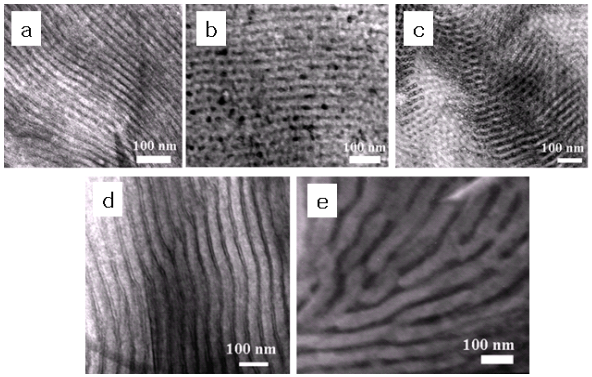
R&D 100

Development of nanostructured electrolytes for high energy lithium batteries

Technical Accomplishments



Measured the effect of morphology and salt concentration on conductivity

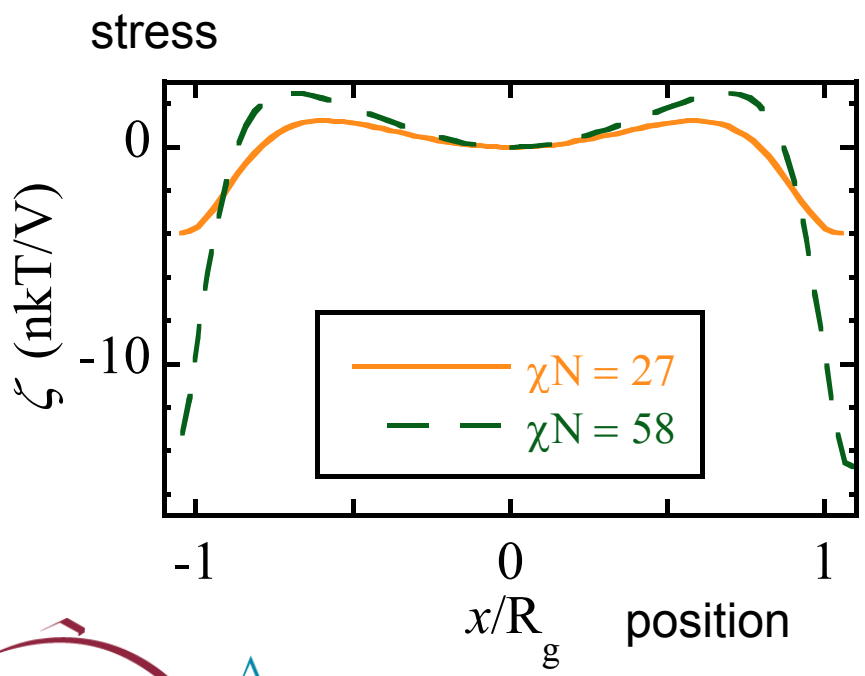


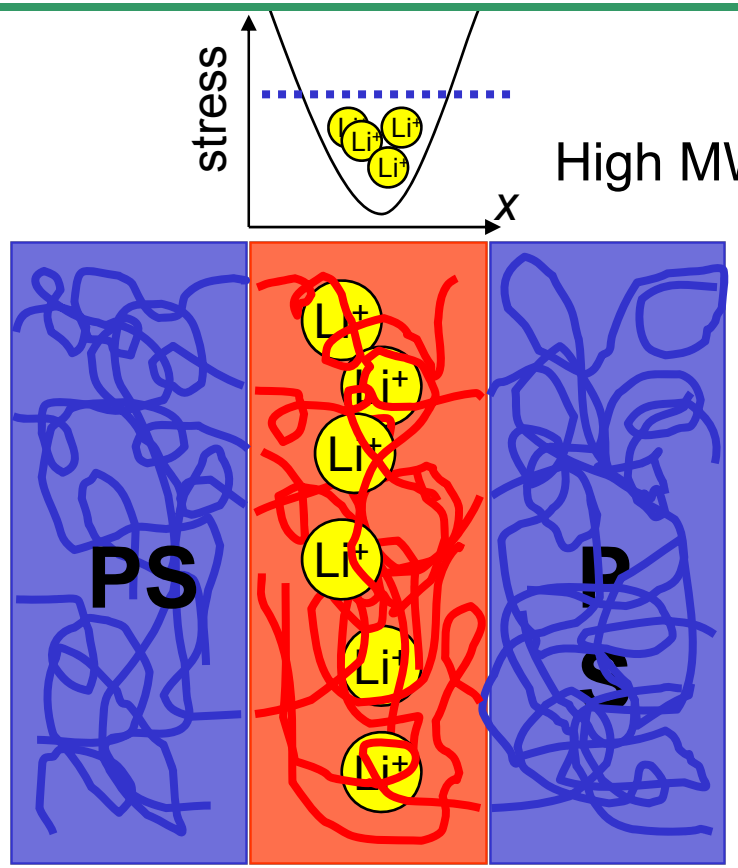
Conductivity increases with polymer molecular weight

Panday, Balsara et al. submitted

Technical Accomplishments

Determined potential reason conductivity increase with polymer molecular weight. Lithium concentration is position-dependent.

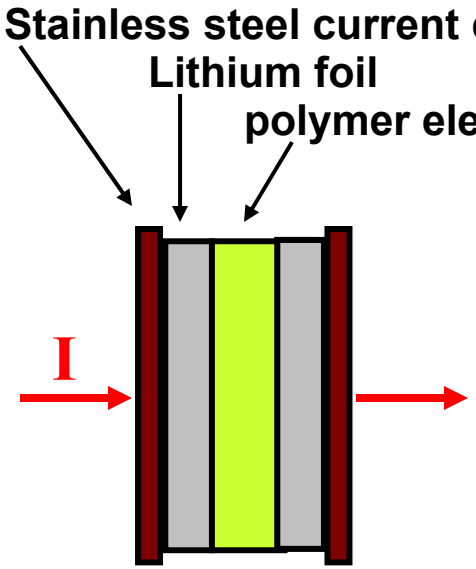


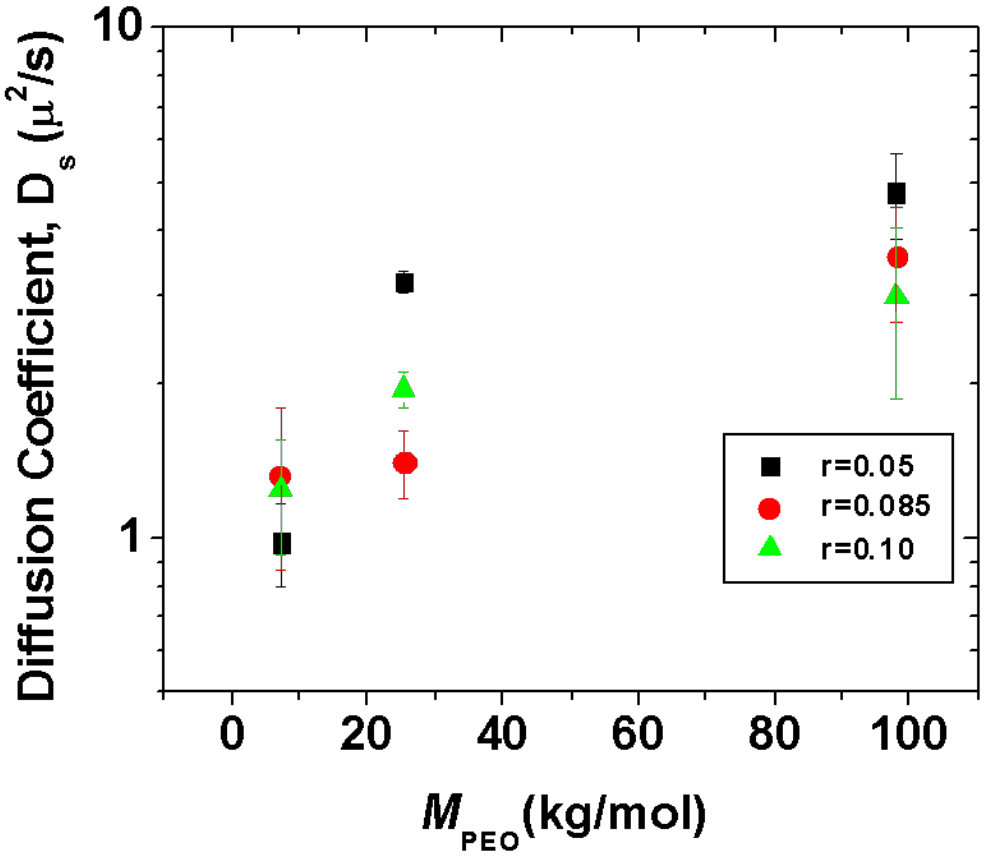


Gomez, Smith, Balsara et al. Nano Letters 2009

Technical Accomplishments

Diffusion coefficient measured by restricted diffusion (Newman 1995)

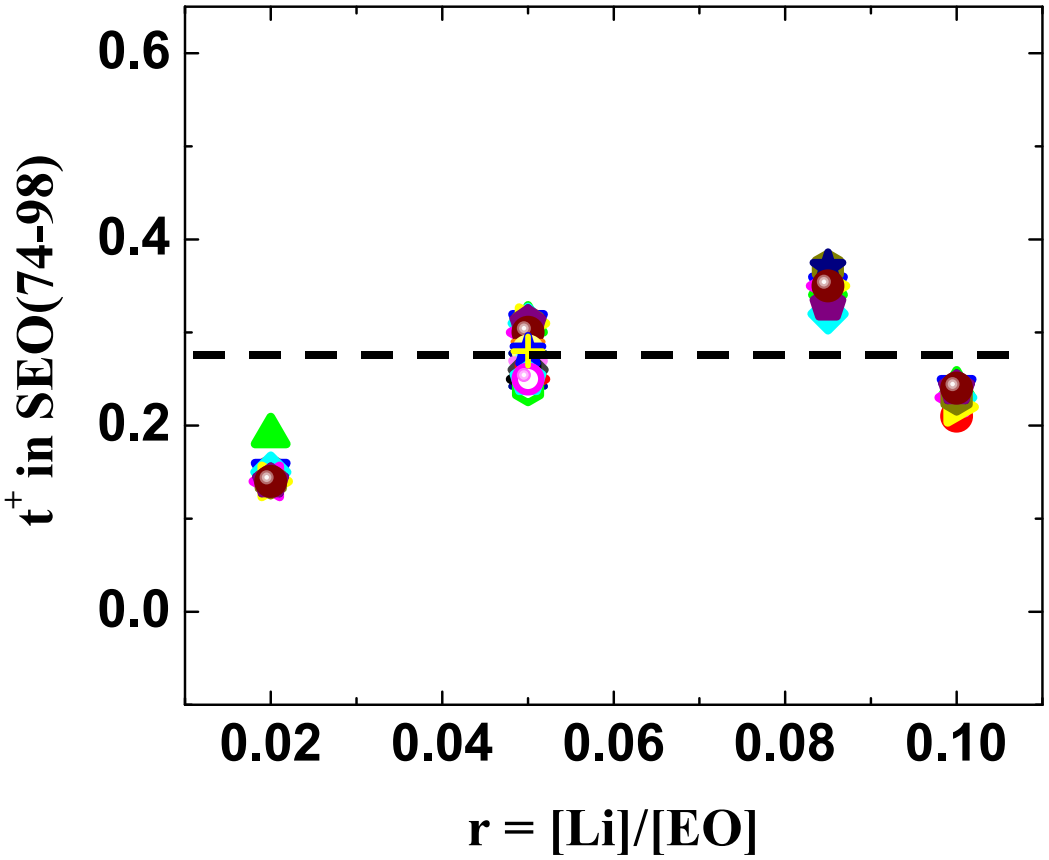




Diffusion coefficient also increases with molecular weight but is not a strong function of salt concentration.

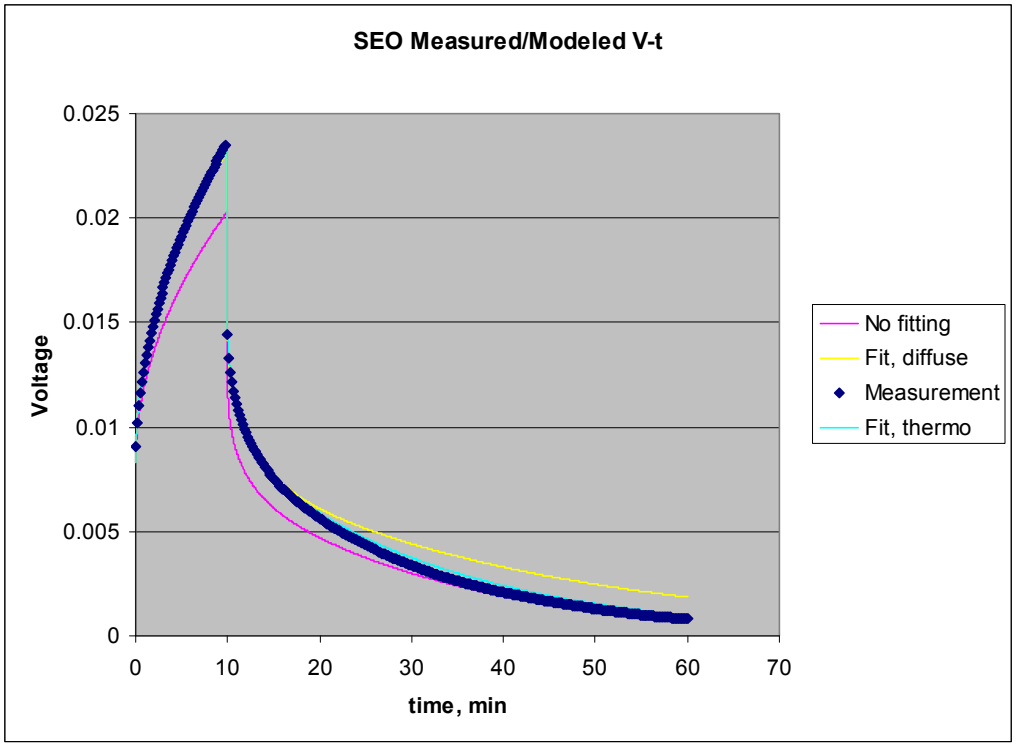
Technical Accomplishments

Li$^+$ transference number, 80 ^{o}C, SEO(74-98)



Technical Accomplishments

σ, D_s, t^+ from independent experiments SEO(75-98)



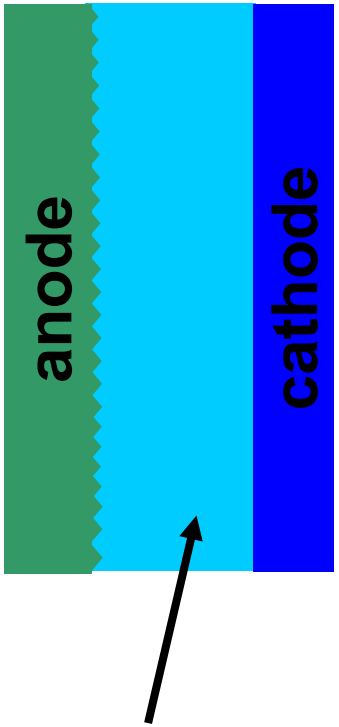
$$\frac{\partial \ln f}{\partial \ln c} = 0.25$$

gives a perfect fit

Not sure of uniqueness of interpretation.

Governing equations taken from Newman's textbook. Solution by Maureen Tang.

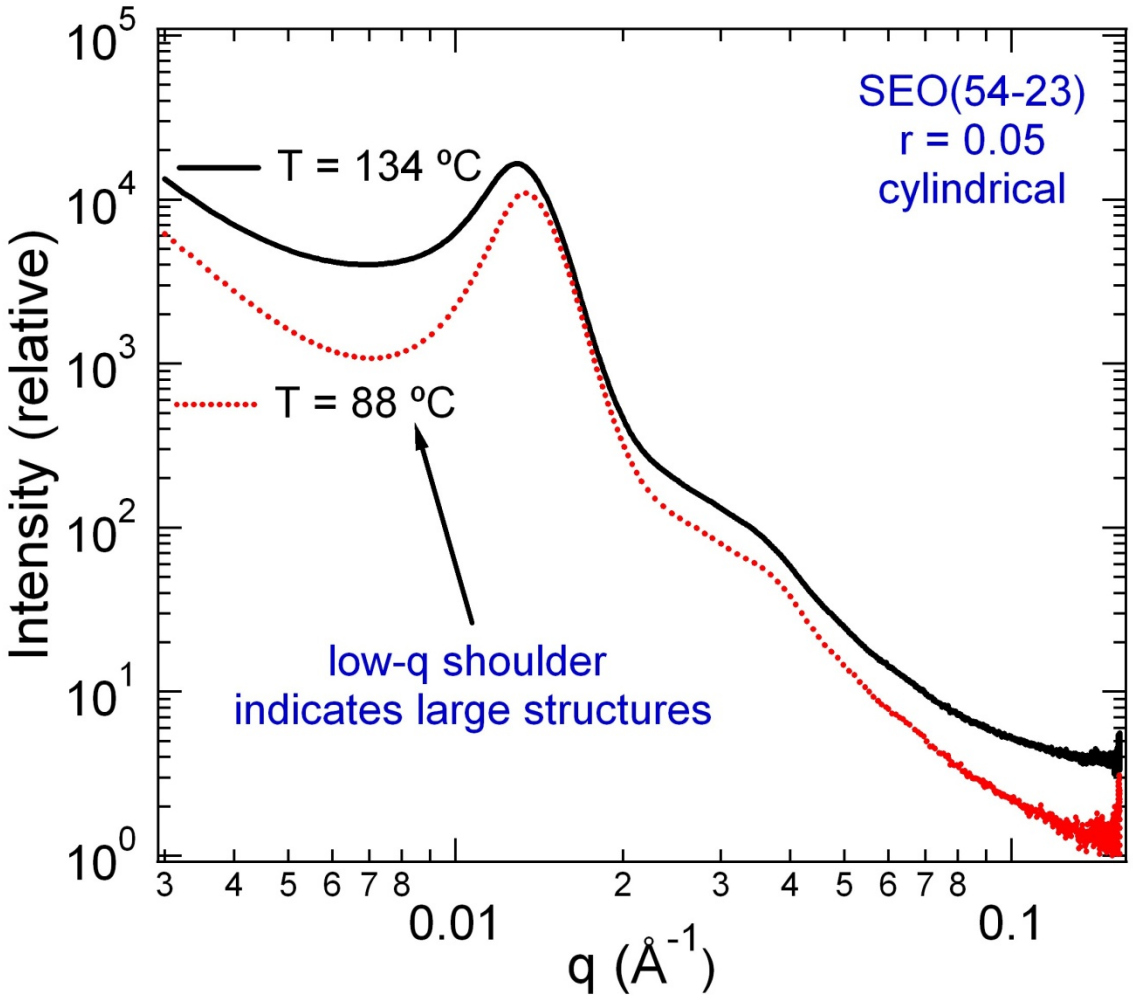
Technical Accomplishments



- High temperature shut-off mechanism for all solid-state batteries.
- In conventional separators pores can be blocked at high temperature.
- But in conventional solids, conductivity increases exponentially with increasing temperature.

Technical Accomplishments

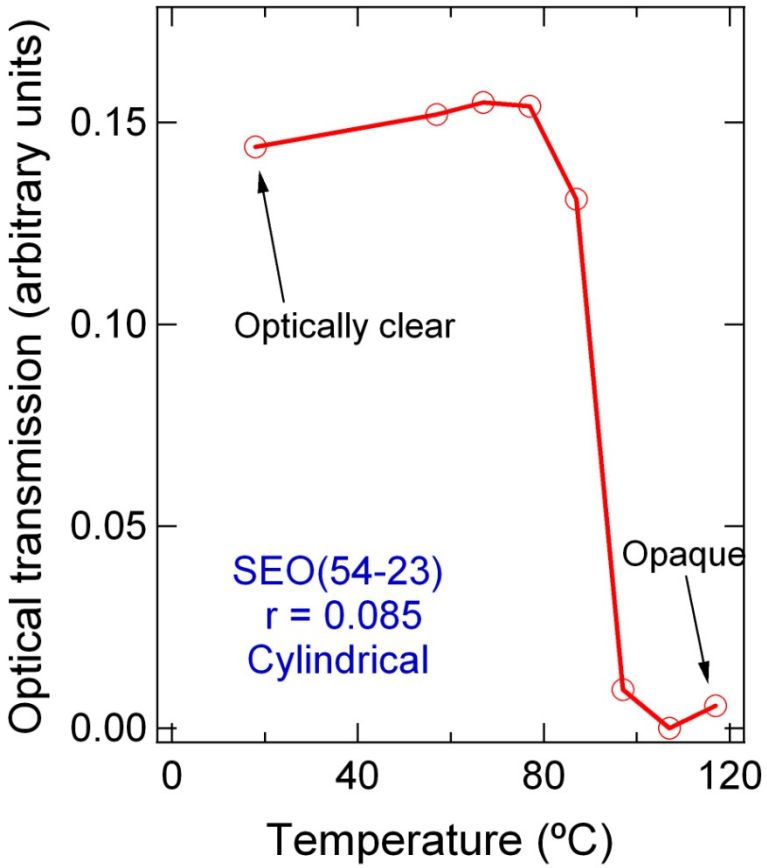
Small-angle X-ray scattering



$$q \propto \frac{1}{d}$$

Mullin

Technical Accomplishments

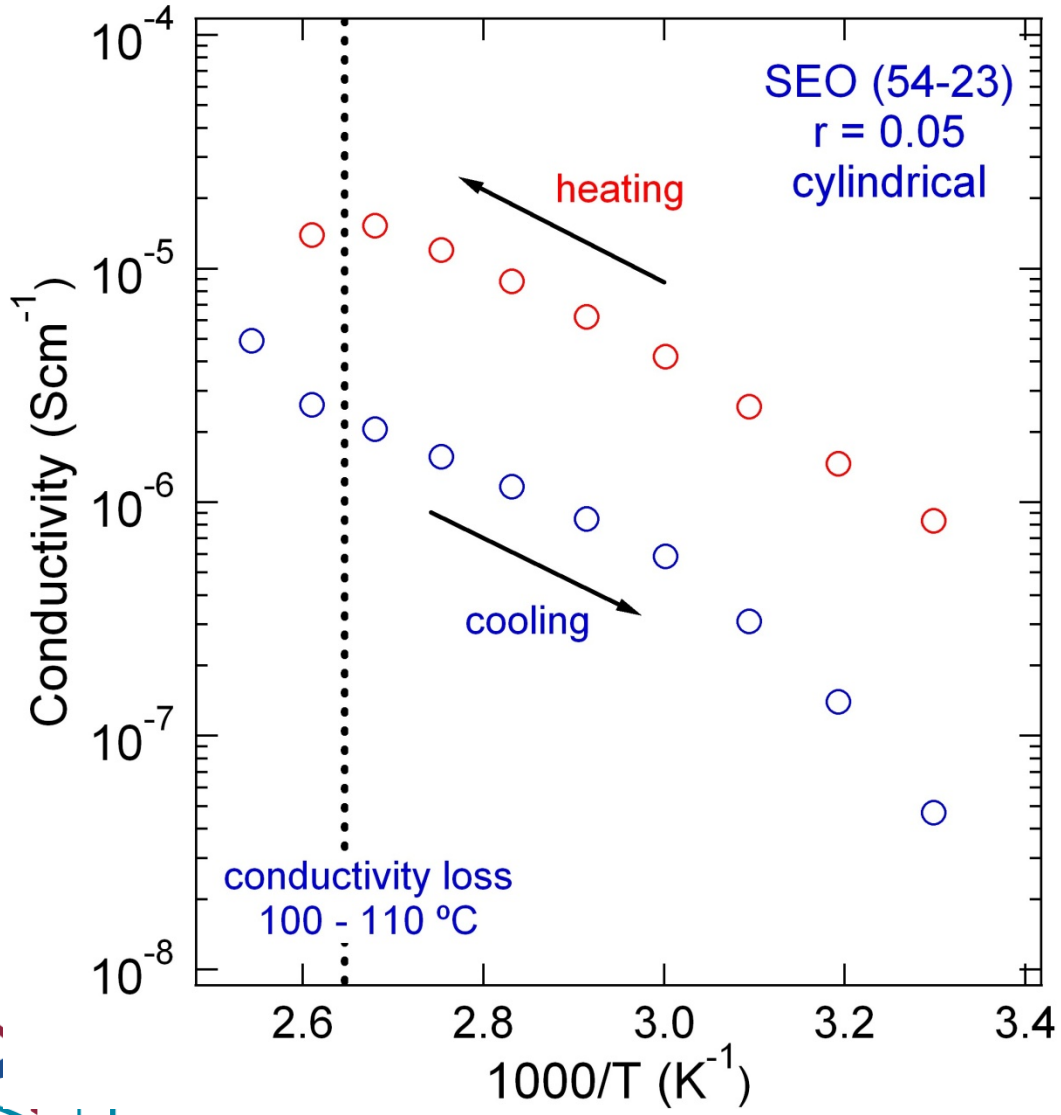


Salt precipitates when temperature increases.

Salt/block copolymer mixtures are certainly non-ideal.

PEO/LiTFSi is miscible at this concentration at all temperatures. PEO chains in block copolymers are fundamentally different from chains in homopolymers

Technical Accomplishments



Self-assembled, responsive nanostructures (not fixed).

Potential for improving safety of solid-state batteries.

Future Work

- Set-up casting equipment to build full cells. Build Li-SEO-$FePO_4$ cells.
- Continue measurement of parameters such as conductivity, transference number, diffusion coefficient of electrolytes, salt activity (Srinivasan, Newman).
- Understand the coordination of lithium ions and block copolymer chains and implication on transport, phase behavior (Smith).
- Unexpected thermodynamics may impact safety of solid-state Li batteries.
- Obtain the first generation of nanostructured porous separators (new project).

Summary

- Creation of all solid-state rechargeable batteries that operate at room temperature and below based on block copolymers milestone accomplished by technology transfer
- Launched an effort to determine all of the transport properties (conductivity, transference number and diffusion coefficient of electrolytes) .
- Unexpected thermodynamics lead to improved safety of solid-state Li batteries.