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

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

\[ r = \frac{[\text{Li}^+]}{[\text{EO}]} \]
Development of nanostructured electrolytes for high energy lithium batteries

- Channels ~10 nm
  - For ion conduction
- Hard matrix
  - For mechanical support

Approach

2008
Conductivity increases with polymer molecular weight.

Measured the effect of morphology and salt concentration on conductivity.

\[ \sigma_n = \frac{\sigma_{SEO}}{2/3 \sigma_{PEO}\phi} \]

\[ r = \frac{[Li]}{[EO]} \]
Determined potential reason conductivity increase with polymer molecular weight. Lithium concentration is position-dependent.
Technical Accomplishments

Diffusion coefficient measured by restricted diffusion (Newman 1995)

Stainless steel current collector
Lithium foil
polymer electrolyte

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

Li$^+$ transference number, 80 °C, SEO(74-98)

\[ r = \frac{[\text{Li}]}{[\text{EO}]} \]
Technical Accomplishments

\[ \sigma, D_s, t^+ \text{ from independent experiments} \quad \text{SEO(75-98)} \]

\[ \frac{\partial \ln f}{\partial \ln c} = 0.25 \]

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.

Solid electrolyte
Mullin

Technical Accomplishments

Small-angle X-ray scattering

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

Intensity (relative)

$10^5$

$10^4$

$10^3$

$10^2$

$10^1$

$10^0$

$10^{-1}$

$10^{-2}$

$10^{-3}$

$10^{-4}$

$10^{-5}$

$q (\text{Å}^{-1})$

$0.01$

$0.1$

$T = 134 \degree C$

$T = 88 \degree C$

low-q shoulder indicates large structures

SEO(54-23)

$r = 0.05$

cylindrical
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.