Block Copolymer Separators for Lithium Batteries

Nitash Balsara

Lawrence Berkeley National Laboratory
Energy and Environmental Technologies Division
Batteries for Advanced Transportation Technologies Program

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Project ID: ES088

Overview

- **Timeline**
  - FY 08
  - FY 10
  - 40%
- **Budget**
  - Total project funding: 1000K
  - Funding received in FY09 and FY10: 700K
- **Technical Barriers / Goals**
  - Available Energy Density (Wh/kg & Wh/l)
  - Short life due to power and capacity fade
  - Cycle Life (safety concerns due to the formation of dendrites when using lithium metal anodes)

DOE Energy Storage Goals		HEV (2010)	PHEV (2015)	EV (2020)
Characteristics	**Unit**			
Available Energy Density	Wh/kg	**5-13**	**30-200**	**100-130**
Available Energy Density	Wh/l	**7-20**	**40-290**	**200-300**
Calendar Life	Year	**15**	**10+**	**10**
Cycle Life	Cycles	**300k, shallow**	**3,000-5,000, deep discharge**	**750, deep discharge**

- **Partners/Collaborators**
  - Project Lead: LBNL
  - Advanced Light Source
  - National Center for Electron Microscopy
  - Stanford Synchrotron Radiation Lightsource
  - NIST Center for Neutron Research
  - Batteries for Advanced Transportation Technologies Program Members

Objectives

- **RELEVANT USABC GOALS:** EV applications goals are a specific energy of 200 Wh/kg and a specific pulse power of 400 W/kg.

- Synthesize and characterize block copolymer-based separators for high energy and high power lithium batteries
  - I) Measure transport properties of dry block copolymer/salt mixtures
  - II) Develop lithium-sulfur batteries with dry block copolymer/salt electrolytes
  - III) Develop lithium-air batteries with dry block copolymer/salt electrolytes
  - IV) Develop grafted porous separators using block copolymer self-assembly.

FY 09 Milestones

Month-Year	Milestone
Dec-08	Complete conductivity measurements on block copolymer electrolytes. Accomplished.
Mar-09	Measure transference number and diffusion coefficient of block copolymer electrolytes. Accomplished.
Jun-09	Improve cathode utilization in dry Li metal/block copolymer/$LiFePO_4$ cells. Accomplished by technology transfer to Seeo, Inc.
Sep-09	Synthesize and determine morphology of block copolymer-based porous separator. Accomplished.

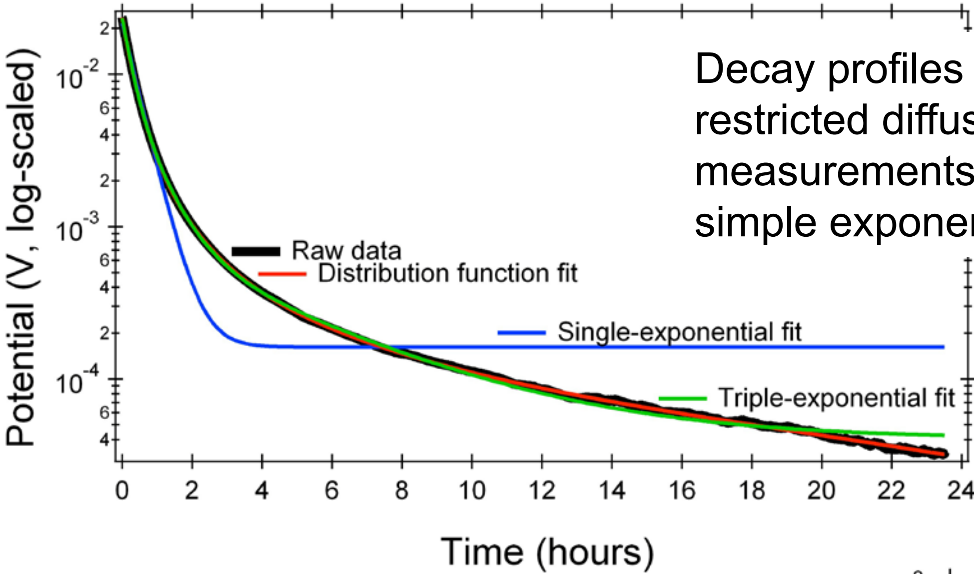
FY 10 Milestones

Month-Year	Milestone
Mar-10	Synthesize and characterize morphology of new PS-PEO-PS. Accomplished.
Sep-10	Cast PS-PEO-PS membranes. Measure ionic conductivity, transference numbers, and diffusion coefficients. Demonstrate battery cycling with PS-PEO-PS and planar cathodes. On track.
Sep-10	Measure ionic conductivity of porous separator/liquid electrolyte mixture. Preliminary data provided here.
Sep-10	Measure solubility of lithium-sulfur compounds in PS-PEO block copolymers. Preliminary data provided here.

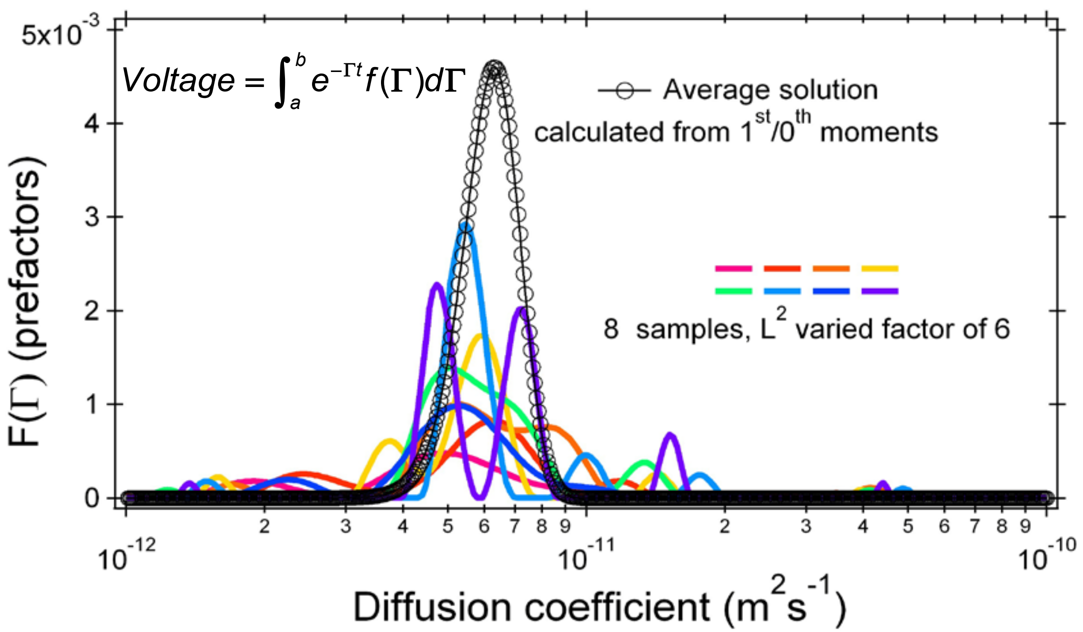
Approach

- Unified approach for creating both active solid electrolyte separators and passive porous separators by block copolymer self-assembly.
- Determine applicability of the solid electrolytes in lithium-sulfur and lithium-air cells.
- Determine morphology of solid electrolyte separators and passive porous separators.
- Complete characterization of ion transport in active solid electrolyte separators and passive porous separators containing liquid electrolytes.
- Solid electrolytes and porous separators will be interfaced with electrodes developed in the VT program.

Accomplishment – Diffusion Measurements



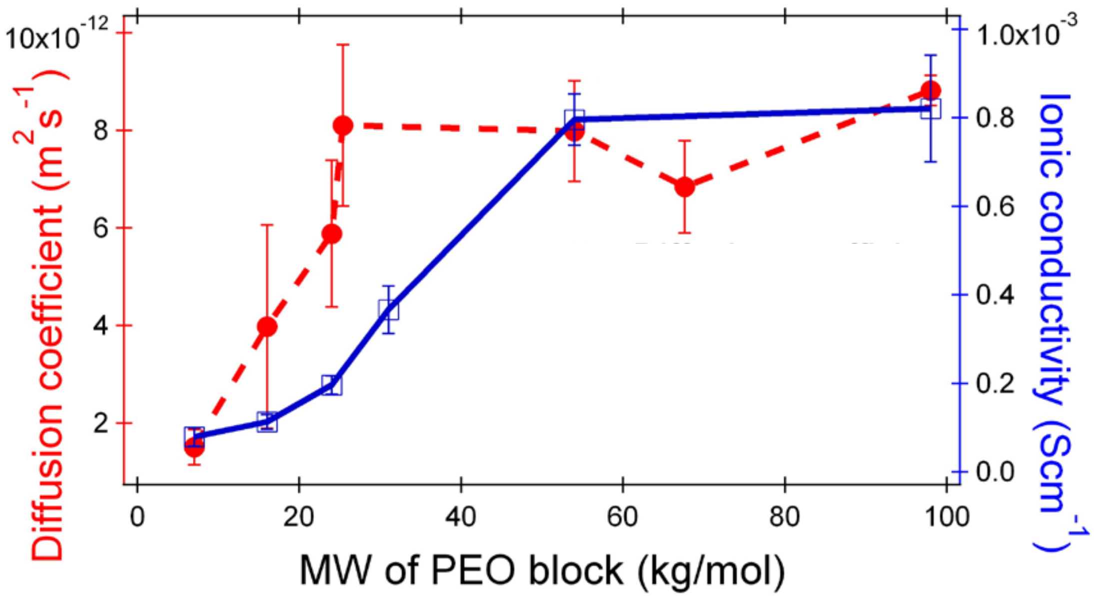
Decay profiles in restricted diffusion measurements are ***not*** simple exponential



Key points:

1. First determination of relaxation in restricted diffusion experiments on block copolymer electrolytes.
2. Complex non-exponential behavior were observed (top).
3. Distributions of relaxation times were determined directly from non-exponential relaxation data (bottom).

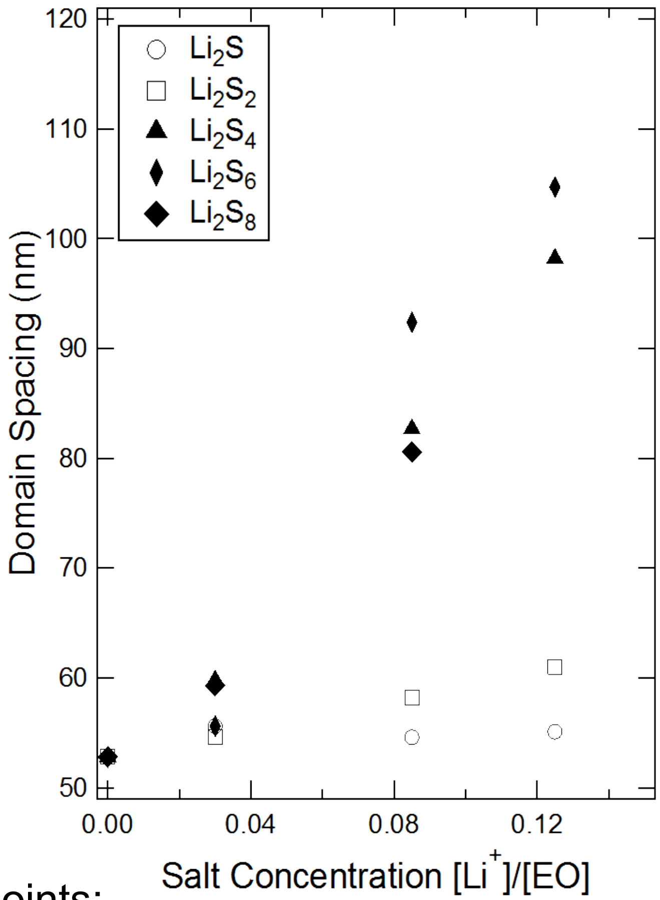
Accomplishment – Discovery of Conductivity-Diffusion Correlation

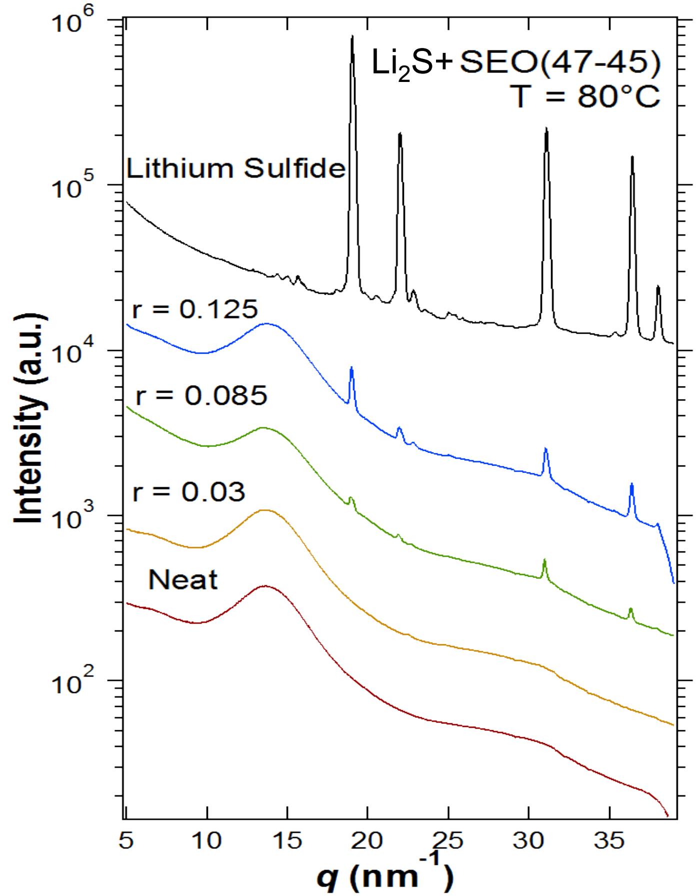


<u>Key points:</u>

1. Diffusion of salt is faster in stiff, high molecular weight block copolymers than in the soft, low molecular weight samples.
2. Dependencies of conductivity and diffusion coefficient on copolymer molecular weights are similar.
3. Ion mobilities must have the same molecular weight dependence.

Accomplishment – Studied solubility of polysulfides in block copolymer electrolytes





Key points:

1. We have discovered that the addition of soluble polysulfides (Li_2S_4-Li_2S_8) results in an unexpectedly large increase in domain size of block copolymer (left).
2. Insoluble polysulfides (Li_2S-Li_2S_2) form small crystallites within block copolymer domains (right).

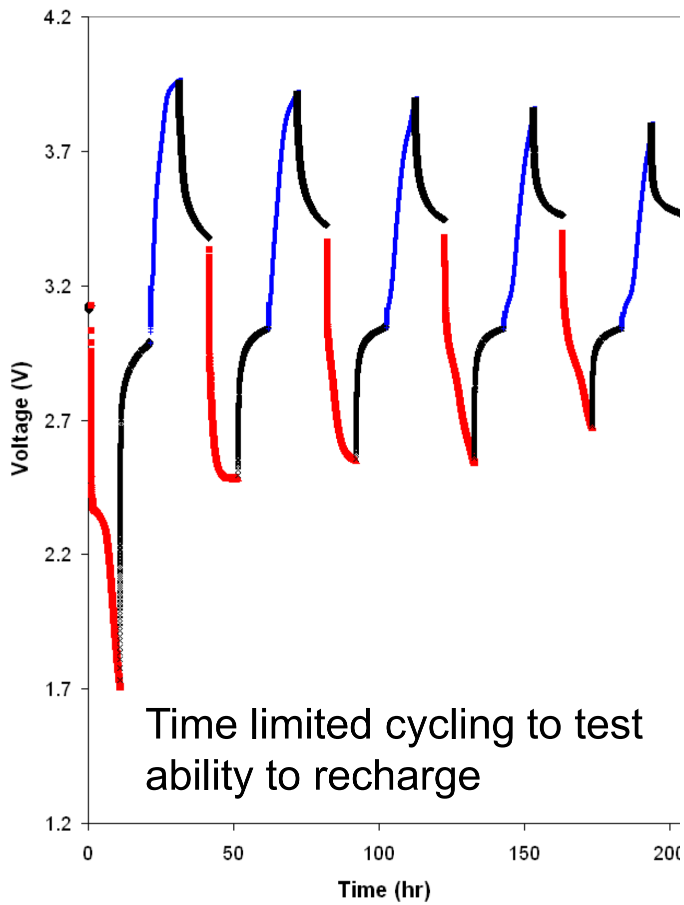
Accomplishment – First cycling data on dry Li-air cells

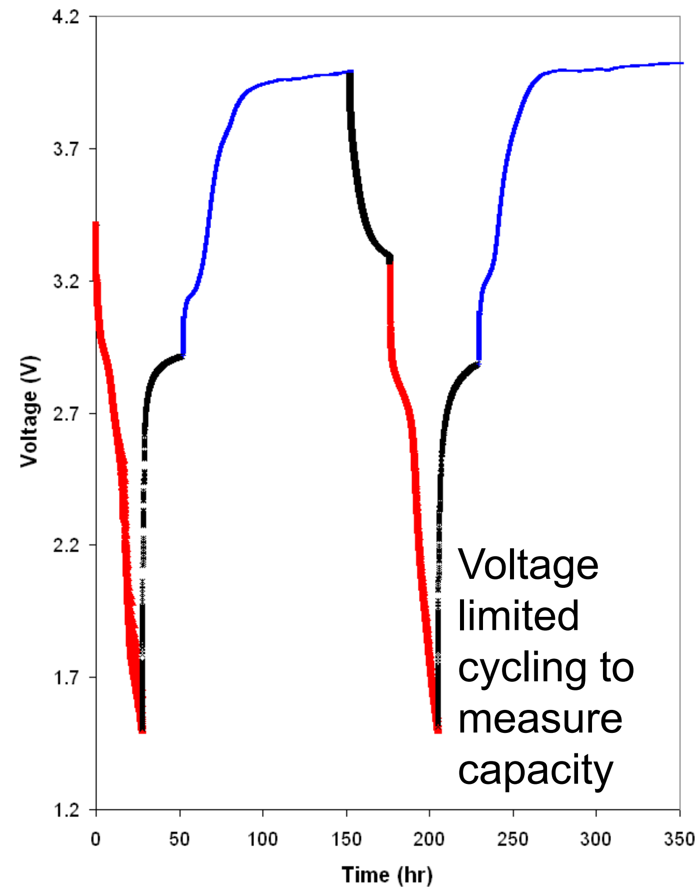
<u>Open Circuit Voltage</u>
3.1 V

<u>Theoretical</u>
Capacity~3,800 mAh/g
Energy~11,000 mWh/g

<u>Actual</u>
Capacity~190 mAh/g
Energy~475 mWh/g

Based on cathode mass only

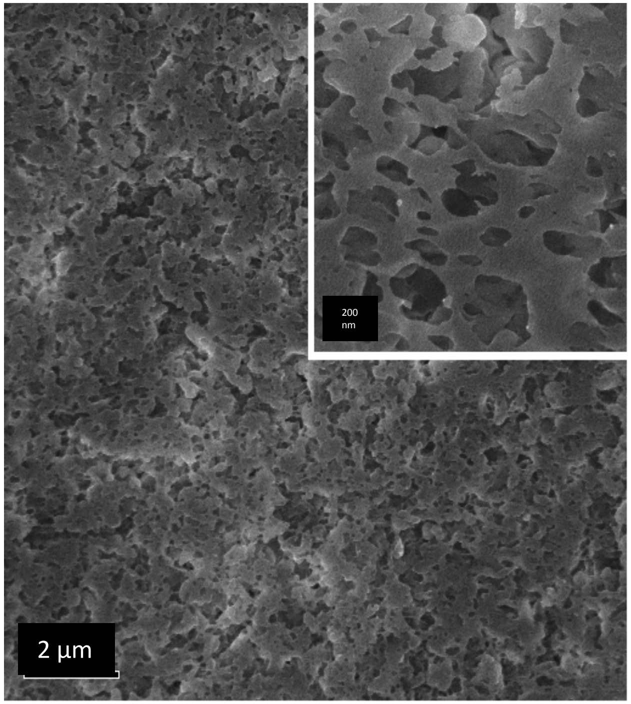


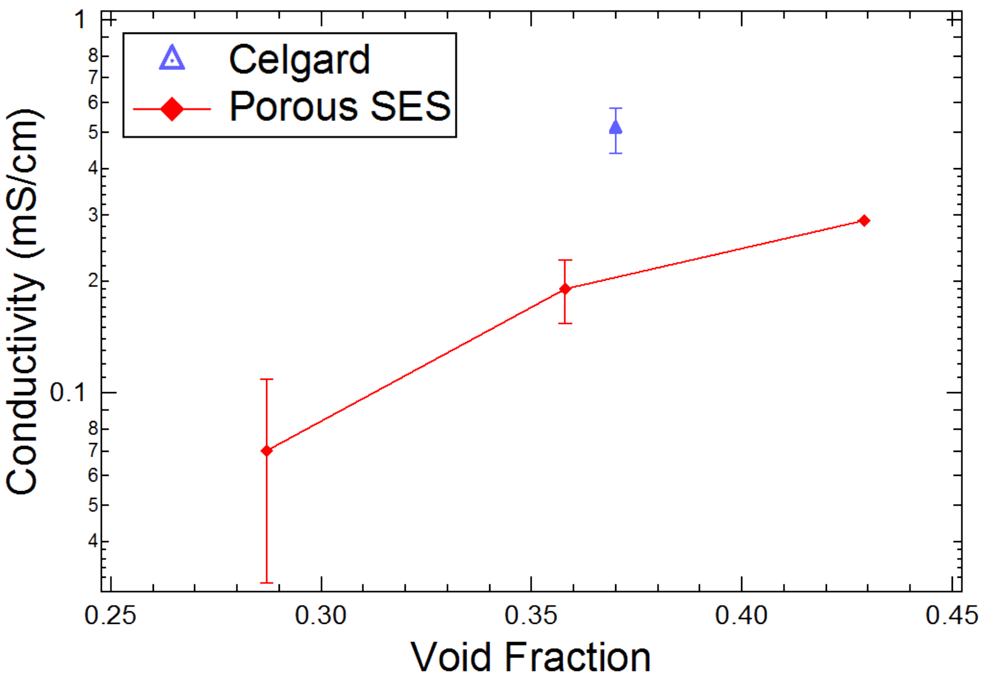


<u>Key points:</u>

1. Assembled solid lithium air cells with block copolymer electrolytes.
2. Preliminary cycling measurements have been made.

Accomplishments – Self-assembled porous separators





Key points:

1. Synthesized and determined morphology of self-assembled porous separators with polystyrene brushes lining the pores (left).
2. Determined conductivity of separators containing a liquid electrolyte (right).

Collaborations

- Technology licensed to Seeo, Inc.
  - Practical aspects of barriers for block copolymer-based EV batteries are being addressed there.
- Advanced Light Source, LBNL (DOE).
  - X-ray scattering from block copolymers
- National Center for Electron Microscopy, LBNL (DOE).
  - Electron microscopy of block copolymer.
- Stanford Synchrotron Radiation Lightsource (DOE).
  - X-ray scattering from block copolymers
- NIST Center for Neutron Research
  - Study thermodynamics of block copolymer/salt mixtures.

Future Work

- Complete measurement of diffusion coefficient and transference numbers of dry block copolymer electrolytes.
  - Evaluate same in full cells.
  - Compare to model predictions.
- Complete study of solubility of polysulfides in block copolymers.
  - Use knowledge of solubility to build Li-S cells with block copolymer electrolytes.
- Continue building and testing Li-air cells.
  - Optimize cathode formulation to maximize capacity and lifetime.
  - Compare to control batteries.
- Continue synthesizing and characterizing grafted porous separators.
  - Seek improvements in conductivity and thermal stability.

Summary

- Established a coherent program to develop block copolymer-based separators for high energy and high power lithium batteries
  - I) Measured transport properties of dry block copolymer/salt mixtures.
  - II) Determined solubility of polysulfides in block copolymer/salt electrolytes.
  - III) Made and tested lithium-air batteries with dry block copolymer/salt electrolytes
  - IV) Made and tested grafted porous separators using block copolymer self-assembly.