Polymer Electrolytes For Advanced Lithium Batteries

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May 15, 2013

Project ID #
ES088

Overview

- **Timeline for projects A and B:**
- Project start date: October 2010
- Project end date: September 2013
- Percent complete: 90%

- **Budget:**
- Total project funding: $1,990K
  - –DOE share (100%)
  - –Contractor share (0%)
- Funding received in FY12 $590K
- Funding for FY13 $590K

- **Barriers:**
  (1) Energy density
  (2) Safety
  (3) Low cycle life

- **Partners:**
- ANL, ALS (at LBNL) and NCEM (at LBNL)

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Objectives

- A) Develop cost-effective method for creating nanoporous separators.
- B) Study the effect of electrolyte nanostructuring on dendrite formation in symmetric and full cells. Also studied gas diffusion through SEO.
- C) Develop a binder that conducts ions and electrons.

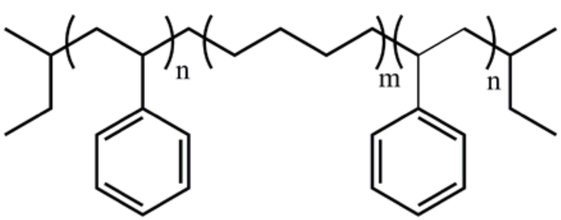
Milestones

- A) Quantify the effect of the nature of the pore structure on conductivity in porous block copolymer separators and Celgard (Dec. 2012). *Completed. David Wong joined ITRI (Taiwan) as a post-doc.*
- B) Quantify effect of nanostructuring on dendrite resistance in full cells (Dec. 2012). *Completed. Dan Hallinan joined Florida State as an Assistant Professor.*
- *Project transitioned to BES to solve "needle-in-a-haystack" problem. [Joint paper with Dan Hallinan (EERE-supported student) and Katherine Harry (BES-supported student) submitted.]*
- C) Quantify diffusion of gases (CO_2, O_2, H_2O) through SEO copolymers to provide insight into failure of solid Li-air cells (Mar. 2013). CO_2 and O_2 *Completed . Humidity controlled experiments turned out to be challenging due to water absorption in SEO.*
- D) Improve on loading of cathodes with conducting binder to 70 wt.%. *Completed. Anna Javier is still in my group, transitioning to a non-BATT project.*

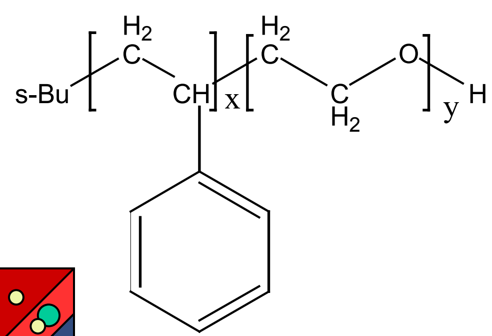
Approach and Deployment

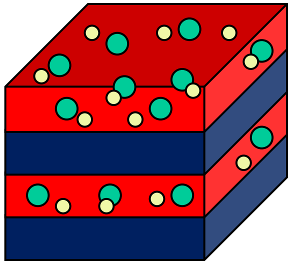
- Synthesize block copolymers
- Study morphology and ion and electron transport
- Build and test full cells
- Work toward commercialization (either by founding start-ups or by working with companies).

Nanoporous separator

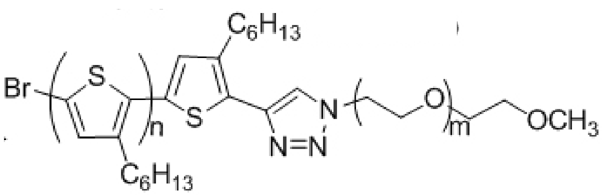


Nanostructured solid electrolyte

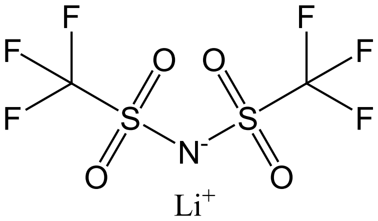




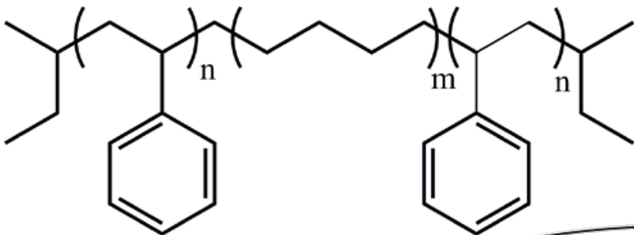
Electron- and ion-conducting binder



Salt, LiTFSI



Technical Accomplishment (A): Self-assembled separators

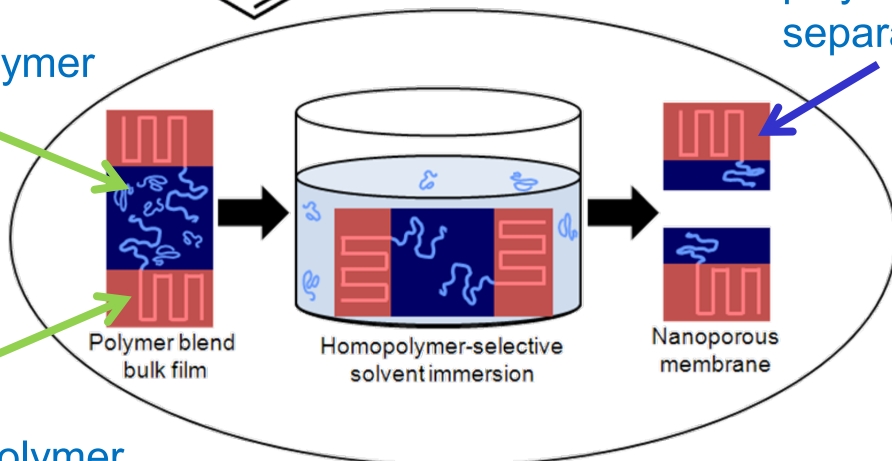


Add PS homopolymer and then wash it out with THF.

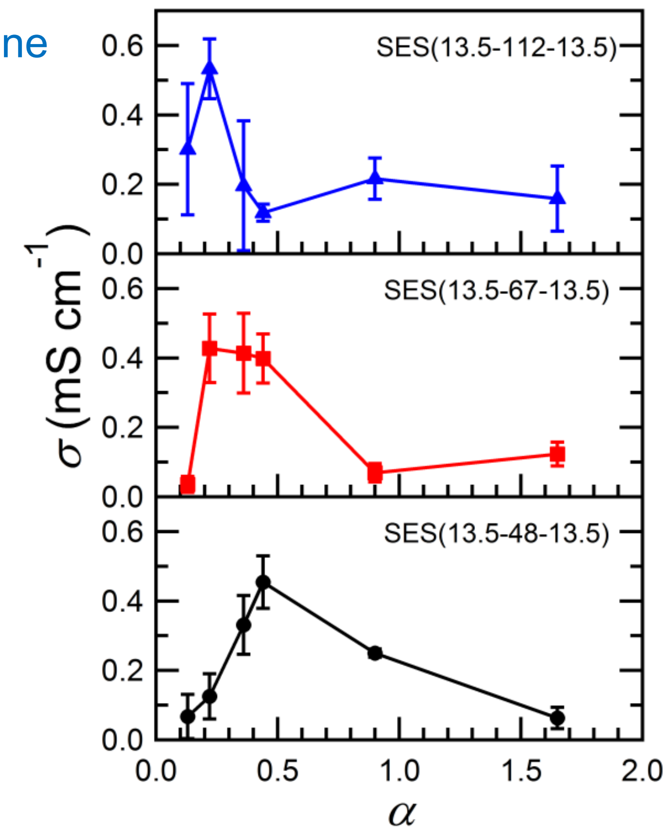
Celgard®, σ=0.42 mS/cm

polyethylene separator

sacrificial polymer



separator polymer



mol. wt. of sacrificial polymer

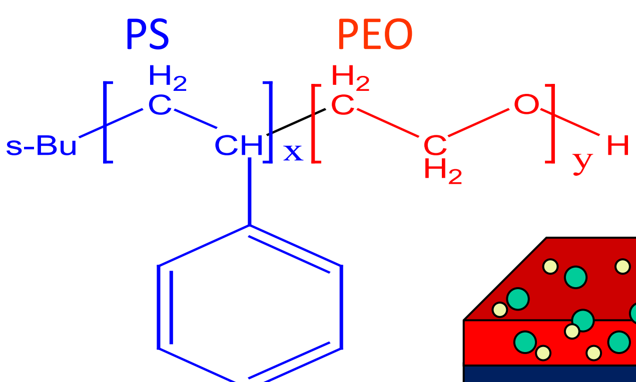
Advantages: Simple wet process (potentially using water) and reduced defect density. Barriers addressed: cost and safety.

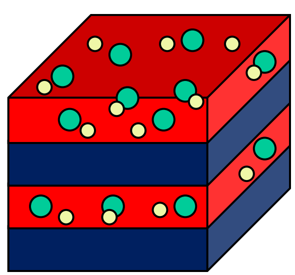
Overall Approach (B): Nanostructured block copolymer electrolytes

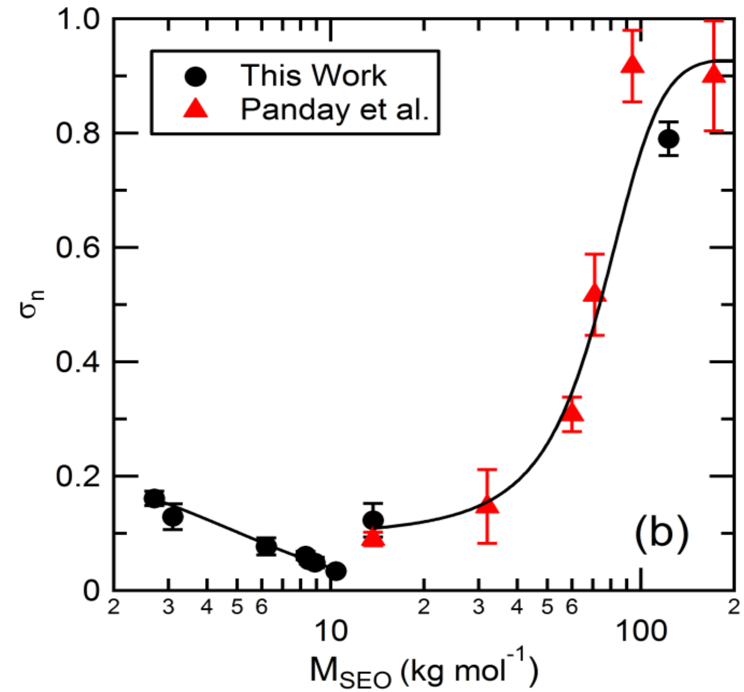
We use a solid block copolymer electrolyte SEO to prevent the formation of Li dendrites. The high modulus of the PS block resists dendrite formation and enables the use of lithium metal as an anode.

high modulus

high conductivity

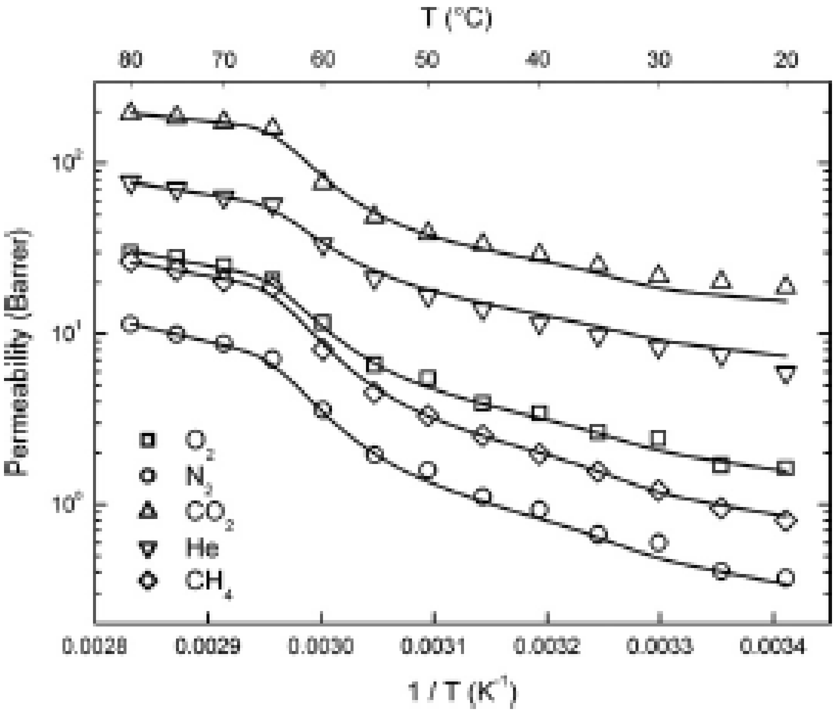






<u>Major Finding</u>: Increasing molecular weight improves both mechanical properties and ionic conductivity.

Technical Accomplishment (B): Quantified gas diffusion through SEO electrolytes



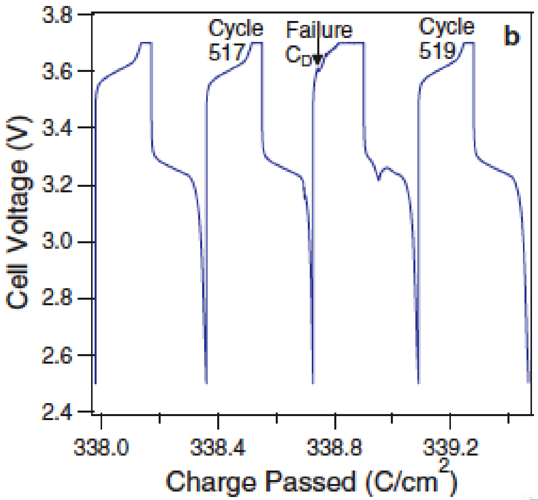
Gas permeability in SEO block copolymer at different temperatures (1 Barrer = 3.464×10^{-16} mol m/(m^2 s Pa)).

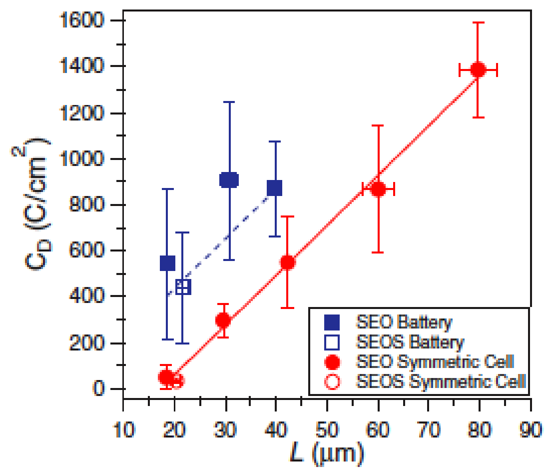
	CO_2	N_2	O_2	CH_4	He	
T_c (°C)[59]	31	−147	−119	−83	−268	
d_k (nm)[60]	0.330	0.364	0.346	0.380	0.260	
T (°C)	P (Barrer)					Selectivity
	CO_2	N_2	O_2	CH_4	He	CO_2/N_2
20	18.7	0.371	1.62	0.801	5.92	50.4
25	20.1	0.406	1.69	0.946	7.49	49.5
30	21.8	0.598	2.42	1.20	8.32	36.5
35	25.1	0.665	2.64	1.55	9.79	37.7
40	29.1	0.930	3.42	1.98	11.5	31.3
45	33.4	1.11	3.92	2.54	14.0	30.1
50	38.8	1.58	5.49	3.32	16.7	24.6
55	48.5	1.96	6.59	4.54	21.1	24.7
60	76.9	3.59	11.6	8.05	33.3	21.4
65	160	7.13	20.5	18.8	57.2	22.4
70	174	8.74	24.9	20.4	63.5	19.9
75	185	9.90	27.9	23.7	70.4	18.7
80	195	11.3	29.8	26.5	77.2	17.3

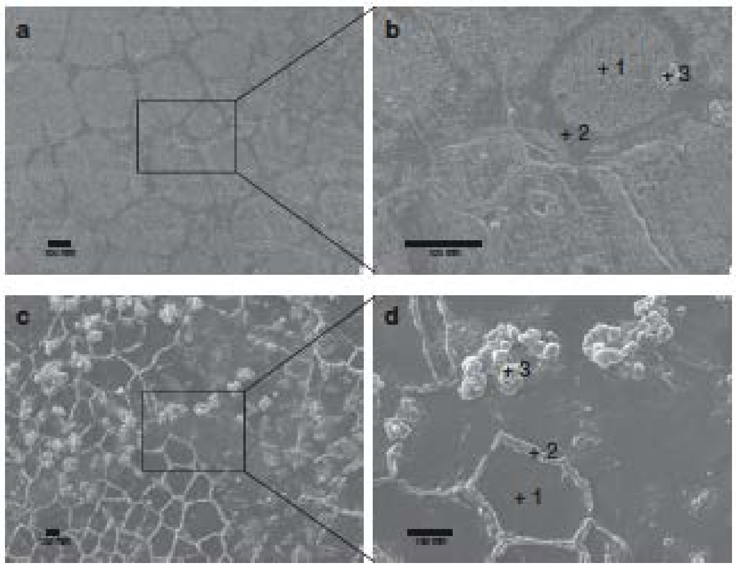
Major Finding: Transport laws developed to understand lithium ion transport also apply to gas diffusion.
SEO is unsuitable for selective transport of lithium ions while blocking CO_2 and N_2, i.e. it cannot help the functioning of the Li-air cell (no go).

M. Minelli, M. Baschetti, D.T. Hallinan, N.P. Balsara, *J. Mem. Sci.*, 2013

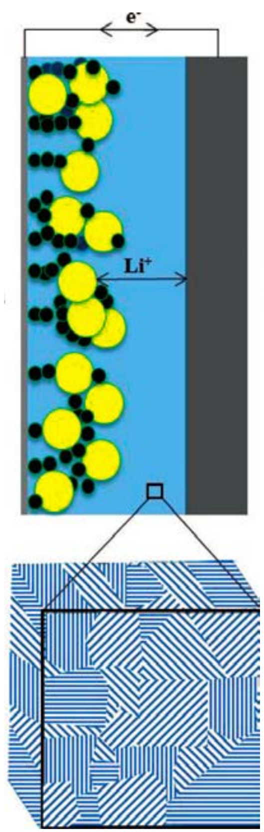
Technical Accomplishment: (B) Studied Failure of Li|SEO|$FePO_4$ and Li|SEO|Li ells







Cathode material: $LiFePO_4$



Anode: Li metal

Nanostructured block copolymer electrolyte

Major Finding:
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.

D.T. Hallinan, S.A. Mullin, G.M. Stone, N.P. Balsara, *J. Electrochem. Soc.*, vol. 160(3) A464-A470, 2013.

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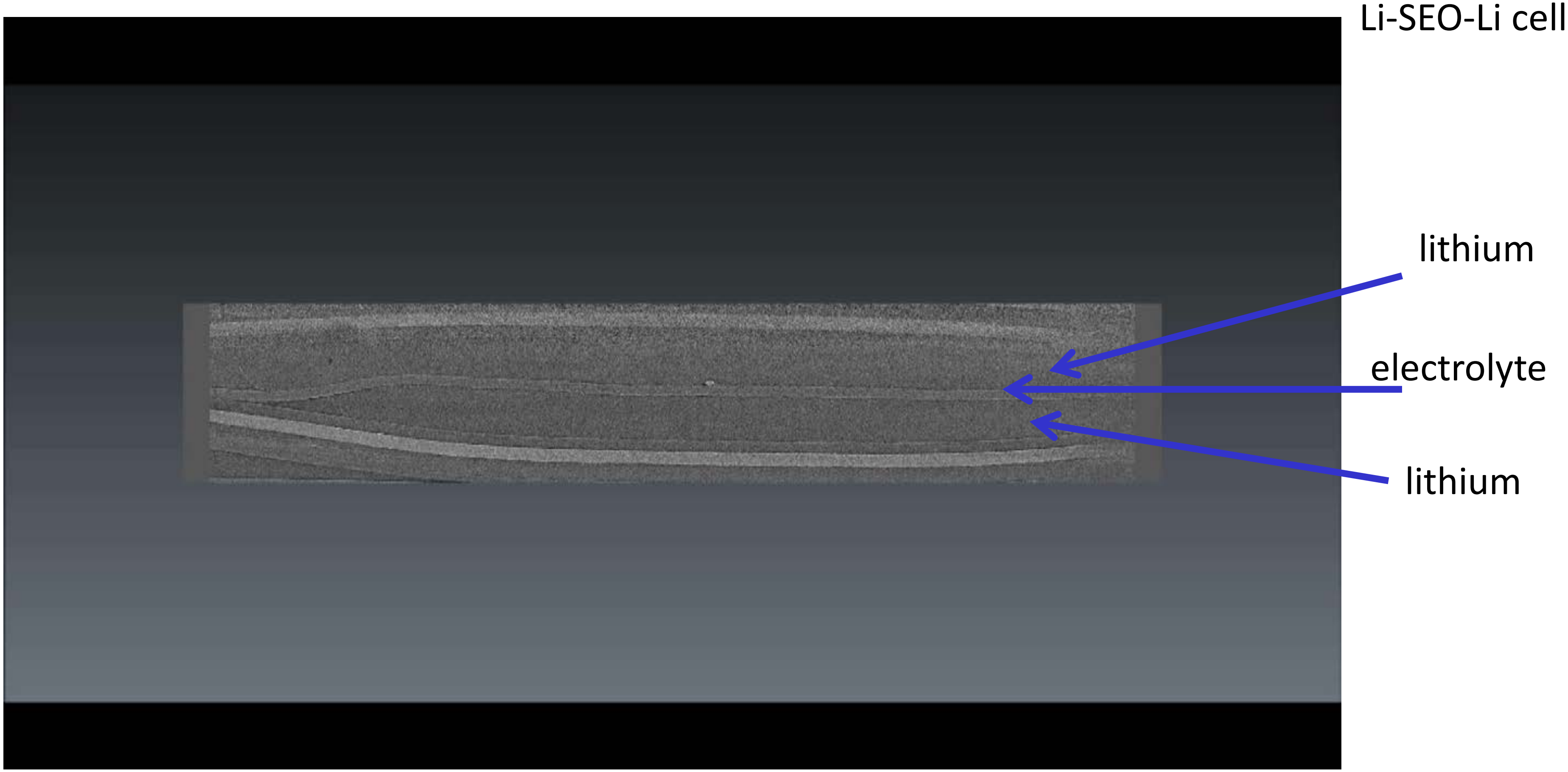
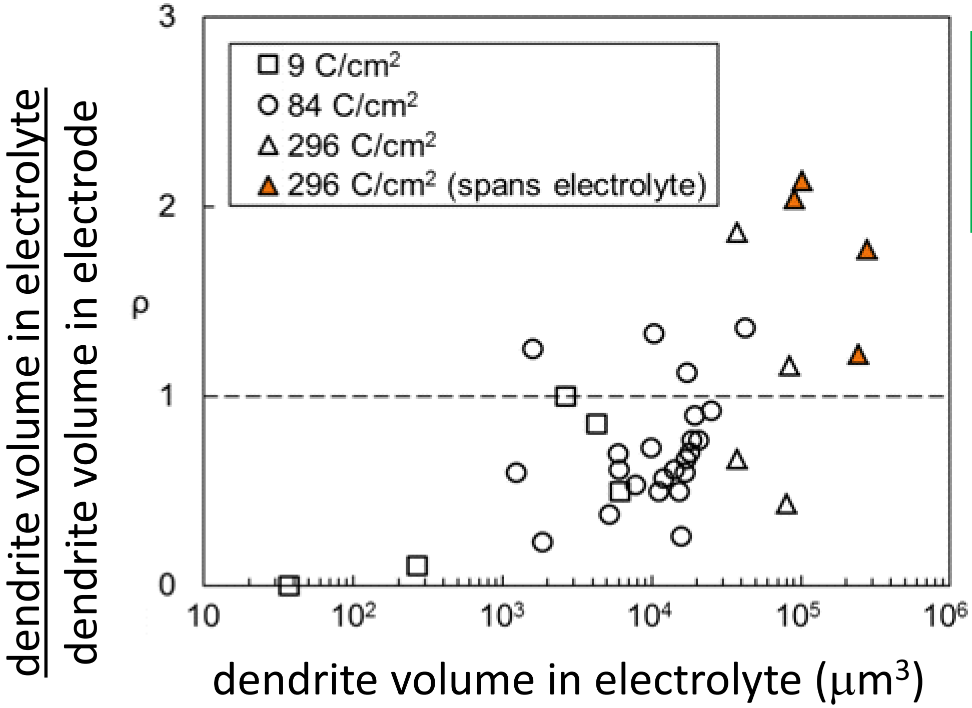
Technical Accomplishment (B): Solved "needle-in-haystack" dendrite problem



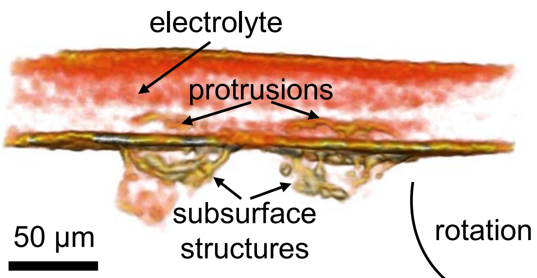
Development of X-ray tomography tool funded by BES (Katherine Harry).
Cell building infrastructure built by BATT/EERE (Dan Hallinan).

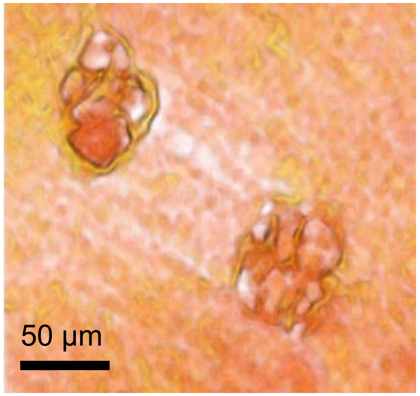
Technical Accomplishment (B): Finding all "needles-in-haystack"

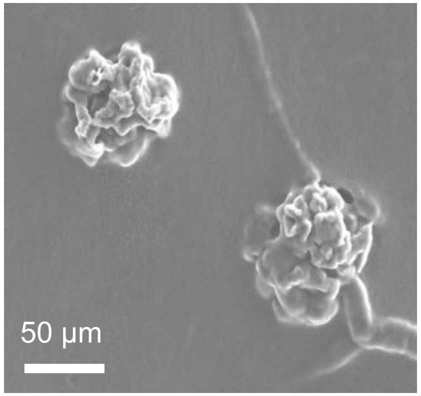


Major Finding: During the early stages of dendrite growth, dendrite is **mainly in the electrode**.

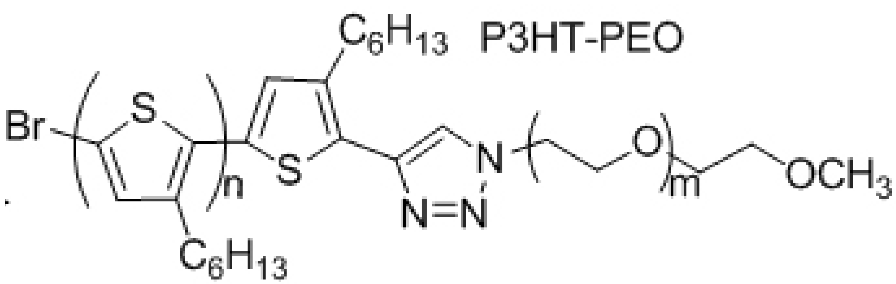
SEM does not reveal sub-surface dendritic structures.

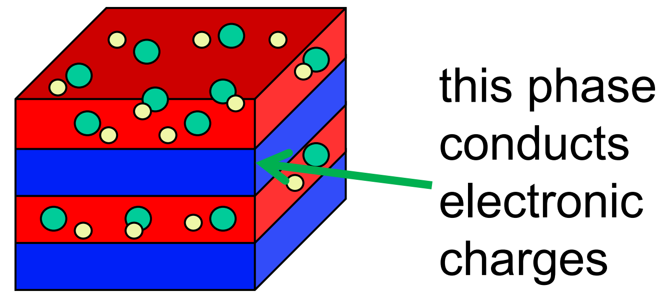


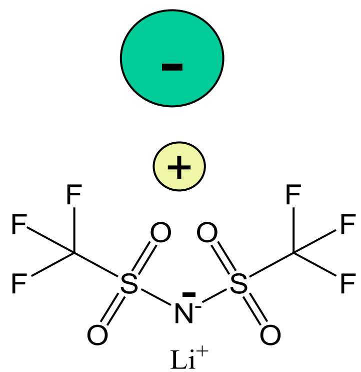




Technical Accomplishment (C): Development of binder that conducts electrons and ions

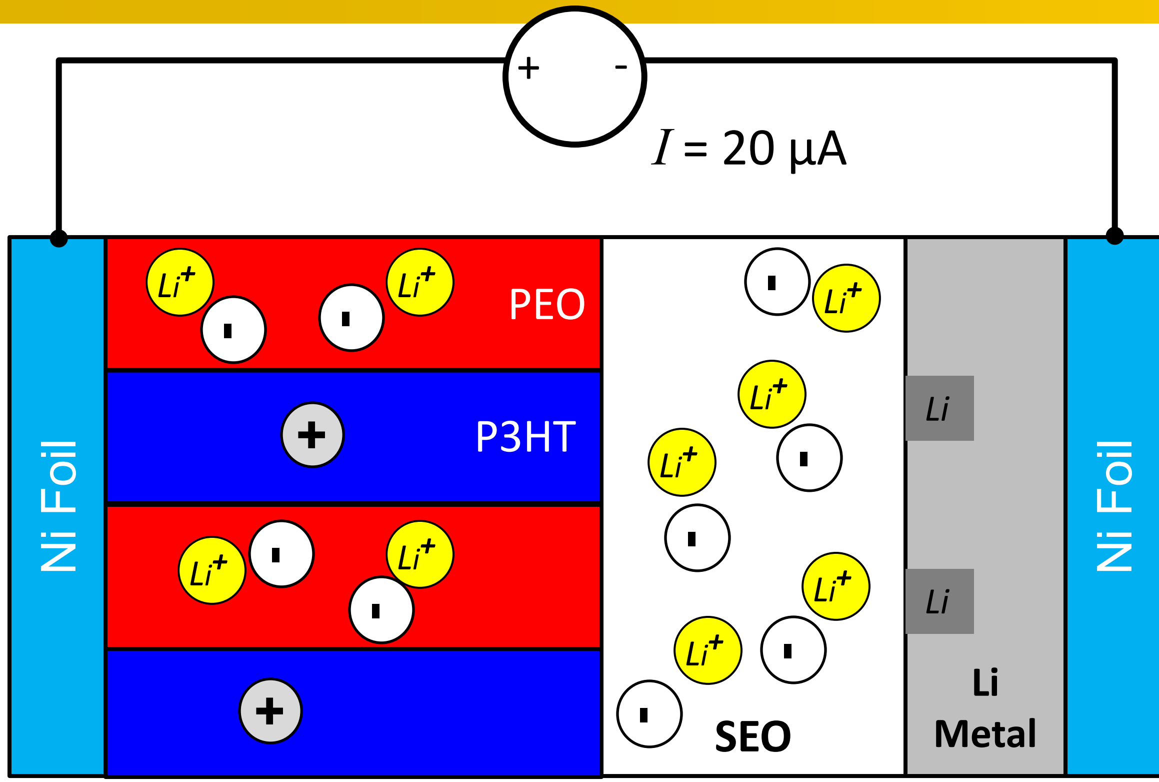






<u>Major Technical Accomplishment</u>:
Measurement of electronic conductivity of binder as a function of potential.

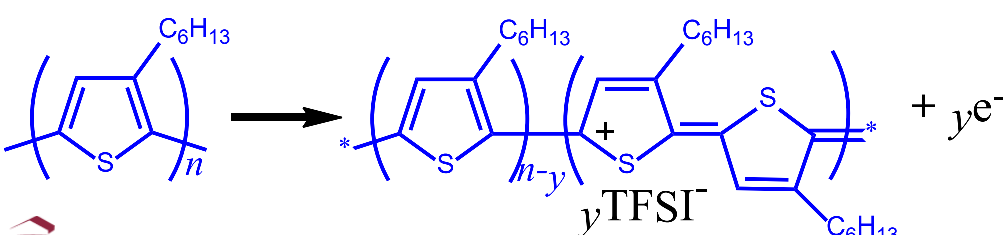
Technical Accomplishment (C): Conceptual cell design for controlled P3HT oxidation



$Li^+ + e^- \rightarrow Li$

$$moles\ e^- = \frac{It}{F}$$

F = 96485 C/mol
Faraday's constant

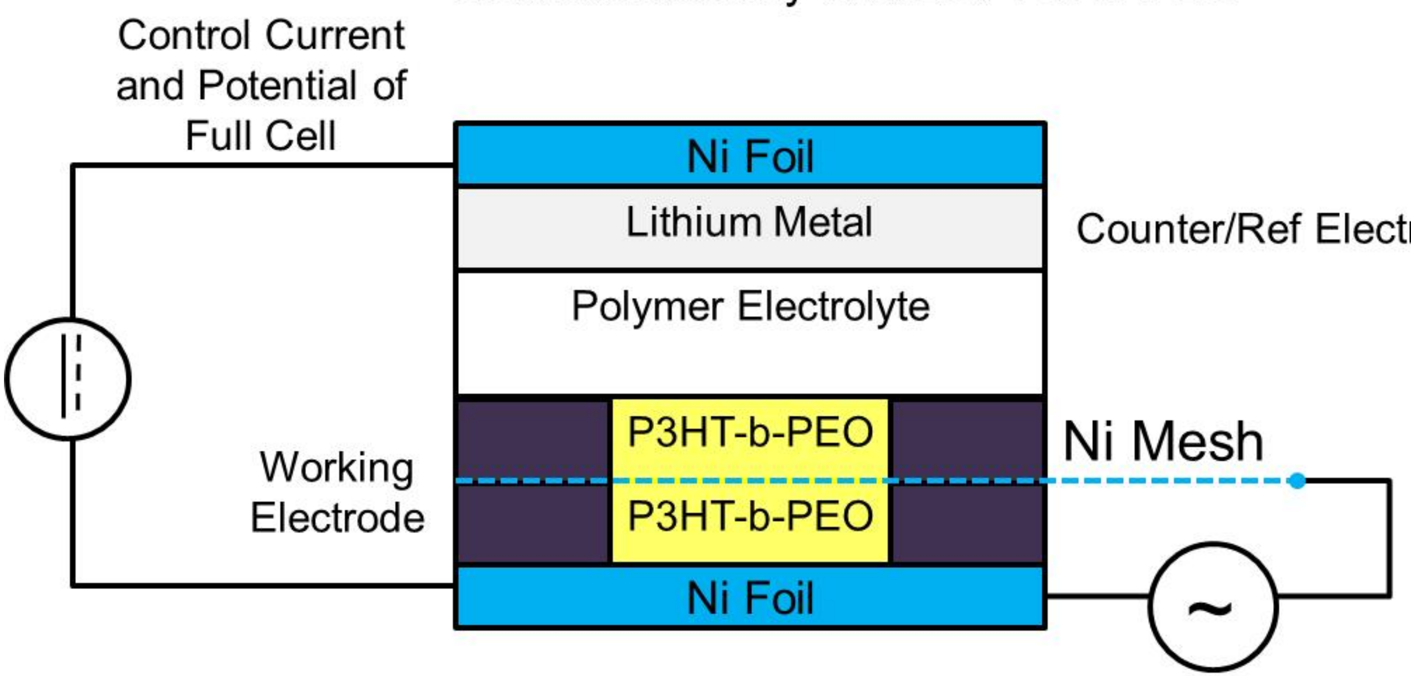


$$SOC = \frac{moles\ e^-}{moles\ thiophene\ monomer}$$

Following Chen and Richardson

Technical Accomplishment (C): Three-terminal cell design

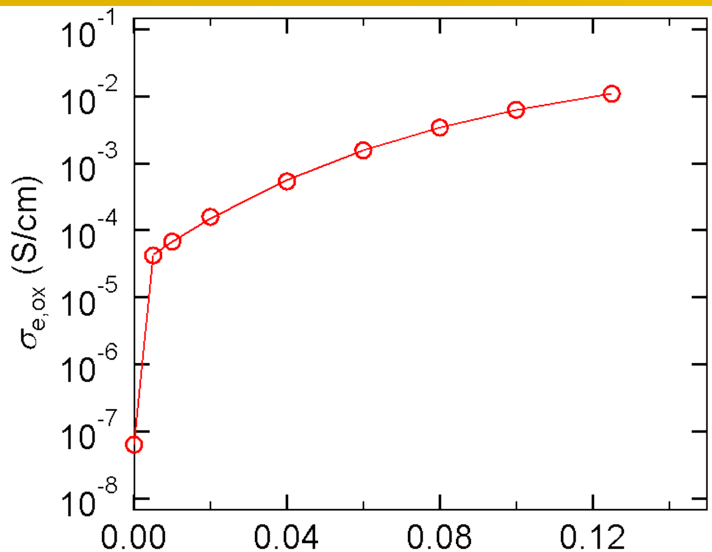
In-situ electronic conductivity measurement of electrochemically oxidized P3HT-PEO

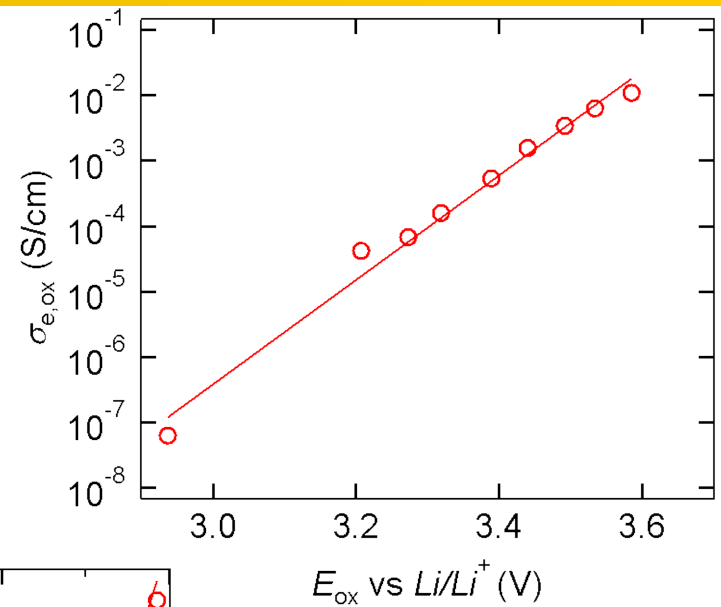


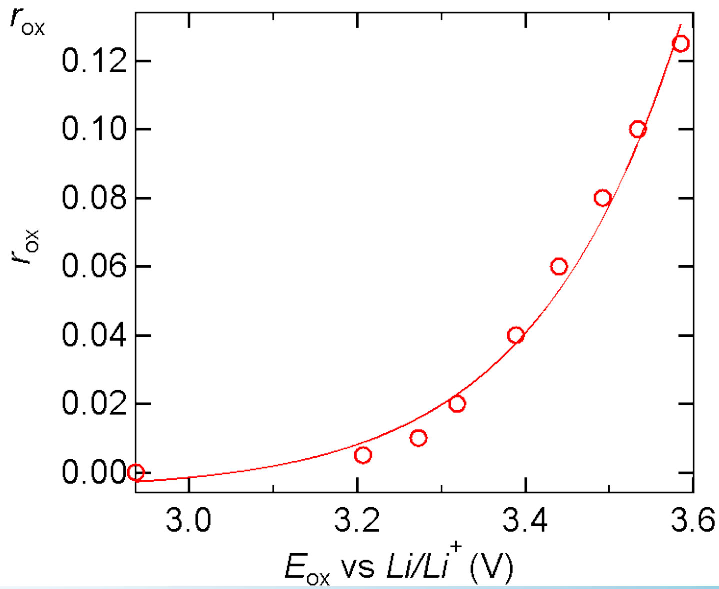
Measurement of electronic conductivity (σ) of P3HT as a function of oxidation state (r_{OX}) and potential (E_{ox}).

measure conductivity of P3HT-PEO layer via AC impedance

Technical Accomplishment (C): Measurement of conductivity as a function of oxidation

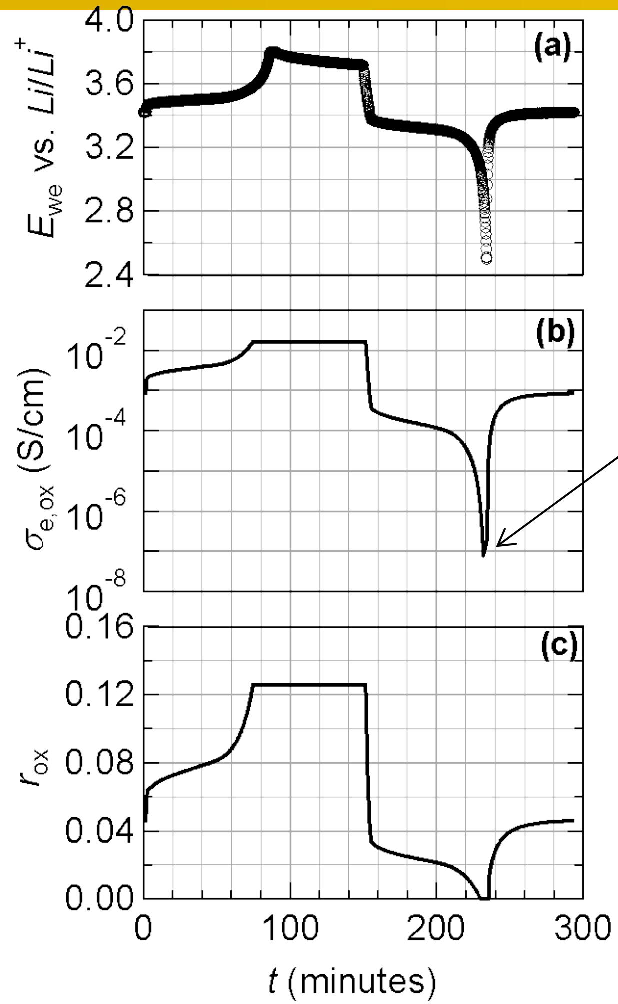




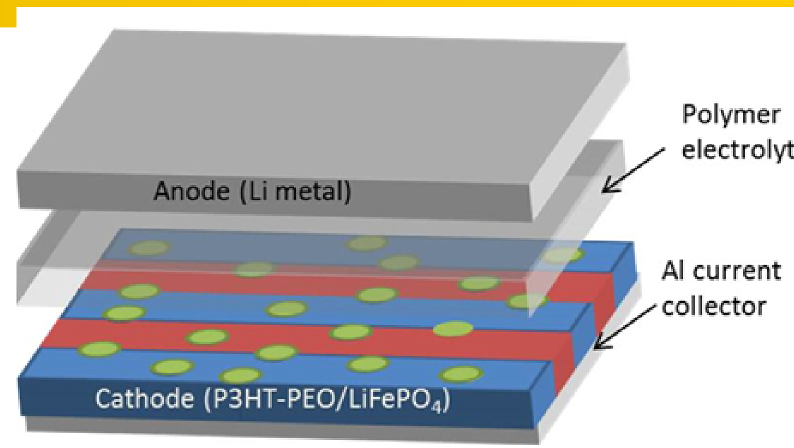


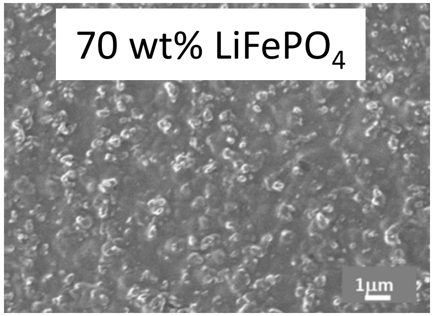
Quantification of factors that control conductivity of binder.

Technical Accomplishment (C): Hypothesis of redox reactions in a full cell

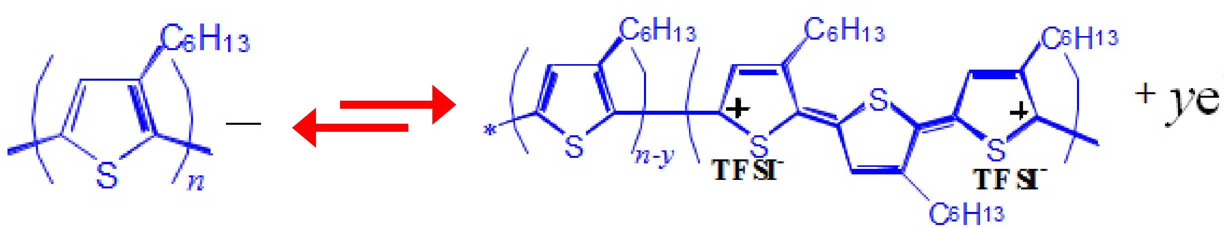


automatic
over-discharge
protection

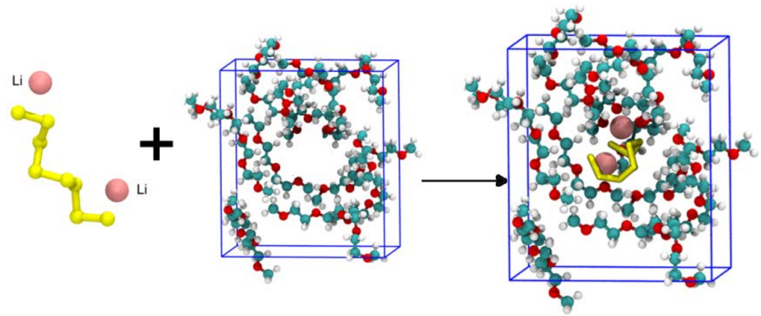


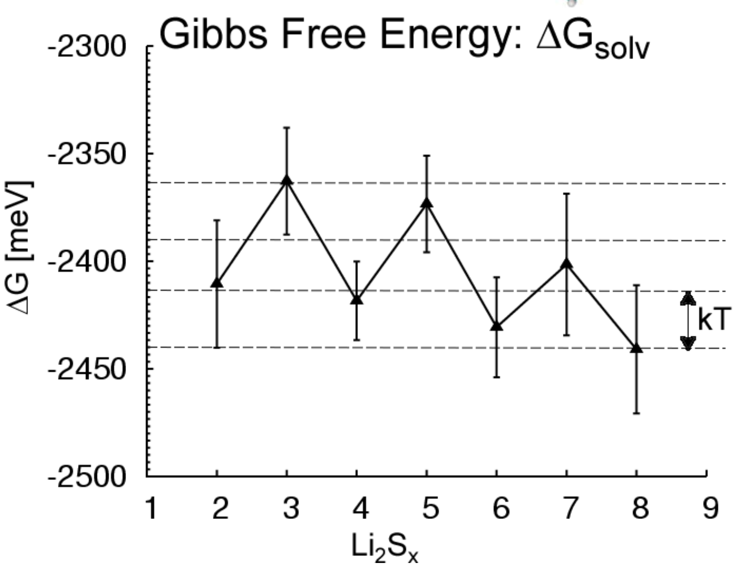


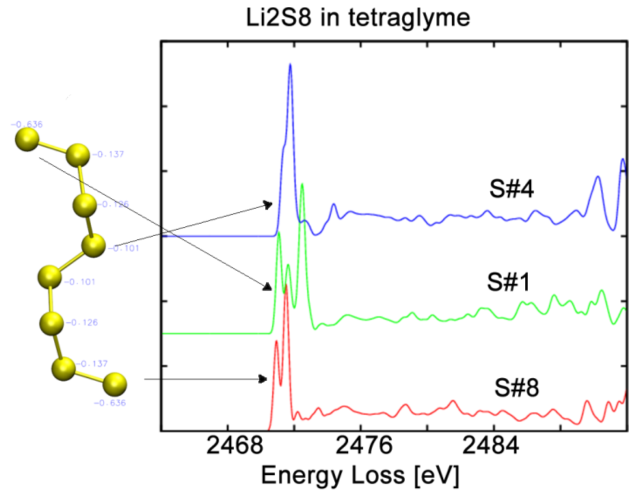
$$LiFePO_4 \rightleftharpoons Li^+ + e^- + FePO_4$$



Future Work: Lithium-Sulfur Speciation Theory (Prendergast)



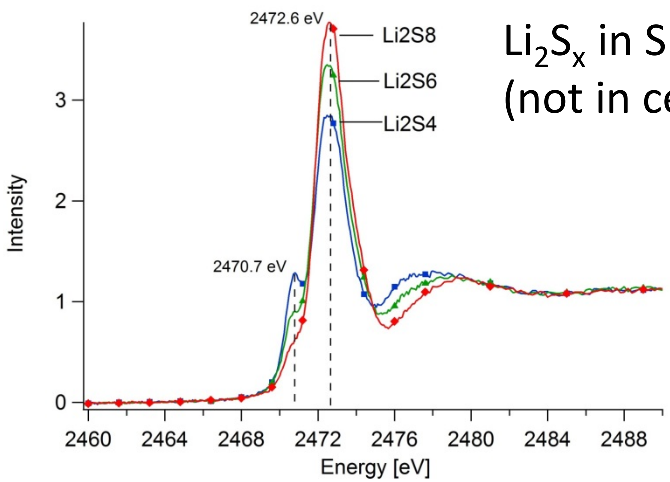




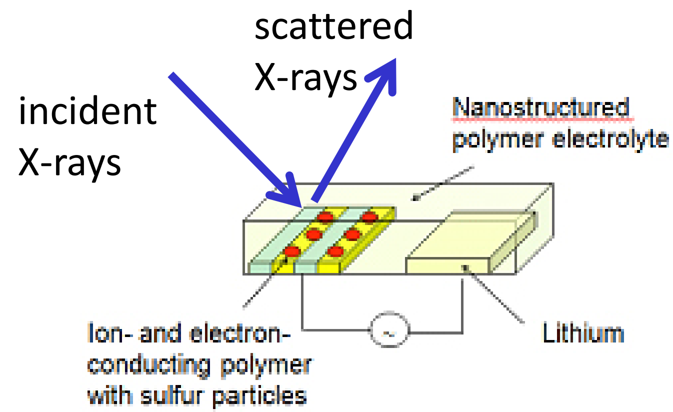
	a1/b1 ratio
S8	0
Li2S8	0.31
Li2S7	0.6
Li2S6	0.8
Li2S5	1.1
Li2S4	1.3
Li2S3	1.5
Li2S2	5

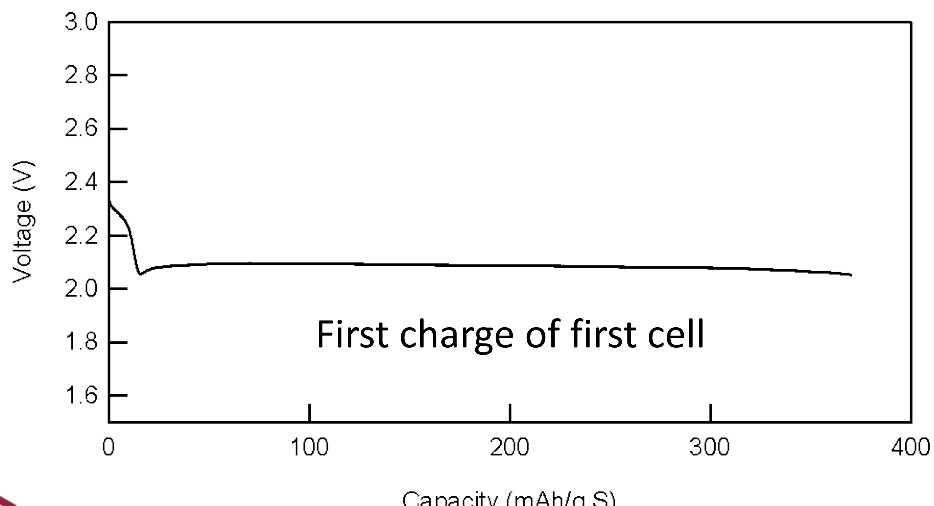
Proposed Modeling: Use molecular dynamics simulations and electronic structure calculations to predict spectra.

Future Work: Lithium-Sulfur Speciation Experiments and Cell Building



Li_2S_x in SEO data (not in cell)





Solid electrolyte being developed with Dudney and Tenhaeff (ONRL)

<u>Proposed Experiment</u>: (1) Measure X-ray spectra while the Li-S cell is charged and discharged. (2) Use fundamental knowledge to make Li-S cells that cycle.

Collaboration and Coordination with Other Institutions

Collaborators:

Vince Battaglia, Venkat Srinivasan, Jordi Cabana, (LBNL, VT Program). *Activity: cell building, testing, and modeling*

David Prendergast, Jinghua Guo, Miquel Salmeron, Alex Hexemer, Alistair MacDowell (LBNL, outside VT Program). *Activity: X-ray spectroscopy and tomography.*

Nancy Dudney and Wyatt Tenhaeff (ONRL). *Activity: Solid polymer/ceramic composites.*

Technology Transfer:

Cofounded Seeo, a battery start-up, in 2007 to commercialize solid-state battery. Company has moved into pilot production in 2011-12. Batteries sent to customers for testing 2013.

Summary

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

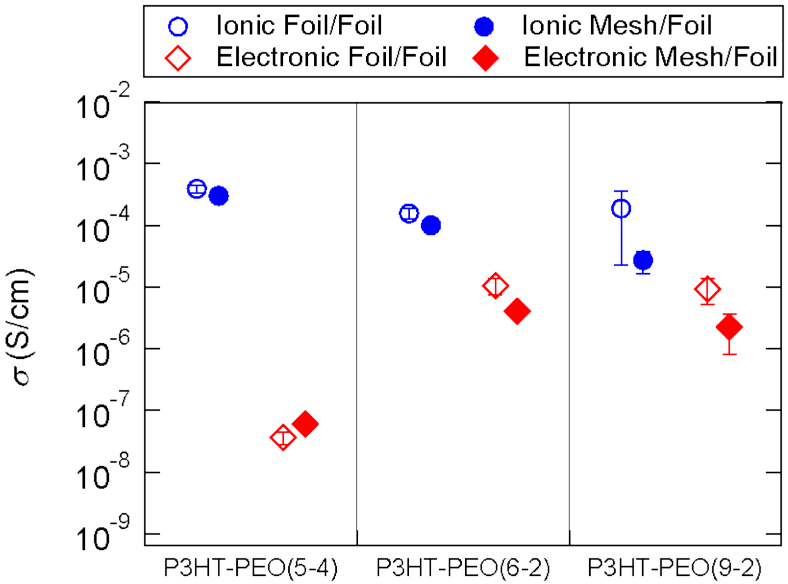
- (A) Established a low-cost approach for creating nanoporous separators.
- (B) Quantified the efficacy of SEO copolymers as electrolytes for the prevention of lithium dendrites in symmetric full cells.
- (D) An active binder that conducts both ions and electrons has been developed, characterized and incorporated into cells.

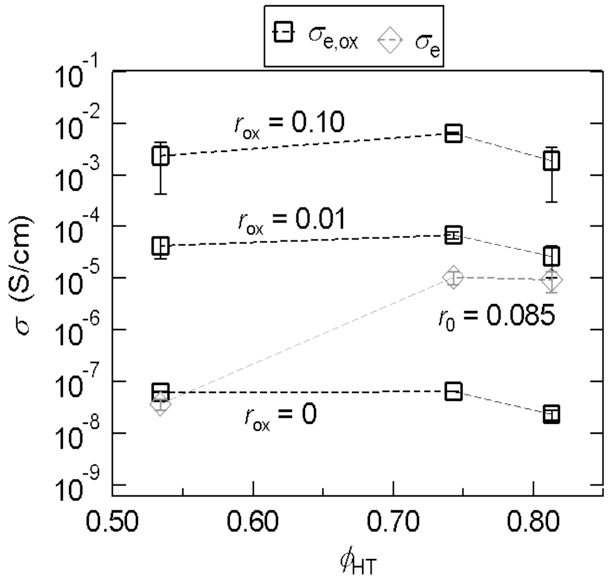
SEO/salt mixture and separator work will be completed by September 2013. (Thank you for your support, critical comments, and guidance.)

Transitioning toward understanding and developing all-solid Li-S cells (new BATT project funded in 2012).

Technical Back-up Slides

E-chem oxidation





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