Polymer Electrolytes for High Energy Density Lithium Batteries

Ashoutosh Panday
Scott Mullin

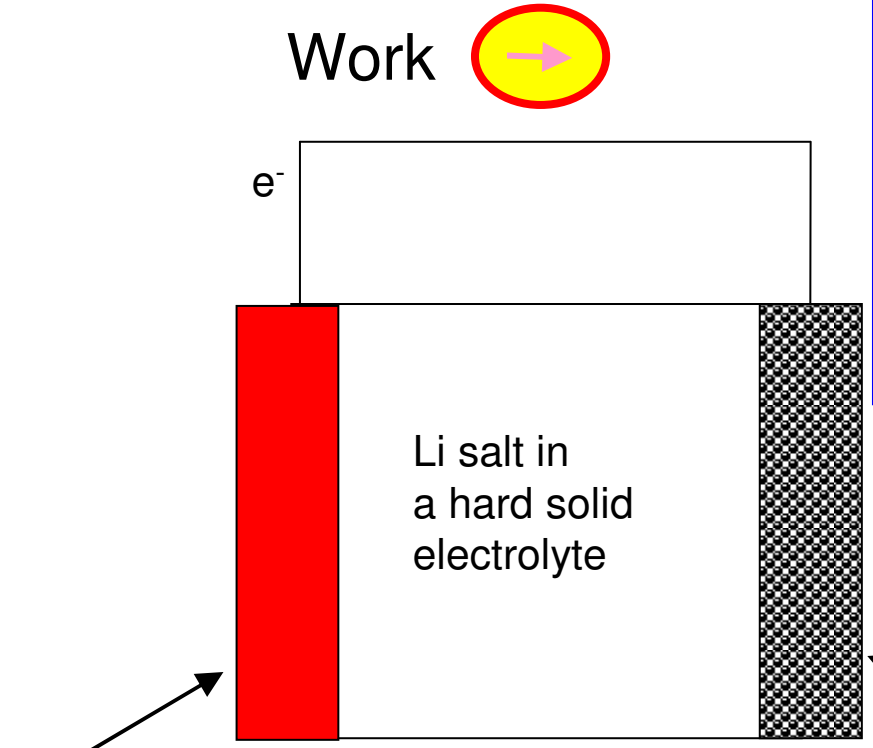
Nitash Balsara

SEEO

THE UNIVERSITY OF CALIFORNIA BERKELEY 1868

BERKELEY LAB

Proposed Battery



Key advantages:

- Non-flammable electrolyte
- Theoretical energy density of 300 Wh/kg.
- No dead weight and no reduction in potential as Li is depleted.

anode (Li metal)

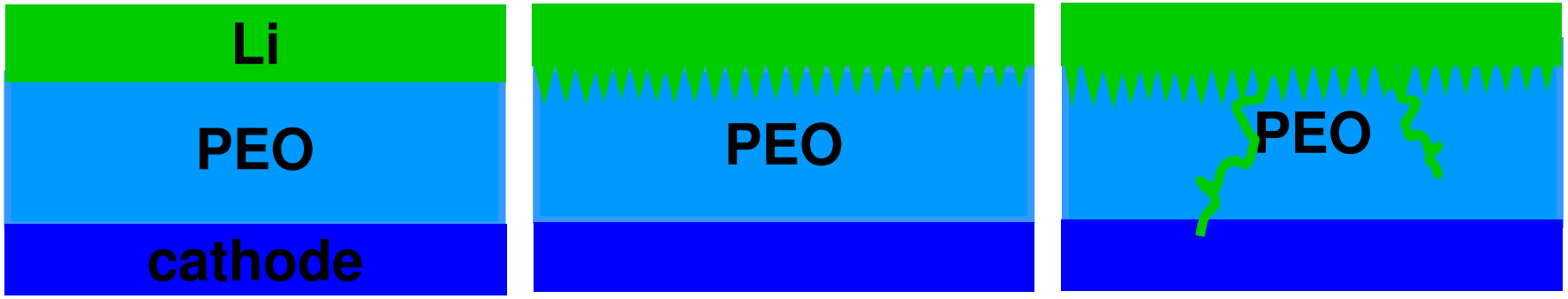
$Li \rightarrow Li^+ + e^-$

cathode (active particles and carbon bound by polymer)

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

Fatal flaw in PEO

Repeated cycling led to the roughening of the Li surface and eventually to catastrophic dendrite growth.



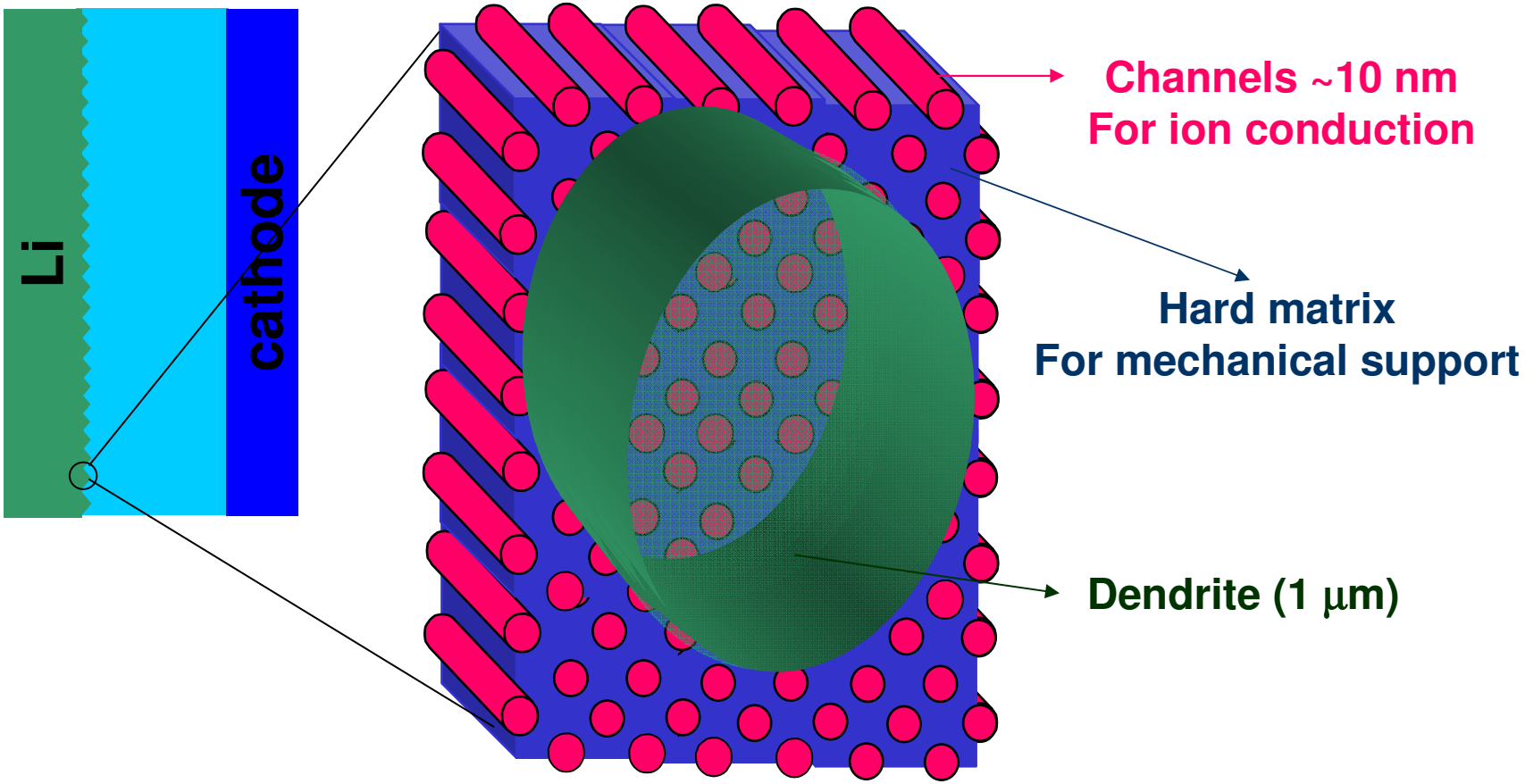
t=0

intermediate times high surface area Li

dendrite short

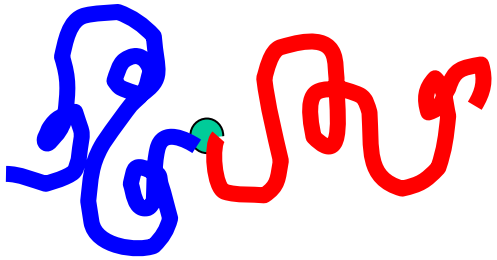
Solution: Make electrolyte hard and mechanically stop dendrites. How hard is hard?
Modulus=10^9 Pa (Monroe, Newman, 2005)

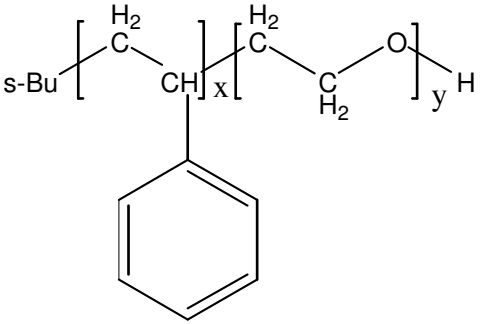
Nanostructured Electrolyte

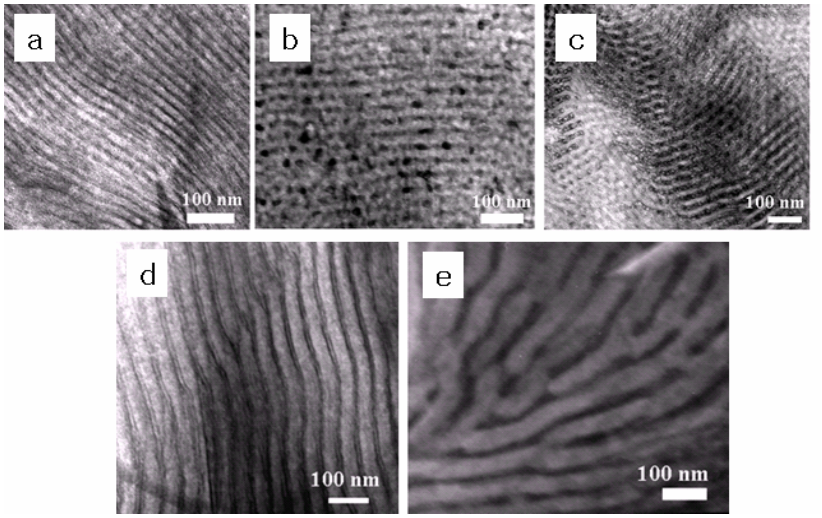


Decouple the mechanical and electrical properties of the electrolyte

Morphology-Conductivity Relation





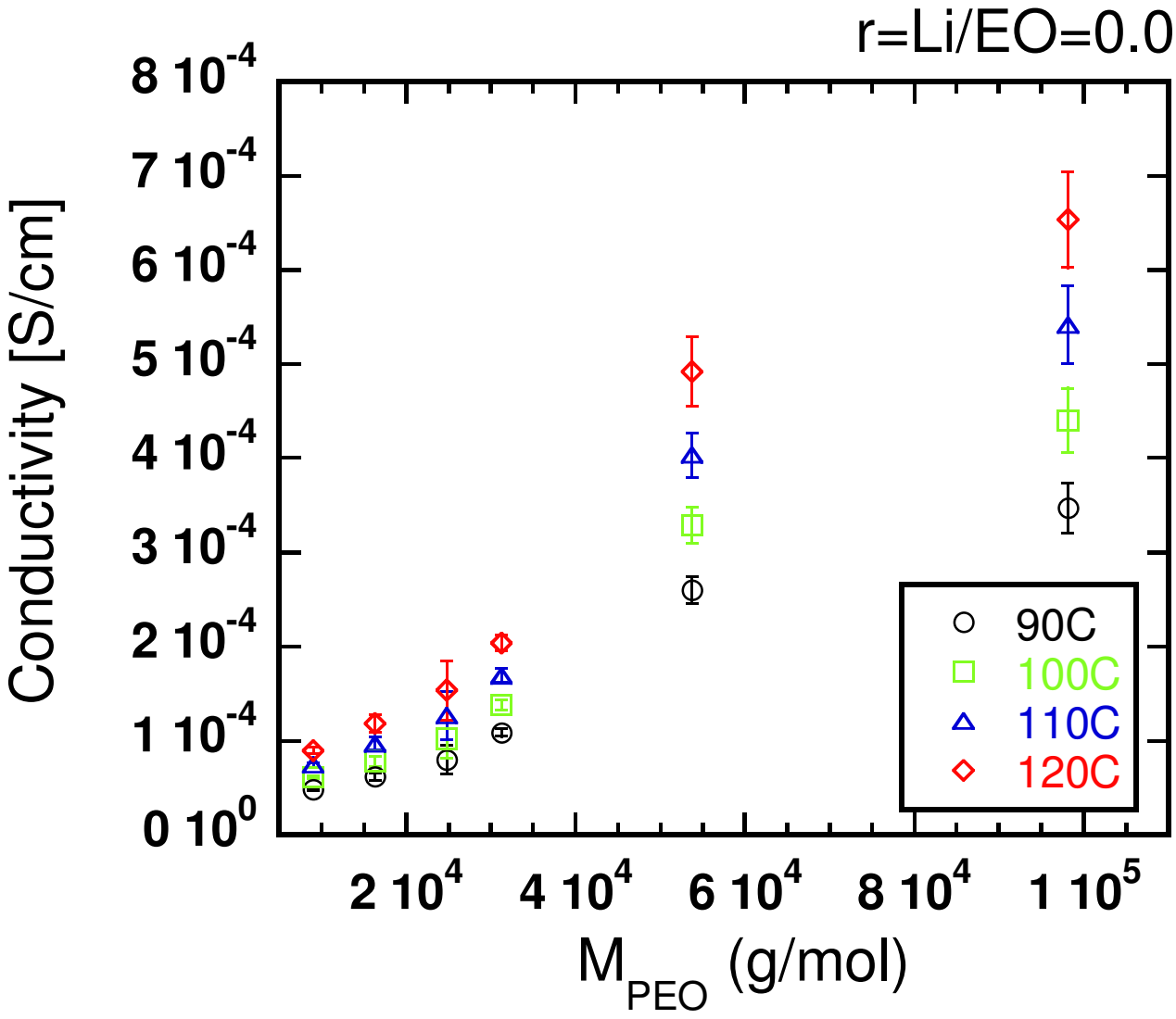


First systematic study of the effect of molecular weight of copolymer on conductivity.

Singh et al., Macromolecules, 2006

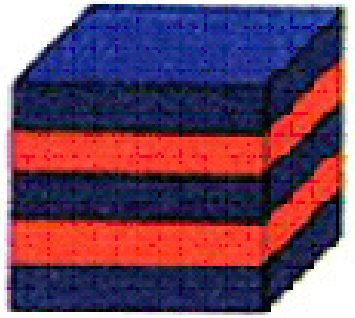
Effective use of nanoscale objects

Conductivity versus M_{PEO}

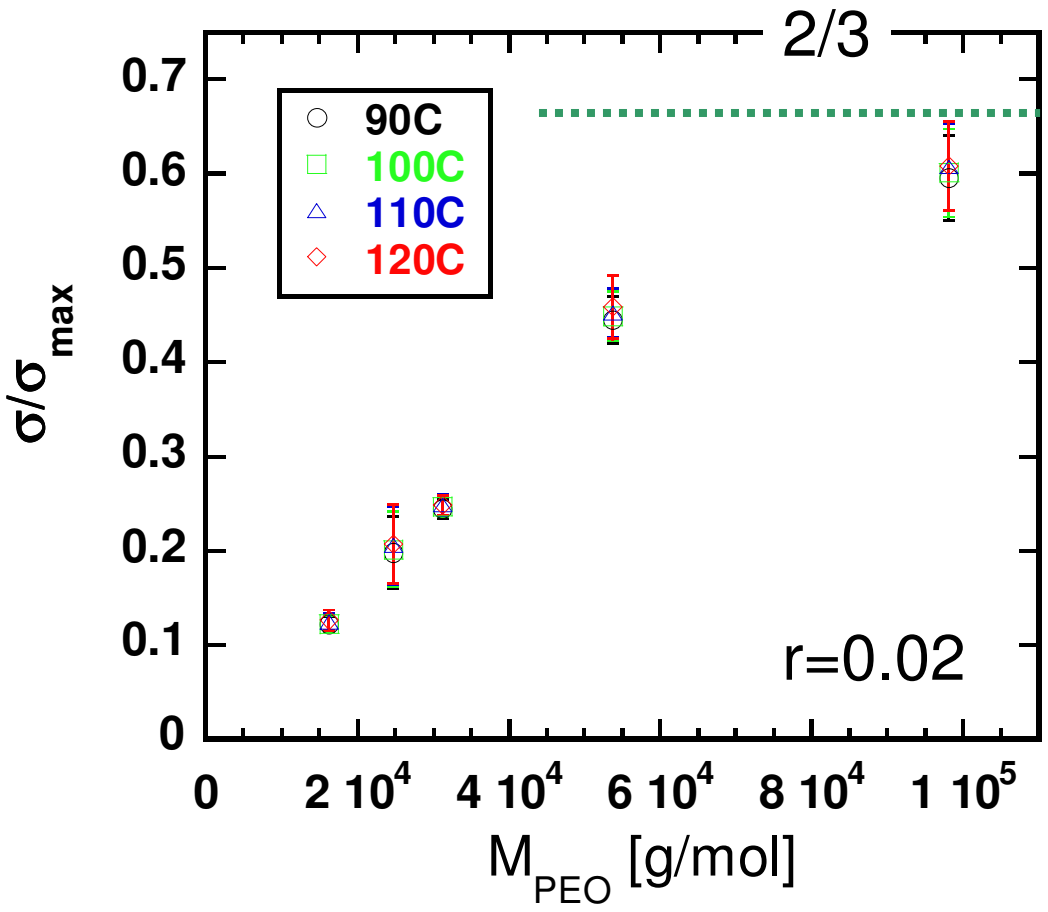


Normalize σ by

$\sigma_{max}=\sigma_{pure\ PEO}\phi_{PEO}$

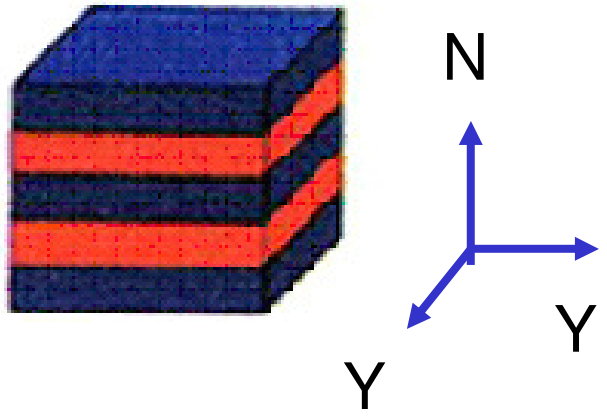


Normalized conductivity



values approaching the theoretical upper limit (0.67)

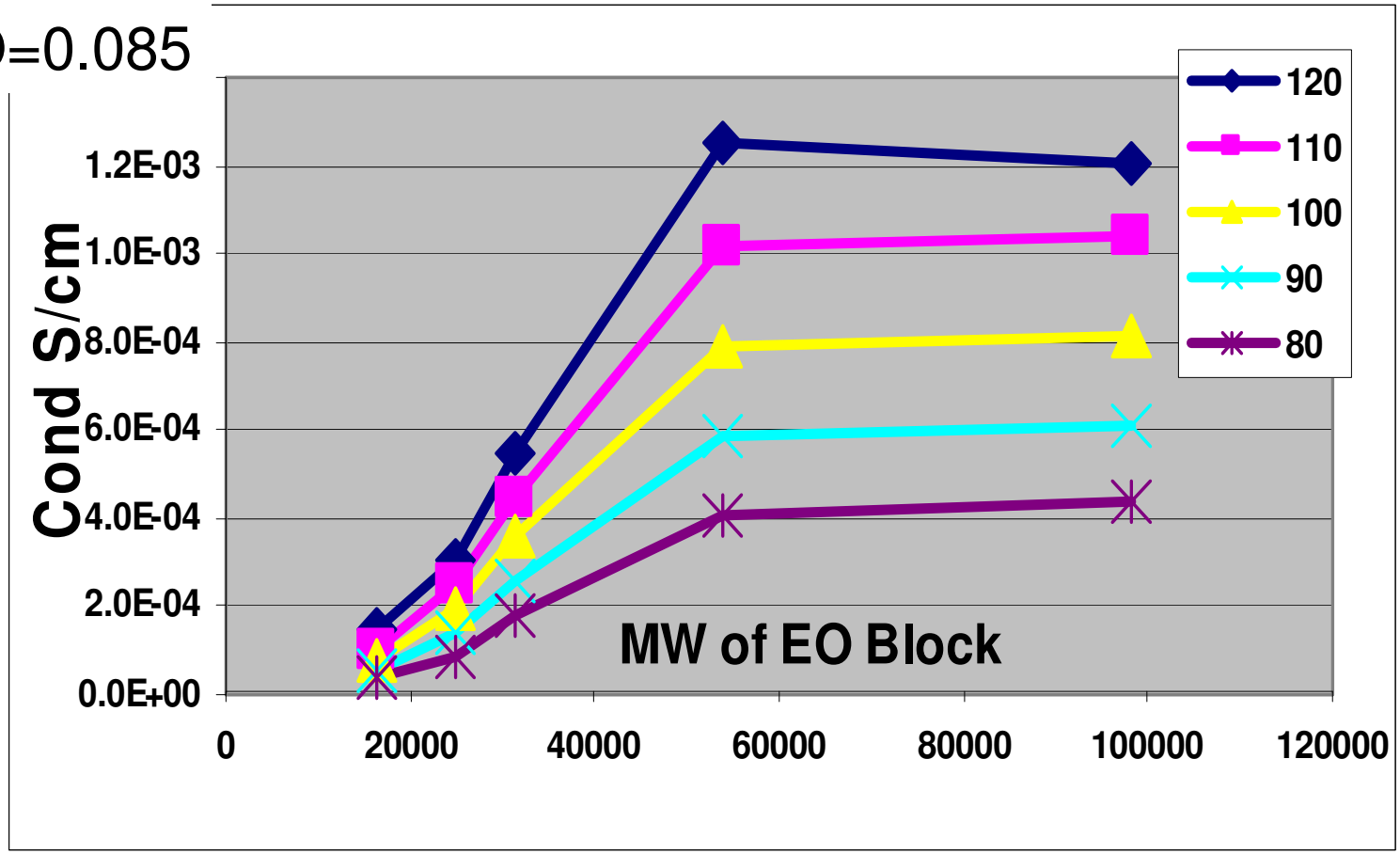
$\sigma_{max}=\sigma_{pure\ PEO}\phi_{PEO}$



Trend holds for other *r* values

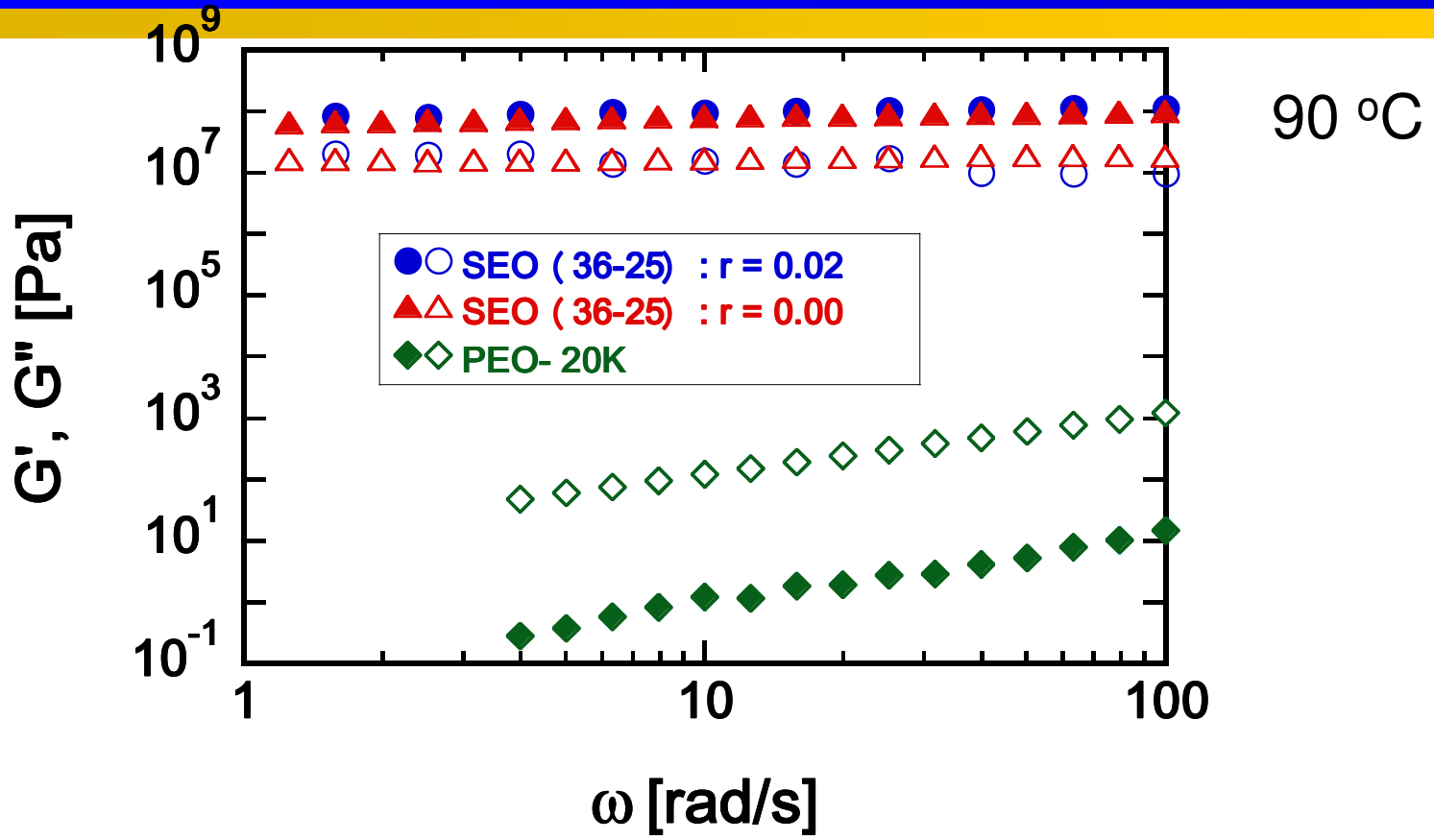
Effect of salt concentration on electrolyte conductivity

r=Li/EO=0.085



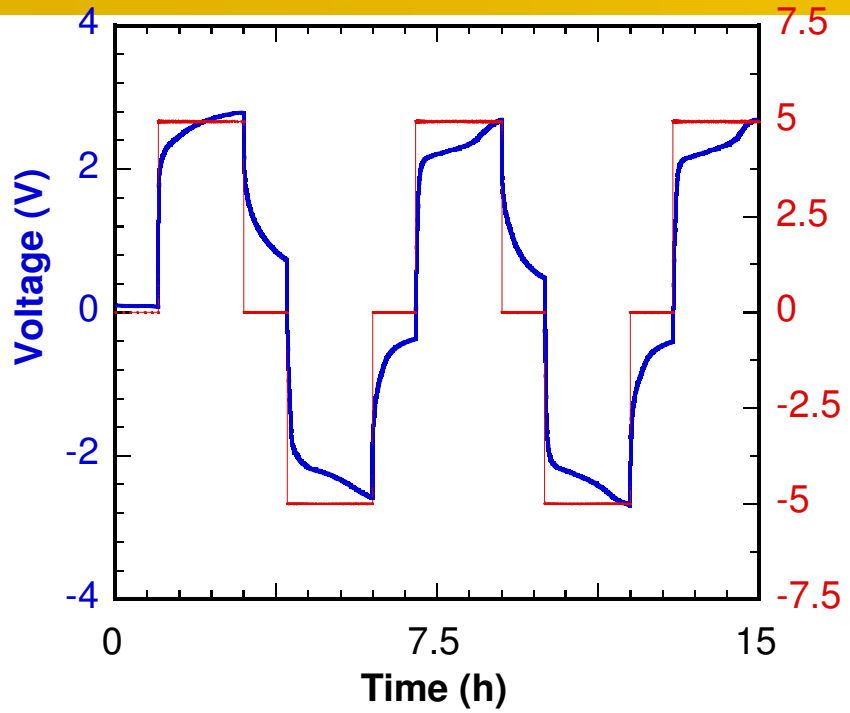
Improved mechanical properties

Mechanical properties



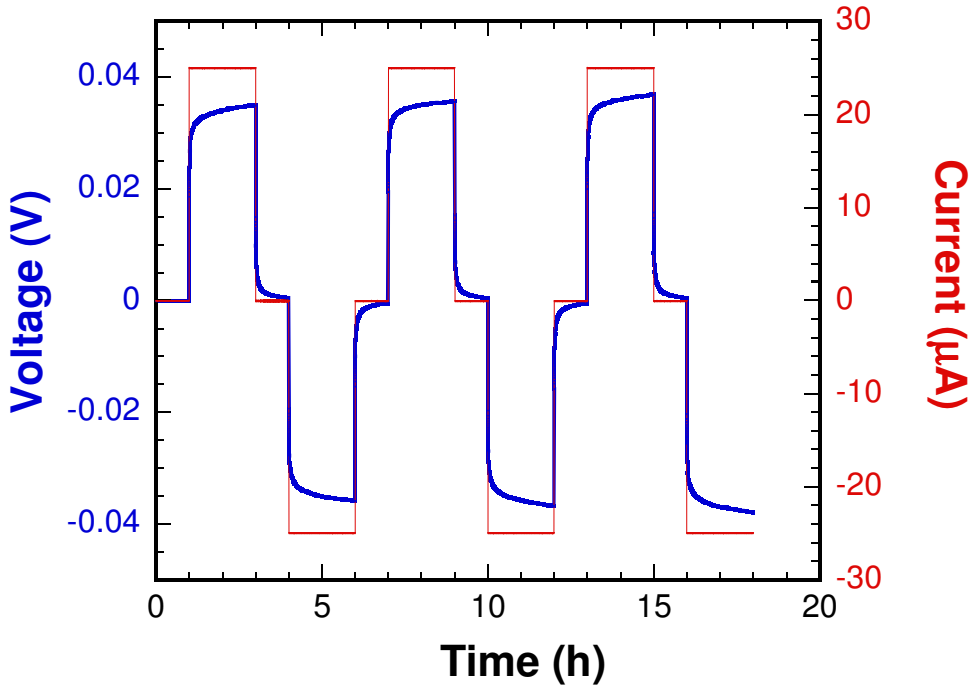
Nanostructured electrolytes have 1/3 the conductivity of PEO but larger shear modulus by several orders of magnitude.

High Overpotential Eliminated

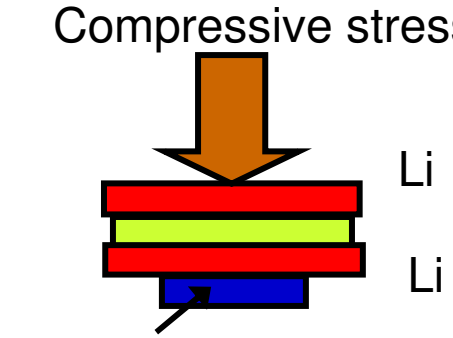


Initial Cycling Data
Overpotential = 3V at 50 uA/cm^2

Cycling Data with spring loaded electrodes
Overpotential = 0.035V at 200 uA/cm^2

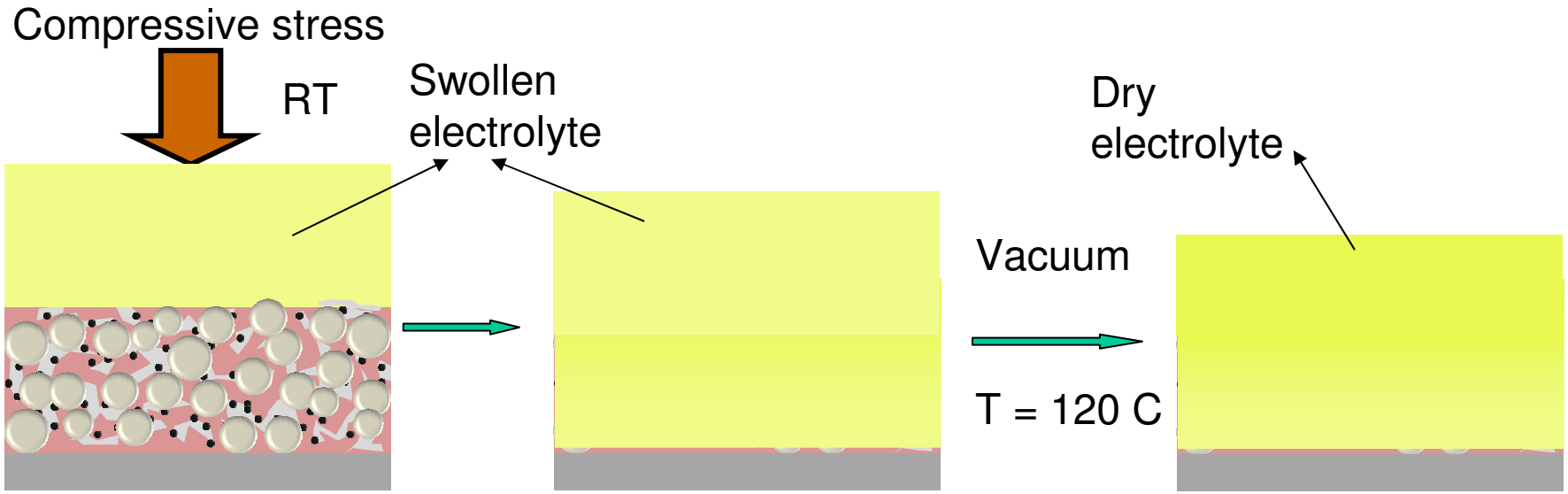


Liu
Battaglia



Interfacing SEO Electrolyte with Cathode

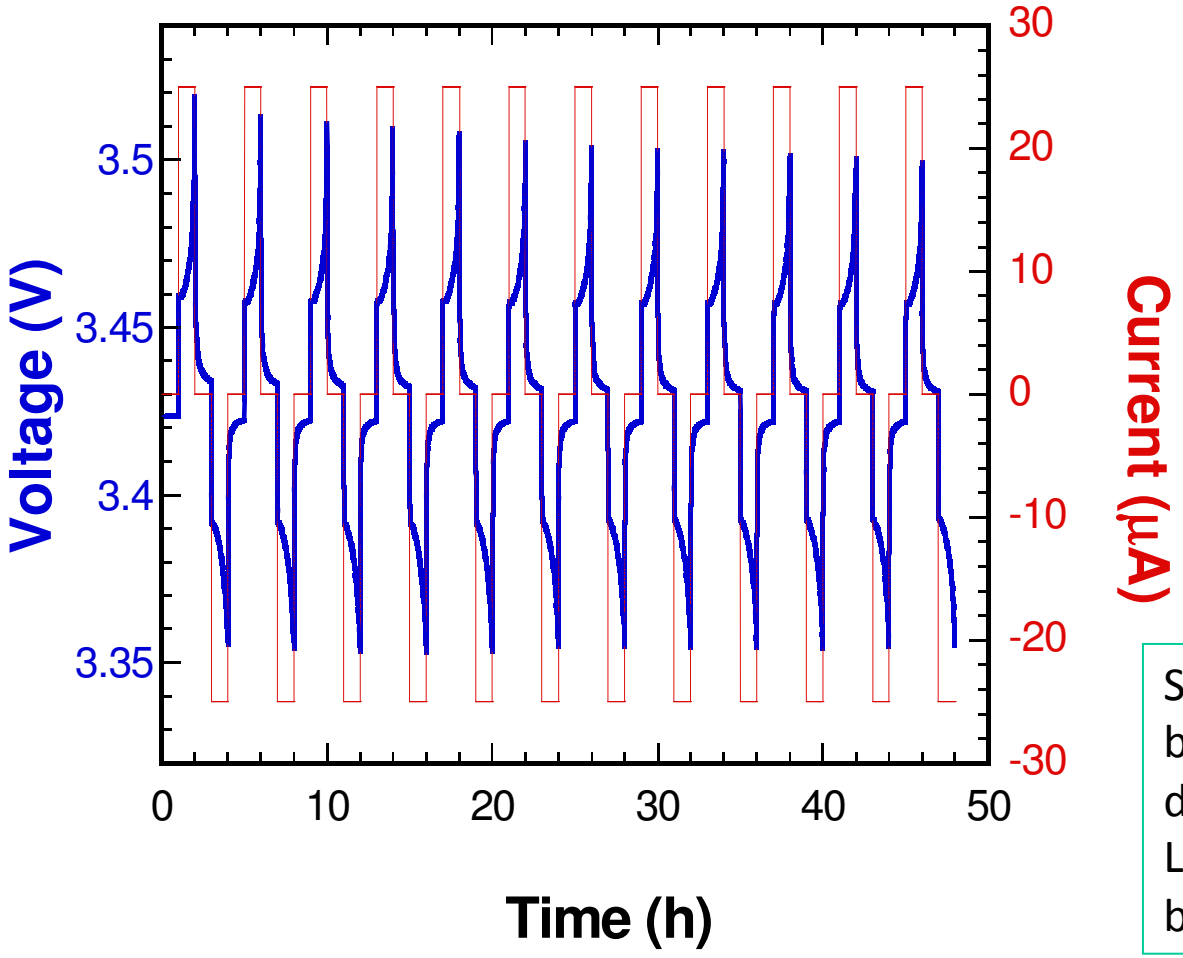
Cathode : $FePO_4$ (HQ)
Solvent: NMP



SEO electrolytes are hard elastic solids at room temperature. In order to "fill" the pores, a compressive stress is applied after the electrolyte has been softened by:
a.) swelling with a solvent that swells both PS and PEO phases
b.) heating the electrolyte above Tg

Liu, Battaglia, Karim

Li/SPE/FePO4 (HQ) Cell



Anode = Li metal
Cathode = $FePO_4$ (HQ)

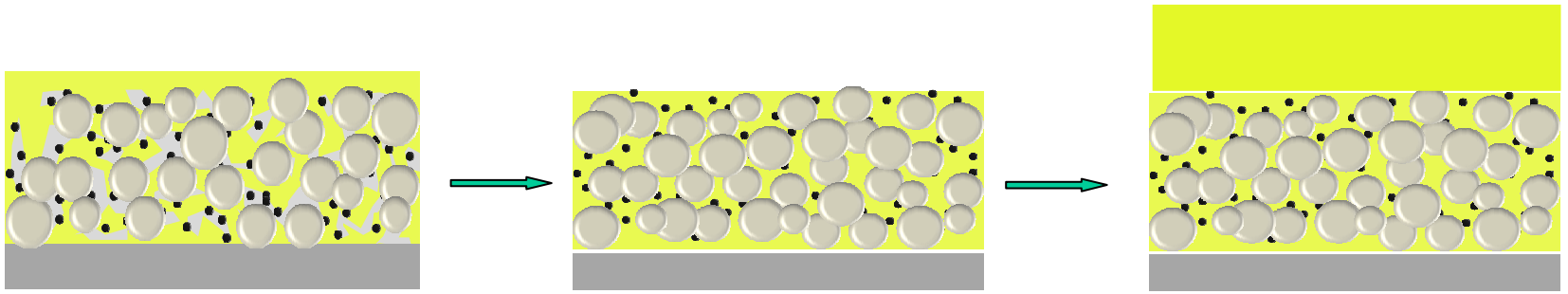
r = 0.067
T = 80°C
i = 200 uA/cm²

SEO electrolyte is stable against both of the electrodes. Low IR drop is maintained when Li/SEO/Li symmetric cell is replaced by Li/SEO/$FePO_4$.

Reviewer: Begin working on full cells.

Cathode casting

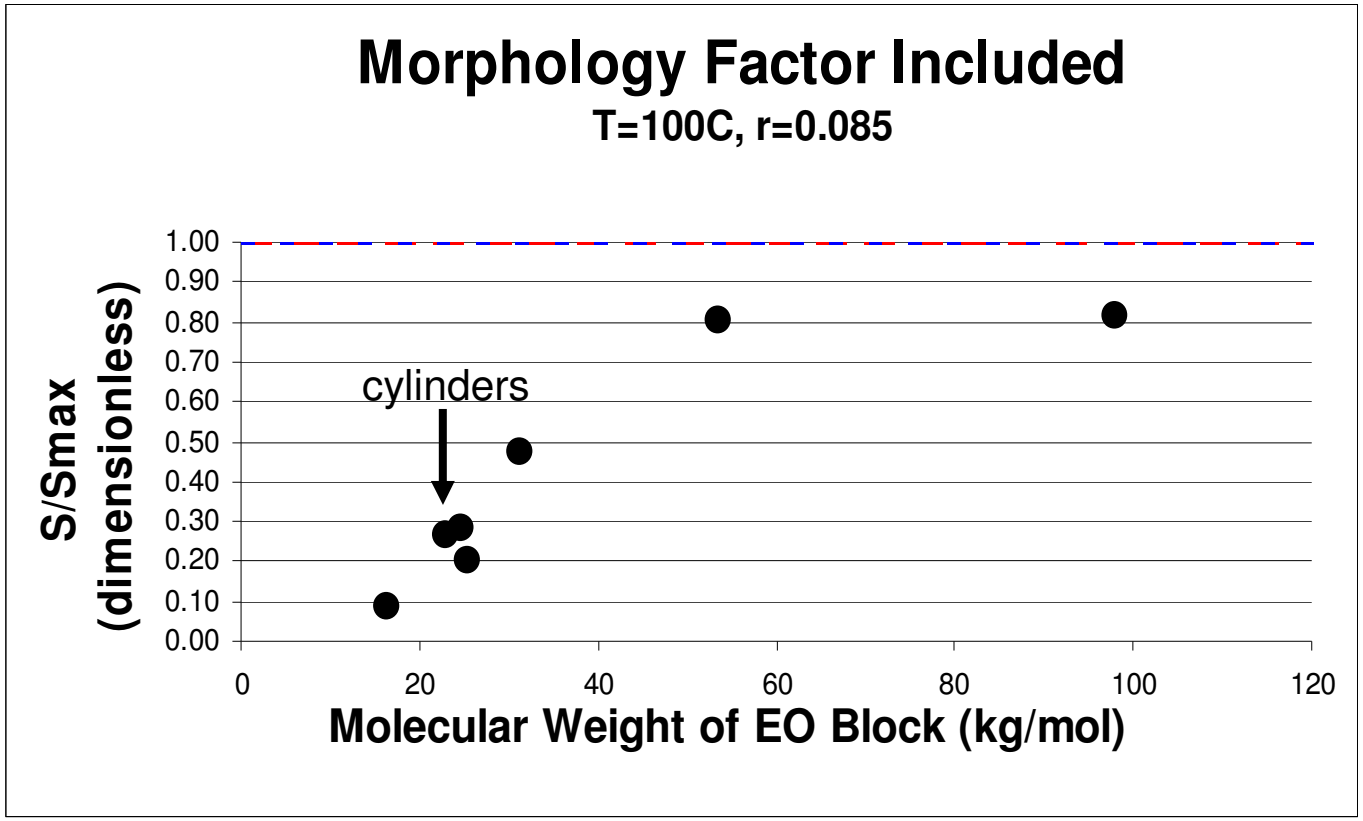
1. Use SEO electrolyte as the binder for the casting cathodes on Al foil
2. Remove the porosity by calendaring
3. Solvent cast SEO electrolyte on the cathode

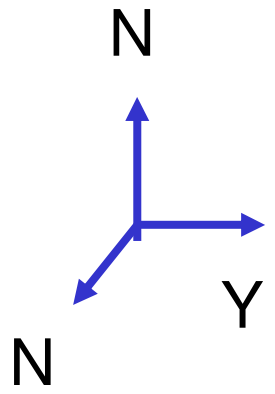


1 2 3

Morphology effects

maximum for both cylinders and lamellae = 1.0

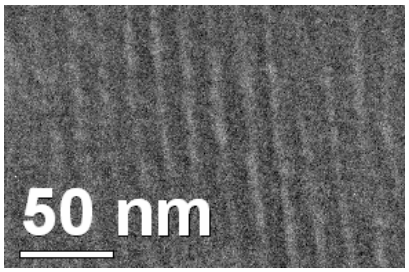


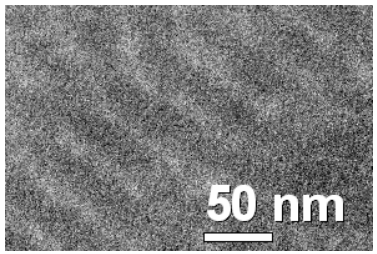


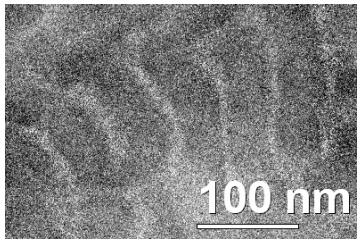
Morphology factor is 1/3 for cylinders and 2/3 for lamellae, corresponding to effective diffusivities

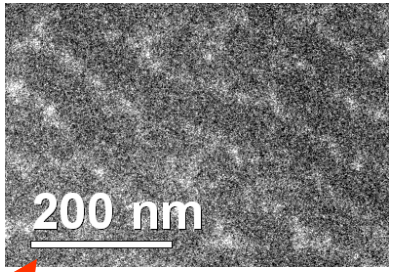
MW effect on Li distribution

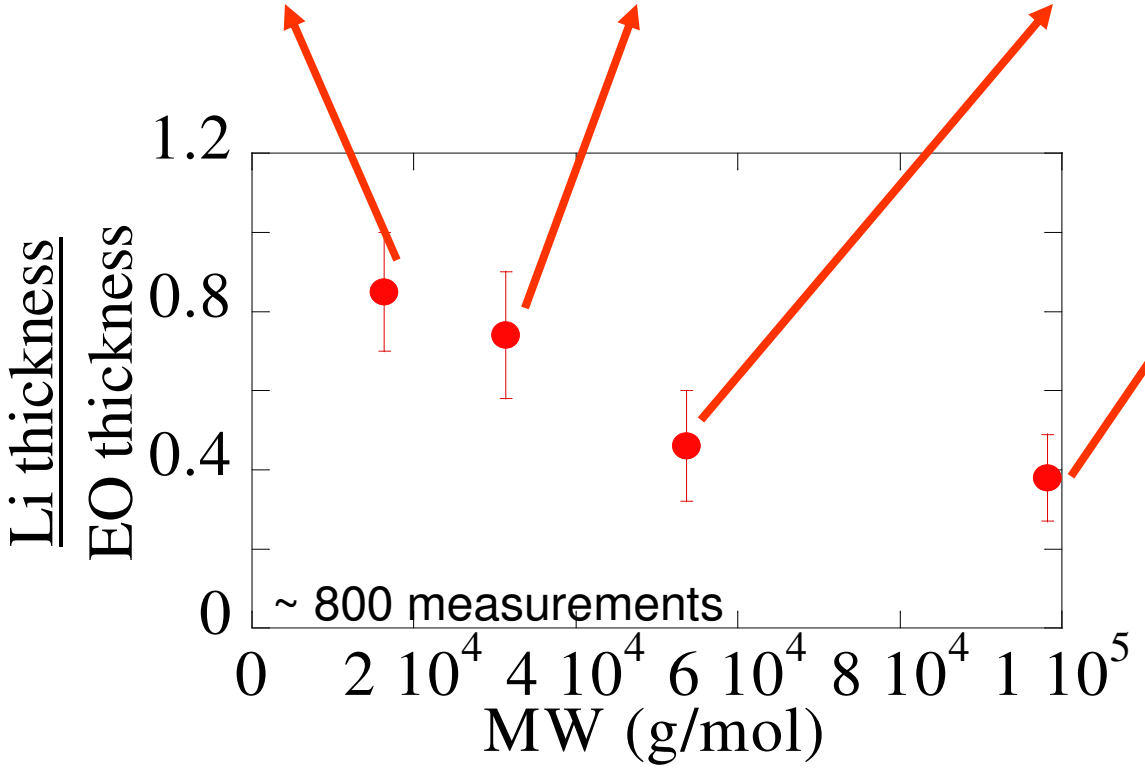
Gomez et al.











Using simulations results and field theory for interpretation.

Reviewer: Explain conductivity results.

Reviewers Comments and Action

Comments:

- Work with simulation groups (Smith) to better understand transport mechanism in the block copolymer materials
- Measure Li transference number to determine if the unusual increase in conductivity is due to higher Li transport or higher anion transport. Focus on explaining increase in σ with increasing MW of PEO
- If successful, abuse tolerance aspects of Li batteries will be enhanced
- Begin work on full cells using Li metal and appropriate cathode materials
- Newman's theory does not support that dry polymers will prevent dendrites. May be discontinued or redirected to Li ion conducting glass R&D to prevent dendrite formation

Actions and Future Plans:

- Preliminary experiments for Li/SPE/Li have been conducted performed. Extended experiments are under way.
- Transference number measurements are underway.
- Initial cathode casting experiments have worked.
- A new lab has been set up at LBL to perform extensive cycling experiments and easy cooperation with other BATT program members.

Technology Transfer

- **A Venture-backed start-up called Seeo, Inc. was founded in May 2007, with two ex-students from my lab (Mohit Singh and Hany Eitouni).**
- **A 5500 square foot facility for making and testing batteries is fully operational with 8 employees.**
- **The proposed battery was chosen by LBNL as one of the entries for the RD 100 Award.**

- **Fundamental characterization of block copolymer electrolytes will be continued within the BATT program, in harmony with the comments of the referees and directions from BATT program management.**

Nitash Balsara does have a financial interest in Seeo

Research Plans

- Continue synthesis and characterization of block copolymer electrolytes.
- Complete characterization if Li-Li symmetric cell cycling.
- Measure Li transference number and diffusion coefficient.
- Make measurements of battery charge/discharge cycles and see how they compare with predictions.