Dry Batteries with Lithium Metal Electrodes

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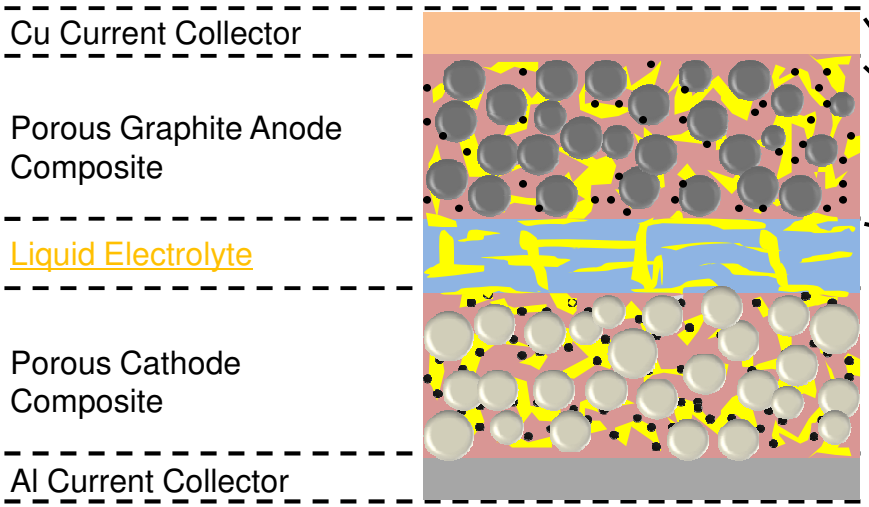
Hany Eitouni and Mohit Singh, Seeo, Inc., Berkeley, CA

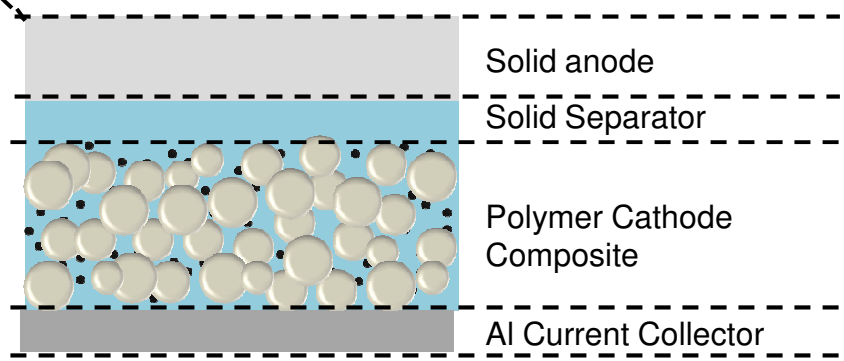
Balsara does have a financial interest in Seeo, Inc.

Replace liquid electrolyte by a solid

Conventional Li Ion



Li Polymer



Flammable liquid electrolyte

Li Ion: <200 Wh/kg

Poor lifetime and capacity fade

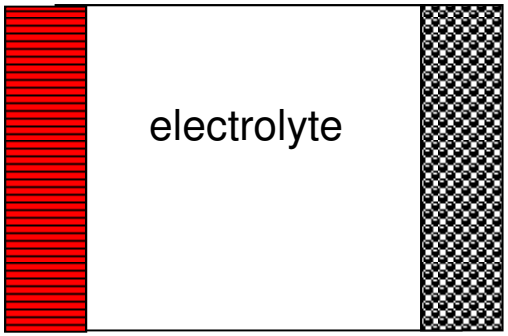
Solid state, no flammables

Li Polymer: ~250 Wh/kg

Stable polymer for best lifetime

Electrolyte properties

1. Must conduct ions.
2. Must be stable against the electrode.
3. Must adhere to the electrode surface (Philippe Steven's earlier talk).



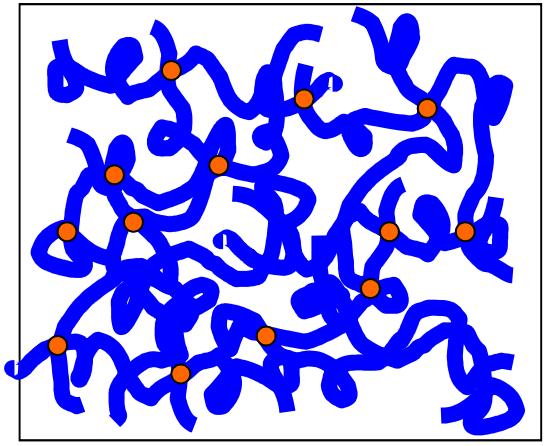
All commercial batteries have a liquid electrolyte.

Previous polymer batteries

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

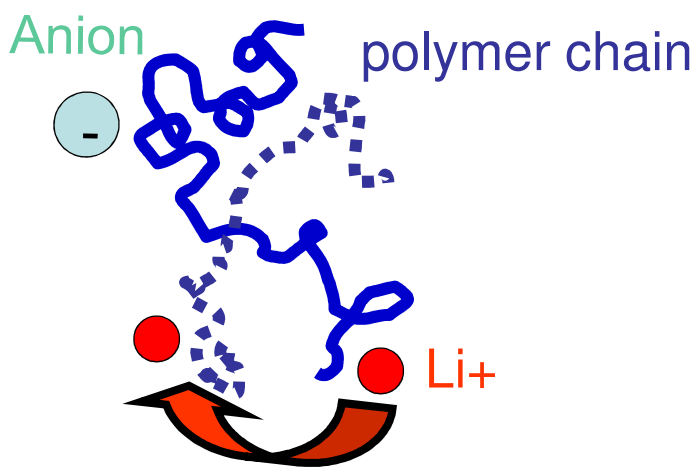
t=0 **high surface area Li** **dendrite short**

Make polymer hard to prevent deformation.
Modulus=10^9 Pa, Monroe and Newman, 2005.

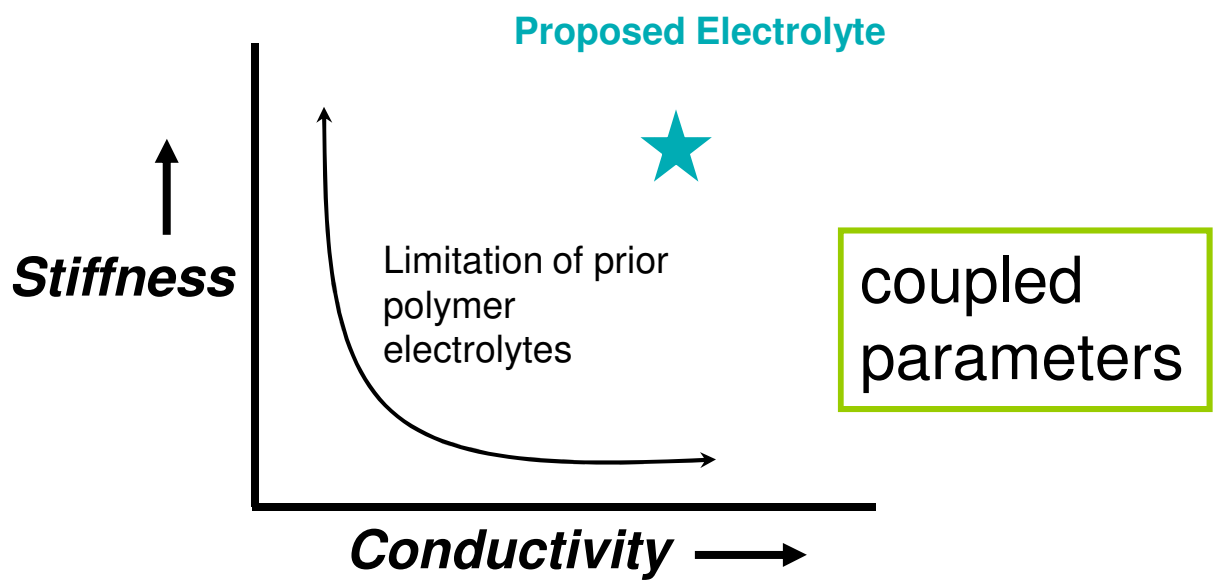


Classical polymer solid

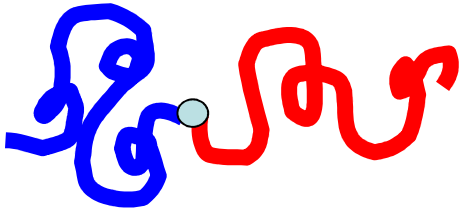
Previous polymer electrolytes

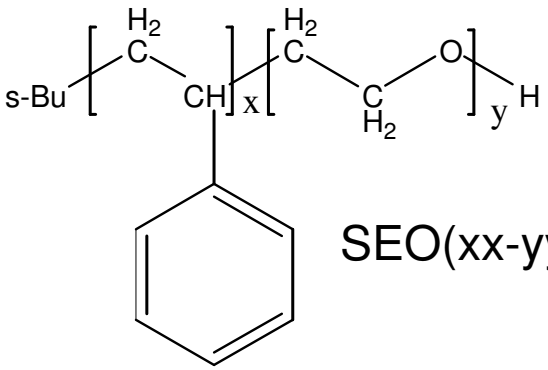


- **Ionic mobility is mediated by polymer chain motion.**
- **Fast polymer motion implies <u>high</u> conductivity and <u>low</u> modulus.**
- **Increasing modulus <u>must</u> decrease conductivity.**



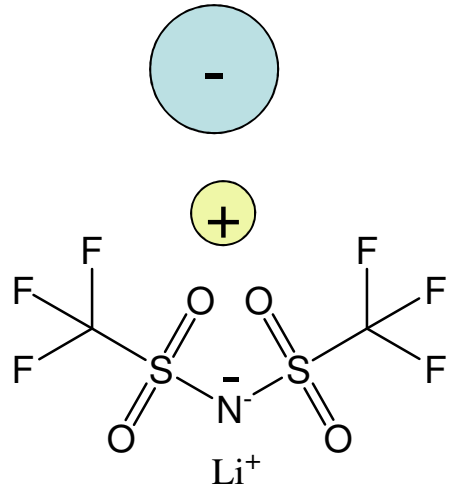
Solid polymer electrolyte





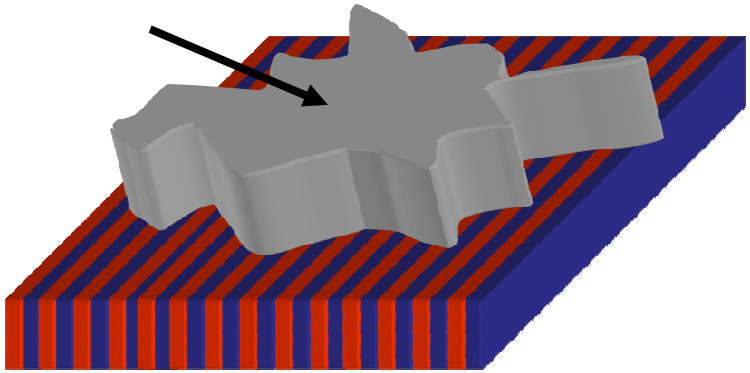
SEO(xx-yy)

+

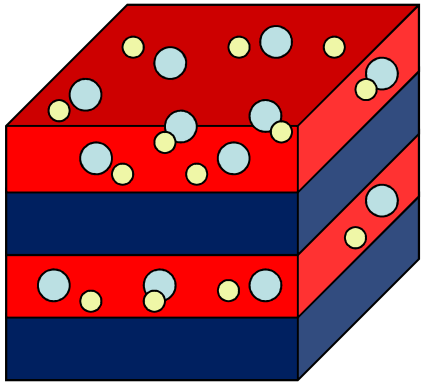


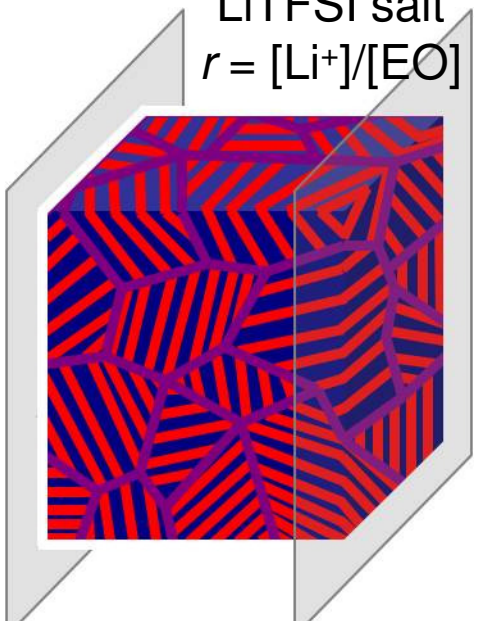
LiTFSI salt
$r = [Li^+]/[EO]$

Dendrites ~ µm



Nanostructured conductor ~ 10 nm





No effort to control alignment

Block Copolymer Electrolyte Characterization

1. Ionic conductivity
2. Salt diffusion coefficient
3. Electrode failure analysis
4. Electrode-electrolyte adhesion

Modulus increases with mol. wt.

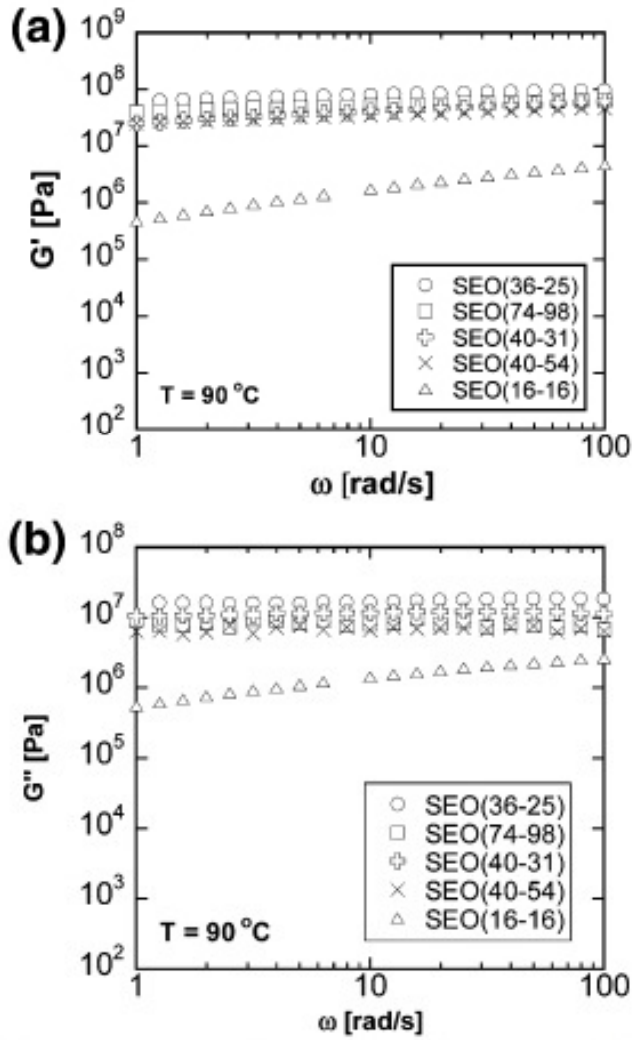
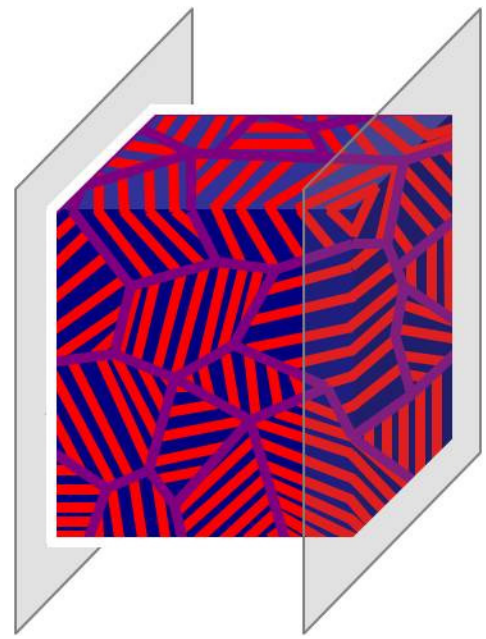
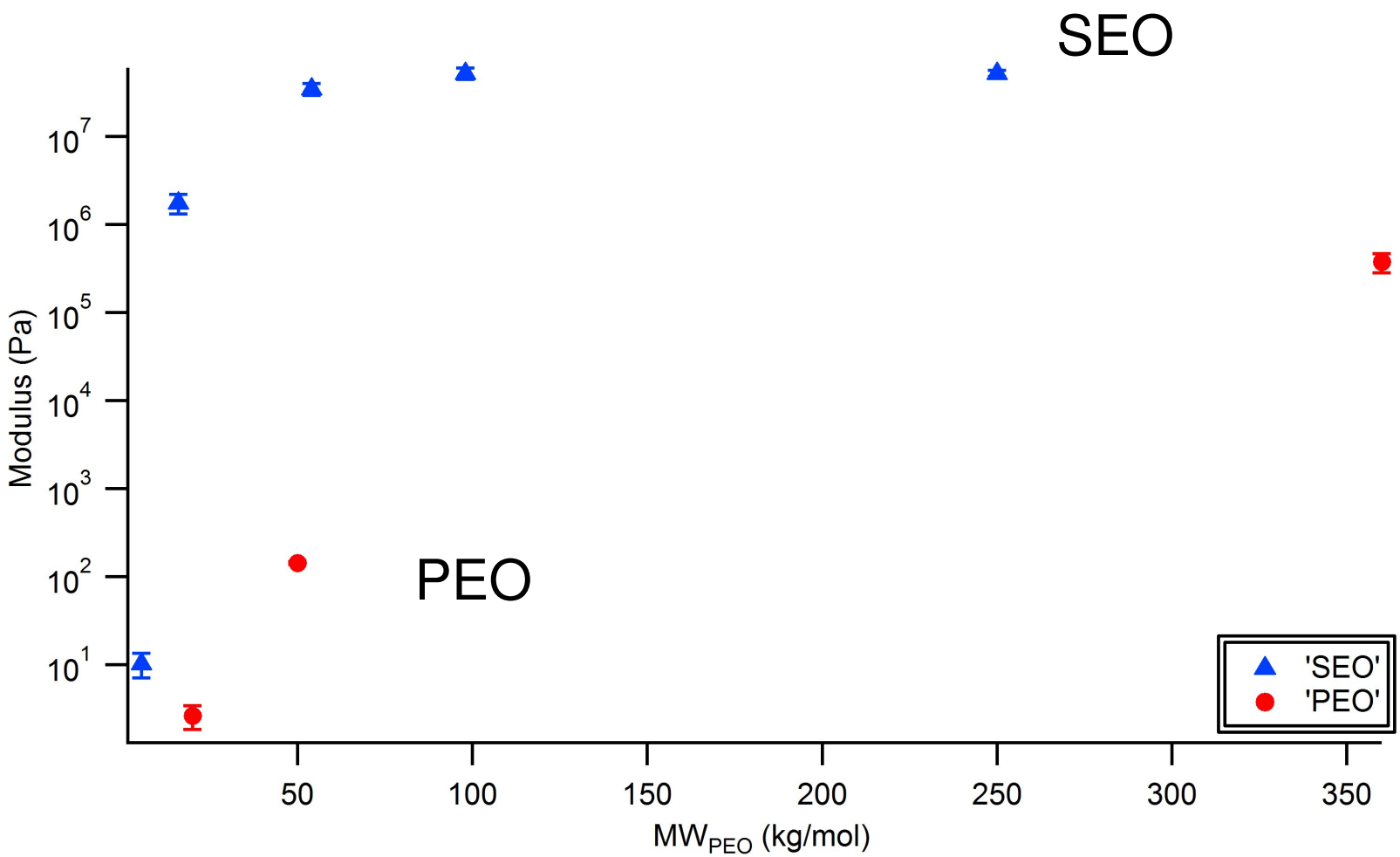


Figure 8. Frequency, ω, dependence of the (a) storage, G', and (b) loss moduli, G'', of SEO copolymers.



$G' \sim \omega^0$, $G'' \sim \omega^0$; $G' >> G''$

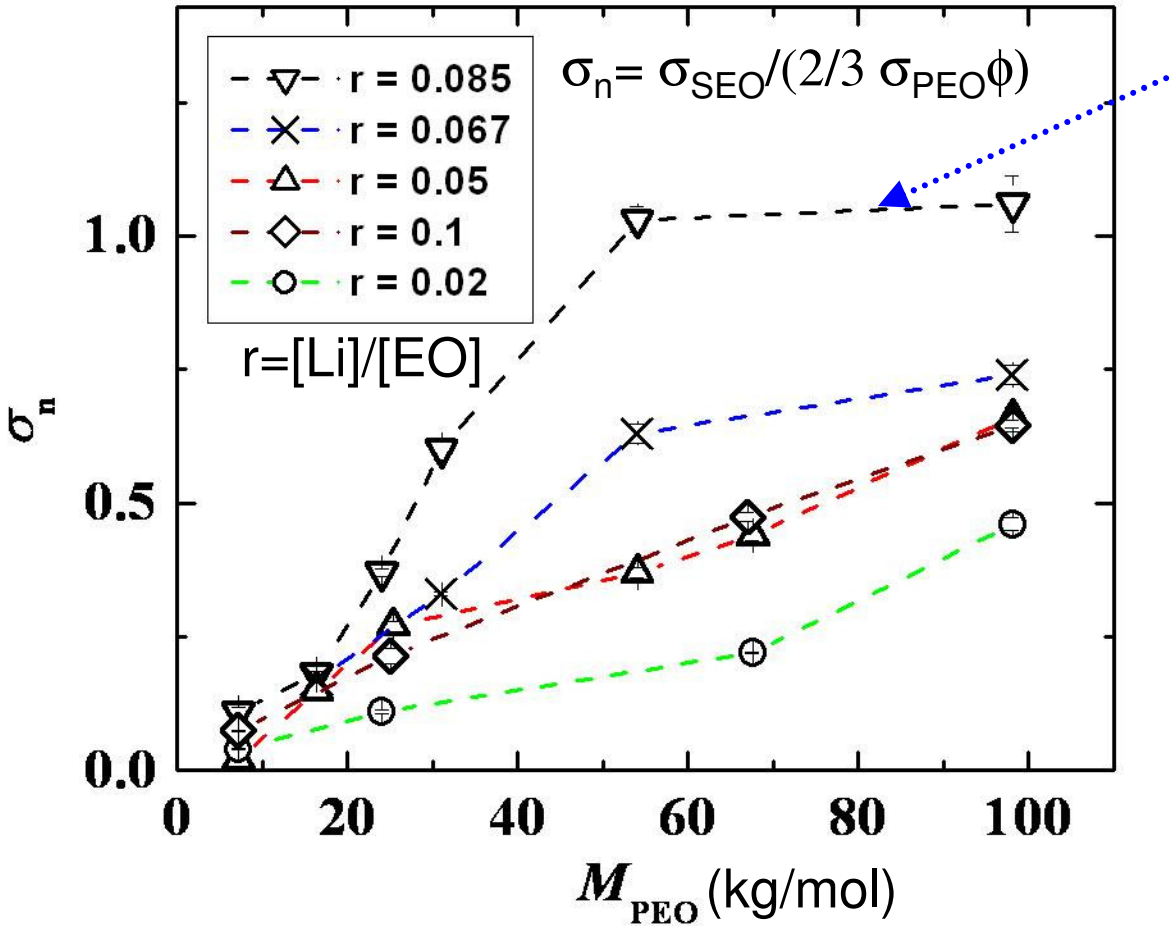
Modulus Data



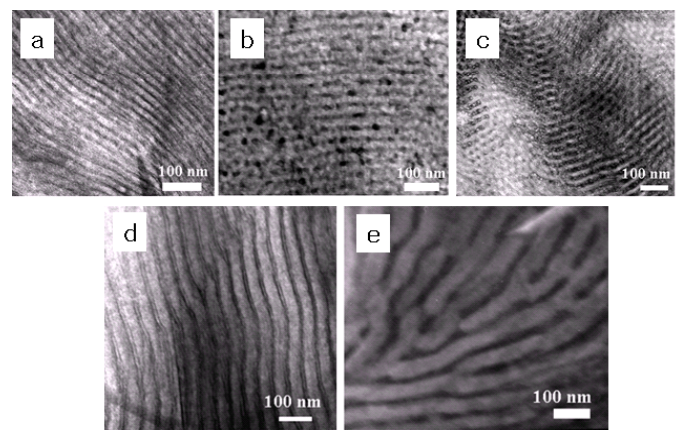
T=90 °C, ω=10 rad/s

1. Conductivity

Singh, Panday



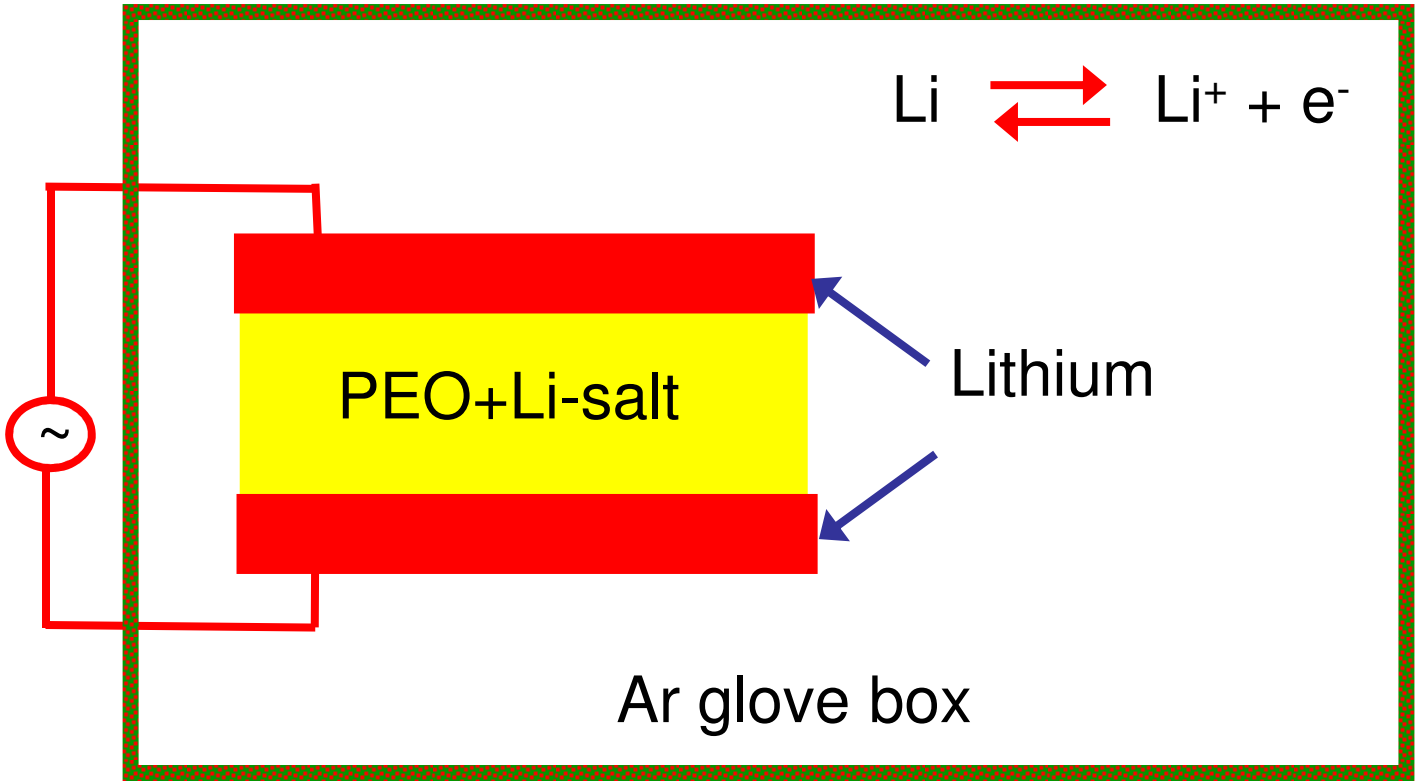
theoretical maximum



σ_n lies between 0.5 and 1.0 at high molecular weights.

You can make the other block as hard as you want.

DC cycling experiments



2. Salt diffusion coefficient

3. Quantifying battery failure

4. Electrode-electrolyte interface stability

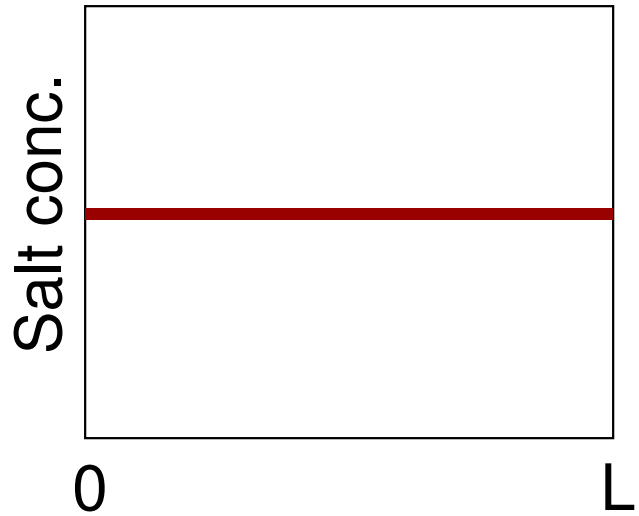
2. Salt Diffusion

Mullin

M. Doeff et al *J. Power Sources* **2000**, *89*, 227-231

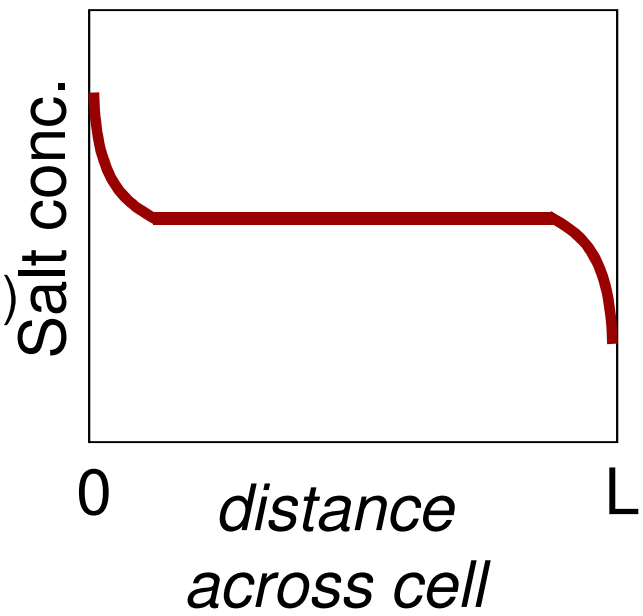
Step 1:

relax cell



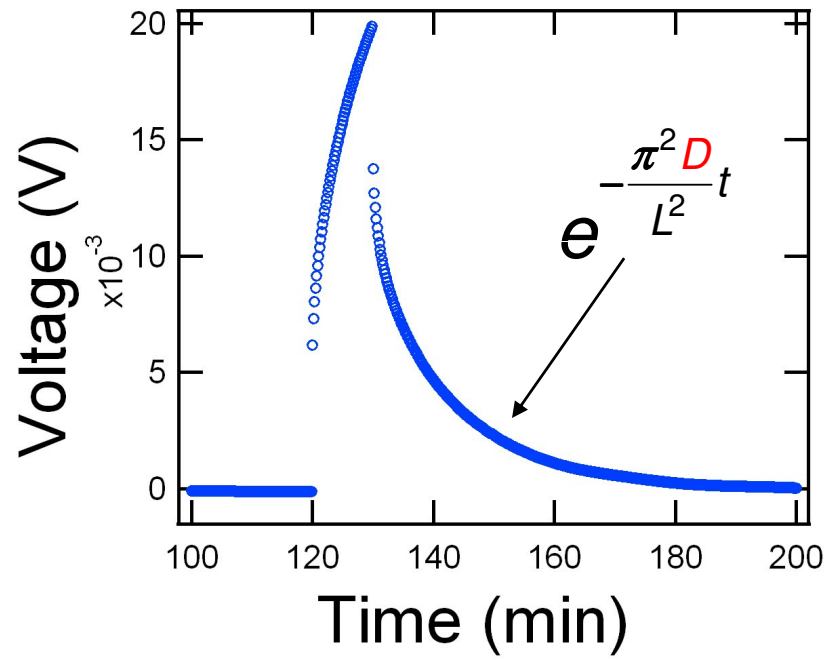
Step 2:

polarize cell
(dc charging)



Step 3: watch voltage decay

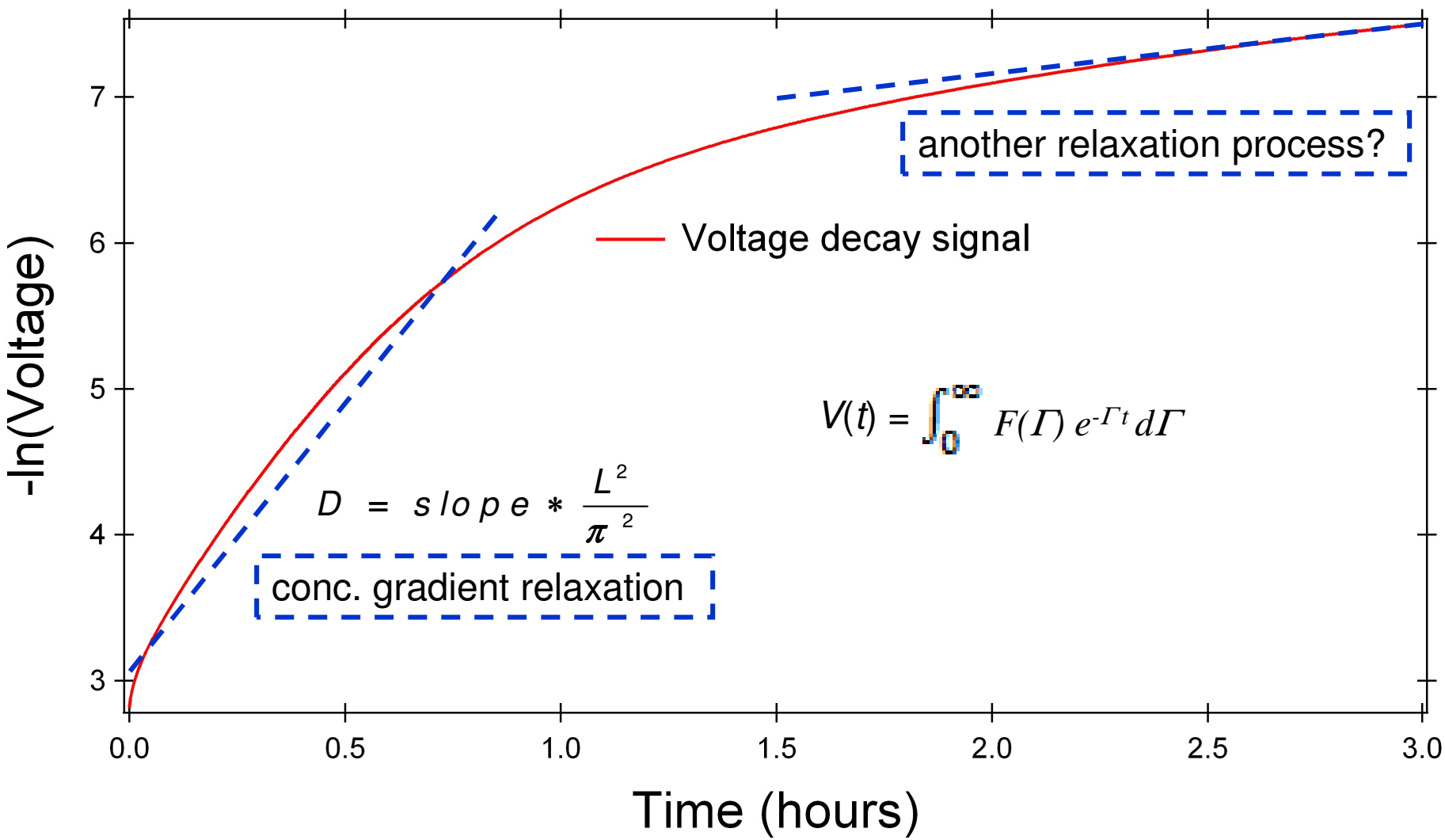
cell voltage with time



Get *D* from slope of

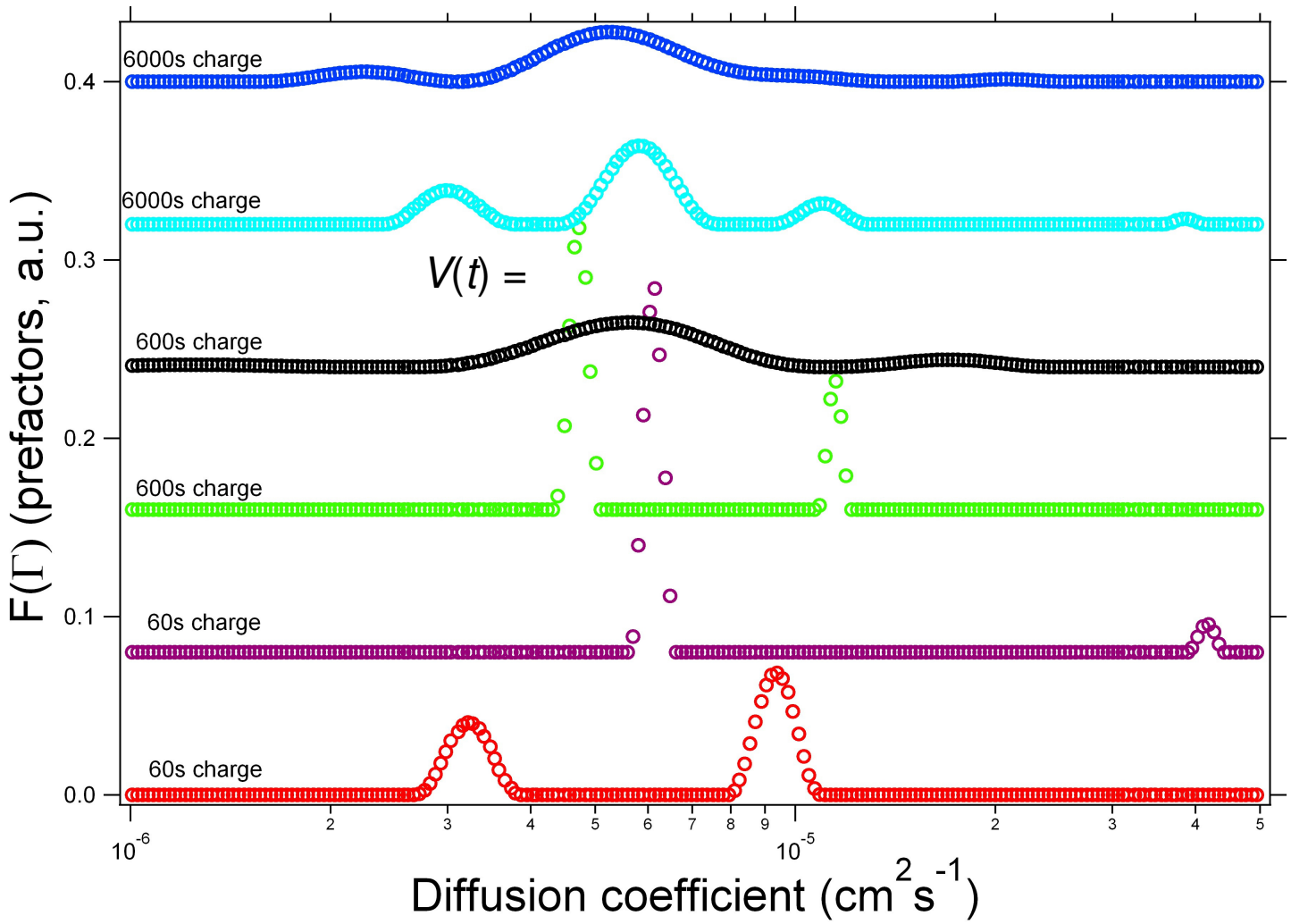
–ln(Voltage) vs time

Multiple exponential data



Multiple exponential analysis

T=90 °C

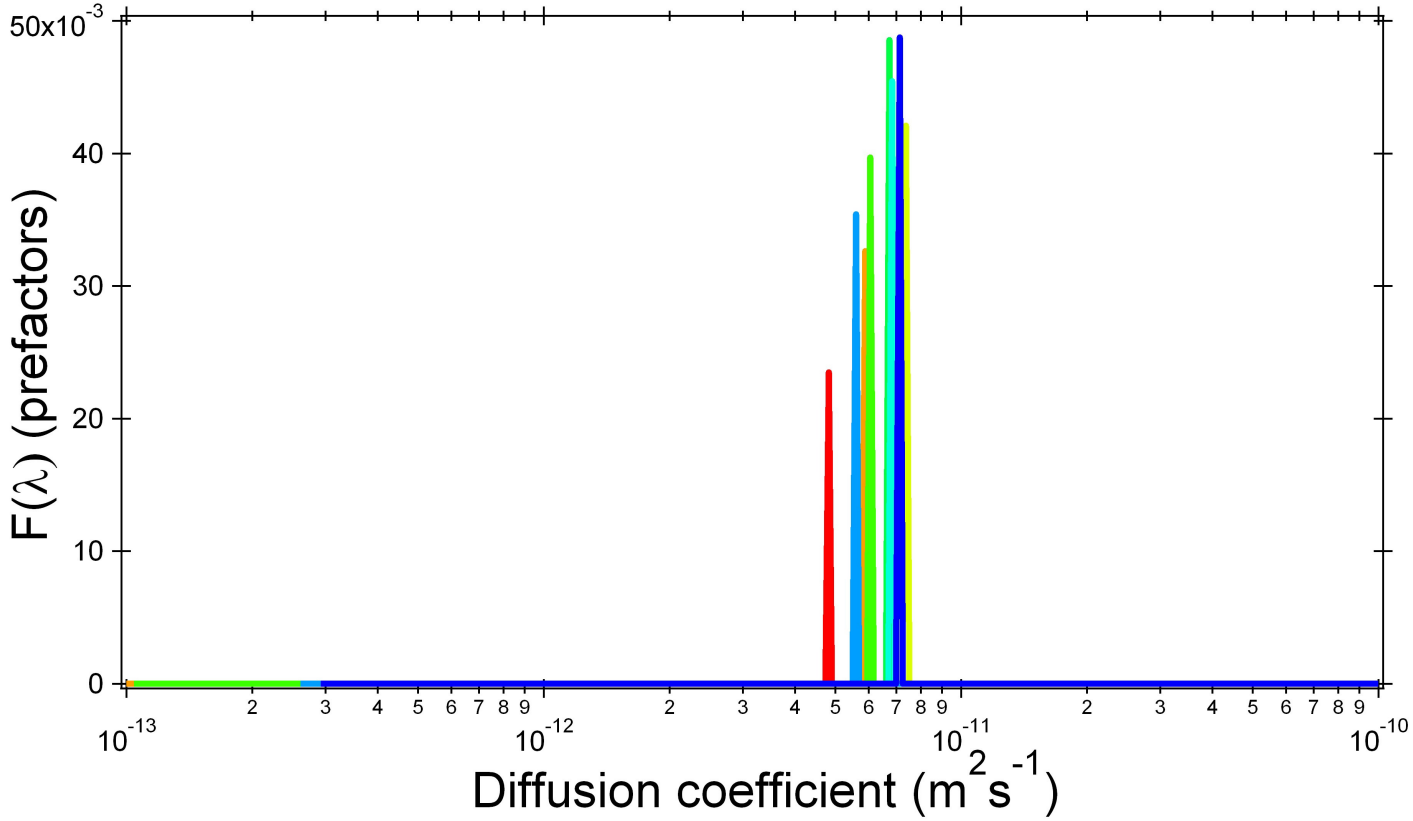


Vary:
Charging time
Cell thickness
Current

Highly varied response, but….

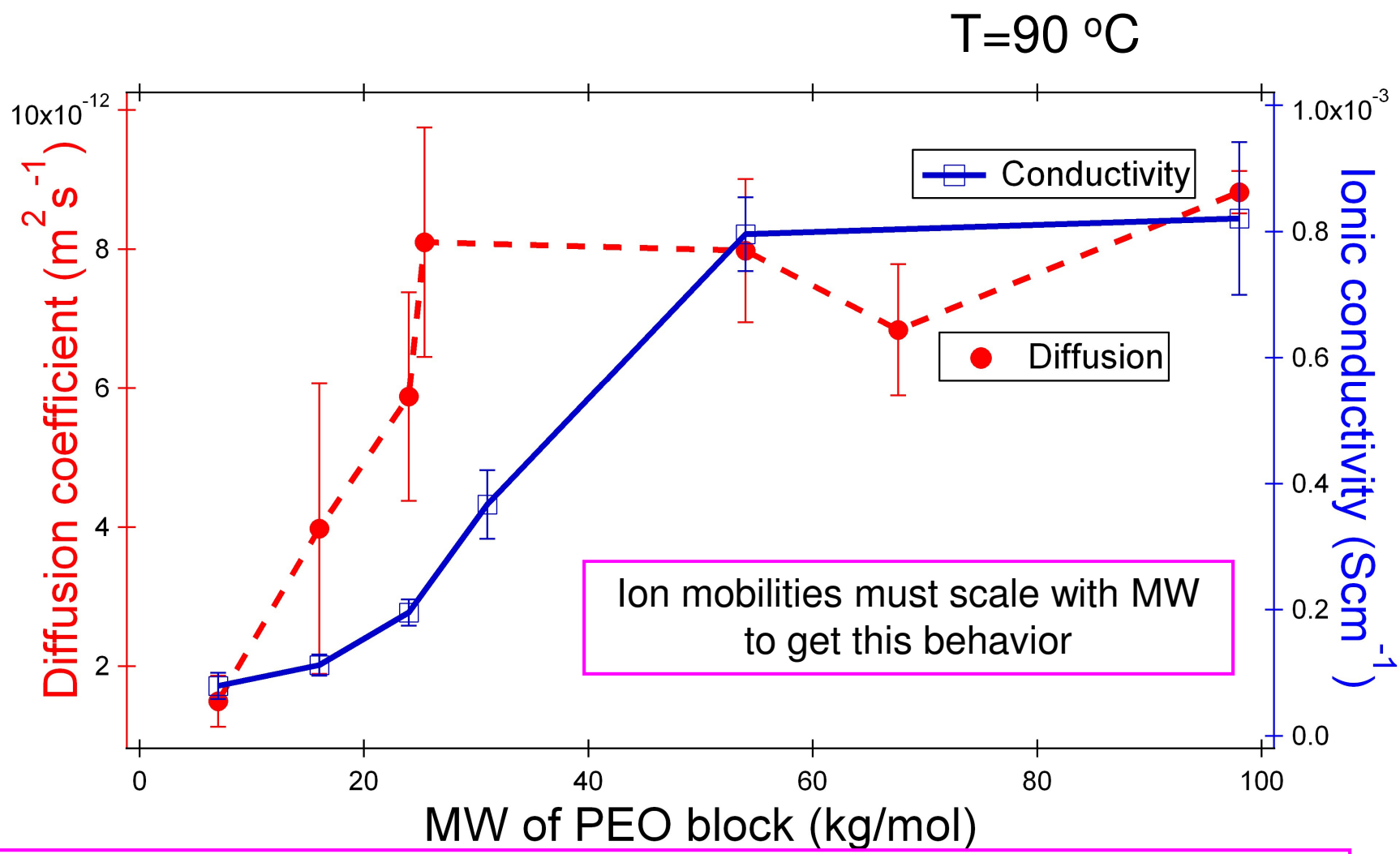
Average is well defined

Average=(First moment)/(Zeroth moment)



Salt Diffusion Coefficient

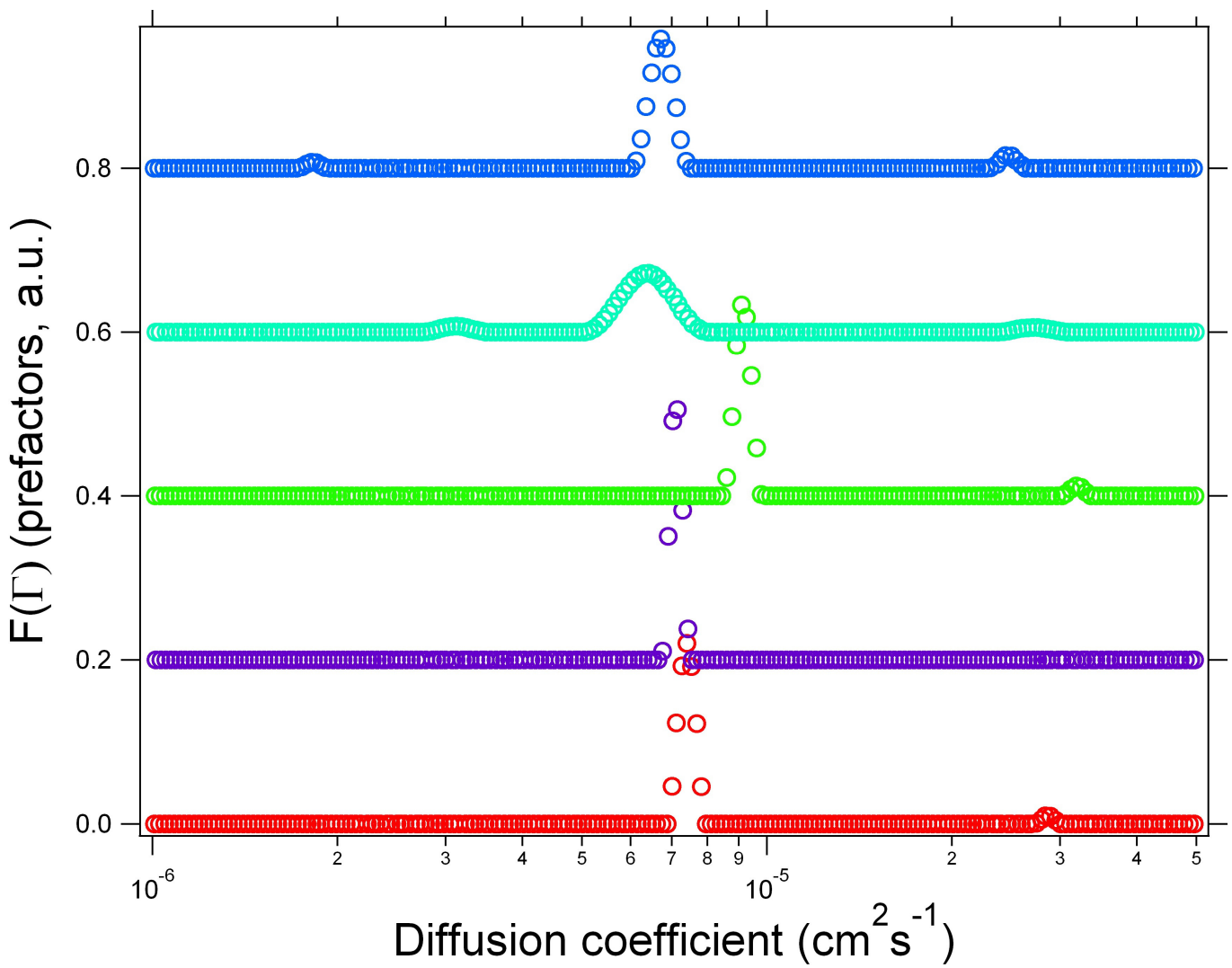
Mullin

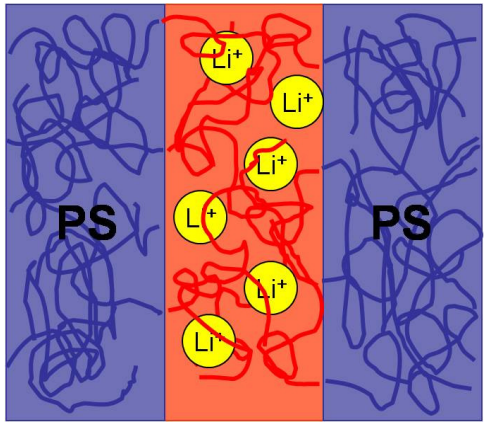


Diffusivity and conductivity scale the same with molecular weight

Temperature effects

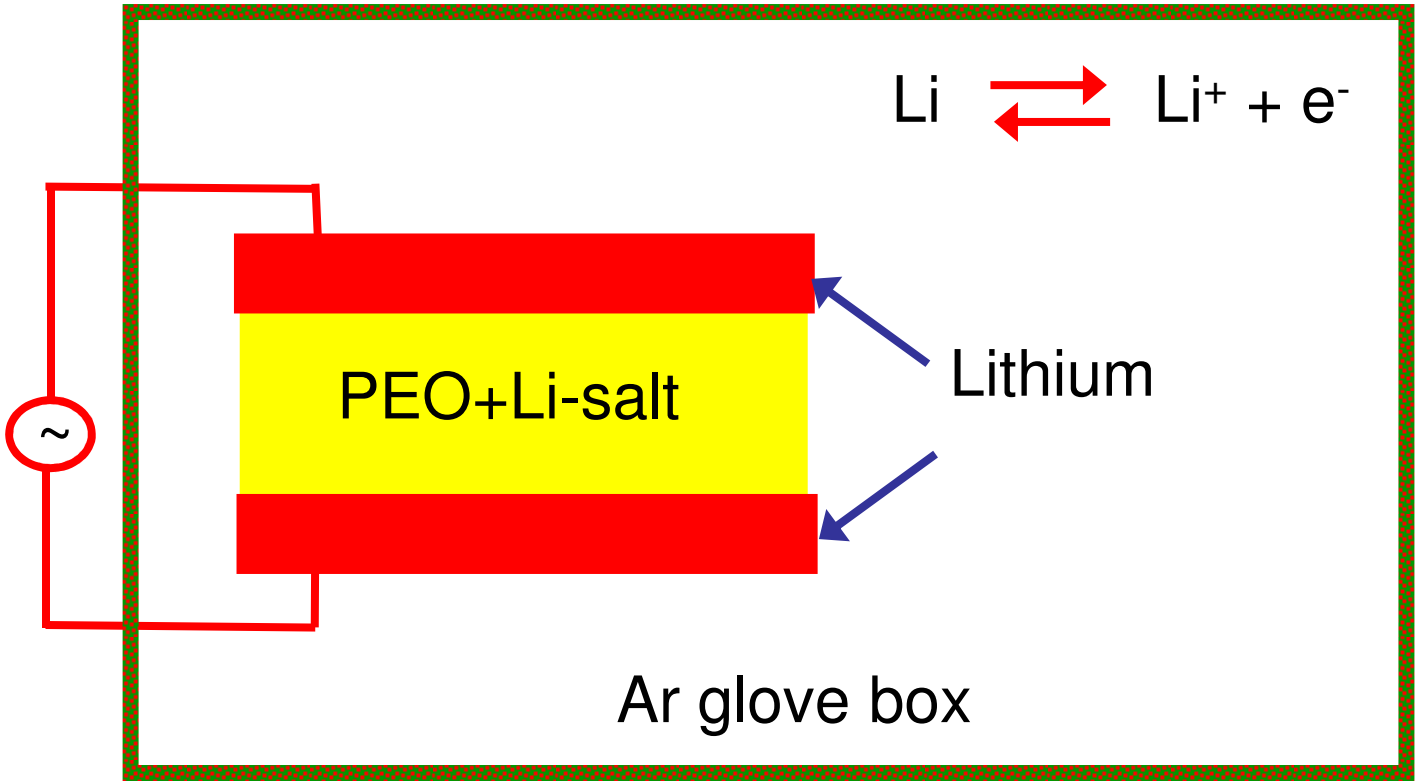
T=130 °C





Keeping ions away from glassy interface may be important.

DC cycling experiments



2. Salt diffusion coefficient

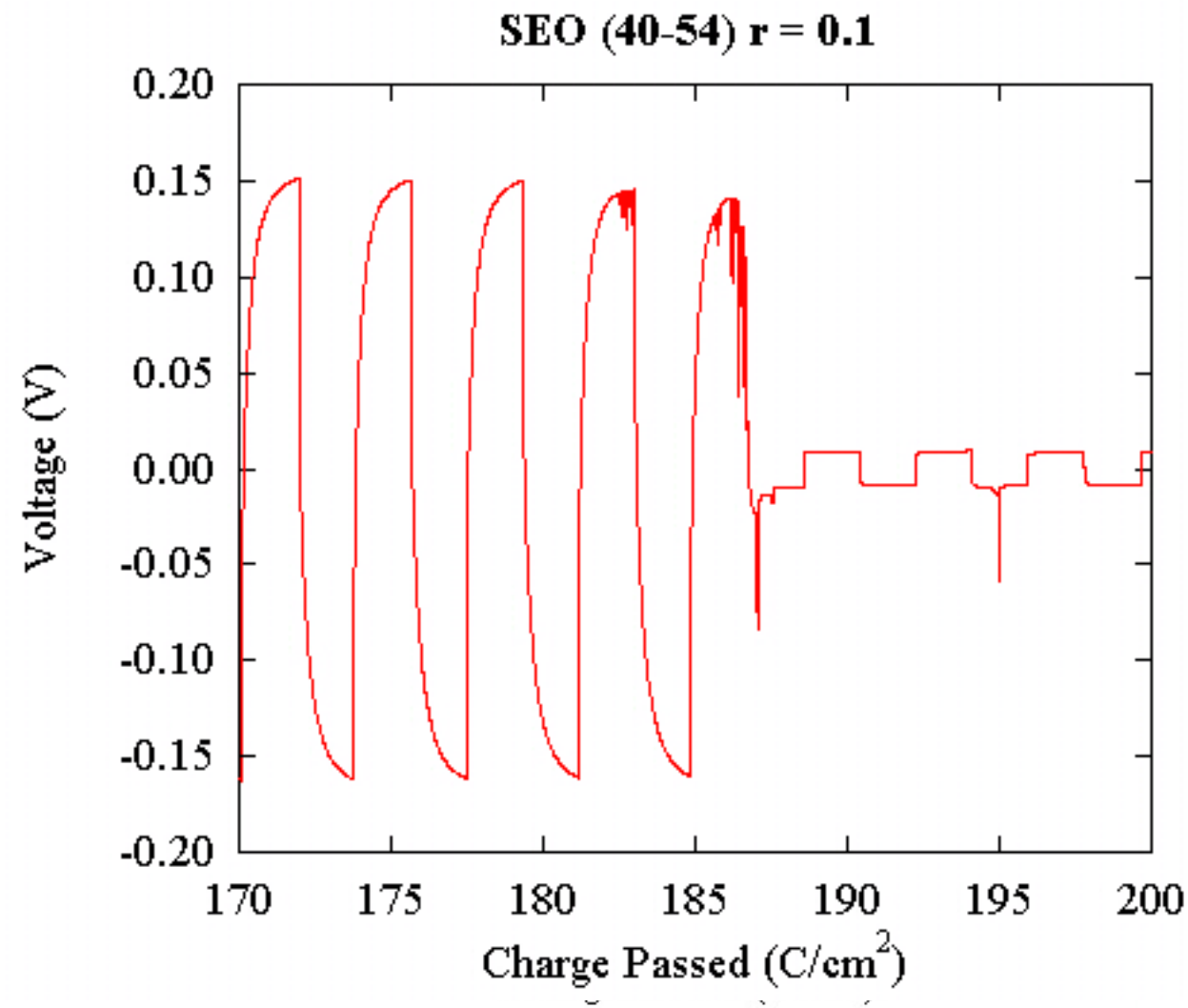
3. Quantifying battery failure

4. Electrode-electrolyte interface stability

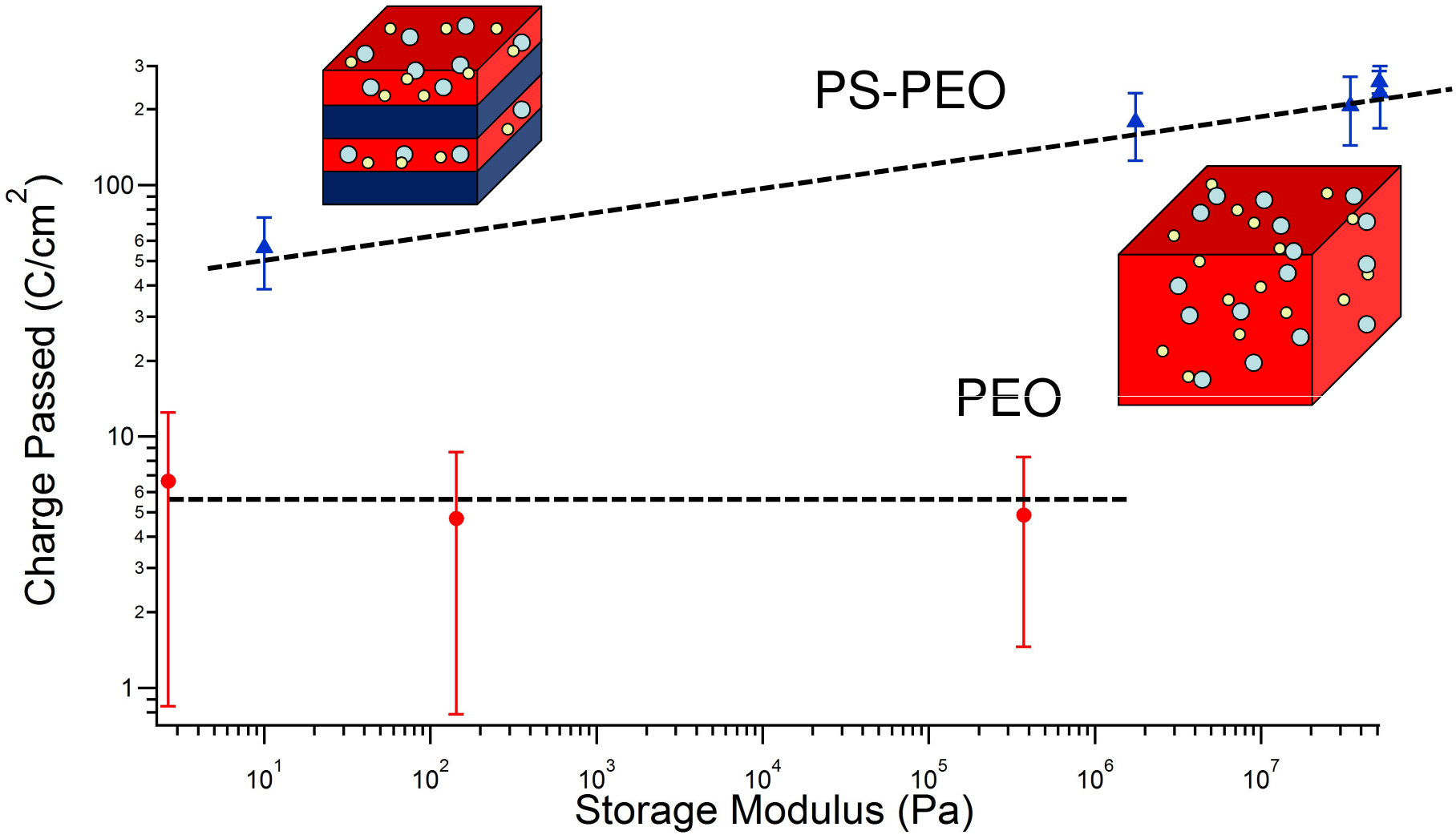
3. Electrode failure analysis

Stone

- Constant current (0.17 mA/cm^2), T=90 ^{o}C

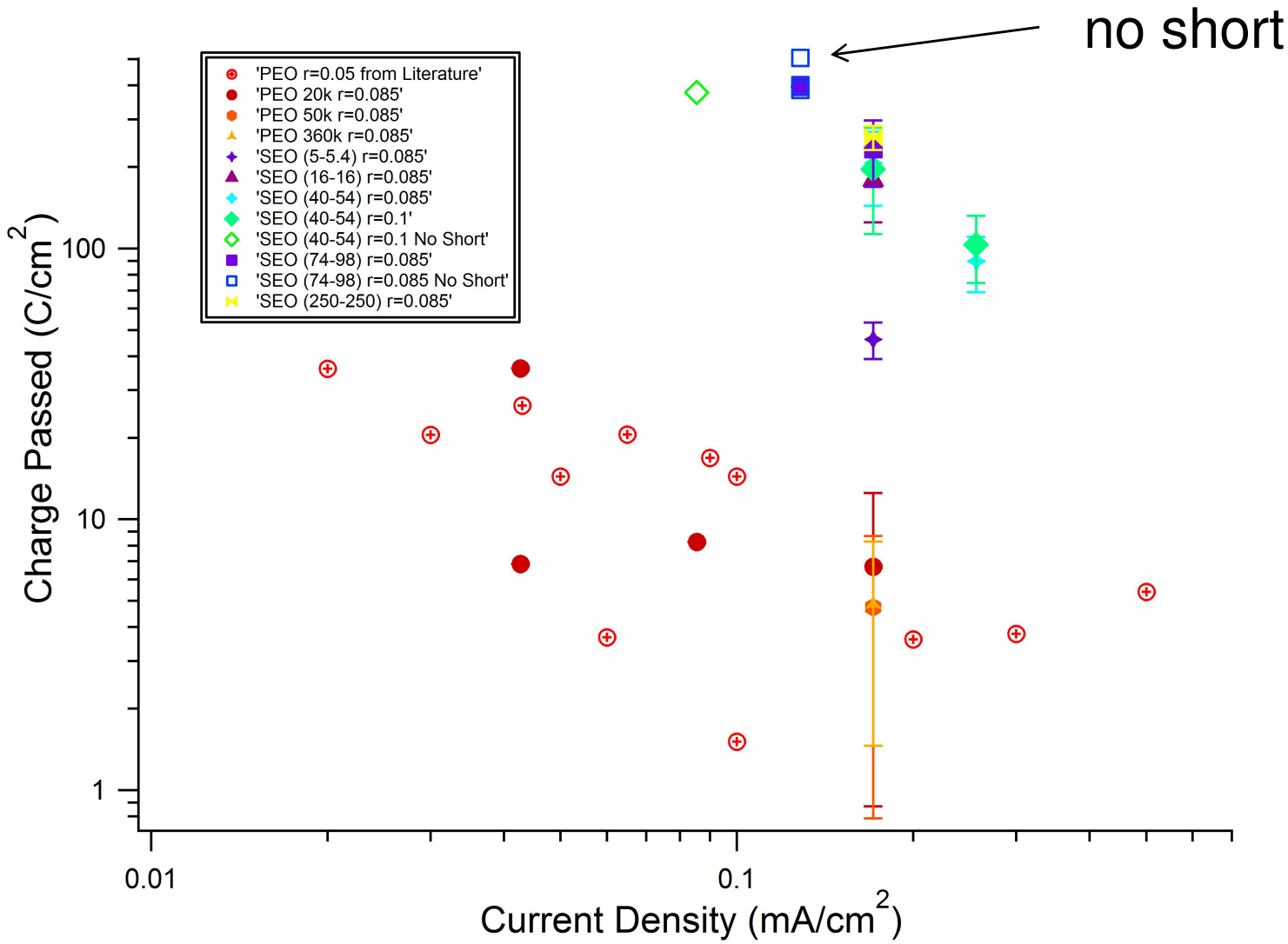


Failure-modulus-structure relationship



Current density=0.17 mA/cm^2, T= 90 ^{o}C

Charge passed at failure



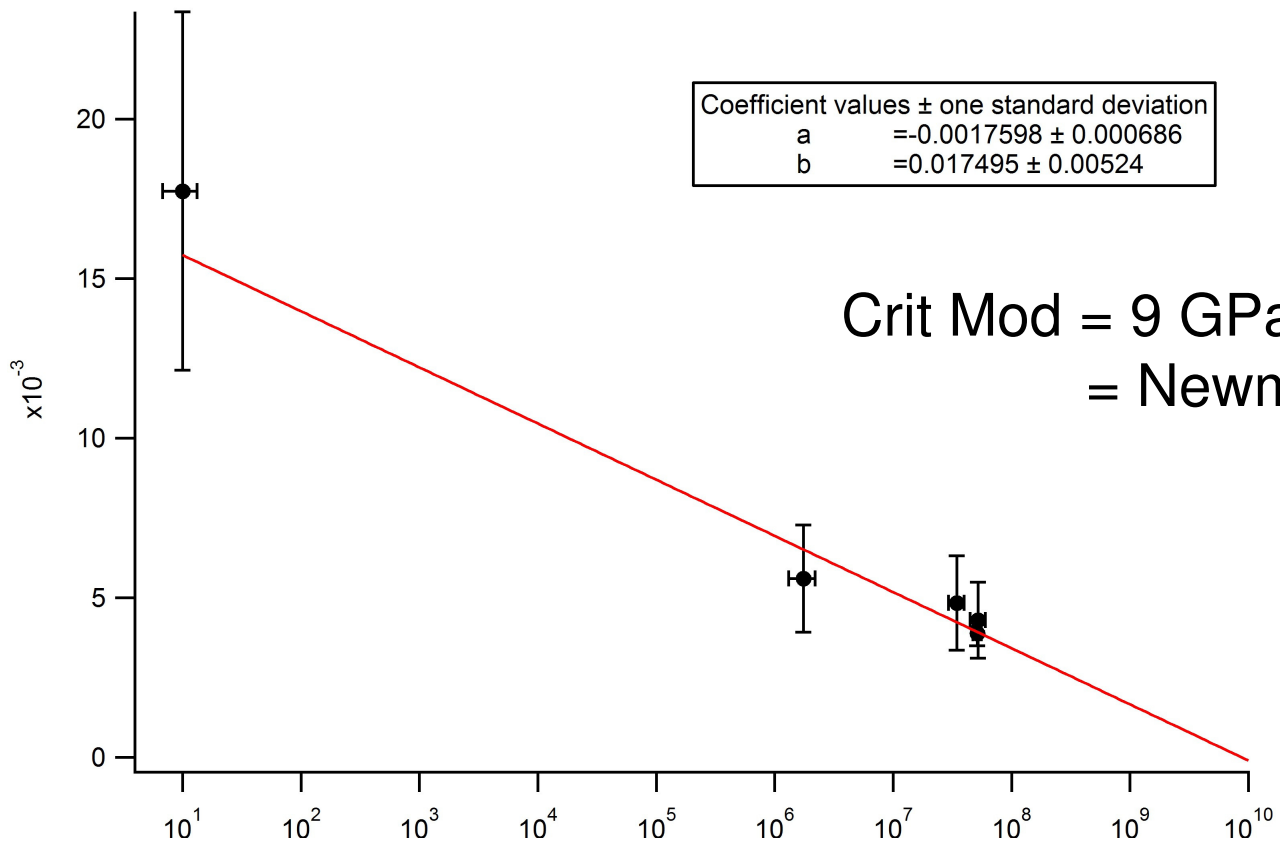
Dollé, M. et. al. *Electrochemical and Solid State* Letters. 2002

Rosso, M. et. al. *Electrochimica Acta 2006*

Rosso, M. et. al. *Jour. Power Sources. 2001*

Critical modulus postulated by Newman

1/[Charge Passed]
(C/cm^2)



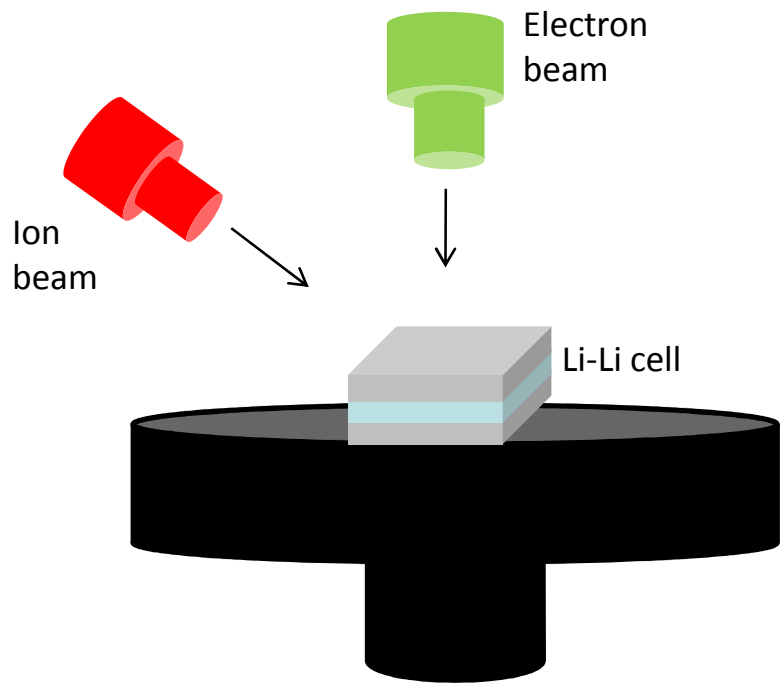
Crit Mod = 9 GPa +/- infinity
= Newman limit

Greg Stone

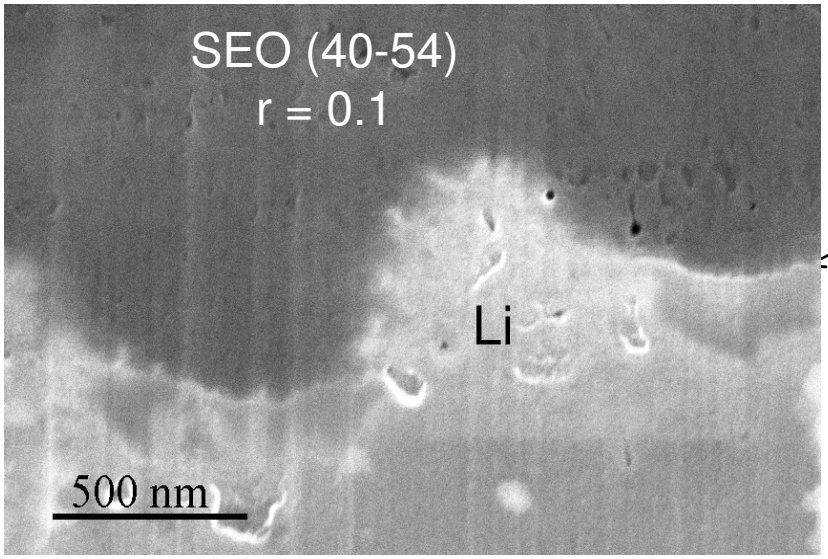
Cross-sectional SEM

Stone

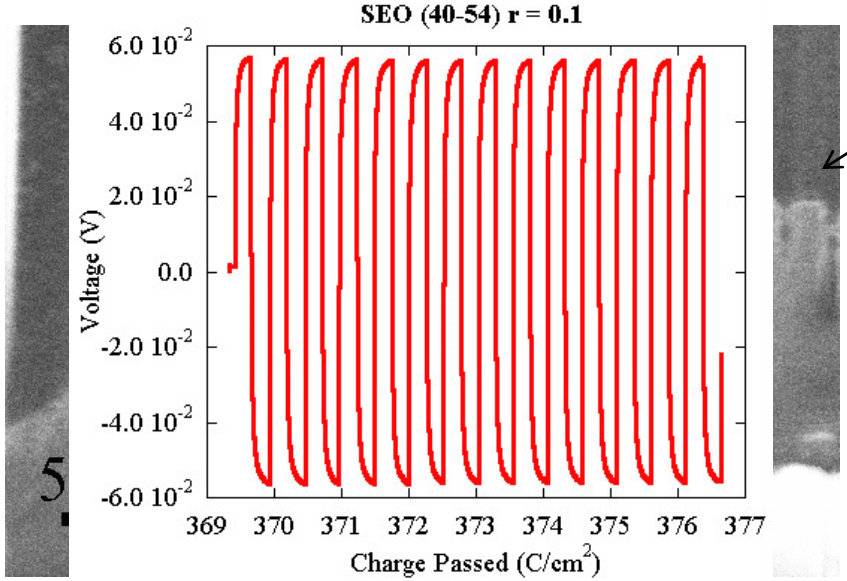
- Cross-section a symmetric Li-Li cell
- Load sample into SEM with focused ion beam (FIB) mill
- Clean cross-section with FIB
- Image with SEM



Interfacial Roughening



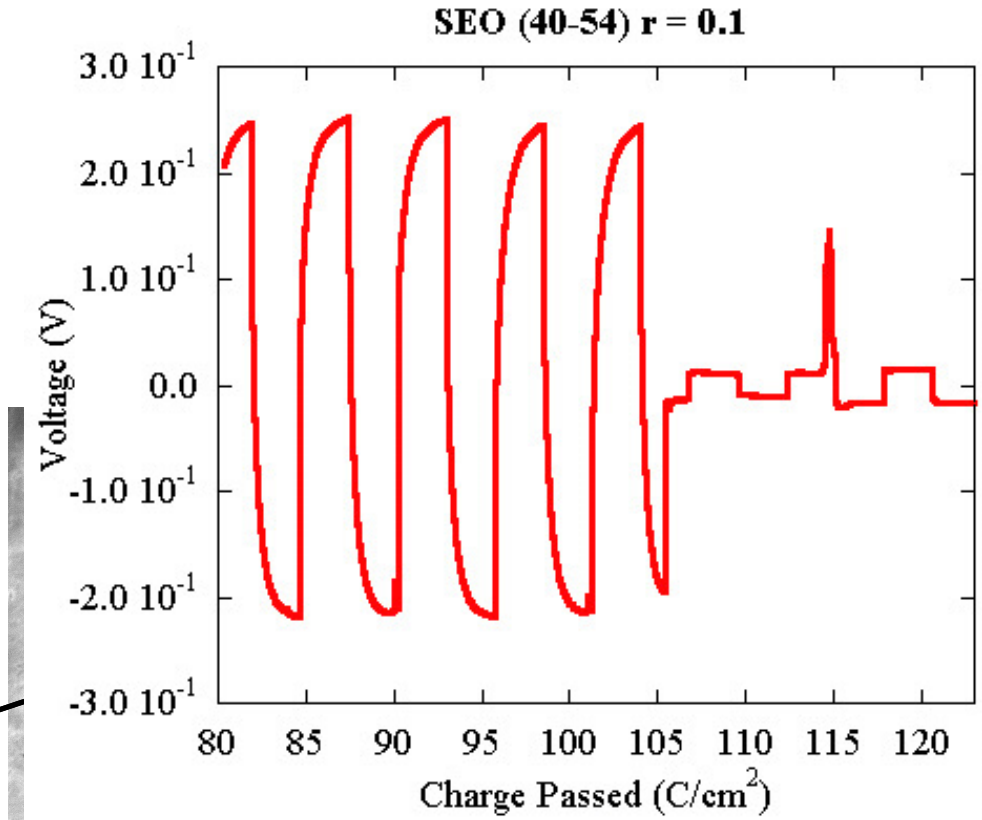
- Uncycled interface
  - Relatively smooth initial surface



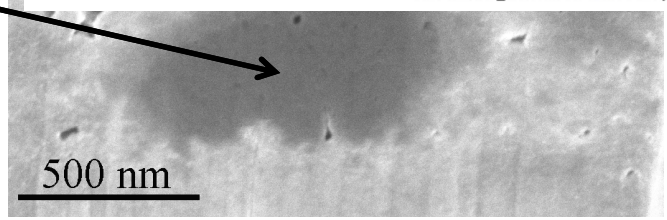
- Cycled interface
  - No dendritic shorting
  - Little to no propagation of initial roughness

Interfacial Roughening

- Cycled Interface
  - Dendrites formed and shorted cell
- No evidence of adhesion failure!

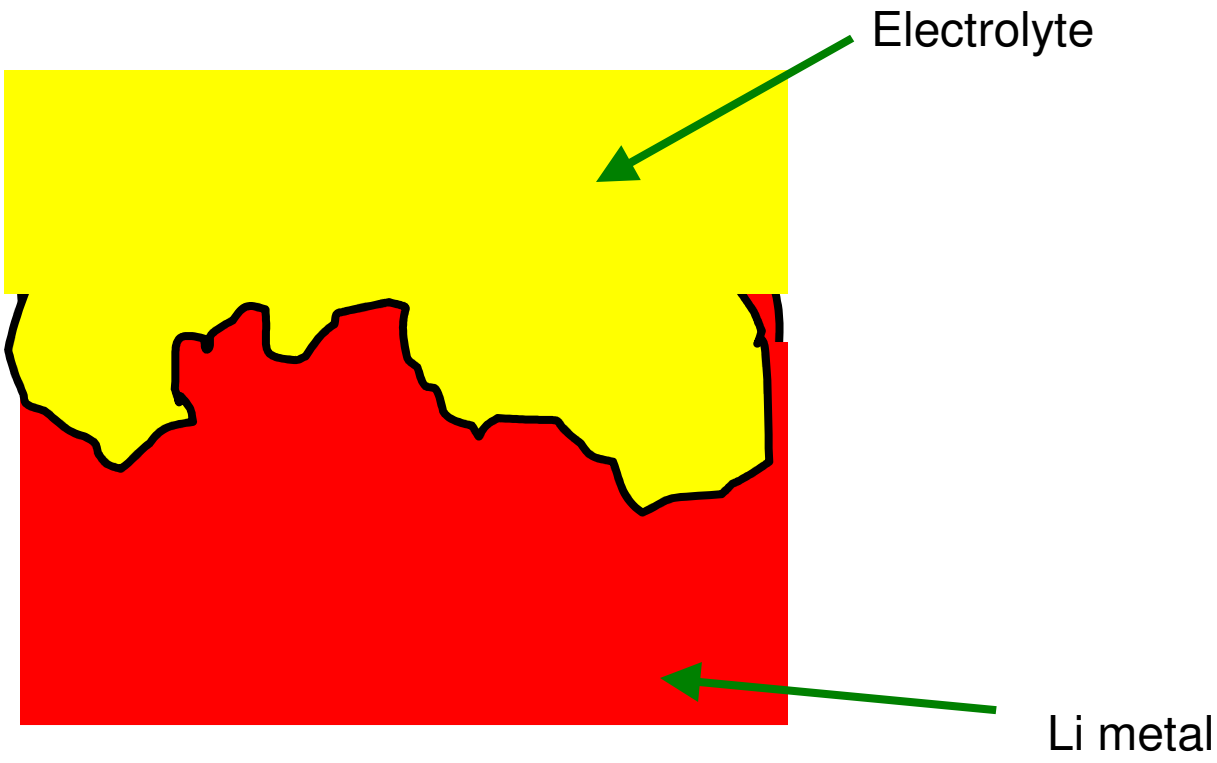


SEO (40-54)
r = 0.1

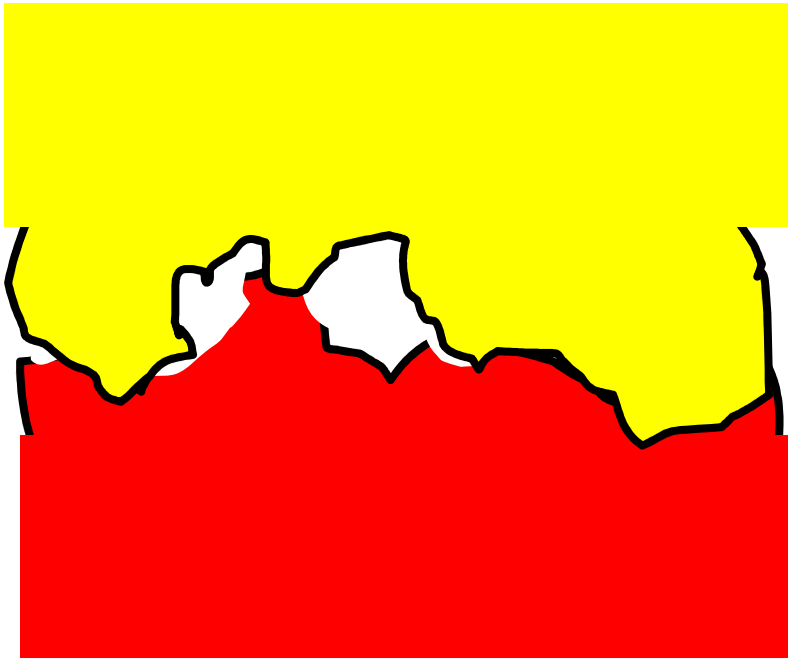


SEO (40-54) domain size = 75 nm

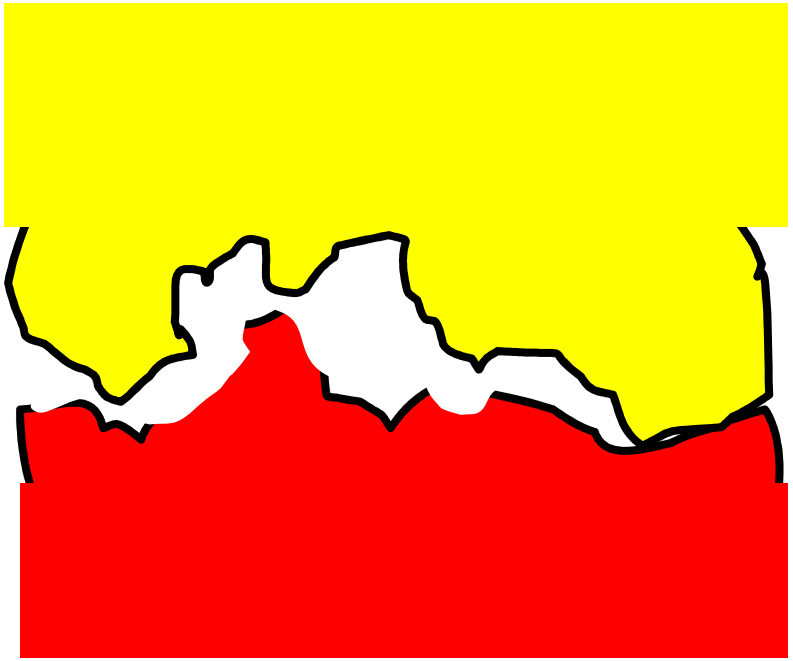
Problem with solid electrolytes



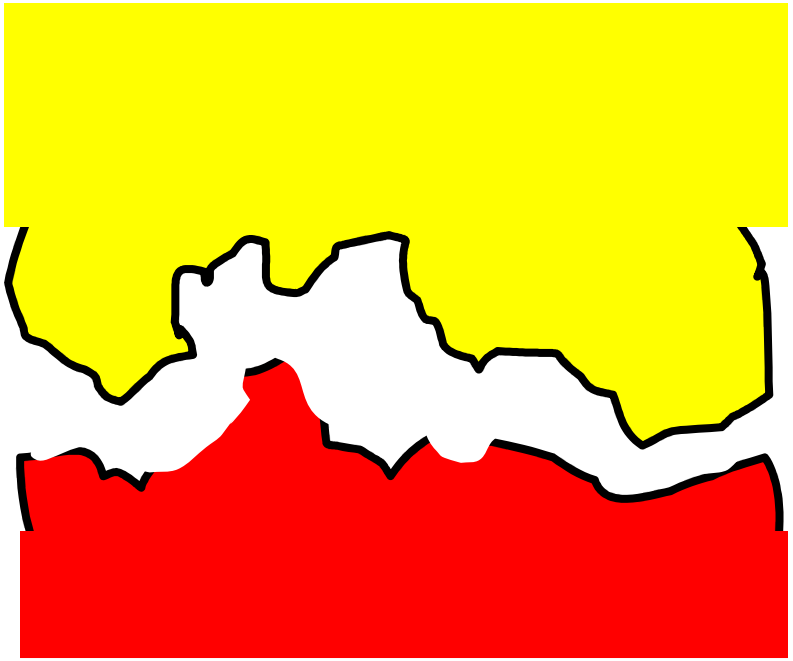
Problem with solid electrolytes



Problem with solid electrolytes



Problem with solid electrolytes



Block copolymers are liquid-crystalline

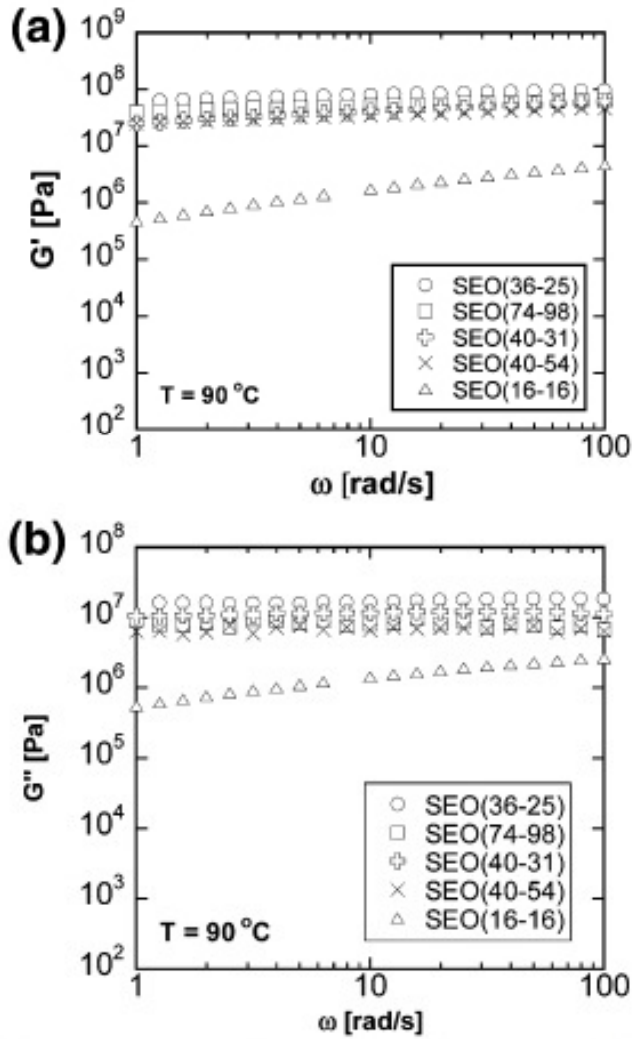
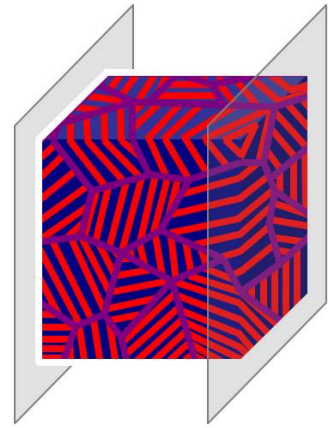


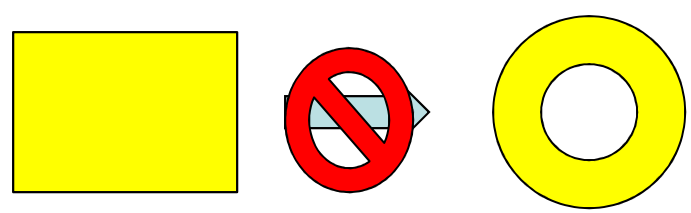
Figure 8. Frequency, ω, dependence of the (a) storage, G', and (b) loss moduli, G'', of SEO copolymers.



Defect-mediated solid

$G' \sim \omega^0$, $G'' \sim \omega^0$; $G' >> G''$

$$\vec{\sigma} = \bar{\bar{E}}\dot{\epsilon}$$



Block copolymers are liquid-crystalline

Macromolecules, Vol. 34, No. 25, 2001

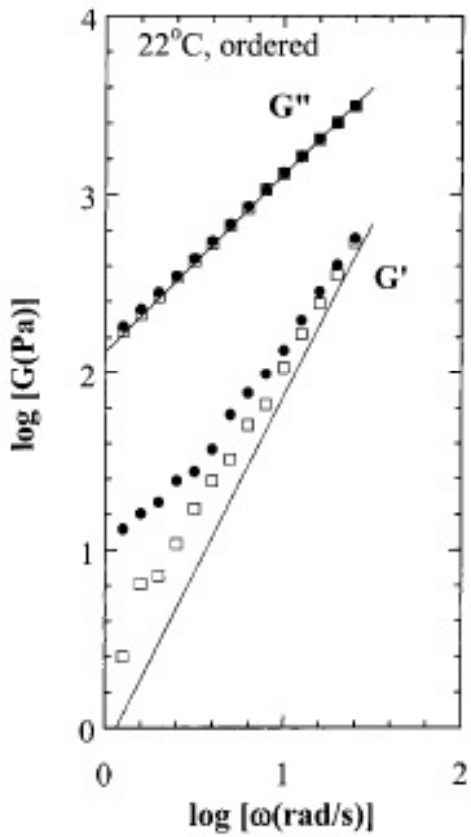
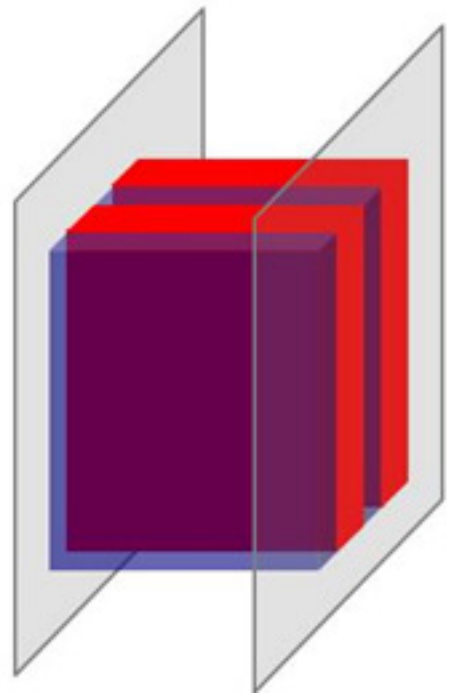


Figure 6. Frequency (ω) dependence of the storage (G') and loss (G'') moduli for ordered sample at 22 °C. Solid symbols: data from the sample with equilibrated defects. Open symbols: data from the best-aligned sample. Solid curves are theoretical fits using Rouse model (eqs 4 and 5) with τ_R as the only fitting parameter.

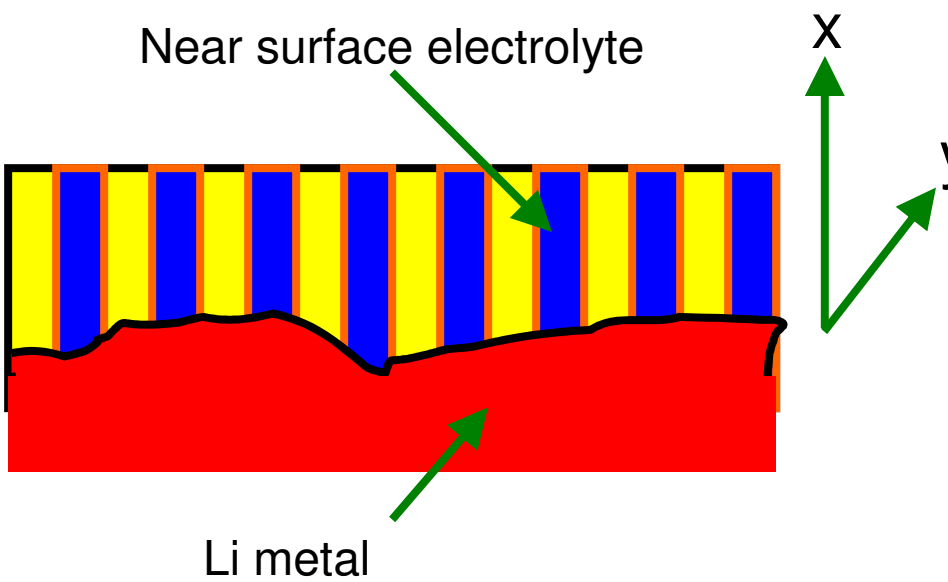


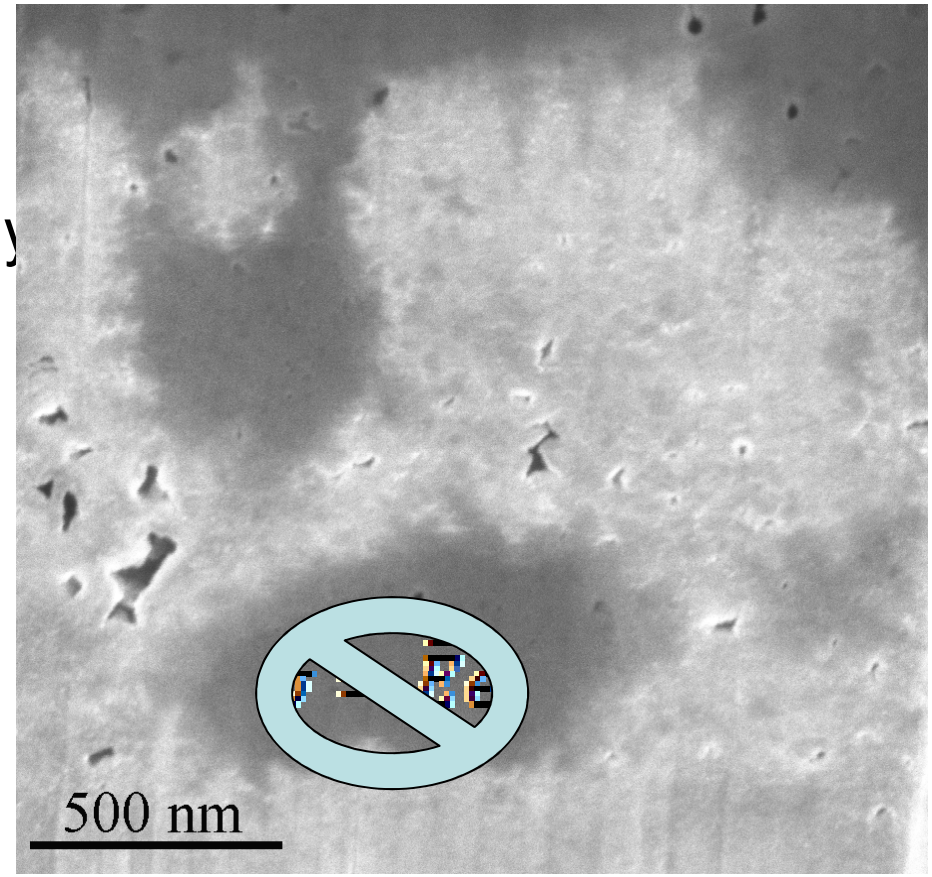
Defect-free liquid

$G' \sim \omega^2$, $G'' \sim \omega^2$; $G'' >> G'$

Hahn, et al. Macromolecules, 2001

Liquid crystalline symmetry of block copolymers

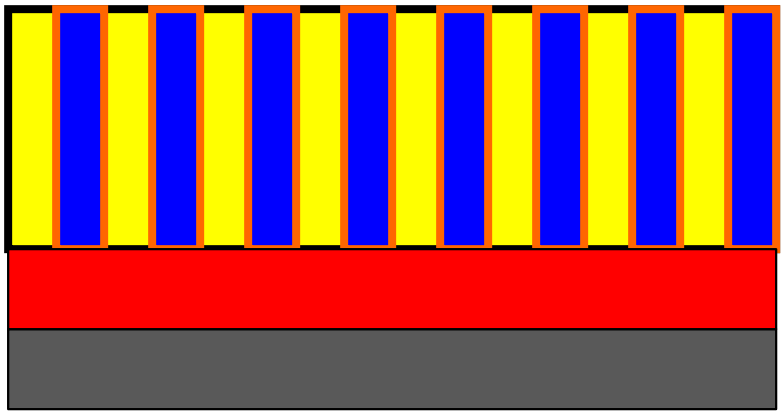




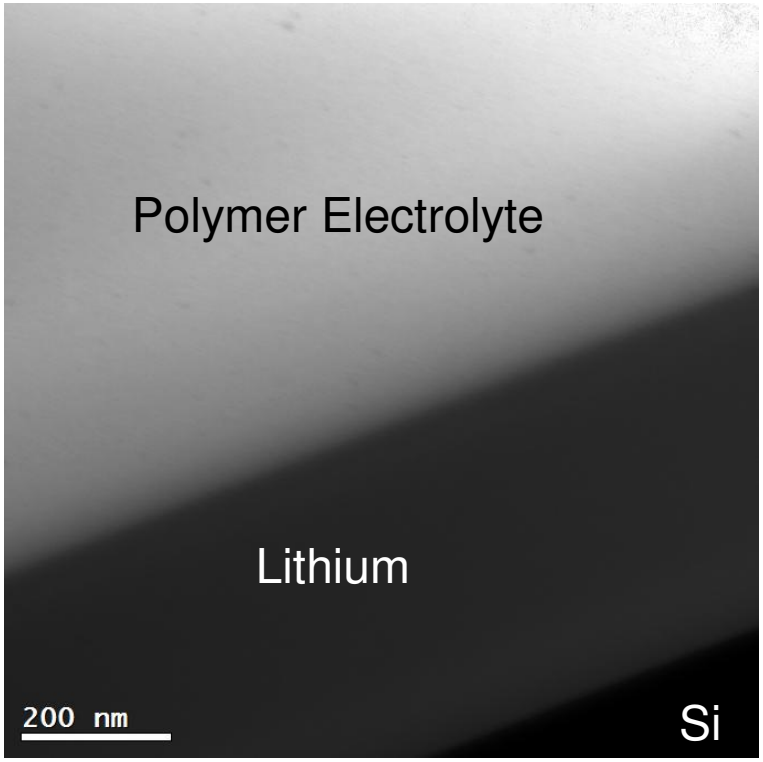
A lamellar block copolymer is:
a solid is sheared in z-direction or compressed in the x direction
a liquid under shear forces in x, y plane

Study alignment near Li surface

Stone



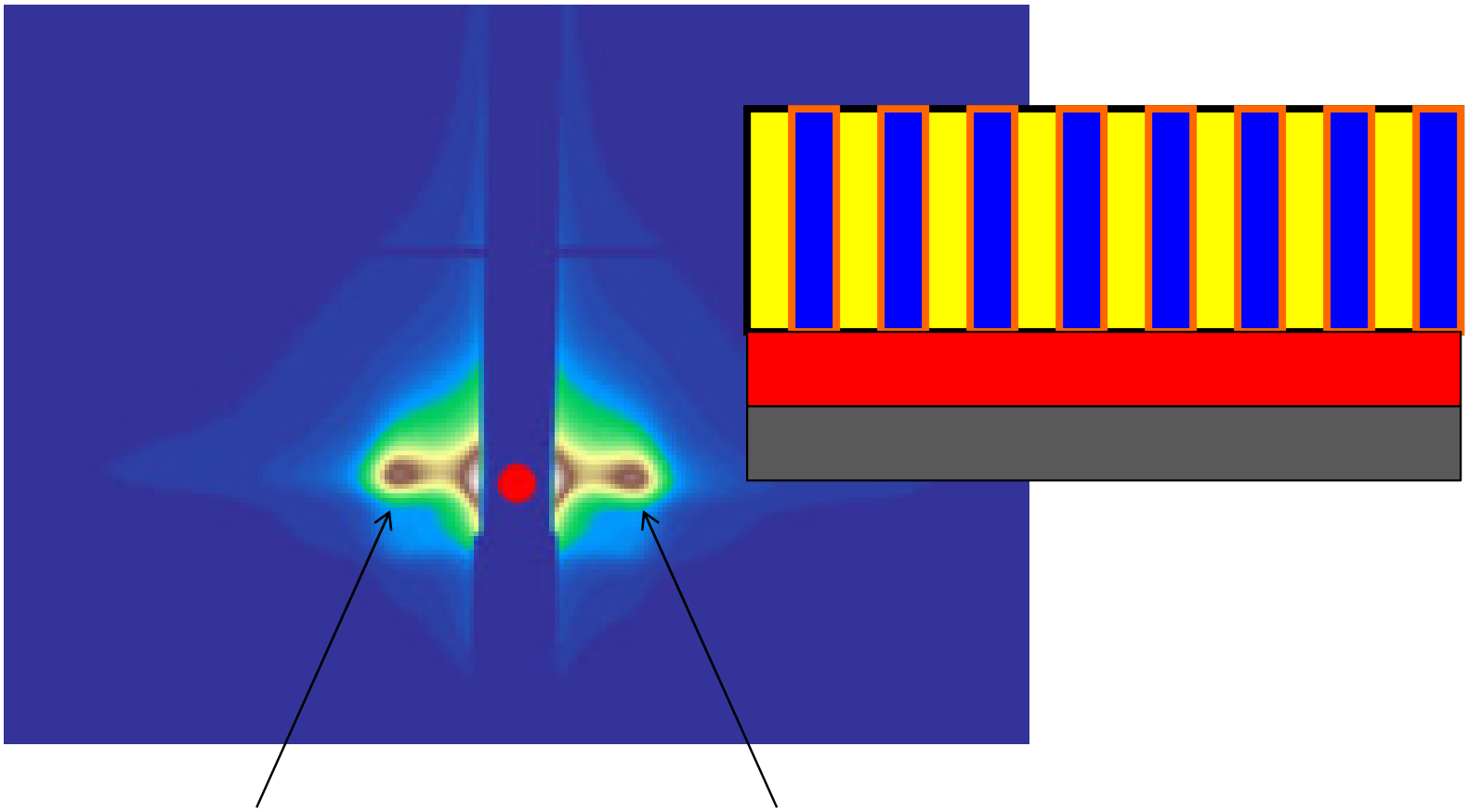
Li film vapor deposited on Si wafer.
SEO spun cast on Li and annealed.
Alignment studied by GISAXS.



GISAXS alignment near Li surface

Stone

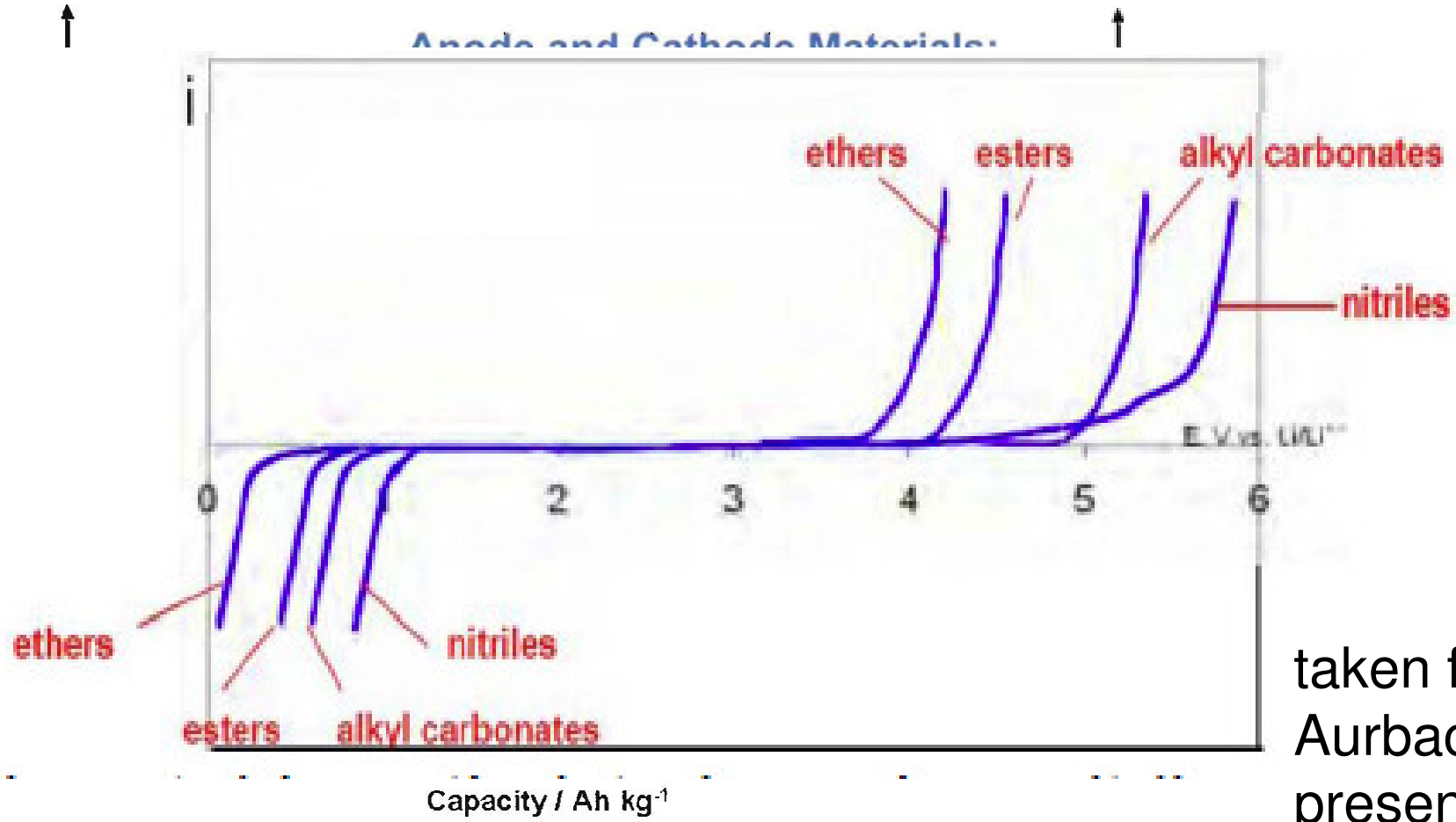
SEO (16-16) r = 0.085 on Lithium Metal



Spots indicative of perpendicular alignment

Grazing Incidence Small-angle X-ray Scattering

Enabling high energy electrodes



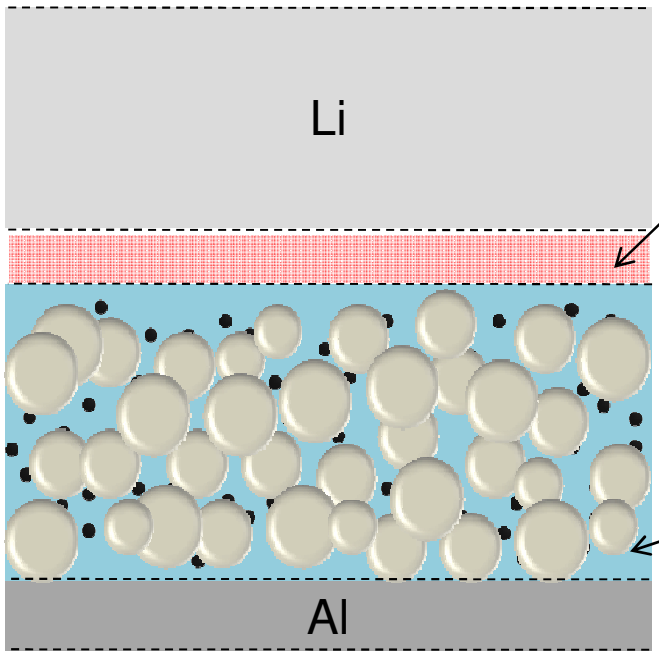
taken from Aurbach presentation

High energy electrodes exist, enabling electrolytes that straddle the potential difference don't.

Layered Electrolytes

Different polymers never mix (Flory)

Li or Li alloy anode



Anode side Polymer

Cathode side Polymer

Anolyte and catholyte optimization is decoupled.

Electrolyte needs to be stable at a particular potential, not a voltage window.

Conclusion

1. Trying to development a rechargeable battery with a dry electrolyte that works. Not easy by any means.
2. Experiments on quantification of electrode failure. At finite current densities, dendrite formation is reduced relative to PEO homopolymer. Establishing requirements for eliminating dendrites is within the realm of possibilities.
3. Recognition that liquid crystalline symmetry is crucial for battery electrolytes (modulus/interfacial adhesion). Solid electrolytes will only work on flat electrodes and will work as long as the roughness does not increase.
4. Better Li ion conductors are needed to enable room temperature Li-polymer batteries. Need to create teams that combine new polymer synthetic techniques (atom transfer, Grubbs catalysts, etc.) with electrochemical characterization.