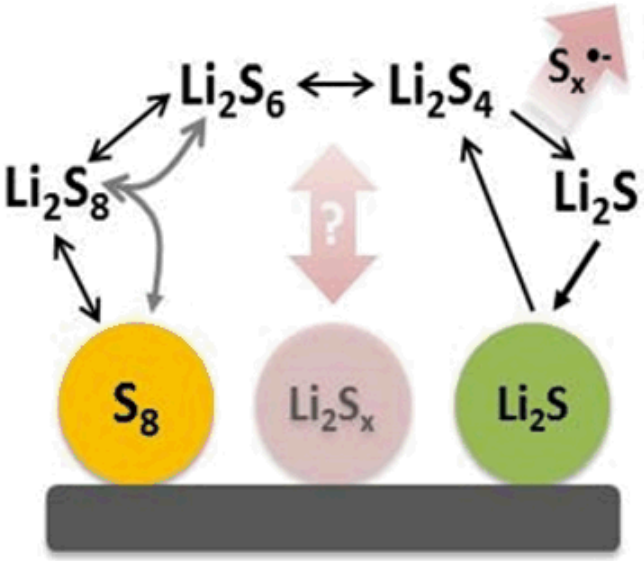
SAND2017-4300C

JCESR | JOINT CENTER FOR ENERGY STORAGE RESEARCH

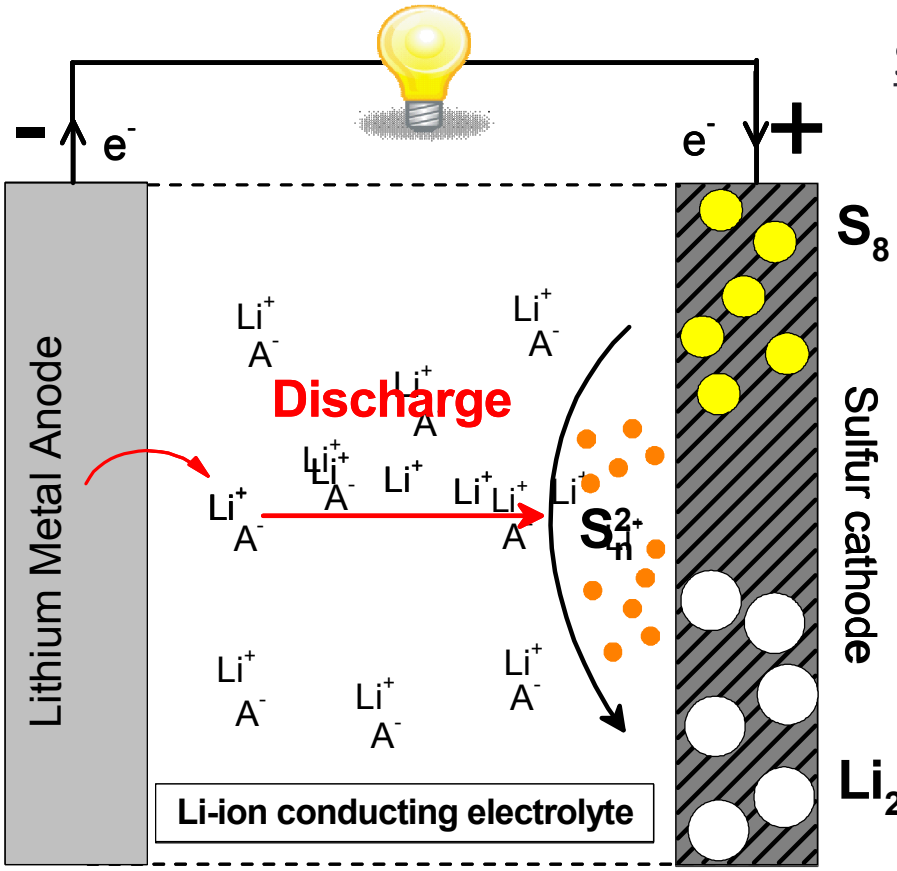
Viable Li-S Batteries: Preserving the Chemical Inventory and Protecting the Li Anode



Kevin R. Zavadil & the JCESR Li-S Team
Materials, Physical and Chemical Sciences
Sandia National Laboratories

2017 MRS Spring Meeting
April 19, 2017

Li-S Cell Redox Chemistry



Successive reduction/oxidation of sulfur:

S_8 (insoluble)

Li_2S_8

Li_2S_n

Li_2S_{n-1}

...

Li_2S_2

Lithium polysulfides in solution

Li_2S (insoluble)

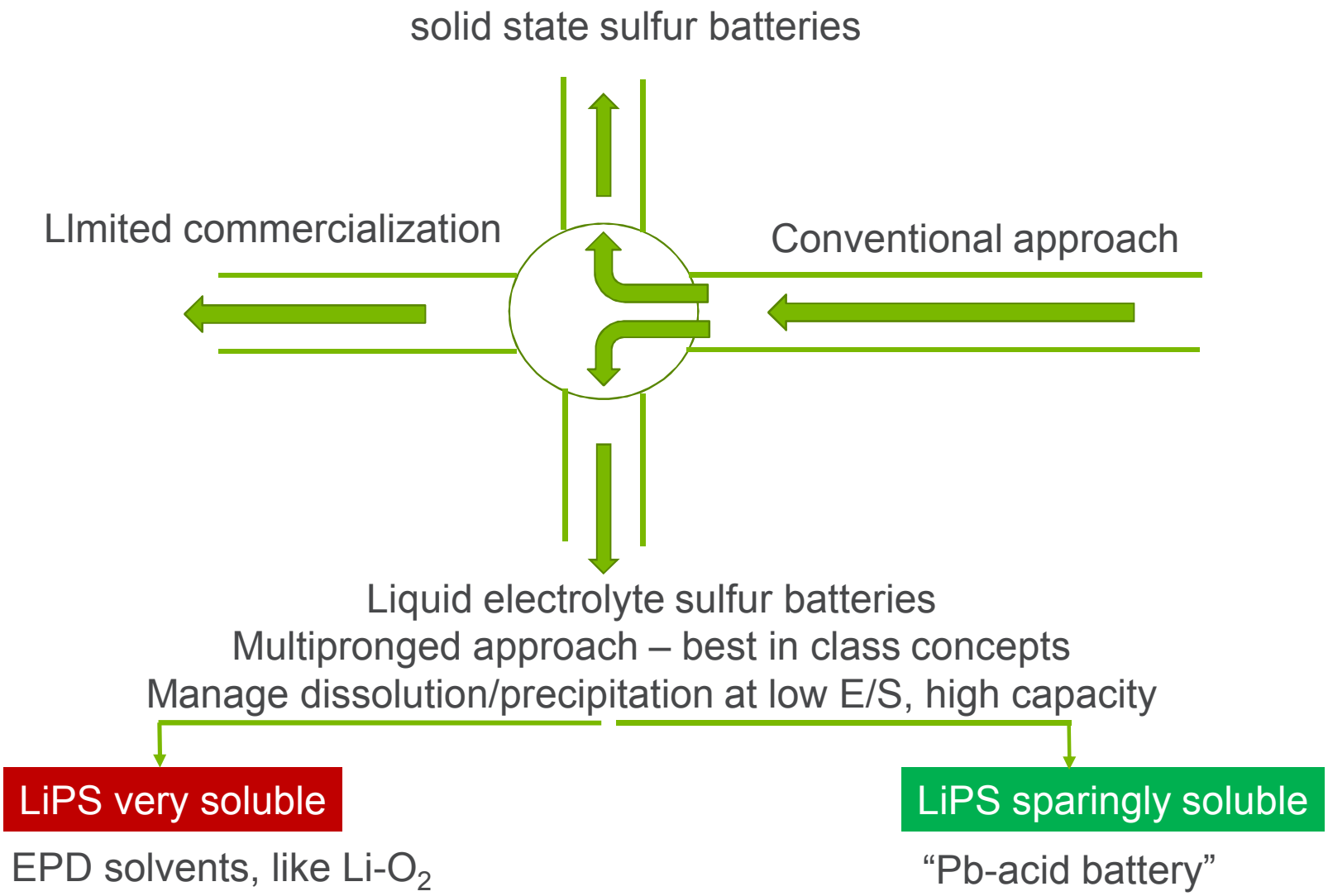
$$S_8 + 16\ Li^+ + 16\ e^- \Leftrightarrow 8\ Li_2S$$

at ~ **2.1V** vs. Li^+/Li – **1672 mAh/g_{sulfur}**

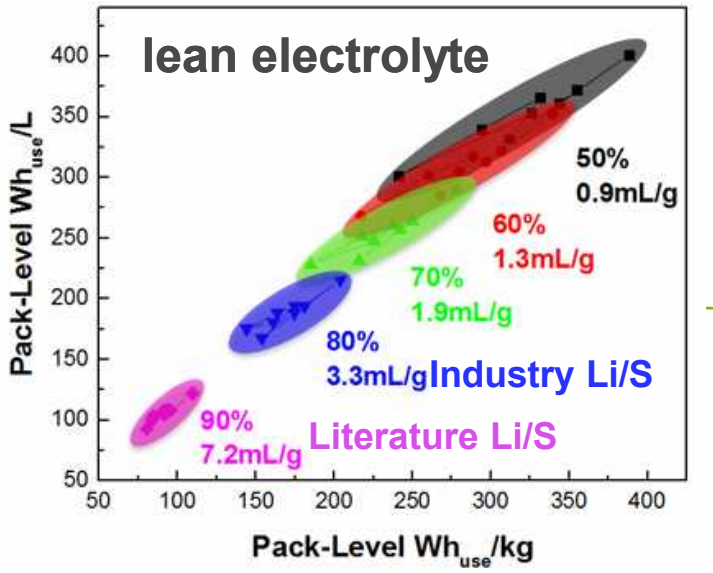
Practical: ~ 1200 mAh/g

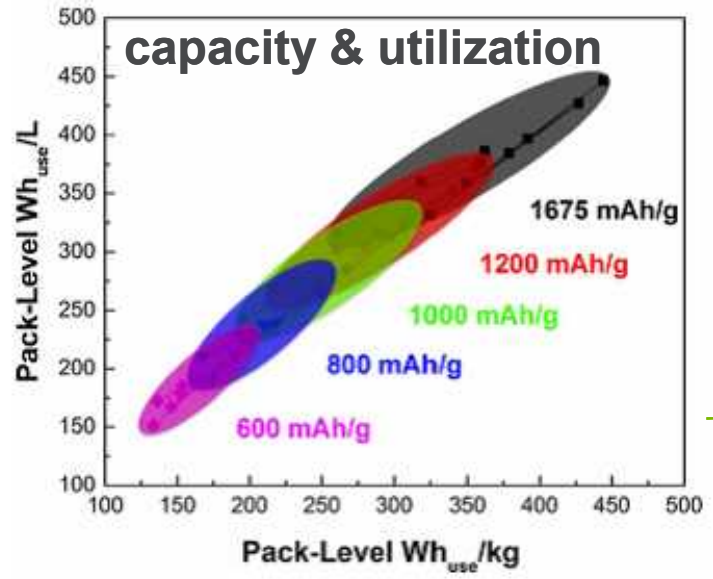
Theoretical: 2567 Wh/kg; 2200 Wh/L

Li-S is at a Crossroad



Three key challenges for practical Li/S batteries





Critical development path:

- Stable Li anode at 6 mAh/cm^2, 6 mA/cm^2 (1C), 50-100% excess
- High capacity cathode with low per cycle loss
- Reduced electrolyte volume fraction approaching 50%, 1 ml/g$_S$

Design guidelines

Couple Li protection strategies with sparingly solvating electrolytes

Capacity • E/S • limited Li

Eroglu et al., J. Electrochem. Soc., 162(6) A982 (2015)

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Advances are made through integration of critical materials concepts

Cathode architecture

e^-/Li^+ continuity

compliant, functional framework

multifunctional binders

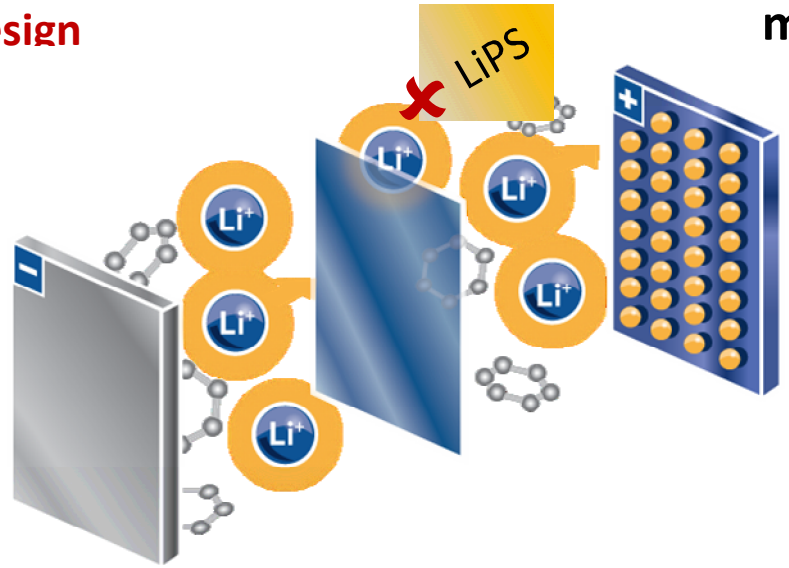
Anode interface design

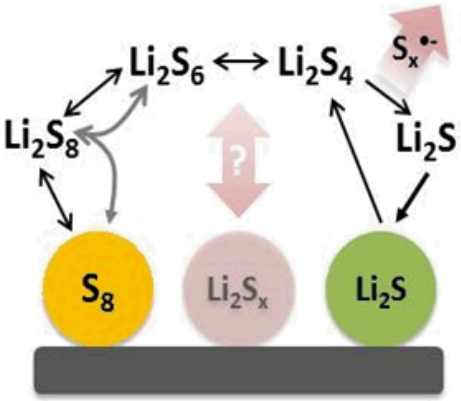
no parasitics

dimensional contr

no dendrites

membranes





:hode interface design

acile kinetics

moderate LiPS binding

polar surfaces

Electrolyte design

control LiPS solubility

control S_8/S^{2-} nucleation & growth

solvates

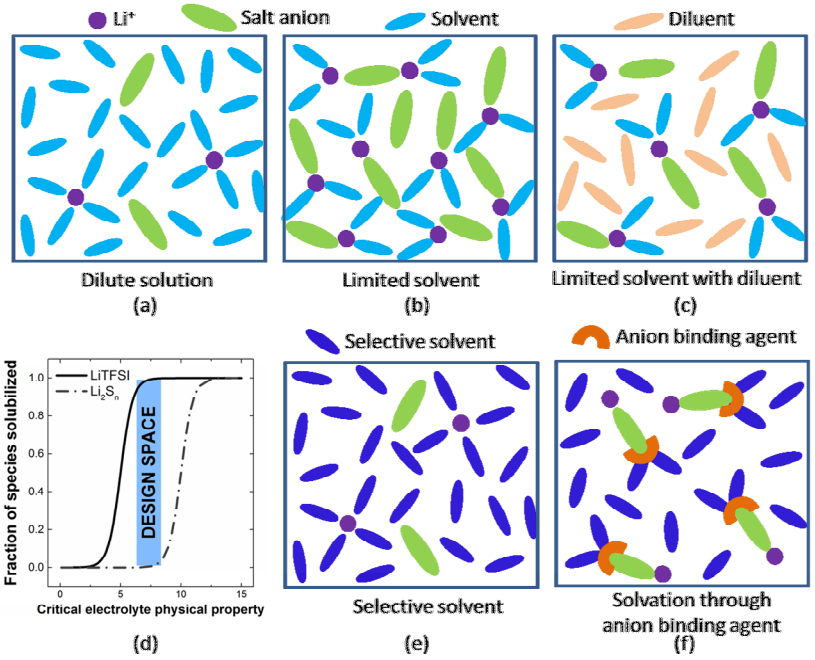
Minimizing Activity Loss with Sparingly Solvating Electrolytes

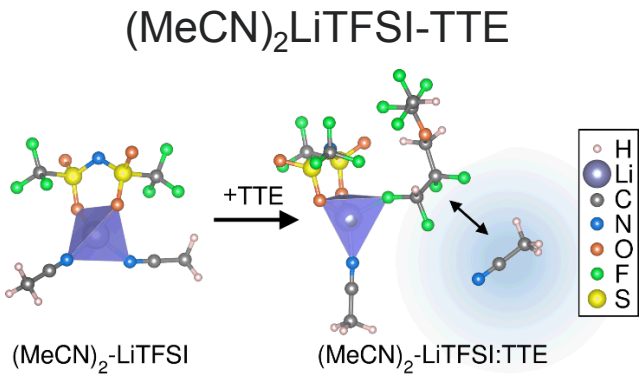
Two strategies:

- Highly solvating electrolytes — $S_8 + 16Li^+ + 16e^- \rightarrow mLi_2S_n \rightarrow 8Li_2S$
- Sparingly solvating electrolytes — LiPS mediate the overall EC reaction

At low E/S, saturation will dominate irrespective of LiPS solubility

Sparingly solvated concept demonstrated to greatly reduce redox shuttle

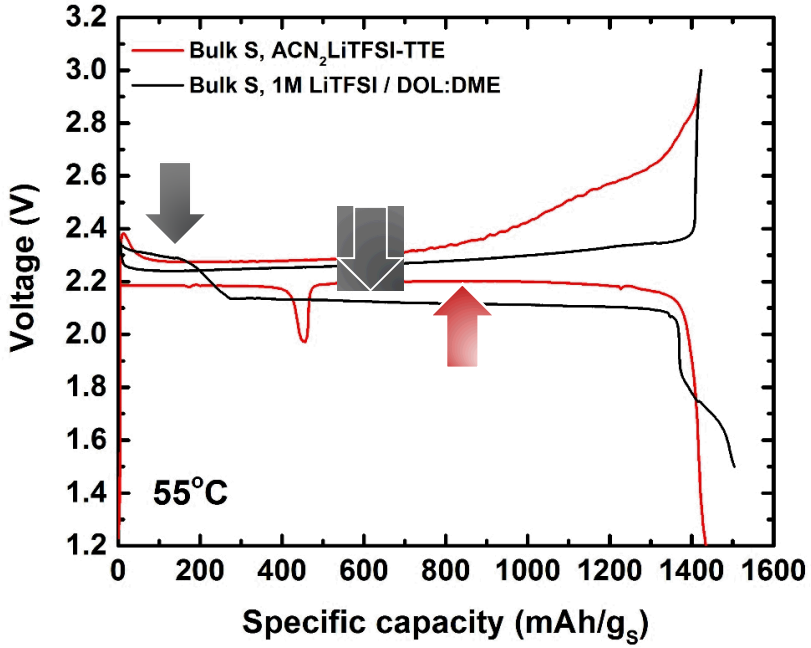




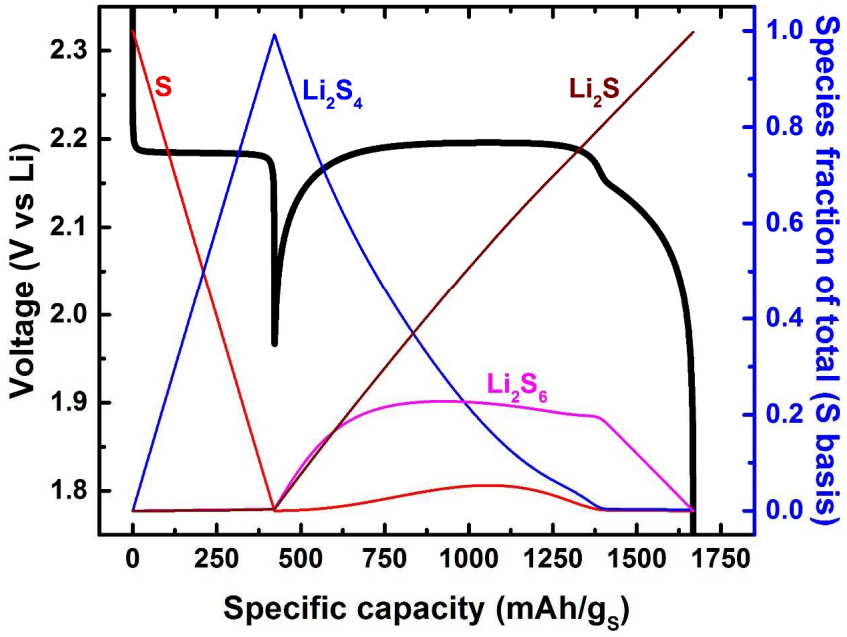
L. Cheng et al. 10.1021/acsenergylett.6b00194

Sparingly Solvating Concept Demonstrated

Dilute ether - solution mediated mechanism



Kinetic model



Solvate - semi-solid state mechanism

Similar results observed in select ether solvates, other sparingly solvating systems

$\frac{1}{2}S_8 + 2Li^+ + 2e^- \leftrightarrow Li_2S_4$ $U^o = 2.2$ V

$\frac{1}{2}Li_2S_6 + Li^+ + e^- \leftrightarrow Li_2S_3$ $U^o = 2.4$ V

$Li_2S_3 + Li_2S_4 \leftrightarrow Li_2S + Li_2S_6$ redox mediation

$Li_2S_3 + 1/8S_8 \leftrightarrow Li_2S_4$ S_8 consumption

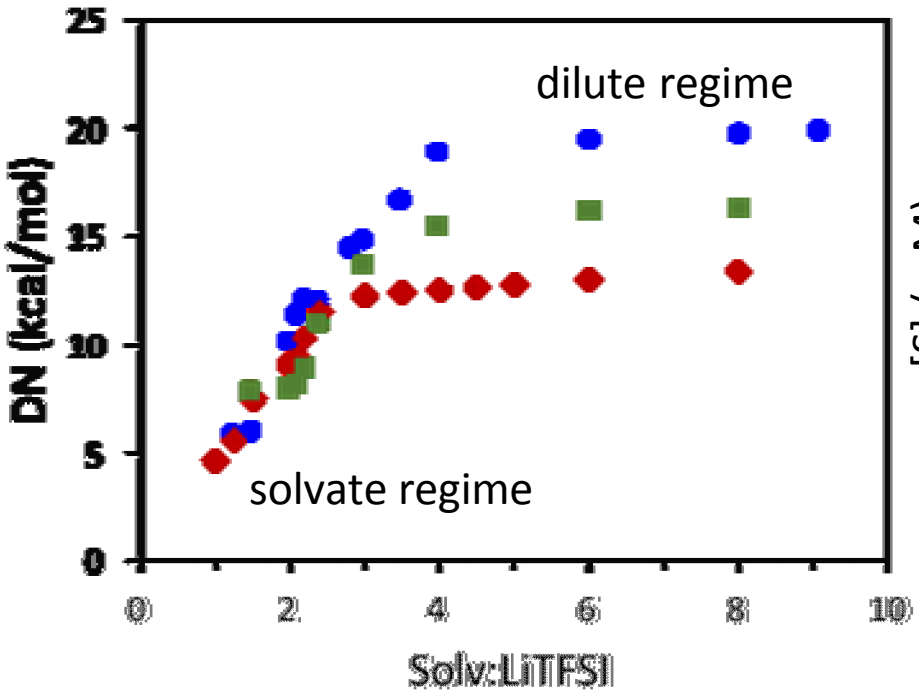
$Li_2S_3 \leftrightarrow Li_2S + \frac{1}{4}S_8$ Li_2S_6 consumption

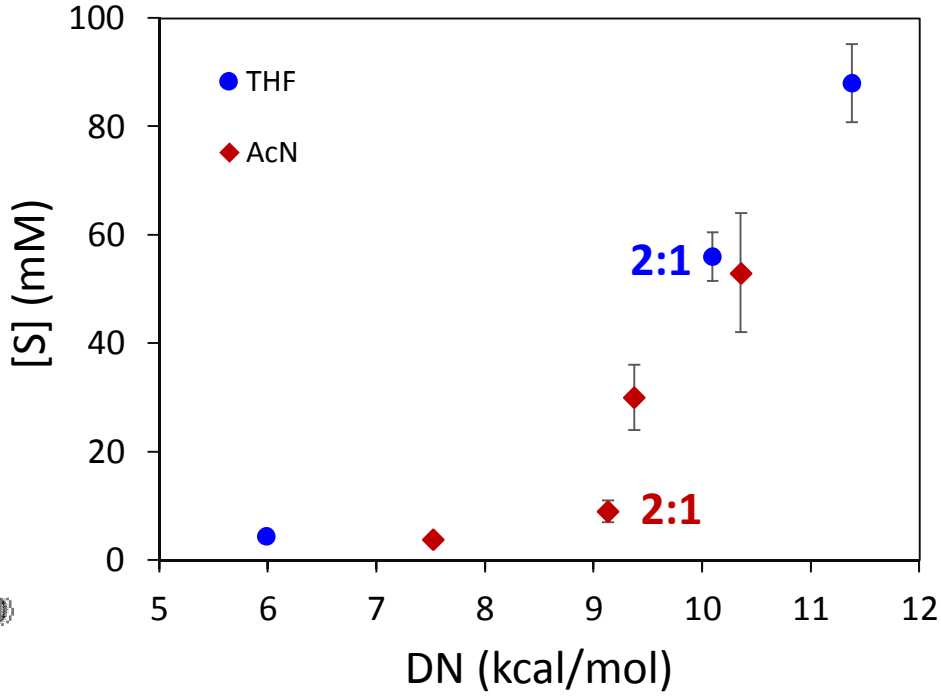
Tune mechanism & kinetics through redox intermediate solubility

Required LiPS Solubilities for Redox Mediation

Clear distinction between dilute and solvate regimes based on donicity of the electrolyte

Solubility is tuned within the solvate regime



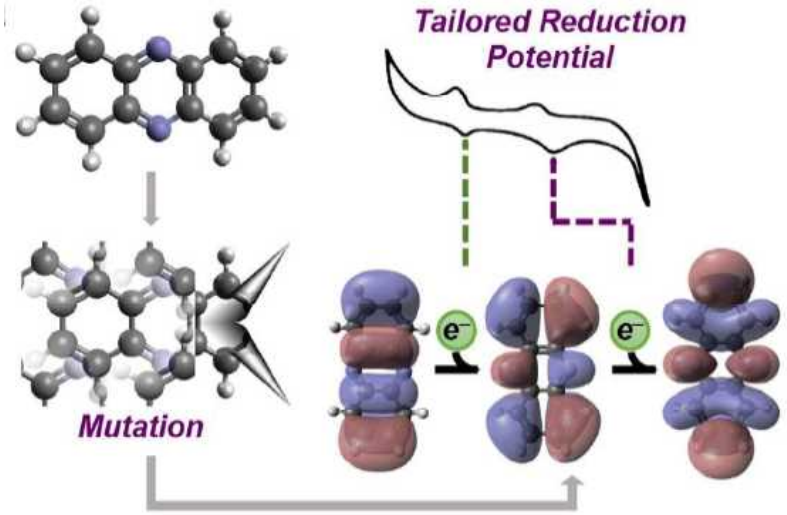


mM equivalent S concentrations – dependent upon solvent and diluent

T. Watkins et al. in preparation

Augmented redox mediation is critical for lean electrolyte operation

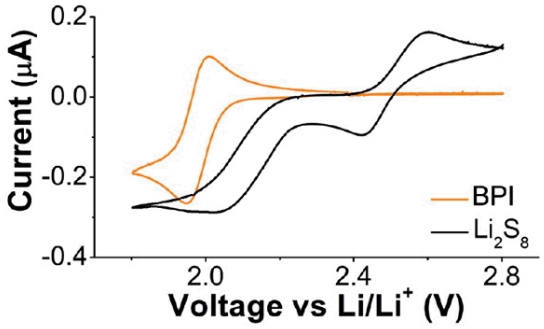
Electrolyte Genome: rational design of a redox mediator

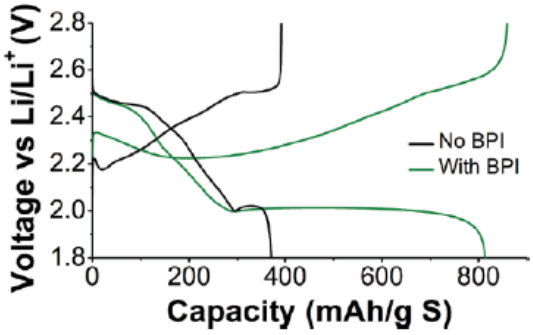


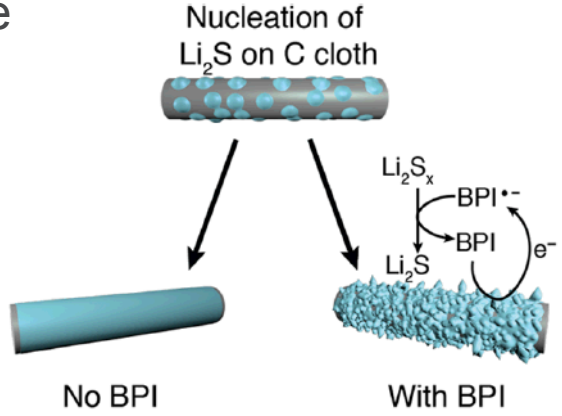
Mutations of PAH molecules and subsequent computational screening for matching charge/discharge potential of a Li−S battery

Directing Li_2S nucleation and growth – porous 3D deposition

6-fold improved sulfur utilization and rate perfo[illegible]ce







L. Gerber et al., 10.1021/acs.nanolett.5b04189

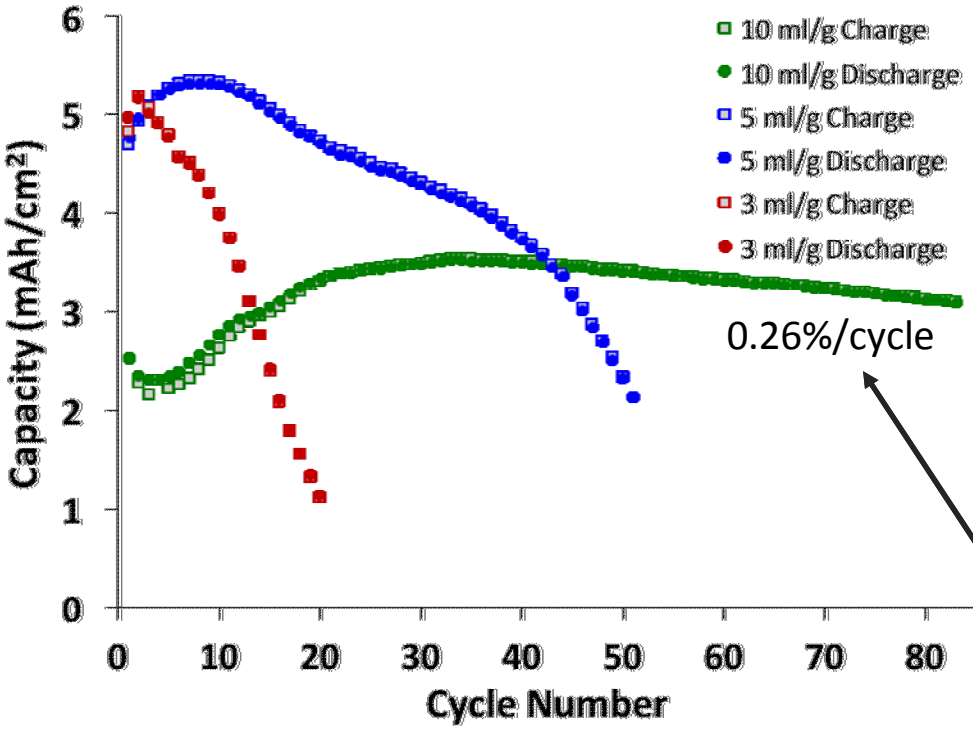
Performance is limited in a solvate

High capacity
High rate
Low E/S

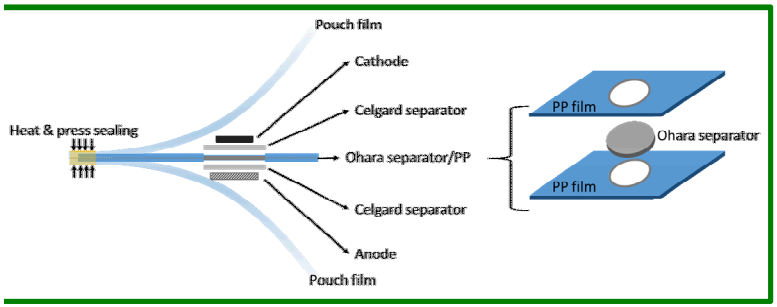
Increasing cycle life

Low capacity
Low rate
High E/S

$Li(MeCN)_2TFSI$ – TTE, 55°C



Decoupling the cathode
Two separated electrolytes
Ohara single ion conductor ($LiTiAlPO_x$)



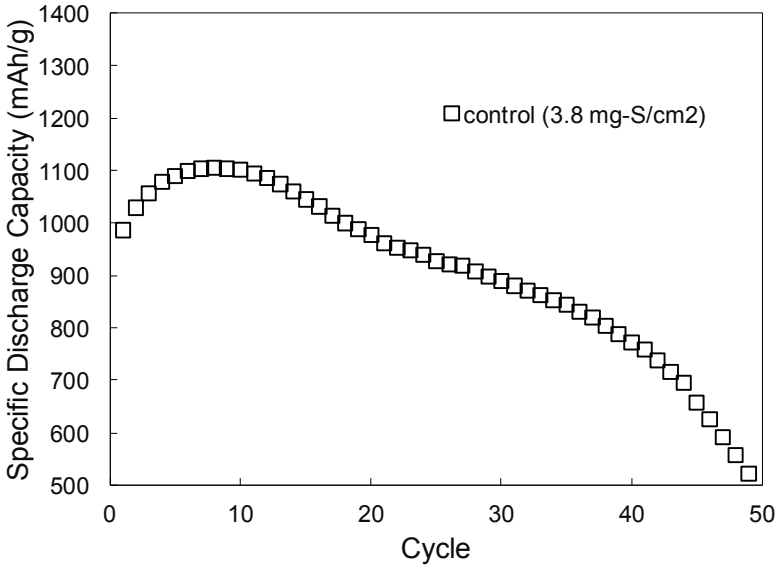
intrinsic cathode fade rate for a moderate capacity cathode

Early cycle fade is an electrolyte/anode limit

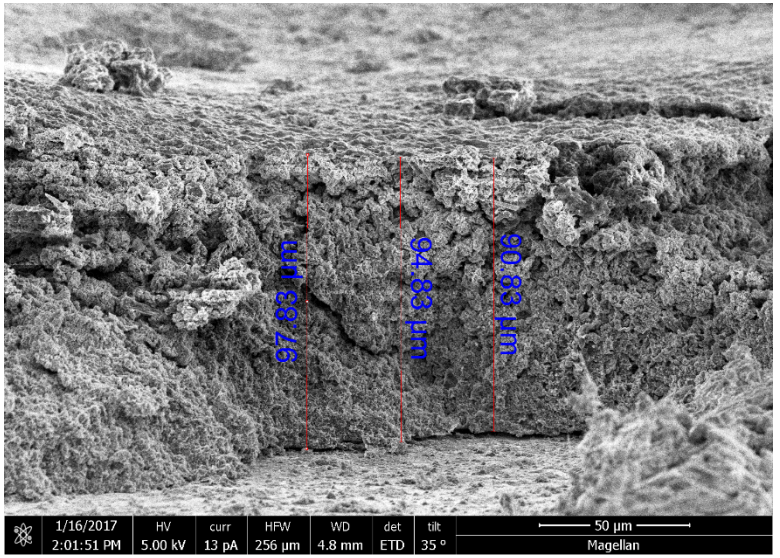
Late cycle fade is a cathode limit

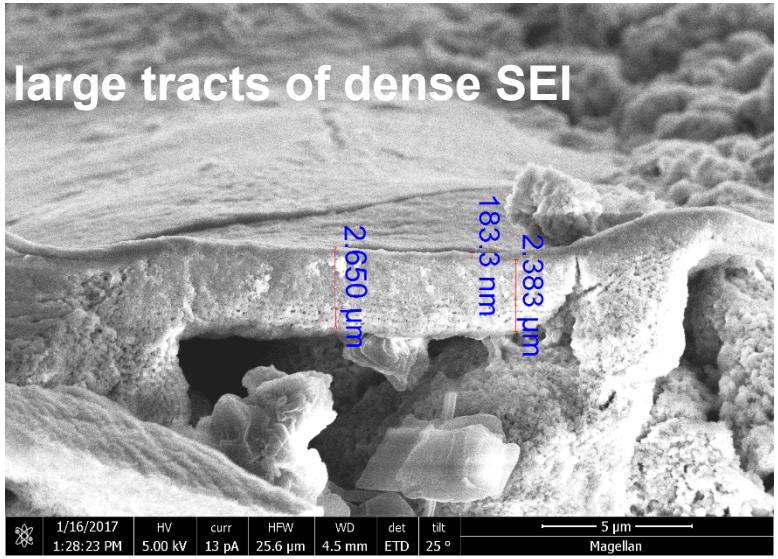
Slow Rate High Capacity Li Cycling in a Solvate

$MeCN_2$:LiTFSI-TTE, 5 ml/g_S, C/30, 5 mAh/cm^2, 0.13 mA/cm^2, 55°C



Fade scales with lower E/S, greater current density/greater capacity





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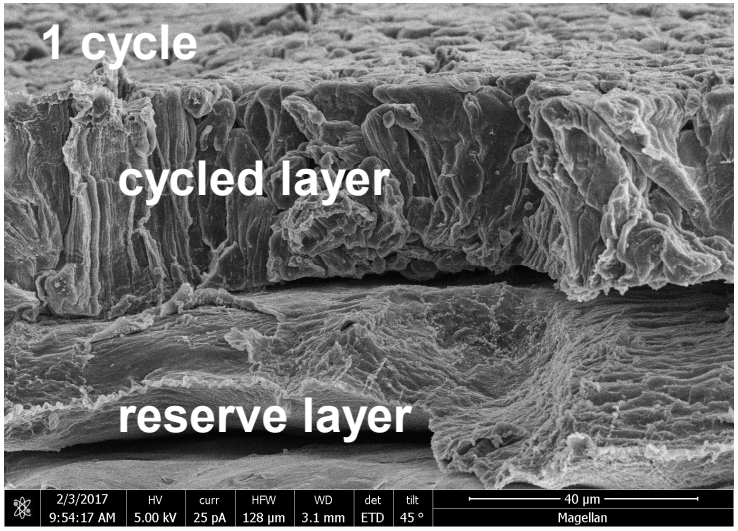
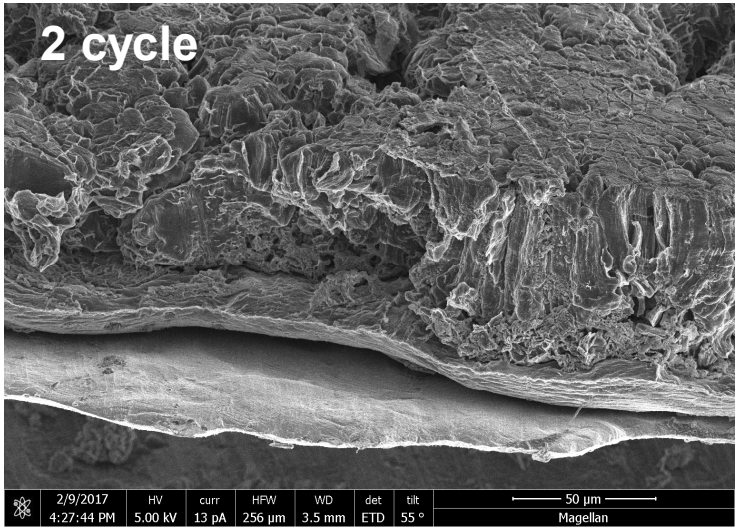
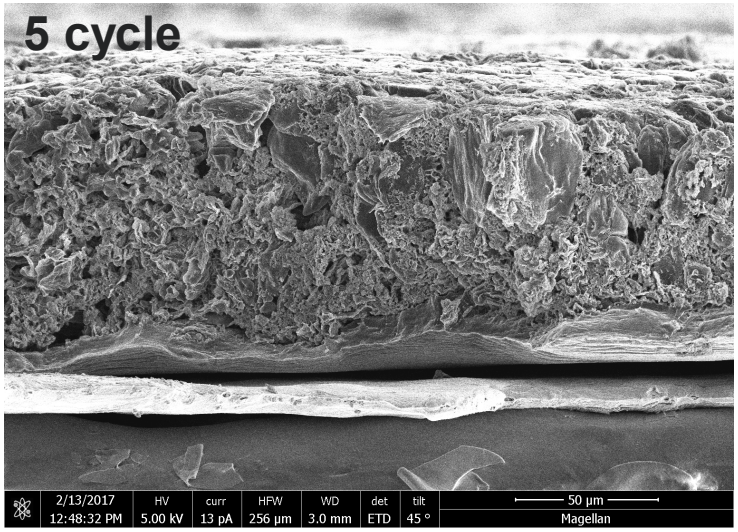
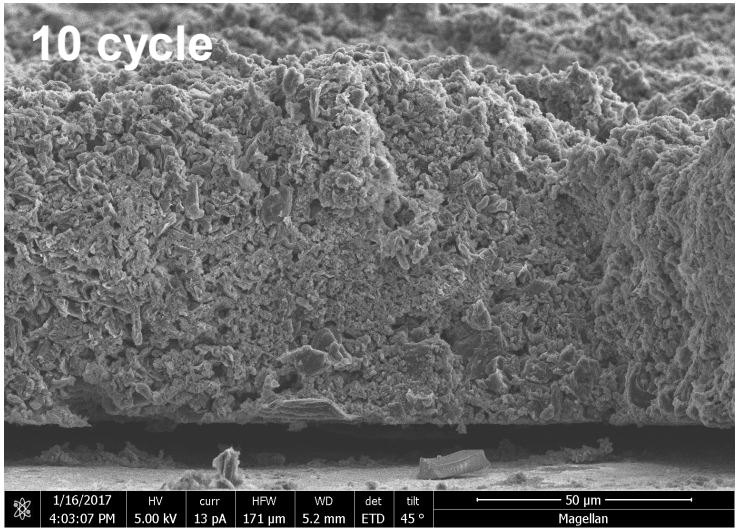
Evolution of Li Anode Morphology in an Solvate Electrolyte

AN_2LiTFSI-TTE, 3 ml/g_S,55°C, 6 mAh/cm^2, 0.6 mA/cm^2



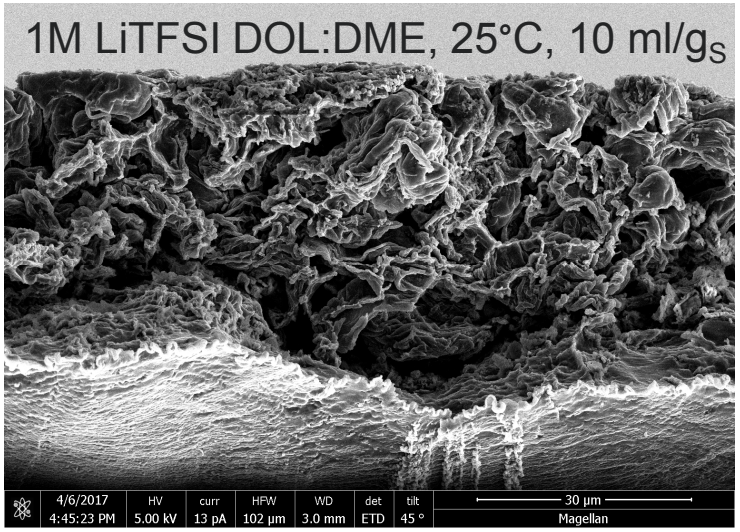


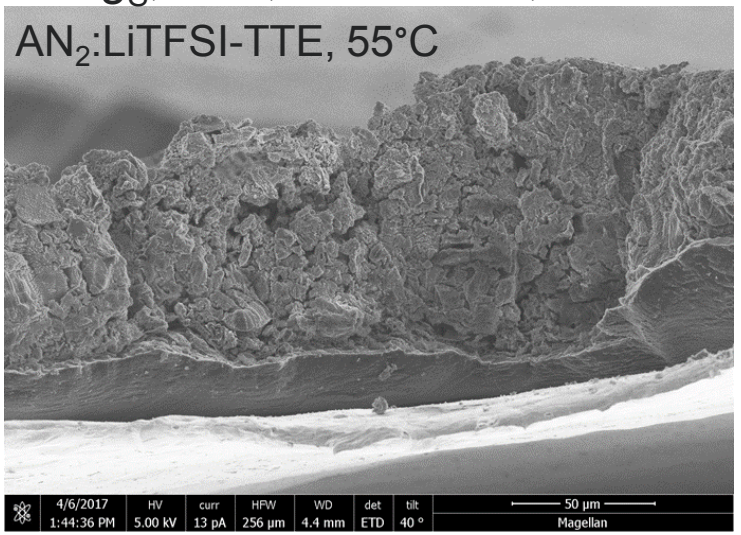


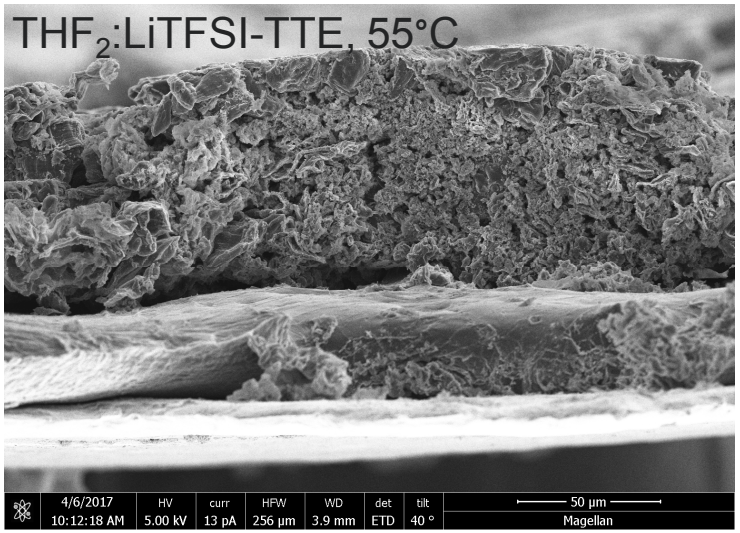


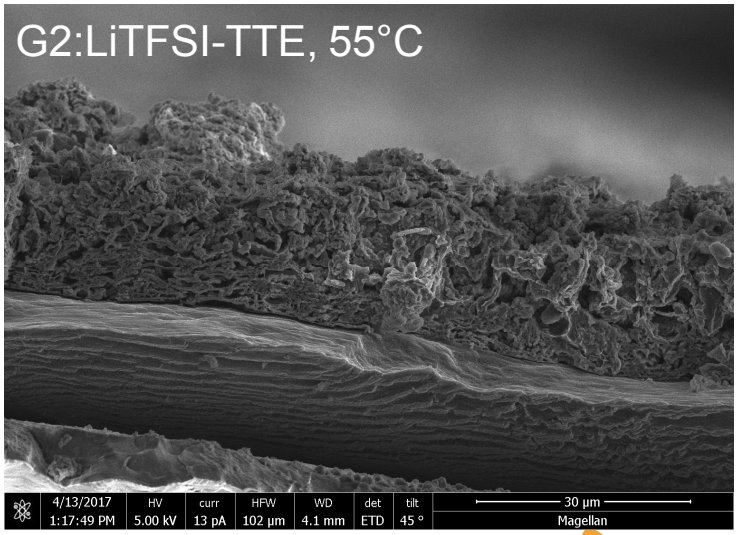
Morphology evolution is not strongly dependent on solvent used

3 ml/g_S,55°C, 6 mAh/cm^2, 0.6 mA/cm^2

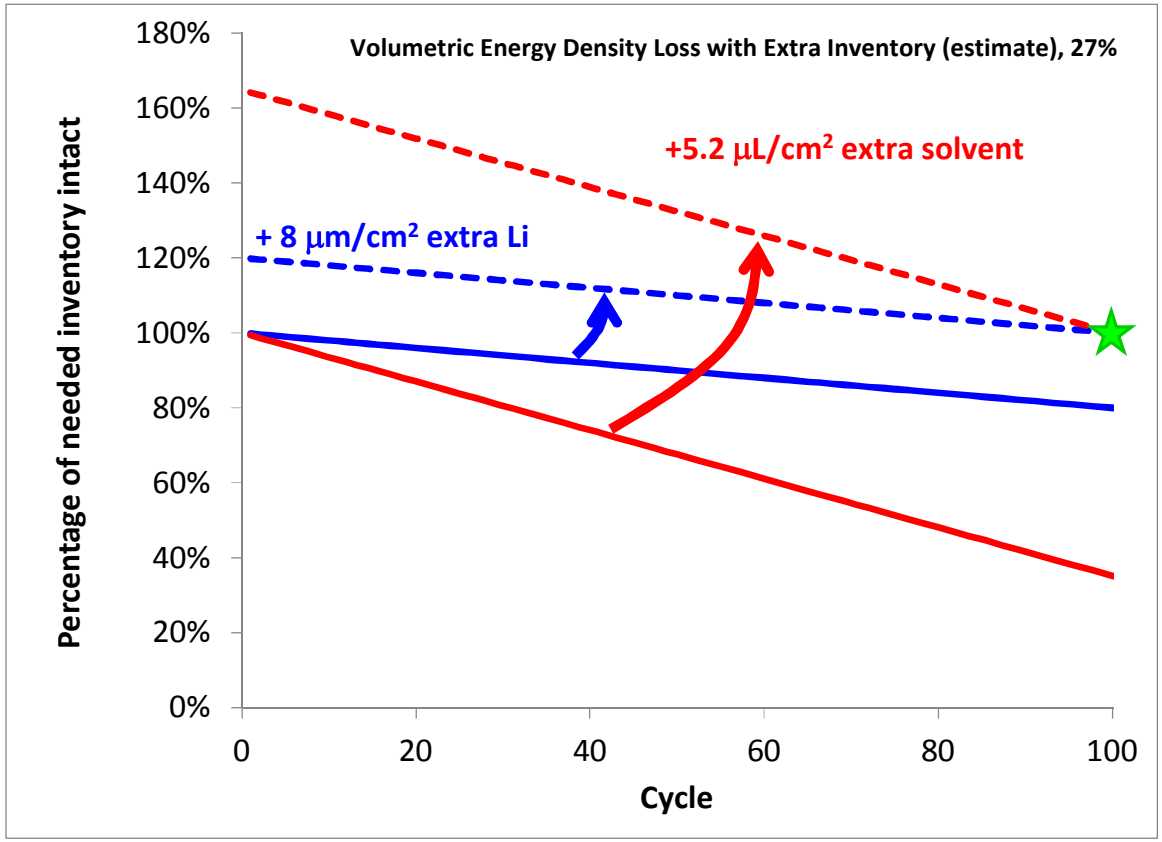








Maintaining material inventory is key



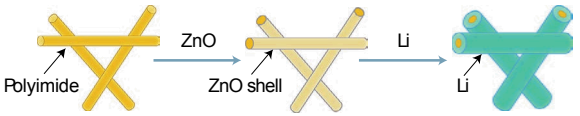
Electrolyte loss is more critical – low density phase

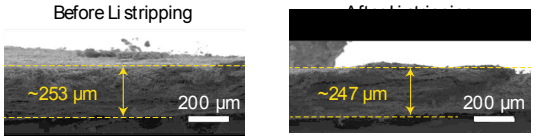
Problem: Finding an optimum electrolyte for Li stripping/plating & S/Li_2S conversion

Approach: Control Electrolyte Contact with the Anode – protect both

Strategies Pursued by the Community

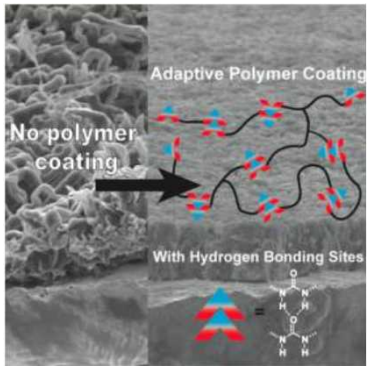
Porous anode hosts
- enhanced surface area to lower current density
- minimum mass and volume





Y. Liu et al. 10.1038/ncomms.10992

Elastic polymer coatings
- accommodate local volume change
- maintain a coherent interface



G. Zheng et al. 10.1021/acsenergylett.6b00456

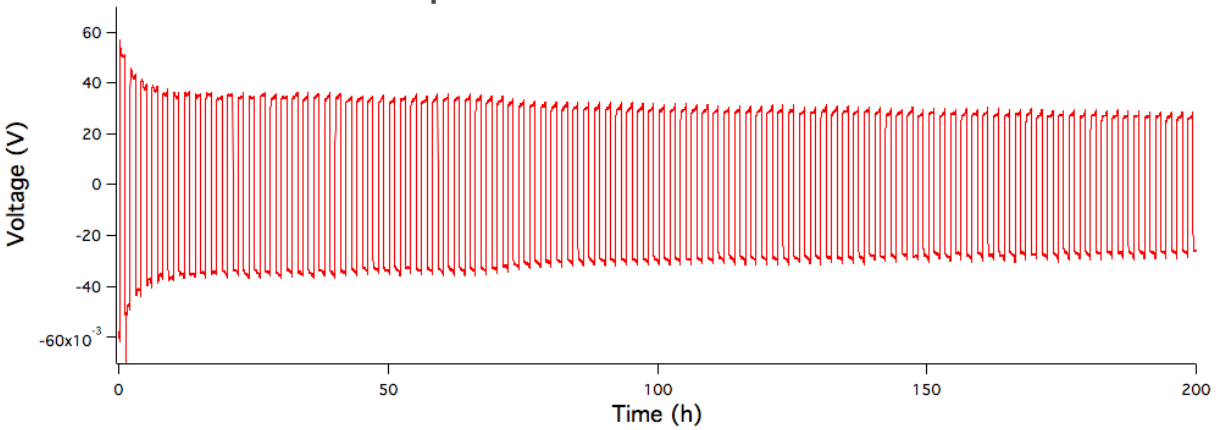
Safety is important – dimensional control issues are a non-starter

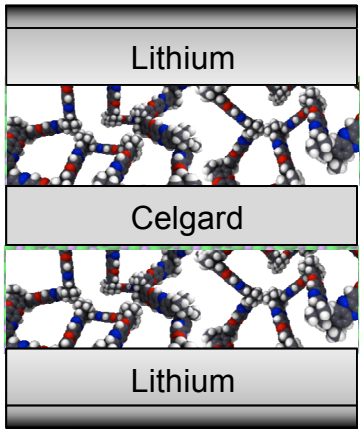
Equally important – low Coulombic efficiency (99.9) is a non-starter
- preserve both electrolyte and lithium

Diverse suite of protection strategies are pursued

Polymer scaffolds for directed SEI growth

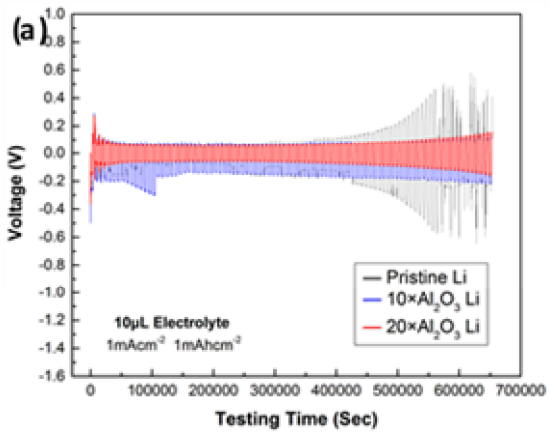
- mechanical compliance and uniform ionic flux



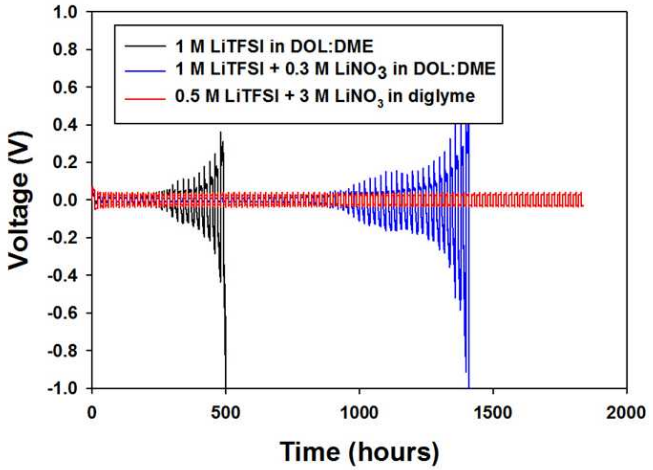


Inorganic or composite films grown on Li

- directed SEI growth

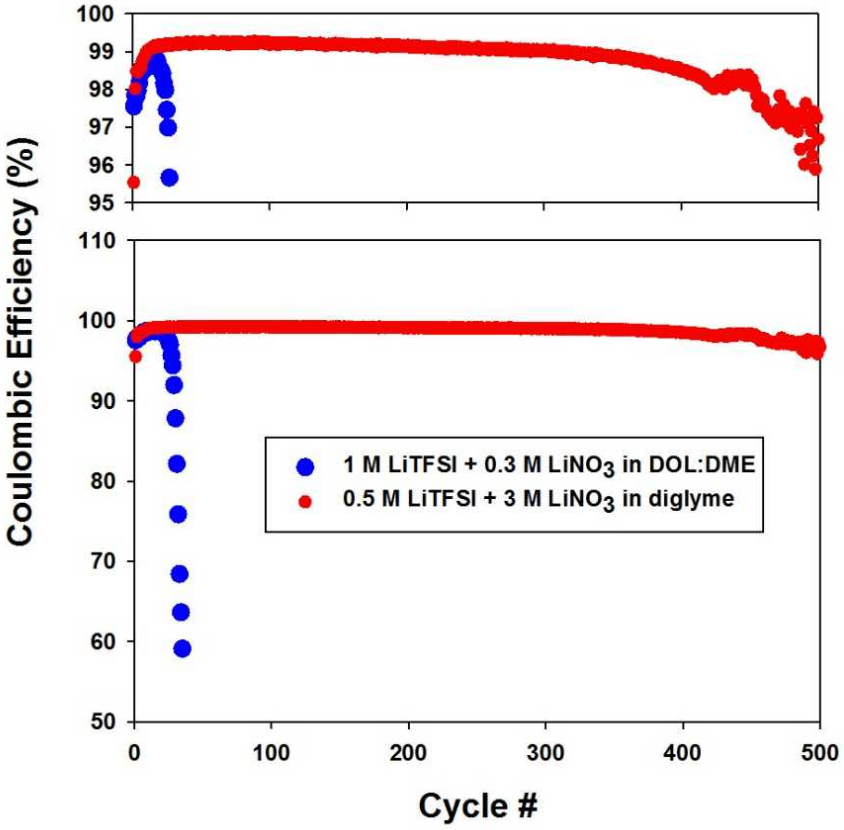


Novel electrolytes – high $LiNO_3$



Designing New Electrolytes

Comparison of Standard DOL:DME electrolyte to high concentration of $LiNO_3$ in diglyme electrolyte



- LiTFSI added as a co-salt in diglyme

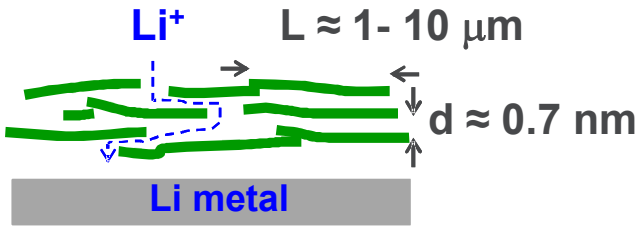
- 0.5 M LiTFSI + 3 M $LiNO_3$ in diglyme
- $LiNO_3$ acts as a sacrificial SEI-forming component
- LiTFSI provides good Li^+ transport for Li deposition and stripping
- >99.0% CE for ~200 cycles
- High CE maintained at >5 mAh/cm^2

B. Adams, J.-G. Zhang et al. in preparation

Protective Membranes from 2D Materials

New approach: Could we block solvent access to Li?
Create a single ion conducting membrane?

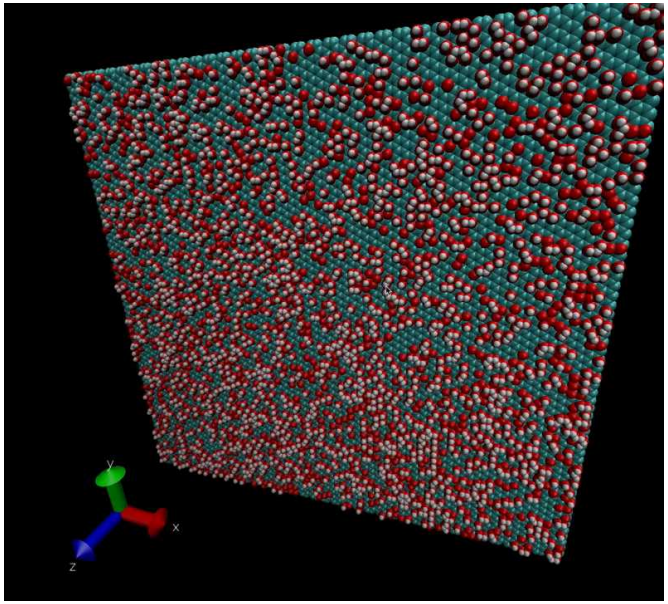
GO Membranes
- laminar assembly
- chemically functional
- compliant, flexible
- high shear modulus



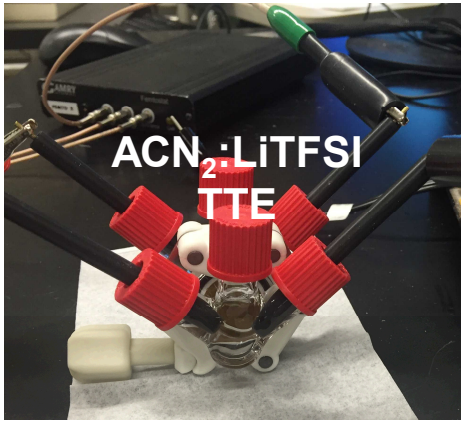
DFT & Classical MD

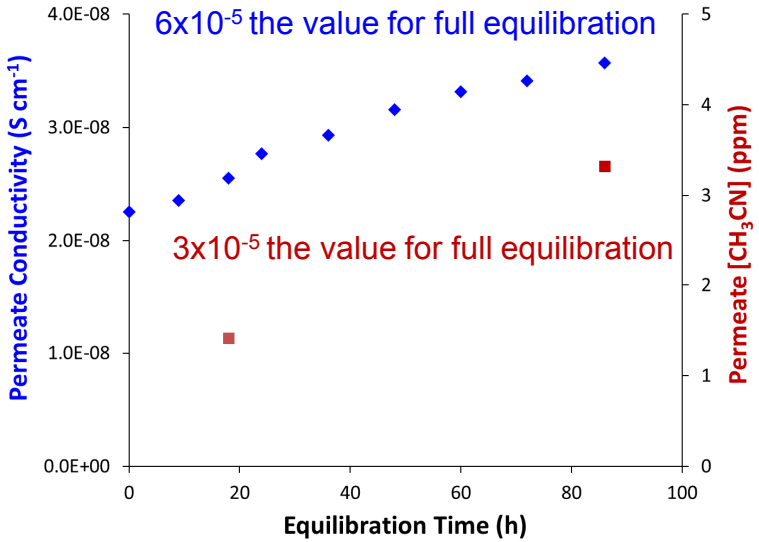
	C:O = 1.8	C:O = 2.7
Bulk Modulus (DFT)	40.7	39.9
Bulk Modulus (=B)	32.2	42.8
Shear Modulus (=G)	38.6	45.7
Young's Modulus (E)	82.7	101.1
Li Shear Modulus	~4	

N. Kumar, D. Siegel in preparation

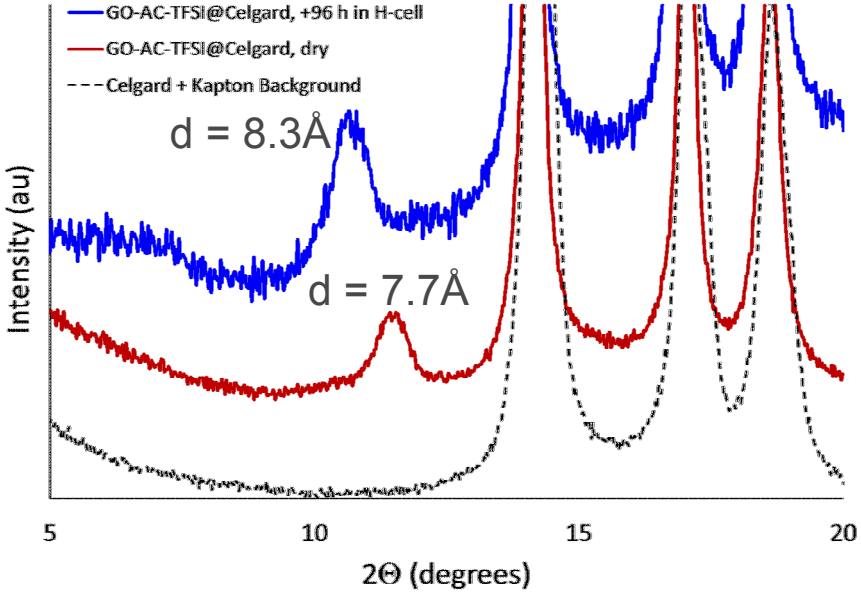


GO can be modified to reject solvent permeation





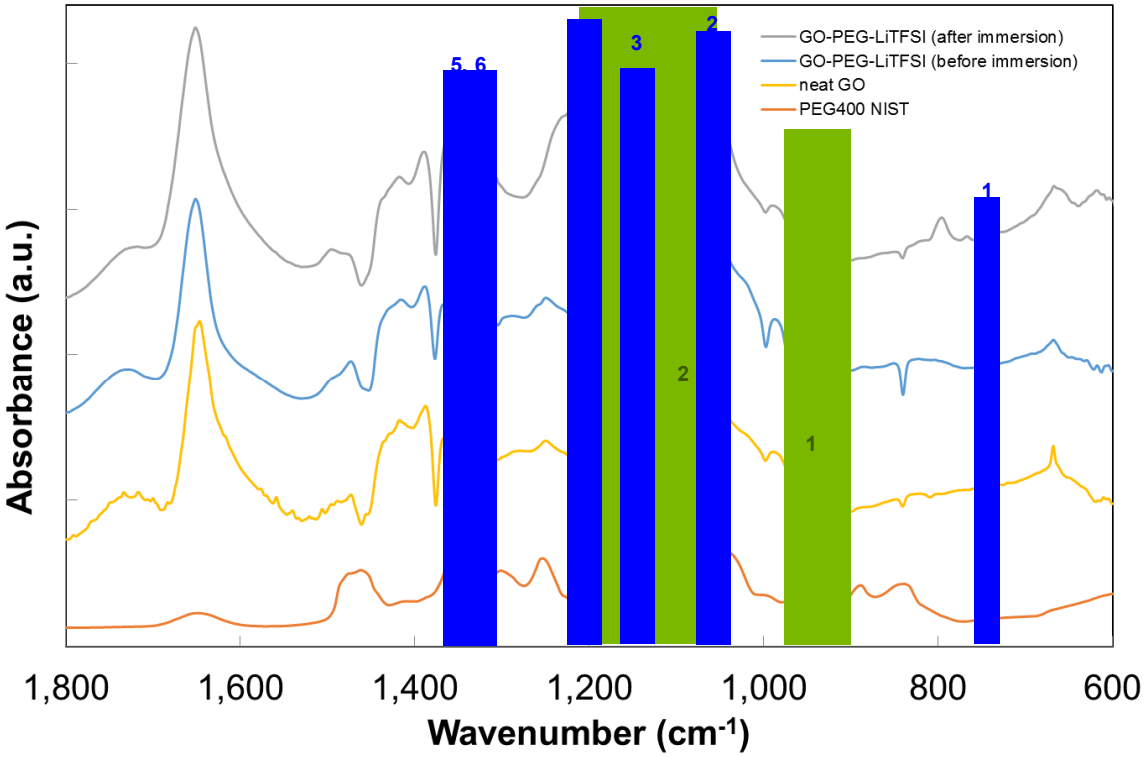
XRD from extracted membrane



- Slow permeation of ACN and LiTFSI through the membrane
- d spacing increase signals solvent uptake in the membrane

Salt infusion provides for ionic conductivity

LiTFSI infusion



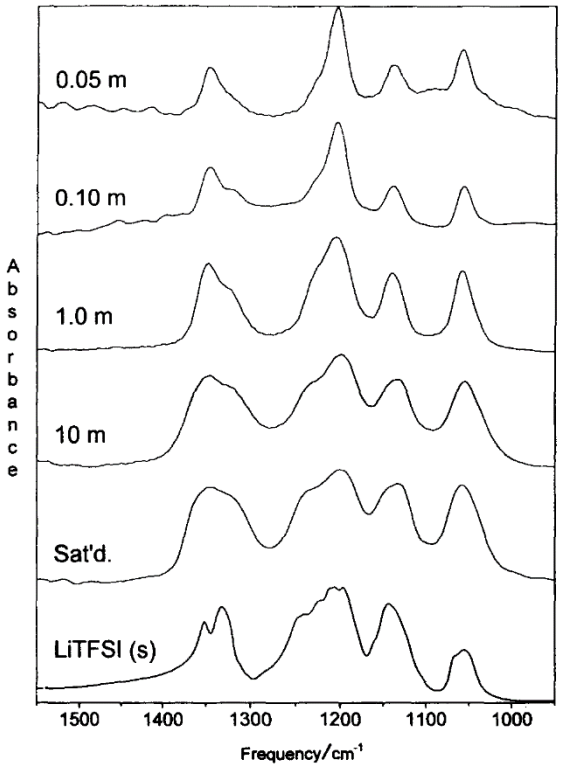


Fig. 8. FTIR absorption spectra of aqueous solutions of LiTFSI.

PEG signature C-O-C ether linkage identified by:

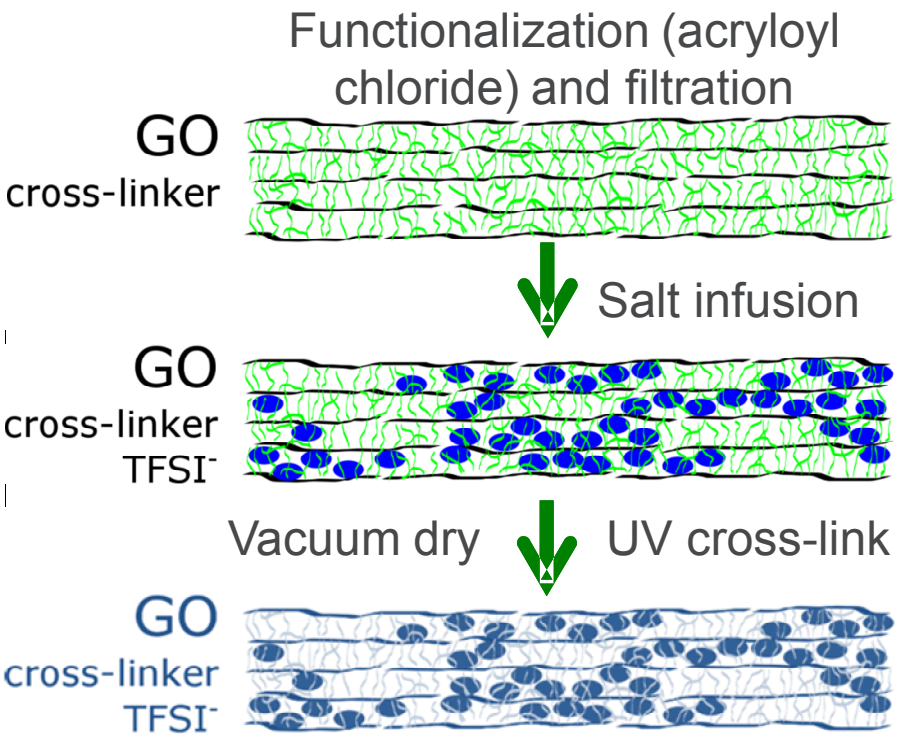
1. band at 950 cm^{-1}
2. broad band between 1,050-1,200 cm^{-1}

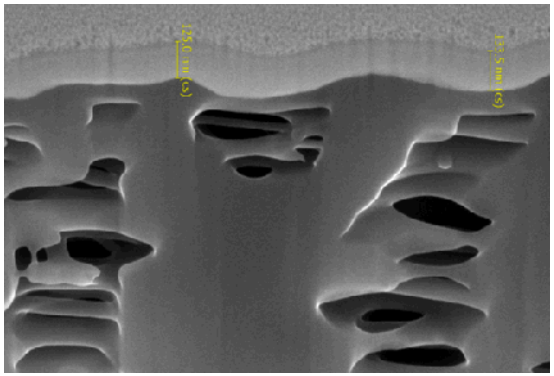
LiTFSI signature

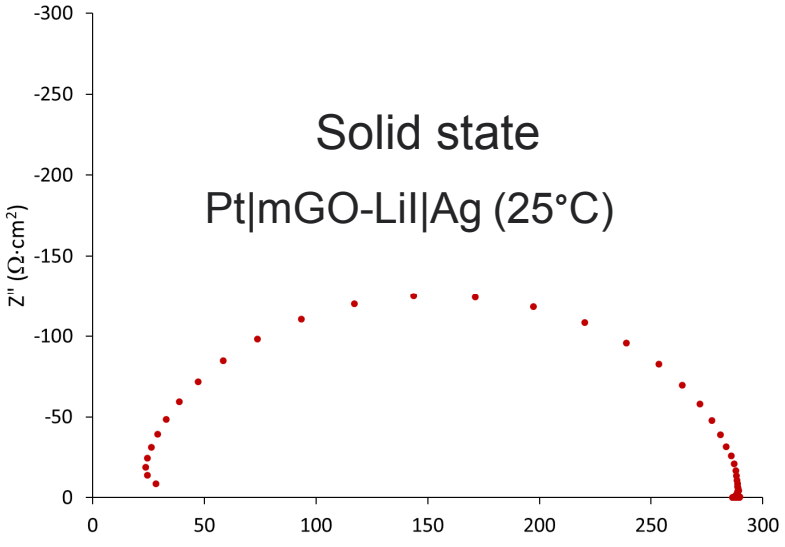
1. 750 cm^{-1} δCF_3 + νC-S + νS-N
2. 1051 cm^{-1} ν_{as}S-N-S
3. 1150 cm^{-1} C-SO_2-N (bonding)
4. 1192 cm^{-1} $\nu_s CF_3$
5. 1335 cm^{-1} C-SO_2-N (deformation)
6. 1364 cm^{-1} $\nu_{as}SO_2$

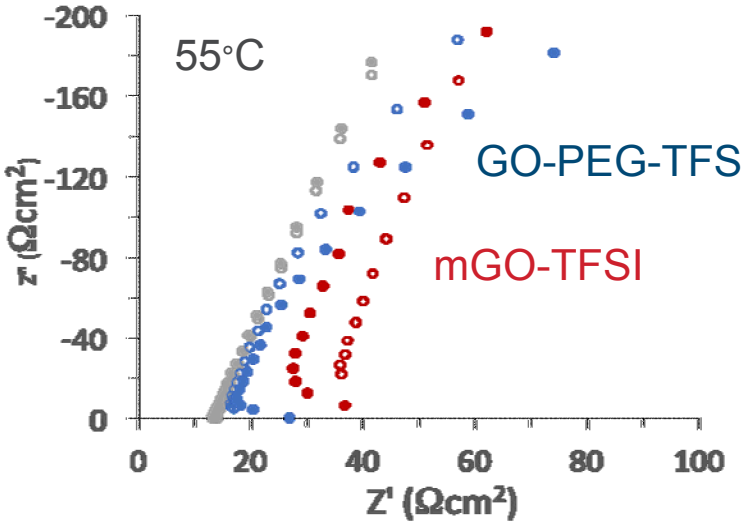
Salt is well dispersed within the intersheet spacing

GO can be modified to support Li^+ Ion conduction

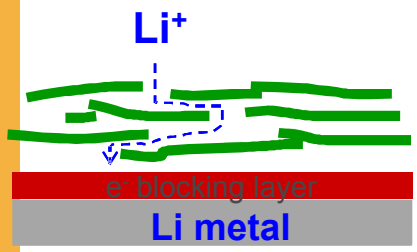


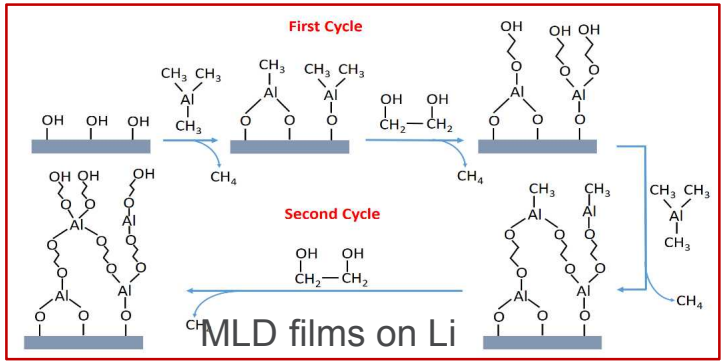


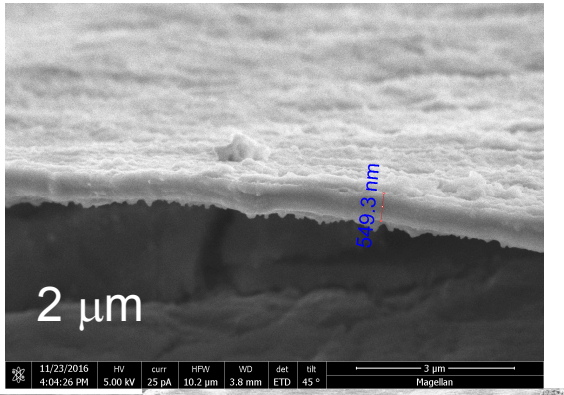


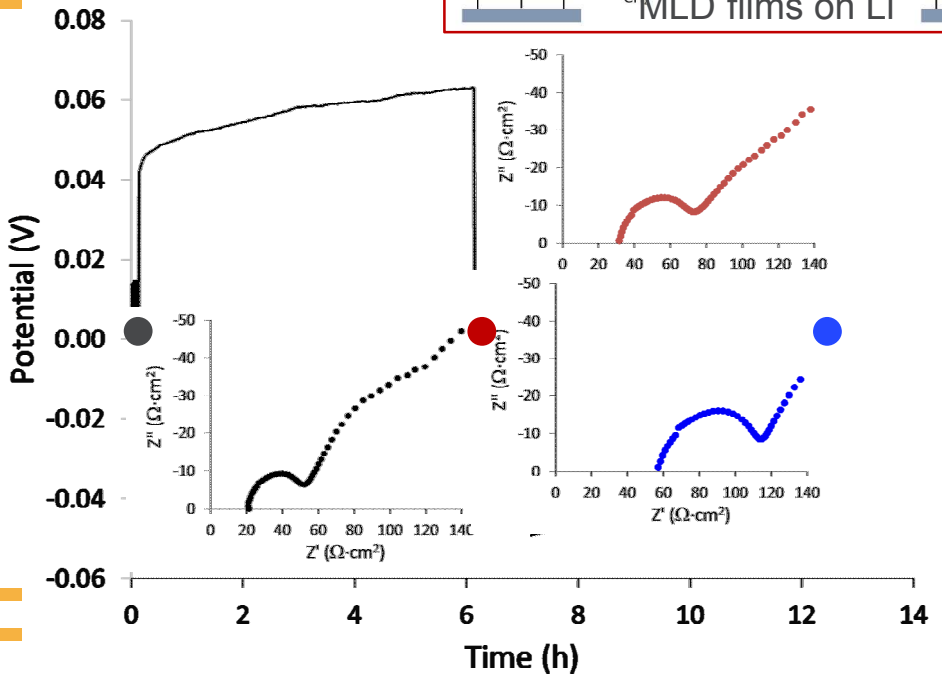


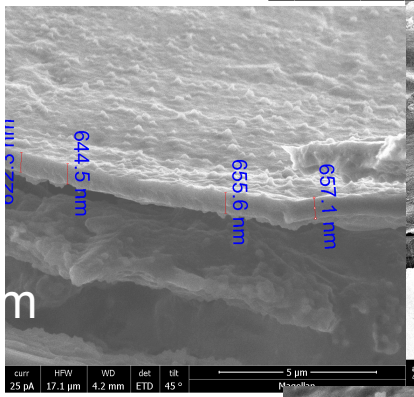
Li morphology is regulated by membrane

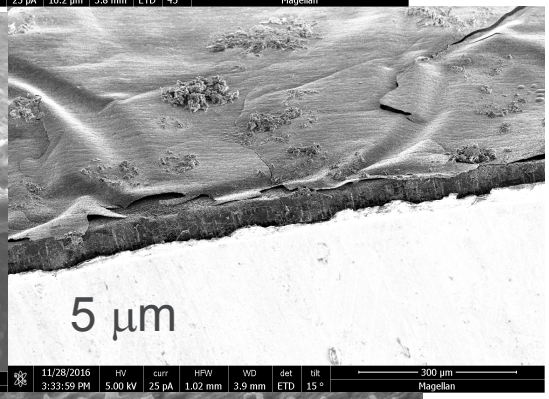


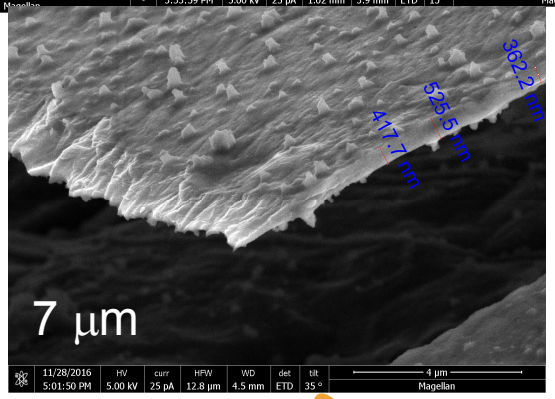












- Li forms a compact layer underneath the mGO
- Alternate barrier layers prevent mGO reduction

K. Klavetter et al. in preparation

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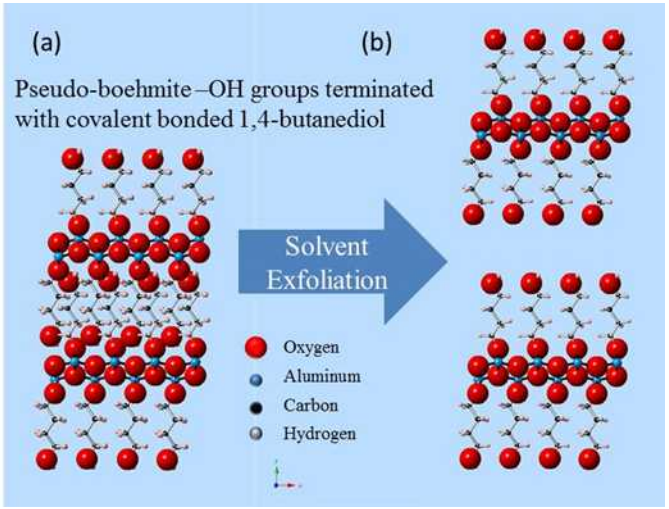
Boehmite as a Barrier Layer to Prevent GO Reduction

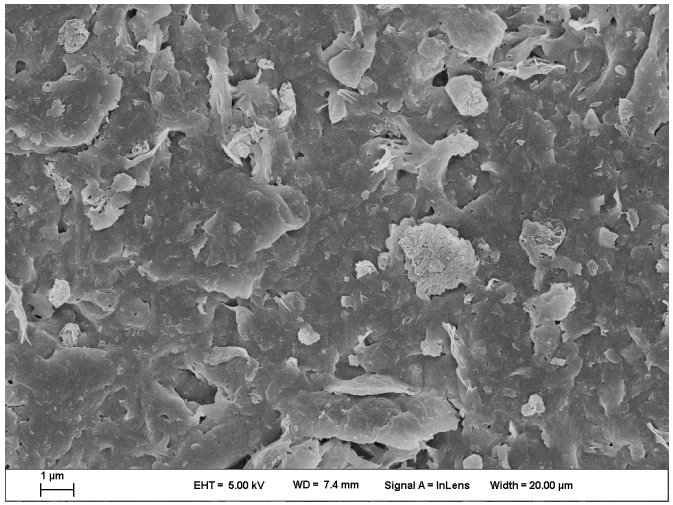


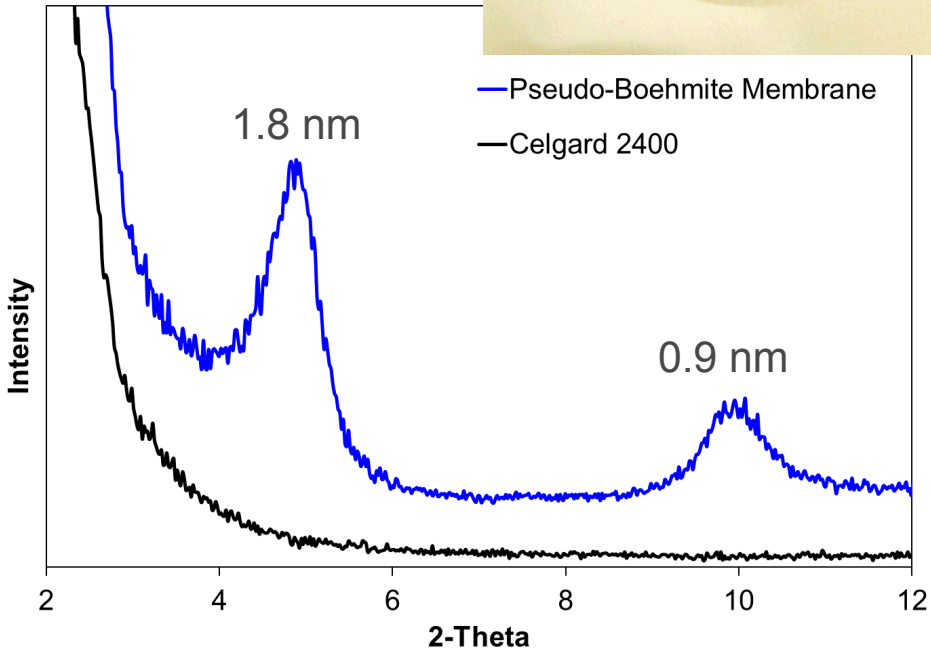
laminar membranes are formed via filtration

mGO

mAlOOLi

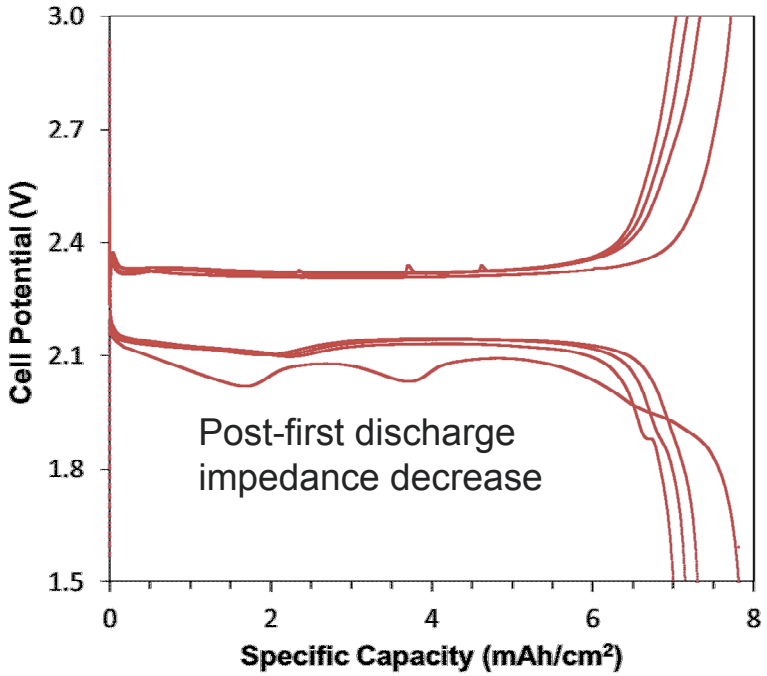
Li



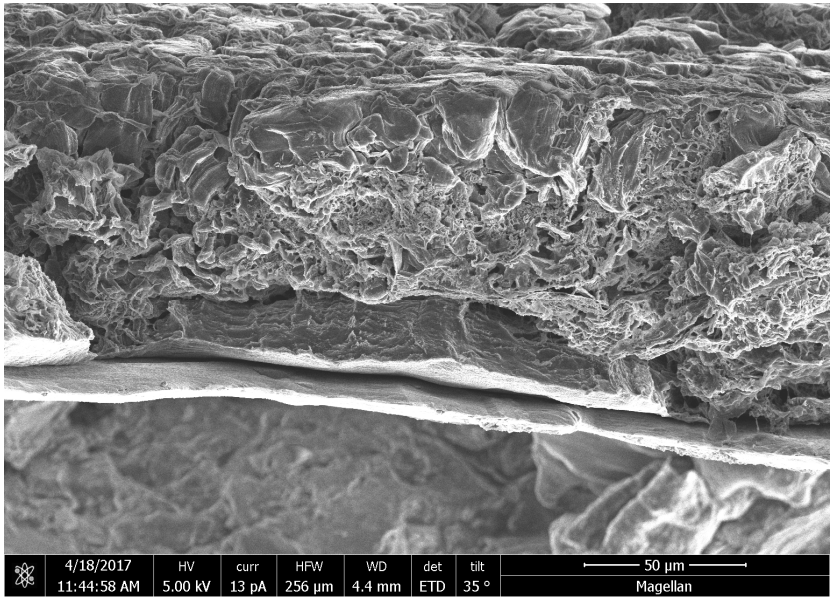


mGO Membranes Stabilized against Reduction

$MeCN_2$:LiTFSI-TTE, E/S 3 ml/g, C/10, 7 mA/cm^2, 0.7 mA/cm^2, 55^{o}C



No sign of Li deposition on membrane



Electrolyte penetrates membrane after first discharge
Morphology indicates liquid coupled
S, F, … are detected in EDS

Moving >30 mm per half cycle: assembly induced flaws or mechanical strain with displacement leads to failure

JCESR'S LI-S TEAM

L. Chen, C.W. Lee, K.C. Lau, M. Balasubramanian, K. Gallagher, L. Curtiss, X. Meng, L. Chen, J. Elam, Z. Zhang, S. Zhang, J. Connell, N. Markovic

Q. Pang, A. Shyamsunder, L.F. Nazar

J. Balachandran, D. Siegel, K. Wood, N. Dasgupta, A. Chadwick, R. Enrique, S. Dewitt, K. Thornton

A. Rojas, I. Villaluenga, N. Balsara, Y. Ji, V. Srinivas Gerber, L. Li, L. Ma, B. Helms

J. Chen, P. Han, Y. Shao, B. Adams, R. Cao, J. Zhang, V. Murugesan, K. Mueller, K.S. Han, J. Liu

C. Zu, G. Zhou, Y. Cui, E. Miller, M. Toney

F. Fan, Y.M. Chiang

H.L. Wu, M. Shin, K. See, A. Gewirth

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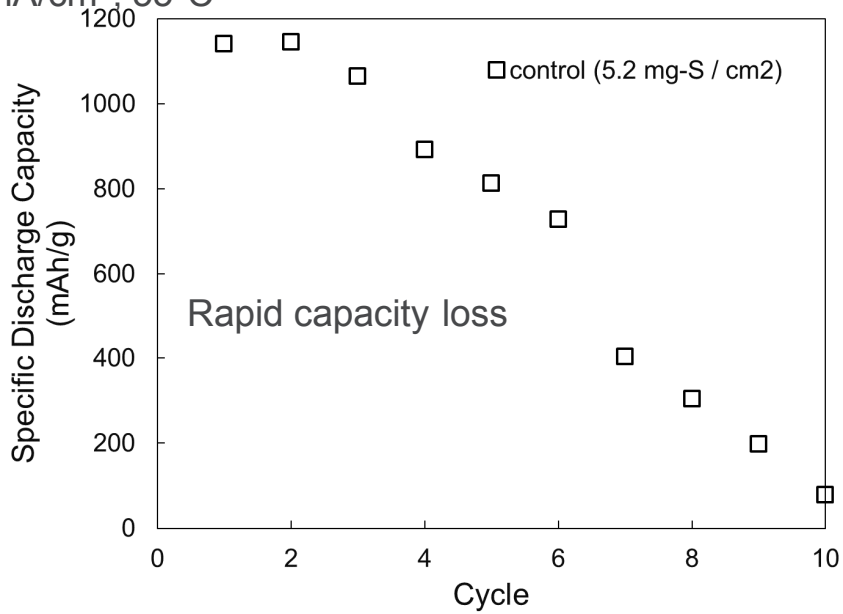
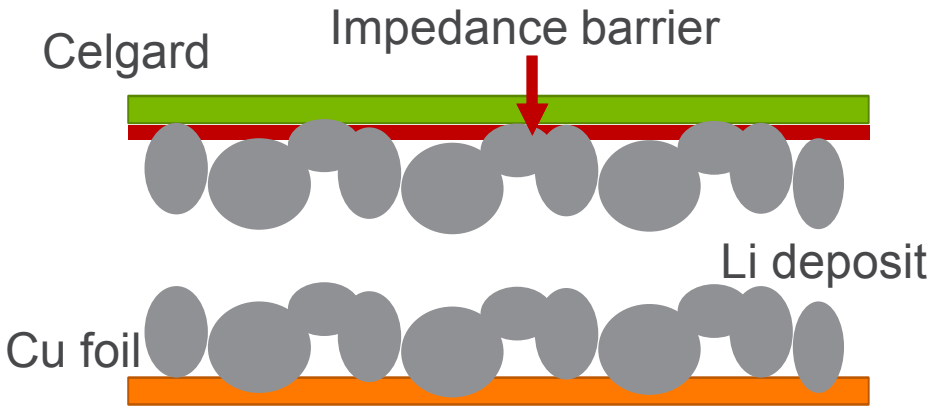
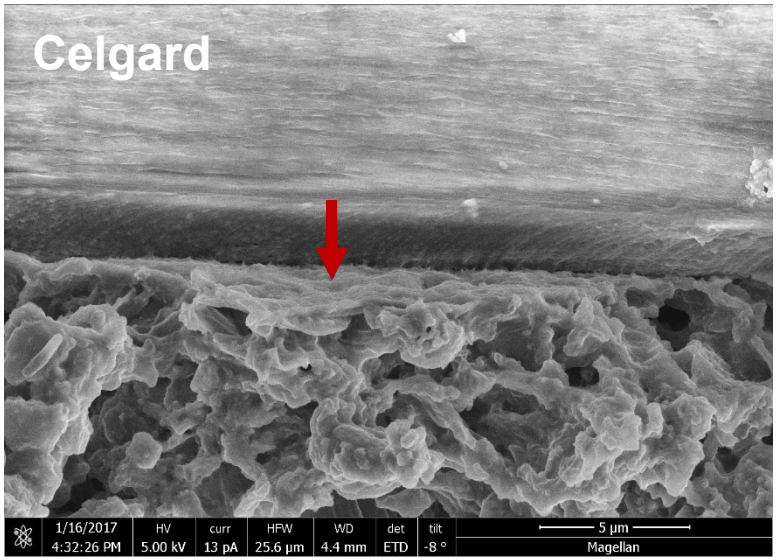
Questions?

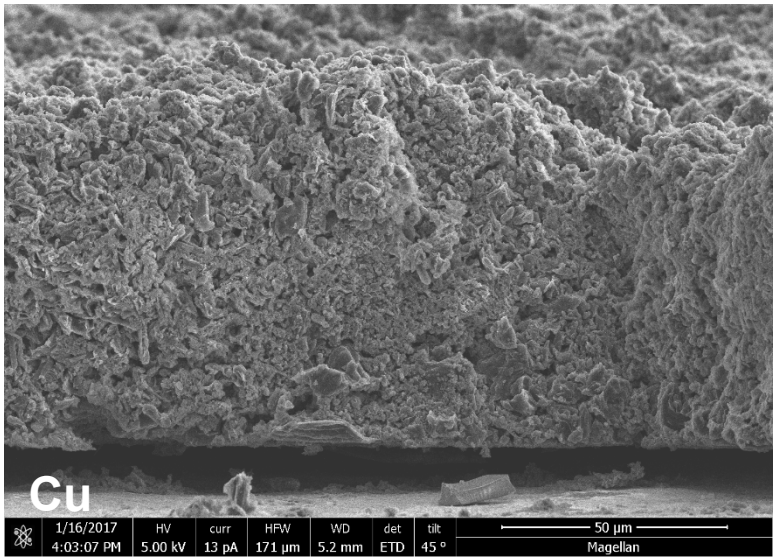
Early Stage Failure Modes at Moderate Rate and Low E/S

$MeCN_2$:LiTFSI-TTE, E/S 3 ml/g, C/10, 5 mAh/cm^2, 0.4 mA/cm^2, 55°C









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