SAND2016-1110C

JCESR | JOINT CENTER FOR ENERGY STORAGE RESEARCH

Overcoming Key Challenges for a Viable Lithium-Sulfur Transportation Battery

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Sandia National Laboratories

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Li-S is a promising transportation storage technology

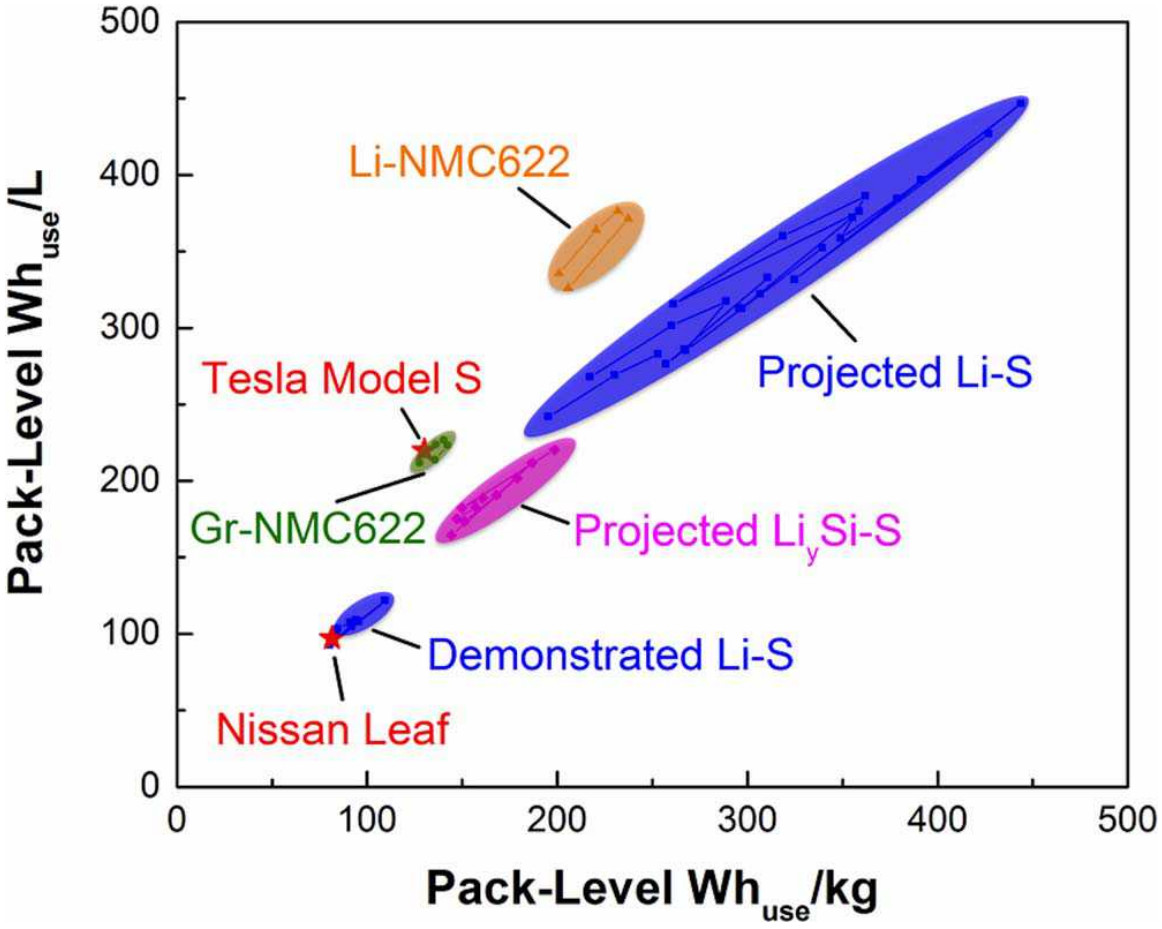
Li-S Theoretical Values

2.1 V

1675 mAh/g_S

2600 Wh/kg

Sulfur is a low cost material

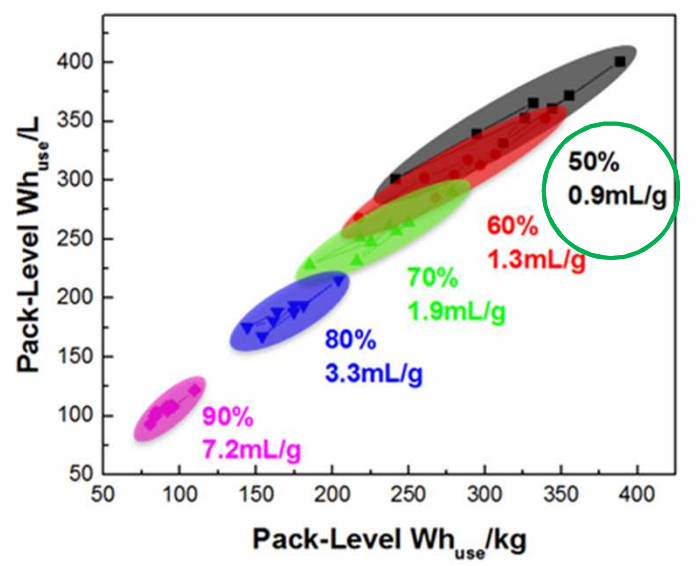


D. Eroglu et. al., *J. Electrochem. Soc.* 2015 10.1149/2.0611506jes

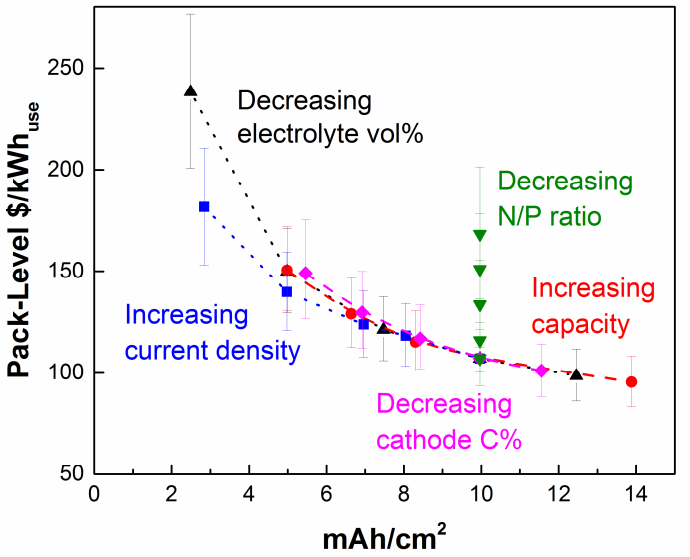
The Road to a 400 Wh/L - $100/kWh Li-S Battery has Barriers

TE modeling provides guidance on setting priorities

1. Reduce the electrolyte volume – S redox chemistry in a lean electrolyte



2. Reduce excess Li – protect the Li metal anode

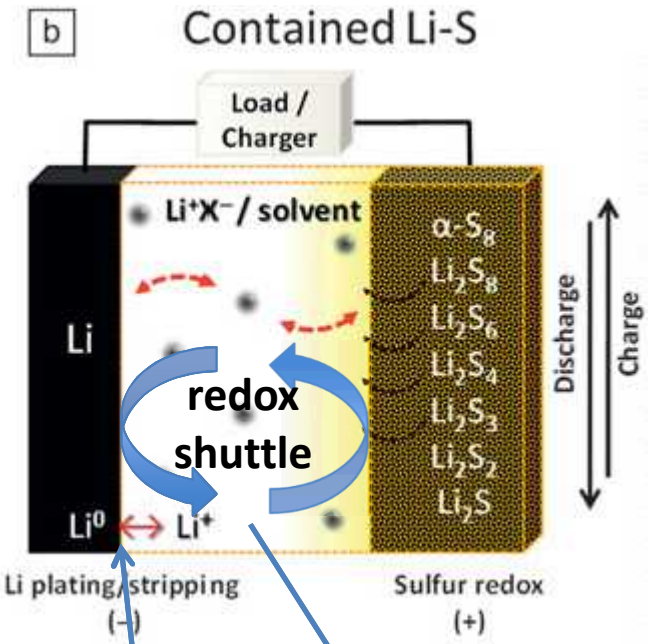


Excess electrolyte and reserve Li metal:

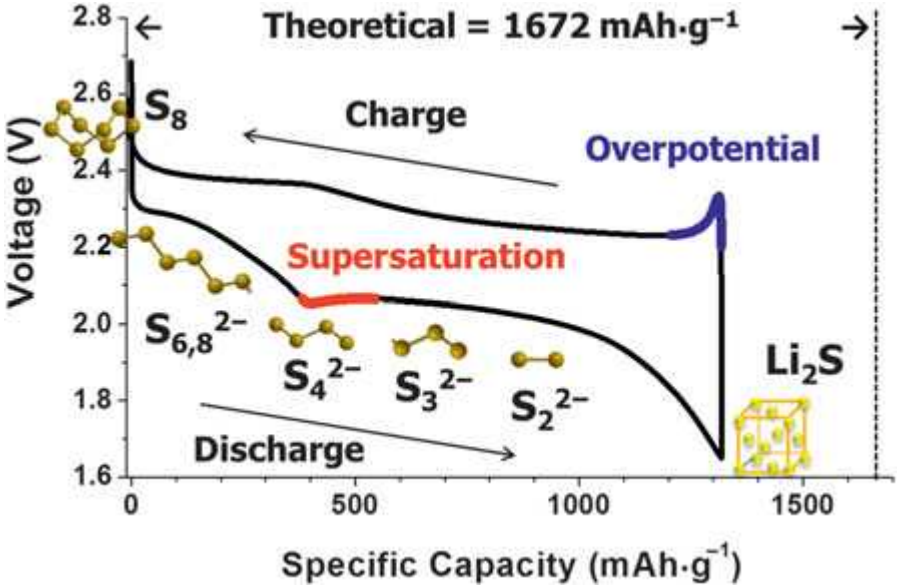
- reduce energy density
- increase cost
- create lost chemical inventory – solubility of polysulfides

D. Eroglu et. al., *J. Electrochem. Soc.* 2015 10.1149/2.0611506jes

Managing inventory to eliminate excess

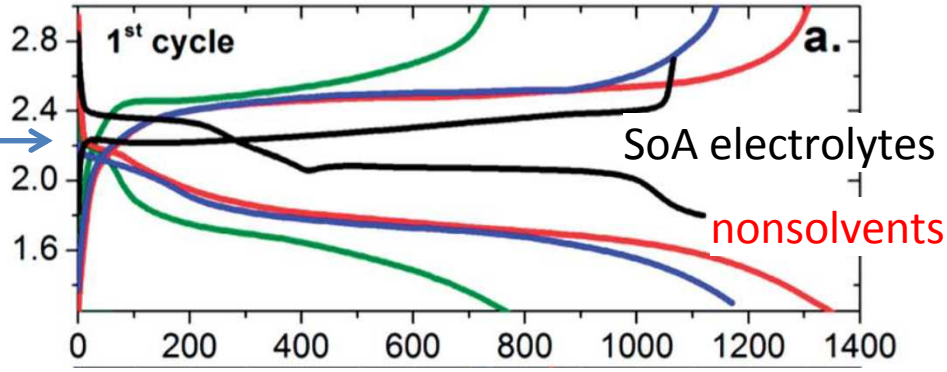


L. Nazar et al. MRS Bulletin 2014



control Li inventory

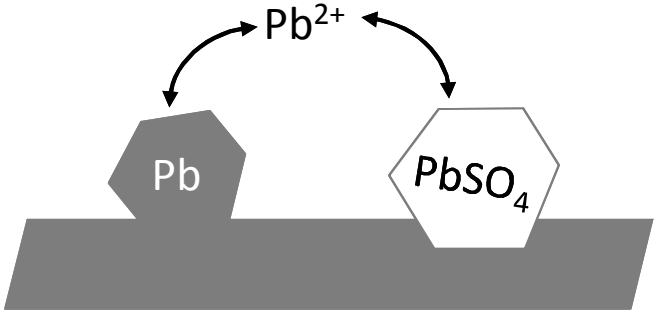
contain through solubility control

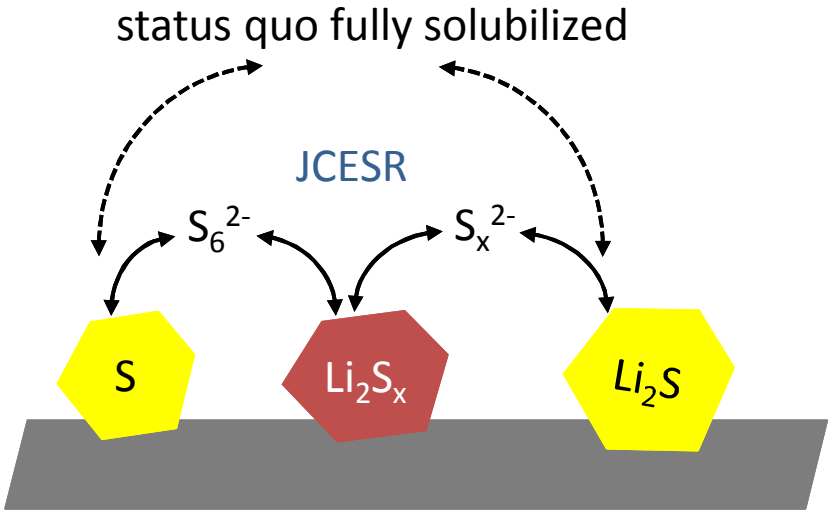


M. Cuisinier et al. Energy Environ Sci 2014

Managing Solubility is Key to a Successful Dissolution/Precipitation Battery

System	Key Attribute	Solubility
commercial Lead Acid	Pb_2SO_4(s) retention	2 – 4 mg/L
Li-S (DOL:DME)	Li_2S_8 solvation (shuttle)	135 g/L (0.5 M)
Li-S new electrolyte	Li_2S_8 retention	sparingly soluble



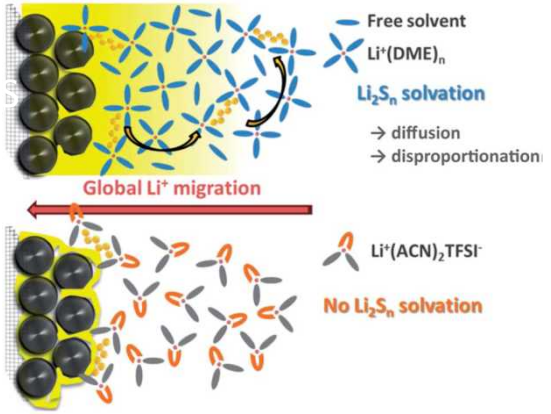


mechanisms of state change

Strategies to Manage Solubility & Enable Performance

- Electrolyte design

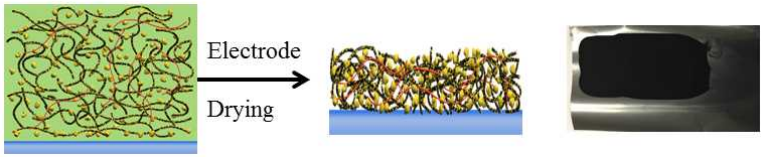
  guide efficient redox processes
  Anions and co-solvents
  solvate IL's



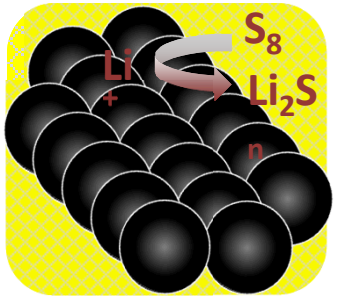
M. Cuisinier et al. Energy Environ Sci 2014

- Architecture development coupled with materials chemistry – multifunctional binder

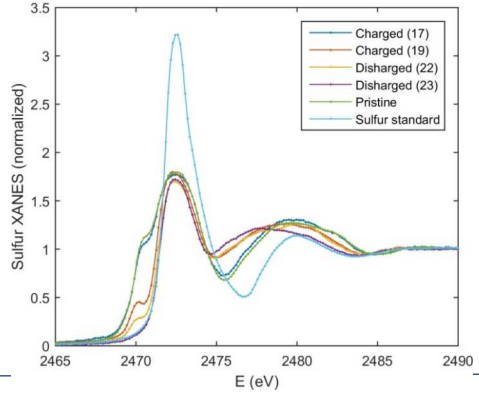
  better way to design a cathode



  porosity, tortuosity, surface wetting control
  increased S electrochemical surface area



binder as an encapsulant and polymer electrolyte

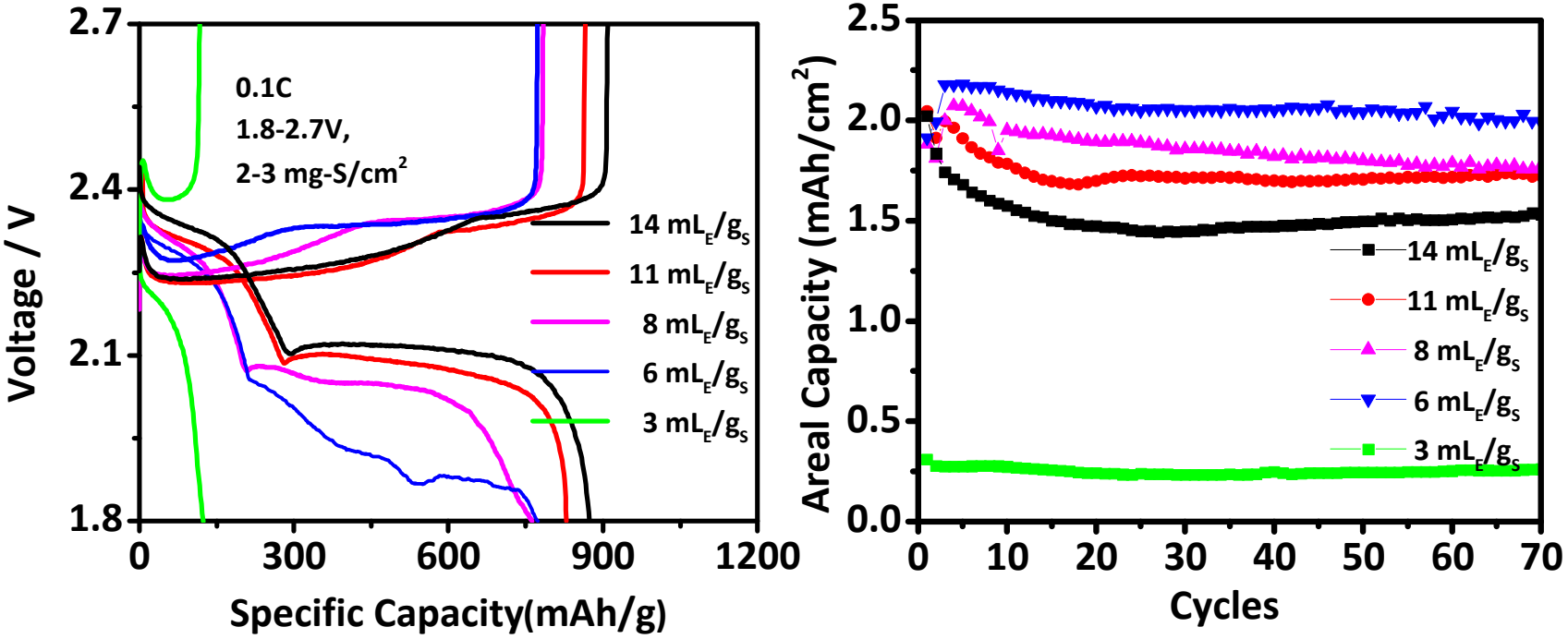


- Knowledge of redox pathways under lean conditions

  discharge product distributions
  methods of electron access

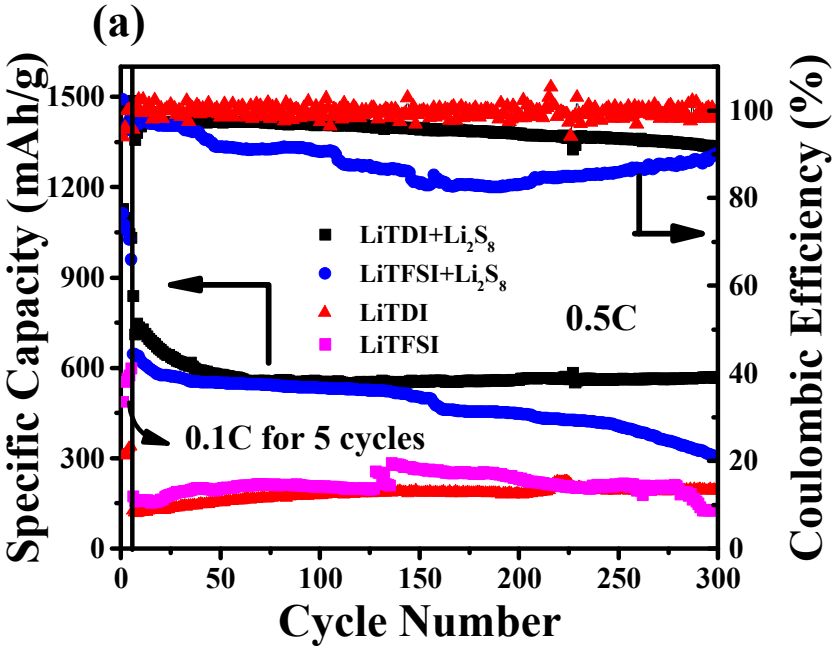
Conventional Materials cannot Support Sufficient Sulfur Activity under Lean Conditions

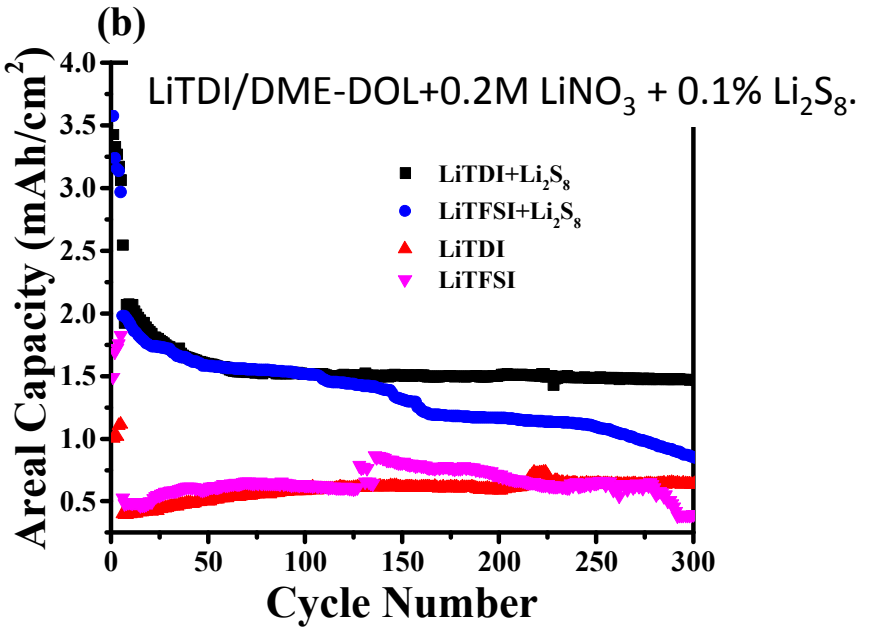
1.0M LiTFSI/DME-DOL+0.2M $LiNO_3$, C/10 rate



Driving to the lean limit: capacity loss and cell polarization

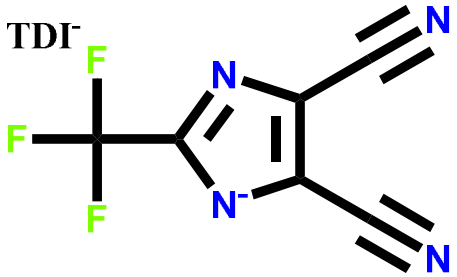
Start with Electrolyte: Control Polysulfide Solubility



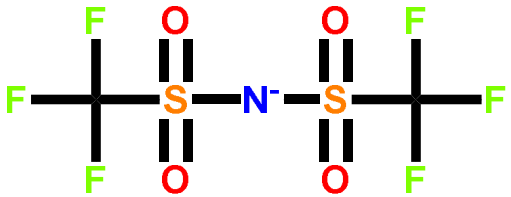


Electrolyte	Conductivity (σ) mS cm^{-1}	viscosity (η) cP	Maximum Li_2S_8 solubility
1M LiTFSI	10.8	1.35	~0.5M
1M LiTDI	6.19	1.31	0.084M

TDI$^-$



TFSI$^-$



- Polysulfide solubility can be tuned by changing lithium salt
- LiTDI decrease s polysulfide solubility, increase cyclability

J. Chen et al. Chem Comm 2015 submitted

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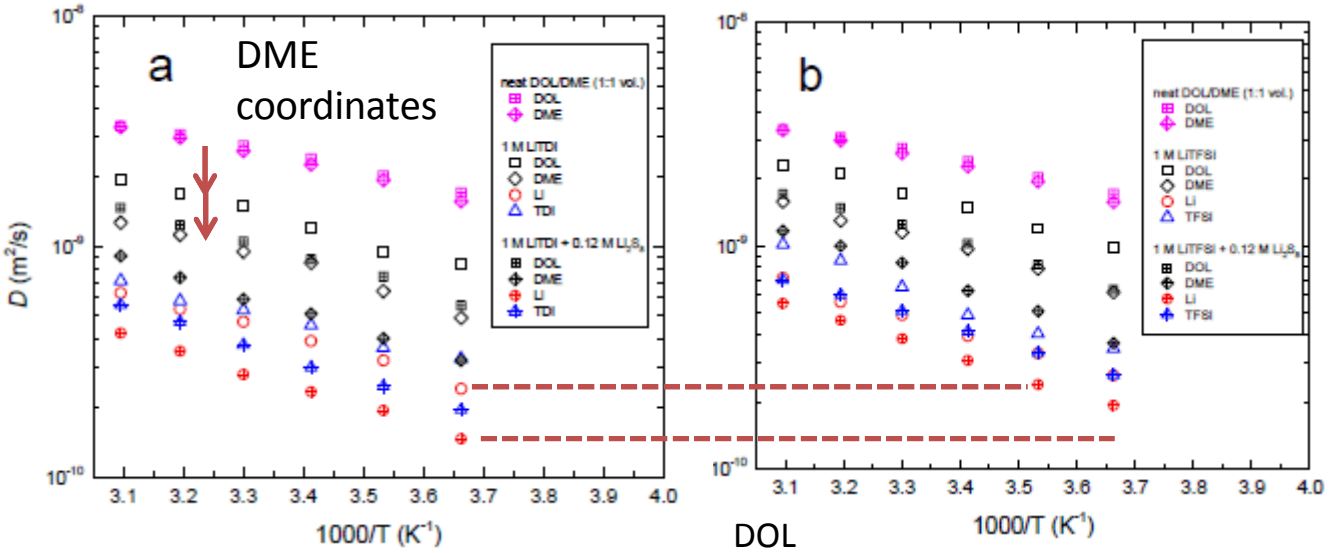
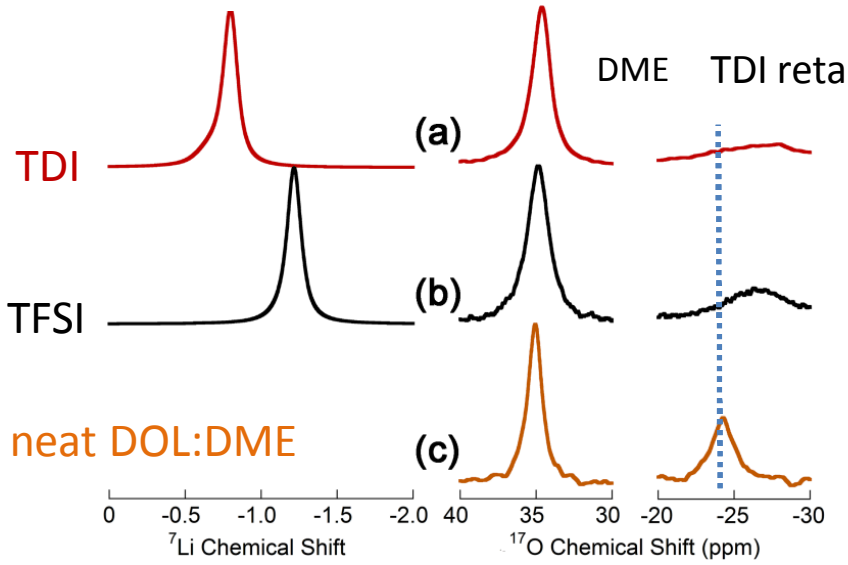
Insights from NMR on Cation and Solvent Coordination



hydrodynamic radius – markedly larger for TDI with Li_2S_8 present

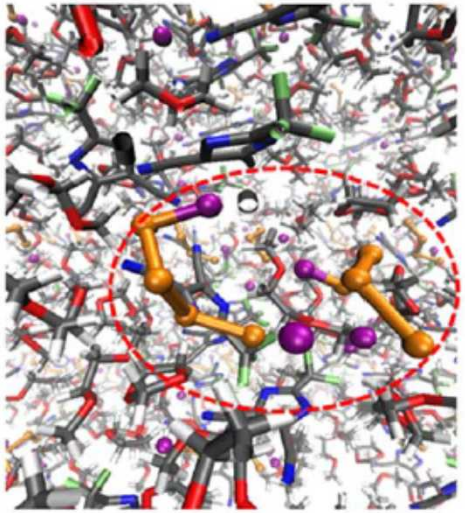


TDI retards both Li and solvent mobility

TDI anion affects Li^+ solvation – impacts solvate structure

J. Chen et al. Chem Comm 2015 submitted

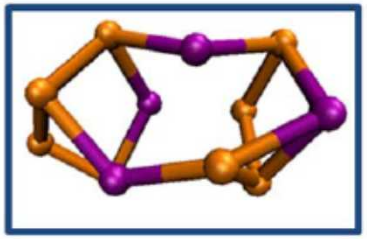
Anion Impacts Disproportionation Reaction



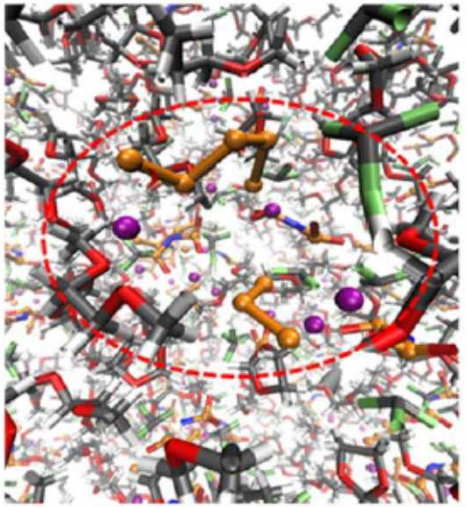
TDI

$Li_2S_8 + 2Li \rightarrow 2\ Li_2S_4$

$(\Delta G_{sol} \sim -6.30\ eV)$



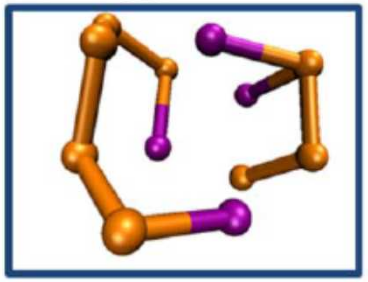
"Li_4S_8-like" agglomerate



TFSI

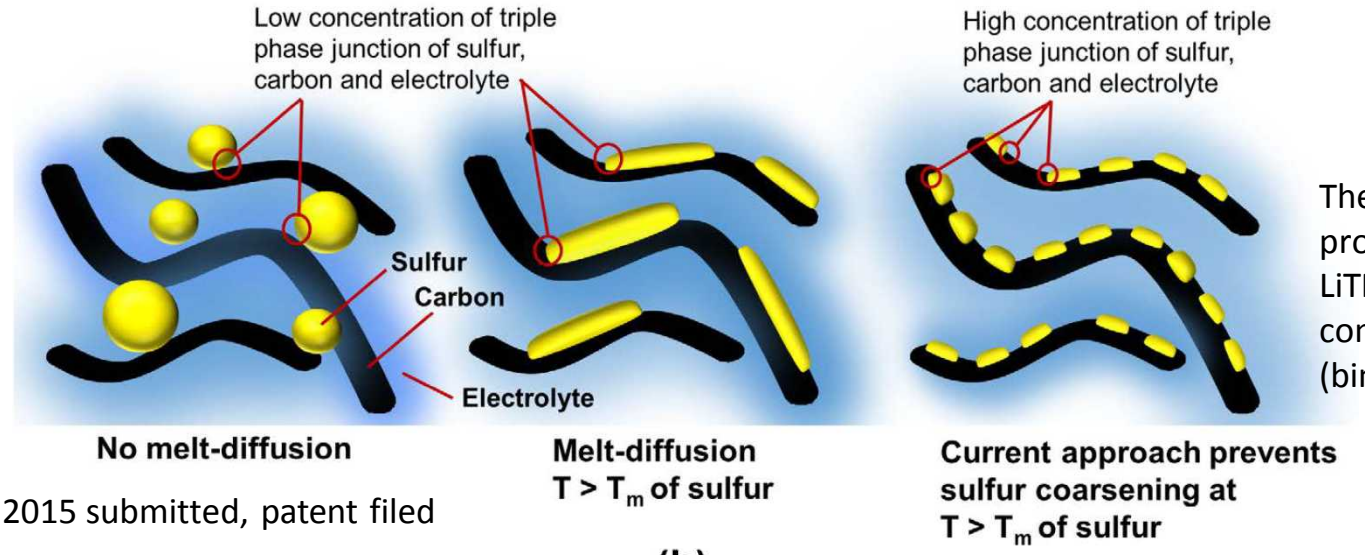
$Li_2S_8 + 2Li \rightarrow Li_2S_3 + Li_2S_5$

$(\Delta G_{sol} \sim -5.78\ eV)$



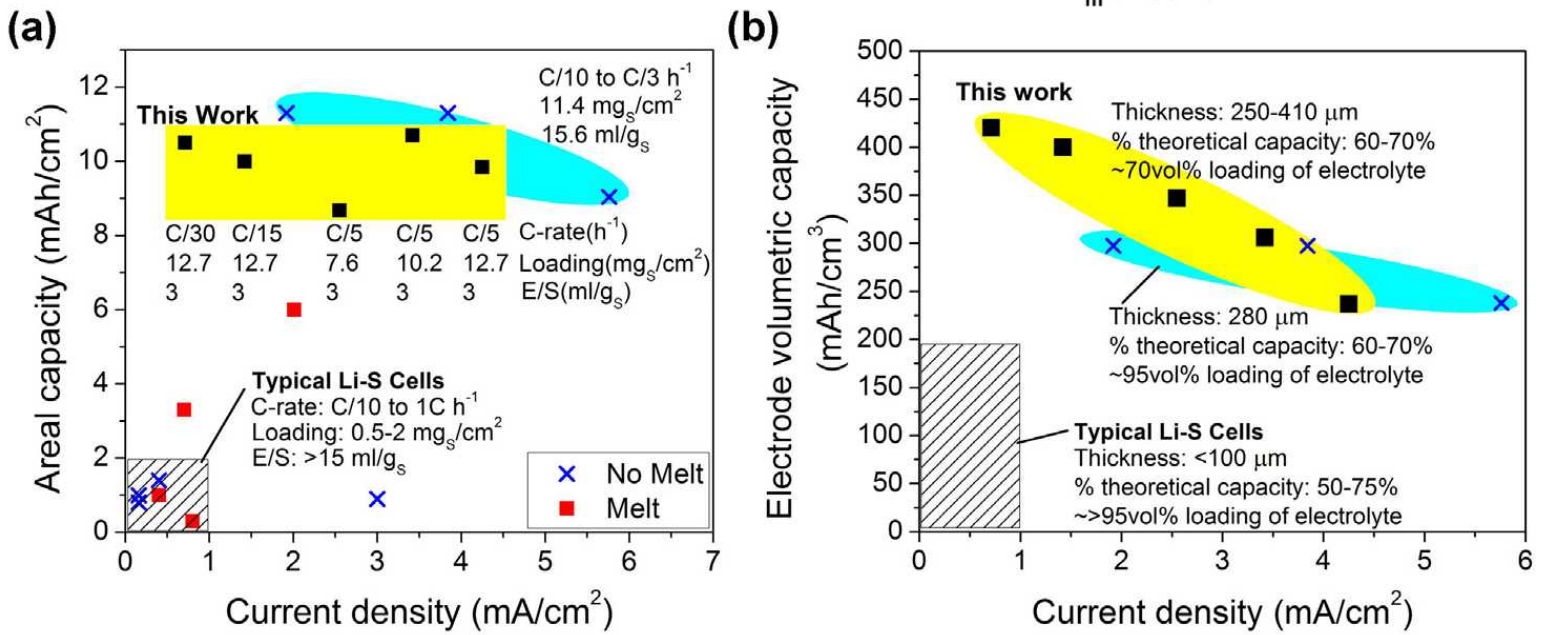
Agglomerate consistent with decreased Li^+ mobility and pS solubility

Lean Electrolyte Requires Attention to Sulfur Distribution



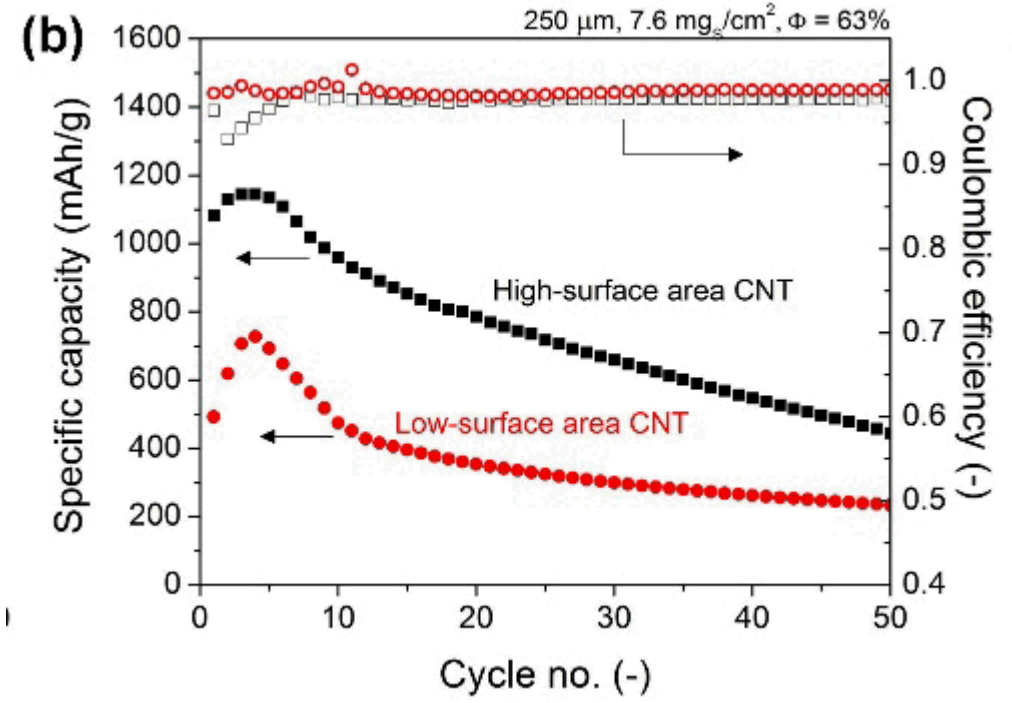
Thermal processing of S, LiTFSI and CNT composits (binder free)

X. Chen et al. 2015 submitted, patent filed



X. Chen et al. A03-0334 Thursday 15:10

Increased S Electrochemical Surface Area Enhances Performance

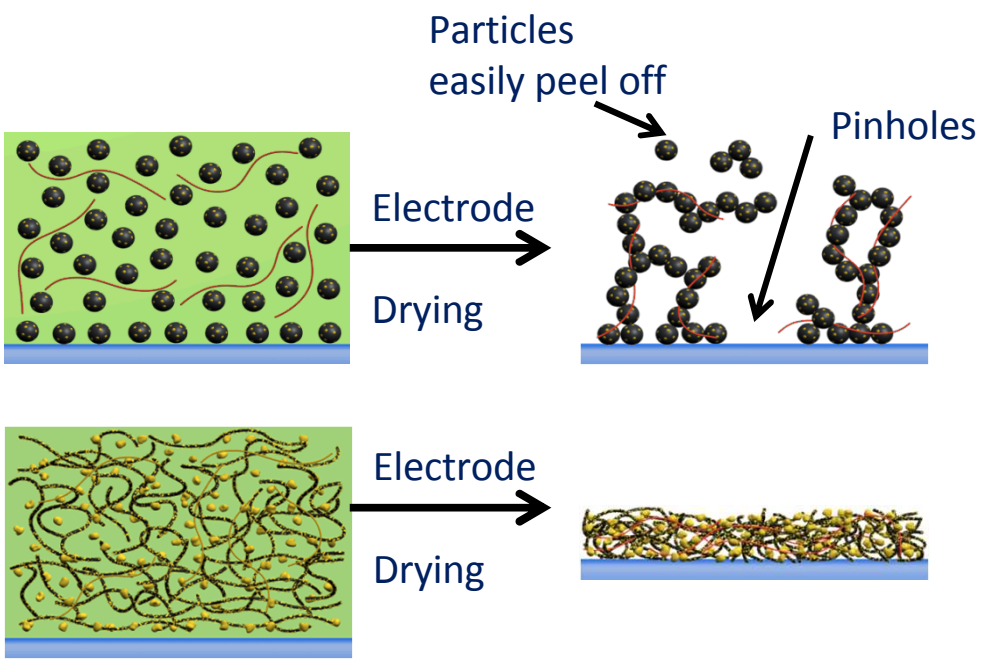


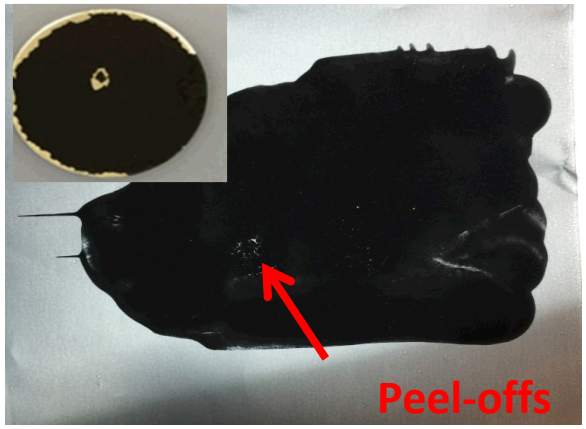
Functional 8 mAh/cm^2 cathode cycled at 2.6 mA/cm^2 (C/5), E/S = 3 ml/g$_S$

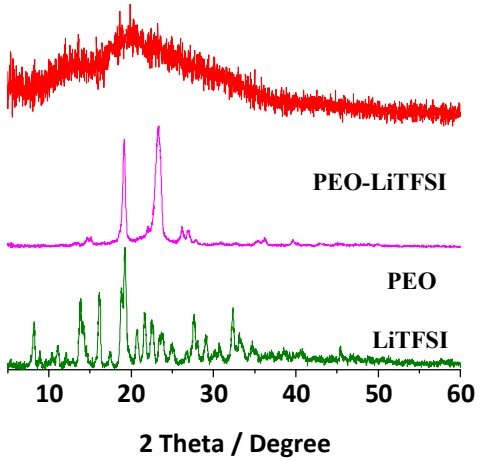
- cathode structure is critical - cathode wetting and electrolyte penetration
- capacity fade (1 M LiTFSI DOL:DME, 0.2 M $LiNO_3$

X. Chen et al. A03-0334 Thursday 15:10

Developing Cathode Structures to Access Greater Capacity

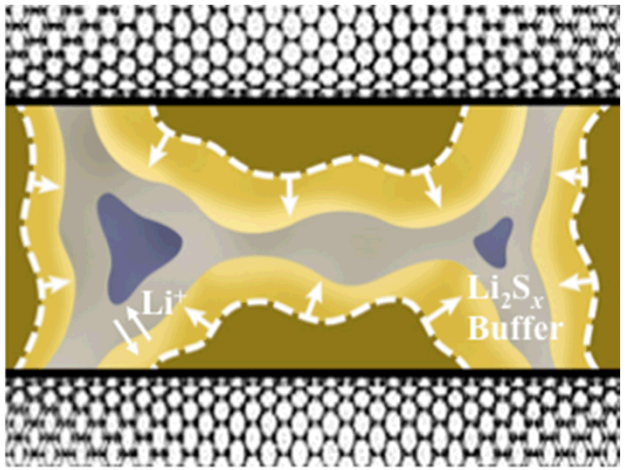




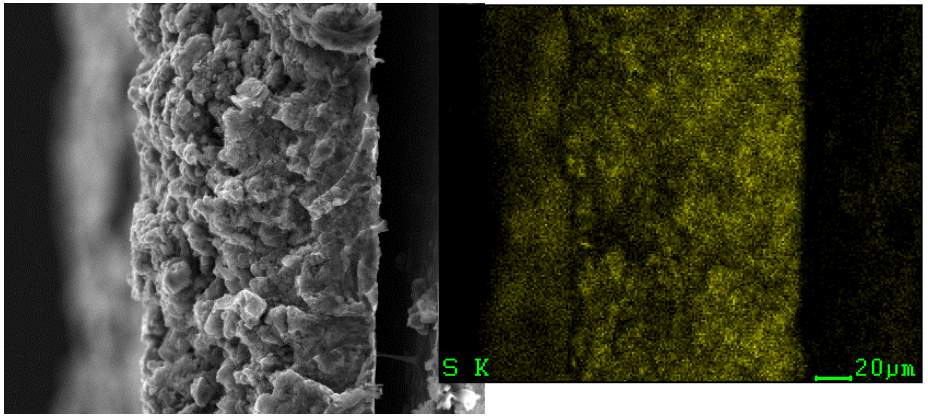


- More dense, uniform electrode coating
- Amorphous stage of PEO revealed a strong binding ability

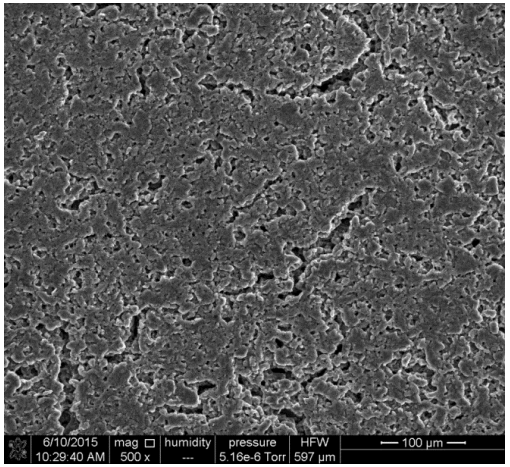
$PEO_6LiTFSI$ Binder Serves as Local Electrolyte - Reducing Polysulfide Transport



$PEO_6LiTFSI$ – sulfur distributed throughout



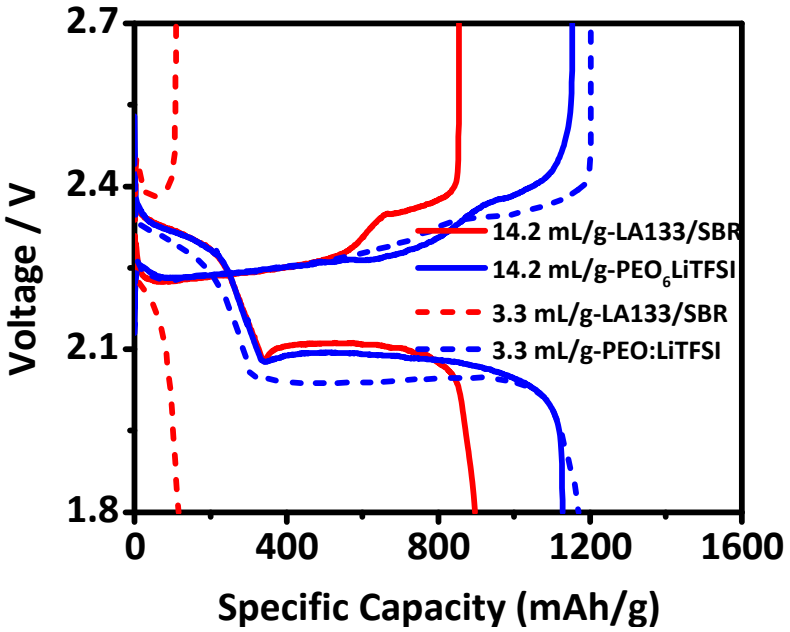
$PEO_6LiTFSI$ swells and maintains structure with cycling

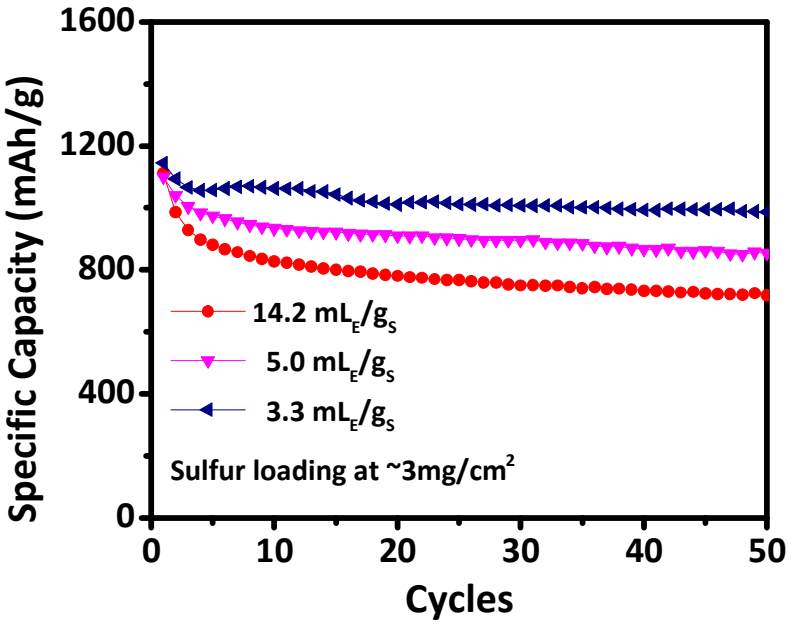


- Encapsulating binder forms a Li^+ conductive network – reducing the amount of liquid electrolyte required in the cathode
- Decreased polysulfide transport with this polymer electrolyte results in retention

State of the art E:S ratios achieved with multifunctional binder

$PEO_6LiTFSI$ electrode, 1.0M LiTFSI/DME-DOL+0.2M $LiNO_3$, C/10 rate

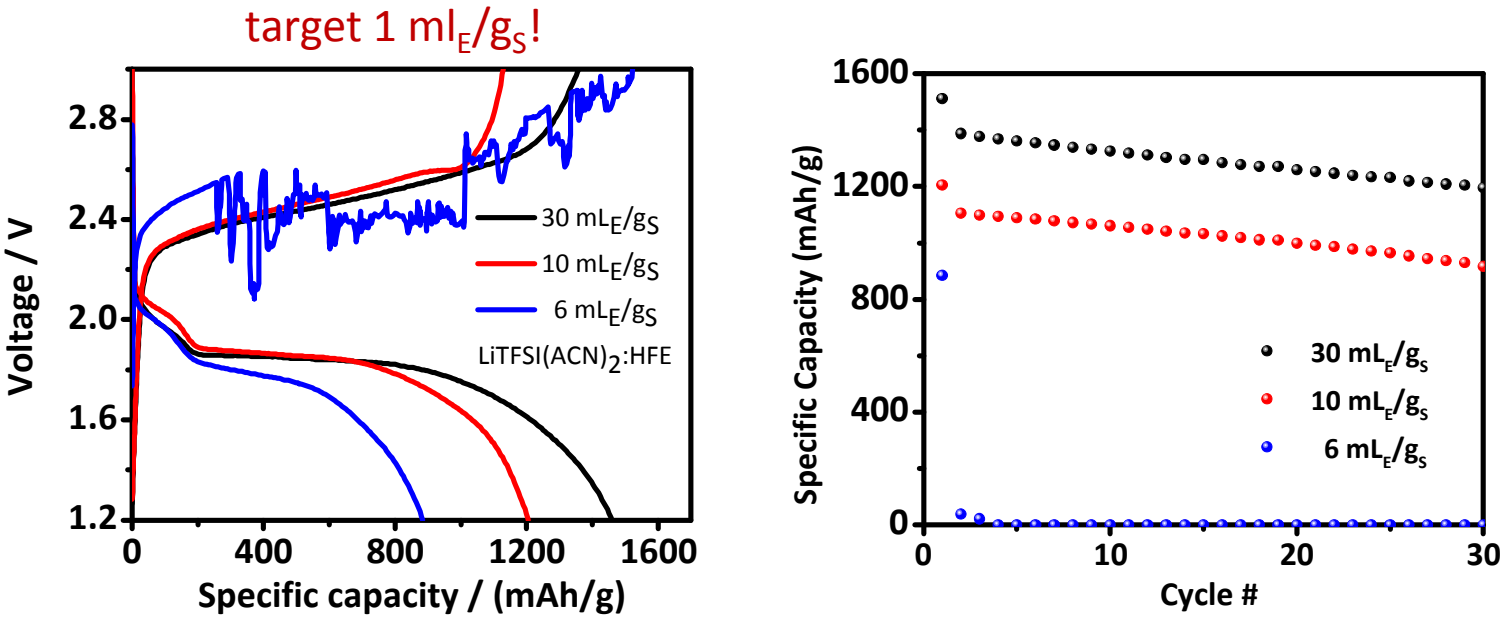




3.3 mL_E/g_S is demonstrated; improvement over 5 mL_E/g_S (state of art)

Not good enough, we need to tailor electrolyte

Sparingly Solvating Electrolytes Exhibit a Limited Activity

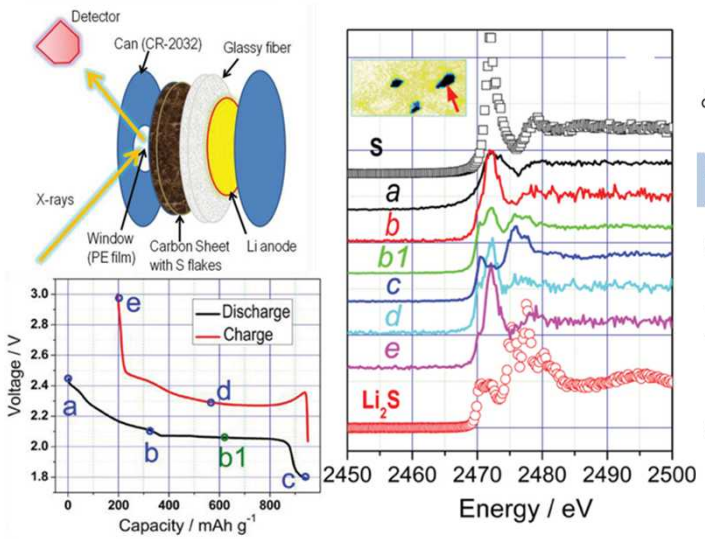


reduced capacity on discharge, increased polarization on charge, instability and cell failure occurs on recharge

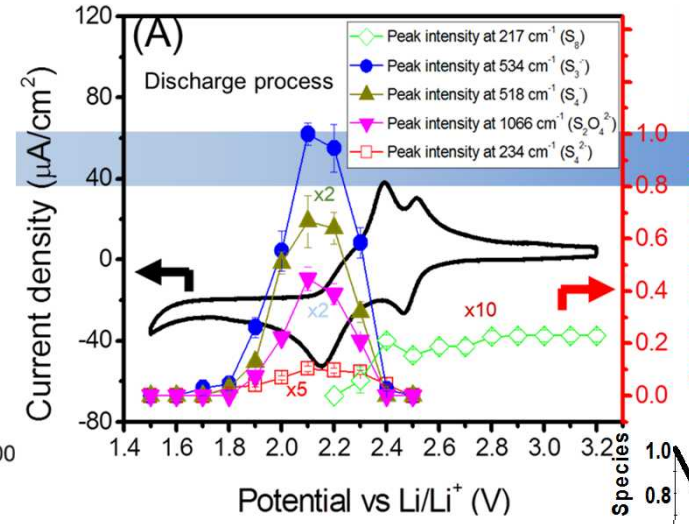
Insight into how the electrolyte functions in this lean limit is required

Understanding Sulfur Redox Chemistry in the Lean Limit

Need to understand how speciation changes in the lean limit



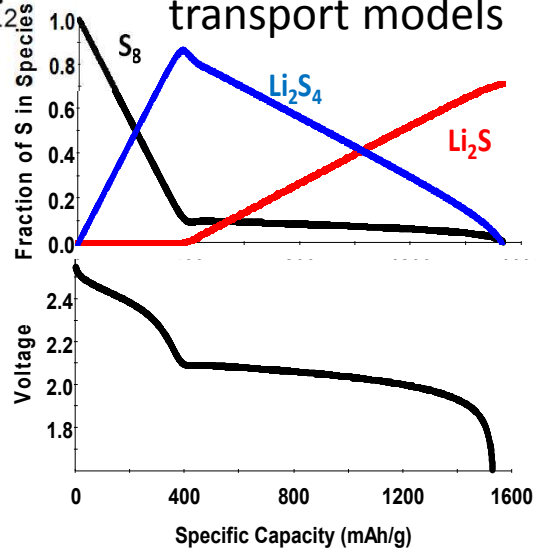
X. Yu, et al. Adv. Energy. Mater. 2015, DOI: 10.1002/aenm.201500072



H.-L. Wu et al., ACS Appl. Mater. Interfaces 2015, 7, 1709−1719

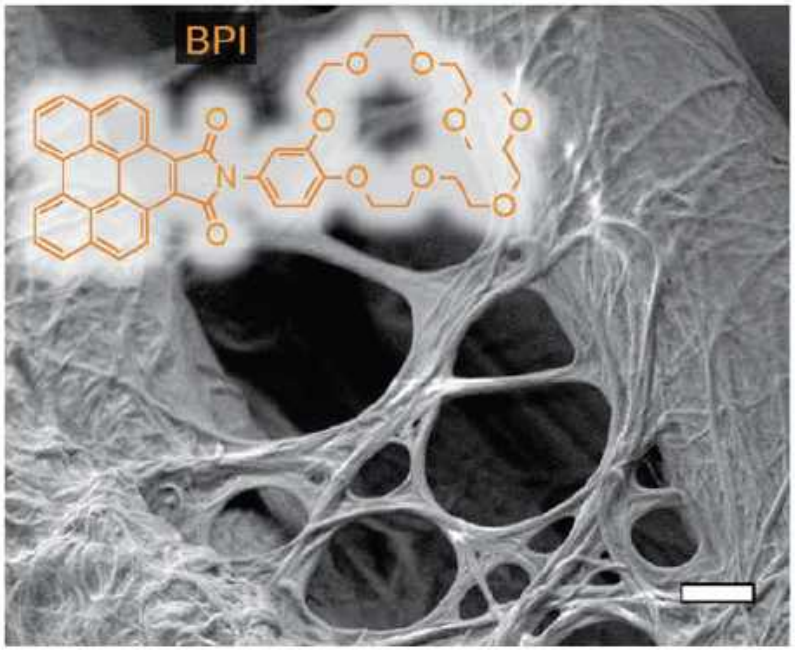
Performance

Kinetic & transport models

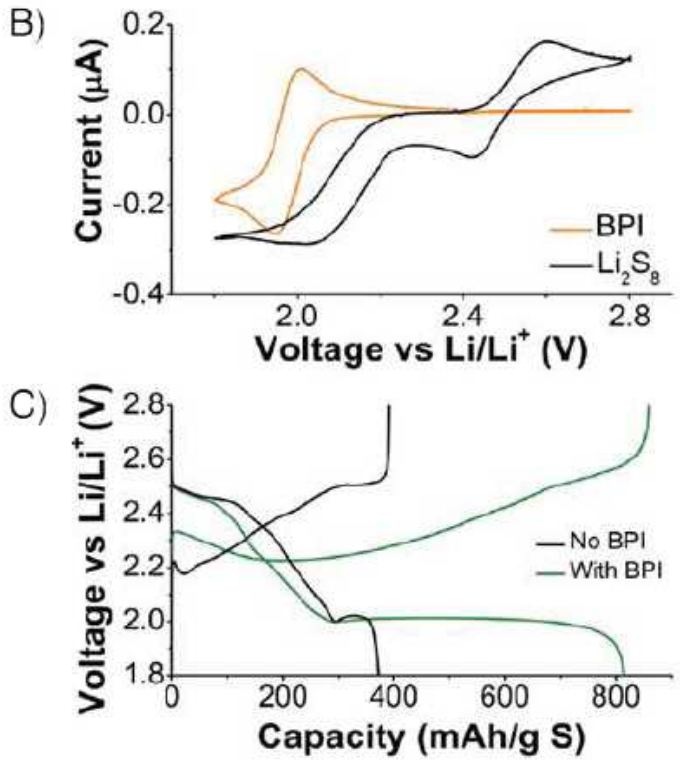


Need to understand how S is redistributed in the cathode – precipitation location (occlusion), electrode proximity, mobility, ...

Accessing discharged products could be achieved through redox mediators



L. Gerber Nano Lett 2015 submitted

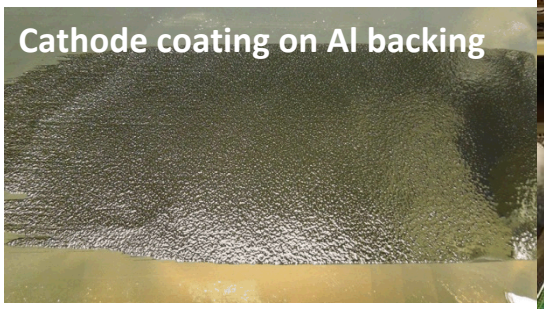


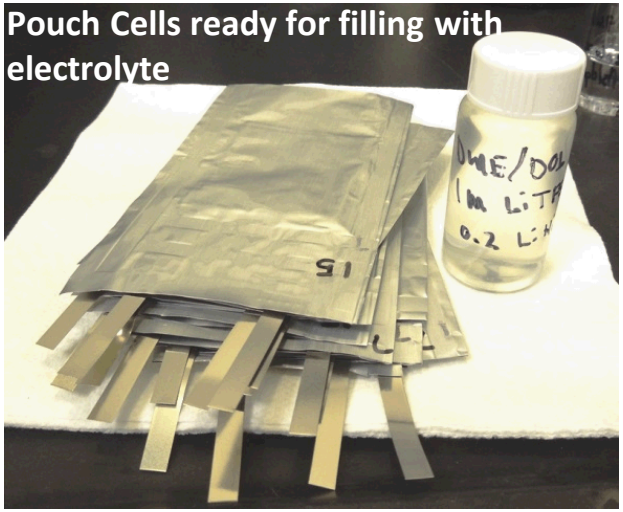
Computational screening to identify target compounds with optimized redox potentials by JCESR's Electrolyte Genome

B. Helms et al. A03-0341 Monday 13:20

Li-S Prototype Pouch Cells Create a Platform for Science and Demonstration

- Benchmark materials set
- Processing to achieve the desired architecture
- Create and transfer fabrication knowledge to JCESR partners
- Translate fabrication knowledge to experimental platforms

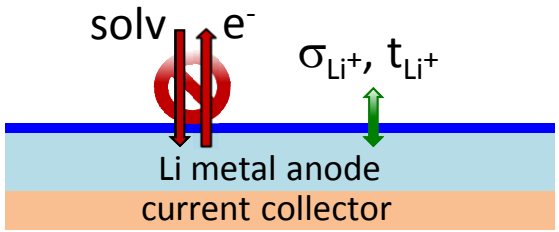




New Strategies to Protect Li Metal Anodes

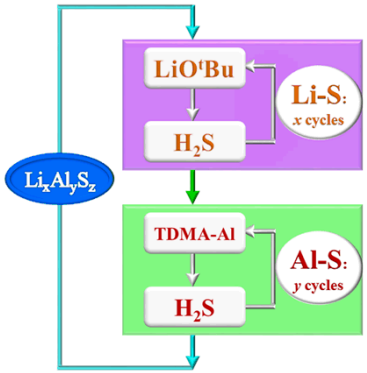
- Intrinsic inorganic membranes

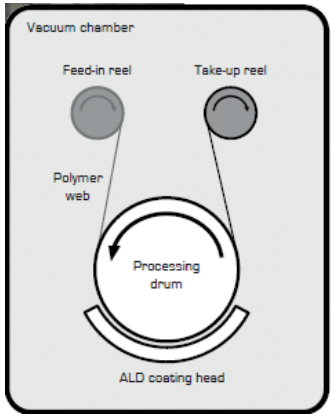
  electrochemically formed compact, amorphous, inorganic solid electrolyte interphases



- Extrinsic inorganic membranes

  atomic layer deposition – nanometric, tunable composition, mechanically compliant, reel-to-reel processing

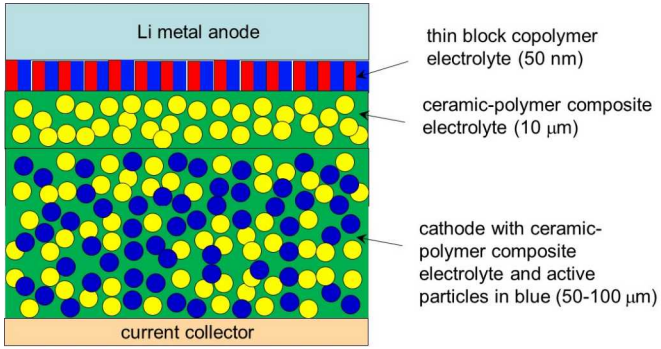




- Composite membranes

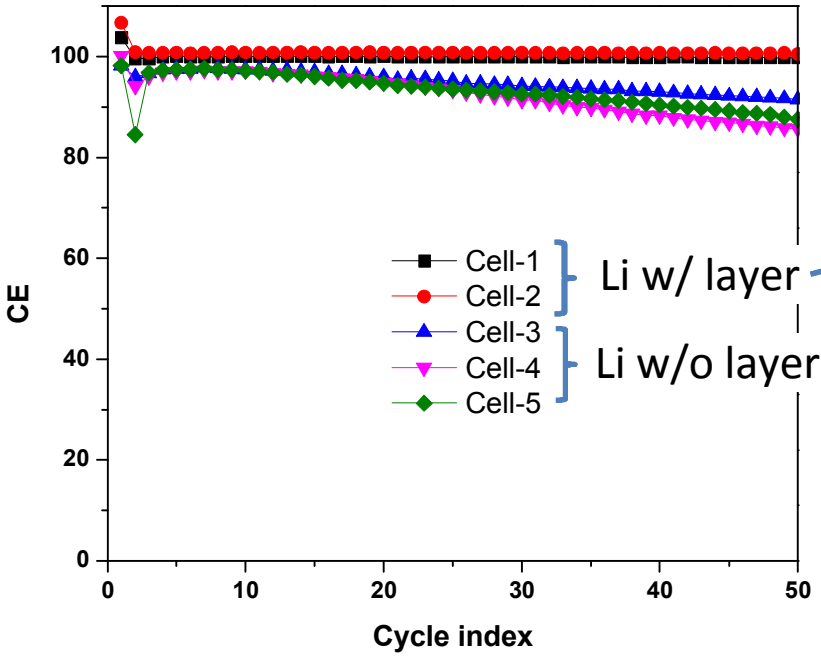
  integrating separator and electrolyte

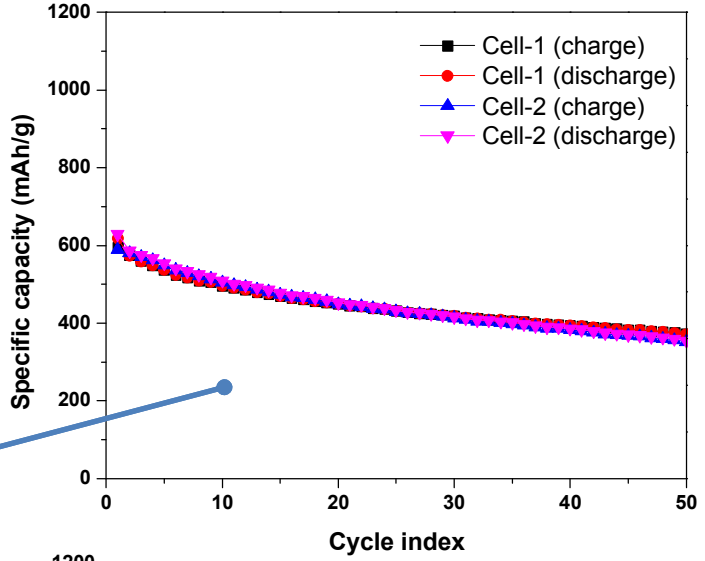
  creating solid state Li-S batteries

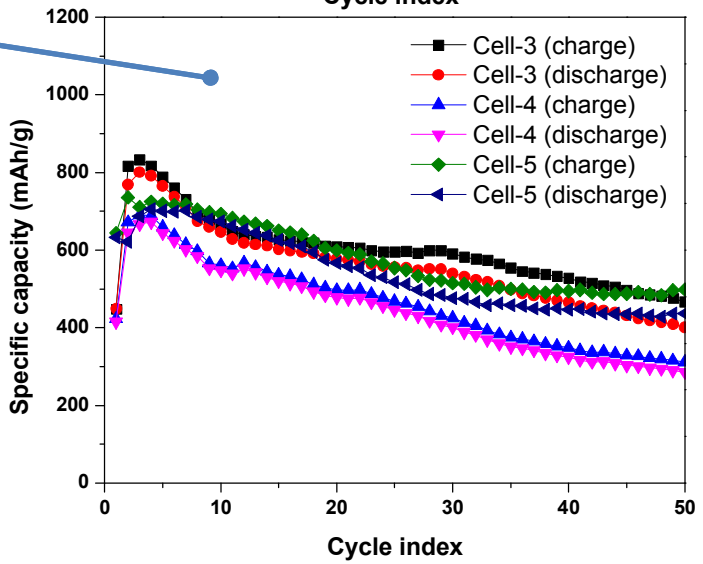


Electrochemically Formed Protective Layers

Cycling in 1 M LiTFSI + 0.2 M $LiNO_3$ in DOL/DME (1:1) with a 1.5 mg_S/cm^2 cathode



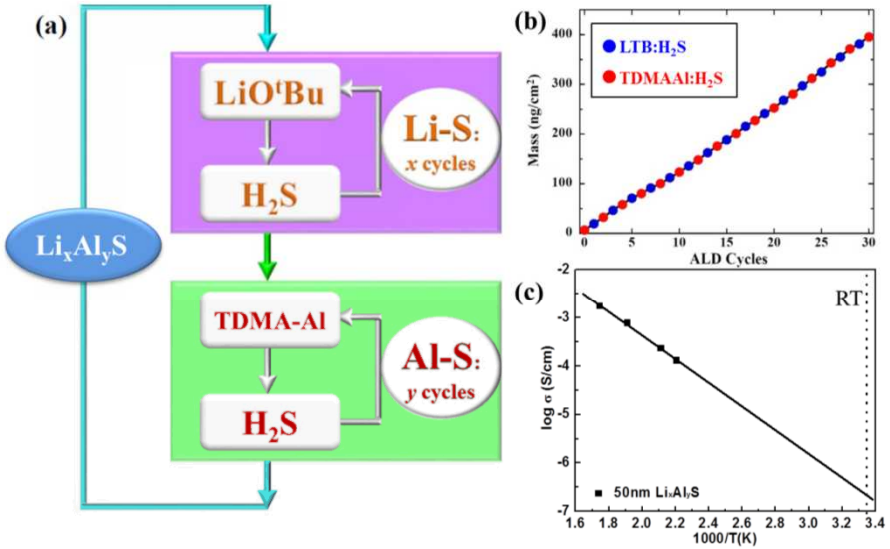




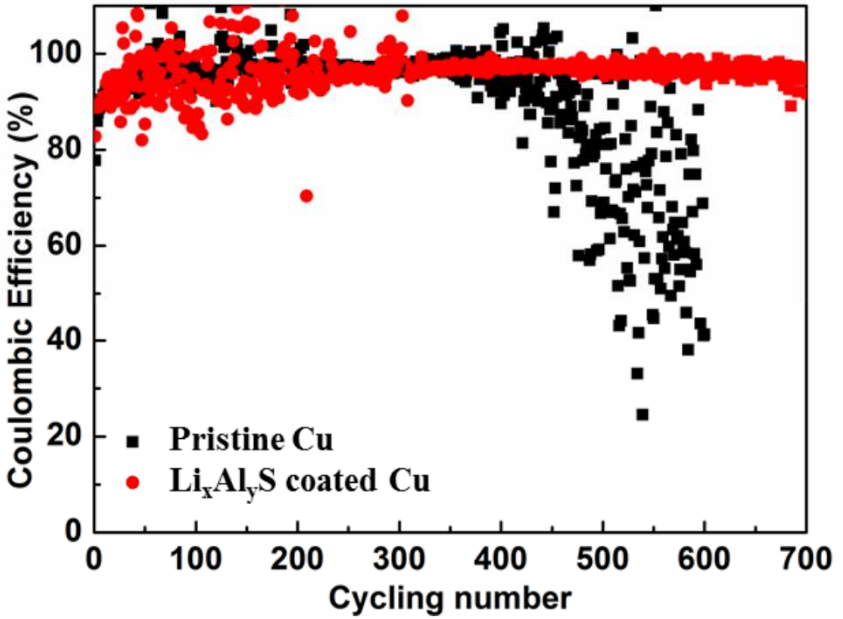
Presence of layer reduces redox shuttle impacts on CE and discharge

ALD Derived Cation Conducting Membranes Protect Li

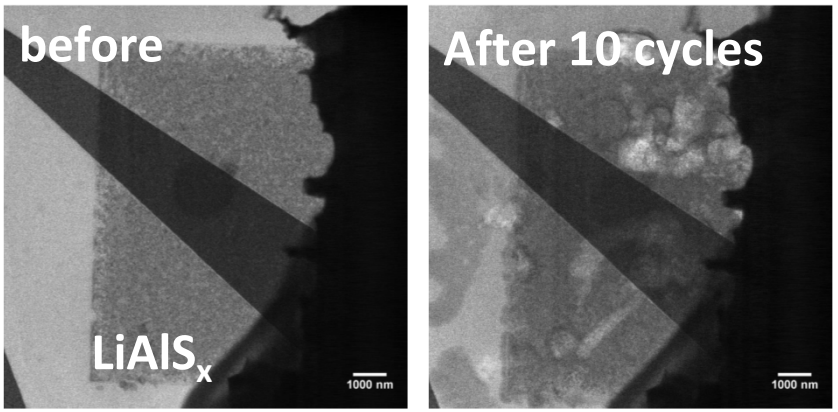
LiAlS$_x$ as Li ion conductor



25 nm thick film cycled in 4M LiFSI DME



- Coulombic efficiency preserved for Li deposition through membrane
- Films remain intact with cycling



Y Cao et al. Adv Mater, 2015 submitted

Our Li-S Work Contributes to JCESR's Legacies

- Library of Knowledge
  - Electroactive ion solvation and stability – electrolyte design
  - charge transport at the electrified interface – interface design
- Prototypes – creating platforms for science & demonstration
  - Multifunctional binder and carbon scaffolds to achieve activity
  - Integration of these materials to achieve new architectures sulfur cathode
- New paradigm
  - Uniting research across multiple areas of focus to surmount barriers

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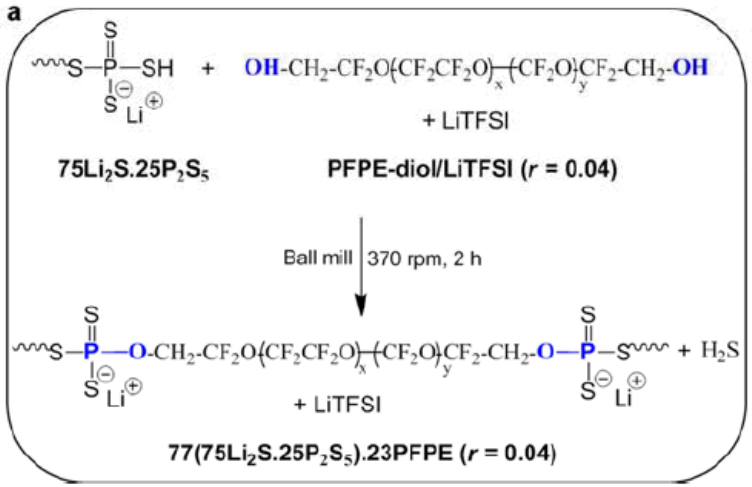
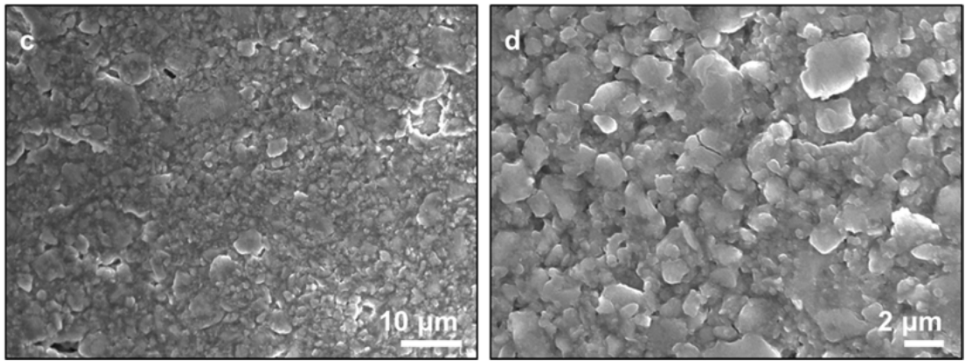
Back-up Slides

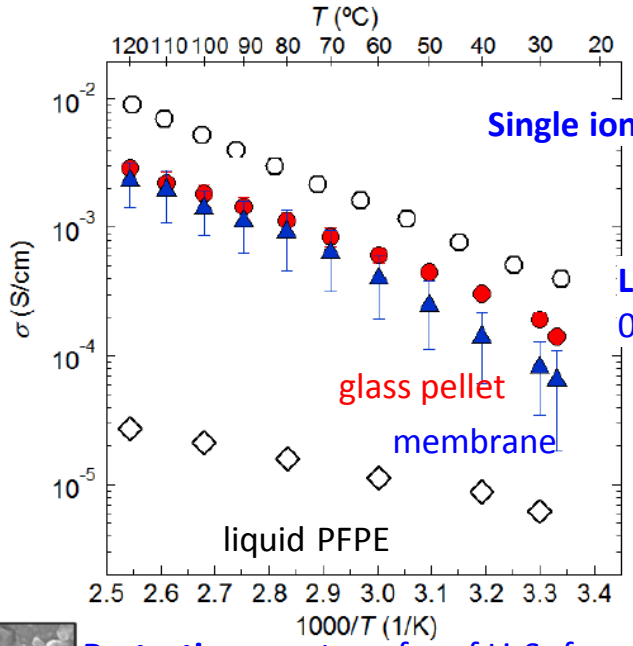
Composite Membranes Provide Protection of Li from Polysulfides



solid composite membranes are created



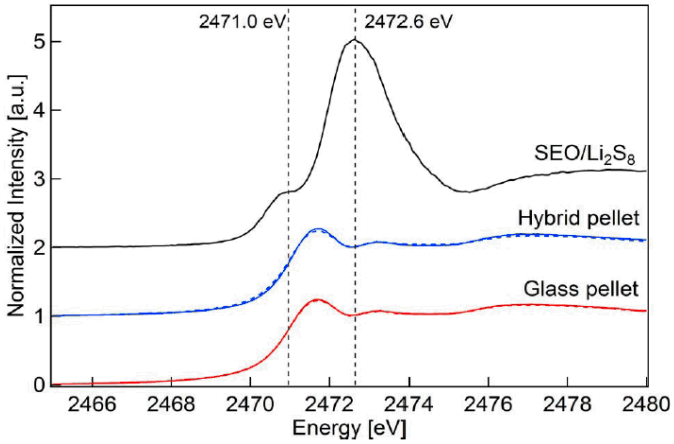
Mechanical compliance - elasticity from rheology



Single ion - t^+ 0.99

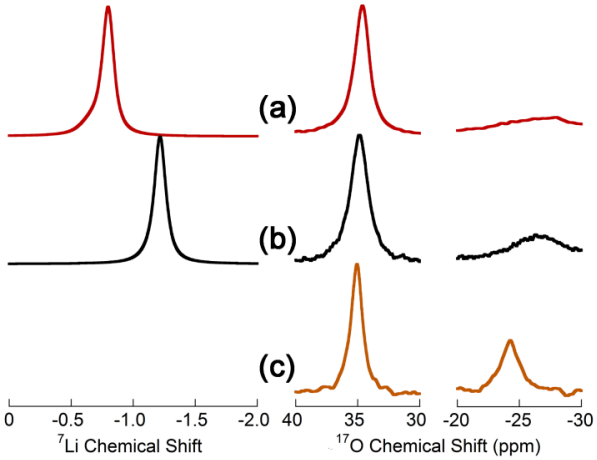
Li^+ Conductivity
0.2 mS/cm @ RT

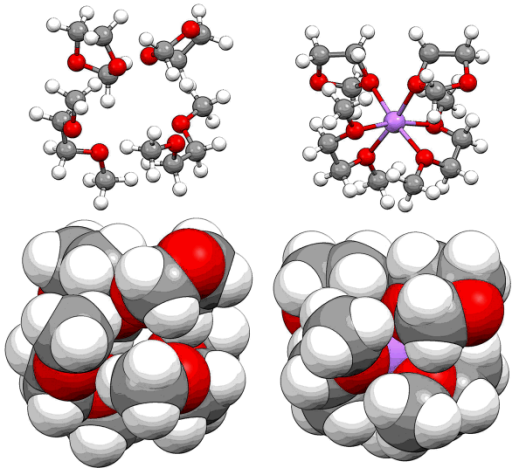
Protection - no transfer of Li_2S_8 from SEO to membrane

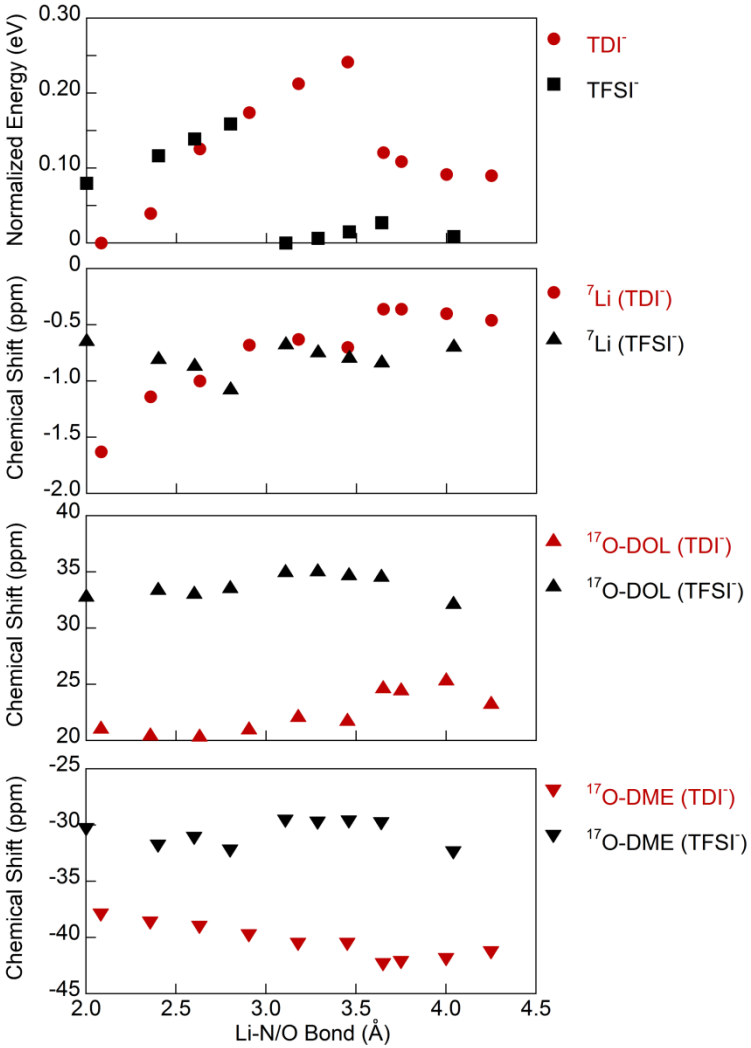


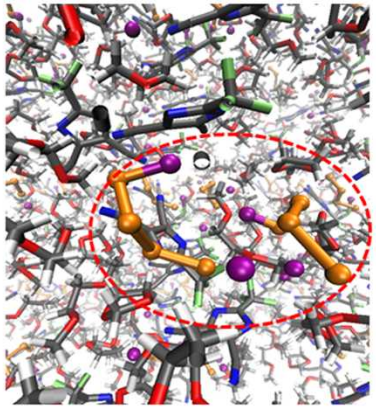
I. Villaluenga et al. PNAS, 2015 submitted

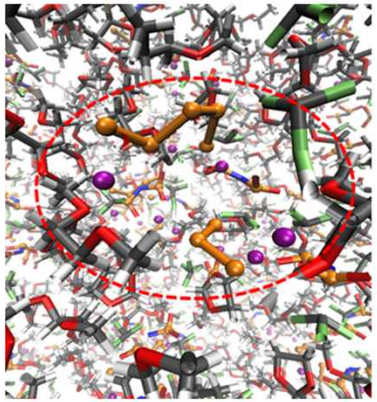
Polysulfide Solubility Control: Solubility mechanism





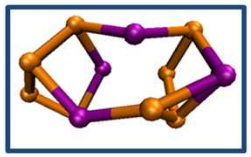






$Li_2S_8 + 2Li \rightarrow 2\ Li_2S_4$

(ΔG_{sol} ~ -6.30 eV)



"Li_4S_8-like" agglomerate

Under dilute concentration, the TDI anion will affect the solvation of Li and the polysulfide disproportion to form Li_4S_8 agglomerate, then decrease the solubility.

JCESR