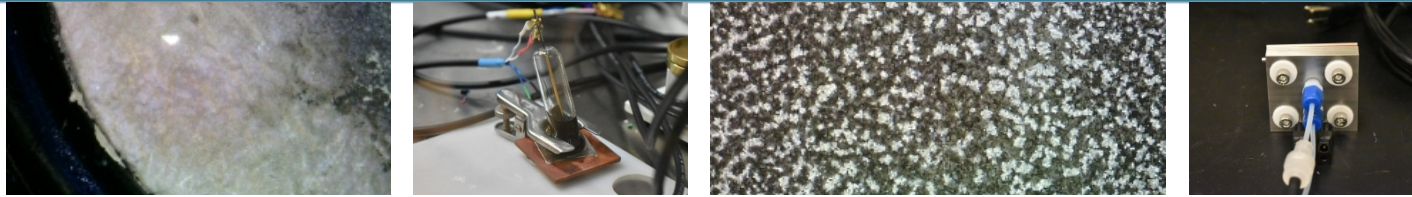




Mediated Li-S Flow Battery for Grid-Scale Energy Storage



Melissa Meyerson,

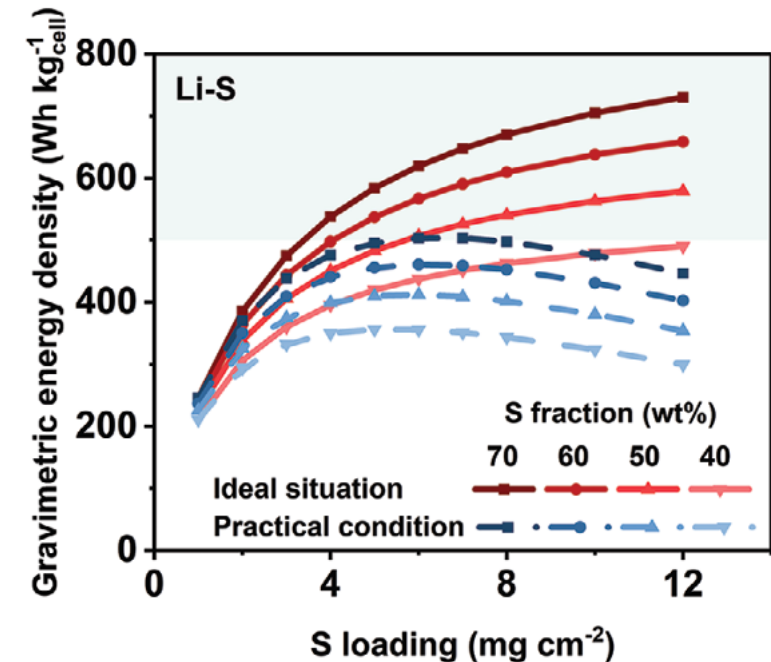
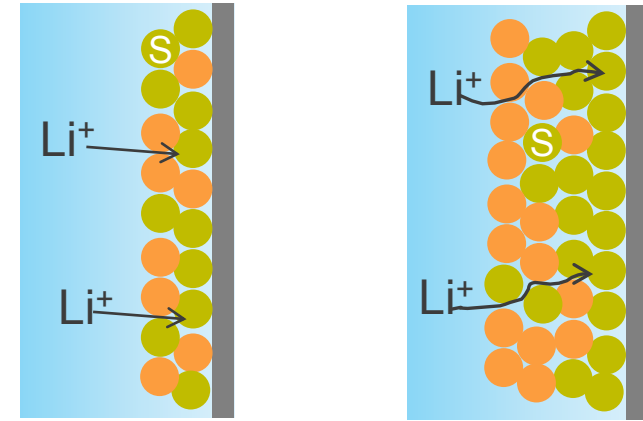
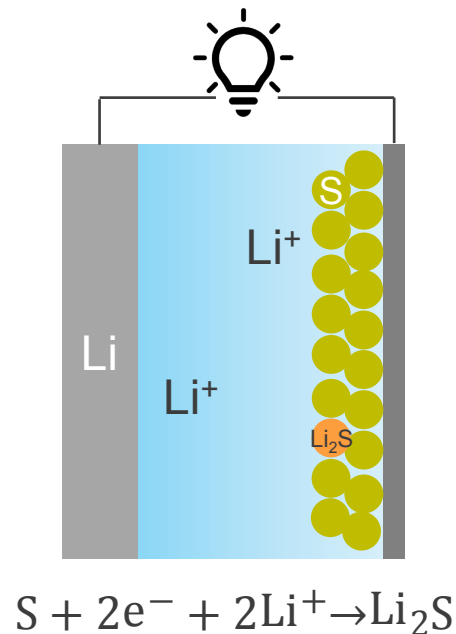
Samantha Rosenberg, Sara Dickens, Leo Small

ACS Southwest Regional Meeting

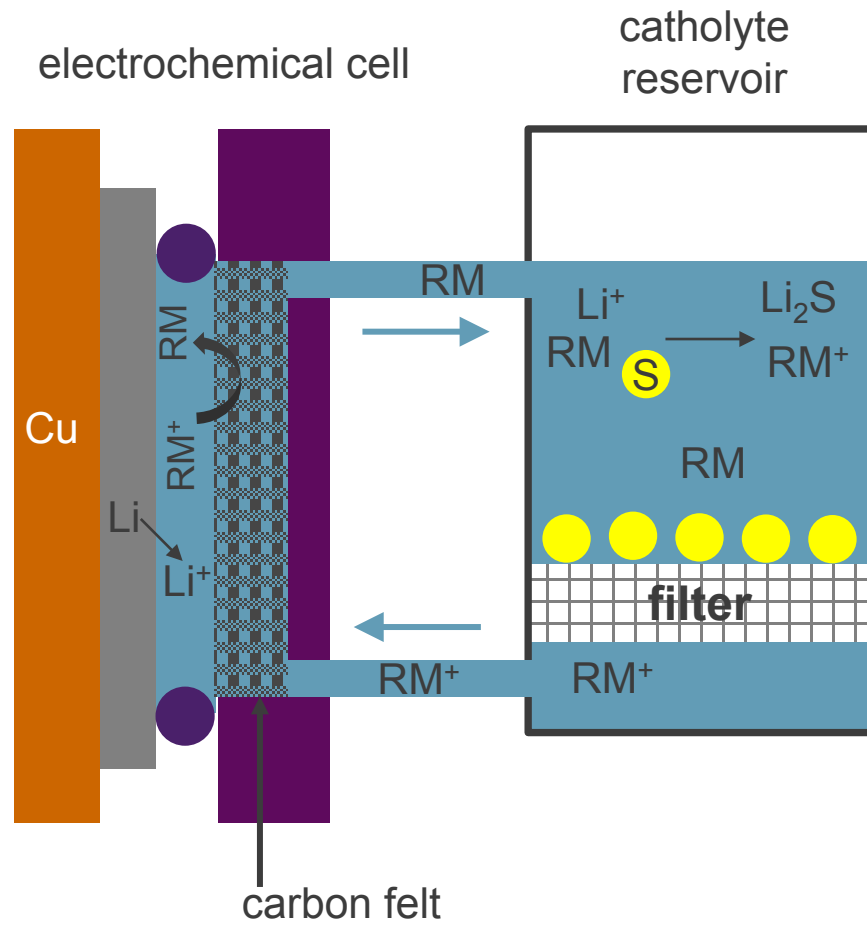
November 2, 2021

Background

- Need for inexpensive, safe, reliable, high-capacity batteries for grid storage
- Li-S is high capacity and low cost
- Increasing to grid scale requires a change in cell design

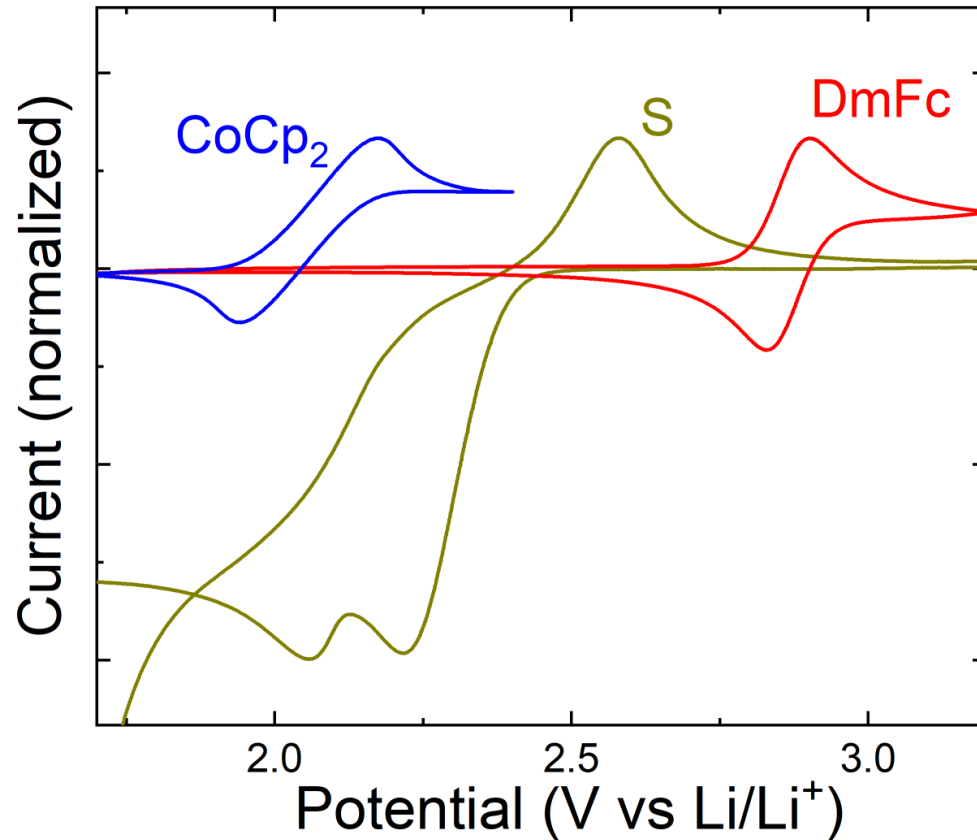


Wu, J., et al. (2021). *Adv Mater* **33**(26): e2101275.



Benefits:

- Improved safety
 - Separation of anode and cathode decreases risk of thermal runaway
- Decreased cost
 - No need for ion selective separators or excess carbon
- Scalability
 - Increased S loading without hindering diffusion

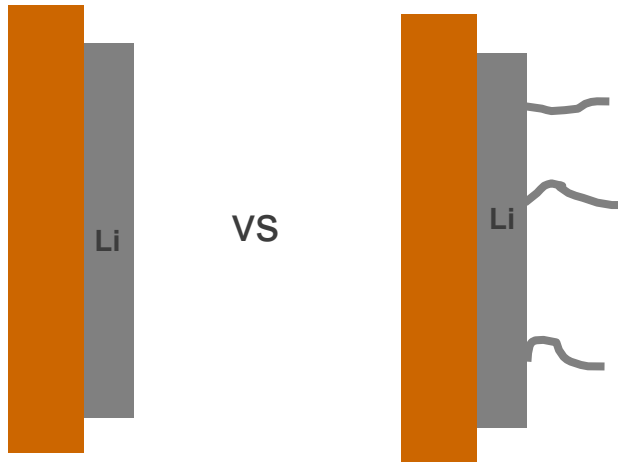


CVs taken at 10 mV/s in 1M LiTFSI 1:1 DOL:DME, glassy carbon working electrode, Pt counter electrode, Li reference electrode.

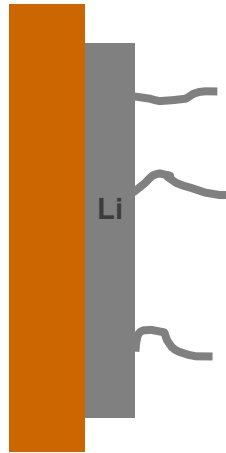
Ideal Redox Mediator

- Close to Li-S reaction (~ 2.4 V vs Li/Li⁺)
 - $E_{\text{DmFc}} = 2.86$ V
 - $E_{\text{CoCp}_2} = 2.06$ V
- Good reaction kinetics
 - $k_{\text{DmFc}}^0 = 4.33 \times 10^{-3} \text{ cm s}^{-1}$
 - $k_{\text{CoCp}_2}^0 = 3.14 \times 10^{-4} \text{ cm s}^{-1}$
- Fast diffusion
 - $D_{\text{DmFc}} = 5.23 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$
 - $D_{\text{CoCp}_2} = 3.70 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$

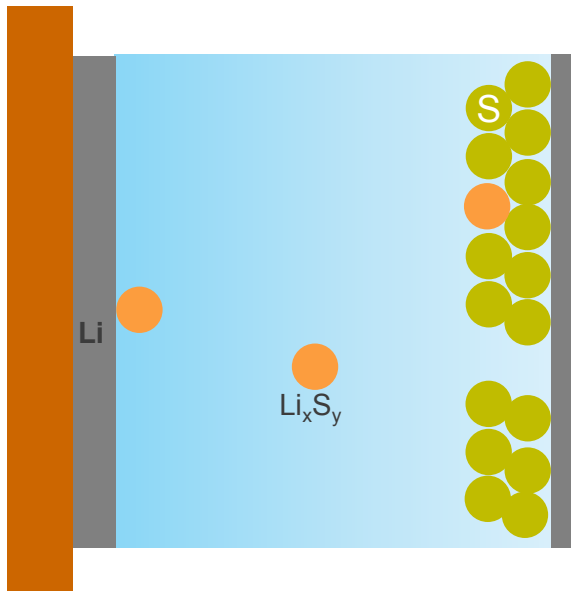
Solid Electrolyte Interphase Engineering



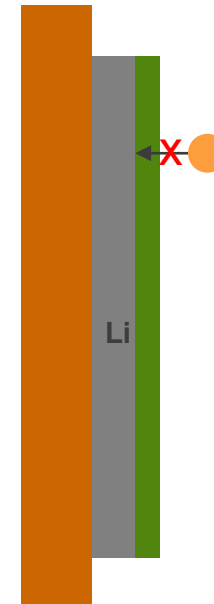
VS



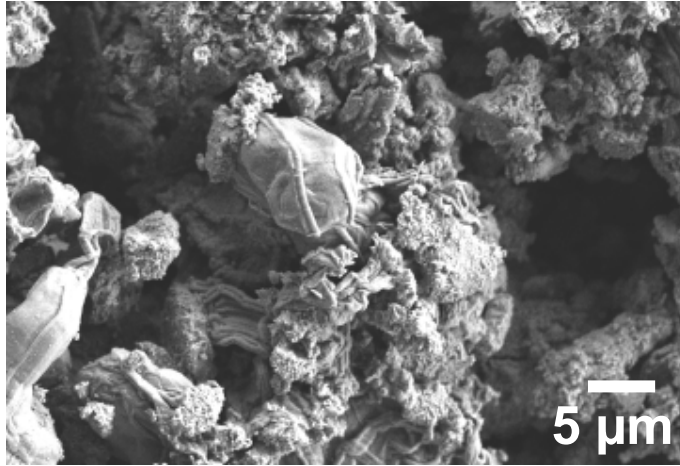
Dendrites decrease battery life and cause short circuits.



Polysulfide shuttling decreases battery life.

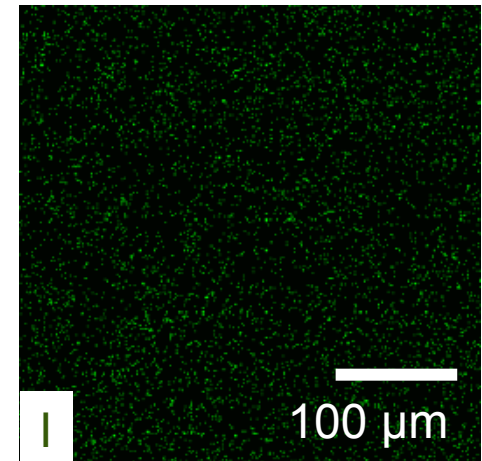
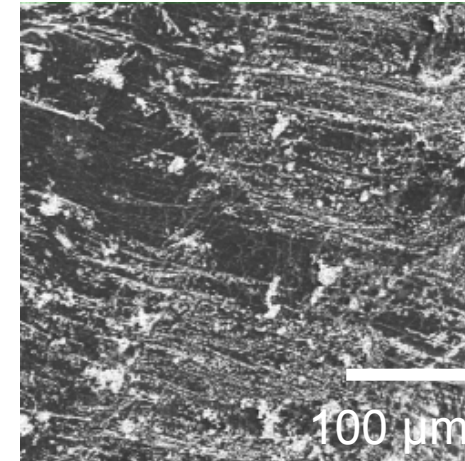
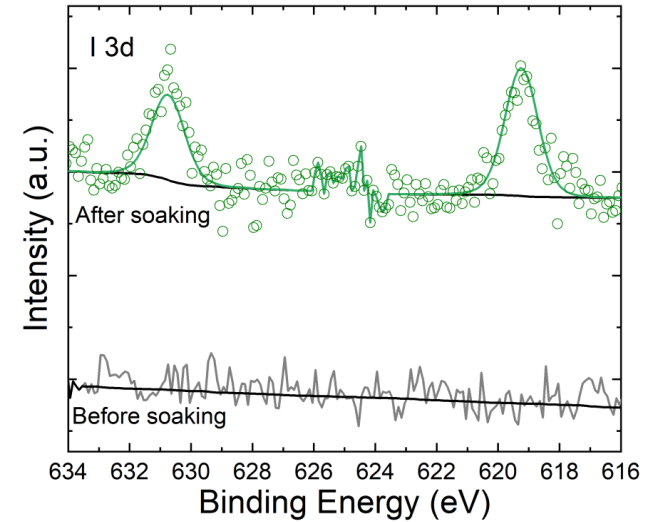


Protective SEI blocks polysulfides from reaching the Li surface and promotes uniform Li deposition.



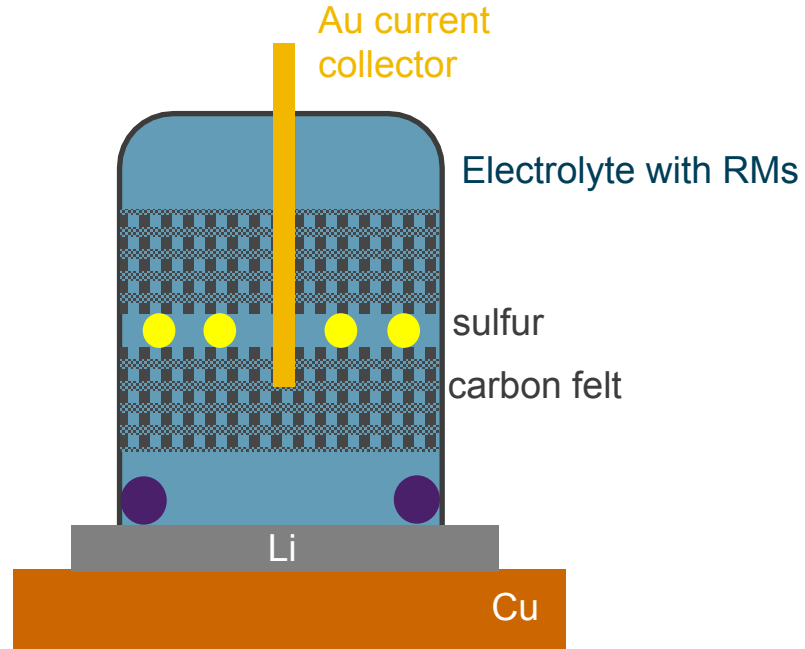
LiNO_3 promotes lower surface area Li deposition.

Additives protect the Li surface, so no ion selective membrane is needed.

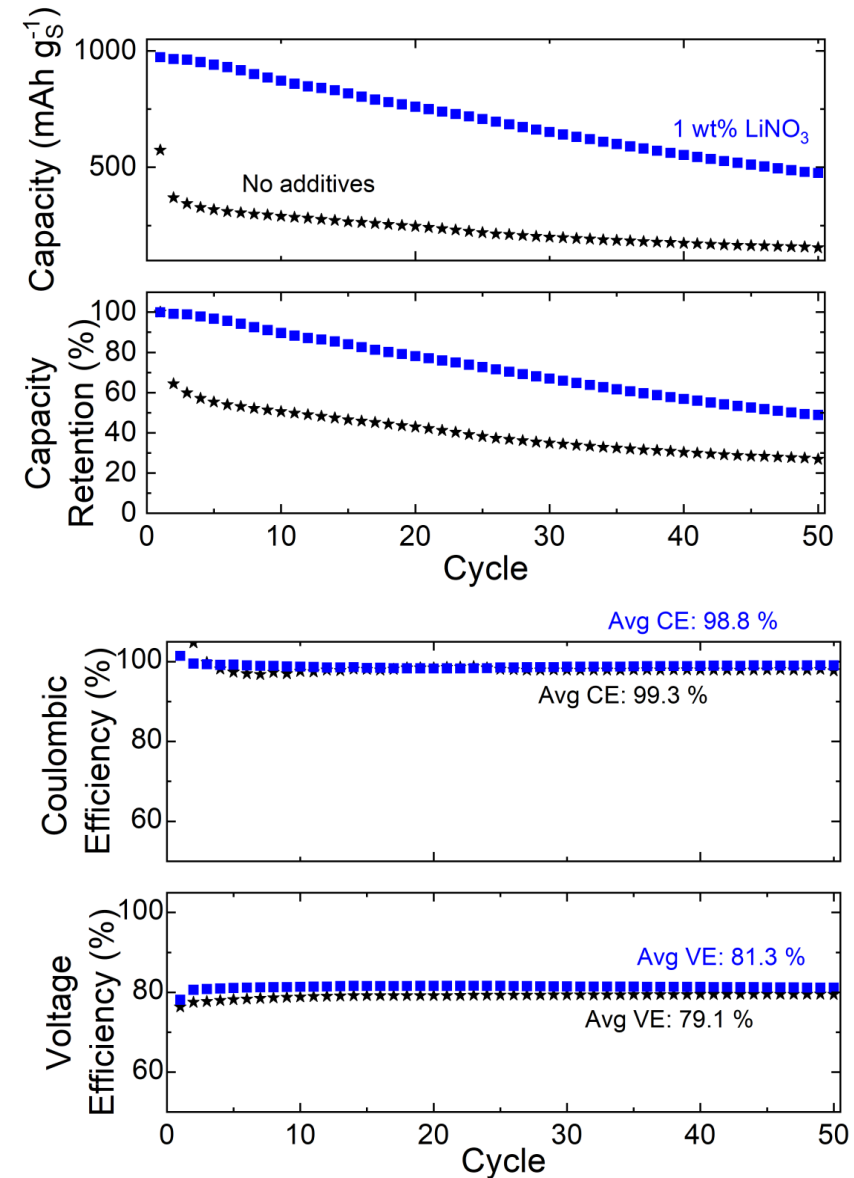


Iodine is uniformly distributed through SEI in the form of LiI .

Static Cell Cycling Performance Improves with Additives



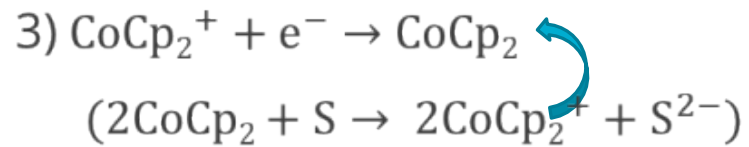
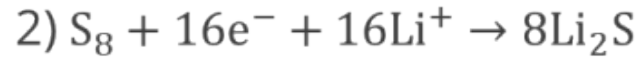
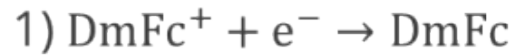
Additives improve capacity retention and voltage efficiency.



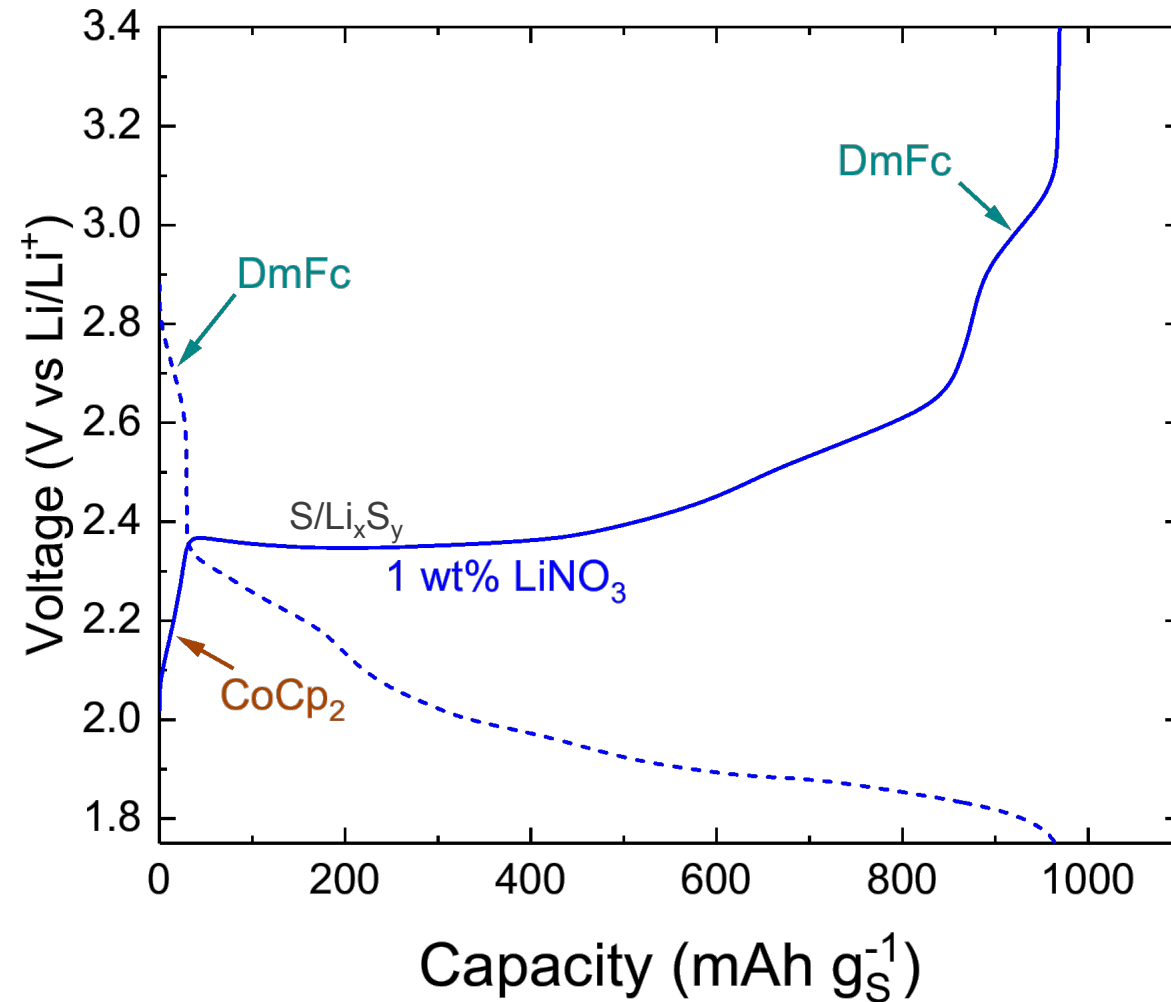
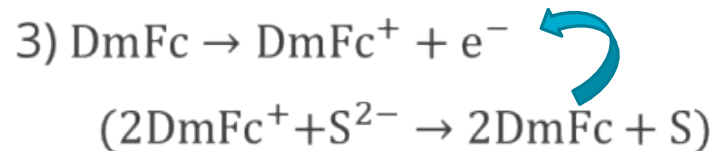
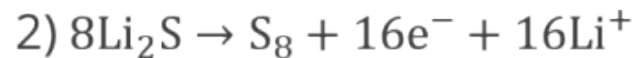
Cells cycled at 0.5 mA cm⁻² with 1 M LiTFSI in 1:1 DOL:DME



Discharge reactions:



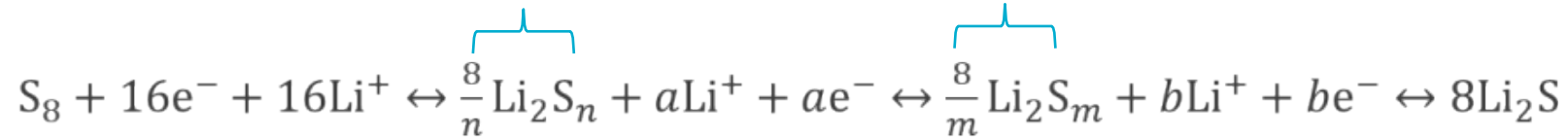
Charge reactions:



Polysulfide Cycling

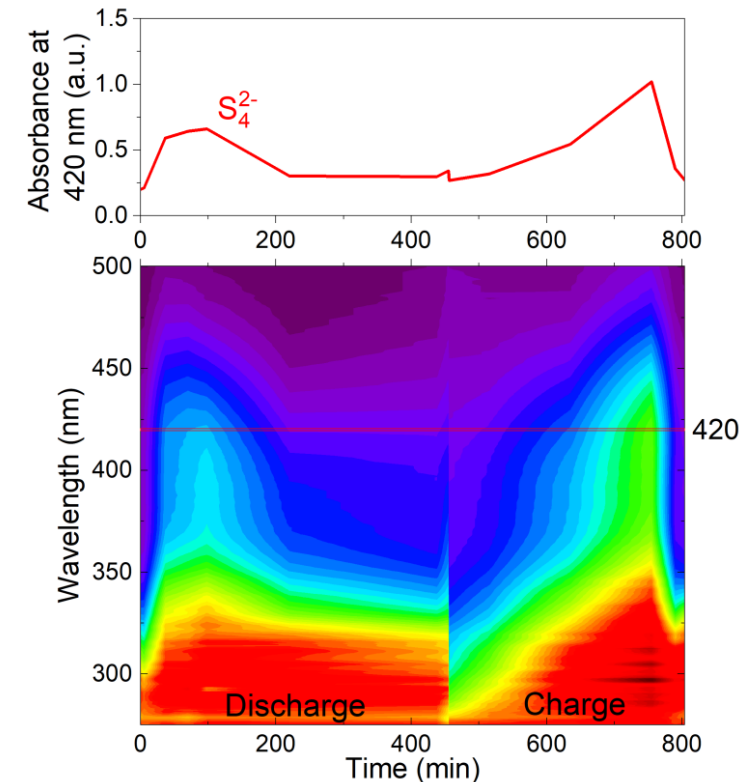
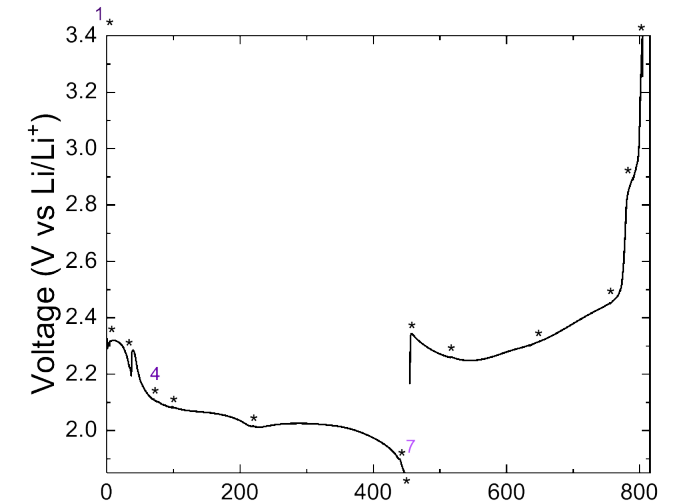
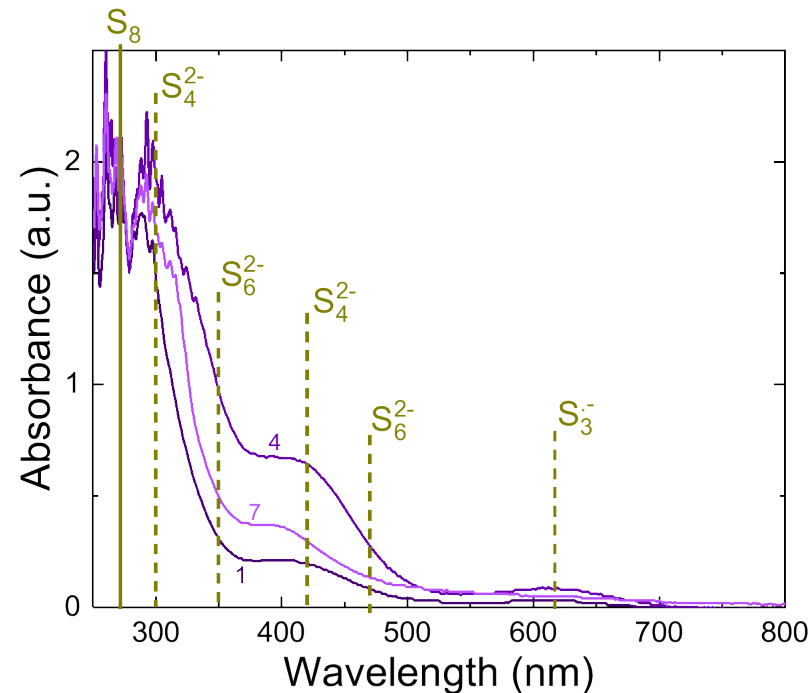
Long chain

Short chain



$$a = \frac{16(n-1)}{n} \quad b = \frac{16(m-1)}{m}$$

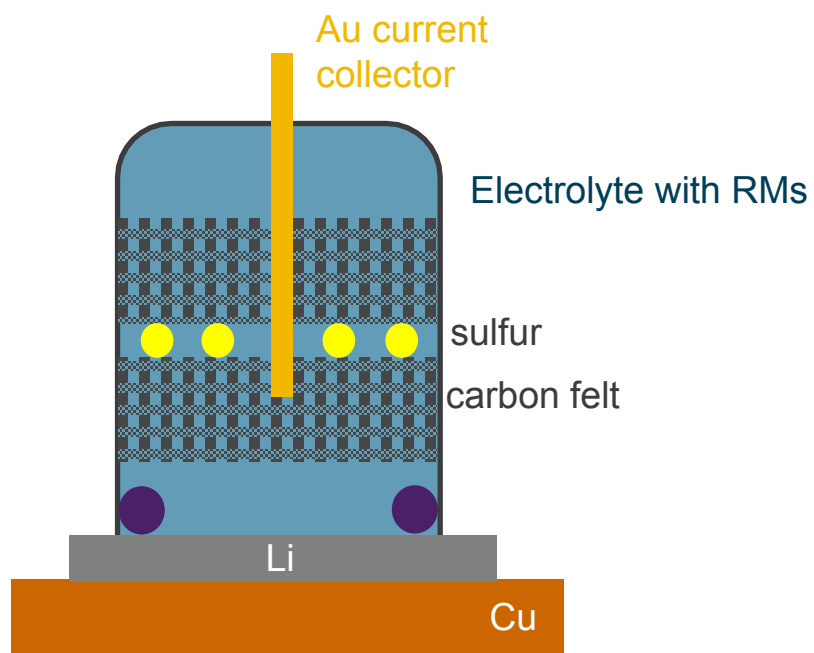
Polysulfide
concentration changes
as cycling progresses.



Scale up to Flow Cell

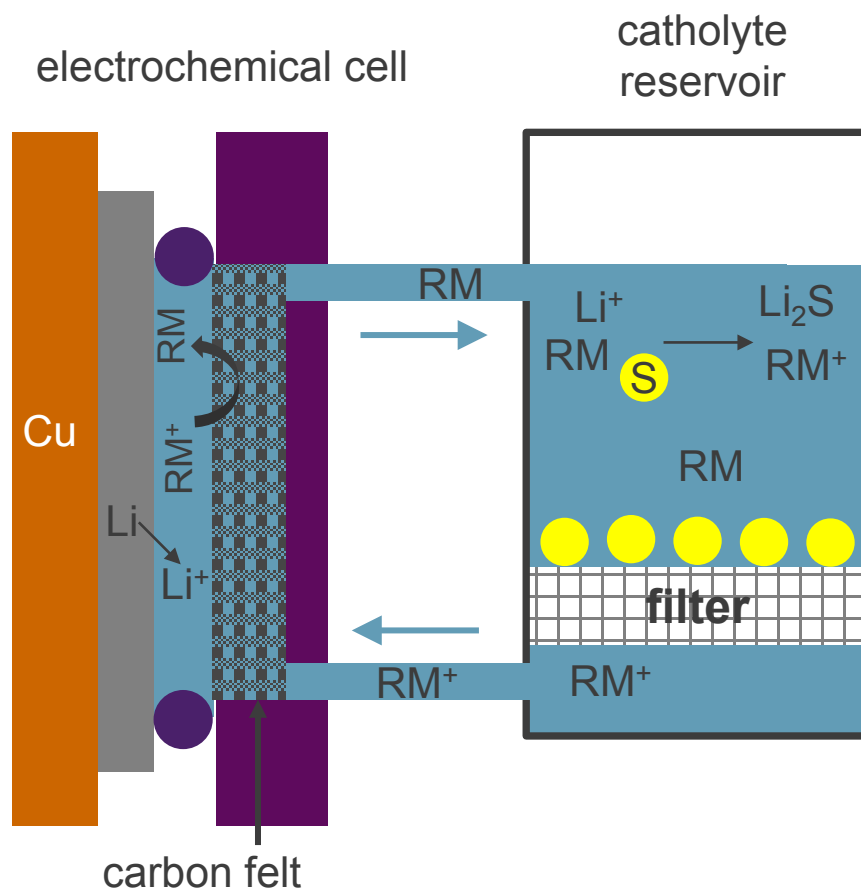


Static cell



S loading: $0.99\text{--}4.4 \text{ mg}_S \text{ cm}^{-2}$

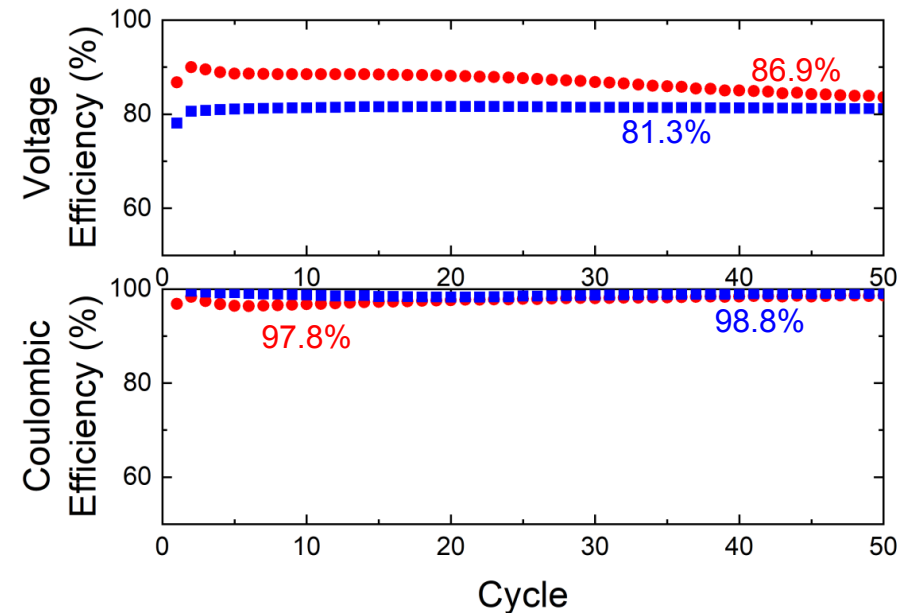
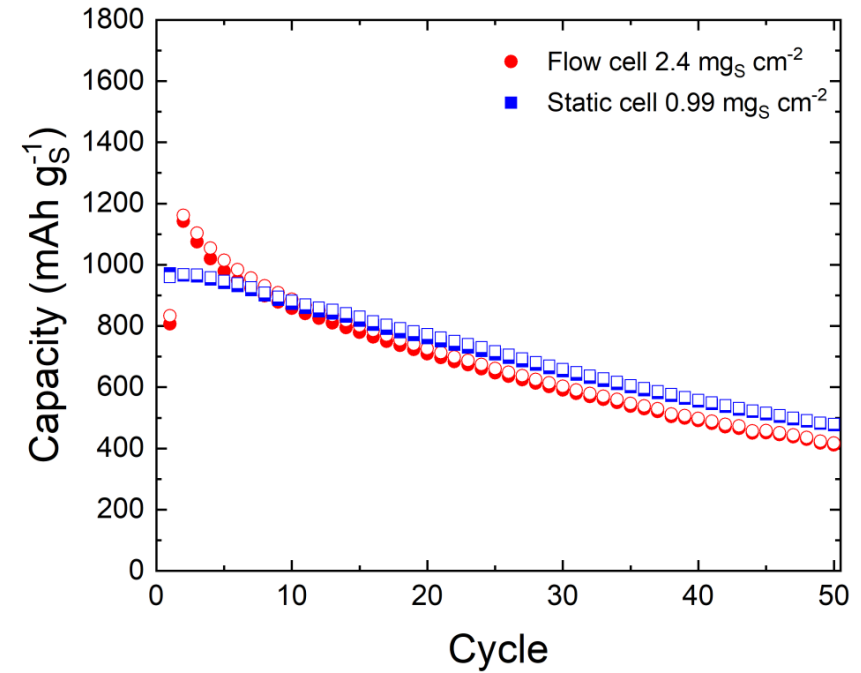
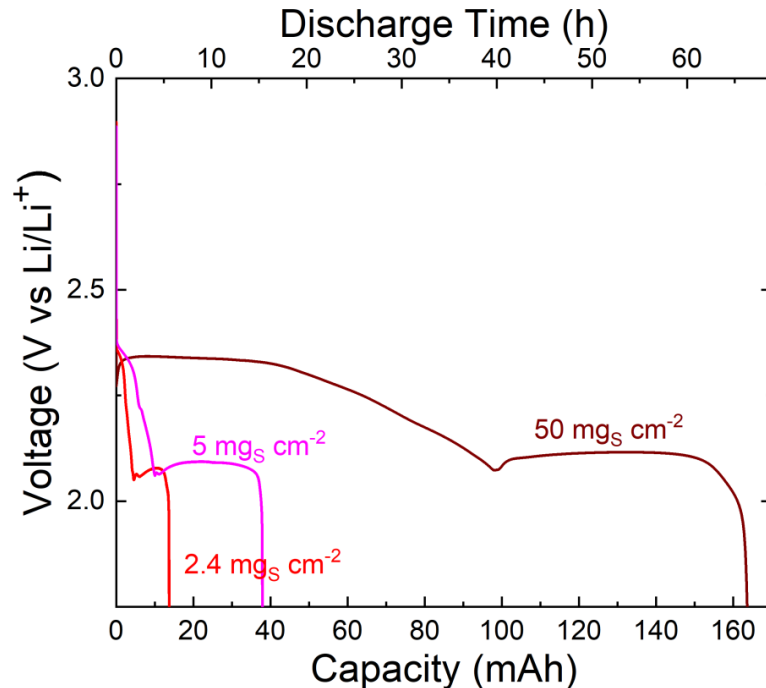
Flow cell



S loading: $2.4\text{--}50 \text{ mg}_S \text{ cm}^{-2}$

Flow Cell Cycling

- Flow cell shows similar capacity to static cell, but improved mass transport improves voltage efficiency
- Increasing S loading increases capacity and enables discharge times over 60 h-showing viability for long duration storage



Conclusions and Future work



- Successfully adapted Li-S chemistry for use in a flow system
- Demonstrated high capacity and voltage efficiency:
 - 973 mAh g_S⁻¹ and 81.3% VE in static cells
 - 1142 mAh g_S⁻¹ and 86.9% VE in flow cells
- Demonstrated viability for long duration storage with > 60h discharge time

Future Work:

- Improve cycling rate by increasing anode surface area
- Scale system up to more realistic S loading

Li-S is a feasible chemistry to use for high capacity, long duration, grid-scale energy storage.

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