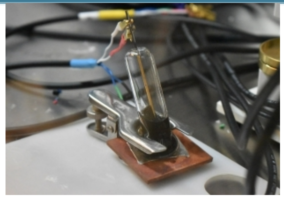
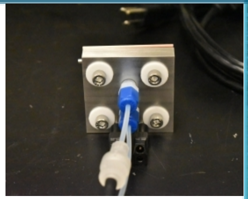
SAND2021-14817C

Sandia National Laboratories

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





Melissa Meyerson,

Samantha Rosenberg, Sara Dickens, Leo Small

MRS 2021 Fall Meeting

December 6, 2021

U.S. DEPARTMENT OF ENERGY NNSA

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

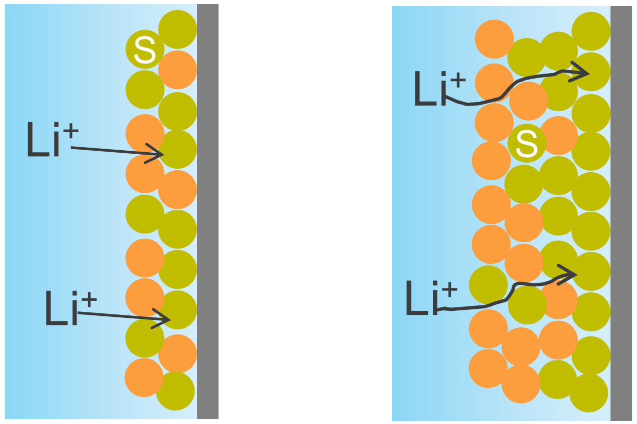
SAND

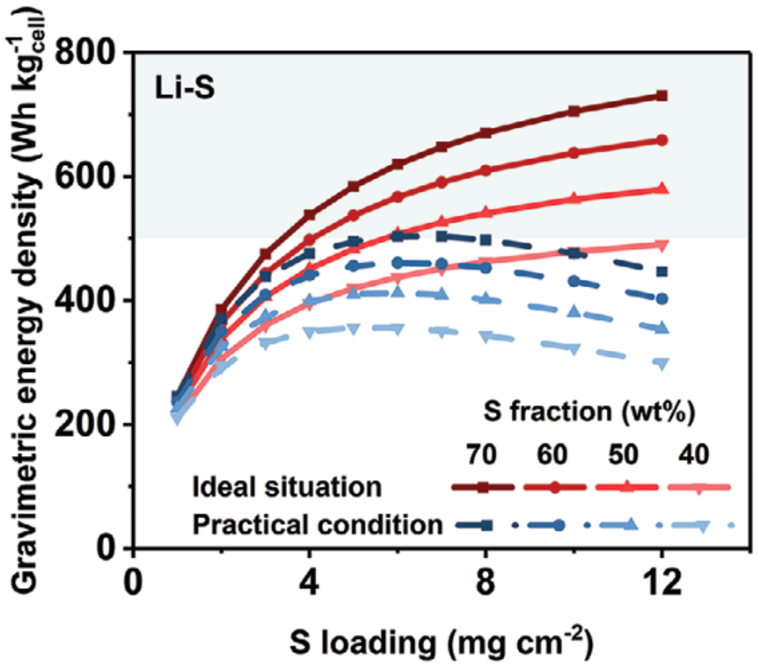
*mlmeyer@sandia.gov

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

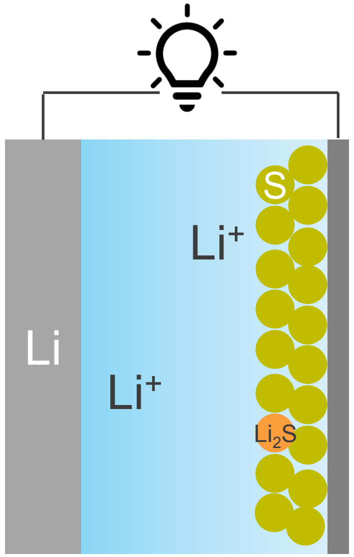
Background

- 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



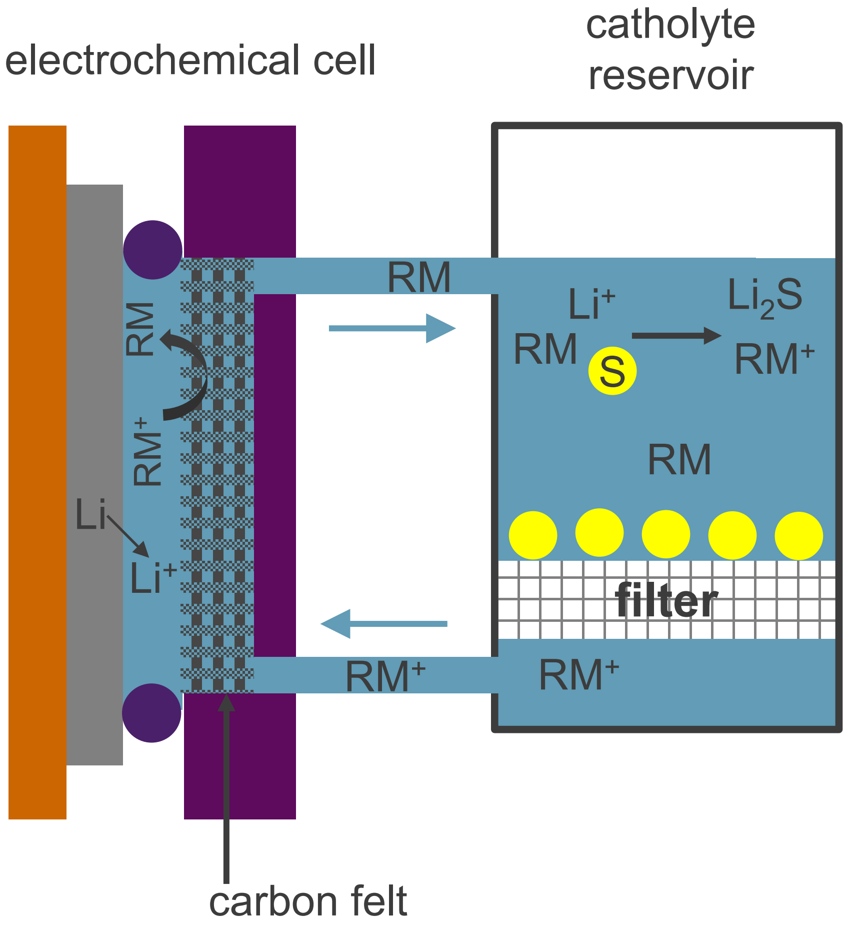


Wu, J., et al. (2021). Adv Mater **33**(26): e2101275.



$$S + 2e^{-} + 2Li^{+} \rightarrow Li_2S$$

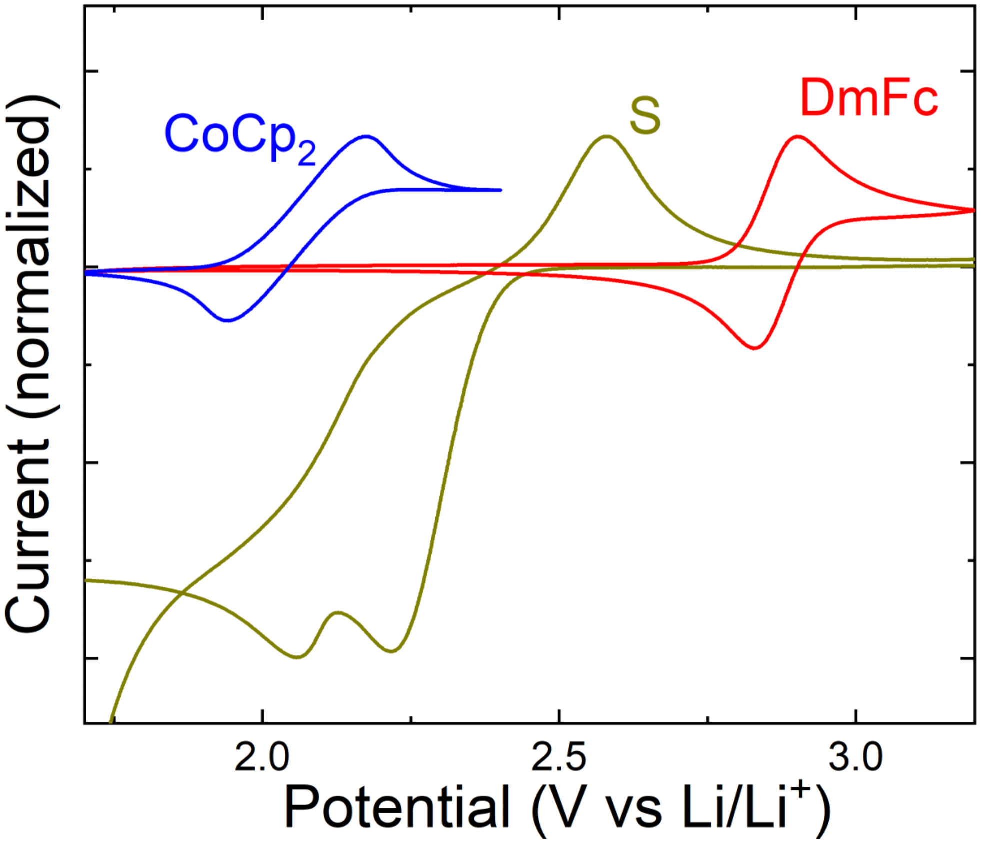
Flow Cell Design



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

Cobaltocene and Decamethyl Ferrocene as Redox Mediators



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_{DmFc} = 2.86 V
  - E_{CoCp2} = 2.06 V
- Good reaction kinetics
  - k^0_{DmFc} = 4.33 x 10^{-3} cm s^{-1}
  - k^0_{CoCp2} = 3.14 x 10^{-4} cm s^{-1}
- Fast diffusion
  - D_{DmFc} = 5.23 x 10^{-6} cm^2 s^{-1}
  - D_{CoCp2} = 3.70 x 10^{-6} cm^2 s^{-1}

Cycling Chemistry

Charge reactions:

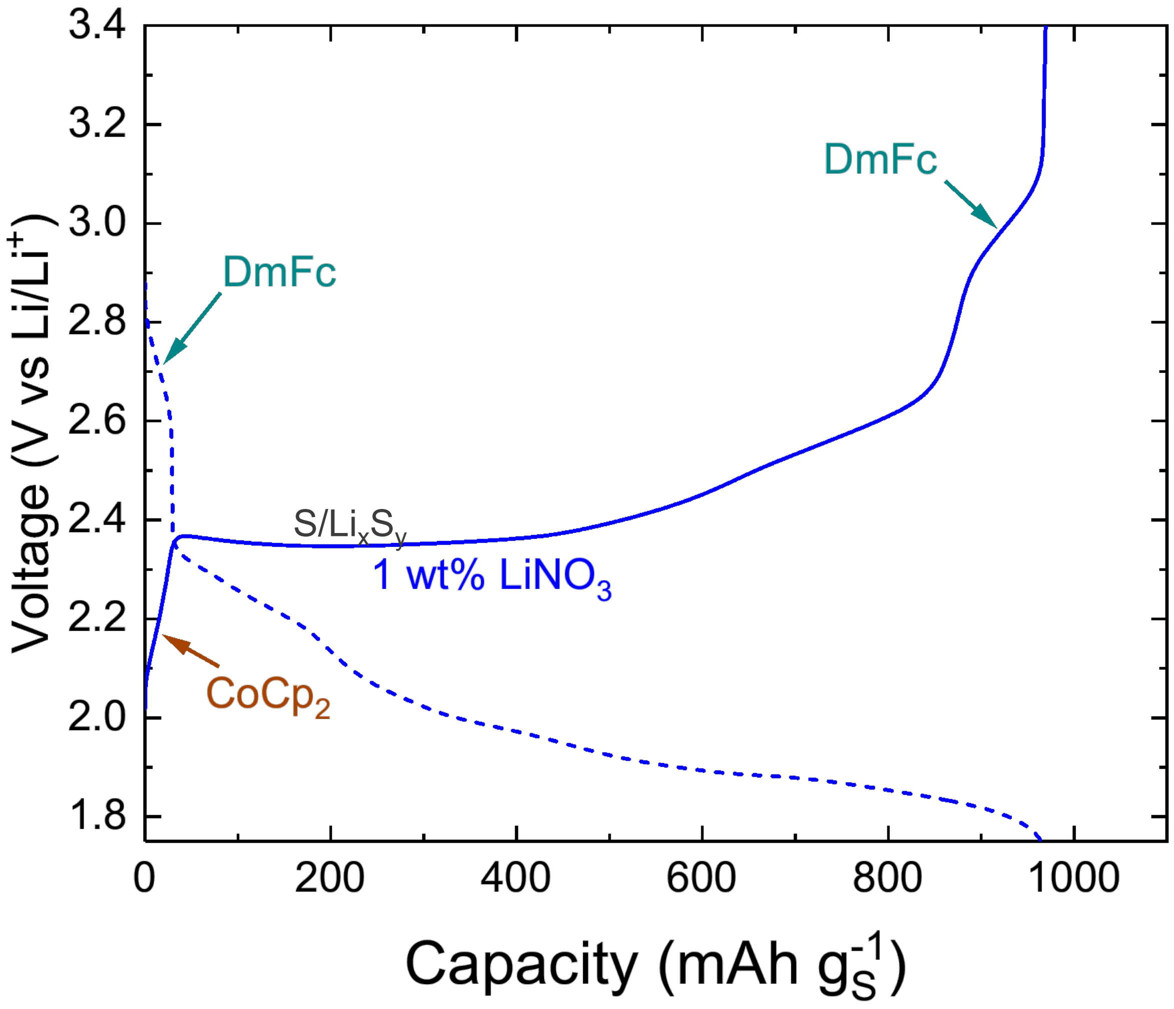
1) $CoCp_2 \rightarrow CoCp_2^+ + e^-$ E= 2.06 V
2) $8Li_2S \rightarrow S_8 + 16e^- + 16Li^+$ E= 2.4 V
3) $DmFc \rightarrow DmFc^+ + e^-$ E= 2.86 V

$(2DmFc^+ + S^{2-} \rightarrow 2DmFc + S)$

Discharge reactions:

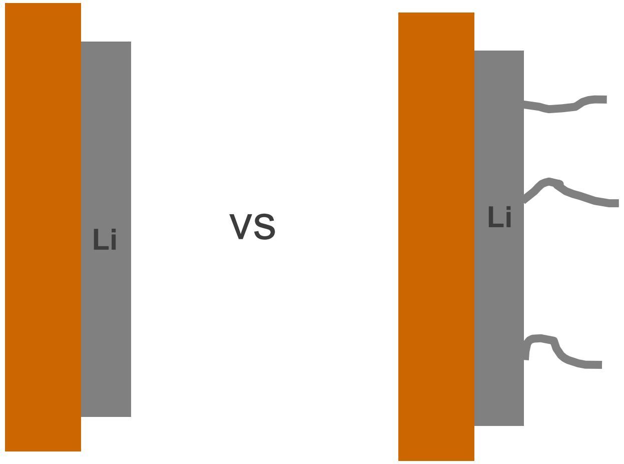
1) $DmFc^+ + e^- \rightarrow DmFc$
2) $S_8 + 16e^- + 16Li^+ \rightarrow 8Li_2S$
3) $CoCp_2^+ + e^- \rightarrow CoCp_2$

$(2CoCp_2 + S \rightarrow 2CoCp_2^+ + S^{2-})$

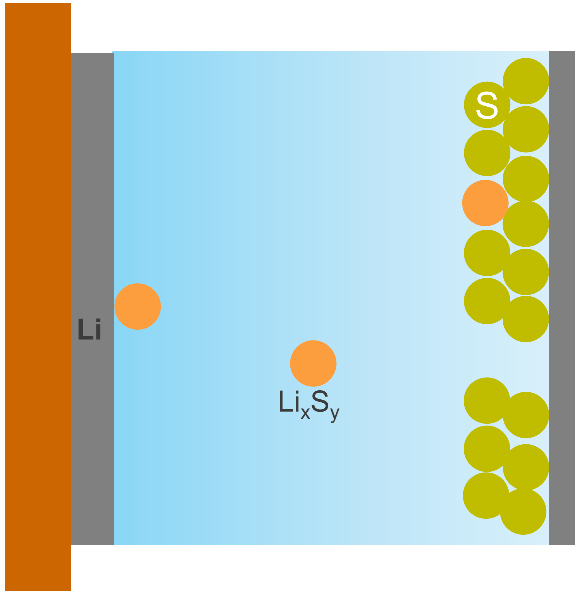


2^{nd} cycle Li vs S, 0.5 mA cm^{-2} with 1 M LiTFSI in 1:1 DOL:DME, 1 wt% $LiNO_3$

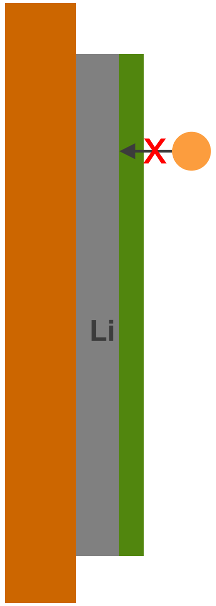
Solid Electrolyte Interphase Engineering



Dendrites decrease battery life and cause short circuits.

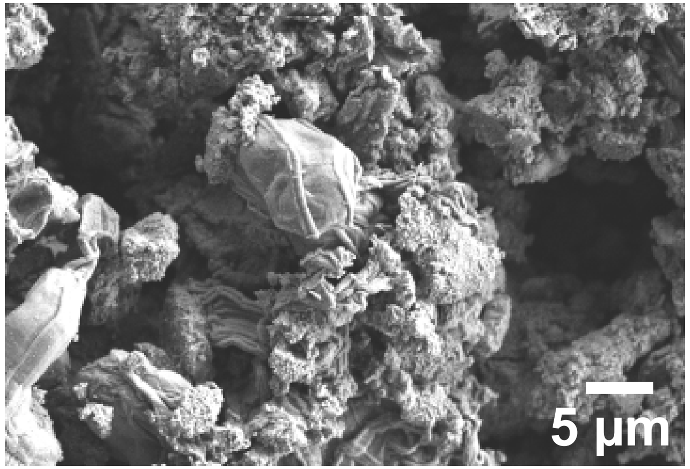


Polysulfide shuttling decreases battery life.



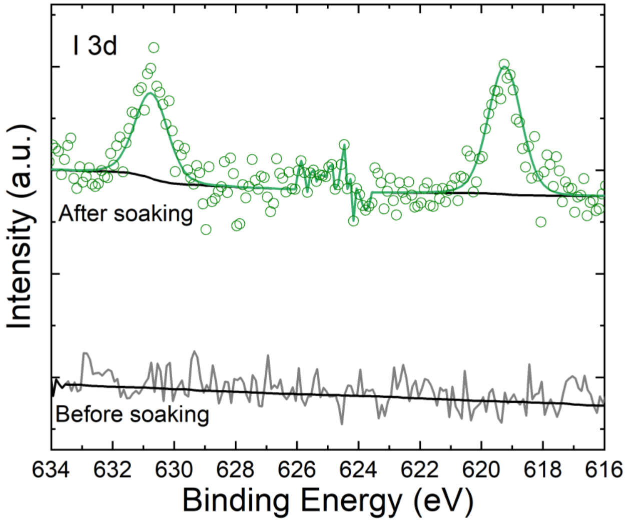
Protective SEI blocks polysulfides from reaching the Li surface and promotes uniform Li deposition.

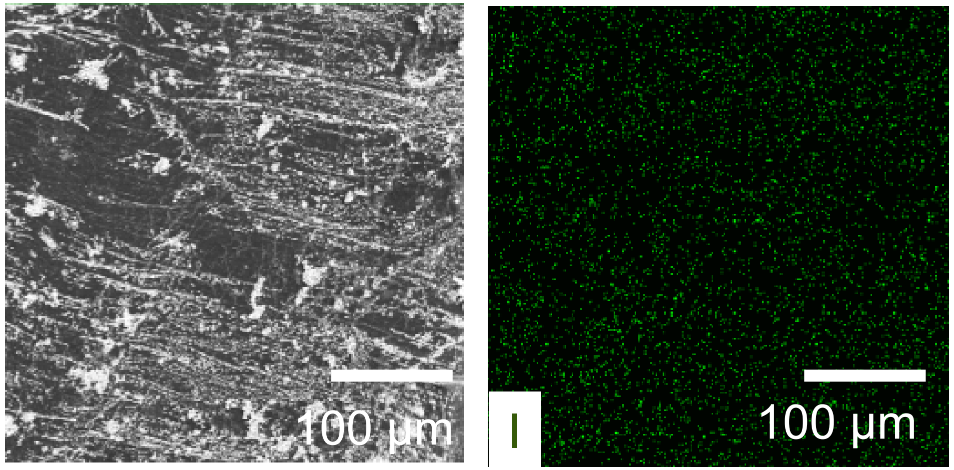
Solid Electrolyte Interphase Engineering



$LiNO_3$ promotes lower surface area Li deposition.

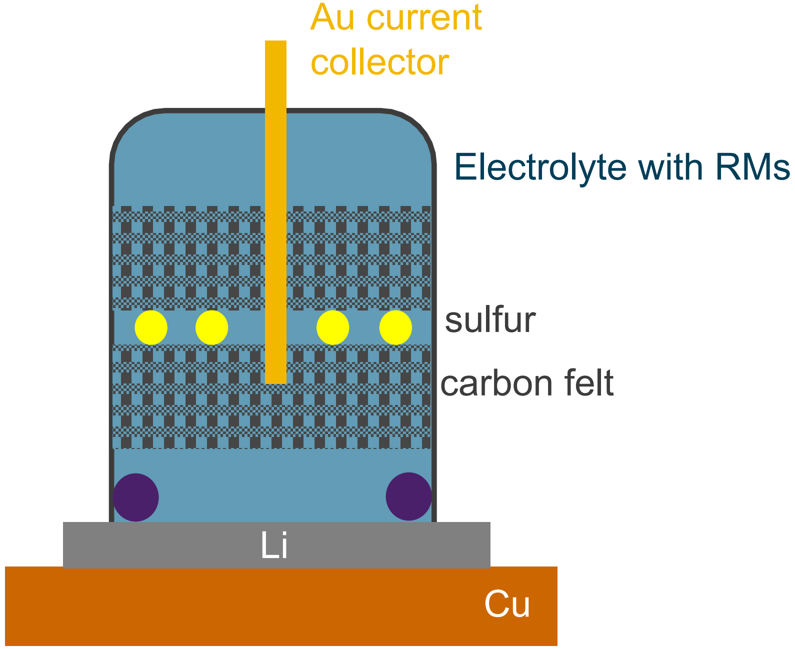
Additives protect the Li surface, so no ion selective membrane is needed.



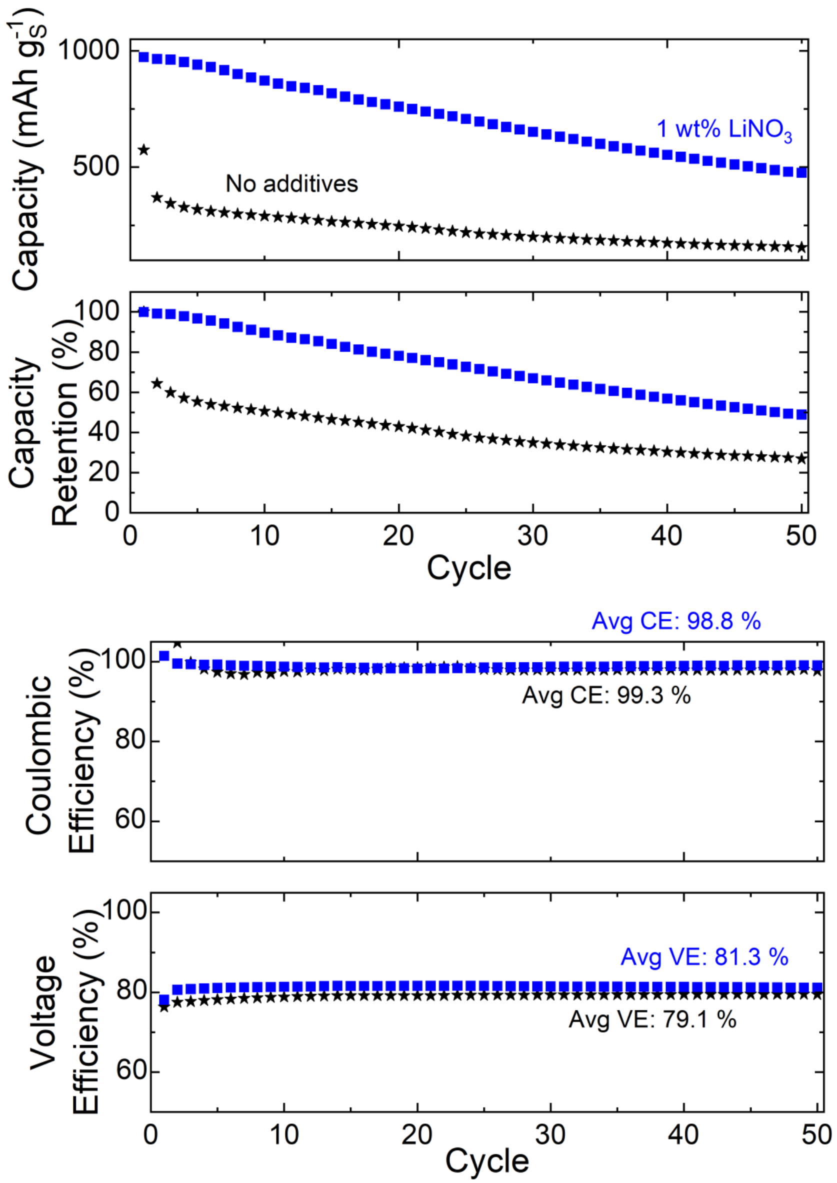


Iodine is uniformly distributed through SEI in the form of LiI.

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

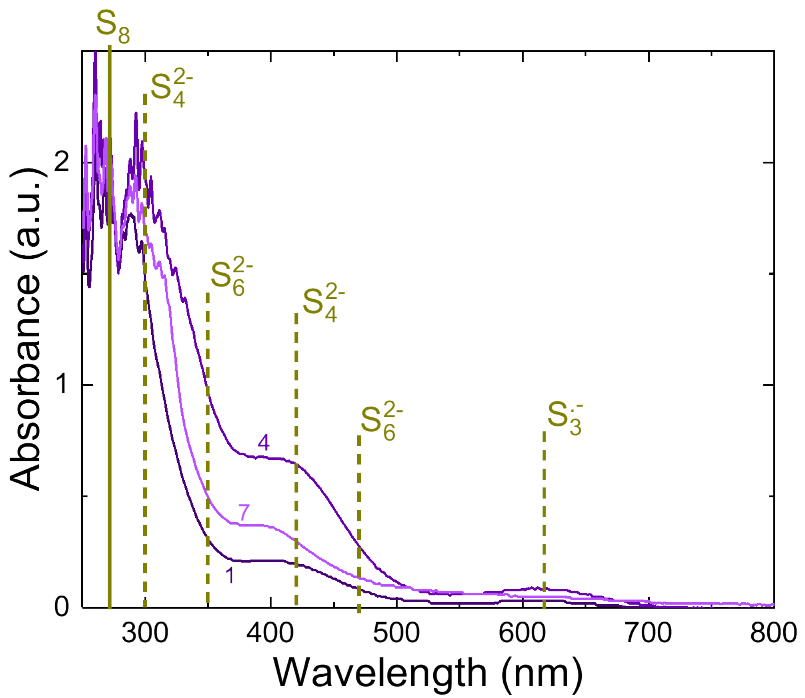
Polysulfide Cycling

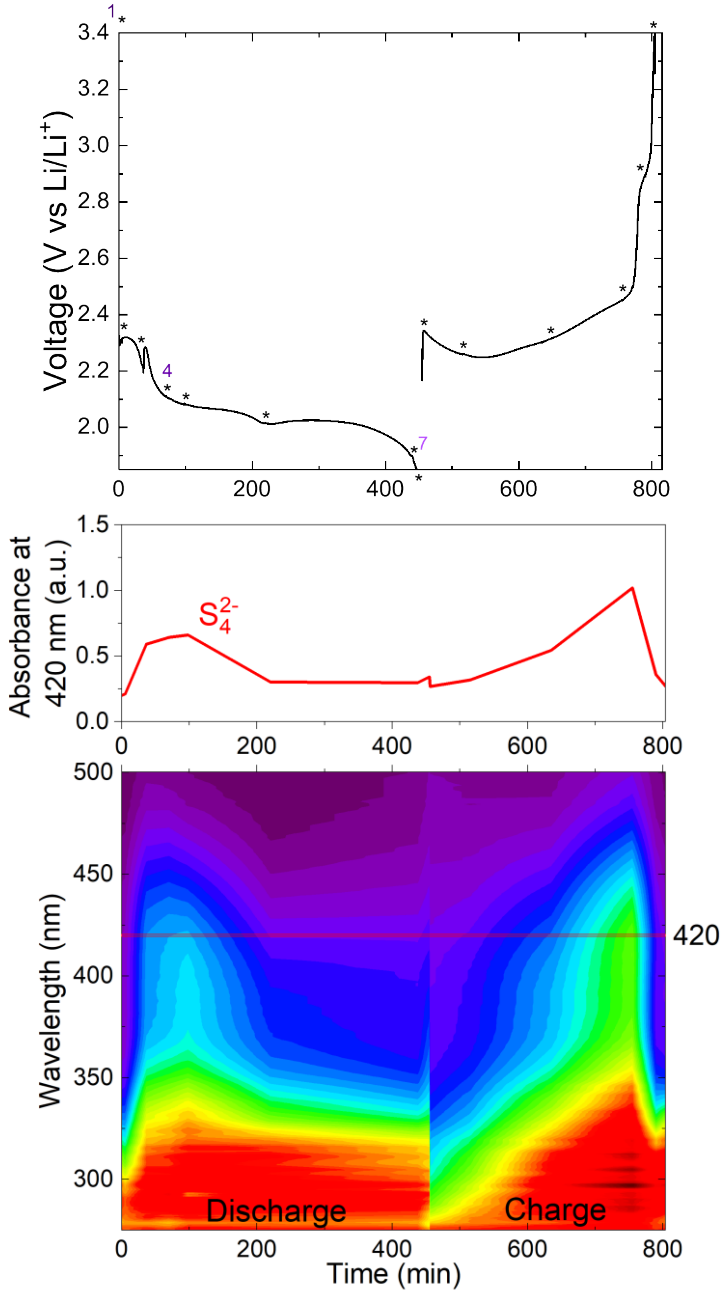
Long chain　　　　Short chain

$$S_8 + 16e^- + 16Li^+ \leftrightarrow \frac{8}{n} Li_2S_n + aLi^+ + ae^- \leftrightarrow \frac{8}{m} Li_2S_m + bLi^+ + be^- \leftrightarrow 8Li_2S$$

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

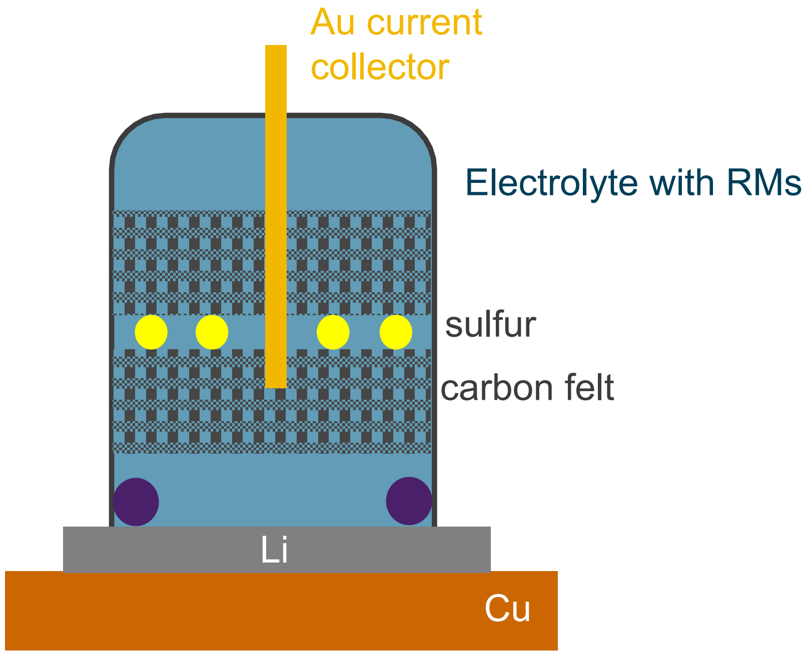
RMs aid in conversion of soluble PSs to insoluble Li_2S.





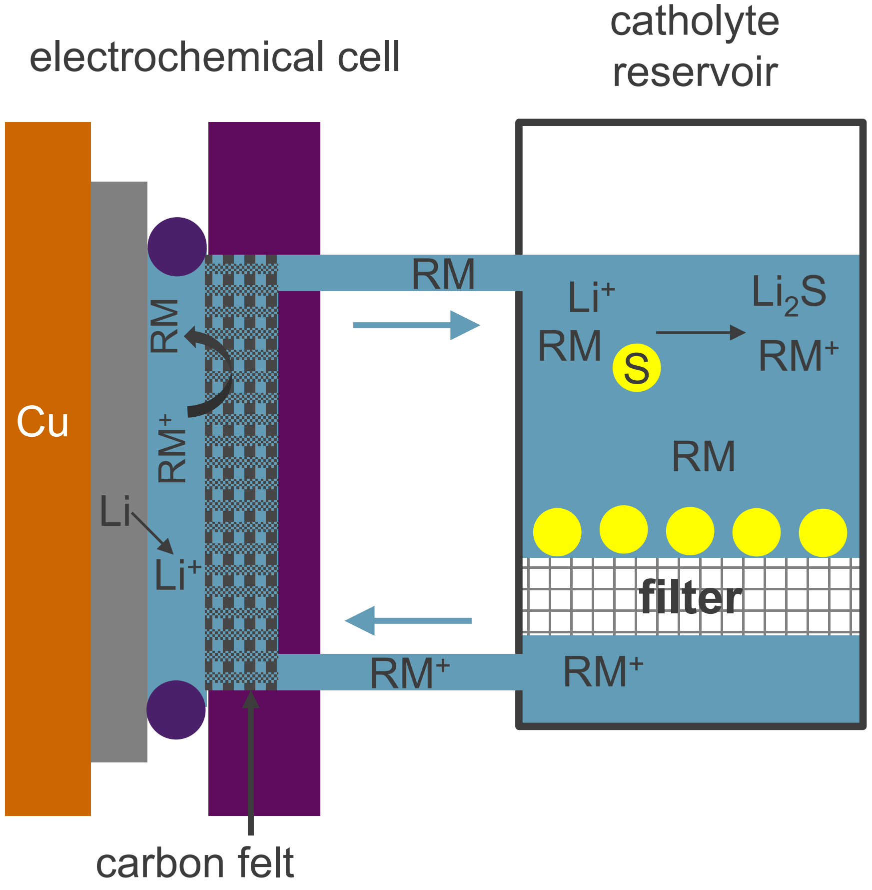
Scale up to Flow Cell

Static cell



S loading: 0.99-4.4 mg_S cm^{-2}

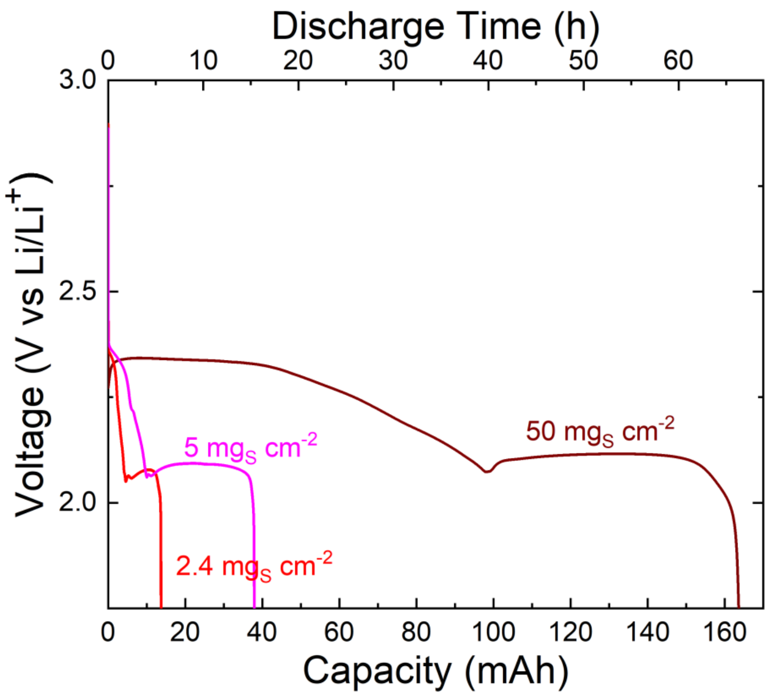
Flow cell

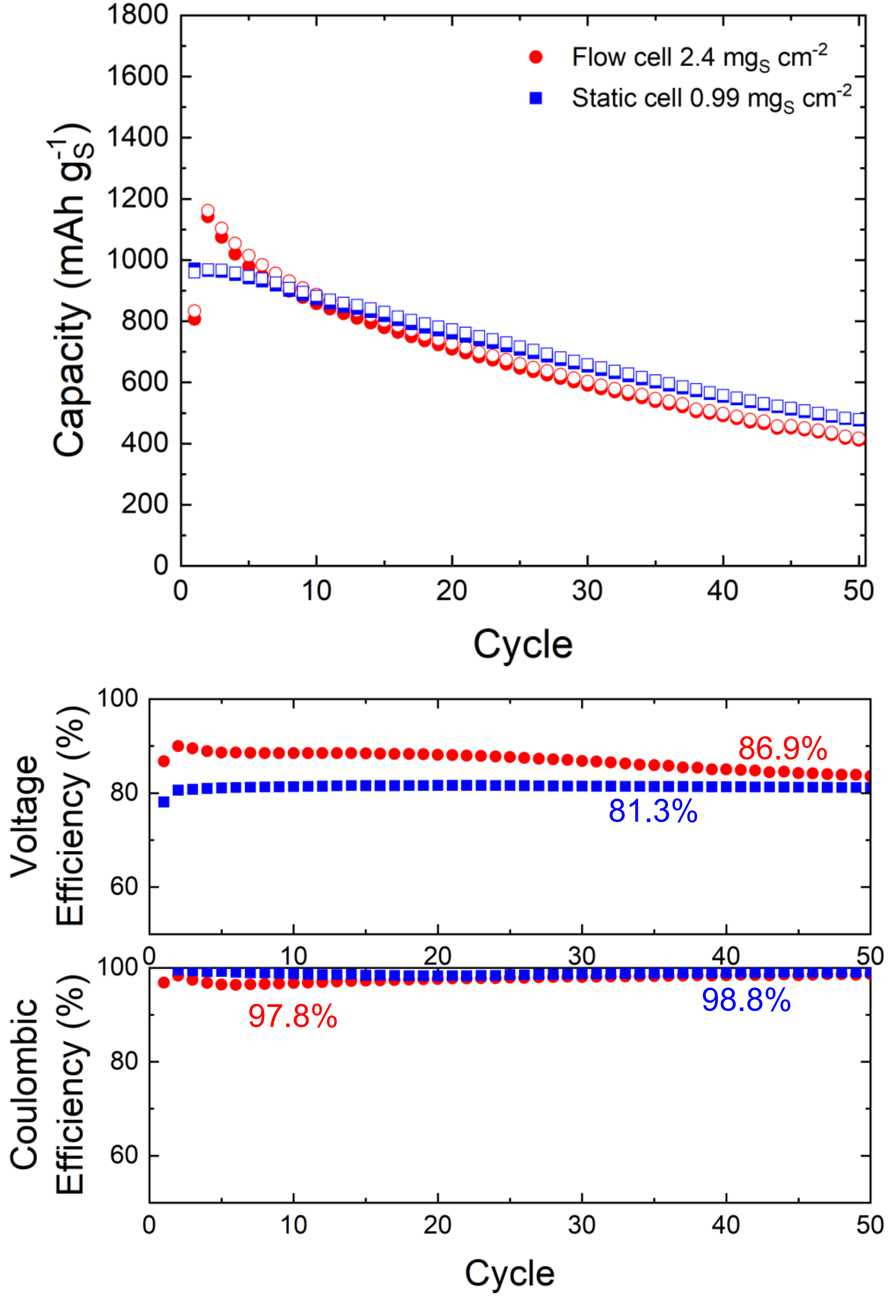


S loading: 2.4-50 mg_S cm^{-2}

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.

Acknowledgments

We thank the DOE Office of Electricity, Energy Storage Program managed by Dr. Imre Gyuk for funding this work!

OFFICE OF ELECTRICITY
ENERGY STORAGE PROGRAM