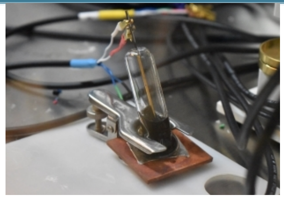
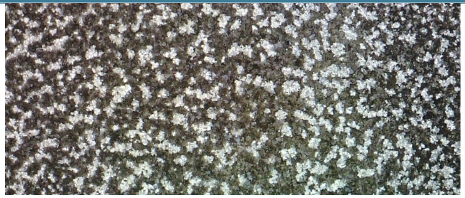
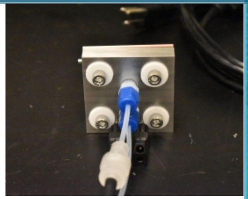
SAND2023-04291C

Sandia National Laboratories

A03-0780: Higher Energy Density Mediated Lithium-Sulfur Flow Batteries





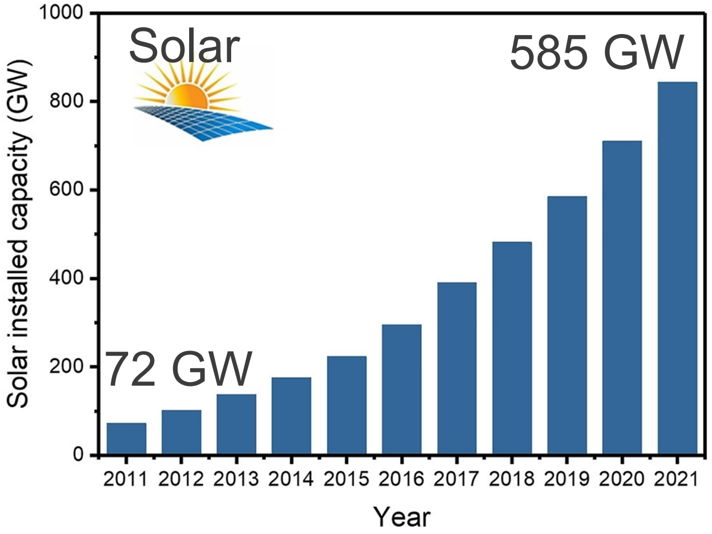


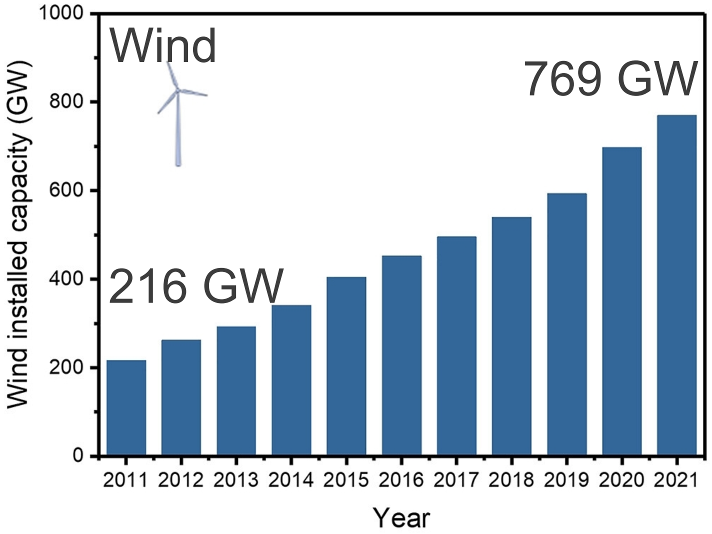
Melissa Meyerson*, Adam Maraschky, and Leo Small

241st ECS Meeting, Spring 2022

May 31, 2022

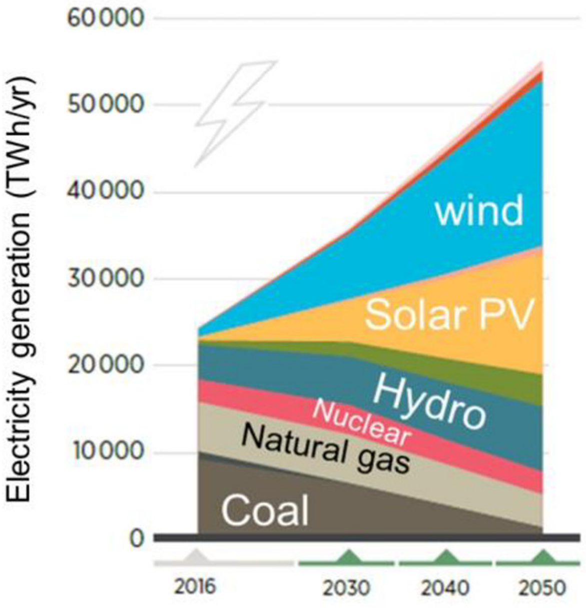
Growing Need for Grid Storage

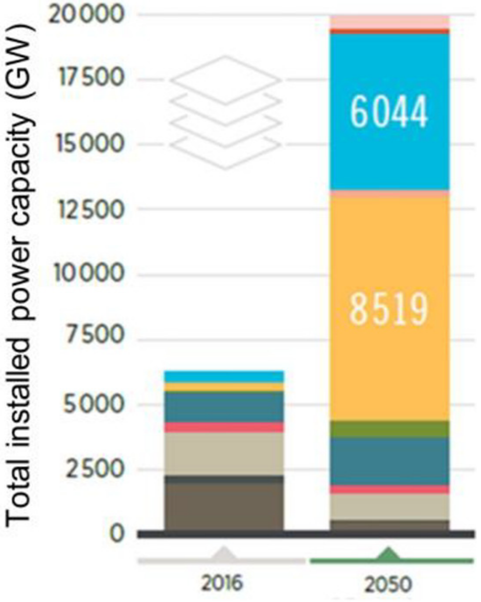




S is high capacity and low cost:

- 1675 mAh g^{-1}
- \$0.1 kg^{-1}





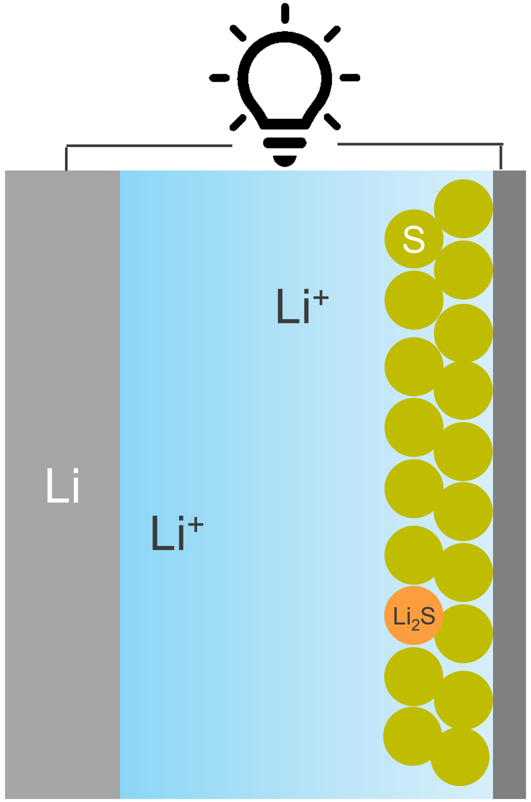
Theoretical energy density of a Li-S battery:

- 2600 Wh kg^{-1}
- 2800 Wh L^{-1}

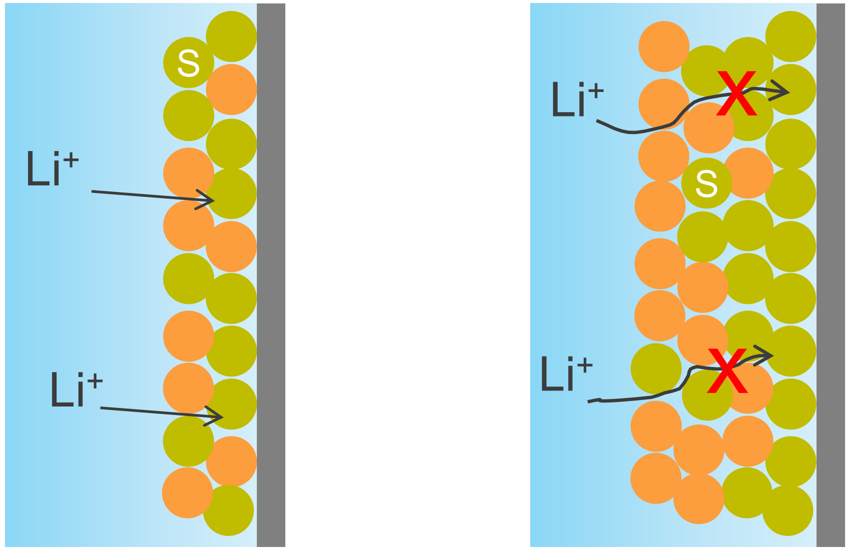
Zhu, Z.; Jiang, T.; Ali, M.; Meng, Y.; Jin, Y.; Cui, Y.; Chen, W. *Chem Rev* **2022,** *122* (22), 16610-16751.

Li-S Battery Design

- Increasing to grid scale requires a change in cell design



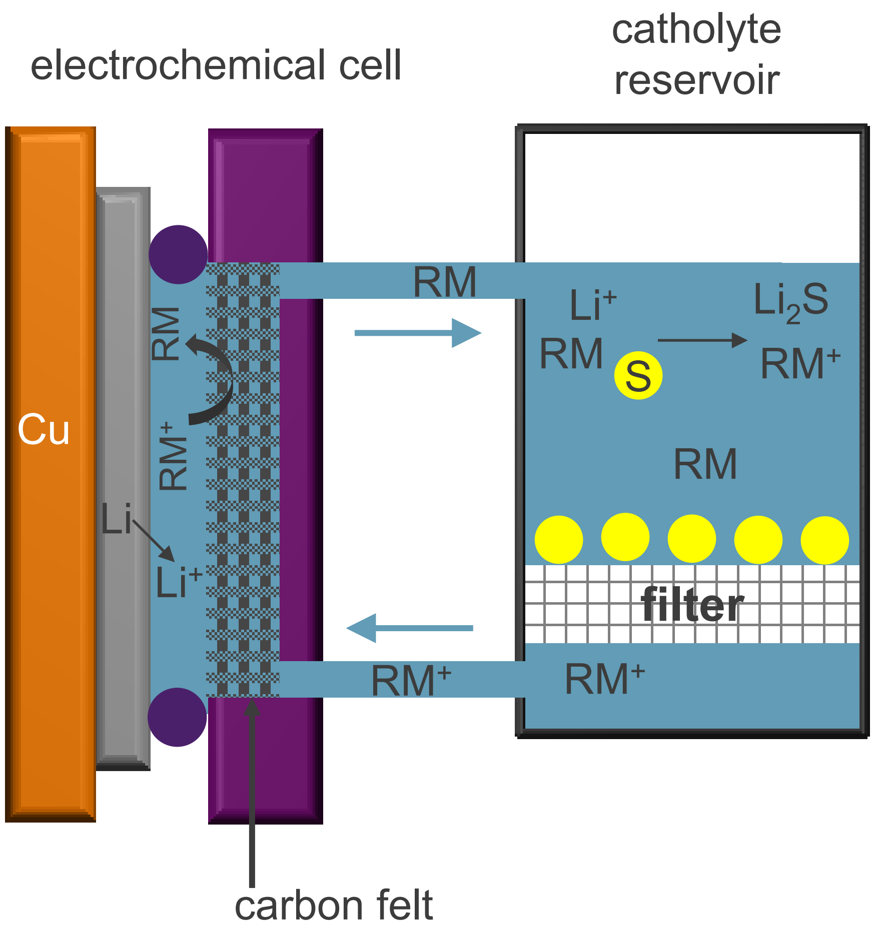
$$S + 2e^{-} + 2Li^{+} \rightarrow Li_2S$$



Energy density plateaus beyond 5 $mg_S\ cm^{-2}$

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

Flow Cell Design



- Hybrid design with solid Li metal anode
- S is chemically reduced with RM
- Electrolyte containing RM^+ is pumped into electrochemical cell where RM^+ is reduced

Discharge:

Echem cell

Felt: $RM^+ + e^- \rightarrow RM$

Metal anode: $Li \rightarrow Li^+ + e^-$

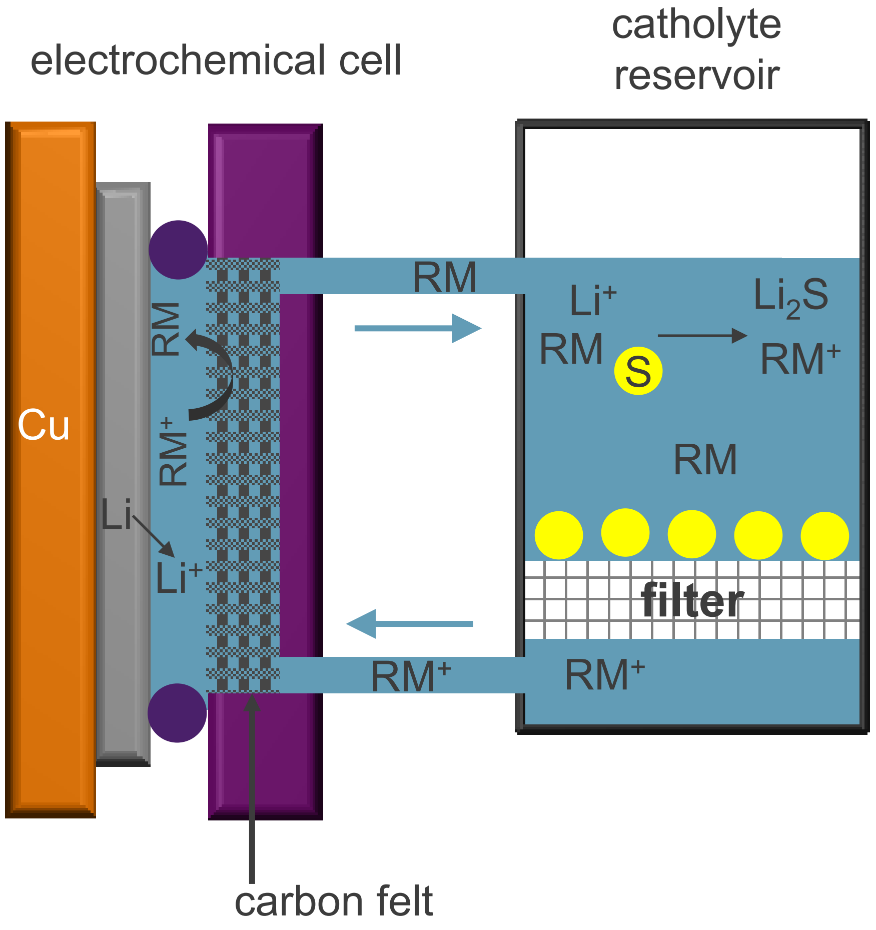
Reservoir

1) $2RM + S \rightarrow 2RM^+ + S^{2-}$

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

Meyerson, M. L.; Rosenberg, S. G.; Small, L. J., *ACS Applied Energy Materials* **2022,** *5* (4), 4202-4211.

Flow Cell Design

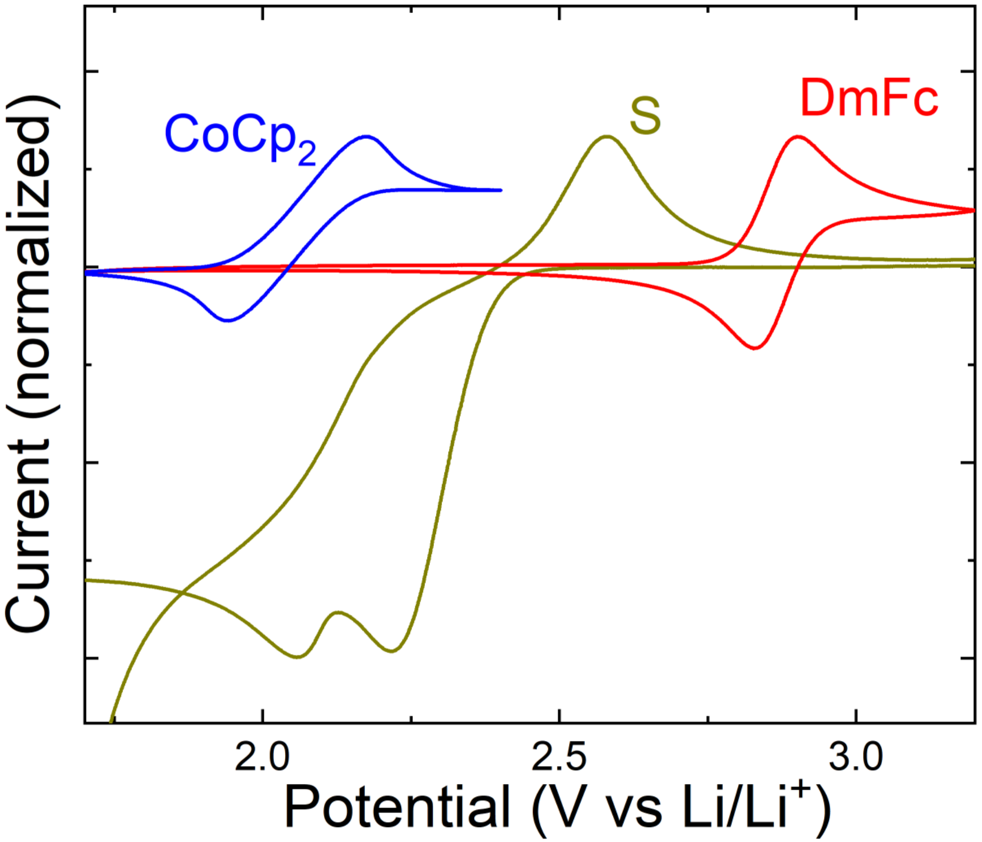


Benefits:

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

Meyerson, M. L.; Rosenberg, S. G.; Small, L. J., *ACS Applied Energy Materials* **2022,** *5* (4), 4202-4211.

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

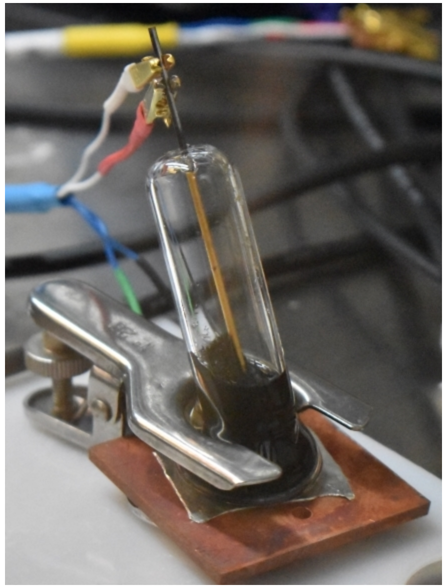
- Close to Li-S reaction (~2.4 V vs Li/Li^+)
  - E_{DmFc}= 2.86 V
  - E_{CoCp2} = 2.06 V
- Good reaction kinetics
  - k^0_{DmFc} = 4.33 x 10^{-3} cm s^{-1}
  - k^0_{CoCp2}= 3.14 x 10^{-4} cm s^{-1}
- Fast diffusion
  - D_{DmFc} = 5.23 x 10^{-6} cm^2 s^{-1}
  - D_{CoCp2} = 3.70 x 10^{-6} cm^2 s^{-1}

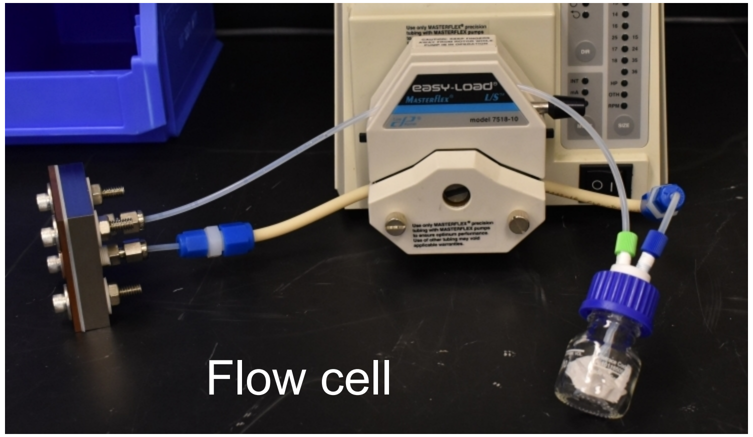
Meyerson, M. L.; Rosenberg, S. G.; Small, L. J., *ACS Applied Energy Materials* **2022,** *5* (4), 4202-4211.

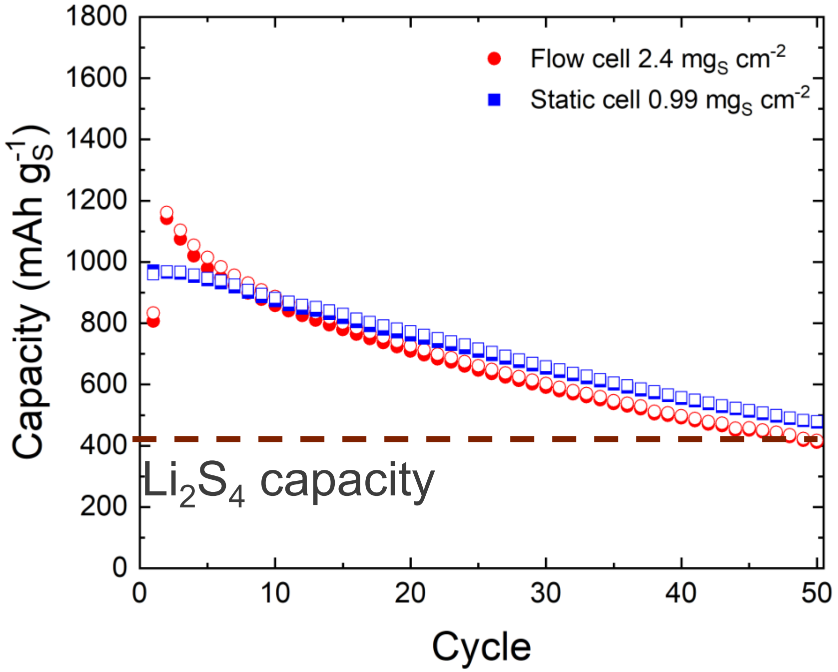
Flow Cell Cycling

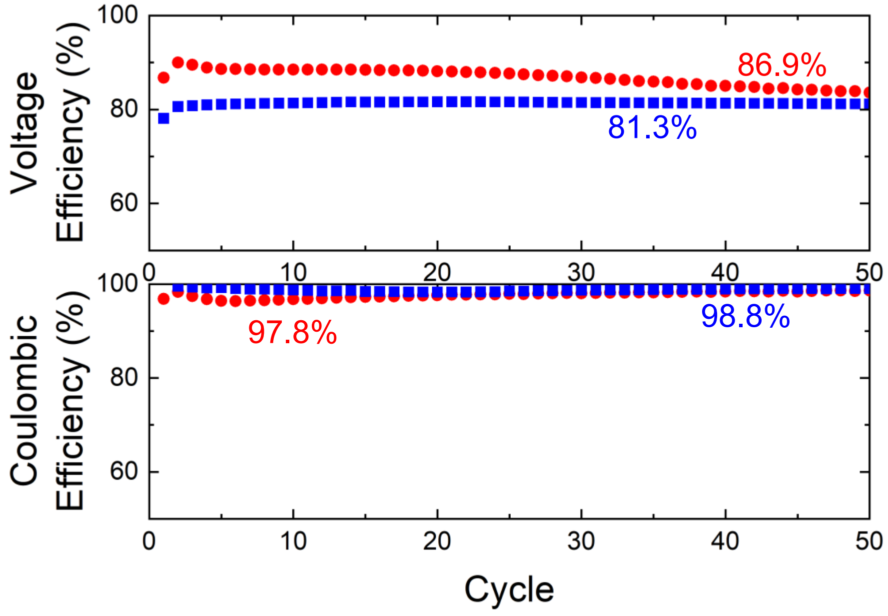
- High capacity
- High coulombic and voltage efficiencies

Static cell





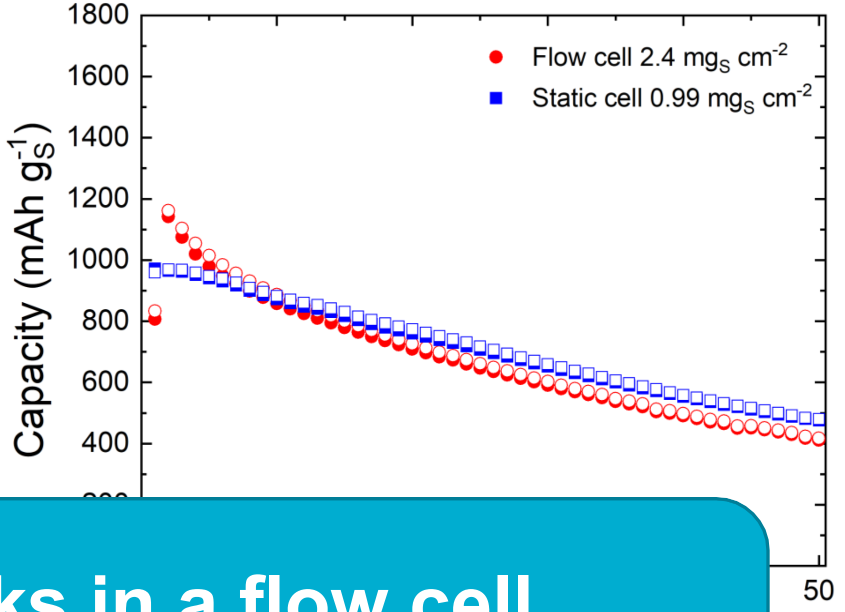




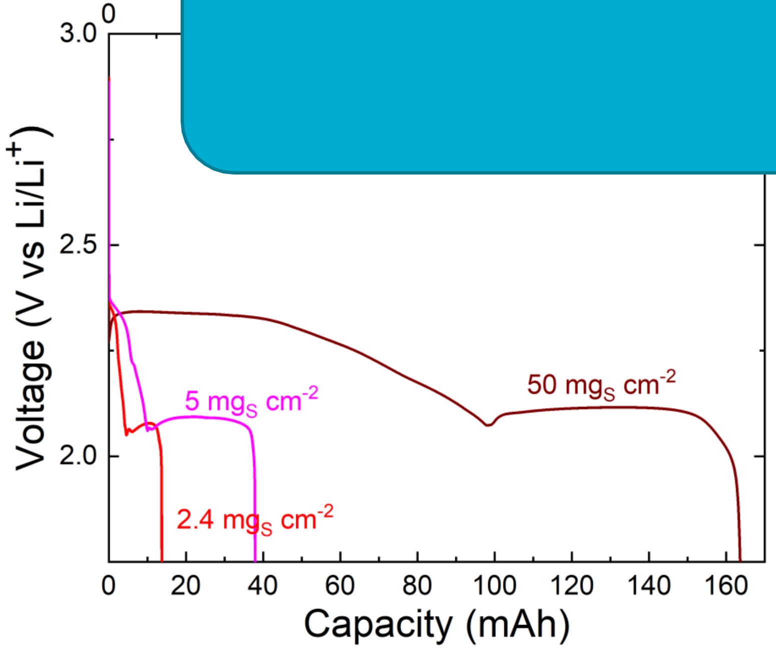
Meyerson, M. L.; Rosenberg, S. G.; Small, L. J., *ACS Applied Energy Materials* **2022,** *5* (4), 4202-4211.

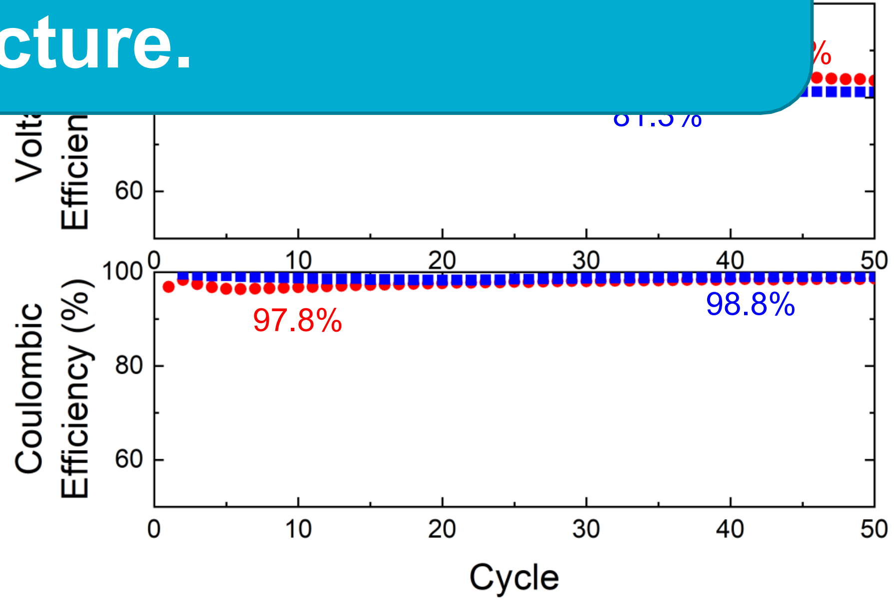
Flow Cell Cycling

- High coulombic and voltage efficiencies
- Increasing S loading increases capacity
- >60 h discharge time shows viability for long duration storage.



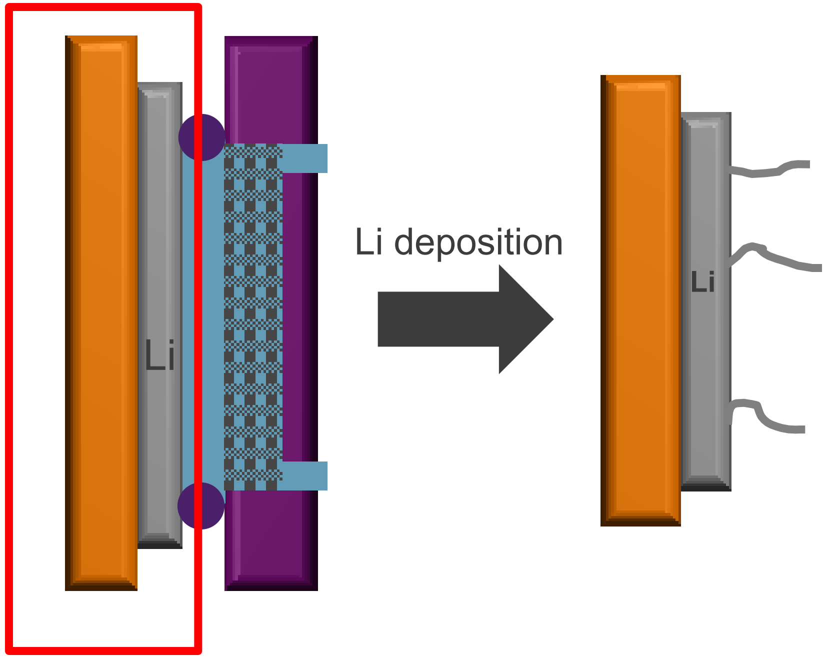
Li-S chemistry works in a flow cell architecture.





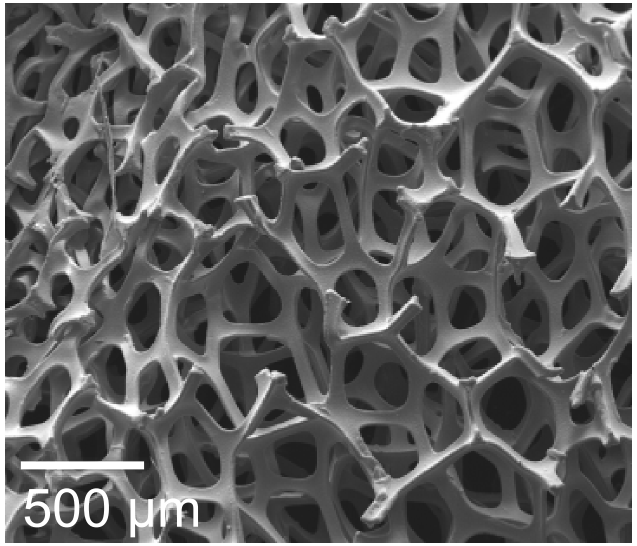
Meyerson, M. L.; Rosenberg, S. G.; Small, L. J., *ACS Applied Energy Materials* **2022,** *5* (4), 4202-4211.

Limitations of Planar Li Anodes: Dendrite formation



Li dendrites

- Dendrites decrease battery life and cause short circuits.
- Increased charge rate exacerbates problems with dendrites.

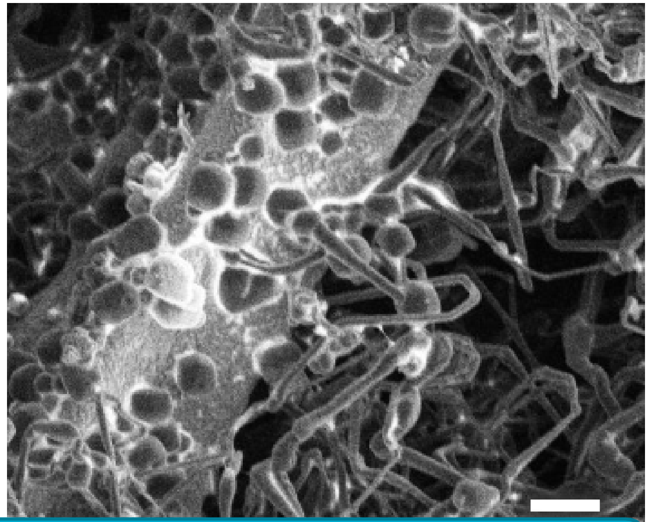


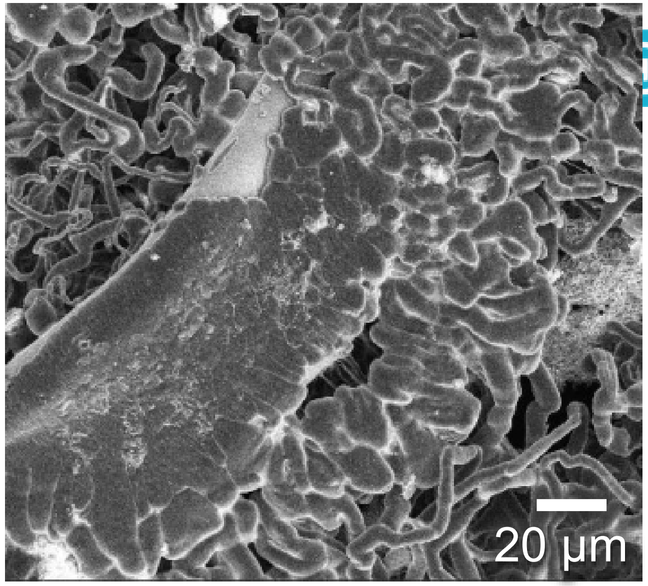
Bare Ni foam

- Ni foam with 97% porosity has ~10x the surface area of planar Ni foil.

Increasing effective surface area decreases the local current density.

Controlling Li Nucleation

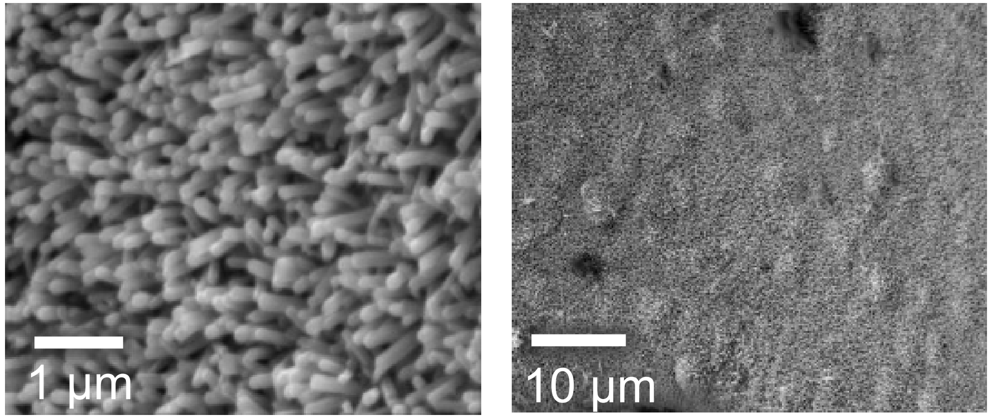




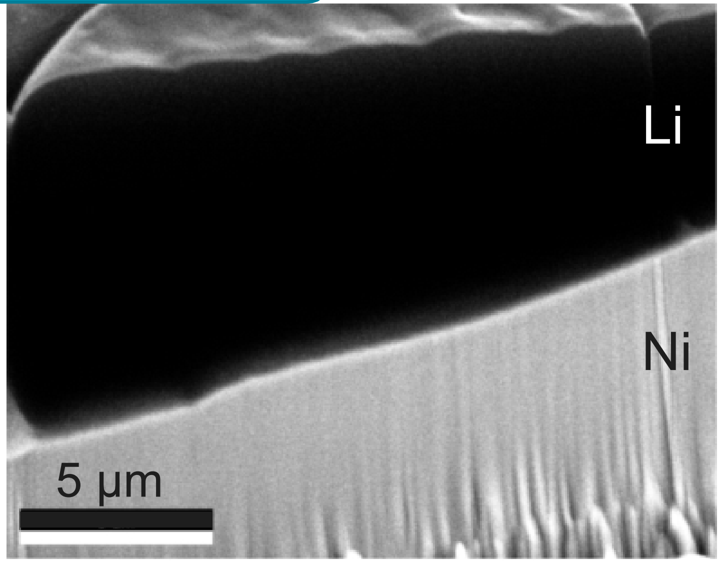
ZnO on Ni Foam

Hydrothermal synt
- 100-150 nm wid
- Uniform coverag

Better wetting leads to lower surface area Li.



SEM of ZnO nanorods

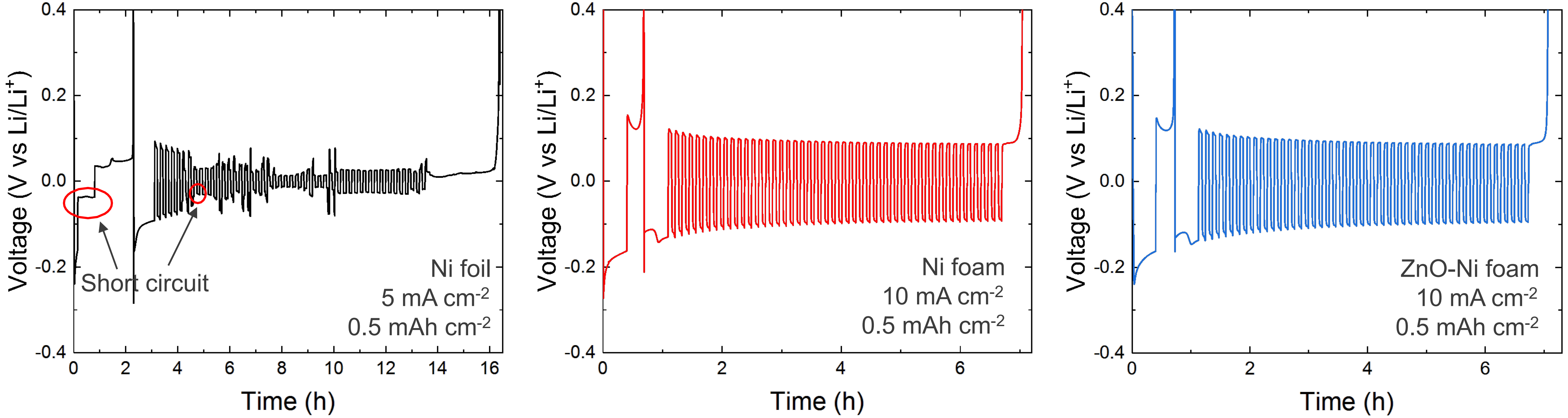


Synthesis procedure: Sun, C.; Li, Y.; Jin, J.; Yang, J.; Wen, Z., *J. Mater. Chem. A* **2019,** *7* (13), 7752-7759.

Meyerson, M.L.; Maraschky, A.M.; Watt, J.; and Small, L.J. “Fast Cycling of “Anode-less”, Redox-mediated Li-S Flow Batteries,” submitted to *J. Energy Storage*.

Increased Surface Area Allows Faster Charging

For planar deposition, charging above 1 mA cm^{-2} results in unstable cycling and shorting

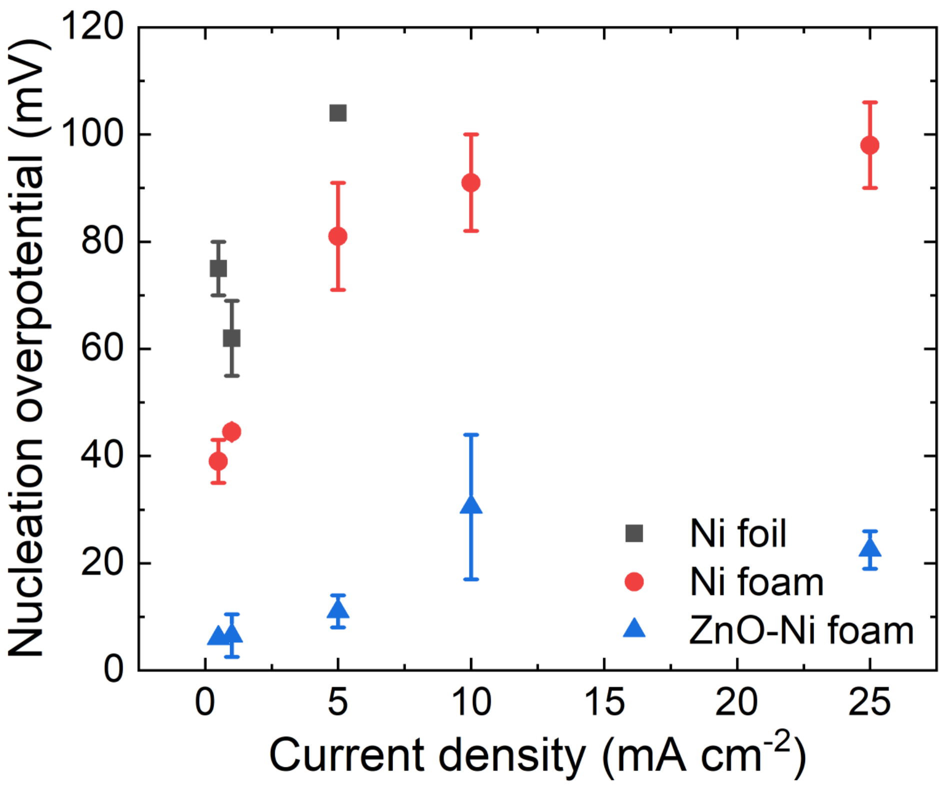


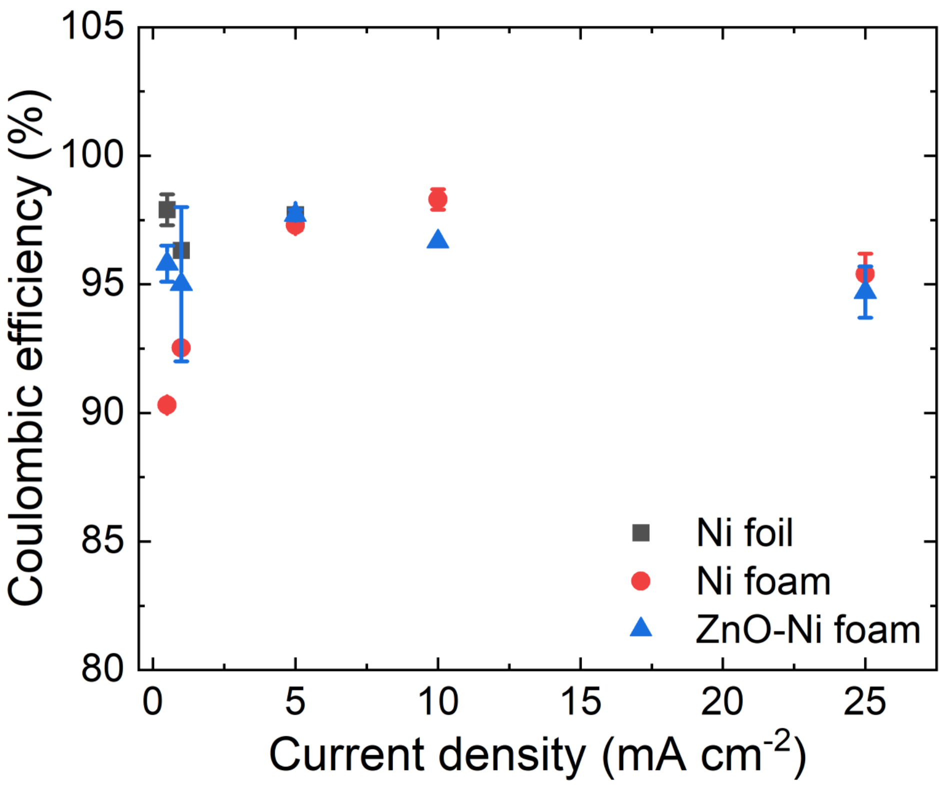
Using high SA foam, charge rate can be 10 times faster.

Meyerson, M.L.; Maraschky, A.M.; Watt, J.; and Small, L.J. "Fast Cycling of "Anode-less", Redox-mediated Li-S Flow Batteries," submitted to *J. Energy Storage*.

ZnO Further Improves System

Nucleation overpotential decreases and CE increases compared to bare Ni foam at low current densities.





ZnO decreases the nucleation overpotential and improves coulombic efficiency.

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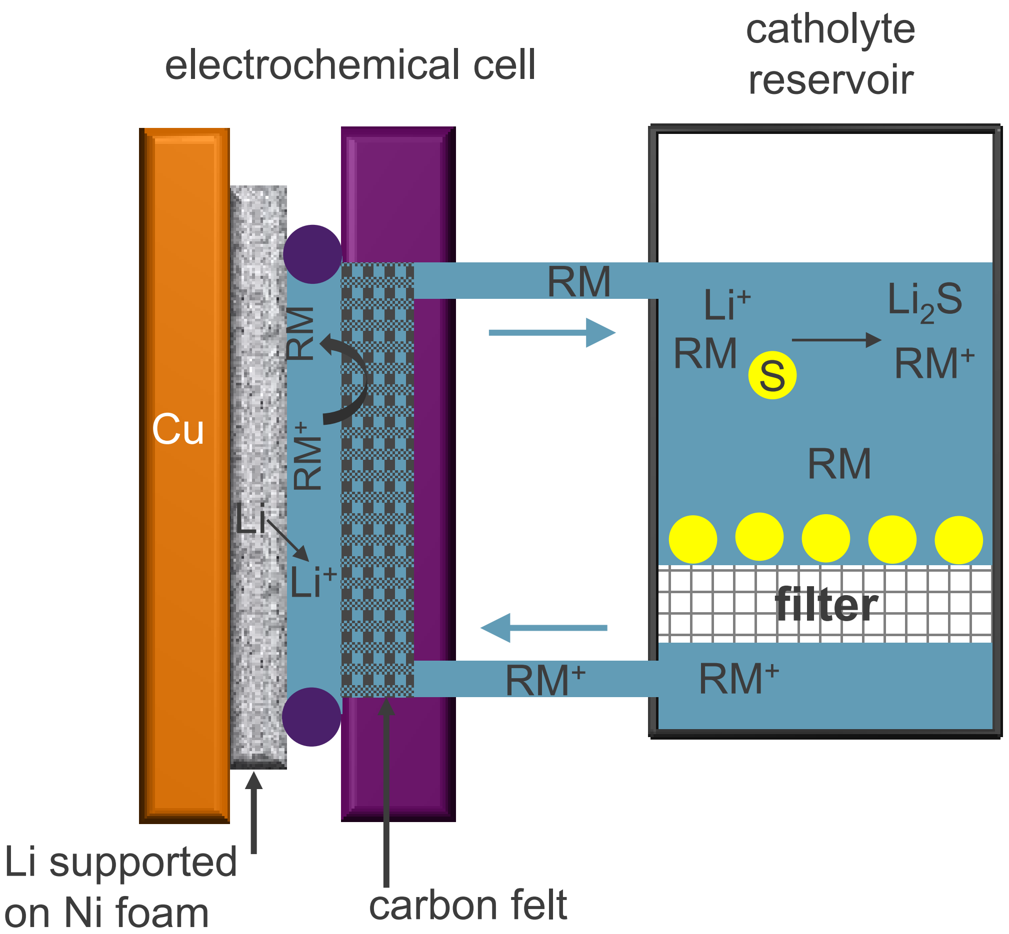
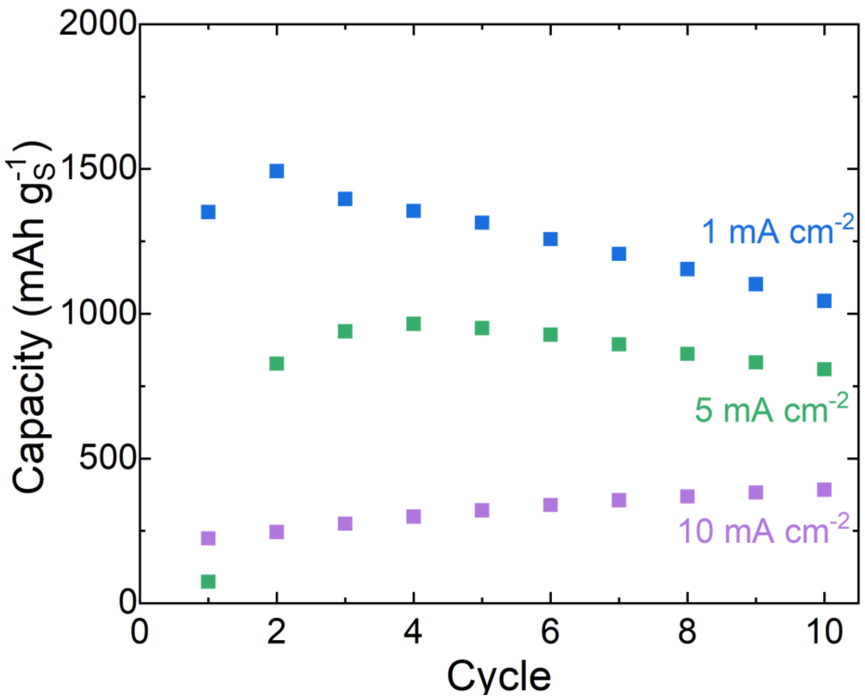
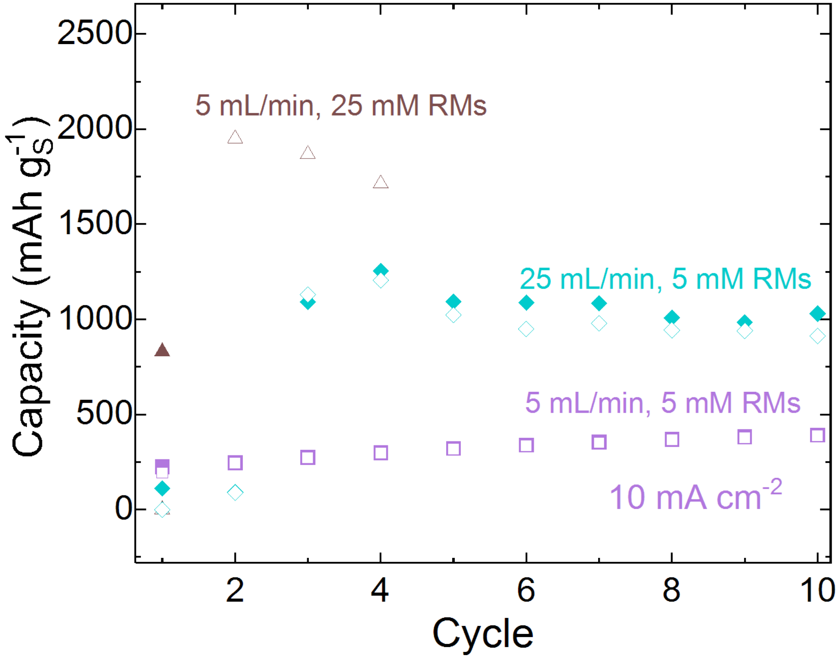
Flow Cells with ZnO on Ni foam



Ni foam enables stable cycling 20x faster than original flow cell.





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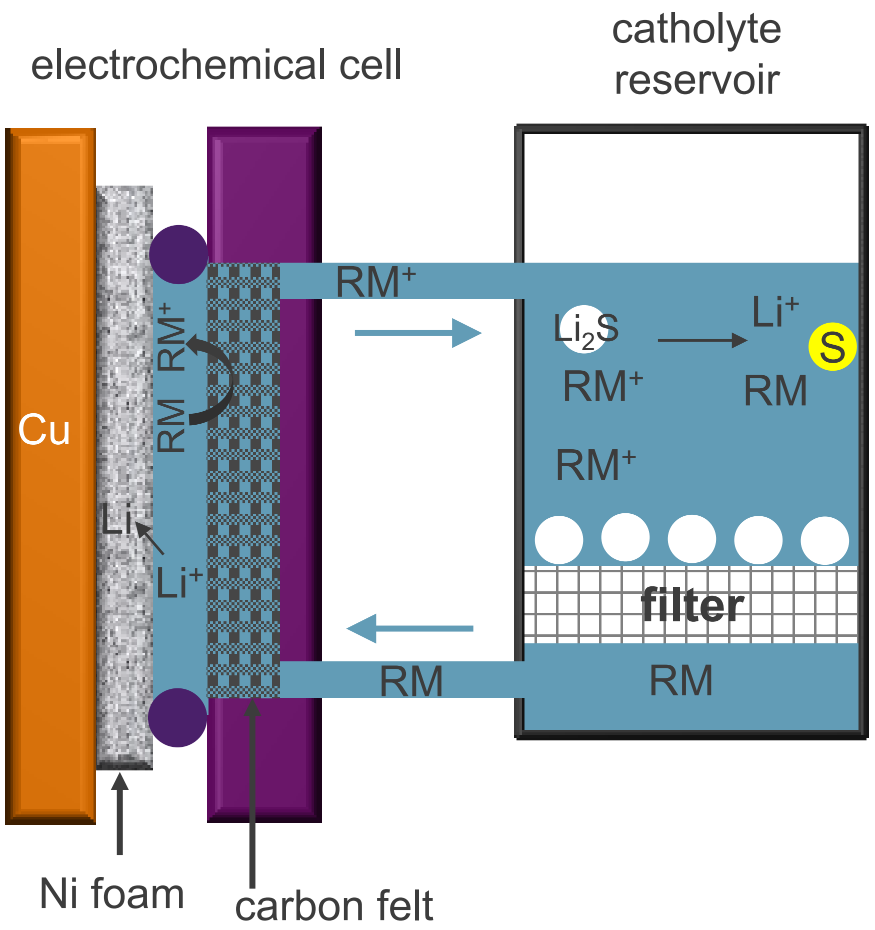
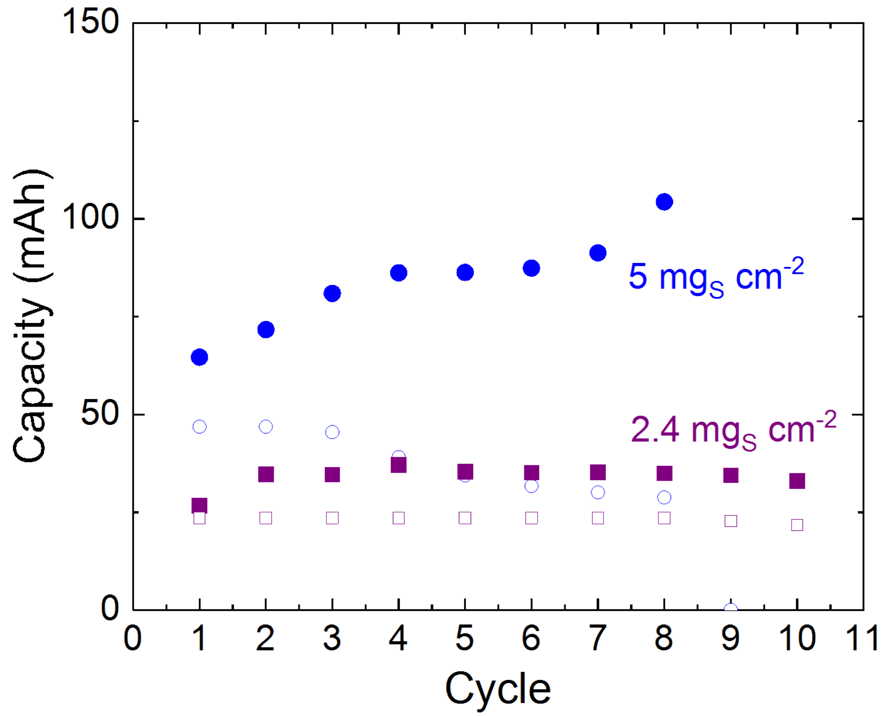
“Anode-less” Flow Cells





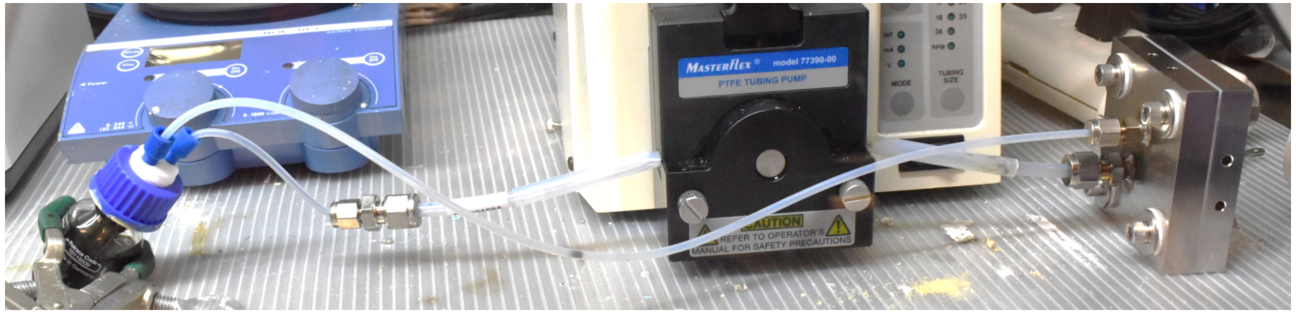
Volumetric energy density: 20.3 Wh L^{-1}

Cells can be scaled up and assembled in the safer Li-less state.

Meyerson, M.L.; Maraschky, A.M.; Watt, J.; and Small, L.J. “Fast Cycling of “Anode-less”, Redox-mediated Li-S Flow Batteries,” submitted to *J. Energy Storage*.

Conclusions

- Redox mediation enables Li-S chemistry to be adapted to work in a flow cell architecture.
- High surface area scaffolds increase the maximum cycling current density 20x.
- Scaled battery increasing energy density to 20.3 Wh L^{-1}.
- Energy density on par with VRBs with room for improvement.



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

Acknowledgments

OFFICE OF ELECTRICITY
ENERGY STORAGE PROGRAM

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

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