Mediated Lithium-Sulfur Flow Batteries

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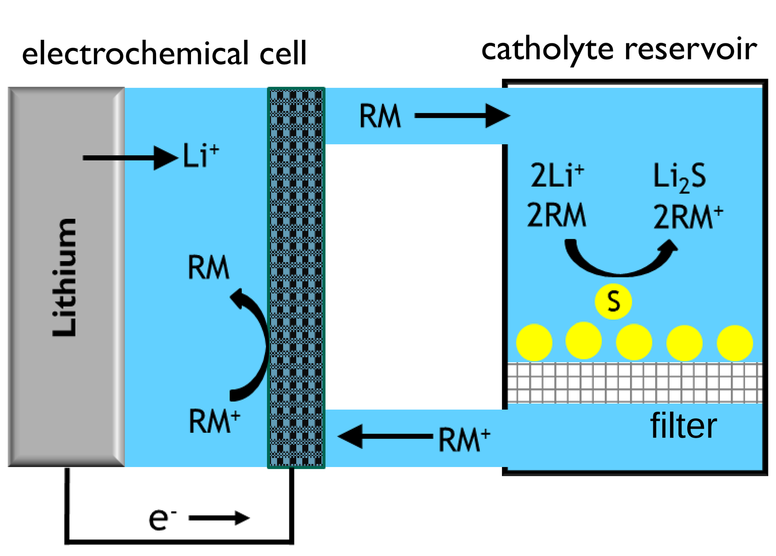
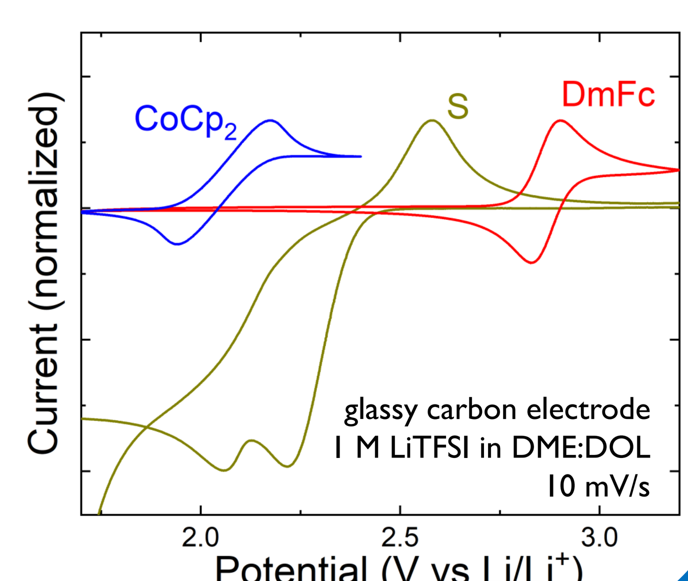
Overview:
Lithium-sulfur is a next-generation battery technology which leverages an inexpensive sulfur cathode to significantly increase specific capacity. We are working to translate this lithium-sulfur technology to a mediated redox flow battery (RFB), where soluble redox-active molecules are circulated, reducing sulfur particles stored in a reservoir. This design also physically separates the anode and cathode, minimizing safety risks in case of failure. While such systems are attractive for cost-competitive long duration energy storage due to their potential for ultra-high sulfur concentrations, the current density of these RFBs need to be increased to reach competitive power outputs.

Operating Principle



Soluble redox mediators (RM) oxidize and reduce solid, energy-storing sulfur particles kept in the catholyte reservoir tank. Catholyte is flowed into an electrochemical cell where electrons are extracted from mediators at a porous carbon electrode.

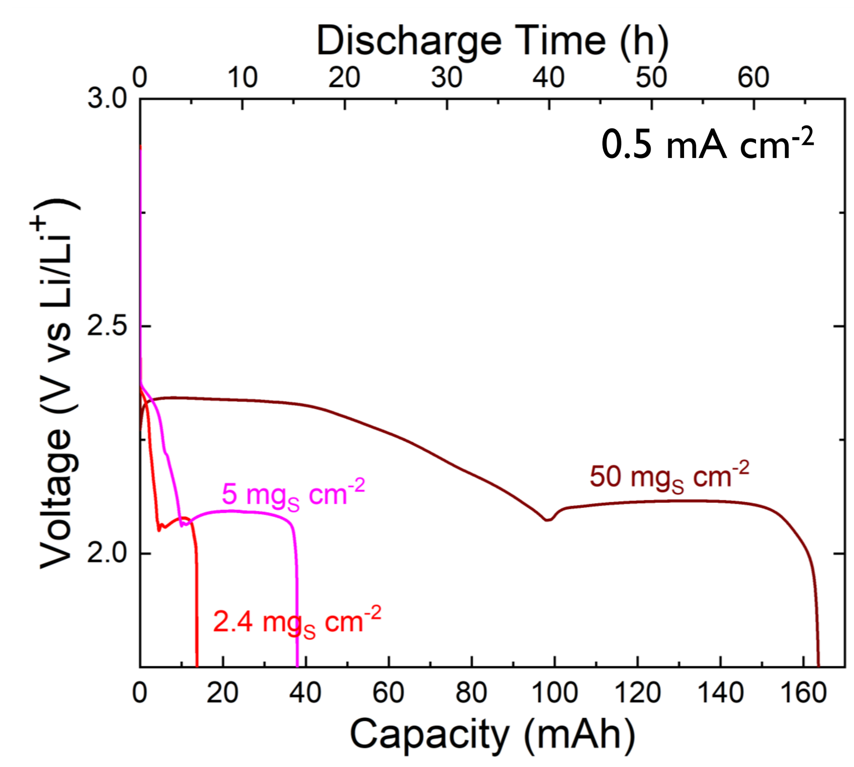
Cobaltocene ($CoCp_2$) was chosen to reduce S to Li_2S, while decamethyl ferrocene (DmFc) was chosen to oxidize Li_2S to S. Cyclic voltammetry (right) demonstrates the relative redox potentials of $CoCp_2$, S, and DmFc.

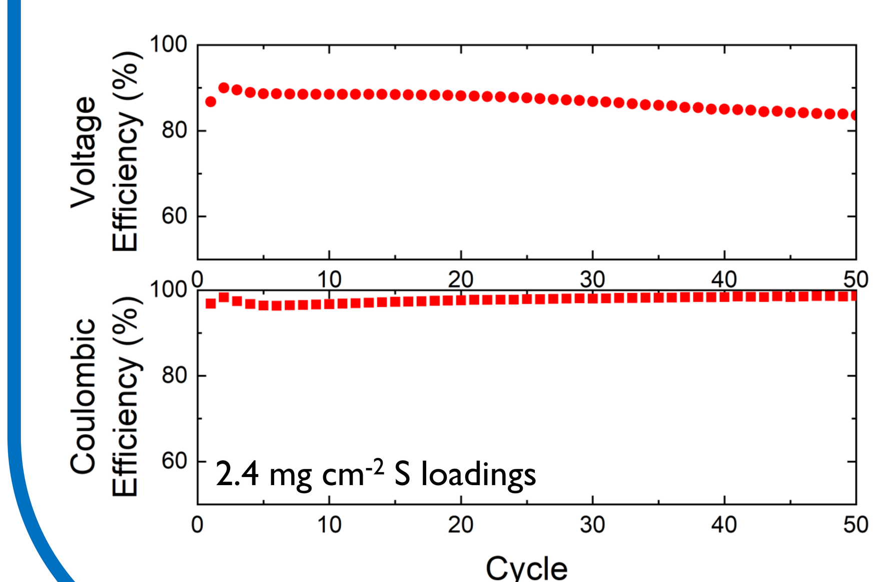


Meyerson et al. *ACS Appl. Energy Mater.* 2022, 5, 4202-4211.
L.J. Small, M.L. Meyerson. US Application No. 17/740,128. May 9, 2022.

Flow Cell Performs Well at Low Current

Redox mediated Li-S flow batteries can be cycled stably over 50 cycles with high capacity and voltage efficiency demonstrated at 2.4 mg_S cm^{-2}: 1142 mAh g_S^{-1} and 86.9% VE. Sulfur loadings of up to 50 mg_S cm^{-2} were achieved enabling a discharge time of over 60 hours.





Li-S chemistry works, but charging speed is limited.

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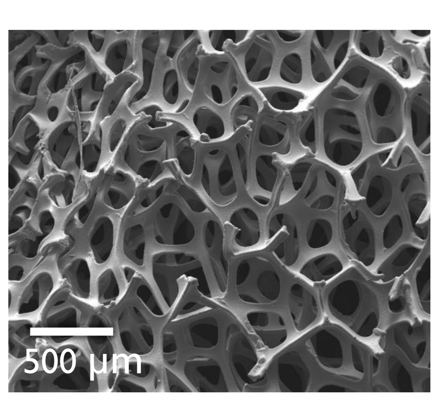
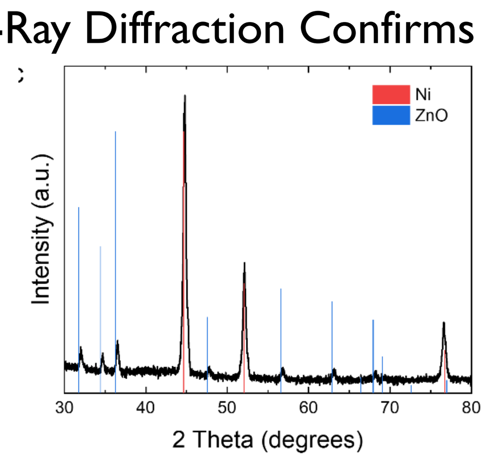
Higher Currents Enabled by a 3D Anode

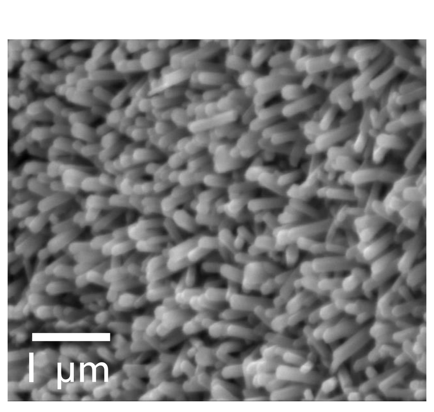
Replacing planar Li foil with high surface area Ni foam decreases the local current.



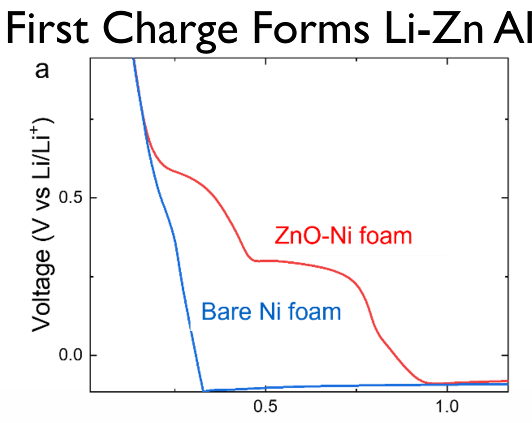
X-Ray Diffraction Confirms ZnO



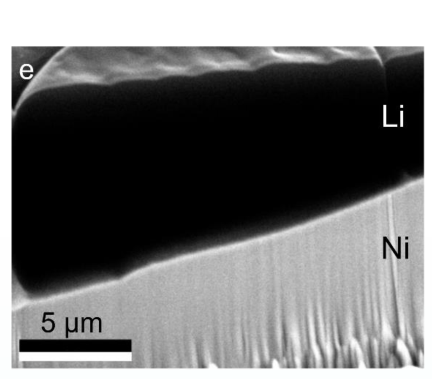
To increase Li wettability and decrease nucleation overpotentials, the Ni foam was decorated with ZnO nanorods.



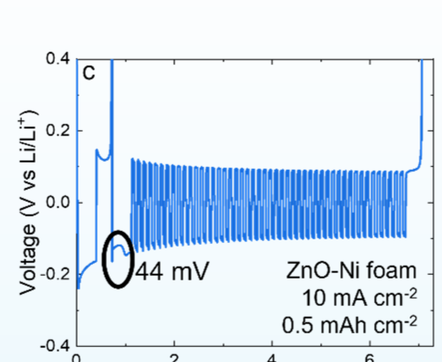
First Charge Forms Li-Zn Alloy



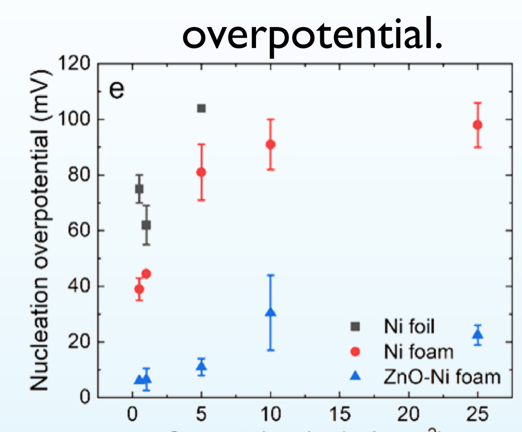
Li-Zn alloy was formed on initial charge, and Li metal was plated on top. (CryoFIB cross section)



Symmetric Li cells were cycled at 10 mA cm^{-2} with 96.7% Coulombic efficiency over 48 cycles.



ZnO lowers the Li nucleation overpotential.

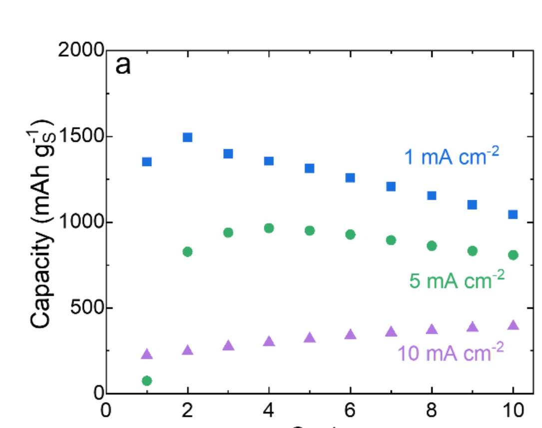


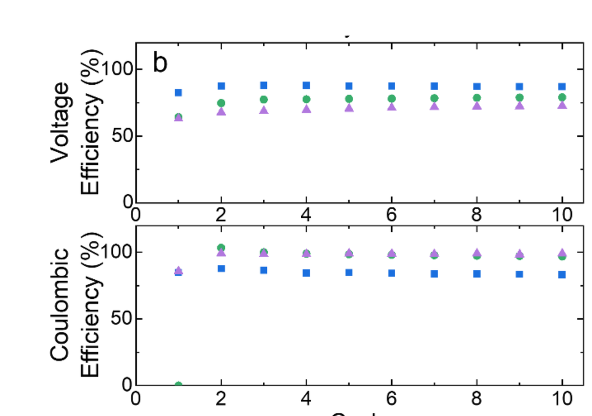
10x increase in current density!

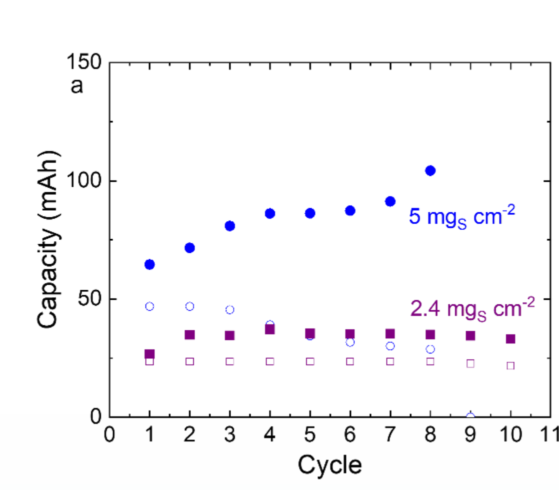
Meyerson et al. *J. Energy Storage* 72 (2023) 108767.

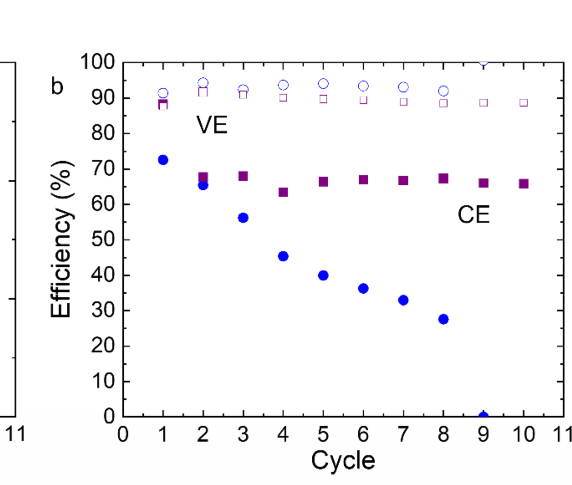
Higher Current RFB Cycling with or without Li Metal

The ZnO-Ni foam was prelithiated with molten Li, and cycled in an RFB at high current. Higher RM concentration or faster pumping can increase capacity at 10 mA cm^{-2}.









RFBs can also be run without any Li metal initially present. Li metal is plated at the anode on initial charge.
Highest S loading achieved 20.3 Wh L^{-1} (8.41 Ah L^{-1}).

Future Work

- Scale up Li-S flow cells to ultra-high S loadings in larger (100 cm^2) cells.
- Improve capacity utilization of cells with ZnO-Ni foam anode at higher rates.
- Improve "anode-less" Li-S RFB capacity utilization.

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