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Mediated Li-S Flow Batteries

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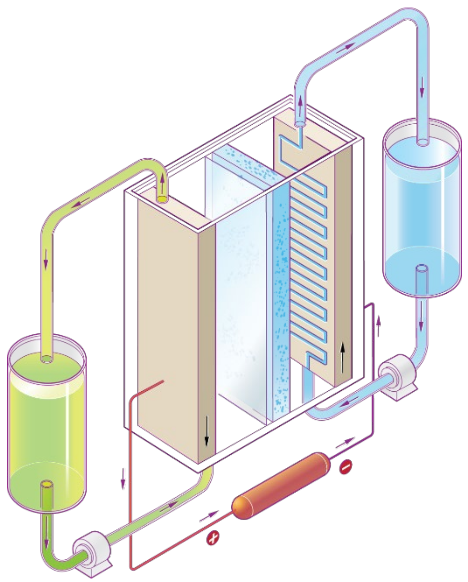
Goal

Adapt **Li-S chemistry** to long duration energy storage using **flow battery** architecture.

- Scalability - adaptable to MWh levels, long duration discharges
- Safety – anode and cathode physically separated
- Cost – larger cell size, less wiring, opportunity for different cell designs

Why Li-S?

- In theory, energy dense **solid materials**: 2600 Wh kg^{-1}
  - Li 3860 mAh g^{-1}, S 1675 mAh g^{-1}
  - Less volume and mass required to store energy!
- Cost of S is essentially "free."
- Large literature available - many great tools, approaches lessons learned!
- Idea is generally applicable to other metal anode – solid mediated systems

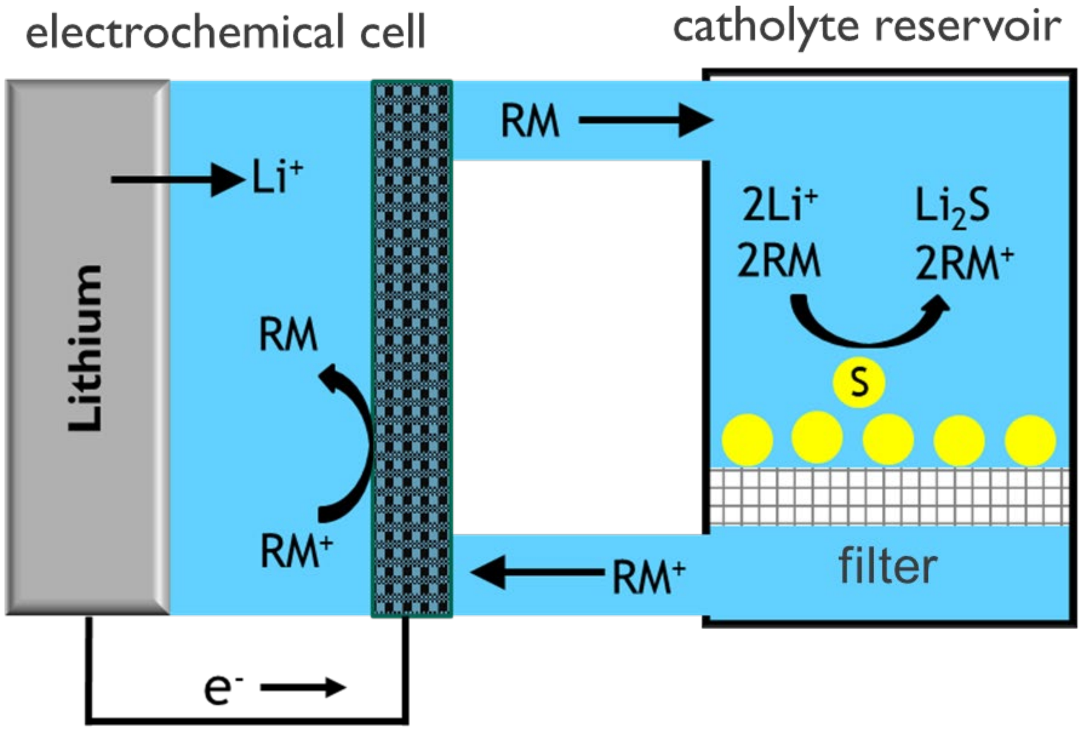


A typical flow battery

Li-S is a promising candidate for adaption into flow batteries for long duration energy storage.

Operating Principle

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



Reactions on Discharge

Echem cell

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

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

Reservoir

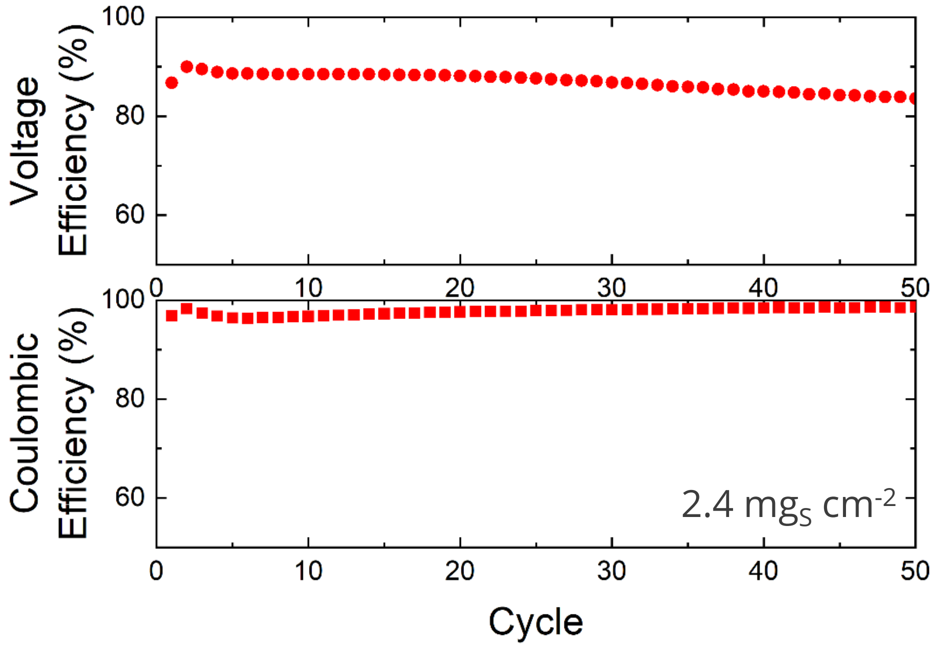
1) $2RM + S \rightarrow 2RM^+ + S^{2-}$

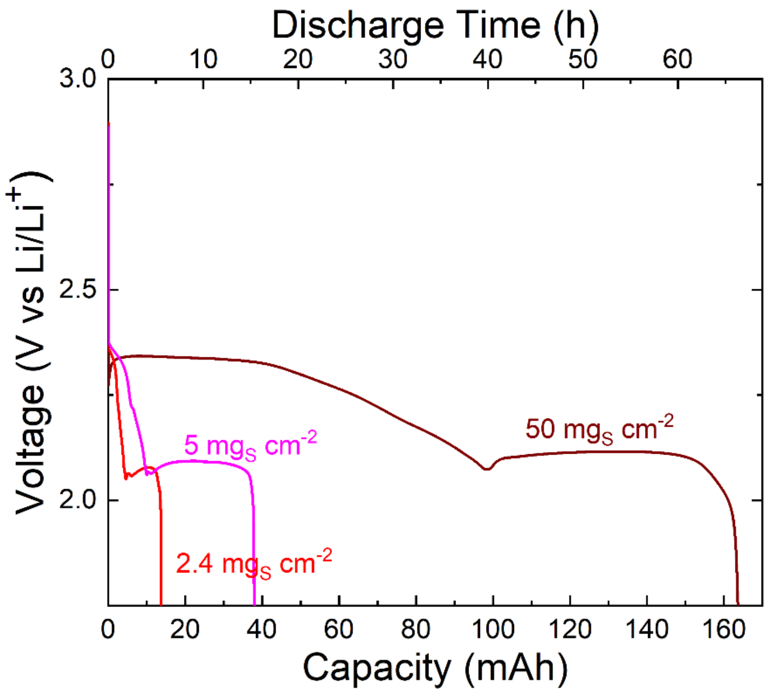
2) $S^{2-} + 2Li^+ \rightarrow Li_2S$

L.J. Small and M.L. Meyerson. US Application No. 17/740,128. May 9, 2022.

Promising Initial Results

- Cycled stably over 50 cycles at 0.5 mA cm^{-2}
- At 2.4 mg$_S$ cm^{-2} sulfur loading: 1142 mAh g$_S$$^{-1}$ (68% theoretical) and 86.9% VE
- Sulfur loadings of up to 50 mg$_S$ cm^{-2} enabled discharge times of over 60 hours.





0.5 mA cm^{-2}
5 mM RM
1M LiTFSI
1wt% $LiNO_3$
1:1 (v/v) DOL:DME

Flow cell performs well at low current density.

M.L. Meyerson, S.G. Rosenberg, L.J. Small. *ACS Appl. Energy Mater.*, **5** (2022) 4202-4211.

Scalability for Long Duration Energy Storage

Key limitations for nonaqueous flow batteries with alkali-metal based anodes[1,2]

- Low current density (<1 mA cm^{-2})
  - Increases cost of flow battery cell stack
  - Solution: increase surface area to enable high rate anode
- Concentration of active species
  - Want >1 M to decrease materials costs
  - Solution: mediation theoretically enables >1 M
  - *Cannot practically test high concentrations in 8-16 h at low current!*

Increase cell area 20×
area of Li metal 5 → 100 cm^2
electrolyte volume 10 → 35 mL

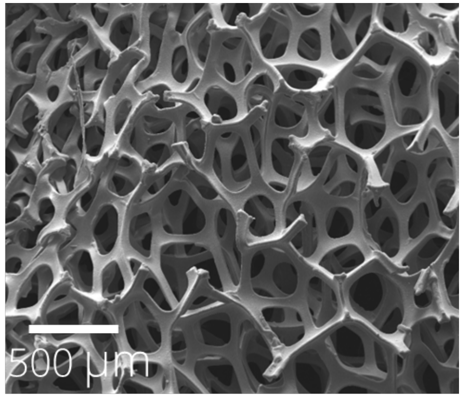
Increase current density 20×
0.5 → 10 mA cm^{-2}
Same geometric area of Li (5 cm^2)
Same electrolyte volume (10 mL)

~100× increase
current / electrolyte volume ratio
Enables testing of higher concentrations of S.

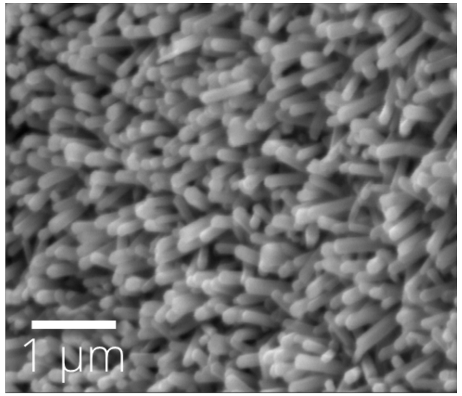
[1]Darling *et al.* Energy. Environ. Sci. 7 (2014) 3459-3477
[2]Darling *Cur. Opin. Chem. Eng.* 37 (2022) 100855

A Higher Rate, Higher Surface Area Anode

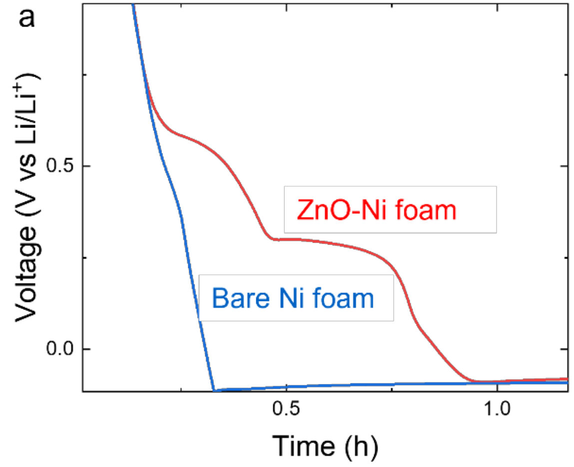
High surface area Ni foam

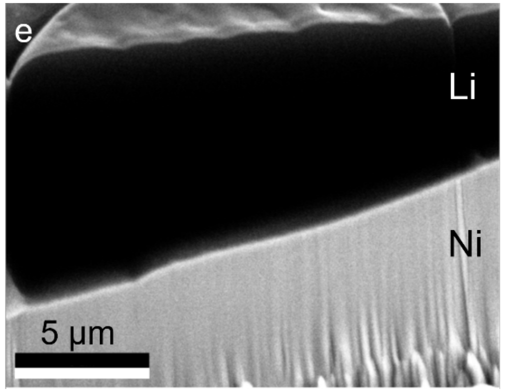


ZnO nanorods to increase Li wettability and decrease nucleation overpotentials.

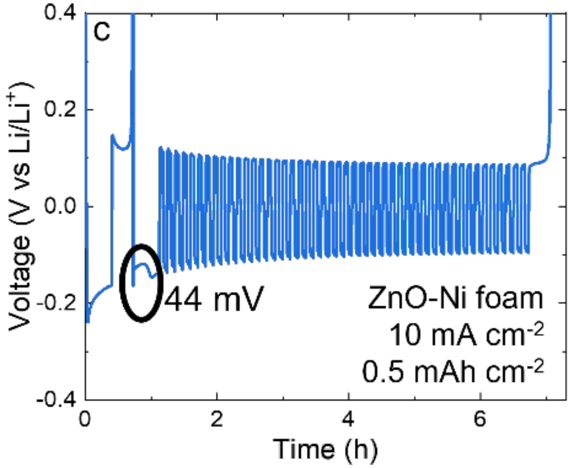


Li-Zn alloy was formed on initial charge





Li metal was plated on top.



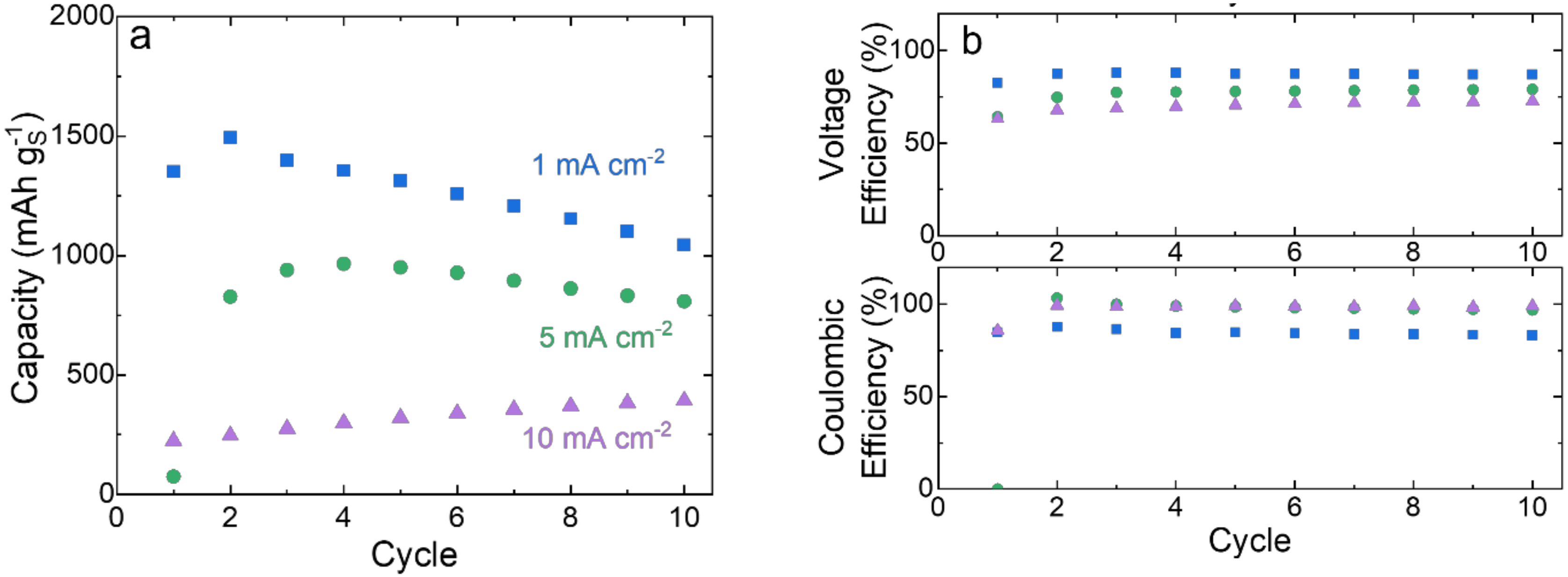
Symmetric Li cells cycled at 10 mA cm^{-2} with 96.7% Coulombic efficiency over 48 cycles.

A ZnO-Ni foam anode scaffold was developed, yielding a 20× increase in current density.

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

Higher Rate Cycling

- ZnO-Ni foam was prelithiated with molten Li and cycled in a flow battery.
- 70-74% energy efficiency
- Higher RM concentration and/or faster pumping speed can increase capacity at 10 mA cm^{-2}.



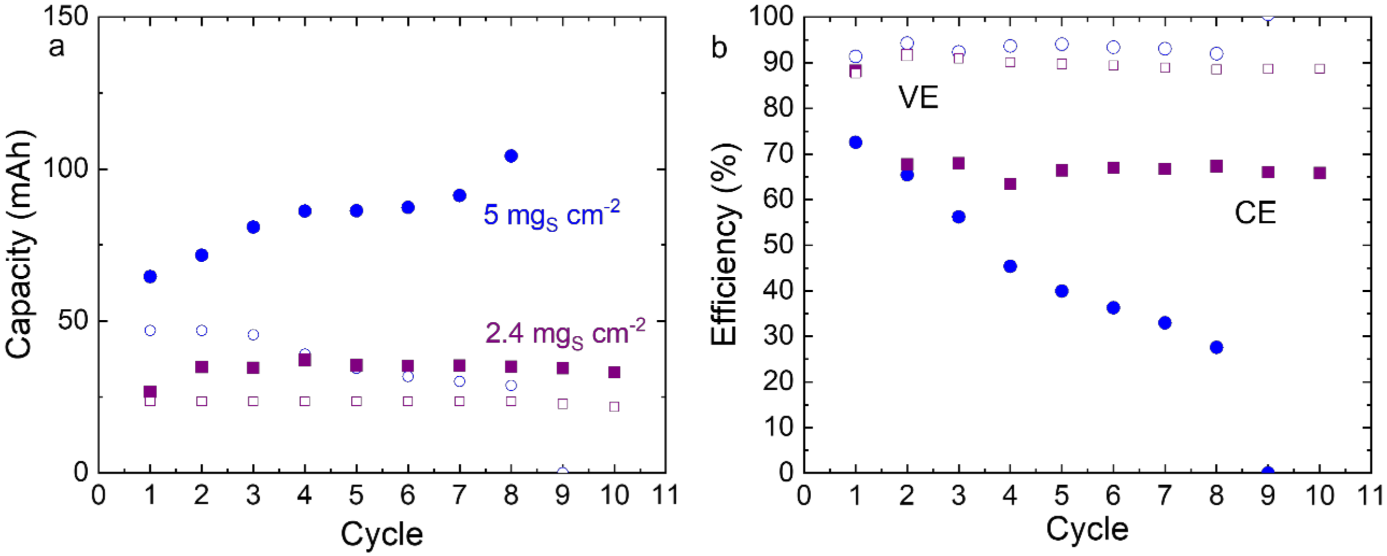
2.4 mg_S cm^{-2}
5 mM RM
1M LiTFSI
2wt% $LiNO_3$
1:1 (v/v) DOL:DME

Flow battery cycles at 10 mA cm^{-2}, a 20× improvement!

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

Cycling Flow Battery without Li Metal Initially Present

- Flow battery assembled in discharged state using ZnO-Ni foam anode and Li_2S in catholyte.
  - S added to increase solubility as Li_2S_4.
  - 20.3 Wh L^{-1} demonstrated
- Li metal plated on initial charge cycle.
- Coulombic efficiency suffers at high sulfur loading.



1 mA cm^{-2}
5 mM RM
1M LiTFSI
2wt% $LiNO_3$
1:1 (v/v) DOL:DME

Possible to start flow battery in discharged state. Initial charge state and mediation need to be better understood.

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

Scalability for Long Duration Energy Storage

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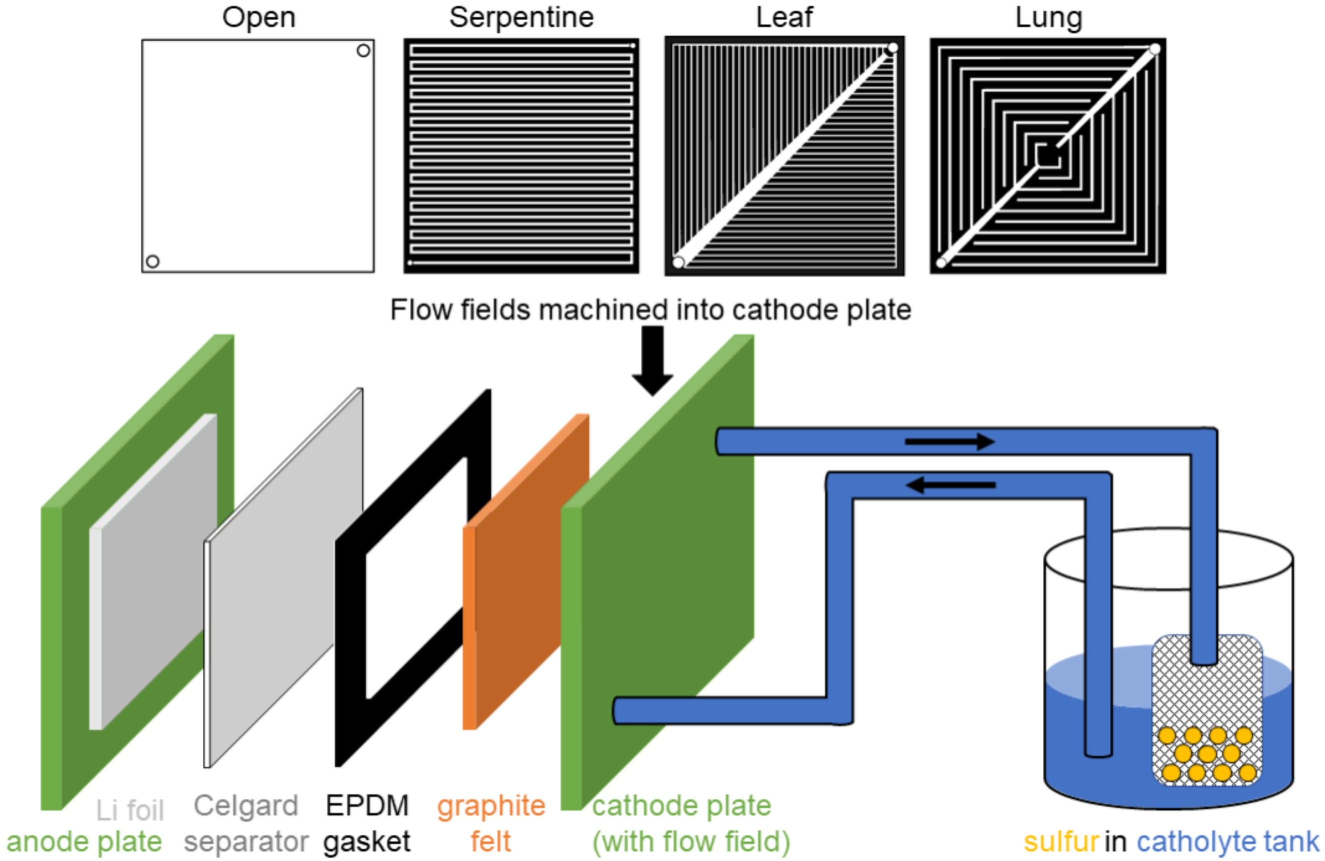
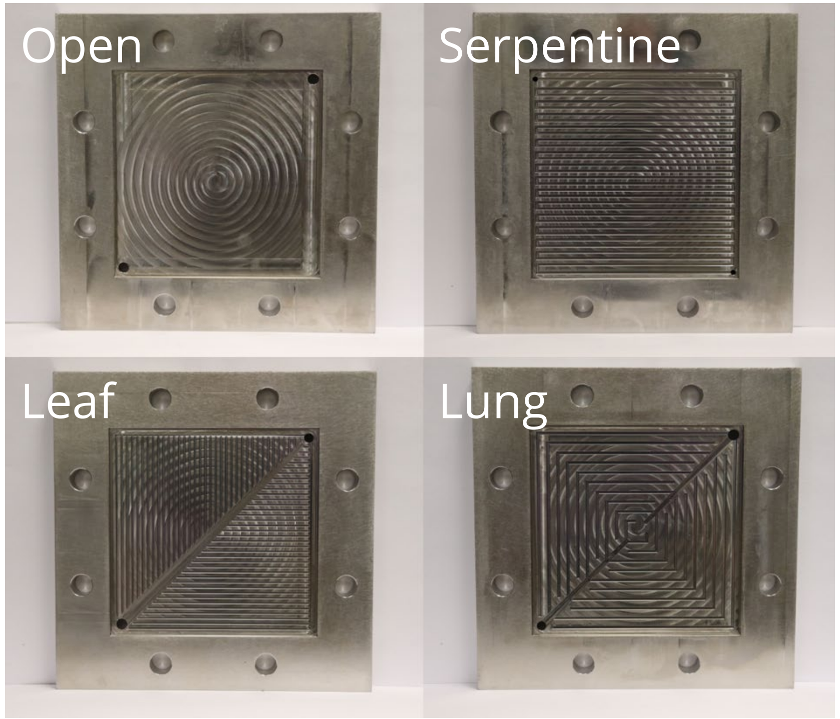
Scaling Up: Bio-inspired Flow Field Designs

Chose four flow field designs. Compare:

- flow battery performance
- fluid velocity
- pressure drop



Flow fields machined in Stainless Steel

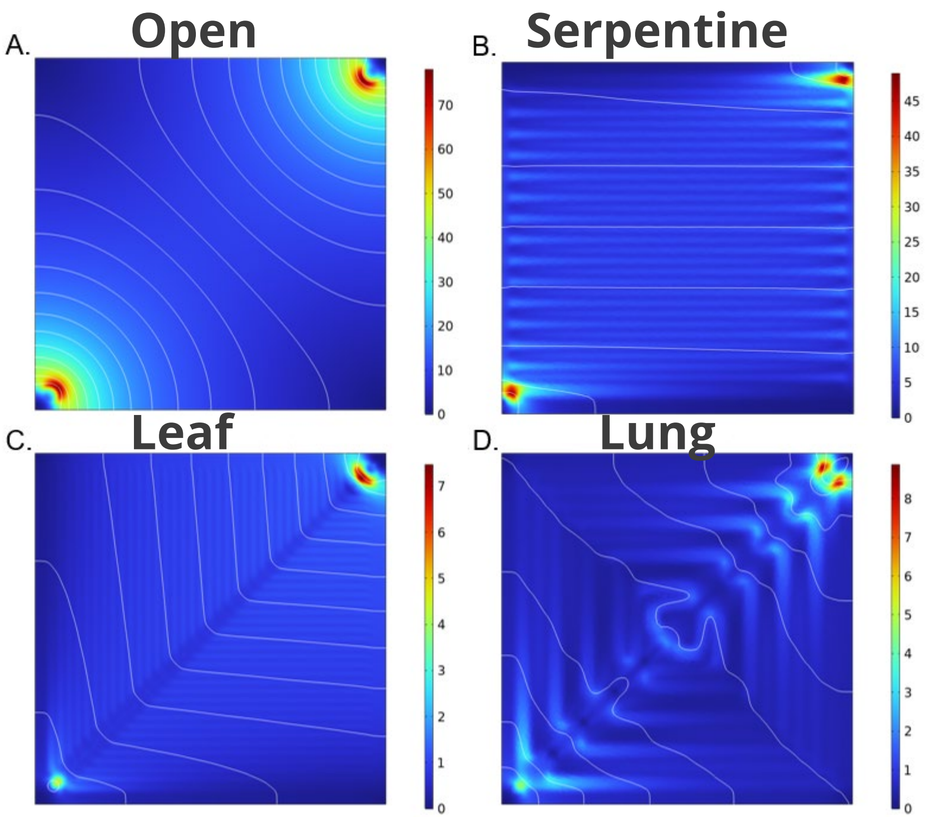


Modeling Fluid Flows in Larger Cell Sizes

- Simulated pressure drop and fluid velocity in flow cells using COMSOL
  - 100 cm^2 area, 100 mL min^{-1}
- Leaf and Lung designs show
  - lowest pressure drop
  - most uniform fluid flow

Flow Field	Pressure / kPa
Open	25.1
Serpentine	9.88
Lung	1.55
Leaf	1.72

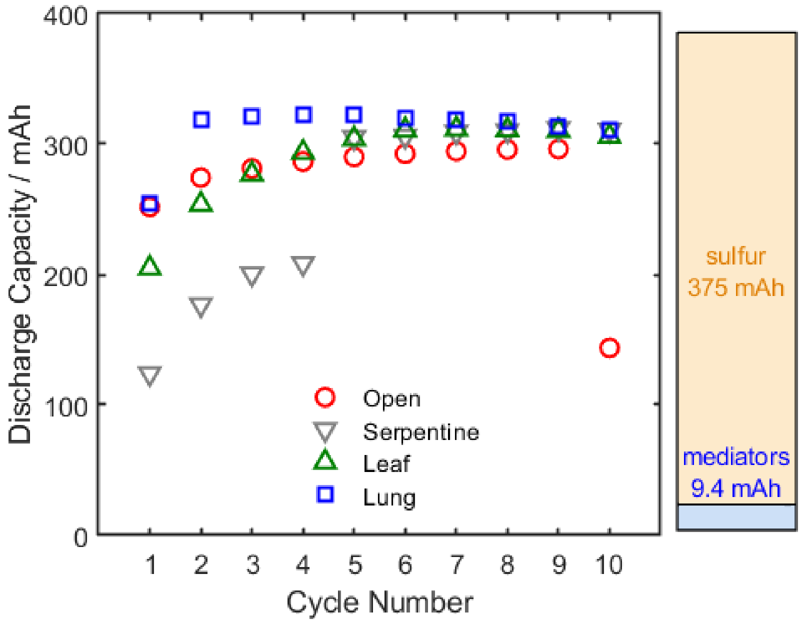
Fluid Velocities in Graphite Felt

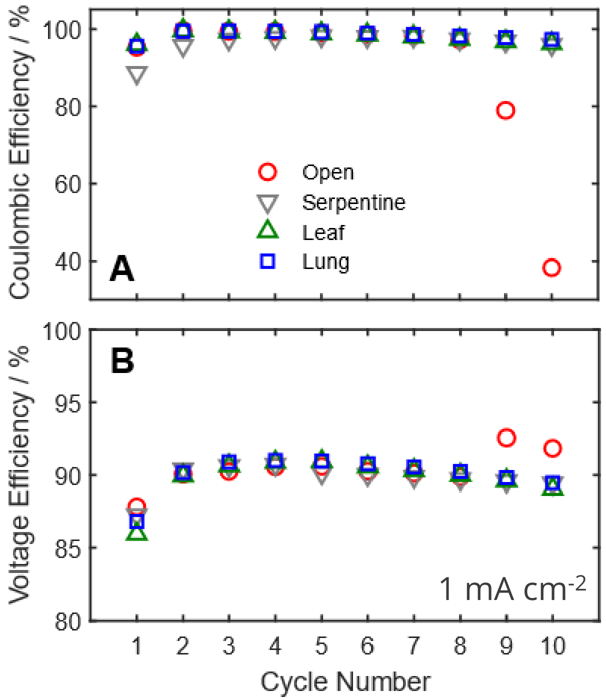


Flow field choice strongly influences cell pressure and uniformity of fluid flow.

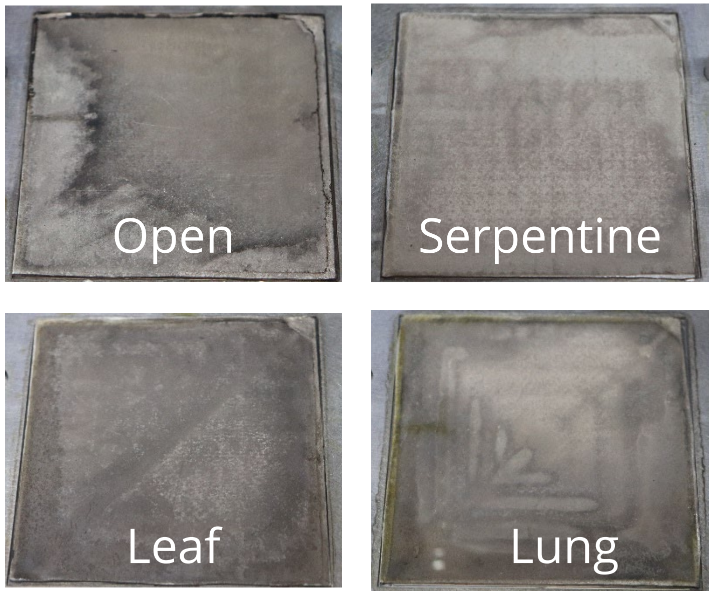
Flow Cell Performance

- Flow cells cycled 10 times, then disassembled and chemical analysis performed.
- After 5 cycles: 80% of theoretical S capacity, CE > 98%, VE > 90%,
- By 9th cycle “open” flow field had shorted





Photographs of Li anodes after cycling



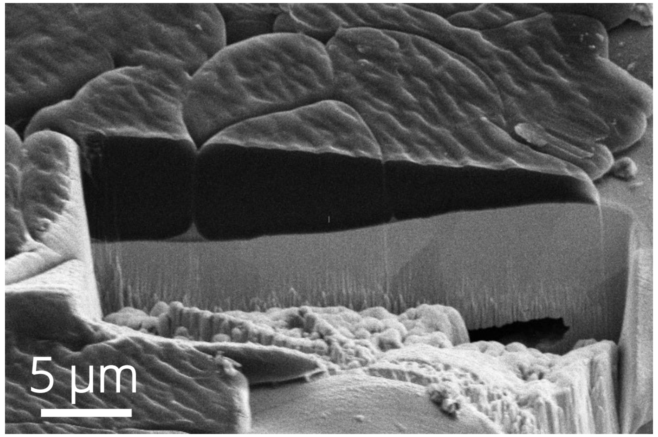
Flow fields influence flow battery performance and failure modes.

Path Forward

This year we…

- developed a flow battery anode for cycling of Li metal 20× faster.
- demonstrated an "anode-less" flow battery with competitive 20.3 Wh L^{-1} and room for improvement.
- increased flow cell size from 5 to 100 cm^2.
- evaluated different flow fields for decreased pressure drop and increased uniformity.

Li on ZnO-Ni Foam



Next year we will…

- integrate high rate anode into 100 cm^2 cell size.
- improve flow cell performance when starting in the discharged state
  - optimize RM concentration and flow rates
  - develop initial "startup" cycle
- test at higher S loadings, ideally 1-5 vol% S.
- evaluate commercial potential via DOE Boost program.

Accomplishments

Publications

- M.L. Meyerson, A.M. Maraschky, J. Watt, and L.J. Small. Fast Cycling of "Anode-less," Redox-mediated Li-S Flow Batteries. *Journal of Energy Storage,* **72** (2023) 108767.
- A.M. Maraschky, M.L. Meyerson, A. Marinelarena-Diaz, C. Poirier, T.M. Anderson, and L.J. Small. Bio-inspired Flow Fields Enhance Performance of Mediated Flow Batteries with Li Metal Anode. *In Preparation.* (2023)

Presentations

- M.L Meyerson, A.M. Maraschky, S.J. Percival, L.J. Small, "Higher Energy Density Mediated Lithium-Sulfur Flow Batteries." 242nd Electrochemical Society Meeting, Atlanta, GA, 10/9-13/2022.
- M.L Meyerson, A.M. Maraschky, S.J. Percival, L.J. Small, "Higher Energy Density Mediated Lithium-Sulfur Flow Batteries." 2022 MRS Fall Meeting, Boston, MA, 11/27/2022 – 12/2/2022.
- M.L Meyerson, A.M. Maraschky, J. Watt, L.J. Small, "Higher Energy Density Mediated Lithium-Sulfur Flow Batteries." 243rd Electrochemical Society Meeting, Boston, MA 5/28-6/2/2023.

Patents

- L.J. Small and M.L. Meyerson. *Mediated Metal-Sulfur Flow Battery for Grid-Scale Energy Storage*. US Application No. 17/740,128. May 9, 2022.

Acknowledgements

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ENERGY STORAGE PROGRAM

Questions?

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