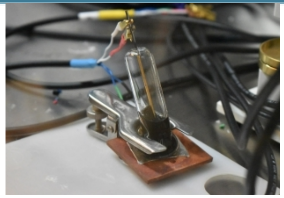
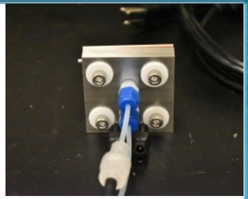
SAND2022-13631C

A02-0109: Higher Energy Density Mediated Lithium-Sulfur Flow Batteries





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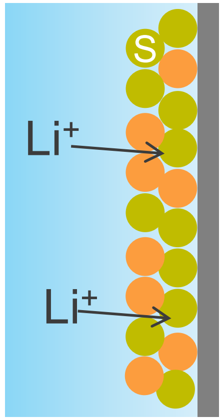
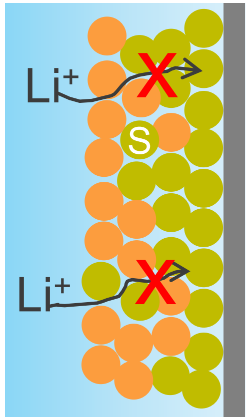
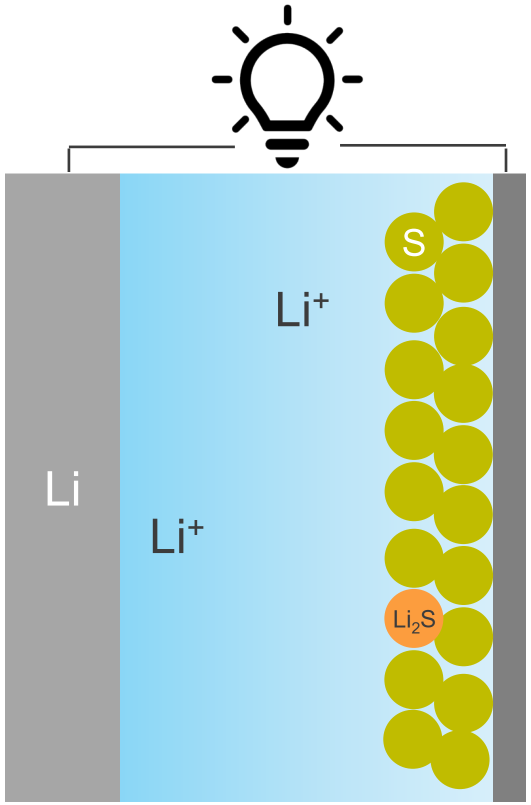
Background

- 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





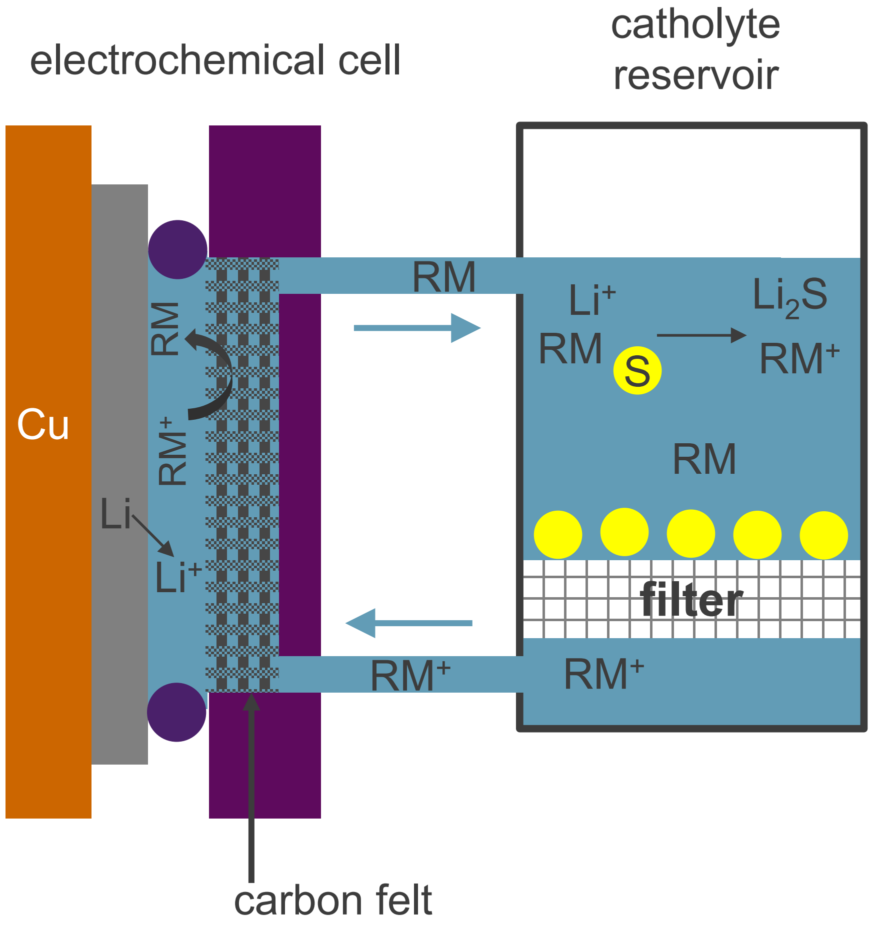


$$S + 2e^{-} + 2Li^{+} \rightarrow Li_2S$$

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

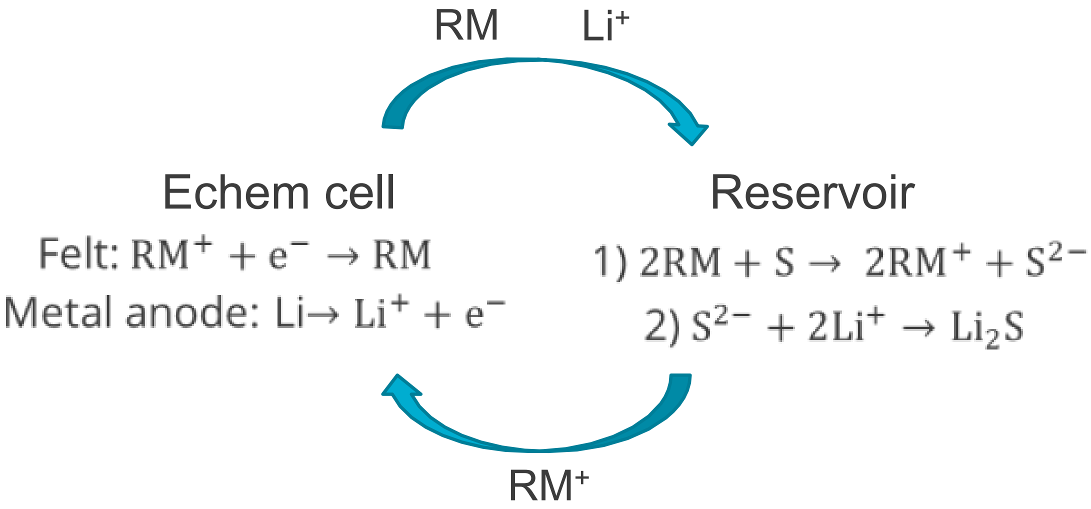
Wu, J., et al. (2021). Adv Mater **33**(26): e2101275.

Flow Cell Design



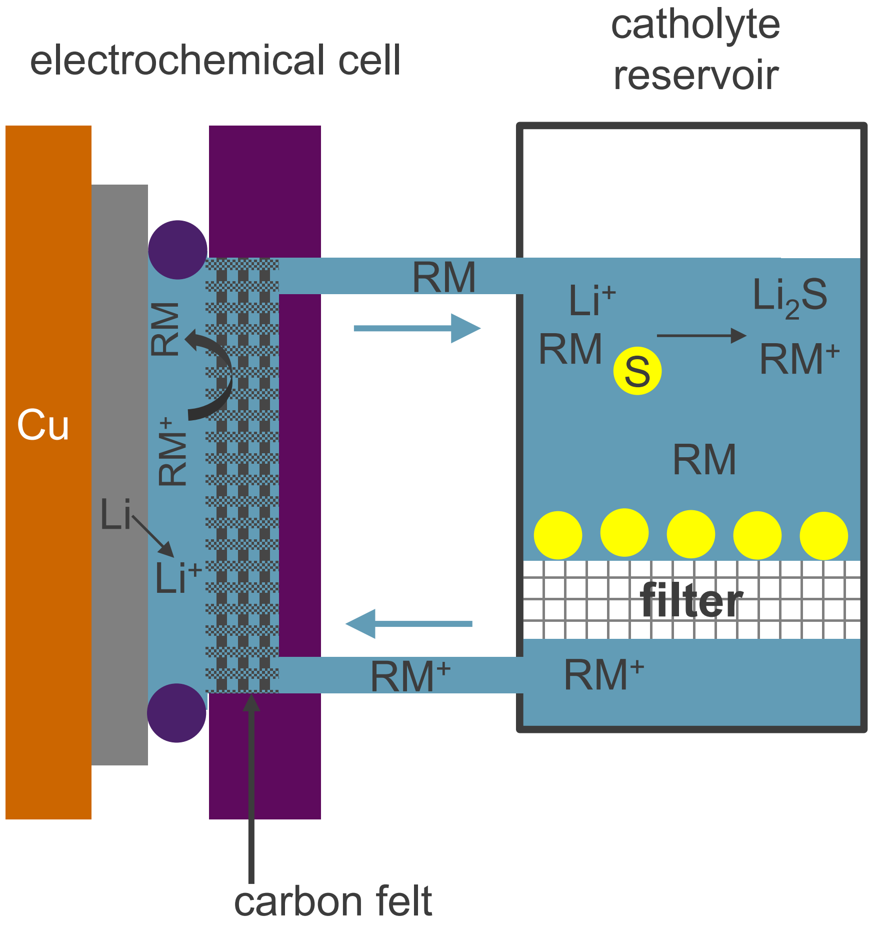
- Hybrid design with solid Li metal anode
- S is chemically reduced with RM
- Electrolyte containing RM^+ is pumped into electrochemical cell where RM^+ is reduced

Discharge:



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

Flow Cell Design

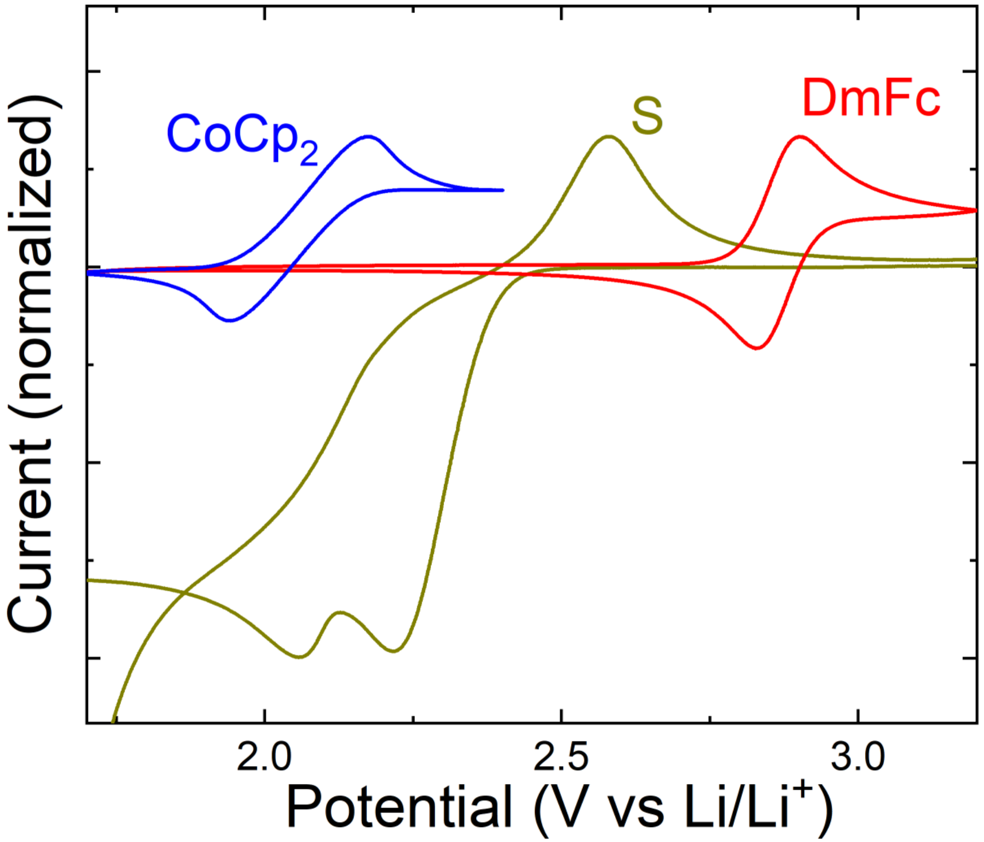


Benefits:

- Improved safety
  - Separation of anode and cathode decreases risk of thermal runaway
- 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.

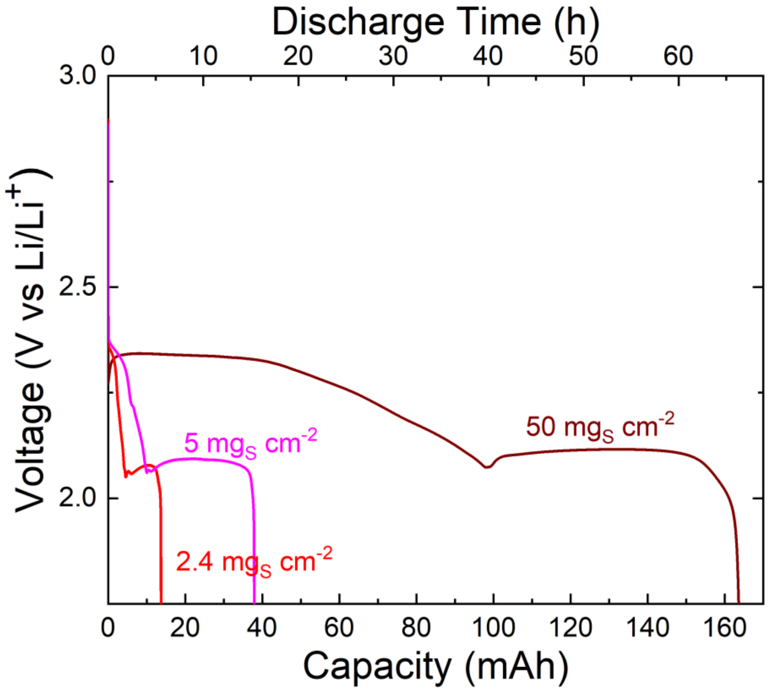
Ideal Redox Mediator

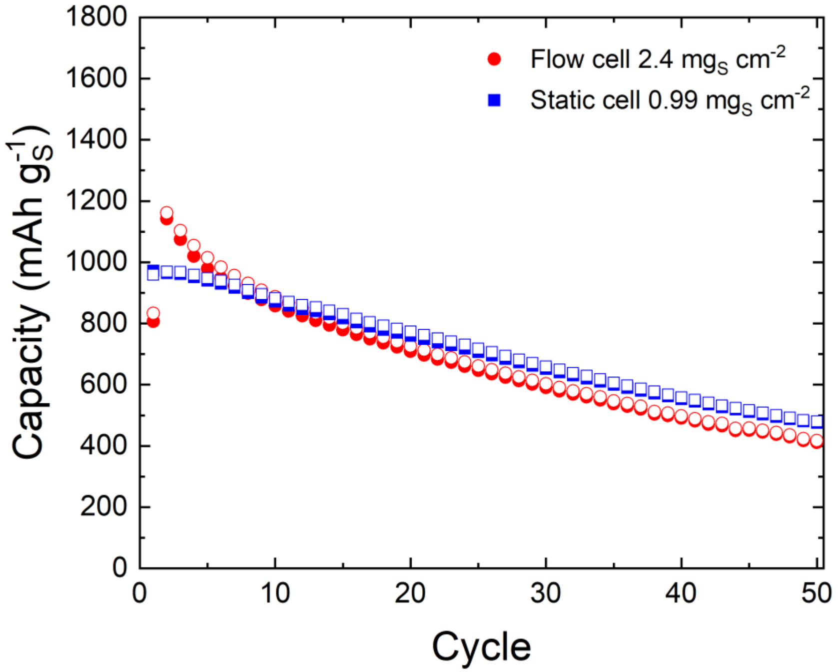
- Close to Li-S reaction (~2.4 V vs Li/Li^+)
  - E_{DmFc}= 2.86 V
  - E_{CoCp2} = 2.06 V
- Good reaction kinetics
  - k^0_{DmFc} = 4.33 x 10^{-3} cm s^{-1}
  - k^0_{CoCp2}= 3.14 x 10^{-4} cm s^{-1}
- Fast diffusion
  - D_{DmFc} = 5.23 x 10^{-6} cm^2 s^{-1}
  - D_{CoCp2} = 3.70 x 10^{-6} cm^2 s^{-1}

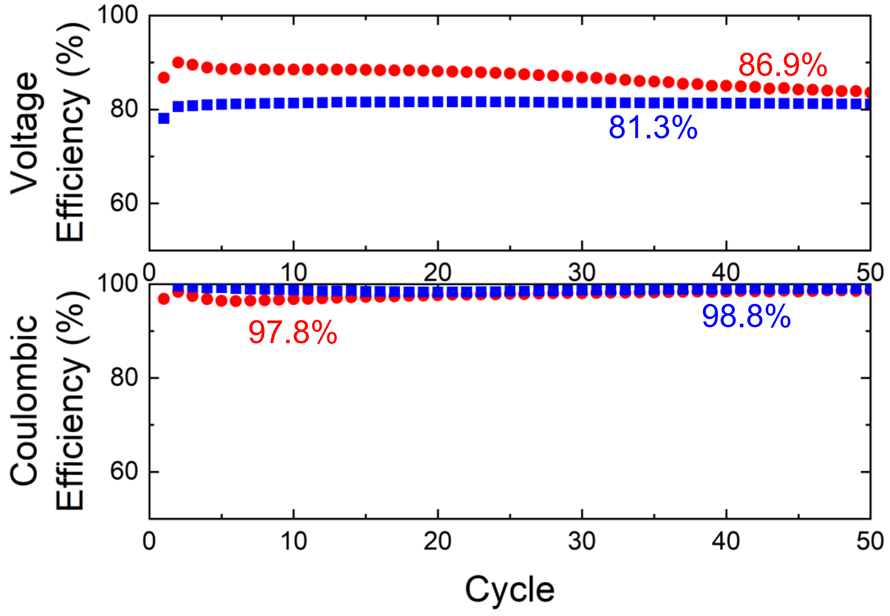
Meyerson, M. L.; Rosenberg, S. G.; Small, L. J., *ACS Applied Energy Materials* **2022,** *5* (4), 4202-4211.

Flow Cell Cycling

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







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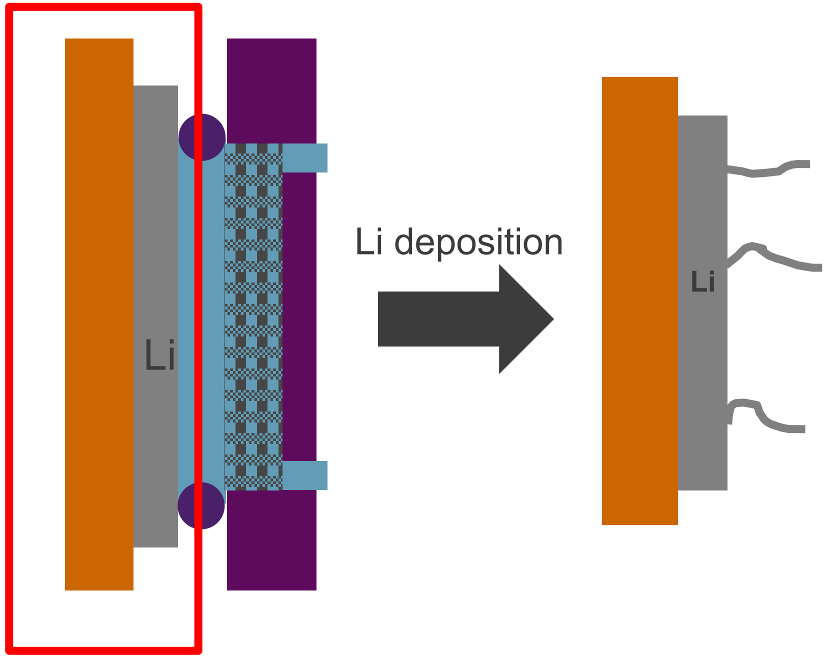
Limitations of Planar Li Anodes



Li dendrites

Causes of dendrite formation:

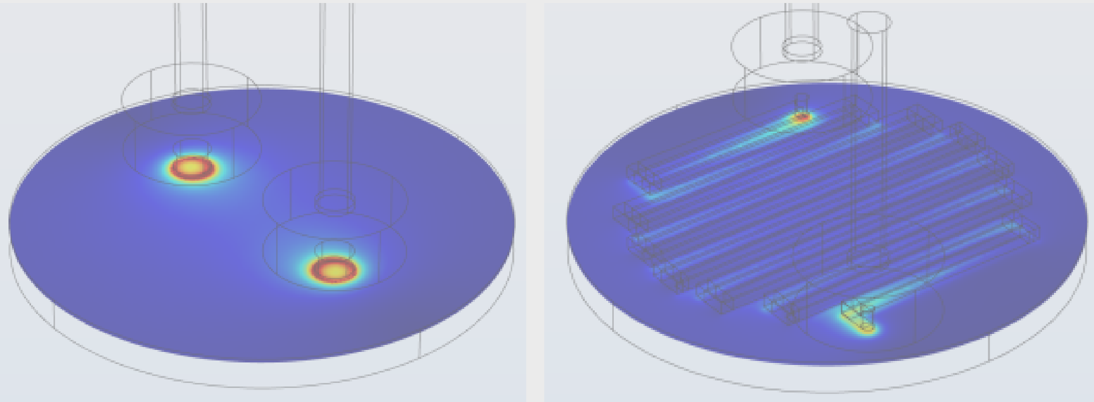
- Inhomogeneous surface chemistry
- Non-uniform Li^+ flux
- Increased charge rate exacerbates problems with dendrites

Dendrites decrease battery life and cause short circuits.

Addressing Limitations of Planar Li Anodes

Non-uniform Li^+ flux

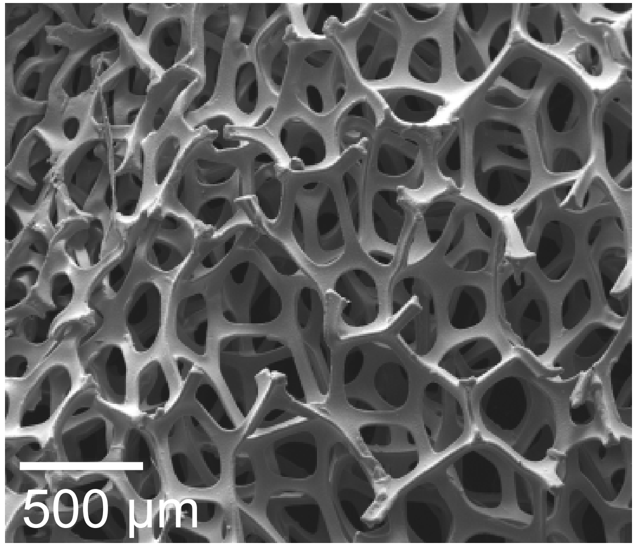
- Use a flow field with more uniform electrolyte flow
- Switching from open to serpentine flow fields increases uniformity of electrolyte flow



More uniform flow leads to more uniform Li deposition.

Limited charge rate

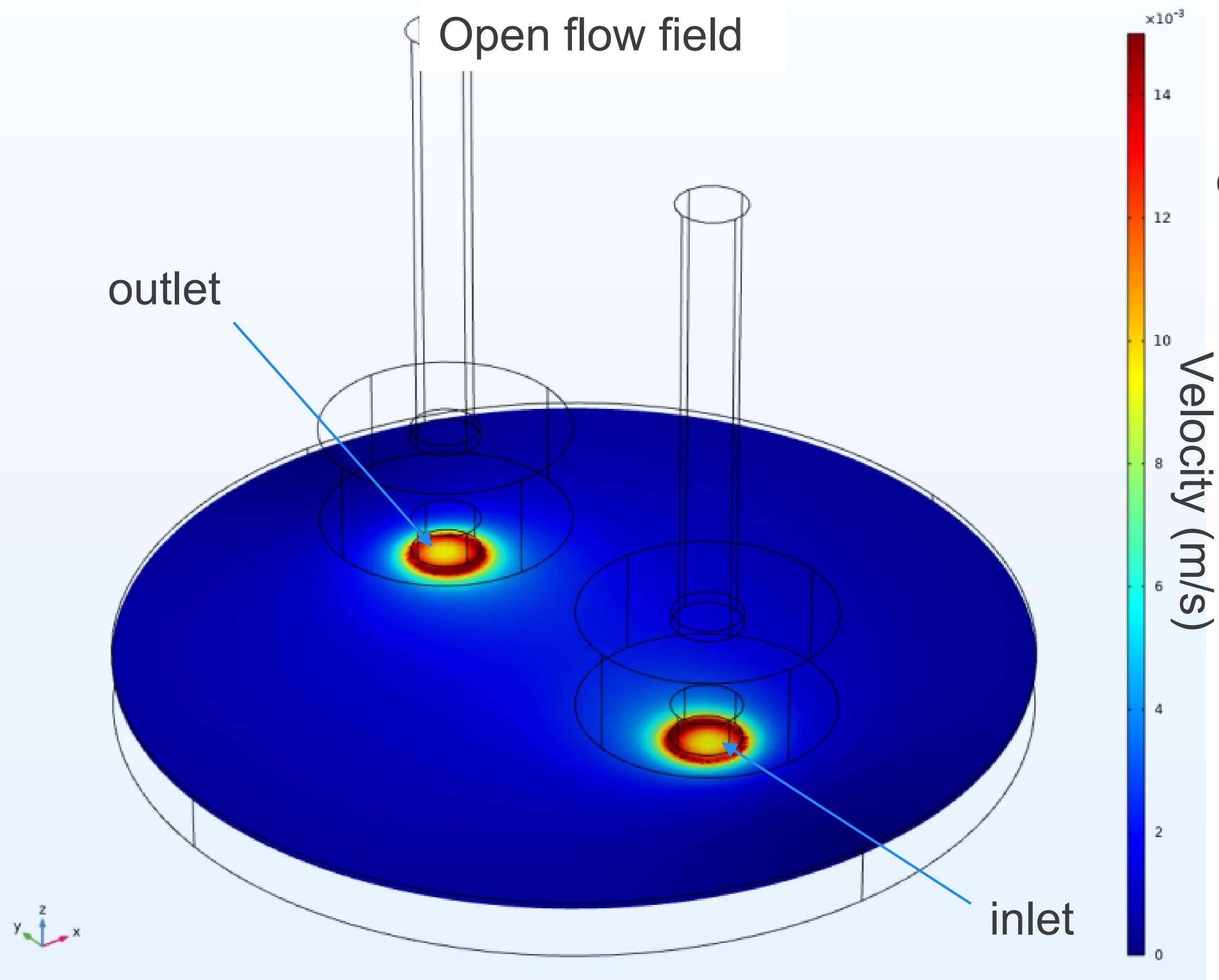
- Replace planar Li foil with high surface area Ni foam
- Ni foam with 97% porosity has ~10x the surface area of planar Ni foil

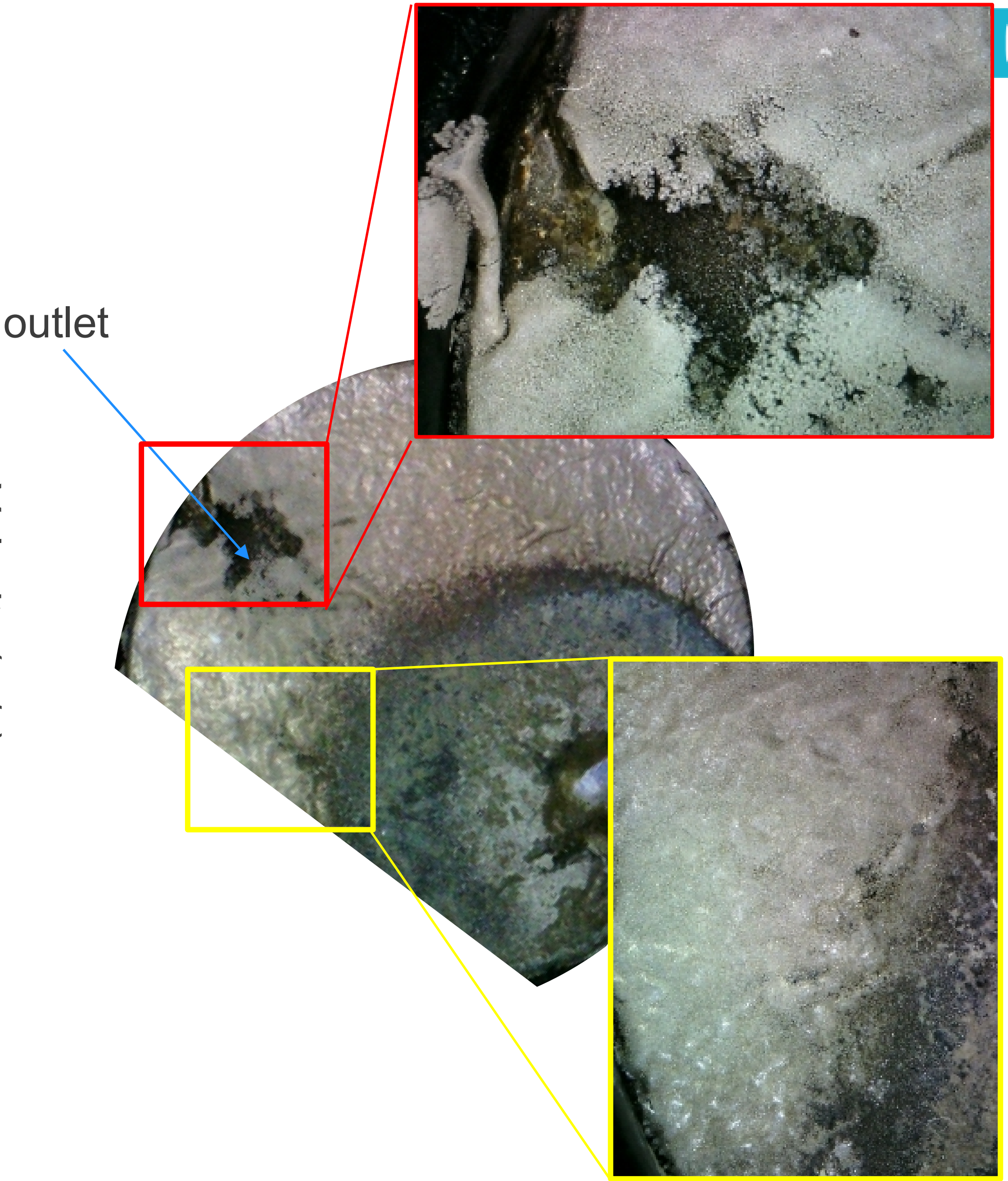


Bare Ni foam

Increasing effective surface area decreases the local current density.

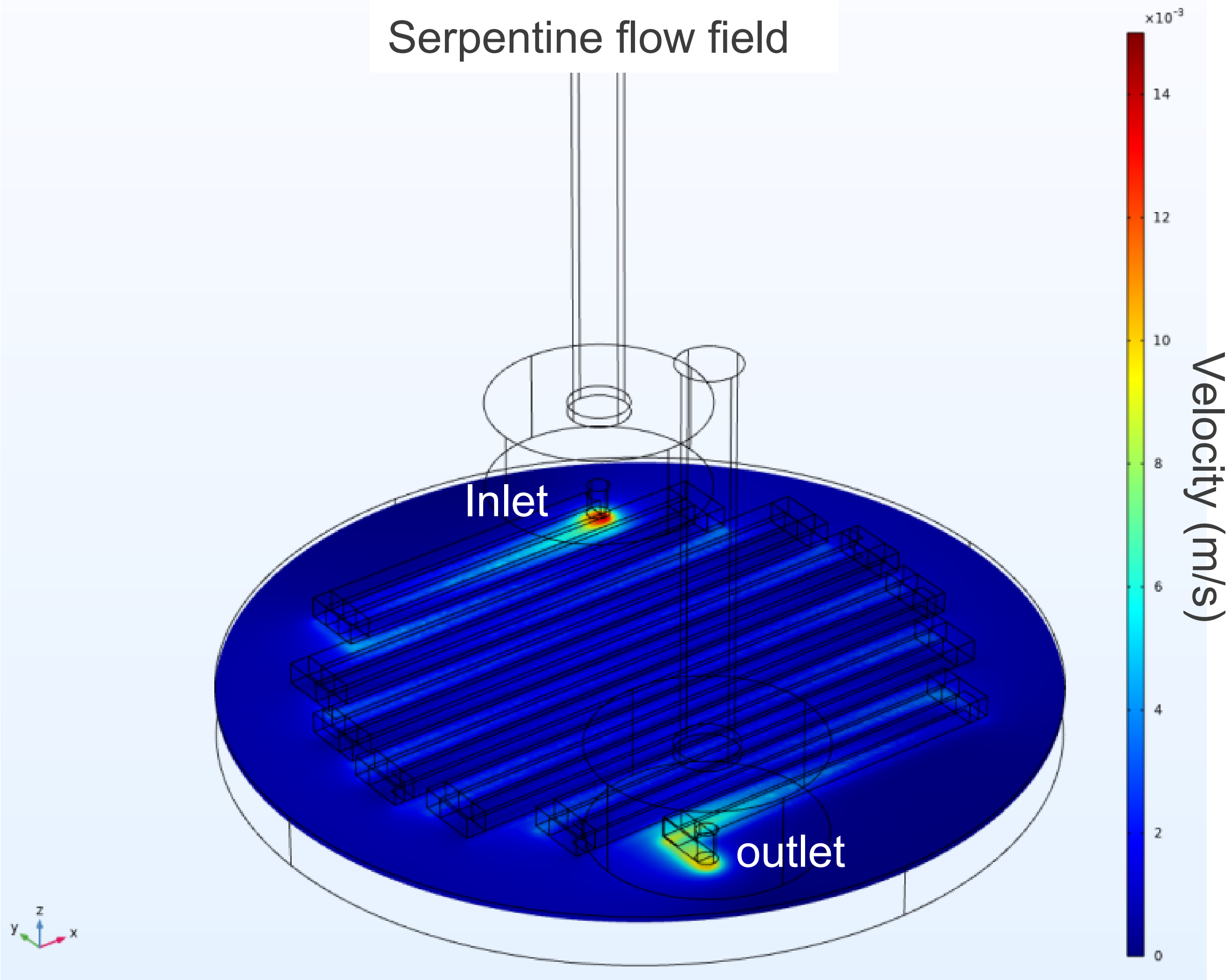
Effect of Flow Field Design

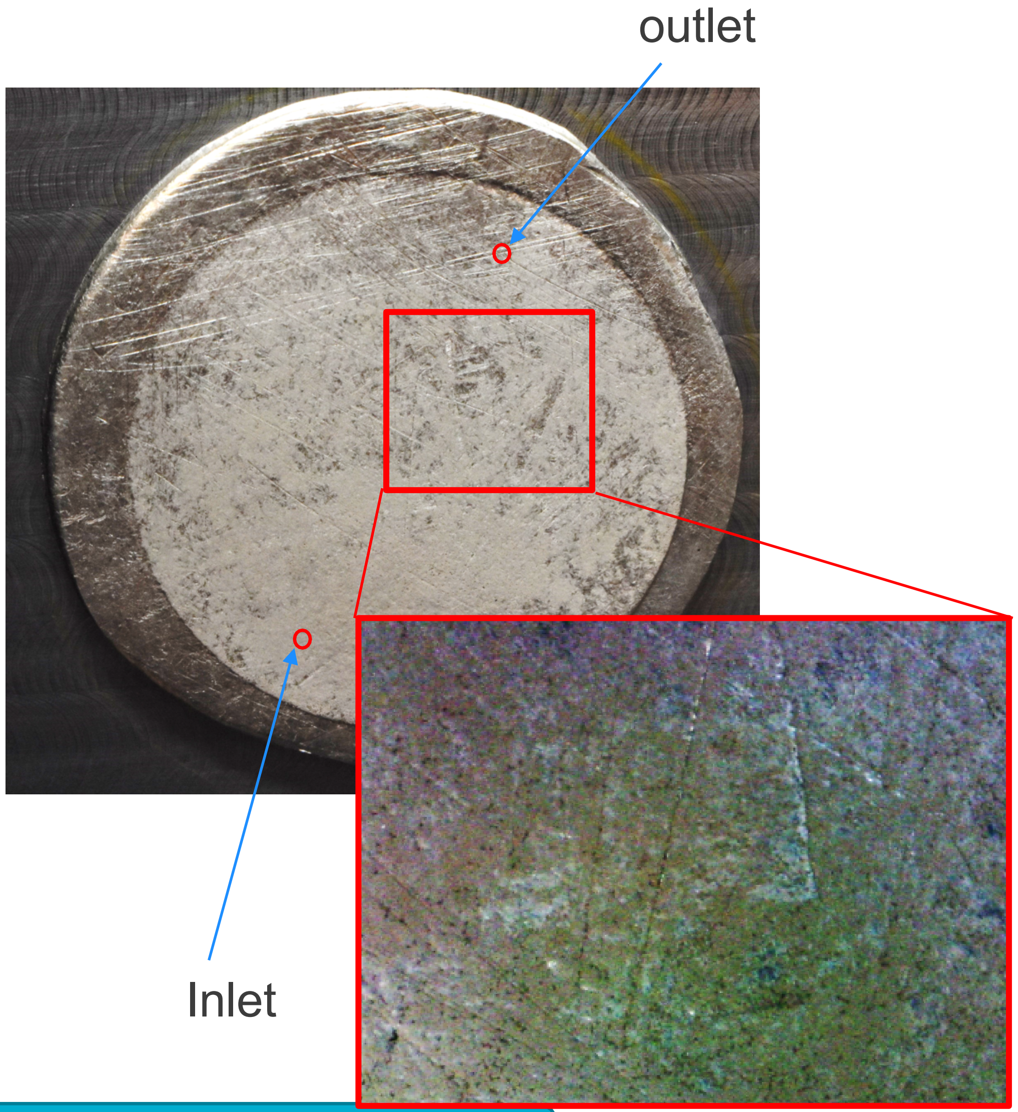




Higher flow corresponds with taller, rougher Li deposition.

Effect of Flow Field Design

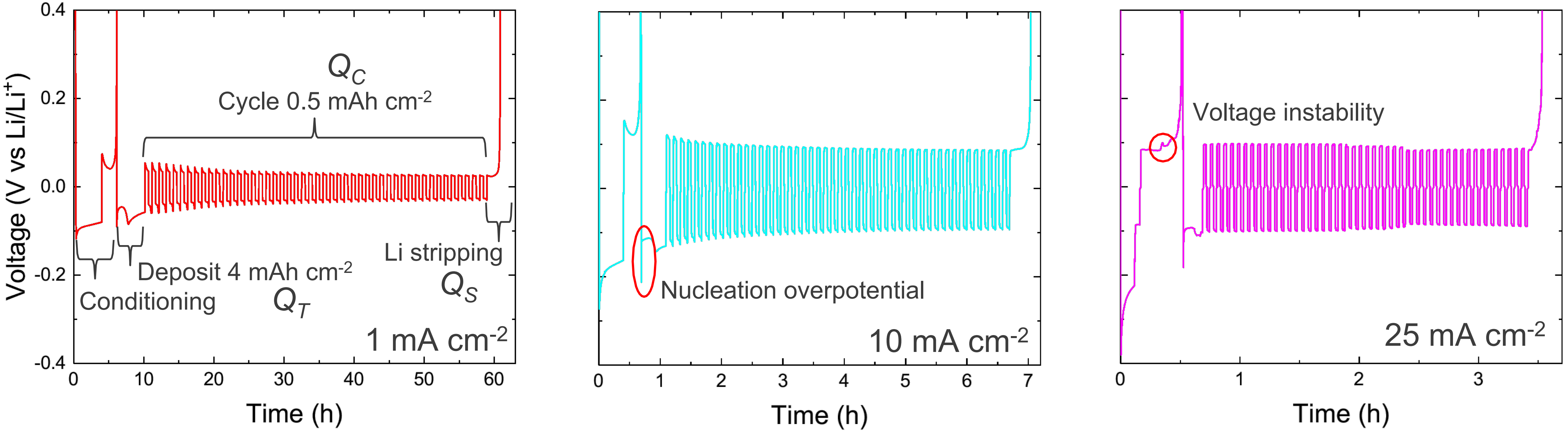




More uniform flow leads to more uniform Li deposition.

Moving from Planar to 3D Anode Scaffolds

- Symmetric cells with Li foil counter electrode and Ni foil or foam as current collector for working electrode
- Test coulombic efficiency at increasing current densities



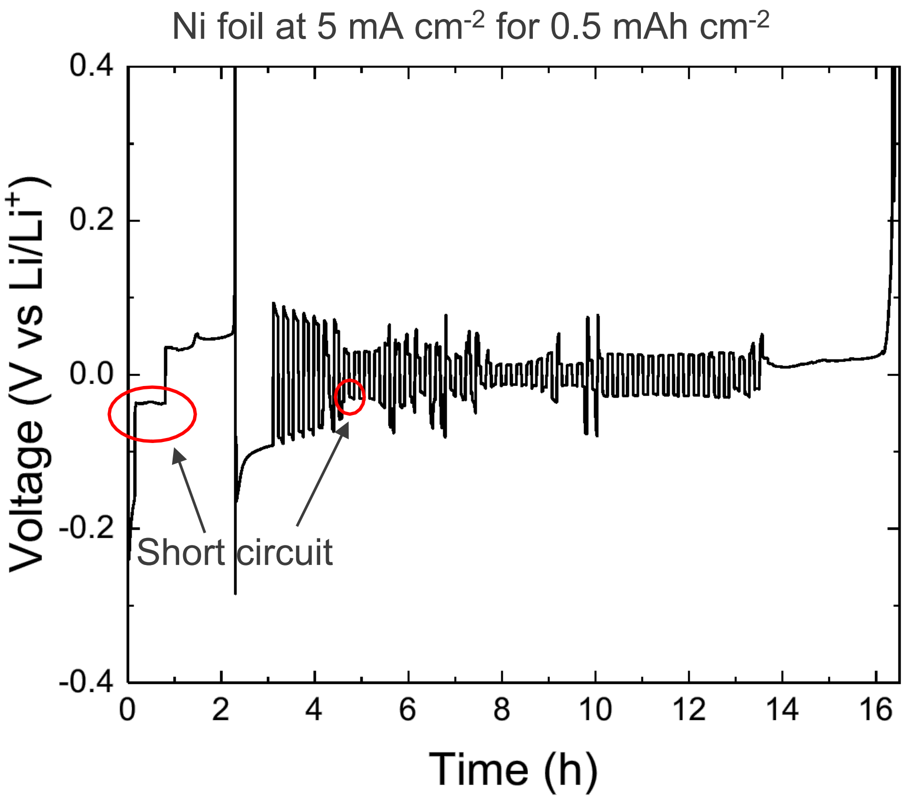
$$\mathrm{CE_{avg}} = \frac{nQ_C + Q_S}{nQ_C + Q_T} \qquad n=48$$

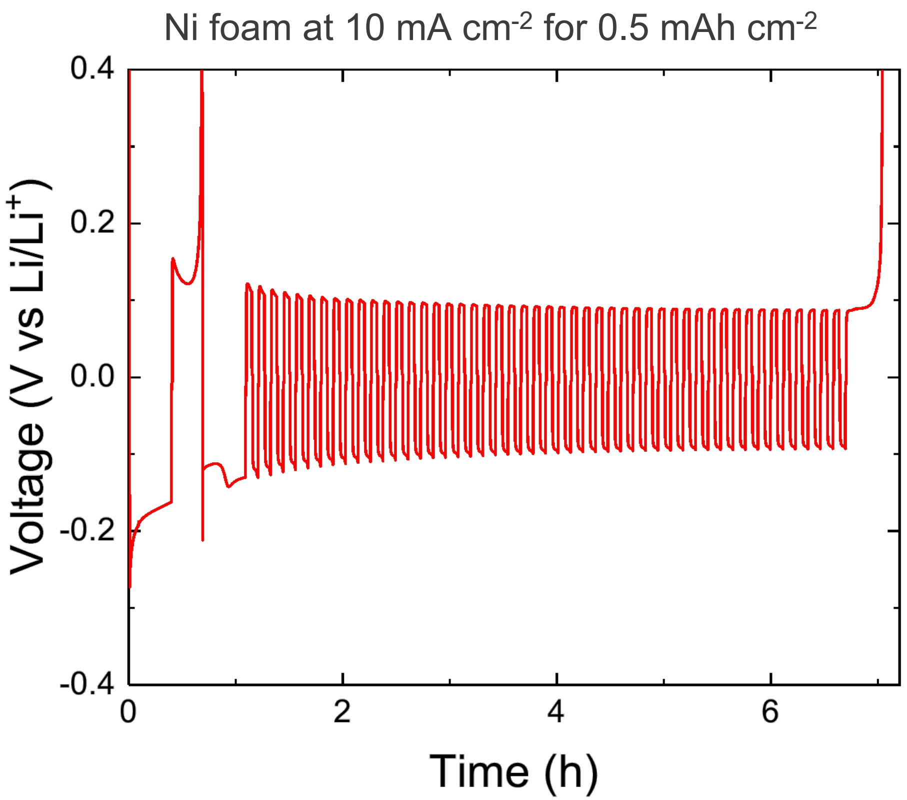
* Ni foam, 1 M LiTFSI with 2 wt % $LiNO_3$ in 1:1 (v/v) DOL:DME

Test procedure: Adams, B. D.; Zheng, J.; Ren, X.; Xu, W.; Zhang, J. G., *Advanced Energy Materials* **2017,** *8* (7).

Increased Surface Area Allows Faster Charging

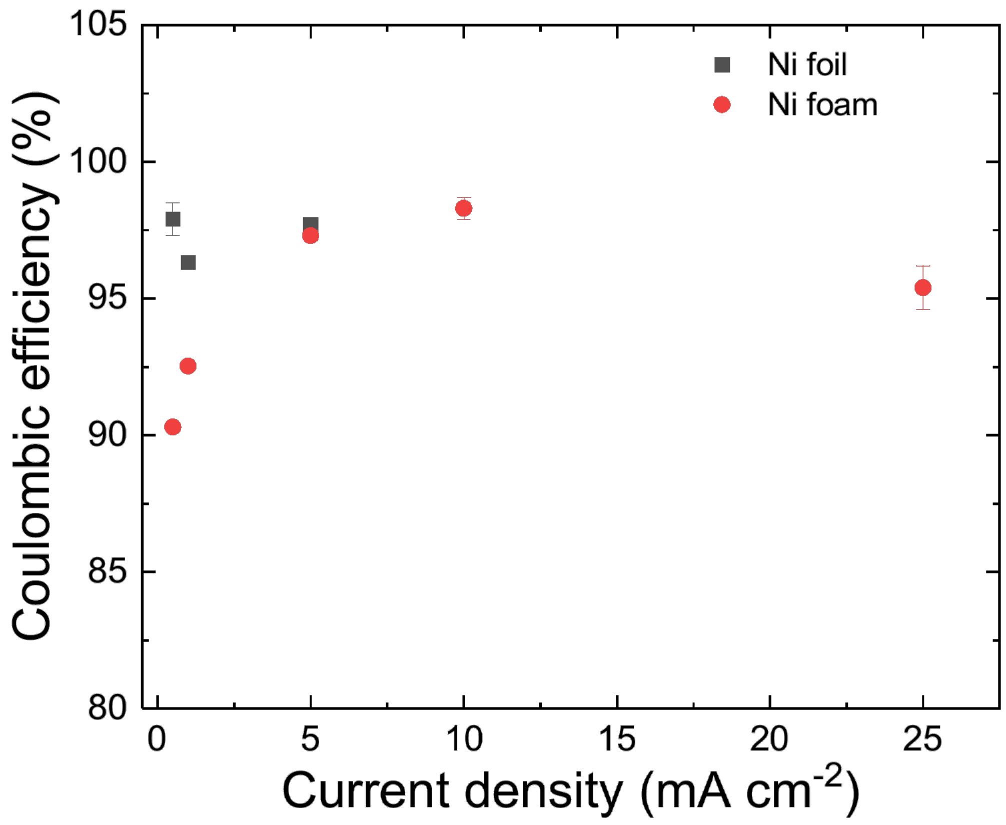
- For planar deposition, charging above 1 mA cm^{-2} results in unstable cycling and shorting



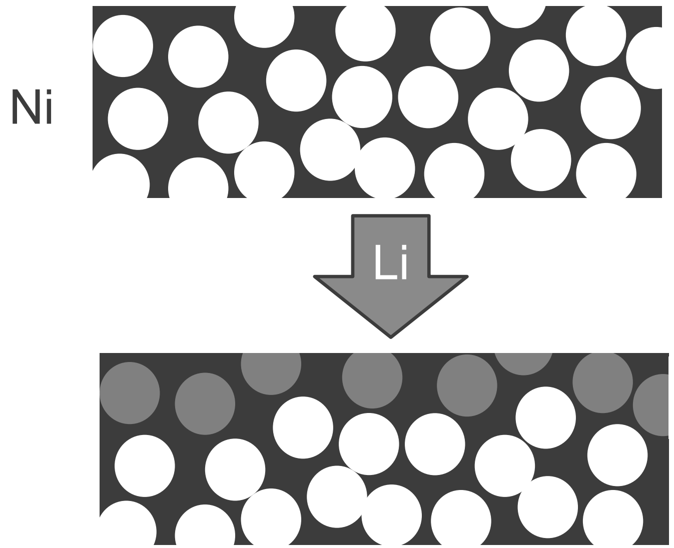


Using high SA foam, charge rate can be 10 times faster.

Increased Surface Area Allows Faster Charging



Lower current densities show better CE on the Ni foil than the bare Ni foam, possibly from low utilization of the foam.

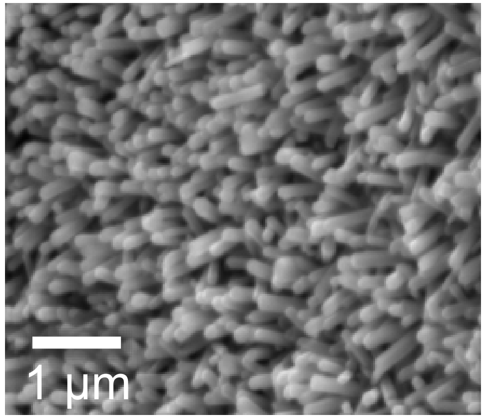


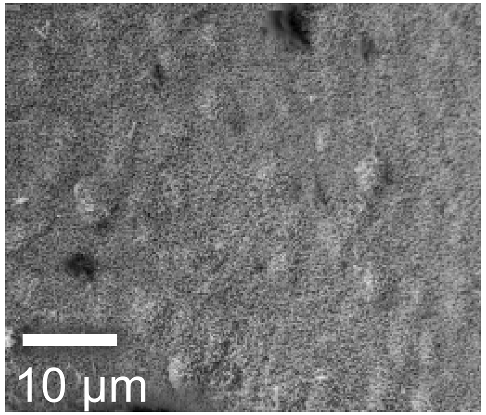
*0.5 mAh cm^{-2}, 1 M LiTFSI with 2 wt % $LiNO_3$ in 1:1 (v/v) DOL:DME

ZnO Synthesis on Ni Foam

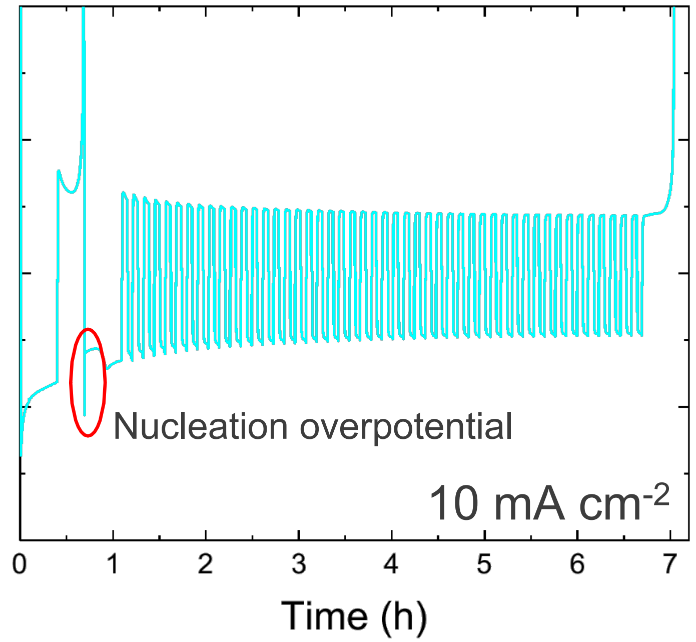
- Lattice mismatch leads to nucleation overpotential
- Li has a lower nucleation overpotential on Zn than Ni

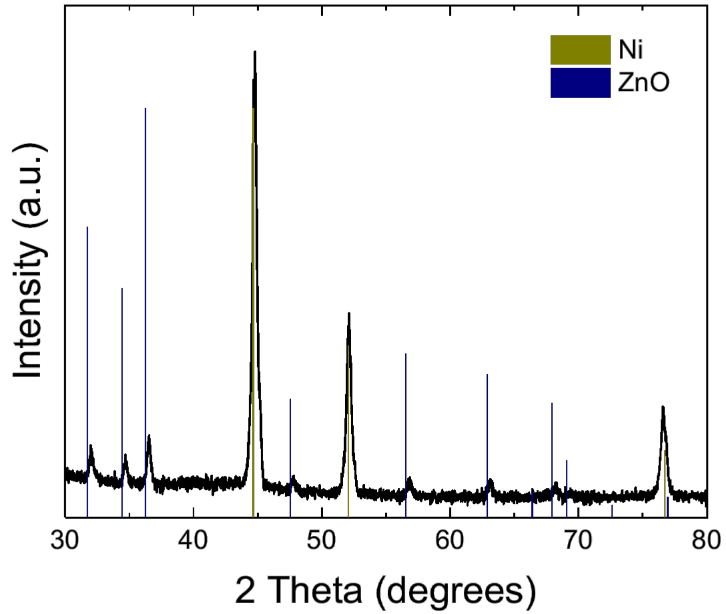
Hydrothermal synthesis of ZnO nano rods
- 100-150 nm wide, 500-800 nm tall
- Uniform coverage of Ni





SEM of ZnO nanorods





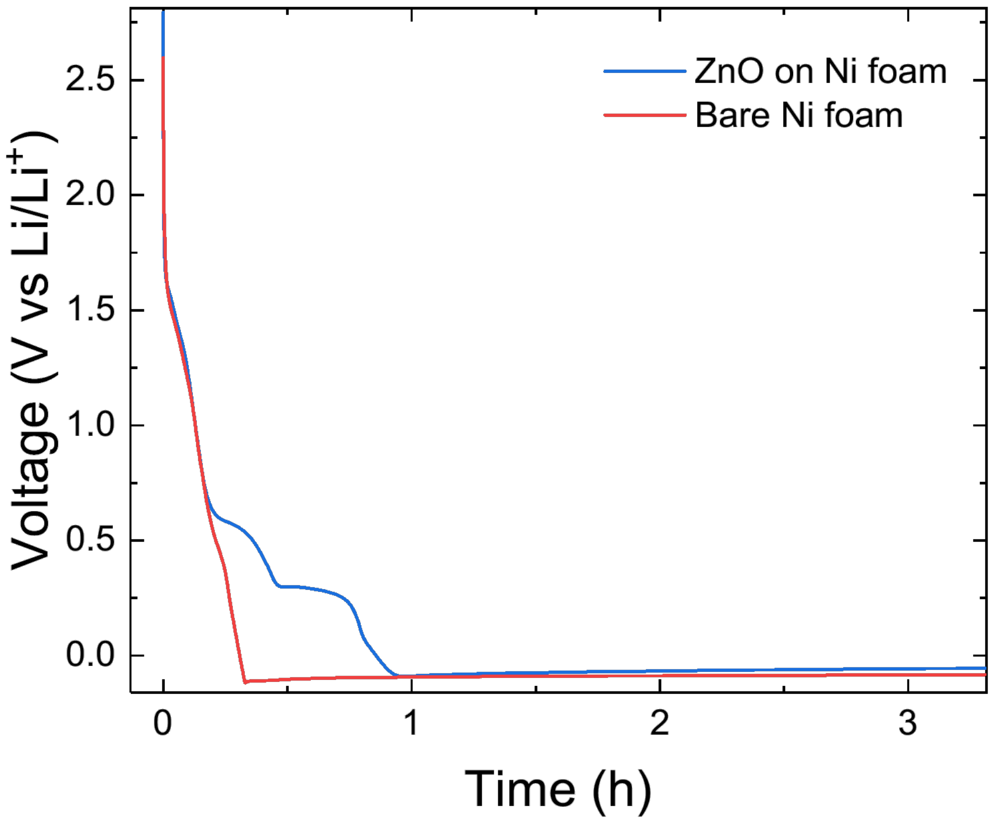
X-ray diffraction of ZnO nanorods on Ni foam

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

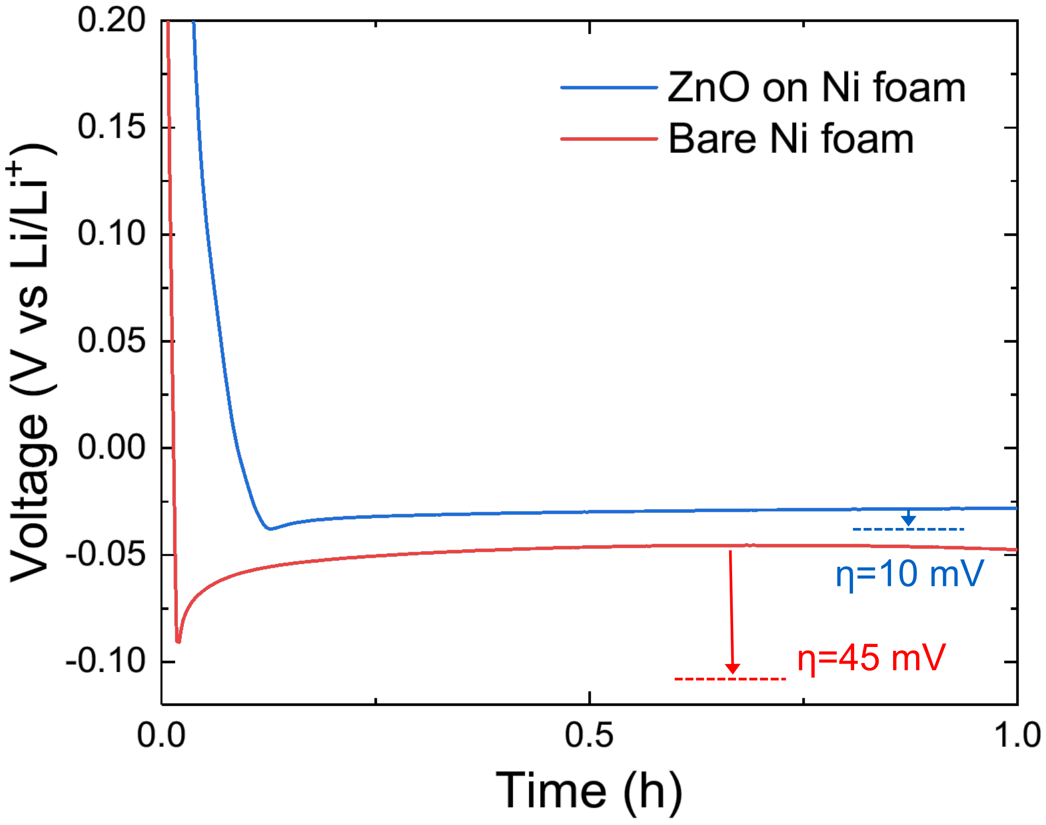
Seeding Li Deposition

Nucleation overpotential of Li on ZnO is lower than Ni, leading to preferential Li deposition on the ZnO.

Li deposition at 1 mA cm^{-2}.



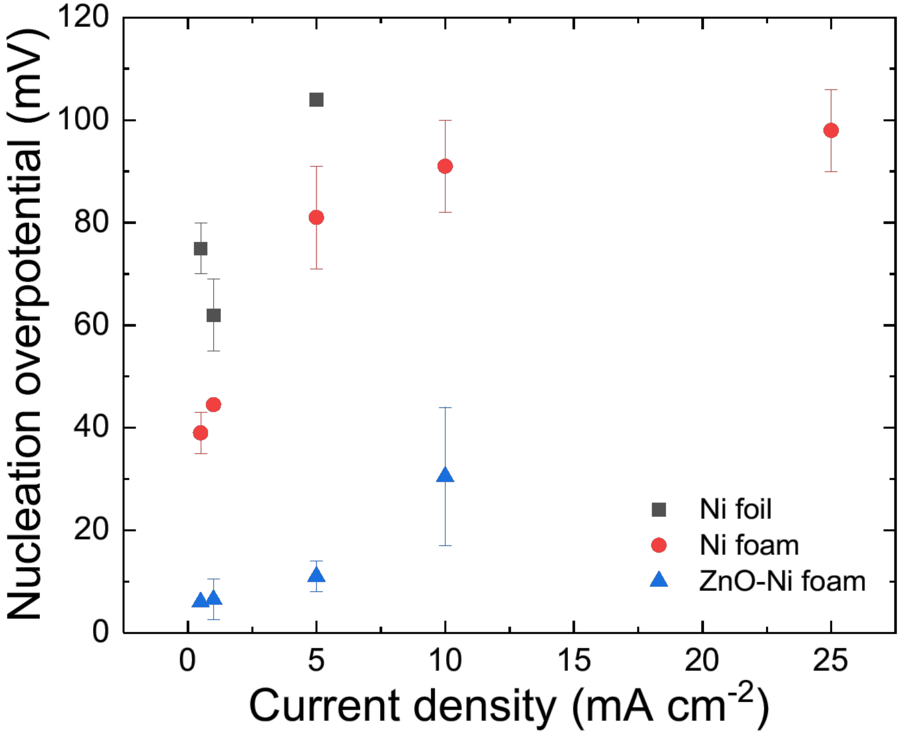
Conditioning deposition

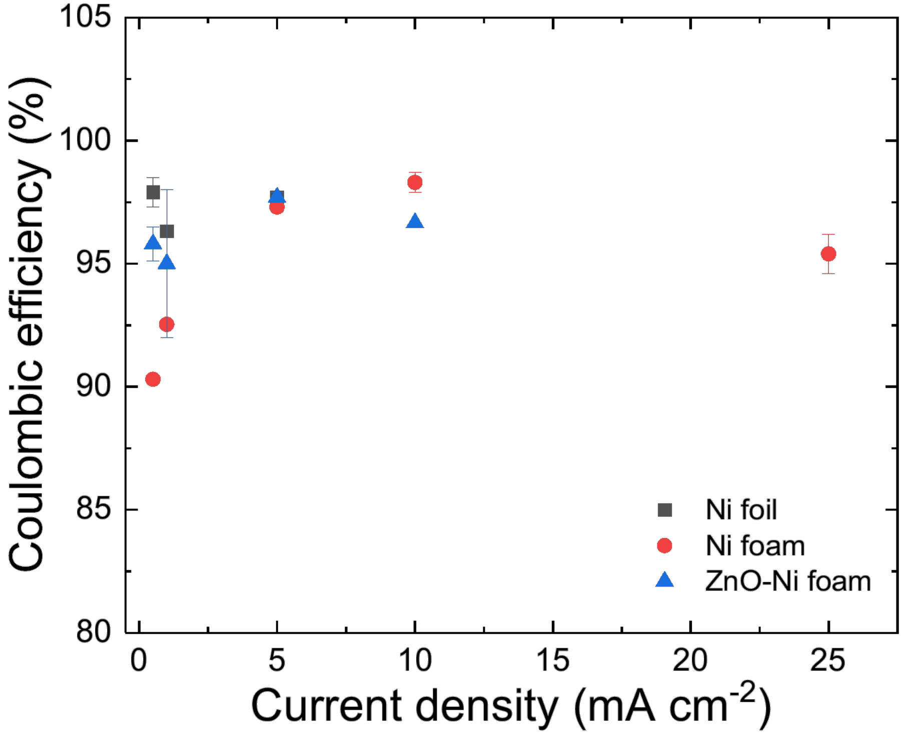


First deposition after conditioning

ZnO Further Improves System

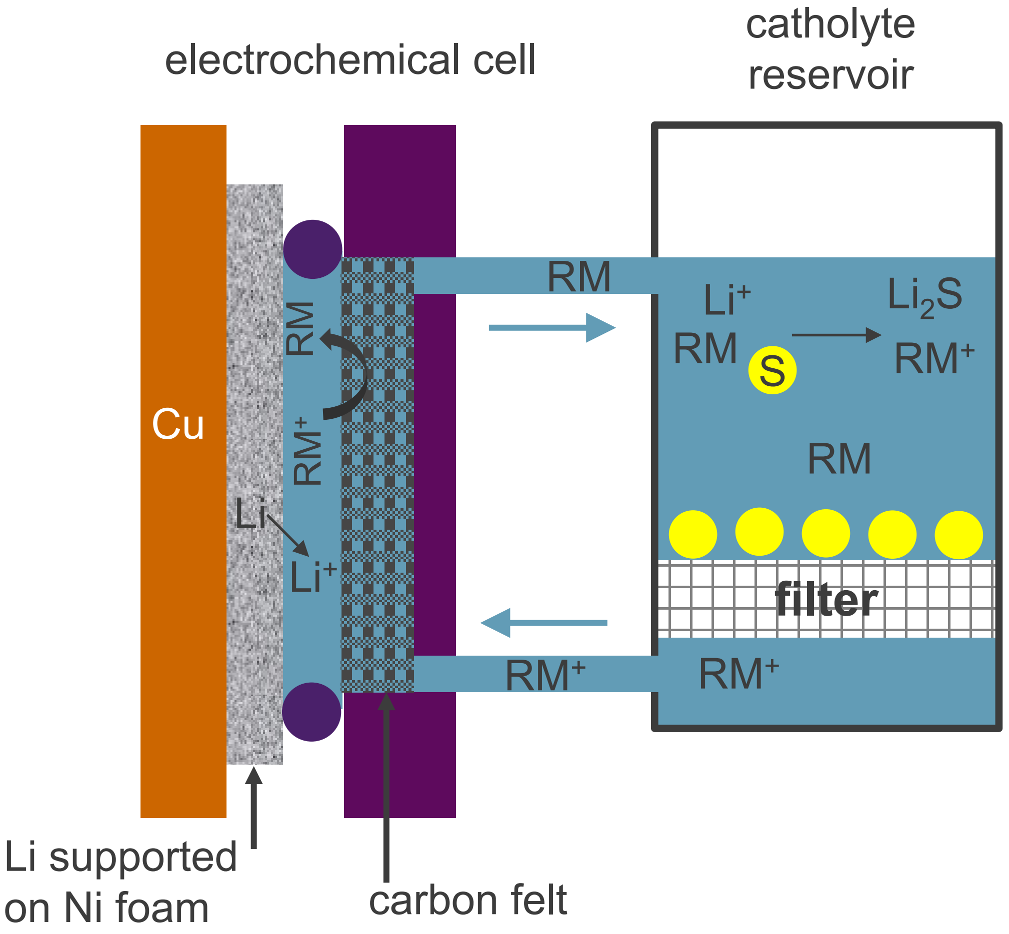
Nucleation overpotential decreases and CE increases compared to bare Ni foam at low current densities.

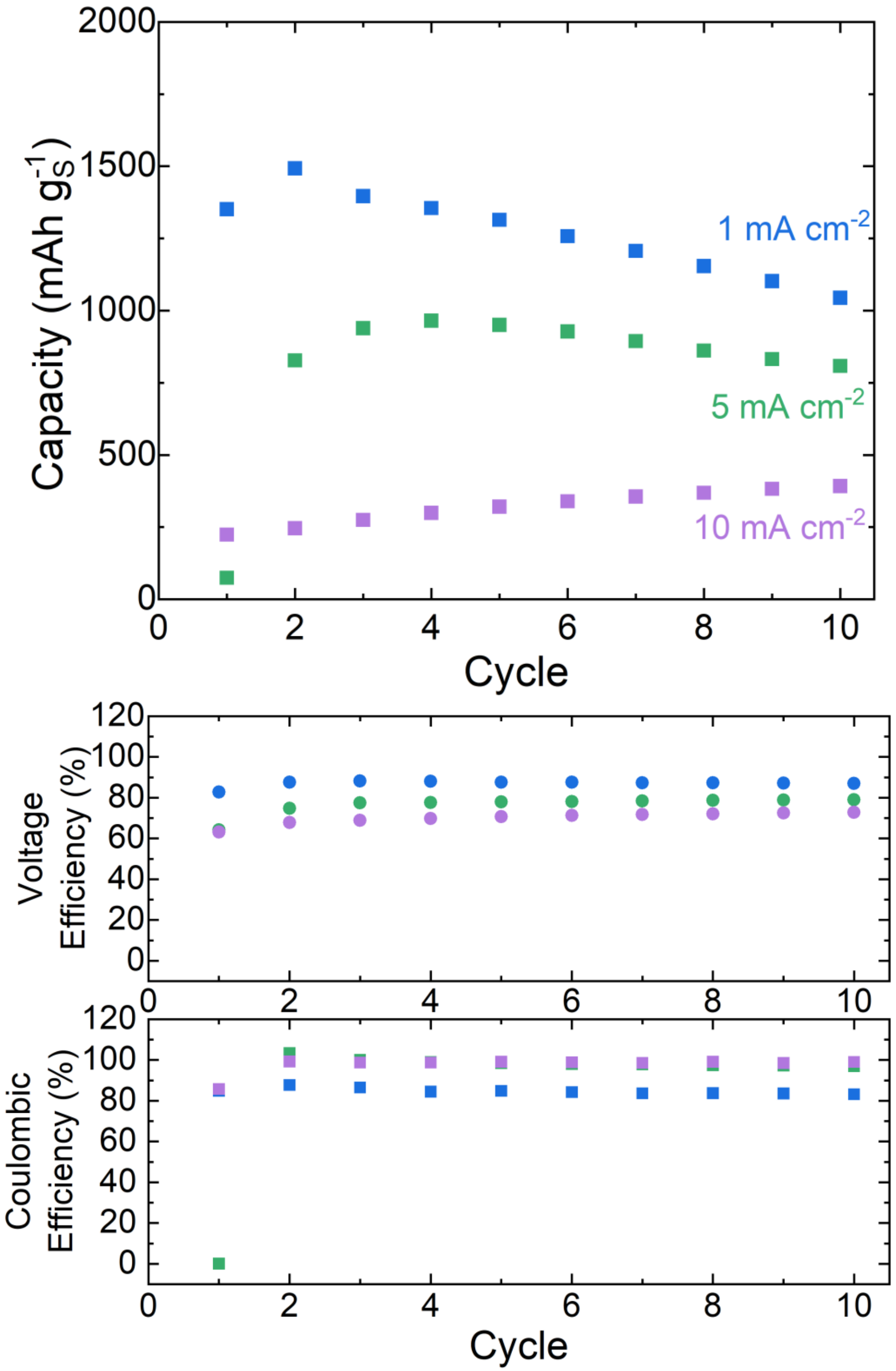




ZnO decreases the nucleation overpotential and improves coulombic efficiency.

Flow Cells with ZnO on Ni foam

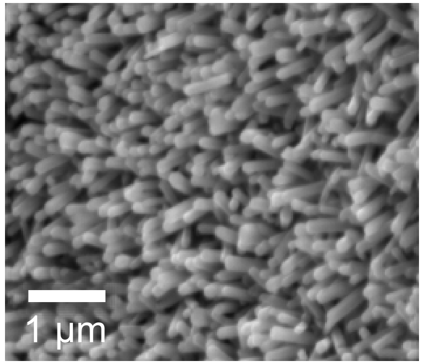


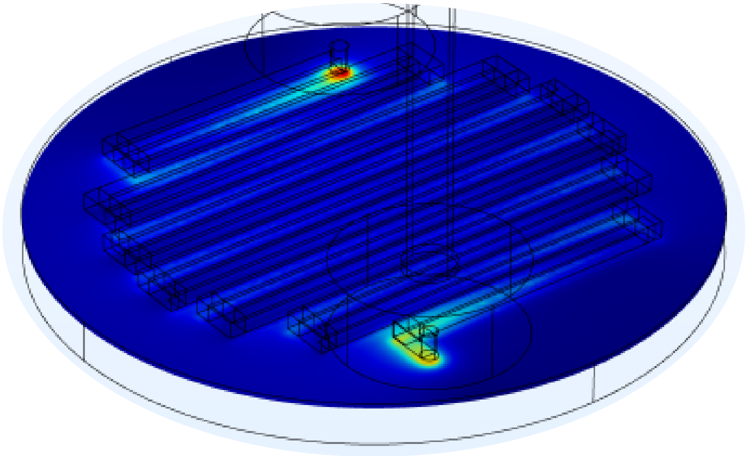


Ni foam enables stable cycling 20x faster than original flow cell.

Conclusions

- Li-S chemistry can be adapted to work in a flow cell architecture.
- High surface area scaffolds increase the maximum cycling current density 20x.
- Serpentine flow field improves uniformity of Li deposition.

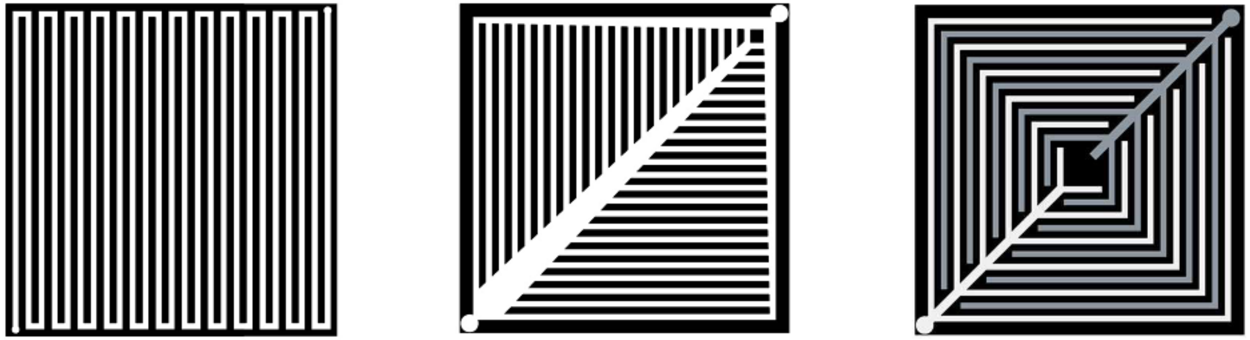




Li-S is a promising chemistry to use for high capacity, long duration, grid-scale energy storage.

Can we improve the system further?

- Evaluate bio-inspired flow fields for Li-plating uniformity.
- Scale up Li-S flow cells to ultra-high S loadings.
- Improve capacity utilization of cells with 3D-Li anode at higher rates.
- Start cells in discharged state using Li_2S instead of S.



Sauermoser, M.; Kizilova, N.; Pollet, B. G.; Kjelstrup, S., *Frontiers in Energy Research* **2020,** *8*.

Acknowledgments

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