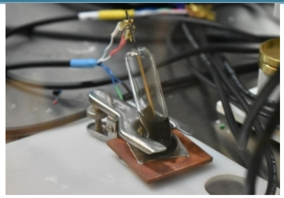
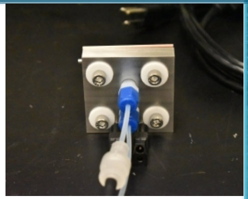
SAND2022-6724C

Sandia National Laboratories

A03-0501: Redox Mediated Li-S Flow Battery for Grid-Scale Energy Storage Applications





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241st ECS Meeting, Spring 2022

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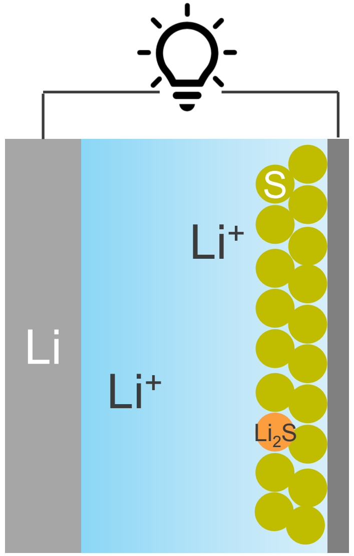
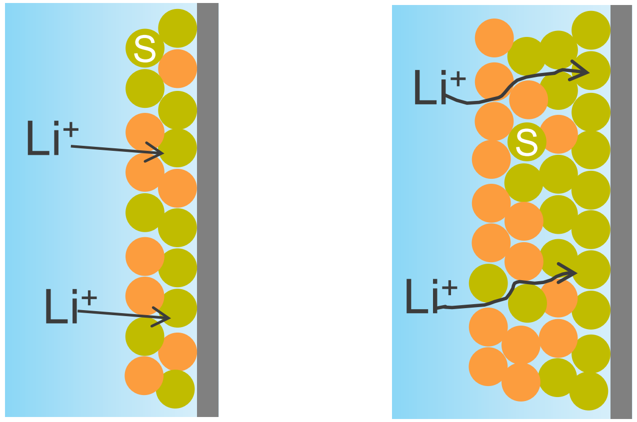
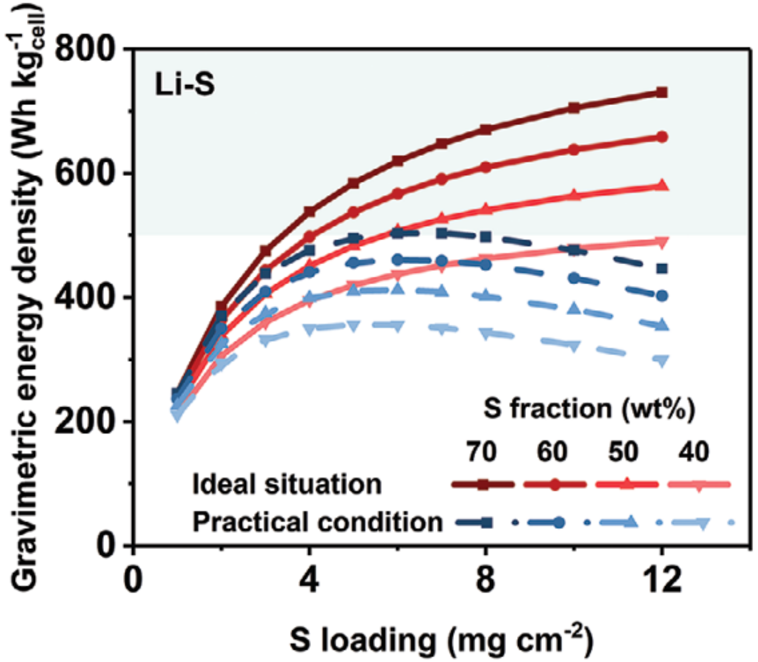
Background

- 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



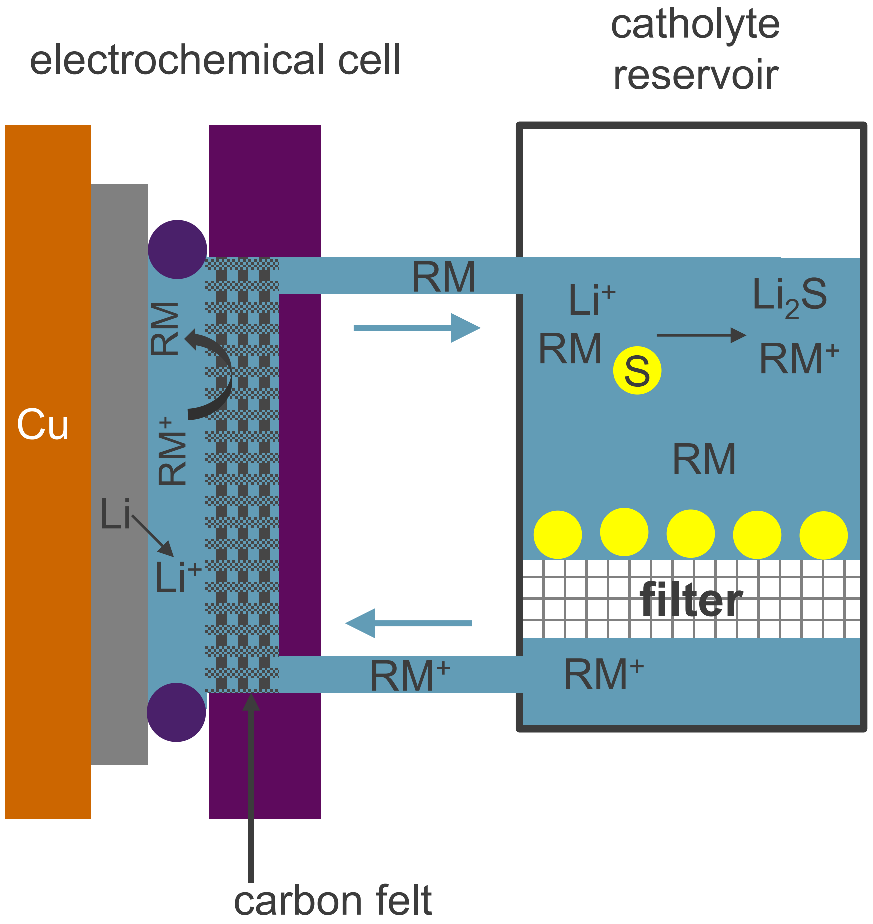
$$S + 2e^- + 2Li^+ \rightarrow Li_2S$$





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

Flow Cell Design

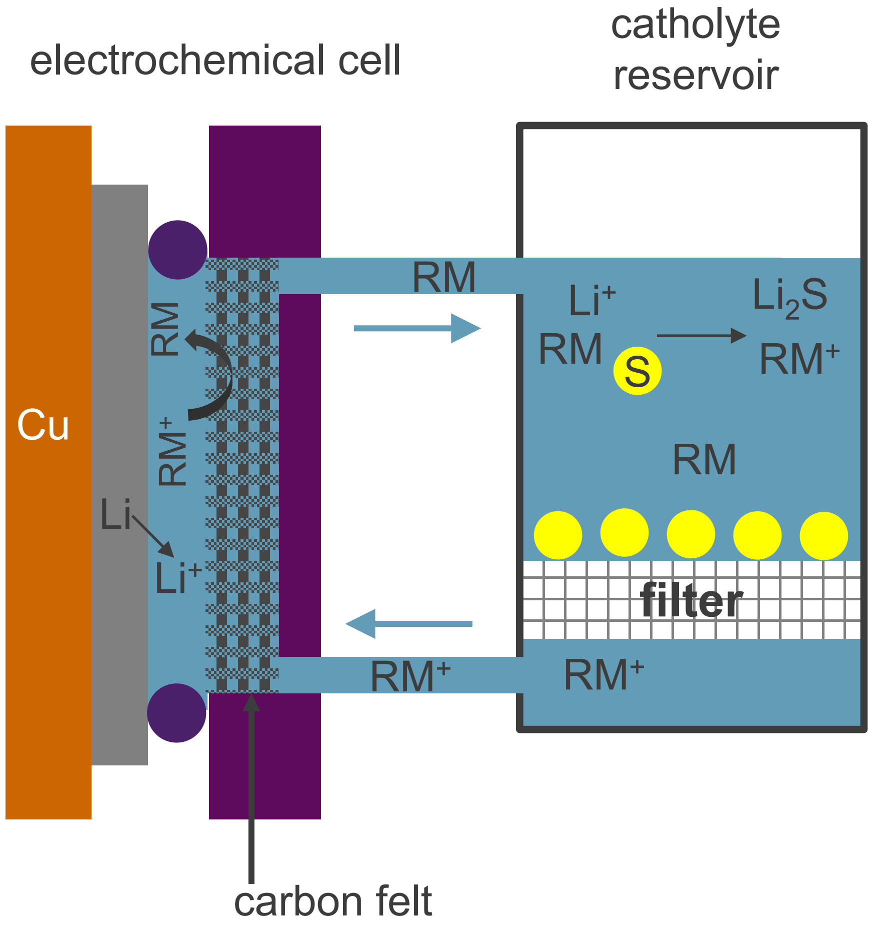


Benefits:

- 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.

Flow Cell Design



- Hybrid design with solid Li metal anode protected from dendrite growth and polysulfide shuttling by LiI and $LiNO_3$.
- Electrolyte containing dissolved redox mediators (RMs) is pumped from the reservoir to the carbon felt electrode.
- The RMs are oxidized or reduced at the carbon felt and returned to the reservoir.

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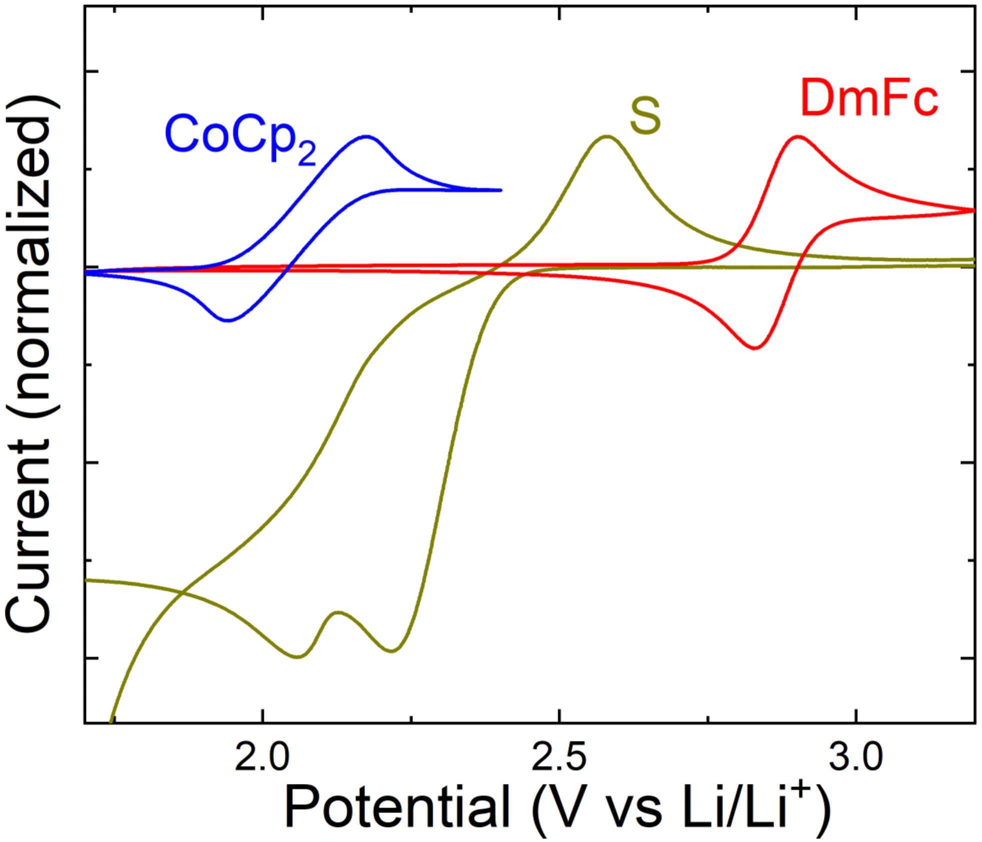
Cobaltocene and Decamethyl Ferrocene as Redox Mediators



CVs taken at 10 mV/s in 1M LiTFSI 1:1 DOL:DME, glassy carbon working electrode, Pt counter electrode, Li reference electrode.

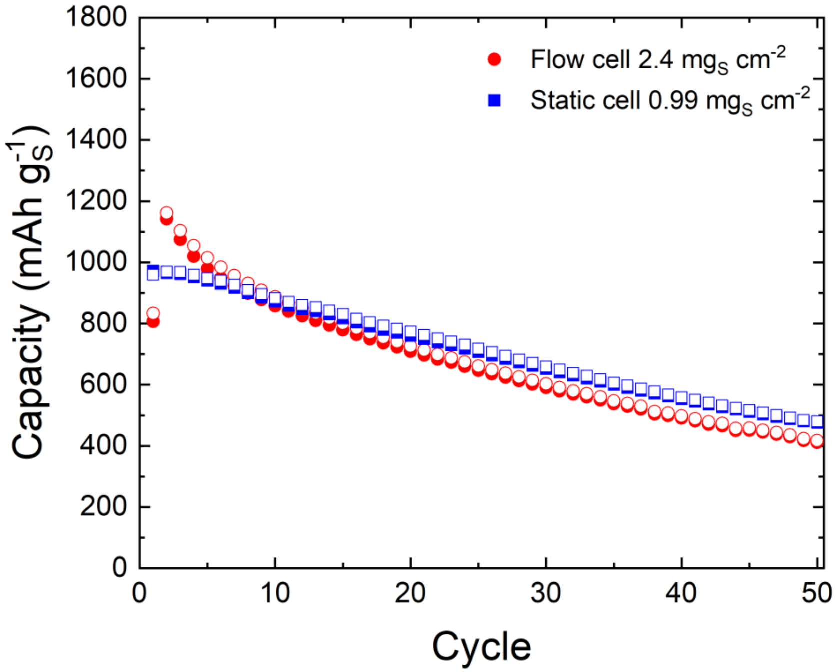
Ideal Redox Mediator

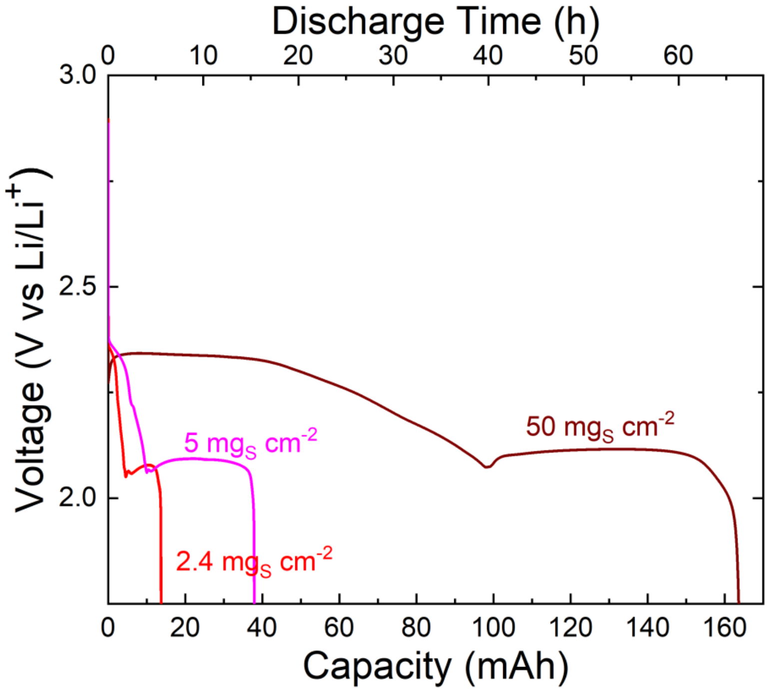
- Close to Li-S reaction (~2.4 V vs Li/Li^+)
  - E_{DmFc} = 2.86 V
  - E_{CoCp2} = 2.06 V
- Good reaction kinetics
  - k^0_{DmFc} = 4.33 x 10^{-3} cm s^{-1}
  - k^0_{CoCp2} = 3.14 x 10^{-4} cm s^{-1}
- Fast diffusion
  - D_{DmFc} = 5.23 x 10^{-6} cm^2 s^{-1}
  - D_{CoCp2} = 3.70 x 10^{-6} cm^2 s^{-1}

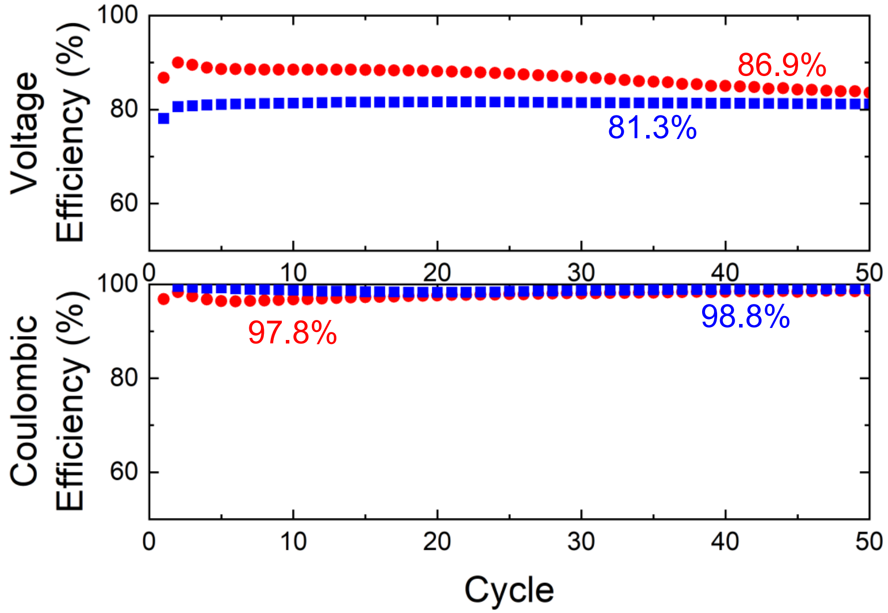
Meyerson, M. L.; Rosenberg, S. G.; Small, L. J., *ACS Applied Energy Materials* **2022,** *5* (4), 4202-4211.

Flow Cell Cycling

- Achieve high coulombic and voltage efficiencies in both static and flow cell configurations.
- Increasing S loading increases capacity and enables discharge times over 60 h-showing viability for long duration storage.







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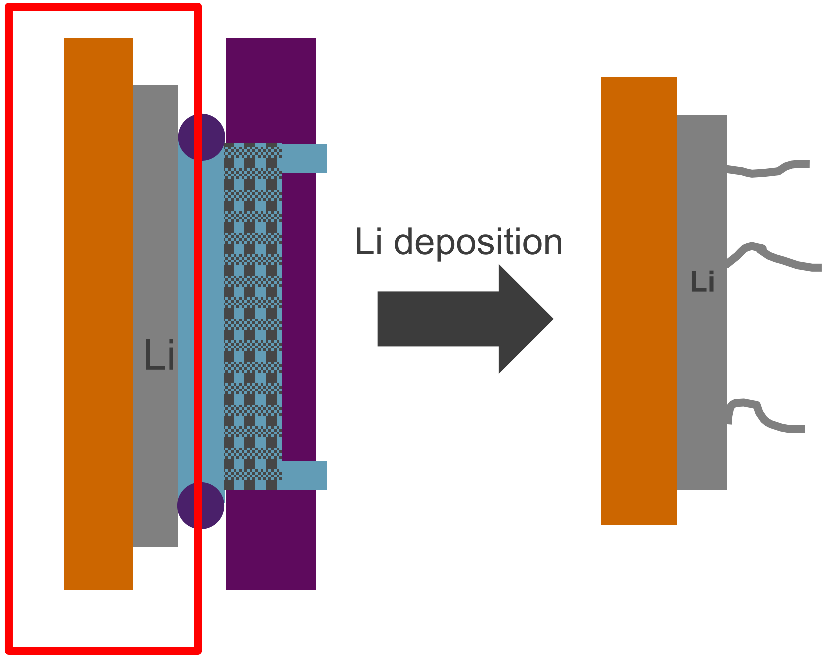
Limitations of Planar Li Anodes

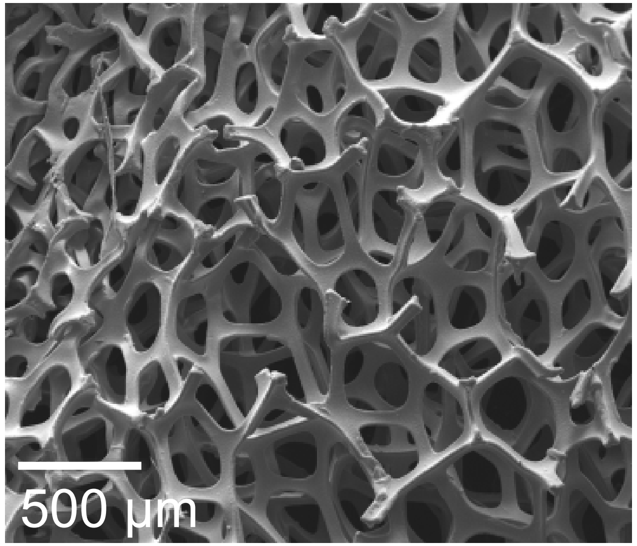


Li dendrites

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

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

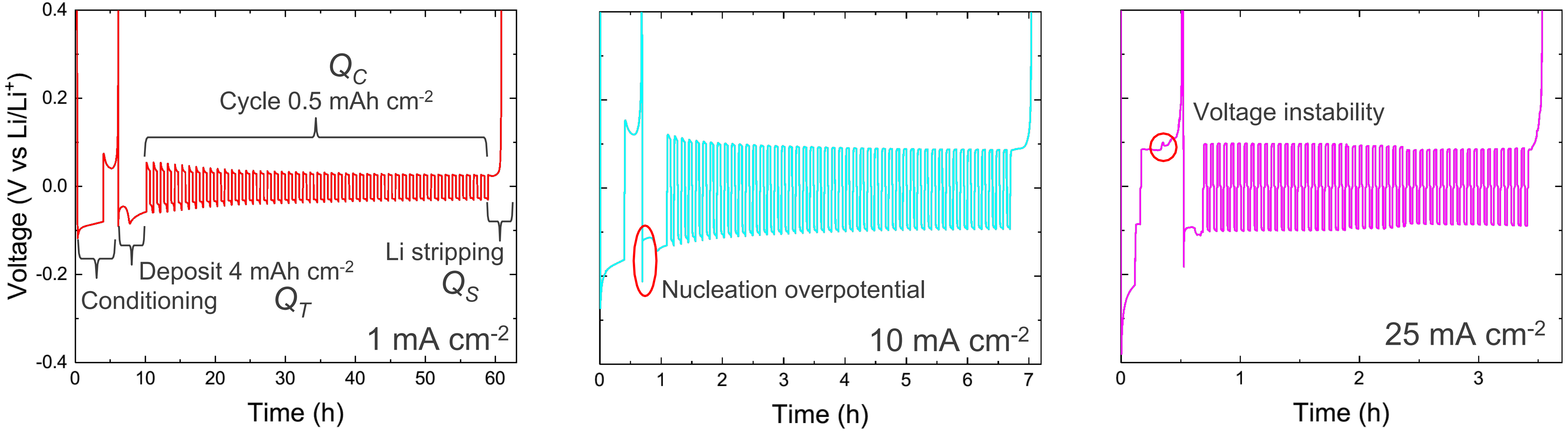
Increasing effective surface area decreases the local current density.



Bare Ni foam

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



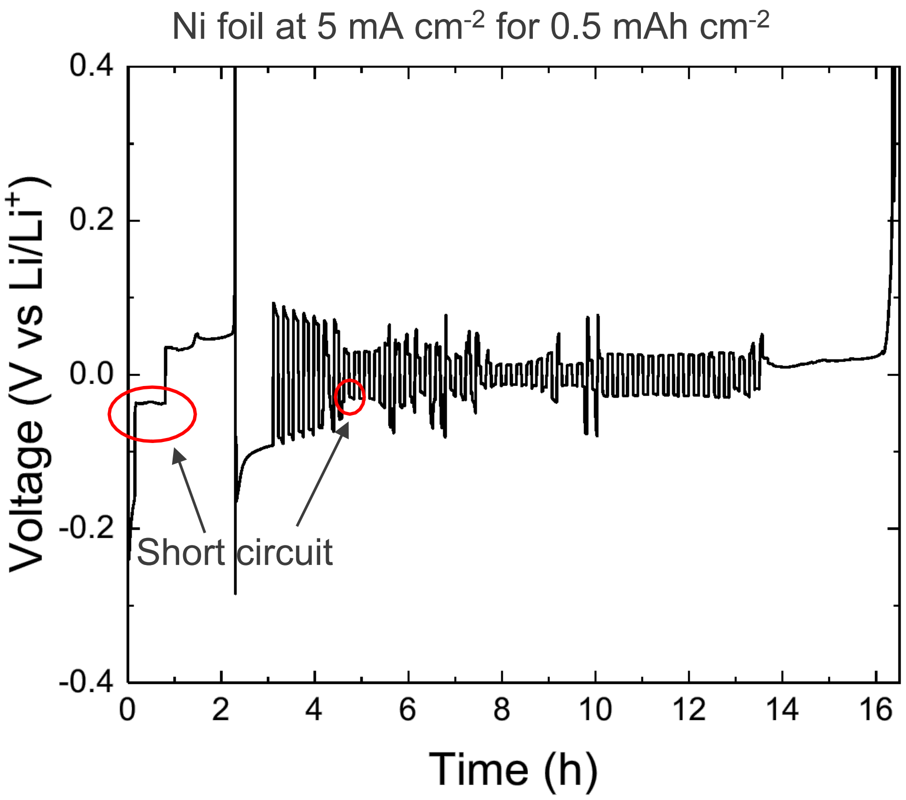
$$\mathrm{CE_{avg}} = \frac{nQ_C + Q_S}{nQ_C + Q_T} \qquad n=48$$

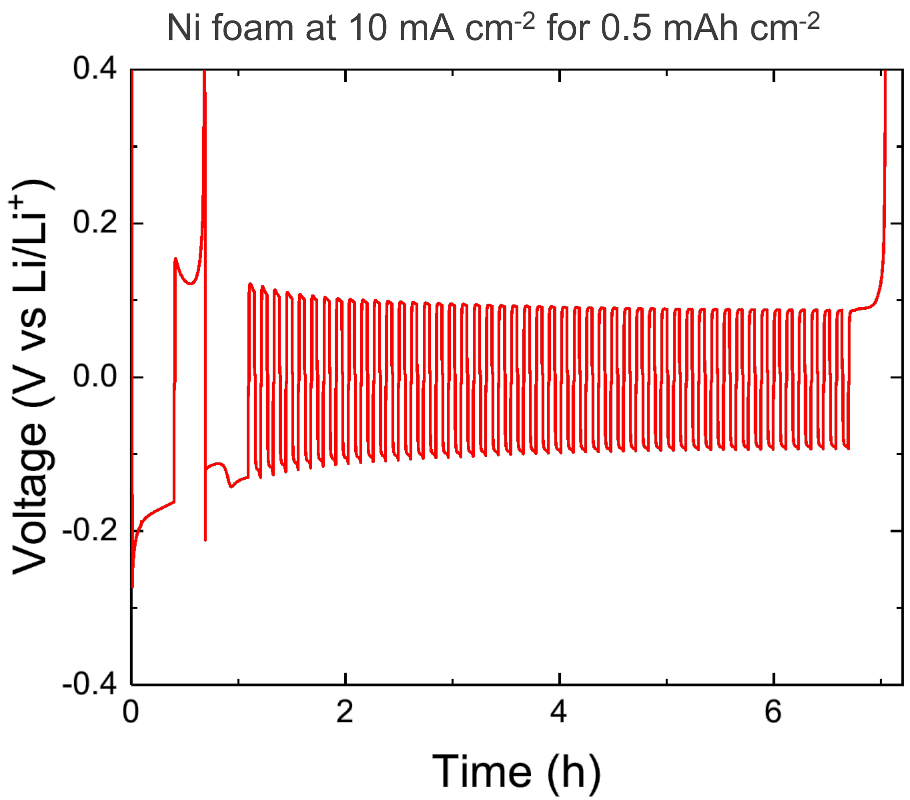
* Ni foam, 1 M LiTFSI with 2 wt % $LiNO_3$ in 1:1 (v/v) DOL:DME

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

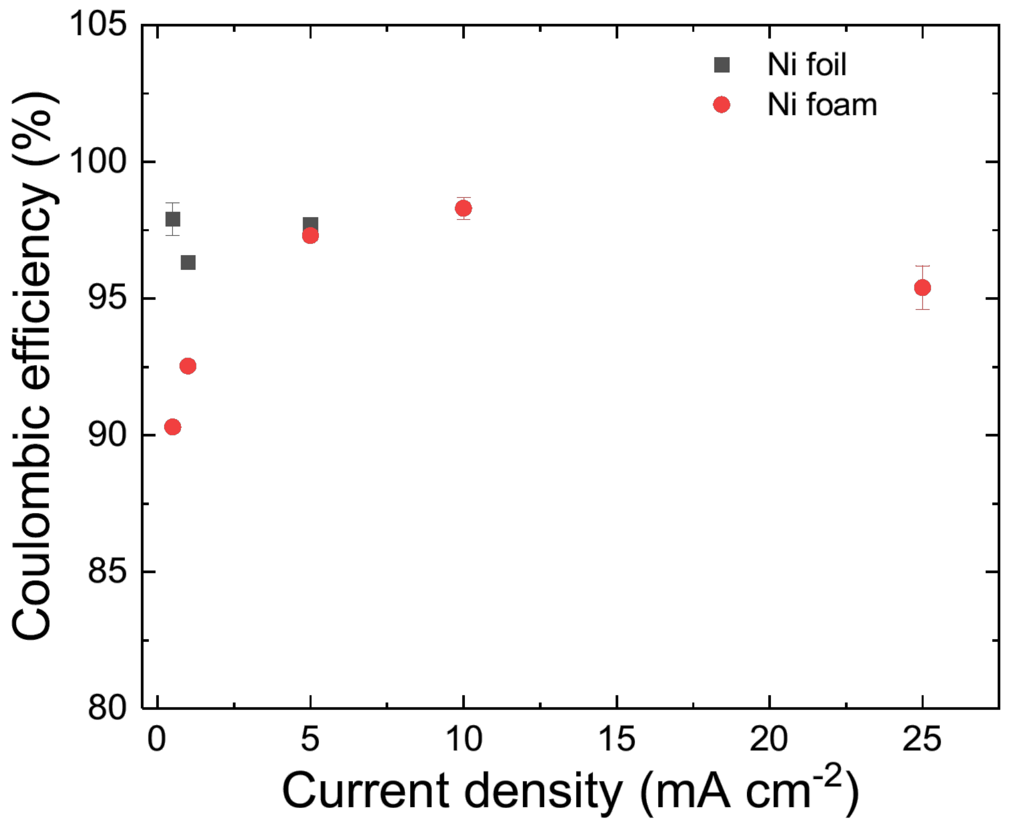
- For planar deposition, charging above 1 mA cm^{-2} results in unstable cycling and shorting.



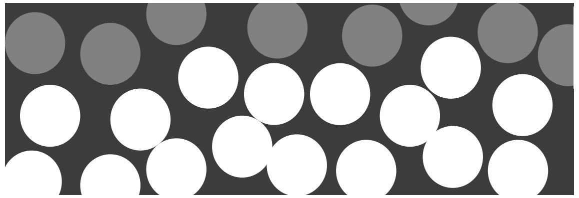


Using high SA foam, charge rate can be 10 times faster.

Increased Surface Area Allows Faster Charging



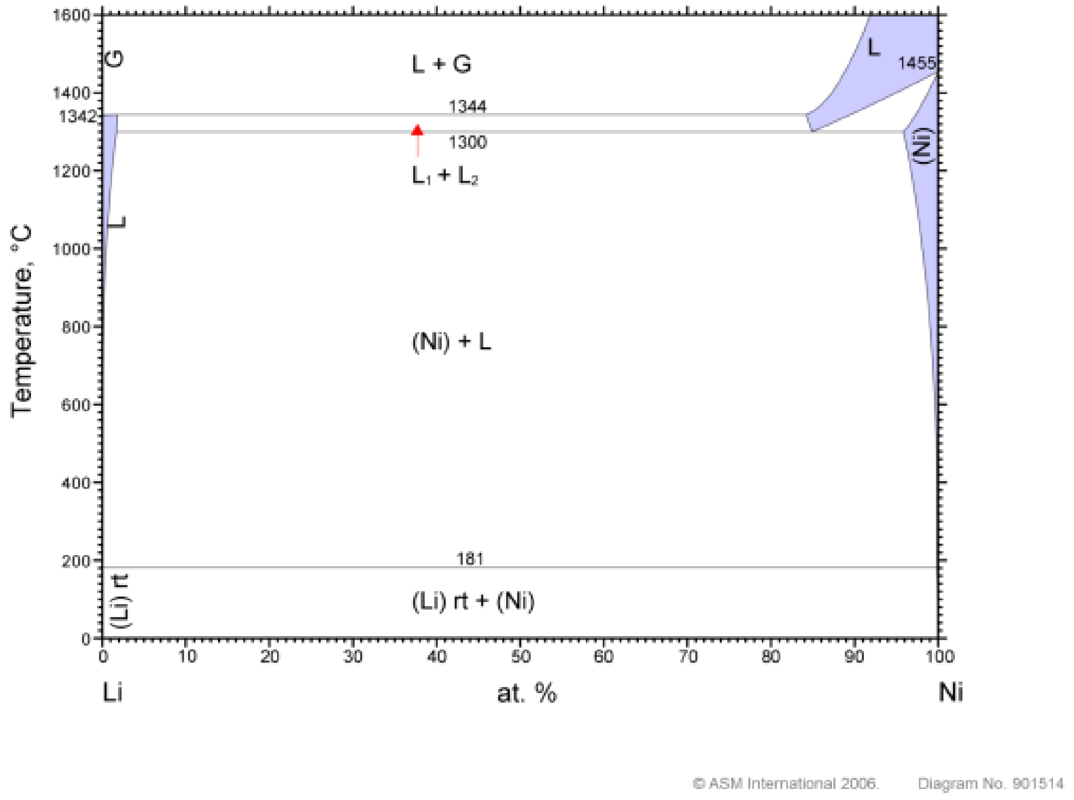
Lower current densities show better CE on the Ni foil than the bare Ni foam, likely from low utilization of the foam.

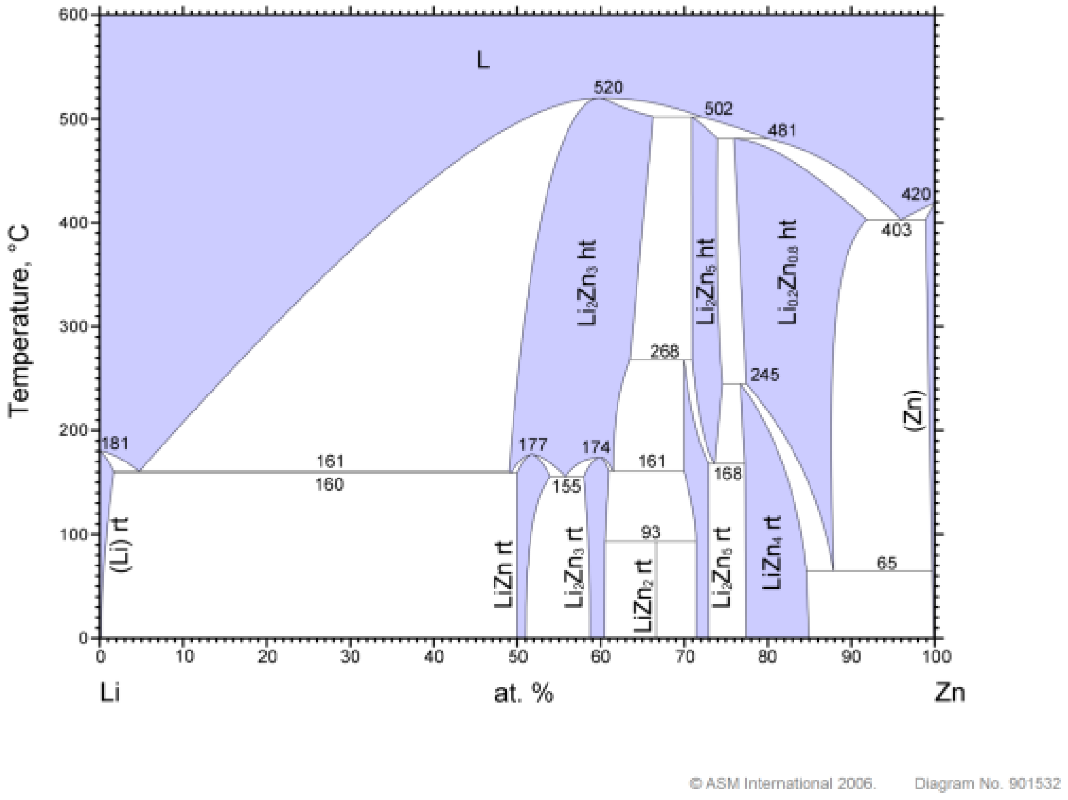


*0.5 mA cm^{-2}, 1 M LiTFSI with 2 wt % $LiNO_3$ in 1:1 (v/v) DOL:DME

Seeding Li Deposition

- Nucleation overpotential on Ni comes from lattice mismatch between the metals.
- Li and Ni do not alloy, but Li and Zn do.

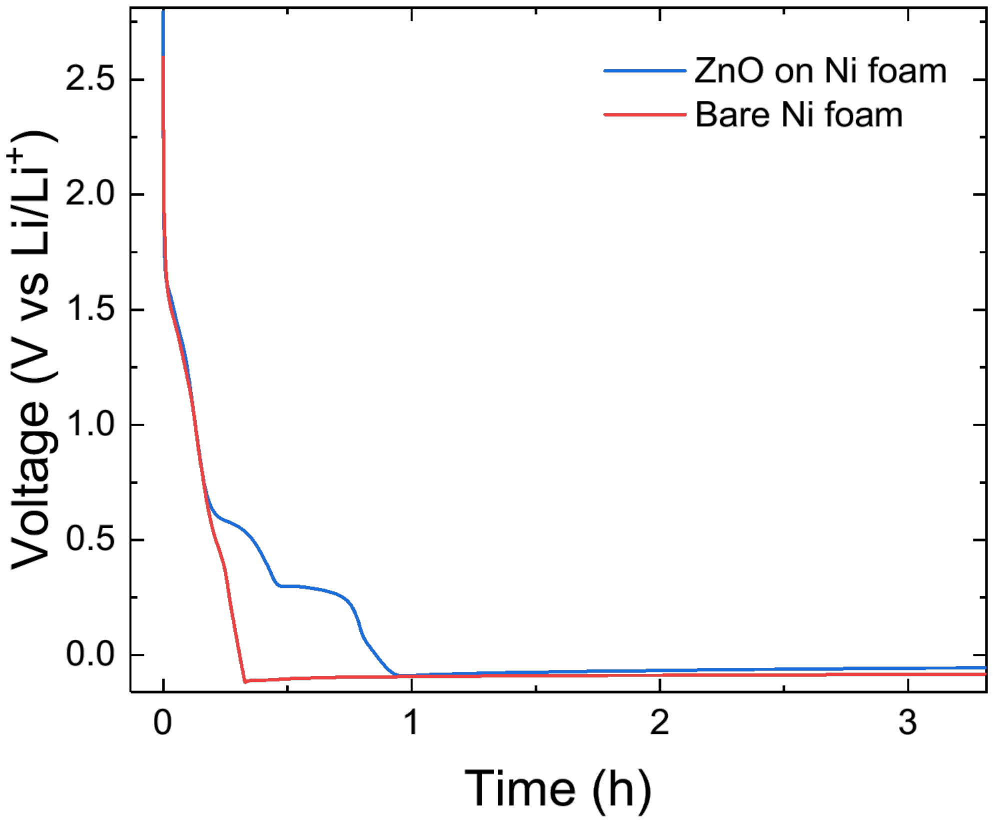




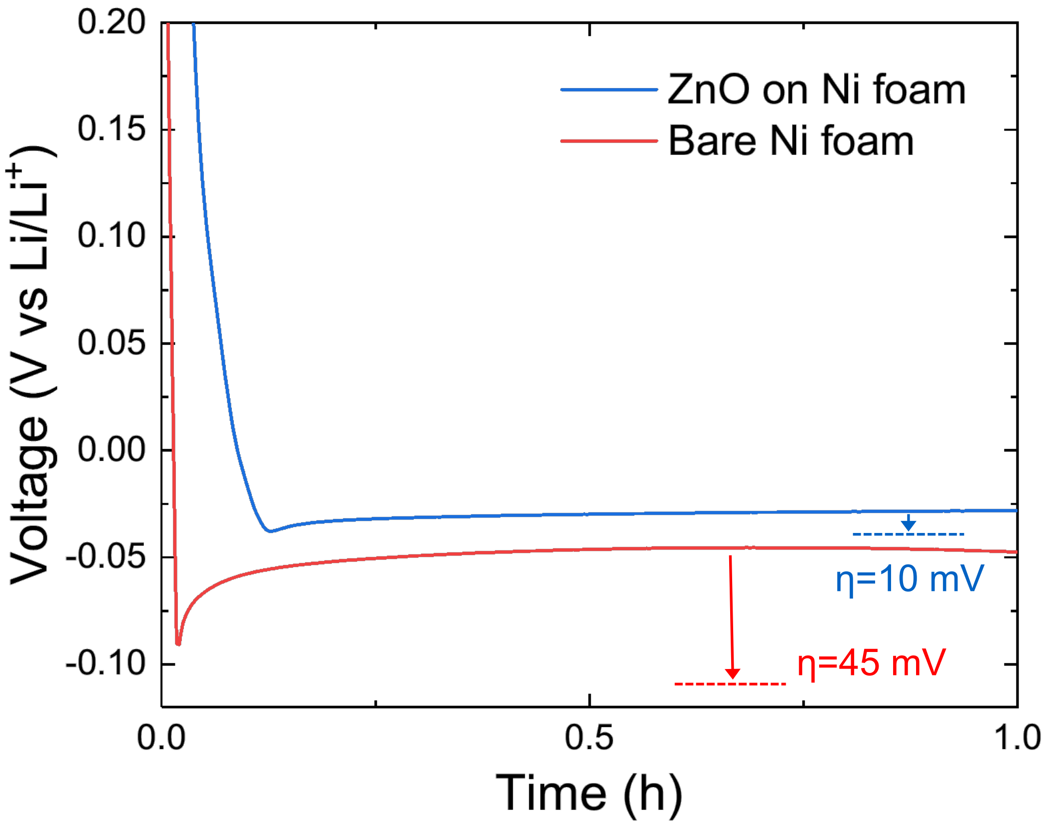
Seeding Li Deposition

- 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

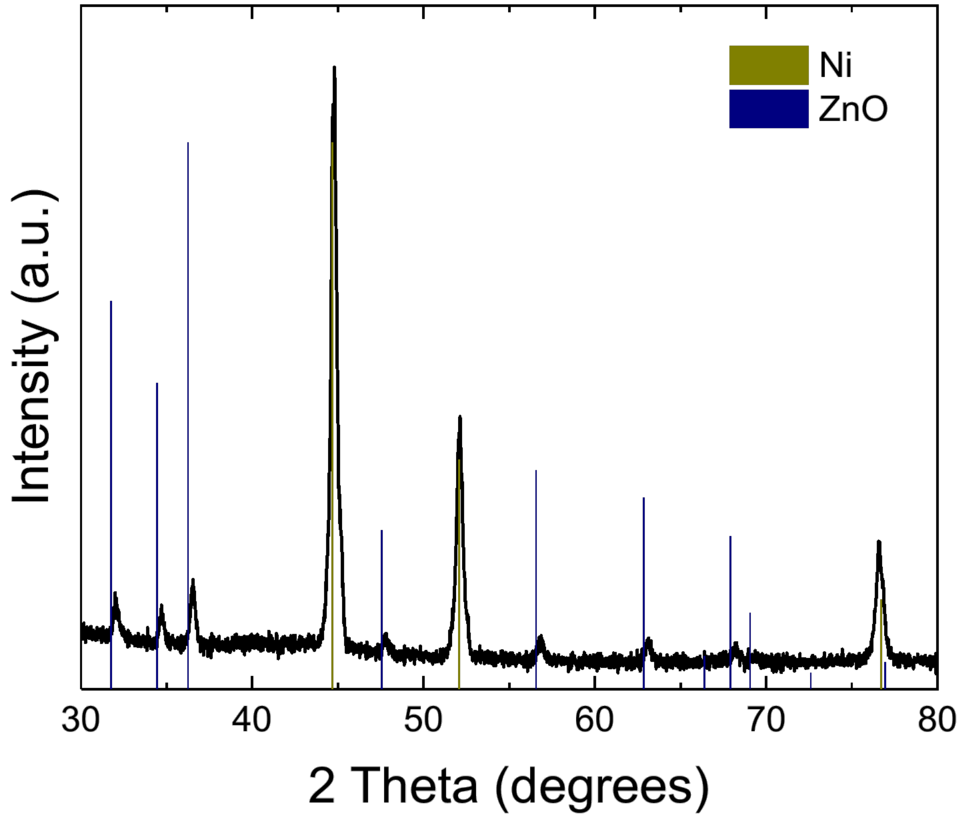


First deposition after conditioning

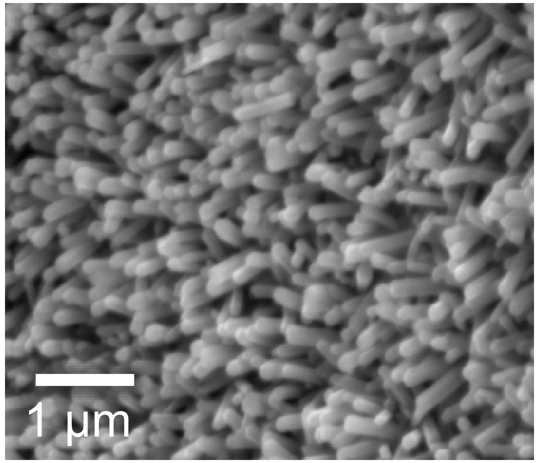
ZnO Synthesis on Ni Foam

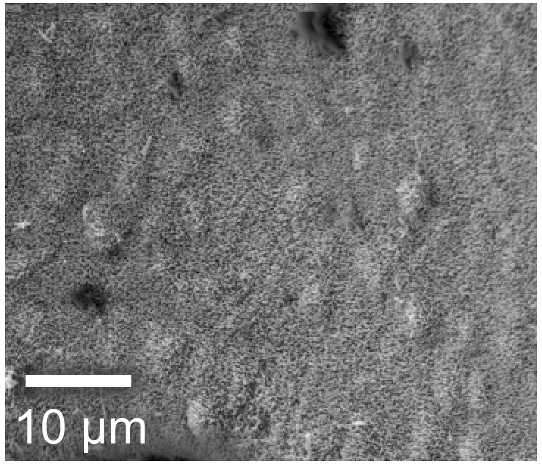
- Hydrothermal synthesis of ZnO nanorods on Ni foam
  - Zinc acetate and hexamine in water

X-ray diffraction of ZnO nanorods on Ni foam



SEM of ZnO nanorods



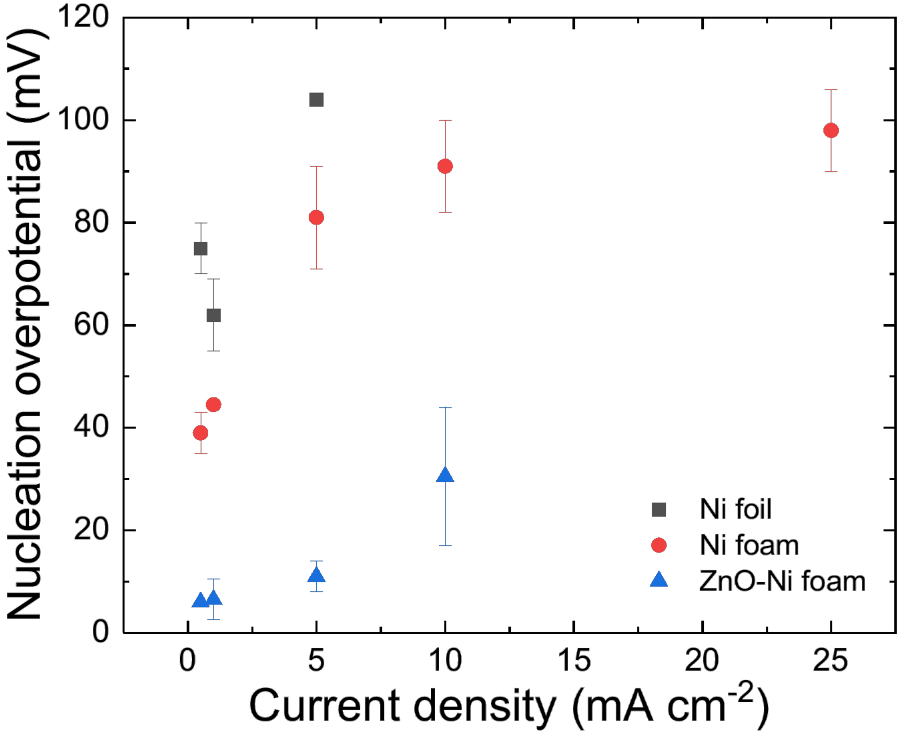


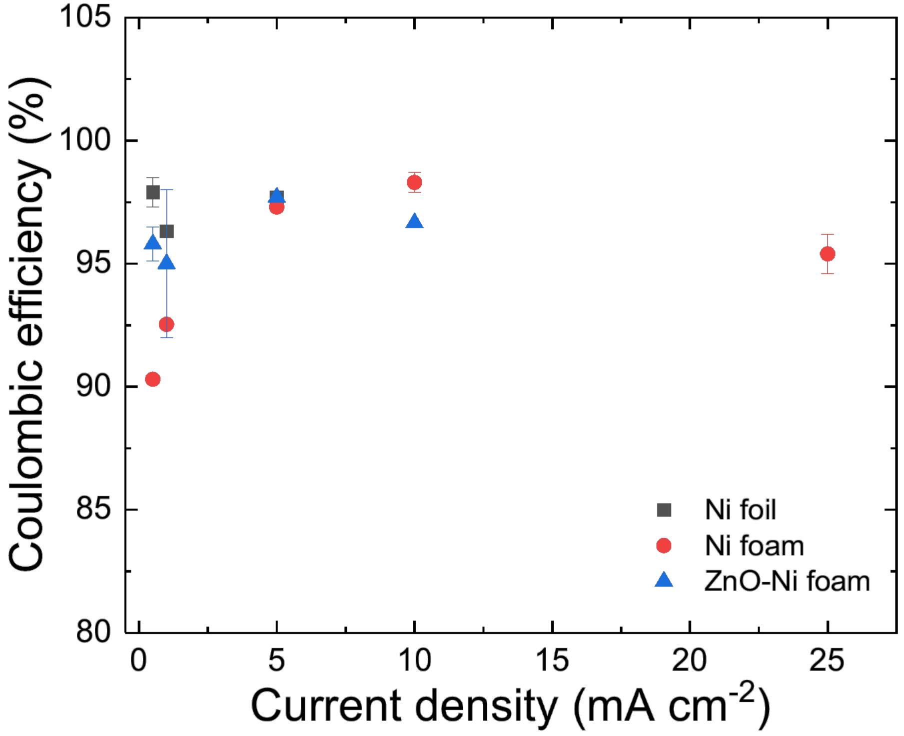
- 100-150 nm wide, 500-800 nm tall
- Uniform coverage of Ni

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

ZnO Further Improves System

- Nucleation overpotential decreases from 68 mV to 10 mV and CE increases compared to bare Ni foam at low current densities.





ZnO decreases the nucleation overpotential and improves coulombic efficiency.

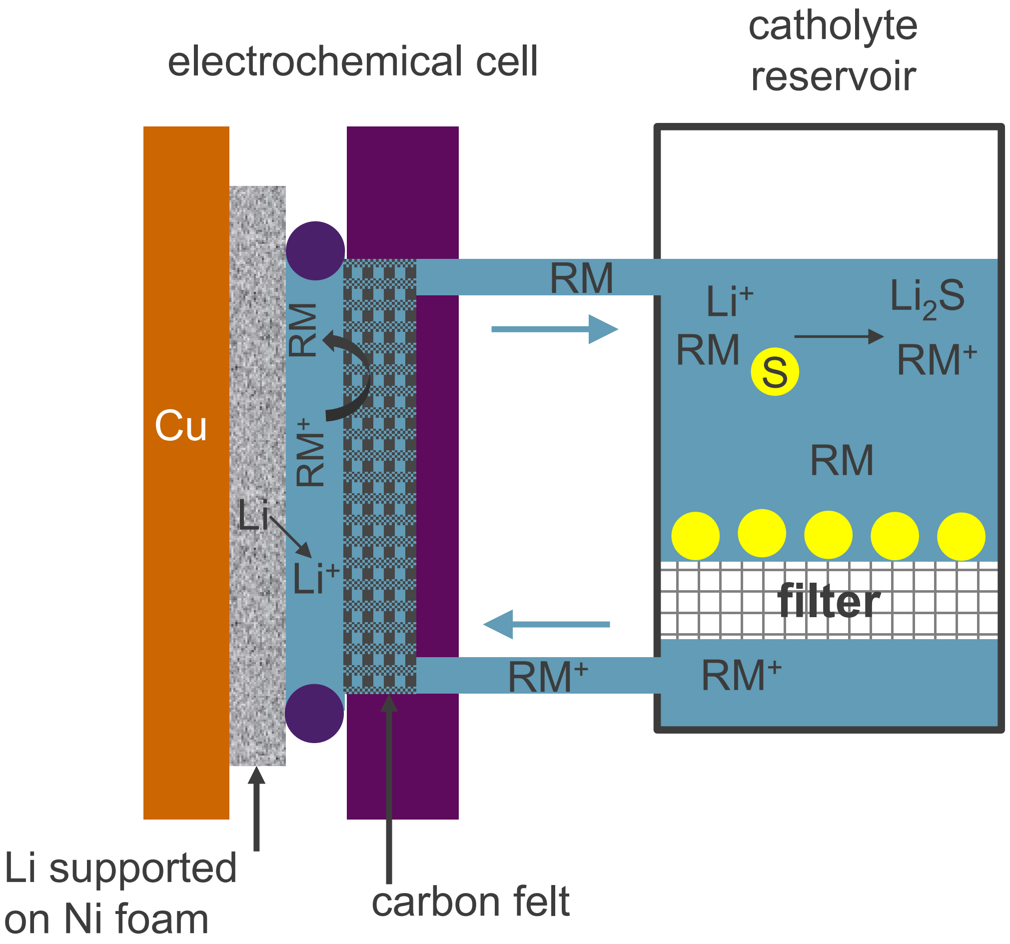
Conclusions

- Li-S chemistry can be adapted to work in a flow cell architecture.
- High S loadings enable long discharge times and show feasibility of use for long duration storage.
- High surface area scaffolds increase the maximum cycling current density.

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

Future Work

Scaling up the flow cell by combining a high S loading flow cell with a ZnO on Ni foam scaffold to enable faster charging and discharging of flow cell at realistic energy densities.



Acknowledgments

OFFICE OF ELECTRICITY
ENERGY STORAGE PROGRAM

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