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Redox Mediated Li-S Flow Battery for Grid Scale Energy Storage

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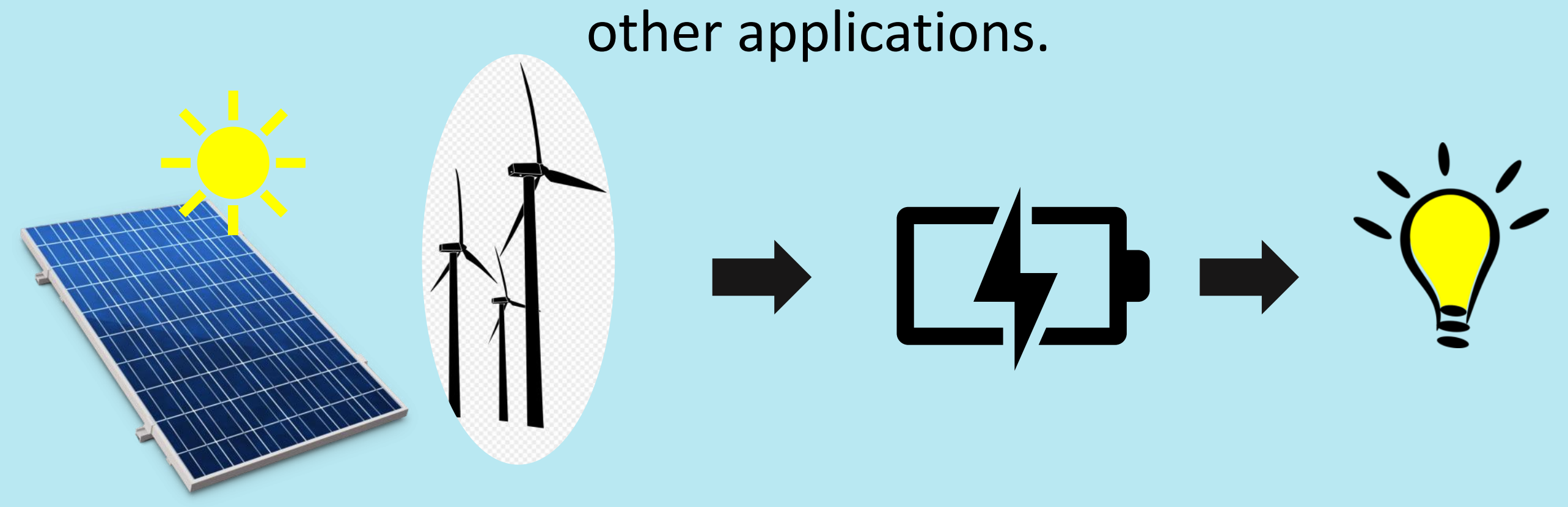
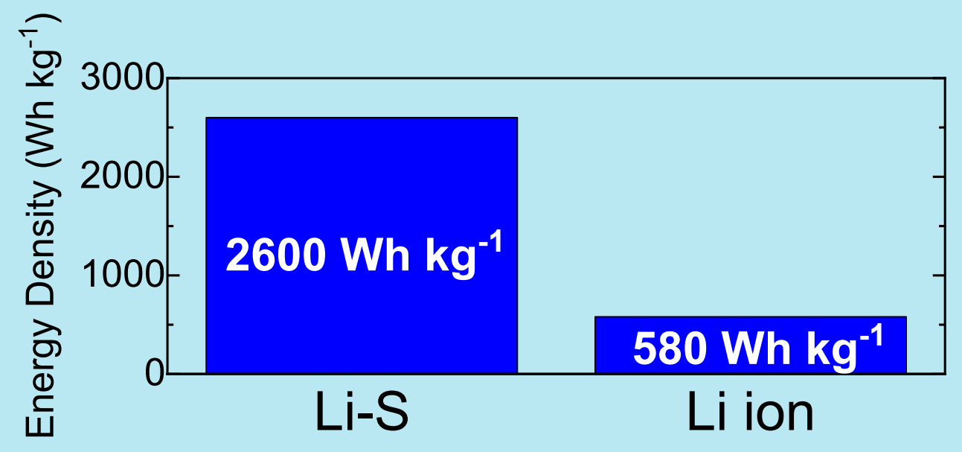
Background

Safe, reliable, grid-scale energy storage is needed to store the energy produced by intermittent renewable sources as well as many other applications.



The low cost and high capacity of S make Li-S batteries a cost-effective solution to this need.[1]



However, S has poor electrical conductivity and typically requires a significant amount of carbon added to enhance the conductivity and Li and S chemistries present a safety hazard.[2,3]

Redox mediators eliminate need for carbon additives

Redox mediators (RMs) enable the redox chemistry of S to occur in solution following the reactions below.[4]

Discharge:
Anode: Li → Li^+ + 1 e^-
Cathode: RM^+ + 1 e- → RM
In solution: $2Li^+ + RM + S \rightarrow Li_2S + RM^+$
Overall reaction: $2Li + S \rightarrow Li_2S$

The RM must have a lower redox potential than S during discharge and a higher redox potential during charge.

To increase power efficiency, the redox potentials of RMs should be as close to that of S as possible.

Decamethyl ferrocene (DmFc) and cobaltocene ($CoCp_2$) were chosen for their redox potentials and stability in the 1 M LiTSFI in 1:1 (vol%) DOL:DME electrolyte.

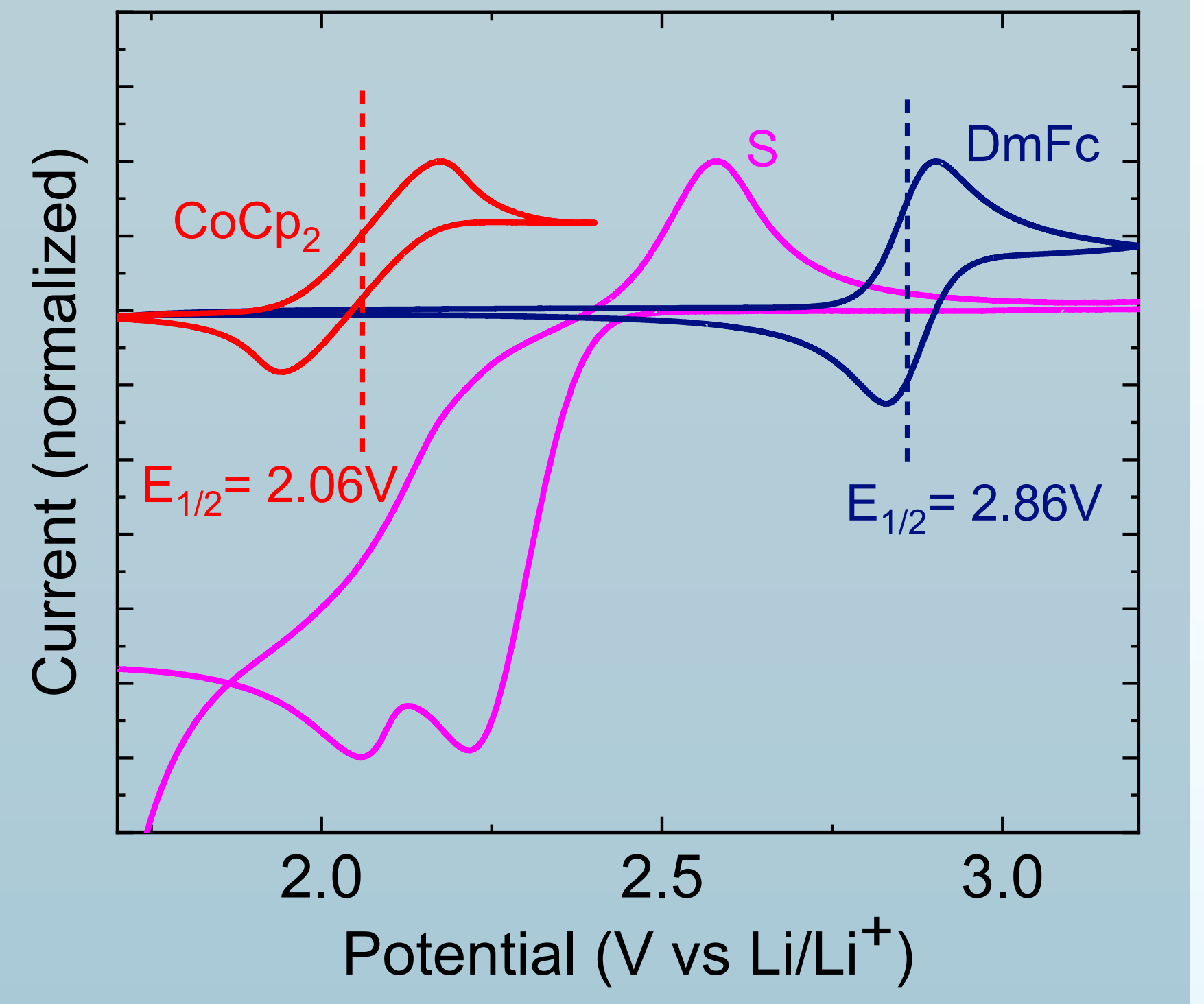
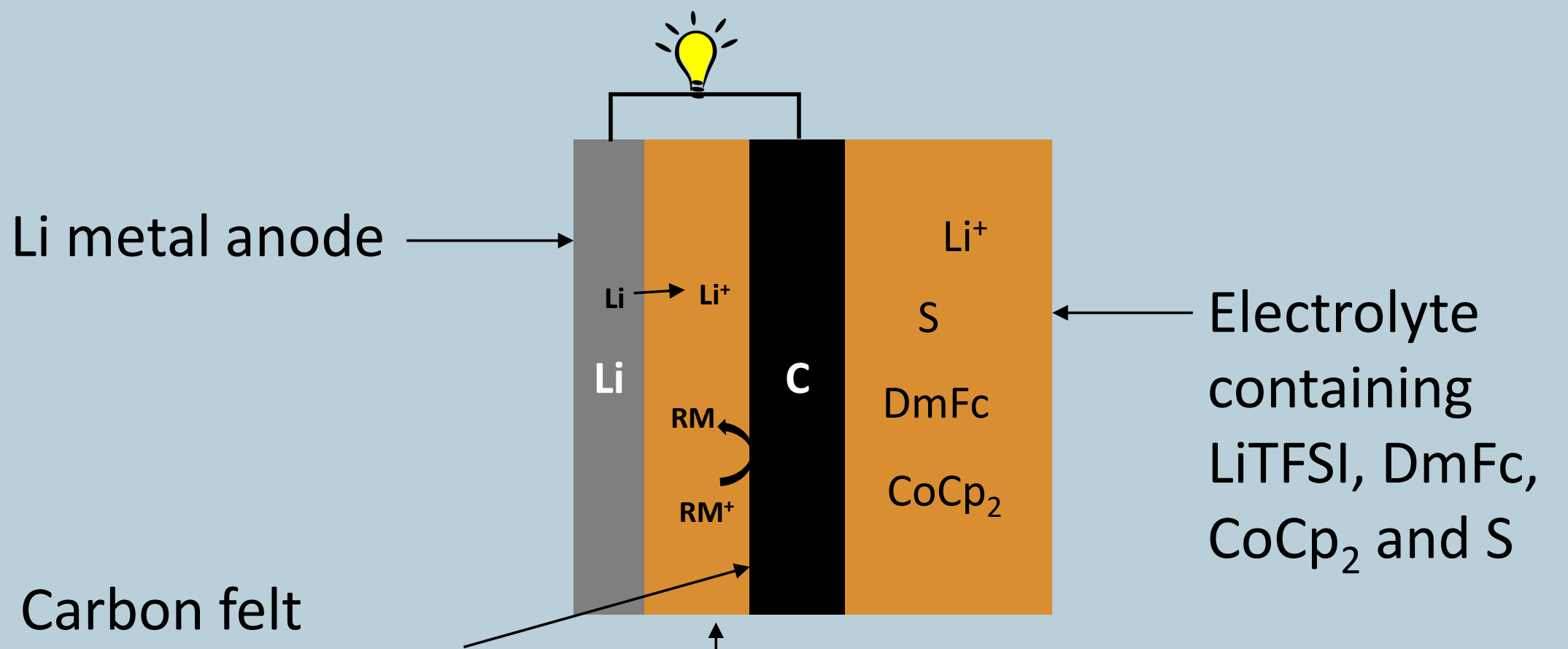


Fig. 1: CVs of 20 mM $CoCp_2$, sulfur, and 8.33 mM DmFc in 1 M LiTFSI in 1:1 DOL:DME at 10 mV/s on glassy carbon in a three-electrode cell.

Small scale cell design



Spatial separation of Li and C removes the need for a separator while reducing risk of short circuiting

Cycling performance

Li metal anodes tend to grow high surface area dendrites during Li electrodeposition unless solid-state electrolytes, additives, or coatings are used.[5,6]

Adding $LiNO_3$ and presoaking the Li in LiI protects the Li surface and improves both the capacity and the capacity retention.

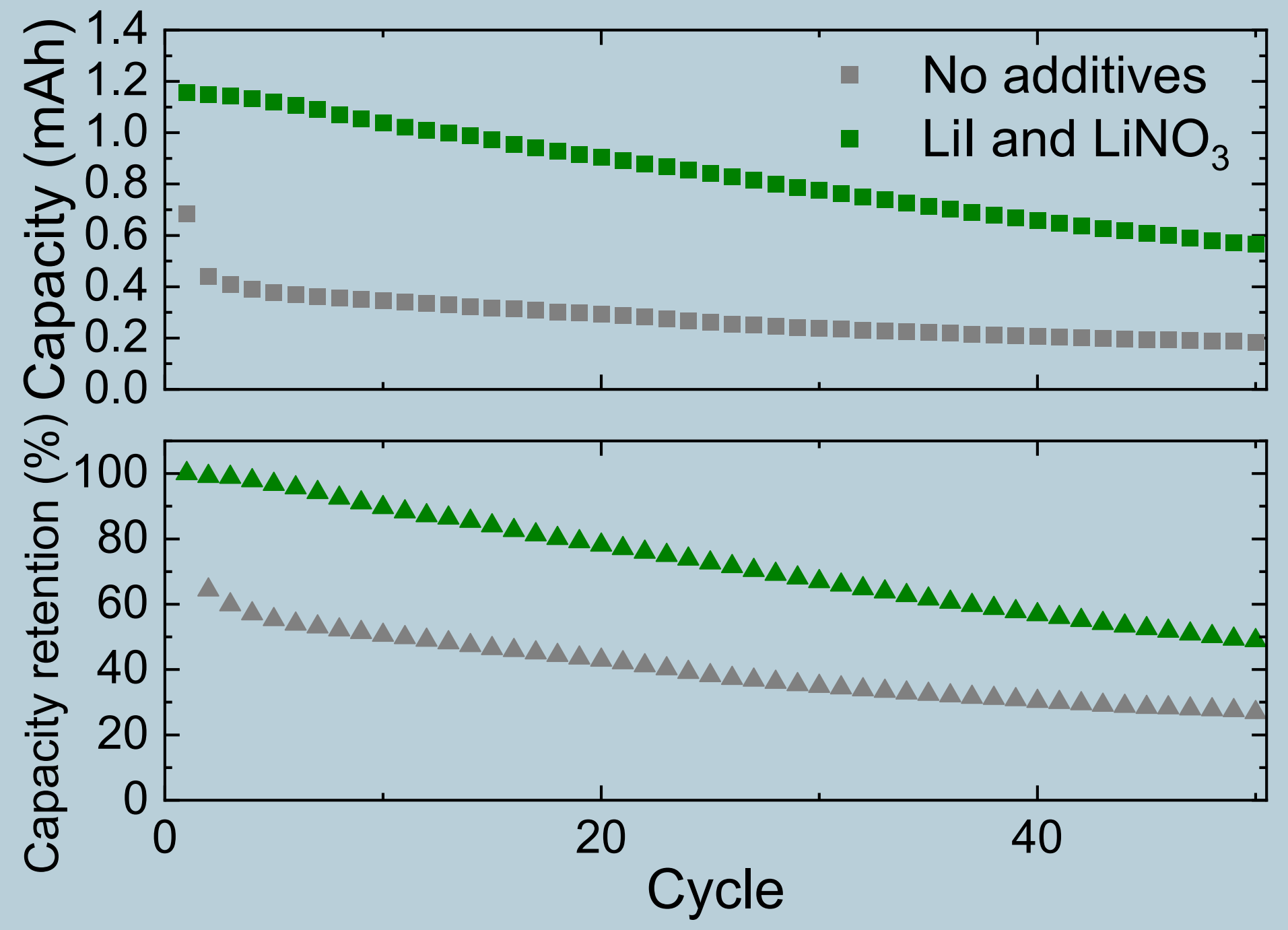


Fig. 2: Cycling performance of Li-S cells with and without additives cycled at 0.5 mA cm^{-2}

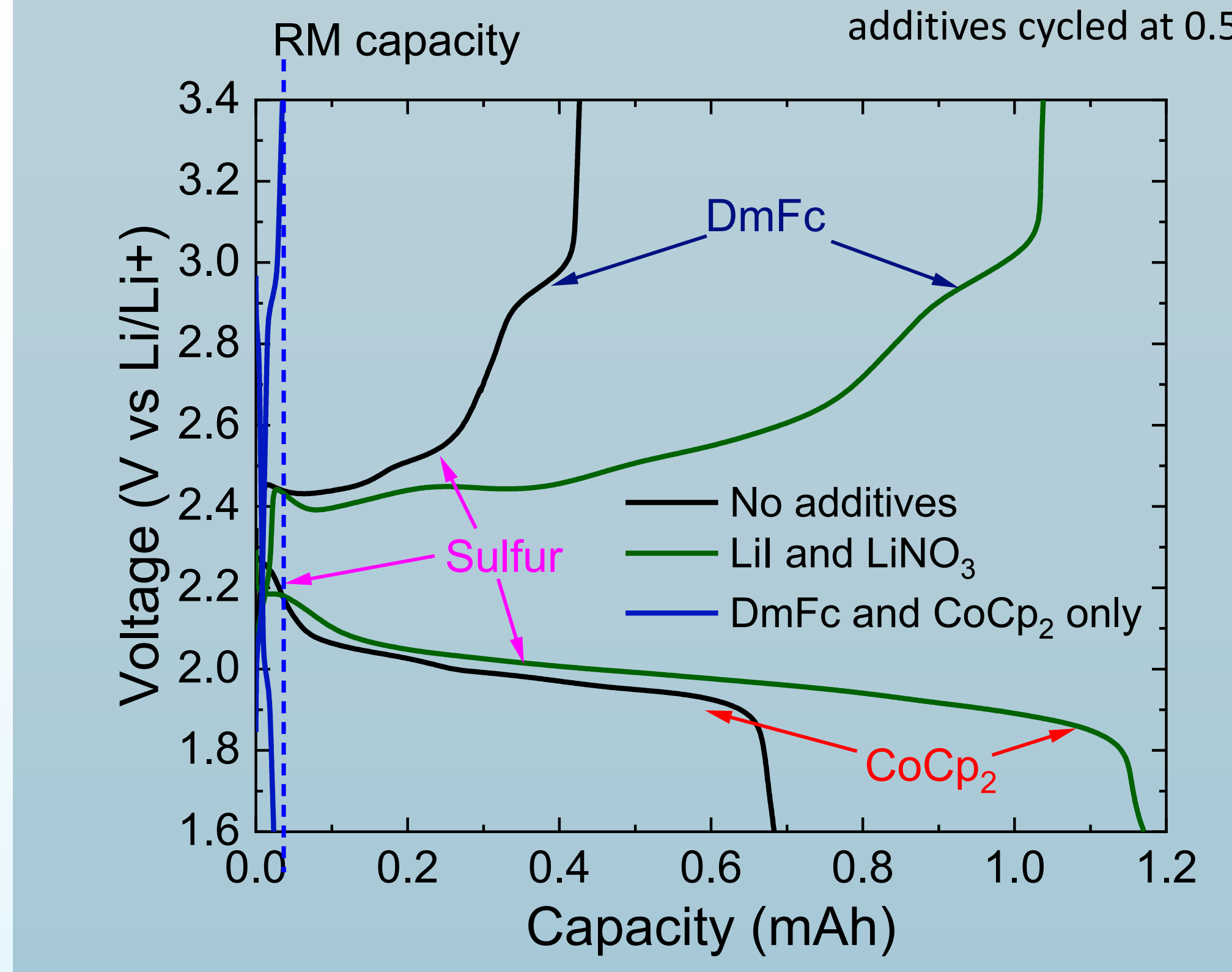


Fig. 3: Charge-discharge curves for Li-S cells cycled at 0.5 mA cm^{-2}

The concentration of RM is kept low, to less than 10% of the total capacity, so **that most of the capacity comes from S, not the RMs.**

Sulfur loss causes capacity fade

After 50 cycles, the capacity has decreased to less than 50% of the initial capacity.

Cyclic voltammetry indicates that:

1) RM peaks remain similar in size after cycling.
2) Some S peaks decrease or disappear.

The decrease in current from S is likely due to **polysulfides diffusing to the Li metal surface and reacting there, which decreases the battery capacity.**

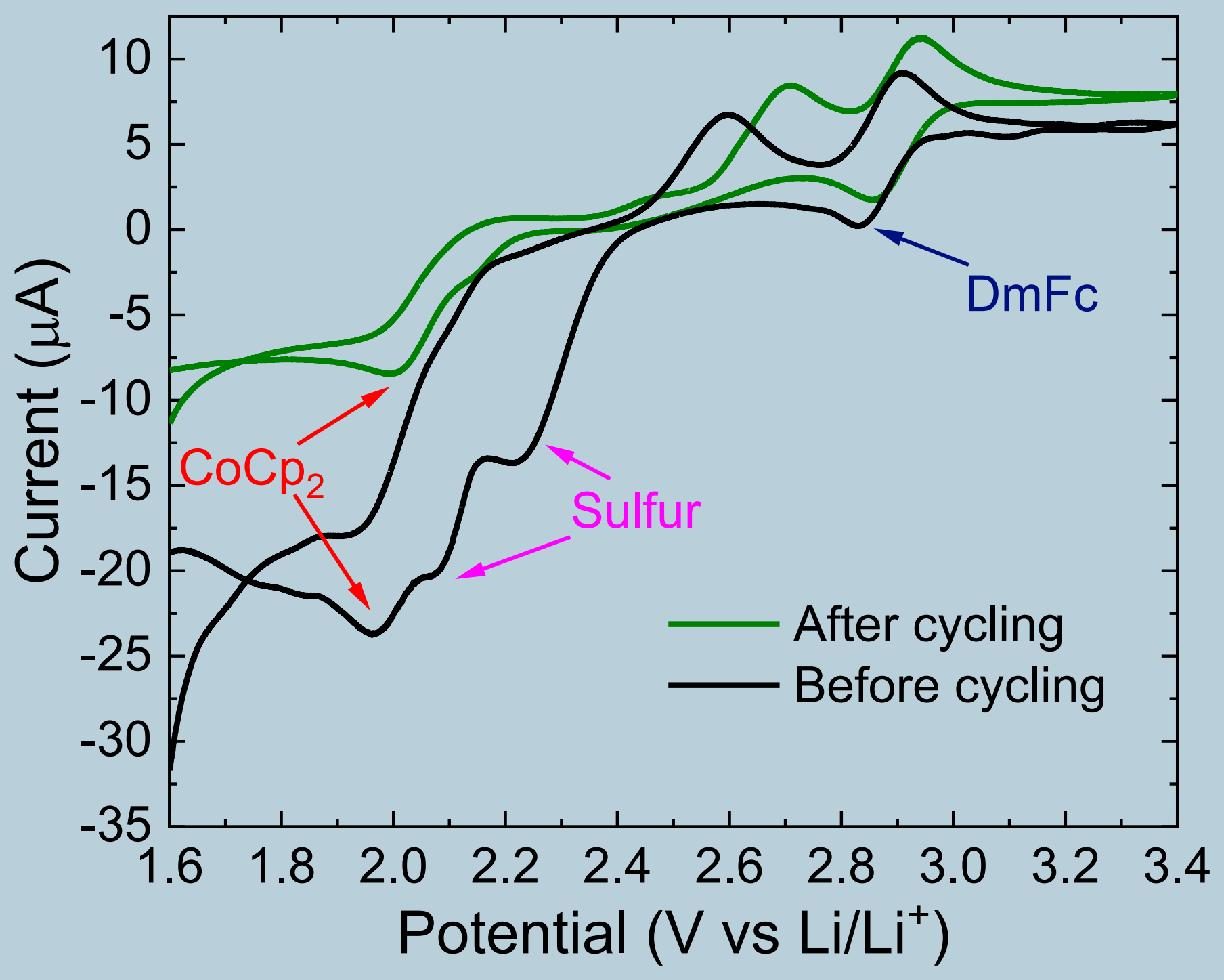


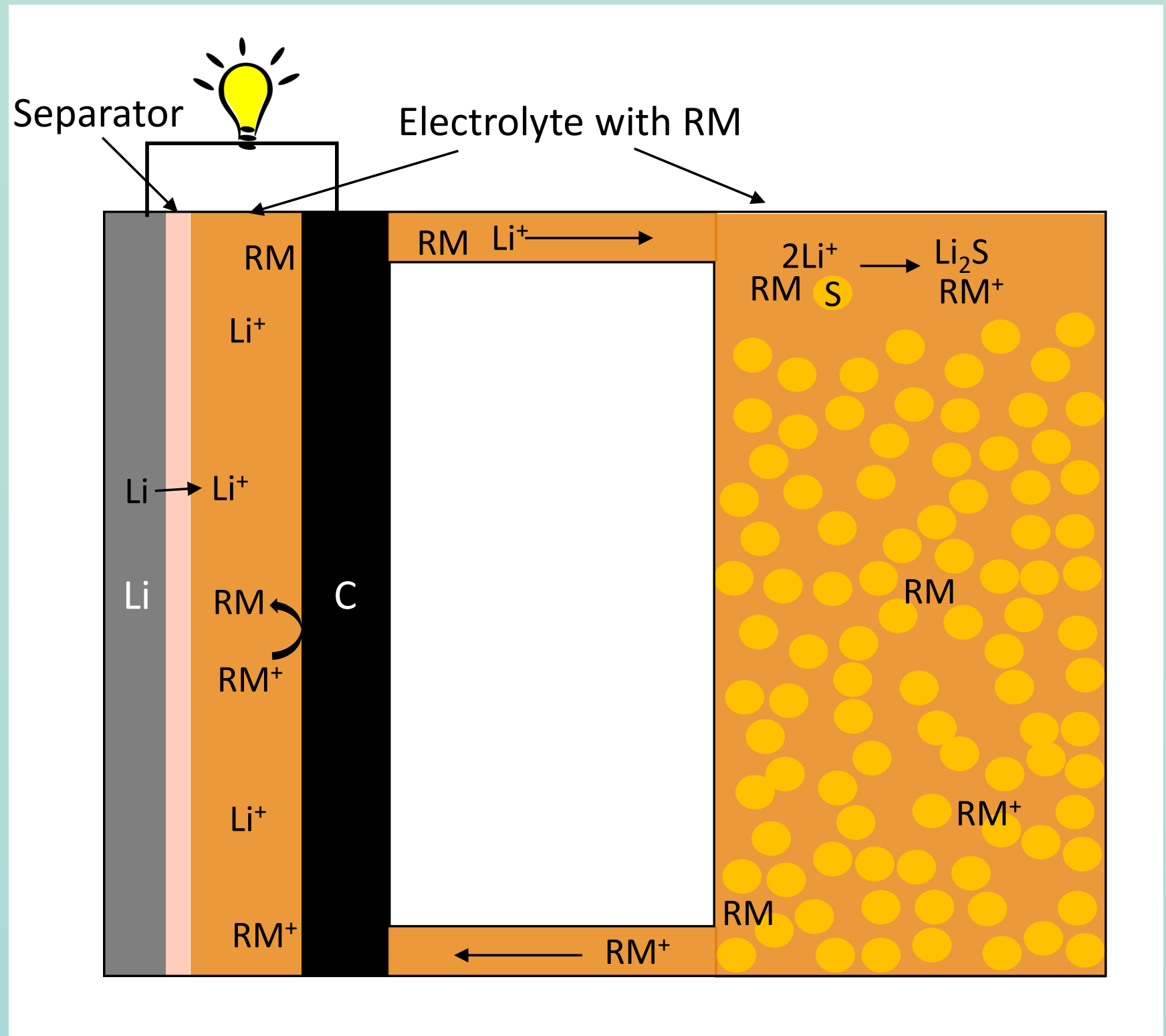
Fig. 4: CVs of electrolyte before and after cycling, scan rate: 10 mV/s

Conclusions and future work

With the small-scale cell, we were able to show that Li metal can be used in a Li-S cell without a solid-state separator, if it is protected by other means.

However, the small-scale cell design allows most of the S to remain in contact with the C electrode.

Separation of sulfur and counter electrode improve safety and allows decoupling of energy and power.



Testing the chosen RMs in a larger scale flow cell would allow us to determine how well they might work in a practical system.

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1.Rana, M.; Ahad, S. A.; Li, M.; Luo, B.; Wang, L.; Gentle, I.; Knibbe, R., Review on areal capacities and long-term cycling performances of lithium sulfur battery at high sulfur loading. *Energy Storage Materials* **2019,** *18*, 289-310.
2.Yin, Y. X.; Xin, S.; Guo, Y. G.; Wan, L. J., Lithium-sulfur batteries: electrochemistry, materials, and prospects. *Angew. Chem. Int. Ed. Engl.* **2013,** *52* (50), 13186-200.
3.Zhang, S.; Guo, W.; Yang, F.; Zheng, P.; Qiao, R.; Li, Z., Recent Progress in Polysulfide Redox-Flow Batteries. *Batteries Supercaps* **2019,** *2* (7), 627-637.
4.Meini, S.; Elazari, R.; Rosenman, A.; Garsuch, A.; Aurbach, D., The Use of Redox Mediators for Enhancing Utilization of Li_2S Cathodes for Advanced Li-S Battery Systems. *J. Phys. Chem. Lett.* **2014,** *5* (5), 915-8.
5.Meyerson, M. L.; Papa, P. E.; Heller, A.; Mullins, C. B., Recent Developments in Dendrite-Free Lithium-Metal Deposition through Tailoring of Micro- and Nanoscale Artificial Coatings. *ACS Nano* **2020**.
6.Meyerson, M. L.; Sheavly, J. K.; Dolocan, A.; Griffin, M. P.; Pandit, A. H.; Rodriguez, R.; Stephens, R. M.; Vanden Bout, D. A.; Heller, A.; Mullins, C. B., The effect of local lithium surface chemistry and topography on solid electrolyte interphase composition and dendrite nucleation. *J. Mater. Chem. A* **2019,** *7* (24), 14882-14894.