



Mediated Lithium-Sulfur Flow Batteries

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Overview:

Energy storage stands to be a key element of the DOE Office of Electricity's drive for grid modernization. Lithium-Sulfur is a next generation battery technology which leverages an inexpensive sulfur cathode to significantly increase battery specific capacity. Scaling a battery technology from consumer-level Wh cells to GWh grid scale energy storage requires re-thinking the battery design for reasons of cost and safety. In this project we are working towards integration of a Li-S chemistry with a redox flow battery (RFB) architecture. RFBs offer a readily scalable solution to grid scale energy storage, physically separating anode and cathode and minimizing safety risks in case of failure. Specifically, we choose a mediated flow battery scheme, where flowing redox-active soluble molecules oxidize and reduce sulfur particles stored in a separate reservoir.

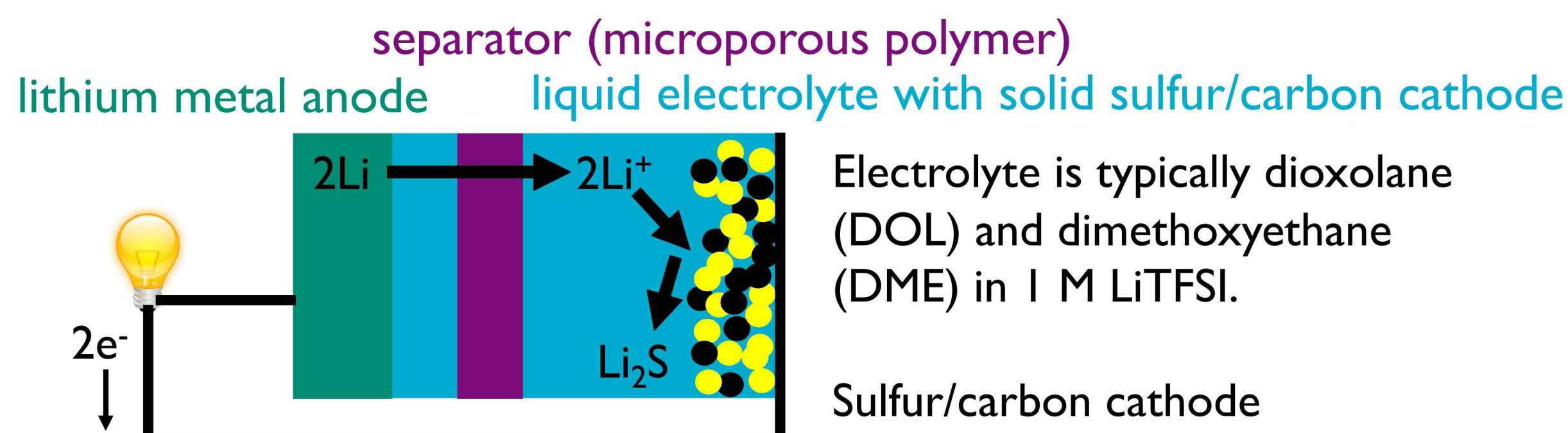
Objectives:

In this first year project, our goals were to (1) establish sulfur battery testing capability and (2) demonstrate proof of concept.

Operating Principle

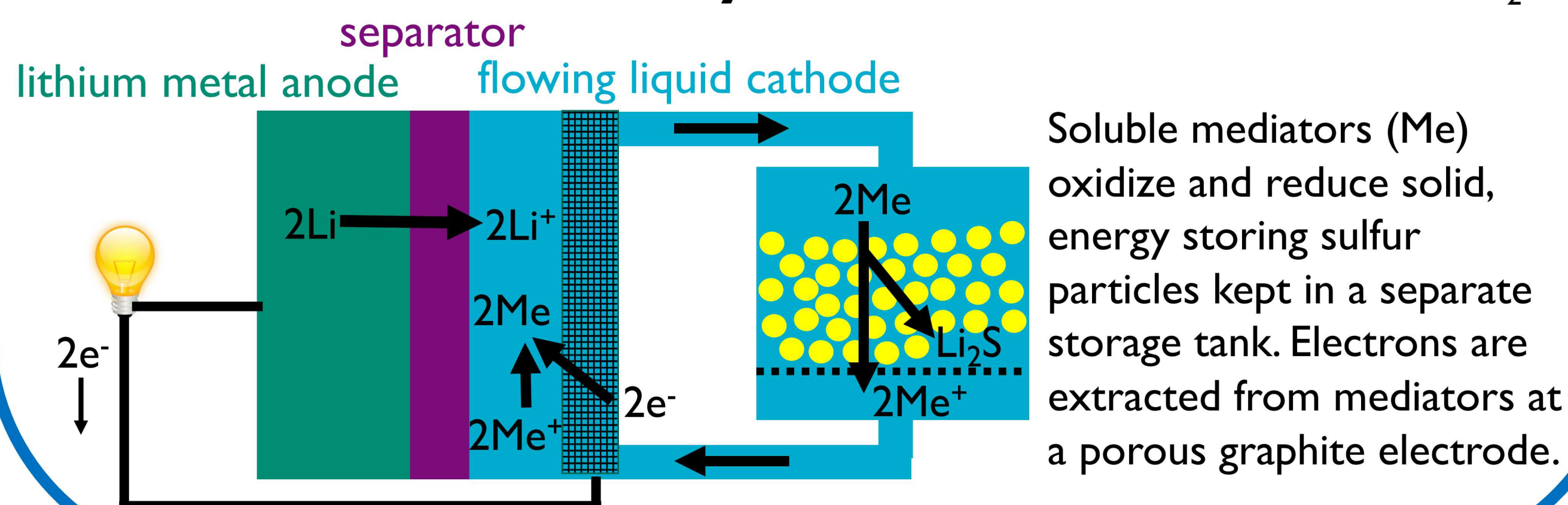
Standard Li-S

Overall Reaction: $2\text{Li} + \text{S} \rightarrow \text{Li}_2\text{S}$



Mediated Flow Battery Li-S

Overall Reaction: $2\text{Li} + \text{S} \rightarrow \text{Li}_2\text{S}$



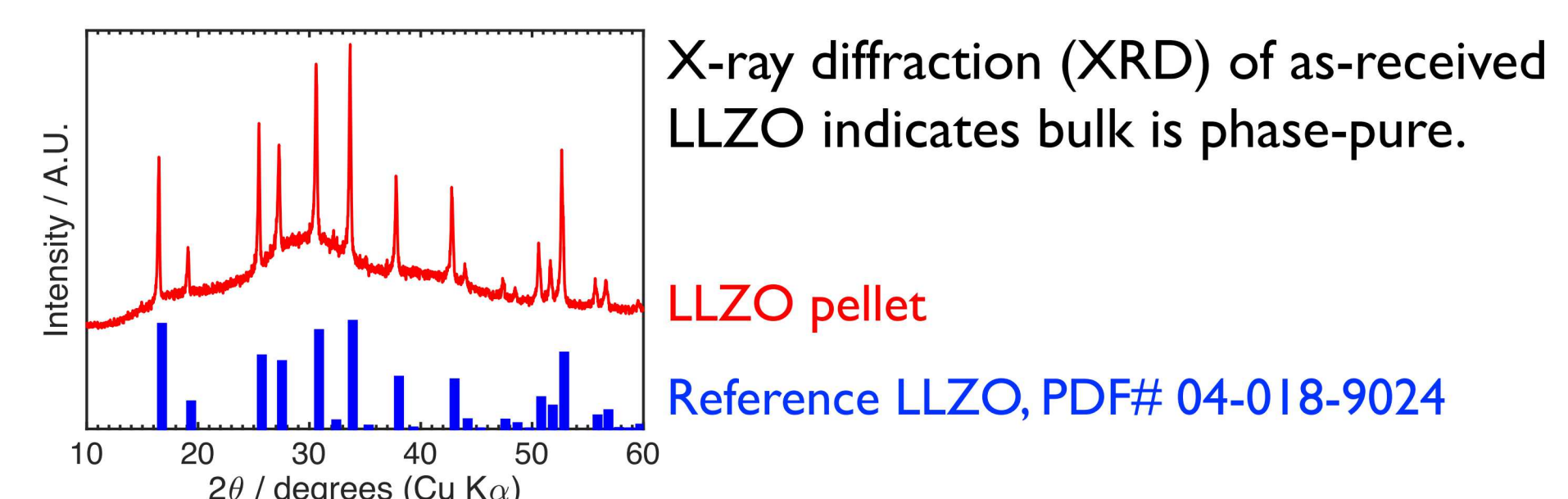
Testing Capabilities

Established new materials handling and battery testing capabilities dedicated for work with sulfur systems, to avoid sulfur cross contamination with other battery chemistries. Comprehensive system includes inert atmosphere glovebox, full electrochemical testing (battery cycling, CV, RDE, conductivity, EIS, etc.) and integrated pump and temperature controls. Also brought online infrared spectroscopy capability for materials analysis in glovebox.

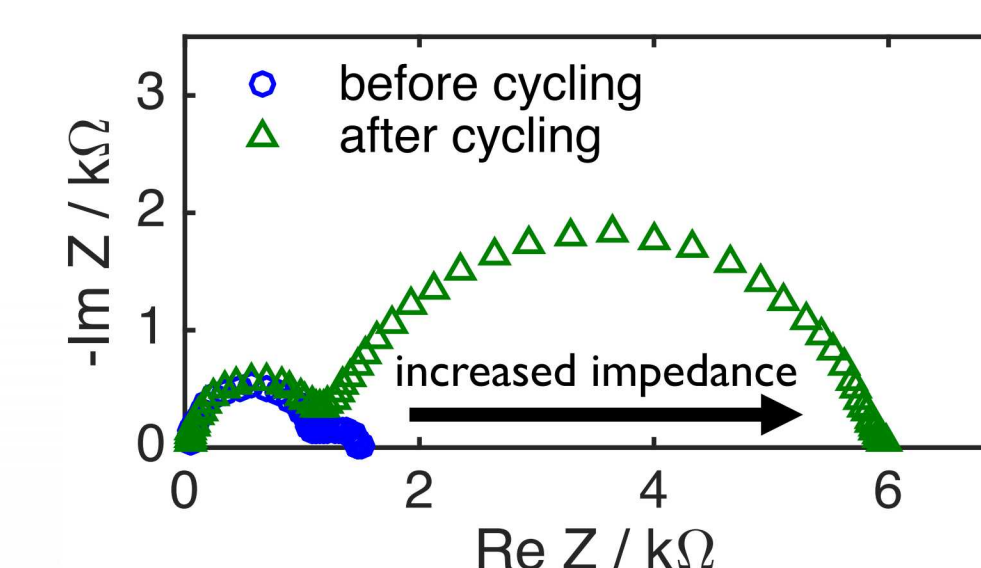
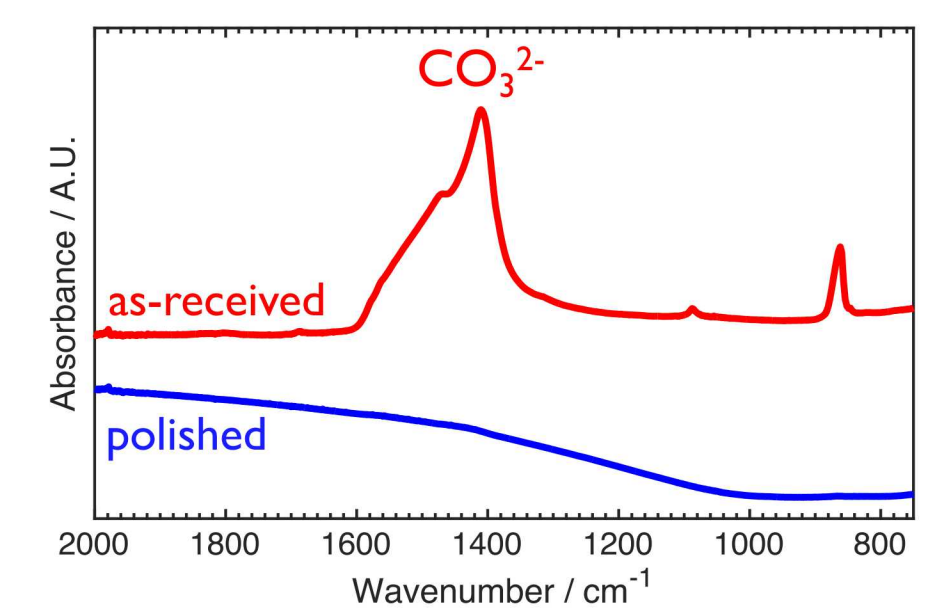


Solid State Separator

$\text{Li}_{6.4}\text{La}_3\text{Zr}_{1.4}\text{Ta}_{0.6}\text{O}_{12}$ (LLZO) was used as the solid state separator to eliminate crossover of anode and cathode. After battery cycling, significant etching of the LLZO and increased cell impedance was observed.



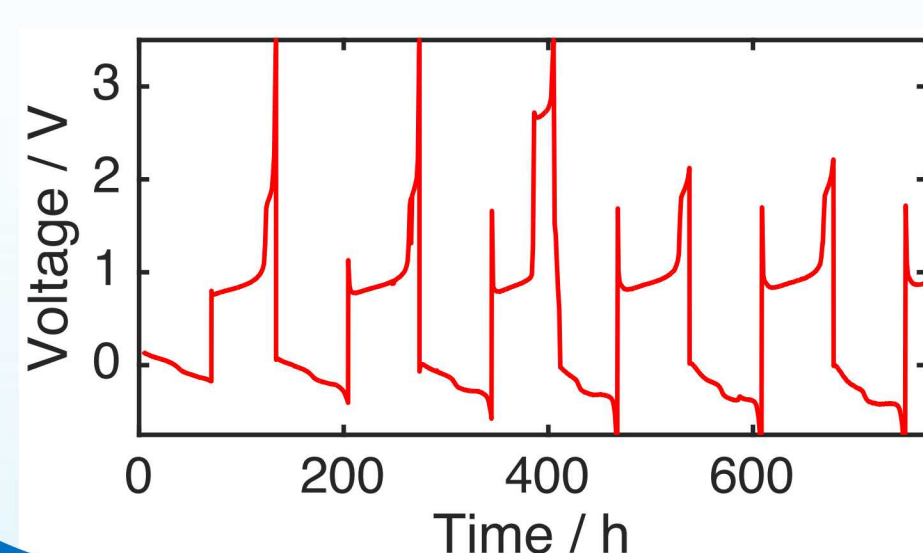
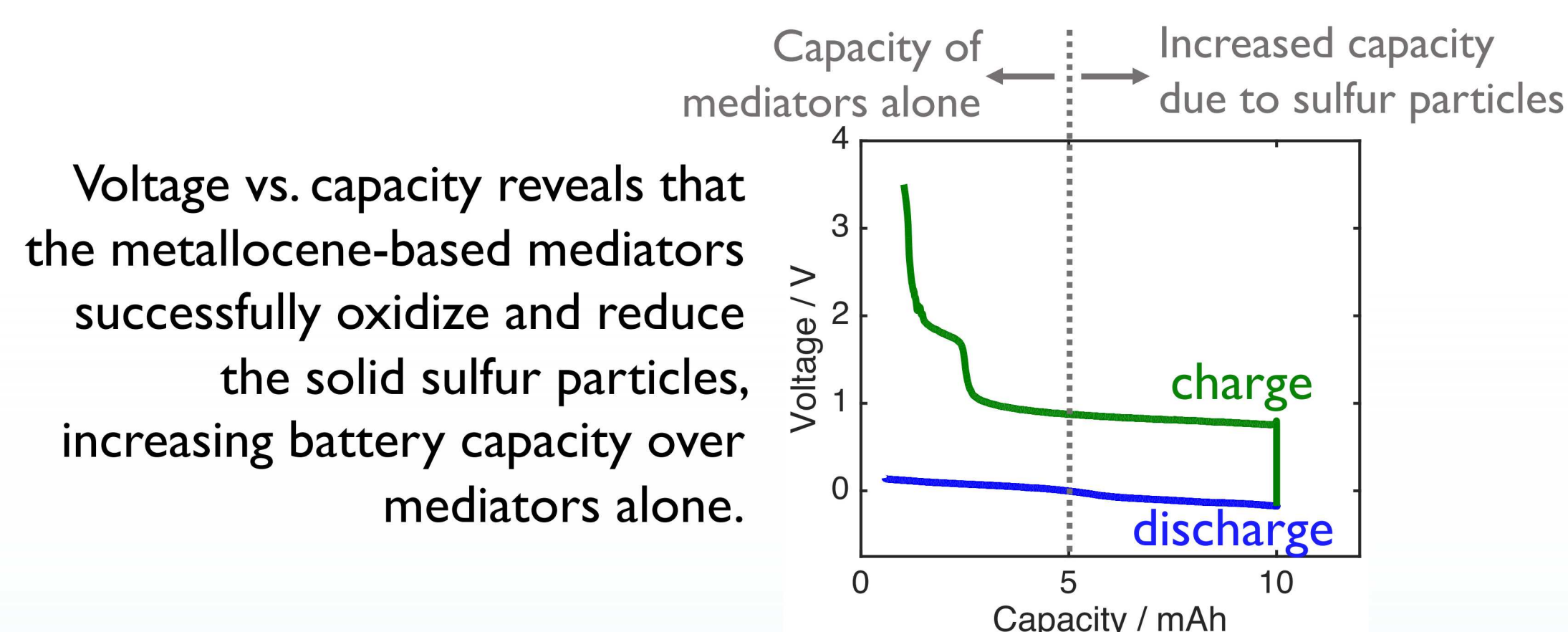
Infrared spectroscopy in glovebox, however, reveals the presence of surface Li_2CO_3 on as-received LLZO. This poorly Li^+ -conductive layer is removed in the glovebox before use via heating to 400 °C or polishing.



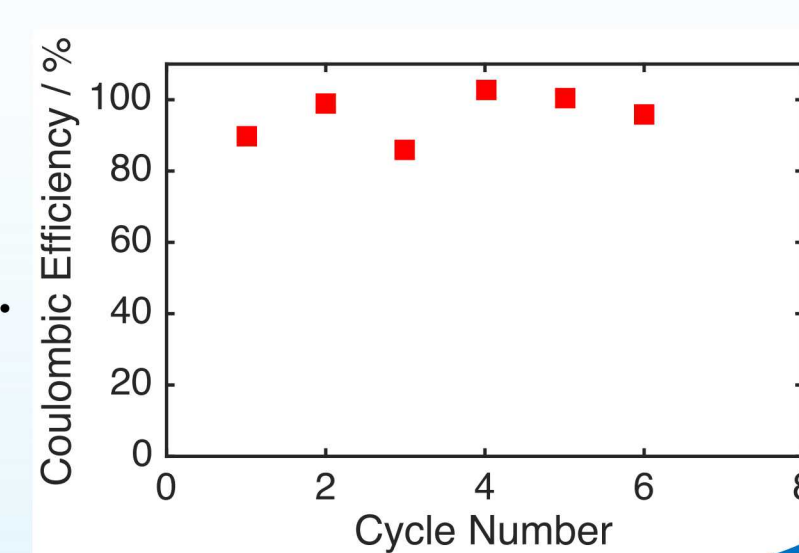
After cycling, etching was observed on the LLZO surface. The etched LLZO surface and resulting solid-electrolyte interface (SEI) are relatively poor Li^+ conductors, as evidenced by increased interfacial resistance in impedance spectroscopy.

Proof of Concept: Cell Cycling

To initially demonstrate the sulfur mediation concept we leveraged traditional Li-S solvent system (DME:DOL 1M LiTFSI) and an anode of the same solvent saturated in cobaltocene, a well-known redox-active metallocene. A Li^+ conducting solid state separator (LLZO) was used to eliminate crossover of anode and cathode. The cobaltocene anode avoids any possible problems at the Li-LLZO interface for this proof of concept, and causes the cell capacity to be limited by the cathode side – the sulfur mediation.



Good cycling over >1 month.



Future Work

- Integrate Li-metal anode
- Protective coating on LLZO separator to stabilize interface and SEI formation
- Optimize mediator potentials
- Safer, lower volatility electrolyte