

Development of High-Energy Lithium-Sulfur Batteries

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Overview

Timeline

- Start date: Oct. 2021
- End date: Sept. 2024
- Percent complete: 85%

Barriers

- Limited cycle life at high energy
- Low volumetric energy density
- Shuttling effect and self-discharge
- Low sulfur (S) utilization rate at high S loading

Partners

- The University of Texas, Austin
- Thermo Fisher Scientific
- Energy Storage Materials Initiative (ESMI)/PNNL

Budget

- Total project funding: \$800k
- DOE share: 100%
- Funding for FY23: \$300k
- Funding for FY24: \$200k

Relevance/Objectives

- Advance materials/electrode development and fundamental understanding to improve energy density and cycle life of Li-S cells at practically high S loading and lean electrolyte conditions.
- Rationalize high-quality and low-porosity S electrode fabrication to extend cell's cycling life.
- Develop S cathode materials and scalable electrodes to support Battery500 Li-S pouch cell.
- Project efforts are directly aimed at key barriers of low practical energy density, shuttling effect, and limited cycling life of realistic Li-S batteries.

Milestones

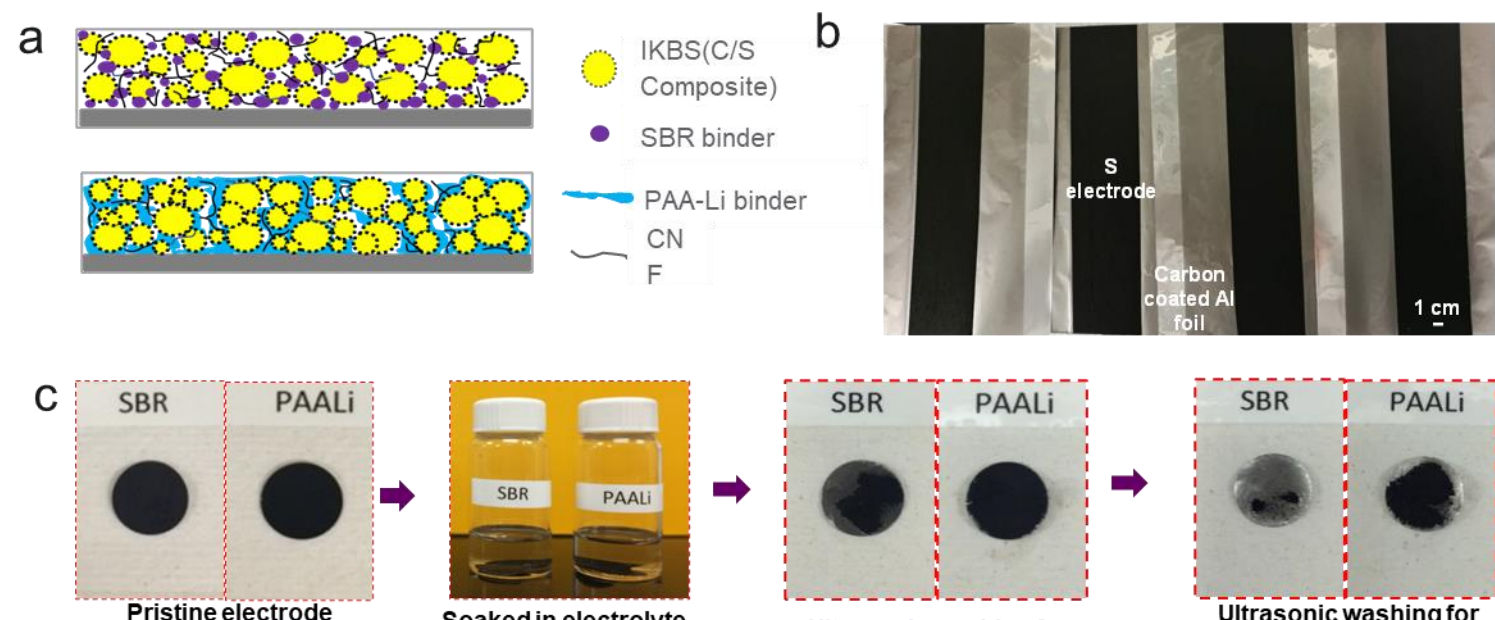
Date	Milestones and Go/No-Go Decisions	Status
December 2023	Develop polymeric binders or composites to enhance both electrode coating quality and sulfur utilization rate of high-mass-loading sulfur cathode (4 mg/cm ²).	Completed
March 2024	Investigate the impact of binder on sulfur cathode structure, sulfur utilization, and cell cycling stability at practical conditions.	Completed
June 2024	Understand electrolyte wetting and replenishing processes in high-loading electrodes by both modeling and experimental approaches.	On track
September 2024	Developed functional electrode additives to extend cell cycle life of high loading electrodes (>4 mg/cm ²) at lean electrolyte conditions.	On track

Approach/Strategy

- Screening study of electrode biners and understand their effects on sulfur utilization rate and cell cycling.
- Investigate surface properties of carbon host tuned by different binders and their impact on reversible sulfur and lithium sulfide nucleation and growth.
- Study effects of material property and electrode architecture on electrode wetting, Li-polysulfide migration, and S reactions at practical conditions.

Binder optimization for high loading S cathode

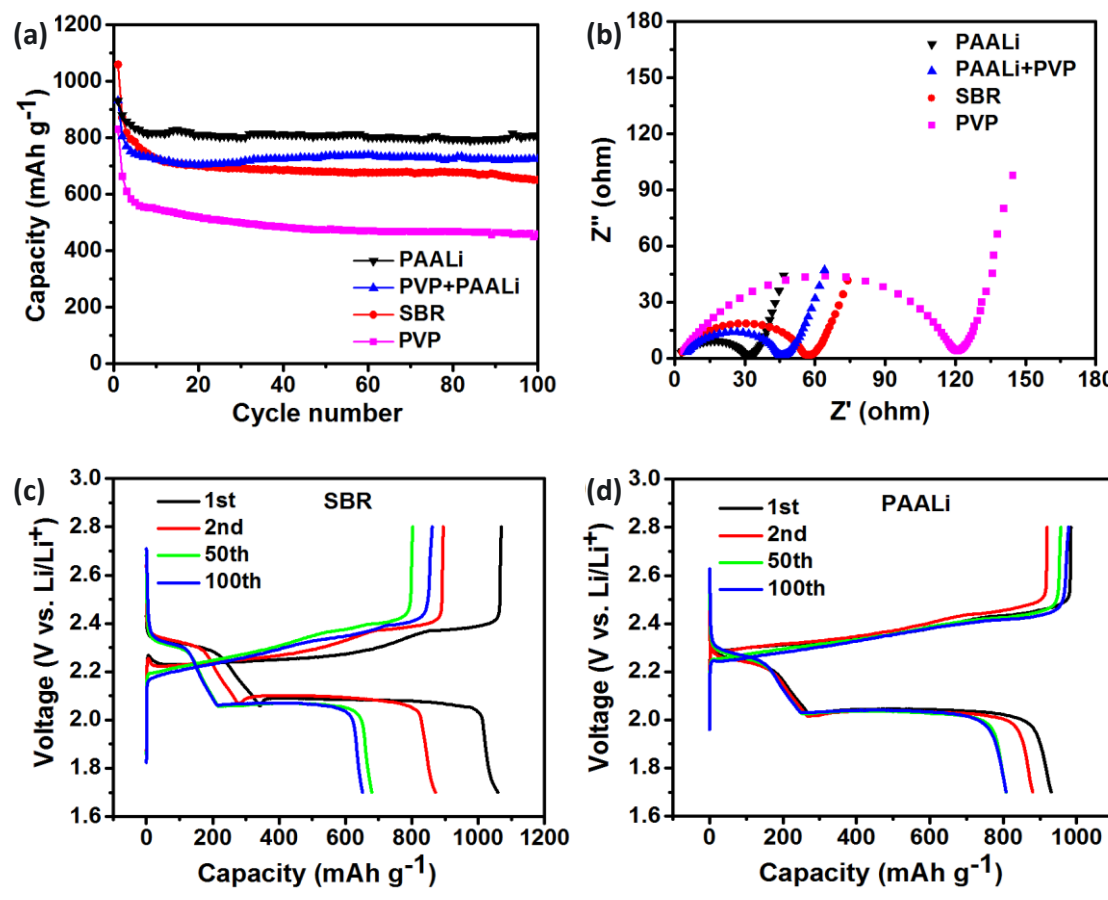
Identified optimal binder for high loading S cathode fabrication



(a) Schematic of S electrodes architecture with PAA-Li and SBR binder, (b) high-loading S electrode fabricated with PAA-Li binder, and (c) adhesion test of S electrodes with PAA-Li and SBR binders.

- Studied and compared alternative aqueous binders—polyvinylpyrrolidone (PVP), styrene-butadiene (SBR), and lithiated-poly(acrylic acid) (PAA-Li) for preparing high-loading sulfur electrodes.
- The PAA-Li binder is superior for large-area, uniform, and crack-free electrode coating with a S loading above 4 mg cm⁻².

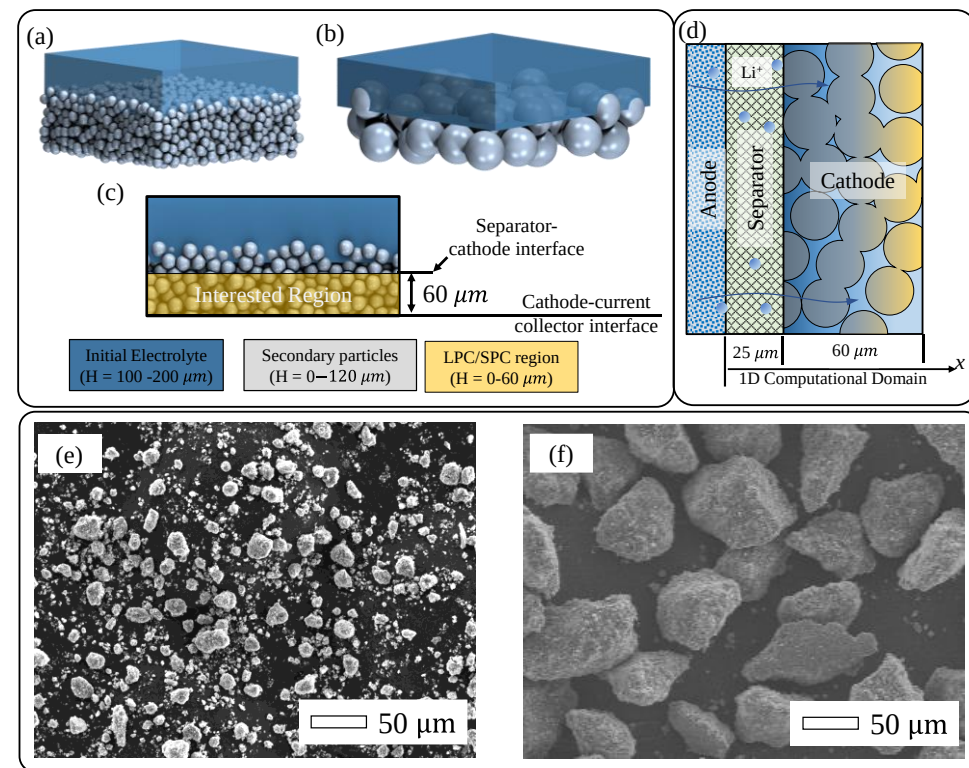
Impacts of binders on performance of high-loading S cathodes



(a) Cycling performance of Li-S cells using different binders at a 0.1 C rate (1C= 1000 mA g⁻¹) and sulfur loading 4 mg cm⁻²; (b) EIS comparison of different binder-based Li-S cells before cycling; Discharge and charge profiles of SBR (c) and PAA-Li (d) binder-based Li-S cells.

Multiscale simulation for Li-S batteries

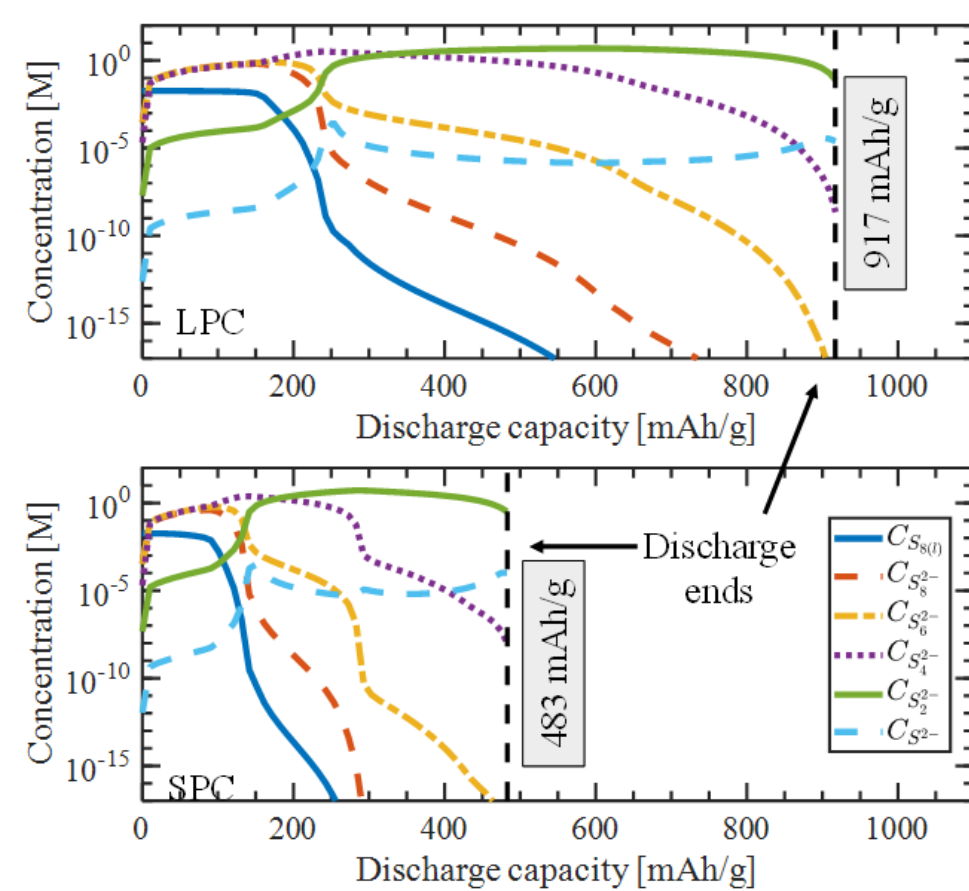
Development of multiscale model for a Li-S battery



Multiscale modeling of a Li-S battery by considering the electrode wettability impacts, materials properties, and electrode structures.

- Developed an integrated three-dimensional (3-D) pore-scale model and 1-D device-scale electrochemical model.
- Performed multiscale modeling of electrode wetting, electrolyte diffusion, and their impacts on sulfur reactions and polysulfide diffusion in Li-S cells.

Cell Modeling by considering materials properties and electrode structures

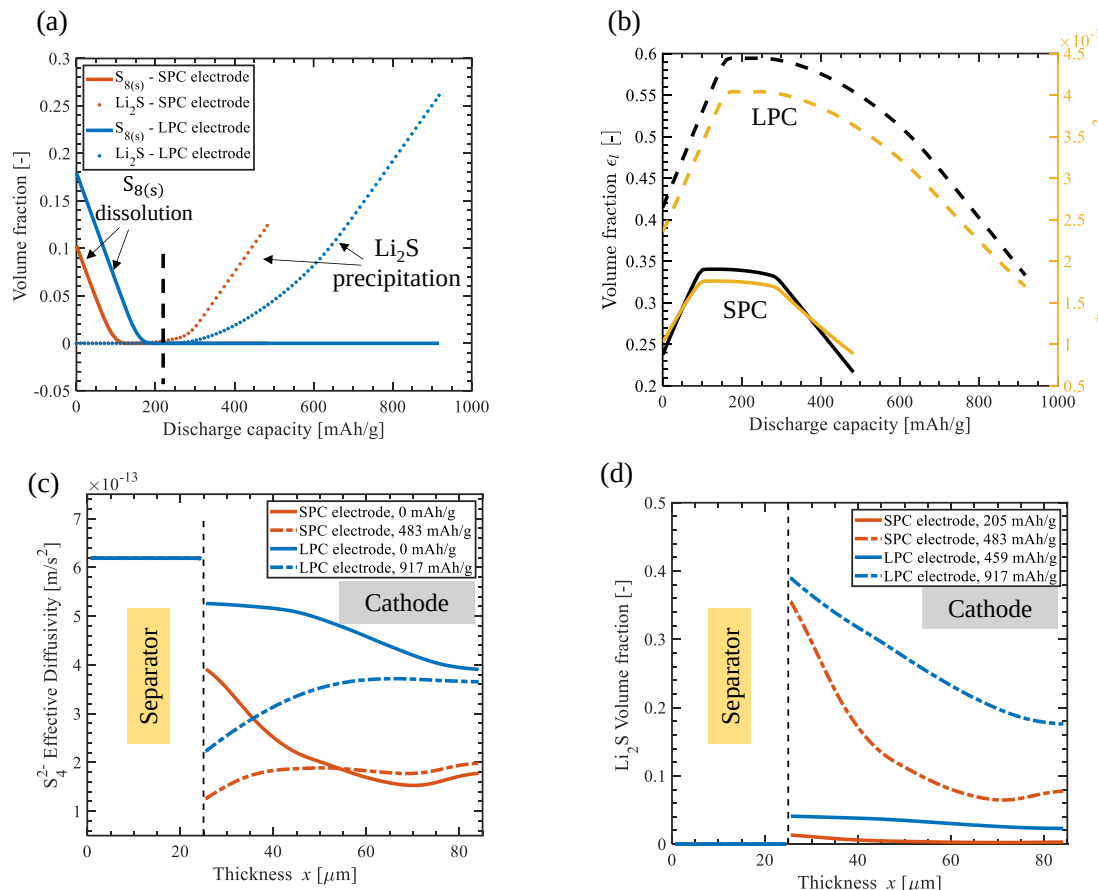


The polysulfides concentration profiles during the discharge for both LPC (up) and SPC (down).

- Modeled cell performance and sulfur/polysulfides species of high-loading sulfur electrodes by considering the electrode wettability impacts and electrode morphologies.
- The large particle cathode (LPC) exhibits a higher sulfur utilization rate compared to the small particle cathode (SPC).

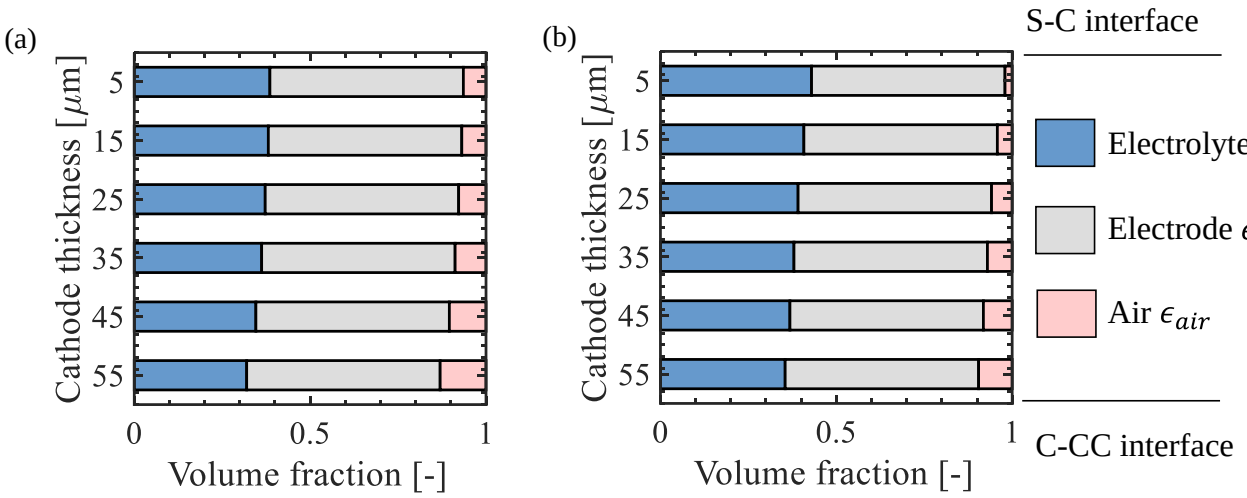
Technical Accomplishments

Evolution of S₈, Li₂S, and polysulfides during discharging process

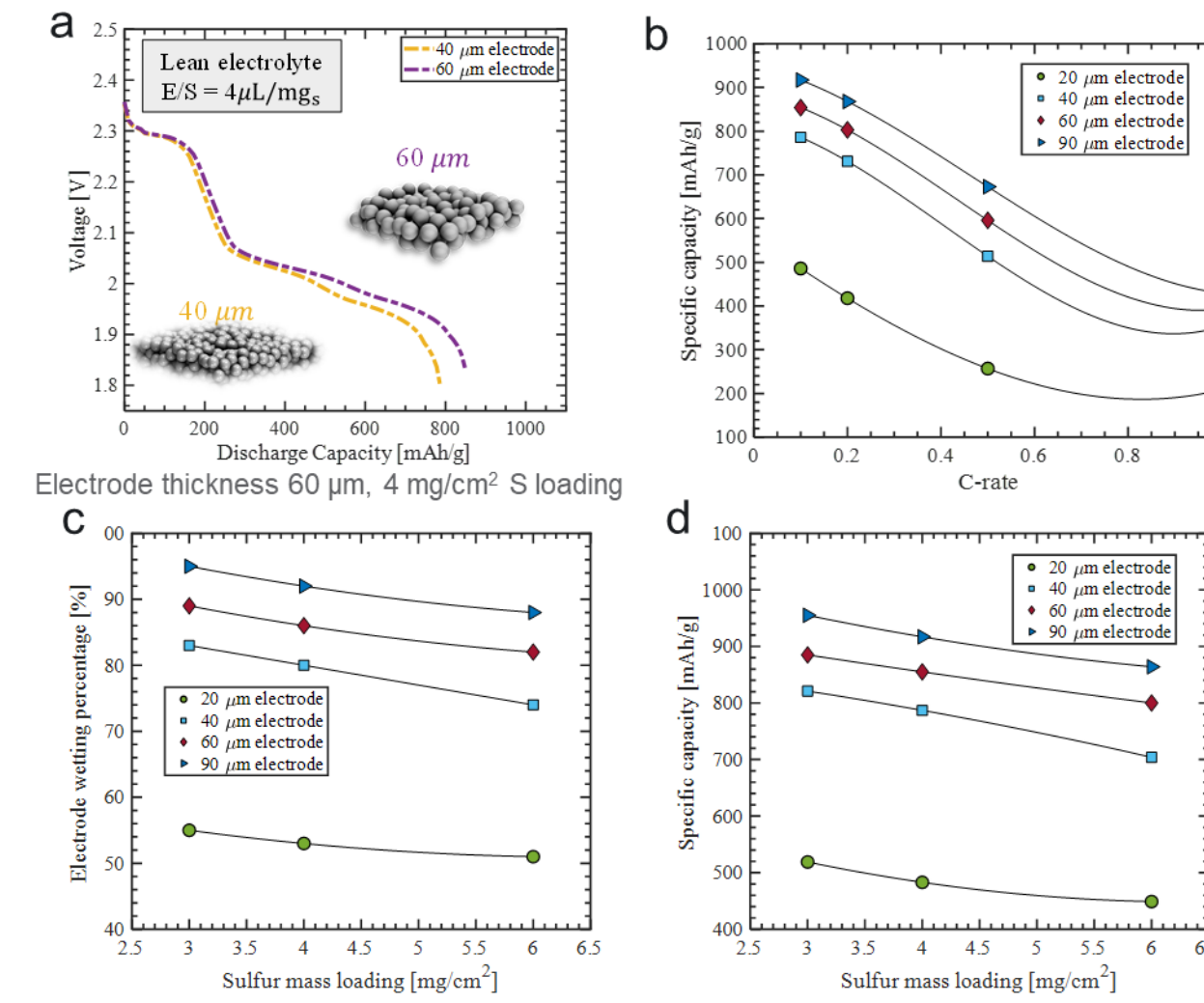


- Modeled temporal evolution of (a) S_{8(s)} and Li₂S, (b) electrolyte volume fraction and Li⁺ effective diffusivity in the discharge process.
- Modeled spatial distribution of (c) S₄²⁻ diffusivity and (d) Li₂S volume fraction at different state of discharge.
- LPC exhibits a higher conversion rate of S_{8(s)}, greater Li⁺ effective diffusivity, and increased concentration of S₄²⁻ and Li₂S deposition compared to SPC.

Electrode wetting, S utilization, and their correlations with particle size

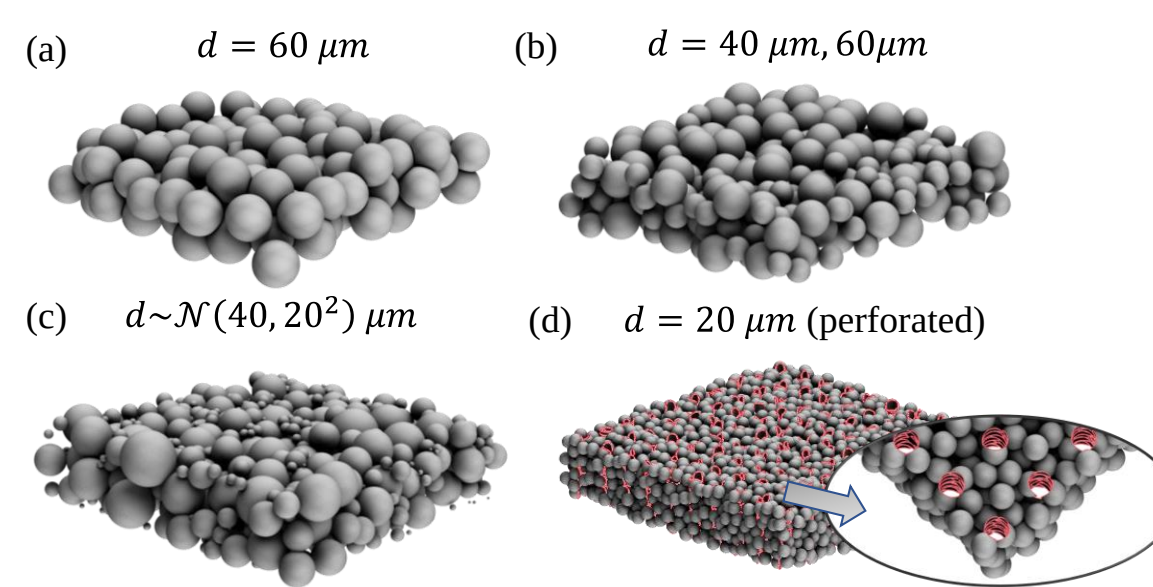


- The electrolyte and air distribution along the electrode thickness x (1-D model coordinate) with (a) 40 μm and (b) 60 μm secondary particles.
- Electrode wetting involves competition of electrolyte infiltration and air flow, where materials properties plays an important role.



- Modeled Li-S discharge curves with electrode using 40 μm and 60 μm secondary particles at 0.1C (a).
- Modeled discharge capacities of the low porosity electrode at different C-rates.
- Studied electrode wetting conditions (c) and specific capacity at different S mass loading conditions (d).
- The 90 μm electrode demonstrates the optimal electrolyte wetting and the highest specific capacity, particularly under elevated S mass loading conditions.

Projected optimal electrode structure



- Visualized low-porosity electrode designs generated by the 3-D pore-scale model. (a) Electrode with 60 μm secondary particles. (b) Electrode with a mix of 40 μm and 60 μm secondary particles. (c) Electrode with secondary particles following a normal size distribution. (d) Perforated electrode with 20 μm secondary particles.
- Mixing particles provides benefits for both electrode wetting and S utilization. Experimental validation is in progress.

Collaboration and Coordination with Other Institutes

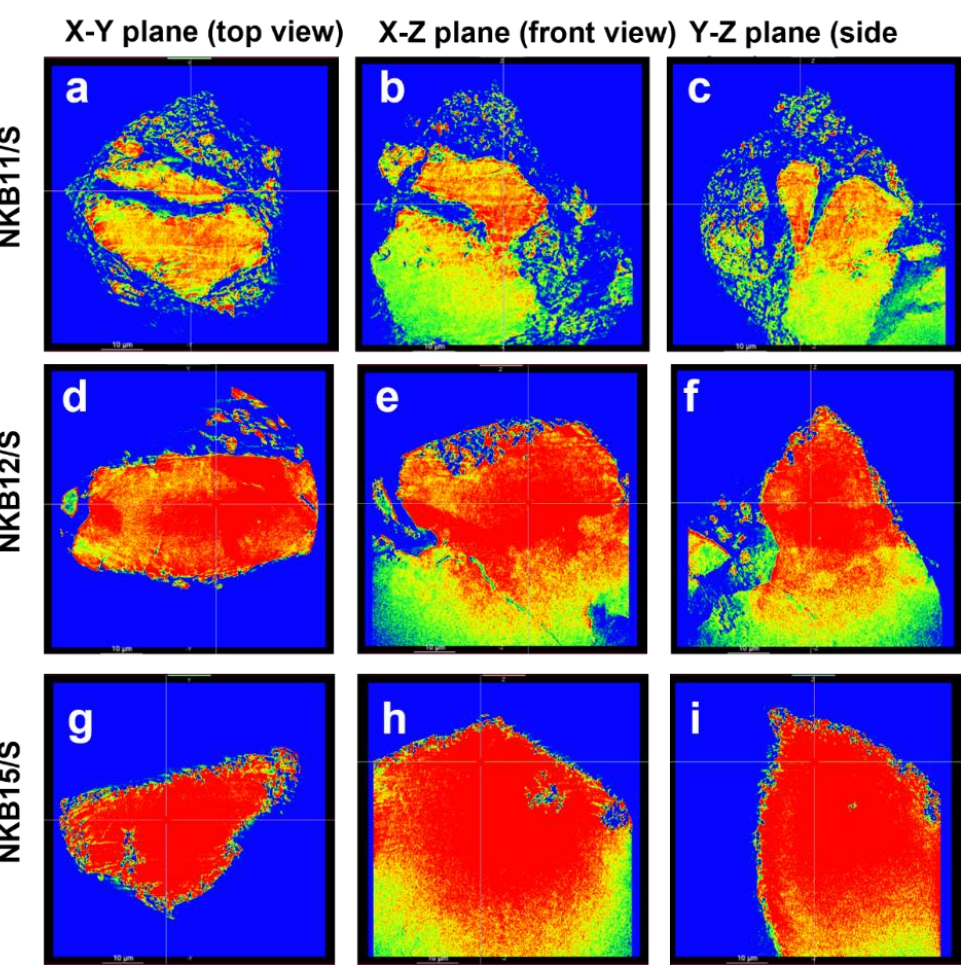
- The University of Texas, Austin: reaction mechanism study
- Thermo Fisher Scientific: electrode characterization
- ESMI/PNNL: multiscale modelling

Remaining Challenges and Barriers

- Short cycle life at simultaneous high-loading S cathodes and lean electrolyte conditions
- Loss of electrolyte in cell's dead volume
- Quick depletion of electrolyte/additive
- Li anode corrosion/dendrite

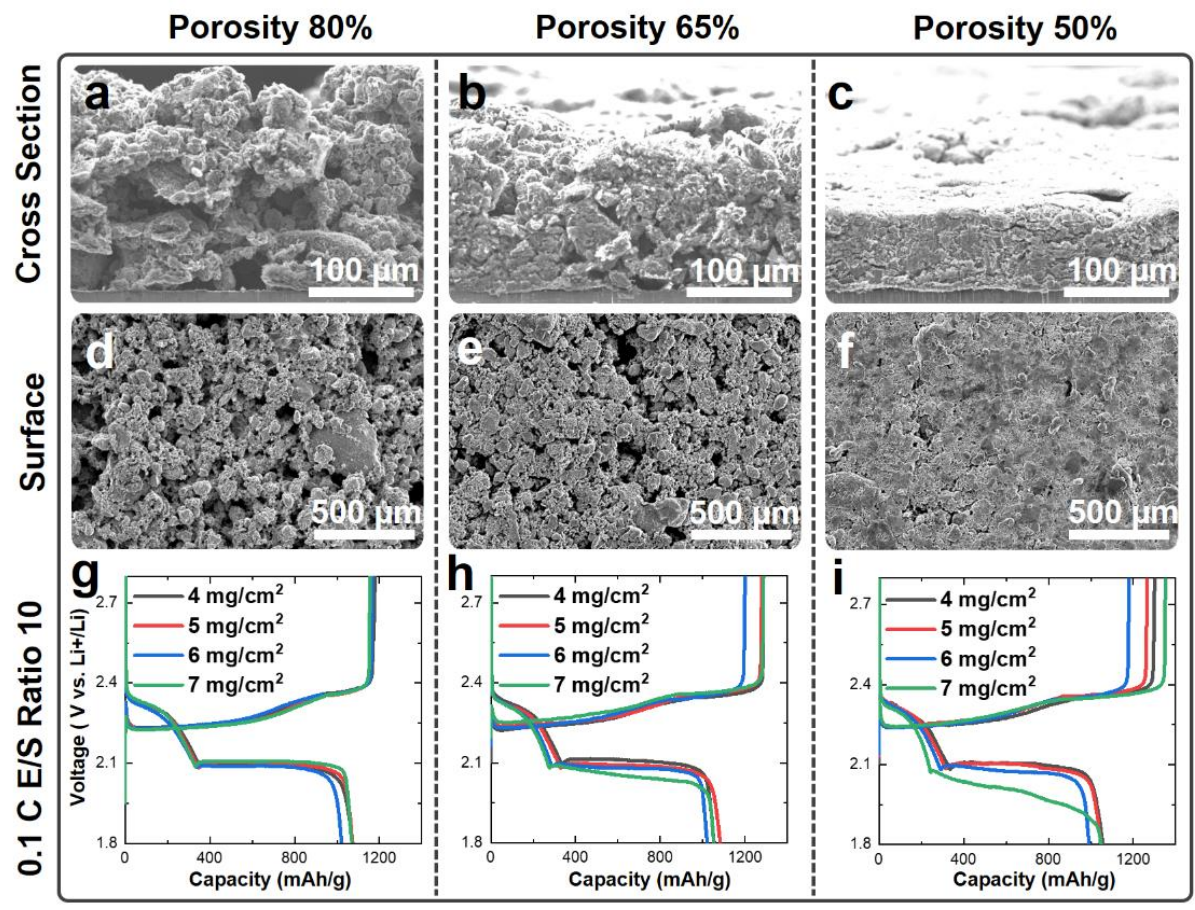
Optimizing S cathode structure and scaling up

Nitrogen-doped porous carbon secondary particles as S host



Multi-view orthographic projections of different NKB/S materials through X-ray Micro Computed Tomography (Micro-CT).

NKB/S secondary particles for high-loading and dense S cathodes

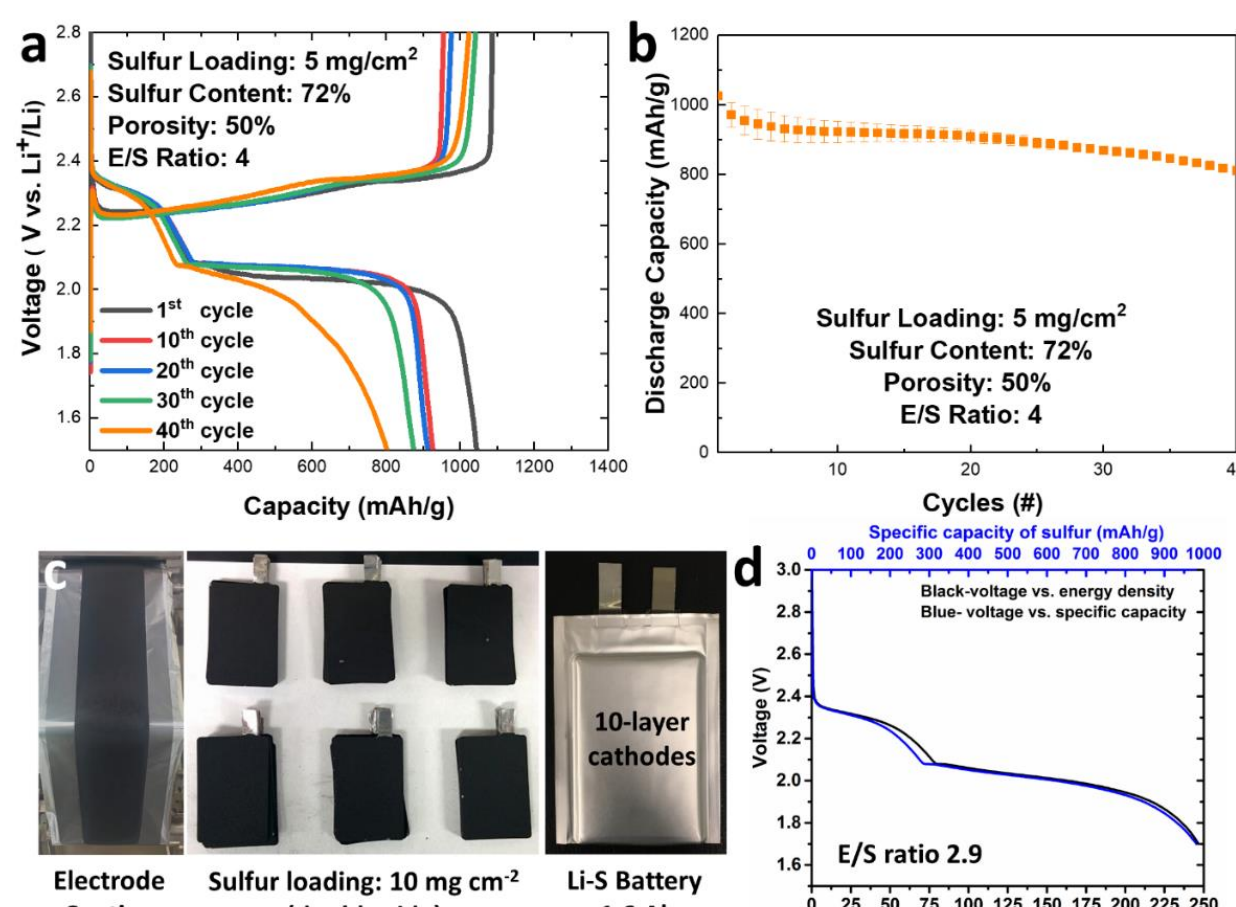


Morphology (SEM images) and discharge/charge curves of S electrodes (NKB11/S) at different porosities (a, d, g) 80% porosity, (b, e, h) 65% porosity, and (c, f, i) 50% porosity.

- Nitrogen-doped Ketjen Black (NKB) was synthesized by integrating KB particles by poly(melamine-co-formaldehyde) methylated (PMF) (NKB11, PMF/KB=2:2; NKB12, PMF/KB=5:2; NKB15, PMF/KB=10:2).
- Higher PMF/KB ratio induces denser NKB particles with lower surface area and pore connectivity, which reduces S reactivity and capacity retention.

- The NKB/S secondary particles are feasible for fabrication of high mass loading S cathodes with good quality.
- The NKB/S cathodes deliver specific capacity > 1000 mAh/g with S loading up to 7 mg/cm² and porosity down to 50%.

NKB/S cathode for practical Li-S pouch cells



(a) Discharge/charge profiles of NKB11/S electrodes at different cycles. (b) Cycling performance of NKB/S cathode. (c) Roll-to-roll preparation of NKB/S electrodes and a 1.6 Ah pouch cell. (d) Discharge capacity of the pouch cell and corresponding energy density.

- The NKB/S cathodes deliver specific capacity > 1000 mAh/g with S content of 72%, mass loading 5 mg/cm², and porosity 50%.
- Demonstrated large-areal S electrode and high-energy pouch cells (250 Wh/kg at cell level).
- Long-term cycling still needs further improvement.

Future Work - FY2024

- Further address material and electrode challenges by using experimental and theoretical simulation tools.
- Reserve liquid electrolyte for extending cell cycle life through low-porosity electrode design.
- Eliminate Li-polysulfide free migration and reduce its interference on Li anode.

Any proposed future work is subject to change based on funding levels

Acknowledgments

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- PNNL: Shuo Feng, Qiuyan Li, Cassidy Anderson, Ji-Guang Zhang, Jie Xiao, Yucheng Fu, Jie Bao, and Zhijie Xu
- The University of Texas, Austin: Venkat Subramanian, Lubhani Mishra
- Thermo Fisher Scientific: Zhao Liu

Summary

- Screened alternative aqueous binders for preparing high-loading sulfur electrodes and identified that PAA-Li binder is superior for large-area, uniform, and crack-free electrode coating with a S loading above 4 mg cm⁻².
- Integrated 3D electrode model and 1D electrochemical model to investigate electrode wetting, electrolyte diffusion, polysulfide diffusion, and their impacts on sulfur reactions at practical cell operation conditions.
- Nitrogen doped secondary carbon particles (NKB) were developed for high loading S electrodes; Integration degree of the NKB affects pore structure and connectivity; materials feasibility was validated through large areal electrode coating and high-energy Li-S pouch cell fabrication (250 Wh/kg).