Project ID#: bat282

Development of High-Energy Lithium-Sulfur Batteries

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Overview

Timeline
- Start date: Oct. 2021
- End date: Sept. 2025
- Percent complete: 70%

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

Budget
- Total project funding: $800k
- DOE share: 100%
- Funding received in FY24: $200k
- Funding for FY25: $200k

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

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

December 2024	Develop new processing methods for high-mass-loading and low-porosity sulfur cathode fabrication (sulfur loading >4 mg/cm^2).	Completed
March 2025	Investigate sulfur cathode structure and its impact on sulfur utilization and rate capability.	Completed
June 2025	Screen compatible liquid electrolytes for the new processed sulfur electrodes and realize sulfur utilization rate >1200 mAh/g with much suppressed Li polysulfide dissolution.	On track
September 2025	Evaluate cell electrochemical performance and recommend optimal electrode/electrolyte combinations to Battery500 consortium for pouch cell fabrication and technology validation.	On track

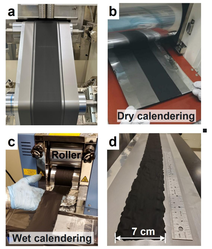
Approach/Strategy

- Develop alternative electrode processing methods to enhance sulfur utilization rate and cell cycling stability.
- Identify liquid electrolytes compatible with the processed sulfur cathodes.
- Study effects of electrode architecture on electrode wetting, Li-polysulfide migration, and S reactions at practical conditions.

Technical Accomplishments

Processing method development for high loading S cathode

New processing methods for high-mass-loading and highly dense S electrodes



➢ **Calendered coated S (CCS) electrodes:**

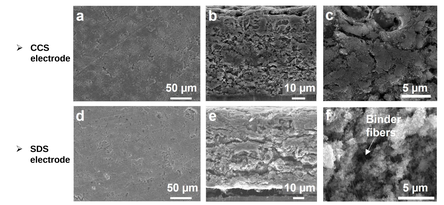
➢ **Shear-force densified S (SDS) electrodes:**

	CCS Electrode	SDS Electrode
S content	64 wt%	70-81%
S loading	2-6 mg cm^{-2}	4-7 mg cm^{-2}
Porosity	65-78%	47%-74%

- The shear-force densified sulfur electrode was developed with higher S content, higher S loading, and lower electrode porosity compared to conventional coated-then-calendered sulfur electrodes.

Fabrication process for high-mass-loading and highly dense sulfur electrodes: (a) using slurry coating-calendering method, (c) using the shear-force densified method. Digital photographs of the prepared sulfur electrodes: (b) CCS electrode, (d) SDS electrode.

Structural analysis of highly dense S electrodes



➢ **CCS electrode**

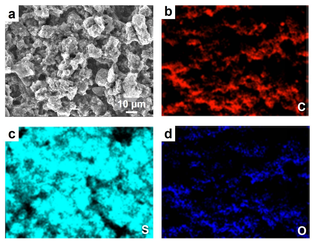
➢ **SDS electrode**

- Both sulfur electrodes exhibit a dense surface.
- The binder deformed into fibers in the SDS electrodes, in contrast to the film-shaped binder in CCS electrode.

Comparison of structural characteristics between CCS (a-c) and SDS electrodes (d-f) in high S loading (4.5 mgS cm^{-2}) and highly dense sulfur electrodes (porosity 47%). a, d, SEM surface images of CCS and SDS electrodes, respectively. b, e, SEM cross-sectional images of CCS and SDS electrodes. c, f, Higher resolution SEM cross-sectional images of CCS and SDS electrodes.

Elemental distribution and electrode homogeneity

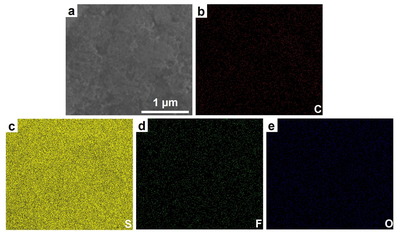
➢ **CCS electrode**



- The distribution of carbon and sulfur in the CCS electrode was not very uniform, potentially due to the inhomogeneous distribution of the binder and carbon conductive additive.

EDX mapping of the CCS electrode (a-d), showing elemental distribution: C (red), S (cyan), and O (blue).

➢ **SDS electrode**

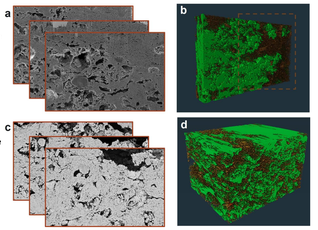


- SDS electrode exhibits uniform distribution of carbon, sulfur, and fluorine, indicating the uniform distribution of the binder and overall structure.

EDX mapping of the SDS electrode (a-d), showing elemental distribution: C (red), S (yellow), F (green), and O (blue).

Shi L, et al., ***Advanced Energy Materials,*** *2025* accepted

Pore structure and connectivity in highly dense S electrodes



➢ **CCS electrode**

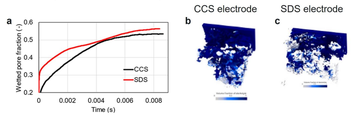
➢ **SDS electrode**

- Highly dense S electrodes were sliced, milled, and re-constructed using pFIB-SEM imaging to investigate the pore structure.
- The SDS electrode shows higher pore connectivity compared to the CCS electrode (80% vs. 60%).

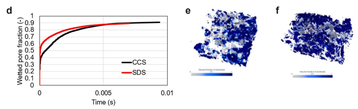
Plasma focused ion beam (PFIB)-scanning electron microscopy (SEM) images of CCS (a) and SDS electrodes (c). 3D reconstructed images of CCS (b) and SDS (d) electrodes, with green representing the connected pores and brown representing closed pores.

Simulated electrolyte wetting in highly dense electrode

➢ **Scenario 1:** liquid flows in from the top



➢ **Scenario 2:** liquid flows in from the top and sides

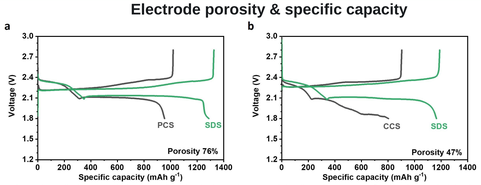


- SDS electrode exhibits faster and more uniform electrolyte wetting compared to the CCS electrode in both simulation scenarios.

Modeled electrolyte wetting fraction variated over time in CCS (a) and SDS electrodes (d). Snapshots of visualized electrode wetting for CCS (b, e) and SDS (c, f) electrodes show blue representing the electrolyte and white representing sulfur electrodes.

Impact of electrode structure on cell performances

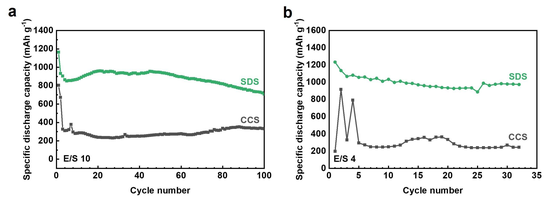
Electrode porosity & specific capacity



Comparison of 1st discharge and charge profiles for S electrodes at an S loading of 4.5 mg cm^{-2}, E/S 10 mL g^{-1}, 0.05 C, and 30 °C. (a) Pristine coated sulfur (PCS) and SDS electrodes at a porosity of 76%. (b) CCS and SDS electrodes at a porosity of 47% (b). The electrolyte used is a conventional electrolyte (CVE, 1 M lithium bis(trifluoromethane)sulfonimide / 1,3-dioxolane+1,2-dimethoxyethane, with 0.3 M lithium nitrate).

- All sulfur electrodes demonstrated high specific capacity at high porosity.
- The SDS electrode maintained higher specific capacity at low porosity compared to CCS electrode.

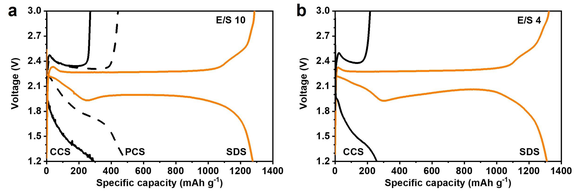
Cell cycle performance of highly dense S electrodes at different E/S ratios



Cycling performances of CCS and SDS electrodes in CVE electrolyte at a porosity of 47%, with varying E/S ratios: a, E/S 10 mL g^{-1}. b, E/S 4 mL g^{-1}.

- SDS electrode exhibits higher specific capacity than CCS electrode at both E/S ratios of 10 and 4 mL g^{-1}.
- However, the cycle life under lean electrolyte conditions (E/S 4 mL g-1) still needs improvement.

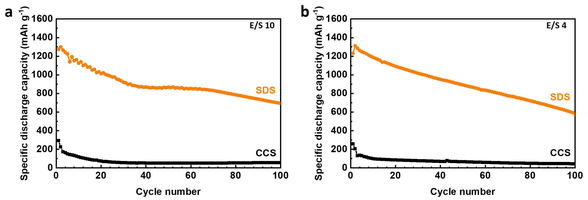
New electrolyte development for SDS electrodes



Comparison of the 1st discharge and charge profiles for S electrodes using localized high concentration electrolyte (LHCE) at a S loading of 4.5 mg cm^{-2}, 0.05 C, and 30 ° C. (a) PCS, CCS, and SDS electrodes at an E/S ratio of 10 mL g^{-1}. (b) CCS and SDS electrodes at an E/S ratio of 4 mL g^{-1}. The PCS electrode has a porosity of 76%, while the CCS and SDS electrodes have a porosity of 47%.

- Coated sulfur electrodes (both PCS and CCS) showed limited specific capacity in LHCE compared to CVE electrolyte, likely due to the higher viscosity of the LHCE electrolyte.
- Highly dense SDS electrode demonstrated high specific capacity in LHCE electrolyte at both E/S ratios of 10 and 4, attributed to their superior pore structure than CCS electrode.

Cycling performances of new S electrodes in new electrolyte



Cycle performances of CCS and SDS electrodes in LHCE electrolyte at a porosity of 47%, with varying E/S ratios: a, E/S 10 mL g^{-1}. b, E/S 4 mL g^{-1}.

- The highly dense SDS electrode using LHCE electrolyte demonstrated a longer cycle life compared to using CVE electrolyte under lean electrolyte conditions (E/S 4 mL g^{-1}).

Collaboration and Coordination with Other Institutes

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

Remaining Challenges and Barriers

- Short cell lifespan 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

Future Work - FY2025

- Optimize electrode material and structure to enhance sulfur utilization and rate capability
- Understand capacity fading mechanism in highly dense electrode
- Develop compatible electrolyte to eliminate Li-polysulfide free migration and reduce its interference on Li anode.

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

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- Thermo Fisher Scientific: Rengarajan Pelapur, Eveline G. Booy, Zhao Liu

Summary

1. Shear-force densified method for high-mass-loading (>4 mg cm^{-2}) and low-porosity sulfur cathode fabrication was developed.
2. Sulfur cathode pore structure was investigated using PFIB-SEM imaging, 3D reconstruction, and fluid flow simulation. Pore connectivity was identified as a critical factor for electrolyte wetting.
3. Compatible liquid electrolyte for the highly dense SDS electrode was developed.
4. Dense sulfur cathodes with sulfur utilization rate >1200 mAh g^{-1} and extended cycling life was achieved under lean electrolyte conditions.