Development of High-Energy Lithium-Sulfur Batteries

Dongping Lu and Jun Liu
Pacific Northwest National Laboratory (PNNL)

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Project ID#: bat282

PNNL is operated by Battelle for the U.S. Department of Energy

Overview

Timeline

- Start date: Oct. 2018
- End date: Sept. 2021
- Percent complete: 89%

Barriers

- Limited cell lifespan at high energy
- High porosity of cathode
- Shuttle effect and self-discharge
- Low sulfur (S) utilization rate at high S loading

Budget

- Total project funding: $1075k
- DOE share 100%
- Funding received in FY21: $275k

Partners

- Brookhaven National Laboratory
- Thermo Fisher Scientific
- Energy Storage Materials Initiative (ESMI)/PNNL

Relevance/Objectives

- Advance the fundamental **understanding of key factors** (material and electrode levels) that affect S reactions and cell lifespan under realistic high S loading and lean electrolyte conditions.
- Rationalize **low-porosity sulfur electrodes** to boost both cell specific energy (Wh/kg) and energy density (Wh/L), and to conserve more electrolyte to extend cell life.
- **Design and scale up S cathode materials** to support Battery500 Li-S pouch cell demonstration.
- Project efforts are directly aimed at barriers of low practical energy density, shuttle effect, low rate-capability, and limited cycling life of Li-S batteries.

Milestones

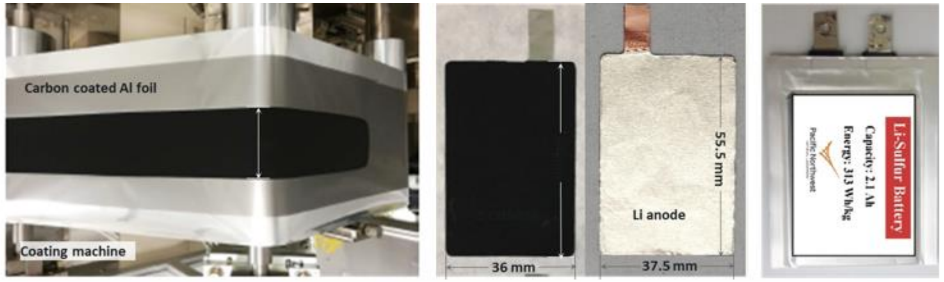
Date	Milestones and Go/No-Go Decisions	Status
December 2020	Optimize electrode architecture to realize discharge capacity of >1000 mAh g^{-1} in high loading S electrode (>4 mg_s cm^{-2}) at very low porosity (< 45%).	Completed
March 2021	Build an electrode model to understand the effects of electrode porosity and tortuosity on the electrode wetting and polysulfide migration.	Completed
June 2021	Enable a quasi-solid electrolyte networks by introducing polymer or sulfide solid electrolytes into the low porosity electrodes and realize cell operation at an extremely low E/S ratio.	On track
September 2021	Identify compatible binder and solvent combinations to enable the scale-up preparation of the quasi-solid electrodes.	On track

Approach/Strategy

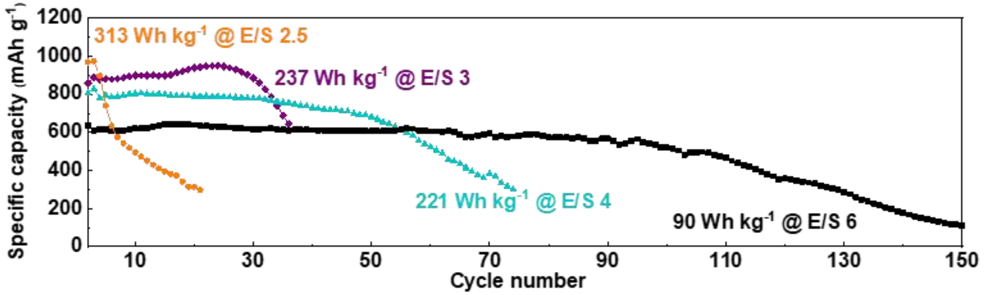
- Build electrode model to simulate the impacts of material property/electrode architecture on electrode wetting, Li-polysulfide migration, and S reaction kinetics.
- Optimize architectures of high-loading and low-porosity S electrode by controlling S/C particle size.
- Study the effects of electrode architecture on cell performance at practical conditions by using electrochemical and advanced characterization tools.
- Integrate polymer or inorganic solid Li^+ conductors into electrode to enhance durability of Li^+ conduction network, extending cell life.

Technical Accomplishments

Identified challenges in realistic Li-S pouch cells



→ IKB/S for pouch cell fabrication



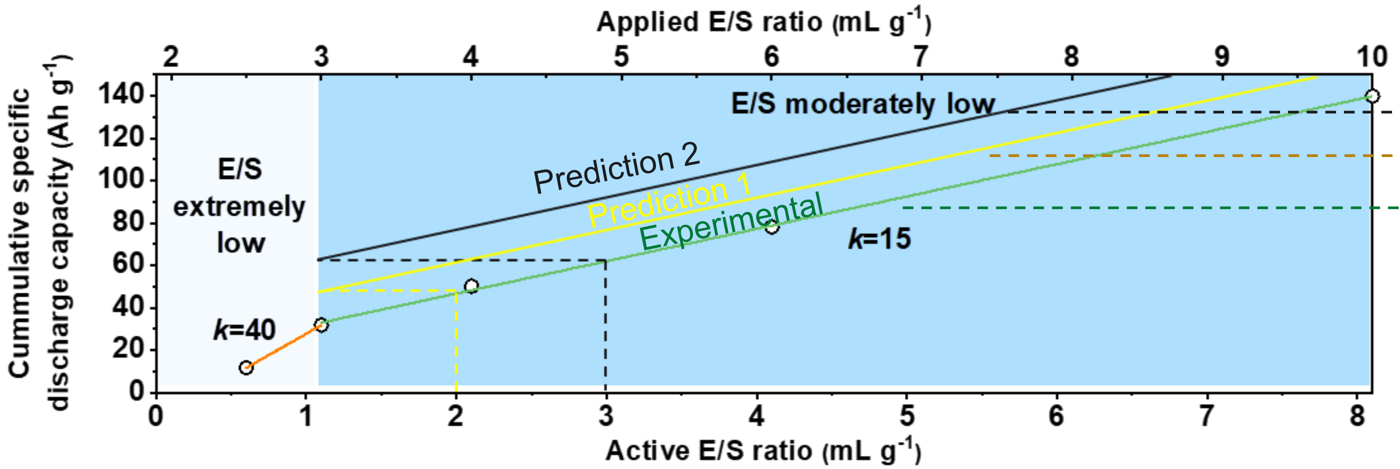
→ Li-S pouch cell results

- The integrated Ketjen Black (IKB)/S composites were processed into high-loading electrodes for pouch cell fabrication and evaluation.
- Shorter cycle life at higher energy: electrolyte depletion at the lean electrolyte conditions.

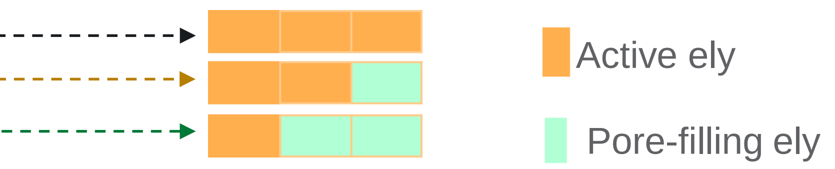
In collaboration with Dr. Lili Shi et. al. Battery500 consortium

Technical Accomplishments

Low-porosity design to conserve more electrolyte for longer cycling



$V_{\text{Active ely}}=V_{\text{Applied ely}}-V_{\text{pore-filling ely}}$



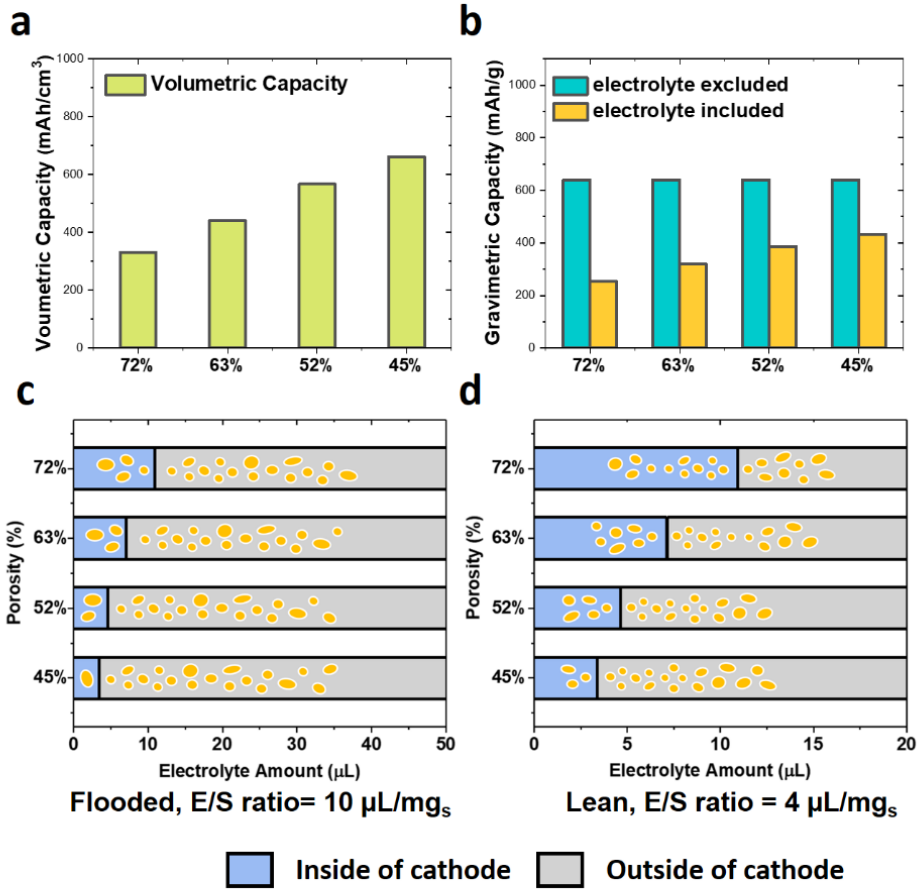
Electrolyte distribution at E/S= 3 mL g^{-1}

- Dependence of cumulative capacities of Li-S pouch cells on E/S ratio.

- In moderately lean electrolyte region (3<E/S<10 mL g_s^{-1}), the cumulative capacity has a linear correlation with E/S ratio.
- In extremely lean region (E/S<3 mL g_s^{-1}), accelerated decay is related to electrolyte distribution issue.
- Saving more electrolyte through reducing electrode porosity to extend cell cycle life.

Technical Accomplishments

Low-porosity cathode to improve energy and extend cell life



Flooded, E/S ratio= 10 μL/mg$_s$

Lean, E/S ratio = 4 μL/mg$_s$

Reducing electrode porosity:

Pros:

- Improved electrode volumetric capacity.
- Improved overall gravimetric capacity, if pore-filling electrolyte is counted.
- Save more electrolyte to support cell cycling.

Cons:

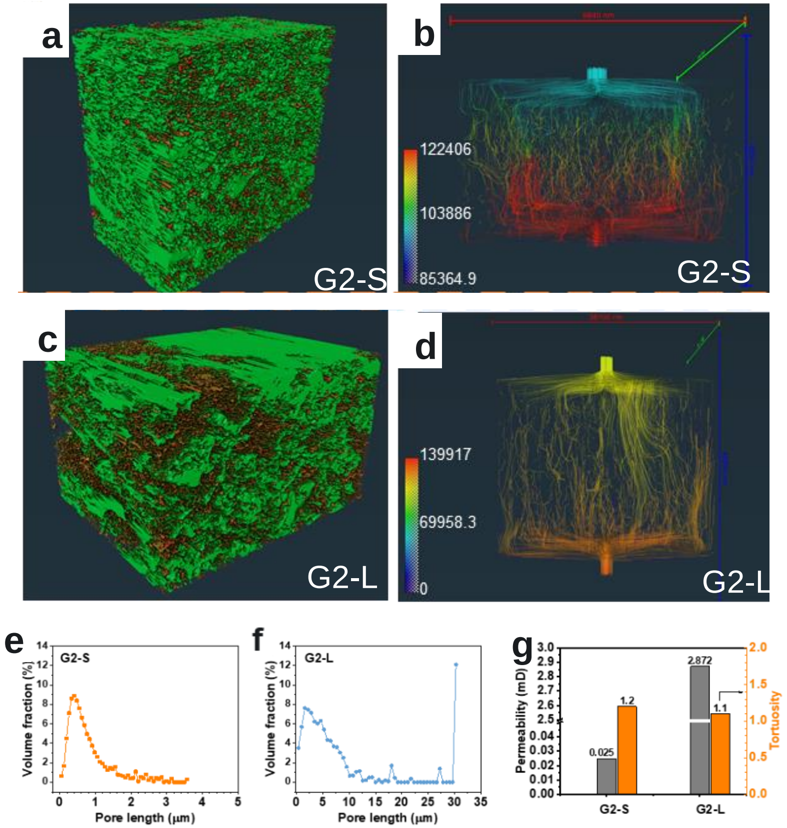
- Worse electrode wetting
- Exaggerated Li-polysulfide shuttling
- Faster electrode passivation

Need:

- Address the cons through material/electrode design

Technical Accomplishments

Identified key factors to enable low-porosity sulfur electrode



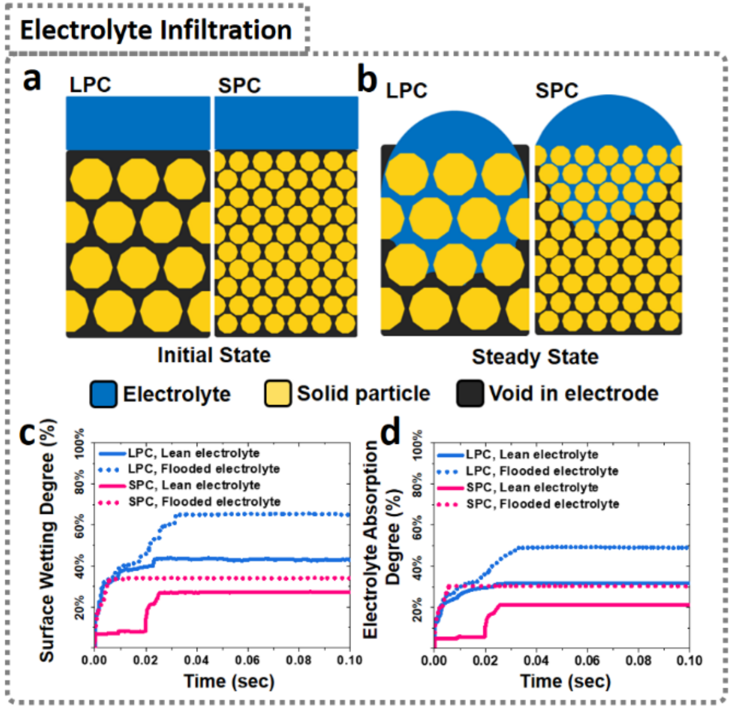
- 3D reconstruction of FIB-SEM of low-porosity sulfur electrode and flow simulation (>5 mg cm^{-2}).

- Electrode architecture dictates electrolyte permeability in low-porosity electrode.
- Electrolyte permeability is determined by not only electrode tortuosity, but also the pore size and its distribution.
- Interconnected porous structures with reasonably distributed pore size are desired.

In collaboration with Dr. Zhao Liu et al. , Thermo Fisher Scientific

Technical Accomplishments

Key considerations of low-porosity electrode: improving electrode wetting



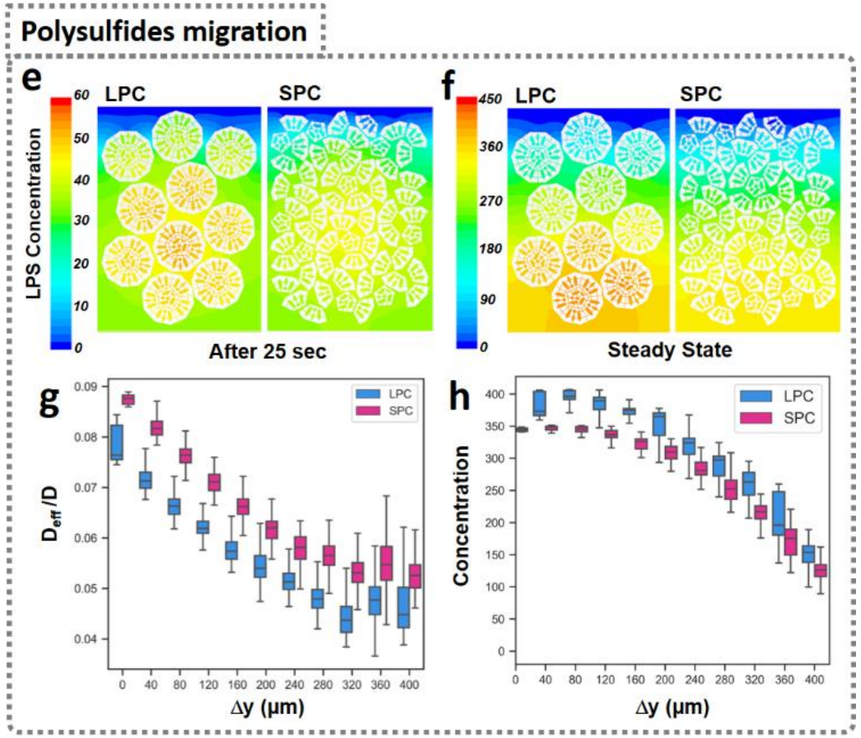
- Simulations of electrolyte infiltration in large particle cathode (LPC) and small particle cathode (SPC) at same electrode porosity.

- Electrode model was built for electrolyte flow simulation.
- Large particle electrode has better wettability compared with the small particle electrode.
- Lean electrolyte conditions worsen electrode wetting for both large and small particle electrodes.

In collaboration with Drs. Jie Bao, Zhijie Xu at PNNL

Technical Accomplishments

Key considerations of low-porosity electrode: suppressing polysulfide migration



- Simulations of Li-polysulfide migration in large particle cathode (LPC) and small particle cathode (SPC) at same electrode porosity.

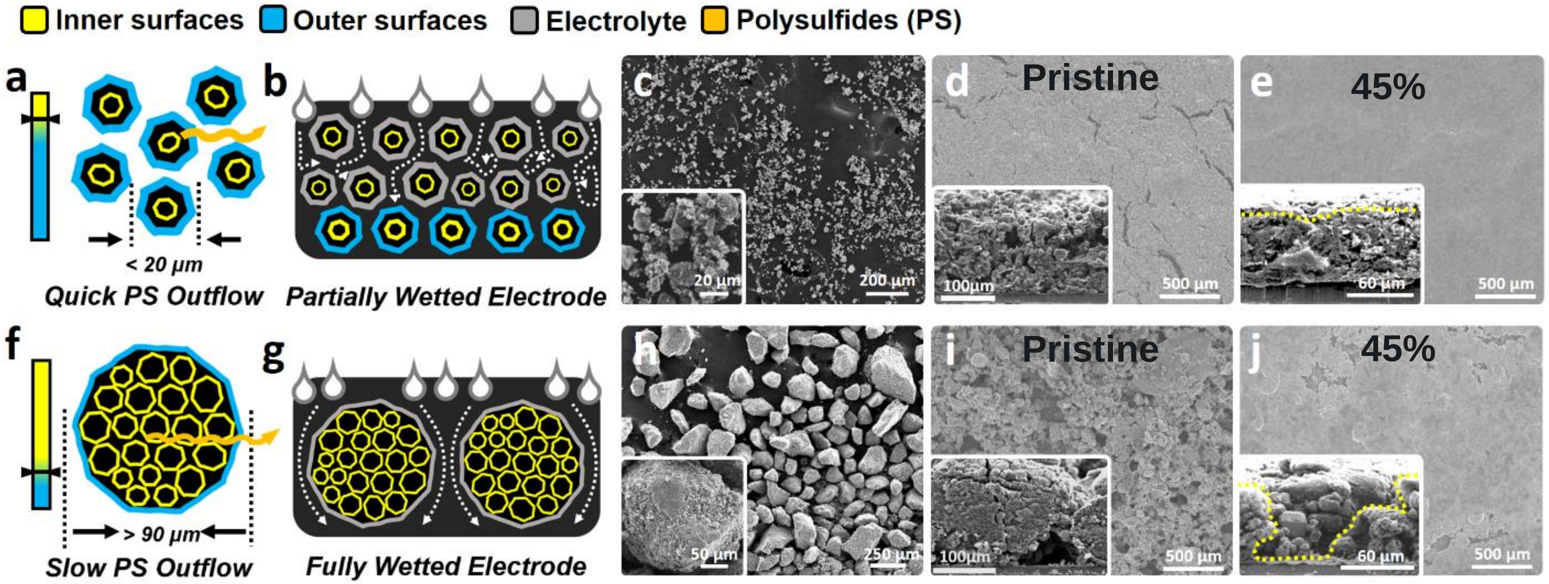
- Electrode model built to simulate Li-polysulfide migration.
- LPC has smaller Li-polysulfide diffusivity compared with the SPC.
- In SPC, Li-polysulfides more easily migrate outside of the particle and electrode than in LPC.

Technical Accomplishments

Design principle of low-porosity electrode: experimental validation

SPC

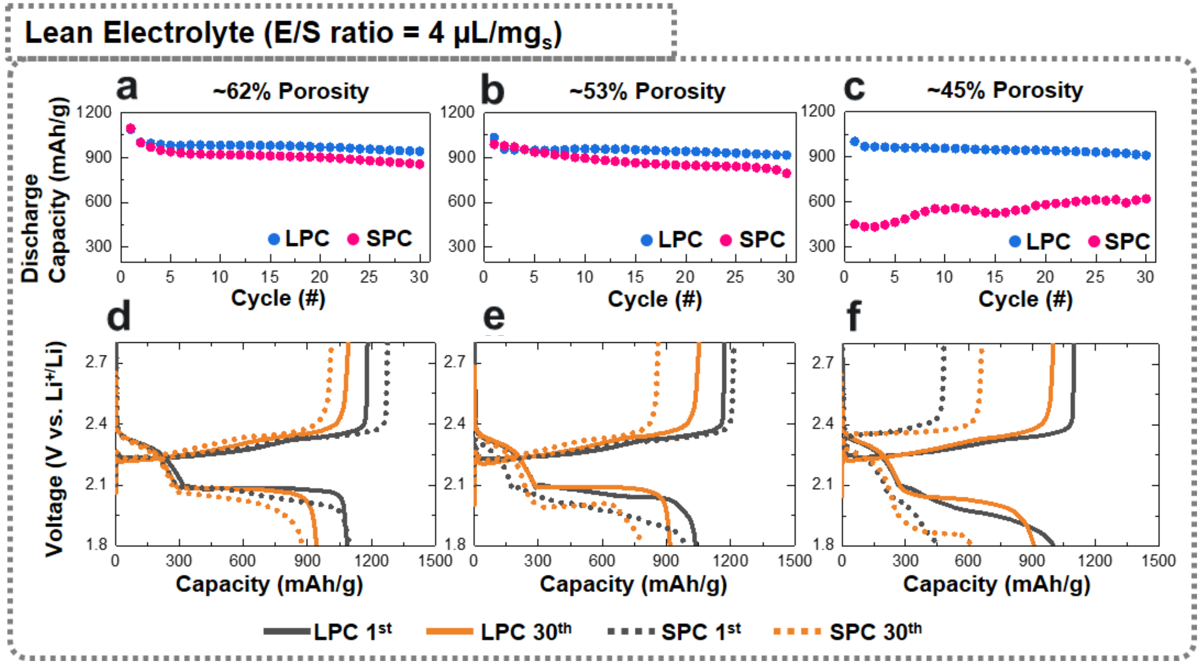
LPC



- S/C composite (IKB/S) with desired particle sizes were synthesized and used as example materials.
- Low-porosity electrode (porosity, ~45%) with large (LPC) and small (SPC) particles were fabricated.

Technical Accomplishments

Impact of electrode architecture on cell performance

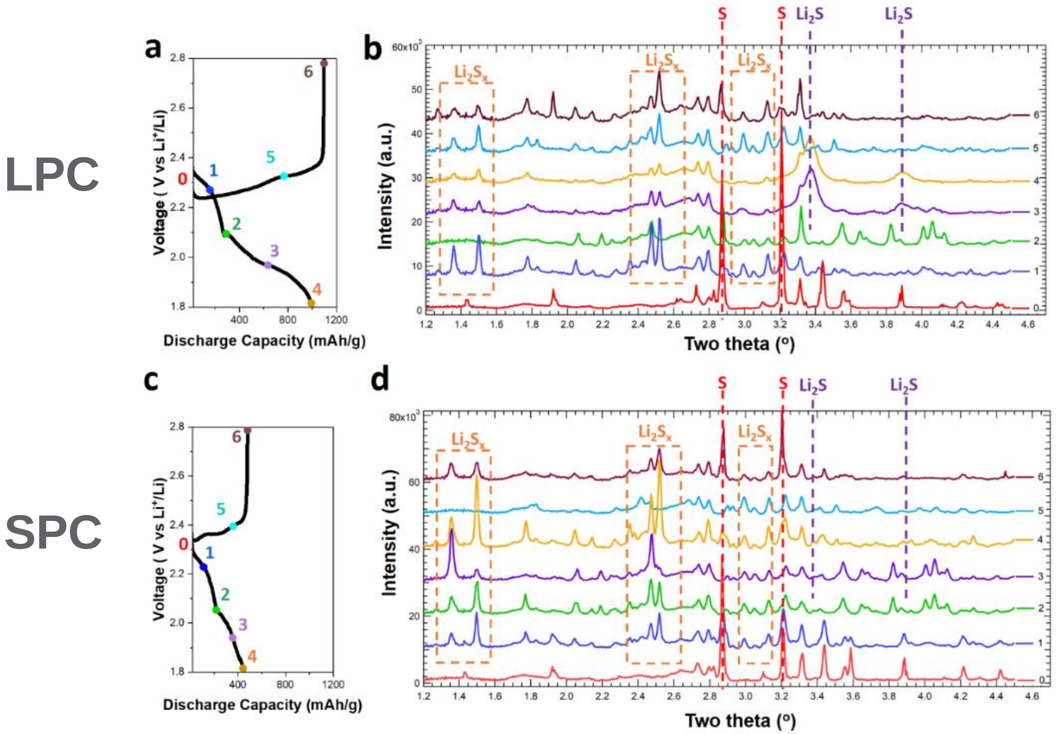


Performance of LPC and SPC cycled at lean electrolyte conditions and different porosities (S loading: 4 mg_s/cm^2, electrolyte/sulfur (E/S) = 4 $\mu L/mg_s$, i=0.1C, room temperature).

- Reducing porosity affects both sulfur utilization and cycling stability, especially for SPC.
- LPC has better tolerance on porosity reduction, thus is desired for low-porosity electrode.

Technical Accomplishments

Impact of electrode architecture on sulfur reactions



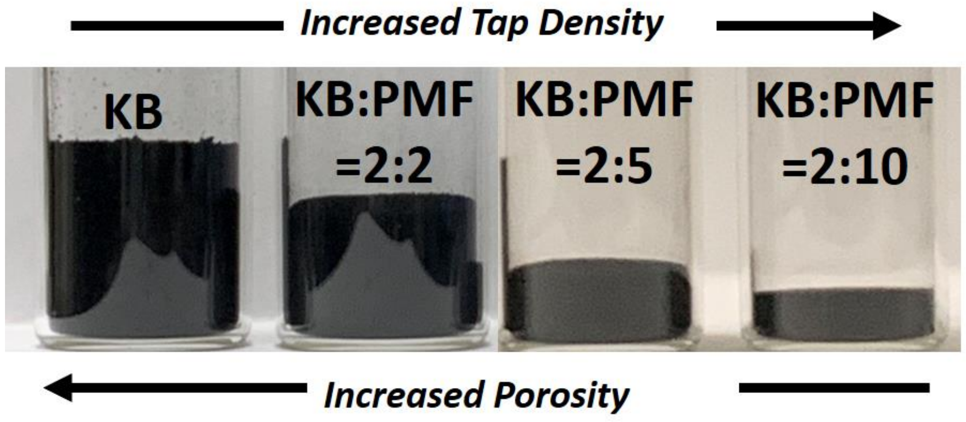
- Phase evolutions in dense LPC and SPC (porosity, 45%) at different depths of discharge monitored by Synchrotron XRD

- Phase evolution of S-polysulfide-Li_2S was identified in dense LPC and SPC.
- LPC has smaller overpotential and higher conversion content compared to SPC.
- SPC has more serious Li-polysulfide migration and electrode passivation (consistent with SEM characterization).

In collaboration with Dr. Peter Khalifah at Brookhaven National Laboratory

Technical Accomplishments

Materials scaling up for Li-S pouch cells



Materials control through synthesis

Scaling-up material synthesis for Battery500 pouch cell

Two Li-S patents licensed by industry this year

- Materials (IKB) with controllable particle size and integration degree.
- Scaling-up synthesis of IKB at 16 g/batch and provided to Battery500.

Collaboration and Coordination with Other Institutions

Partners:

- Brookhaven National Laboratory: reaction mechanism study
- Thermo Fisher Scientific: material/electrode characterization
- ESMI/PNNL: electrode-level simulation
- Environmental Molecular Sciences Laboratory (EMSL)/PNNL: characterization

Remaining Challenges and Barriers

- Short cycle life at both high-loading S cathodes and lean electrolyte conditions
- Depletion of electrolyte/additives
- Instability of Li metal anode and lack of effective strategies

Future Work - FY2021

- Continue to understand material and electrode barriers by using experimental and theoretical simulation tools.
- Improve electrode wettability and sulfur utilization rate at realistic conditions through optimizing material functionality and electrode architecture.
- Suppress Li-polysulfide migration and redistribution and reduce its interference on Li anode.
- Identify optimal solid Li-ion conductor and liquid electrolyte combinations to extend the cell cycle life at extremely lean electrolyte conditions.

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

Summary

1. Rationale of low-porosity electrode design was elucidated by theoretical simulation and validated experimentally; S/C particle determines electrode architecture and affects electrolyte permeability, Li polysulfide migration and sulfur reaction kinetics.

2. At a low porosity, the electrode comprising of large particles delivers superior sulfur utilization, lower overpotential and better capacity retention over the small particle electrode.

3. By controlling material microstructure, high-mass-loading S electrodes (4 mg cm^{-2}) with porosity of ~45% were demonstrated to deliver a high sulfur utilization rate (>1000 mAh g^{-1}) at very lean electrolyte conditions (E/S=4 µL mg^{-1}).

4. Optimized S/C cathode materials were scaled-up synthesized and transferred to Battery500 for pouch cell fabrication.

Acknowledgments

- Support from the DOE/OVT/BMR program is greatly appreciated
- Team Members: Shuo Feng, Zhaoxin Yu, Lili Shi, Cassidy Anderson, Ji-Guang Zhang and Jie Xiao

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Technical Backup Slides

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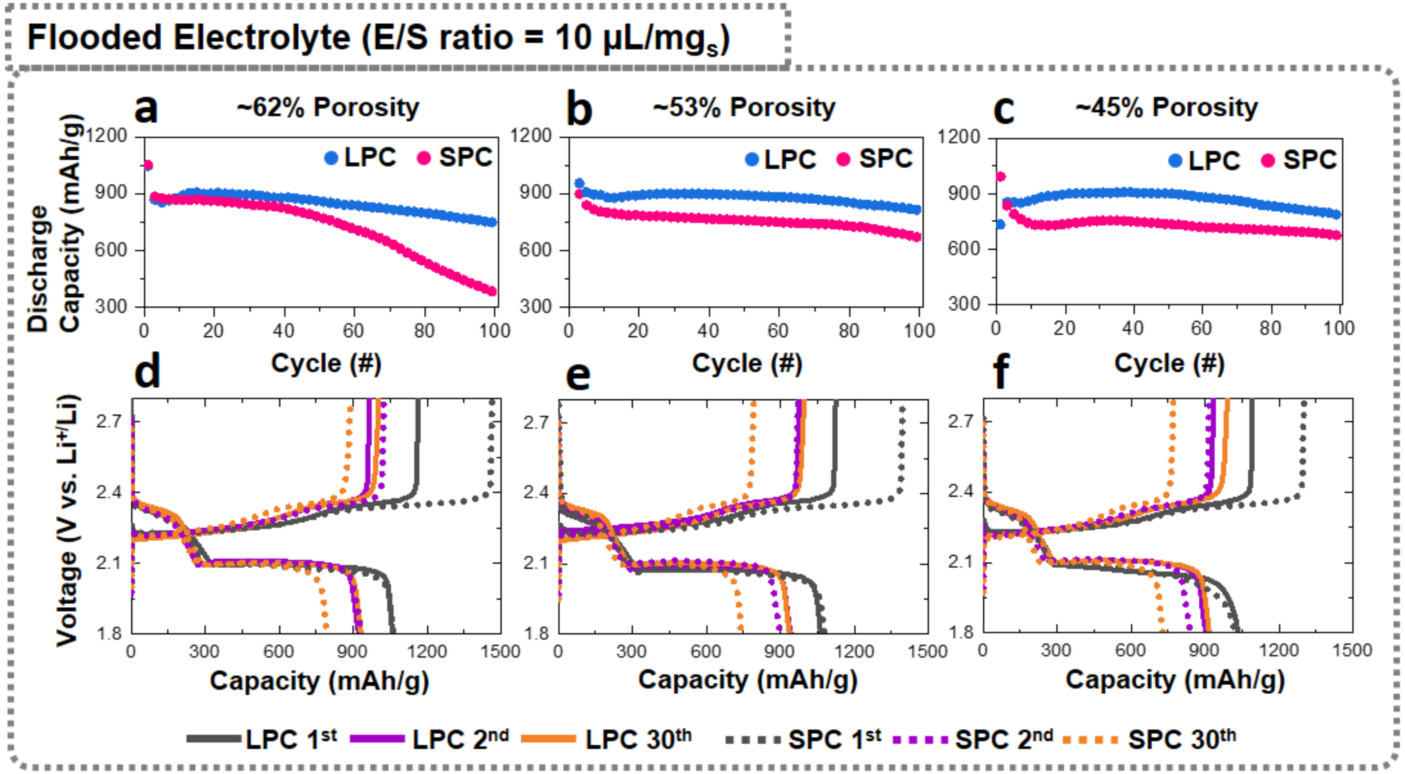
Technical Accomplishments



Performance of LPC and SPC cycled at flooded electrolyte conditions and at different electrode porosities (Electrode: 4 mg_s/cm^2, electrolyte/sulfur (E/S) = 10 $\mu L/mg_s$, i=0.1C, room temperature).