Development of High-Energy Lithium-Sulfur Batteries

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2020 DOE VTO AMR
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PNNL is operated by Battelle for the U.S. Department of Energy

Overview

Timeline

- Start date: Oct. 2016
- End date: Sept. 2020
- Percent complete: 89%

Budget

- Total project funding: $1200k
- DOE share 100%
- Funding received in FY20: $400k

Barriers

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

Partners

- Brookhaven National Laboratory
- University of Michigan
- General Motors
- The Chemours Company
- Environmental Molecular Sciences Laboratory/PNNL

Relevance/Objectives

- Advance the fundamental understanding of key factors (material and electrode levels) that affect S reactions and cell lifespan at realistic high S loading cathode and lean electrolyte conditions.
- Optimize electrode structure and realize a high S utilization rate in low-porosity S cathodes to boost both cell specific energy (Wh/kg) and energy density (Wh/L).
- Tackle the challenges of low ionic-conductivity of sulfide-based solid electrolytes and compatible liquid electrolytes and construct hybrid Li^+ conductive networks to improve S reaction kinetics at extremely lean electrolyte conditions.
- 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

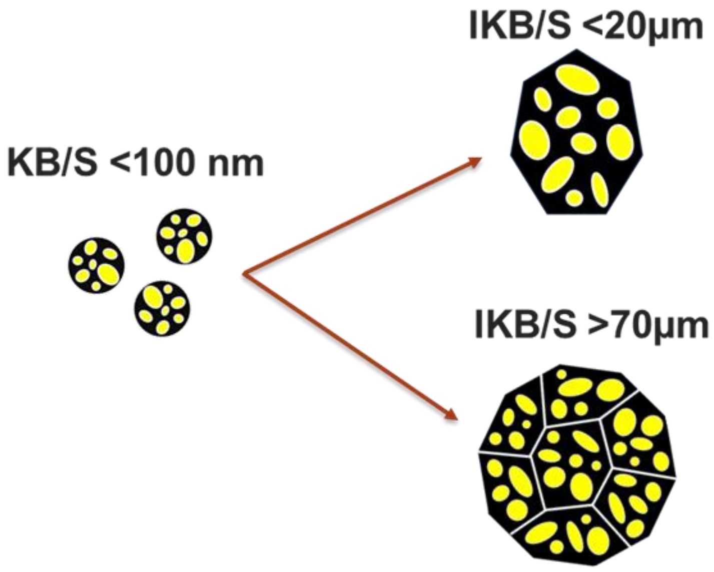
Date	Milestones and Go/No-Go Decisions	Status
December 2019	Controllable synthesis of carbon/S secondary particles from 5 to 100 µm for high-loading S electrodes (>4 mg S/cm^2).	Completed
March 2020	Realize S utilization rate >1000 mAh/g in dense S electrodes (S > 4 mg/cm^2, porosity≤50%) at an E/S≤4 µL/mg through electrode architecture control.	Completed
June 2020	Demonstrate >80 cycles (80% capacity retention) in dense S electrodes at E/S≤4 µL/mg through the hybrid electrode design.	On track
September 2020	Complete evaluation of high-loading S electrodes at E/S≤3 µL/mg and transfer sufficient materials to Battery500 for high-energy pouch cell demonstration.	On track

Approach/Strategy

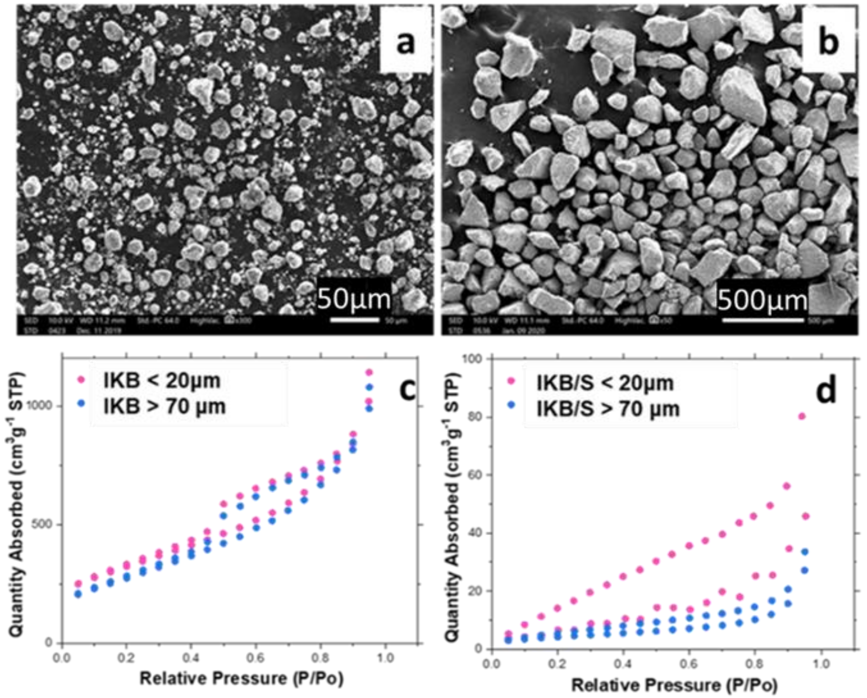
- Synthesize S/C composites with controllable particle size for high-loading and dense S cathode fabrication.
- Understand the effects of cathode particle size on electrode wetting, polysulfide diffusion, and S utilization rate at different electrode porosities.
- Study the limiting factors of S reactions in large-size S electrodes, with high S loading, through experimental and simulation approaches.
- Evaluate functional separator coating to enhance electrolyte distribution and thus S reaction uniformity.
- Develop high Li^+ conductive solid conductors and compatible liquid electrolytes and use both to enhance sulfur reaction kinetics at lean electrolyte conditions.

Technical Accomplishments

Controllable synthesis of C/S materials for high-loading sulfur cathode



Controllable synthesis of IKB

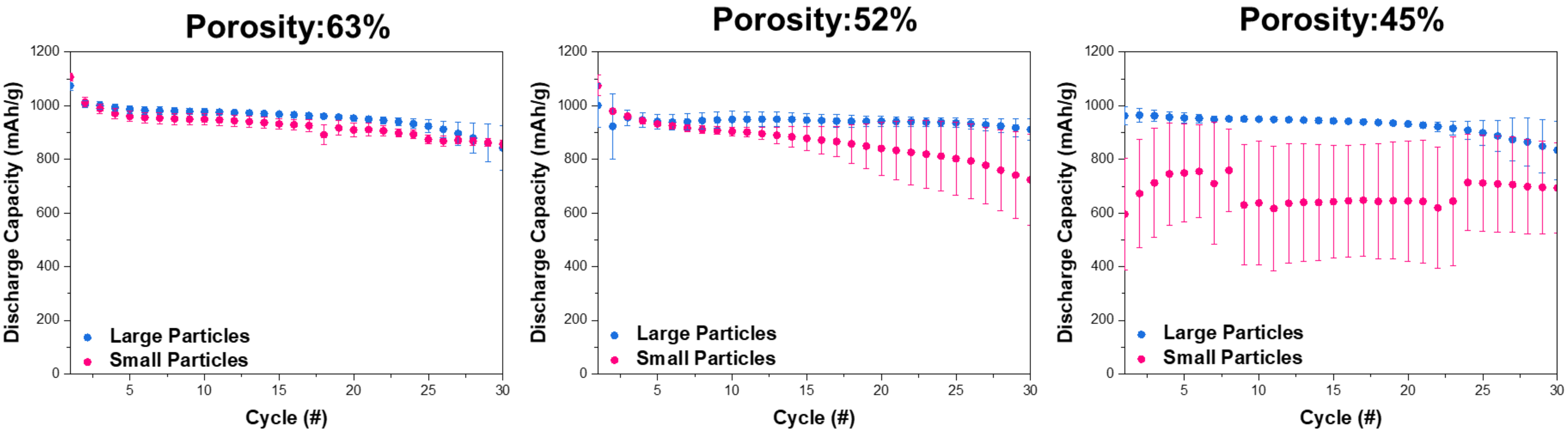


Morphology and surface area of IKB and IKB/S

- Integrated Ketjen Black (IKB)/S composites with different particle sizes were synthesized through a facile and scalable synthesis route.
- IKB composites with typical particle size <20 µm and >70 µm were used as example materials to understand the effects of particle size on cell performance.

Technical Accomplishments

Effects of cathode particle size on S reactions in high-loading electrodes at lean electrolyte conditions

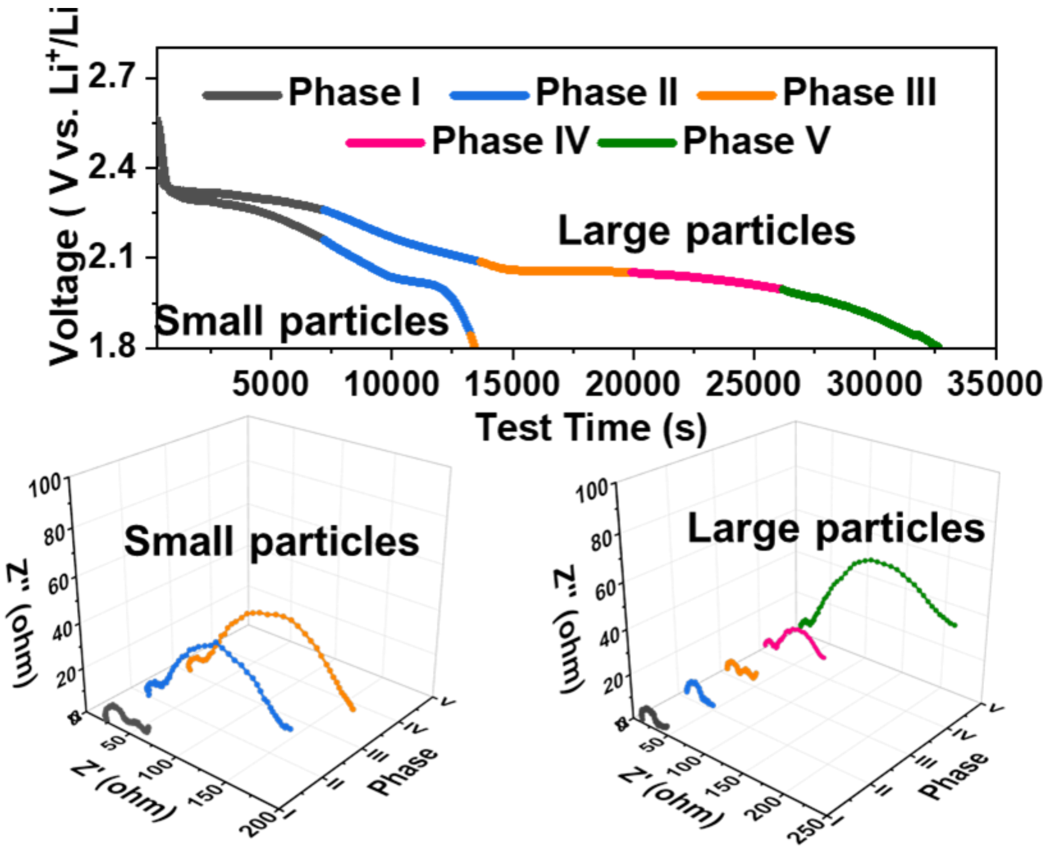


Performance of S electrodes comprised of small and large particles, cycled under lean electrolyte conditions and at different electrode porosities (Electrode: 4 mg_s/cm^2, electrolyte/sulfur (E/S) = 4 $\mu L/mg_s$, i=0.1C, room temperature).

- With lean electrolyte (4 µL/mg), the cathode particle size has significant impact on both sulfur utilization and capacity retention (six parallel coin cells for each porosity test).
- Particle size plays a more important role when electrode porosity is decreased to low practical level.

Technical Accomplishments

How does particle size affect the performance of dense electrodes at lean electrolyte conditions?

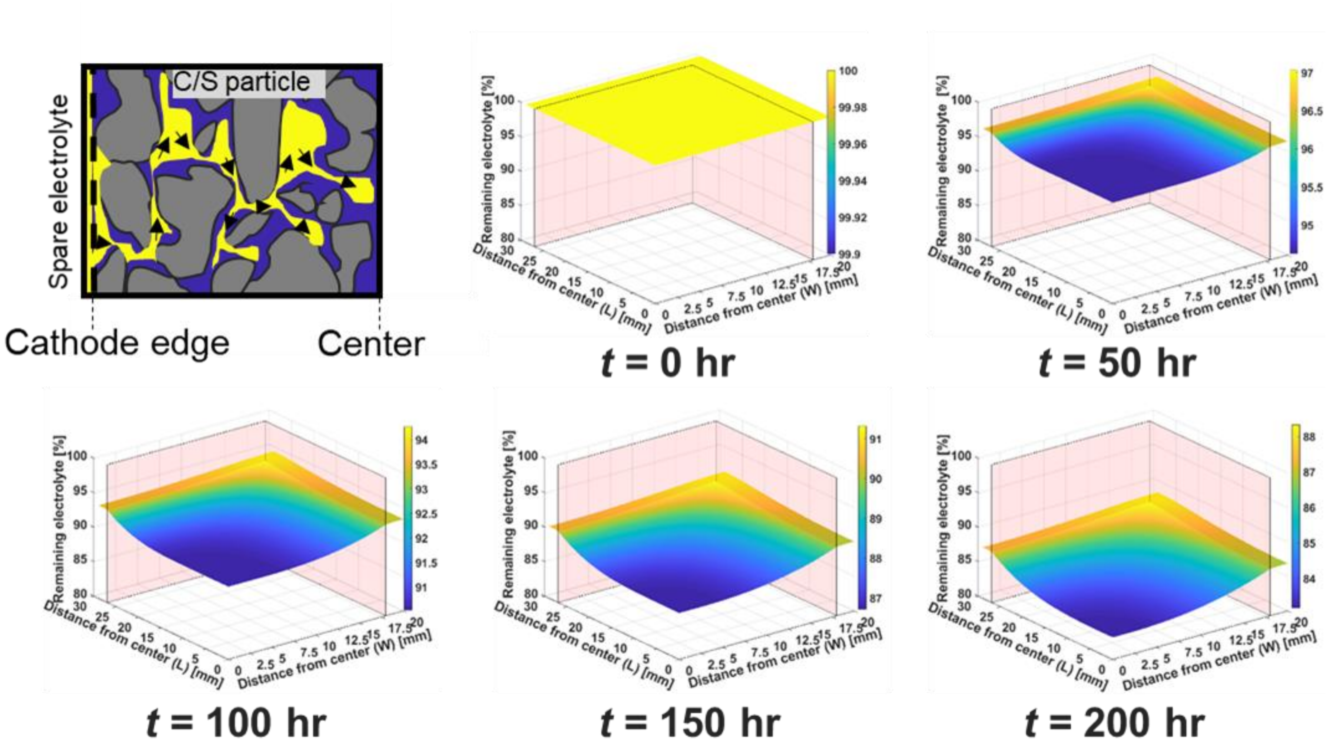


- *In situ* electrochemical impedance spectroscopy was performed to track the kinetic evolution of electrodes with small and large particles.
- Higher overall charge transfer resistances (R_{ct}) were identified for the electrodes with small particles compared with those with large particles.
- High R_{ct} observed in small-particle electrodes is mainly due to hindered electrolyte infiltration.

Discharging profiles and *in situ* electrochemical impedance spectroscopy of electrodes with <20 μm and >70 μm particles (Electrode: 45% porosity, 4 mg_s/cm^2, and E/S = 4 $\mu L/mg_s$, i=0.1C, room temperature).

Technical Accomplishments

Hindered electrolyte redistribution caused by high tortuosity of the high-loading S cathodes



t = 0 hr

t = 50 hr

t = 100 hr

t = 150 hr

t = 200 hr

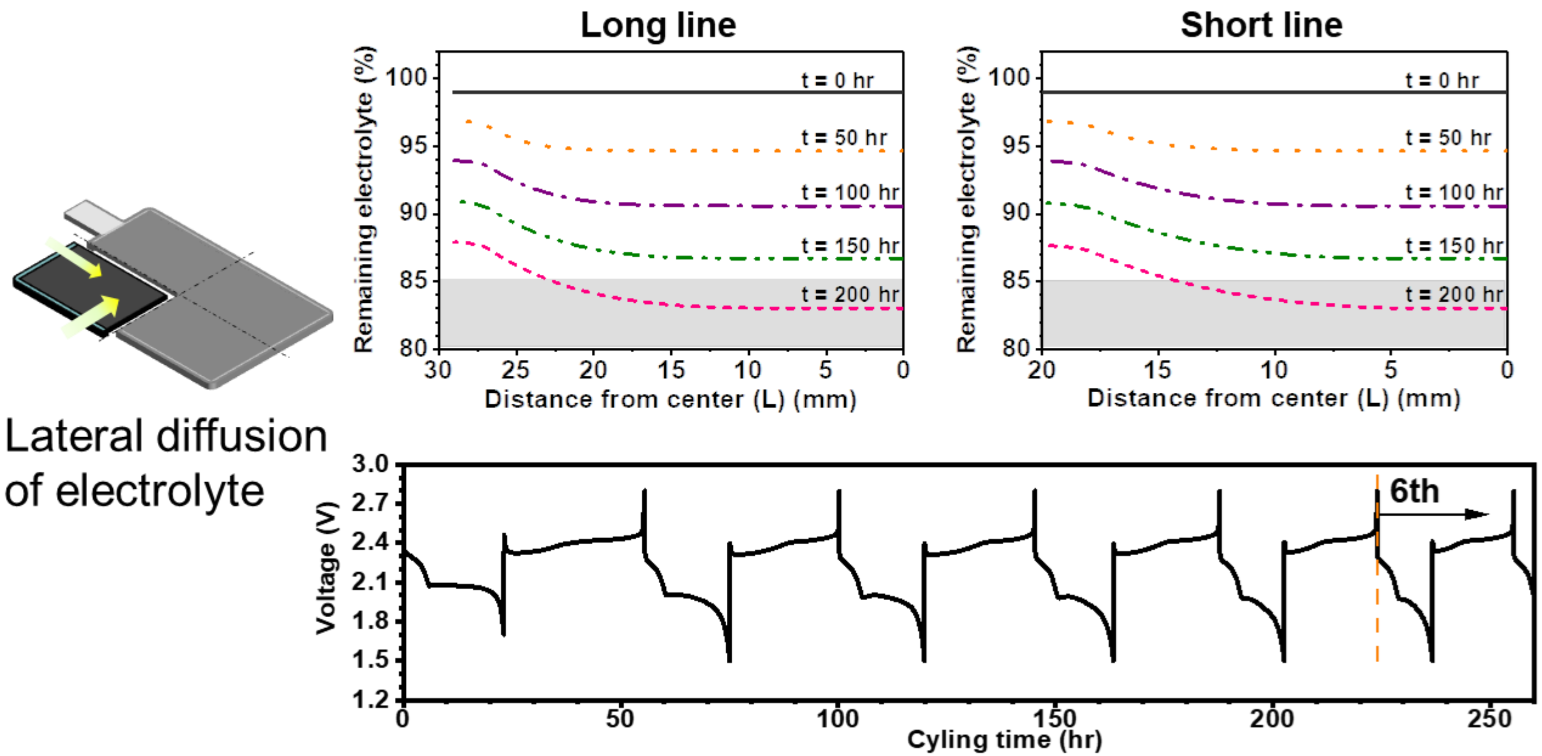
- The electrolyte gets depleted gradually upon cycling; replenishing process occurs from the electrode edge to the center.
- The electrolyte replenishment is hindered due to the high electrode tortuosity and deteriorates over time.

Multiphysics simulation of the electrolyte diffusion and redistribution along the lateral direction of a large-size pouch cell upon cycling.

In collaboration with Battery500 consortium and University of Michigan

Technical Accomplishments

Hindered electrolyte redistribution along the lateral direction of large-size S cathode due to the high electrode tortuosity



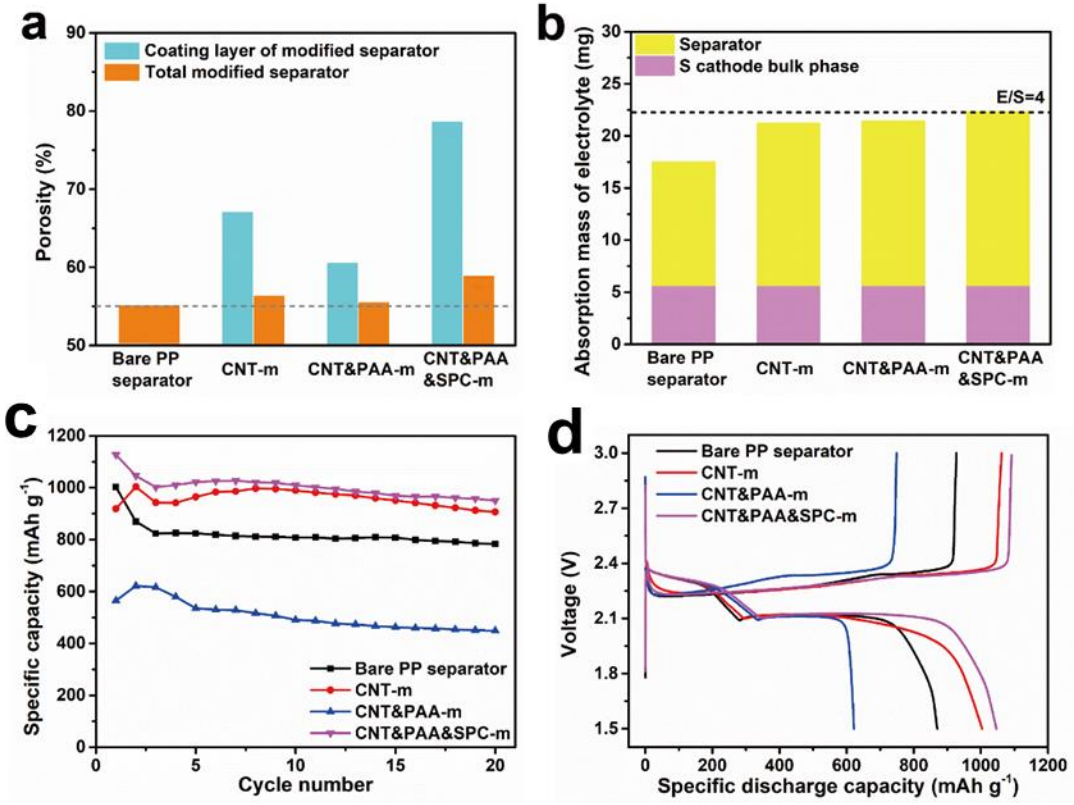
Simulation results of electrolyte diffusion and redistribution along the lateral direction of a large-size electrode upon cycling and cycling of a practical 300 Wh/kg Li-S pouch cell (bottom).

- After 200 hours, half of the electrode area (50.3%) has less than 85% electrolyte content.
- The inhomogeneous electrolyte distribution along lateral direction deteriorates over time, which is consistent with the increased polarization and capacity decay in Li-S pouch cells.

In collaboration with Battery500 consortium and University of Michigan

Technical Accomplishments

Functional and ultra-thin coating of separator to improve electrolyte distribution and S reaction uniformity

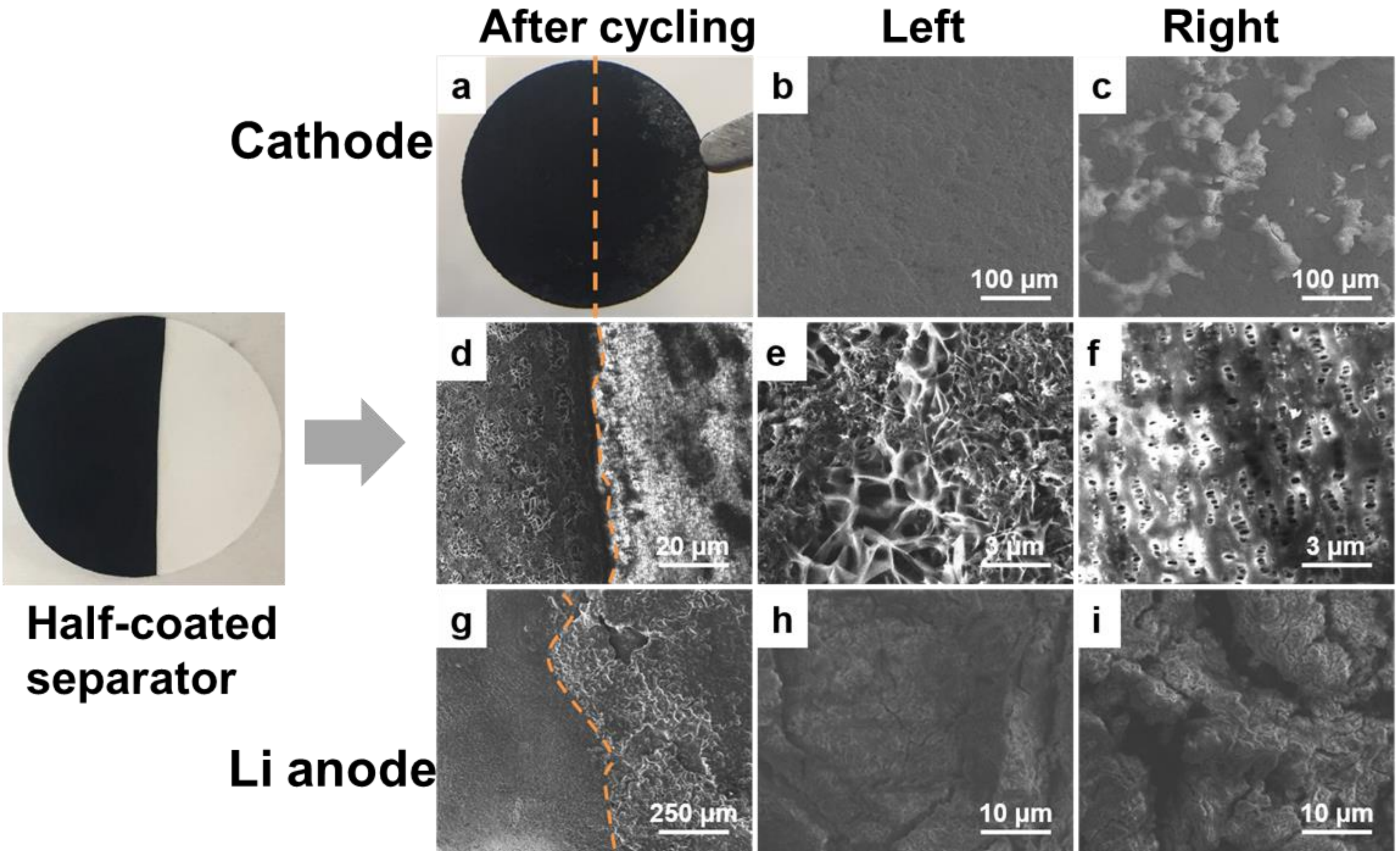


Properties of the coated separators and their effects on cell performance (Cathode: 4 mg$_s$/cm^2, and E/S = 4 µL/mg$_s$, i=0.1C, PAA-polyamic acid).

- Separators coated by ultra-thin layers of CNT (CNT-m), CNT&PAA (CNT&PAA-m), and CNT&PAA&Super-P carbon (CNT&PAA&SPC-m) were prepared and compared with bare PP separator (Coating weight: 0.2 mg/cm^2).
- Functional PAA coating with appropriate porosity control is essential to improve electrolyte distribution while suppressing polysulfide crossover.

Technical Accomplishments

Effects of the functional separator coating on both cathode and Li anode

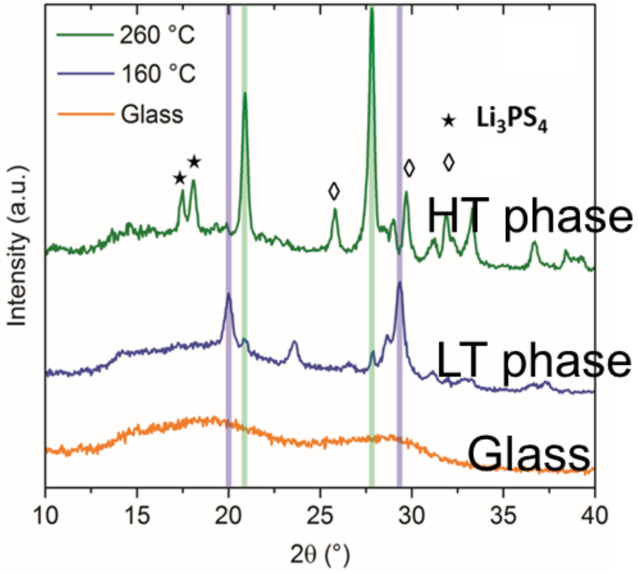


Morphological characterization of cycled sulfur cathode, separator, and lithium anode using the half-coated separator.

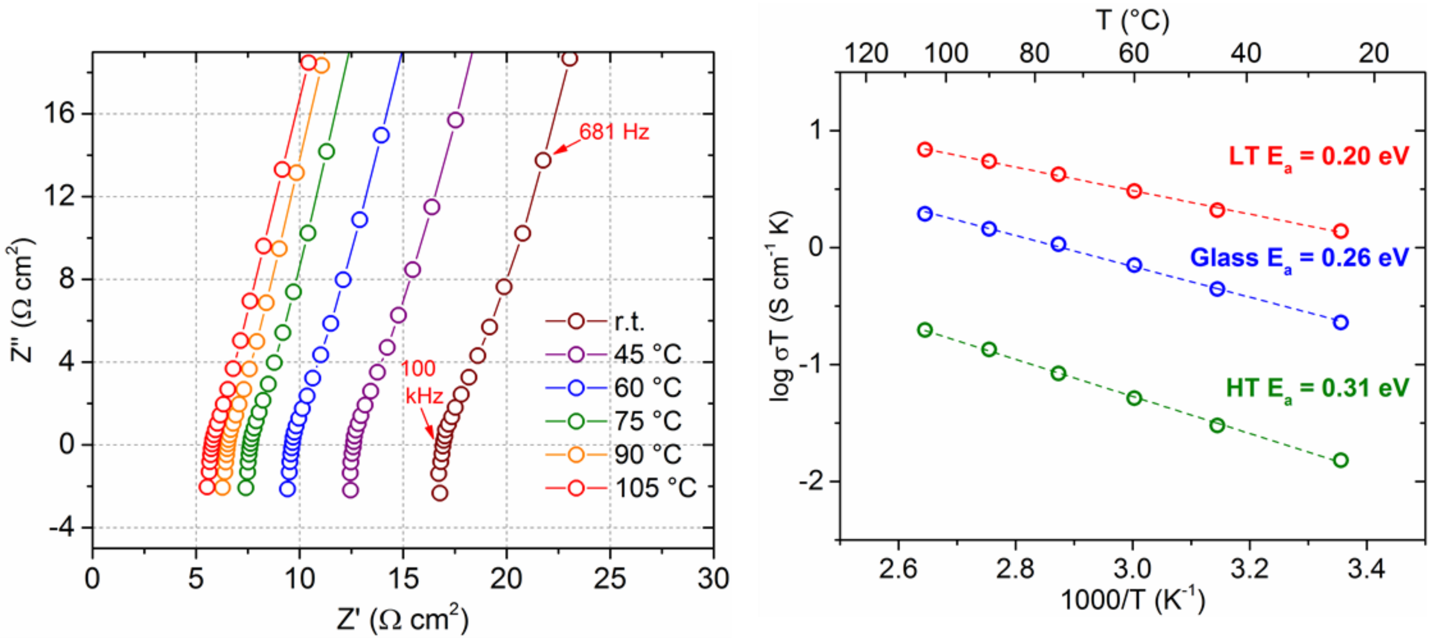
- Significant effects of separator coating were observed by a morphological study using a half-side coated separator in a Li-S cell.
- The ultra-thin PAA/CNT/Super-P coating can effectively regulate the electrolyte distribution and suppress polysulfide crossover, which improves reaction uniformity on both the sulfur cathode and Li anode.

Technical Accomplishments

Highly conductive Li-ion conductors to enhance the S cathode ionic conductivity



XRD pattern of different phases

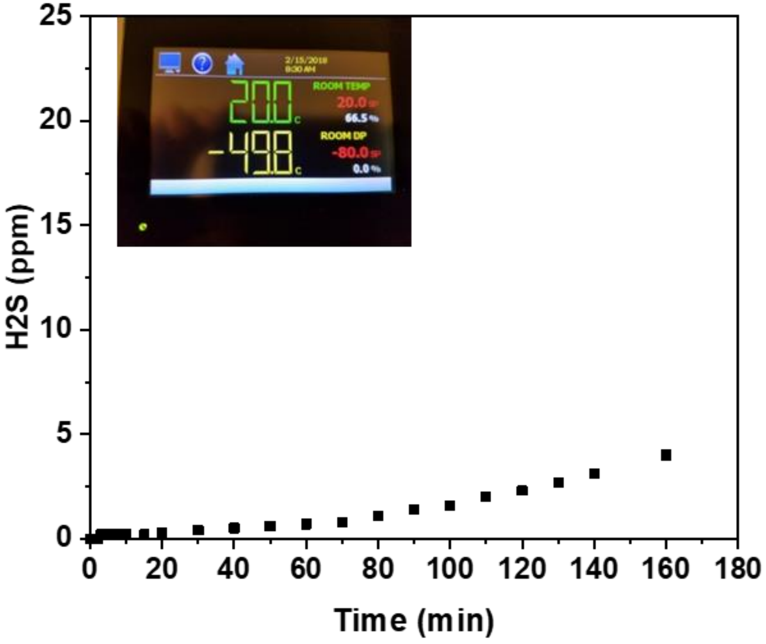


Ionic conductivity and activation energy through EIS test.

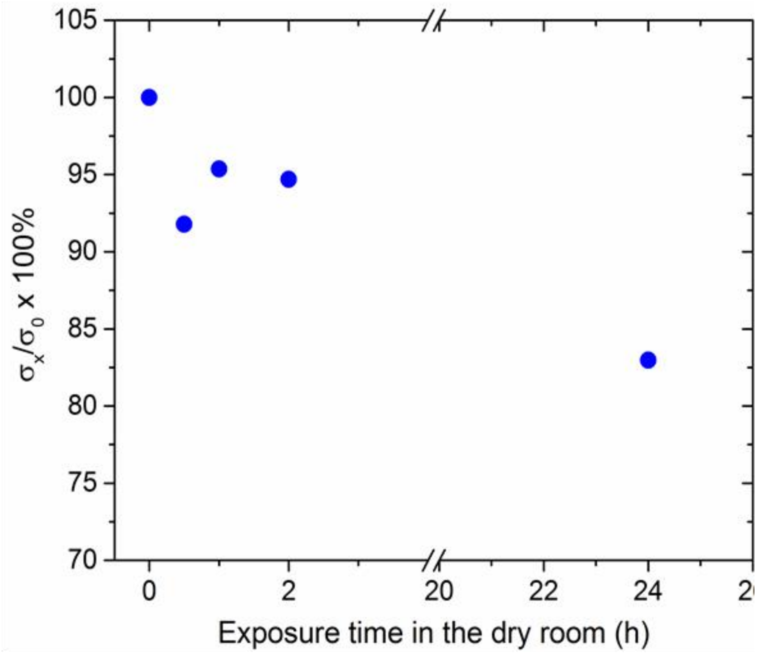
- Low-temperature phase $Li_7P_2S_8Br_{0.5}I_{0.5}$ was prepared through a mechanochemical approach.
- High Li^+ conductivity of 4.7 mS/cm was achieved at room temperature on a cold-pressed pellet.

Technical Accomplishments

Improved air stability of the sulfide solid electrolytes enables direct processing in dry room



H_2S vs. exposure time

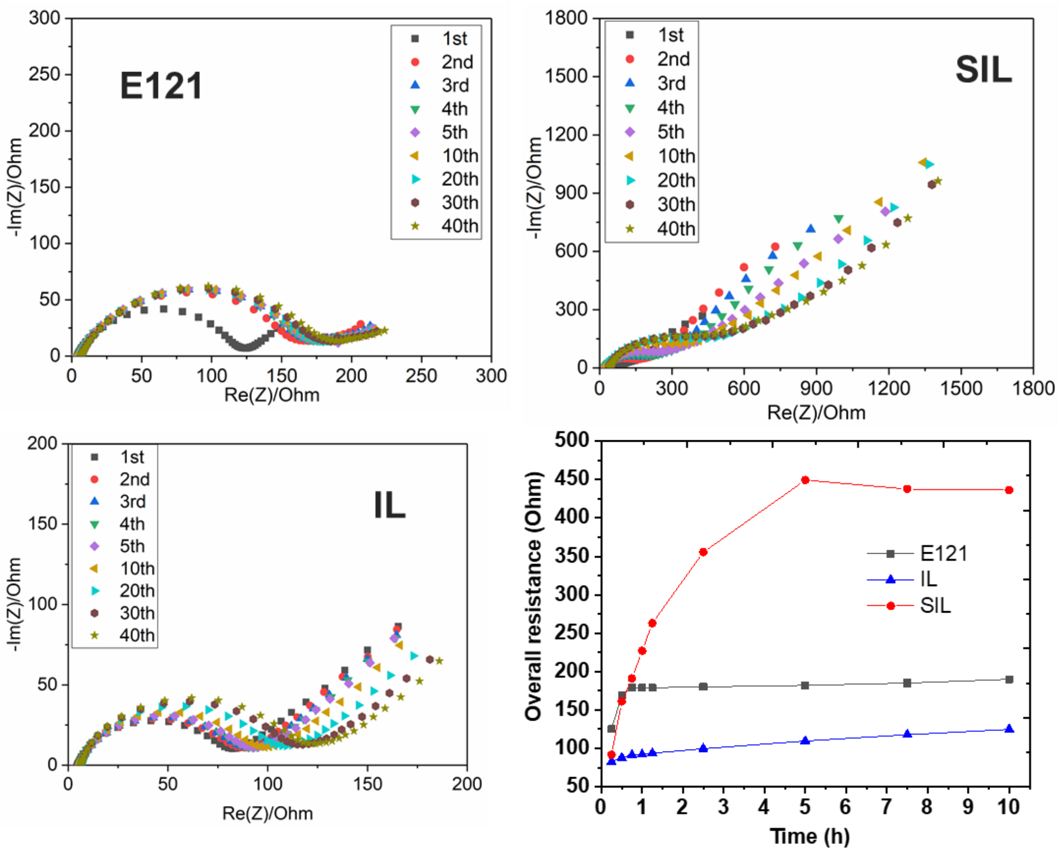


Ionic conductivity vs. exposure time

- Two hours of exposure in the dry room atmosphere ONLY generates limited H_2S (< 5 ppm) and causes negligible decrease of ionic conductivity (<5%) (Test in powder form).
- The high air stability and low level of H_2S release enable the direct processing of the material in a dry room.

Technical Accomplishments

Compatible liquid electrolytes with the $Li_7P_2S_8Br_{0.5}I_{0.5}$ solid conductors for the hybrid Li-ion conduction S cathode



Nyquist plots of solid electrolyte contained S cathode in contact with different electrolytes (E/S = 2 µL/mg_s)

- Sulfur cathode (6 mg/cm^2) containing $Li_7P_2S_8Br_{0.5}I_{0.5}$ solid conductors was prepared through a dry processing for Li-S cells.
- Compatibility of $Li_7P_2S_8Br_{0.5}I_{0.5}$ with ether-based electrolyte (E-121), solvated ionic liquid electrolyte (E-SIL), and room-temperature ionic liquid electrolyte (E-IL) was evaluated for 10 hours.
- Ionic liquid shows the best overall compatibility and wettability.

Collaboration and Coordination with Other Institutions

Partners:

- Brookhaven National Laboratory: reaction mechanism study
- General Motors: material/electrode test
- The Chemours Company: separator coating development
- University of Michigan: electrode-level simulation
- Environmental Molecular Sciences Laboratory at Pacific Northwest National Laboratory: materials characterization and electrochemical *in situ* study

Remaining Challenges and Barriers

- Long-term cycling stability of Li-S battery at both high-loading sulfur cathodes and lean electrolyte conditions
- Durable electrolyte/additives to enable long-term cell cycling
- Instability of Li metal anode and effective protection strategies

Future Work - FY2020

- Address the technical challenges of scale-up synthesis of integrated KB particles with controllable large secondary particle sizes for the preparation of high-loading (> 4 mg S/cm^2) and dense sulfur electrode (<50% porosity) at relevant scales.
- Understand key factors (material and electrode levels) that affect sulfur reactions at realistic high S loading cathode and lean electrolyte conditions through the combined experimental and theoretical simulation approaches.
- Develop effective approaches to further improve the air stability/moisture sensitivity of sulfide solid electrolytes to facilitate their applications in batteries.
- Identify optimal combinations of solid and liquid electrolytes to extend the cycle life of Li-S at extremely lean electrolyte conditions.

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

Summary

1. IKB/S composites with different particle sizes were synthesized through a facile and scalable synthesis route and were used as example materials to understand roles of the materials' properties on cell performance.
2. Materials' particle size and porosity were verified to play a very critical role in electrolyte diffusion, S utilization rate, and polysulfide shuttling, especially for electrodes with lower porosities. The electrodes comprising large particles deliver both higher-specific capacities and better capacity retention compared to those comprising small particles.
3. A physical model of large-size pouch cell electrode (36mm×54mm in dimension) was built and simulated to understand limiting factors in large-size and high-loading S cathodes; the electrolyte distribution along the electrode lateral direction, instead of perpendicular direction, is hindered and deteriorates the reaction uniformity over time, which is consistent with the experimental results of Li-S pouch cell.
4. Functional PAA separator coating with appropriate porosity control is essential to regulate electrolyte distribution and suppress polysulfide crossover, which improves reaction uniformity on both the S cathode and Li anode.
5. Low-temperature phase $Li_7P_2S_8Br_{0.5}I_{0.5}$ with high conductivity of 4.7 mS/cm^2 was synthesized with improved dry-room air stability and was used to enhance ionic conductivity of S electrodes after identifying the compatible ionic liquid electrolytes.

Acknowledgments

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- Team Members: Jie Xiao, Ji-Guang Zhang, Zhaoxin Yu, Shuo Feng, Lili Shi, Yuxing Wang, Jian Qin, Arthur Baranovskiy, and Cassidy Anderson

Technical Backup Slides

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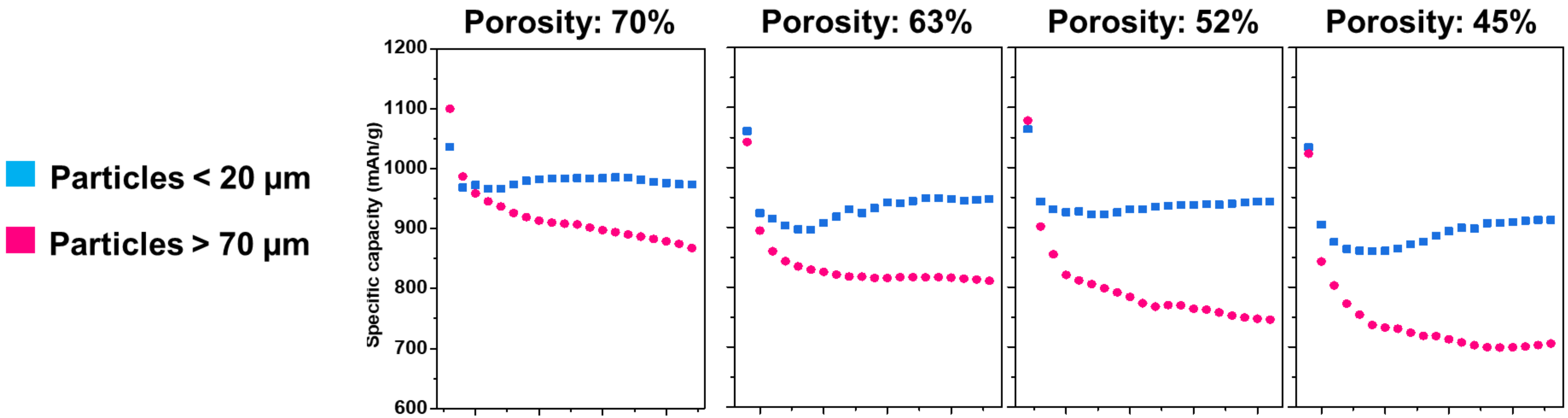
Technical Accomplishments

Effects of particle size on S reactions in the high-loading S electrodes at different porosities



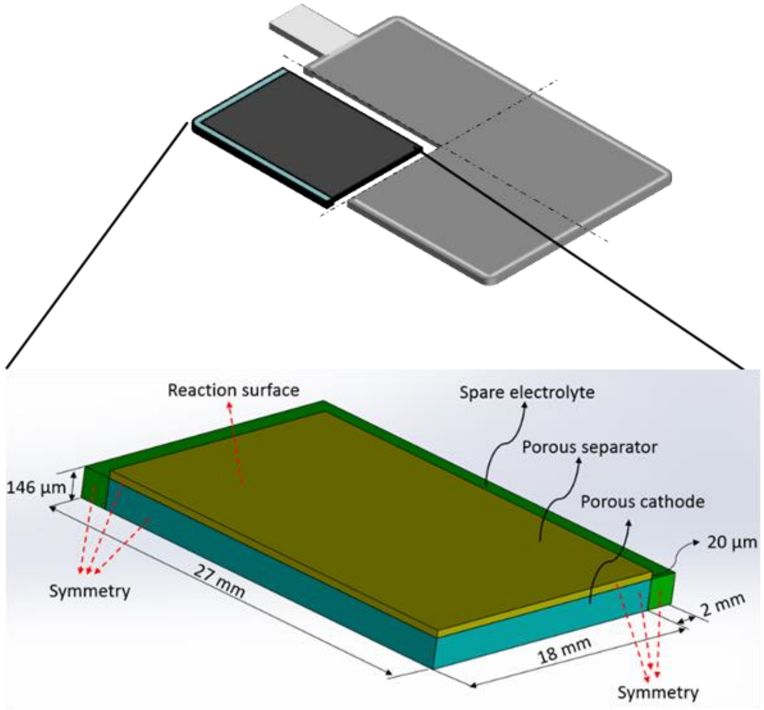
Cycling performance of IKB/S with small and large particles at different porosities

(Electrode: 4 mg$_s$/cm^2, Electrolyte/sulfur: 10 μL/mg$_s$, i=0.1C)

- The electrodes comprising large particles deliver both higher-specific capacities and better capacity retention compared to those with small particles.
- Particle size plays a more important role when electrode porosity is decreased.

Technical Accomplishments

Understanding reactions in large-size electrodes of pouch cells



Physical model of a large-sized, single-layer pouch cell

- A physical model of large-size pouch cell electrode (36mm × 54mm in dimension) was built for simulation.
- Chemical reactions between the electrolyte and Li anode occur and deplete the electrolyte.
- The reaction rate was estimated based on the cycle life of practical Li-S pouch cells.
- An effective diffusion coefficient D_e was adopted, considering the electrode porosity and tortuosity, and an electrolyte diffusion coefficient D_0.

In collaboration with Battery500 consortium and University of Michigan