PennState

Developing Materials for High-Energy-Density Solid-State Lithium-Sulfur Batteries

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The Pennsylvania State University

2021 DOE Annual Merit Review

Date: June 24, 2021

Project ID # bat487

Overview

Timeline

- Project start date: October 1st, 2019.
- Project end date: September 30th, 2022.
- Percent completed: 50%

Barriers

- **Barriers addressed**
  - Novel solid-state electrolytes with high ionic conductivity and good stability against lithium metal
  - Sulfur cathode with high energy density, high sulfur content and long cycle life (> 1000 cycles)

Budget

- Total project funding:
  - DOE share: $1M
  - Contractor share: $250K
- Funding for FY 2020: $416,022
- Funding for FY 2021: $412,367

Partners

- Project Lead: Pennsylvania State University
- University of Illinois at Chicago

Relevance

Overall Objective

- Develop new materials to enable lithium-sulfur all-solid-state batteries (Li-S ASSBs) with high energy density and excellent cycling stability and thus to build knowledge for fabrication of prototype Li-S ASSBs batteries.

Objective of FY 2020

- Acquire knowledge of Li-S ASSBs on both material level and electrode level.
- Identify materials suitable as conductive framework, solid state electrolyte and additives for Li-S ASSBs.
- Demonstrate sulfur cathode with >1000 mAh g^{-1} at 0.3 C for 50 cycles at 60°C
- Demonstrate new solid-state electrolyte with good ionic conductivity (> 2 mS cm^{-1}, at 25 ^{o}C).

Impact

- The DOE funding will make this innovative project possible and enable the team to demonstrate safe, low-cost, high-performance Li-S ASSBs. Meeting the technical targets will potentially promote the development of high-energy-density Li-S ASSBs and their practical application in EVs and PHEVs and reduce petroleum consumption in the transportation sector by helping battery-powered vehicles become more accepted by consumers as a reliable source of transportation.

Milestones

Milestones for FY 2021

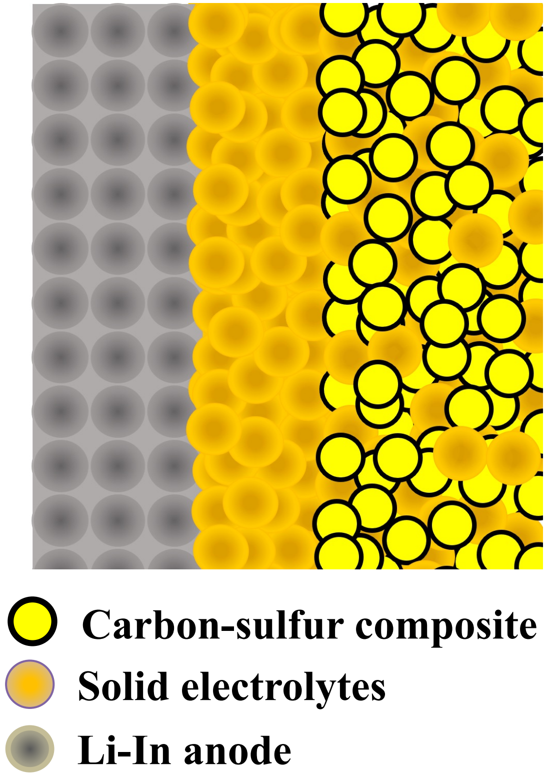
Date	Description	Status
Dec. 2020	Demonstrate sulfur cathode with > 1000 mAh g^{-1} capacity at 0.2 C at 60 ^{o}C.	Complete
Mar. 2021	Demonstrate new anion-doped electrolyte with ionic conductivity > 2 mS cm^{-1} at 25°C. Demonstrate sulfur cathode with > 1000 mAh g^{-1} at 0.3 C use solid additives for 50 cycles.	Complete
Jun. 2021	Demonstrate sulfur cathode with > 1000 mAh g^{-1} at 0.3 C for 50 cycles at 60 ^{o}C using hybrid conductive materials.	In progress
Sep. 2021	Demonstrate sulfur cathode with > 1000 mAh g^{-1} at 0.1 C for 100 cycles at room temperature. (Go/No Go for FY 2021) Demonstrate anion-doped solid electrolytes with ionic conductivity > 3 mS cm^{-1} at 25 ^{o}C.	In progress

Milestones for FY 2022

Date	Description	Status
Dec. 2021	Demonstrate sulfur cathode (≥ 5 mg cm^{-2}) with > 1000 mAh g^{-1} at 0.1 C for 10 cycles at room temperature.	In progress
Mar. 2022	Demonstrate new cation and anion co-doped solid electrolytes with ionic conductivity of above 3 mS cm^{-1}.	In progress
Jun. 2022	Demonstrate sulfur cathode (≥ 5 mg cm^{-2}) with > 1000 mAh g^{-1} at 0.3 C for 50 cycles at room temperature.	In progress
Sep. 2022	Demonstrate sulfur cathode (≥ 5 mg cm^{-2}) with > 1200 mAh g^{-1} at 0.3 C for 500 cycles at room temperature. Demonstrate new cation and anion co-doped solid electrolytes with ionic conductivity of above 5 mS cm^{-1} and improved moisture stability.	In progress

Approach

Solid-State Li-S Batteries



Novel solid-state electrolytes (SSEs)

- Synthesis approaches
  - ✓ Solid-phase method
  - ✓ Liquid-phase method
- Targets
  - ✓ Superior ionic conductivity (> 3 mS cm^{-1} at room temperature)
  - ✓ Stable against lithium (low interfacial resistance)

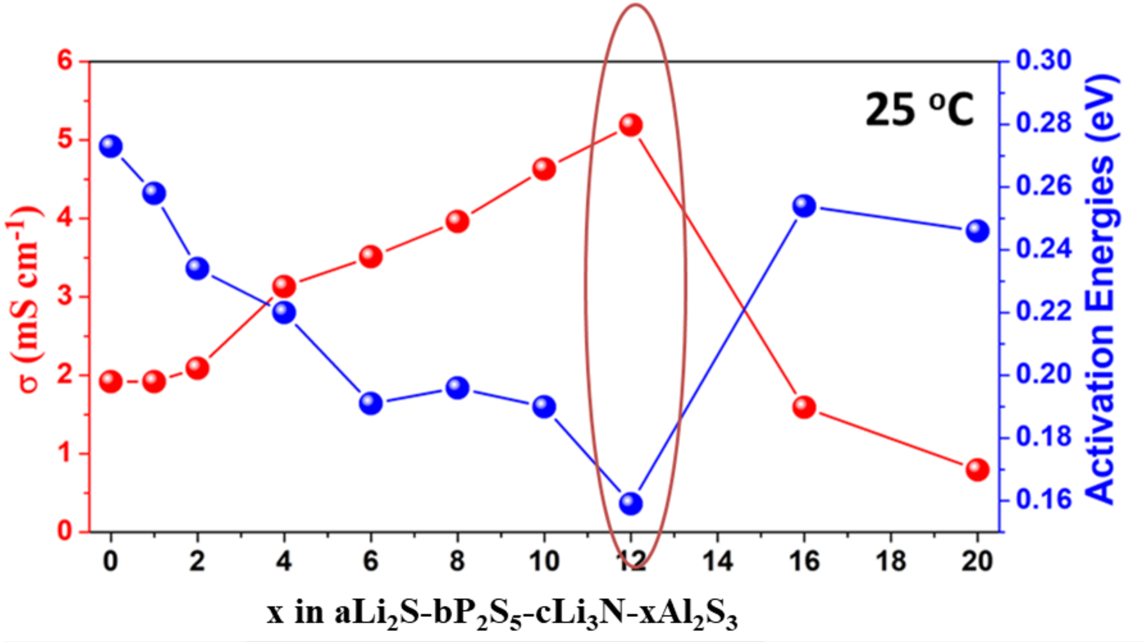
High-energy-density sulfur cathode

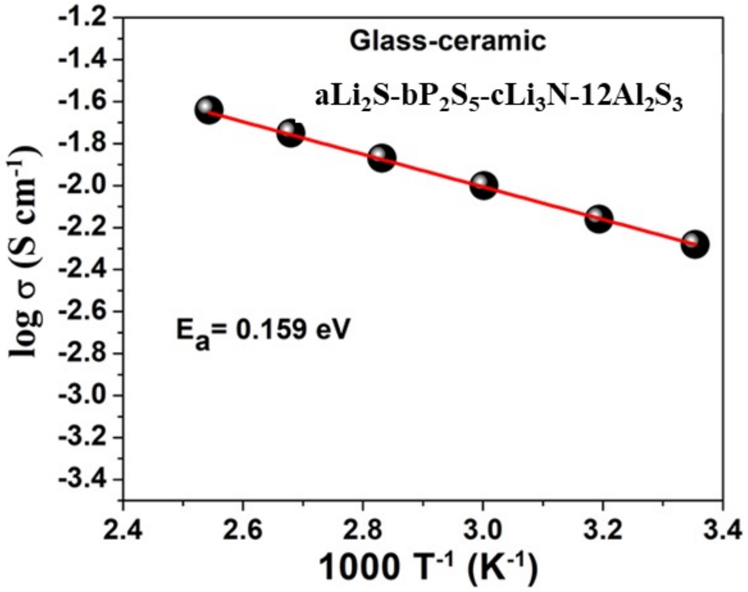
- Rational design and development of cathode components (sulfur, carbon & SSE)
  - ✓ High sulfur content (≥ 50 wt%)
  - ✓ Low carbon content (≤ 20 wt%)

Technical Accomplishments – Glass-Ceramic SSEs

Glass-ceramic solid electrolytes aLi_2S-bP_2S_5-cLi_3N-xAl_2S_3

- Highest ionic conductivity was achieved at $x = 12$ (SSE-1).
  - ✓ **5.19 mS cm^{-1}, at 25 ^{o}C**
- Low activation energy of 0.159 eV.

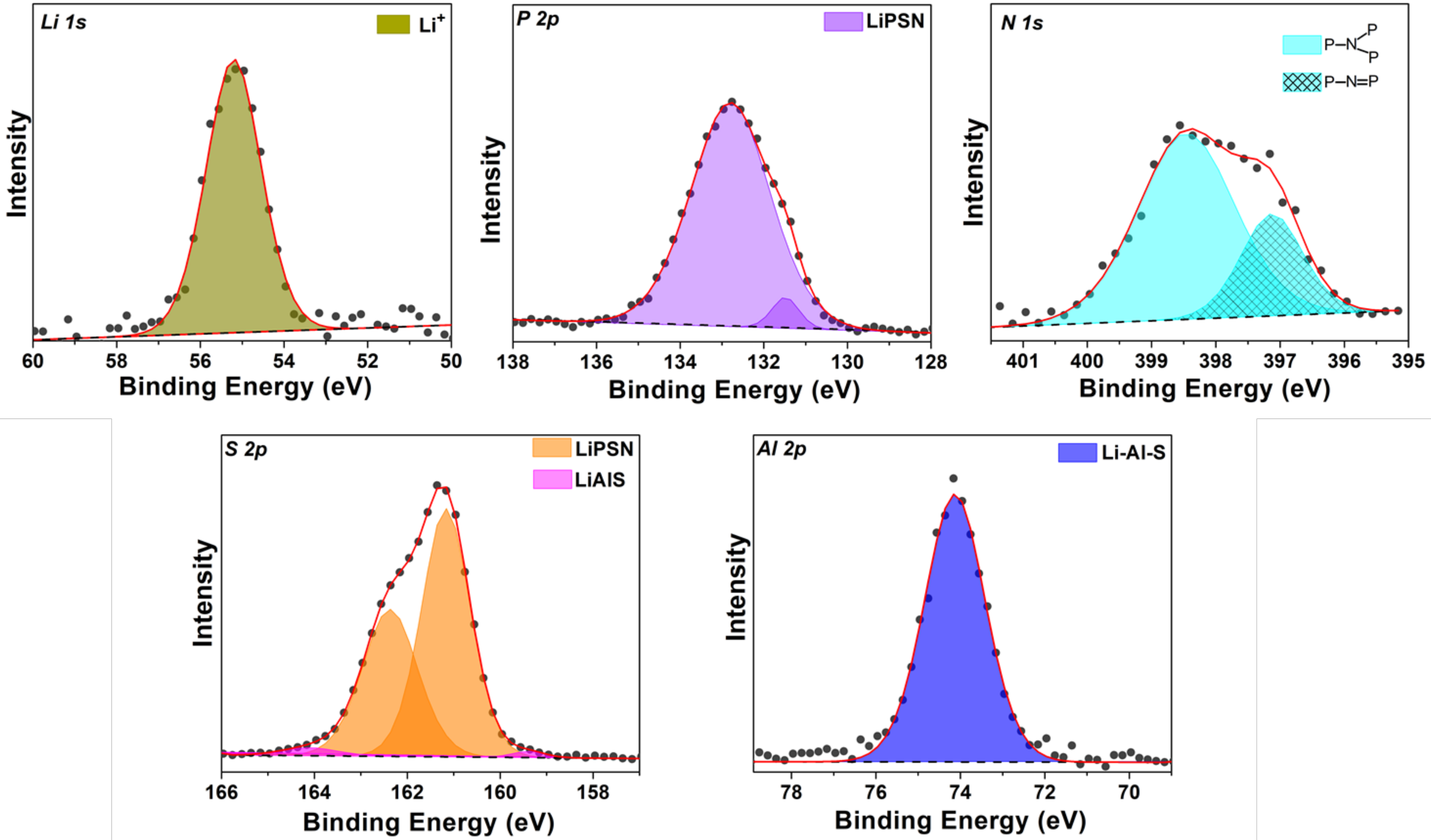




Technical Accomplishments – Glass-Ceramic SSE-1

Chemical environment of aLi_2S-bP_2S_5-cLi_3N-$12Al_2S_3$ (SSE-1)

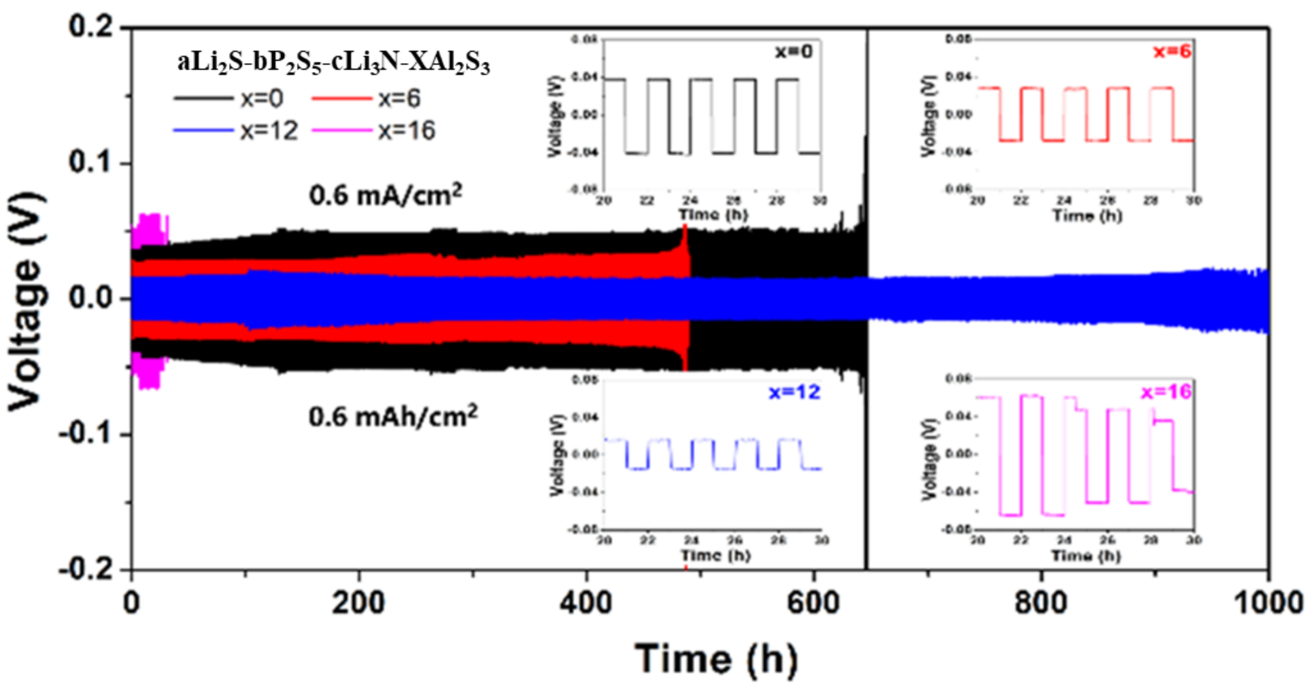
- Formation of P-N, P=N, and Li-Al-S bonds.

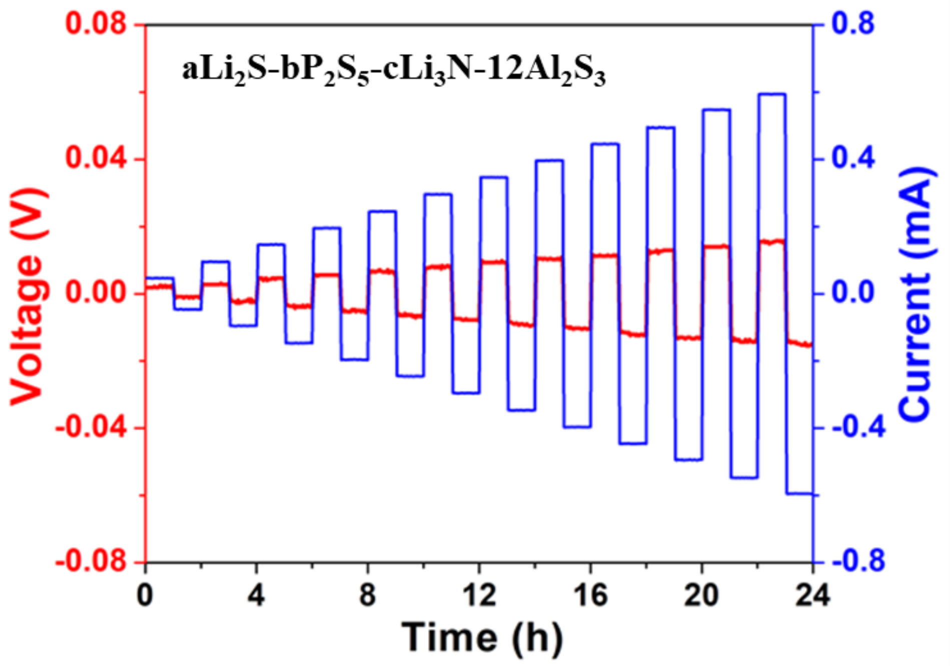


Technical Accomplishments – Glass-Ceramic SSE-1

Stability against lithium metal anode - Li/SSE/Li symmetric cell

- Compared with other composition, SSE-1 demonstrated best stability against lithium and lowest interfacial resistance.
- Over 1000 hours stable cycling was enabled.
- At 0.6 mA cm^{-2}, polarization resistance (R_p) is merely 25 Ω cm^2

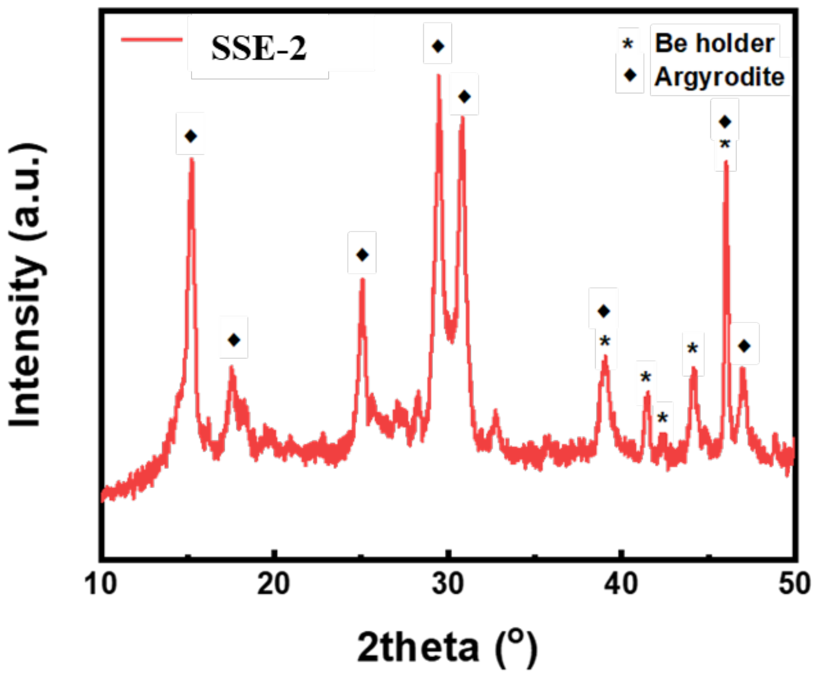


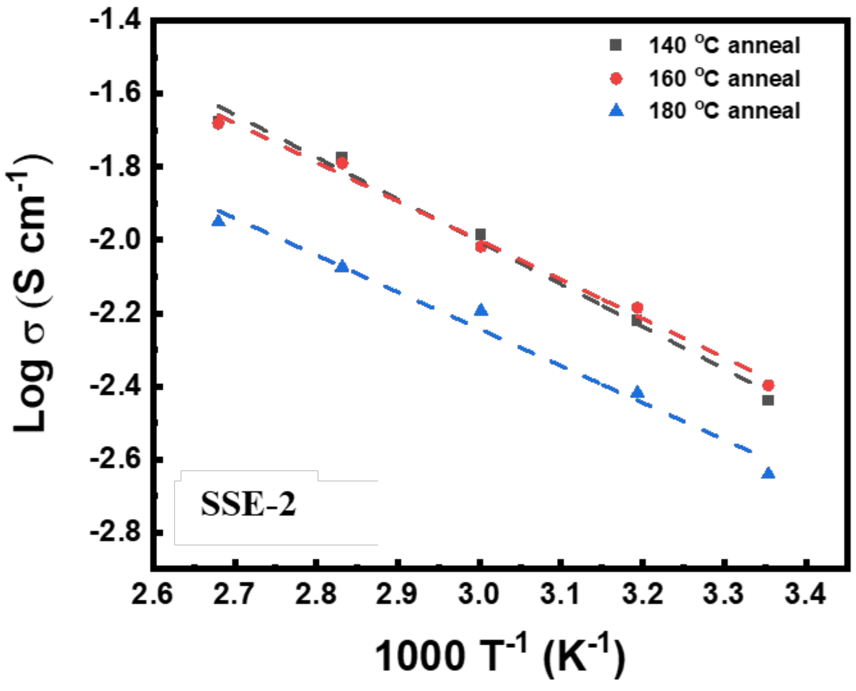


Technical Accomplishments – Liquid-Phase Synthesis of SSE-2

Liquid-phase synthesis of argyrodite thiophosphate solid electrolyte (SSE-2)

- Facile and scalable approach
- Low sintering temperature of 160 °C
- Argyrodite structure
- High ionic conductivity of **4.01 mS cm^{-1}** at 25 °C

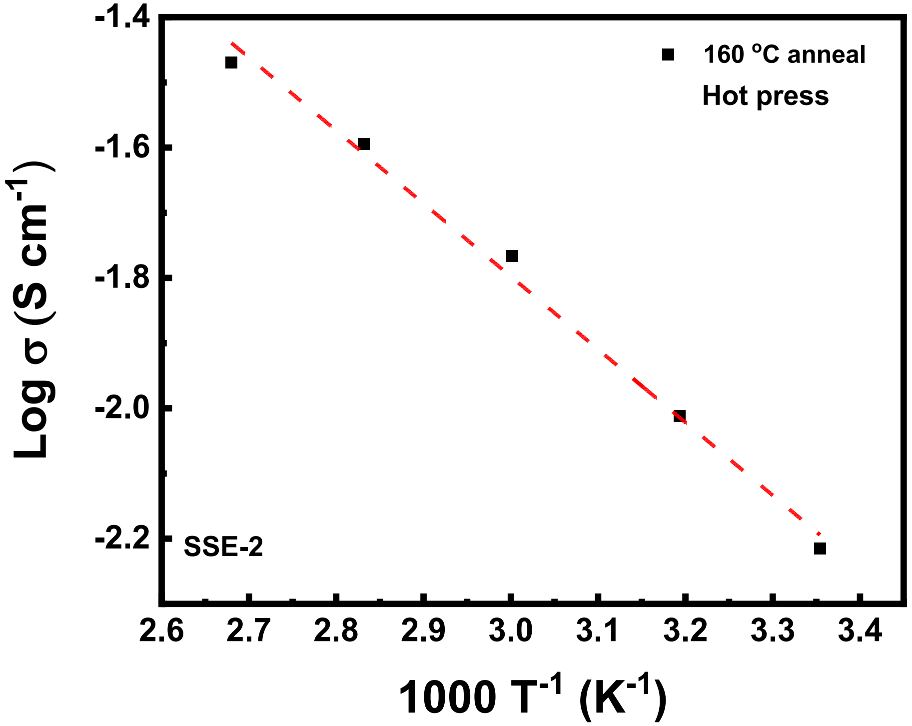


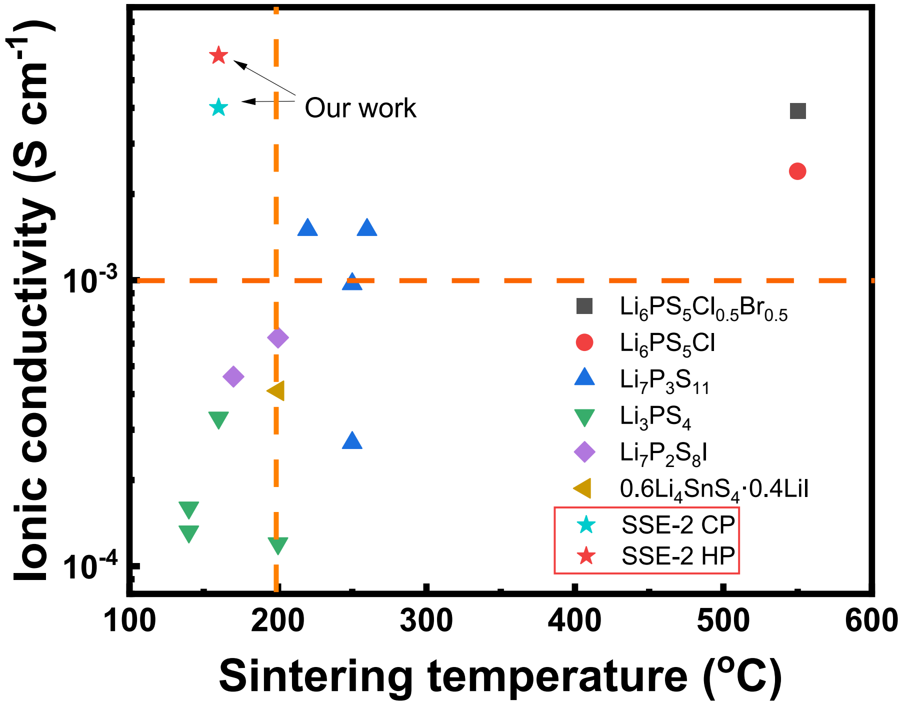


Technical Accomplishments – Liquid-Phase Synthesis of SSE-2

Hot pellet press

- High ionic conductivity **6.09 mS cm^{-1}** at 25 ^{o}C
- Low activation energy: 0.222 eV

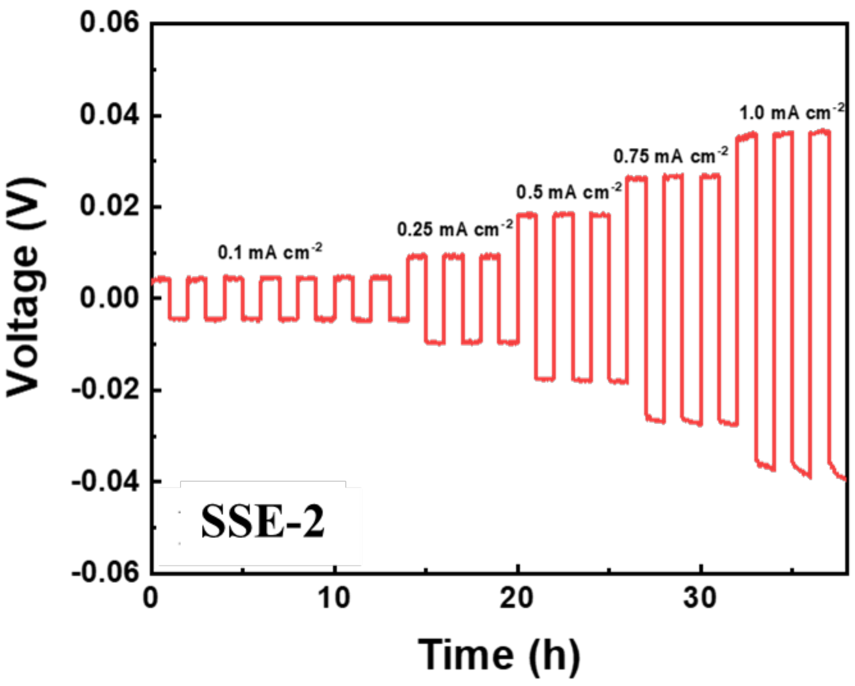


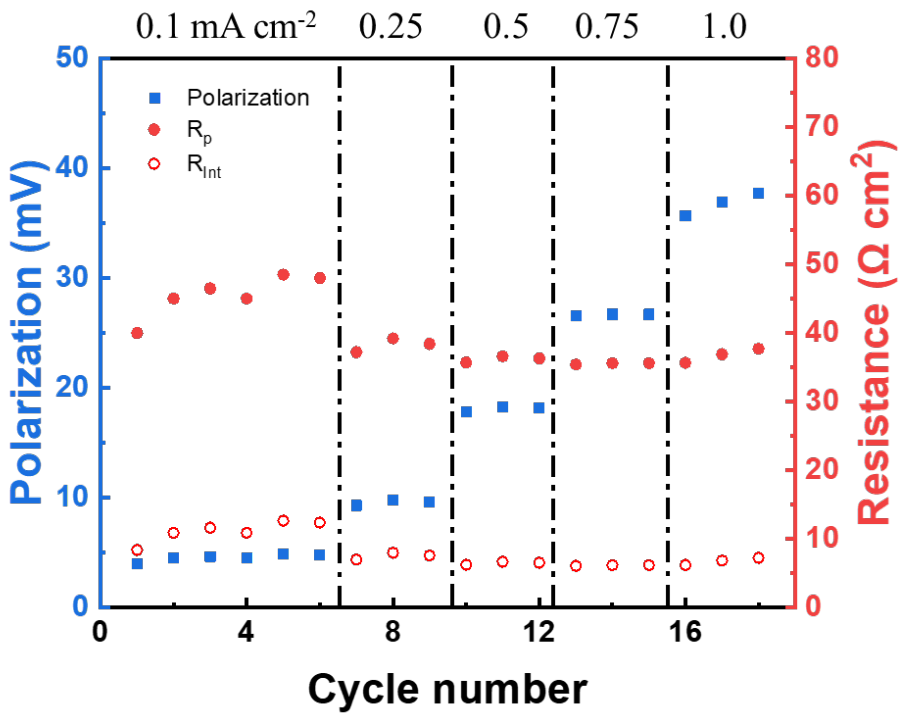


Technical Accomplishments – Liquid-Phase Synthesis of SSE-2

Stability against lithium metal anode - Li/SSE-2/Li cell

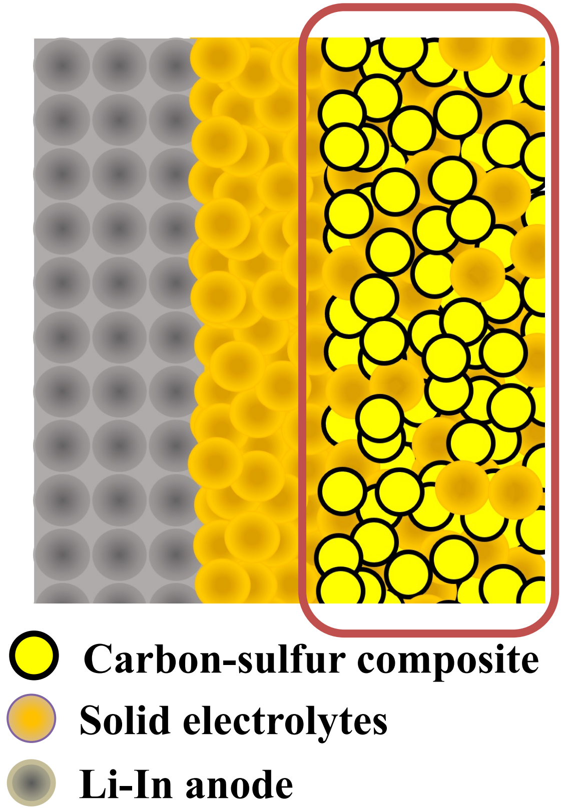
- Stable against lithium metal anode
- Low areal interfacial resistance at around 6 ~ 7 Ω cm^2





Technical Accomplishments – Sulfur Cathode

Solid-State Li-S Batteries



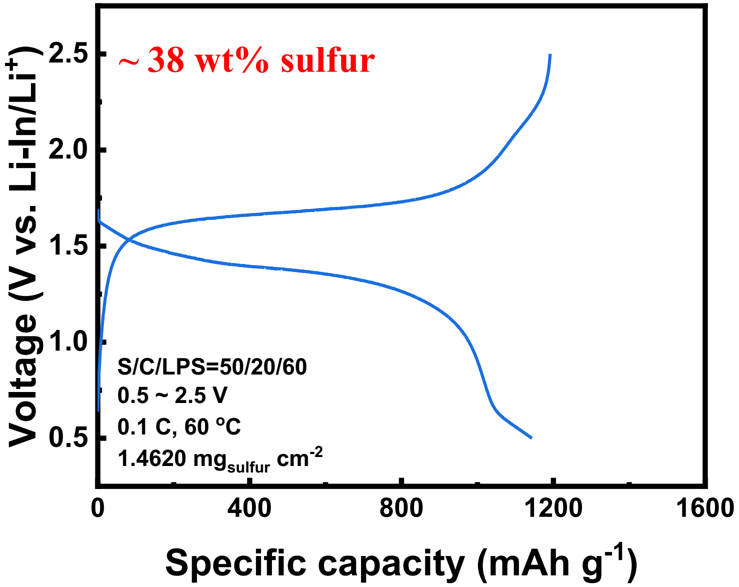
Achieving high-energy-density sulfur cathode

1. Increase sulfur content (≥ 50 wt%) & decrease carbon content (≤ 20 wt%)
2. Increase sulfur utilization (specific capacity of sulfur)

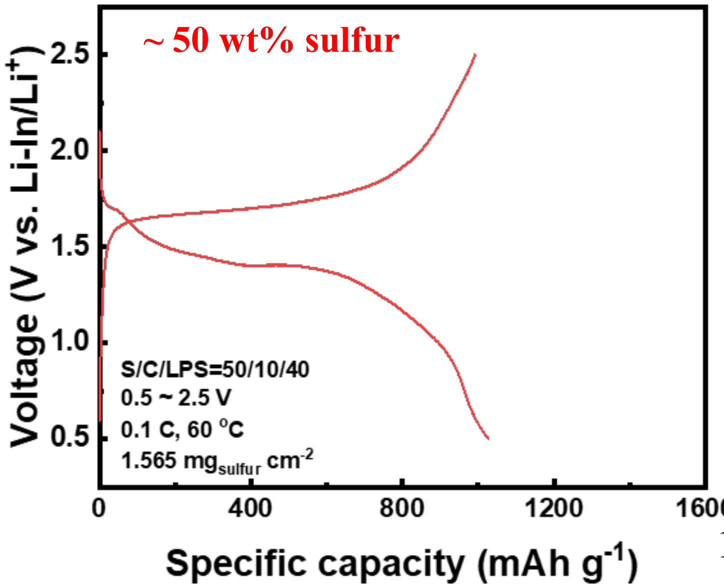
Sulfur cathode performance – baseline cell optimization

$75Li_2S{\cdot}25P_2S_5$ glass (LPS)

- Optimization of cathode compositions, preparation procedures, etc.
- Sulfur cathode (50 wt% sulfur & 10 wt% carbon) with ~ 1000 mAh g^{-1} specific capacity.



Optimization

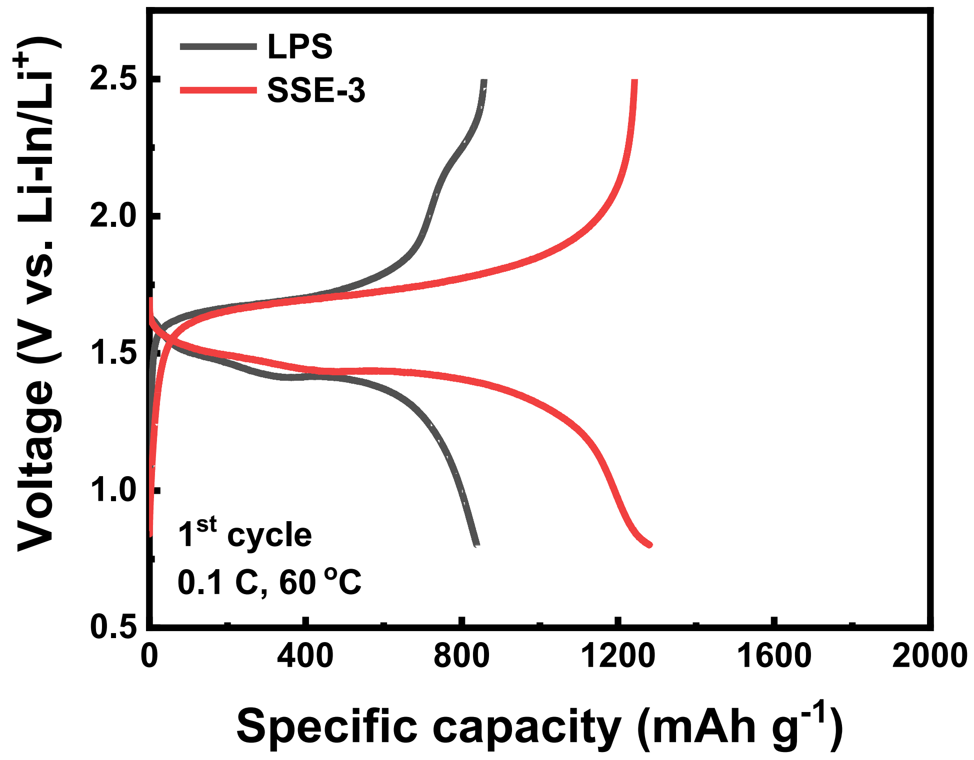


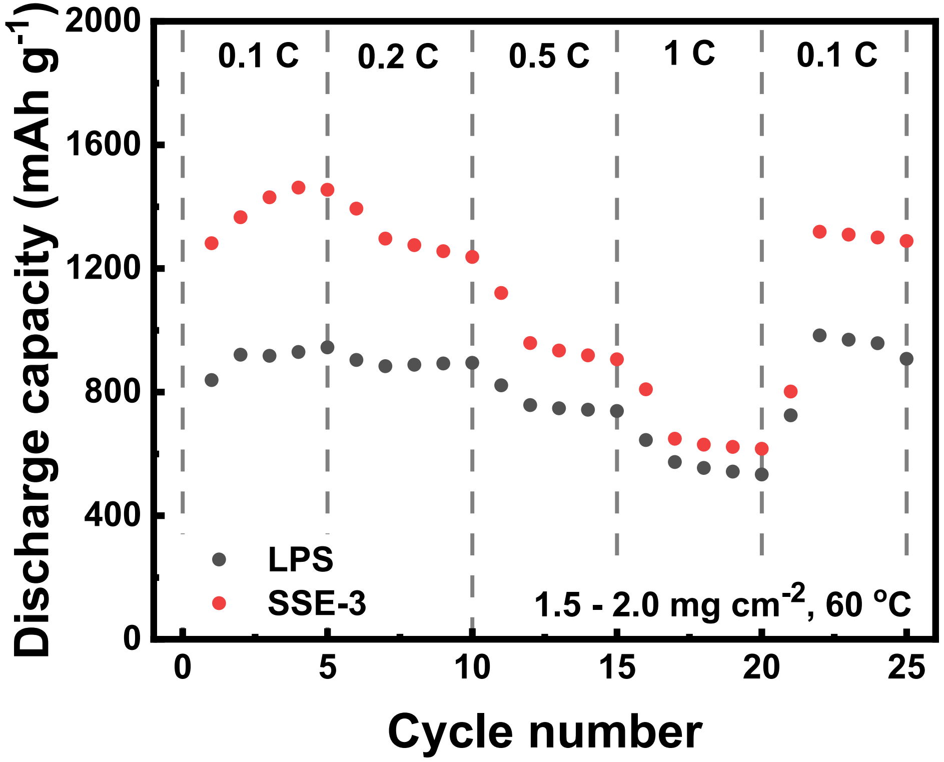
Technical Accomplishments – High-Energy Sulfur Cathode

Sulfur cathode:

1. Carbon/Sulfur/Solid electrolyte = 10/50/40 (weight ratio), 1.5 ~ 2.0 mg_{sulfur} cm^{-2} loading
2. Two different solid electrolytes were compared: $75Li_2S{\cdot}25P_2S_5$ (LPS) and SSE-3

Electrochemical window: 0.8 ~ 2.5 V vs. Li-In/Li^+



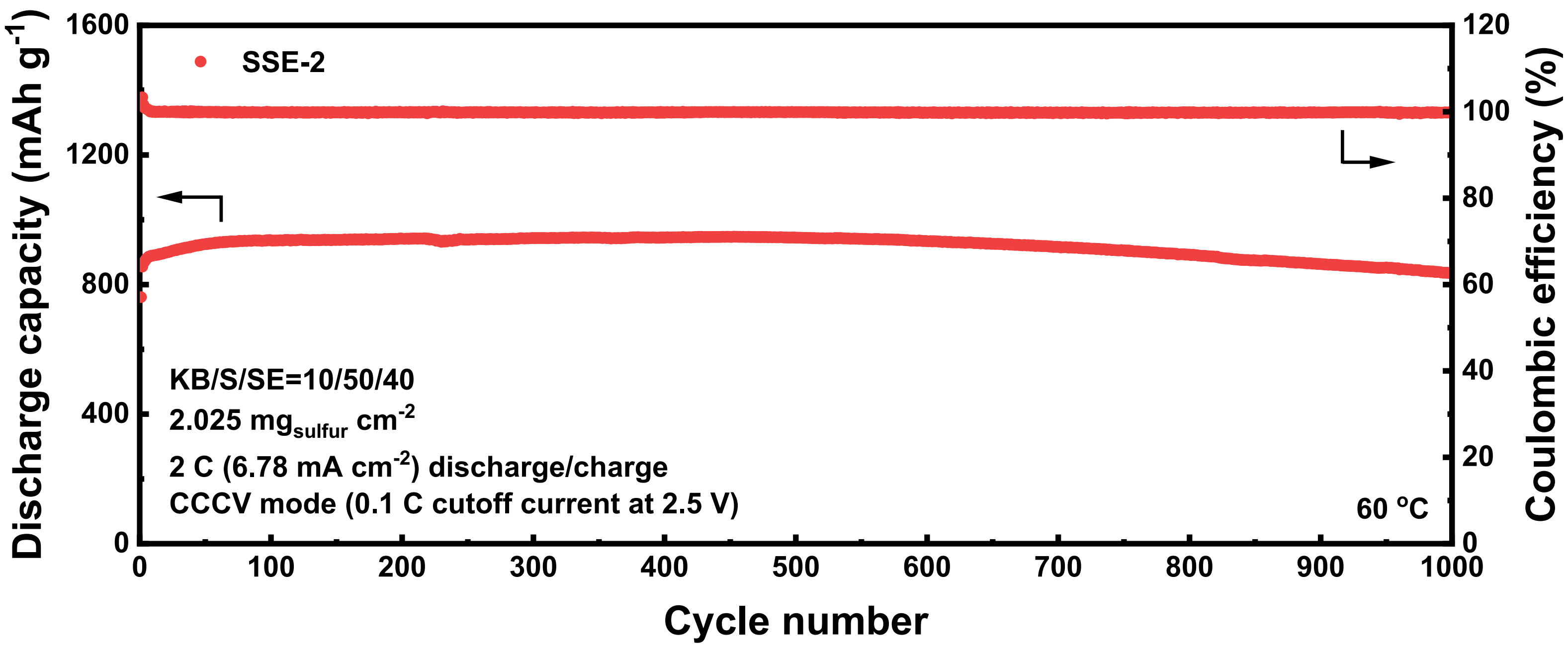


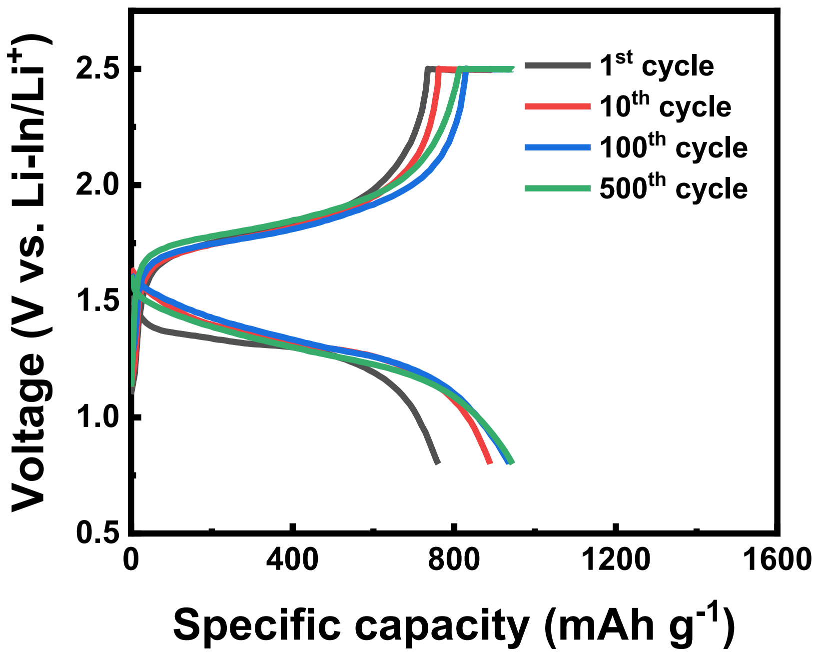
Technical Accomplishments – High-Energy Sulfur Cathode

Electrochemical testing at 2 C (CCCV mode, cutoff current is 0.1 C at 2.5 V)

Capacity retention after 1000 cycles:

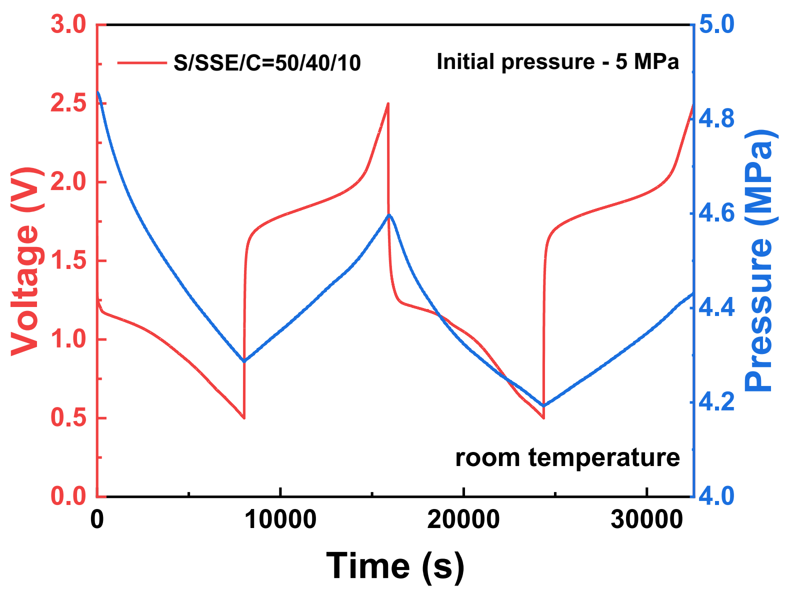
- **88.07 % (based on highest discharge capacity 947.5 mAh g^{-1})**
- **97.57% (based on 2^{nd} cycle discharge capacity 855.3 mAh g^{-1})**





Technical Accomplishments – Mechano-Electrochemical Property

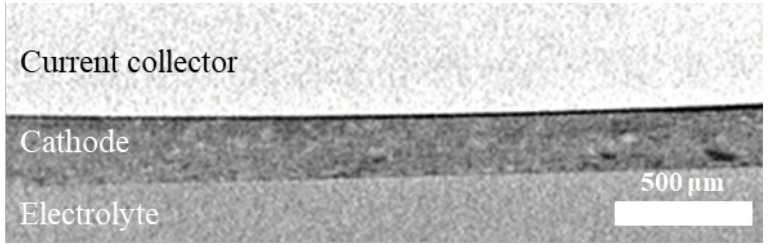
In-situ pressure monitoring



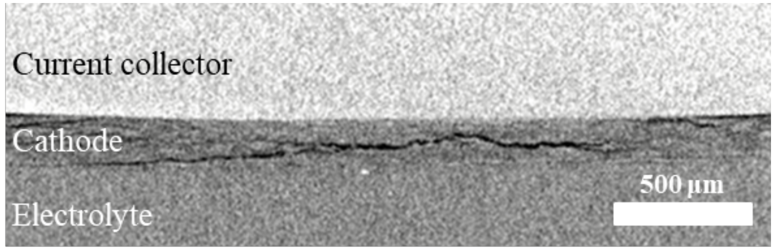
Volume change on both anode and cathode should be characterized to illustrate the pressure variation and crack formation.

X-Ray CT Characterization

After discharge
Cathode Thickness
~ 180 µm



After charge
Cathode Thickness
~ 140 µm



Generation of cracks in the cathode after charge

Discharge →

Specific Volume 0.50 $cm^3/g\ S_8$ | $16Li + S_8 \leftrightarrow Li_2S_n \leftrightarrow 8Li_2S$ | Specific Volume 0.60 $cm^3/g\ Li_2S$

← Charge

Response to Previous Year Reviewer's Comment

This project was not reviewed last year.

Remaining Challenges

- **The moisture stability of lithium thiophosphate solid-state electrolyte is still not satisfactory.**

- **The cycling stability issue of sulfur cathode at high areal sulfur loading (≥ 5 mg_{sulfur} cm^{-2}) need to be resolved.**

- **Achieving the superior performance of sulfur cathode at room temperature.**

Proposed Future Research

- **Development of new SSEs as electrolyte membrane**
  - High ionic conductivity (> 5 mS cm^{-1} at 25 ^{o}C) and good stability against lithium metal anode
  - Improved moisture stability
- **Development of new carbon materials, solid additives and SSEs for sulfur cathode**
  - Electrochemical performance at room temperature (> 1000 mAh g^{-1} at 0.1 C for 100 cycles)
  - High-areal-loading sulfur cathode (≥ 5 mg_{sulfur} cm^{-2}, > 1000 mAh g^{-1} at 0.1 C)
- **In-depth characterization of Li-S ASSBs**
  - X-ray CT characterization

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

Summary

- **Development of new solid-state electrolytes**
  - Two new thiophosphate solid electrolytes were successfully synthesized
    - Solid-phase synthesis & liquid-phase synthesis
    - High ionic conductivity > 4 mS cm^{-1} at 25 ^{o}C
    - Superior stability against lithium metal anode
- **Development of new carbon materials and solid-state electrolytes for high-energy sulfur cathode**
  - Cathode composition & preparation process optimization
  - Solid electrolytes design & development for sulfur cathode
    - 50 wt% sulfur content, 10 wt% carbon content
    - High sulfur utilization (~ 1400 mAh g^{-1} at 0.1 C)
    - Stable cycling for 1000 cycles at 2 C (800 ~ 950 mAh g^{-1})

Acknowledgement

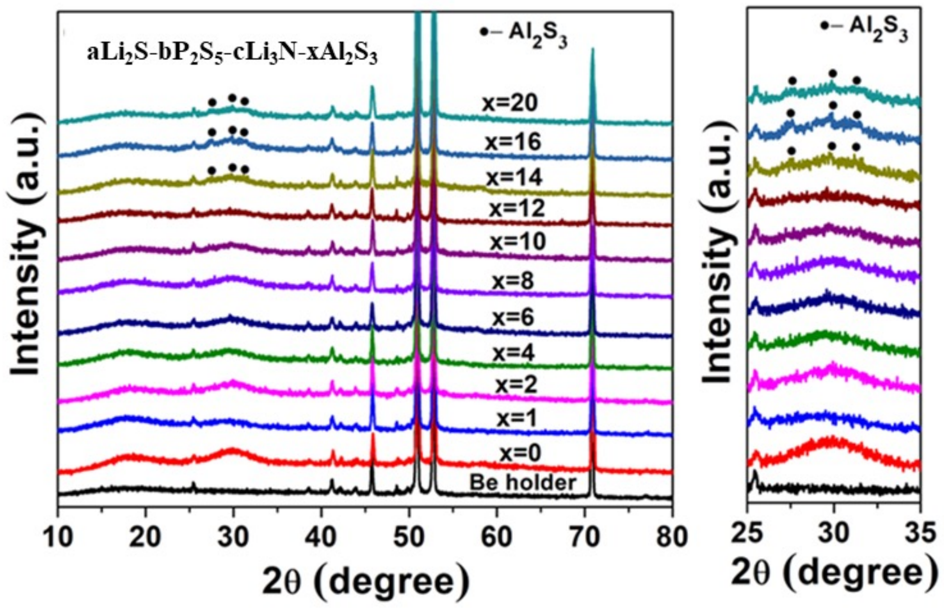
**Support from David Howell and Tien Duong
at the US Department of Energy's Office of Vehicle Technologies
is greatly appreciated.**

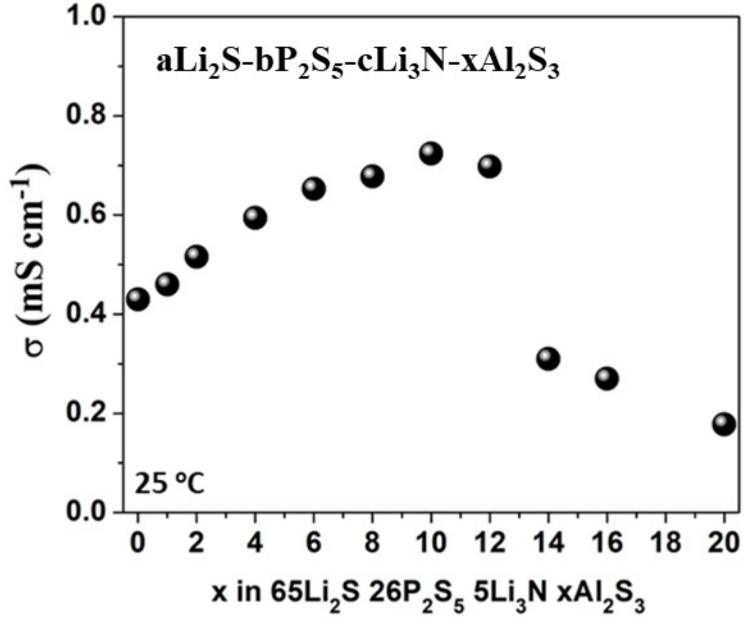
Technical Back-Up Slides

Technical Back-Up Slides

Glass-type solid electrolytes aLi_2S-bP_2S_5-cLi_3N-xAl_2S_3

- Solid-phase synthesis
- When $x \geq 14$, residual Al_2S_3 was observed in solid electrolyte glass and will lead to low ionic conductivity
- Highest ionic conductivity was achieved at $x = 10$ at room temperature (0.71 mS cm^{-1})

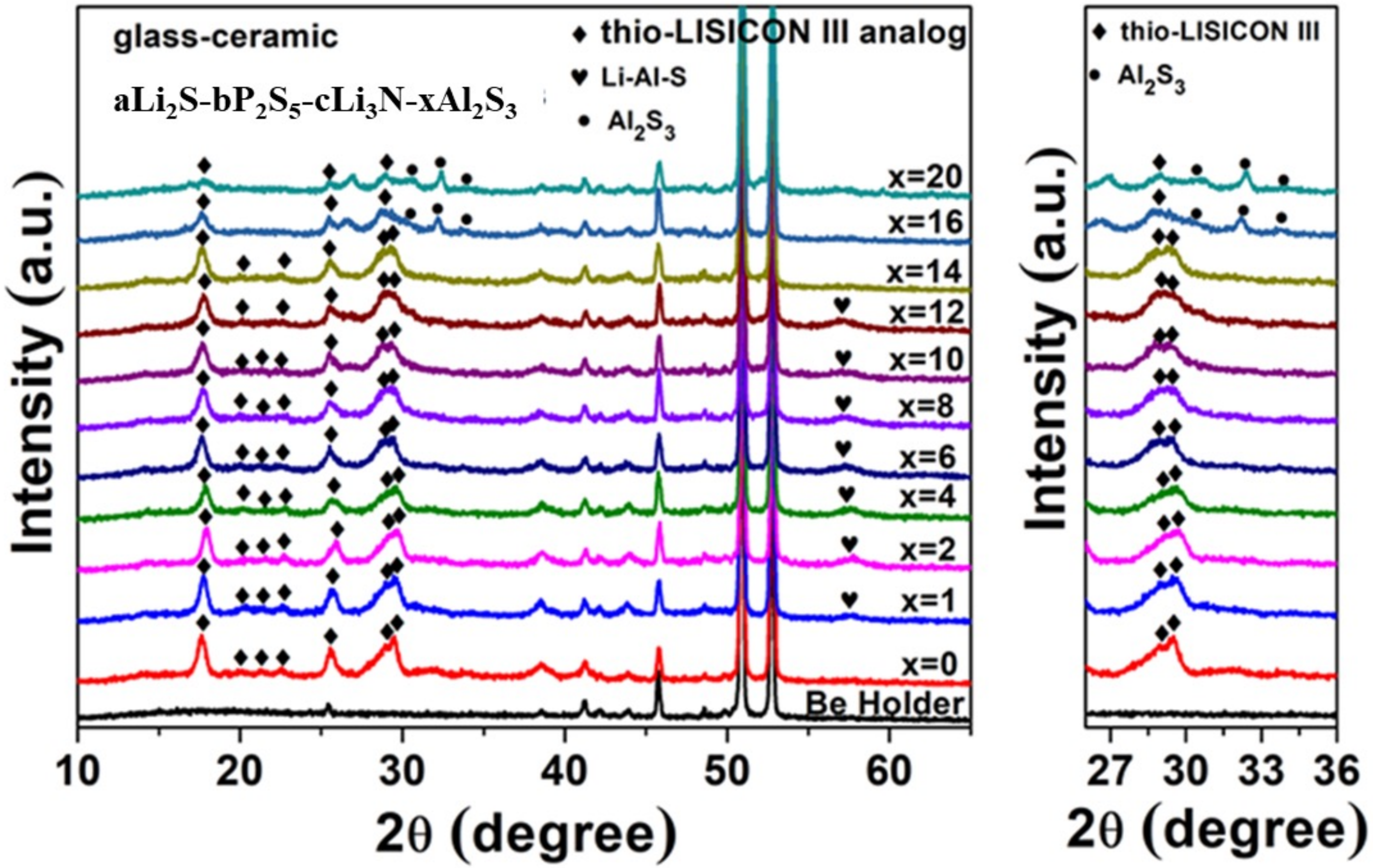




Technical Back-Up Slides

Glass-ceramic solid electrolytes $aLi_2S\text{-}bP_2S_5\text{-}cLi_3N\text{-}xAl_2S_3$

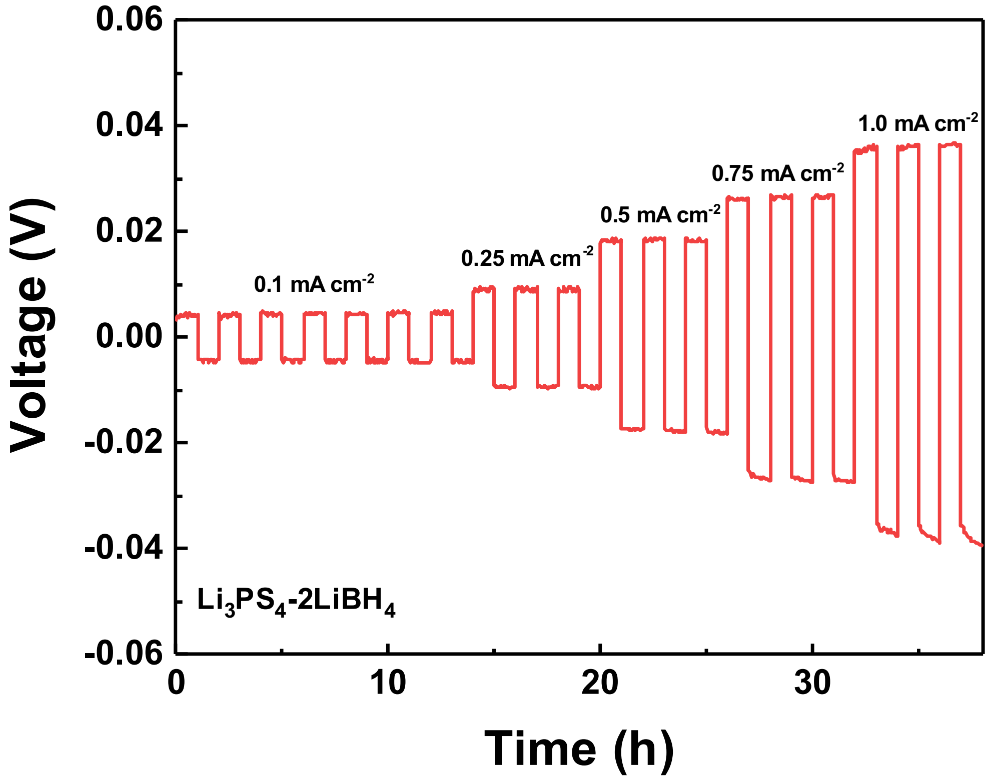
- The thio-LISICON III analog phase formation were observed.



Technical Back-Up Slides

Calculation of polarization resistance & interfacial resistance (SSE-2)

Li vs. Li symmetric cell (cycled at 6 ~ 8 MPa)



$$R_p = \frac{U}{I} = R_{bulk} + 2R_{int}$$

$$R_{bulk} = \frac{l}{\sigma S}$$

R_p, polarization resistance
R_{bulk}, bulk resistance from electrolyte pellet
R_{int}, interfacial resistance (lithium/SE)
l, pellet thickness