Improving Cell-Level Specific Energy for All-Solid-State Lithium Sulfur Batteries

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243rd Electrochemical Society (ECS) Meeting

June 1, 2023
Boston, MA

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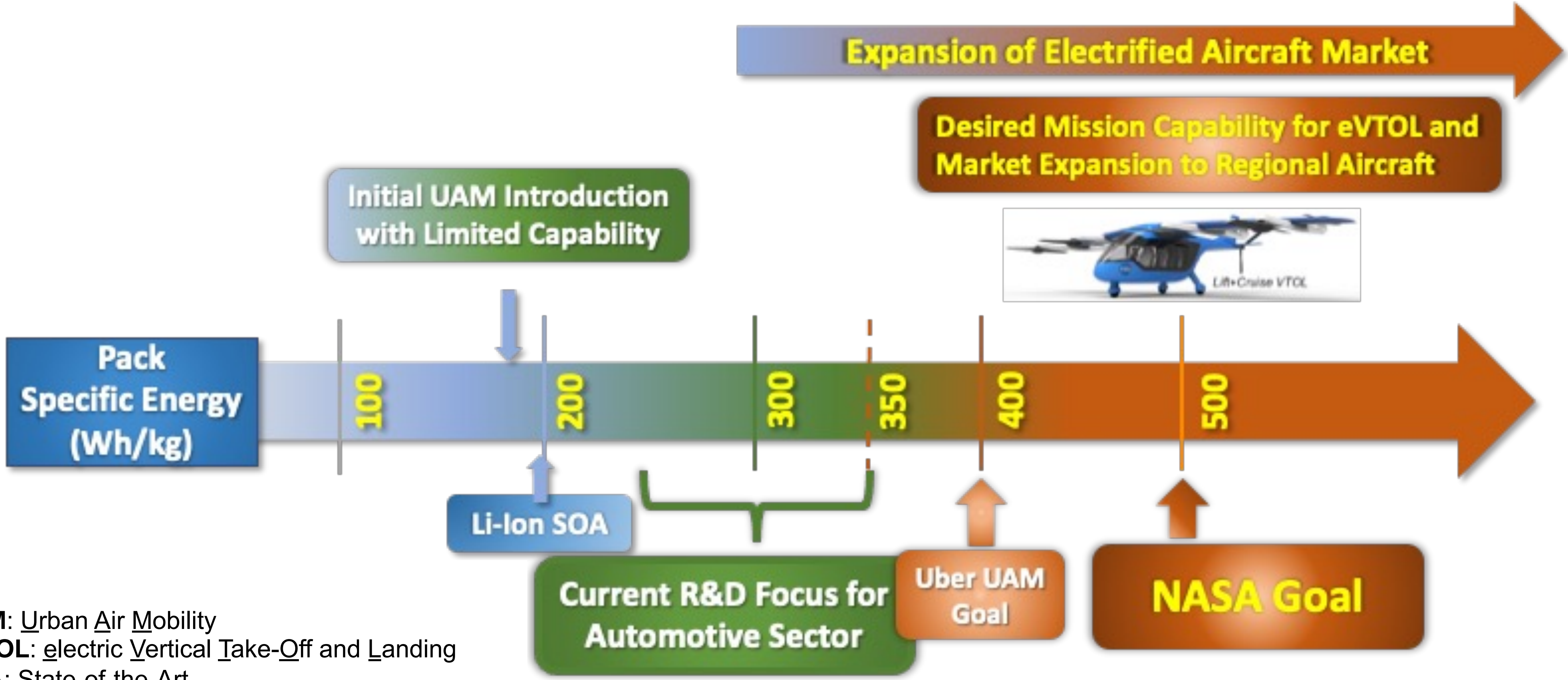
Why is NASA Interested in Solid-State Batteries?



Expansion of Electrified Aircraft Market

Desired Mission Capability for eVTOL and Market Expansion to Regional Aircraft

Initial UAM Introduction with Limited Capability

Pack Specific Energy (Wh/kg)

Li-Ion SOA

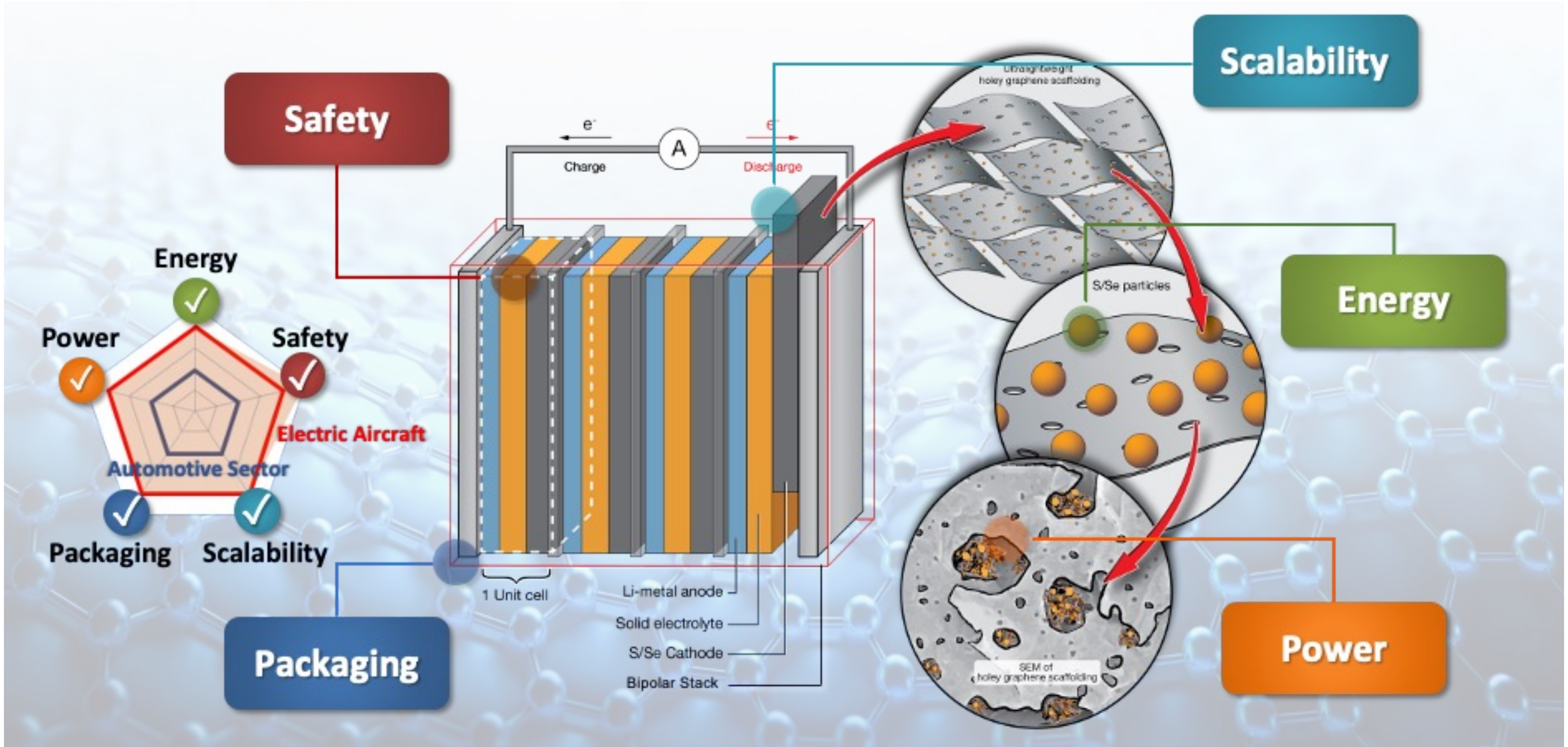
Current R&D Focus for Automotive Sector

Uber UAM Goal

NASA Goal

UAM: Urban Air Mobility
eVTOL: electric Vertical Take-Off and Landing
SOA: State-of-the-Art
R&D: Research & Development

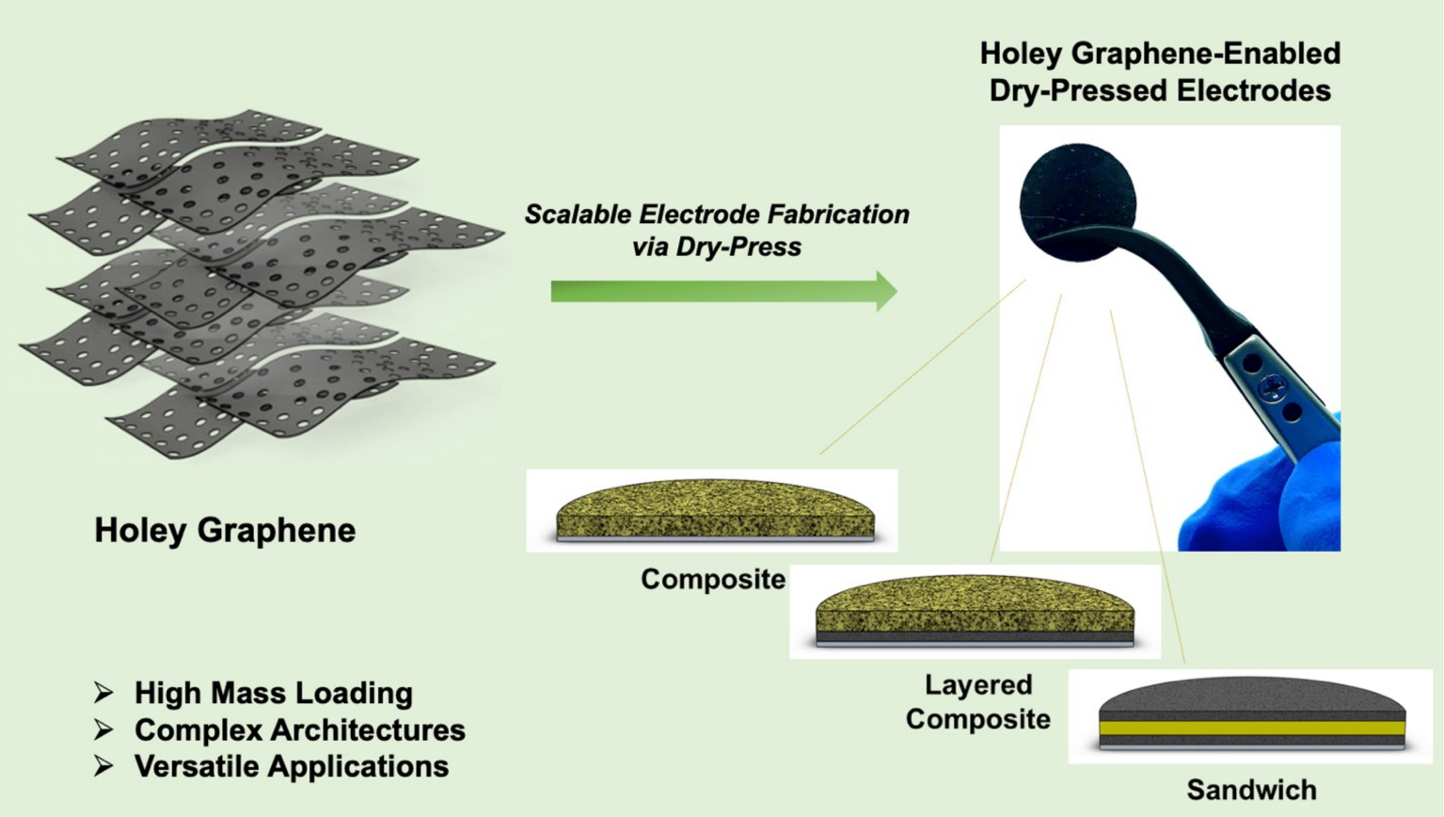
Why is NASA Interested in Solid-State Batteries?



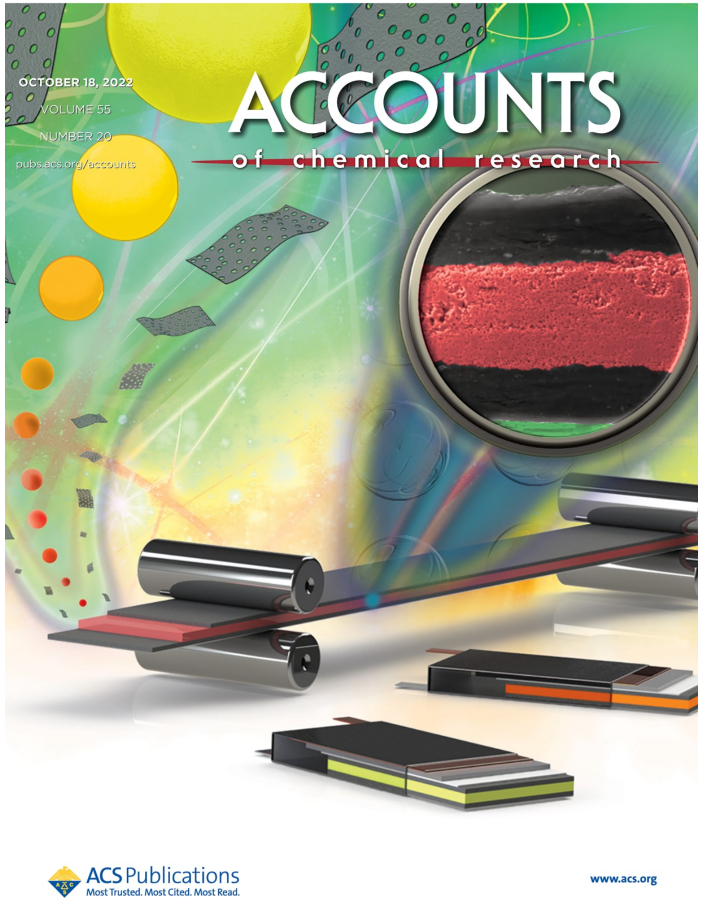
Combination of unique materials technologies to achieve performance goals

SABERS: Solid-state Architecture Batteries for Enhanced Rechargeability and Safety

Dry-Pressed Electrodes Enabled by Holey Graphene

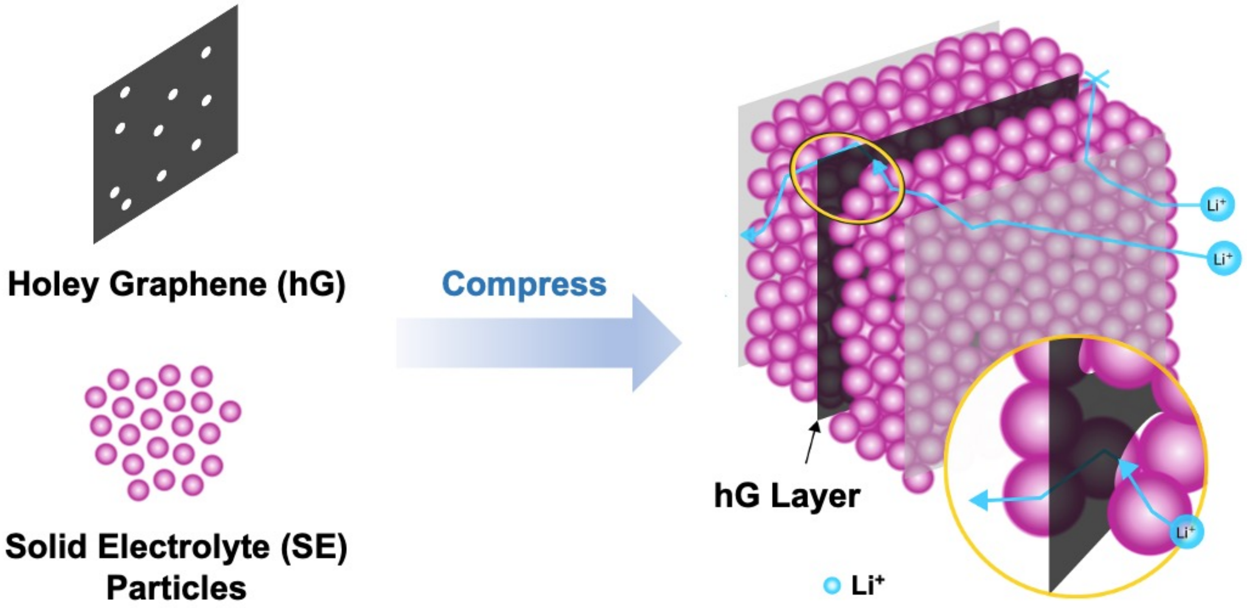


- High Mass Loading
- Complex Architectures
- Versatile Applications



Acc. Chem. Res. **2022**, *55*, 3020-3031.

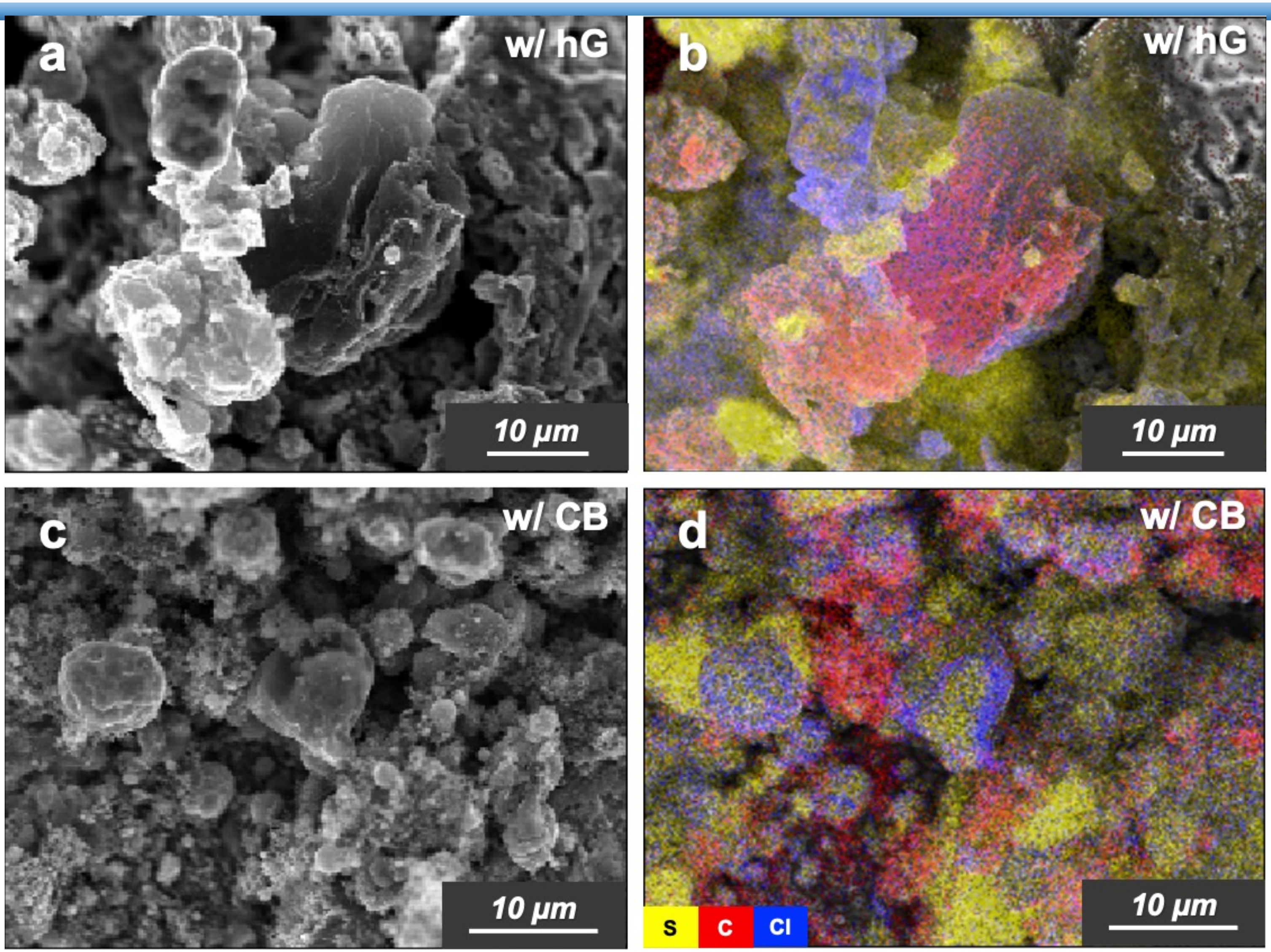
Li Ion Conductivity through hG Sheets



- ☐ Li ion can conduct through the thickness of holey graphene (hG) – as long as the holes are at least 25% in size of the solid-state electrolyte particles.

ACS Appl. Mater. & Interfaces **2022**, *14*, 21363-21370.

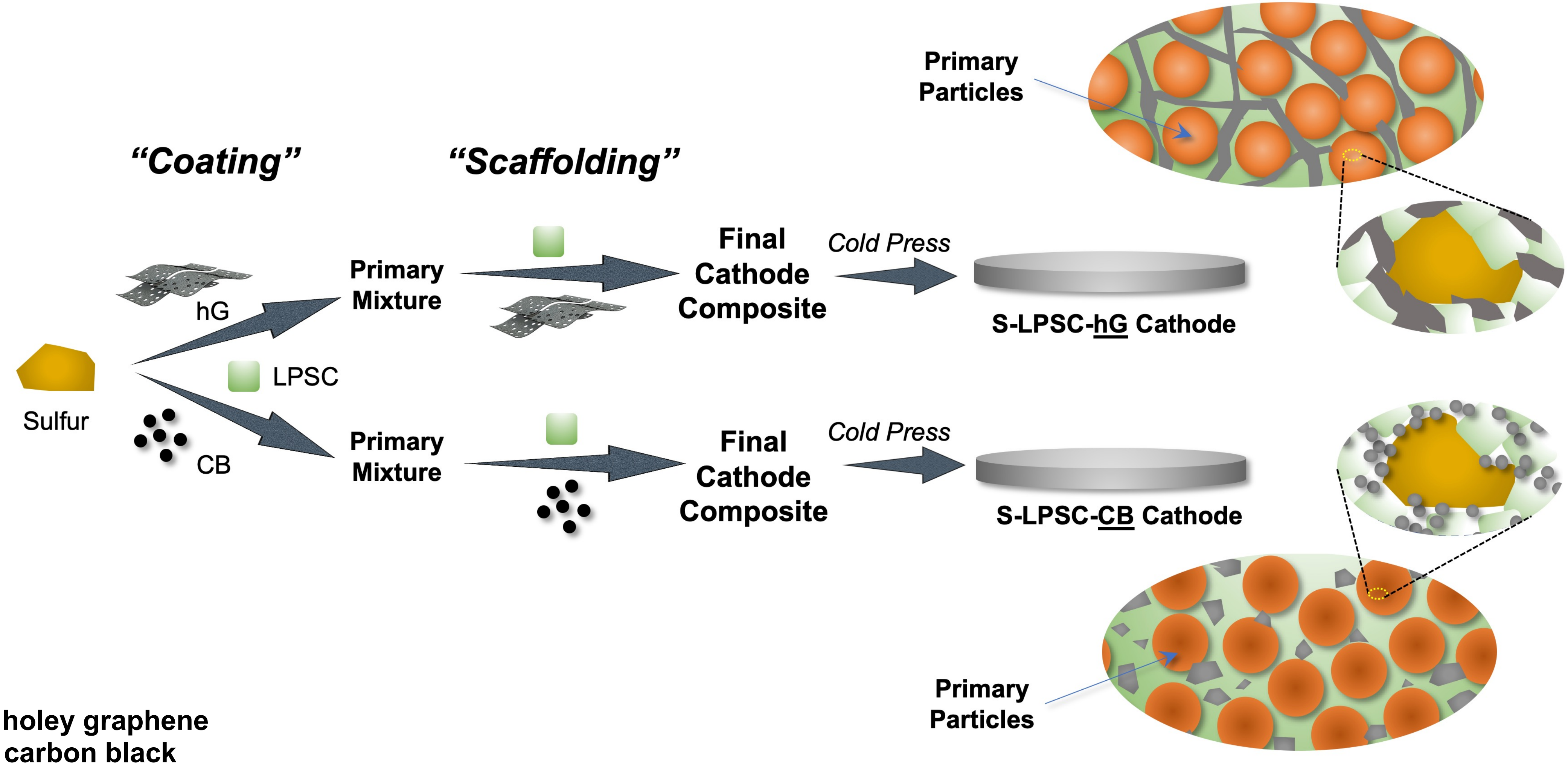
Composite Solid-State Cathode Powder



- ☐ Active material: **S**
- ☐ Solid electrolyte (SE): **Li_6PS_5Cl (LPSC)**
- ☐ Carbon: **CB (carbon black) vs hG (holey graphene)**

CB: Super C45

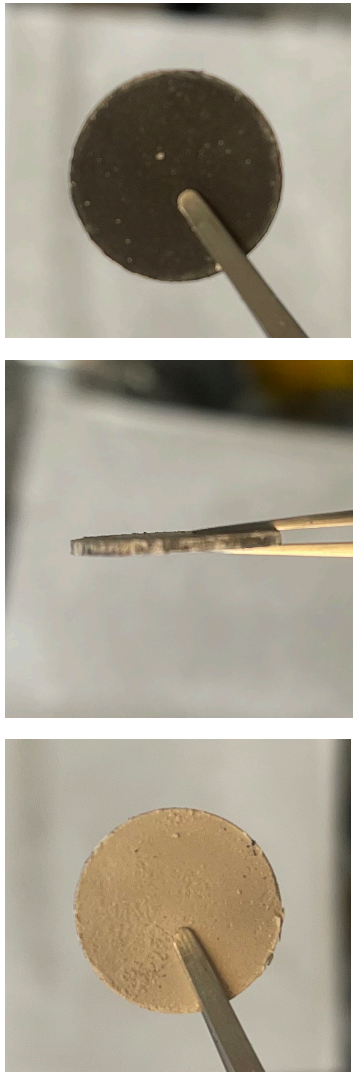
All-Solid-State S Cathodes



- ❑ **hG: holey graphene**
- ❑ **CB: carbon black**

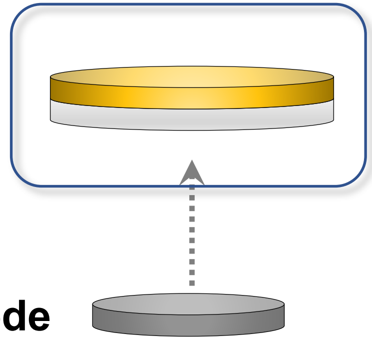
Dry-Pressed Cathode/SE Bilayer Discs

CB



hG

- ☐ Both composites are compressible to form robust cathode/SE bilayer discs
- ☐ LPSC glass electrolyte serves as binder
- ☐ hG as "cold pressable hosts" is not an obvious advantage…?

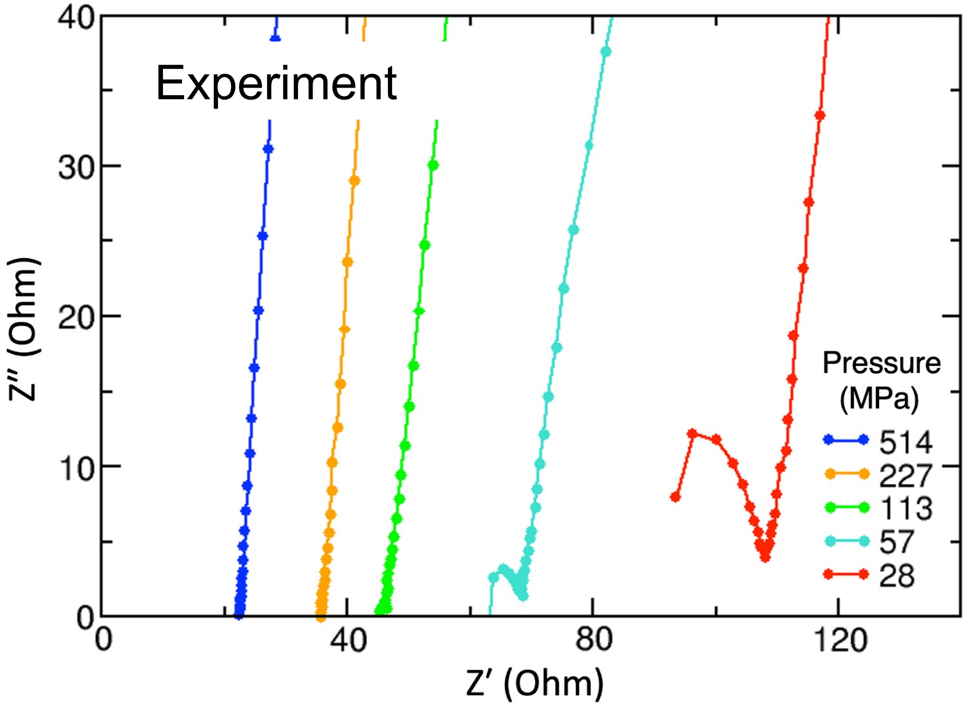


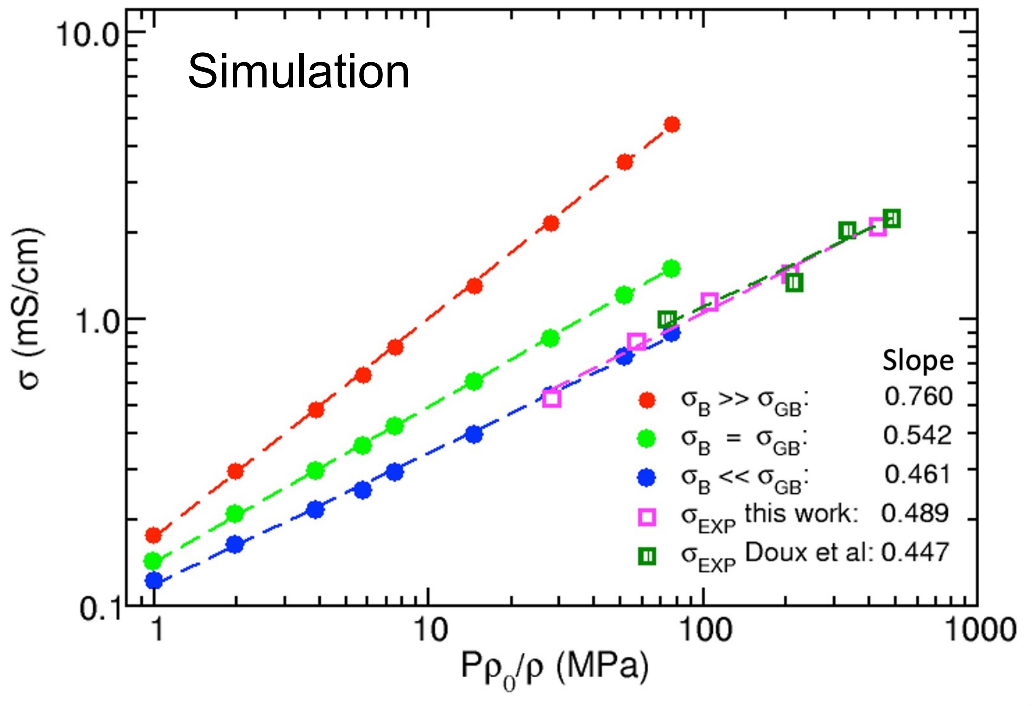
Cathode/SE Bilayer

Lithium (Li) metal anode

Fabrication Pressure Dependence

- ❑ σ_B: bulk conductivity
- ❑ σ_{GB}: grain boundary conductivity
- ❑ σ_{EXP}: experimentally measured conductivity

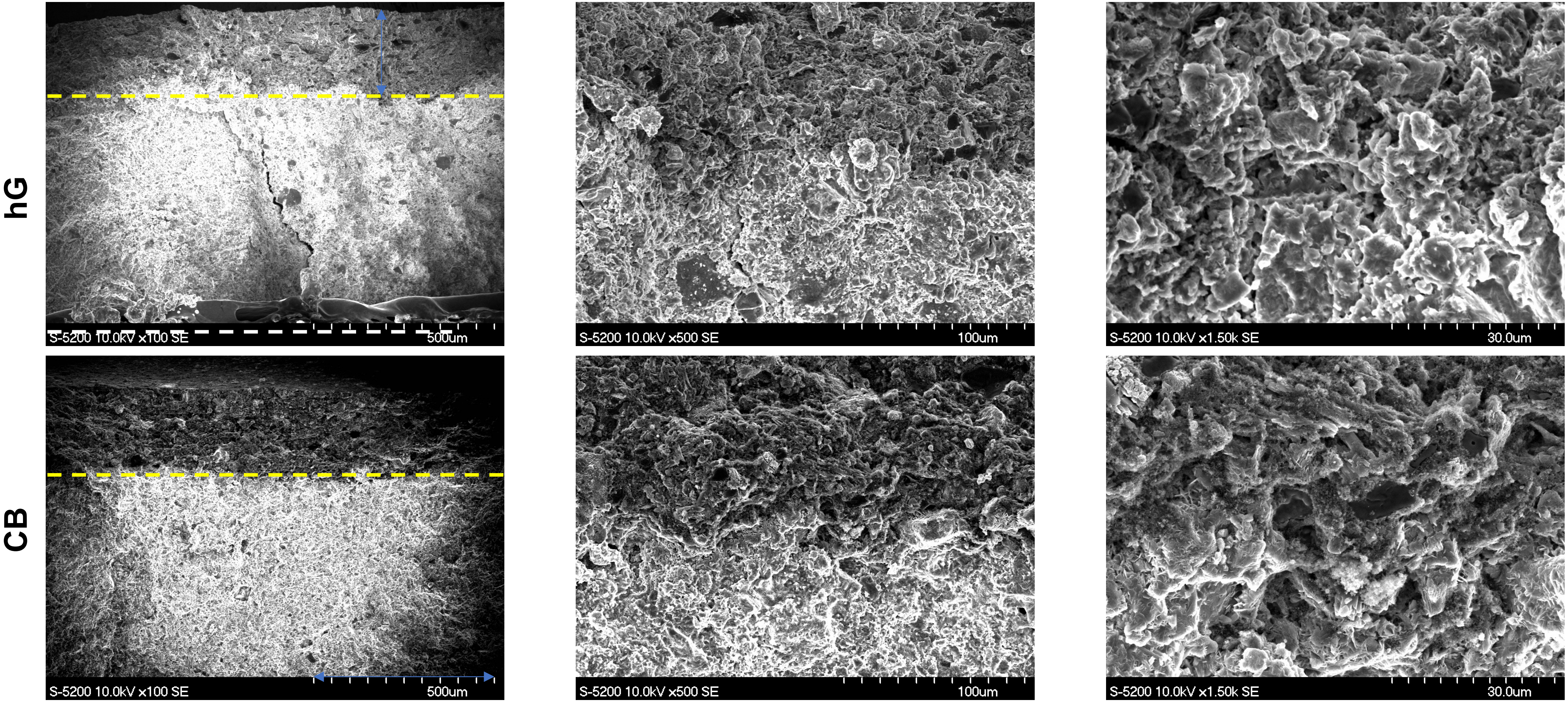




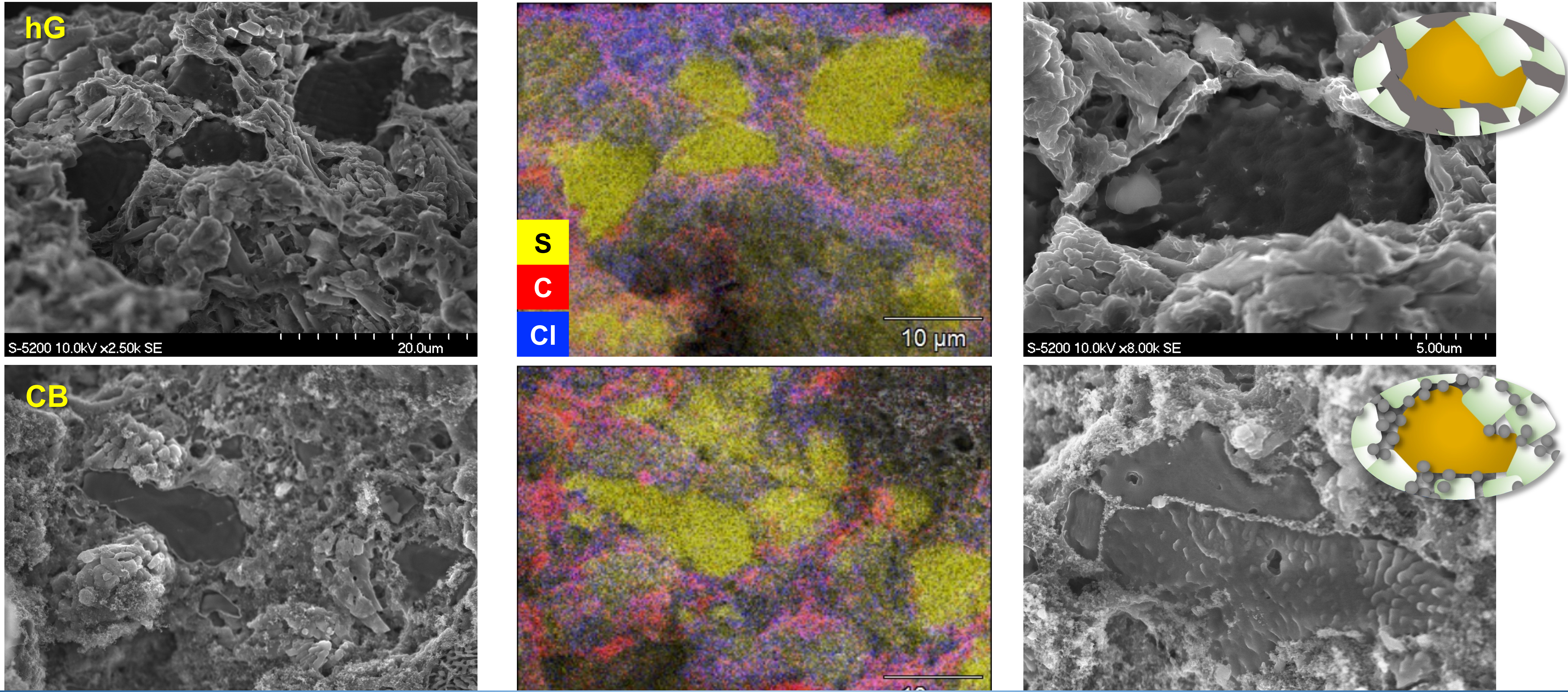
- ❑ Ionic conductivity of solid electrolytes from different fabrication pressure can be described using a particle dynamics model

ACS Appl. Mater. & Interfaces ***2023****, accepted for publication*

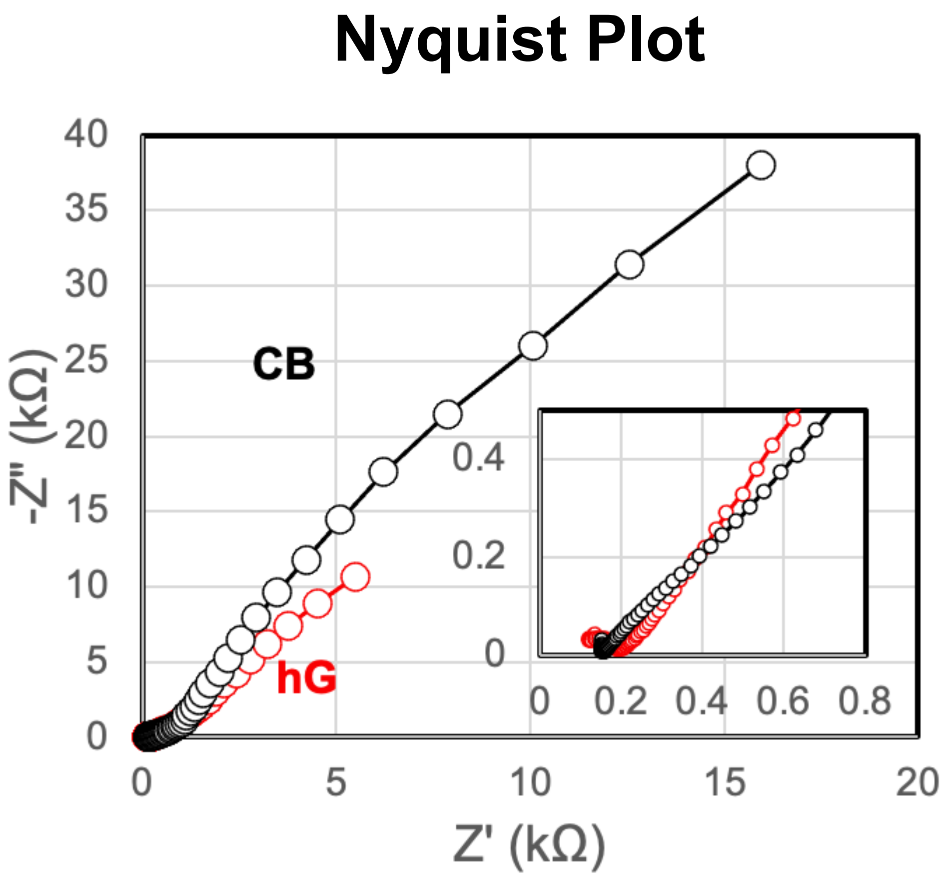
Dry-Pressed Cathode/SE Bilayers

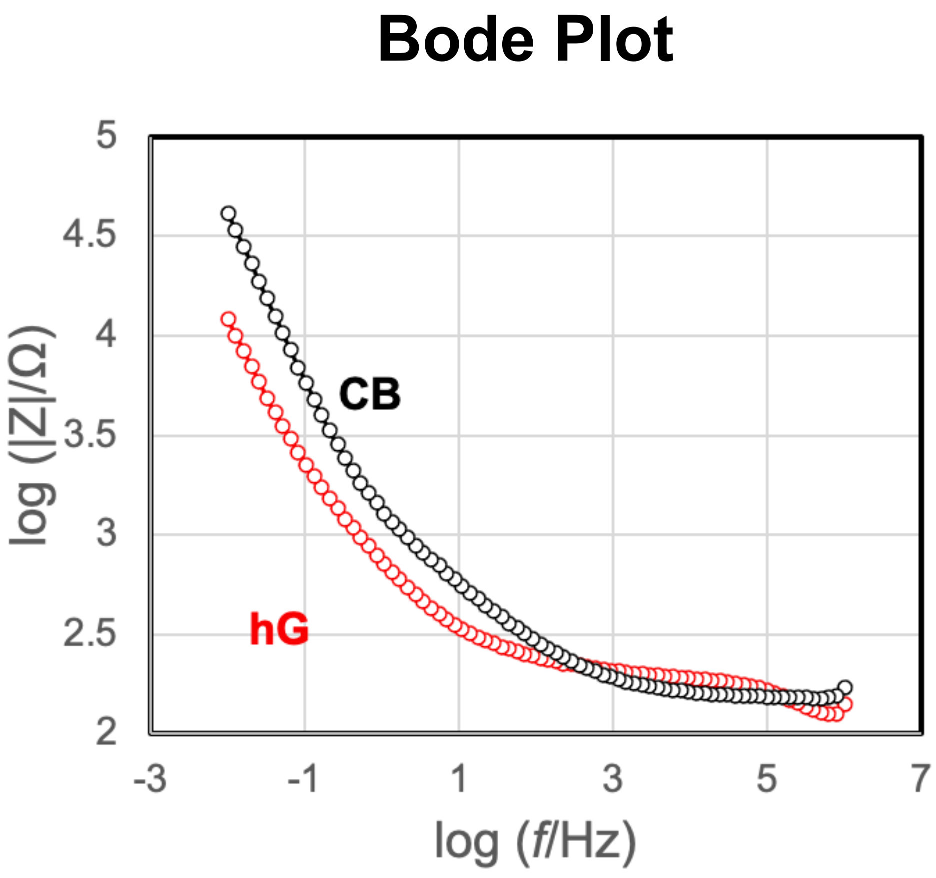


Cathode Microstructures



All-Solid-State Li-S Cell Impedance Characteristics

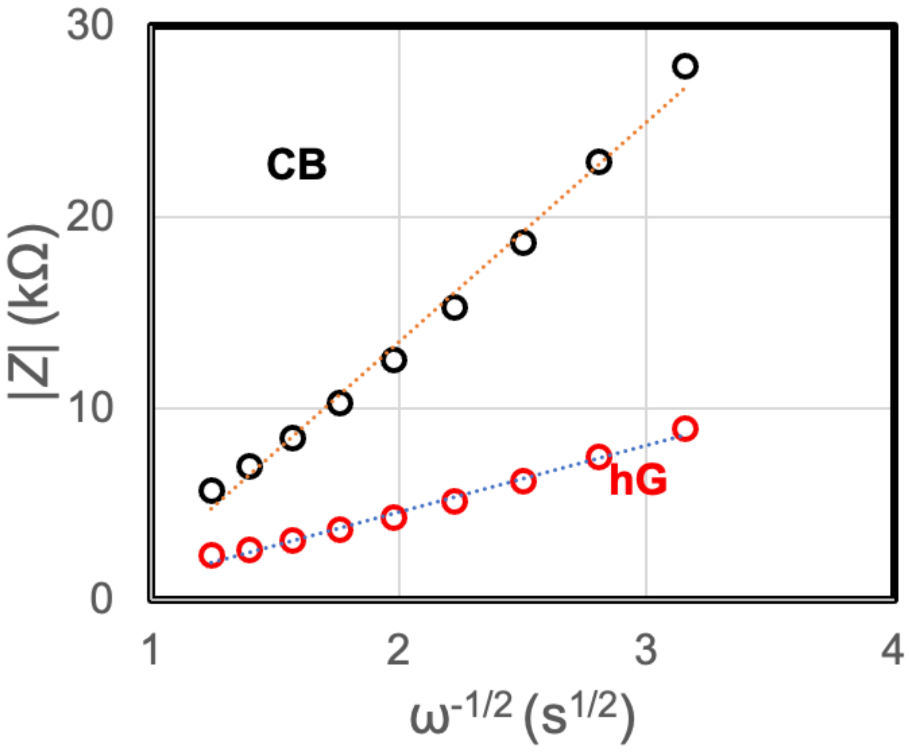




- ☐ The use of hG provides much lower impedance, especially in low frequency region.

Li Ion Diffusion Properties

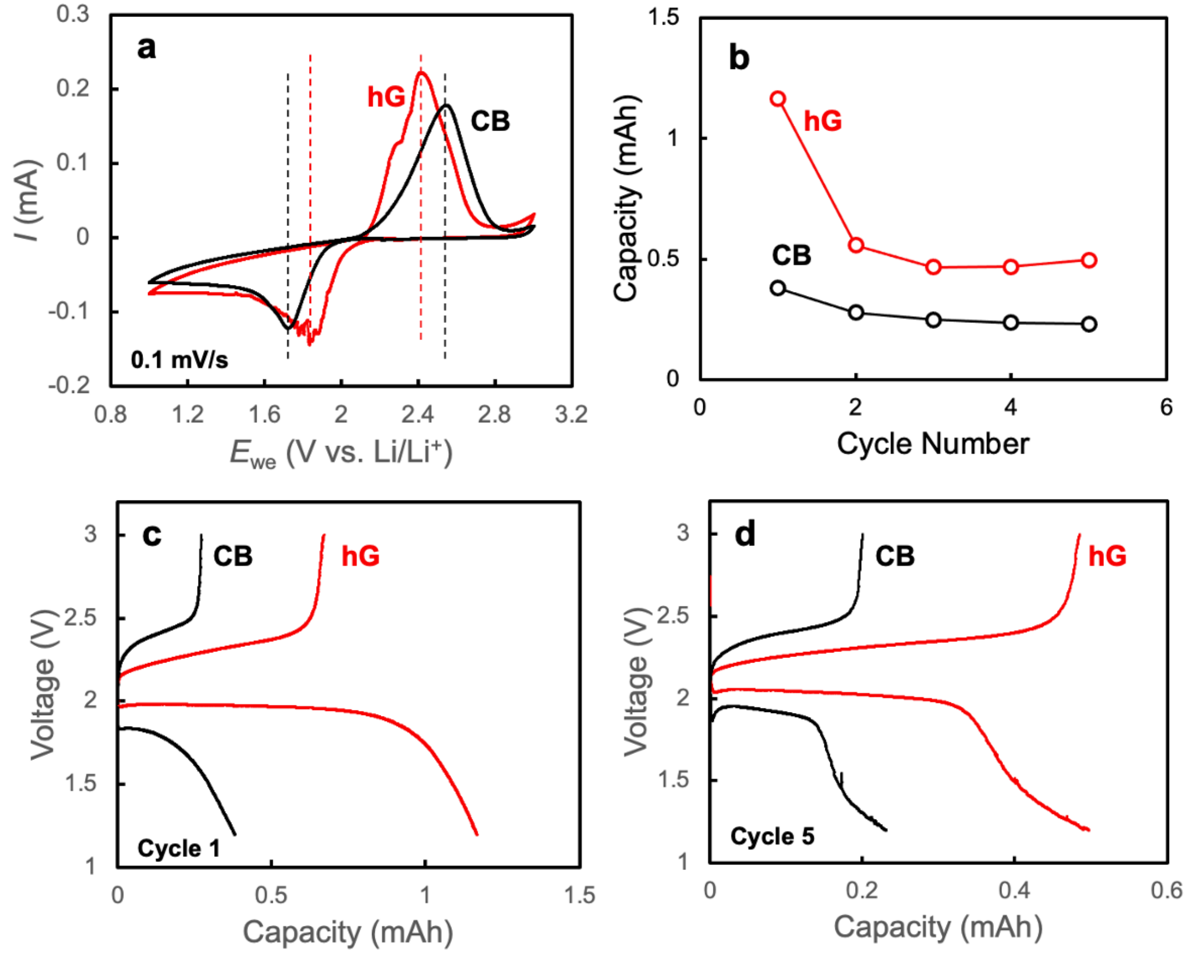
$$D_{Li^+} = \frac{R^2T^2}{2A^2n^4F^4c^2\sigma_w^2}$$

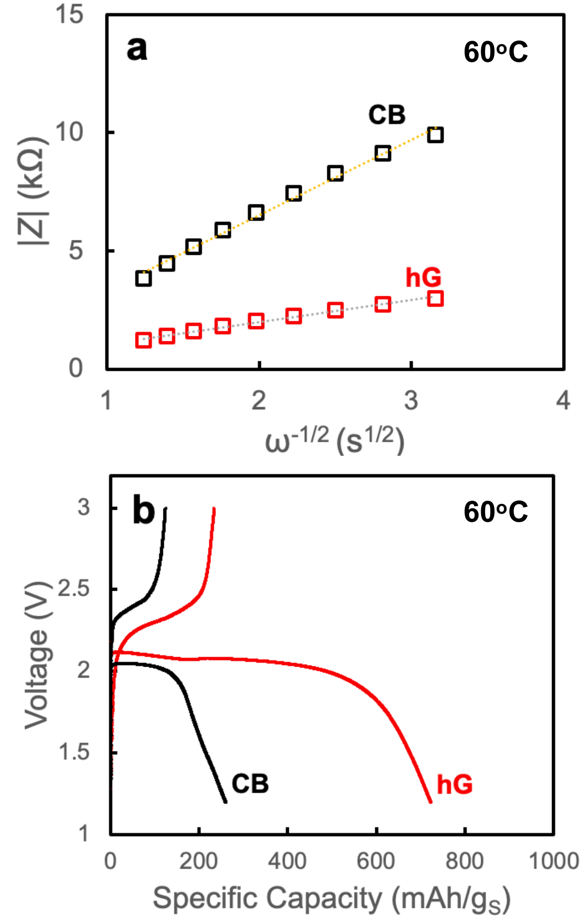


	D_{Li+} (cm²/s)
CB	3.0×10^{-18}
hG	3.9×10^{-17}

- The use of hG allows one magnitude higher Li ion diffusion through the cathode.

All-Solid-State Li-S Cell Performance





- ☐ Li metal anode
- ☐ No additional stack pressure

Room Temperature

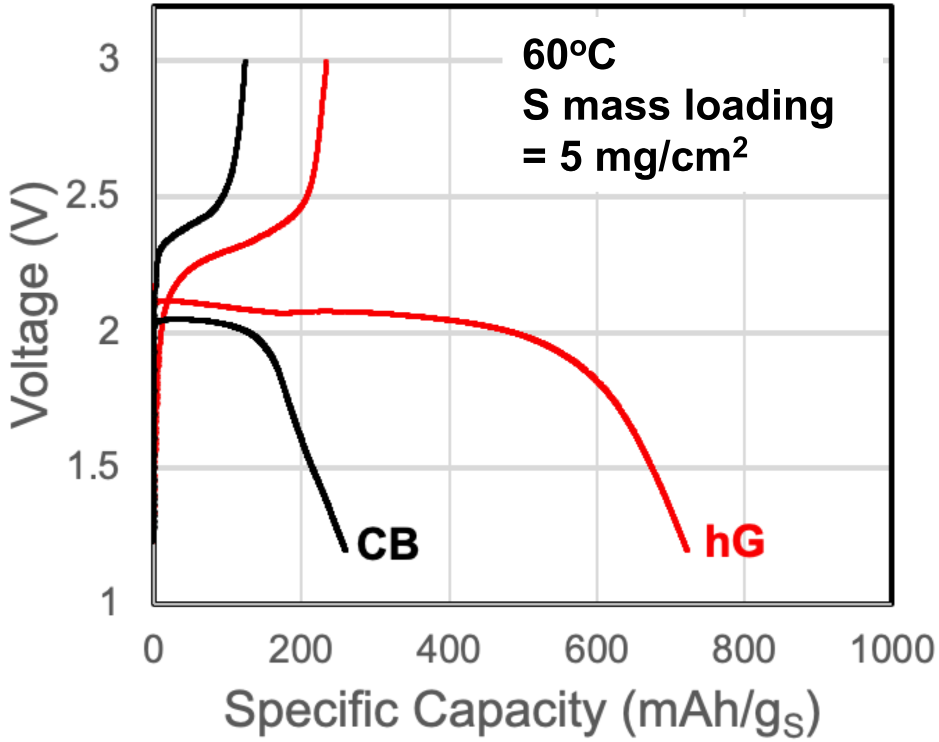
12 mg/cm²

60°C

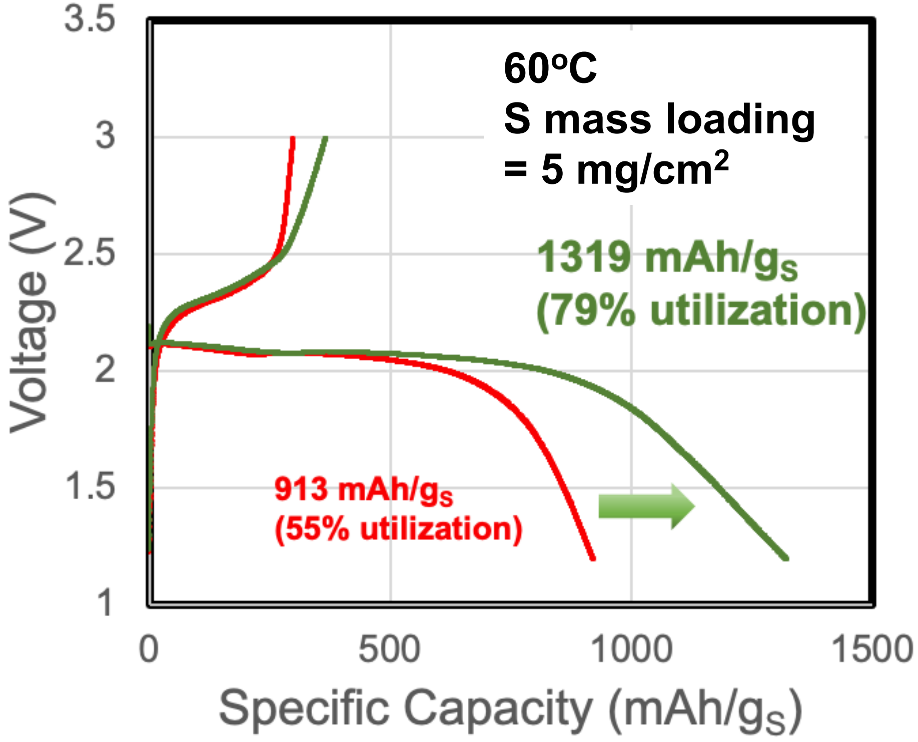
5 mg/cm²

Strategies toward High S Utilization

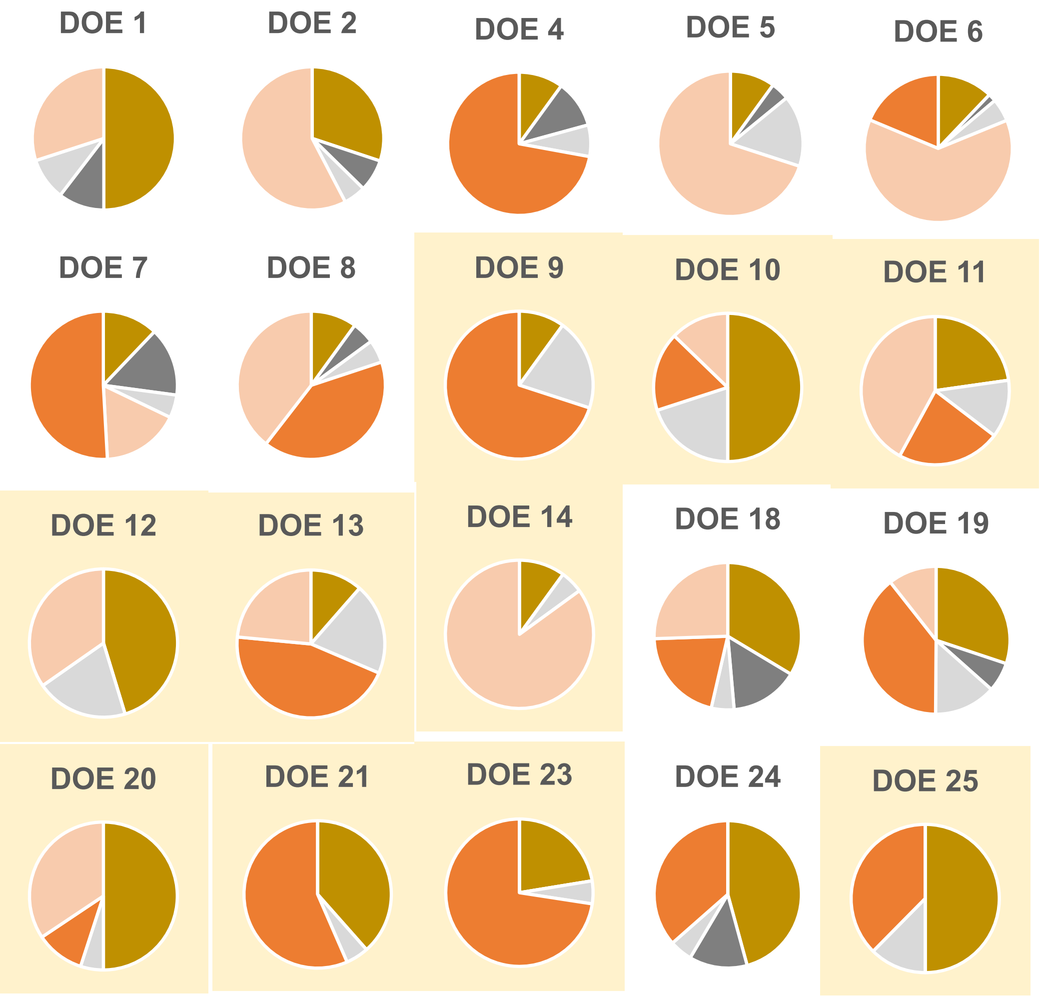
Increase Operation Temperature

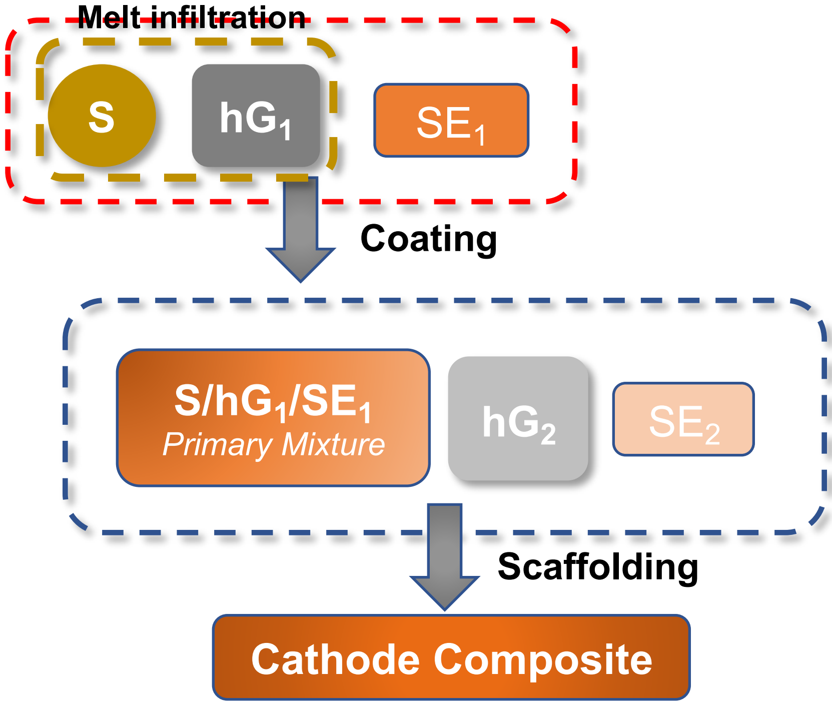


S Melt Infiltration



Composition/Process Optimization





Melt infiltration

S

hG_1

SE_1

Coating

$S/hG_1/SE_1$
Primary Mixture

hG_2

SE_2

Scaffolding

Cathode Composite

- A Design-of-Experiment (DOE) study
- 20 unique compositions
  - S: 10 – 50%
  - hG_1+hG_2: 5-20%; hG_1: 0-15%; hG_2: 0-20%
  - SE_1+SE_2: 30-85%; SE_1: 0-75%; SE_2: 0-70%
  - No hG_1 = no melt infiltration

S Cathode Design Principles from DOE

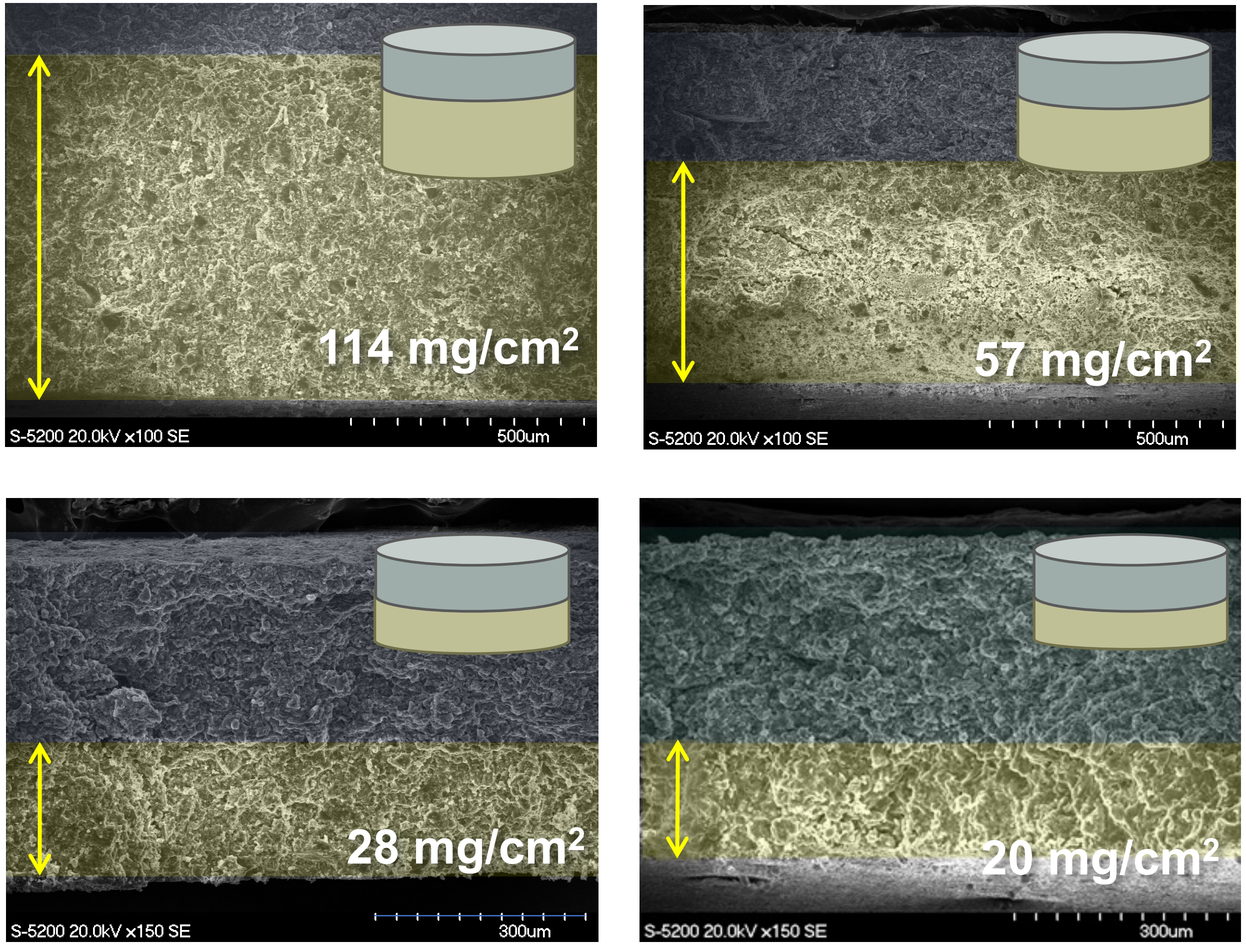
- ❑ High Discharge Capacity
  - ➢ Low S content
  - ➢ High hG:S ratio in melt infiltration

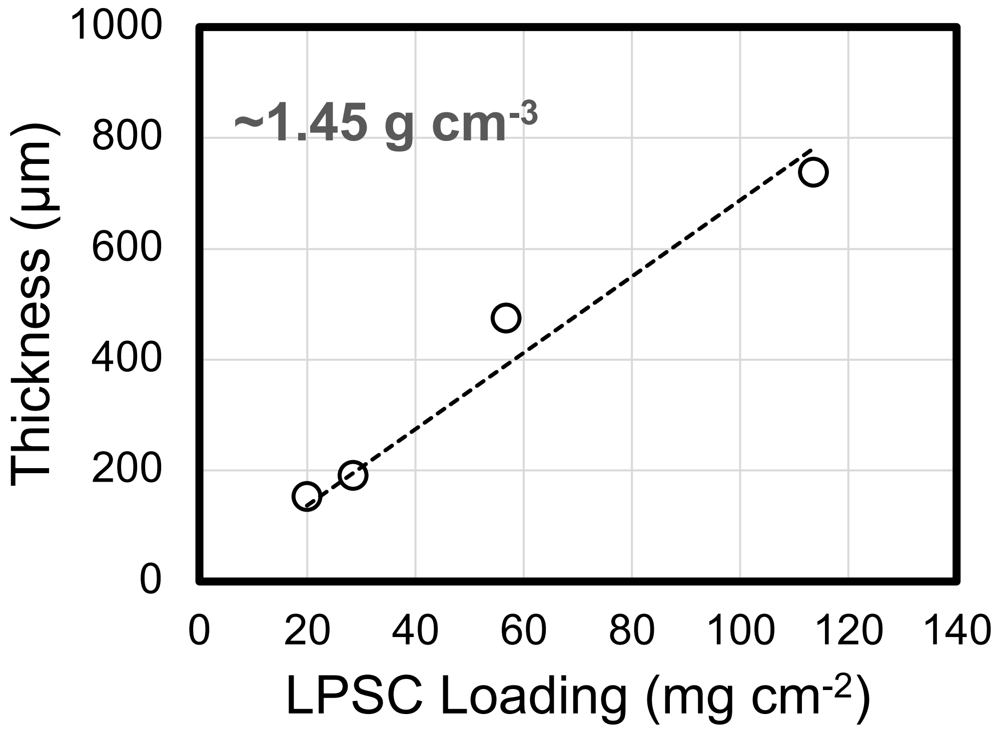
- ❑ Low Overpotential
  - ➢ Low S content
  - ➢ Medium hG:S ratio in melt infiltration

- ❑ Low impedance
  - ➢ High scaffolding-step hG content
  - ➢ High coating-step SE content

- ❑ High Li^+ Diffusion Coefficient
  - ➢ High hG:S ratio during melt infiltration
  - ➢ High coating-step SE content

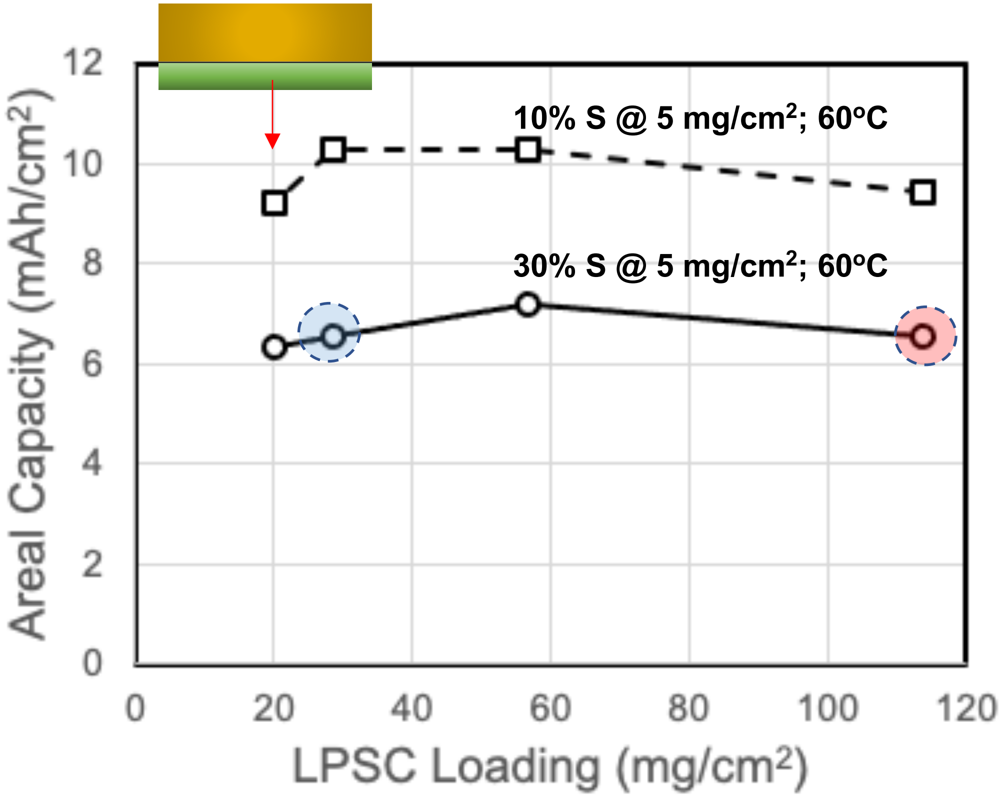
Reducing SE Thickness in Dry-Press

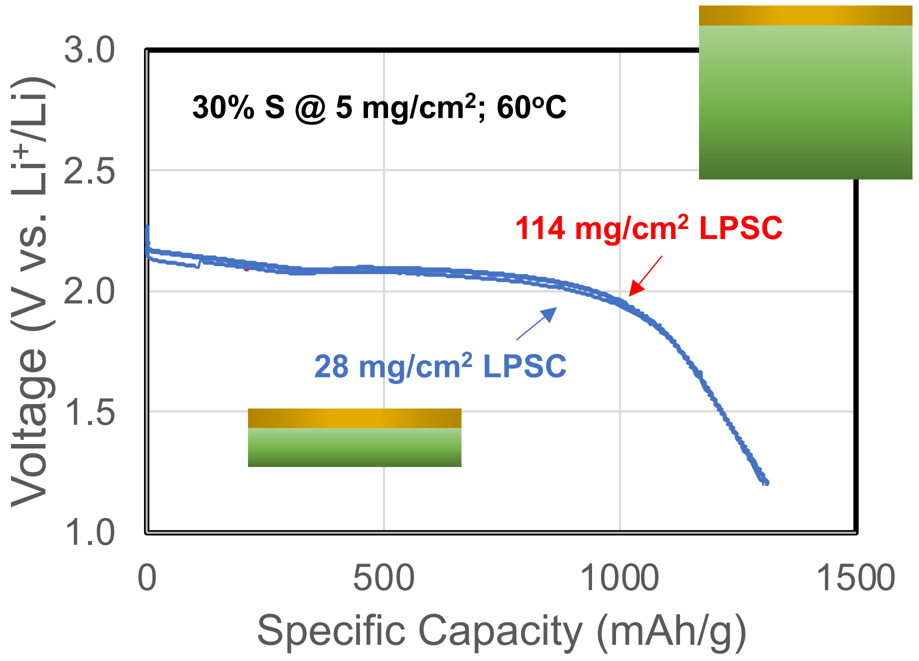




Improved Energy Density

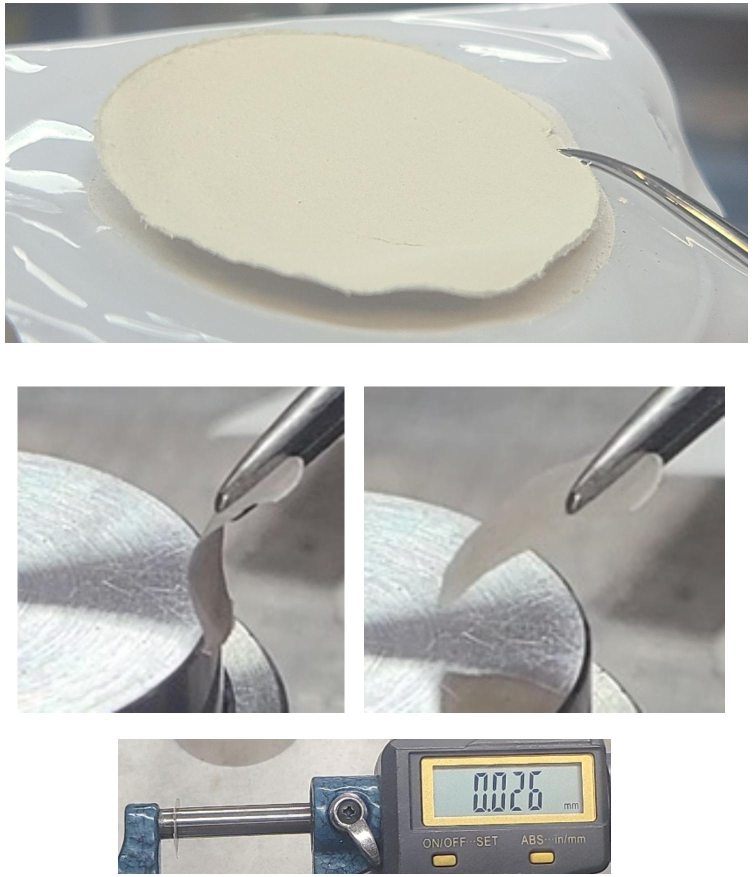
❑ Reduction in SE thickness + Increasing cathode S content with retained S utilization = <u>**Improved Energy Density**</u>





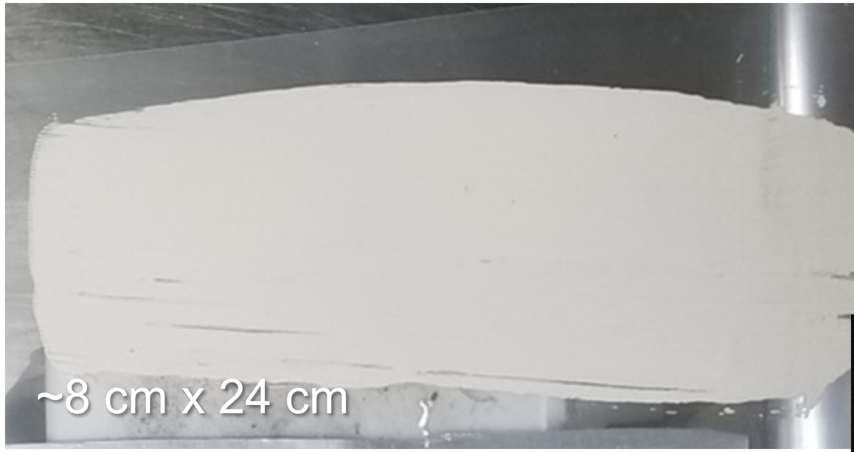
- ➢ All dry-pressed cathodes
- ➢ No additional stack pressure
- ➢ 0.032 mA/cm^2

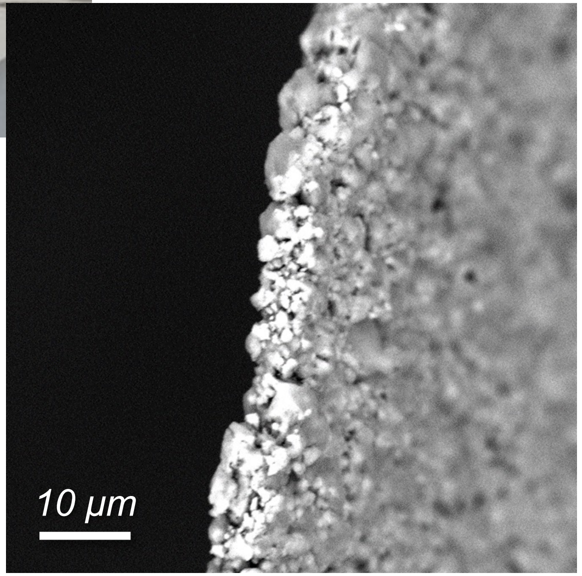
Reliable Reductions of SE Thickness



Free-standing LPSC Thin Films
(~26 µm in thickness)

Tape-Casted LPSC Films
(~25 µm in thickness)





- ❖ Future development and direction: 5-10 µm
- ❖ Feasible? Reliable? Safe?

Summary

- ☐ Solid-state S cathodes were prepared by **solvent-free pressing** a mixture of S, solid electrolyte, and carbon
- ☐ **Holey graphene** provides robust composite cathode architecture, thus enhanced electrochemical performance (in comparison to carbon black)
- ☐ **High S utilization** was achieved at **high mass loading (> 5 mg/cm^2)** in all-solid-state cells
- ☐ **Optimization** of all-solid-state S cathodes was achieved via **DOE studies**
- ☐ Cell-level (electrochemical) **energy density** was improved by **reducing solid electrolyte thickness and increased cathode S content**

Acknowledgements

- NASA Convergent Aeronautics Solutions (**CAS**) Project
- NASA Transformational Tools and Technologies (**TTT**) Project

- NASA **SABERS** Team:
  - John Connell (retired)
  - Vesselin Yamakov, Ji Su, Rodolfo Ledesma, Jin Ho Kang, Lopamudra Das, Glen King
- Student Interns:
  - 2019 – 2022: Christian Plaza-Rivera, Brandon Walker
  - 2022: Abigail Durgin, Bona Kim, Lucy Somervill, Rehan Rashid