Toward 500 Wh/kg with All-Solid-State Lithium Sulfur Batteries

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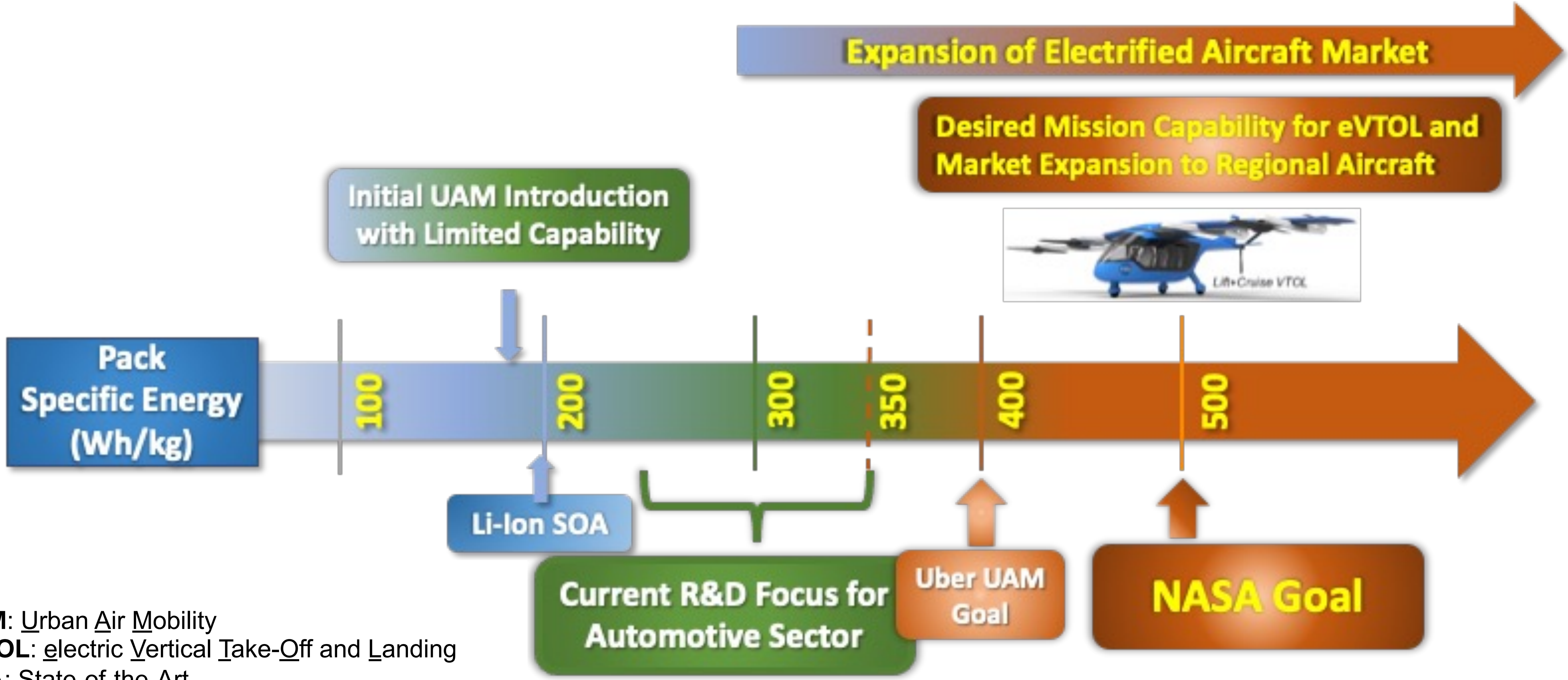
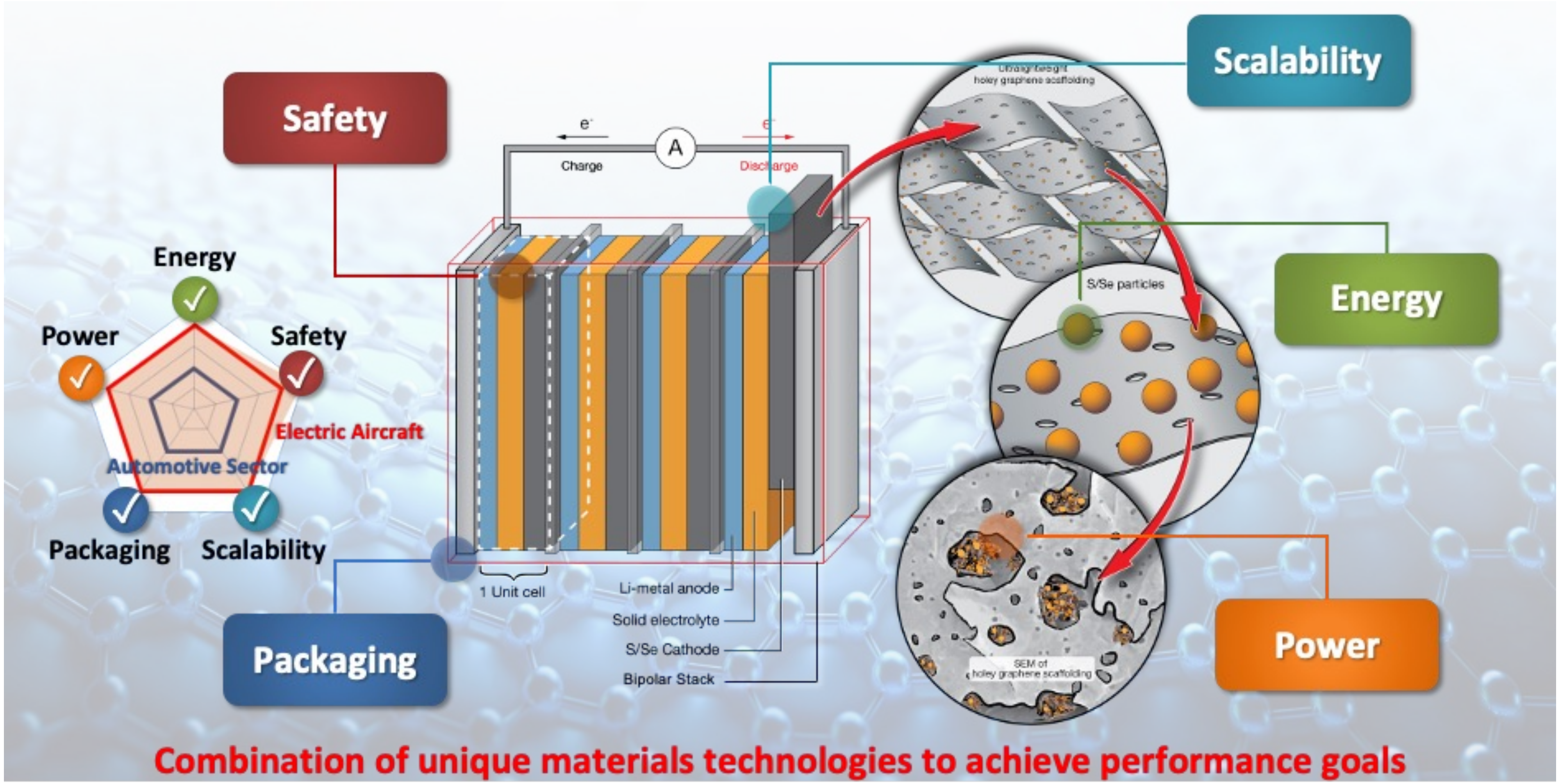
Why is NASA Interested in Solid-State Batteries?



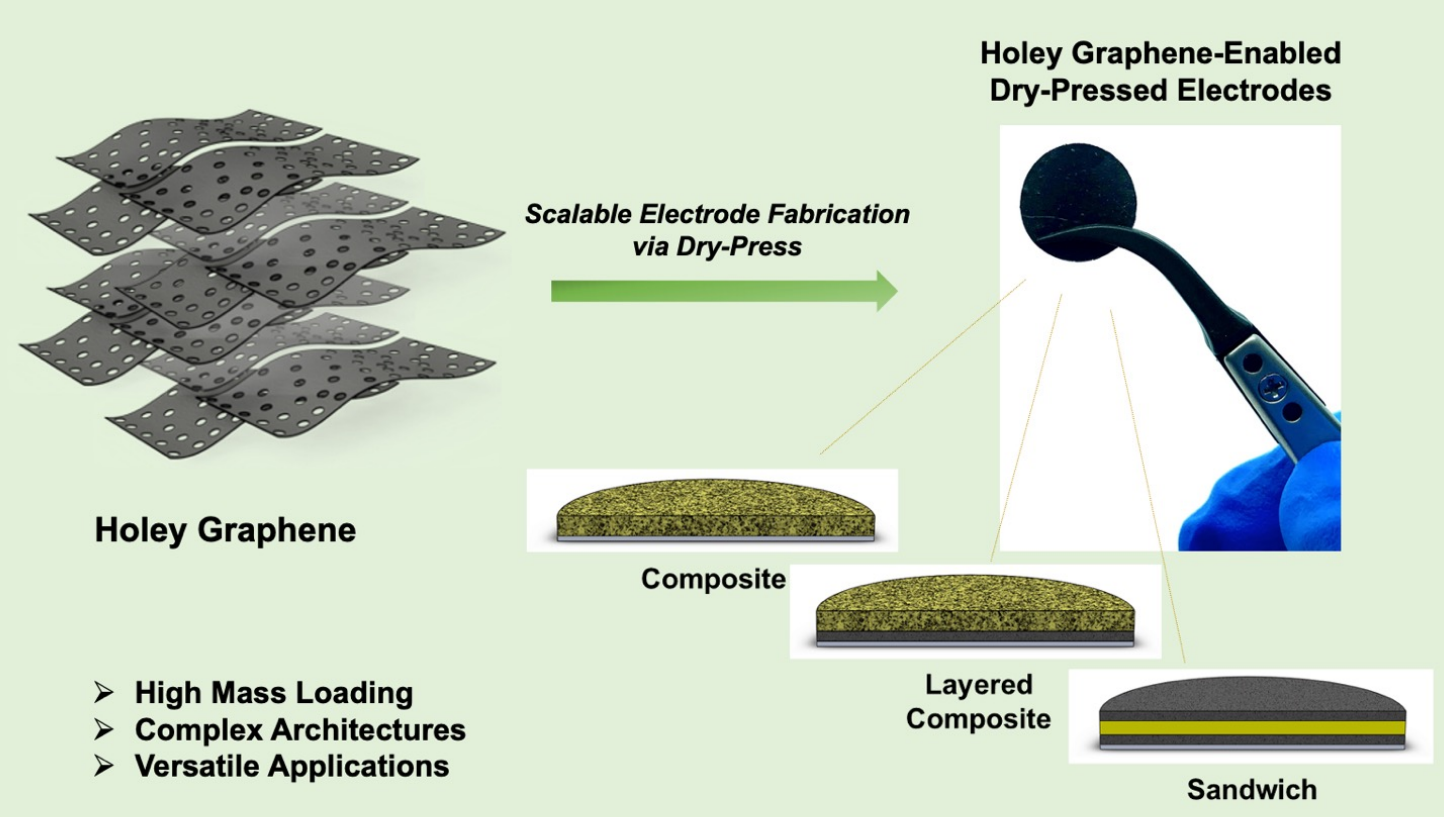
UAM: Urban Air Mobility
eVTOL: electric Vertical Take-Off and Landing
SOA: State-of-the-Art
R&D: Research & Development

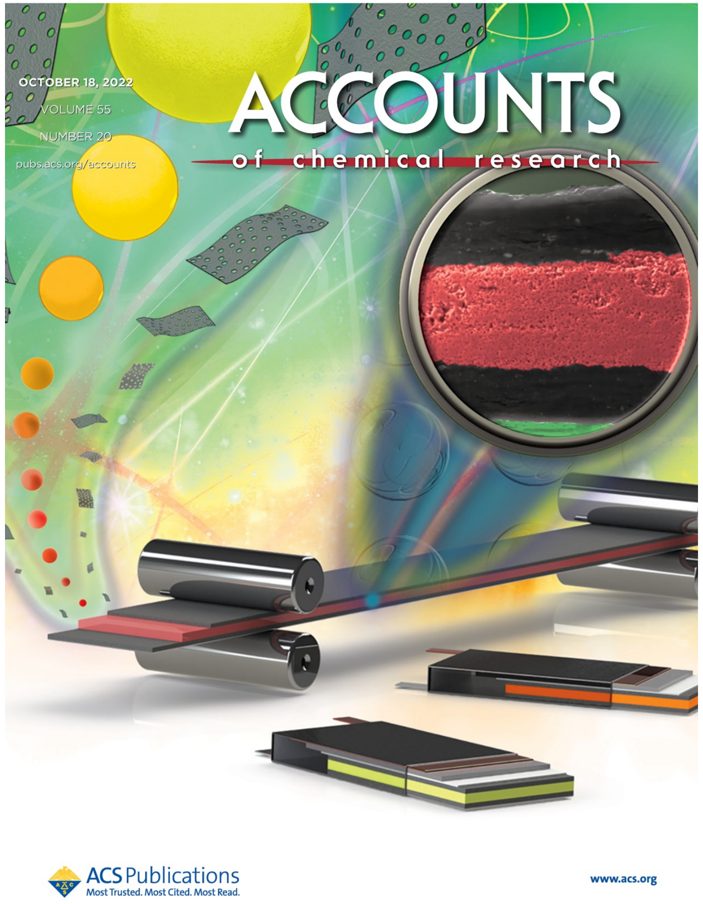
Why is NASA Interested in Solid-State Batteries?



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

Dry-Pressed Electrodes Enabled by Holey Graphene





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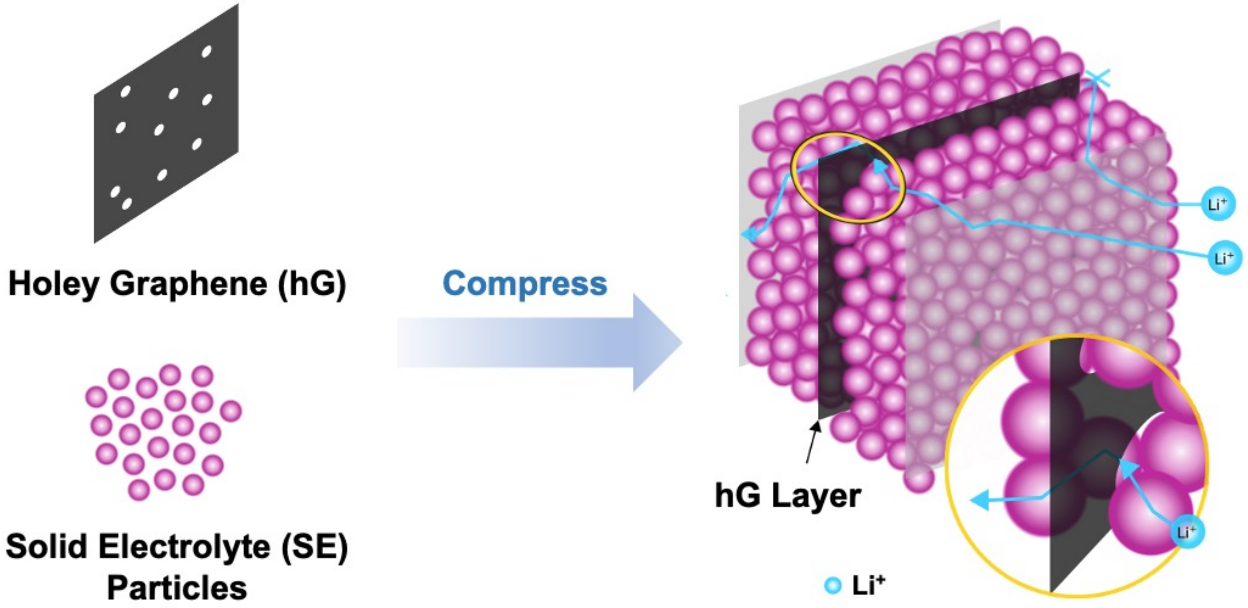
Li Ion Conductivity through hG Sheets



❑ 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.

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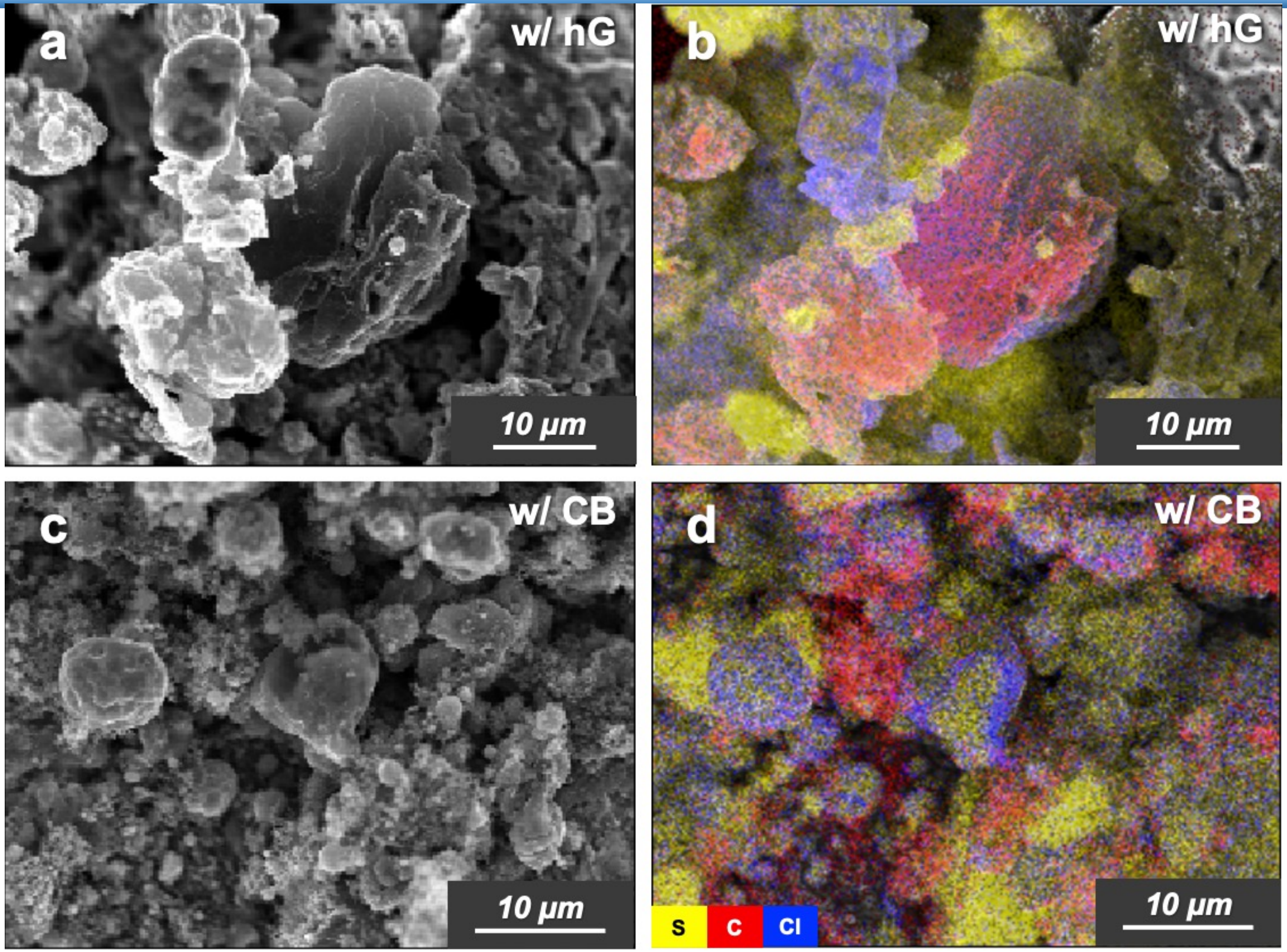
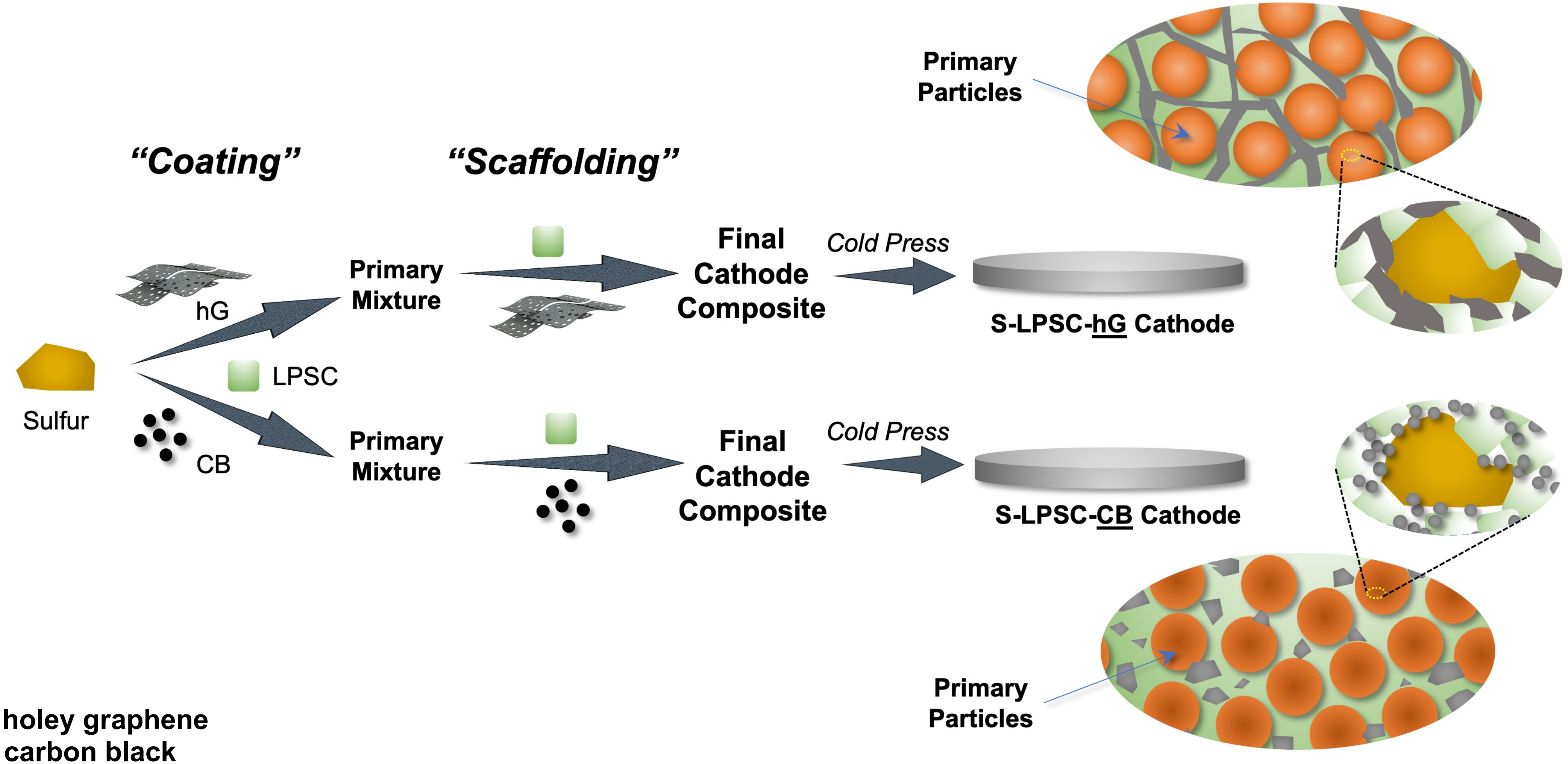
Composite Solid-State Cathode Powder



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

CB: Super C45

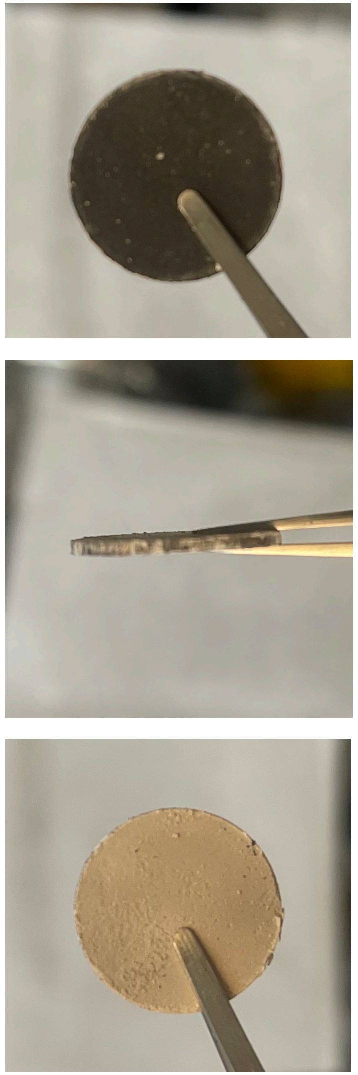
All-Solid-State S Cathodes



- hG: holey graphene
- CB: carbon black

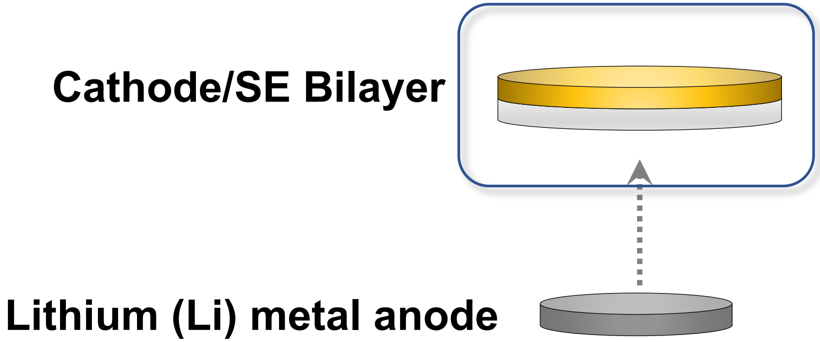
Dry-Pressed Cathode/SE Bilayer Discs

CB



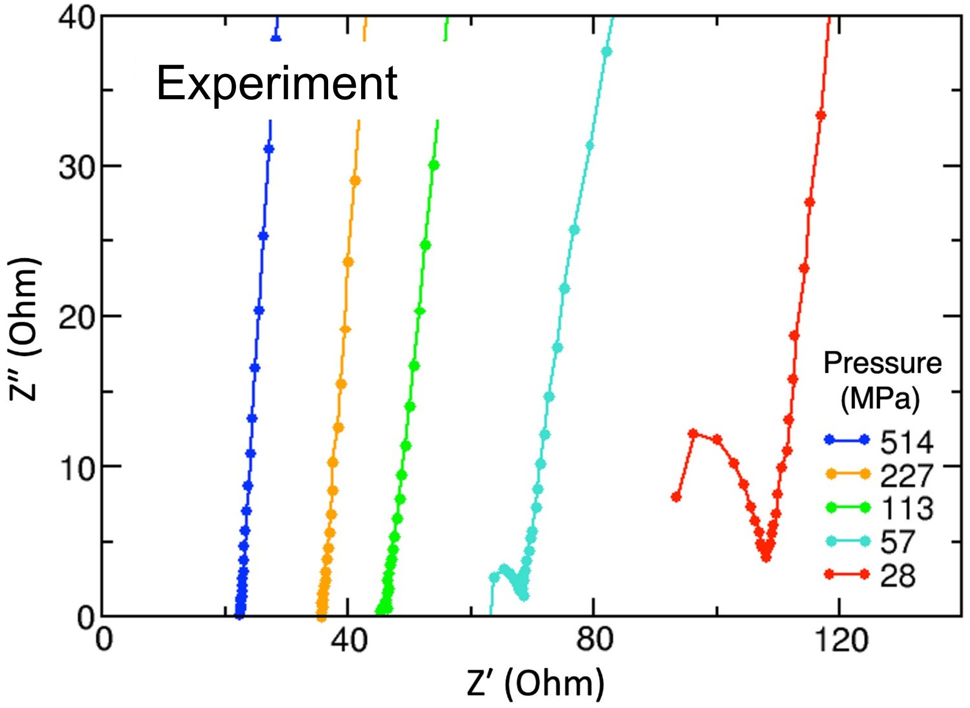
hG

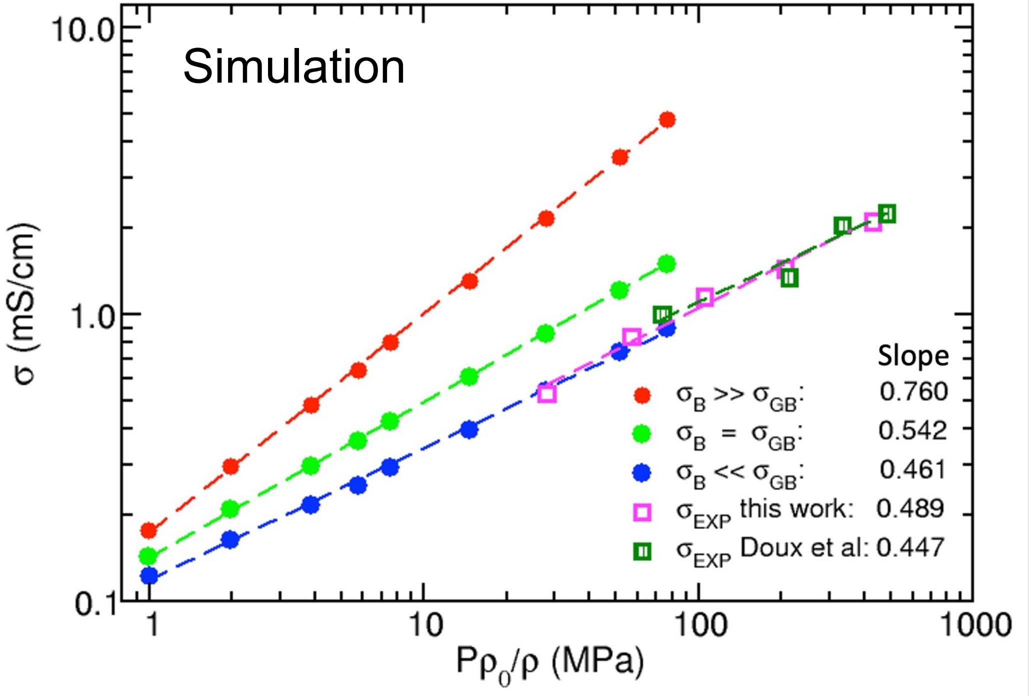
- ❑ Both composites are compressible to form robust cathode/SE bilayer discs
- ❑ LPSC glass electrolyte serves as binder
- ❑ hG as “cold pressable hosts” is not an obvious advantage…?



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

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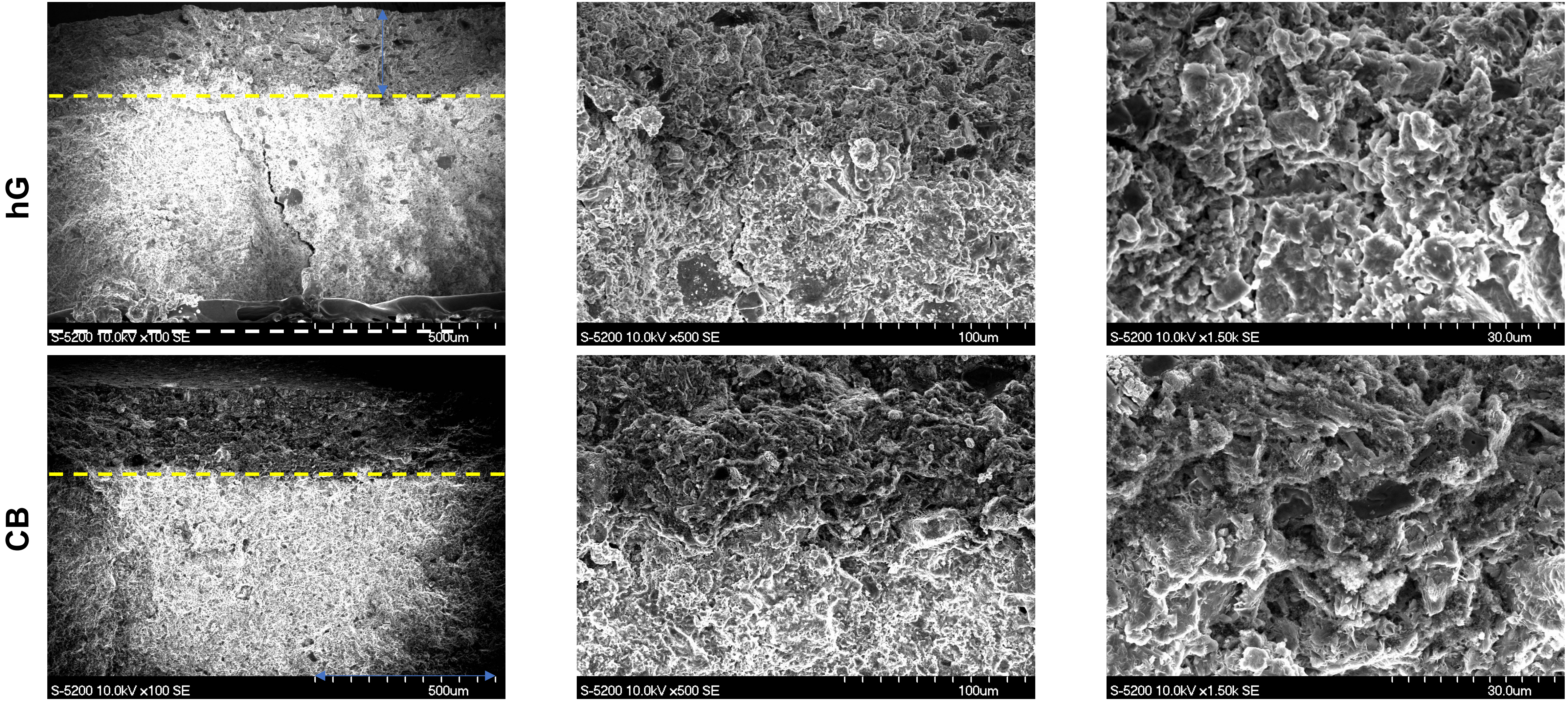
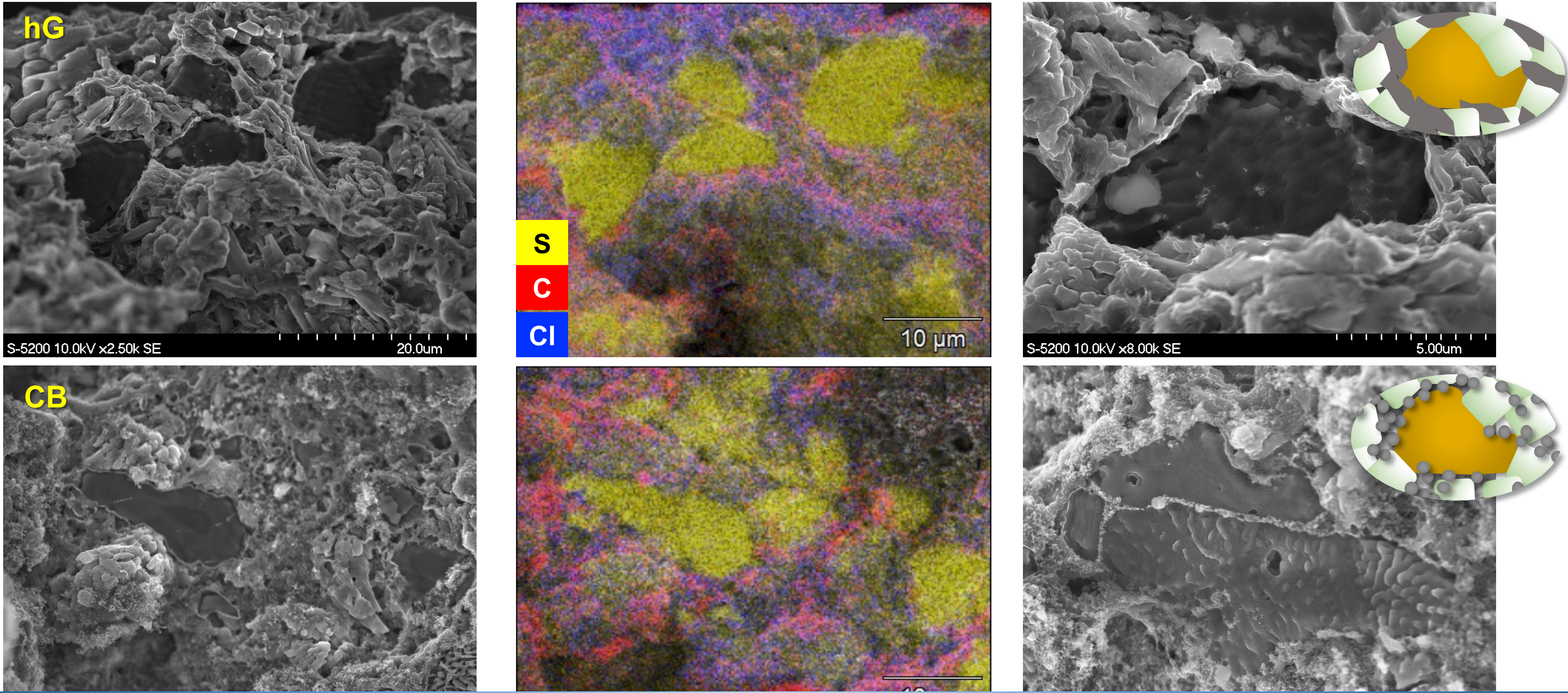
Dry-Pressed Cathode/SE Bilayers

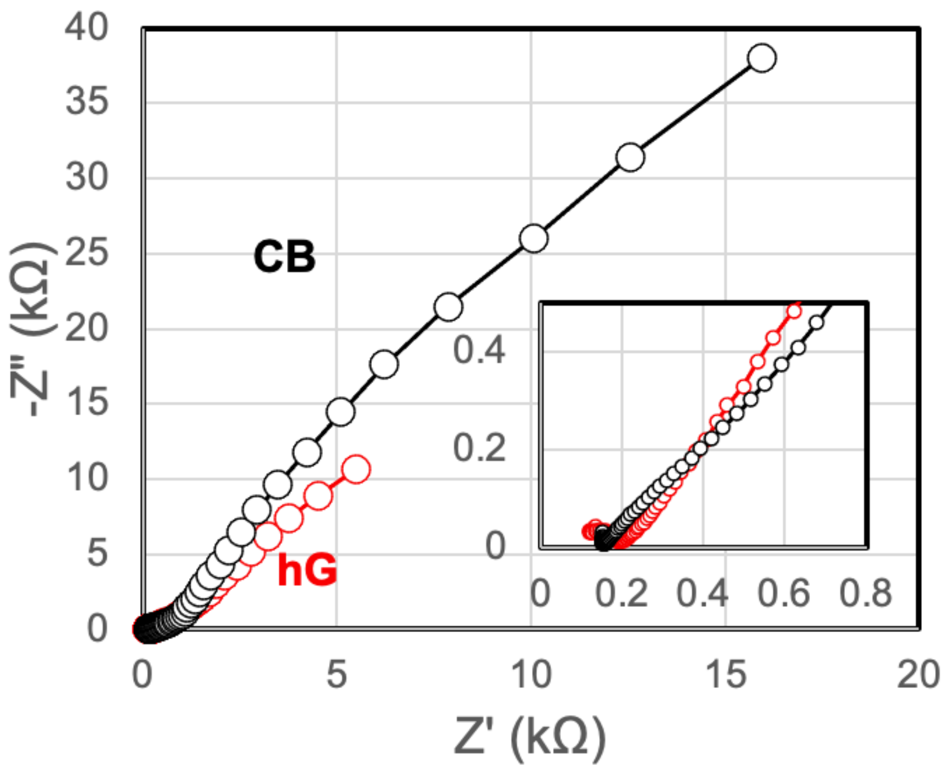


Cathode Microstructures

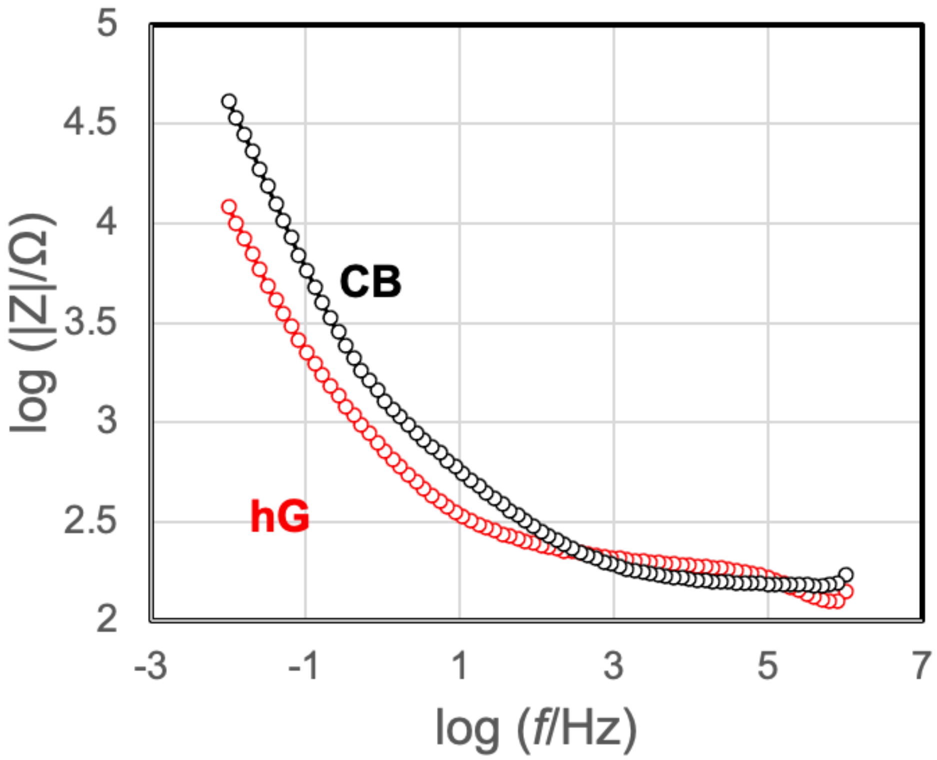


All-Solid-State Li-S Cell Impedance Characteristics

Nyquist Plot

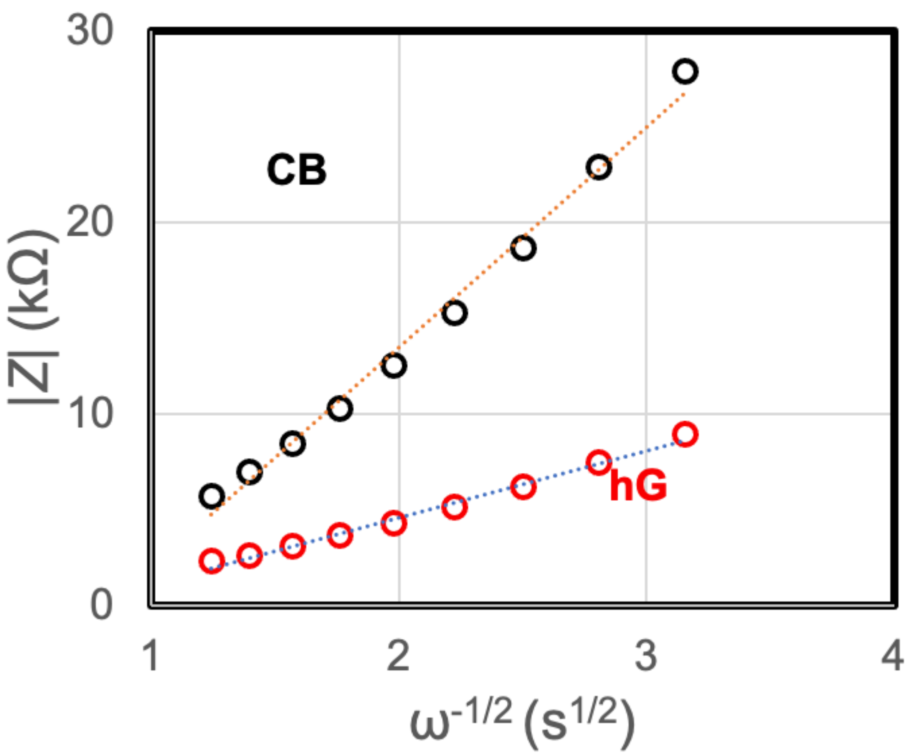


Bode Plot



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

Li Ion Diffusion Properties

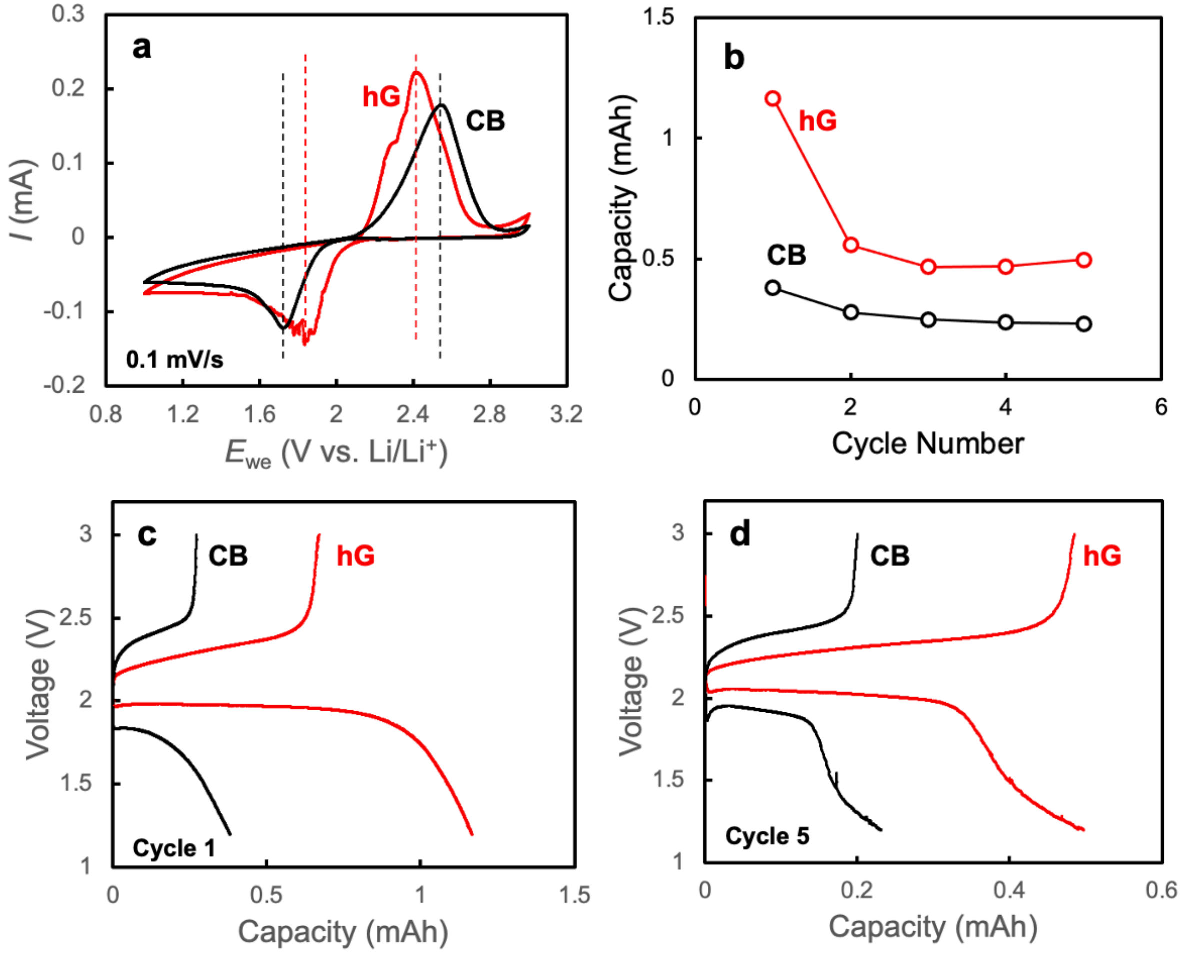


$$D_{Li^+} = \frac{R^2T^2}{2A^2n^4F^4c^2\sigma_w{}^2}$$

	D_{Li+} (cm^2/s)
CB	3.0×10^{-18}
hG	3.9×10^{-17}

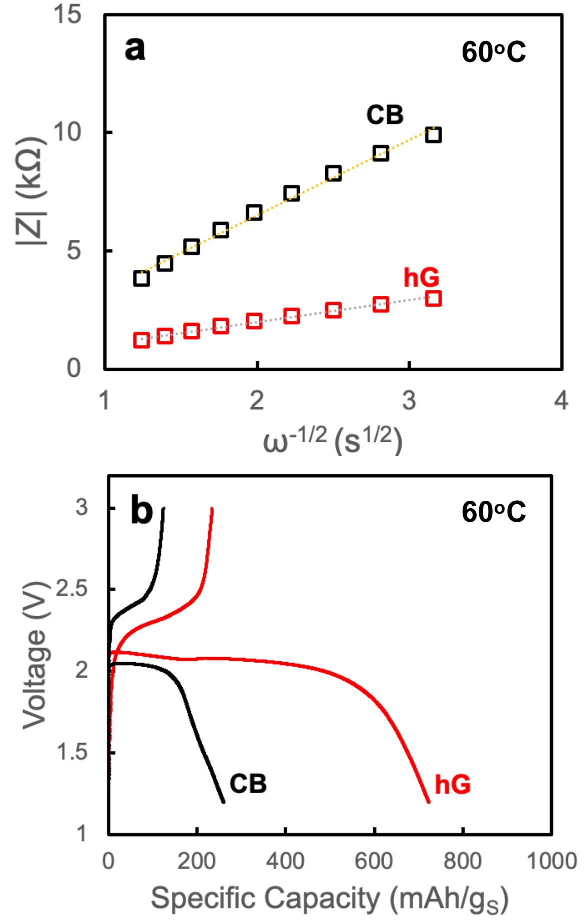
- ❑ The use of hG allows one magnitude higher Li ion diffusion through the cathode.

All-Solid-State Li-S Cell Performance



Room Temperature

12 mg/cm²



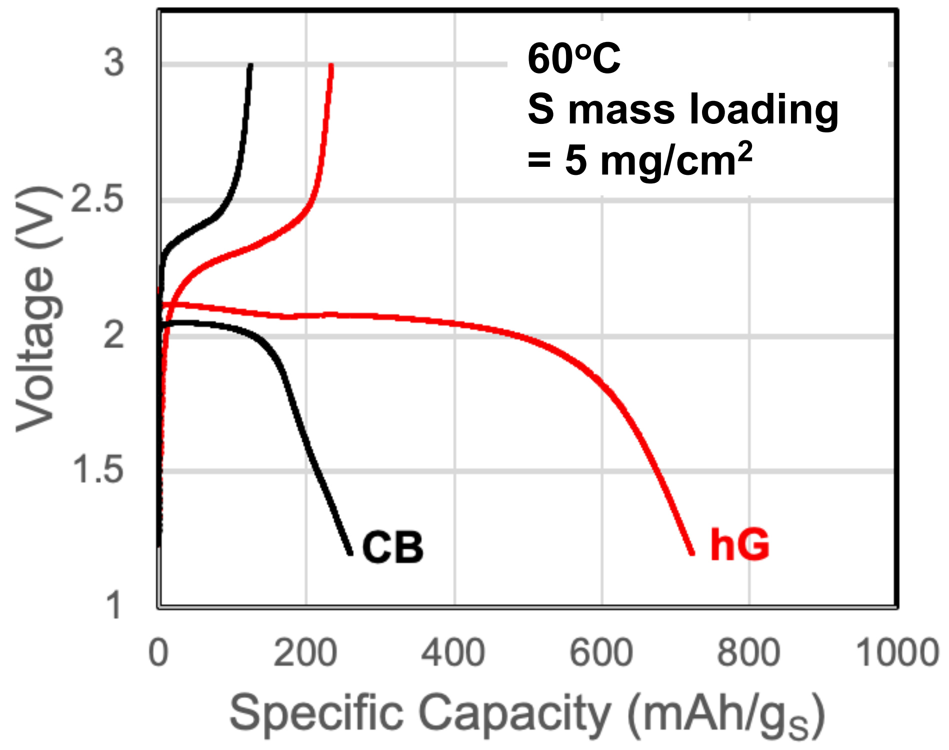
60°C

5 mg/cm²

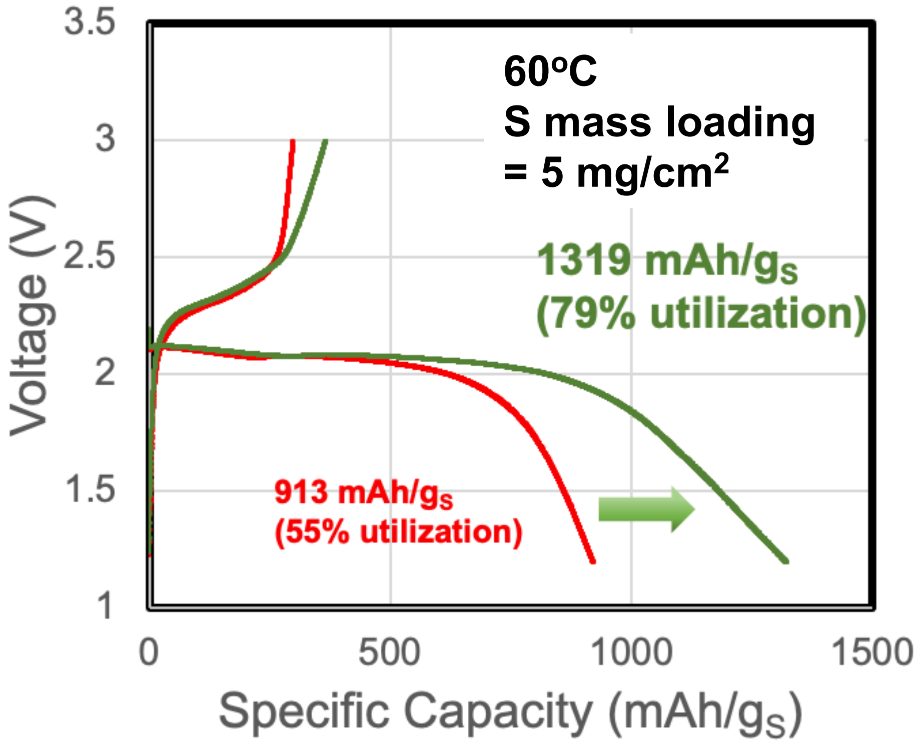
- ❑ Li metal anode
- ❑ No additional stack pressure

Strategies toward High S Utilization

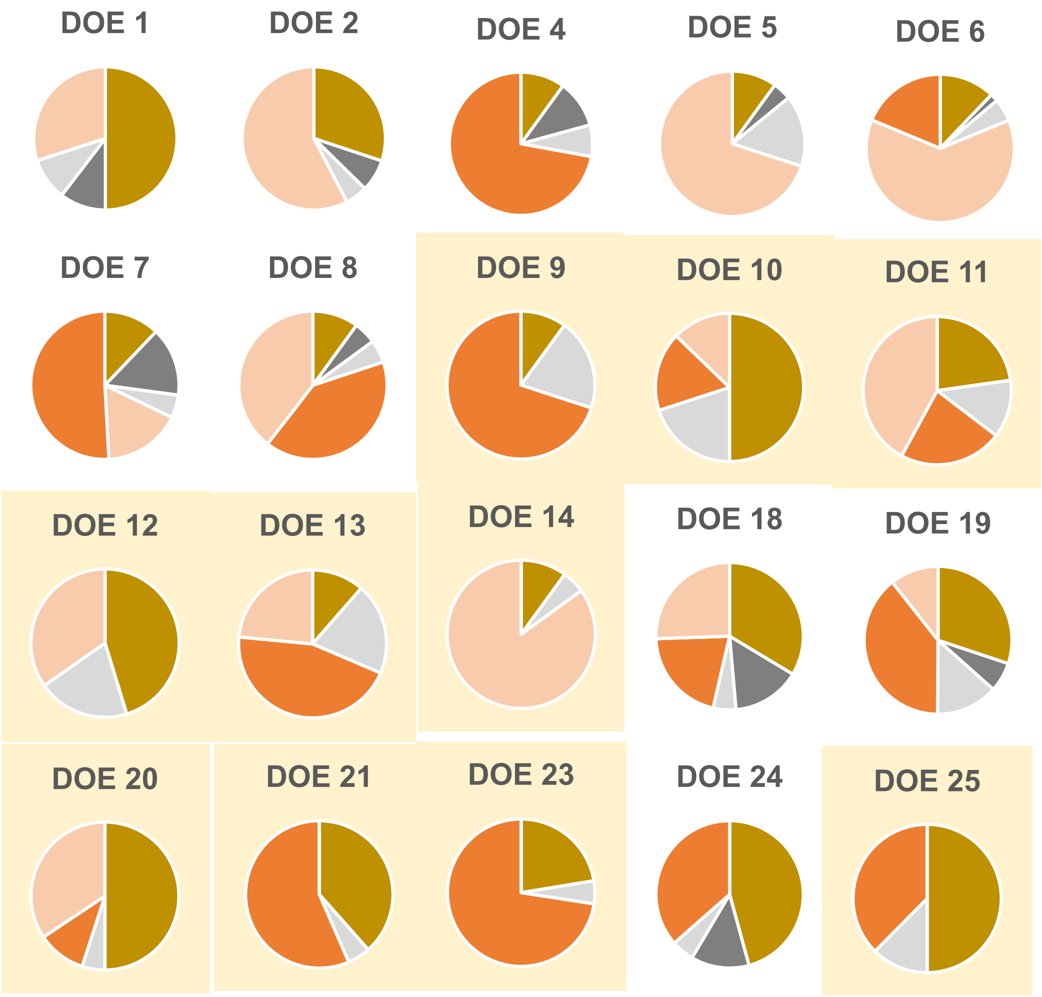
Increase Operation Temperature

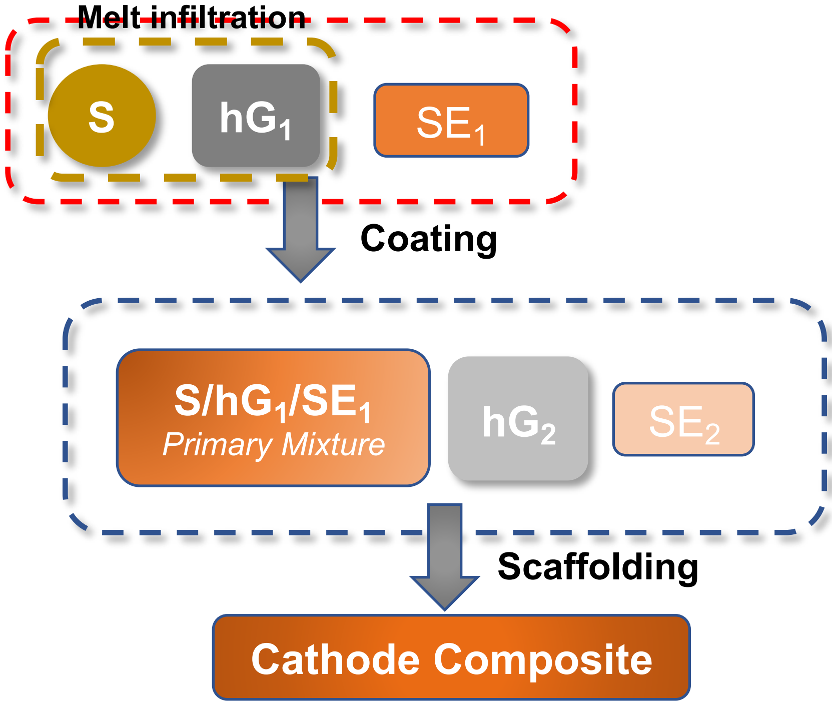


S Melt Infiltration



Composition/Process Optimization





- 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

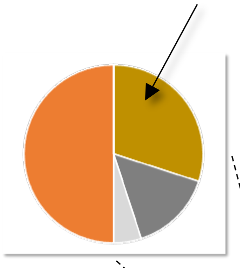
- High Discharge Capacity
  - Low S content
  - High hG:S ratio in melt infiltration
- Low Overpotential
  - Low S content
  - Medium hG:S ratio in melt infiltration
- Low impedance
  - High scaffolding-step hG content
  - High coating-step SE content
- High Li^+ Diffusion Coefficient
  - High hG:S ratio during melt infiltration
  - High coating-step SE content

Cell Integration to Improve Specific Energy

$$E = \frac{W \cdot h}{kg} = \frac{V \cdot mA \cdot h}{g(C + SE + xLi)} = \frac{V \cdot Capacity}{g(C^{*} + SE + xLi)}$$

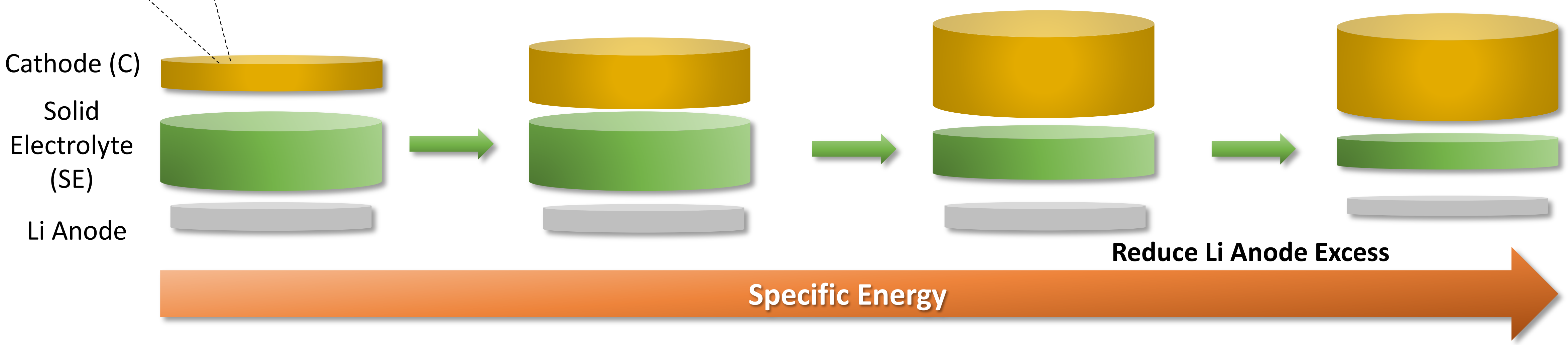
$$^{*}g(C) = g[S + SE(C) + hG]$$

Maximize S Content & Utilization

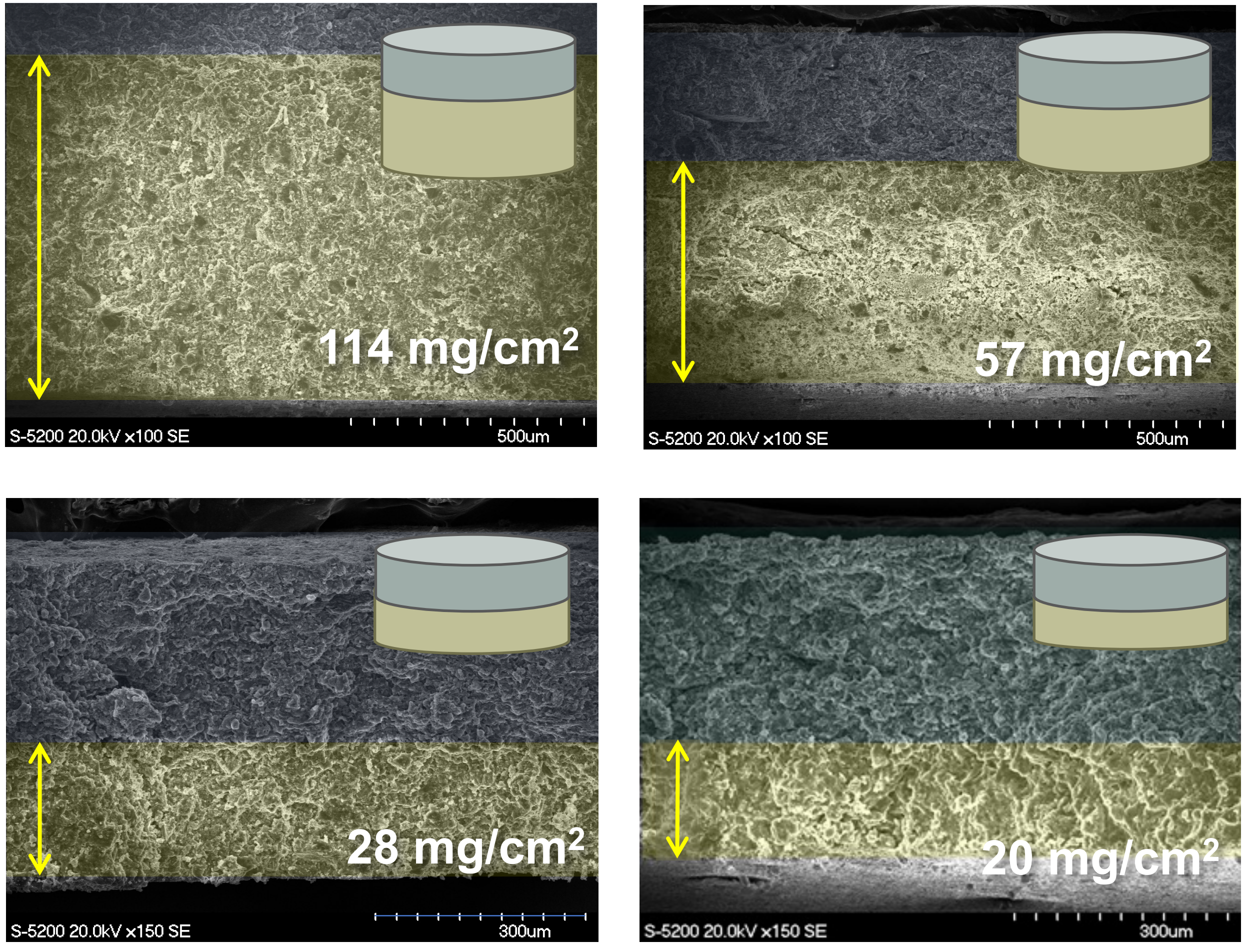


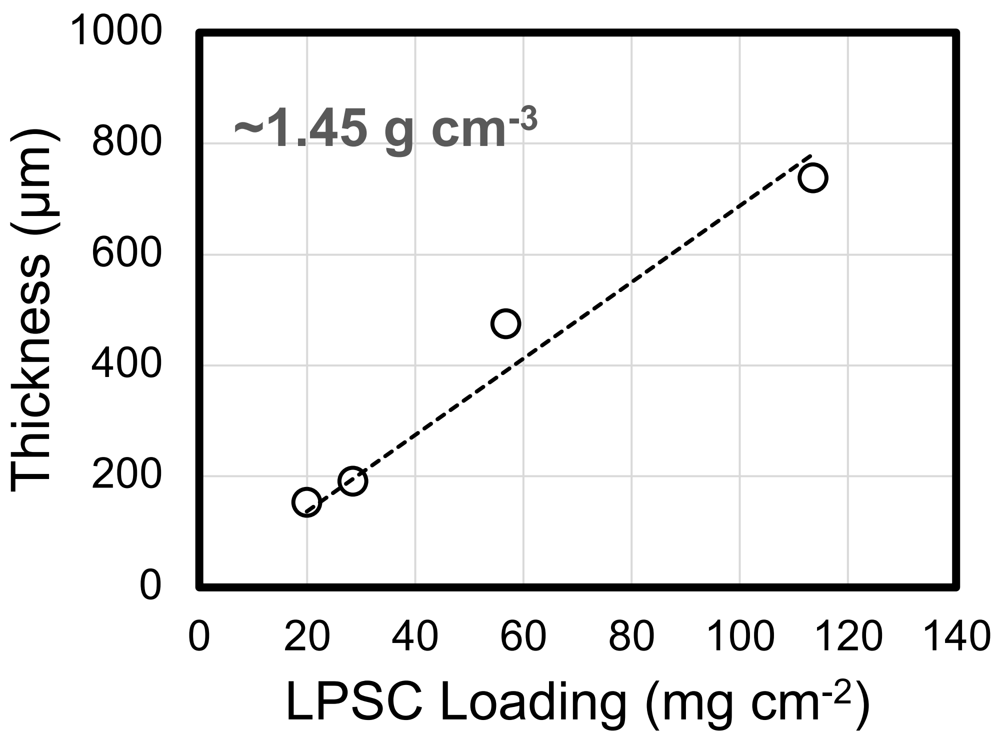
Increase Cathode Loading

Decrease Solid Electrolyte Loading



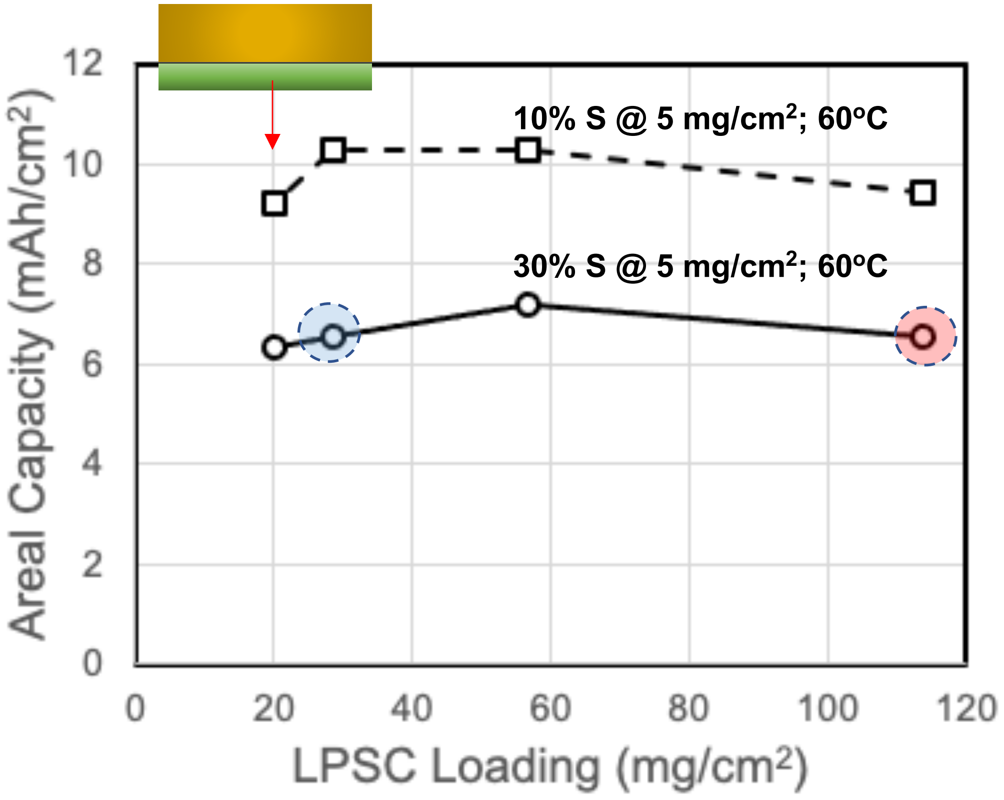
Reducing SE Thickness in Dry-Press

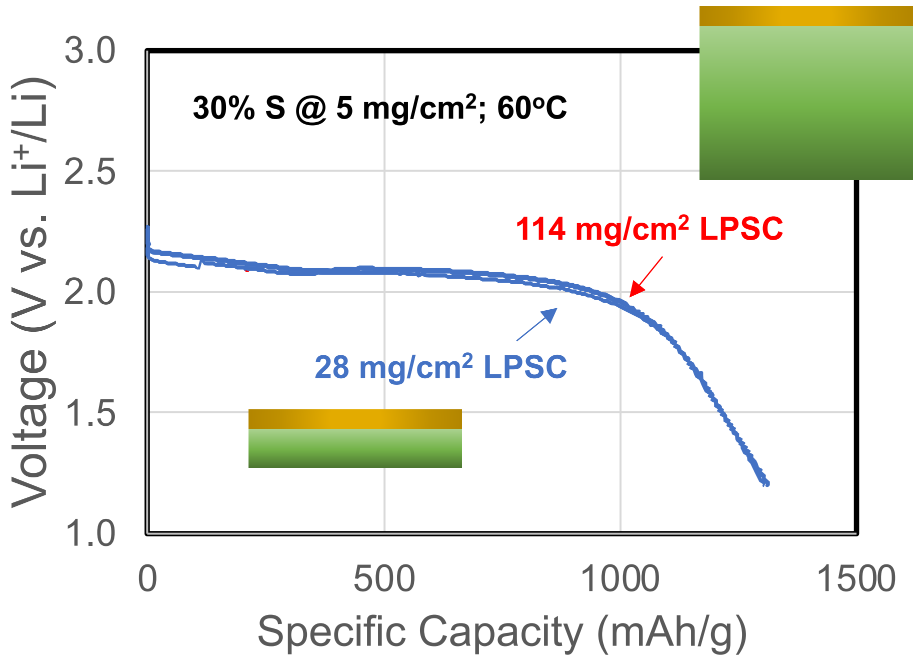




Improved Energy Density

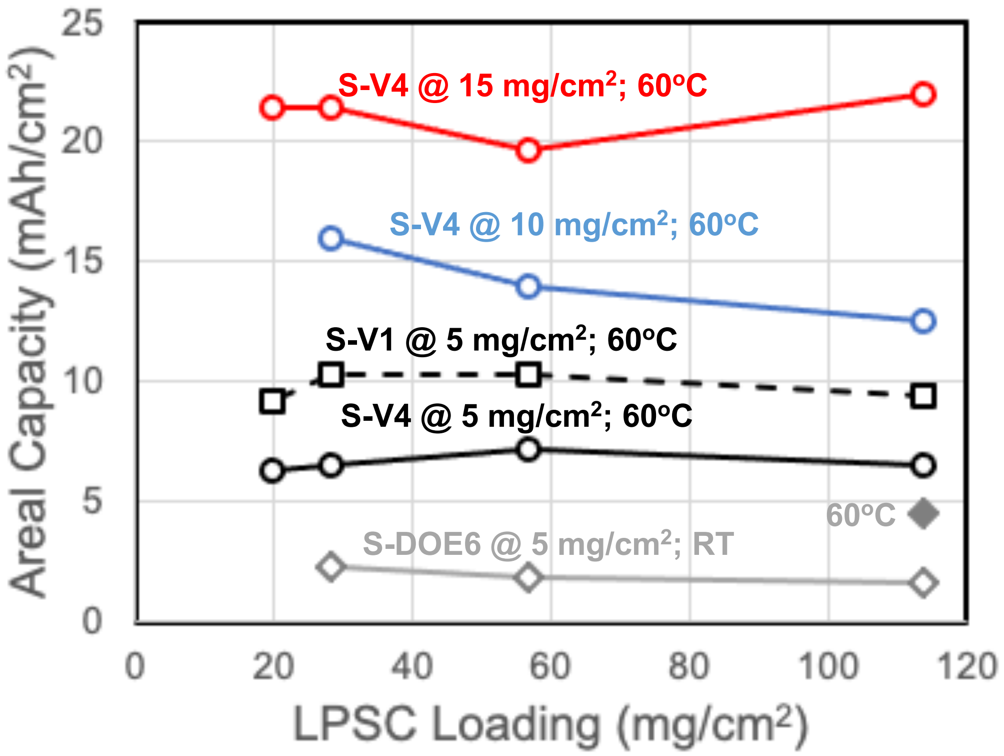
❑ Reduction in SE thickness + Increasing cathode S content with retained S utilization = **Improved Energy Density**

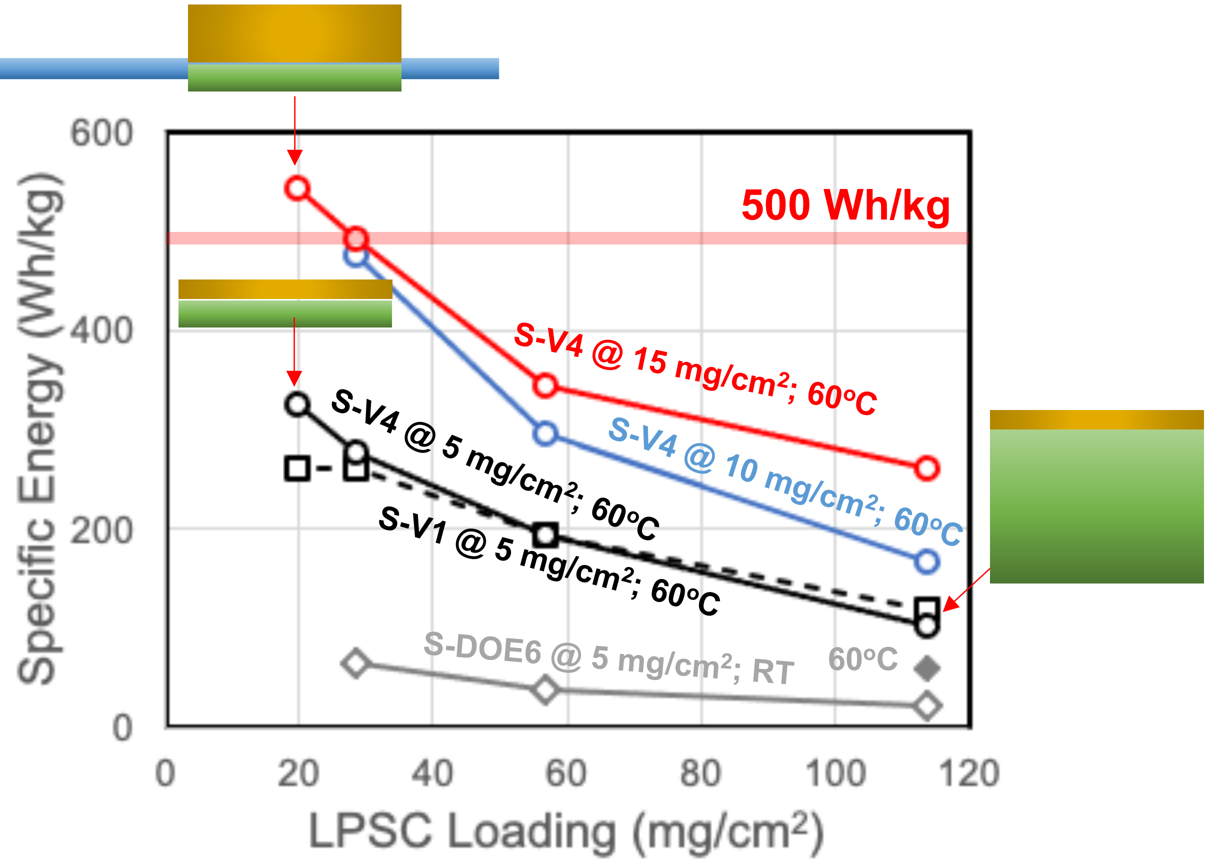




- ➢ All dry-pressed cathodes
- ➢ No additional stack pressure
- ➢ 0.032 mA/cm^2

Toward 500 Wh/kg



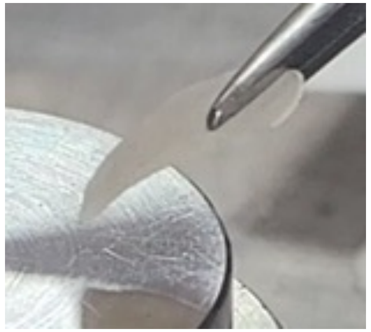


- ❑ "DOE6": 12% S
- ❑ "V1": 10% S
- ❑ "V4": 30% S
- ❑ All dry-pressed

- ❑ Calculated based on N:P = 2:1 (or 2x Li)
- ❑ Anode to be further optimized for cyclability

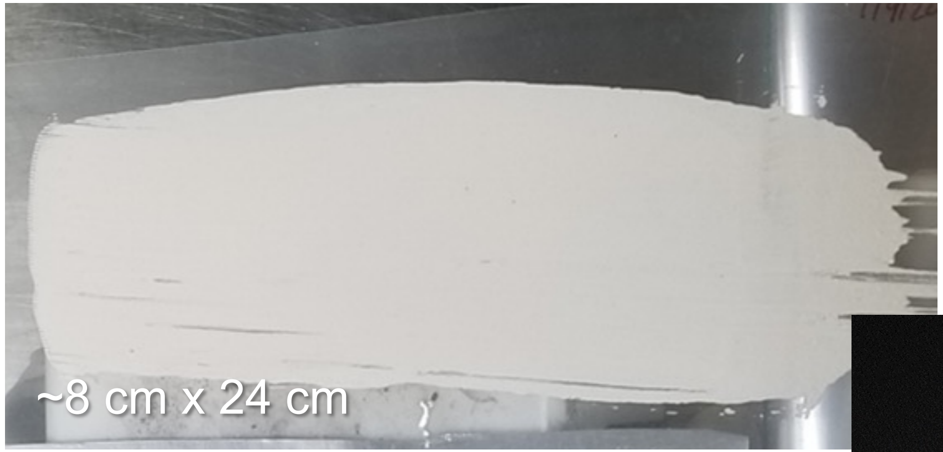
Increasing cathode S content and loading and reducing solid electrolyte thickness pushed specific energy pass 500 Wh/kg.

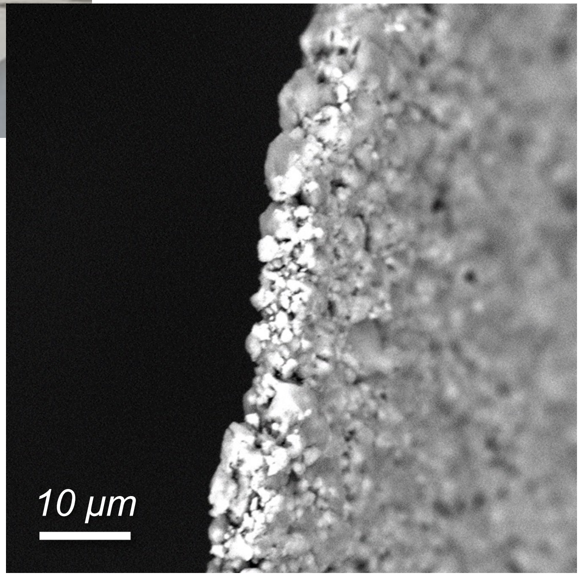
Reliable Reductions of SE Thickness



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

Tape-Casted LPSC Films
(~25 μm 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**

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  - 2022: Abigail Durgin, Bona Kim, Lucy Somervill, Rehan Rashid
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