High Performance Solid-State Batteries with Solvent-Free Processing

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Perspectives from Future Electric Aviation

Battery Performance Requirements

- The primary barrier to electric aviation is battery performance
- Aerospace batteries require: safety, high energy density, fast discharge rate, lightweight packaging, and scalability
- Sulfur (S) has ultra-high theoretical energy density (2510 Wh/kg)

Battery Safety Requirements

- Typical lithium (Li)-Ion batteries use flammable organic liquid electrolytes
- State-of-the-art batteries possess narrow operational temperature range and may undergo thermal runaway when heated or overcharged
- Solid-state electrolytes are intrinsically much safer

Solid-state Li-S chemistry could be the most plausible option for electric aviation.

Battery Sustainability Preferences

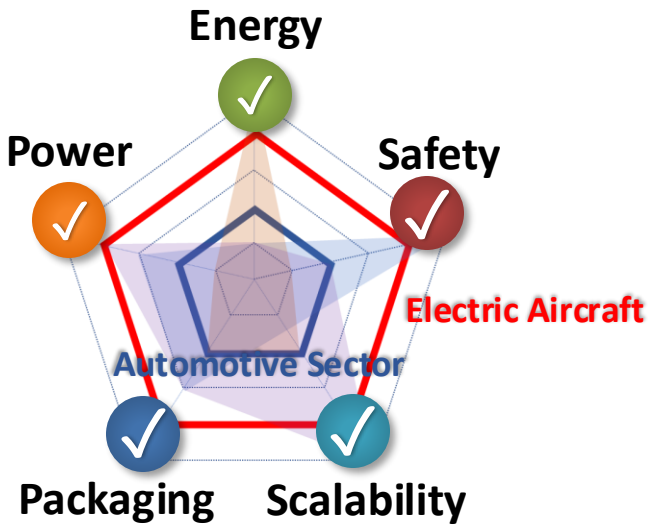
- More than 80% of the S supply is a waste product, extracted from fossil fuels
- If left in the environment, S converts to sulfur dioxide, the gas that causes acid rain

Battery Supply Chain Preferences

- Nickel (Ni)- and Cobalt (Co)-free chemistry
- U.S. has enough Li to meet battery needs (750,000 tonnes)
- Carbon (C) is widely accessible in the U.S.
- S is highly abundant and inexpensive in the U.S.

NASA SABERS Concept

- State-of-the-art lithium-ion batteries
- Lithium sulfur batteries
- Solid state batteries



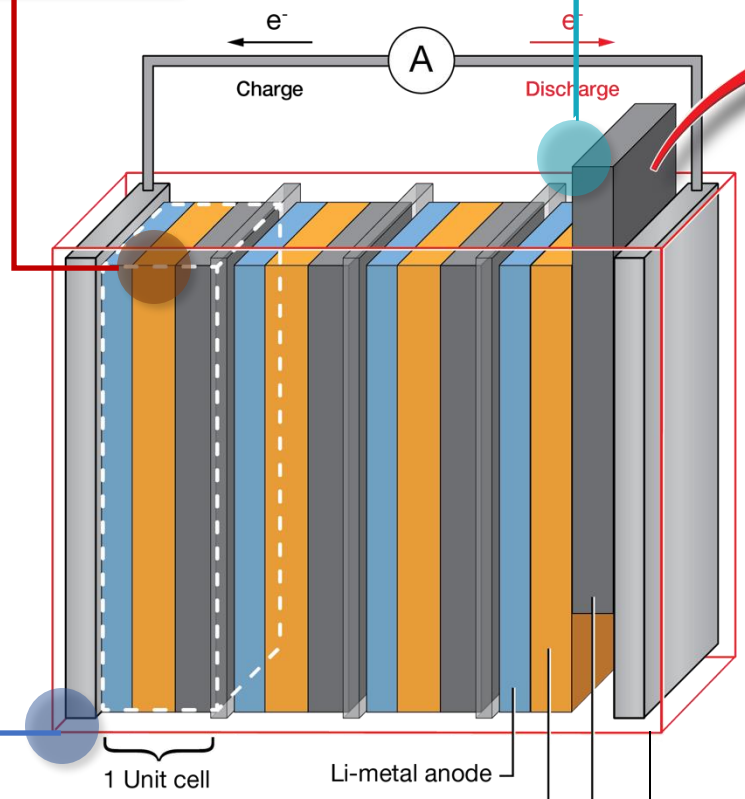
Safety

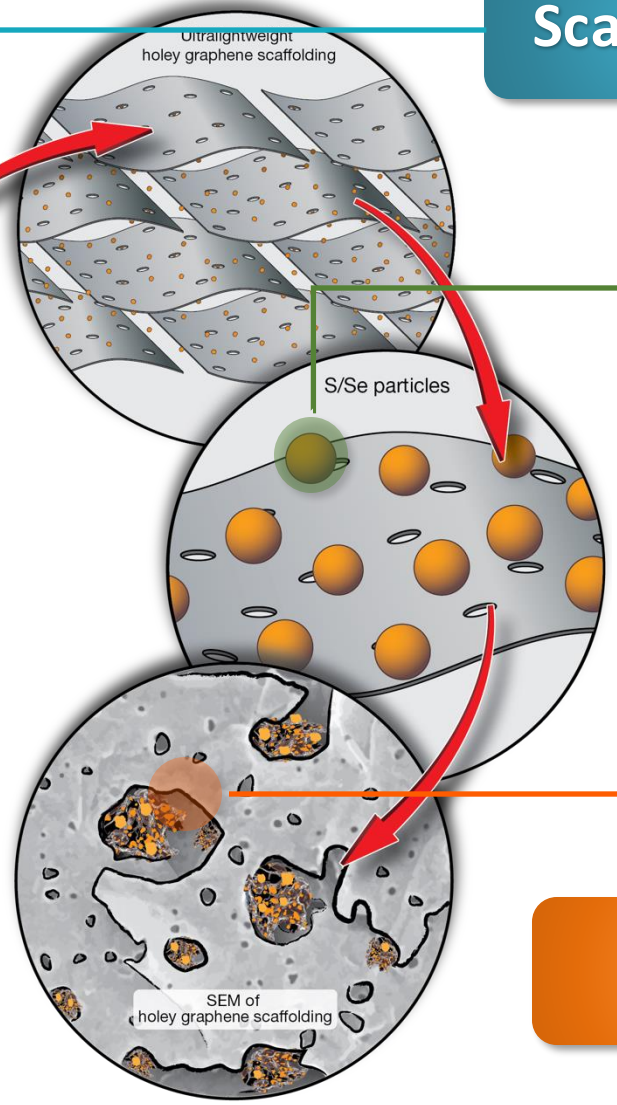
Scalability

Energy

Power

Packaging

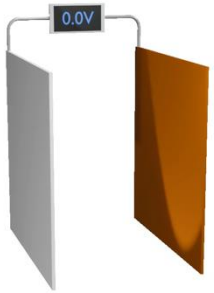


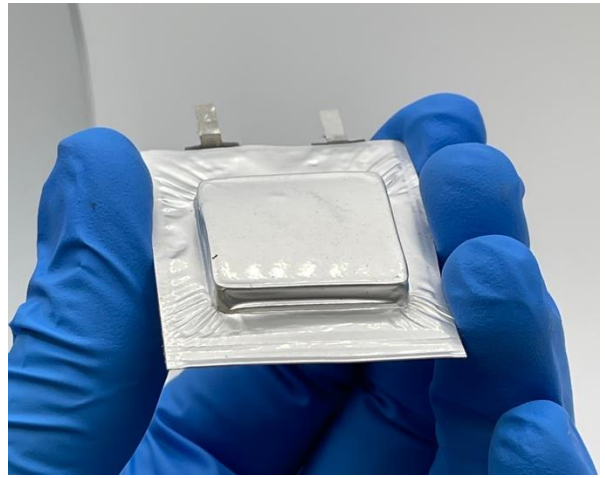


SABERS: Solid-state Architecture Batteries for Enhanced Rechargeability and Safety

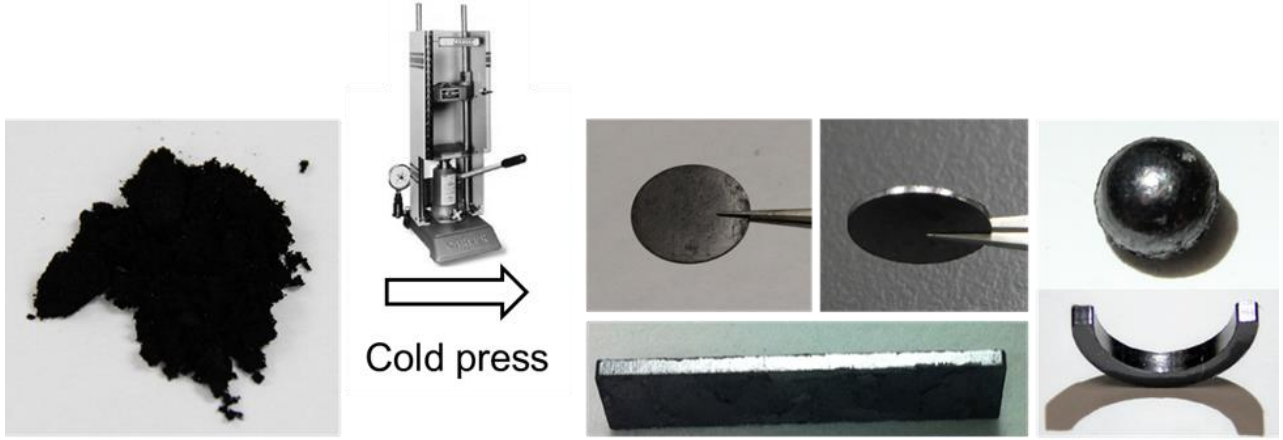
NASA SABERS Research Interest

- ❑High performance composite S cathodes
- ❑Thin, robust solid electrolyte membranes
- ❑High areal capacity Li anodes
- ❑Pouch cells and bipolar stacks
- ❑Aviation-specific performance conditions



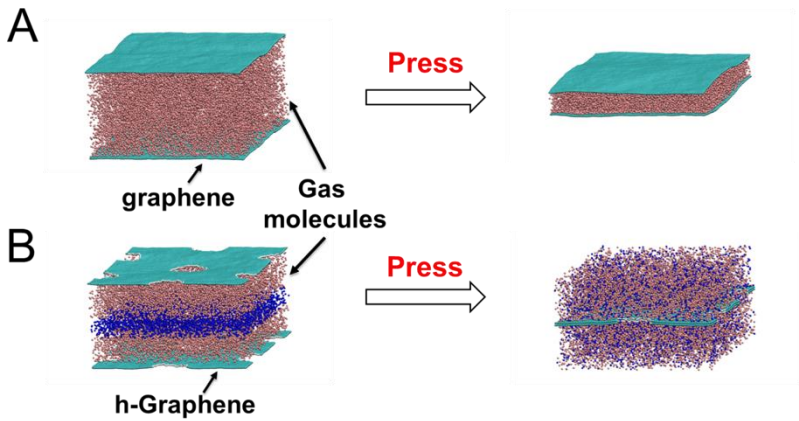


Dry Compressible Holey Graphene (hG)

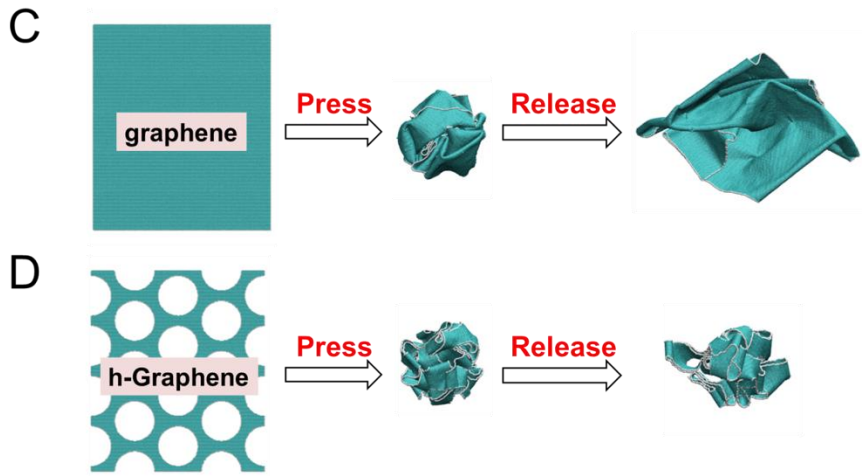


Holey Graphene Powder

Holey Graphene Monolithic Architectures



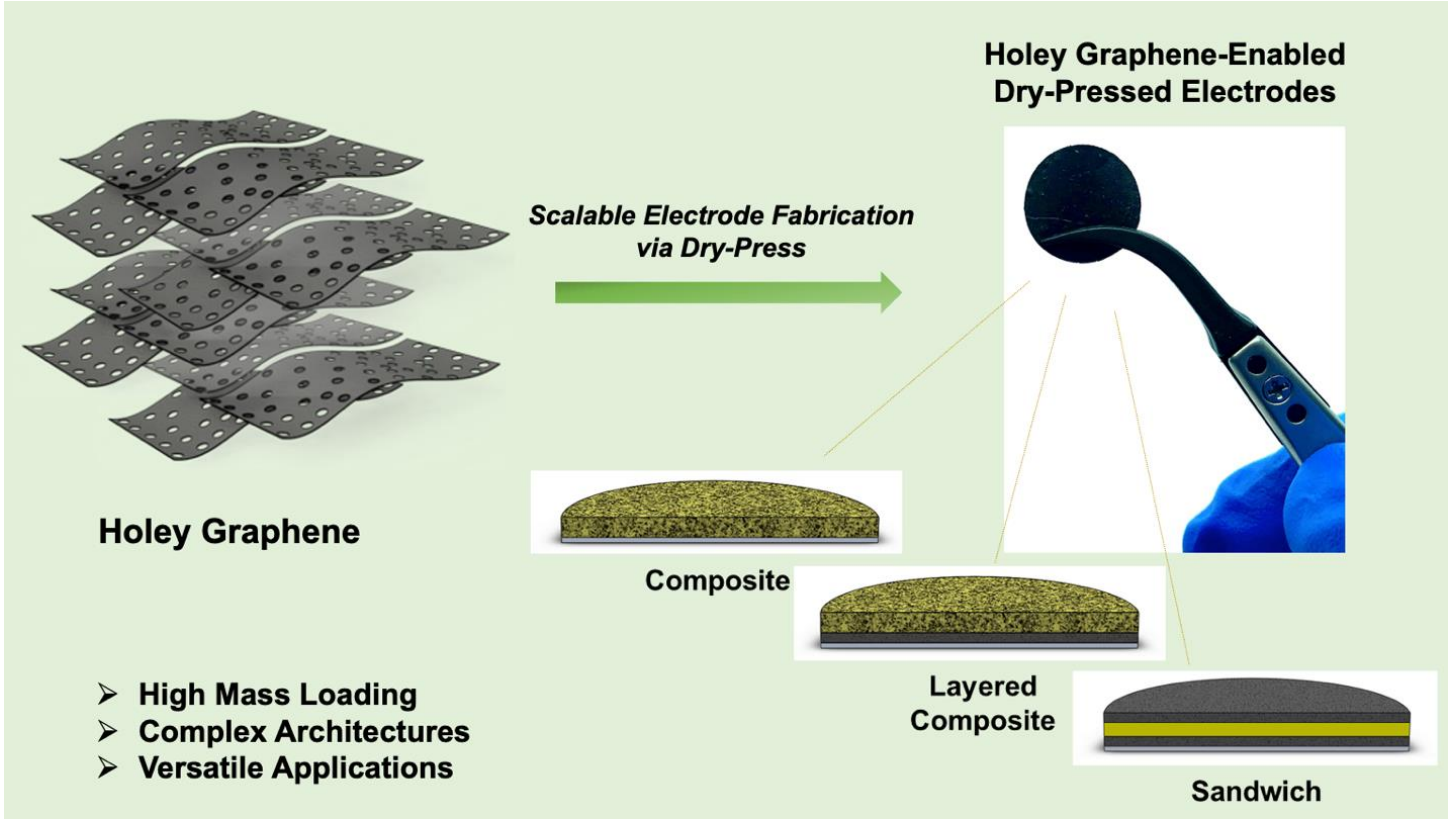
Facile air escape upon compression

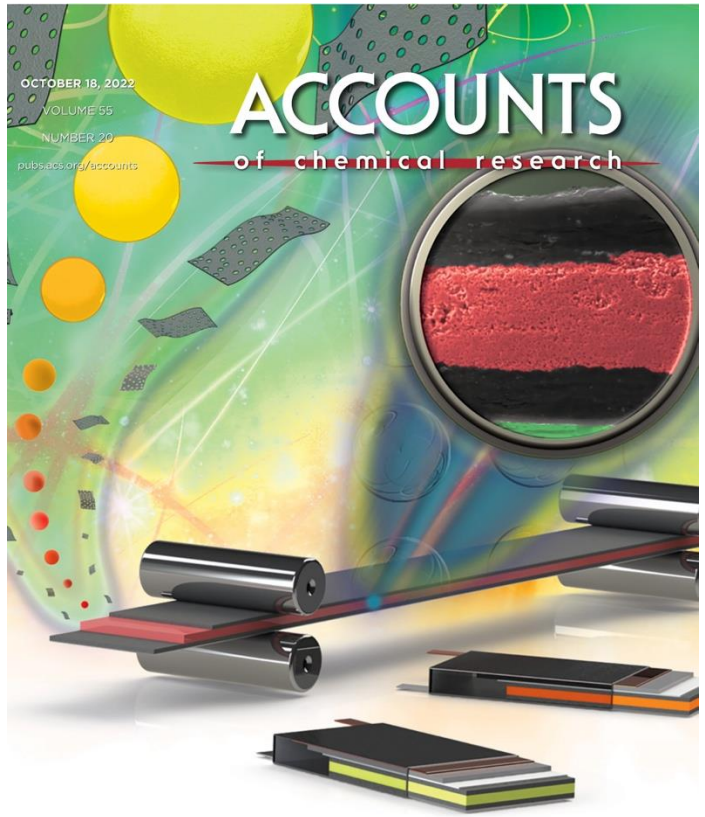


Minimal volume rebound upon release

ACS Nano **2017**, *11*, 3189. (In collaboration with Prof. Liangbing Hu)

Dry Compressible hG for Batteries





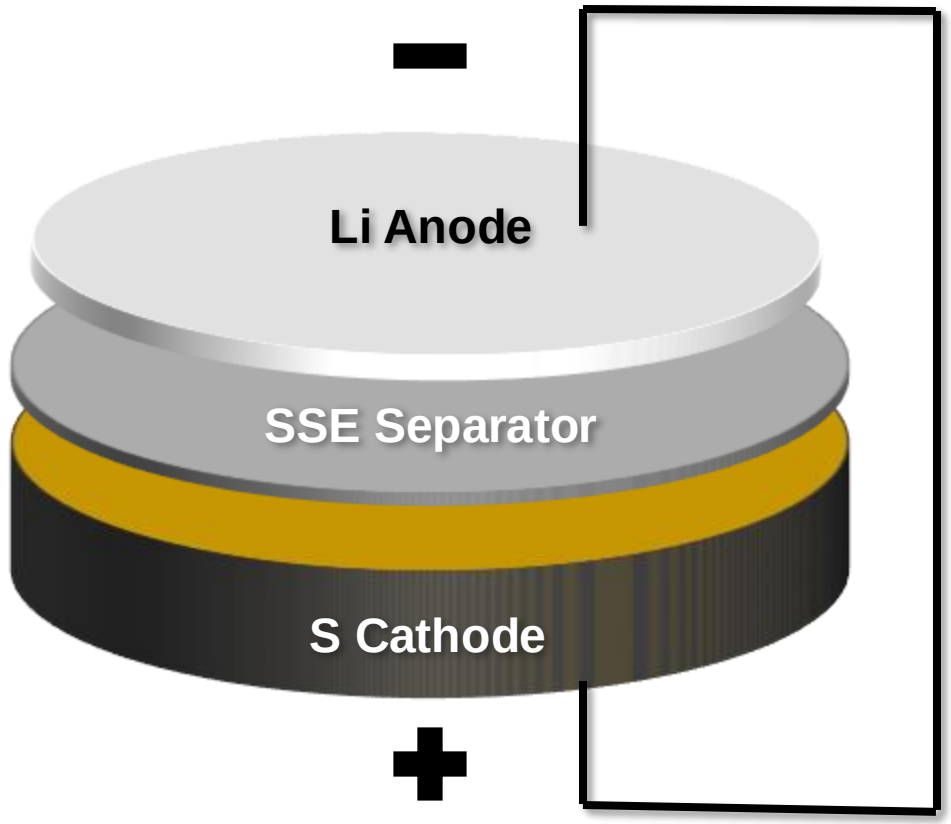
Acc. Chem. Res. **2022**, *55*, 3020-3031.

- Holey graphene is a unique conductive scaffold that can be **directly dry-pressed** into robust, high mass loading electrodes by itself or as a host for active battery materials.

A Solid-State Li-S Battery Cell

In solid-state Li-S batteries:

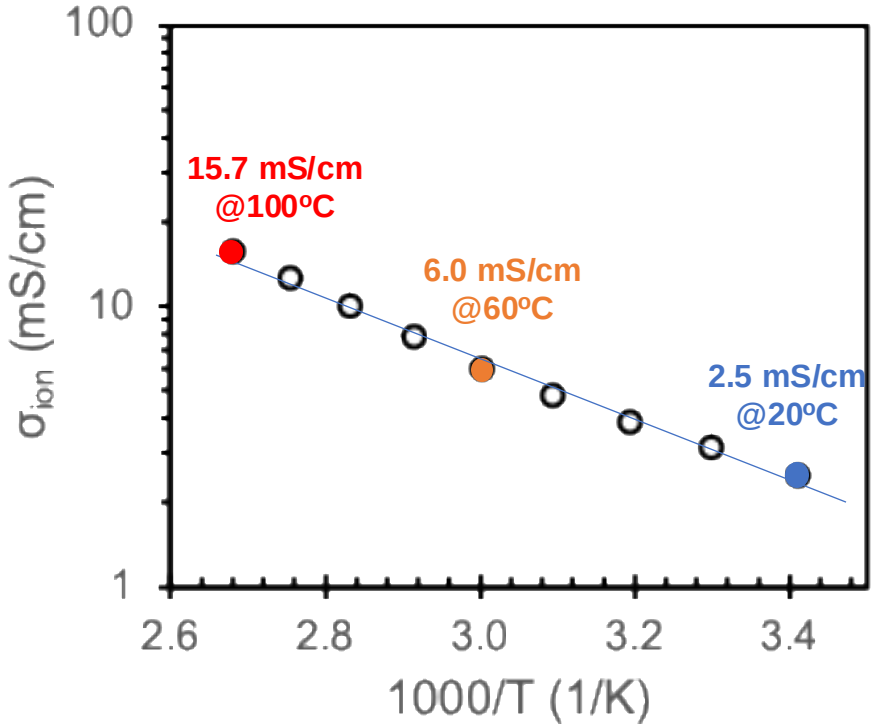
- **Anode**: Li metal
- **Solid state electrolyte (SSE) separator**: A solid layer that conducts Li ion but insulates electrons
- **Cathode**: S *and* necessary additives to make it electrically (thus carbon) and ionically (thus solid electrolyte) conductive



Commercially Available Sulfide Electrolytes

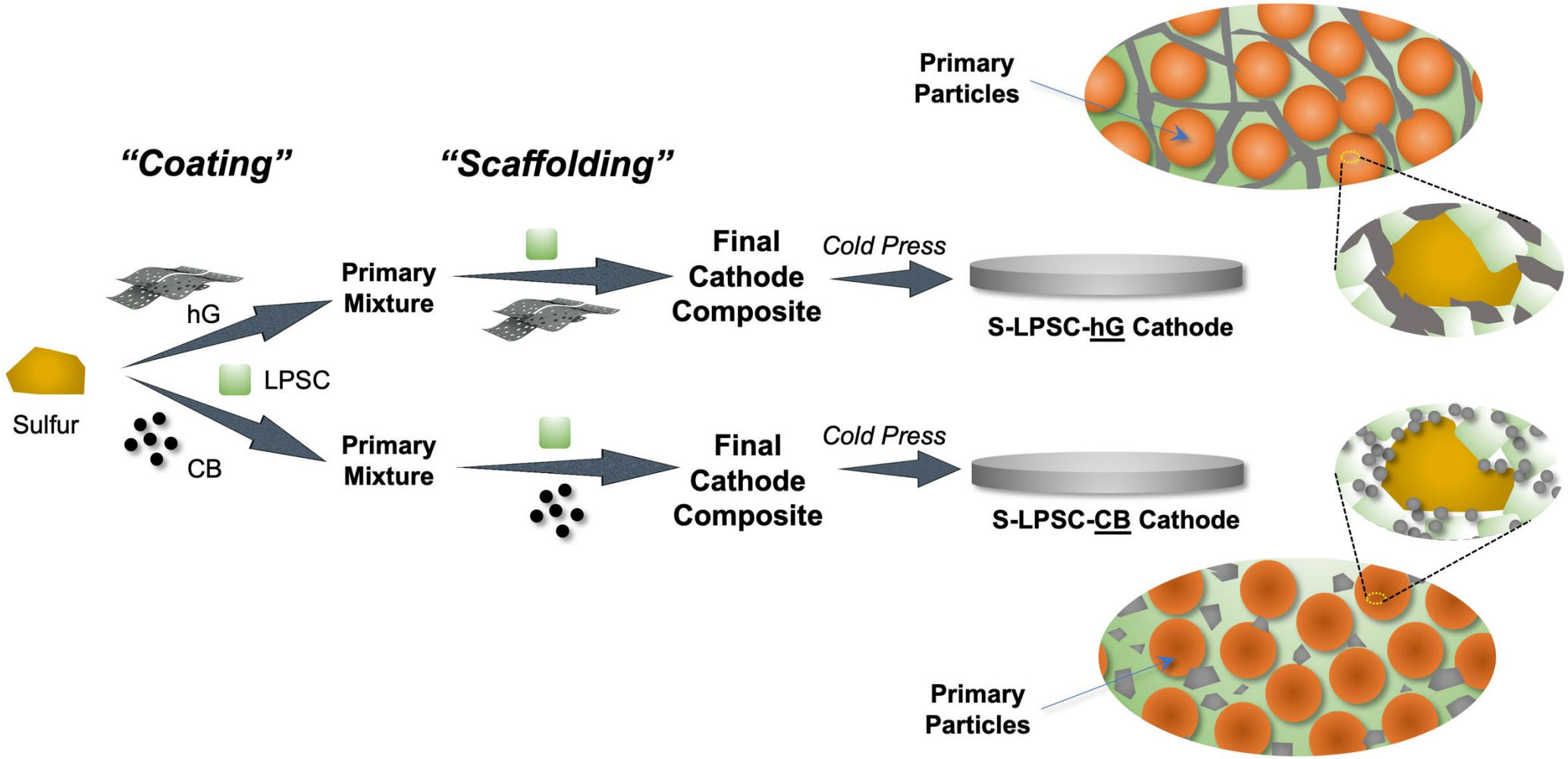
Sulfide Electrolytes	Vendor
$Li_{10}SnP_2S_{12}$ (LSPS)	NEI
$Li_6PS_5Cl_{0.5}Br_{0.5}$	MSE
$Li_6PS_5Cl_{0.9}I_{0.1}$ (LPSC-I)	NEI
Li_6PS_5Cl (LPSC)	NEI
$Li_7P_3S_{11}$	MSE
$Li_{10}GeP_2S_{12}$-Fine	MSE
$Li_{10}GeP_2S_{12}$-Coarse	MSE

- NEI: NEI Corporation (http://neicorporation.com)
- MSE: MSE Supplies LLC (http://msesupplies.com)



- Sulfide electrolytes are typically of high ionic conductivity (> 1 mS/cm)
- Sulfide electrolytes are soft and highly feasible for dry processing
- Li_6PS_5Cl (LPSCl; LPSC) is the most studied sulfide electrolyte and commercially available in large quantities (~$10/g)

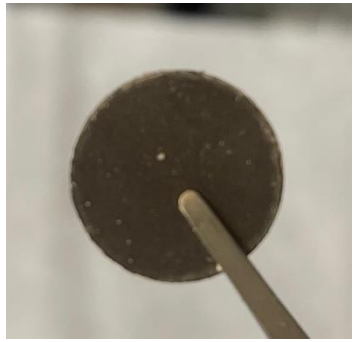
All-Solid-State S Composite Cathodes

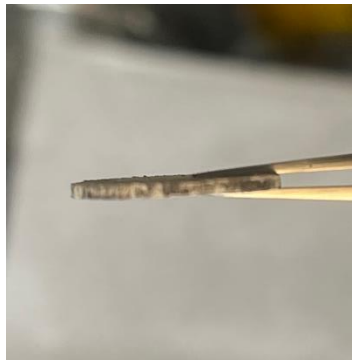


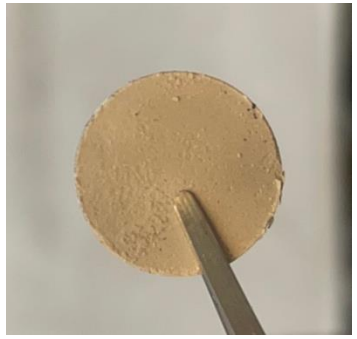
- CB: carbon black
- SSE: LPSC (Li_6PS_5Cl)

Dry-Pressed Cathode/SSE Bilayer Discs

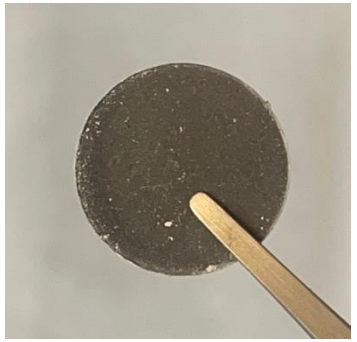
CB

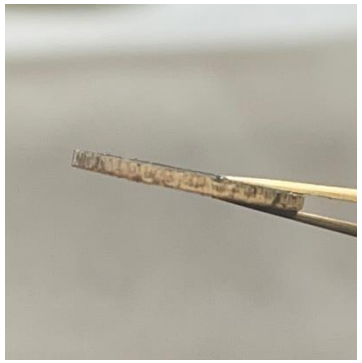






hG

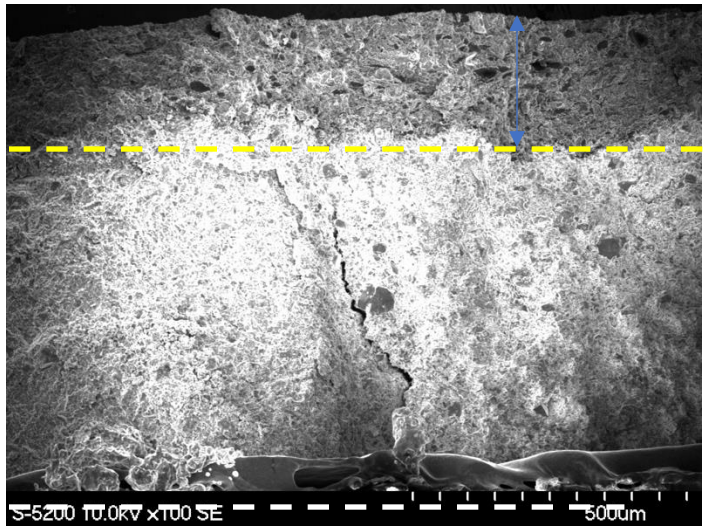


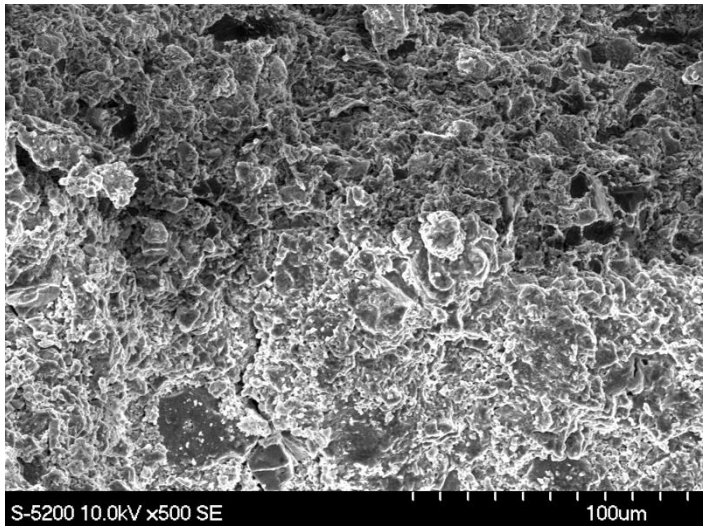


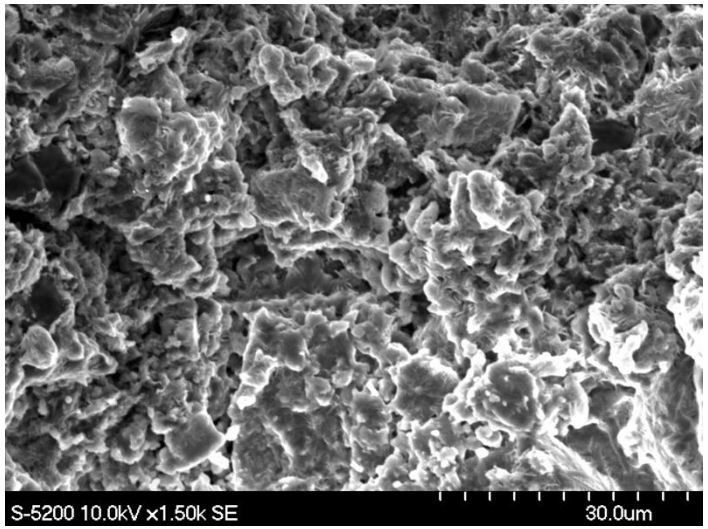
- Both composites are compressible to form robust cathode/SSE bilayer discs
- LPSC glass electrolyte serves as binder
- hG as “cold pressable hosts” is not an obvious advantage…?

Dry-Pressed Cathode/SSE Bilayer Discs

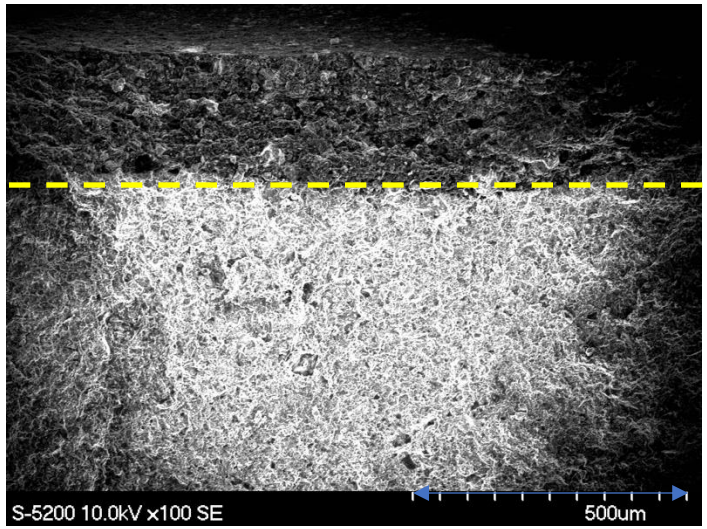
hG

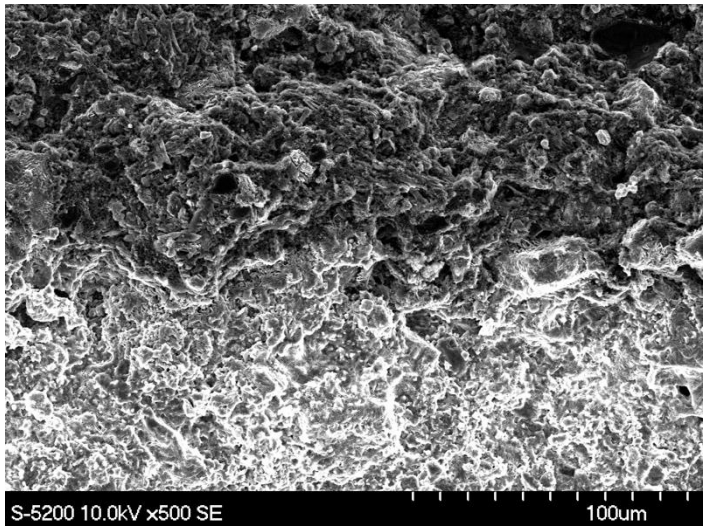


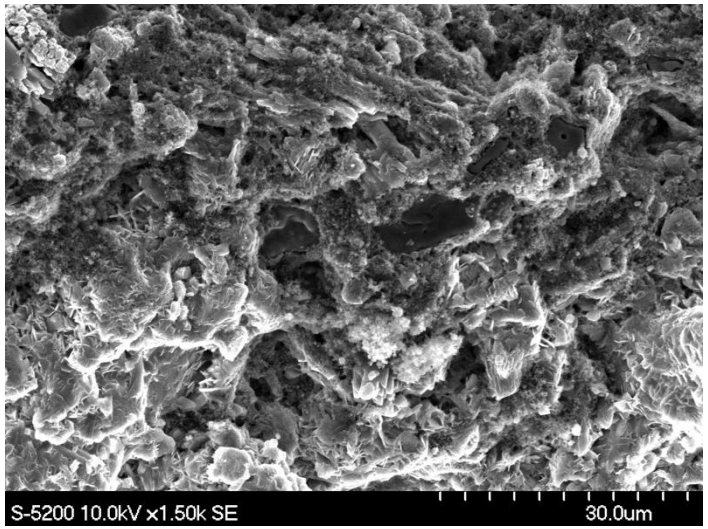




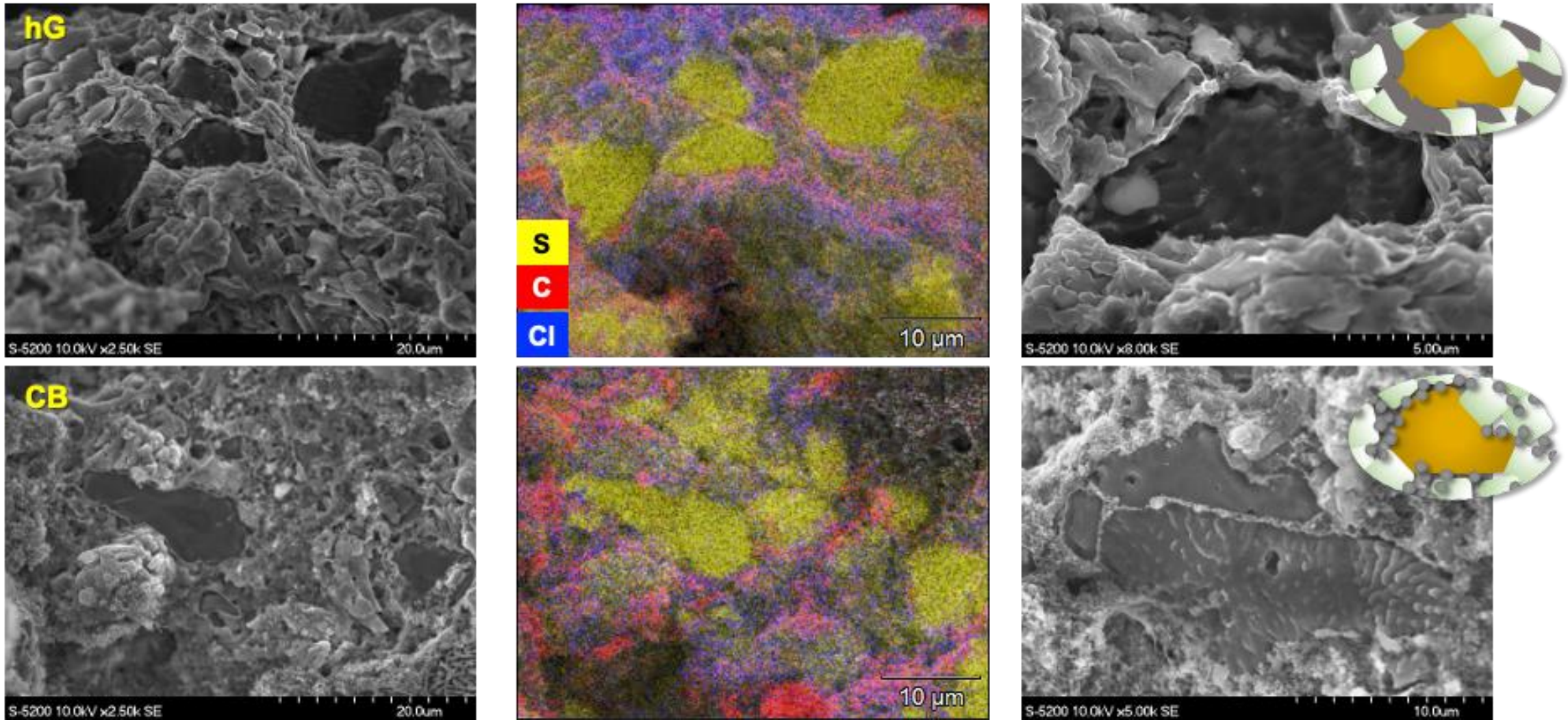
CB



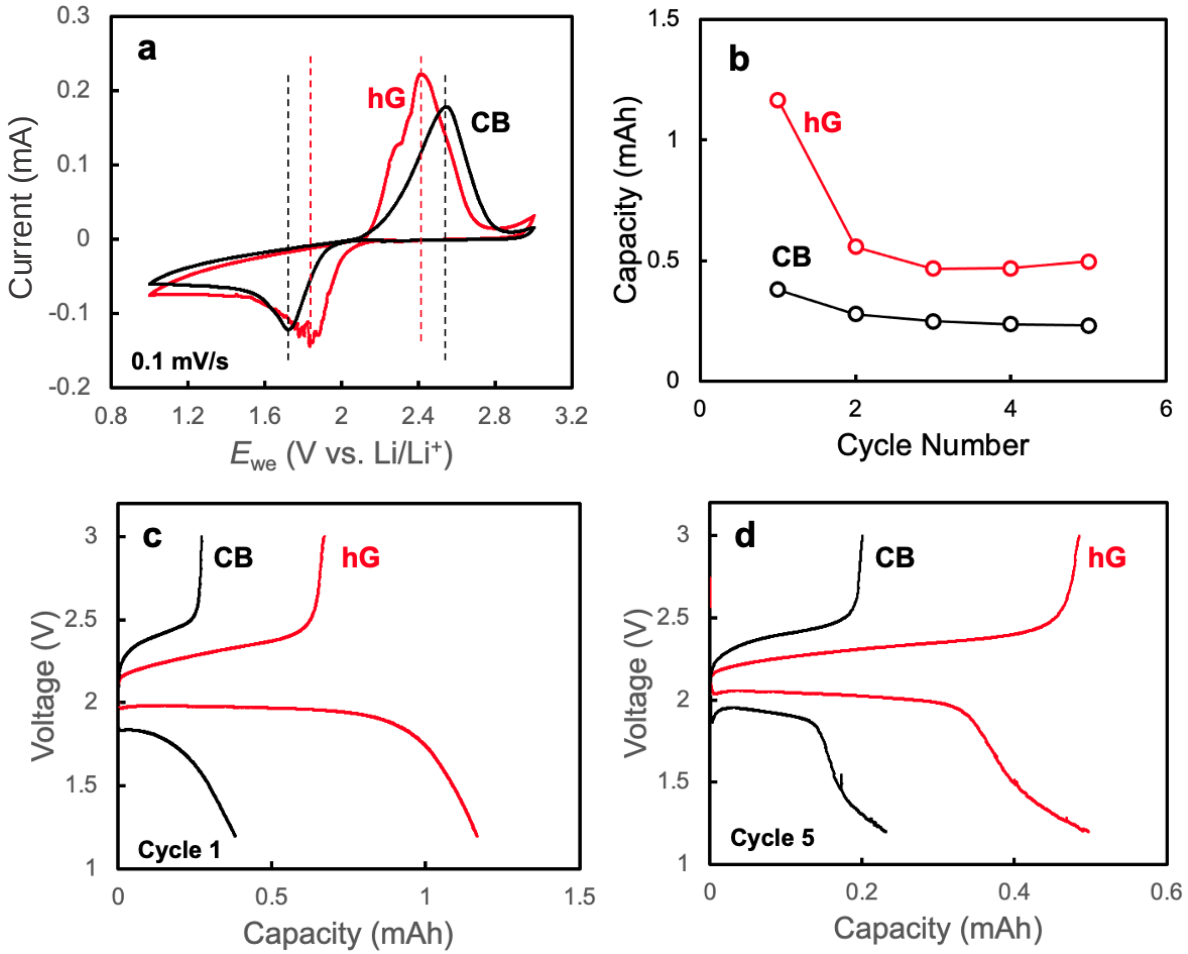




S Cathode Microstructures

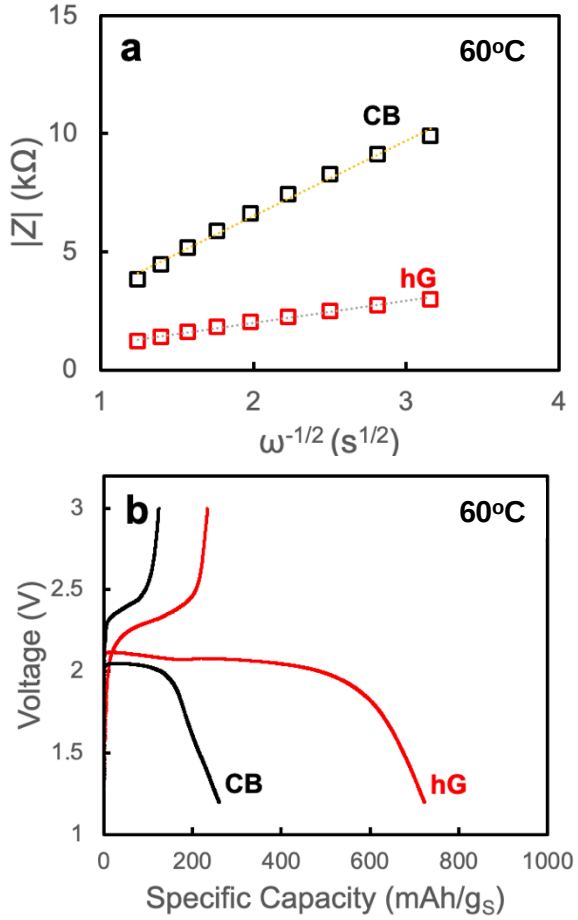


hG vs. CB



Room Temperature

12 mg/cm²



60ºC

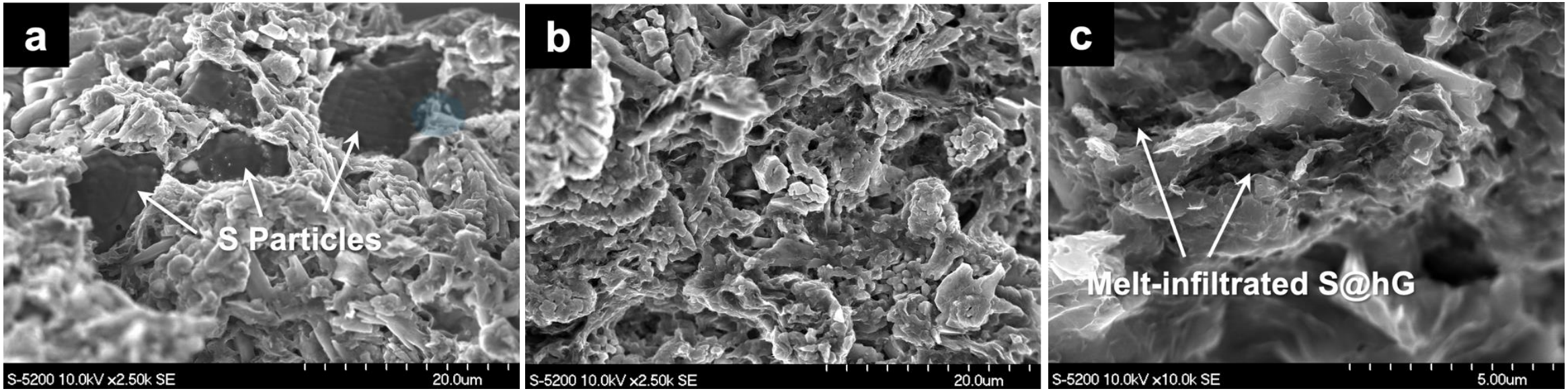
5 mg/cm²

- ❑ Li metal anode
- ❑ Coin cells (< 2 MPa stack pressure)

Cathode Composite with Melt Infiltrated S

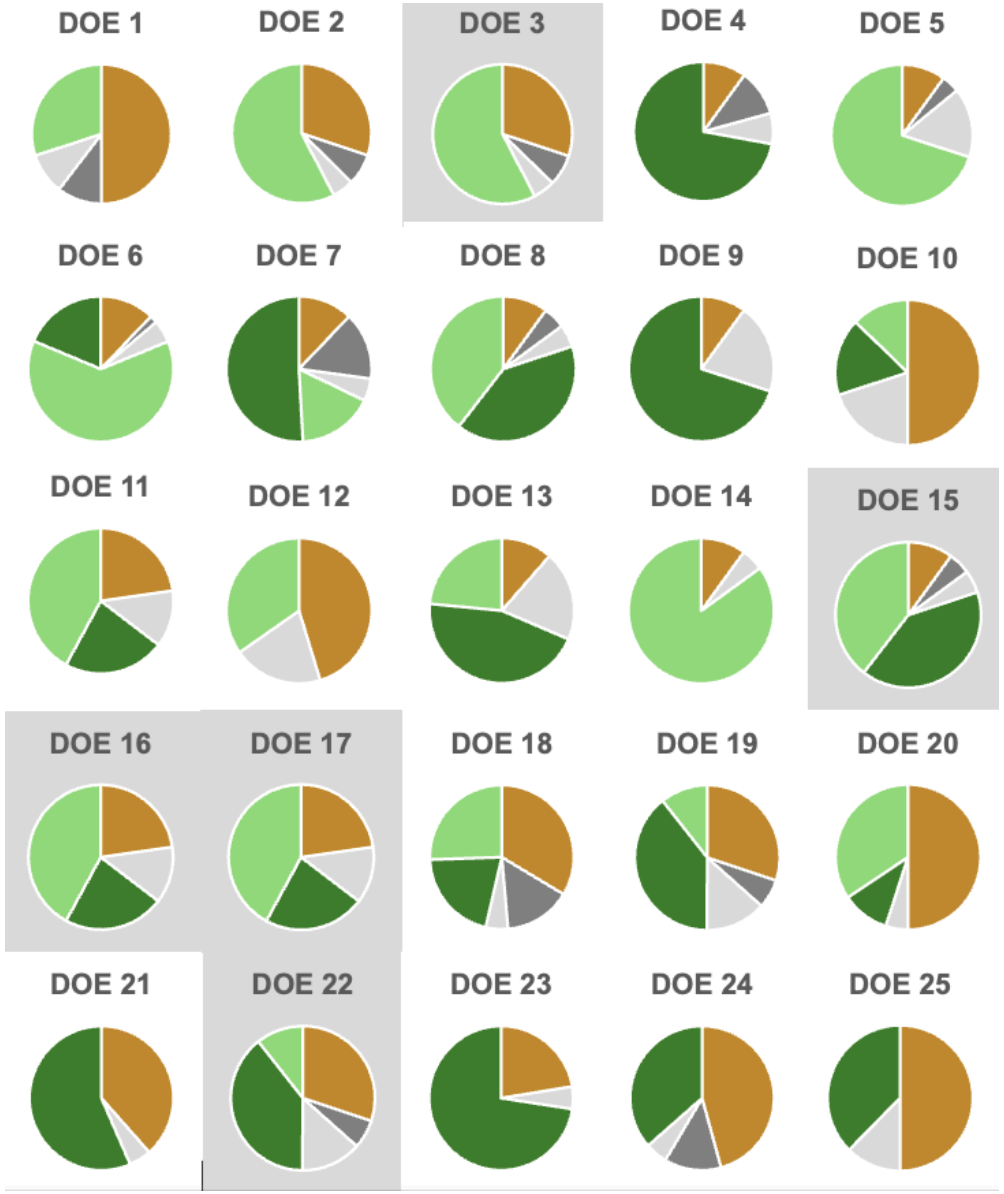
Mixing with Pristine S Particles

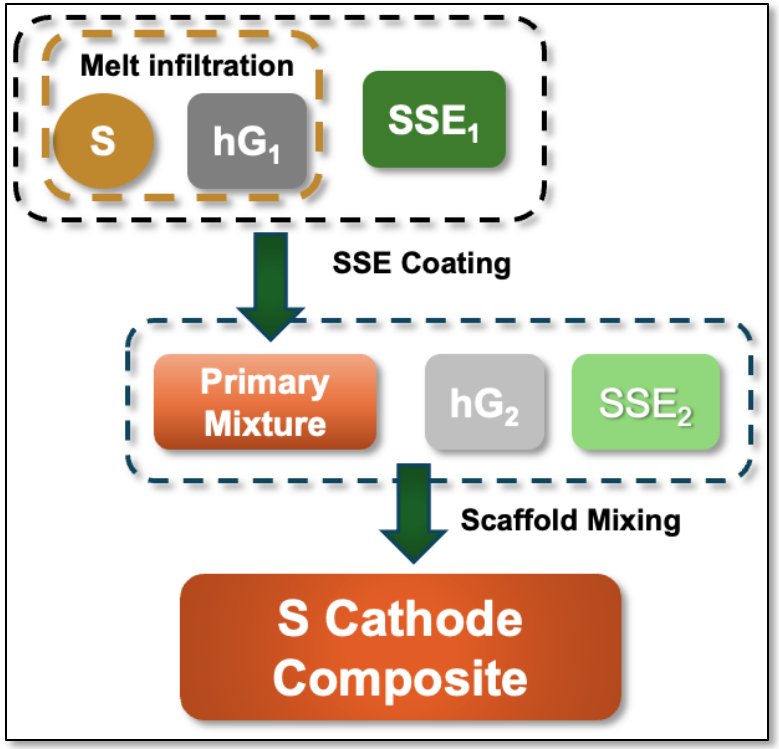
Melt Infiltrating S onto hG Sheets



- Melt infiltration of S onto hG sheet surface significantly improves electrical and ionic contact area of sulfur with hG and SSE, respectively

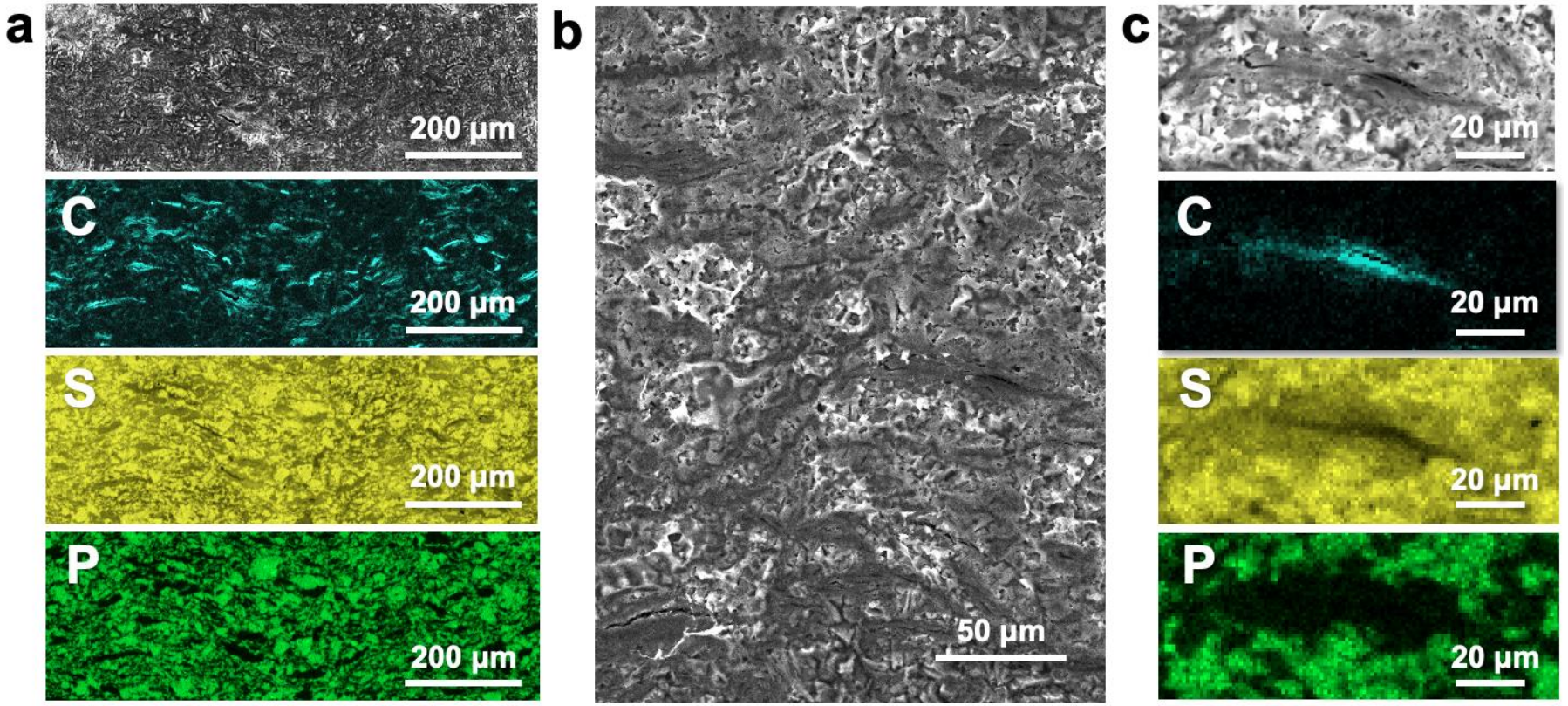
Optimizing Dry Processing of S Cathode





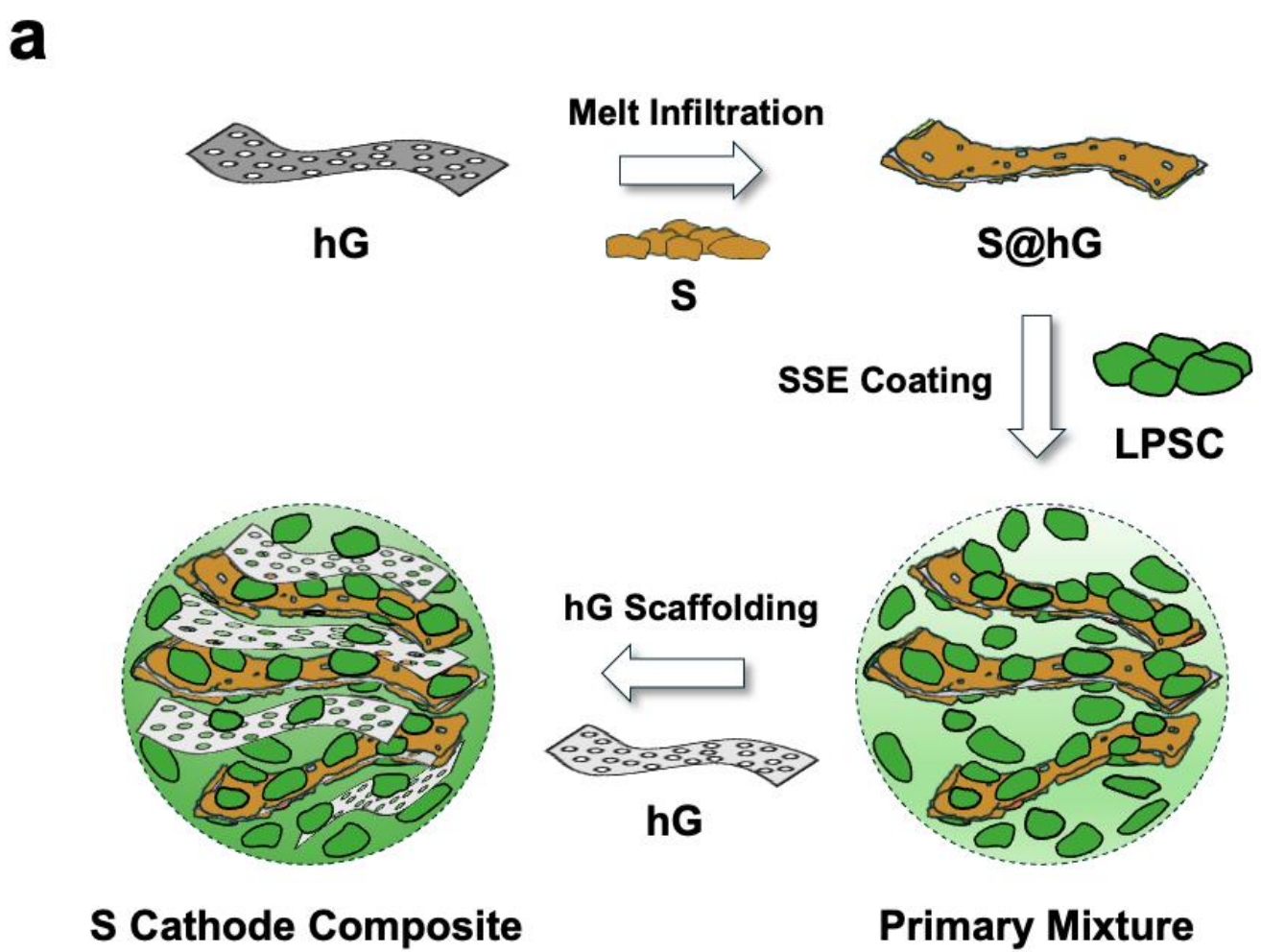
- A Design-of-Experiment (DOE) study
- 20 unique compositions
  - S: 10-50%
  - hG_1+hG_2: 5-20%; hG_1: 0-15%; hG_2: 0-20%
  - SE_1+SE_2: 30-85%; SE_1: 0-75%; SE_2: 0-70%
  - No hG_1 = no melt infiltration

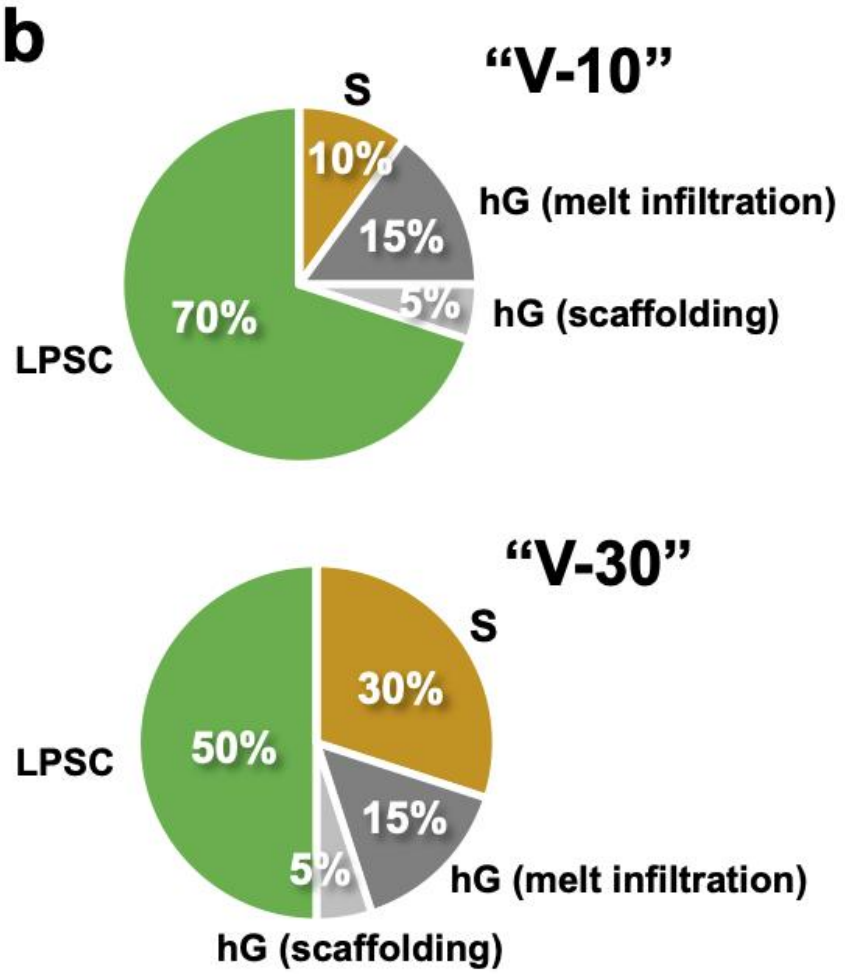
S Composite Cathode Design Principles



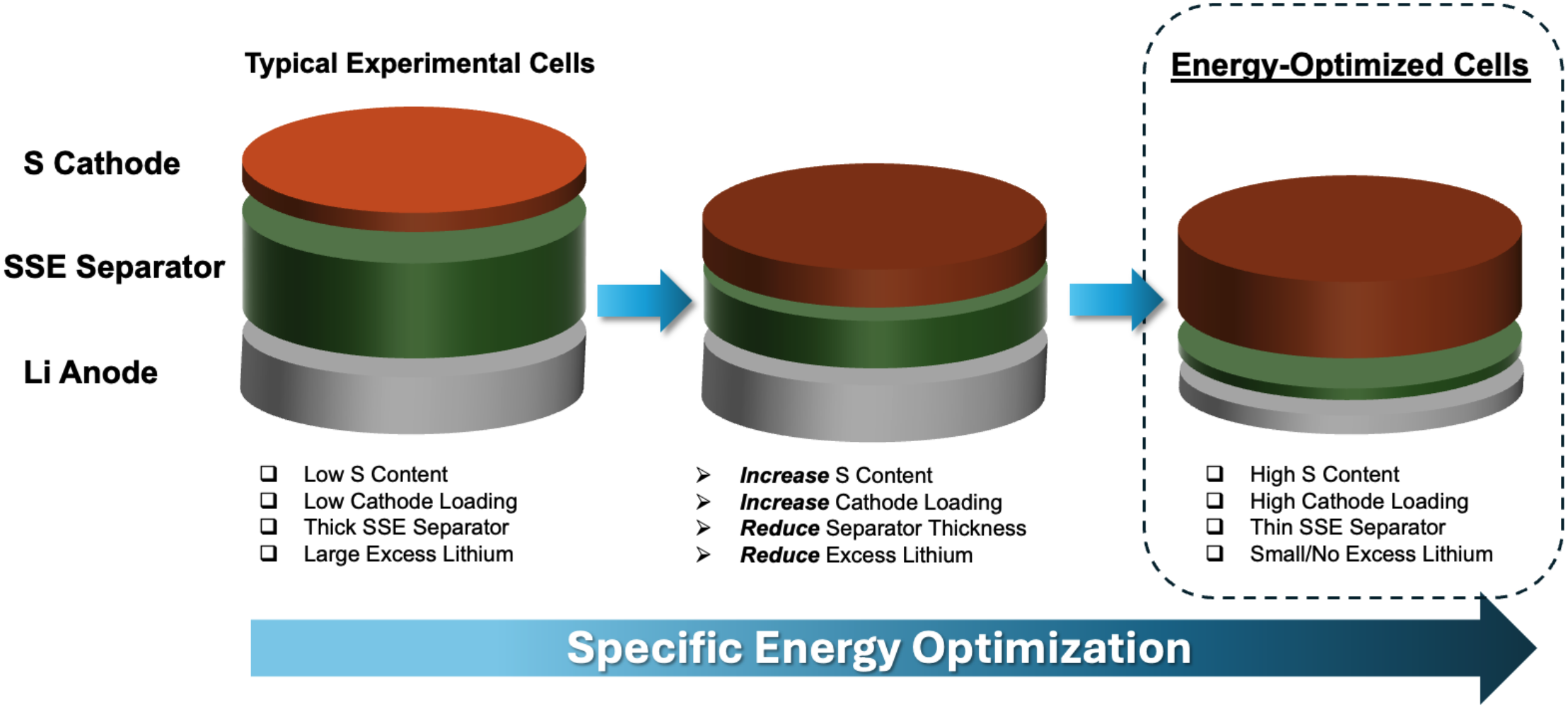
- ❑ High Discharge Capacity
  - ➢ Low S content
  - ➢ High hG:S ratio in melt infiltration
- ❑ Low Overpotential
  - ➢ Low S content
  - ➢ Medium hG:S ratio in melt infiltration
- ❑ Low Impedance
  - ➢ High scaffolding-step hG content
  - ➢ High coating-step SE content
- ❑ High Li^+ Diffusion Coefficient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

S Composite Cathodes Optimization

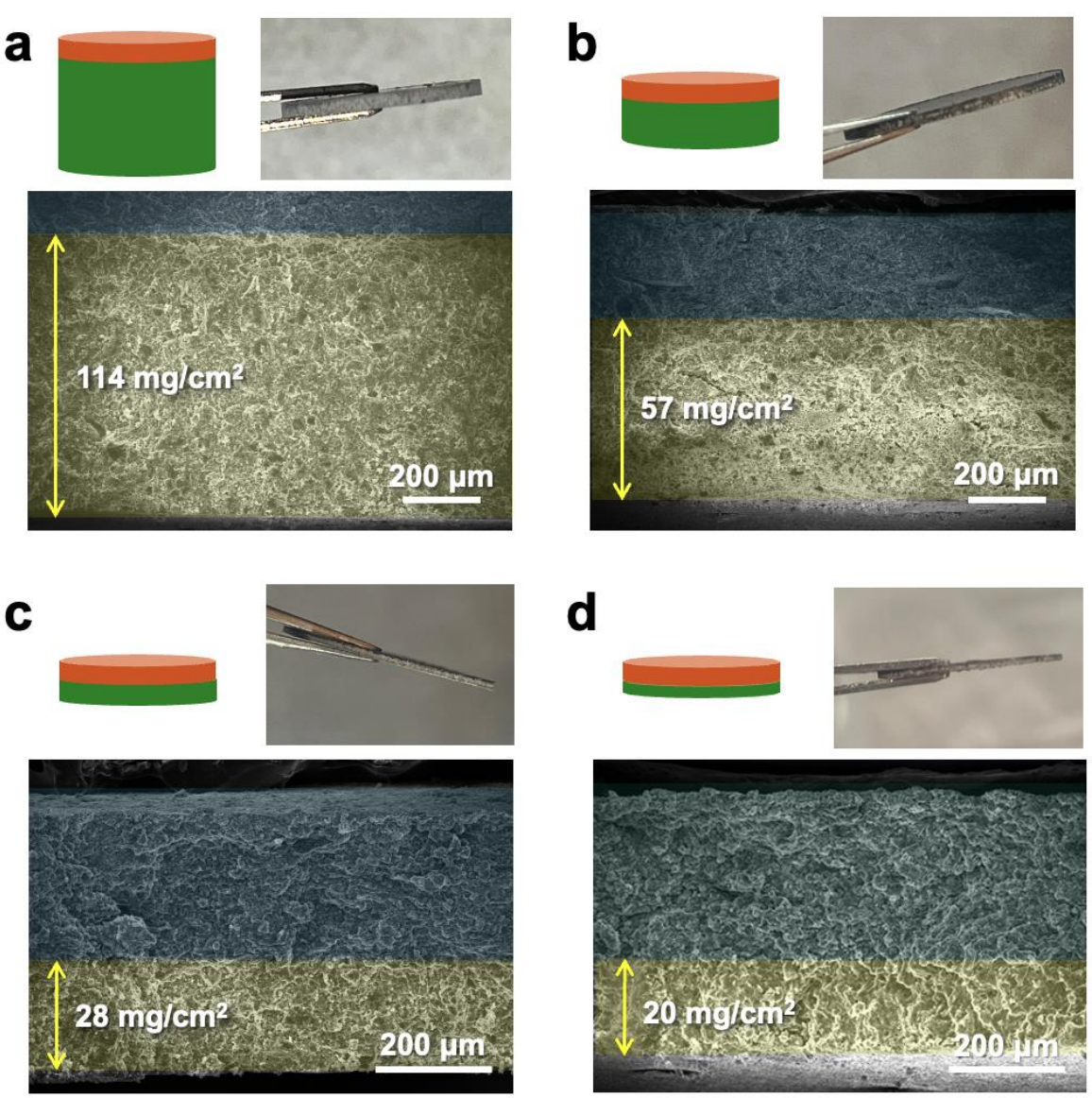


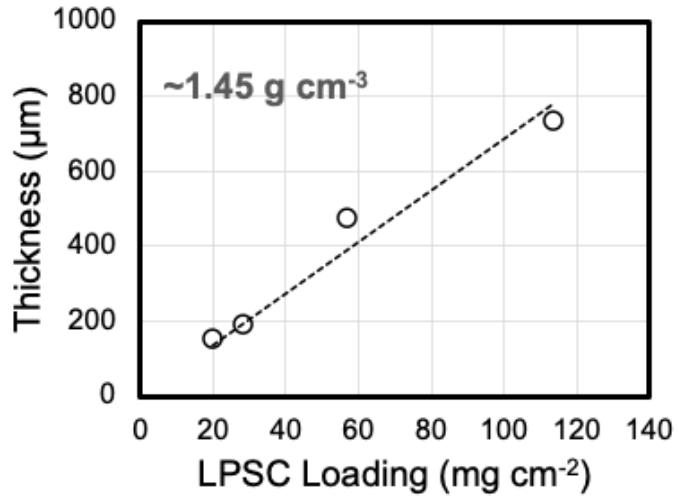


Cell Integration to Improve Specific Energy



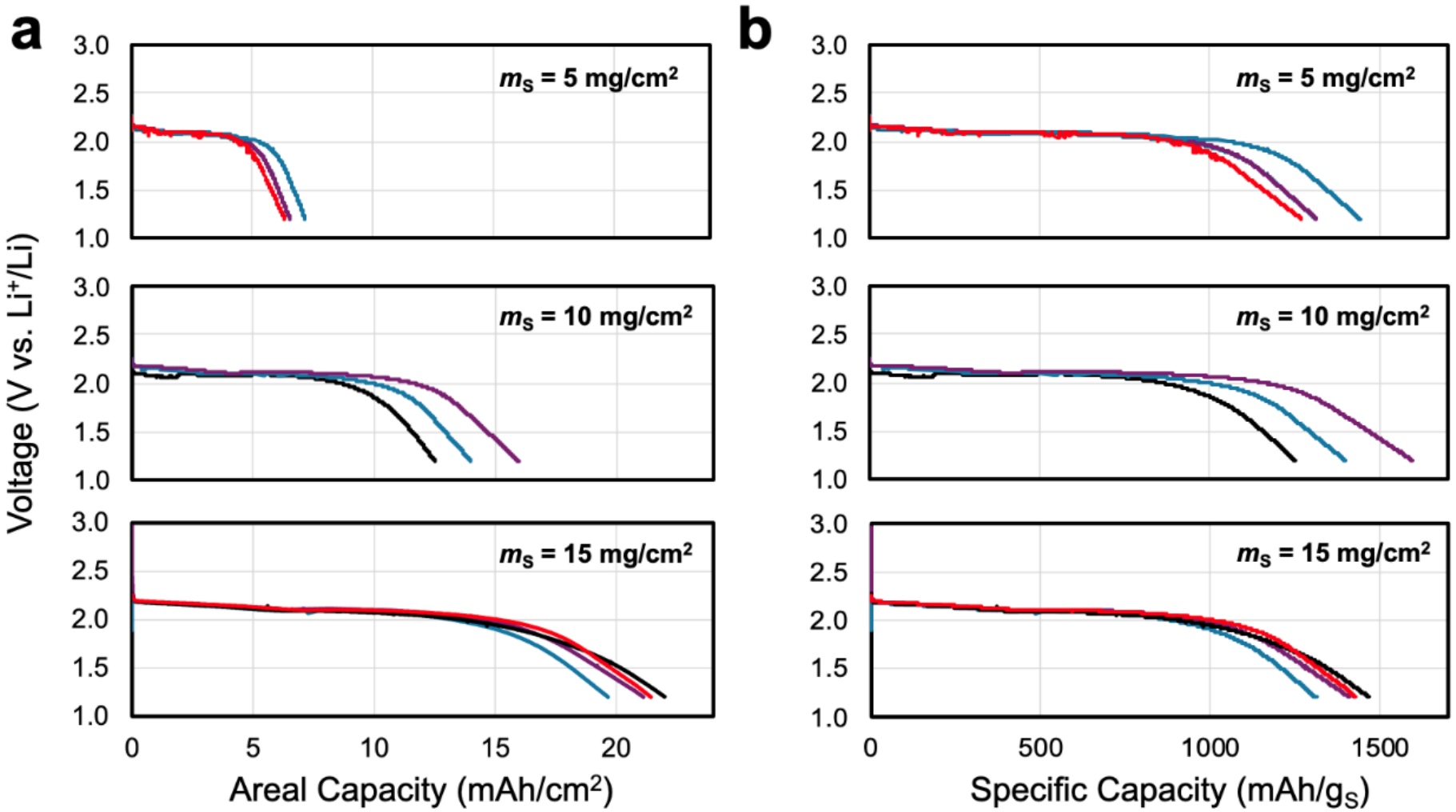
Reduce SSE Thickness with Dry Pressing





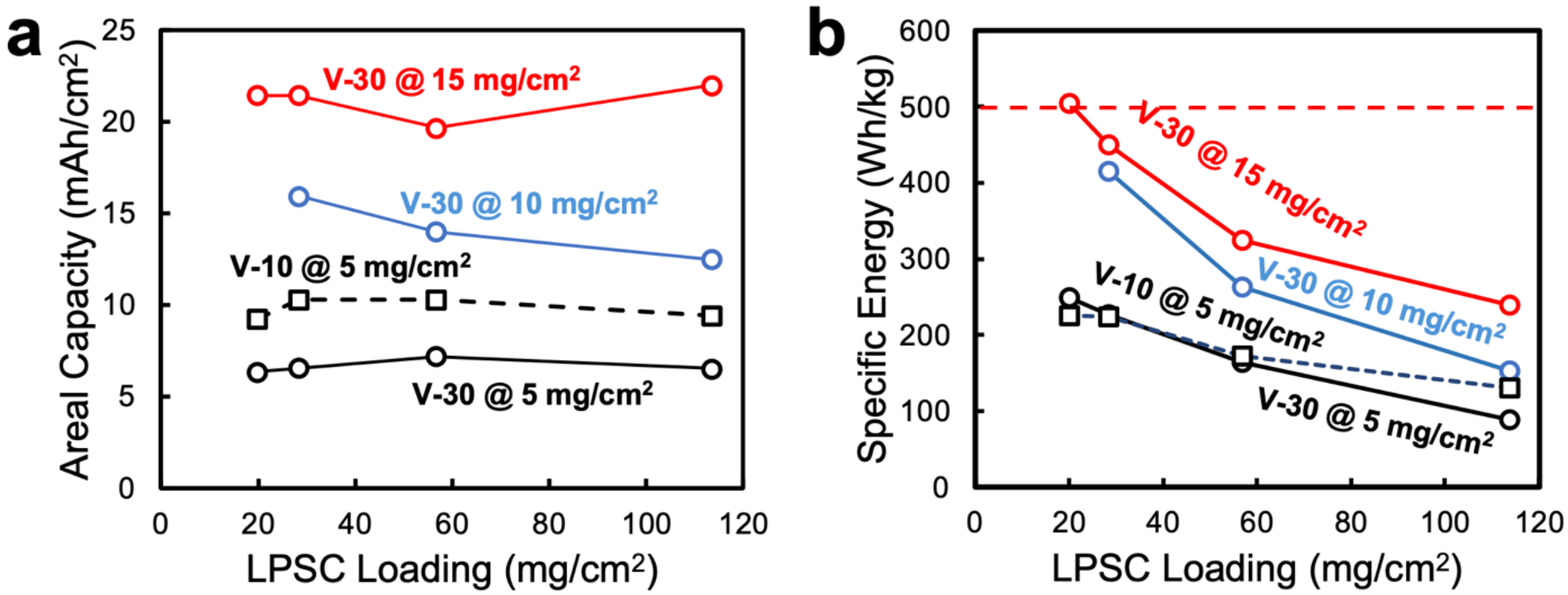
- ❑ Proof-of-concept experiments
- ❑ Doable yet extremely challenging

Ultrahigh Areal Capacity S Cathodes



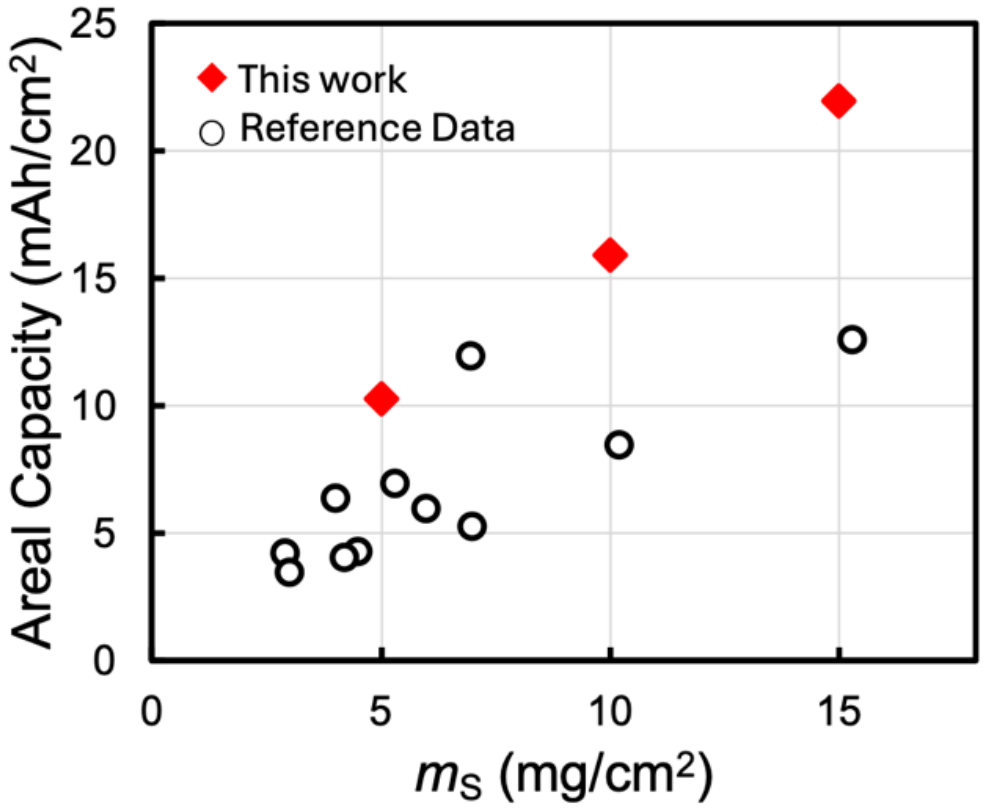
- Increase the areal capacity of S cathodes by increasing the S mass loading (more V30 cathode used)
- Capacity performance is consistent despite various SSE loadings (114 (black), 57 (blue), 28 (purple), and 20 (red) mg/cm²)

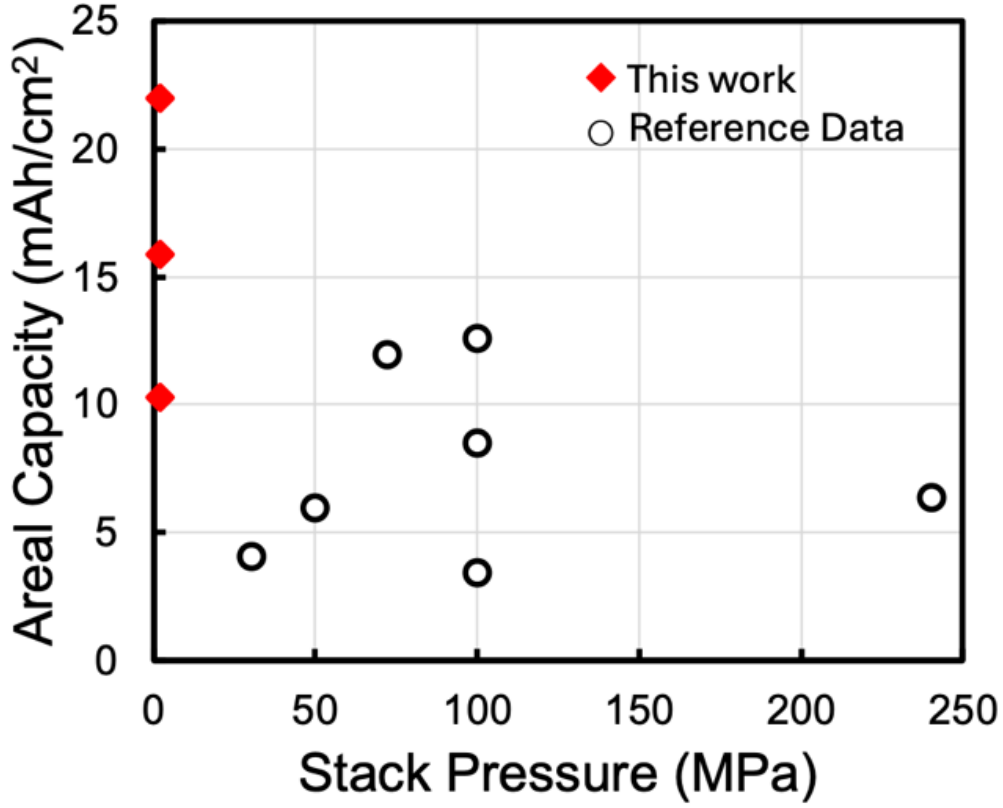
Toward 500 Wh/kg



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

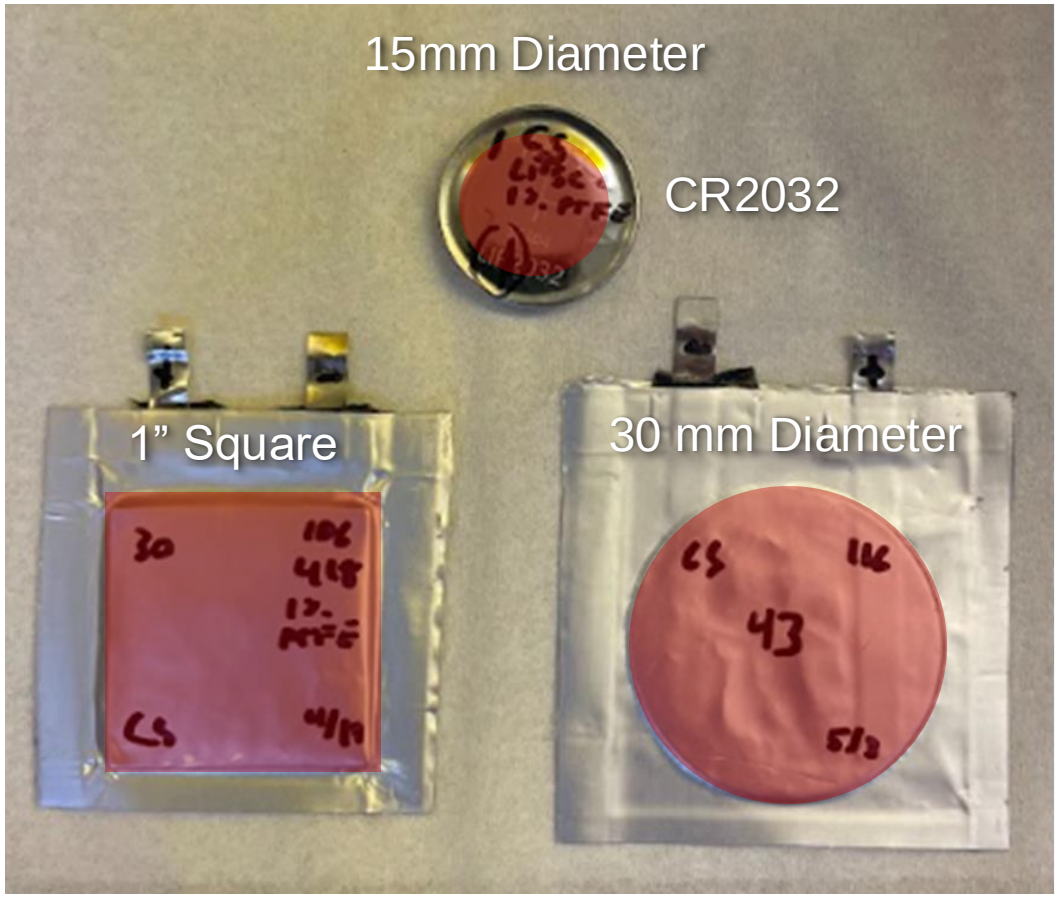
High Areal Capacity with Low Stack Pressure

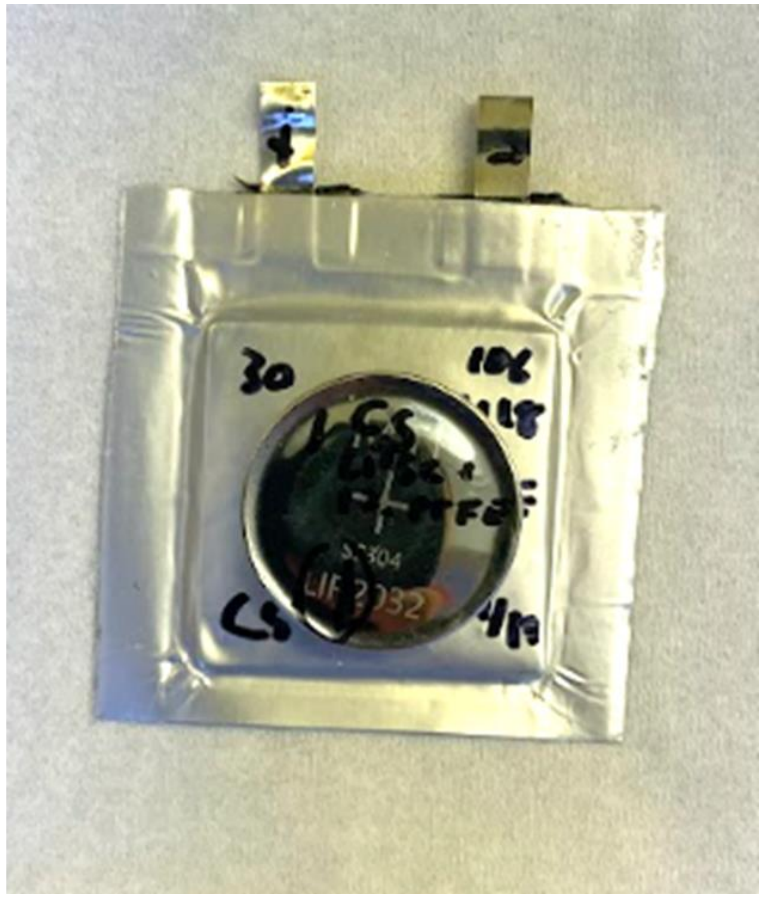




Cyclability at low stack pressure needs to be addressed: cathode, SSE, Li anode

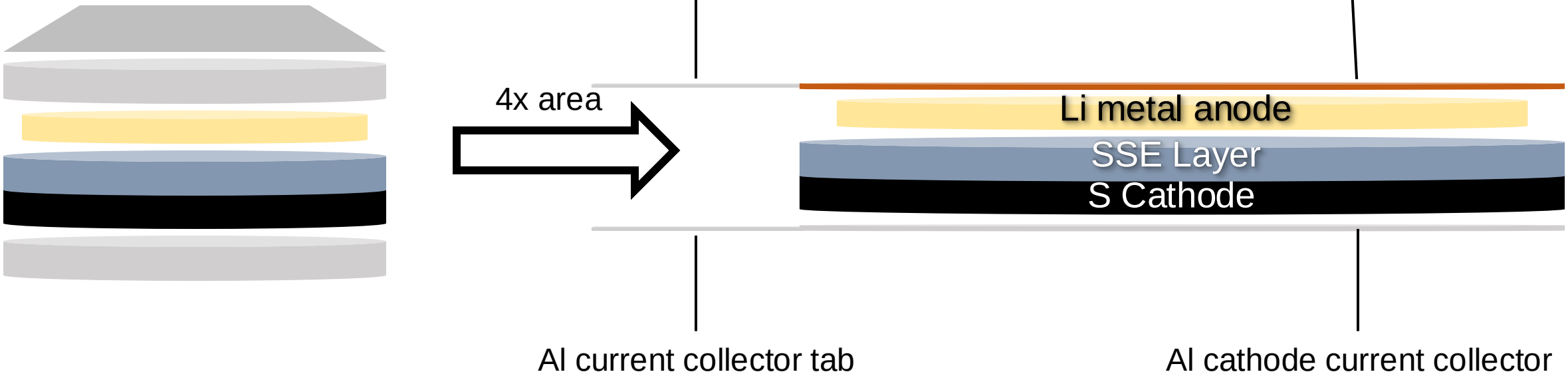
From Coin Cells to Pouch Cells





- Small format pouch cell allows scale-up materials engineering studies with (currently) costly chemicals conducted at an affordable scale

From Coin Cells to Pouch Cells

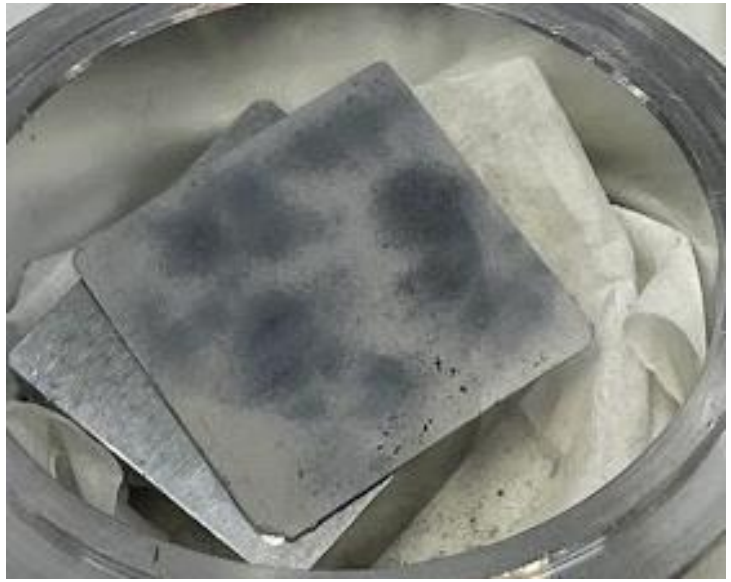


Dry Processing Improvements

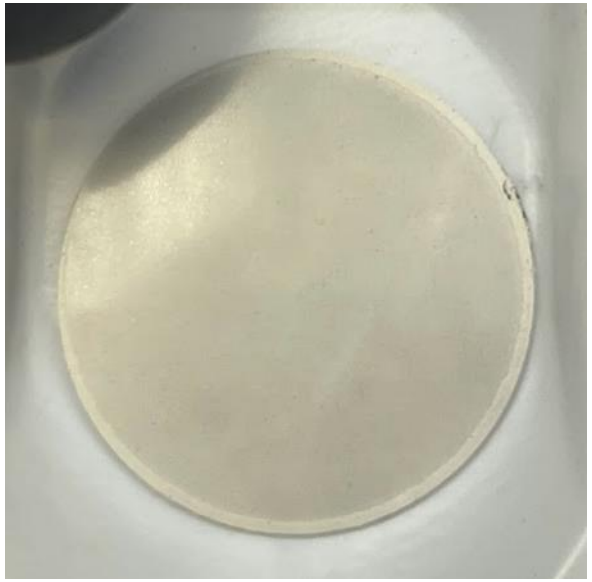
Generation 1

Direct scale-up from coin cell studies

Generation 2



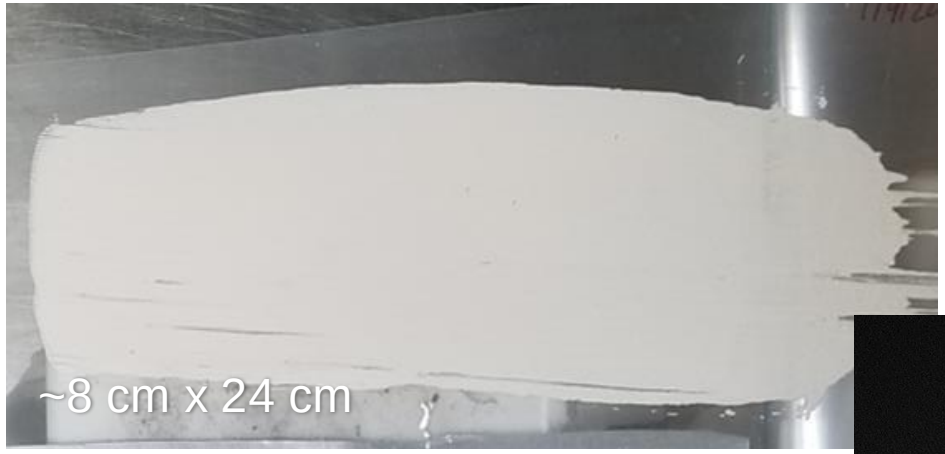
Generation 3



Improved dry-processing via proper use of polymer binders

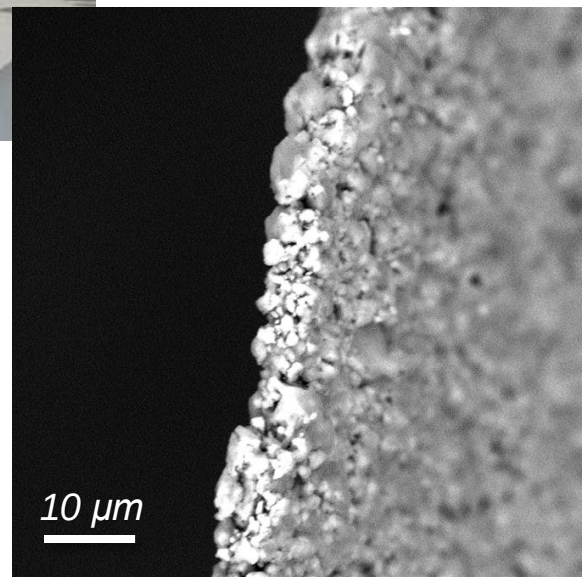
Development of SSE Films

Free-standing LPSC Thin Films

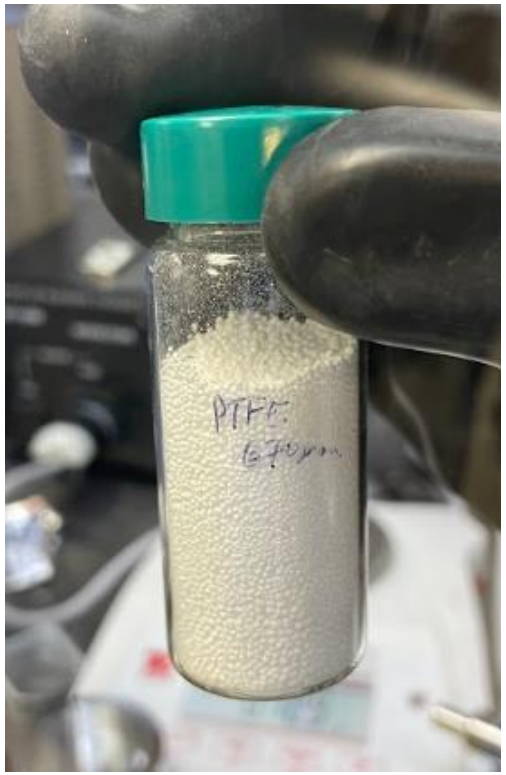


Tape-Casted LPSC Films
(~25 μm thickness)

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

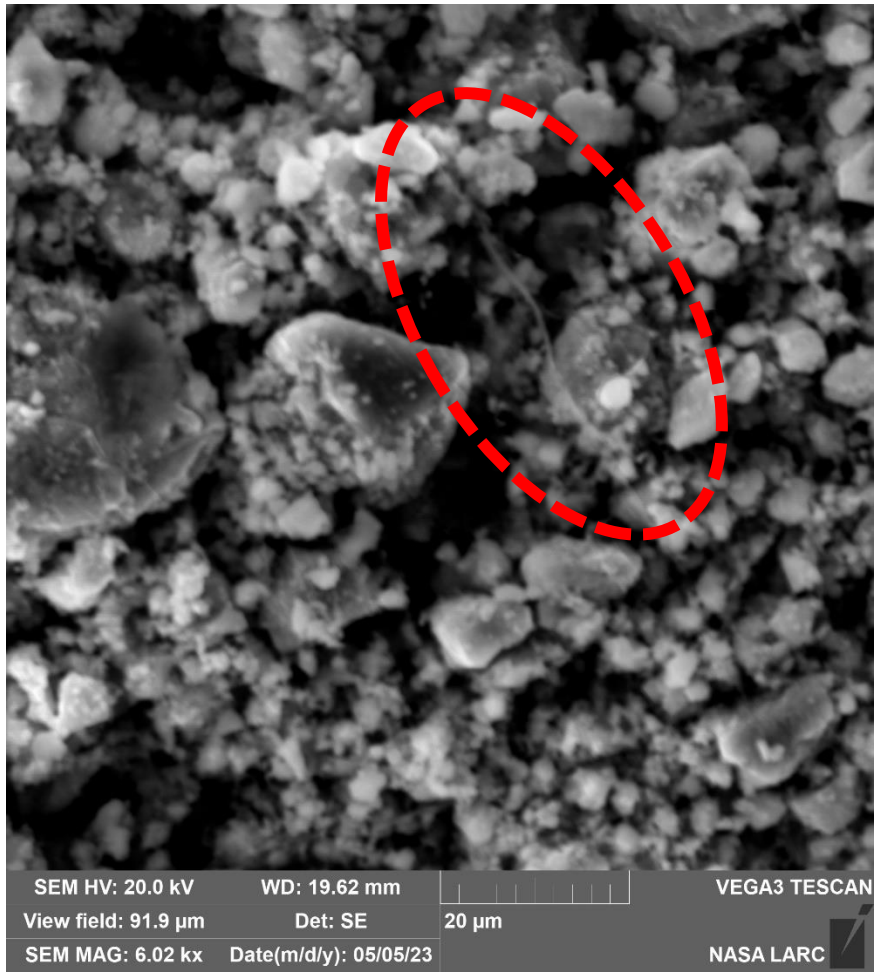


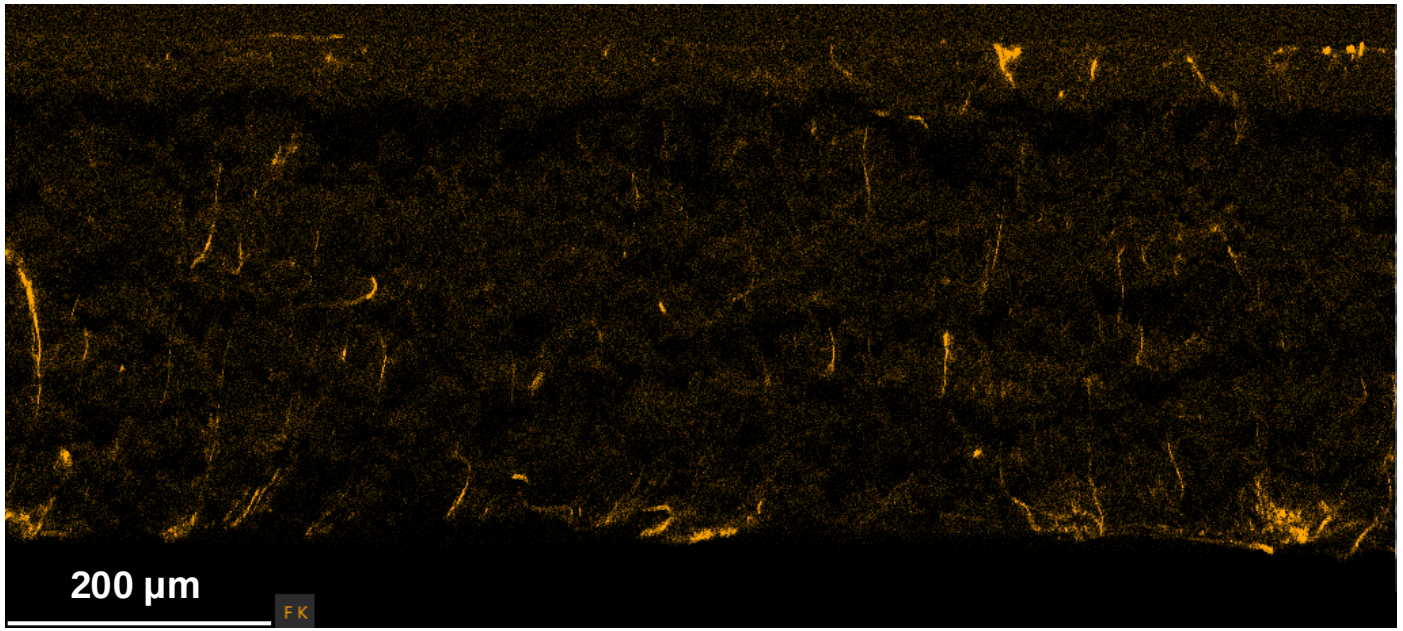
Dry Processing of LPSC Films



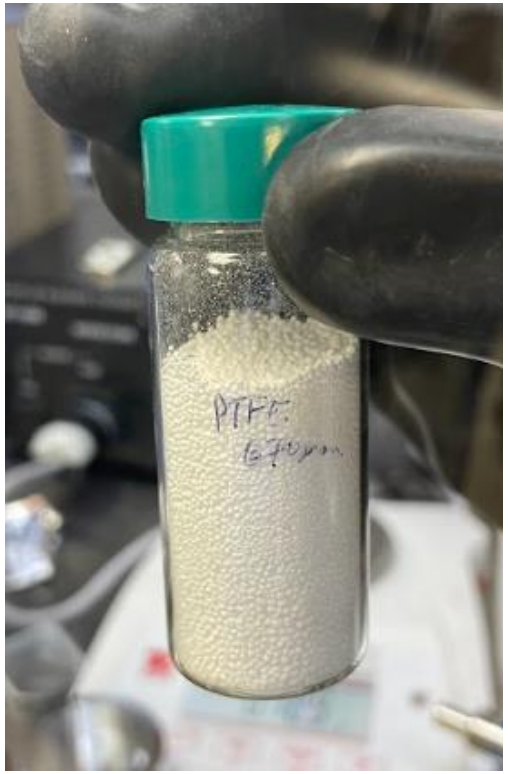
PTFE: Polytetrafluoroethylene

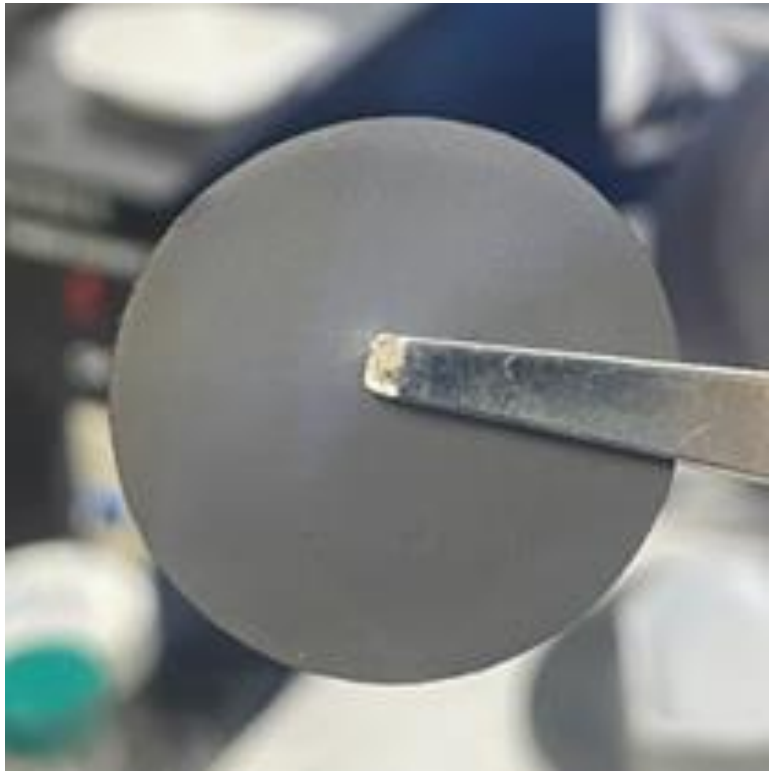
PTFE Fibers Provide Mechanical Support





Dry Processing of S Cathode Films

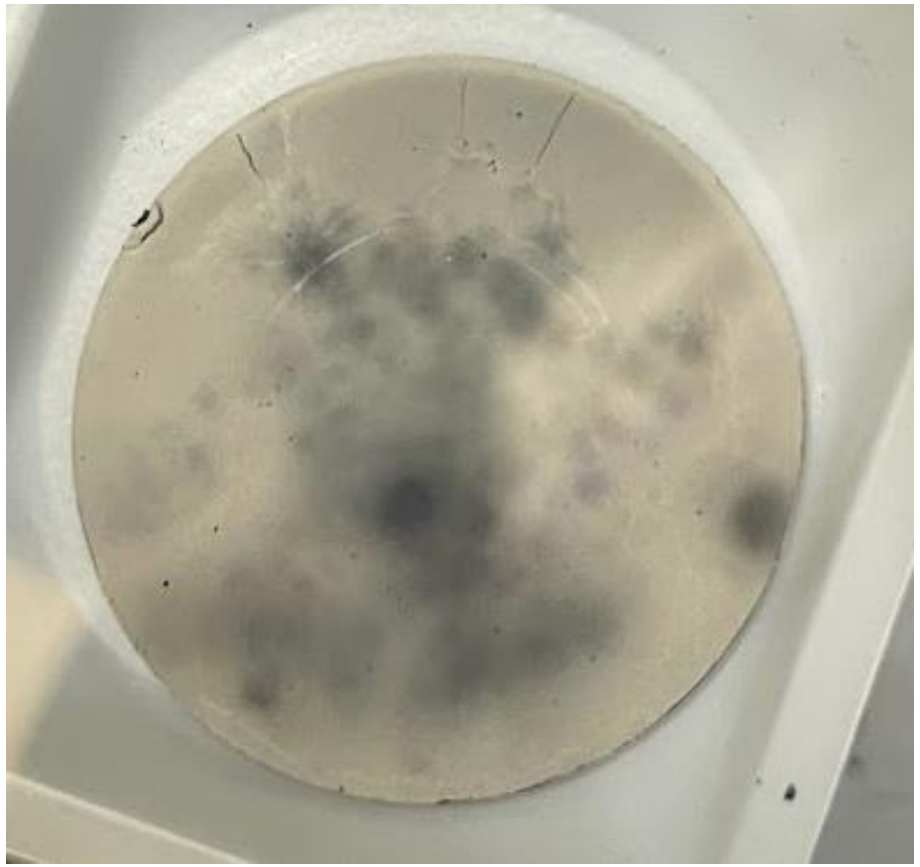




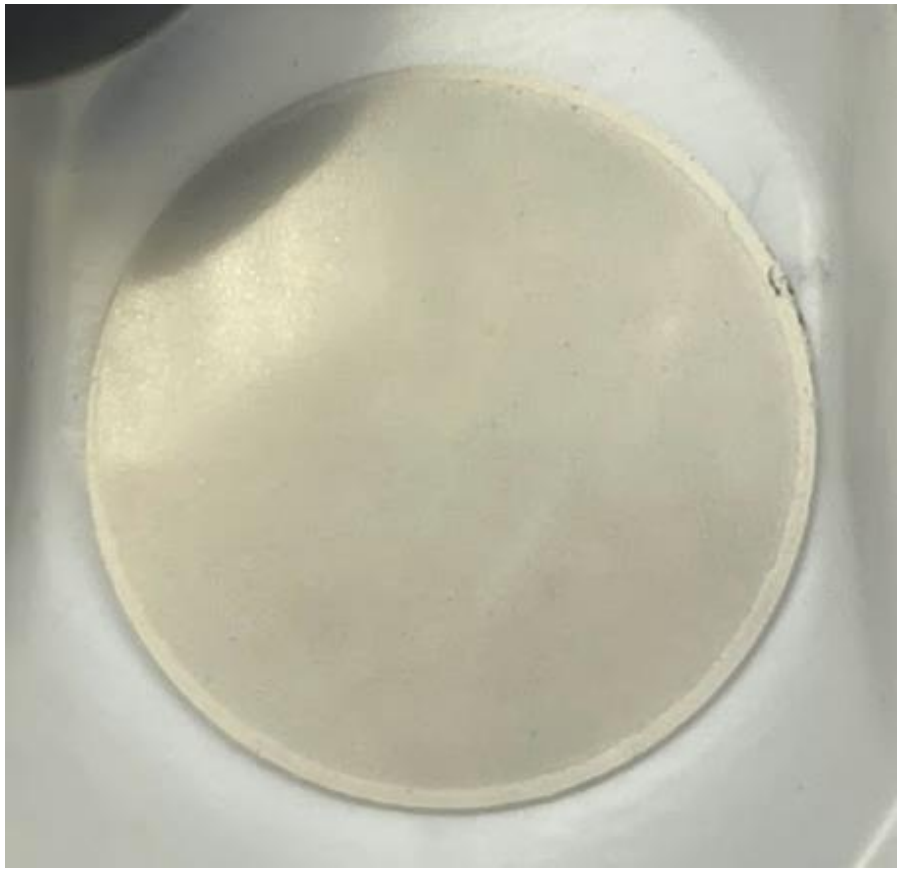
- PTFE binder is also compatible with dry processing of sulfur cathode

Cathode-SSE Bilayer Fabrication

Generation 2 Pouch Cell



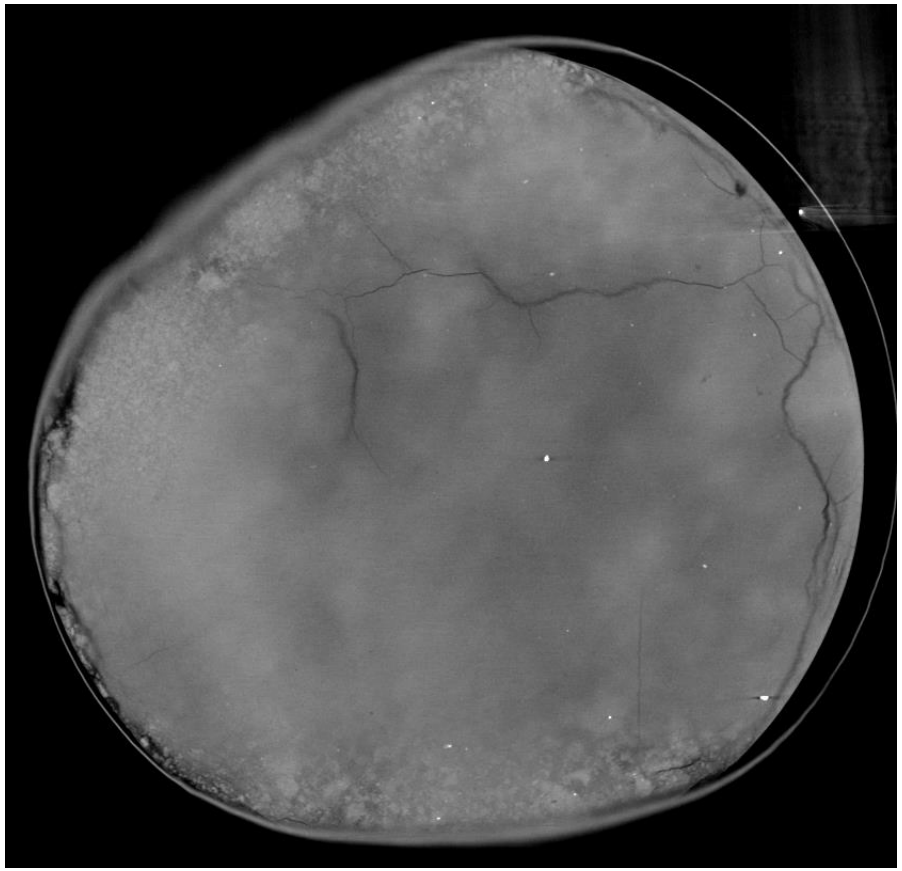
Generation 3 Pouch Cell



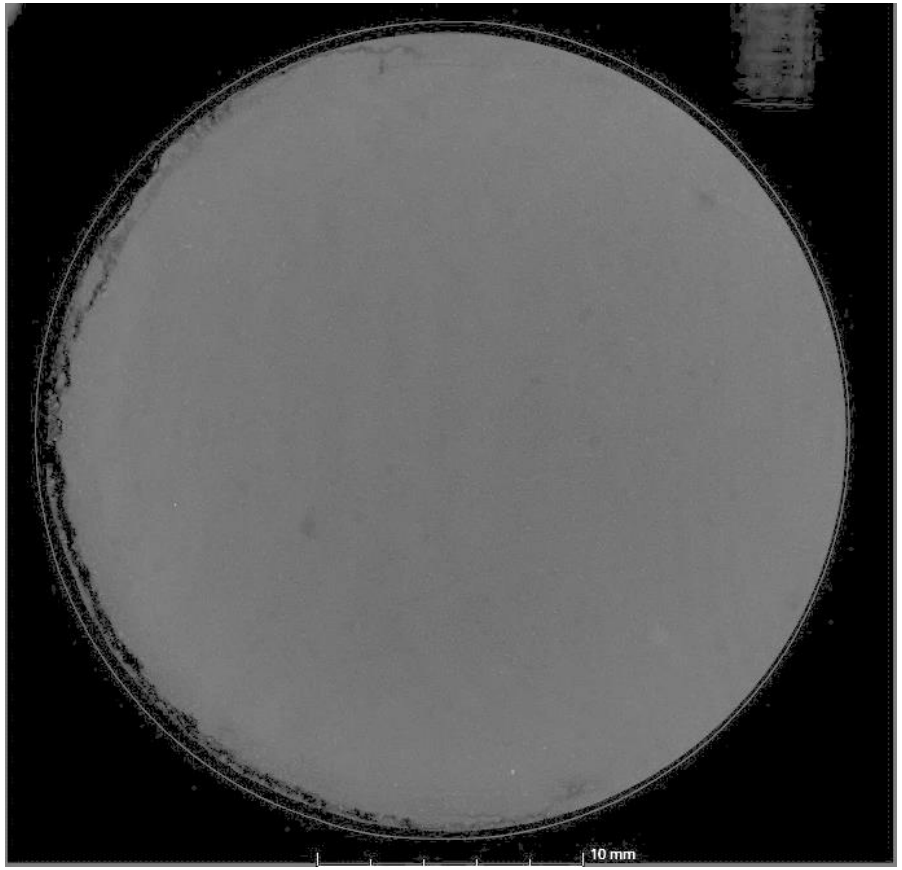
- Discs are all 3 cm in diameter

X-Ray Computed Tomography (CT)

Generation 2 Pouch Cell



Generation 3 Pouch Cell

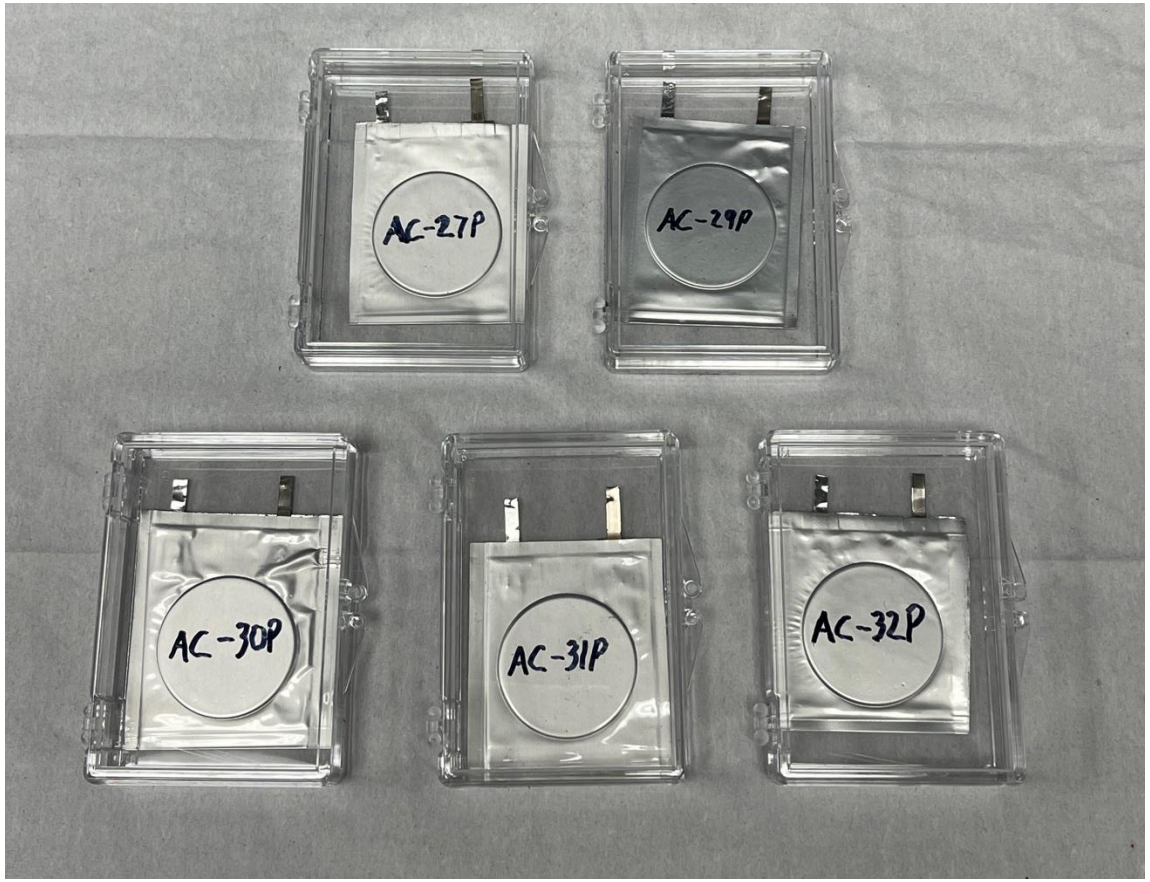


Courtesy: Dan Perey
NASA Langley Research Center (LaRC)

- Discs are all 3 cm in diameter

Small Format All-Solid-State Pouch Cells

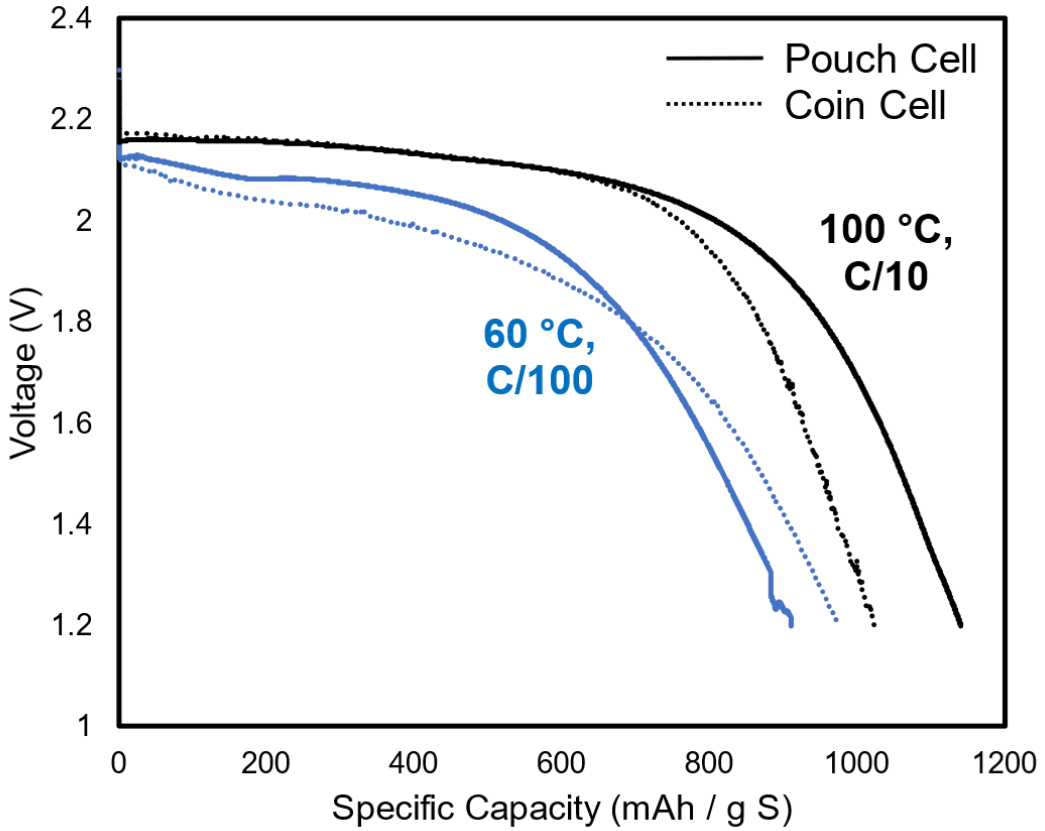
30-mm Diameter Li-S Pouch Cells

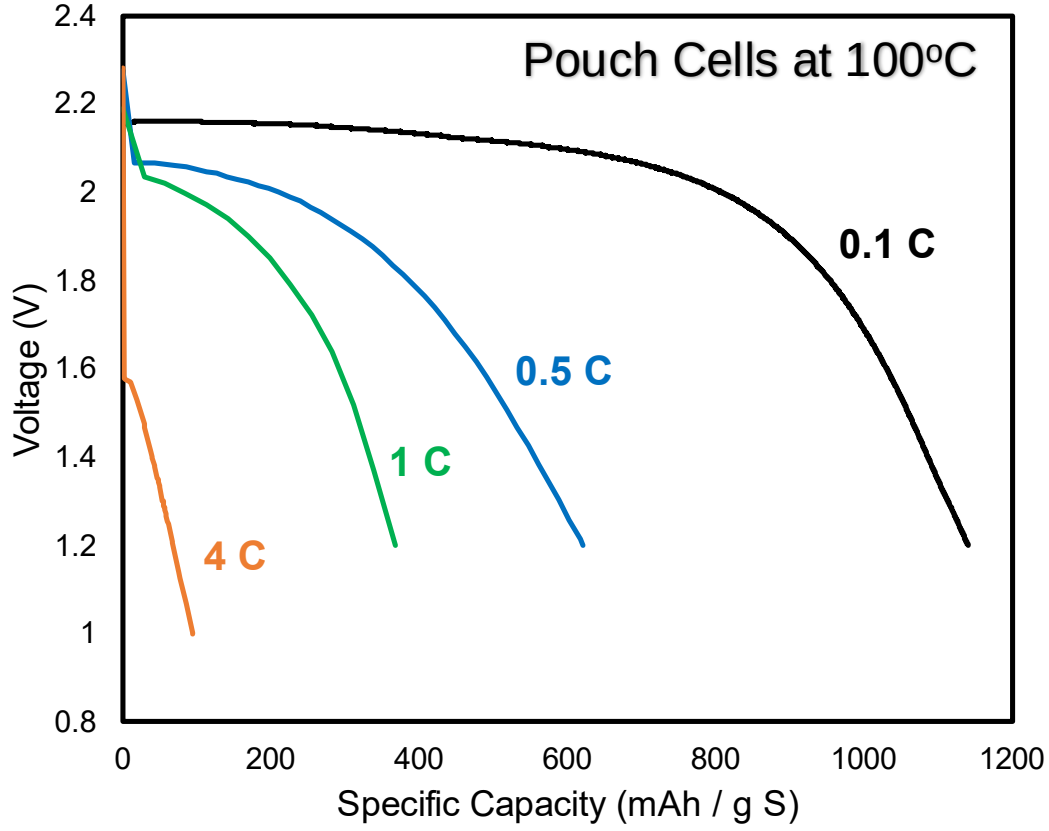


A 1”x1” Li-S Pouch Cell

- Routine fabrications of high quality, small format all-solid-state pouch cells

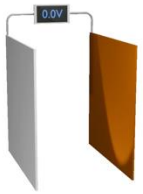
From Coin Cells to Pouch Cells



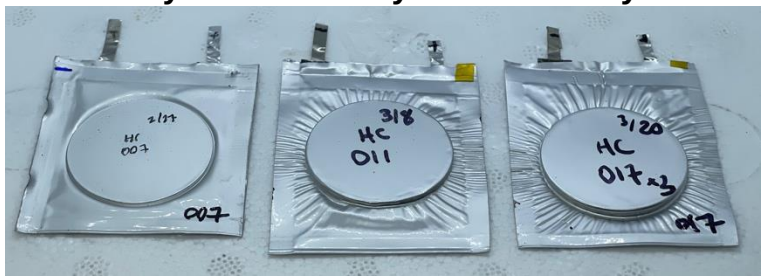


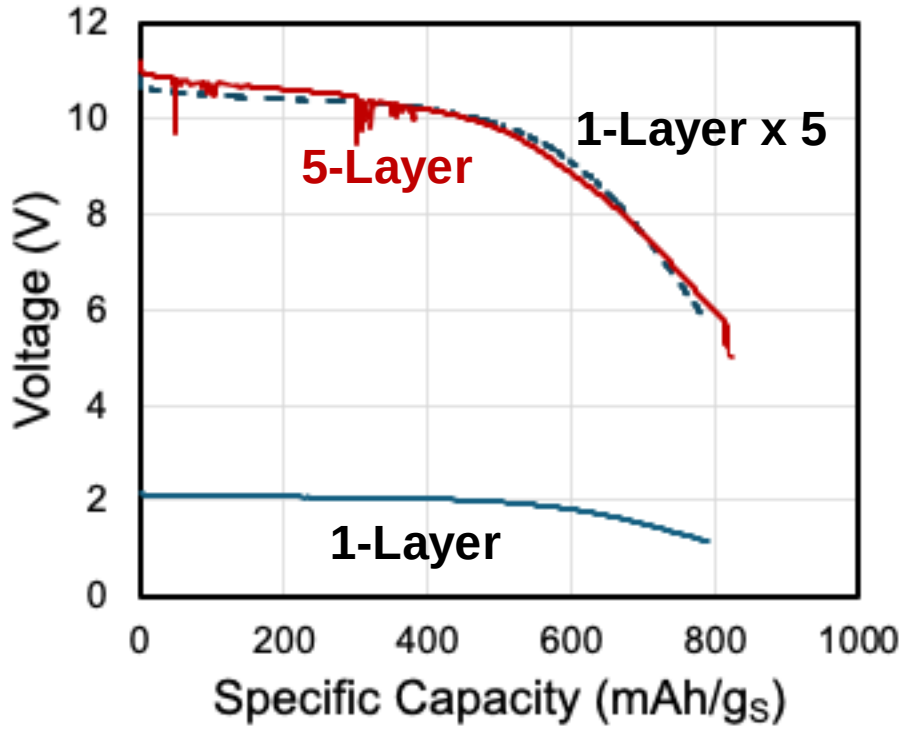
- Small format all-solid-state pouch cells exhibit expected performance in comparison to coin cells

Solid State Bipolar Stack Pouch Cells



1-Layer 2-Layer 3-Layer

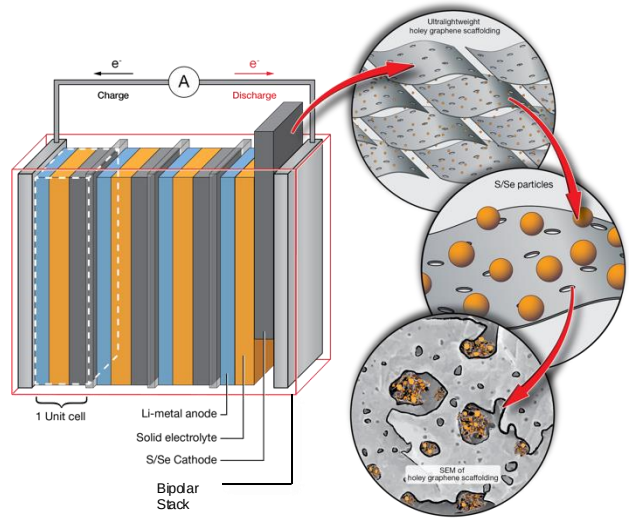




- Multi-layer bipolar stack pouch cells exhibited expected voltage multiplications of single-layer cells and similar capacity performance.

Summary

- High performance solid-state Li-S battery cells were fabricated via **dry processing** of solid electrolyte and cathode.
- The use of **holey graphene** as the solid-state cathode scaffold significantly improved the dry processibility and performance.
- Various all-solid-state Li-S **test cells**, including coin cells and pouch cells, as well as those with bipolar stack architectures, were fabricated and tested.



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