



All-Solid-State Lithium-Sulfur Batteries: *from Cathode Architecture to Pouch Cell Engineering*

Yi Lin,¹ Coby Scudder,² Hanjing Chen,² Vesselin Yamakov,³ Jin Ho Kang,¹ Ji Su,¹ Rodolfo Ledesma,³
Donald A. Dornbusch,⁴ Rocco P. Viggiano⁴

¹Advanced Materials & Processing Branch, NASA Langley Research Center, Hampton, VA 23681; ²NASA Office of STEM Engagement (OSTEM) Internship Program, NASA Langley Research Center, Hampton, Virginia 23681; ³Analytical Mechanics Associates (AMA), Hampton, VA 23666; ⁴Materials Chemistry and Physics Branch, NASA Glenn Research Center, Cleveland, OH 44135.

Pacific Rim International Meeting of Electrochemical Society (PRIME)

October 10, 2024

All images & videos credit: NASA

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.

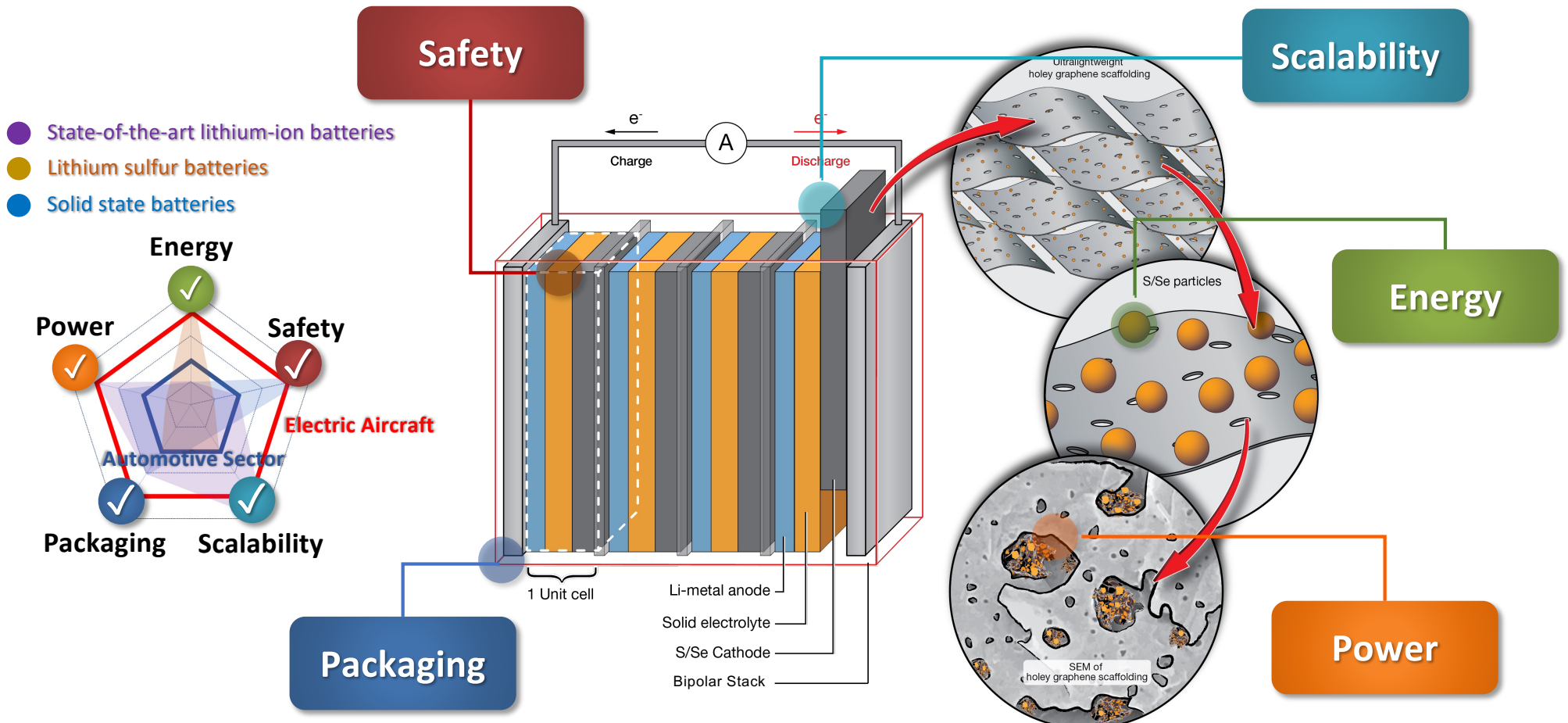
Battery **Sustainability** Preferences

- ❑ **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

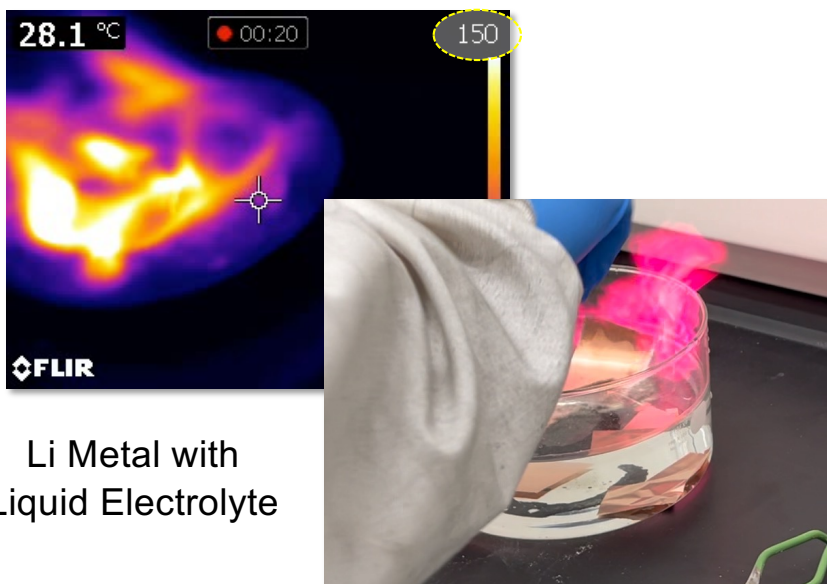
- ❑ Nickel (Ni)- and Cobalt (Co)-free chemistry
- ❑ U.S. has enough Li to meet battery needs (750,000 tonnes)
- ❑ Carbon (C) is widely accessible in the U.S.
- ❑ **S is highly abundant and inexpensive in the U.S.**

NASA SABERS Concept



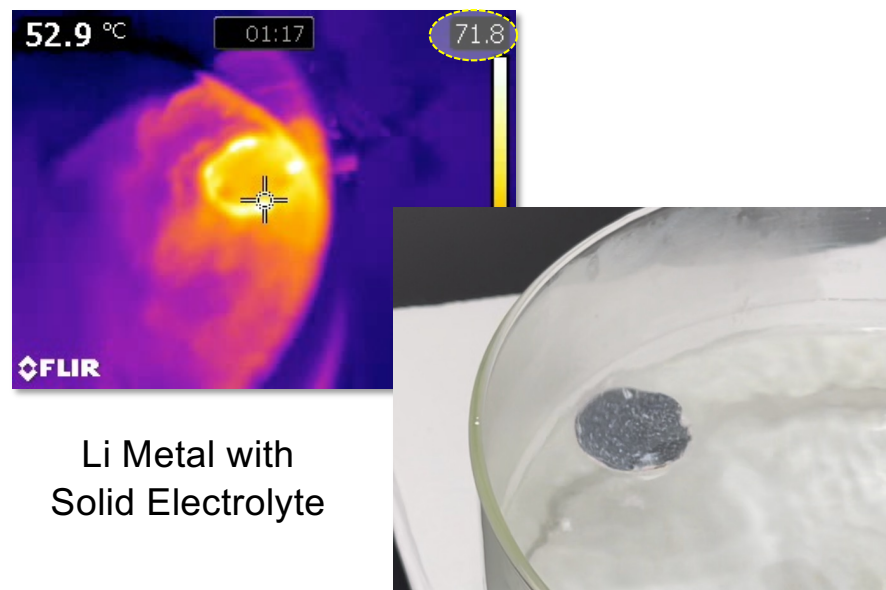
SABERS: Solid-state Architecture Batteries for Enhanced Rechargeability and Safety

Safety in Water: Li Metal in Liquid vs. Solid Electrolytes



Li Metal with Liquid Electrolyte

- ❑ Reaction of Li metal and water resulted in local temperature exceeding the flash point (<math><40^{\circ}\text{C}</math>) of organic solvents that catch fire.



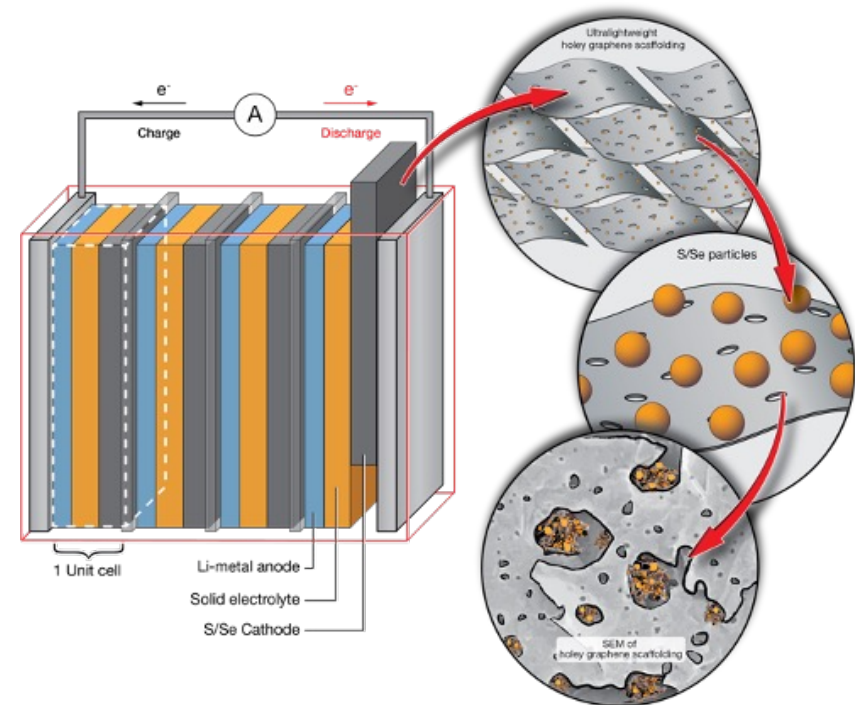
Li Metal with Solid Electrolyte

- ❑ Reaction of Li metal and water resulted in local temperature increase and hydrogen release, but no flammable material to catch fire.

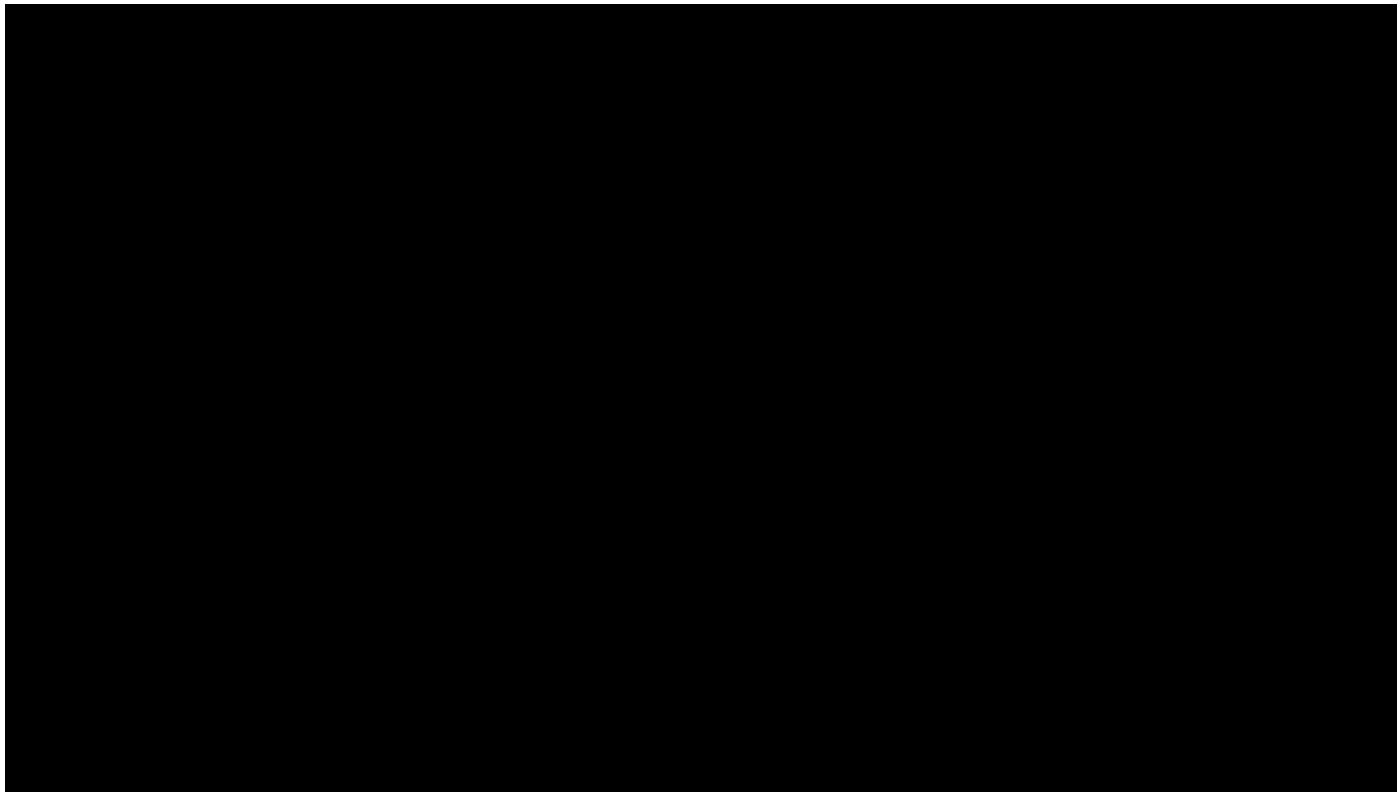
NASA SABERS Research Interest



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



Holey Graphene (hG)

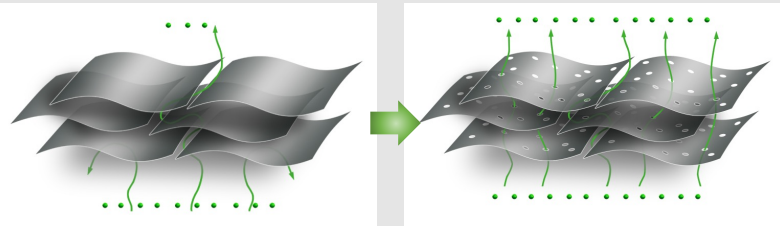


Full version: <https://www.youtube.com/watch?v=OGyn2PjBTN0>

hG for Advanced Electrodes



Supercapacitors



Intact Graphene

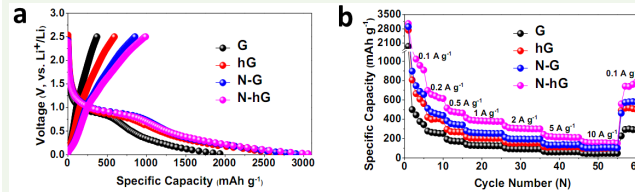
Holey Graphene

ACS Nano 2014, 8, 8255.

As-Prepared hG

Liangbing Hu
(U Maryland)

Li-Ion Battery (Anode)

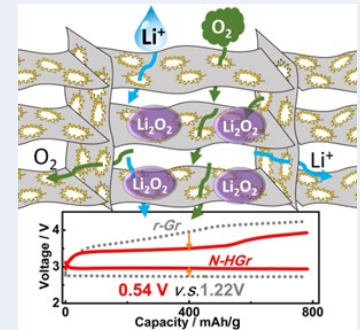


Small 2015, 11, 6179.

N-doped hG

Liming Dai
(CWRU)

Li-Oxygen (O₂) Batteries

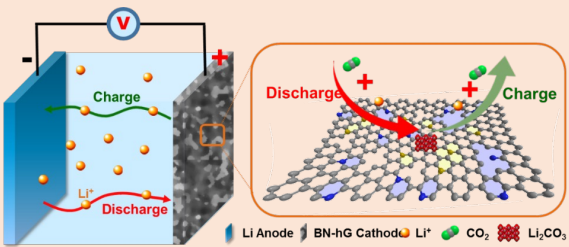


ACS Energy Lett 2016, 1, 260.

N-doped hG

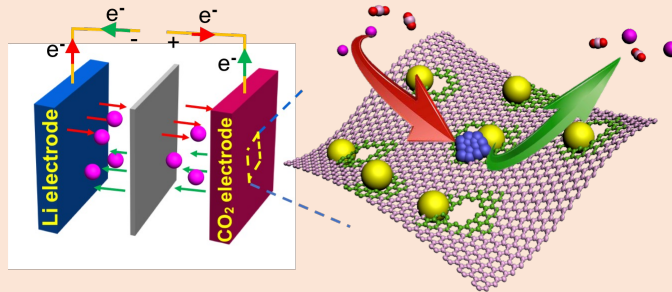
Liming Dai
(CWRU)

Li-Carbon Dioxide (CO₂) Batteries



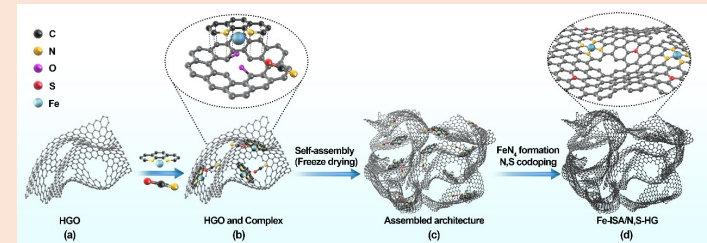
Angew. Chem. Int. Ed. 2017, 56, 6970.

B,N-codoped hG



Adv. Func. Mater. 2018, 28, 1804630

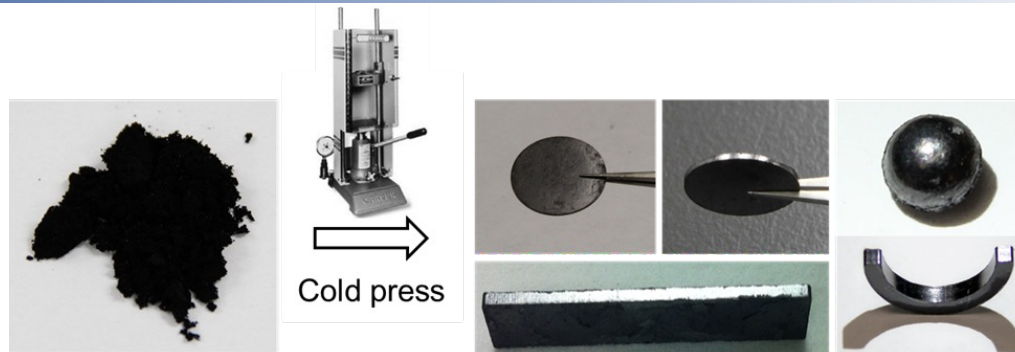
Carbon Dot-Supported on hG



Adv. Mater. 2020, 32, 1907436.

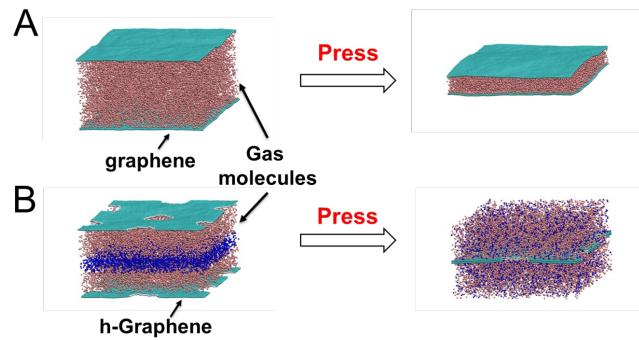
Single Fe Atom Catalysts Supported on hG

hG is Dry Compressible

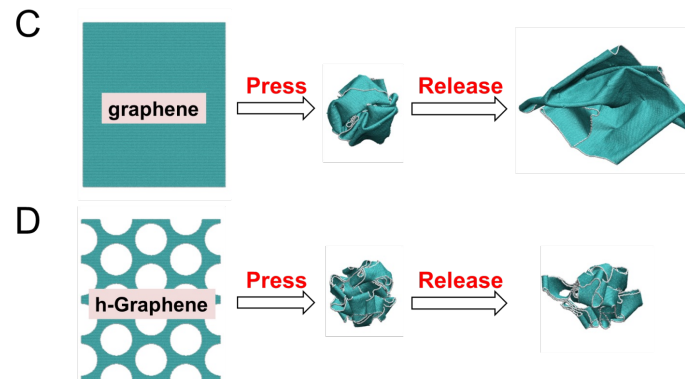


Holey Graphene Powder

Holey Graphene Monolithic Architectures



Facile air escape upon compression



Minimal volume rebound upon release

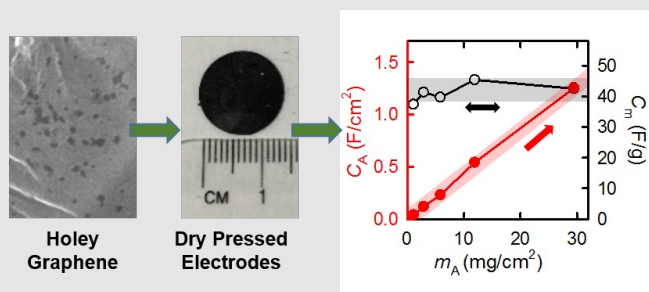
ACS Nano 2017, 11, 3189. (In collaboration with Prof. Liangbing Hu)

A New Narrative in Electrode Preparation



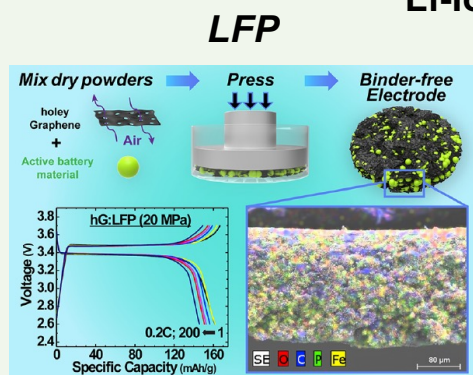
Dry-pressed hG is applicable in various energy storage platforms for ultrahigh areal capacities.

Supercapacitors



ACS Appl. Mater. Interfaces **2016**, 8, 29478.

Li-Ion Batteries



LFP: Lithium iron phosphate

ACS Appl. Energy Mater. **2019**, 2, 2990.

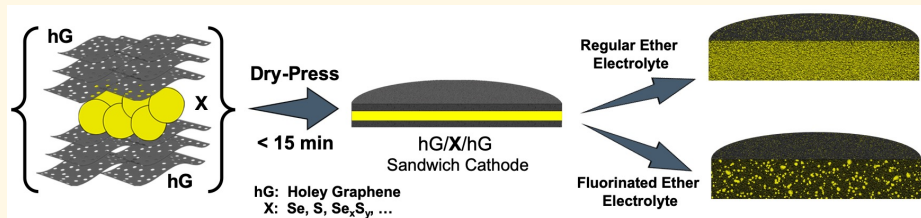
NCM



NCM: Lithium nickel cobalt manganese oxide

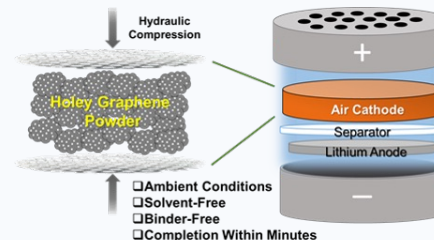
Electrochim. Acta **2020**, 362, 137129

Li-Sulfur/Selenium (Li-S/Se) Batteries

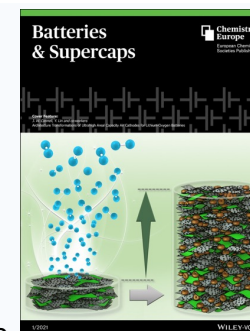


Batteries & Supercaps **2019**, 2, 774; *ACS Appl. Energy Mater.* **2020**, 3, 6374; *Front. Energy Res.* **2021**, 703676.

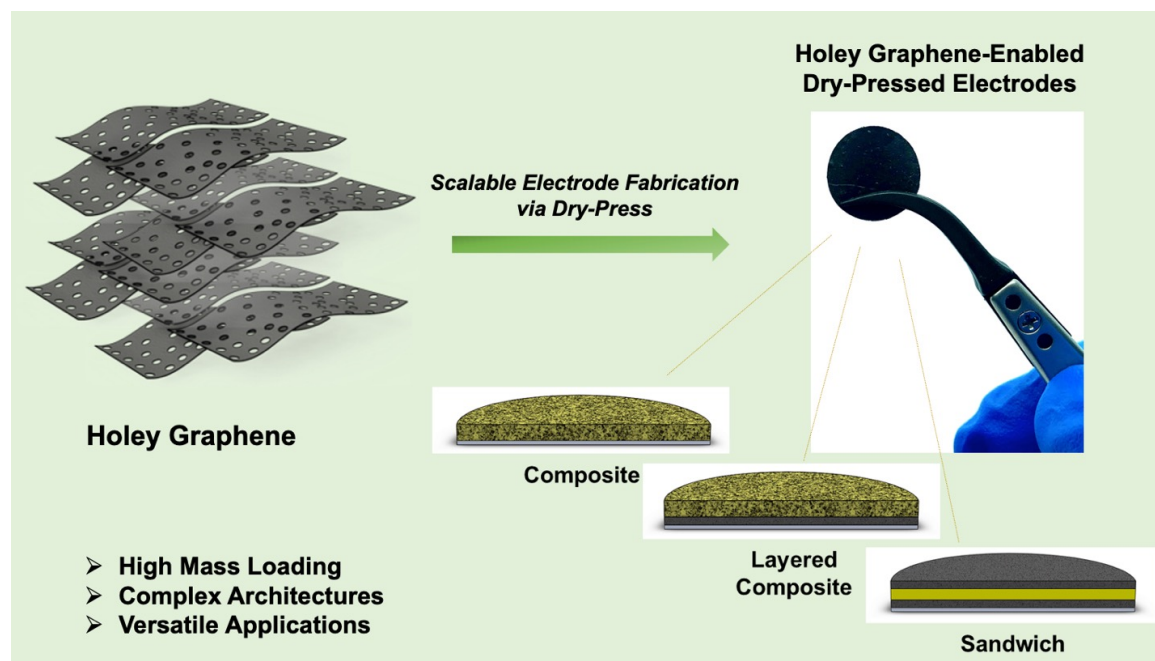
Li-O₂ Batteries



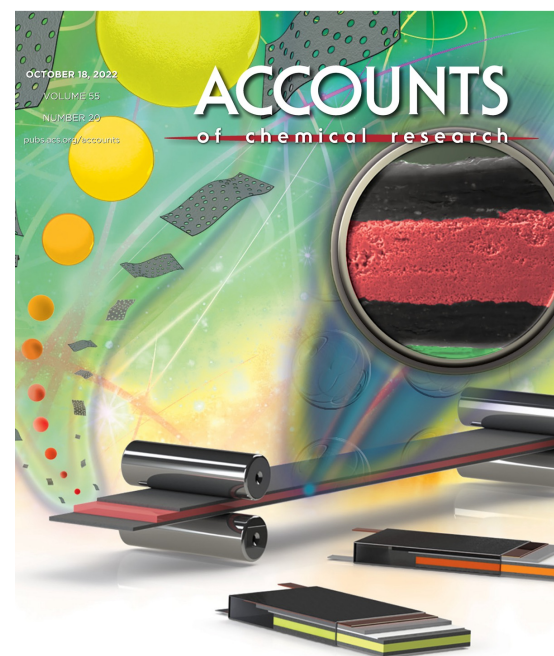
Nano Lett. **2017**, 17, 3252; *Nano Energy* **2017**, 31, 386; *J. Electrochem. Soc.* **2020**, 167, 080522; *Batteries Supercaps* **2021**, 4, 120.



Dry-Pressible hG for Batteries



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

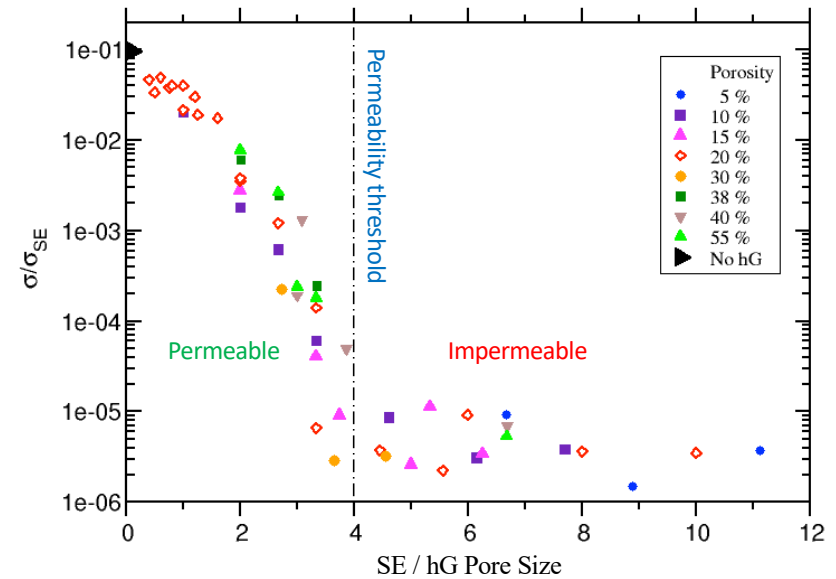
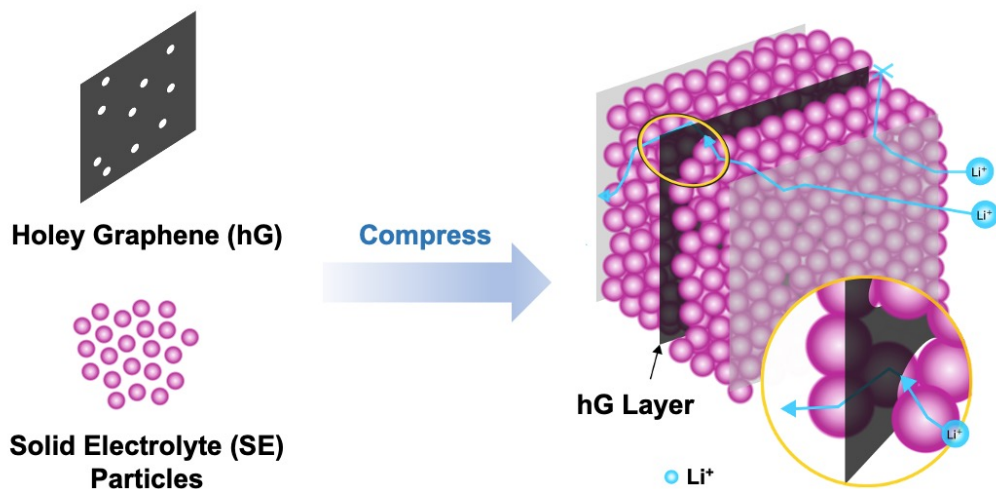


ACS Publications
Most Trusted. Most Cited. Most Read.

www.acs.org

- ❑ 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.

Li Ion Conductivity Through hG Sheets



Hole size [nm]: 9 – 200
Porosity [%]: 5 - 55

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

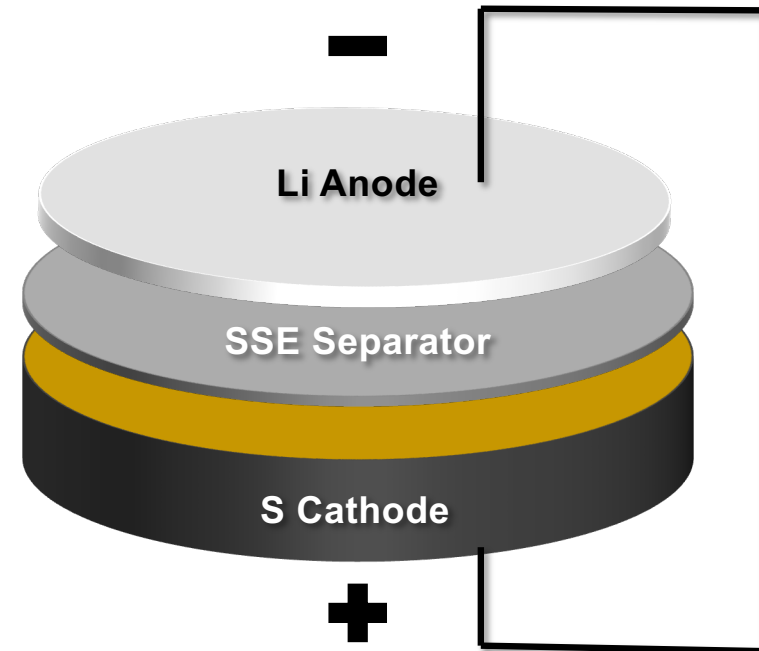
ACS Appl. Mater. & Interfaces **2022**, 14, 21363-21370.

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

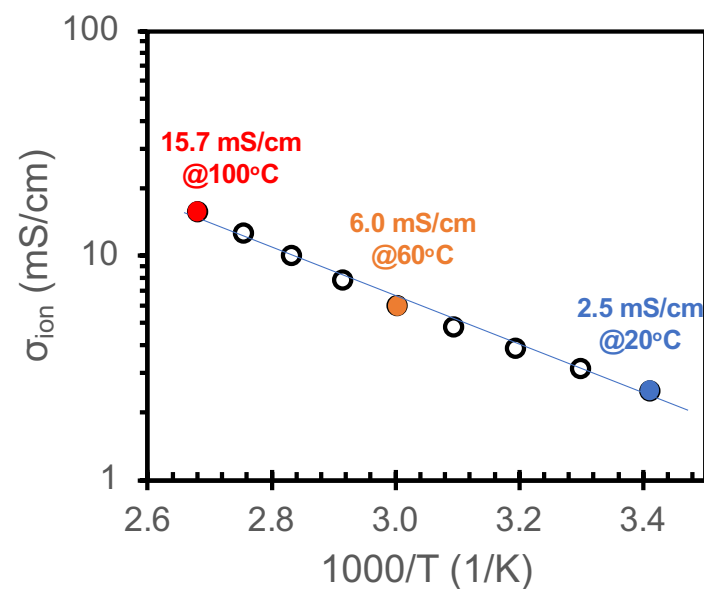


- ❑ **A battery is an electrochemical device that converts chemical energy into electric energy.**
- ❑ **Materials chemistry, processing, and engineering are keys to develop new battery technology.**

Commercially Available Sulfide Electrolytes



| Sulfide Electrolytes | Vendor |
|--|--------|
| $\text{Li}_{10}\text{SnP}_2\text{S}_{12}$ (LSPS) | NEI |
| $\text{Li}_6\text{PS}_5\text{Cl}_{0.5}\text{Br}_{0.5}$ | MSE |
| $\text{Li}_6\text{PS}_5\text{Cl}_{0.9}\text{I}_{0.1}$ (LPSC-I) | NEI |
| $\text{Li}_6\text{PS}_5\text{Cl}$ (LPSC) | NEI |
| $\text{Li}_7\text{P}_3\text{S}_{11}$ | MSE |
| $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ -Fine | MSE |
| $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ -Coarse | MSE |



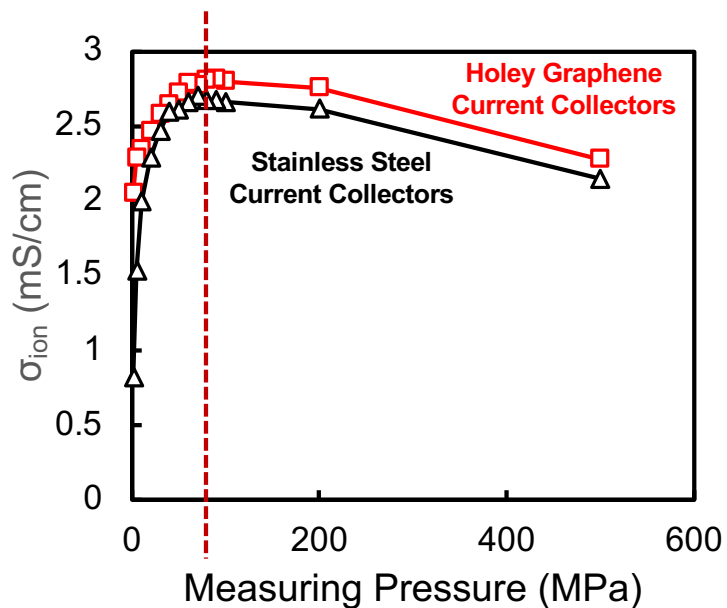
- ❑ NEI: NEI Corporation (<http://neicorporation.com>)
- ❑ MSE: MSE Supplies LLC (<http://msesupplies.com>)

- ❑ Sulfide electrolytes are typically of high ionic conductivity (> 1 mS/cm)
- ❑ $\text{Li}_6\text{PS}_5\text{Cl}$ (LPSC; LPSC) is the most studied sulfide electrolyte and commercially available in large quantities ($\sim \$10/\text{g}$)

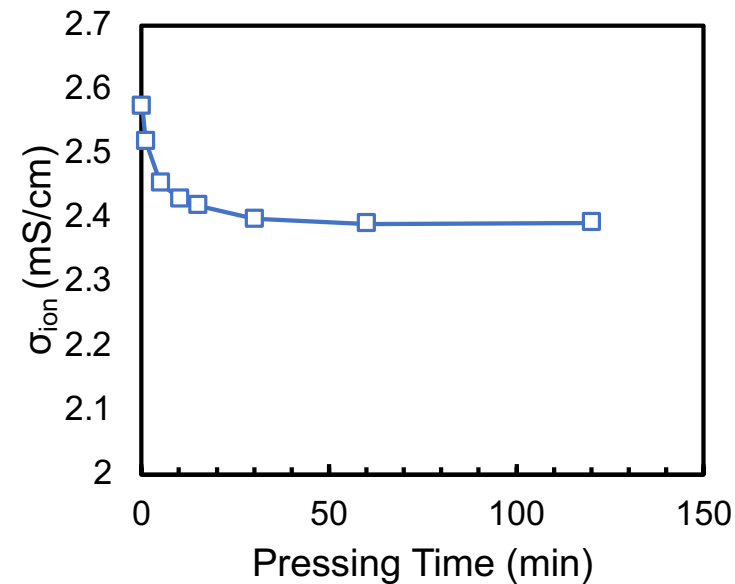
LPSC Ionic Conductivity Measurements



Effect of Stack Pressure and Current Collectors

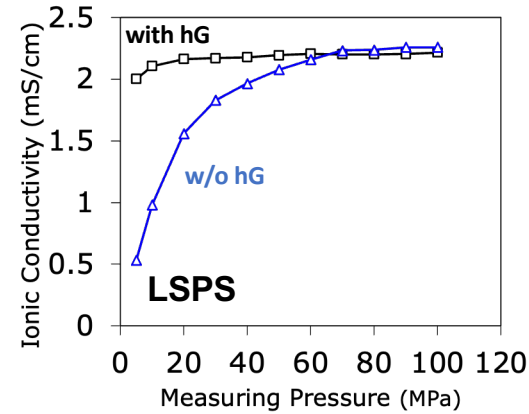
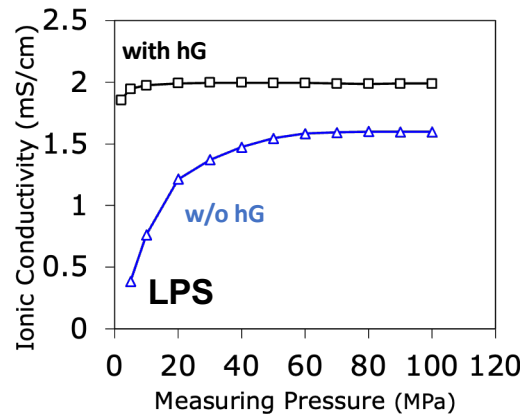
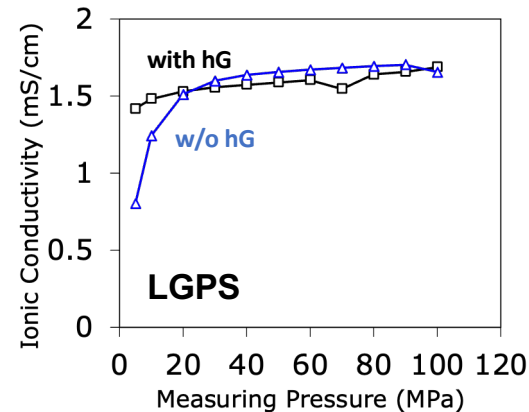
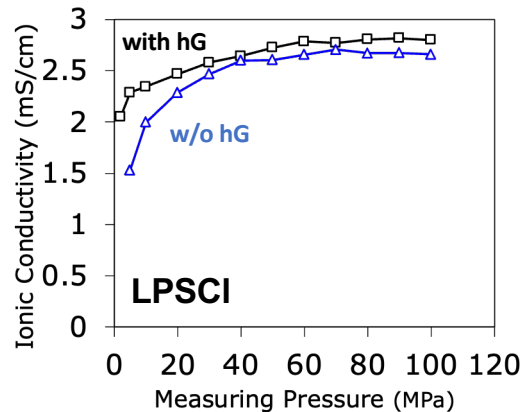


Effect of Pressing Time



- ❑ Measured ionic conductivity values are strongly dependent upon the measuring pressure
- ❑ Contact at current collector could also make a difference in measurements, especially at low stack pressures (<20 MPa)
- ❑ Compression time also affects the measured values

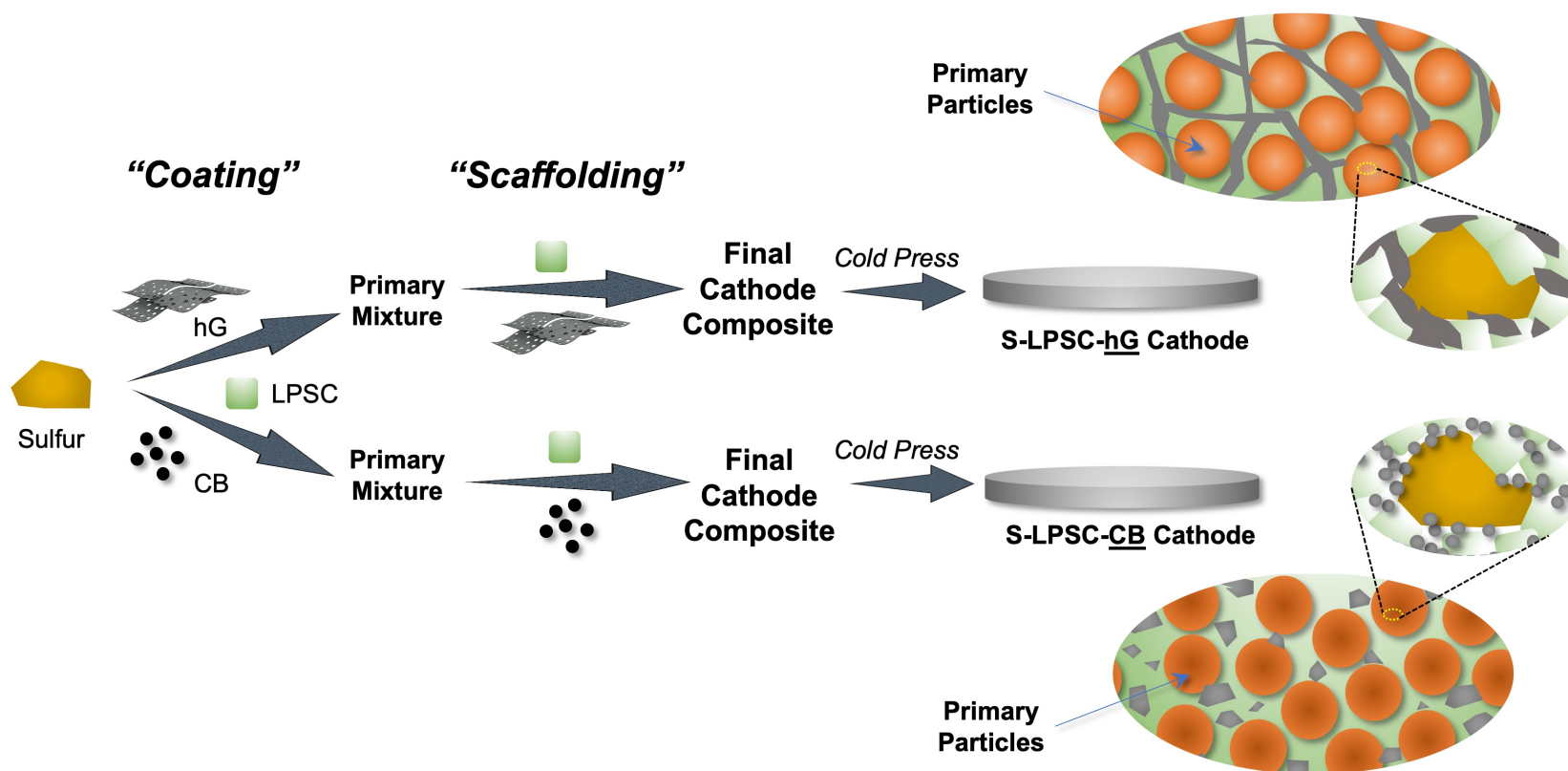
hG Current Collectors



- LPSC: $\text{Li}_6\text{PS}_5\text{Cl}$ (NEI)
- LGPS: $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (MSE)
- LPS: $\text{Li}_7\text{P}_3\text{S}_{11}$ (MSE)
- LSnPS: $\text{Li}_{10}\text{SnP}_2\text{S}_{12}$ (NEI)

➤ The use of hG as the current collectors (black symbols) consistently provided with stable ionic conductivity readings despite the measurement pressure.

All-Solid-State S Composite Cathodes

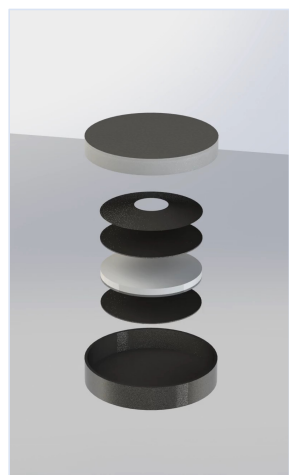
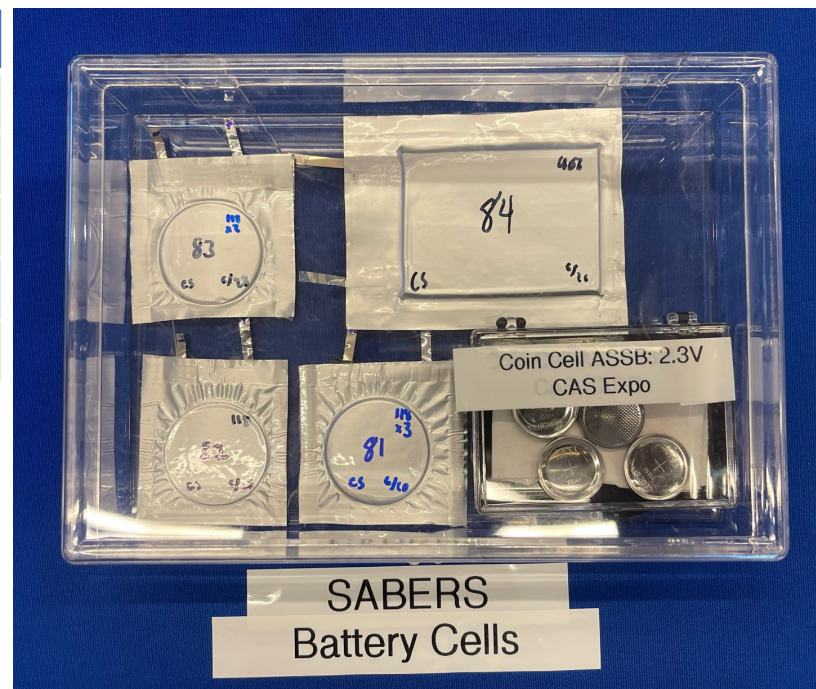


- CB: carbon black
- SSE: LPSC (Li₆PS₅Cl)

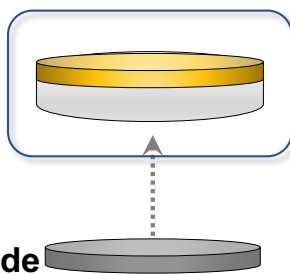
All-Solid-State Li-S Test Cells



| | Split Cells | Coin Cells | Pouch Cells |
|--------------------------|------------------|------------|-------------------|
| Stack Pressure Control | Excellent | Low | Excellent |
| Industry Standard Casing | No | Yes | Customized |
| Commercial Availability | Yes | Yes | Yes |
| Cost | High | Low | Moderate |
| Field Testing Capable | No | Yes | Yes |



Freestanding Cathode/SSE Layers/Bilayer



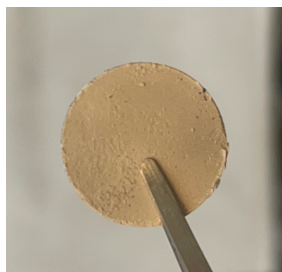
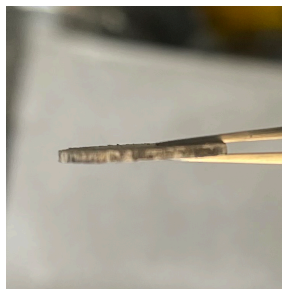
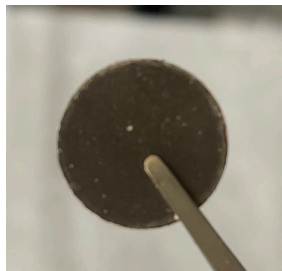
Lithium (Li) metal anode

- ☐ Coin cells are desirable formats for materials screening with high efficiency at a low cost

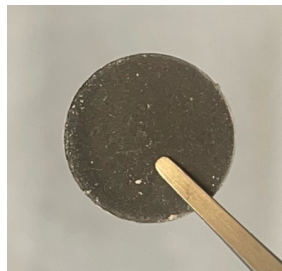
Dry-Pressed Cathode/SSE Bilayer Discs



CB

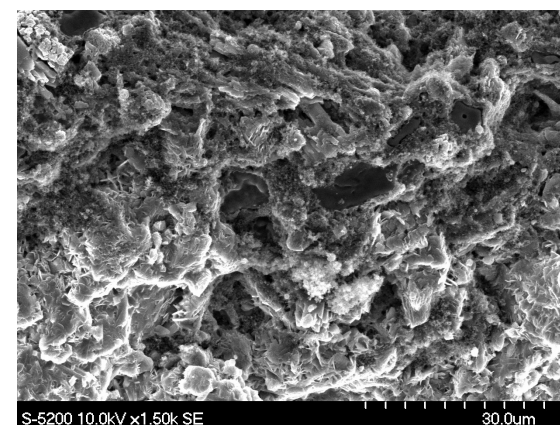
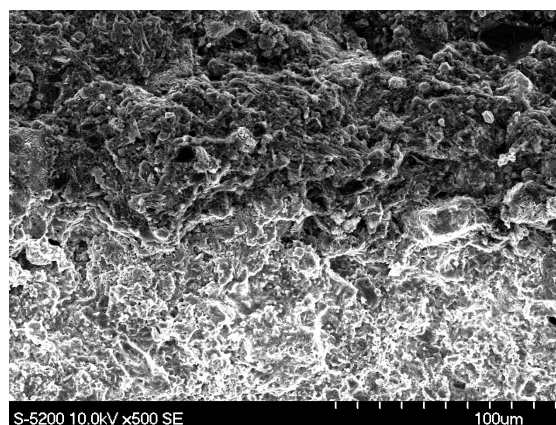
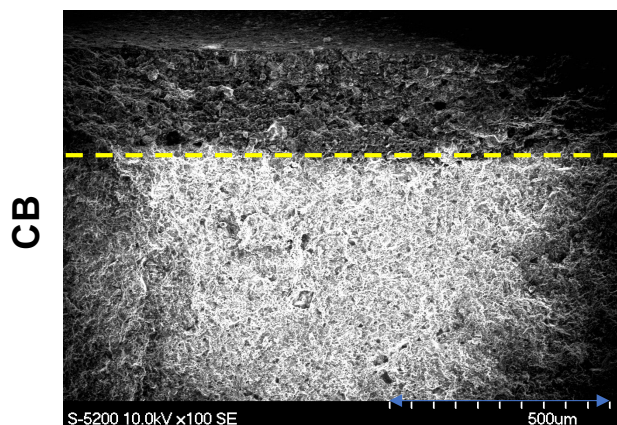
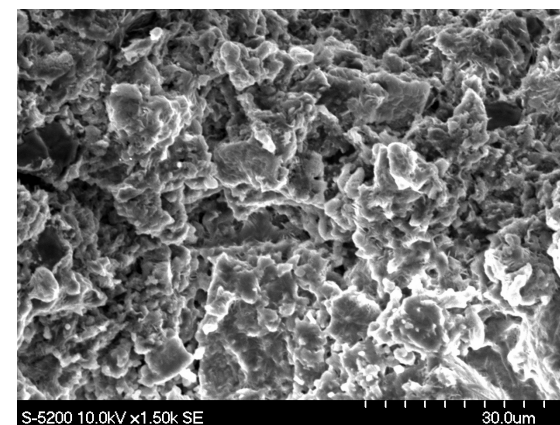
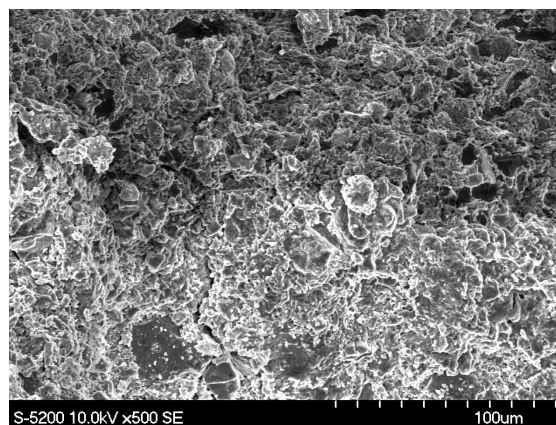
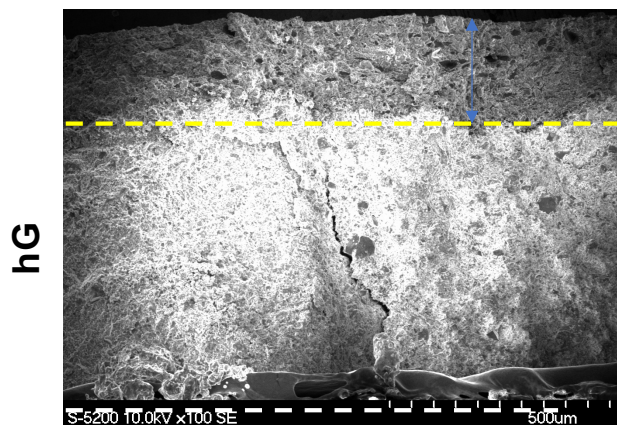


hG

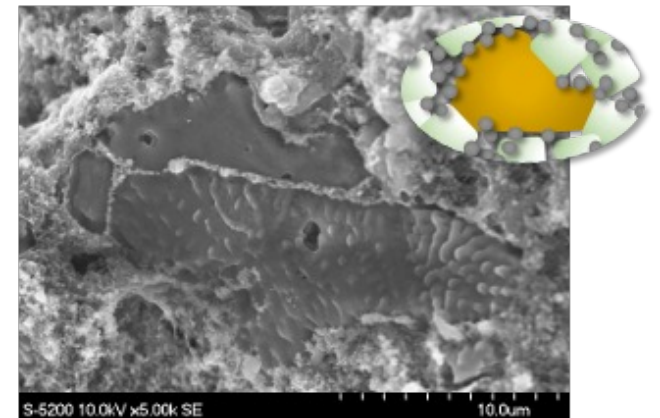
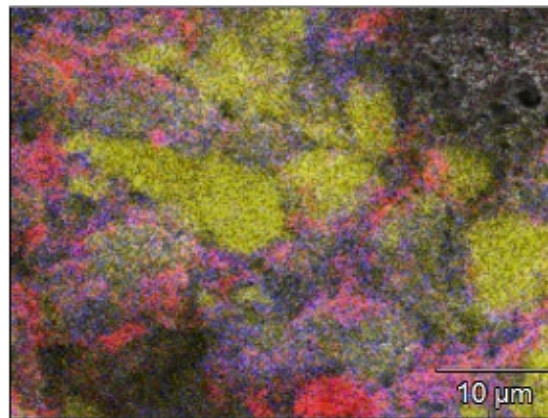
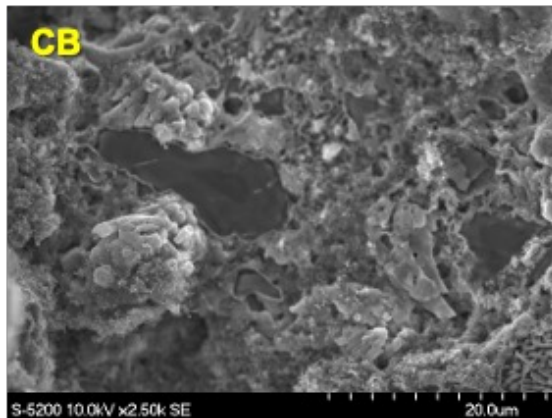
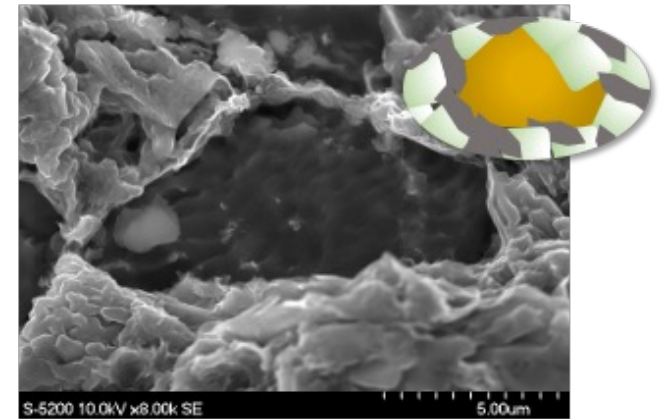
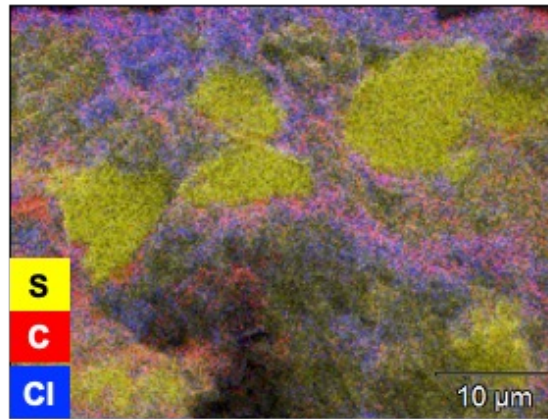
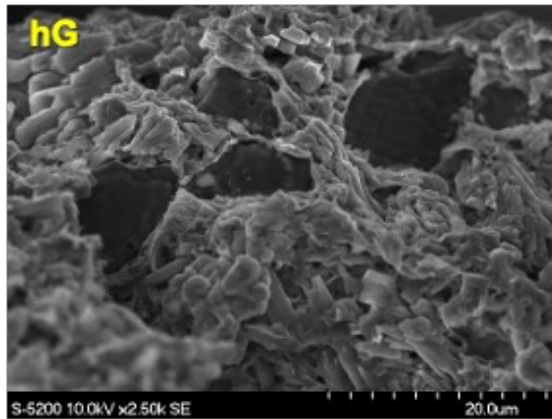


- ❑ Both composites are compressible to form robust cathode/SSE bilayer discs
- ❑ LPSC glass electrolyte serves as binder
- ❑ hG as “cold pressable hosts” is not an obvious advantage...?

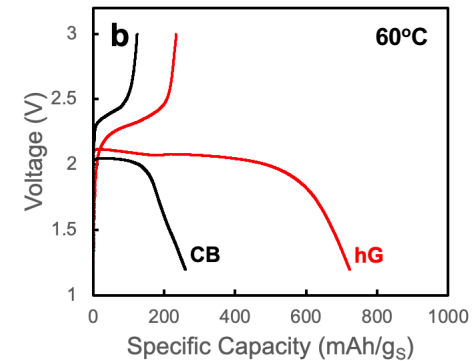
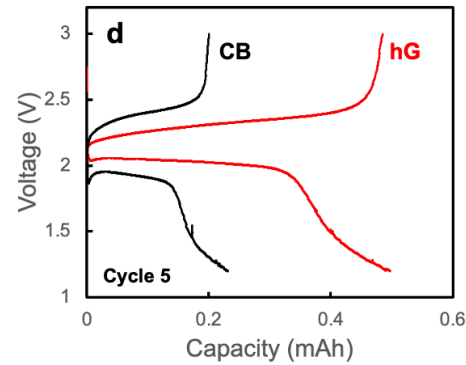
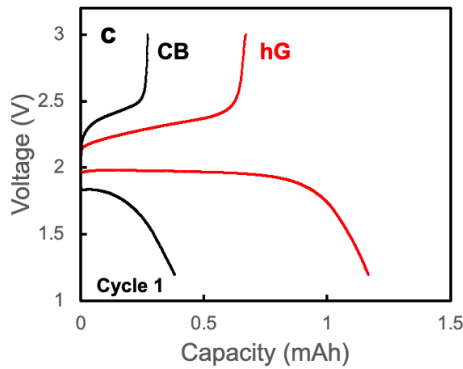
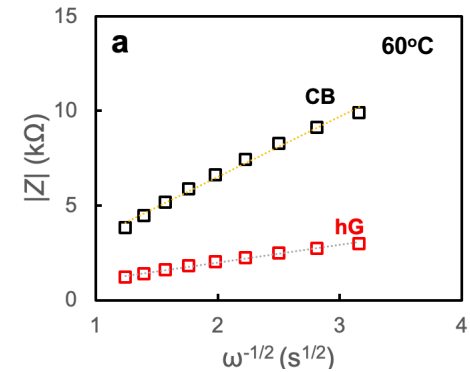
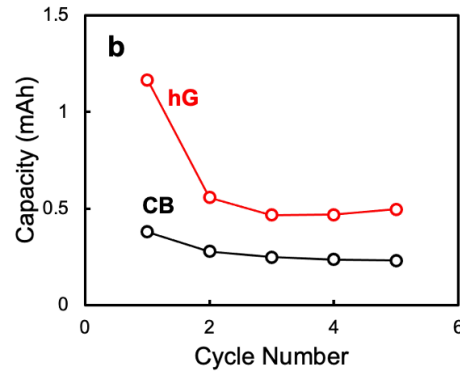
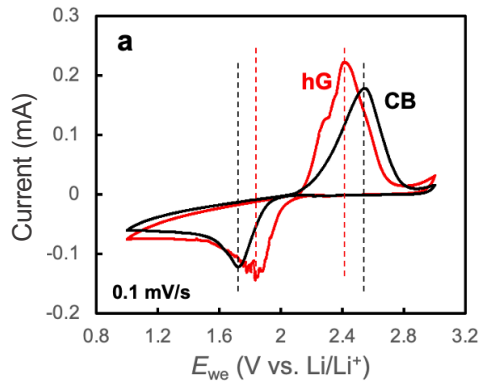
Dry-Pressed Cathode/SSE Bilayer Discs



S Cathode Microstructures



hG vs. CB



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

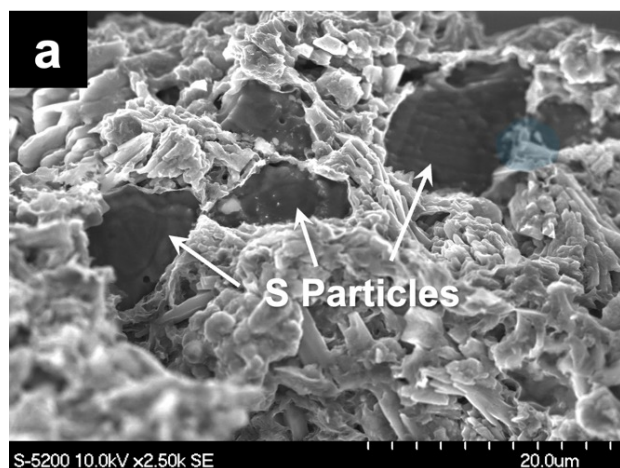
Room Temperature
12 mg/cm²

60°C
5 mg/cm²

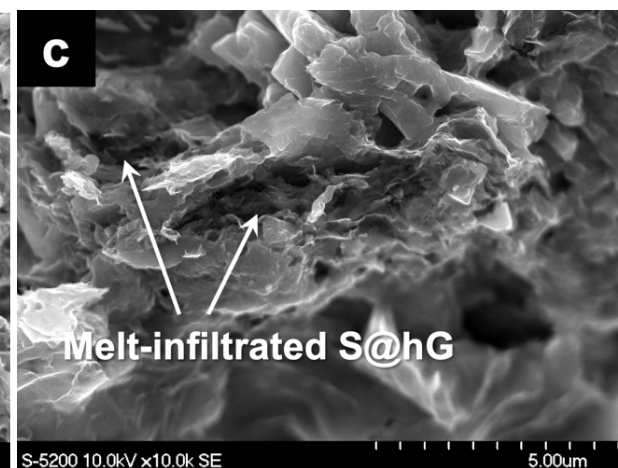
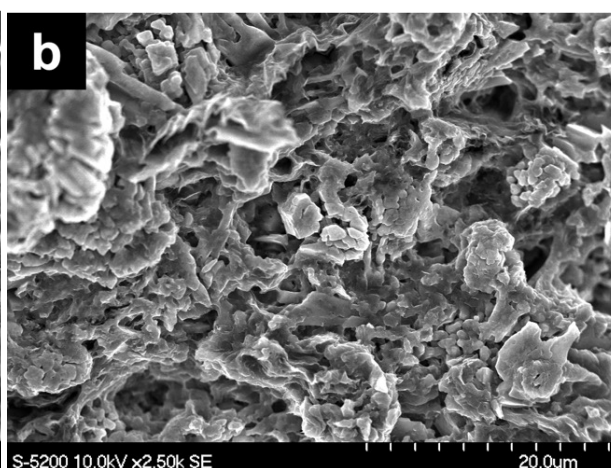
Cathode Composite with Melt Infiltrated S



Mixing with Pristine S Particles

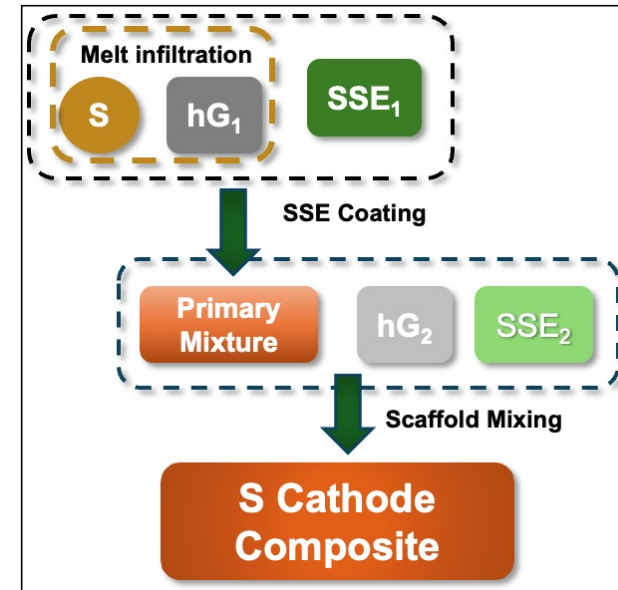
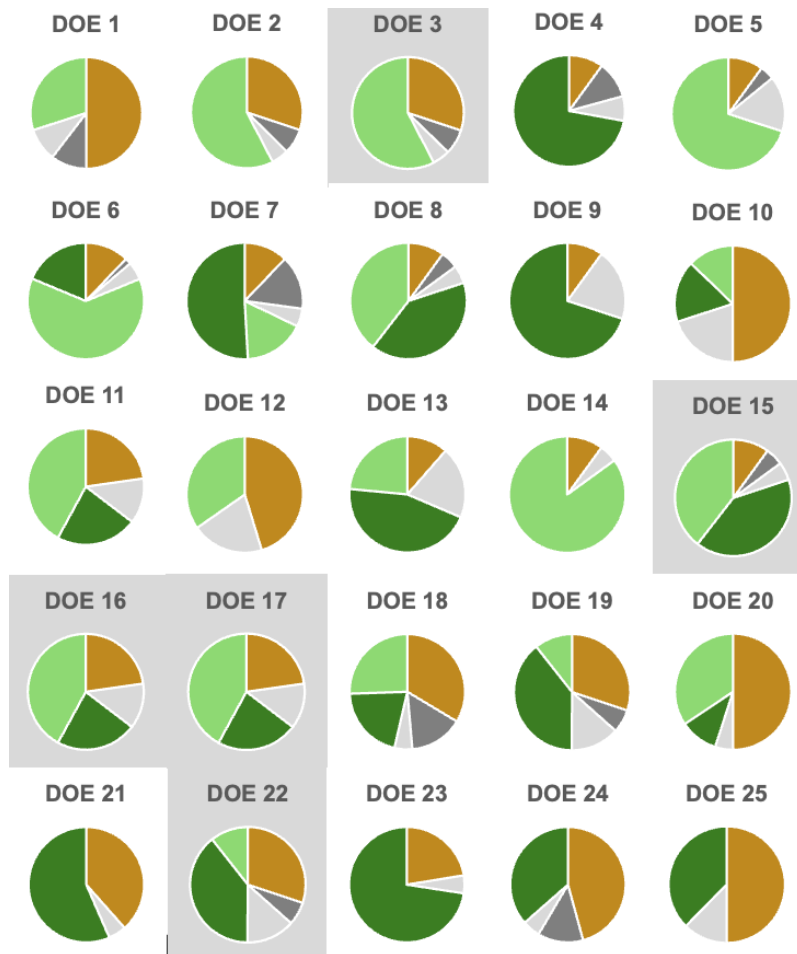


Melt Infiltration S onto hG Sheets



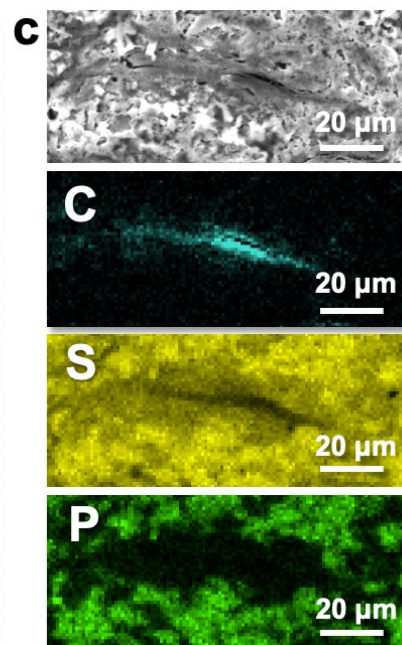
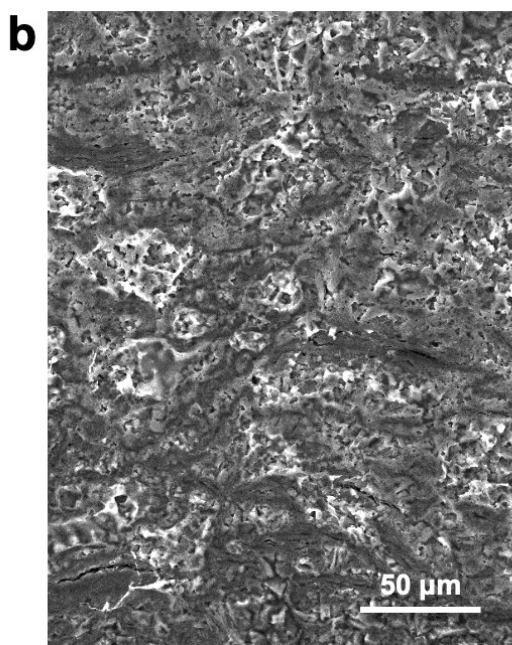
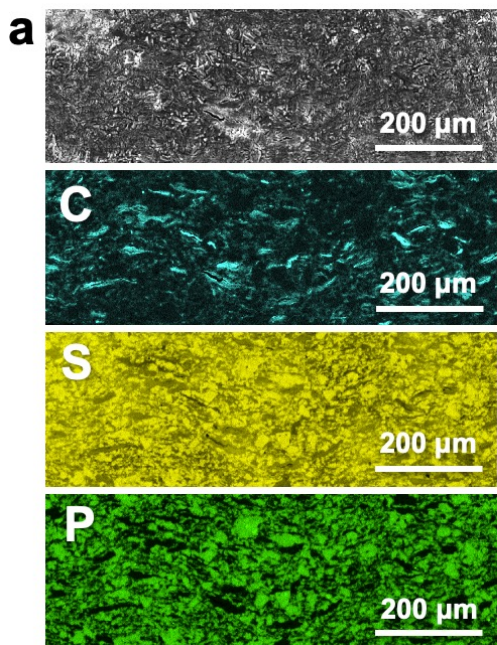
- ❑ Melt infiltration of S onto hG sheet surface significantly improves electrical and ionic contact area of sulfur with hG and SSE, respectively

S Cathode Optimization



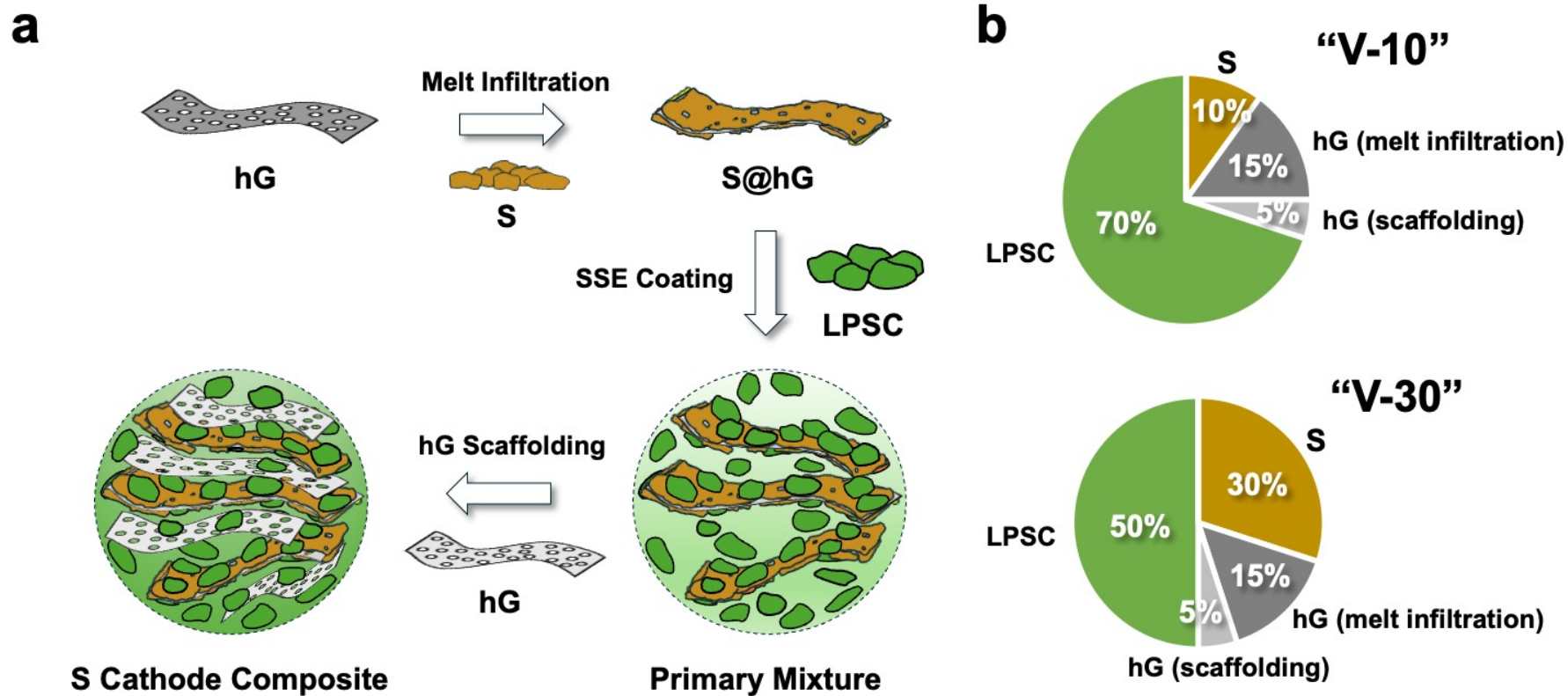
- ❑ A Design-of-Experiment (DOE) study
- ❑ 20 unique compositions
 - ❖ S: 10-50%
 - ❖ $hG_1 + hG_2$: 5-20%; hG_1 : 0-15%; hG_2 : 0-20%
 - ❖ $SE_1 + SE_2$: 30-85%; SE_1 : 0-75%; SE_2 : 0-70%
 - ❖ No hG_1 = no melt infiltration

S Composite Cathode Design Principles

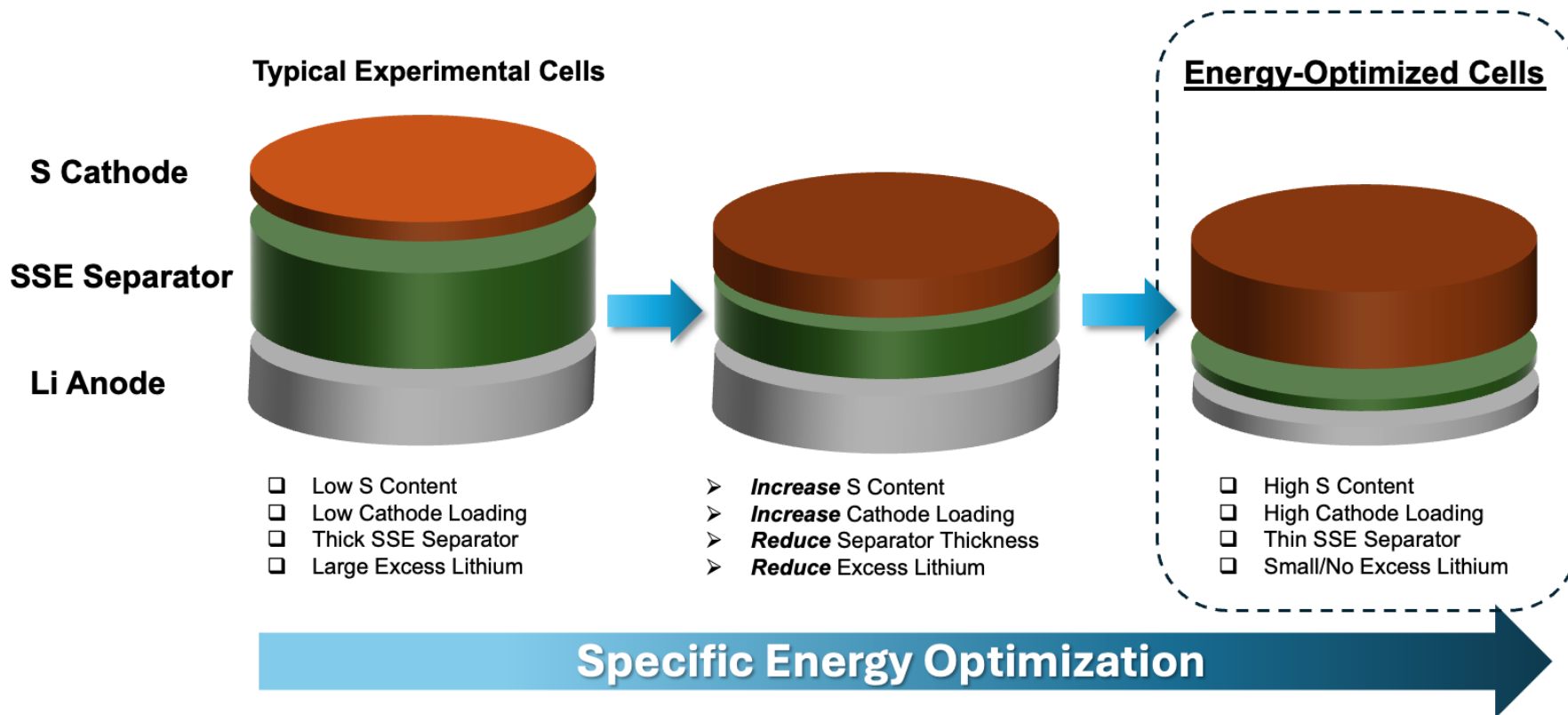


- High Discharge Capacity
 - Low S content
 - High hG:S ratio in melt infiltration
- Low Overpotential
 - Low S content
 - Medium hG:S ratio in melt infiltration
- Low Impedance
 - High scaffolding-step hG content
 - High coating-step SE content
- High Li^+ Diffusion Coefficient
 - High hG:S ratio during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

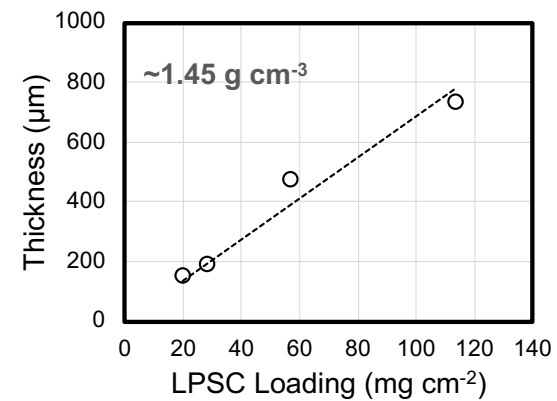
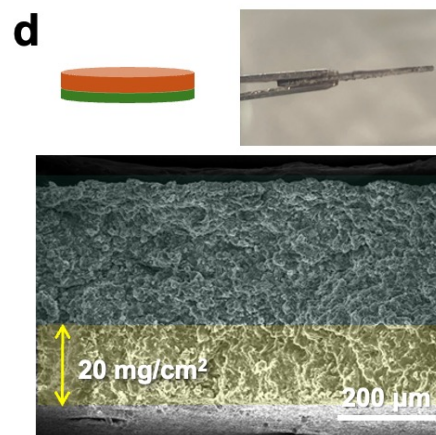
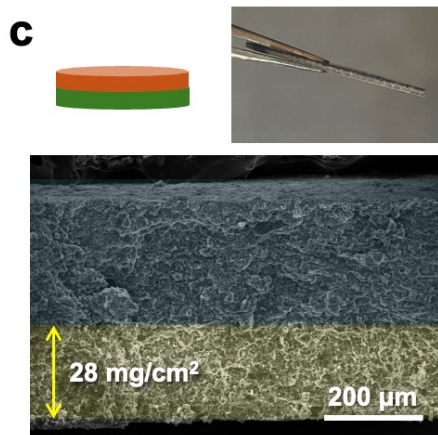
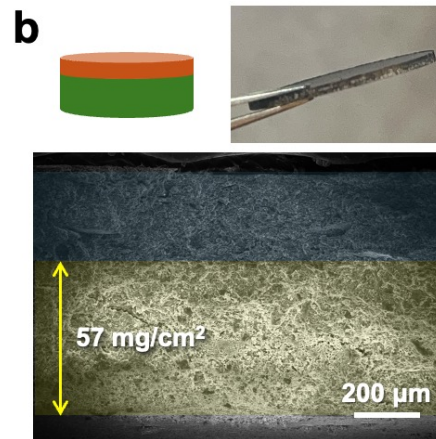
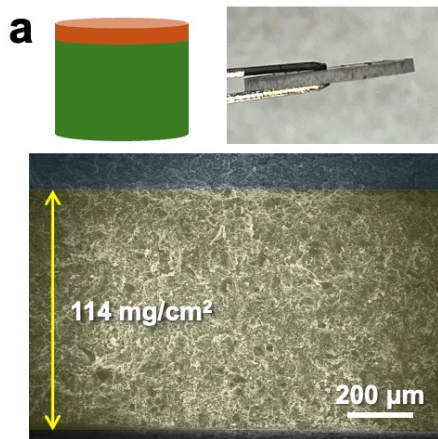
S Composite Cathodes Optimization



Cell Integration to Improve Specific Energy



Reduce SSE Thickness with Dry Pressing

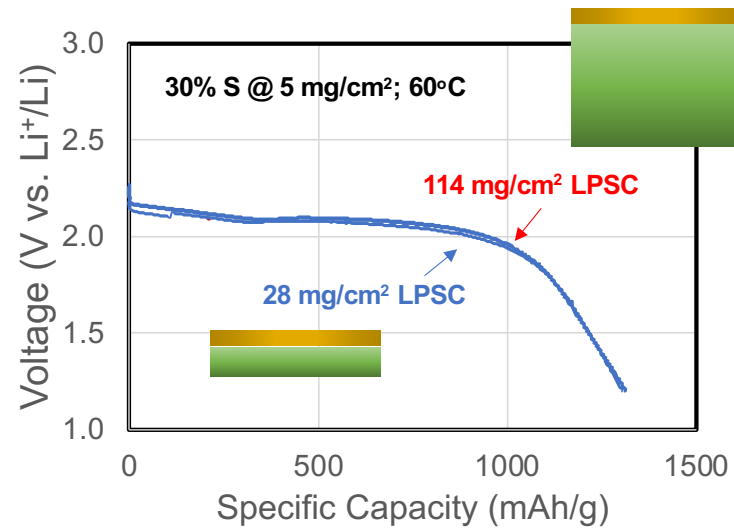
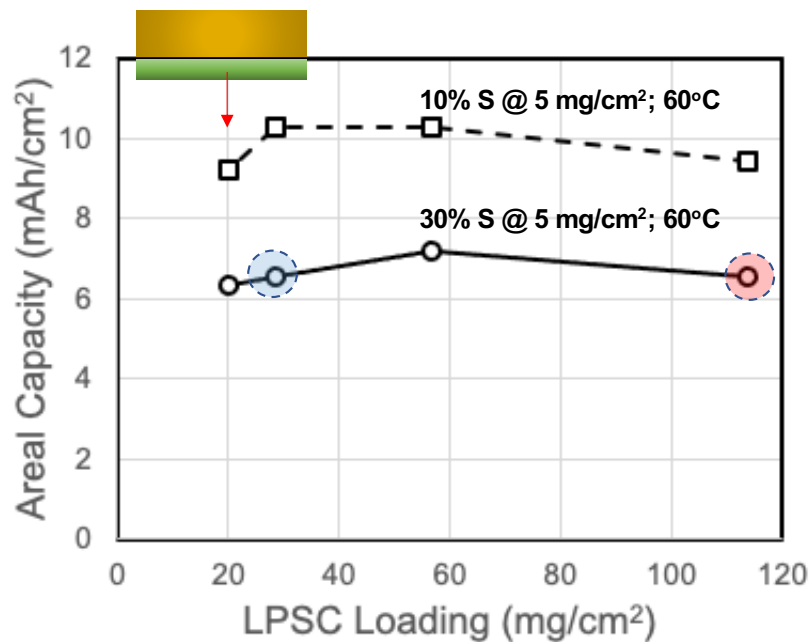


- Proof-of-concept experiments
- Doable yet extremely challenging

Improving Overall Specific Energy

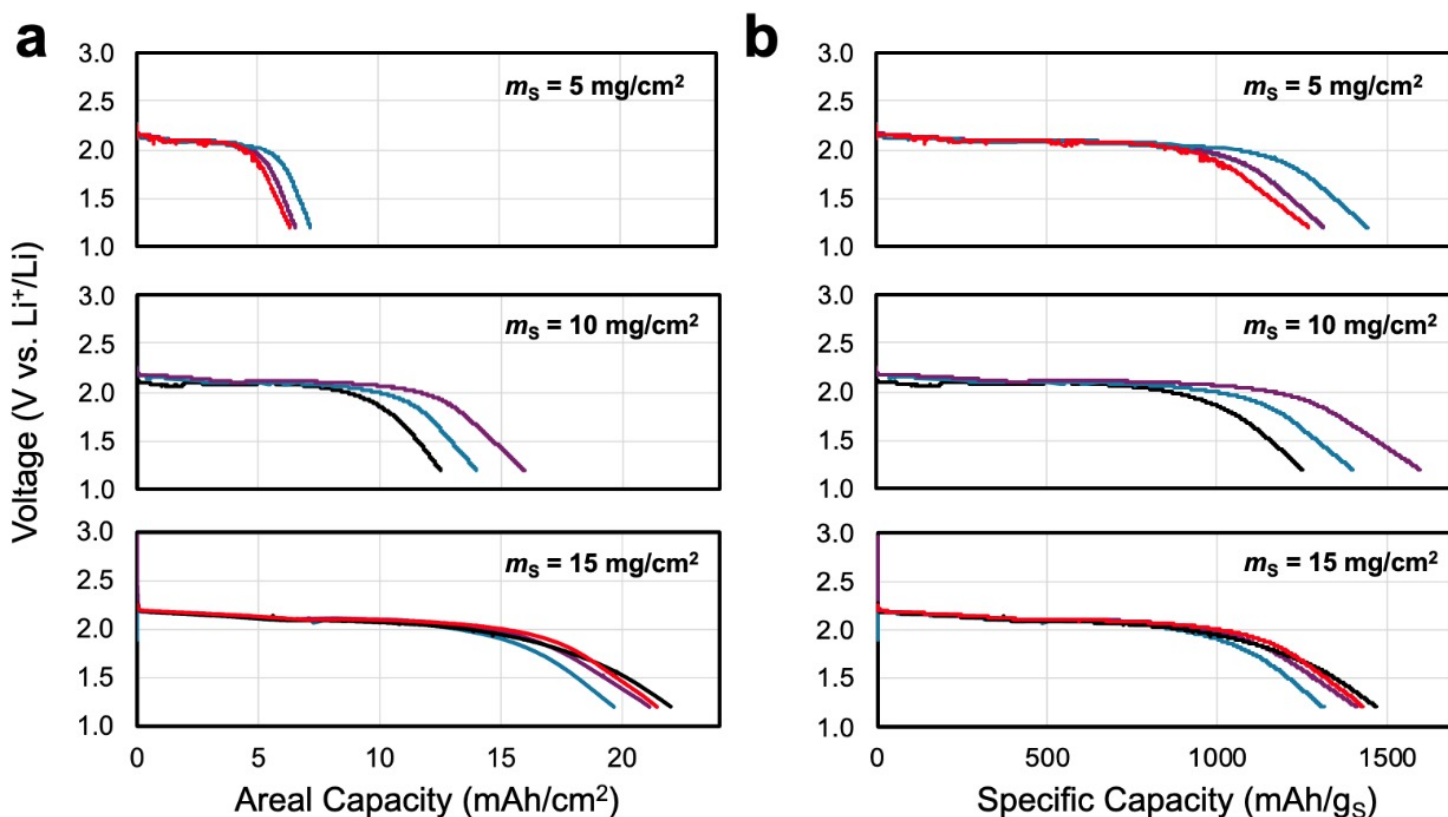


- Reduction in SSE thickness + Increasing cathode S content with retained S utilization = **Improved Specific Energy**



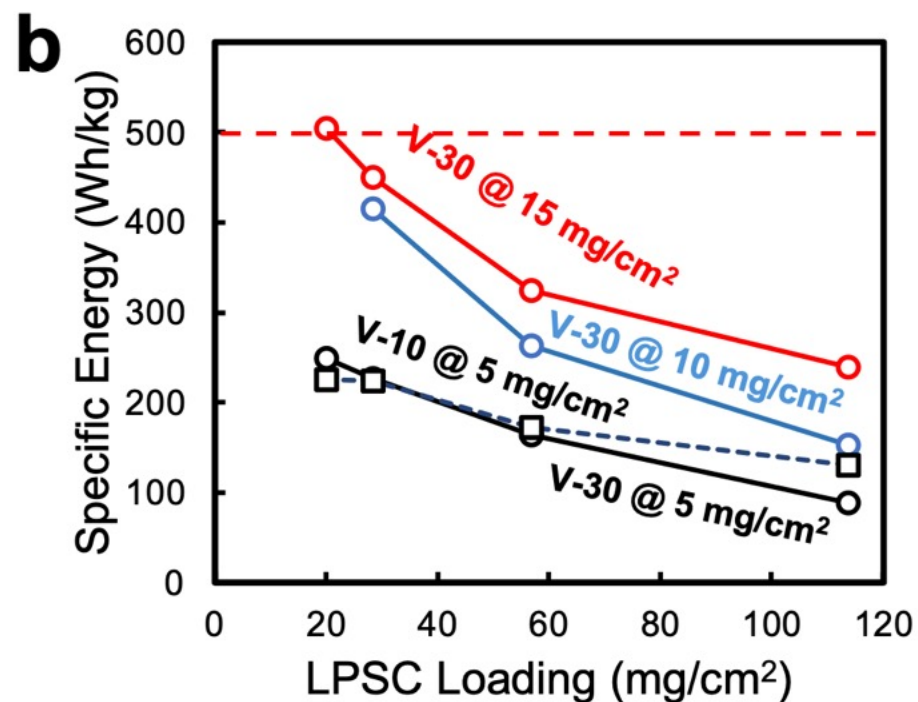
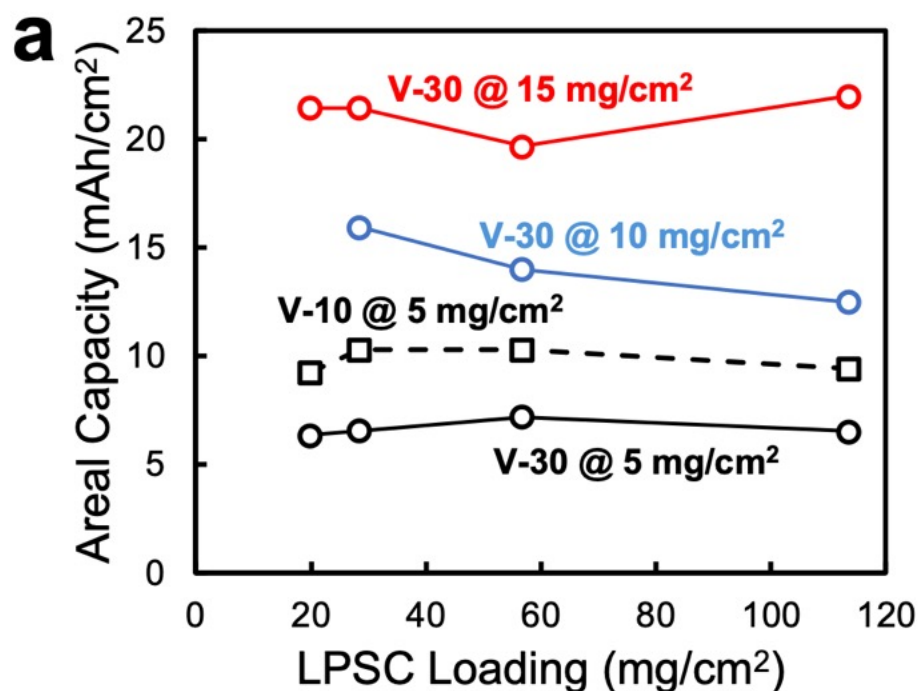
- All dry-pressed cathodes
- Coin cell tests
- 0.032 mA/cm²

Ultrahigh Areal Capacity S Cathodes



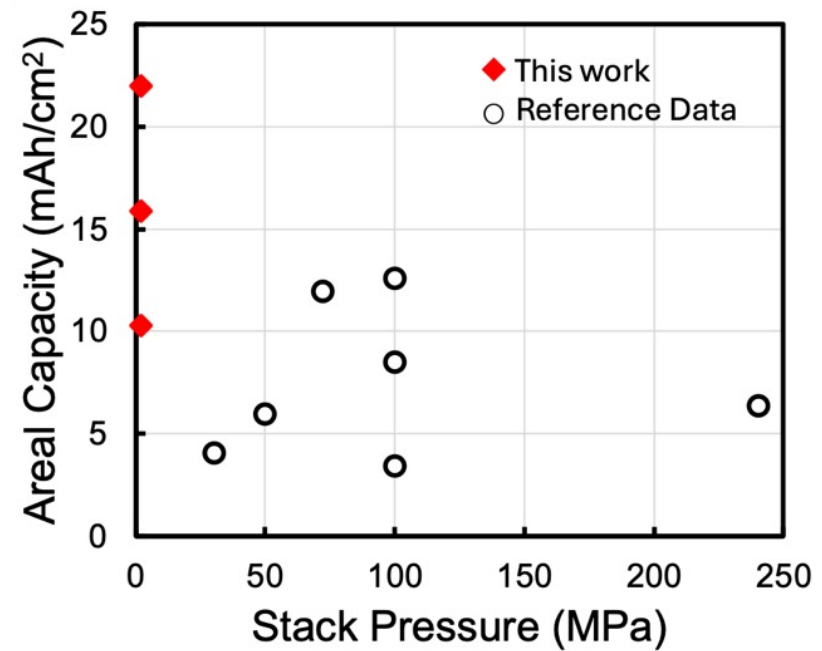
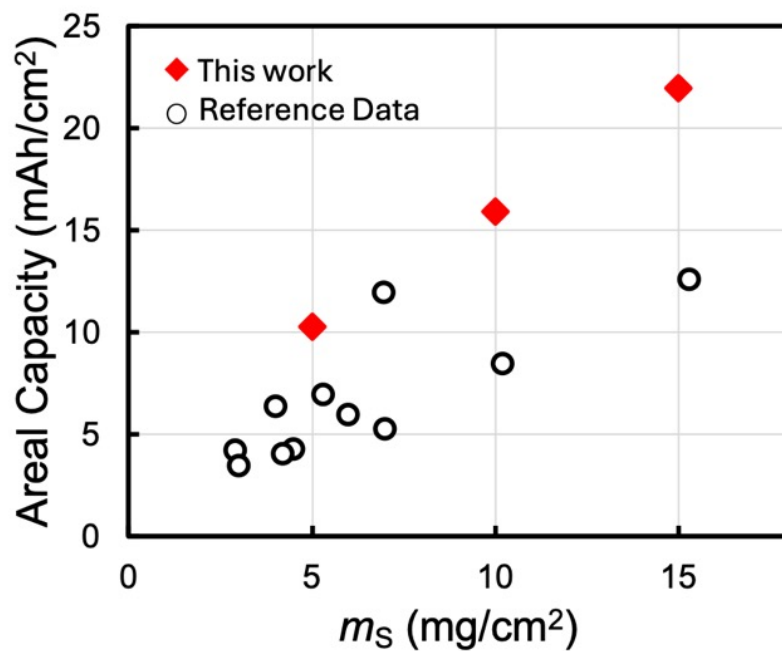
- ❑ Increase the areal capacity of S cathodes by increasing the S mass loading (more V30 cathode used)
- ❑ Capacity performance is consistent despite various SSE loadings (114 (black), 57 (blue), 28 (purple), and 20 (red) mg/cm²)

Toward 500 Wh/kg



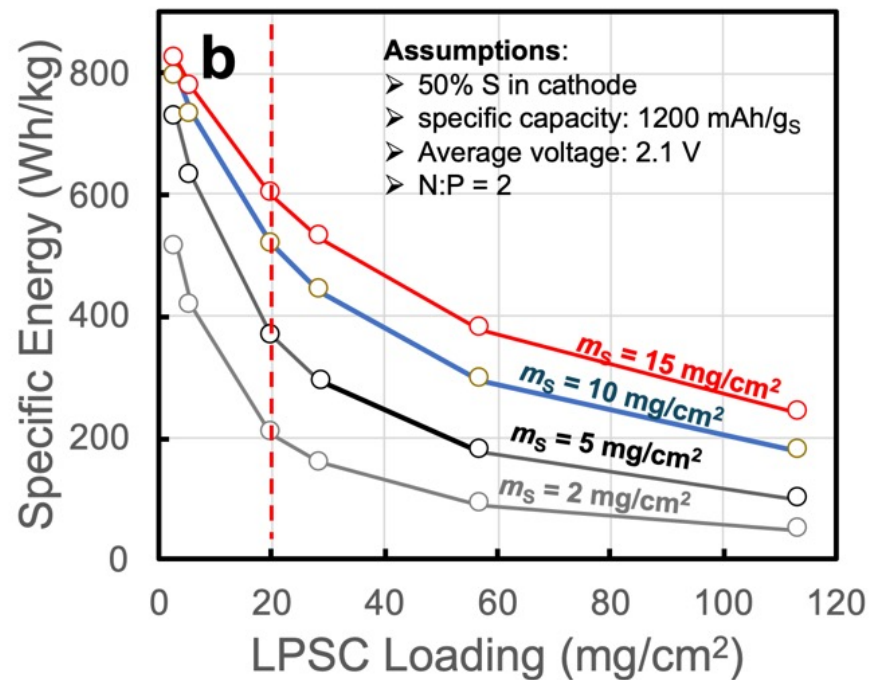
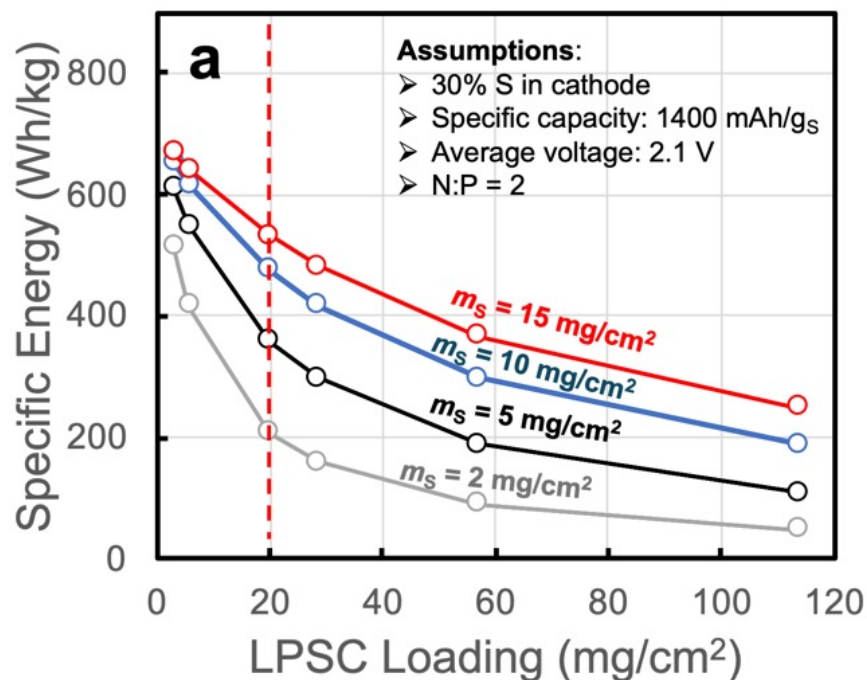
Increasing cathode S content and loading and reducing solid electrolyte thickness pushed specific energy pass 500 Wh/kg.

High Areal Capacity with Low Stack Pressure



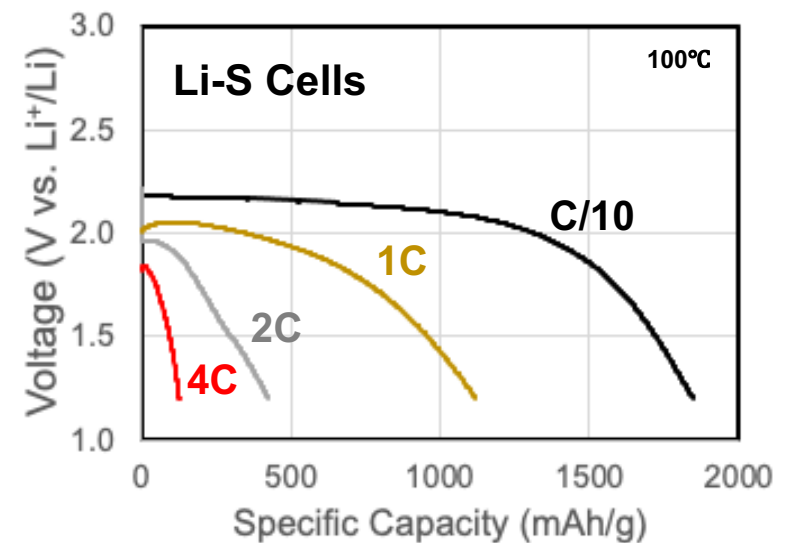
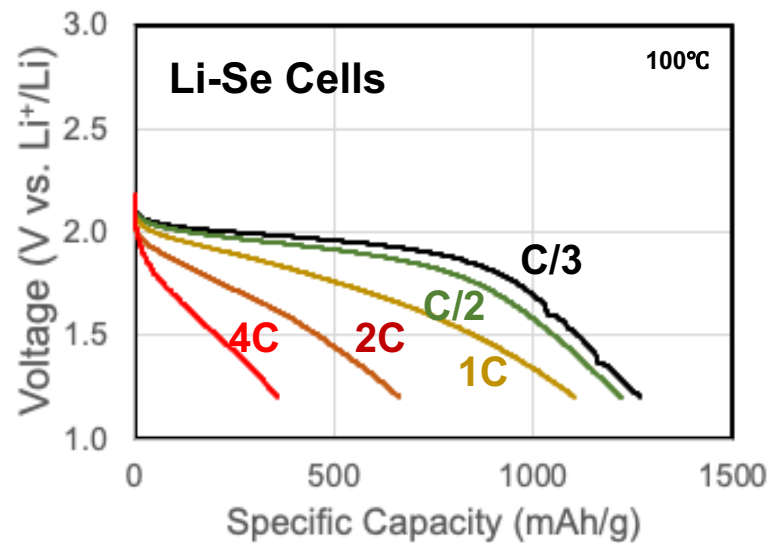
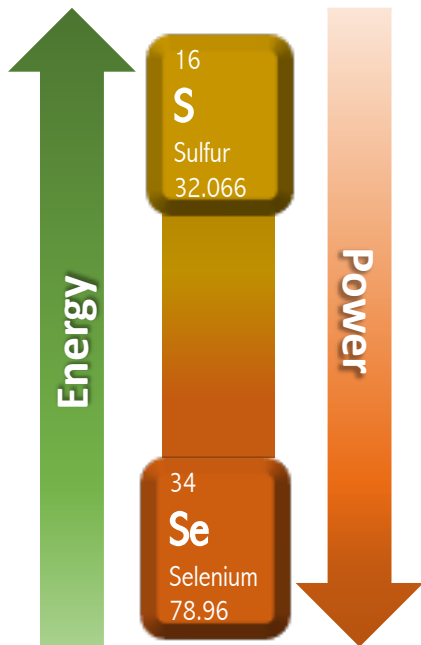
Cyclability at low stack pressure needs to be addressed: cathode, SSE, Li anode

Projection Beyond 500 Wh/kg



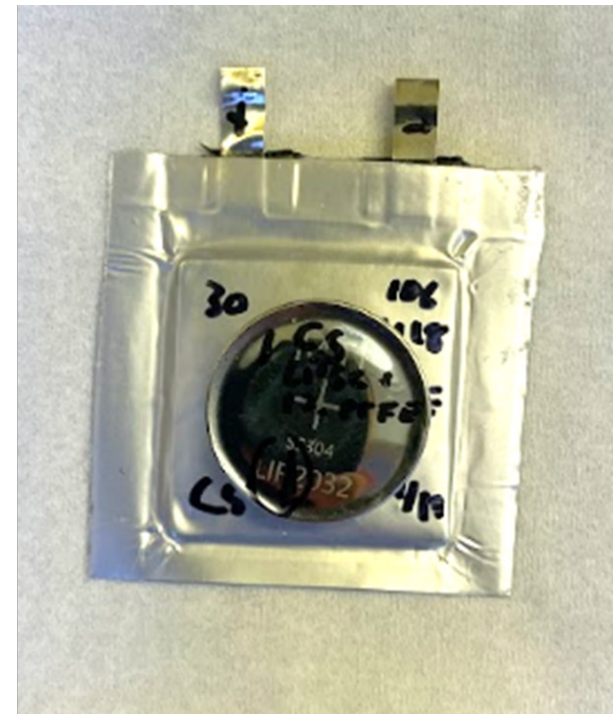
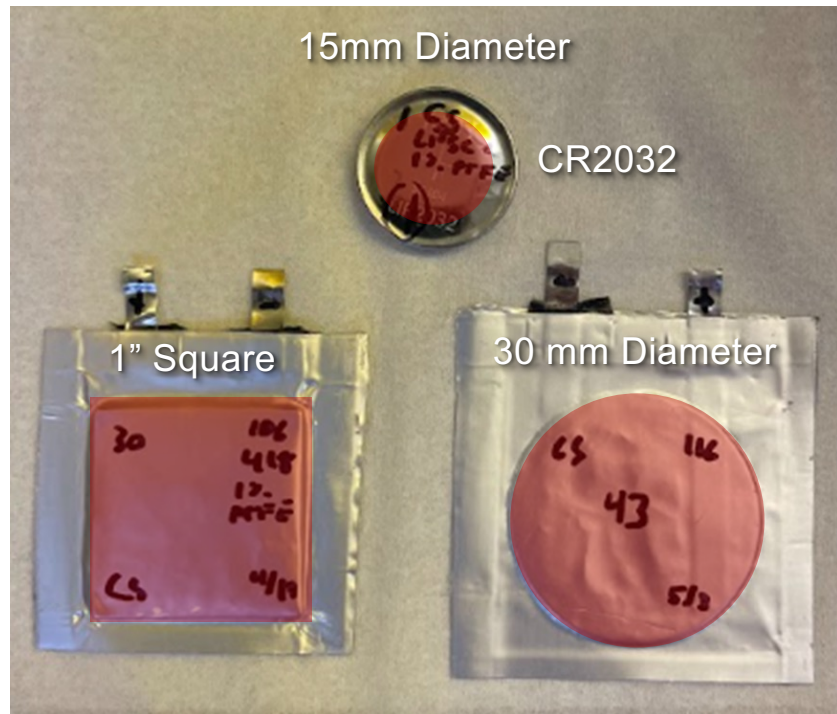
Increasing cathode S content and loading and reducing solid electrolyte thickness pushed specific energy pass 500 Wh/kg.

High Temperature, High Power Cells



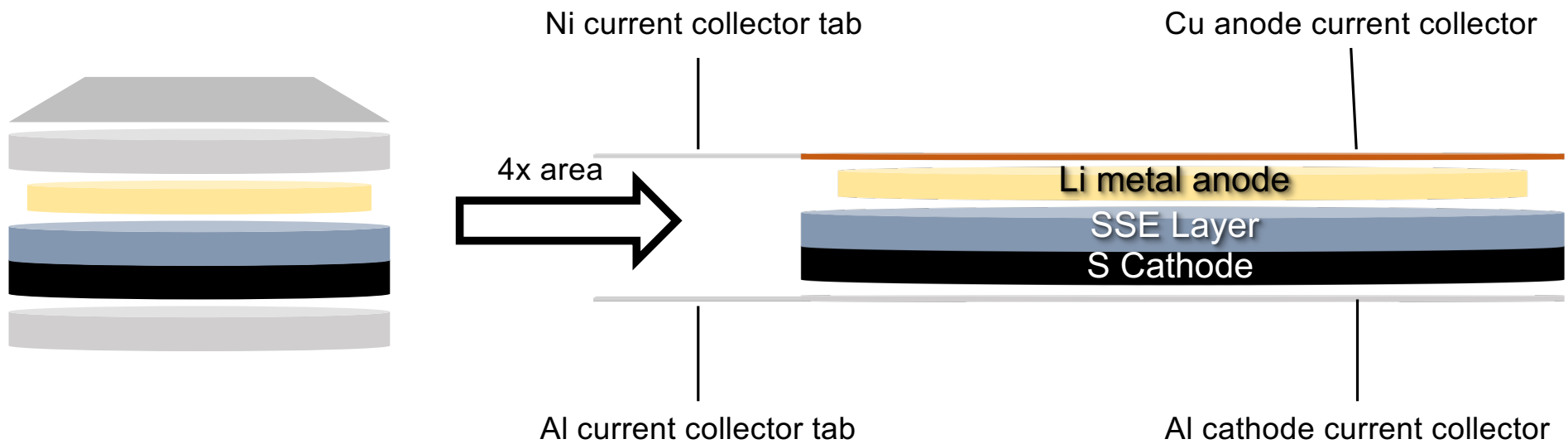
SABERS cells can operate at and above 100°C with high power performance.

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



Process Improvements



Generation 1



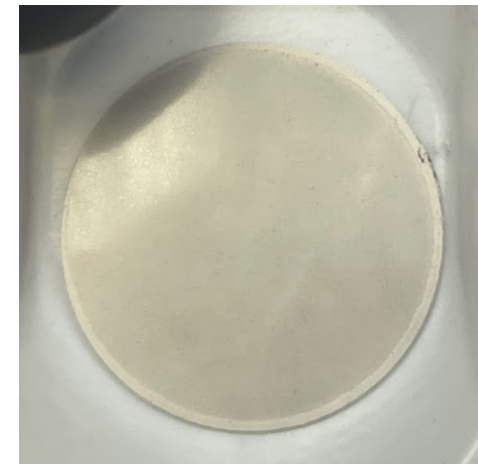
Direct scale-up from coin cell studies

Generation 2



Improved dry-processing via proper use of polymer binders

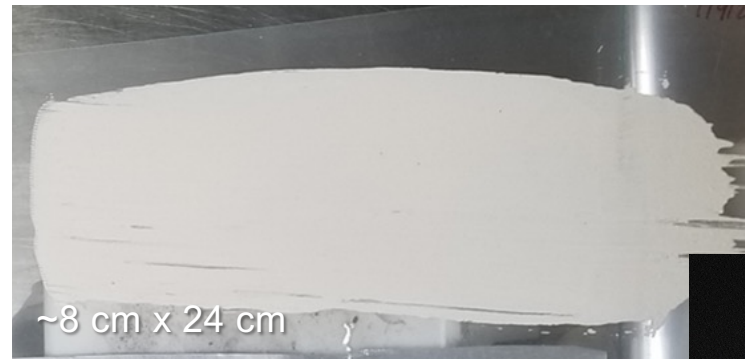
Generation 3



Development of SSE Films

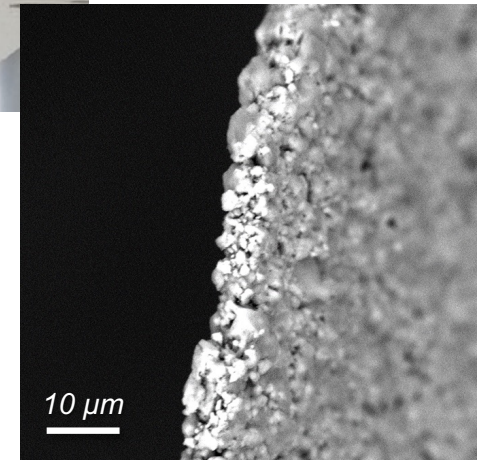


Free-standing LPSC Thin Films

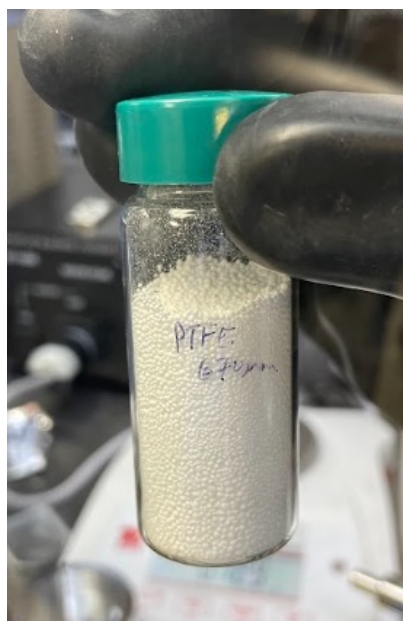


Tape-Casted LPSC Films
(~25 μm thickness)

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

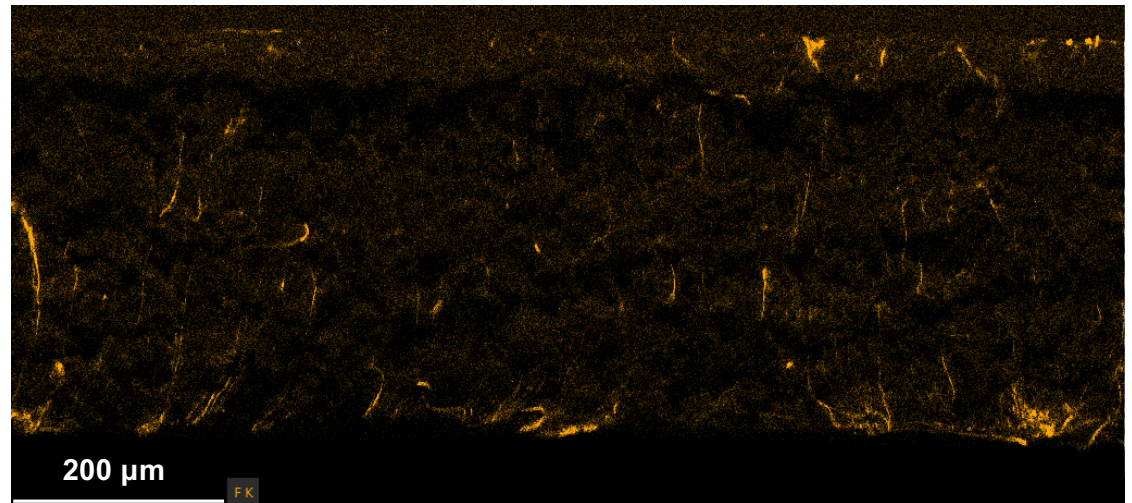
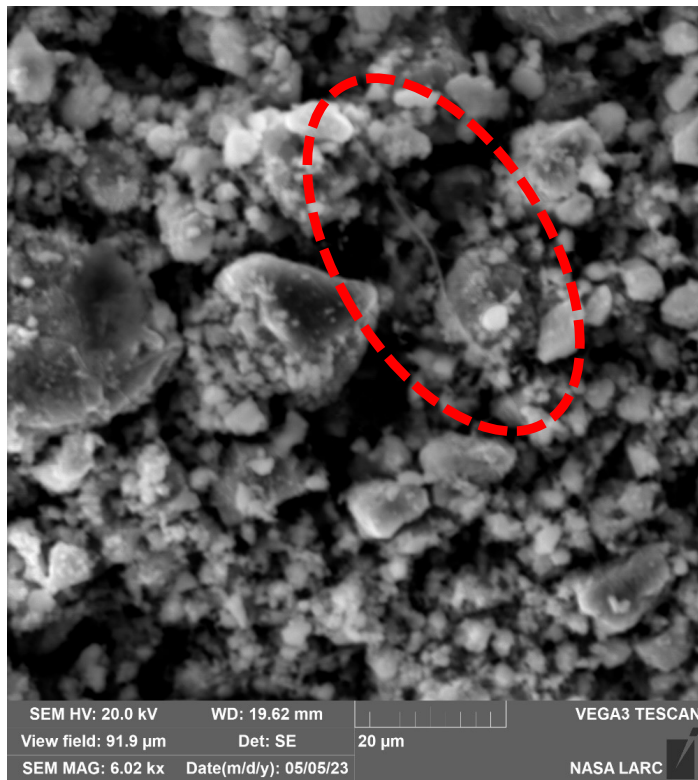


Dry Processing of LPSC Films

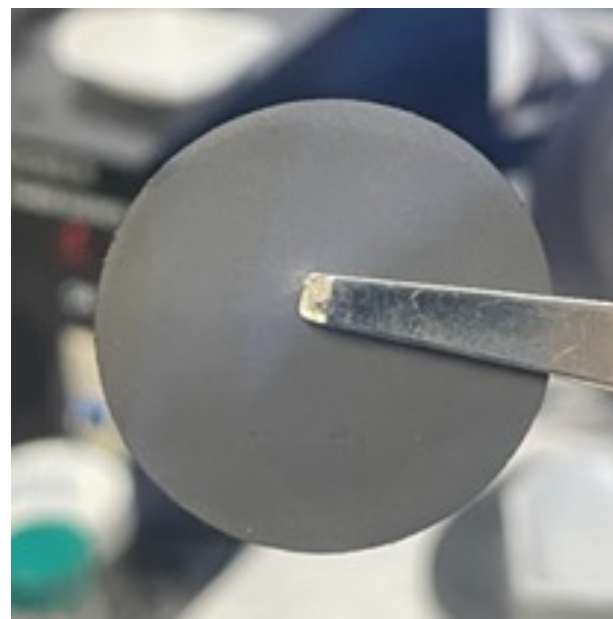
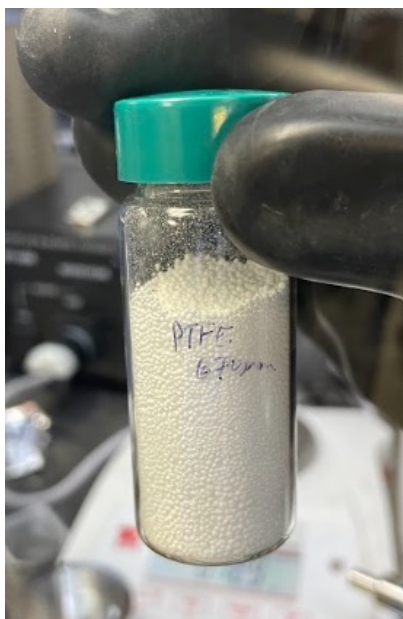


PTFE: Polytetrafluoroethylene

PTFE Fibers Provide Mechanical Support



Dry Processing of S Cathode Films

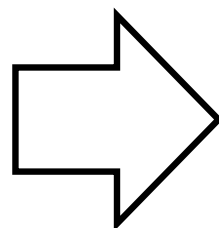
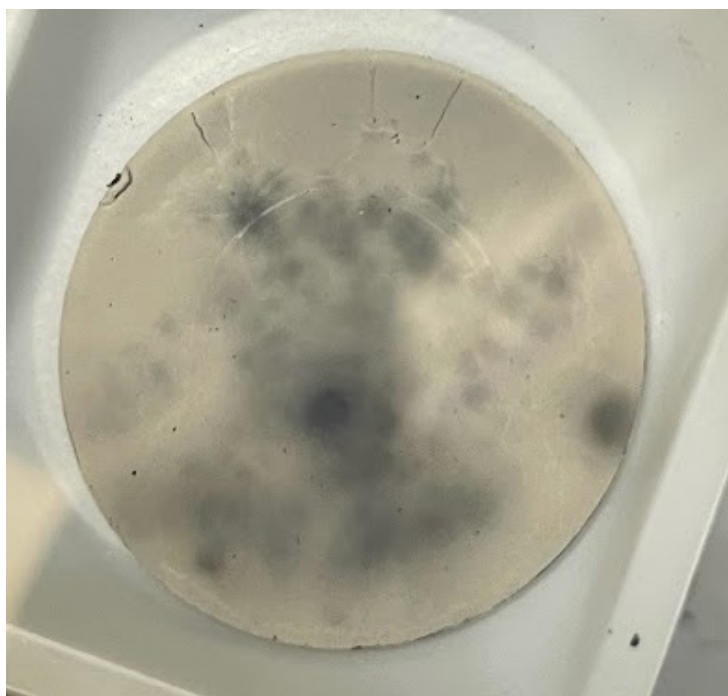


- PTFE binder is also compatible with dry processing of sulfur cathode

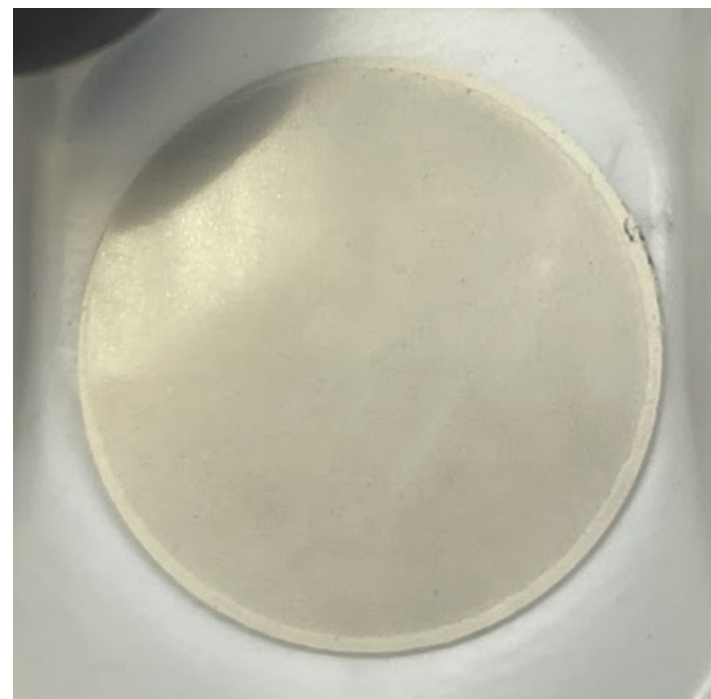
Cathode-SSE Bilayer Fabrication



Generation 2 Pouch Cell



Generation 3 Pouch Cell

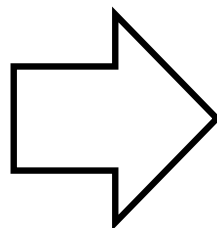
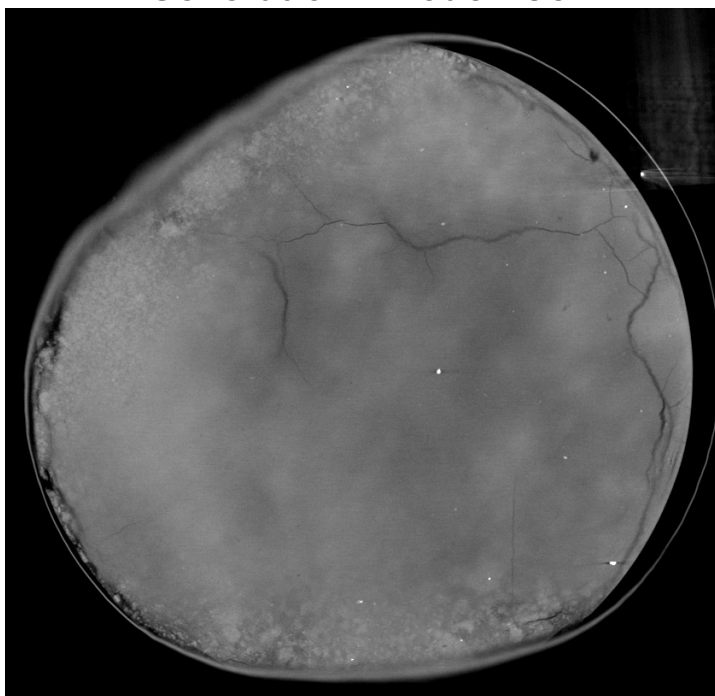


- ❑ Discs are all 3 cm in diameter

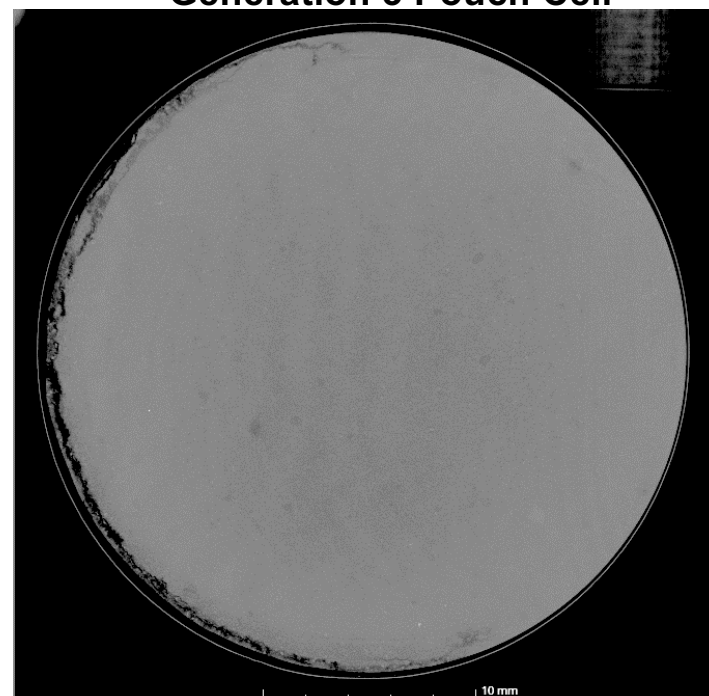
X-Ray Computed Tomography (CT)



Generation 2 Pouch Cell



Generation 3 Pouch Cell



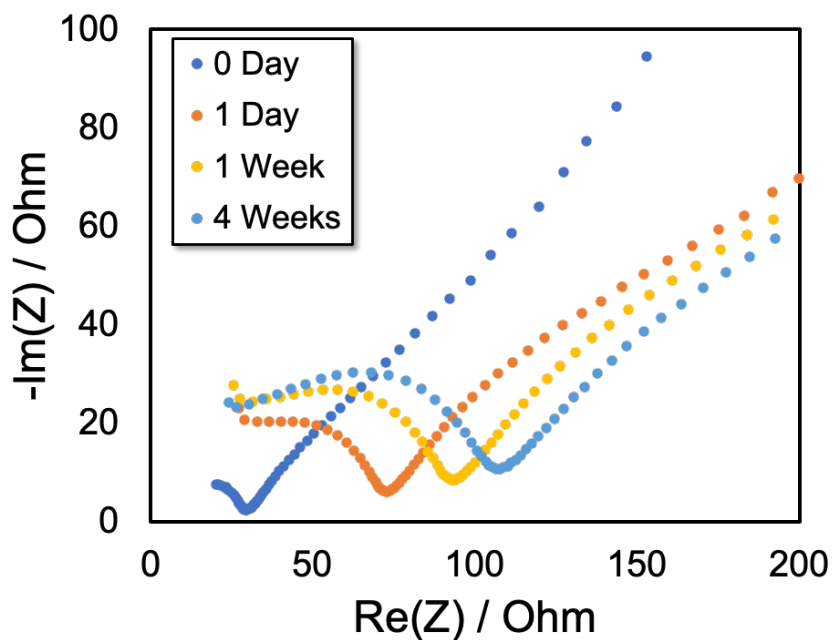
- ❑ Discs are all 3 cm in diameter

Courtesy: Dan Perey
NASA Langley Research Center (LaRC)

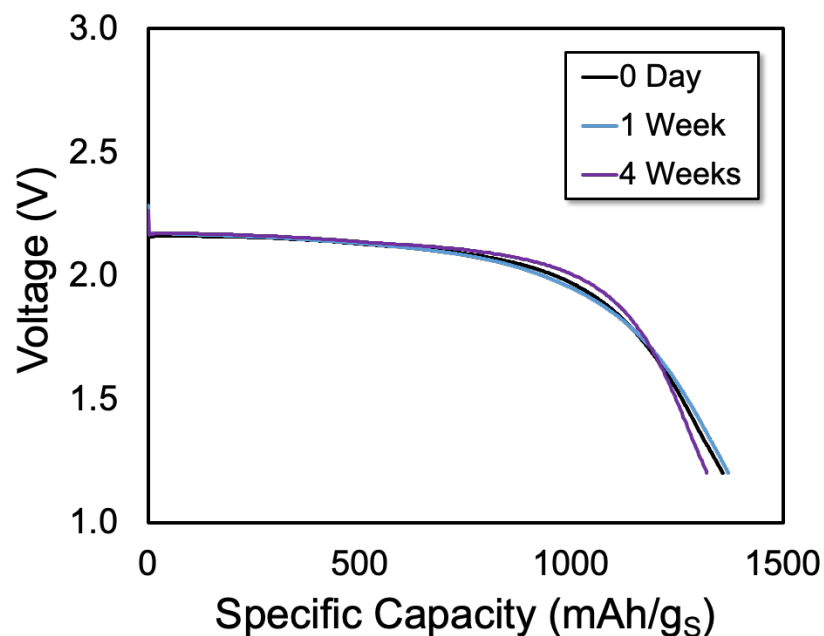
Pouch Cells with Improved Shelf Life



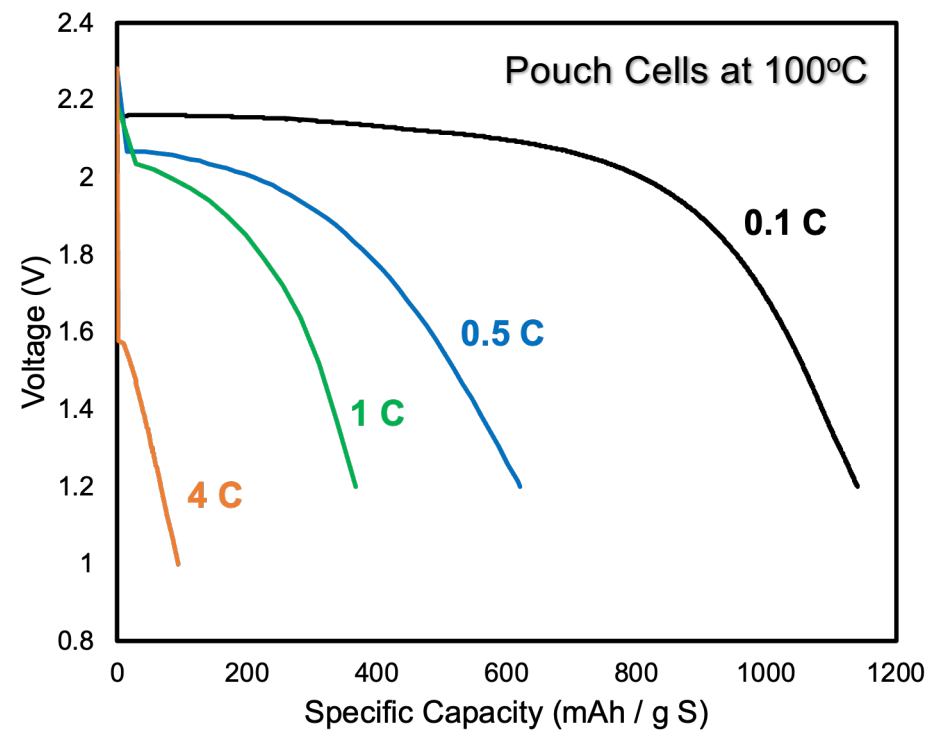
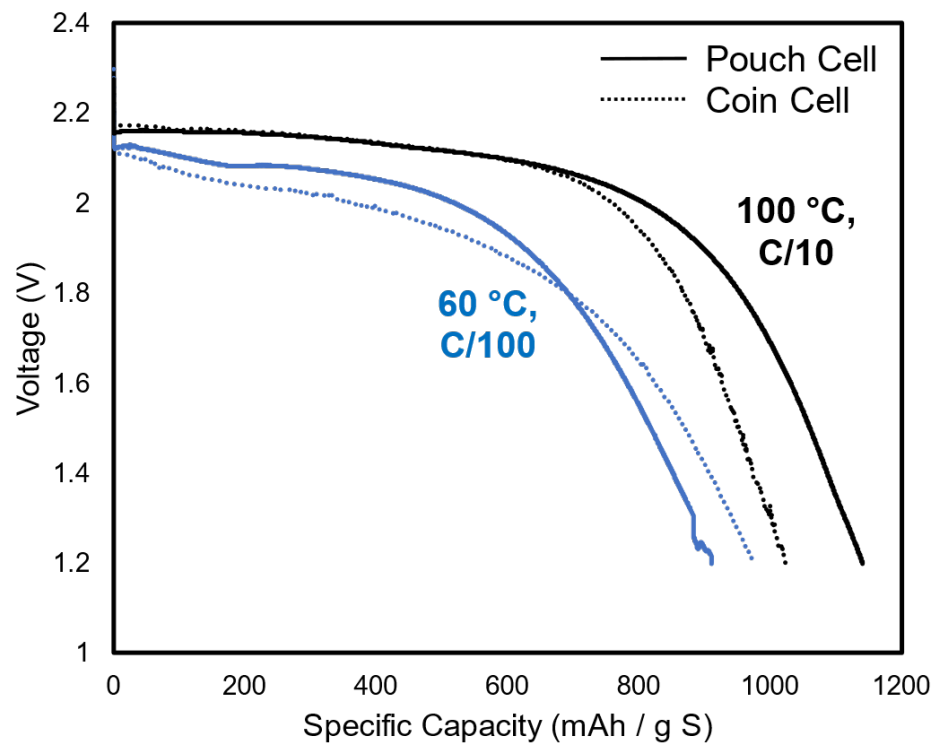
Electrochemical Impedance Spectroscopy (EIS)



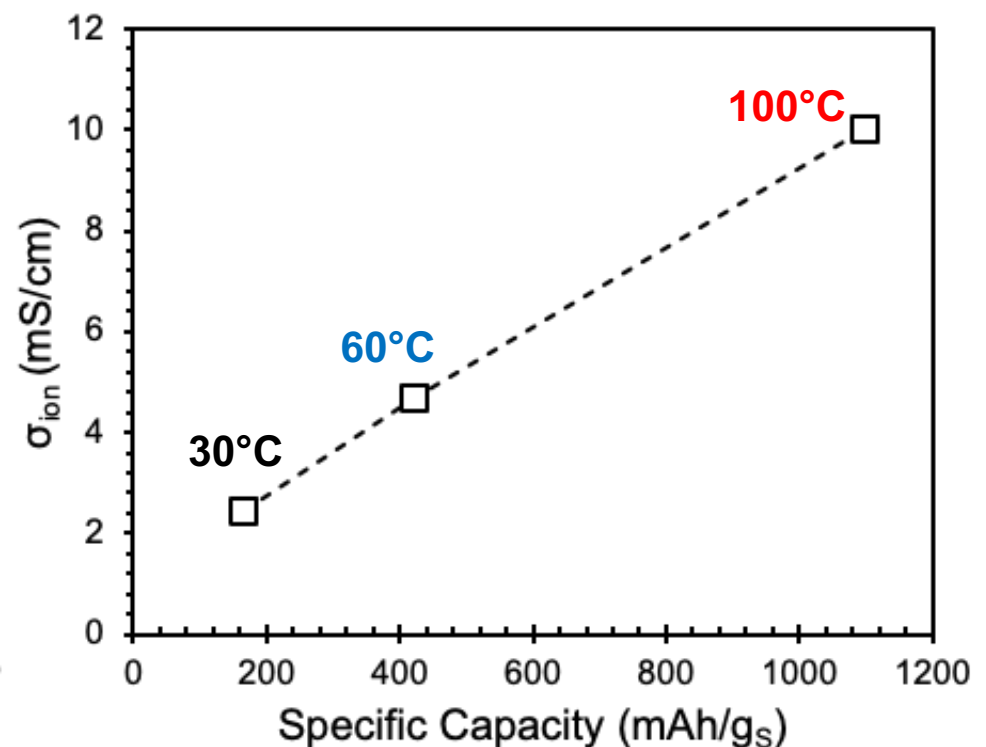
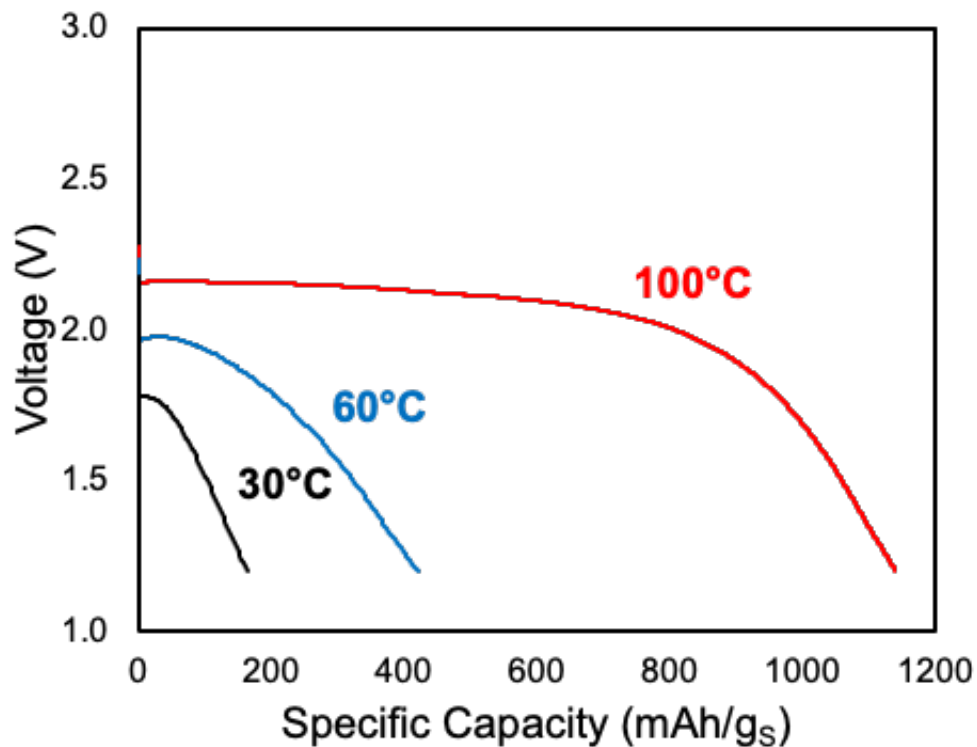
Constant Current Discharge



From Coin Cells to Pouch Cells

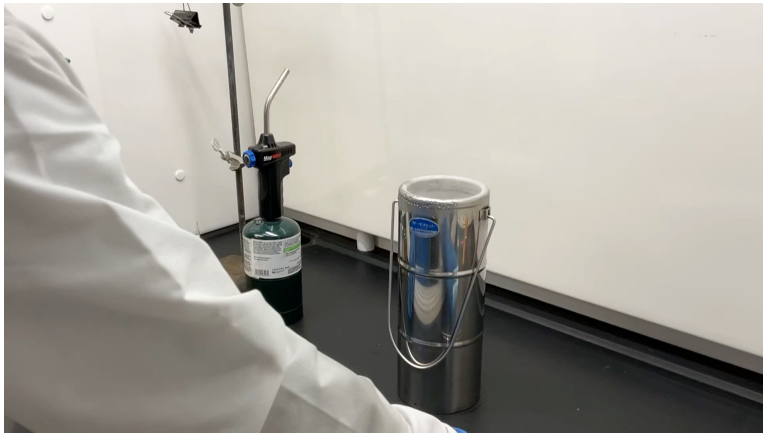


Key Roles of SSE Ionic Conductivity

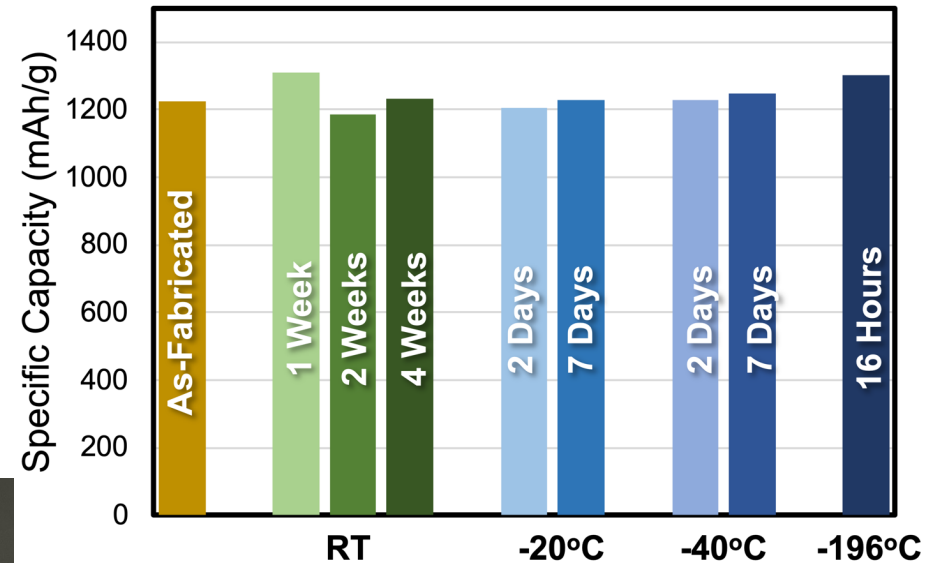


- Battery capacity linearly correlates with solid electrolyte (LPSC) conductivity
- Solid electrolyte with higher ionic conductivity should result in enhanced battery performance

Shelf Life and Low Temperature Storage



SABERS Cells Removed from Liquid Nitrogen Reservoir

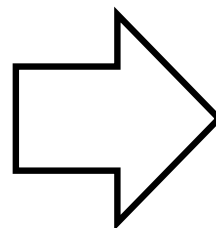
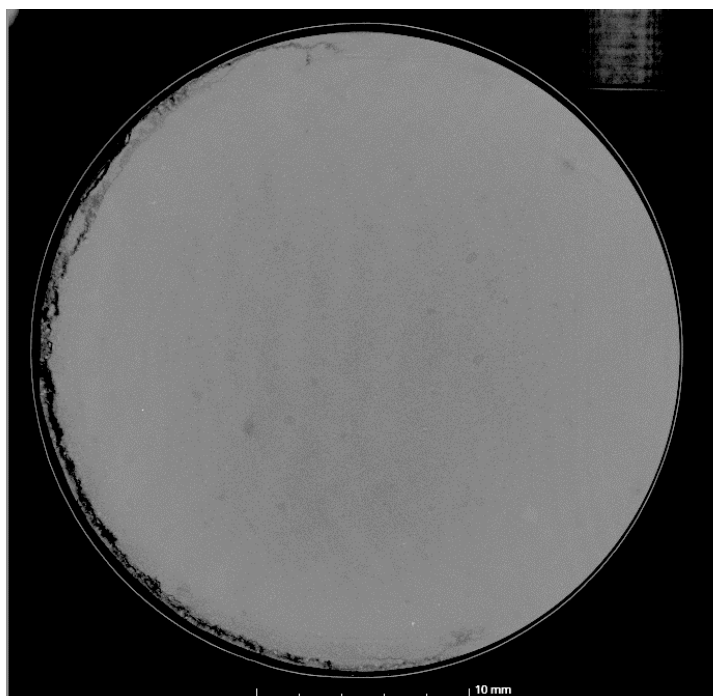


- SABERS all-solid-state battery cells exhibit excellent shelf life and survive from low and extremely low temperatures (exhibit normal functions after warming up).

More Challenges!



Before Discharge



After Discharge



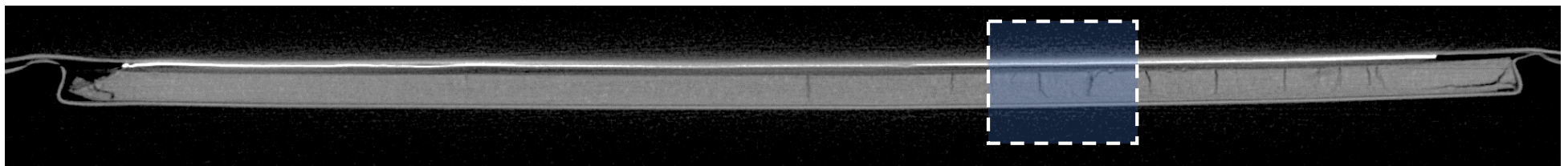
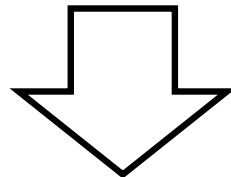
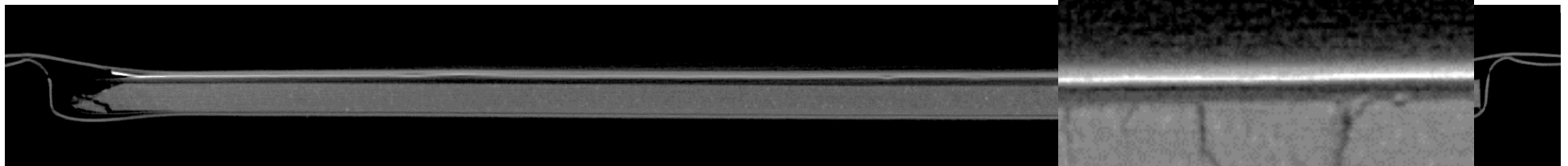
- ❑ Discs are all 3 cm in diameter

Courtesy: Dan Perey (NASA LaRC)

More Challenges!



Before Discharge



After Discharge

Courtesy: Dan Perey (NASA LaRC)

- ❑ Discs are all 3 cm in diameter

Summary

- ❑ **High areal capacity (>22 mAh/cm²)** all-solid-state Li-S cells were demonstrated, providing a viable pathway to **>500 Wh/kg** in specific energy.
- ❑ Li-S and Li-Se cells exhibited **wide operation temperature** range up to at least 100°C, at which the cells also exhibited high power capability.
- ❑ High capacity all-solid-state Li-S (small-format) **pouch cells** were demonstrated from processing development of both solid electrolyte and cathode layers.



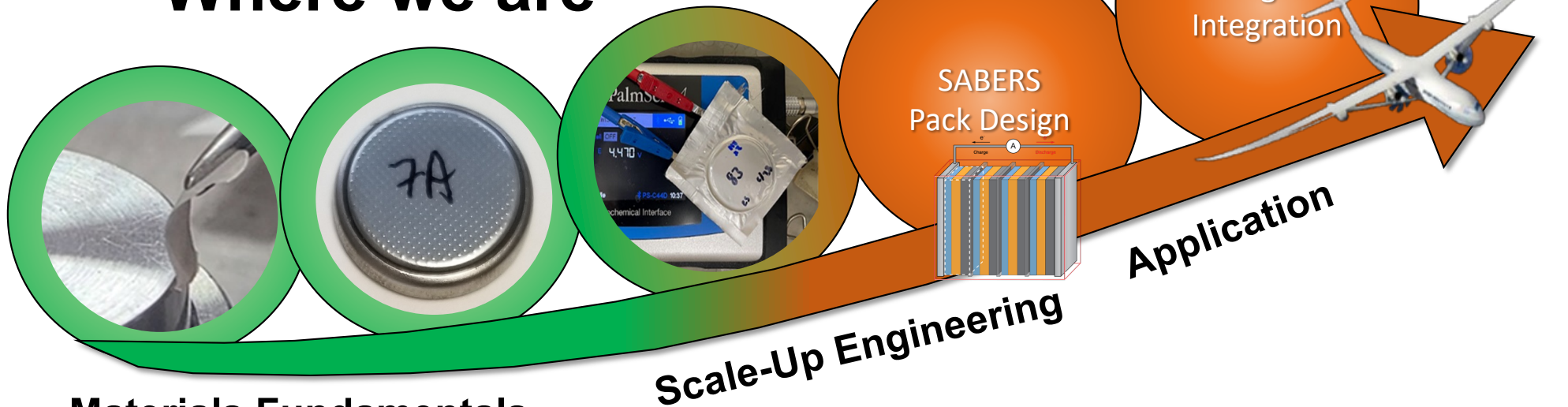
Future of SABERS



Addressing Materials Challenges to Power the Future of Aerospace

What's Next?

Where we are



Materials Fundamentals

Scale-Up Engineering

SABERS Pack Design

Flight Integration

Application

Acknowledgments



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



- ❑ Dan Perey
- ❑ Joshua Brown
- ❑ Lopamudra Das
- ❑ Glen King
- ❑ John Hopkins
- ❑ Student Interns:
 - ❑ 2019 – 2022: April Rains, Christian Plaza-Rivera, Brandon Walker
 - ❑ 2022: Abigail Durgin, Sophie Kiley, Bona Kim, **Lucy Somervill**, **Rehan Rashid**
 - ❑ 2023: Melissa Chang, William Dai, Sayyam Deshpande, Ethan Higginbotham, Shane Lindsey, Claudia Lopez, Alanis Matias-Perez, Abraham Nicolson, **Coby Scrudder**
 - ❑ 2024: **Hanjing Chen**, Kelsey Crawford, David Forslof, **Jason Packard**, Autumn Avery, Alan Cancel, Demetrius Burns, Kelton McGrath, Alison Kavanagh, Ashley Gomez, Vergil Schreiber, Daniel Thornton