



High Energy and High Power All-Solid-State Batteries toward Electric Aircraft Applications

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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.

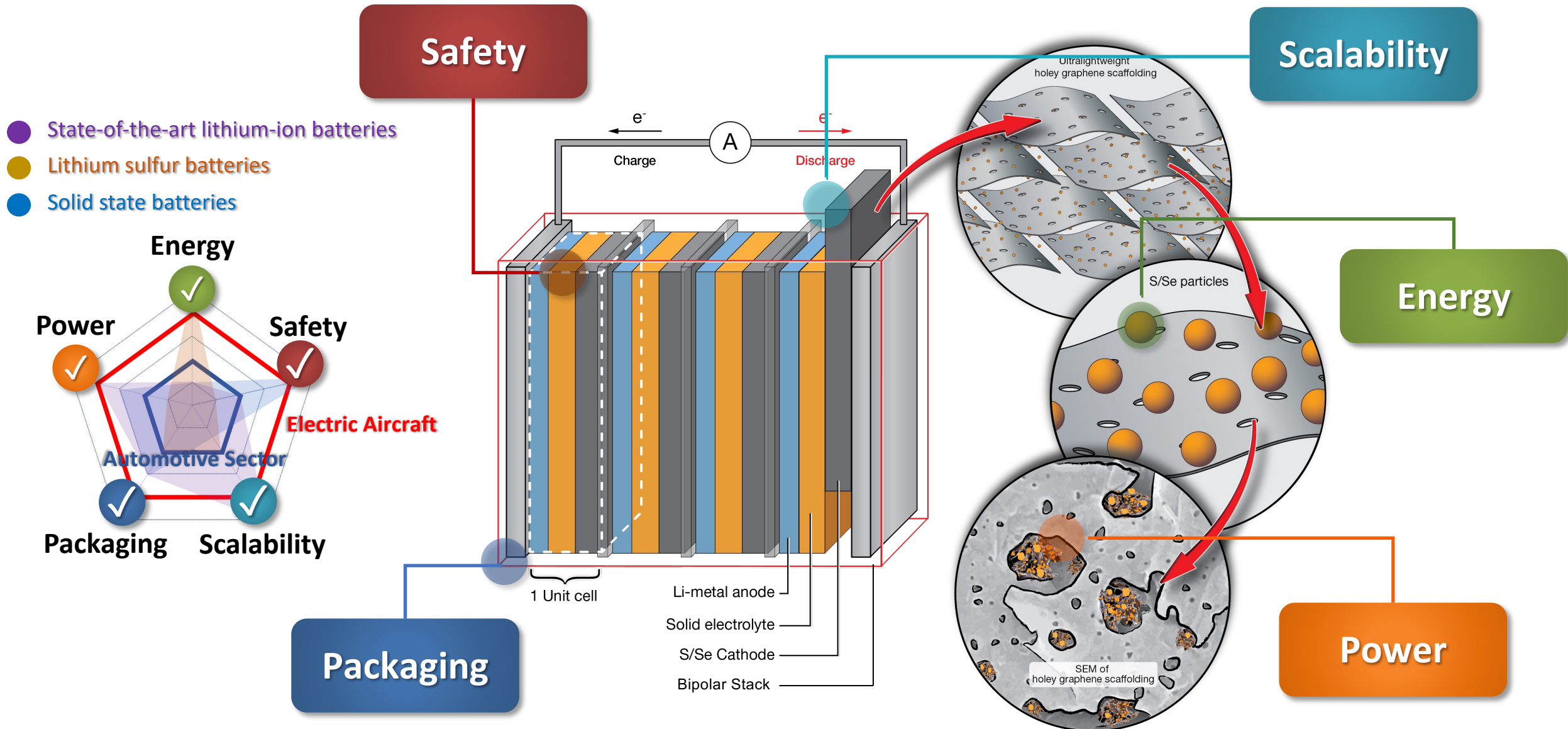
Battery **Sustainability** Preferences

- ❑ **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

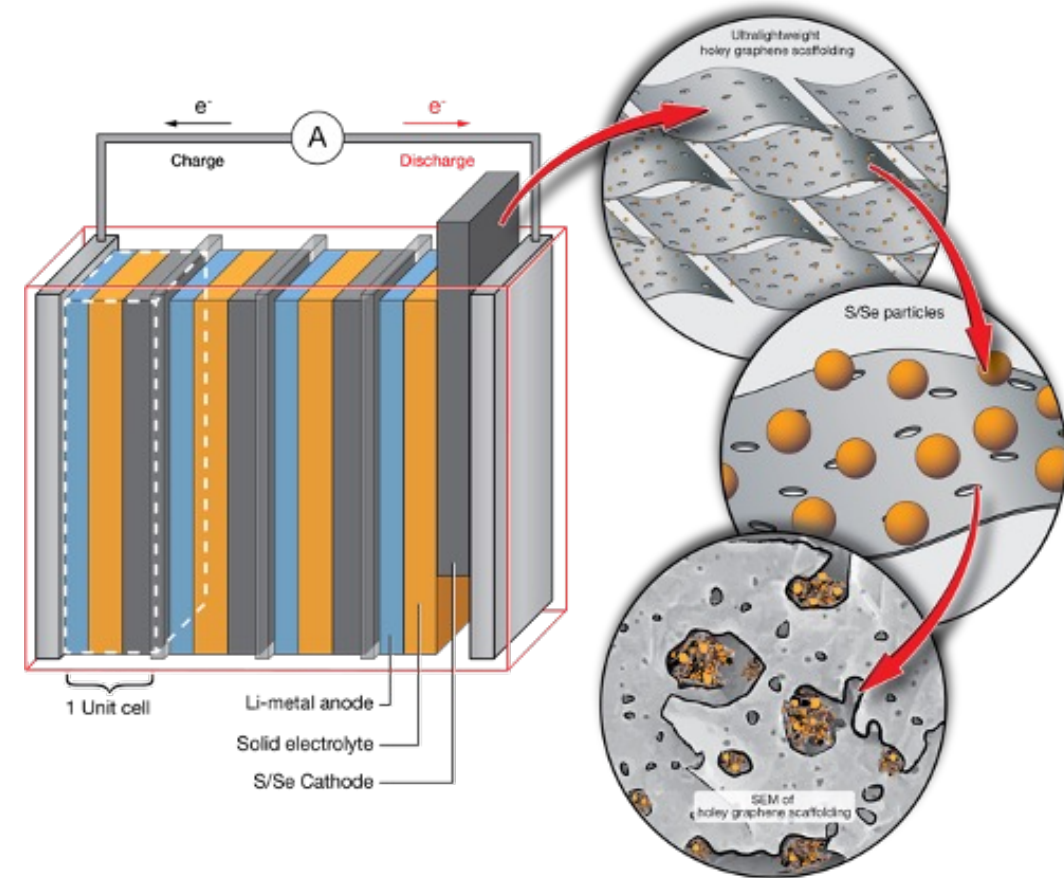


SABERS: Solid-state Architecture Batteries for Enhanced Rechargeability and Safety

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

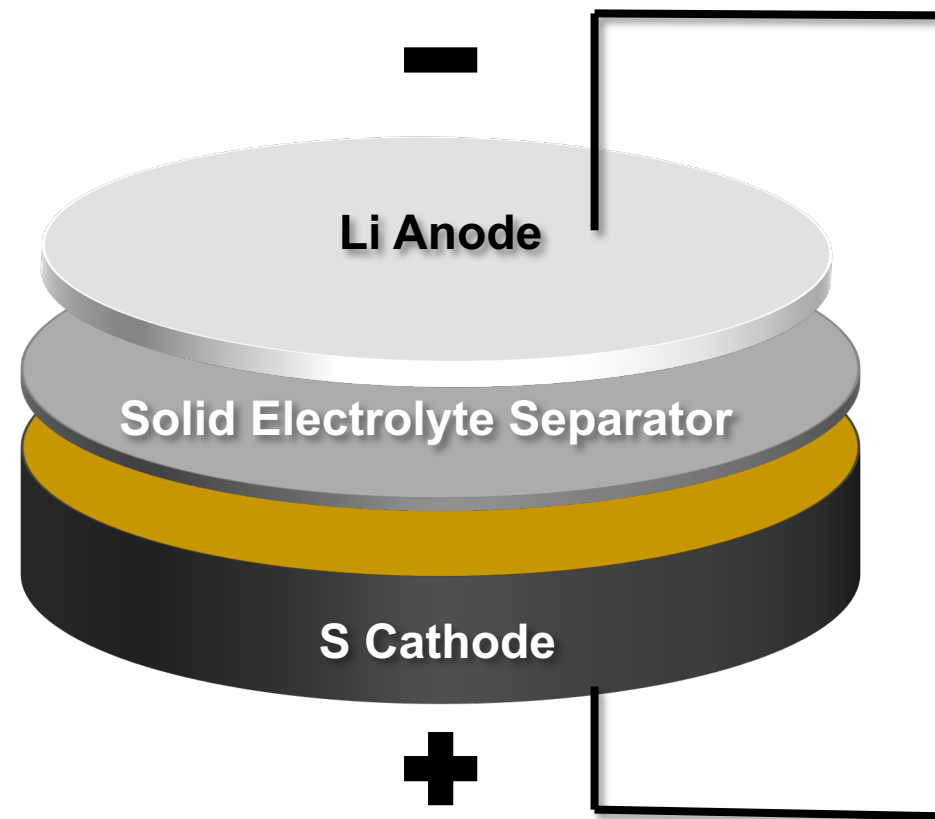


A Solid-State Li-S Battery Cell



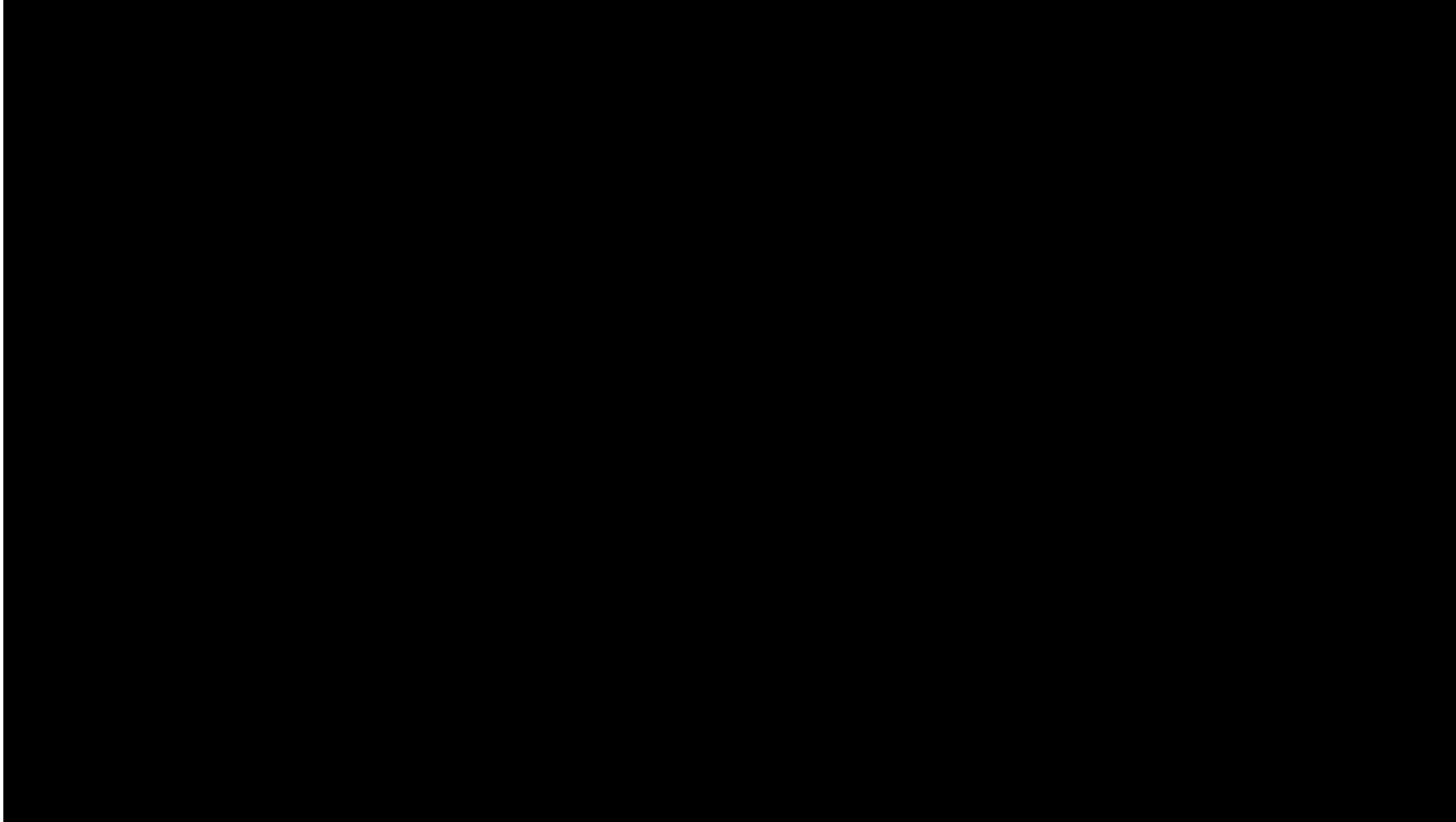
In solid-state Li-S batteries:

- ❑ **Anode:** Li metal
- ❑ **Solid electrolyte (SE) 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.**

Holey Graphene (hG)

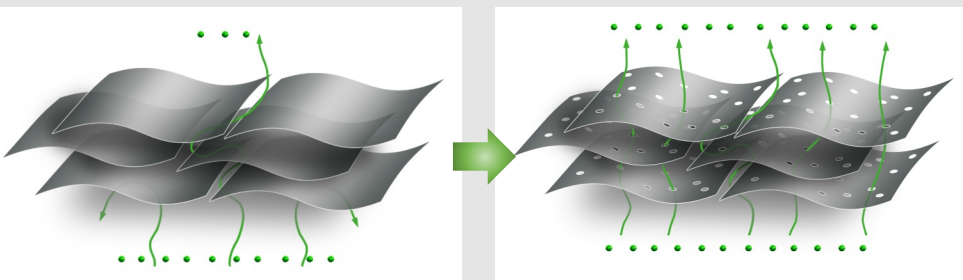


Full version: <https://www.youtube.com/watch?v=OGyn2PjBTN0>

hG for Advanced Electrodes



Supercapacitors



Intact Graphene

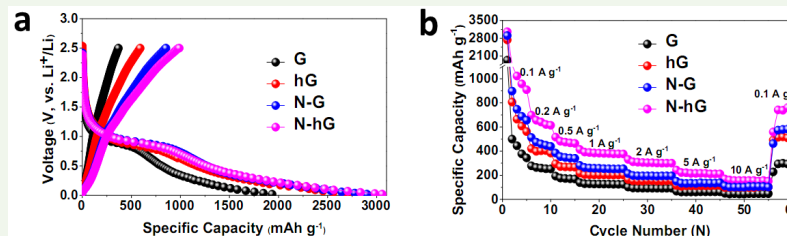
Holey Graphene

ACS Nano **2014**, 8, 8255.

As-Prepared hG

Liangbing Hu
(U Maryland)

Li-Ion Battery (Anode)

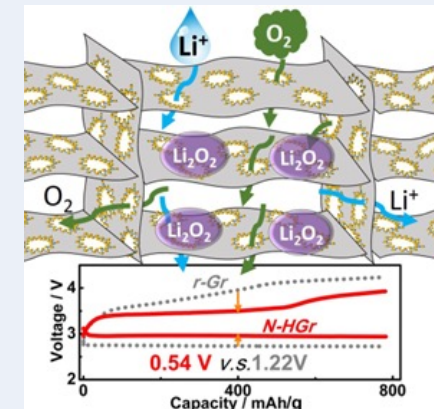


Small **2015**, 11, 6179.

N-doped hG

Liming Dai
(CWRU)

Li-Oxygen (O_2) Batteries

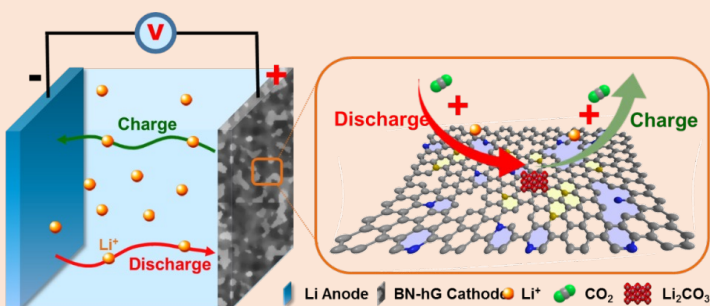


ACS Energy Lett **2016**, 1, 260.

N-doped hG

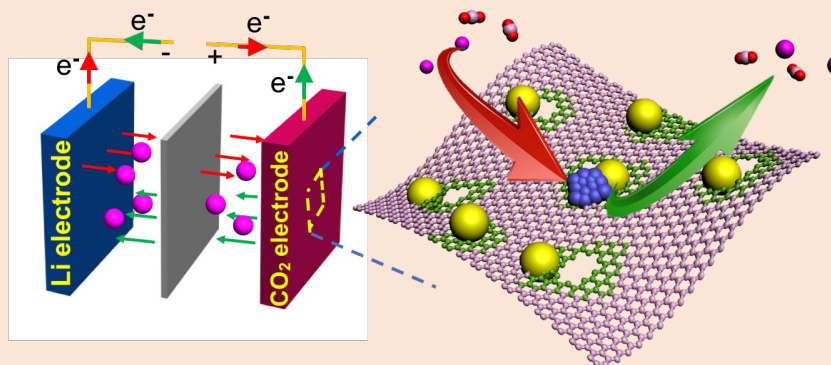
Liming Dai
(CWRU)

Li-Carbon Dioxide (CO_2) Batteries



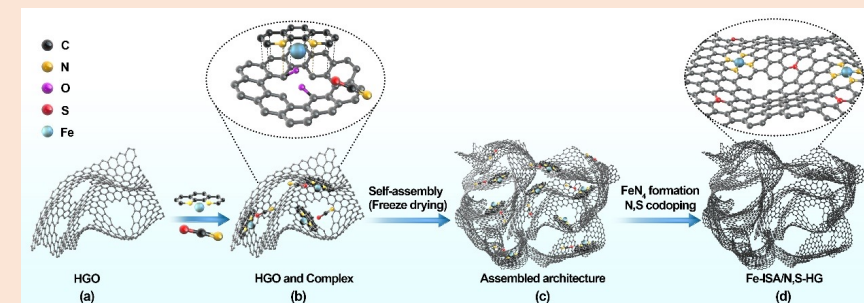
Angew. Chem. Int. Ed. **2017**, 56, 6970.

B,N-codoped hG



Adv. Func. Mater. **2018**, 28, 1804630

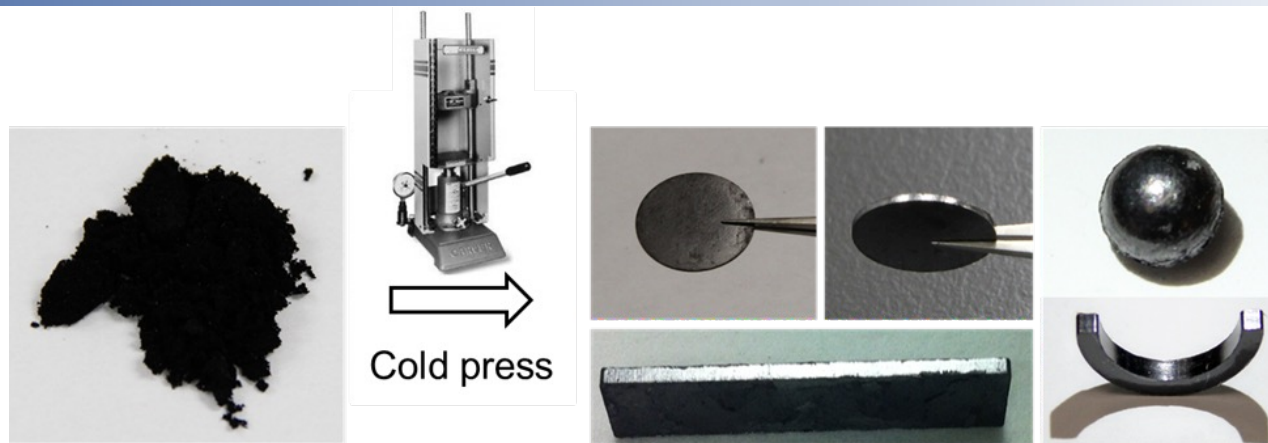
Carbon Dot-Supported on hG



Adv. Mater. **2020**, 32, 1907436.

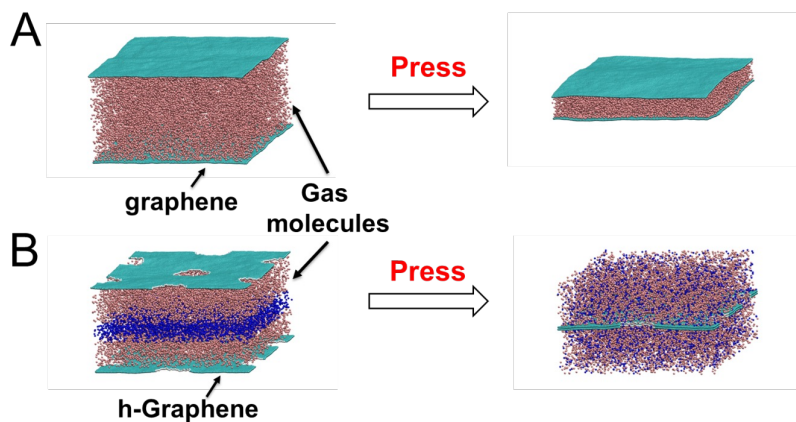
Single Fe Atom Catalysts Supported on hG

hG is Dry Compressible

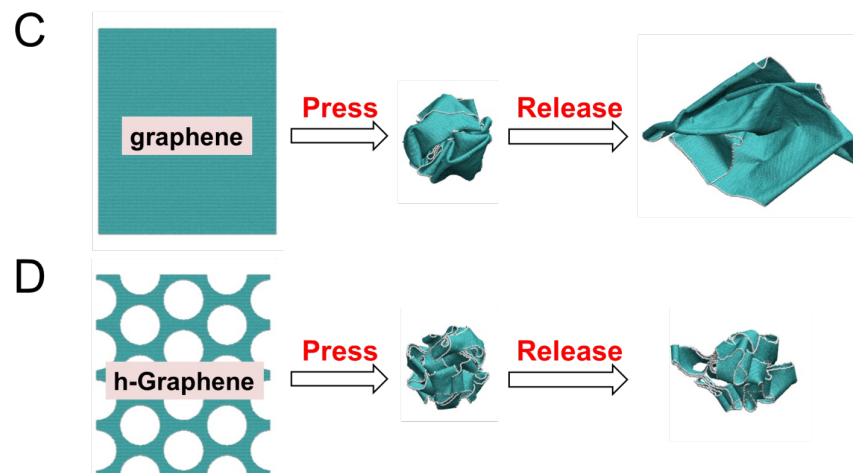


Holey Graphene Powder

Holey Graphene Monolithic Architectures



Facile air escape upon compression



Minimal volume rebound upon release

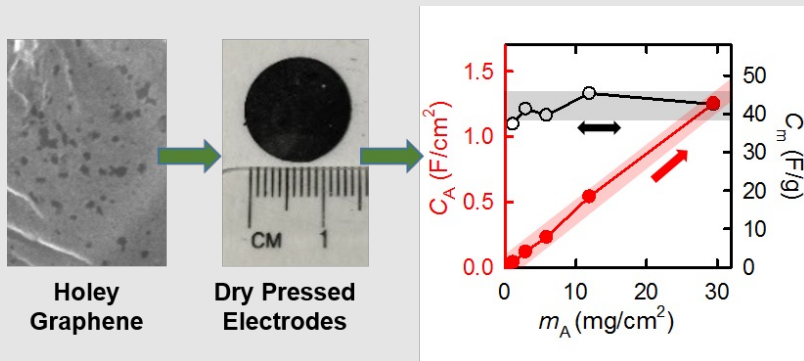
ACS Nano **2017**, 11, 3189. (In collaboration with Prof. Liangbing Hu)

A New Narrative in Electrode Preparation



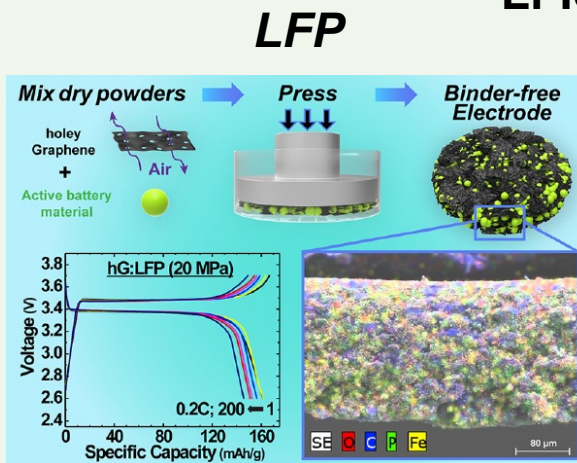
Dry-pressed hG is applicable in various energy storage platforms for ultrahigh areal capacities.

Supercapacitors



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

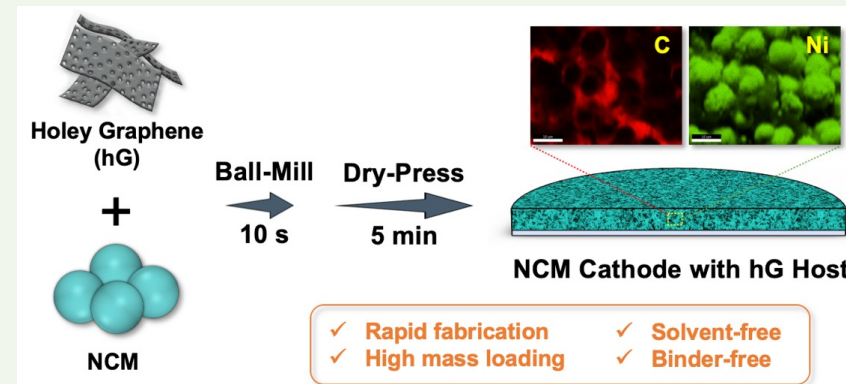
Li-Ion Batteries



LFP: Lithium iron phosphate

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

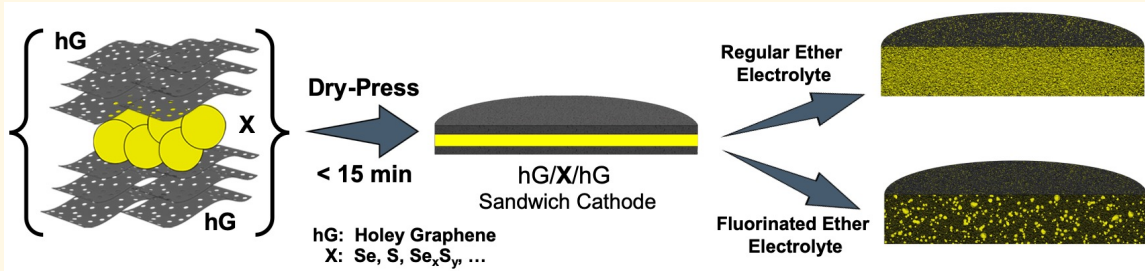
NCM



NCM: Lithium nickel cobalt manganese oxide

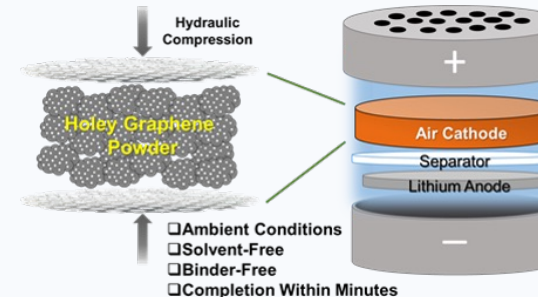
Electrochim. Acta **2020**, 362, 137129

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

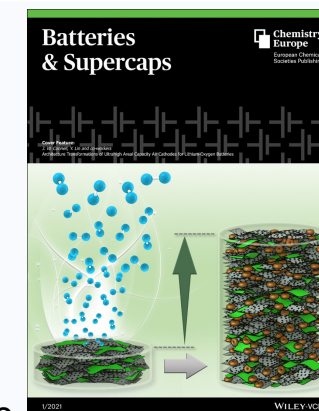


Batteries & Supercaps **2019**, 2, 774; ACS Appl. Energy Mater. **2020**, 3, 6374; Front. Energy Res. **2021**, 703676.

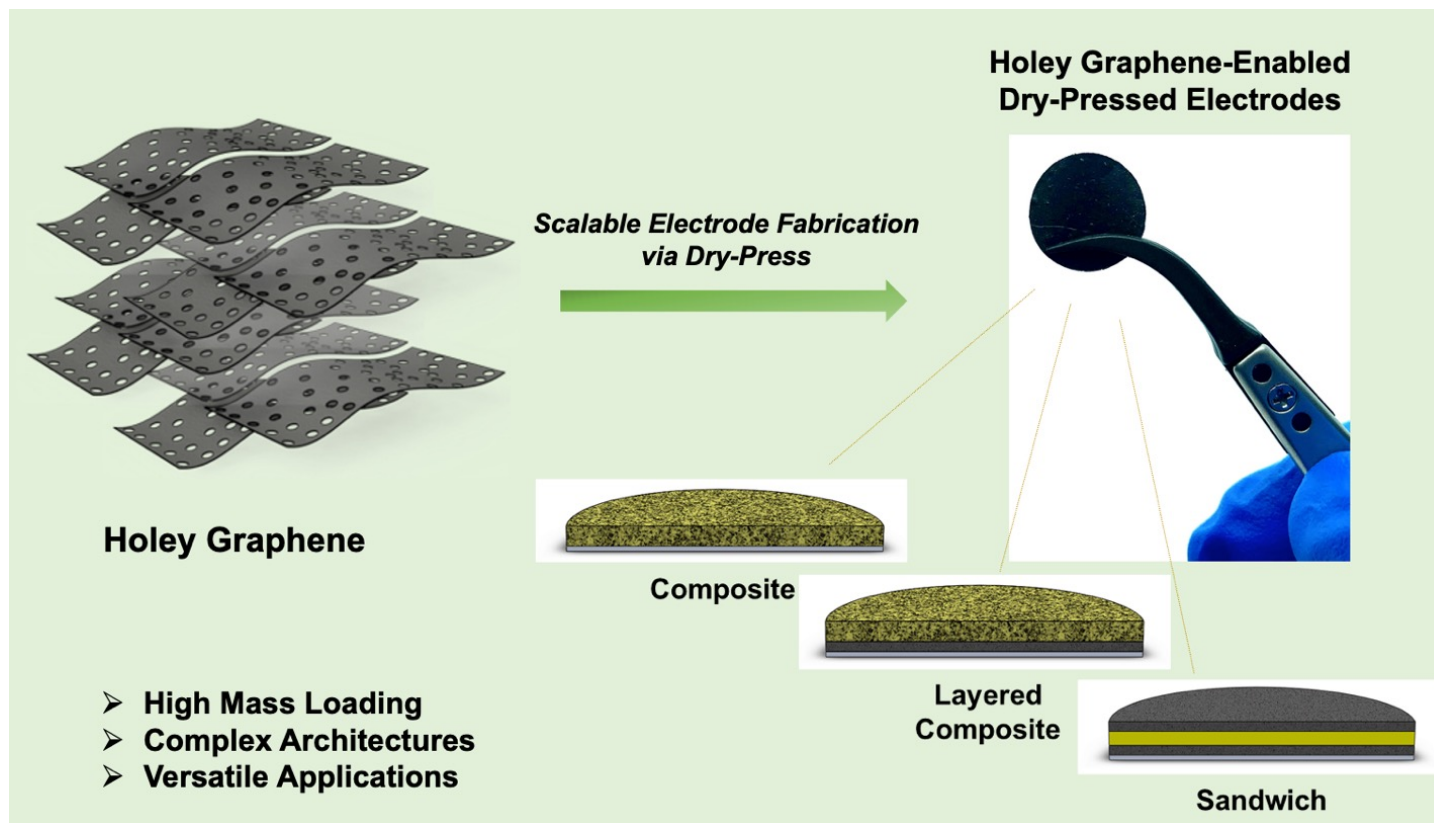
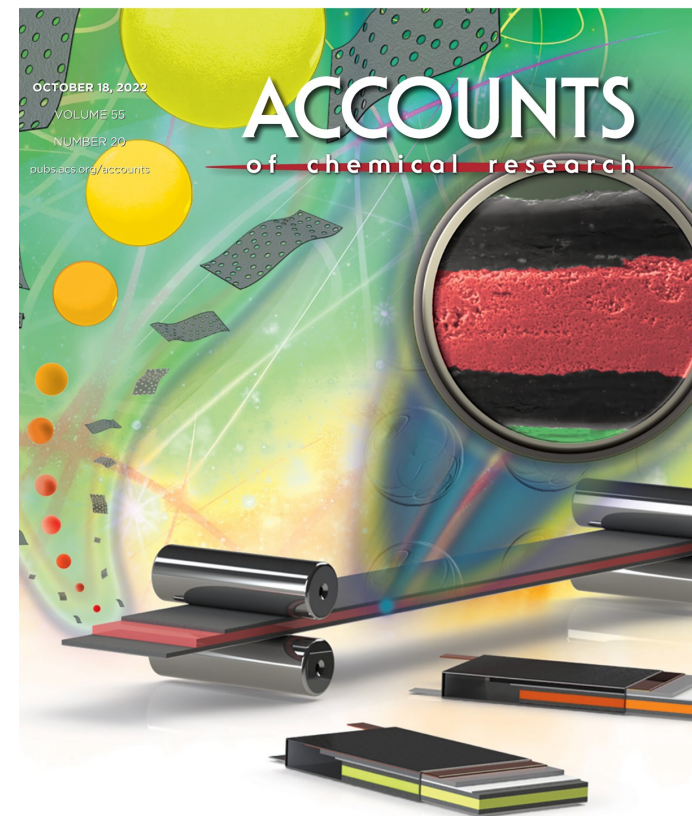
Li-O₂ Batteries



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



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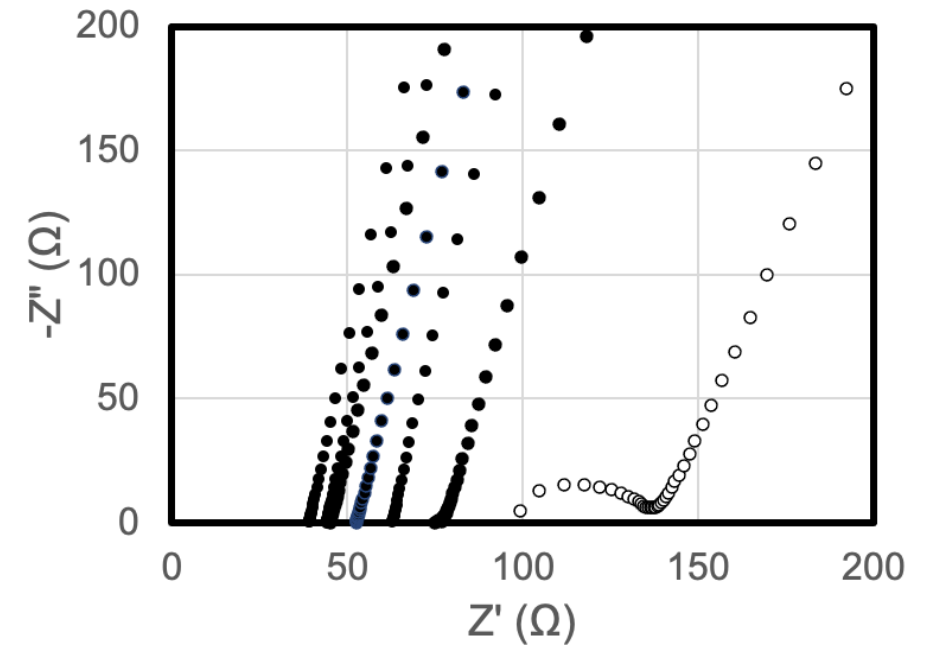
Acc. Chem. Res. **2022**, 55, 3020-3031.

- ❑ 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.

Commercially Available Sulfide Electrolytes



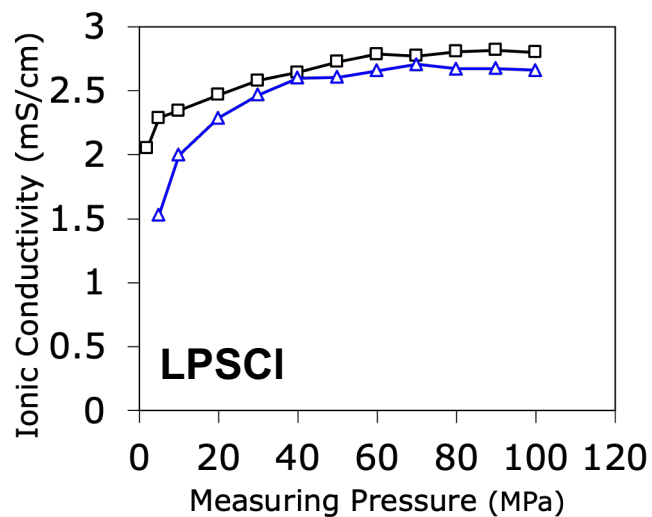
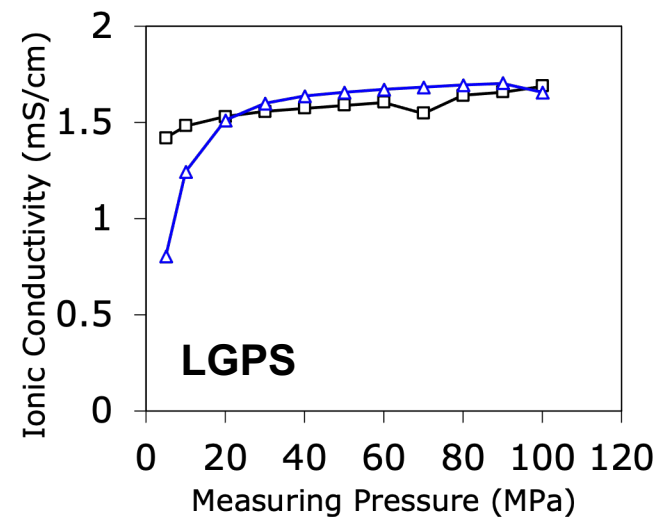
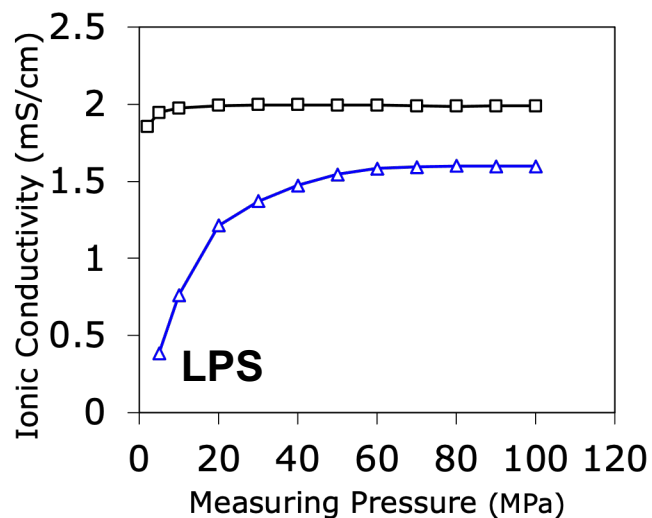
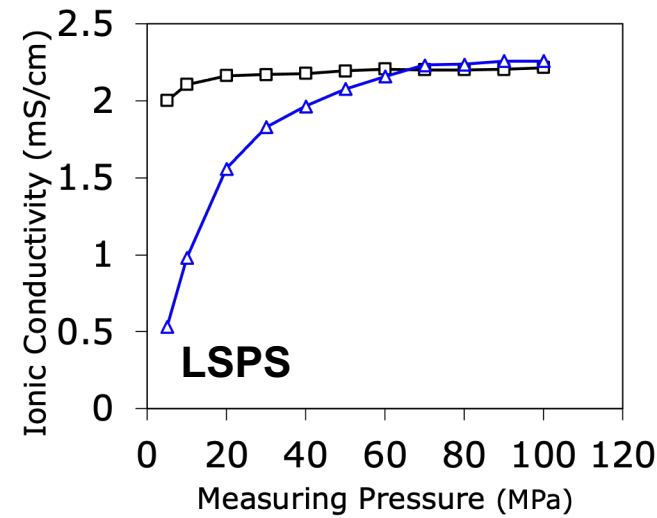
Sulfide Electrolytes	Vendor	Density (g/cm ³)	Ionic (mS/cm)	Electrical (μS/cm)
Li ₁₀ SnP ₂ S ₁₂ (LSPS)	NEI	1.47	1.75	0.159
Li ₆ PS ₅ Cl _{0.5} Br _{0.5}	MSE	1.37	1.65	0.142
Li ₆ PS ₅ Cl _{0.9} I _{0.1} (LPSCII)	NEI	1.48	1.50	0.106
Li ₆ PS ₅ Cl (LPSCI)	NEI	1.32	1.44	0.132
Li ₇ P ₃ S ₁₁	MSE	1.32	1.19	0.095
Li ₁₀ GeP ₂ S ₁₂ -Fine	MSE	1.55	0.86	0.060
Li ₁₀ GeP ₂ S ₁₂ -Coarse	MSE	1.44	0.51	0.006



- ❑ Sulfide electrolytes are typically of high ionic conductivity (> 1 mS/cm)
- ❑ Li₆PS₅Cl (LPSCI; LPSC) is the most studied sulfide electrolyte and commercially available in large quantities (~\$10/g)

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

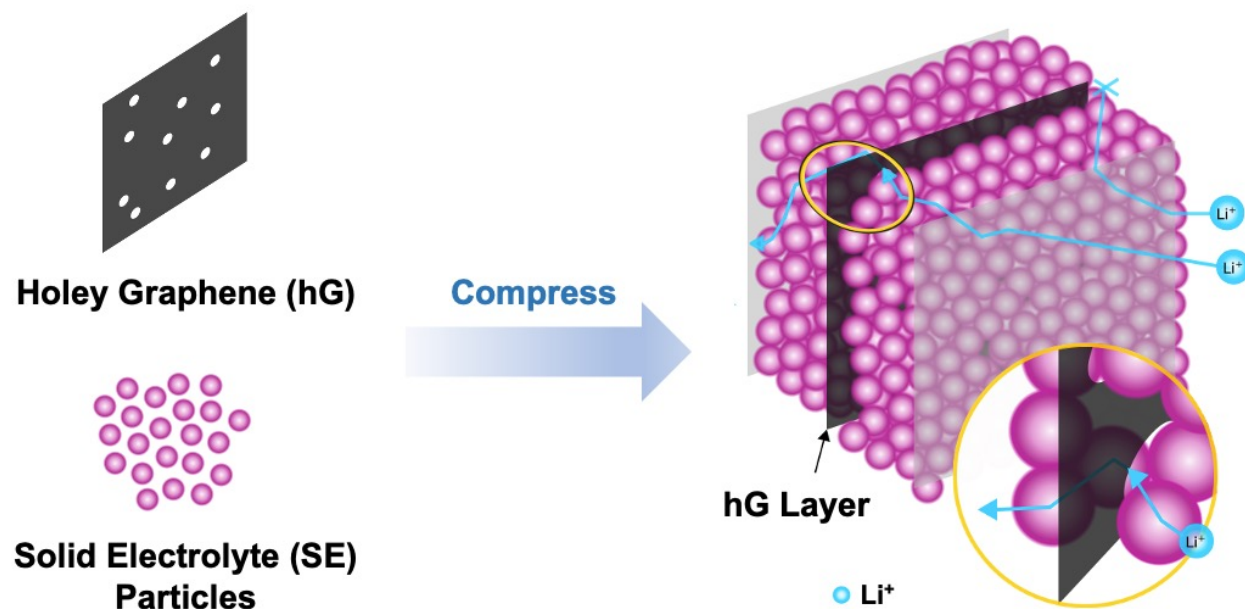
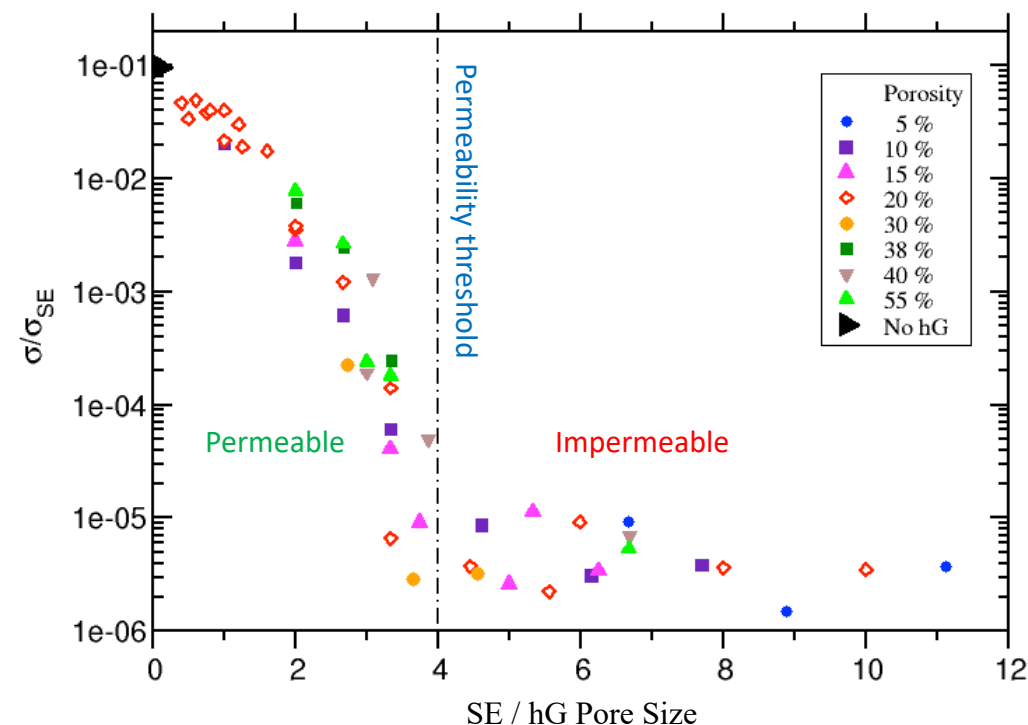
hG Current Collectors



- 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.

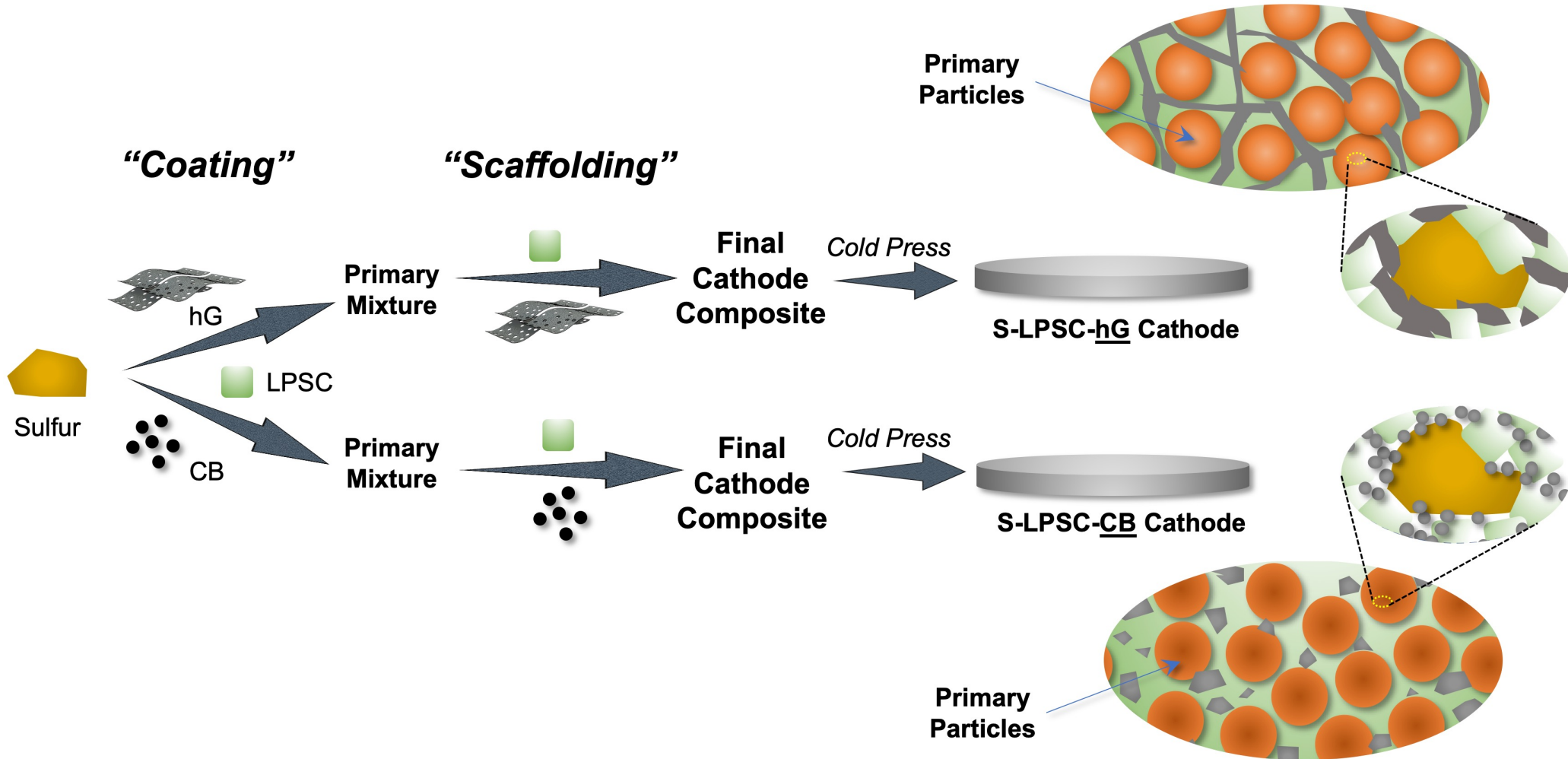
Li Ion Conductivity Through hG Sheets



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

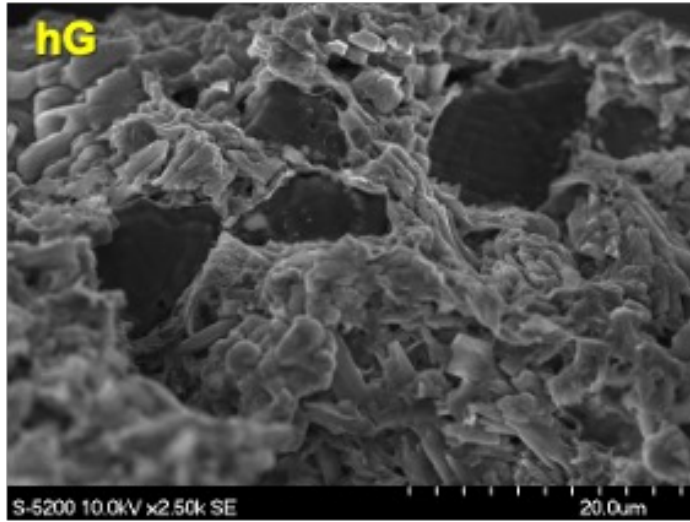
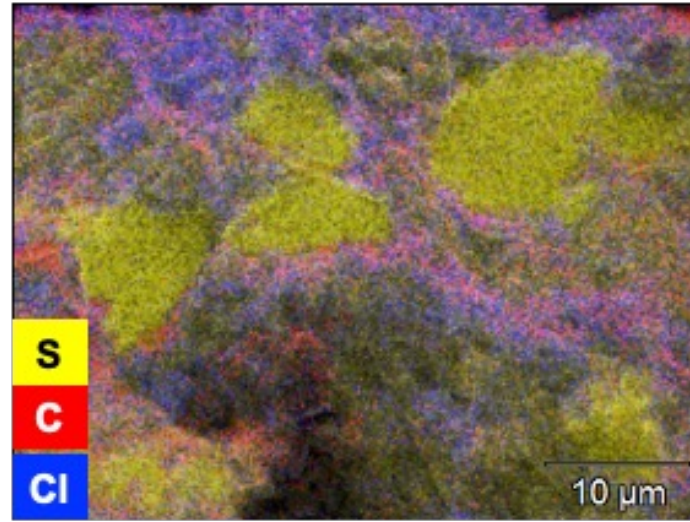
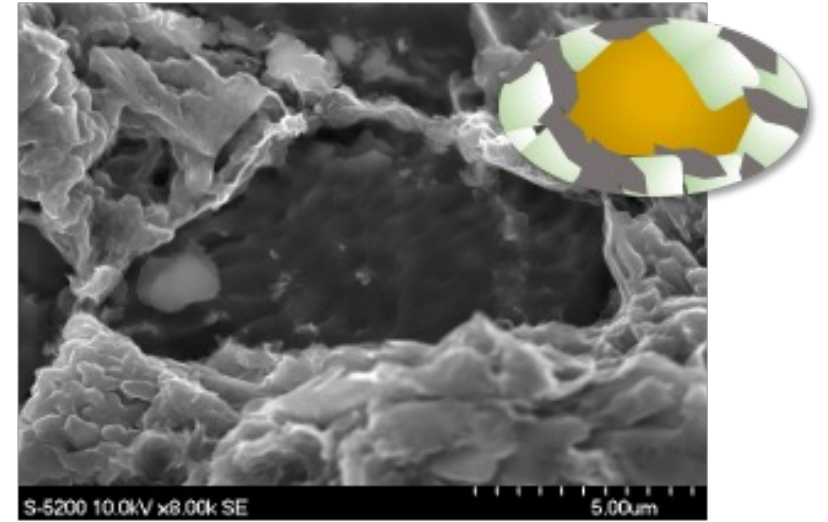
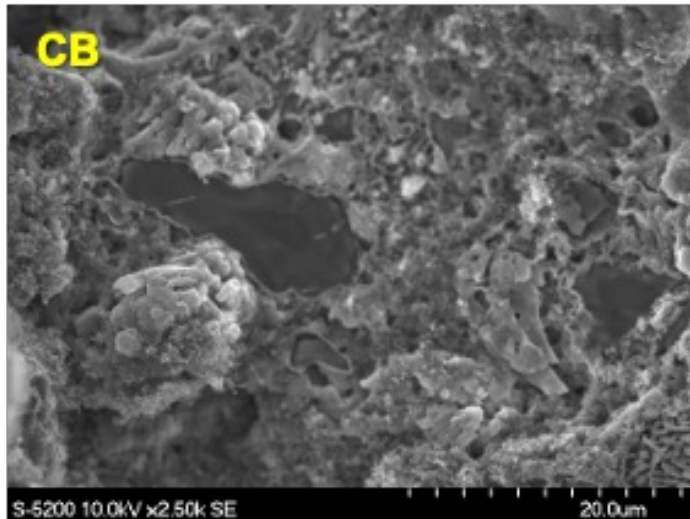
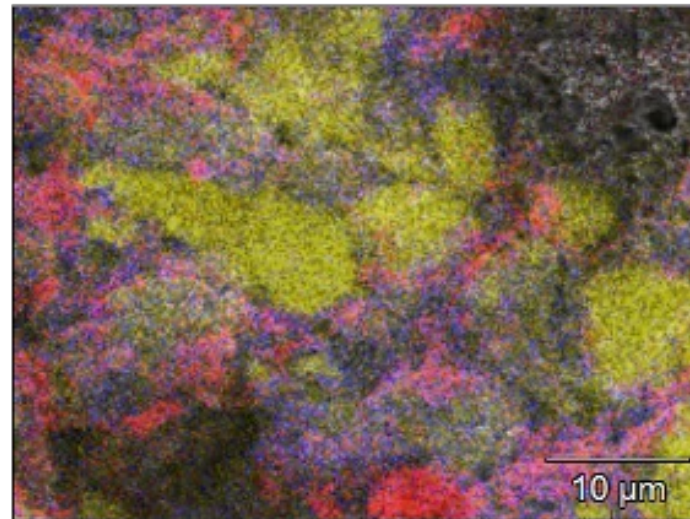
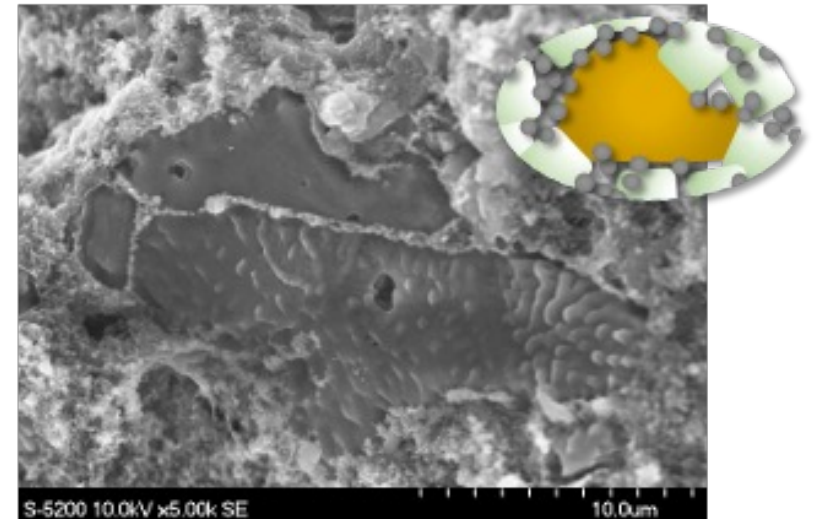
- ❑ Li ion can conduct through the thickness of hG – as long as the holes are at least 25% in size of the solid-state electrolyte particles.

All-Solid-State S Composite Cathodes

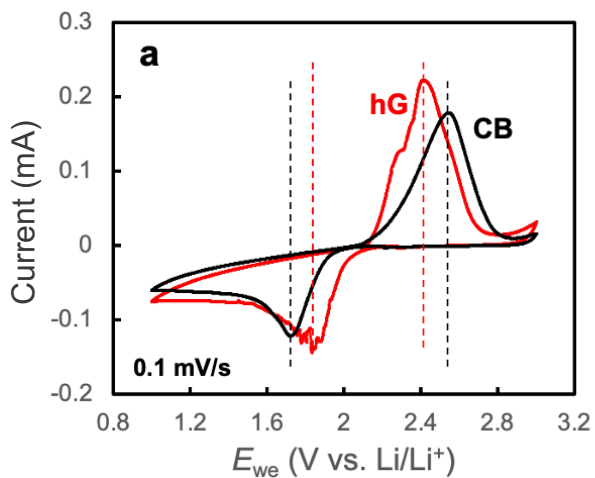
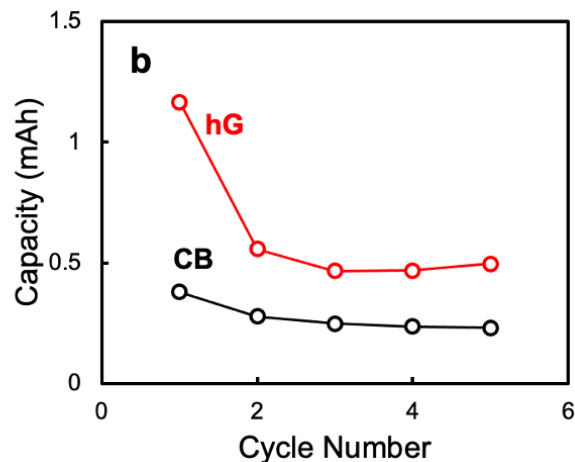
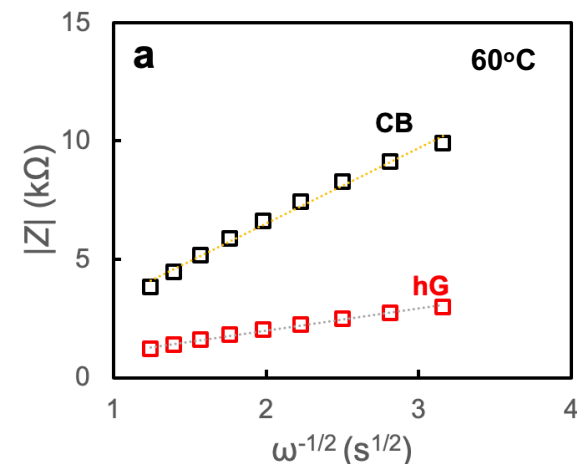
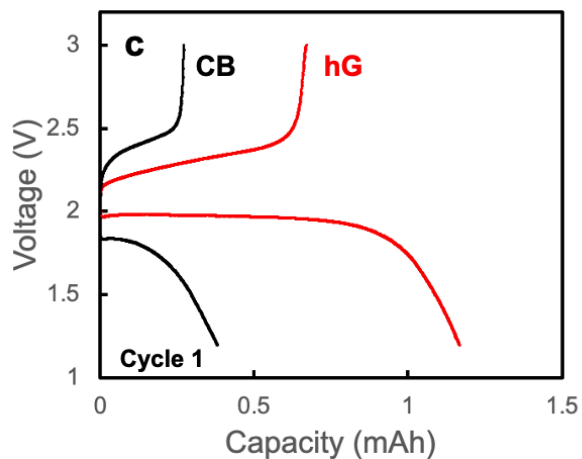
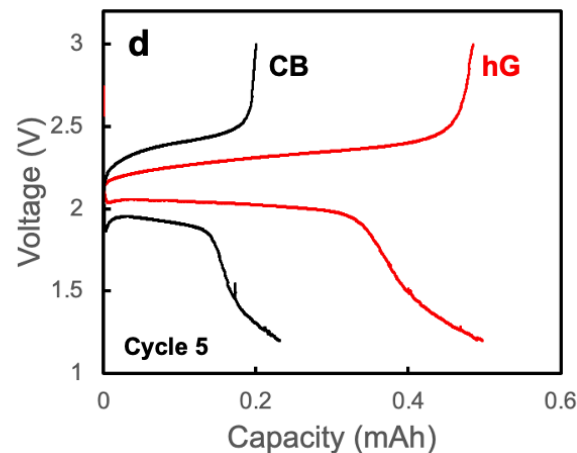
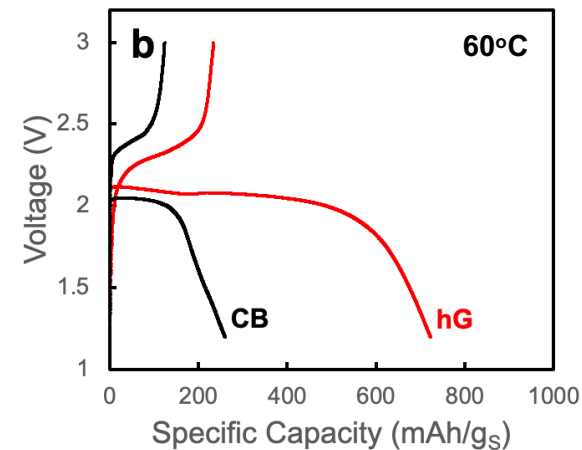


- CB: carbon black
- SE: LPSC ($\text{Li}_6\text{PS}_5\text{Cl}$)

S Cathode Microstructures



hG vs. CB

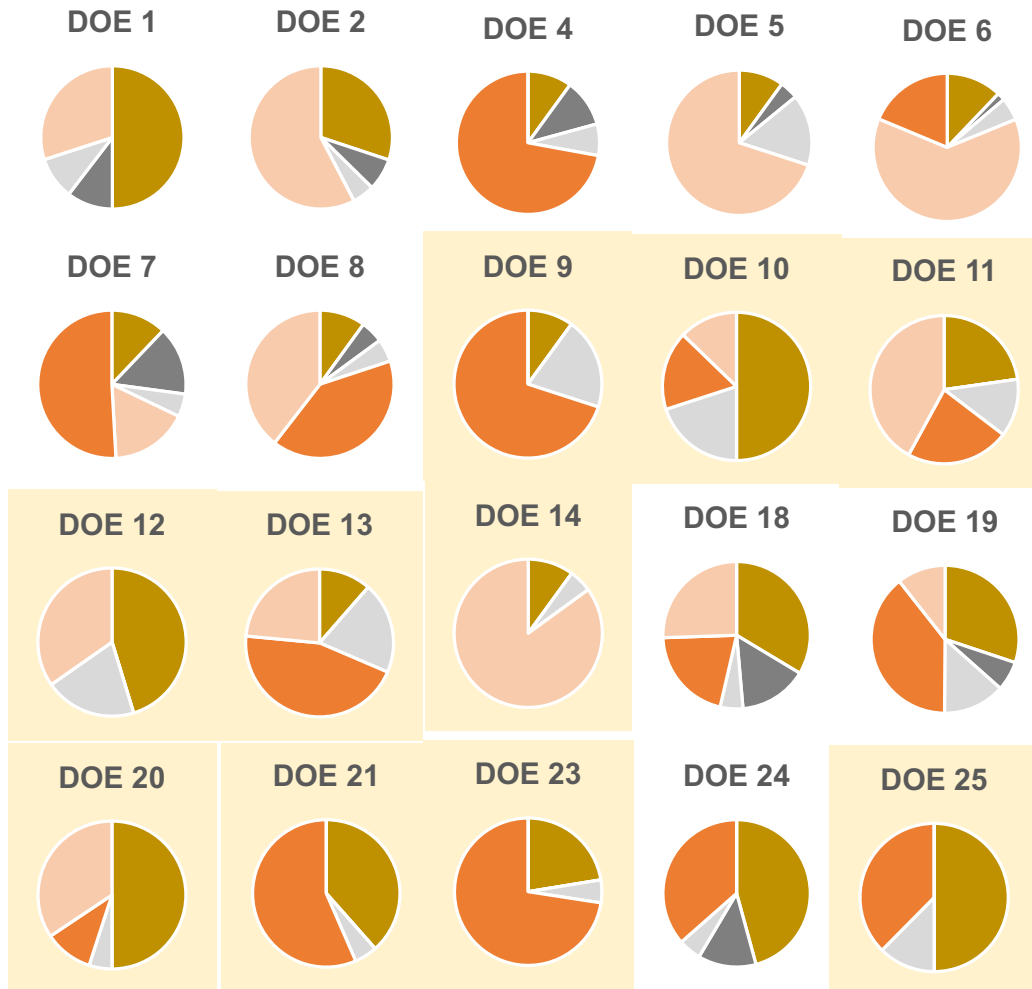
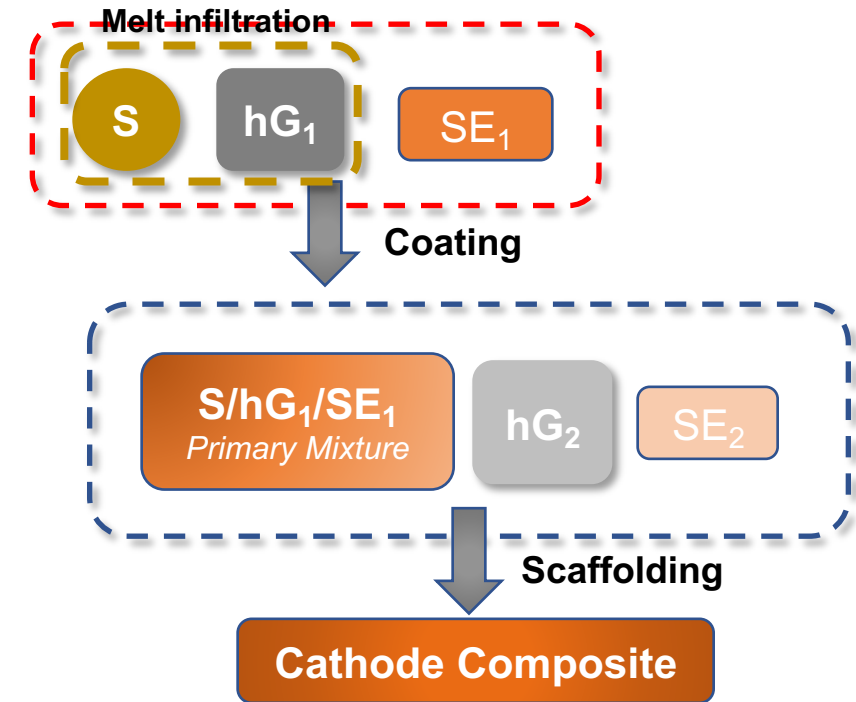


Room Temperature
12 mg/cm²

60°C
5 mg/cm²

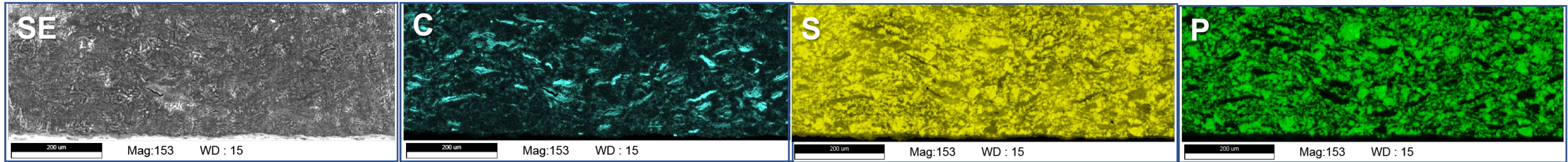
- Li metal anode
- Coin cells (< 2 MPa stack pressure)

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



Scale bars = 200 μm

☐ High Discharge Capacity

- Low S content
- High hG:S ratio in melt infiltration

☐ Low Impedance

- High scaffolding-step hG content
- High coating-step SE content

☐ Low Overpotential

- Low S content
- Medium hG:S ratio in melt infiltration

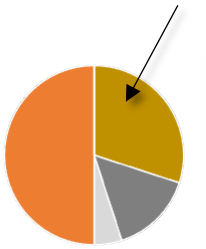
☐ High Li^+ Diffusion Coefficient

- High hG:S ratio during melt infiltration
- High coating-step SE content

Cell Integration to Improve Specific Energy



Maximize S Content and Utilization



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

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

Increase Cathode Loading

Decrease Solid Electrolyte Loading

Cathode (C)

SE

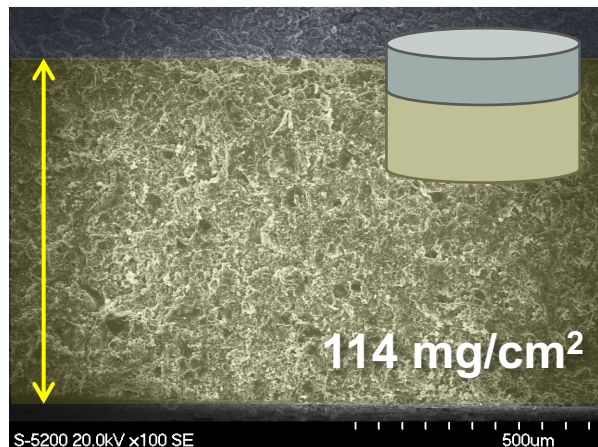
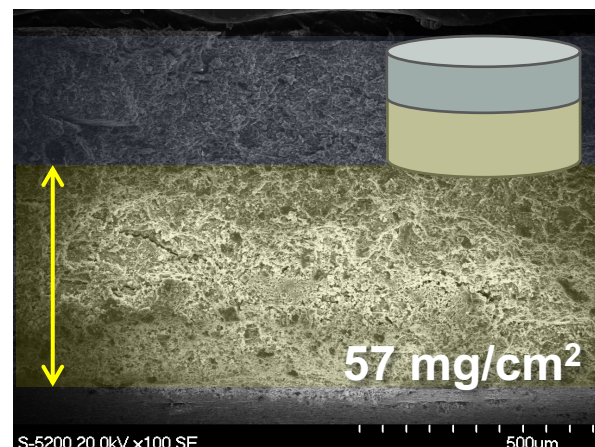
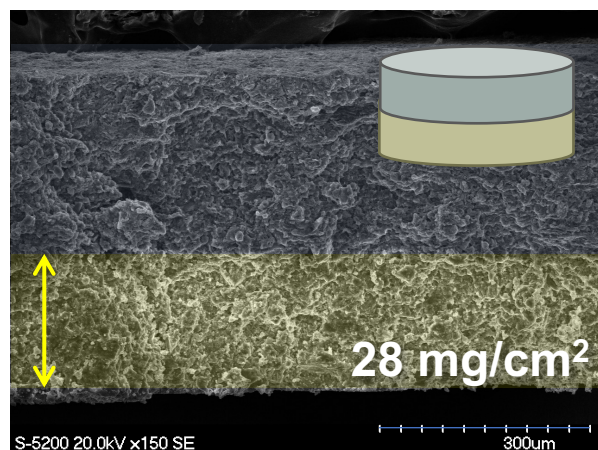
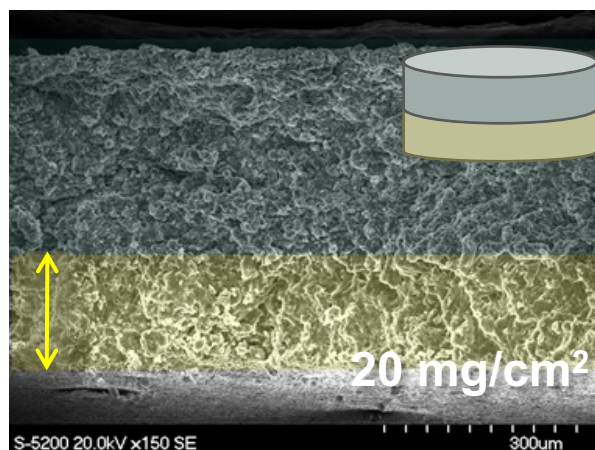
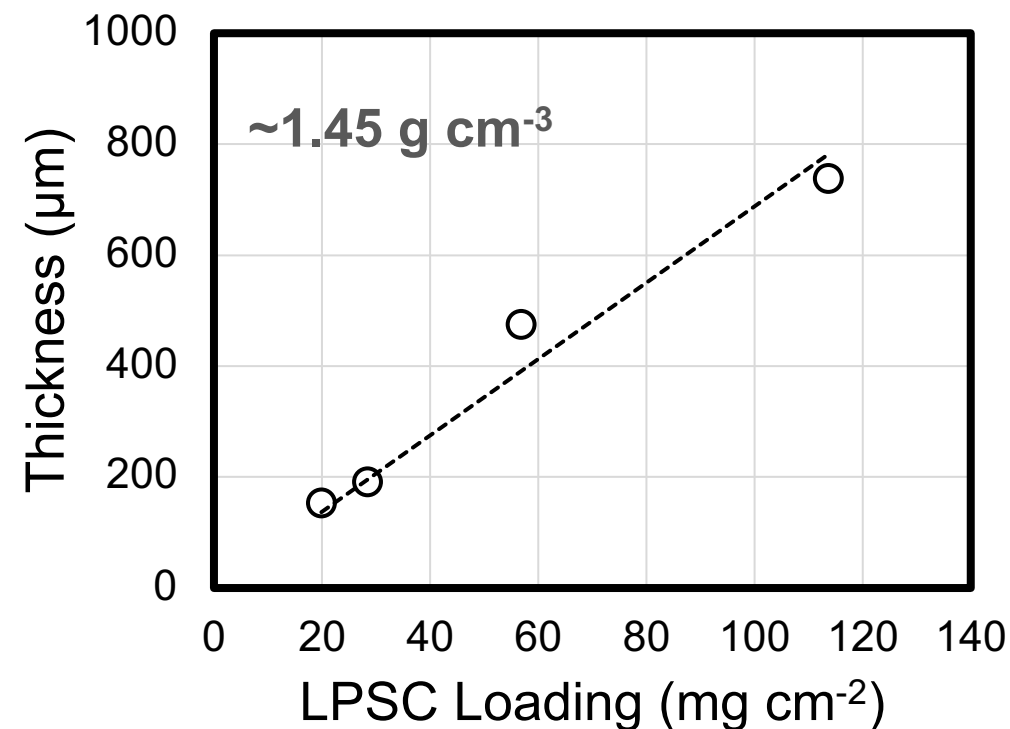
Li Anode

Reduce Li Anode Excess

Specific Energy



Reduce SE Thickness with Dry Pressing

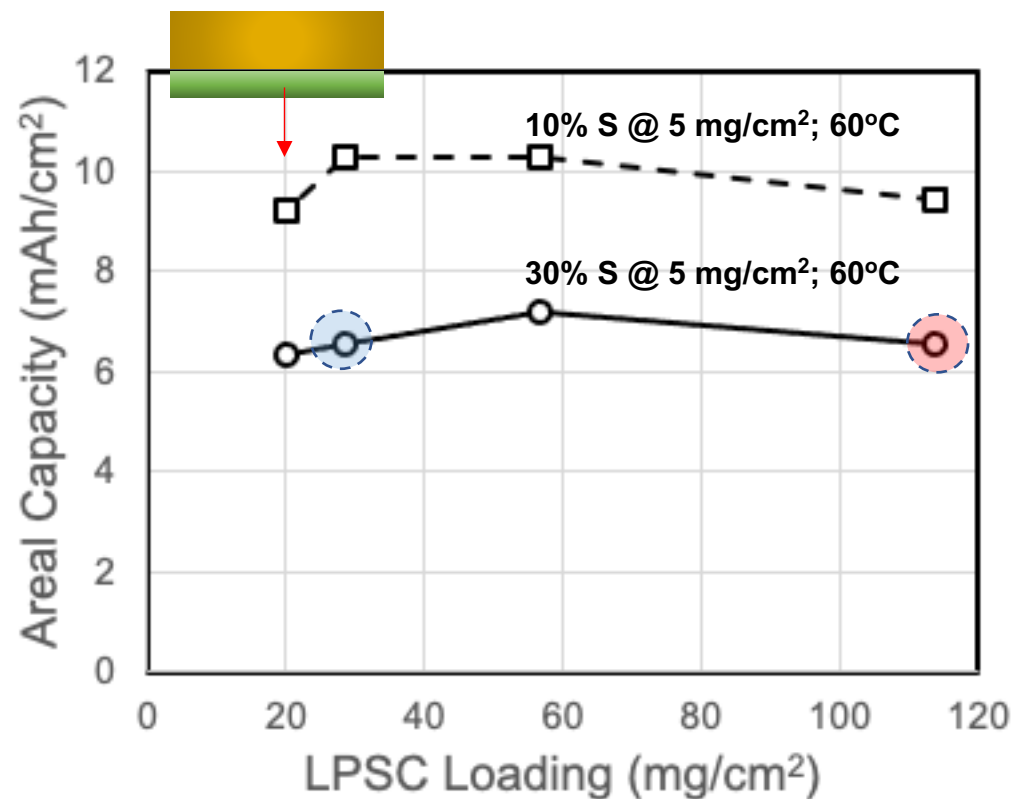
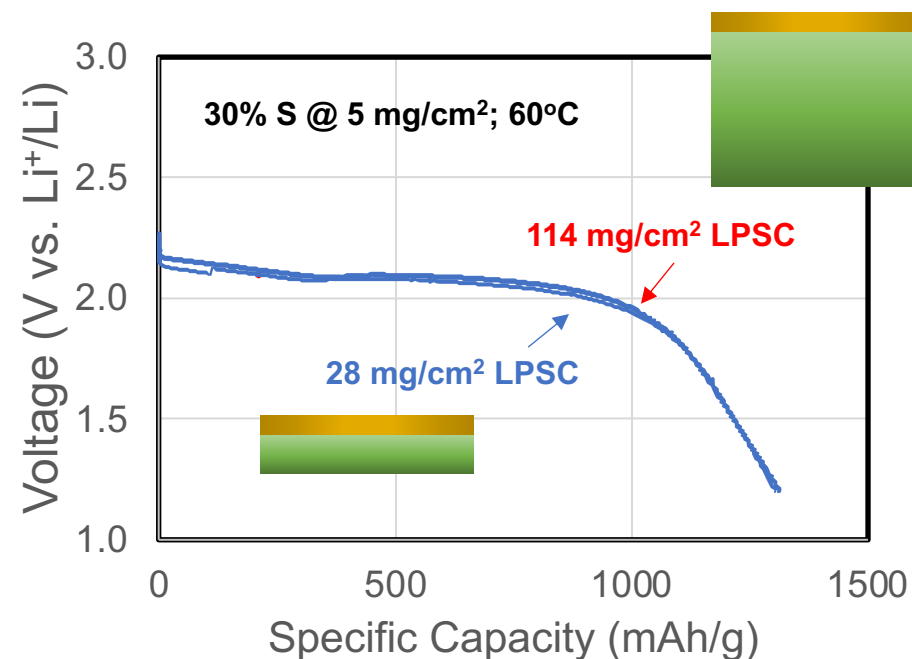


- ☐ Proof-of-concept experiments
- ☐ Doable yet extremely challenging

Improving Overall Specific Energy

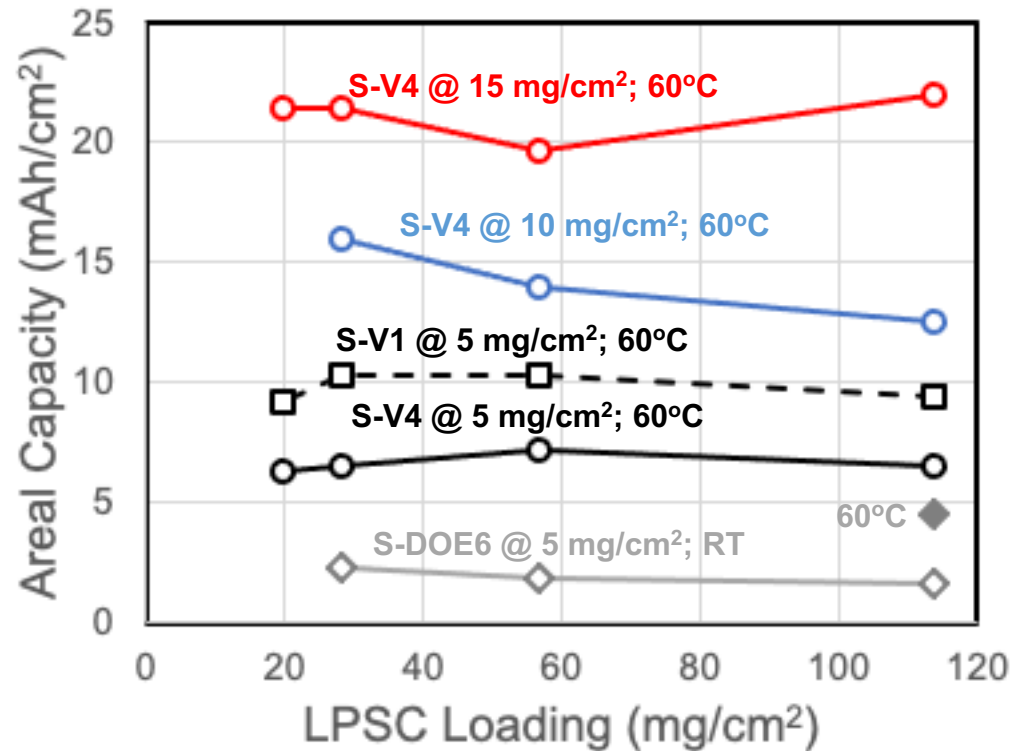
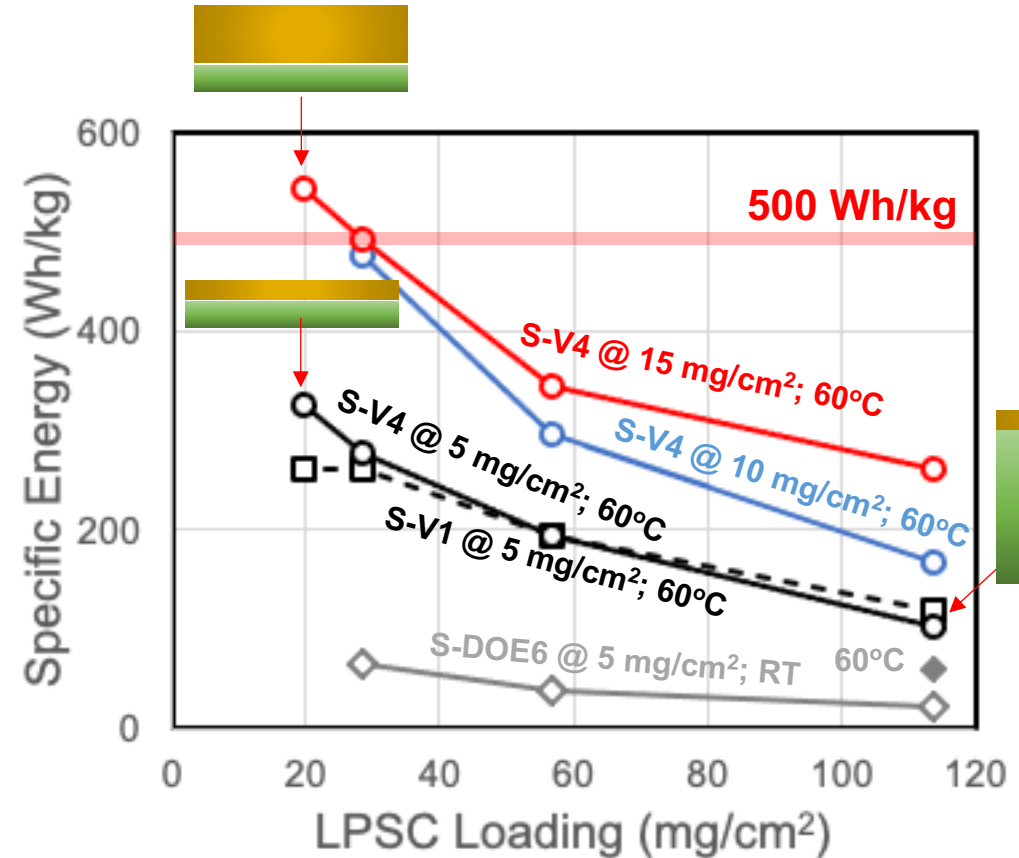


❑ Reduction in SE thickness + Increasing cathode S content with retained S utilization = **Improved Specific Energy**



- ❑ All dry-pressed cathodes
- ❑ No additional stack pressure
- ❑ 0.032 mA/cm²

Toward 500 Wh/kg

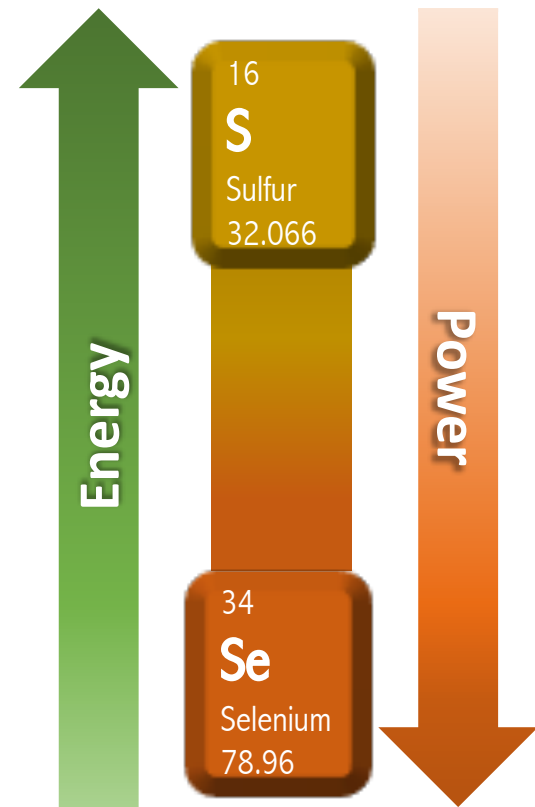
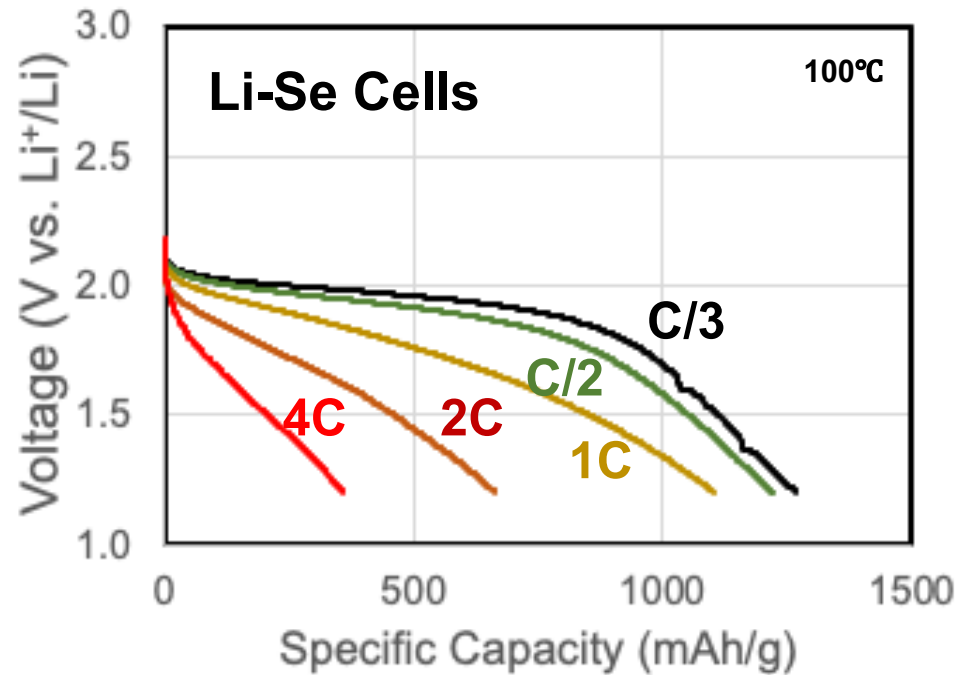
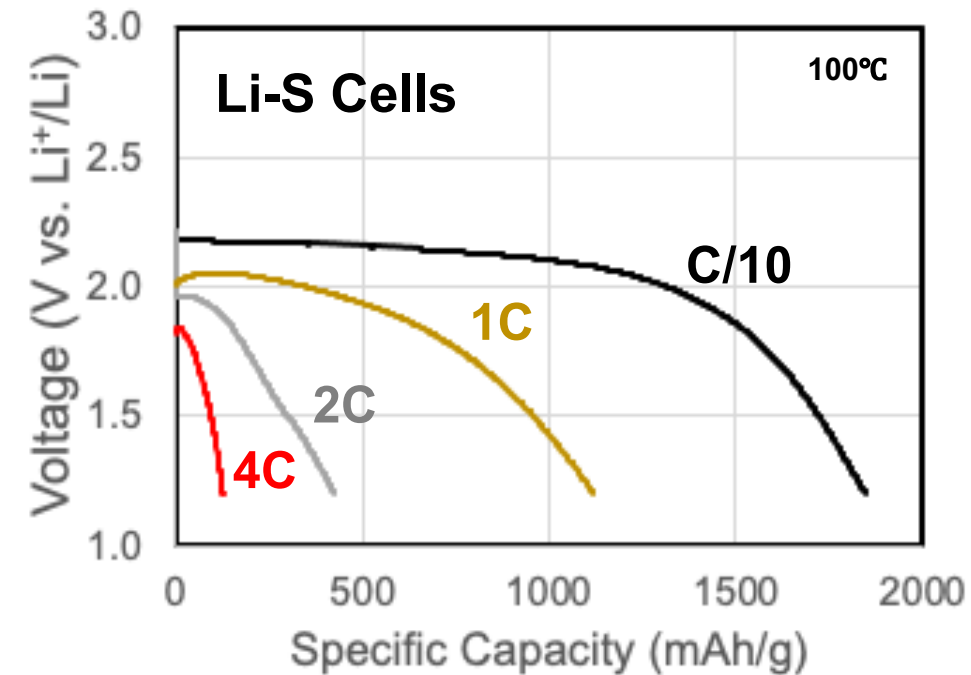


- "DOE6": 12% S
- "V1": 10% S
- "V4": 30% S
- All dry-pressed

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

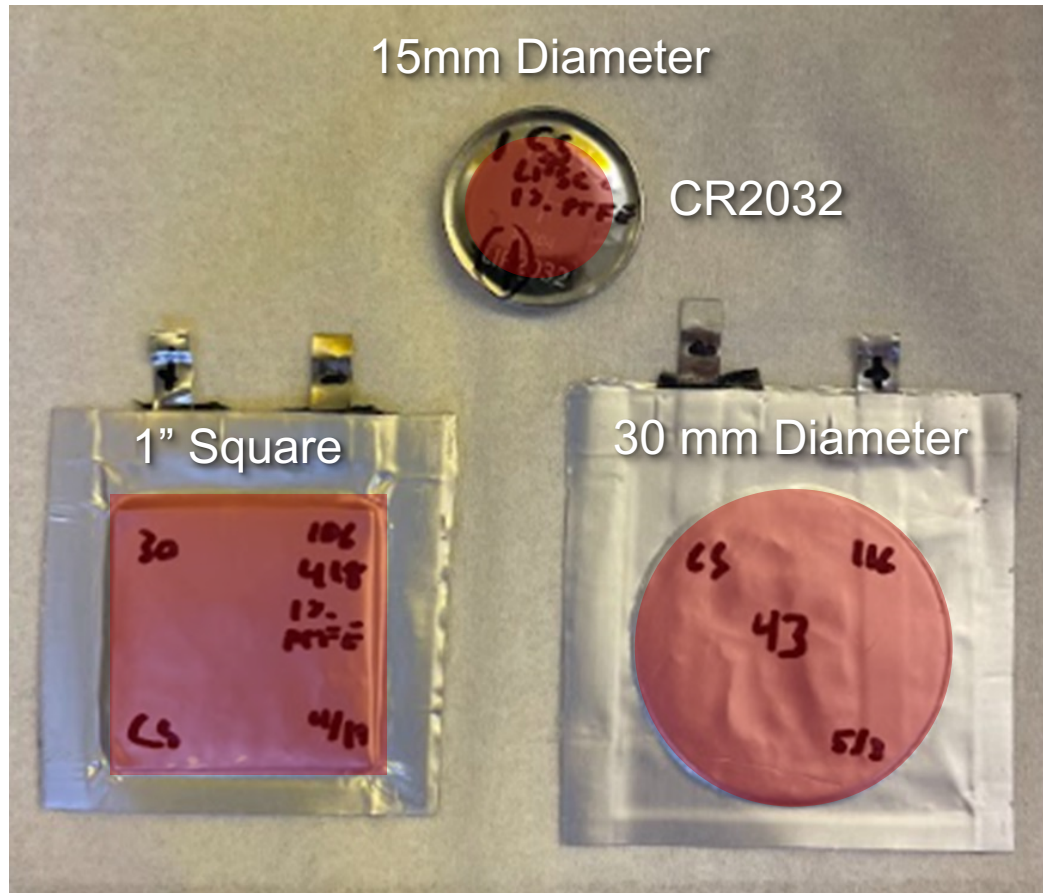
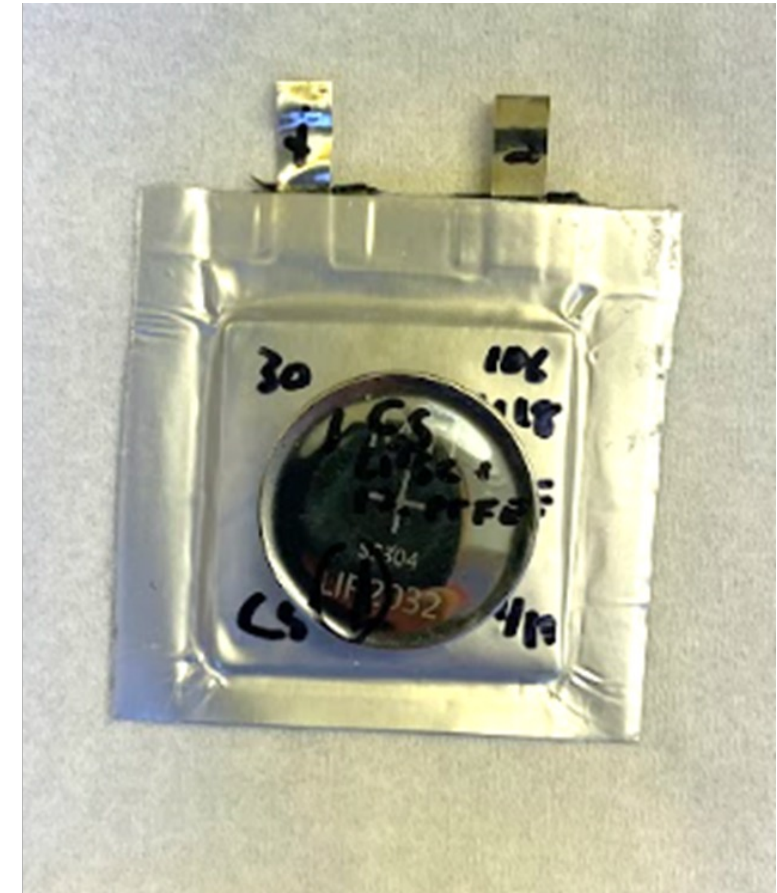
Increasing cathode S content and loading and reducing solid electrolyte thickness pushed specific energy pass 500 Wh/kg.

High Temperature, High Power Cells



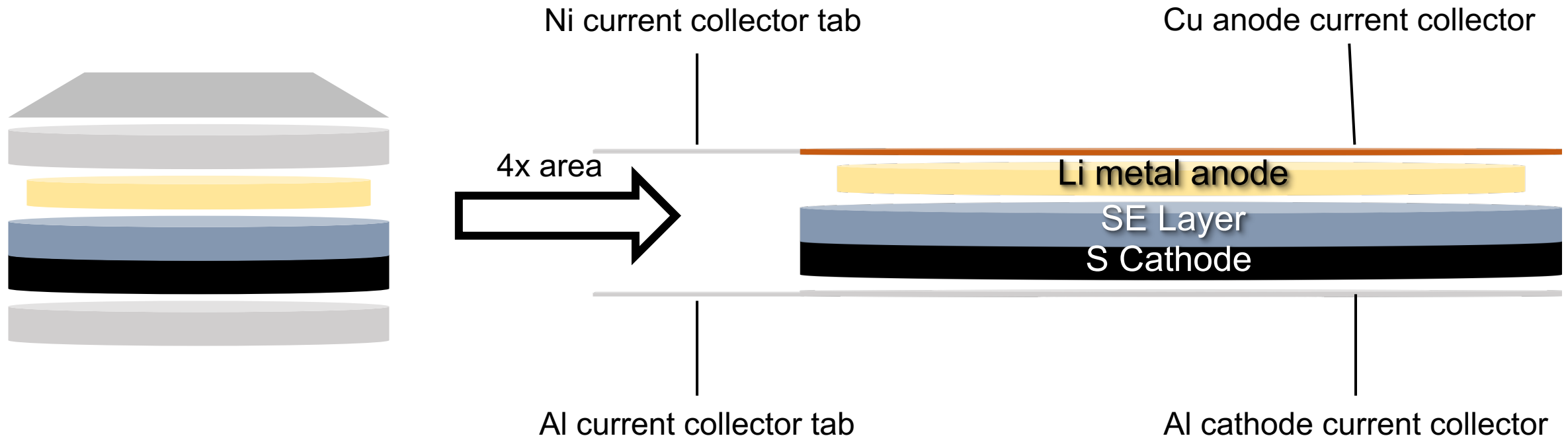
SABERS cells can operate at and above 100°C with high power performance.

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

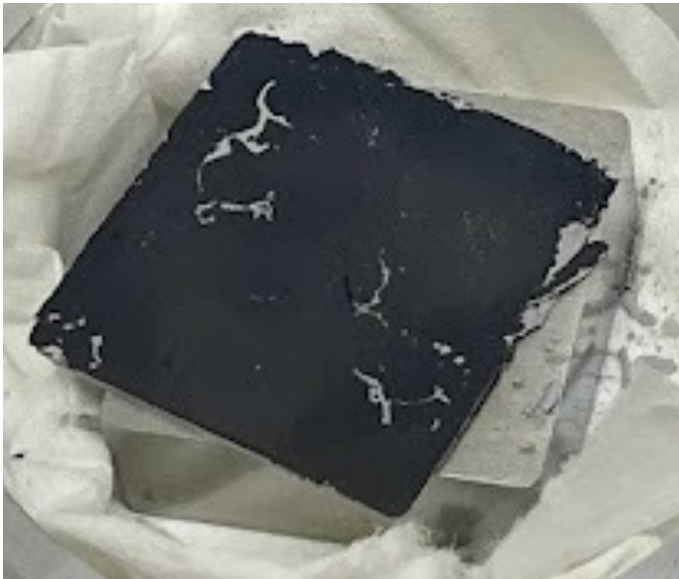
From Coin Cells to Pouch Cells



Process Improvements



Generation 1



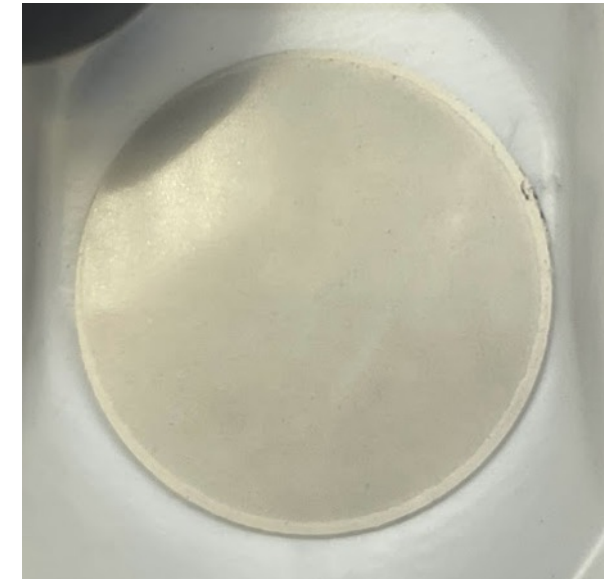
Direct scale-up from coin cell studies

Generation 2

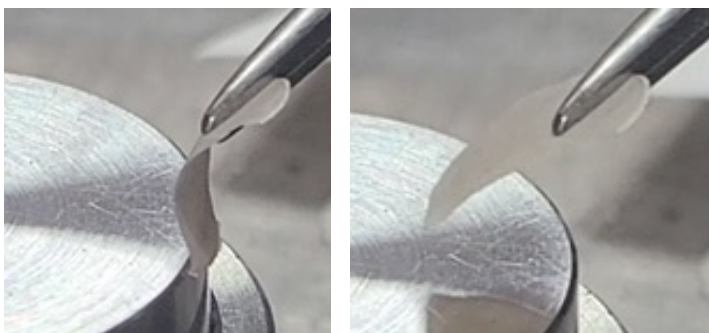


Improved dry-processing via proper use of polymer binders

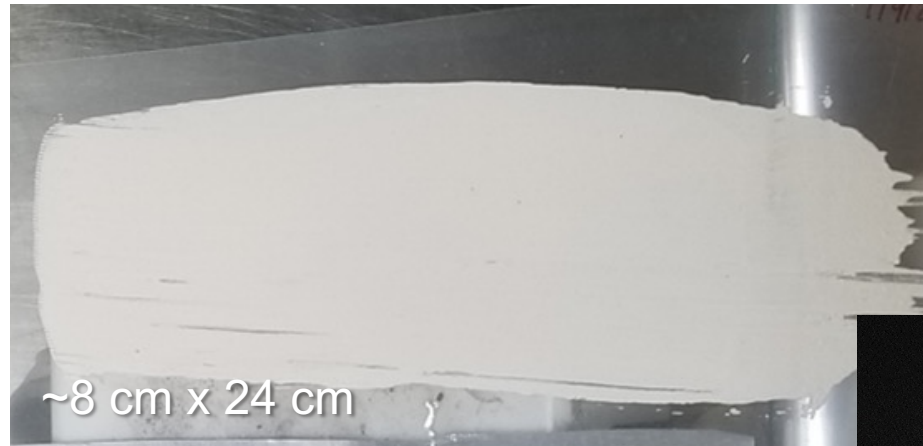
Generation 3



Development of SE Films

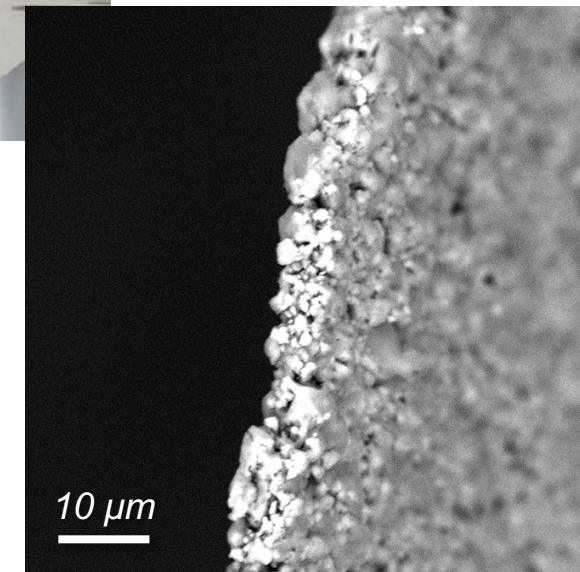


Free-standing LPSC Thin Films

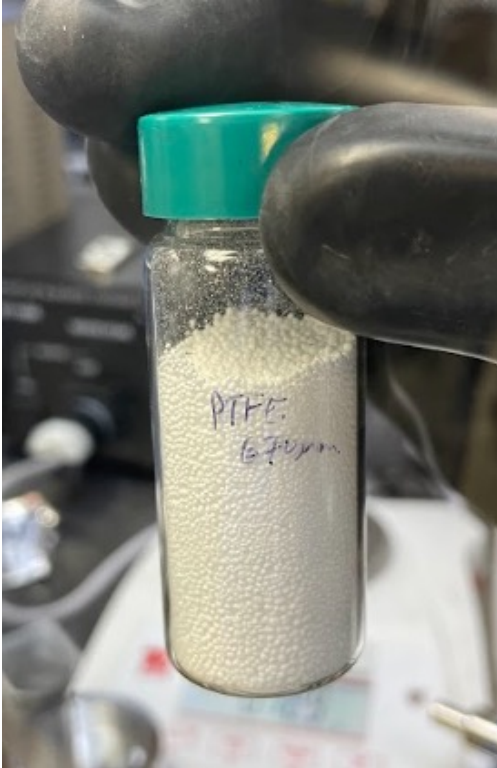


Tape-Casted LPSC Films
(~25 μm thickness)

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

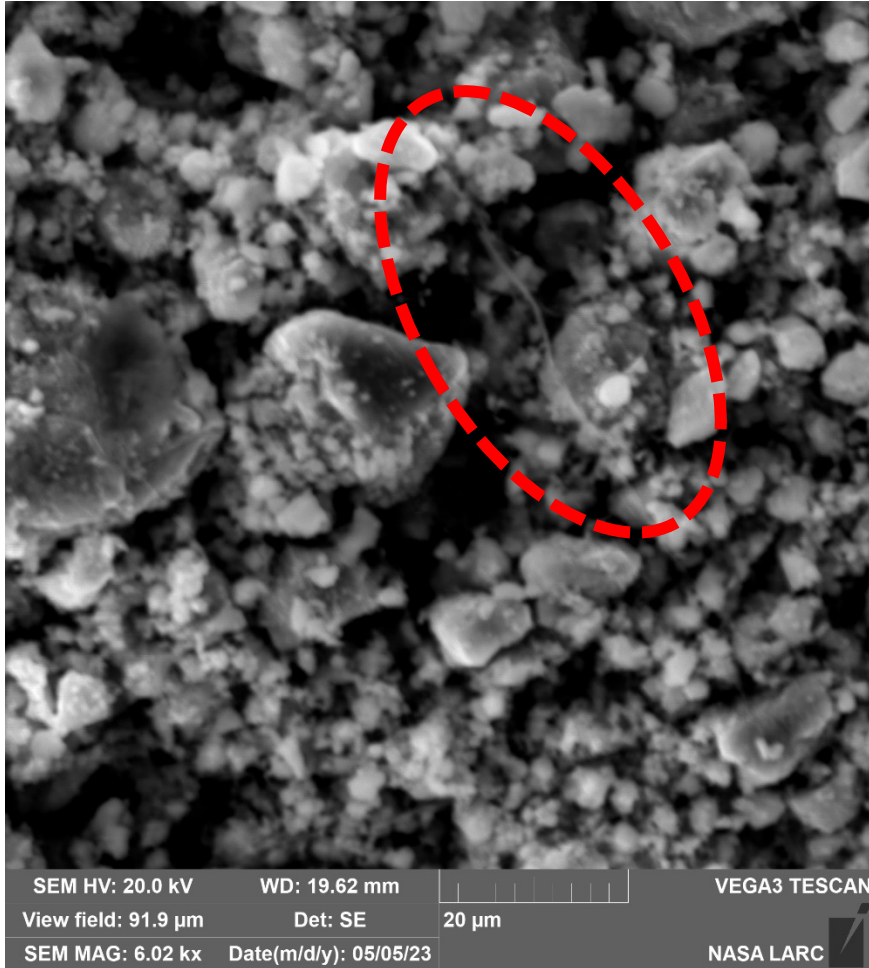
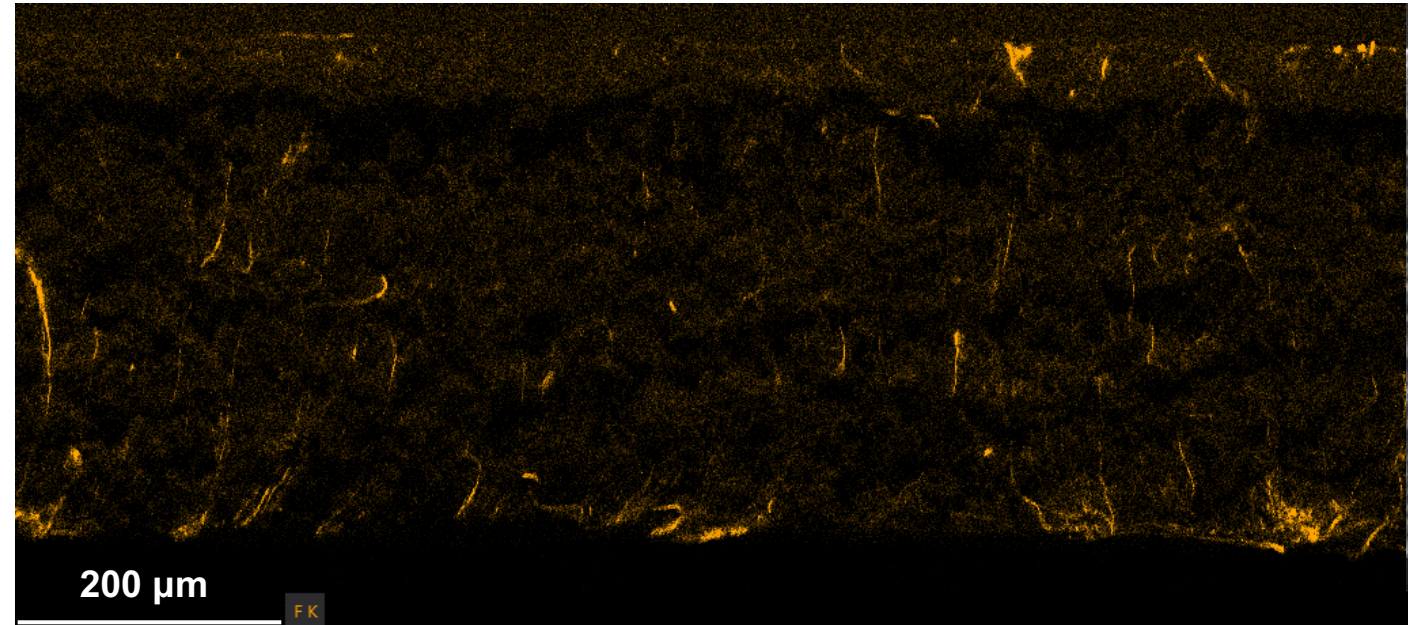


Dry Processing of LPSC Films

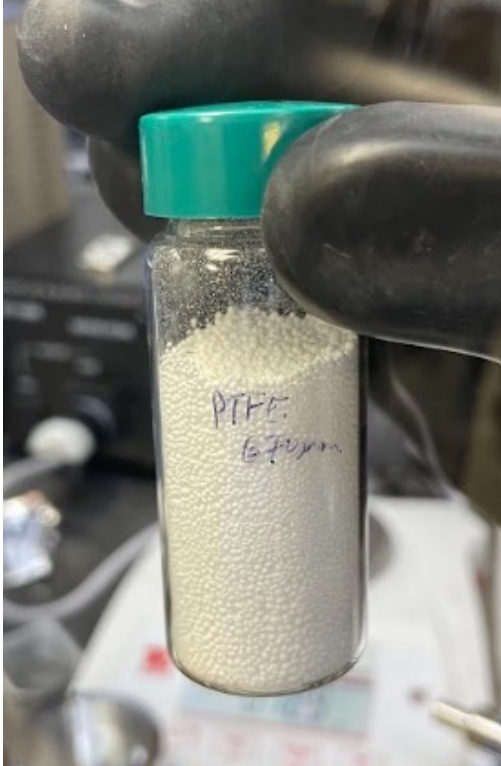
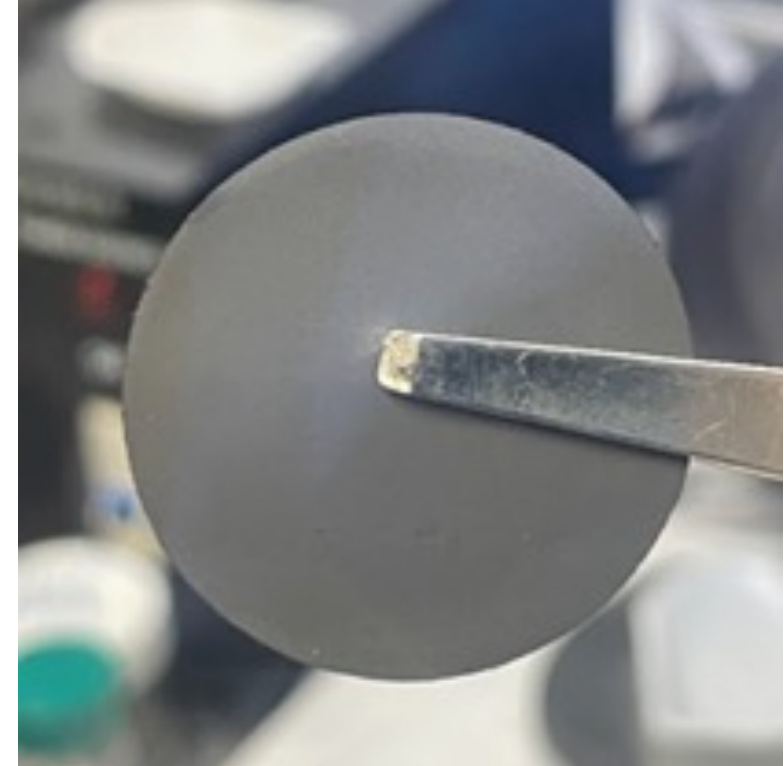


PTFE: Polytetrafluoroethylene

PTFE Fibers Provide Mechanical Support



Dry Processing of S Cathode Films

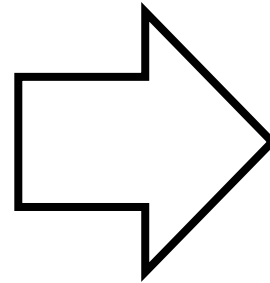


- ❑ PTFE binder is also compatible with dry processing of sulfur cathode

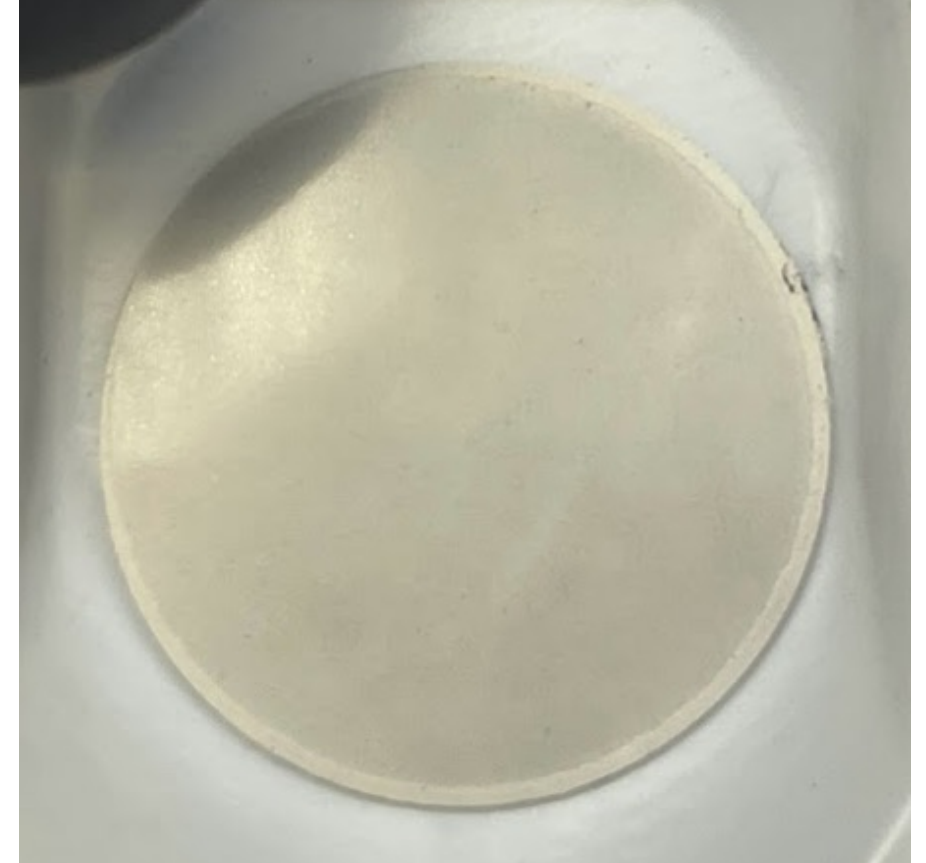
Cathode-SE Bilayer Fabrication



Generation 2 Pouch Cell



Generation 3 Pouch Cell

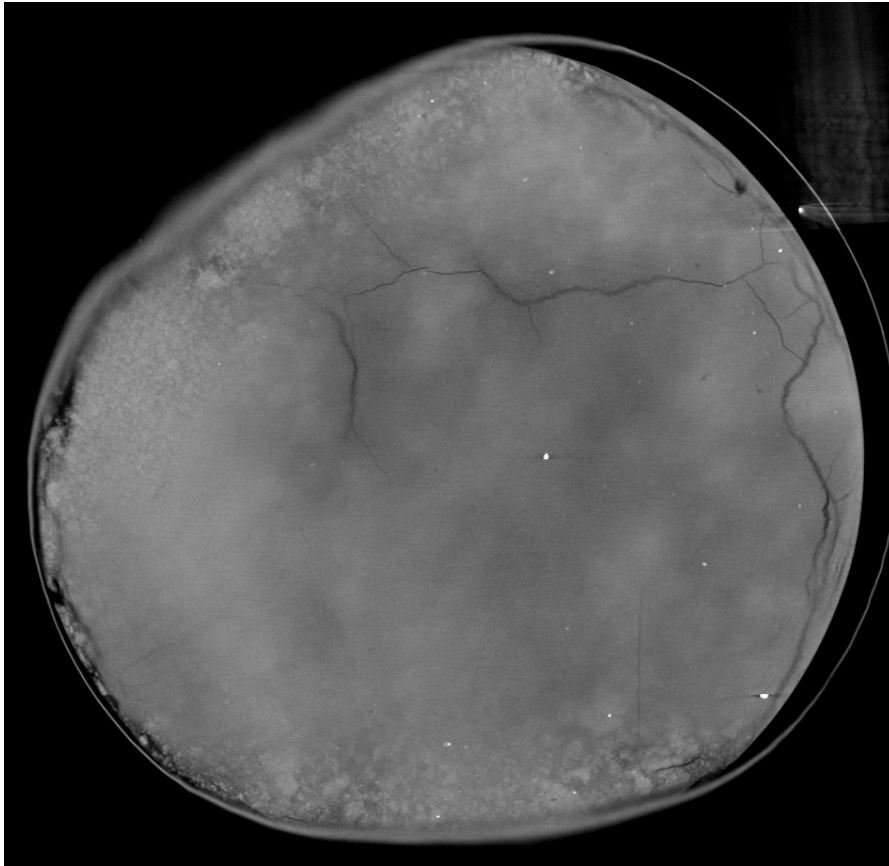
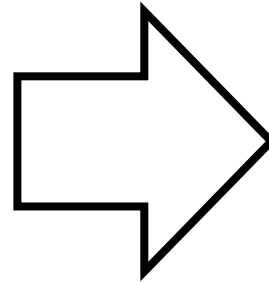


❑ Discs are all 3 cm in diameter

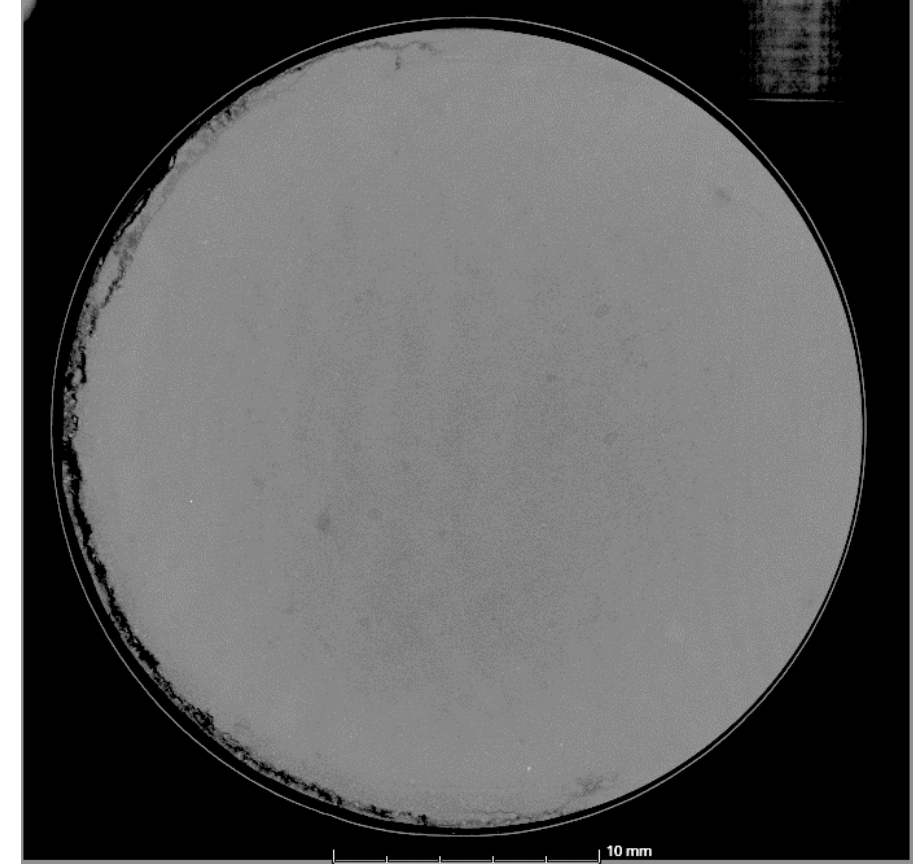
X-Ray Computed Tomography (CT)



Generation 2 Pouch Cell



Generation 3 Pouch Cell



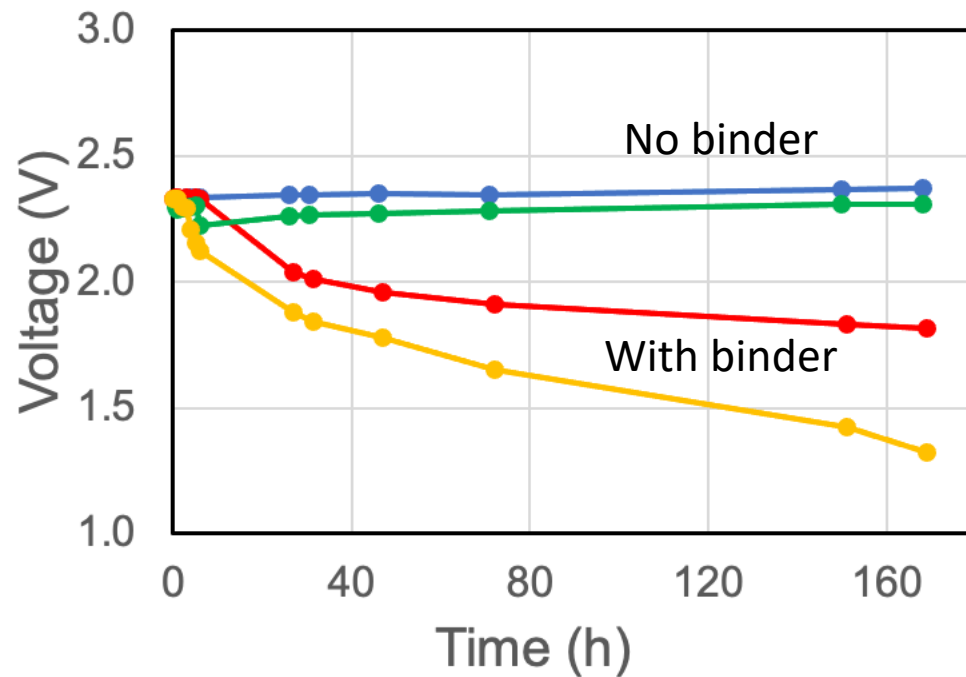
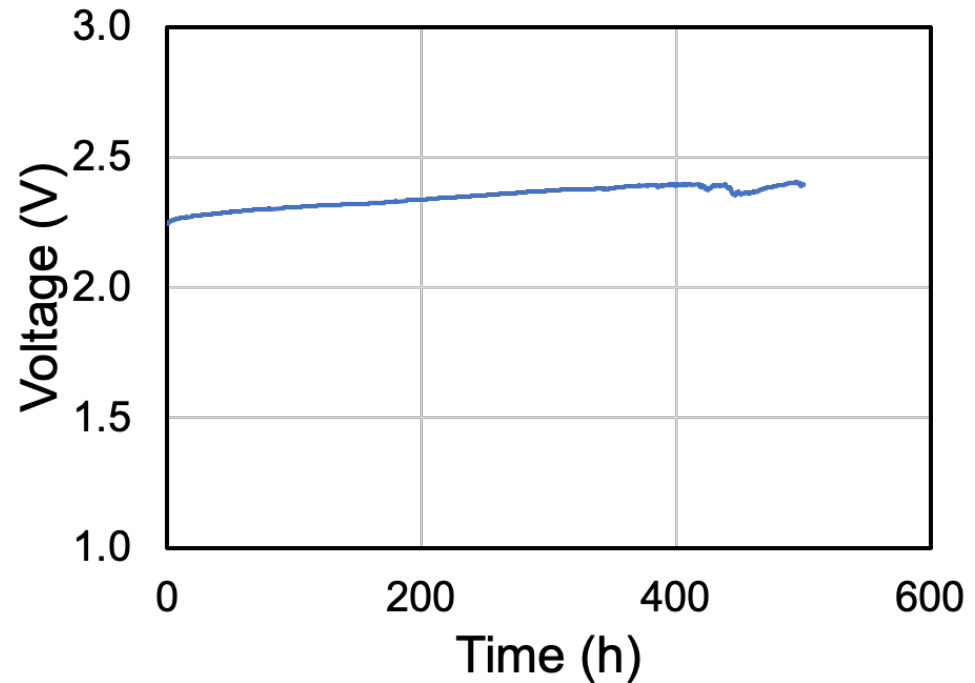
❑ Discs are all 3 cm in diameter

Courtesy: Dan Perey
NASA Langley Research Center (LaRC)

Self-Discharge Issues



- ❑ Polymer binder reacts with Li metal, resulting in self-discharge overtime

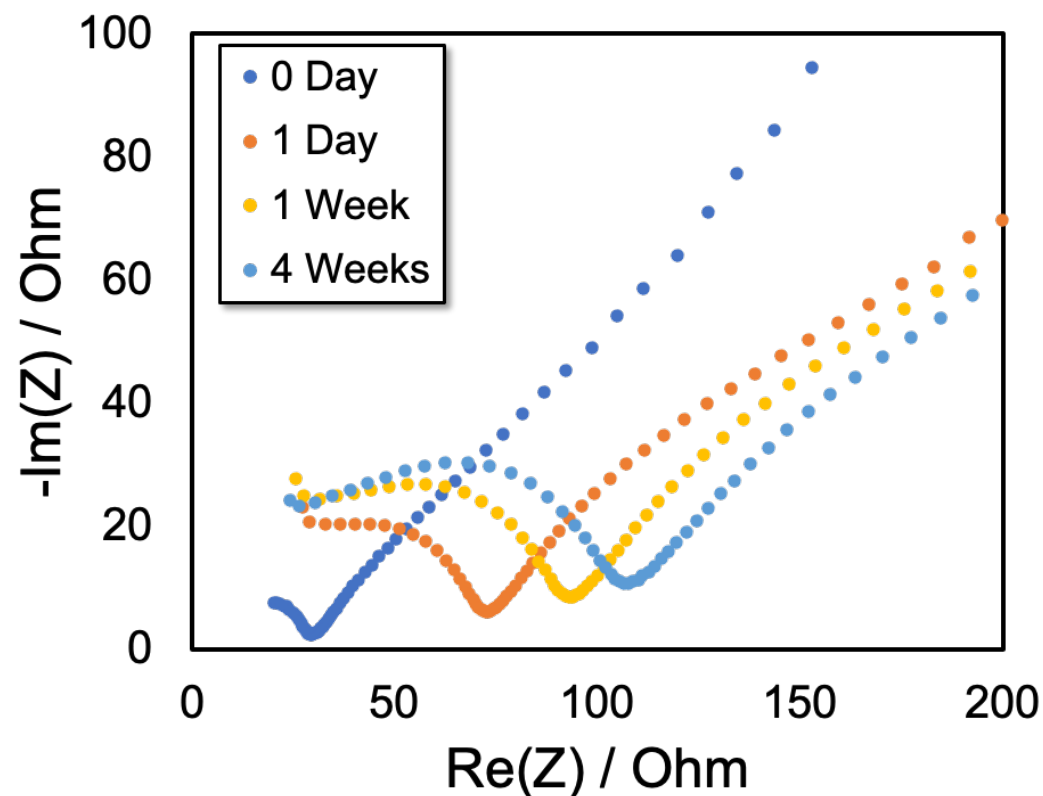


- ❑ Optimized binder processing eliminates self-discharge

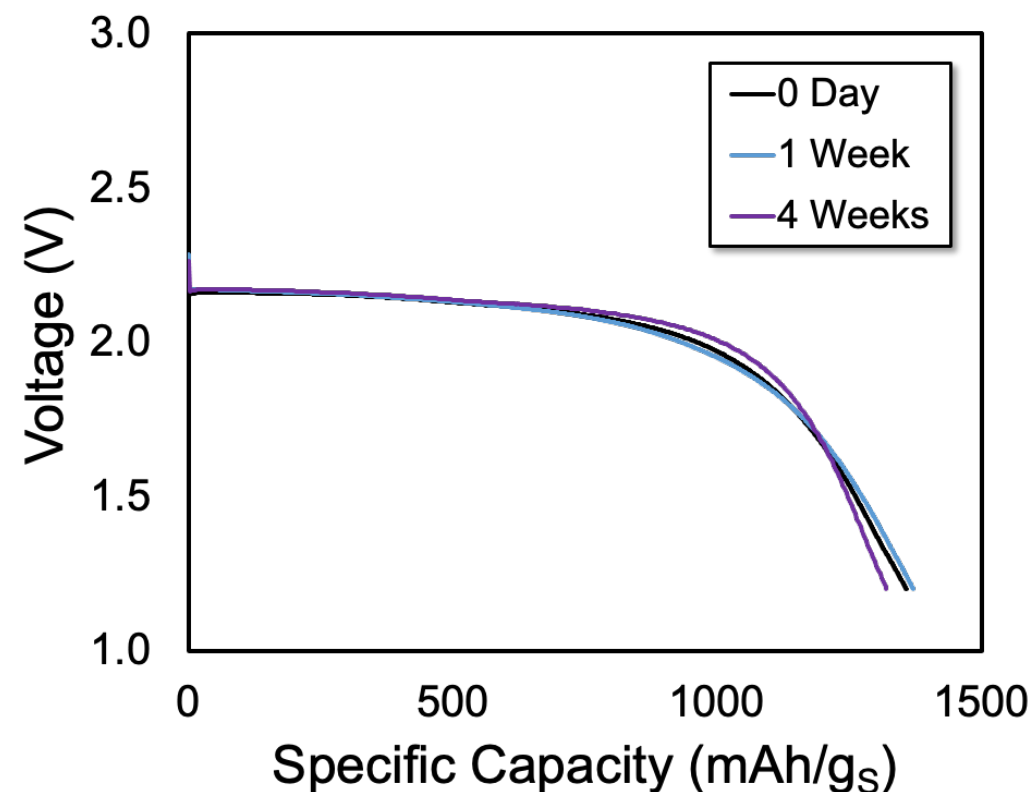
Pouch Cells with Improved Shelf Life



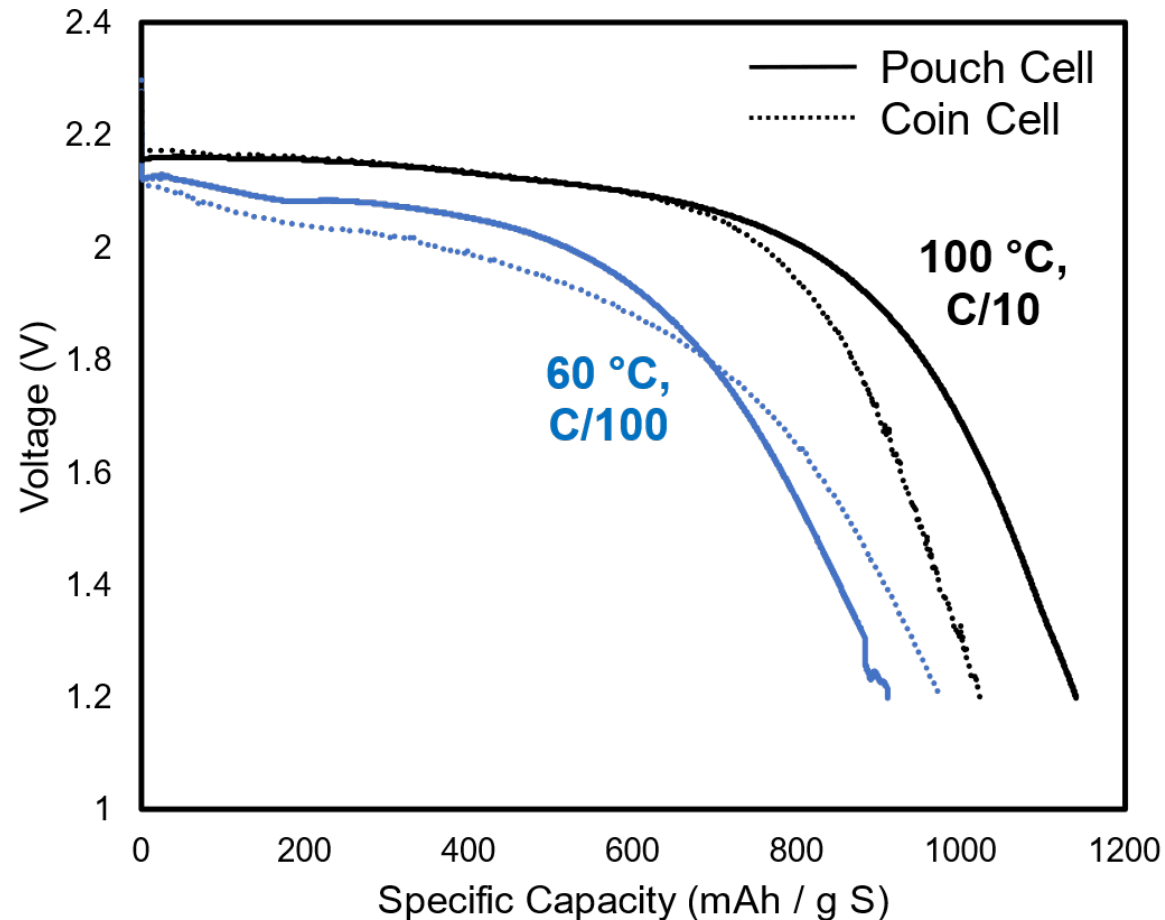
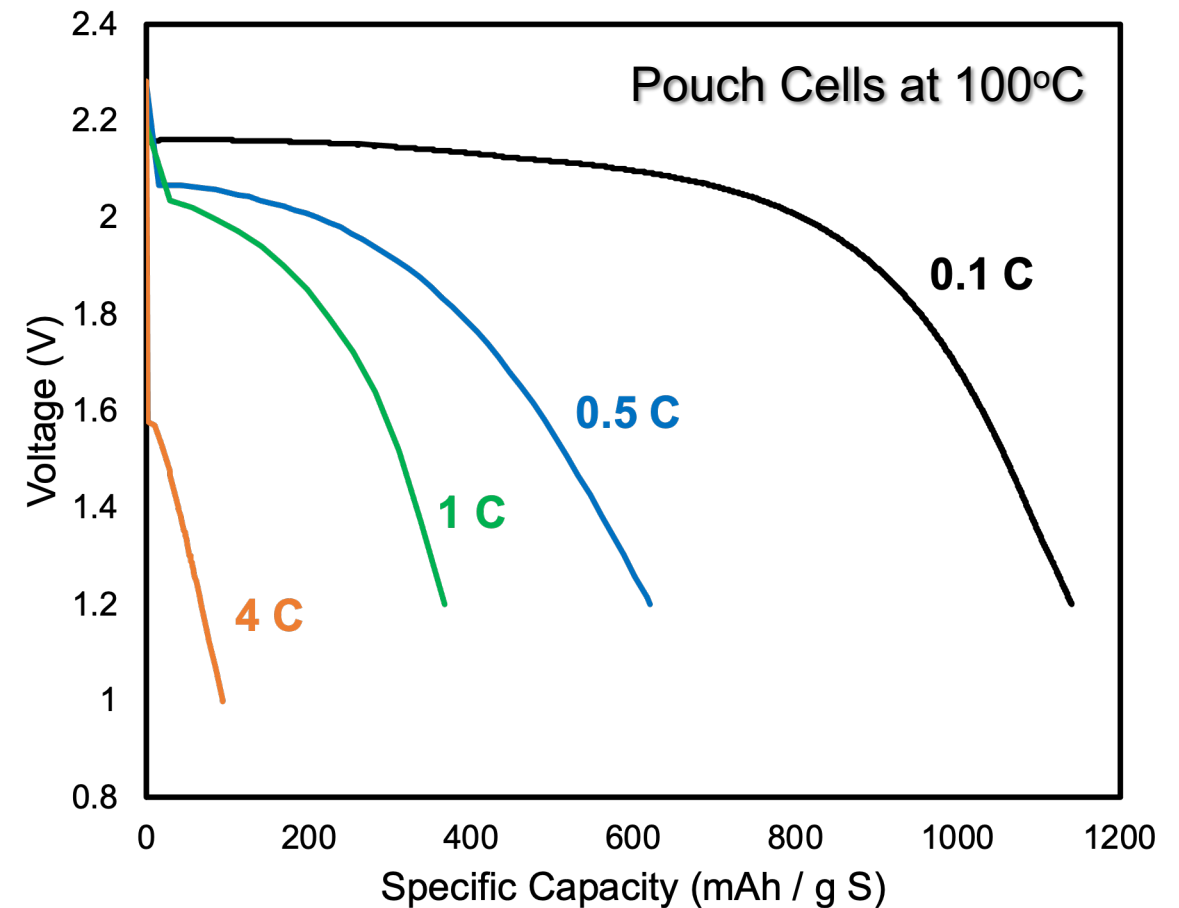
Electrochemical Impedance Spectroscopy (EIS)



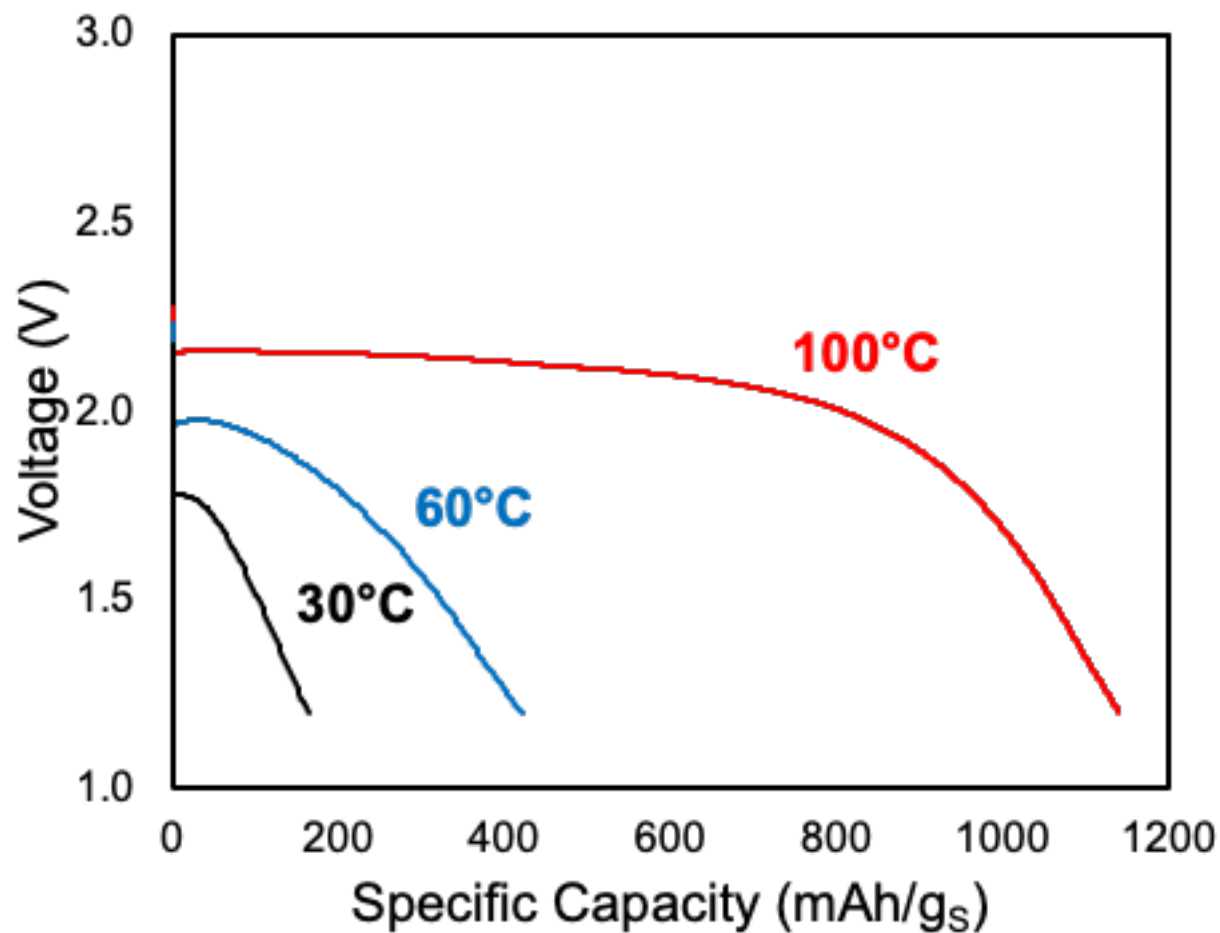
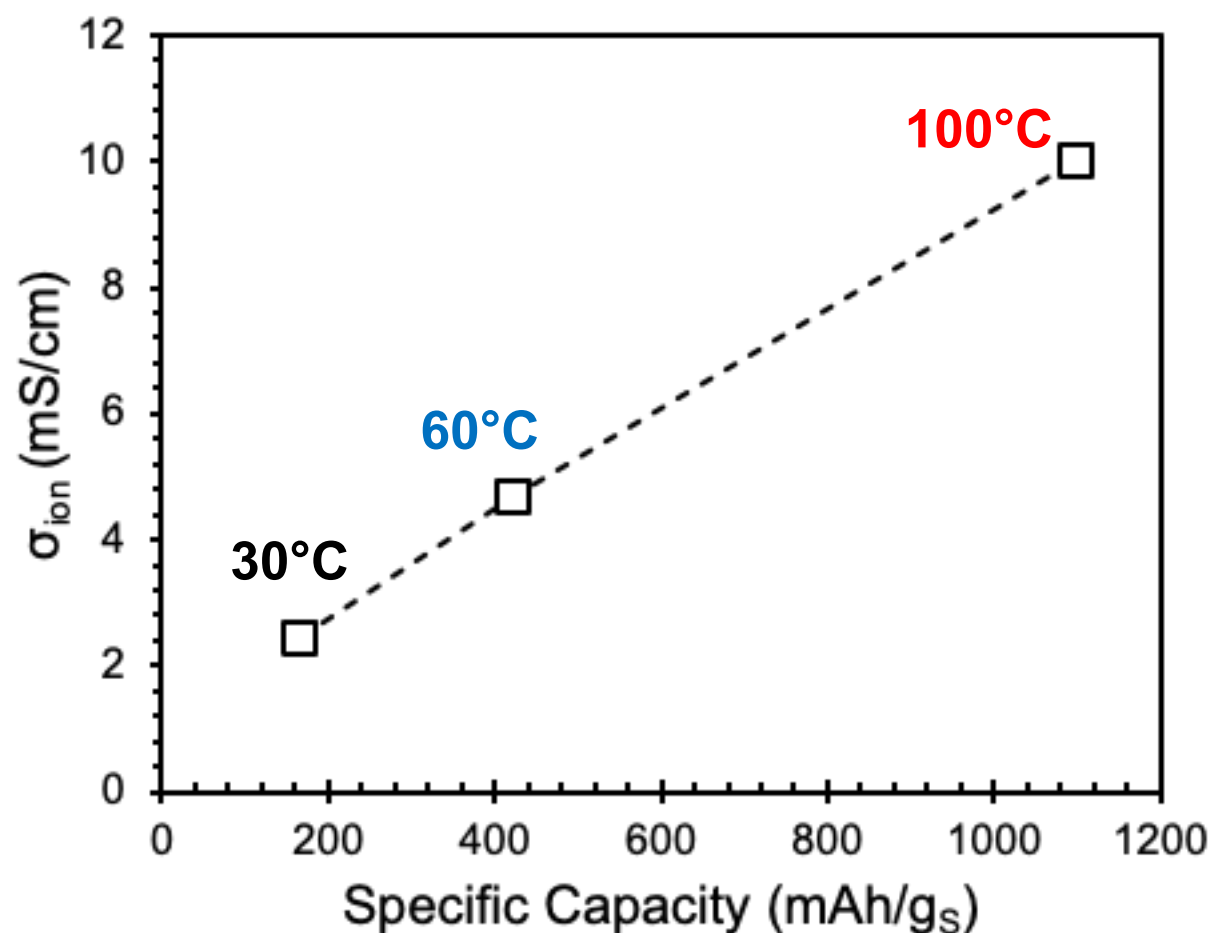
Constant Current Discharge



From Coin Cells to Pouch Cells



Key Roles of SE Ionic Conductivity

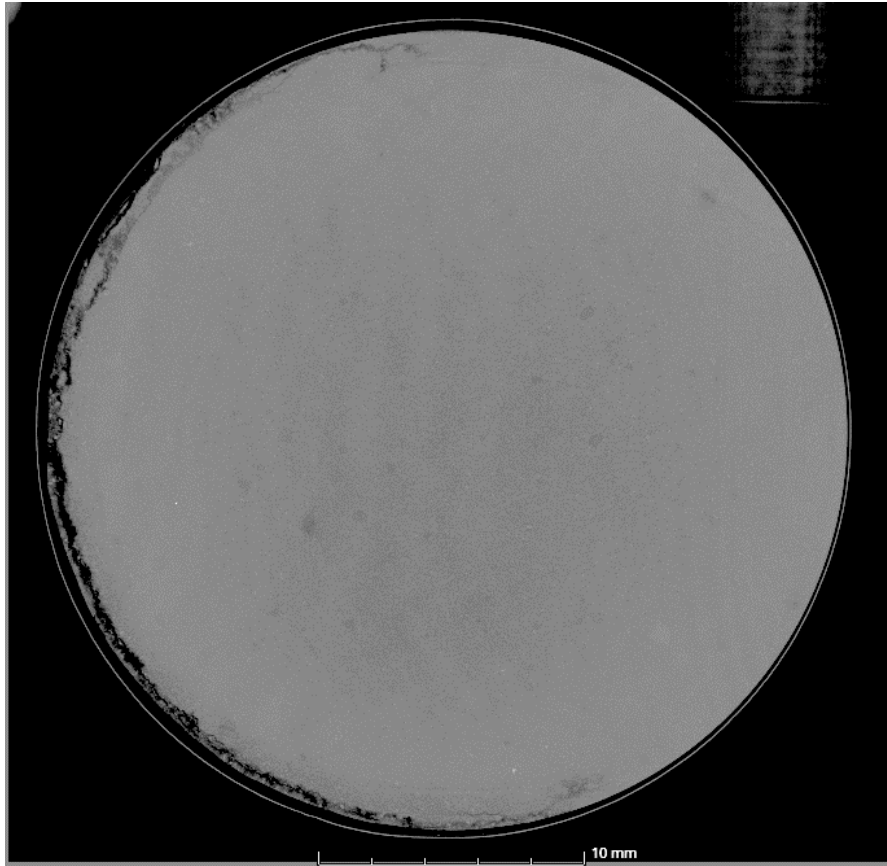
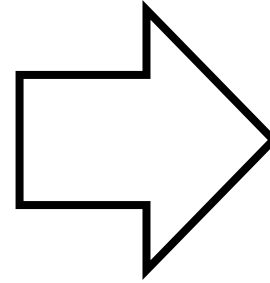


- ❑ Battery capacity linearly correlates with solid electrolyte (LPSC) conductivity
- ❑ Solid electrolyte with higher ionic conductivity should result in enhanced battery performance

More Challenges!



Before Discharge



After Discharge



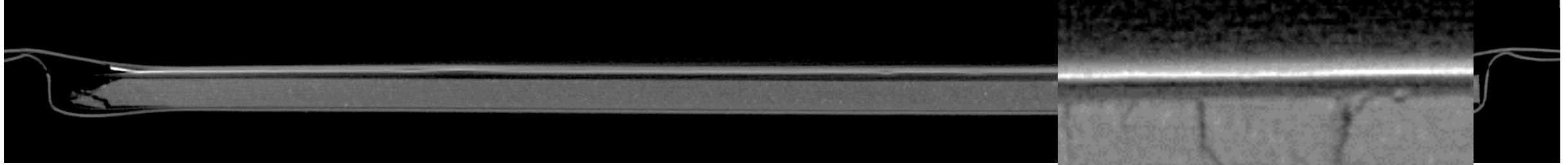
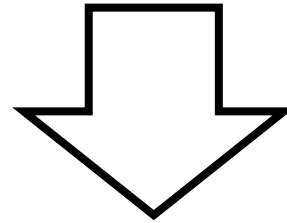
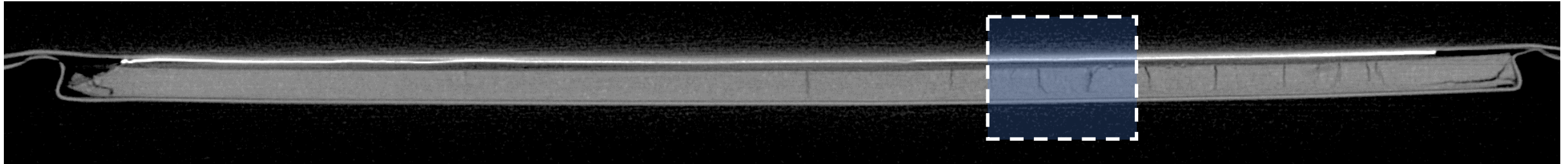
❑ Discs are all 3 cm in diameter

Courtesy: Dan Perey (NASA LaRC)

More Challenges!



Before Discharge



After Discharge

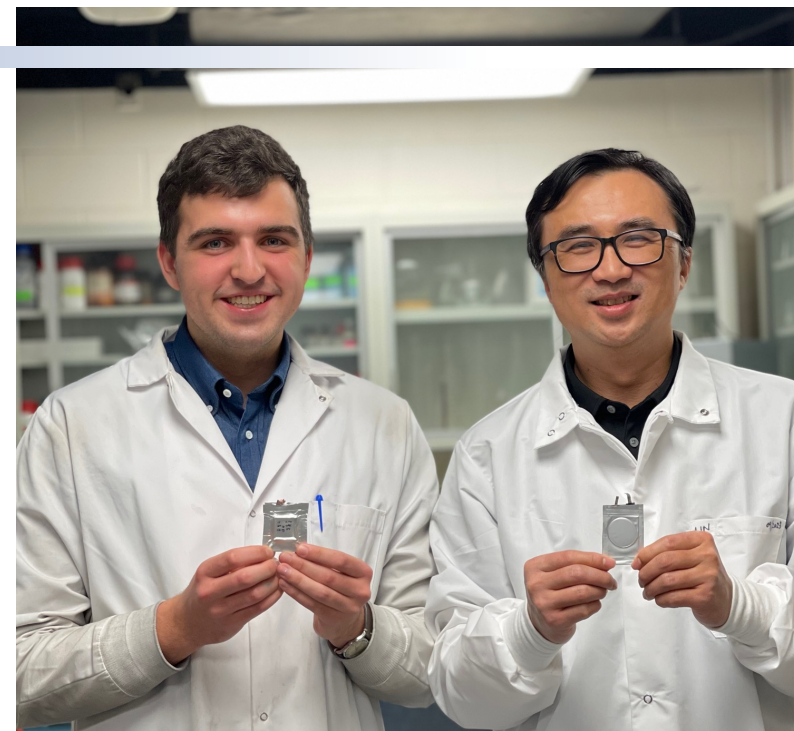
❑ Discs are all 3 cm in diameter

Courtesy: Dan Perey (NASA LaRC)

Summary



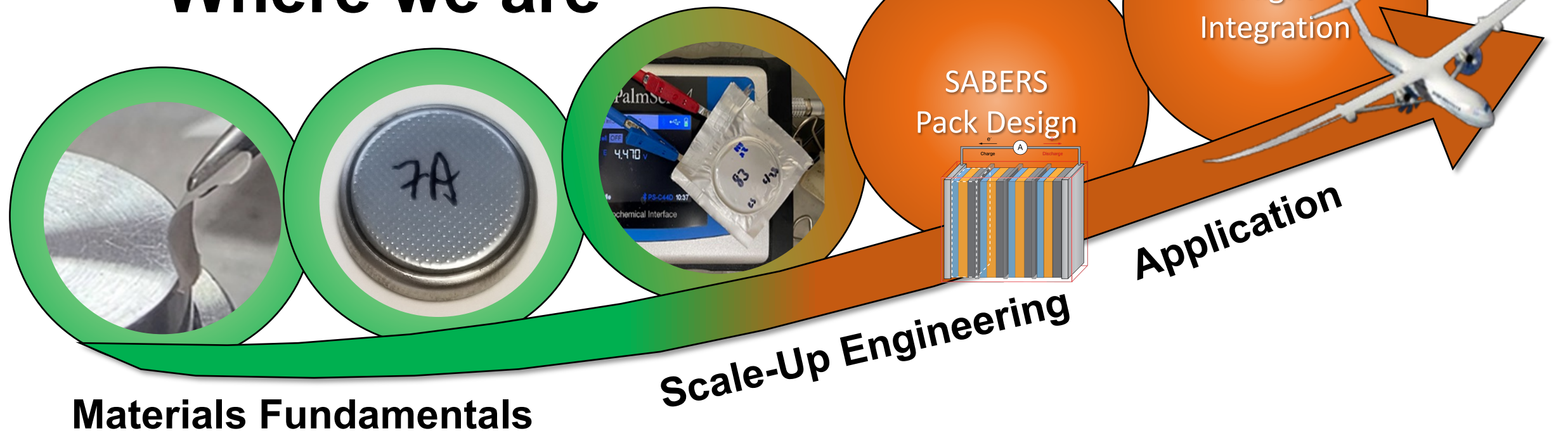
- ❑ High areal capacity ($>22 \text{ mAh/cm}^2$) all-solid-state Li-S cells were demonstrated, providing a viable pathway to $>500 \text{ Wh/kg}$ in specific energy.
- ❑ Li-S and Li-Se cells exhibited wide operation temperature range up to at least 100°C , at which the cells also exhibited high power capability.
- ❑ High capacity all-solid-state Li-S (small-format) pouch cells were demonstrated from processing development of both solid electrolyte and cathode layers.



Addressing Materials Challenges to Power the Future of Aerospace

What's Next?

Where we are



Acknowledgments



- ❑ NASA Convergent Aeronautics Solutions (**CAS**) Project
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- ❑ Lopamudra Das (AMA)

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 - ❑ 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
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