Toward Full Active Material Utilization in All-Solid-State Lithium-Sulfur Batteries with Sulfide Electrolytes

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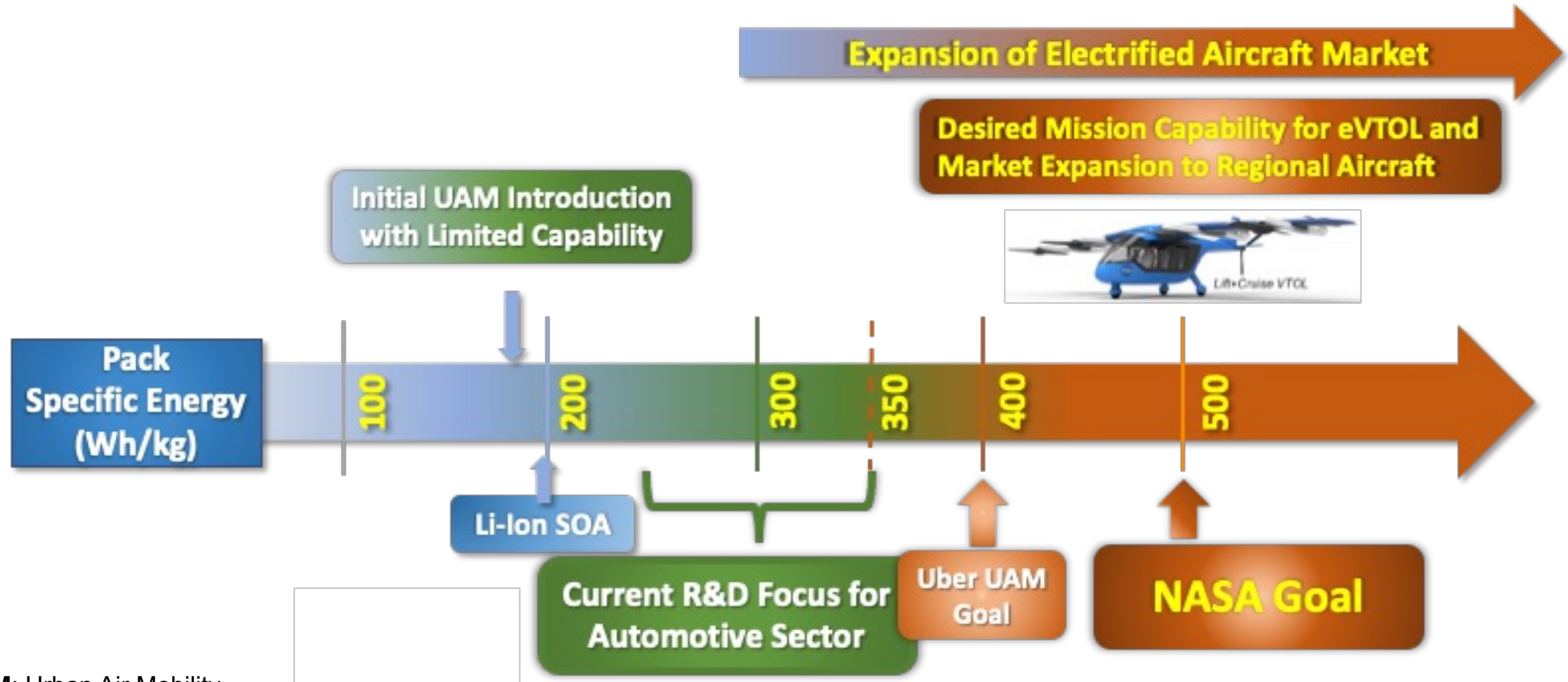
2022 American Chemical Society (ACS) Fall Meeting & Exhibit

August 21, 2022

Chicago, IL

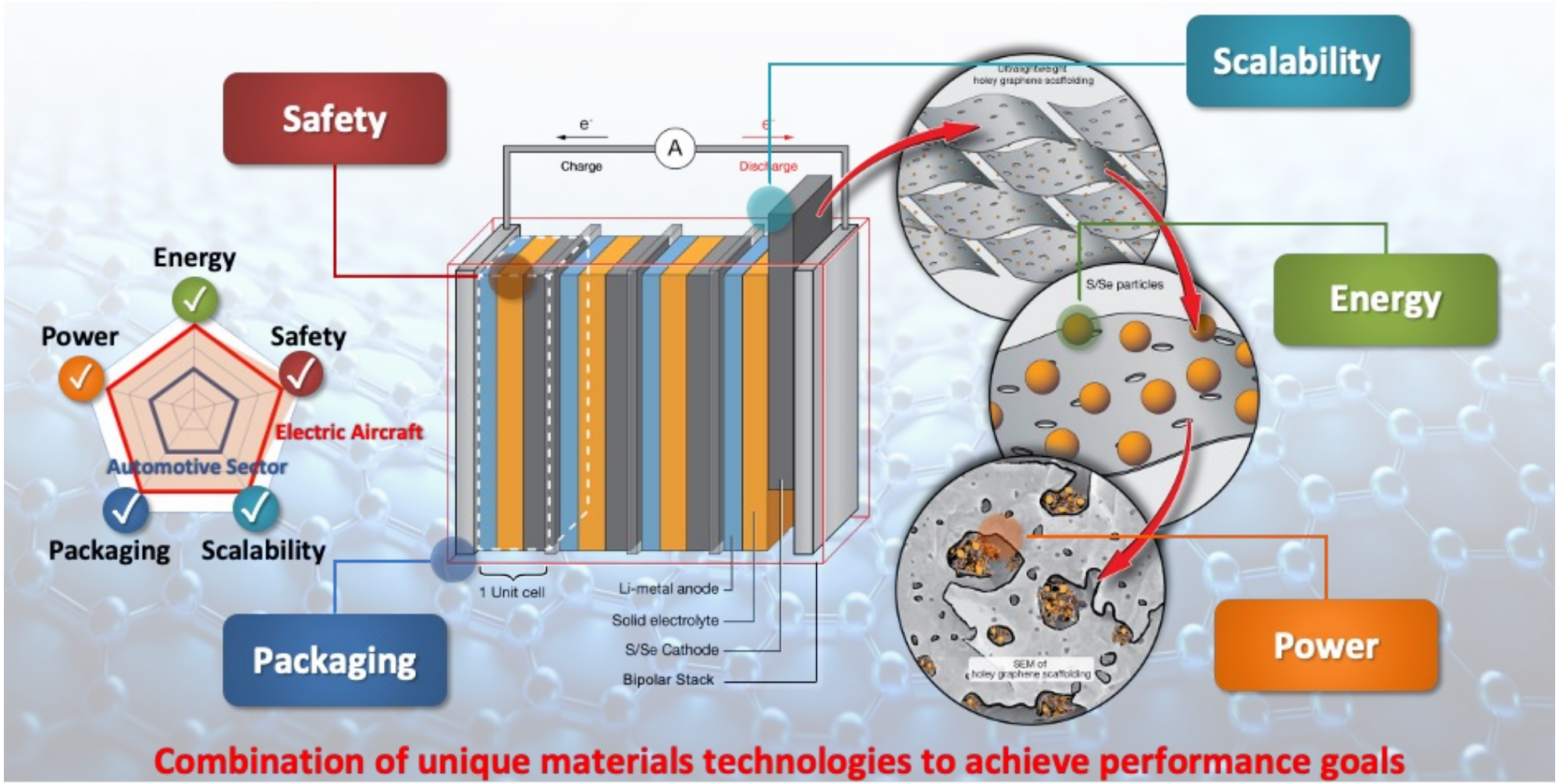
All images & videos credit: NASA

NASA's Interest in Solid-State Batteries



UAM: Urban Air Mobility
eVTOL: electric Vertical Take-Off and Landing

NASA's Interest in Solid-State Batteries



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

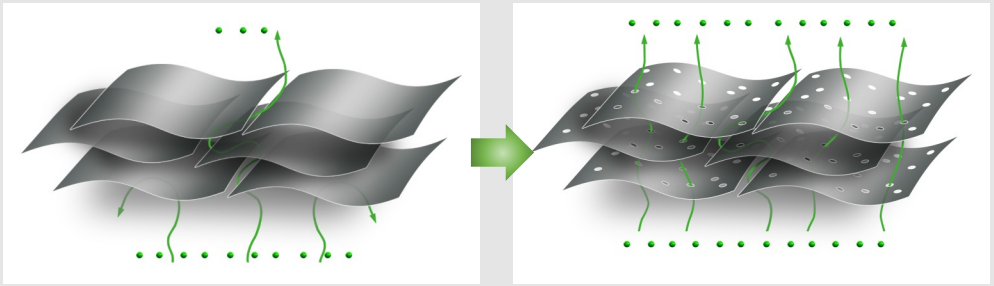
Holey Graphene (hG)



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

Holey Graphene: An Advanced Electrode Material

Supercapacitors

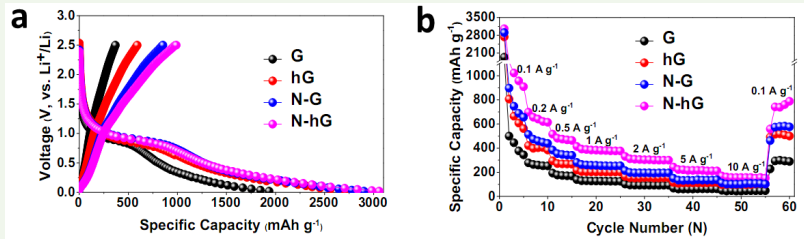


ACS Nano **2014**, *8*, 8255.

Liangbing Hu (U Maryland)

As-Prepared hG

Li-Ion Battery (Anode)



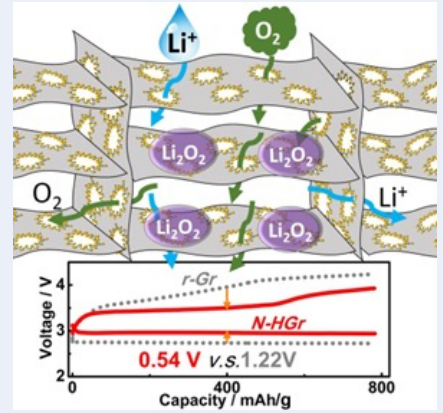
Small **2015**, *11*, 6179.

Liming Dai (CWRU)

N-doped hG

$Li-O_2$ Batteries

Liming Dai (CWRU)

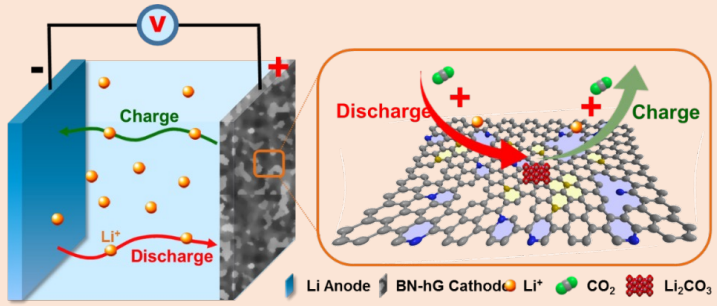


ACS Energy Lett **2016**, *1*, 260.

N-doped hG

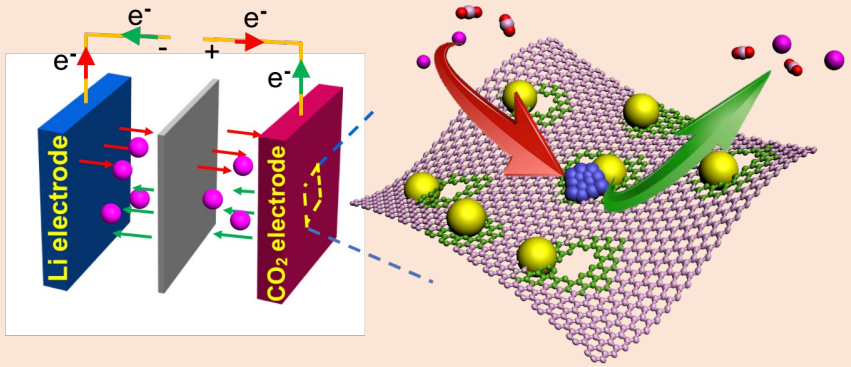
$Li-CO_2$ Batteries

Liming Dai (CWRU)



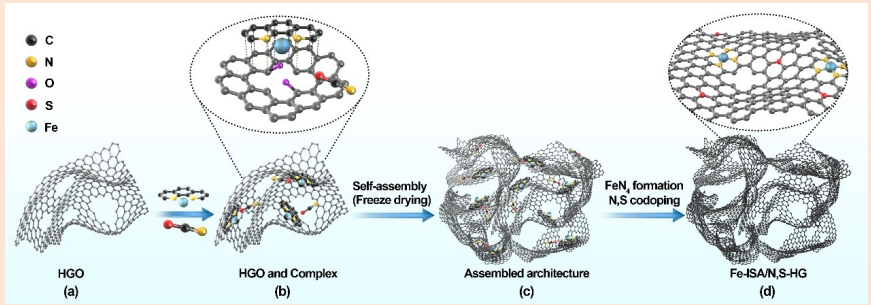
Angew. Chem. Int. Ed. **2017**, 56, 6970.

B,N-codoped hG



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

Carbon Dot-Supported on hG



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

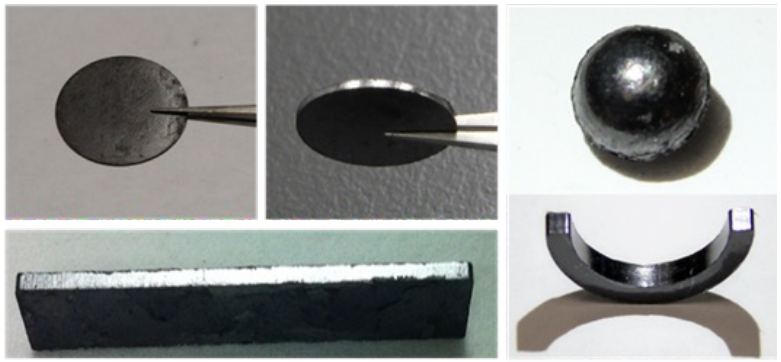
Single Fe Atom Catalysts Supported on hG

A Dry Compressible Carbon Scaffold: Holey Graphene

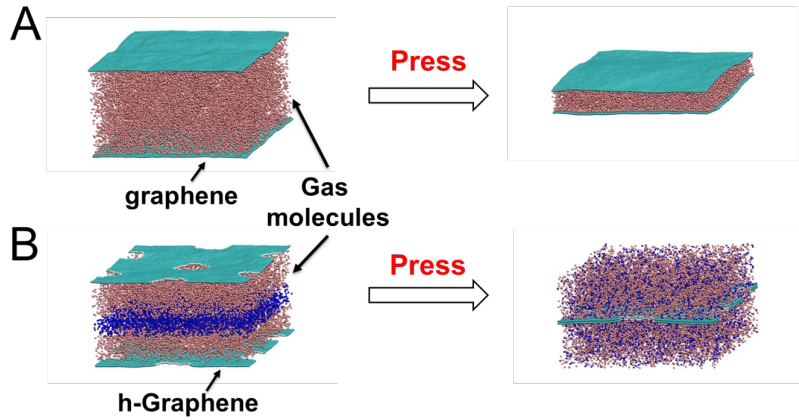


Holey Graphene Powder

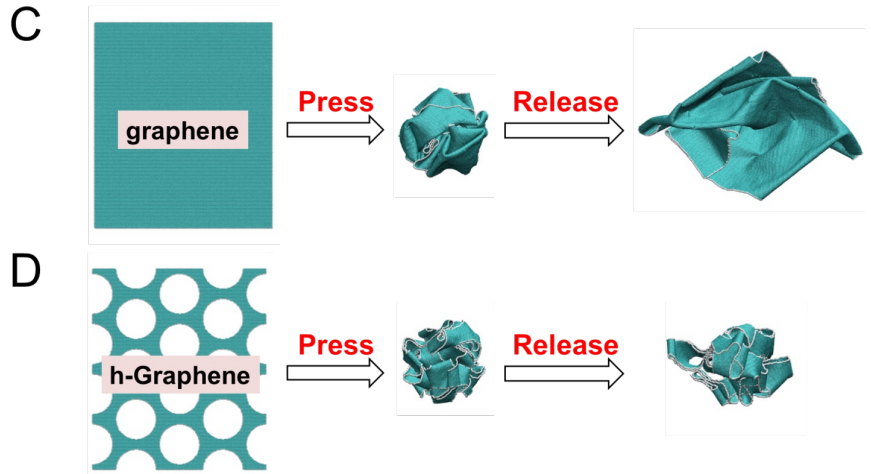




Holey Graphene Monolithic Architectures



Facile air escape upon compression



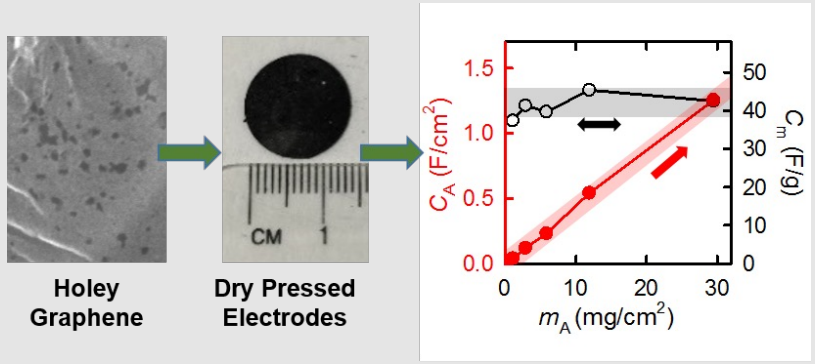
Minimal volume rebound upon release

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

A Game Changer in Electrode Preparation

Versatile Applications

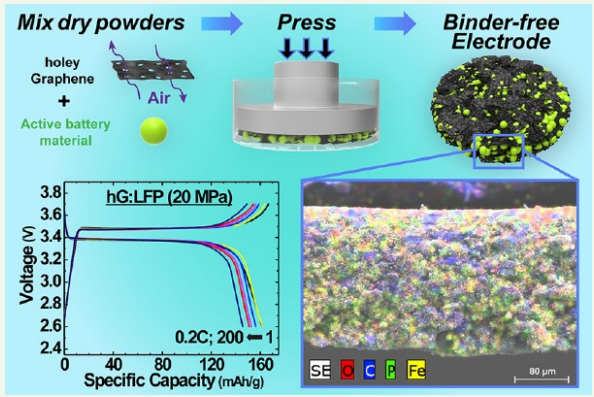
Supercapacitors



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

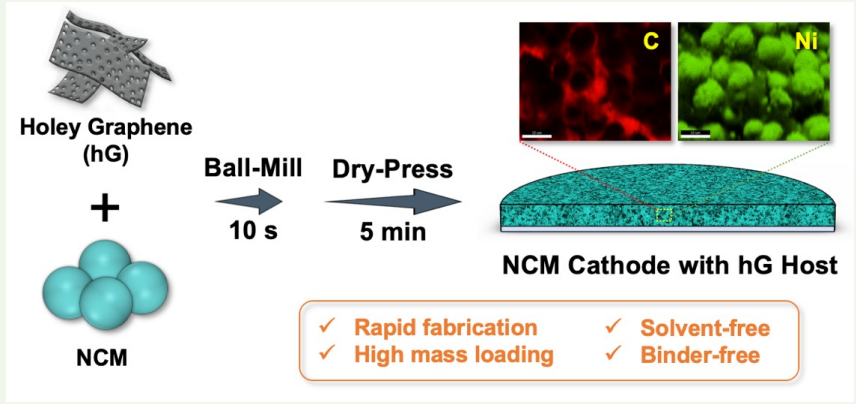
Li-Ion Batteries

LFP



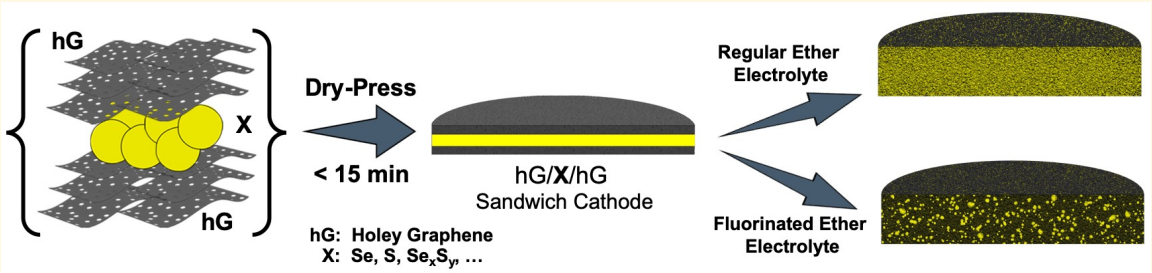
ACS Appl. Energy Mater. **2019**, *2*, 2990.

NCM



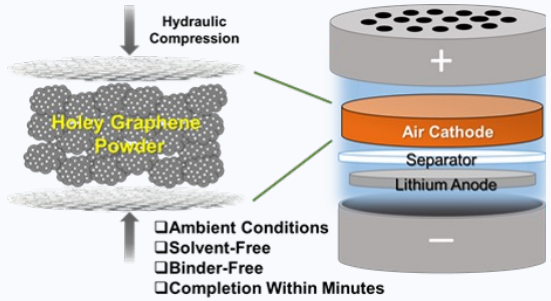
Electrochim. Acta **2020**, *362*, 137129.

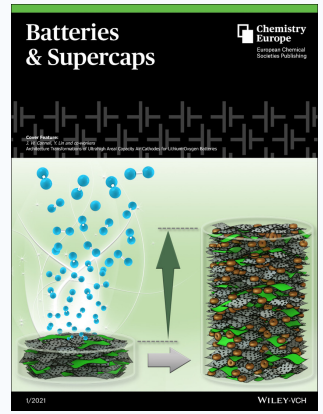
Li-S/Se Batteries



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

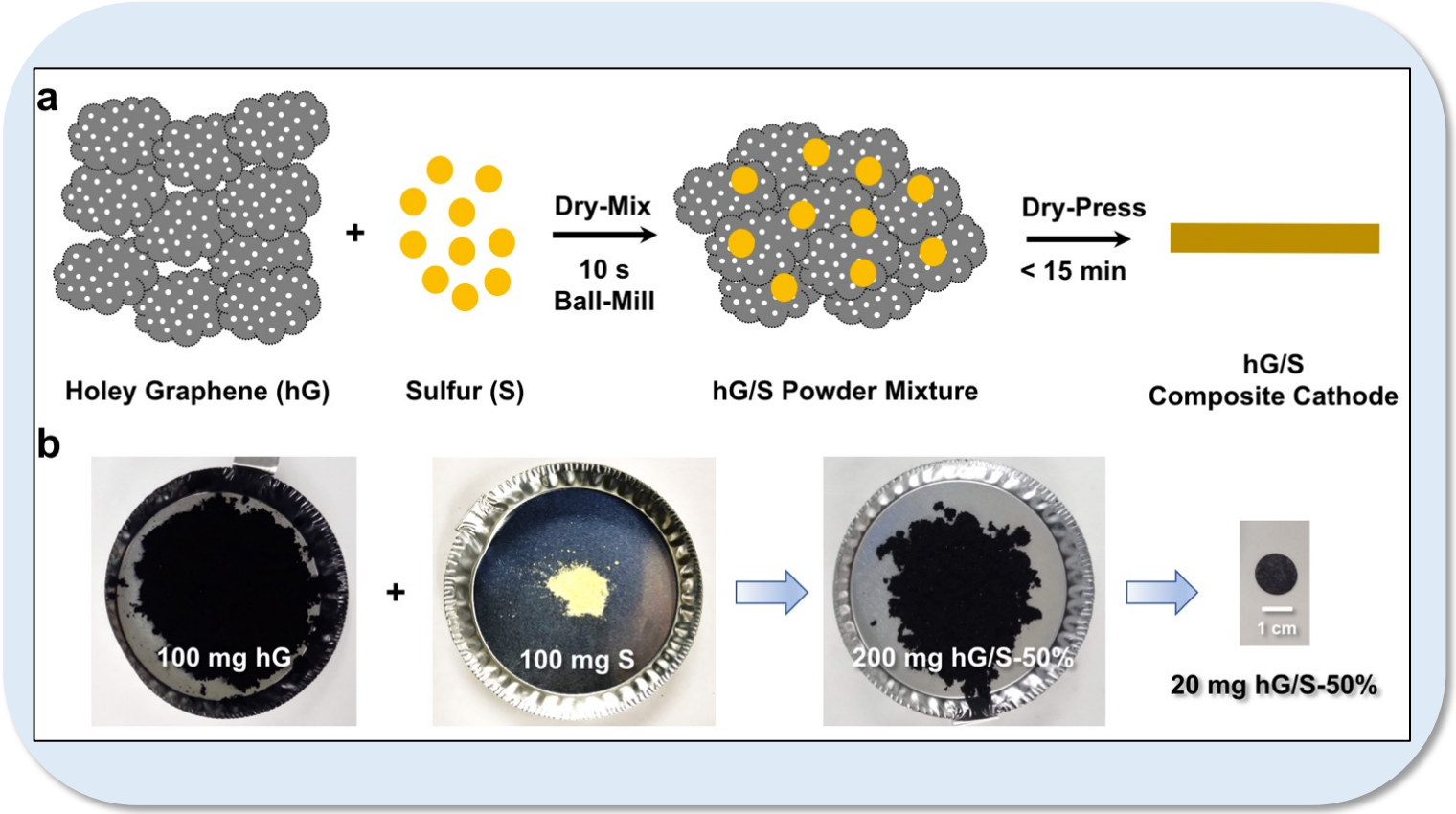
Li-O_2 Batteries

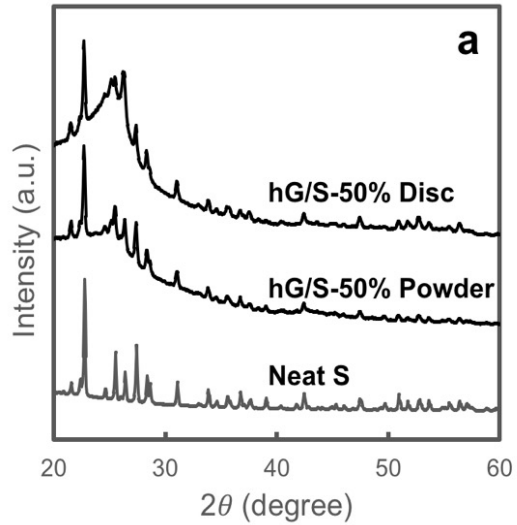


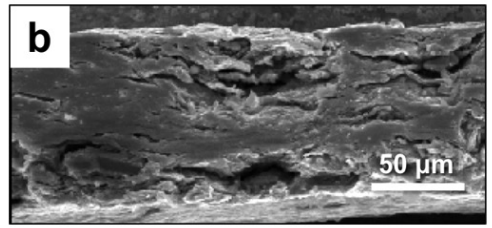


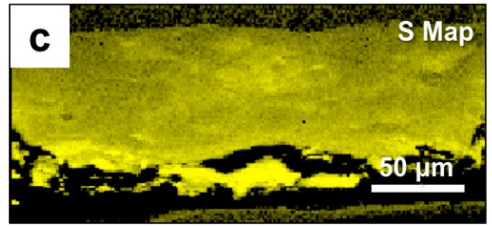
Nano Lett. **2017**, *17*, 3252; *Nano Energy* **2017**, *31*, 386; *J. Electrochem. Soc.* **2020**, *167*, 080522; *Batteries Supercaps* **2021**, *4*, 120.

Dry Pressed S Cathodes Enabled by hG





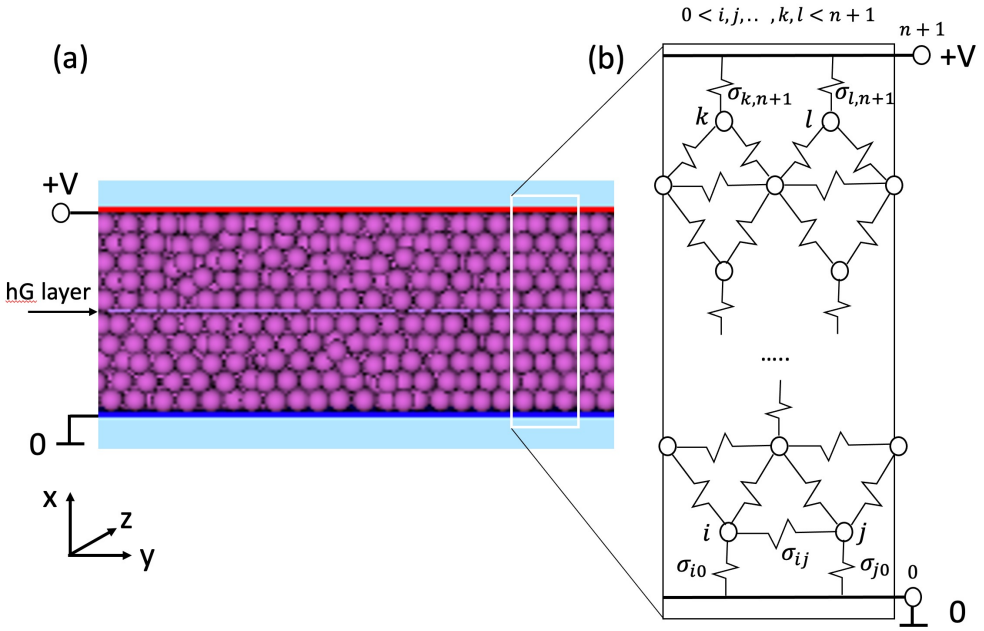


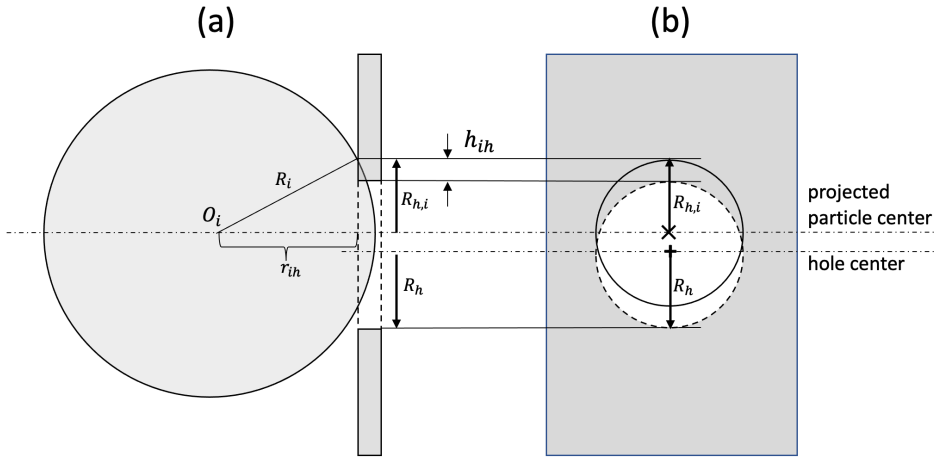


❑ Facile solvent-free preparation of high S content, high mass loading S cathodes.

Batteries & Supercaps, **2019**, *2*, 774-783.

Solid State Li-ion Transport Through hG



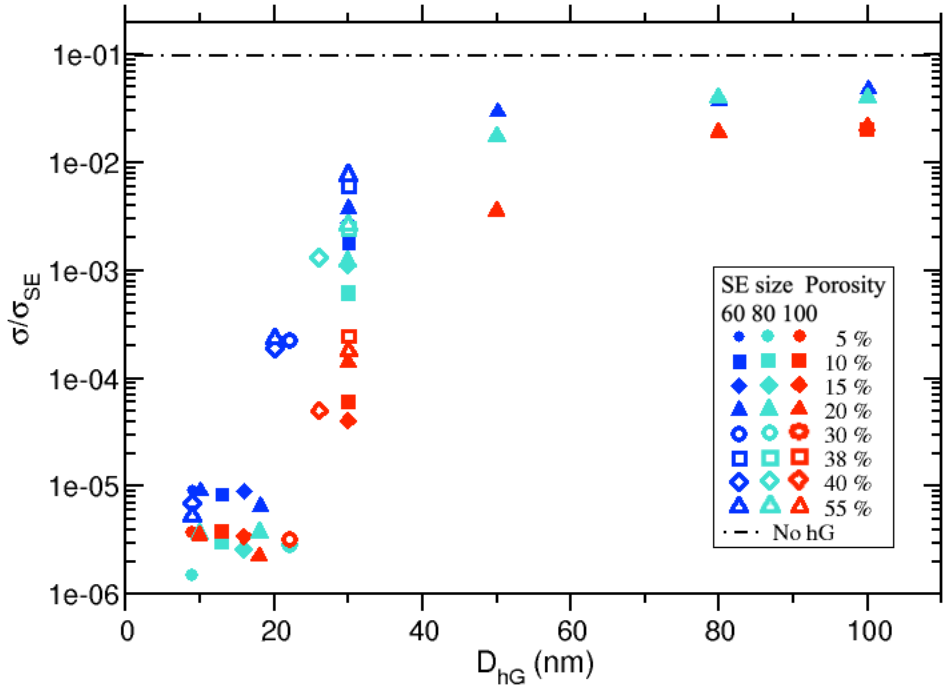


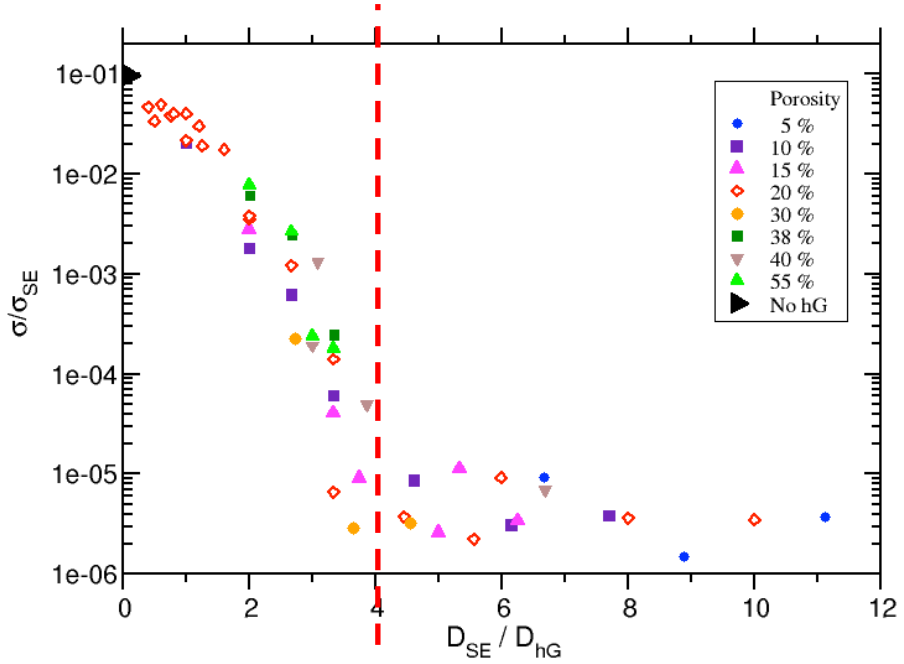
- ❑ Solid electrolyte (SE) particles: 60 nm
- ❑ hG layer: 10 - 100 nm holes

- ❑ Interaction of a SE particle and a hG hole

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

hG Hole Parameter: Porosity or Size?



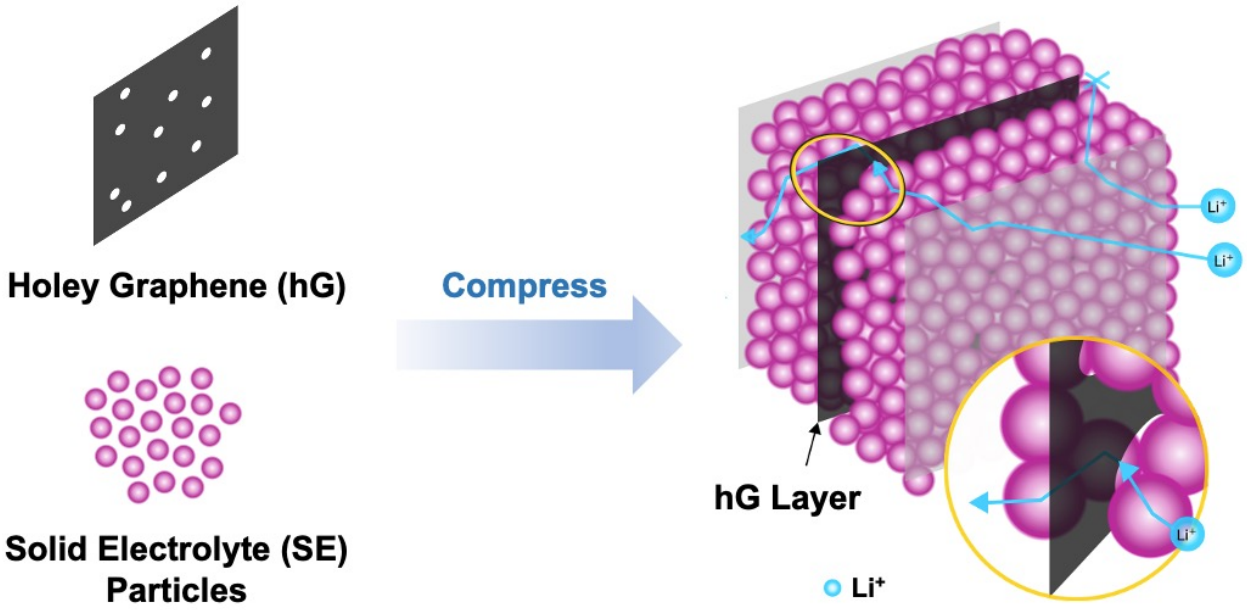


- ❑ Porosity of the hG is not a governing parameter for the permeability
- ❑ Permeability is governed by the ratio between the SE particles size (D_{SE})and the pore size of the hG (D_{hG})

- σ: ionic conductivity of hG/SE system
- σ_{SE}: ionic conductivity of SE

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

Question Answered

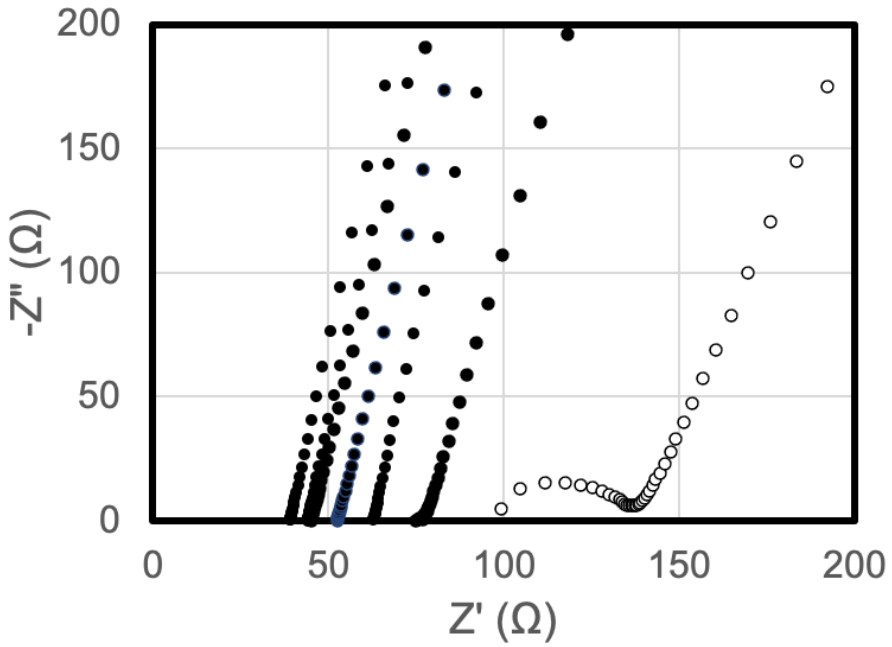


- Li ion can conduct through the thickness of holey graphene – as long as the holes are at least 25% in size of the solid-state electrolyte particles.

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

Commercially Available Sulfide Electrolytes

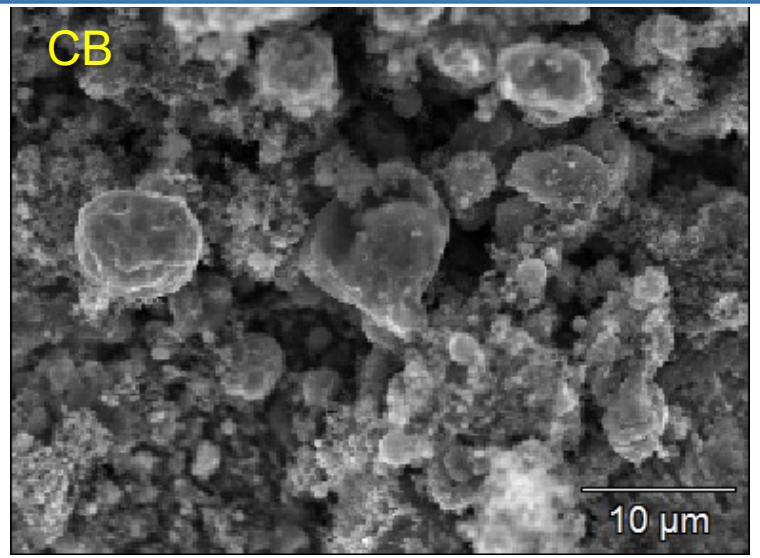
Sulfide Electrolytes	Vendor	Density (g/cm^3)	Ionic (mS/cm)	Electrical (μS/cm)
$Li_{10}SnP_2S_{12}$	NEI	1.47	1.75	0.159
$Li_6PS_5Cl_{0.5}Br_{0.5}$	MSE	1.37	1.65	0.142
$Li_6PS_5Cl_{0.9}I_{0.1}$	NEI	1.48	1.50	0.106
Li_6PS_5Cl	NEI	1.32	1.44	0.132
$Li_7P_3S_{11}$	MSE	1.32	1.19	0.095
$Li_{10}GeP_2S_{12}$-Fine	MSE	1.55	0.86	0.060
$Li_{10}GeP_2S_{12}$-Coarse	MSE	1.44	0.51	0.006
β-Li_3PS_4	NEI	Fine white powder; do not form disc		

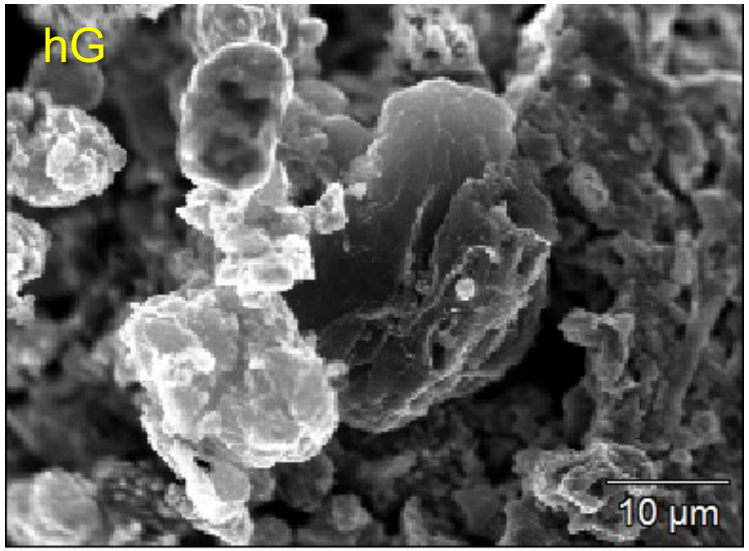


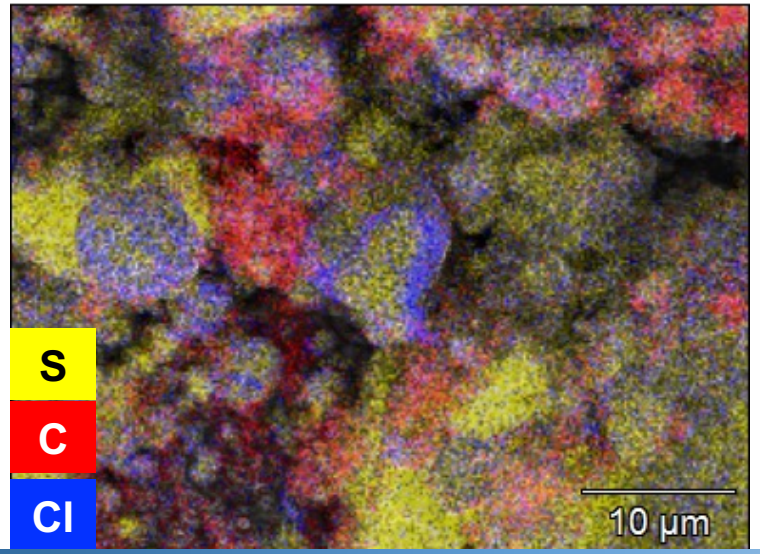
- Sulfide electrolytes are typically of high ionic conductivity (> 1 mS/cm)
- Li_6PS_5Cl (LPSCl; LPSC) is the most studied sulfide electrolyte and commercially available in large quantities (~$10/g)

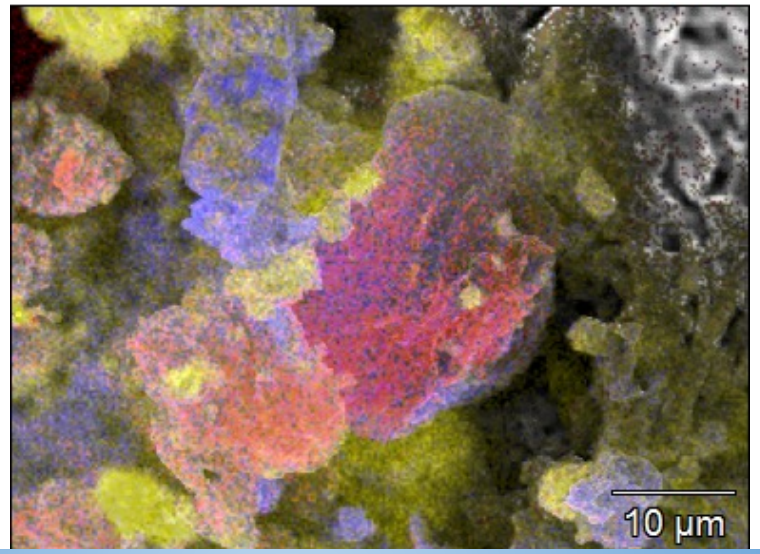
- NEI: NEI Corporation (http://neicorporation.com)
- MSE: MSE Supplies LLC (http://msesupplies.com)

Composite Solid-State Cathode Powder







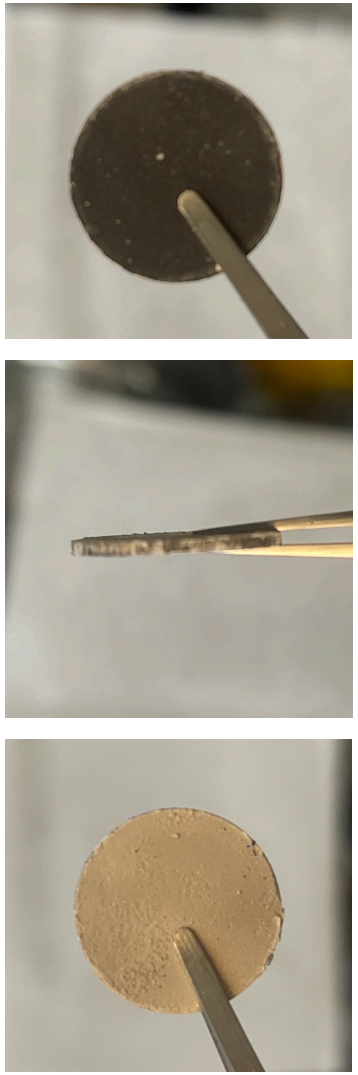


- Active material: **S**
- Solid electrolyte (SE): **Li_6PS_5Cl (LPSCl)**
- Carbon: **CB (carbon black) vs hG (holey graphene)**
- Multistep mixing process

CB: Super C45

Dry-Pressed Cathode/SE Bilayer Discs

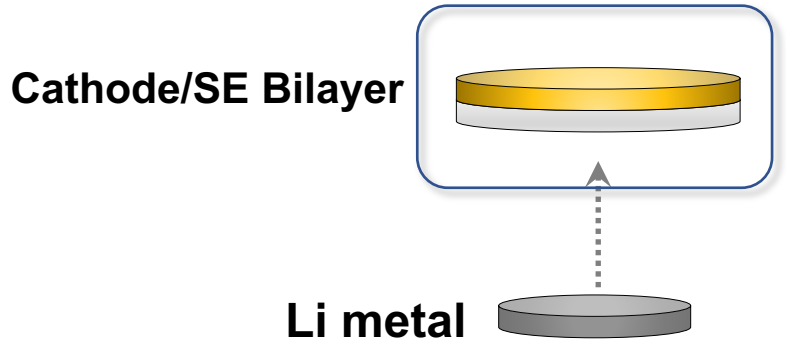
CB



hG

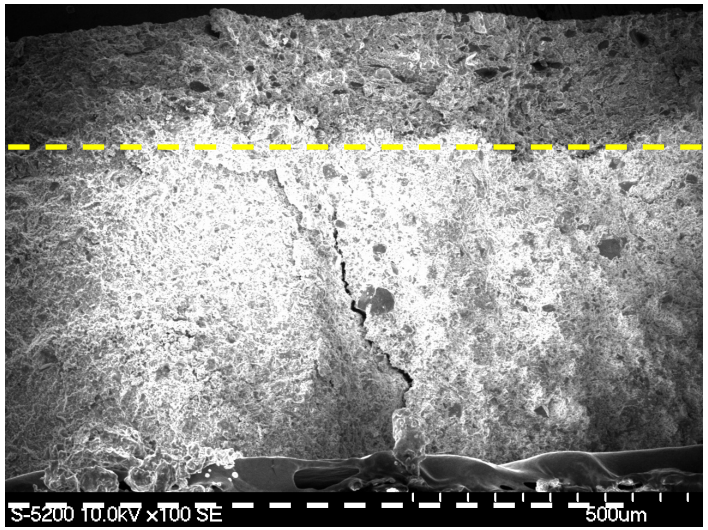


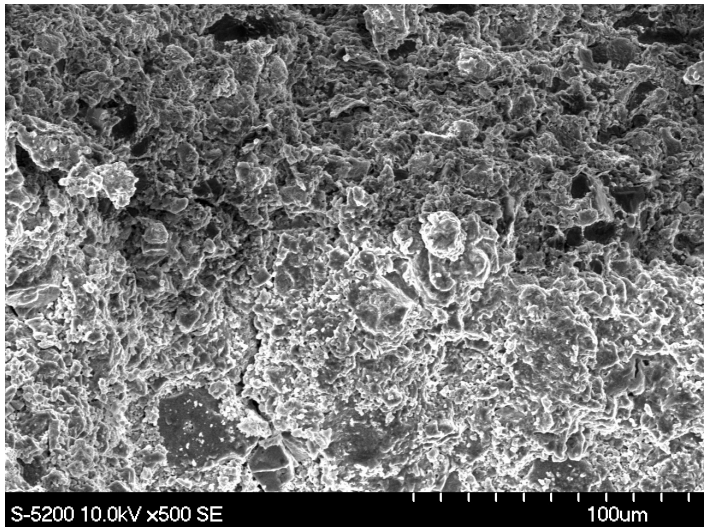
- Both composites are compressible to form robust cathode/SE bilayer discs
- LPSC glass electrolyte serves as binder
- hG as “cold pressable hosts” is not an obvious advantage…?

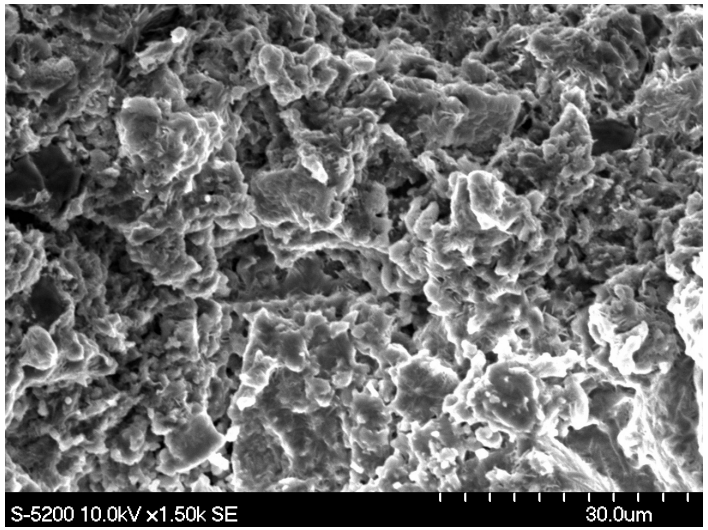


Dry-Pressed Cathode/SE Bilayers

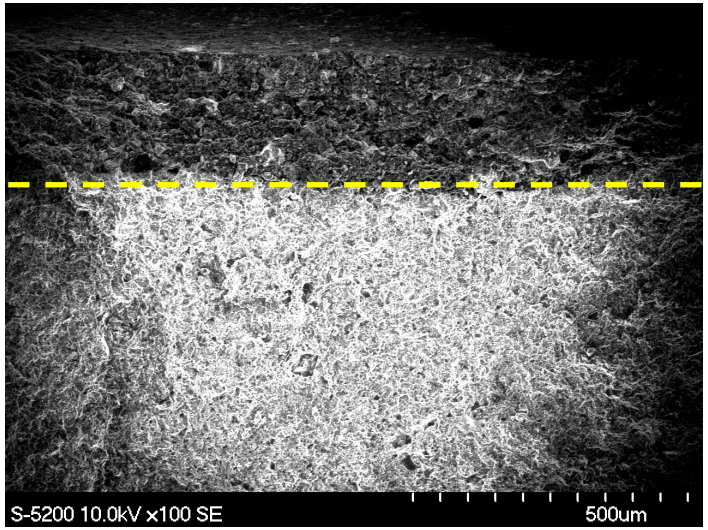
hG

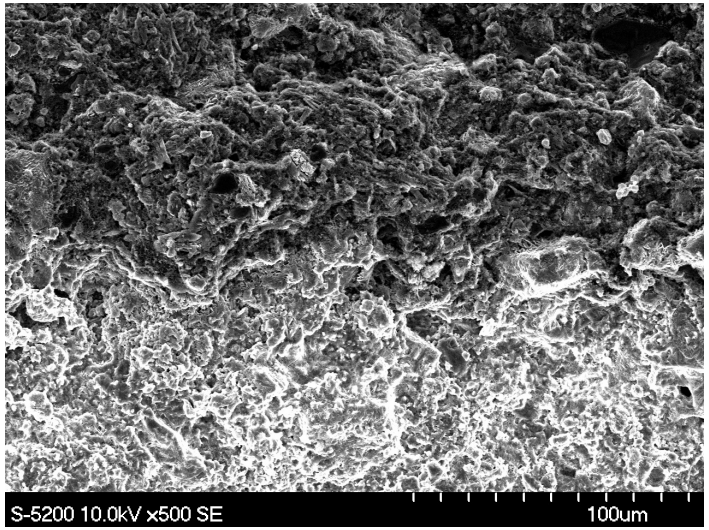


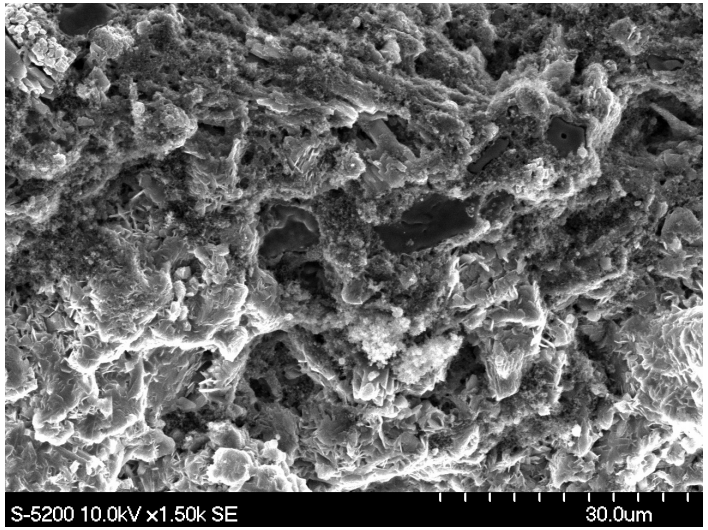




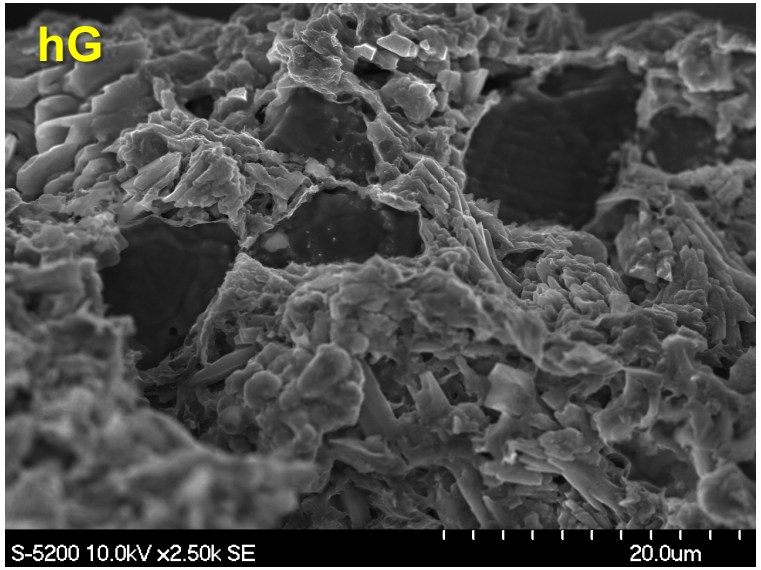
CB

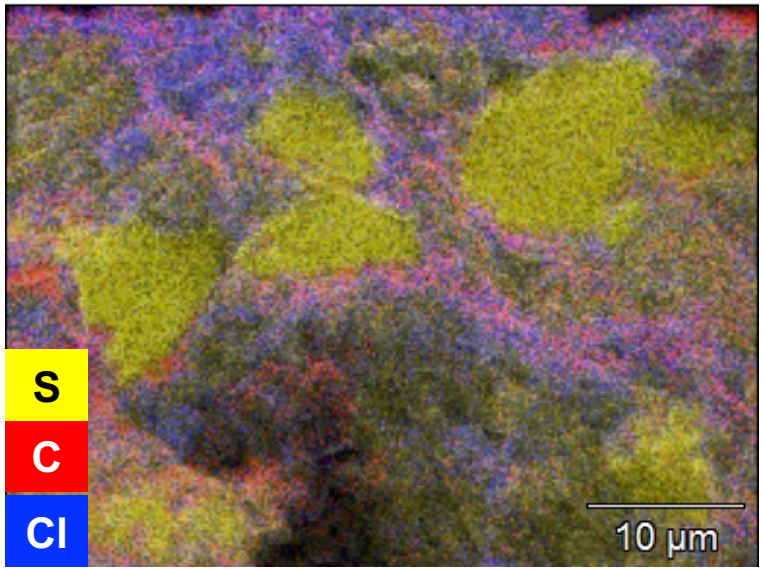


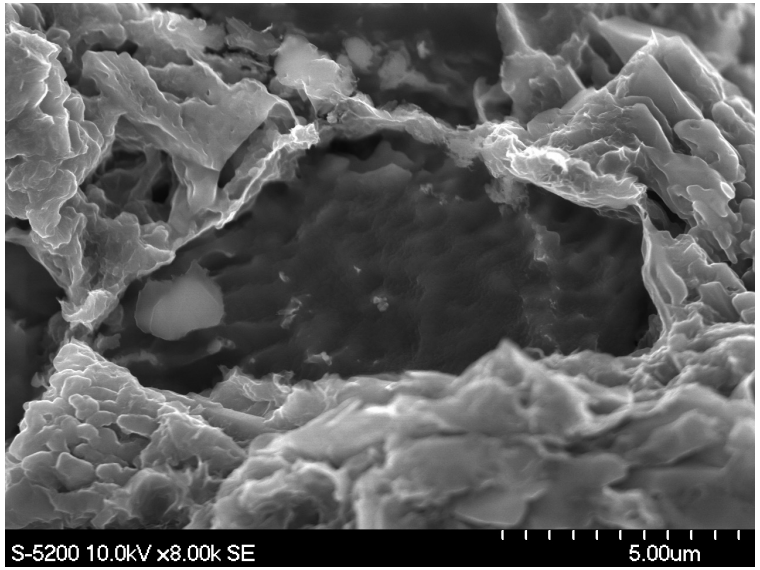


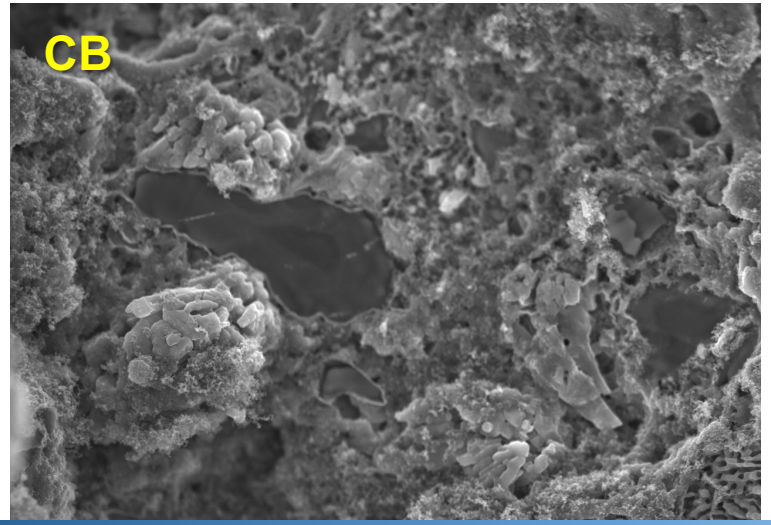


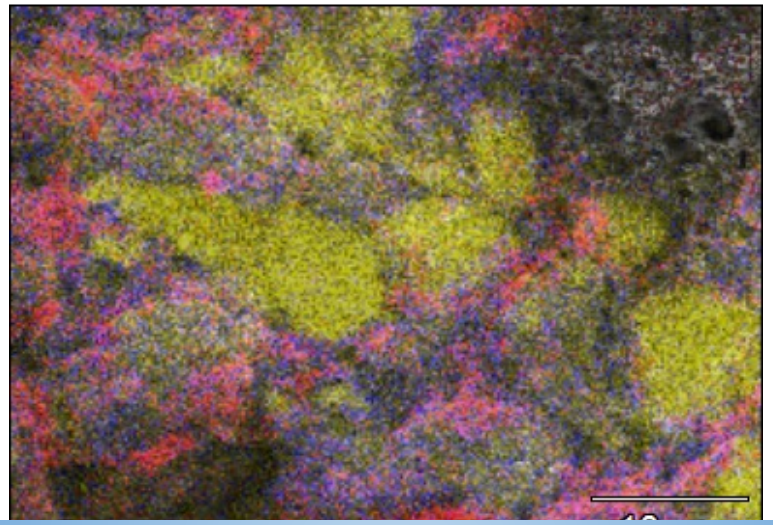
Cathode Microstructures

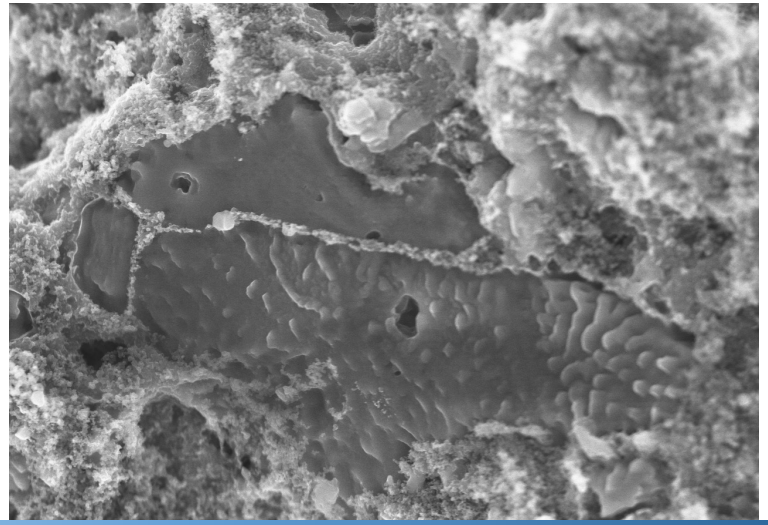






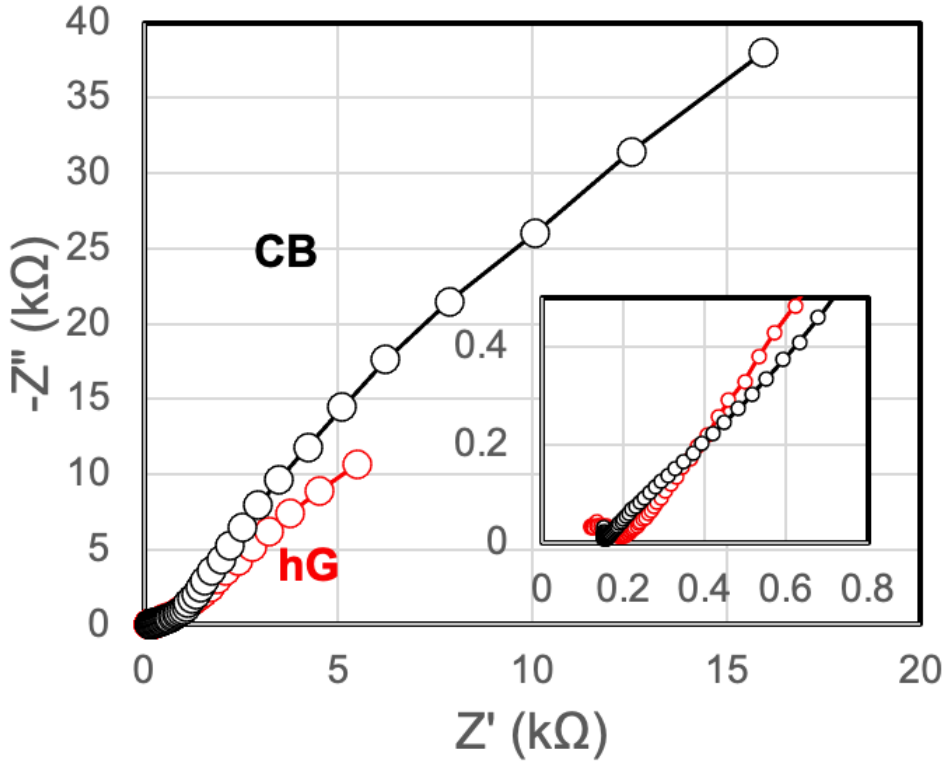




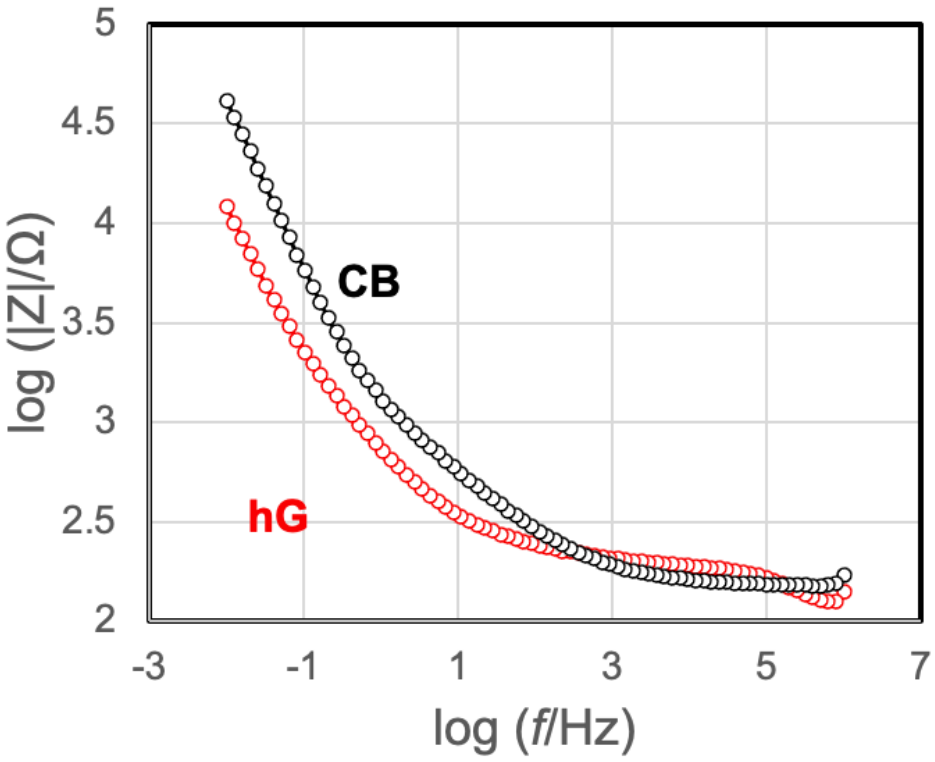


All-Solid-State Li-S Cell Impedance Characteristics

Nyquist Plot



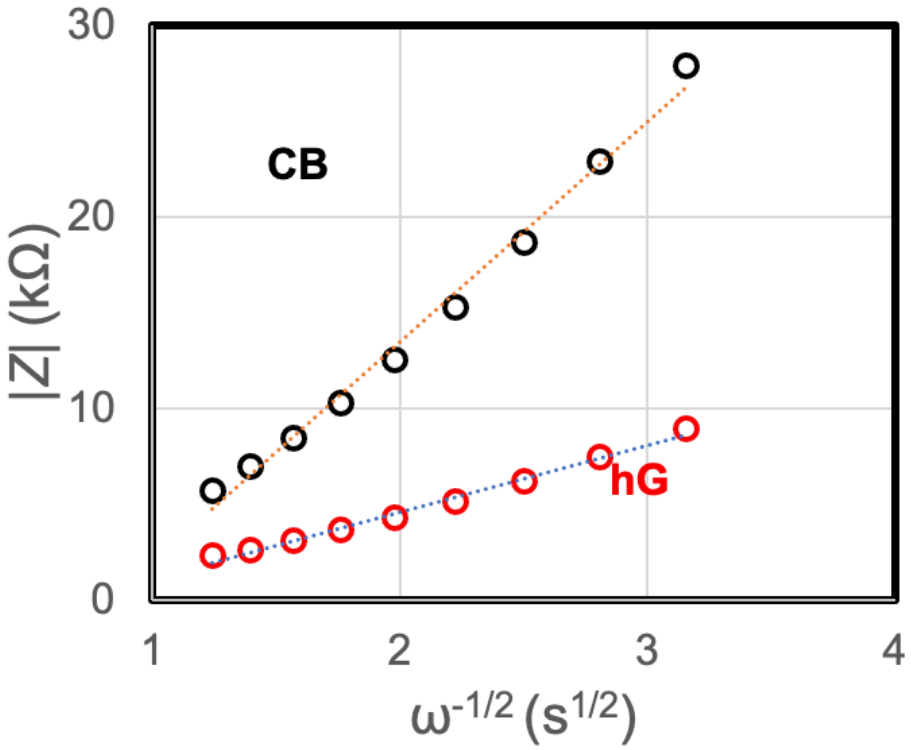
Bode Plot



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

Li Ion Diffusion Properties

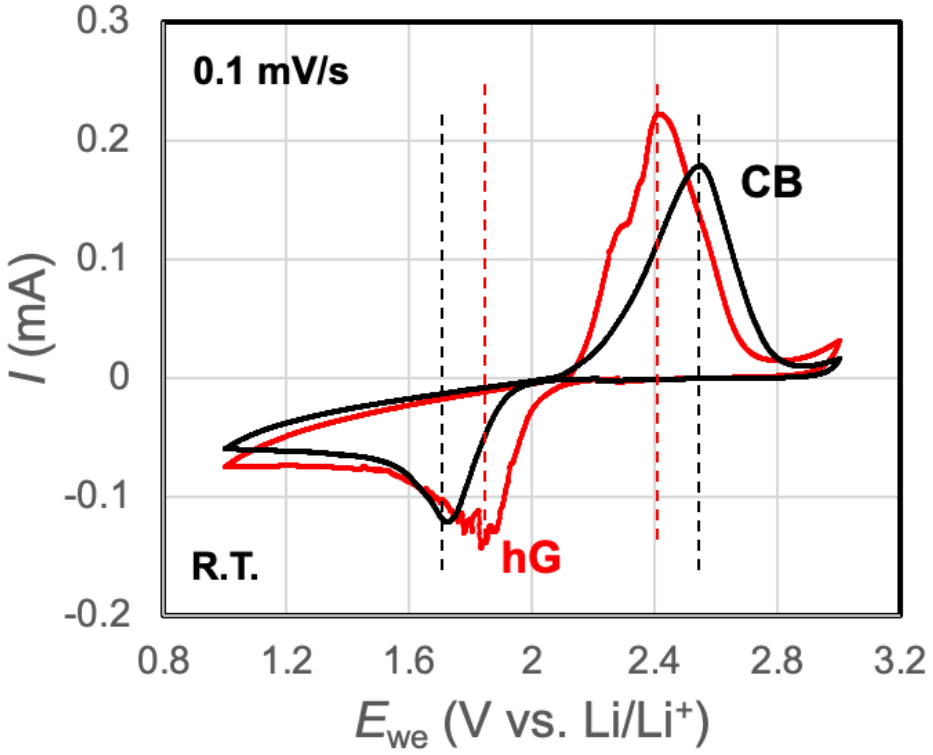
$$D_{Li^+} = \frac{R^2T^2}{2A^2n^4F^4c^2\sigma_w^{\ 2}}$$

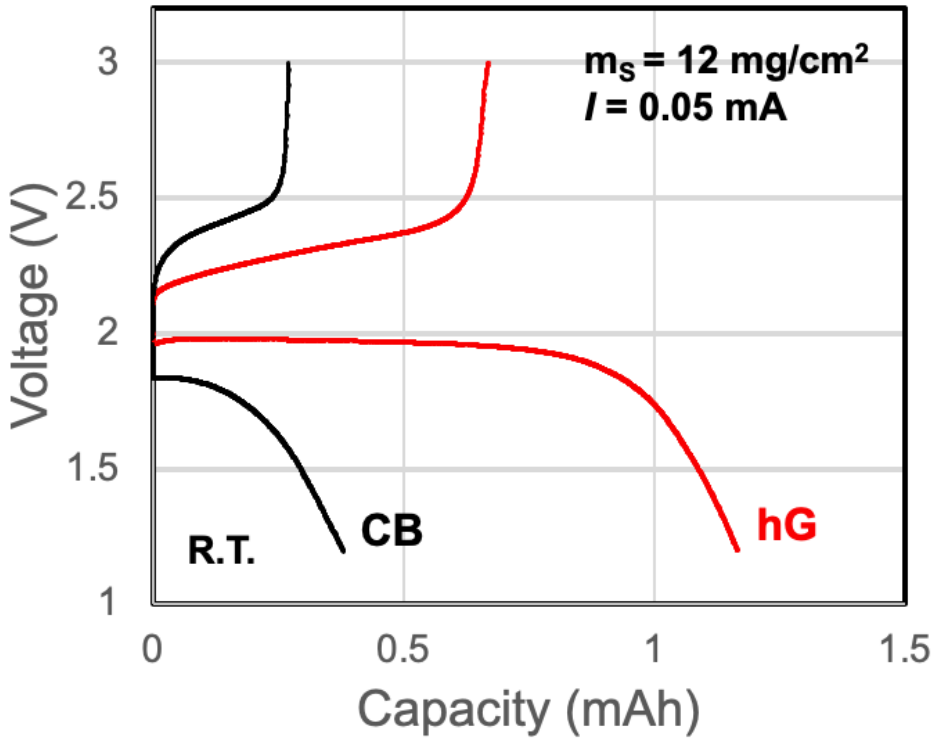


	D_{Li+} (cm^2/s)
CB	3.0×10^{-18}
hG	3.9×10^{-17}

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

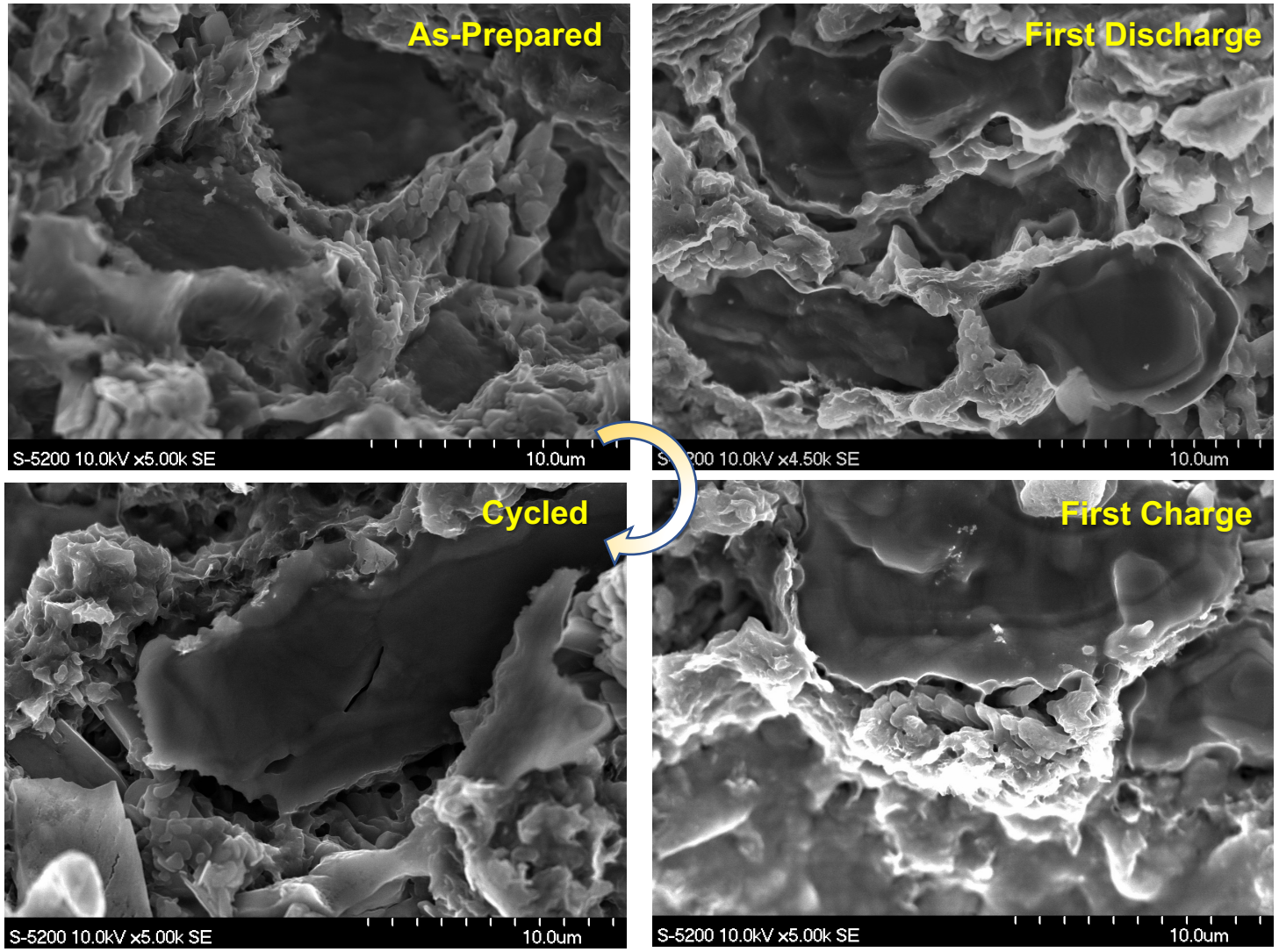
All-Solid-State Li-S Cell Performance





- The use of hG in comparison to CB results in :
  - Lower overpotential
  - Higher discharge capacity

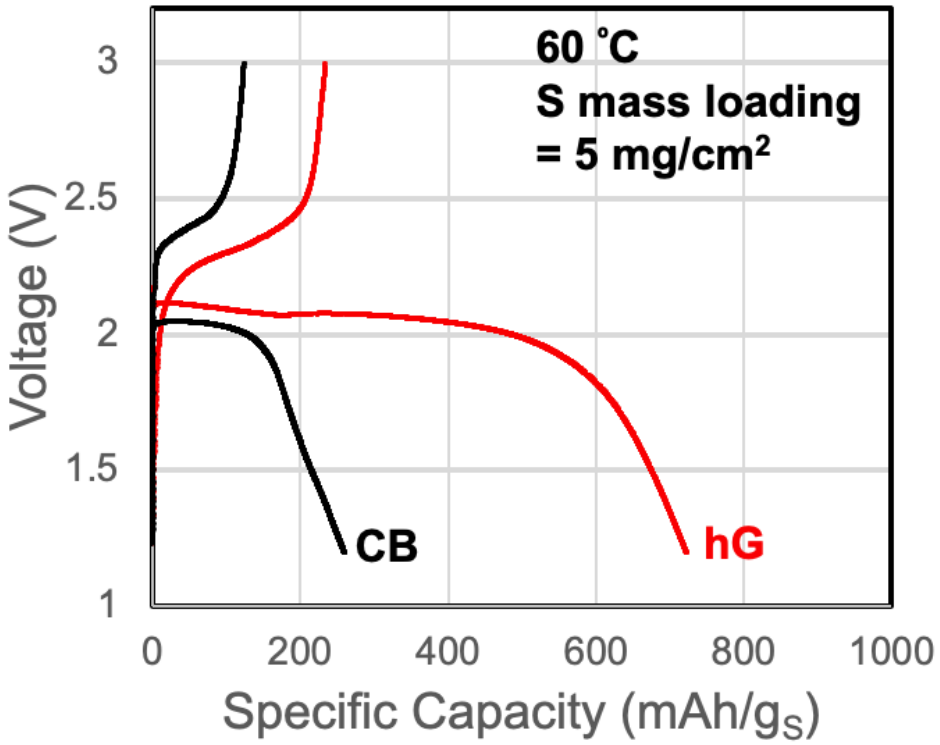
Cathode Post-Mortem Morphology



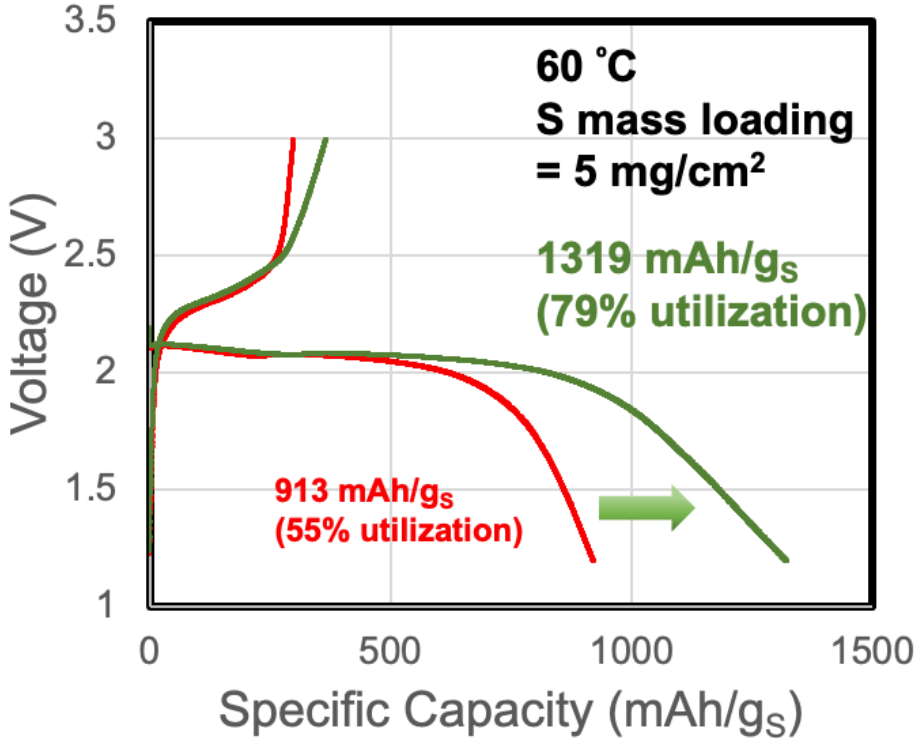
- Expected volume expansion and contraction of S upon discharge and charge
- Low total S utilization at current conditions
- Detachment of S with surrounding ion (SE) and electrical (C) conductors
- Better S-conductor contacts are needed

Strategies toward High S Utilization

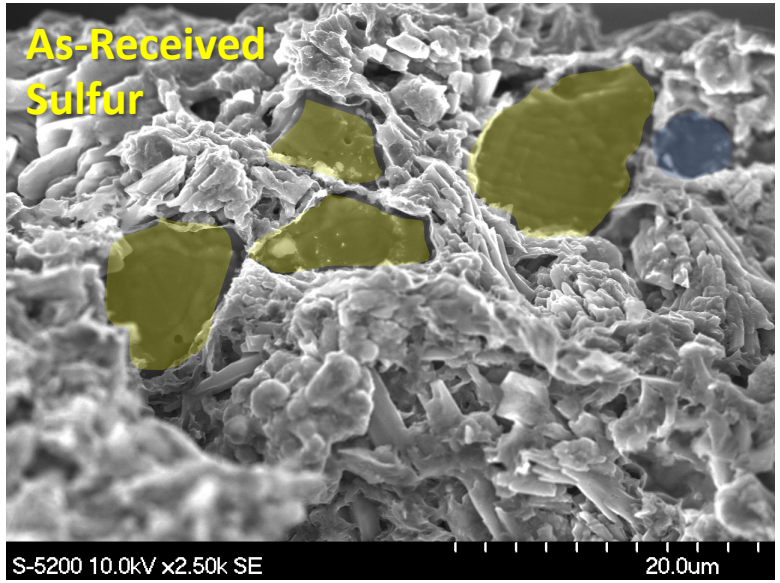
Increase Operation Temperature

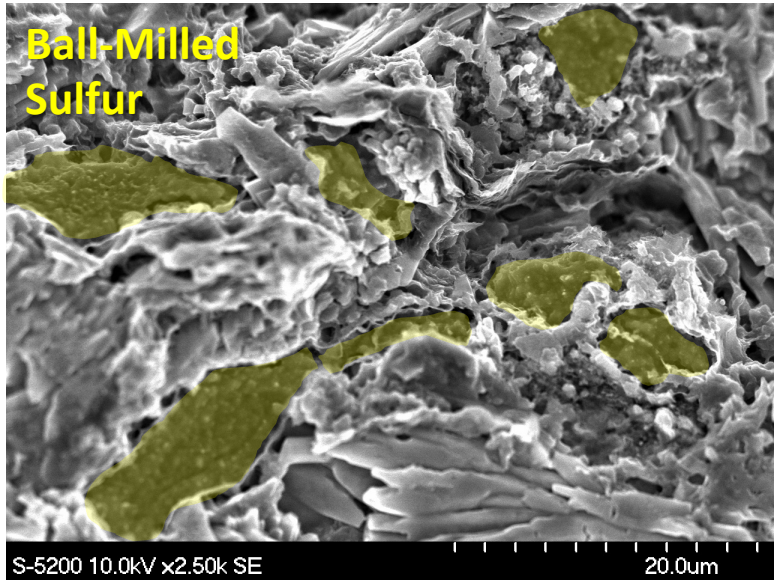


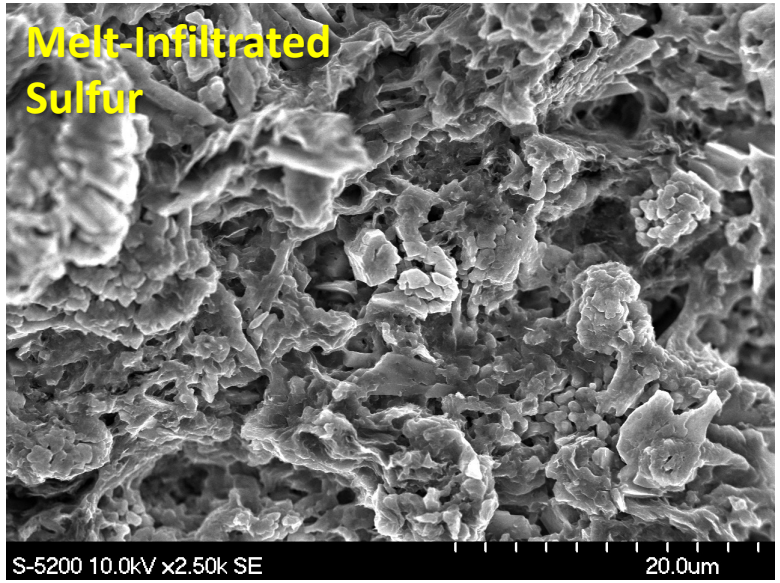
S Melt Infiltration



Morphology of mS in Cathode Discs

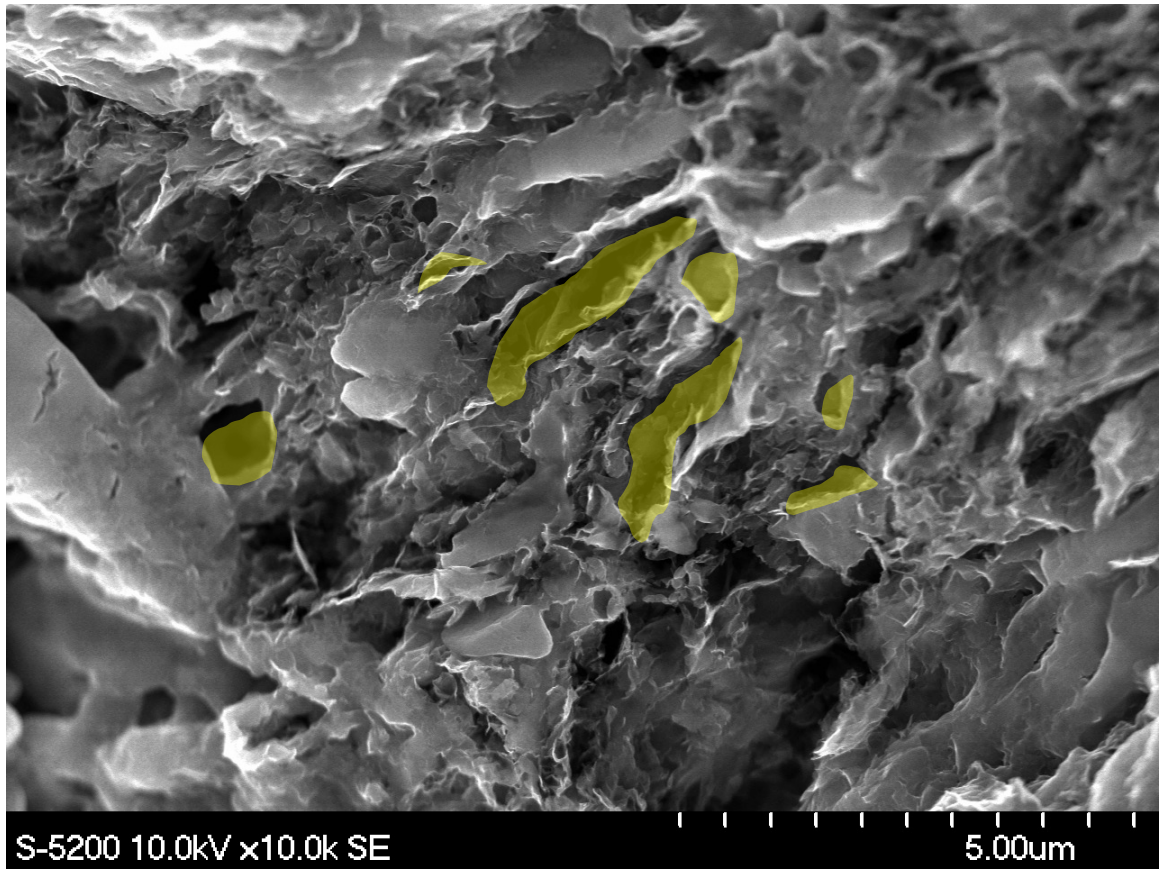






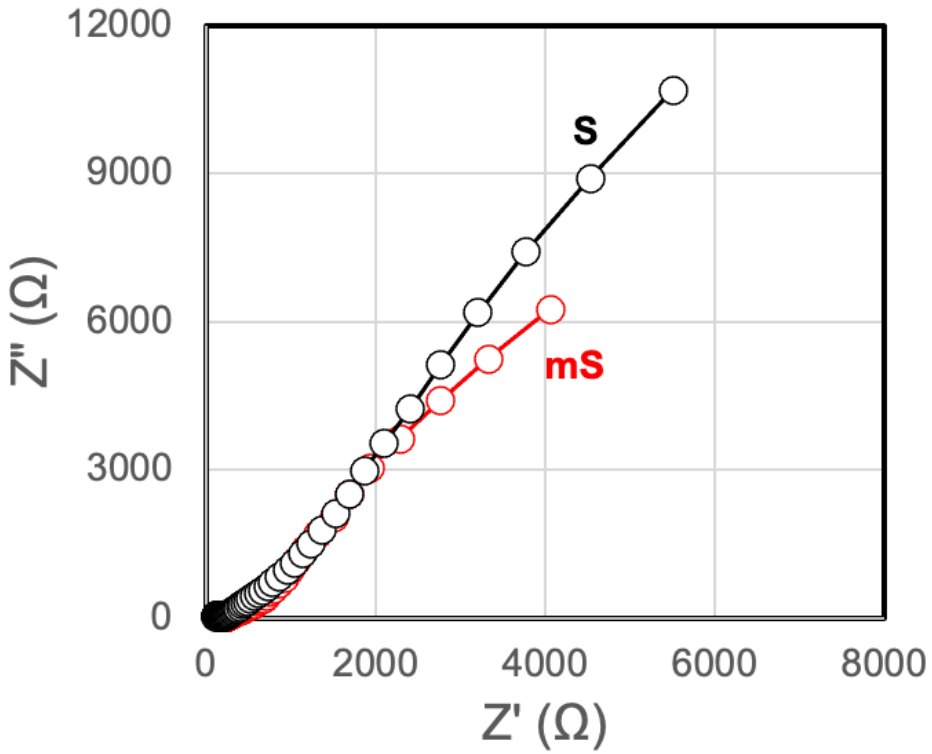
mS = melt-infiltrated S

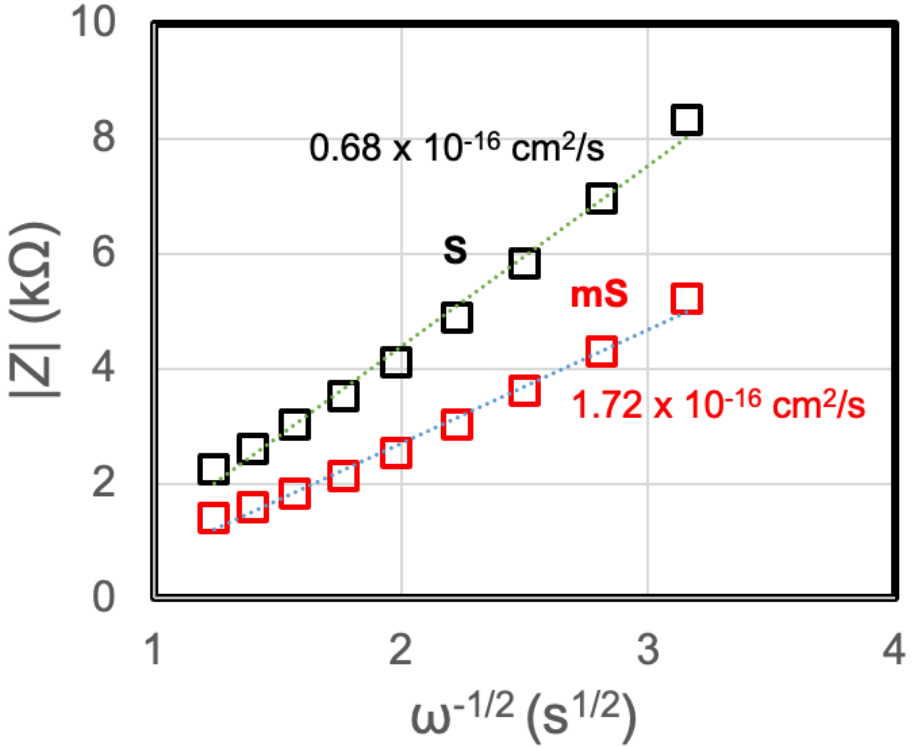
Morphology of mS in Cathode Discs



mS = melt-infiltrated S

mS Improves Cathodic Interphase Contacts

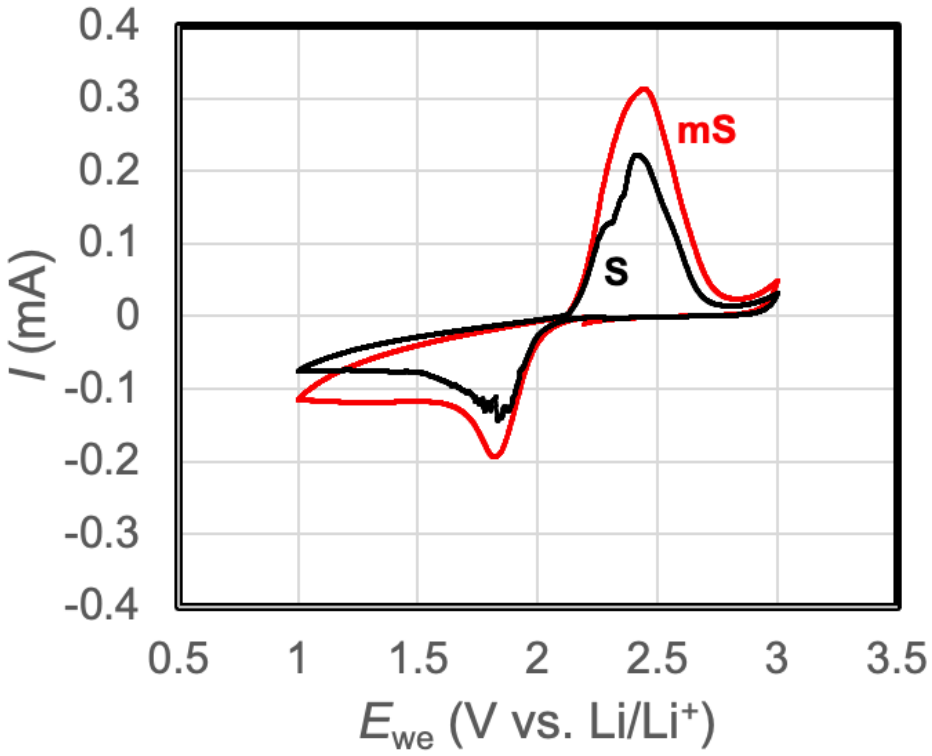


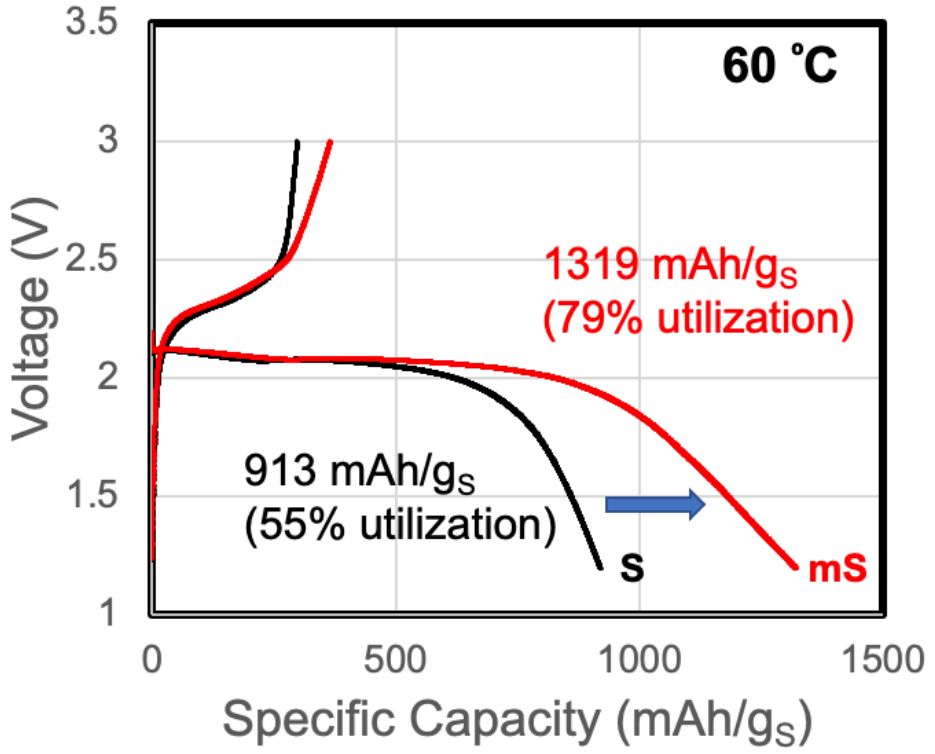


- ~3 times Li^+ diffusivity

mS = melt-infiltrated S

mS Improves Utilization

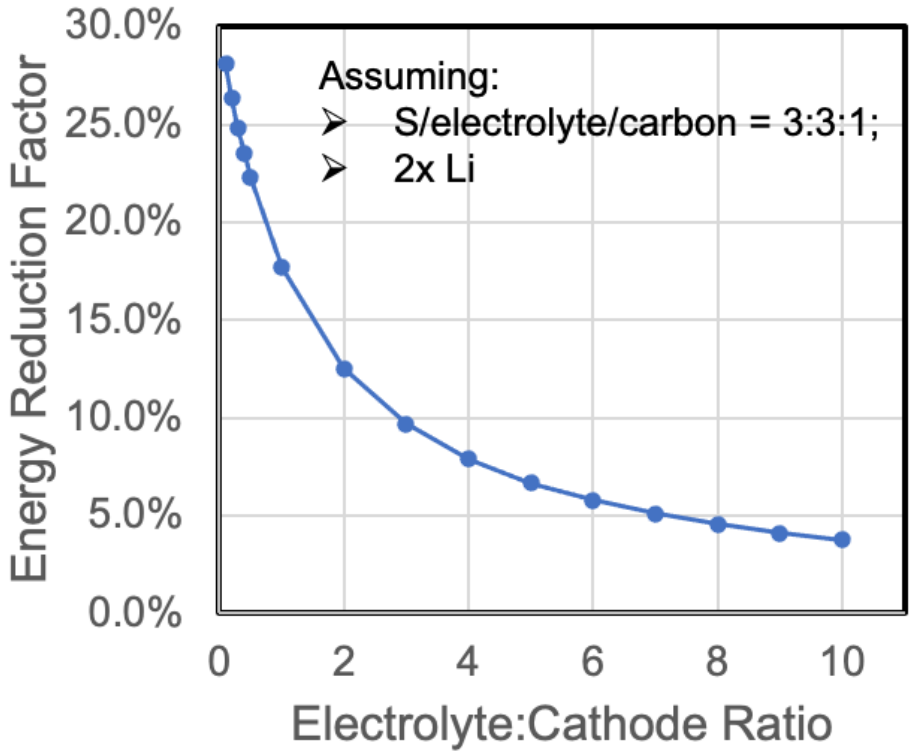


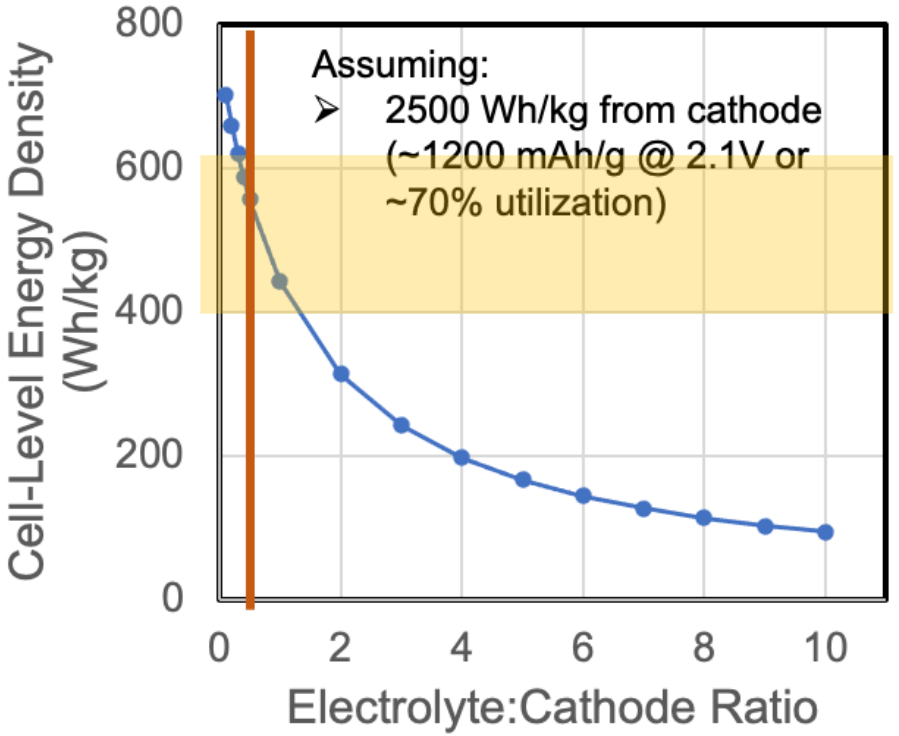


mS vs. S:

- ❑ Higher utilization @ 5 mg/cm^2 (i.e., more active materials are available)
- ❑ Similar overpotential (i.e., active material has similar electrochemical surroundings)

Toward 500 Wh/kg

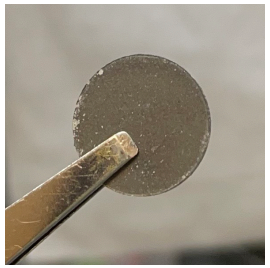


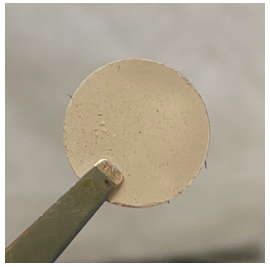


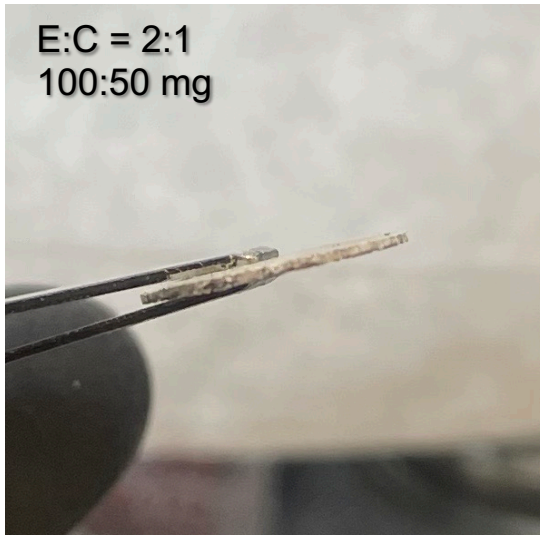
- Thinnest dry-press LPSC currently achieved experimentally: ~20 mg/cm^2
- High mass loading can dilute the requirement of absolute electrolyte thickness and also help with the pack-level energy density
- To reach 500 Wh/kg, it would require, for example, a minimum S mass loading of 8.6 mg/cm^2 @ E:Cathode = 1:1
- Higher mass loading would lead to lower rate and utilization

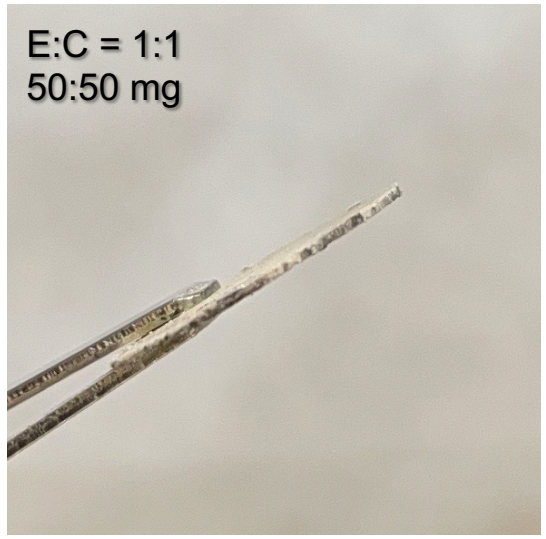
Challenges in Fabrication

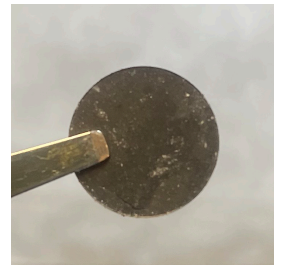


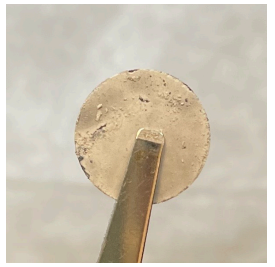




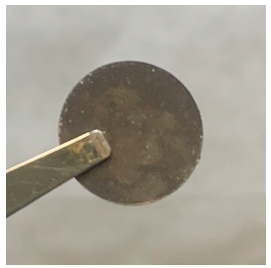


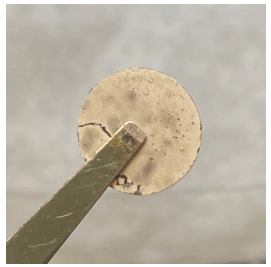


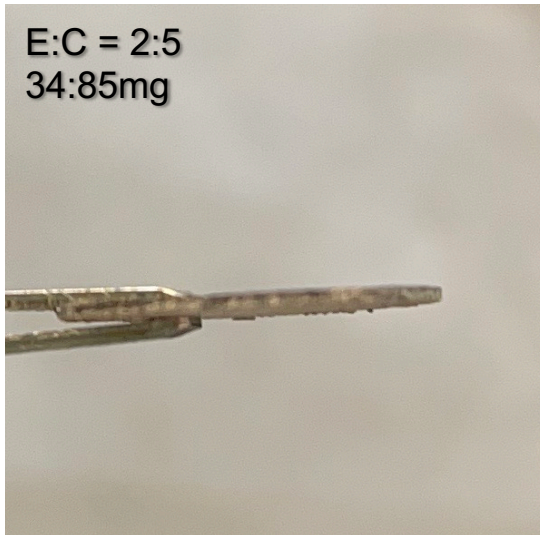


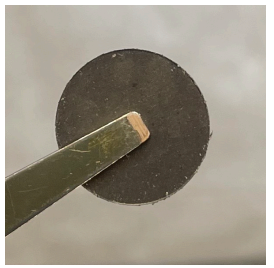


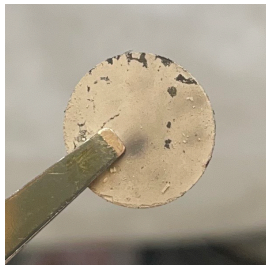






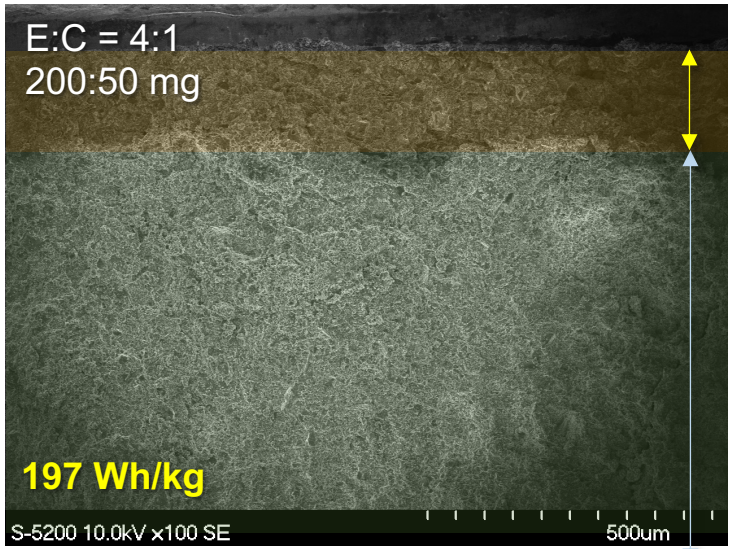


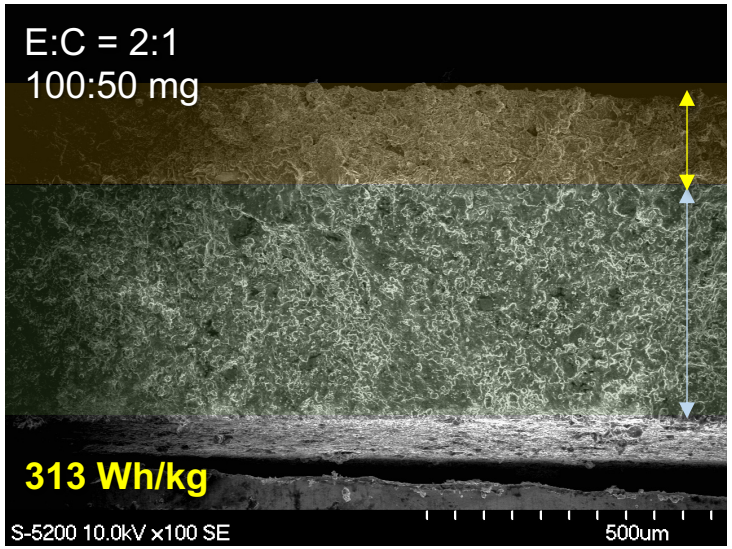


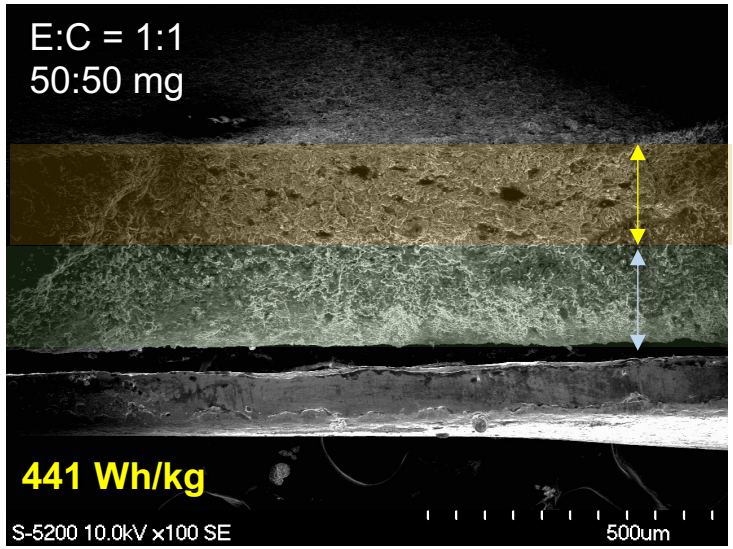


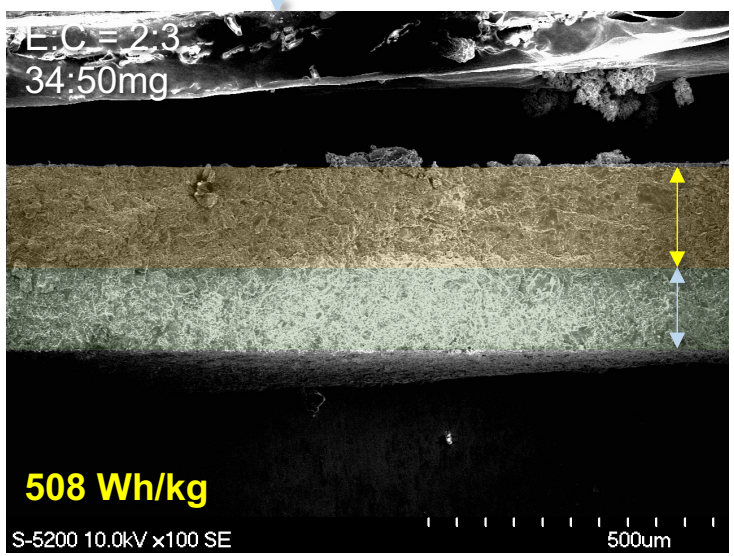
E: solid electrolyte
C: cathode

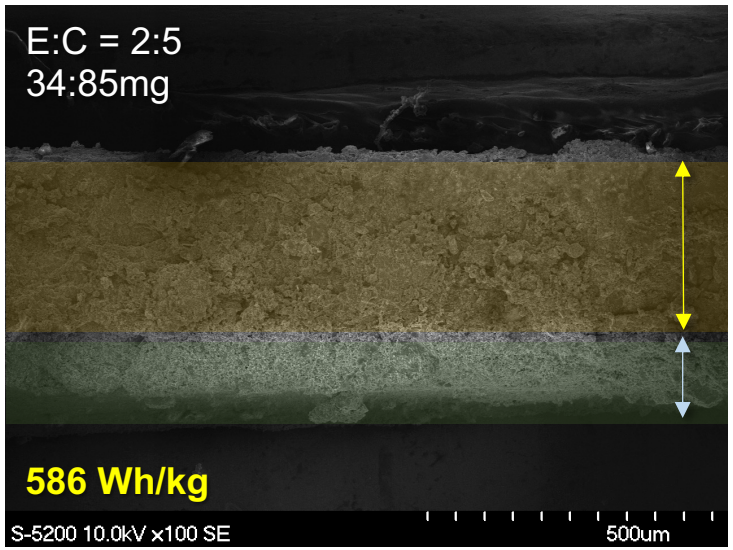
Pushing the Limit in Specific Energy











~300 um **Cathode Layer**

~140 um **SE Layer**

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
- A specific energy path toward **500 Wh/kg** may be feasible

Acknowledgements

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- NASA **SABERS** Team

- Student Interns:
  - 2015: Evan Walsh; Steven Lacey
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  - 2017: Sterling Baird; Kobi Jones; Marina Chang; Joshua Jack
  - 2018: Francisco Mendez Sosa; Louisa Greenburg
  - 2019-2020: Christian Plaza-Rivera; Nam Tran; Bryson Clifford
  - 2020-current: Brandon Walker; April Rains