



Holey Graphene for Advanced Batteries

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Outline

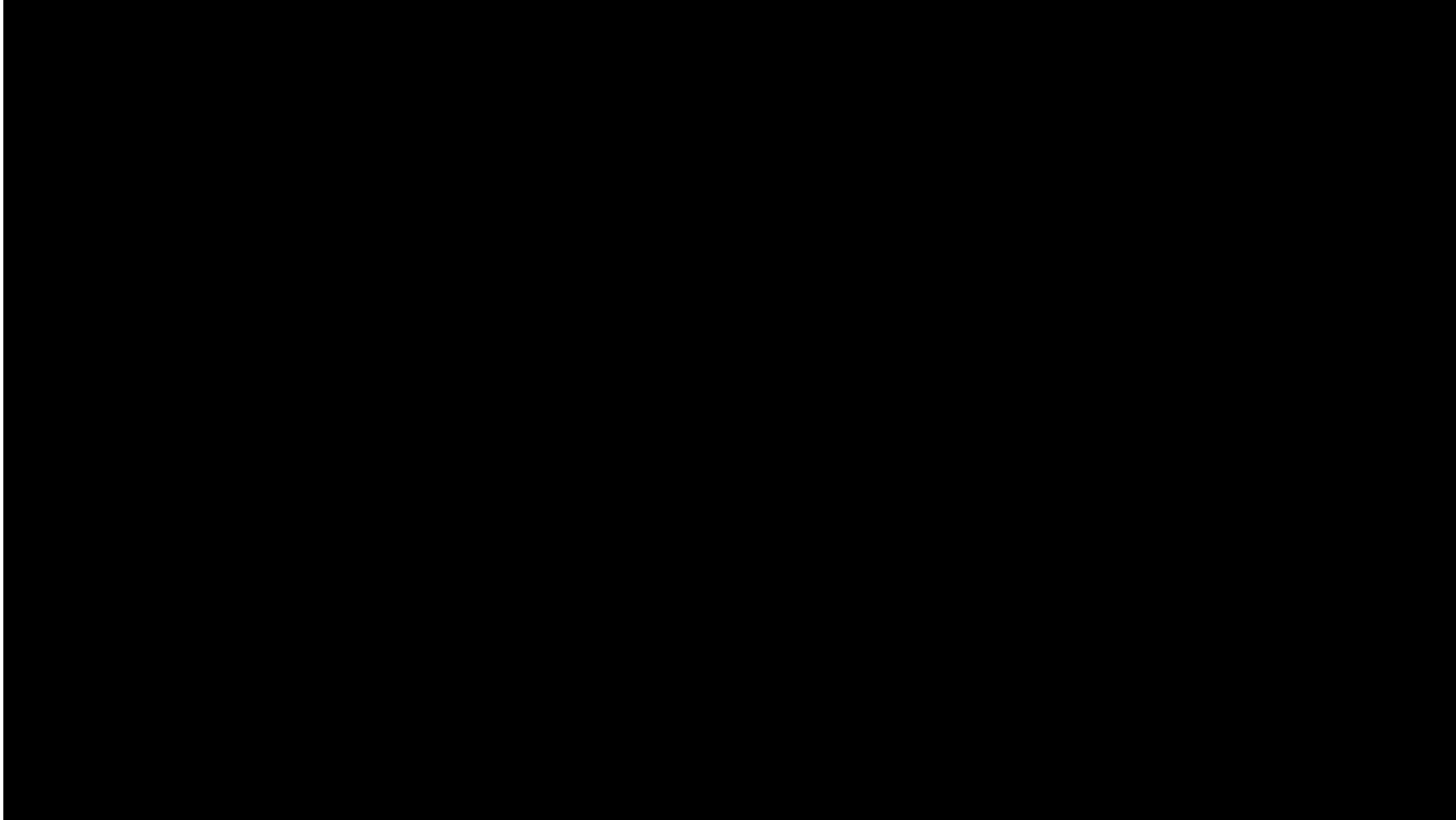
- ❑ Holey graphene: A brief history

- ❑ Holey graphene for dry-press fabrication of advanced electrodes
 - ❑ Li-air batteries
 - ❑ Li-sulfur/selenium batteries
 - ❑ Solid-state batteries

- ❑ Summary

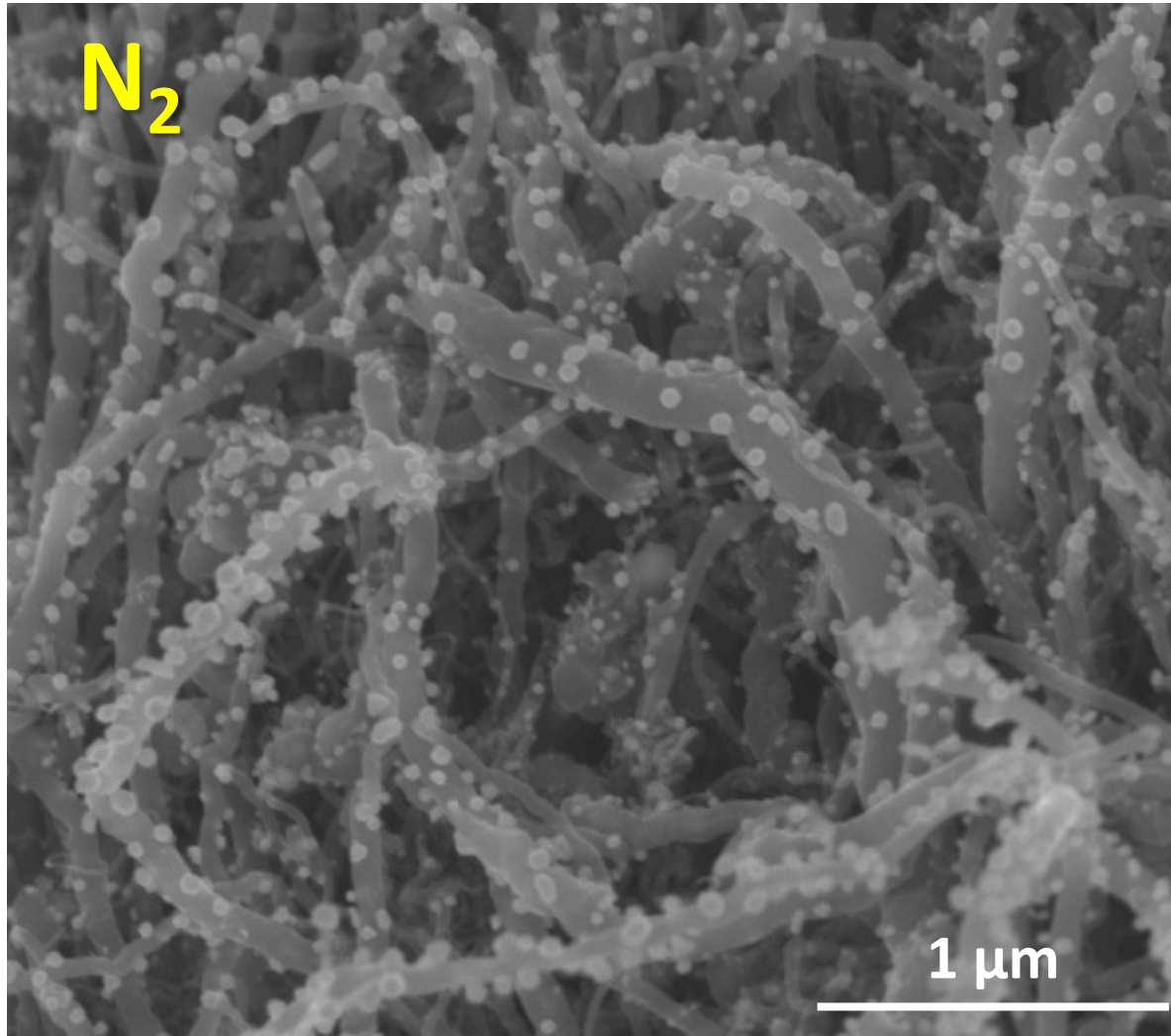
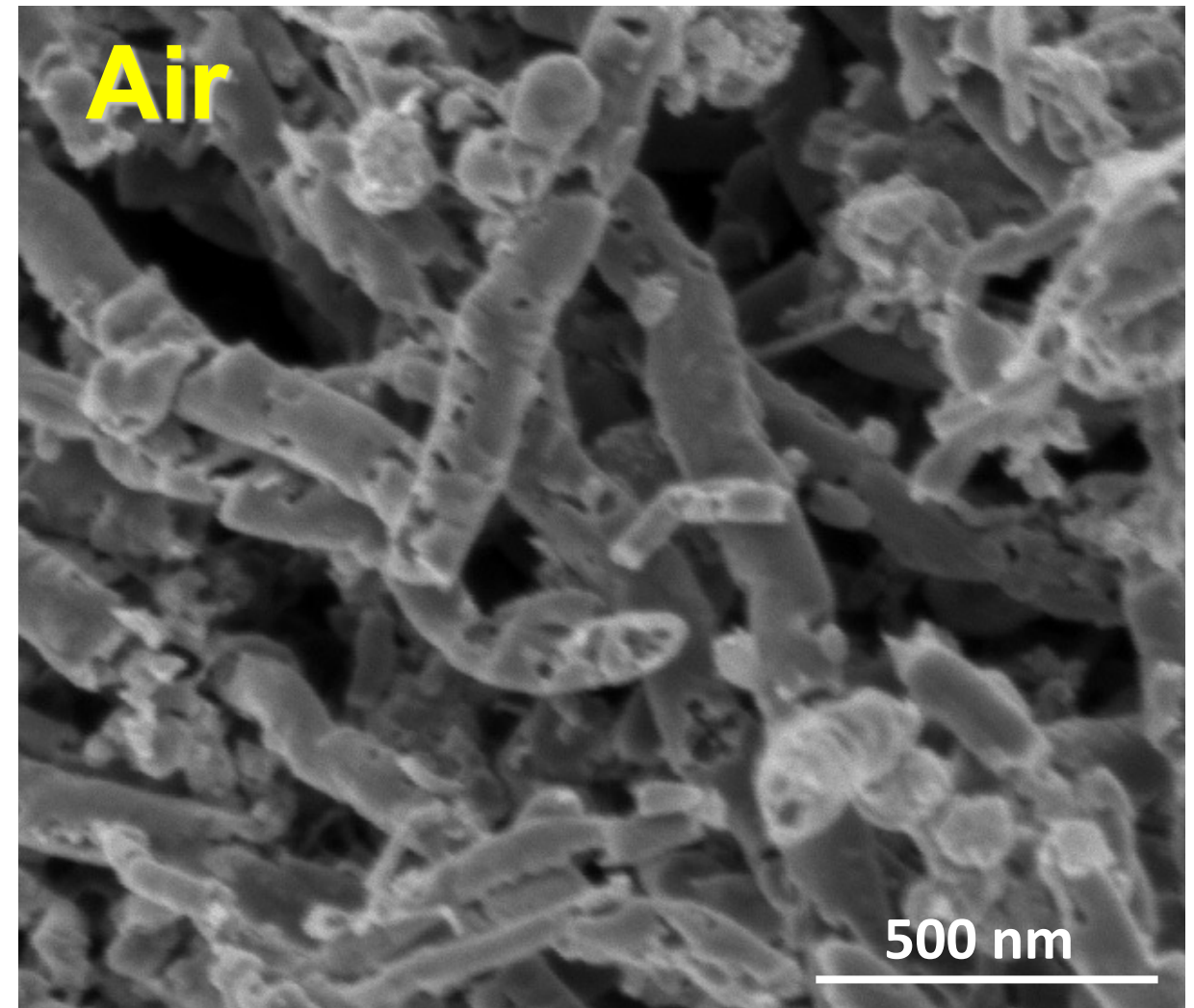
- ❑ Acknowledgements

Holey Graphene

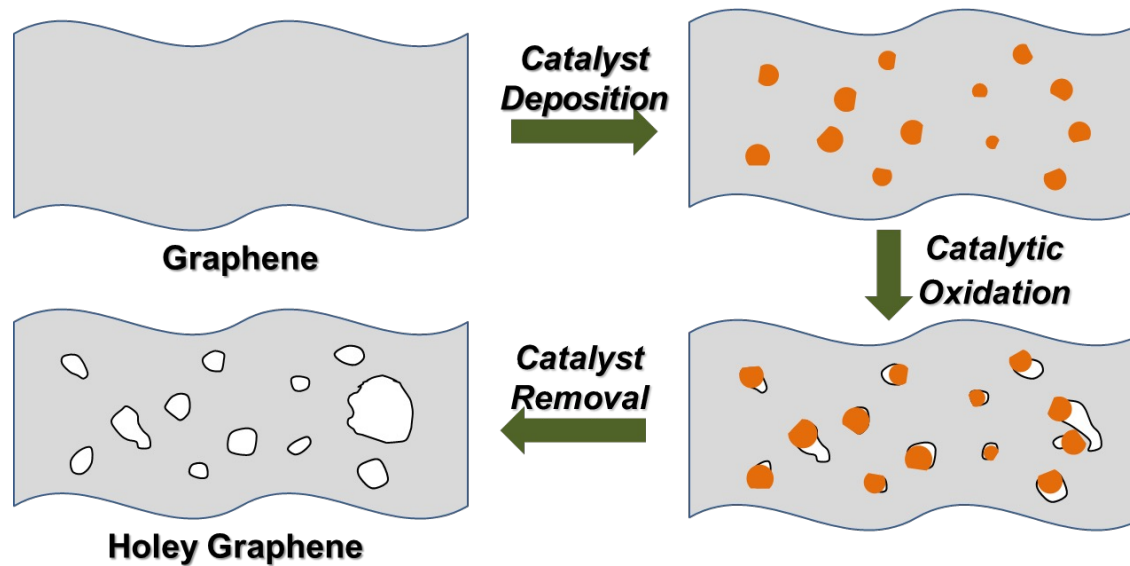


Full version: <https://www.youtube.com/watch?v=OGyn2PjBTN0>

Punching Holes at Nanoscale

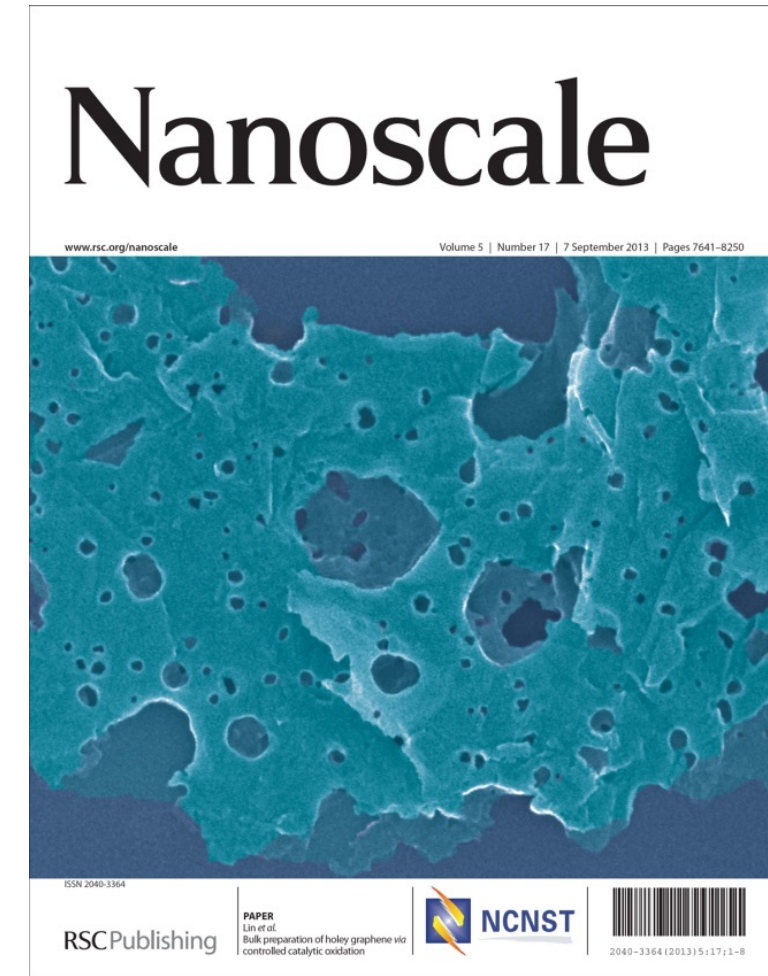


Catalytic Preparation of Holey Graphene



Controlled Catalytic Oxidation

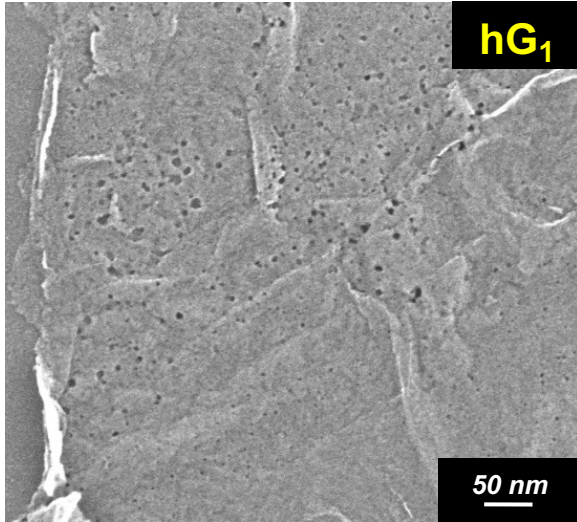
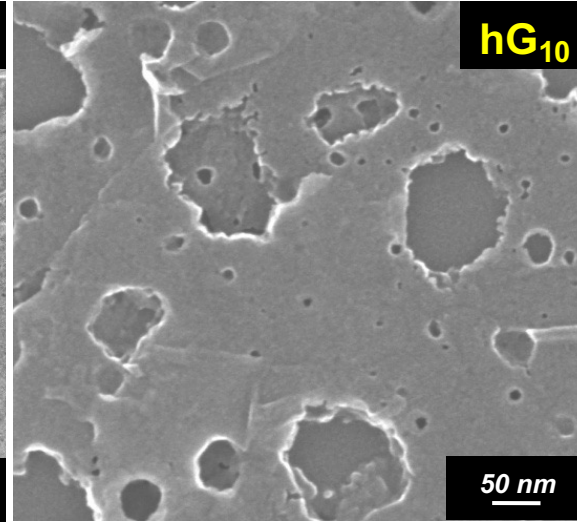
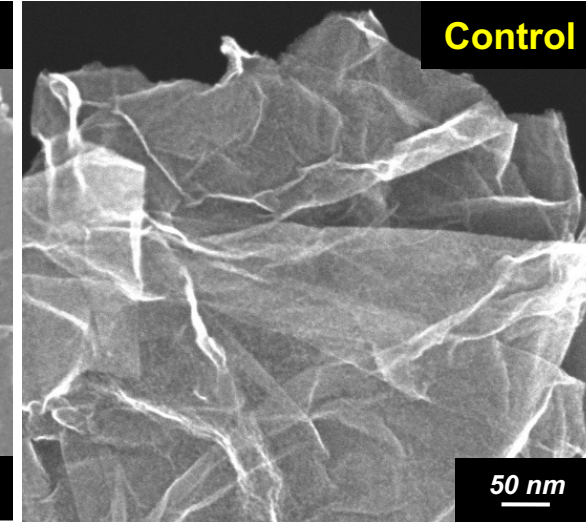
Holey Graphene = hG = h-Graphene



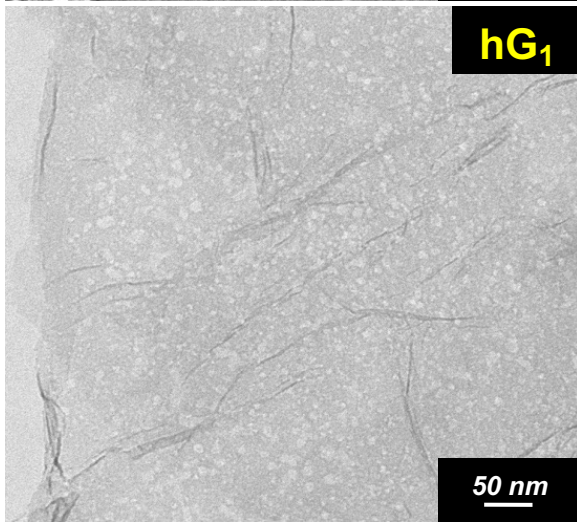
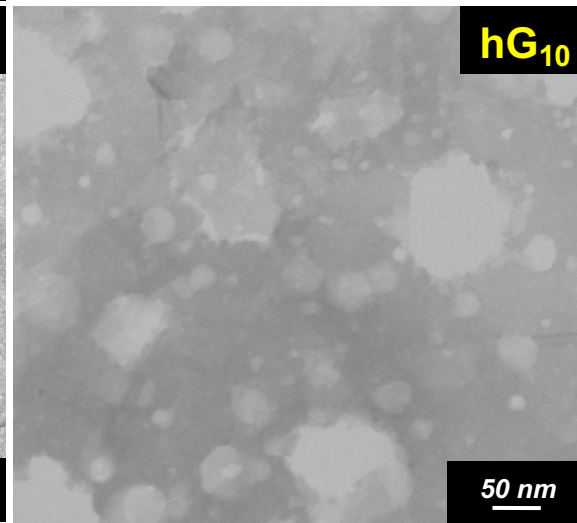
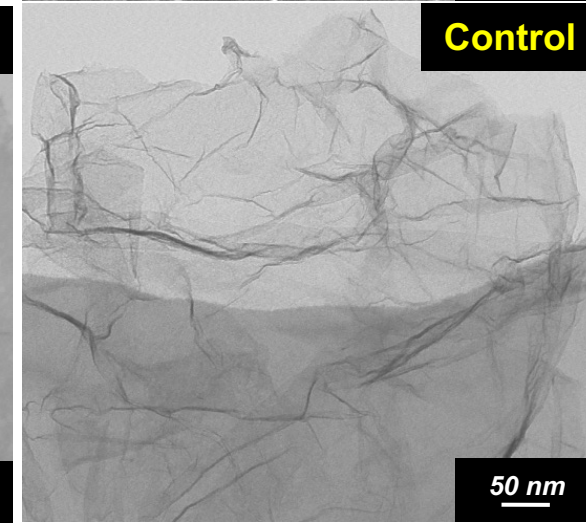
Nanoscale **2013**, 5, 7814.

Hole Size Control

SEM

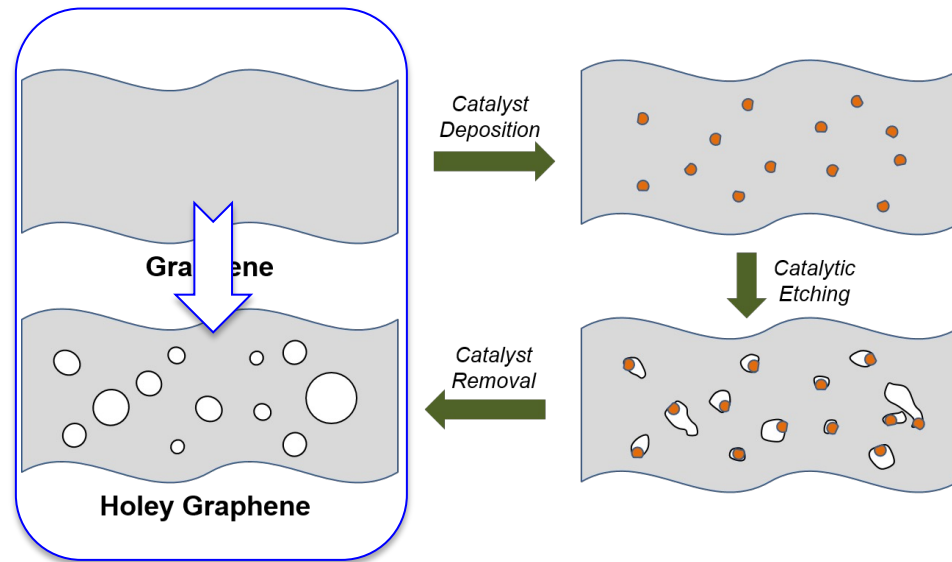


TEM

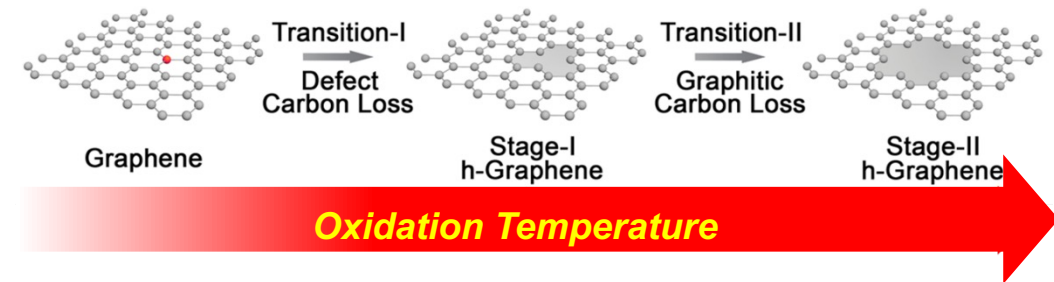


- ☐ **Catalyst Removal:** HNO₃ (2.6 M), 2h reflux
- ☐ **hG_x** (X: Starting Ag Content)

Catalyst-Free Synthesis of Holey Graphene



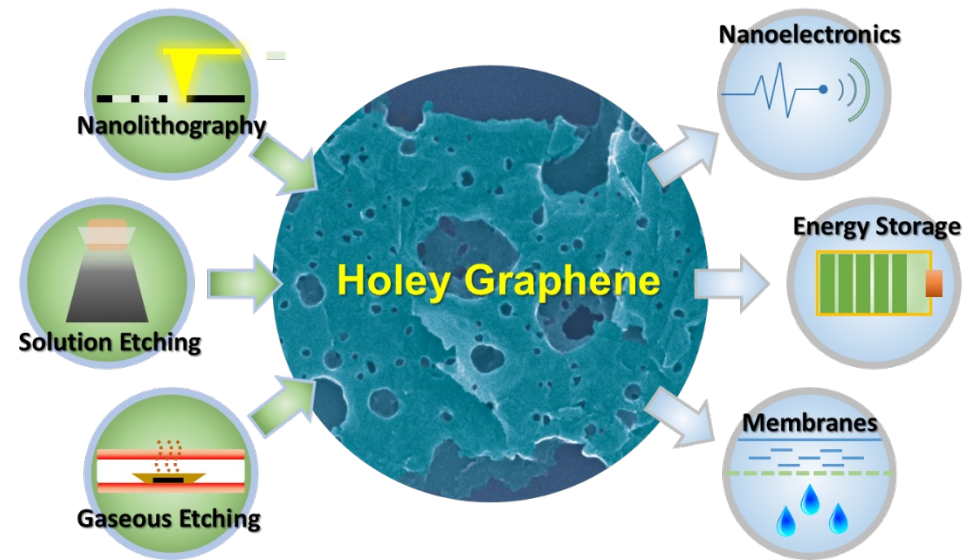
“Generation II”



Single Step + Catalyst-Free = Highly scalable!

ACS Nano **2014**, 8, 8255; *Adv. Func. Mater.* **2015**, 25, 2920.

hG: A Structural Derivative of Graphene



Holey graphene ≠ Porous graphene

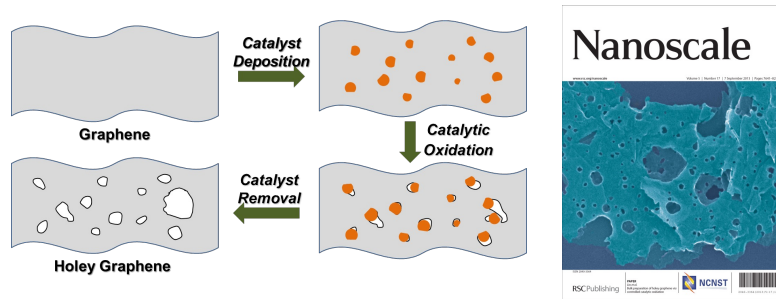
- “Holes”: large graphitic structural defects and pertinent to the graphitic sheet structure
- “Pores”: Empty spaces between the individual graphene sheets

Mater. Res. Lett. **2017** (open access).
(DOI: 10.1080/21663831.2016.1271047)

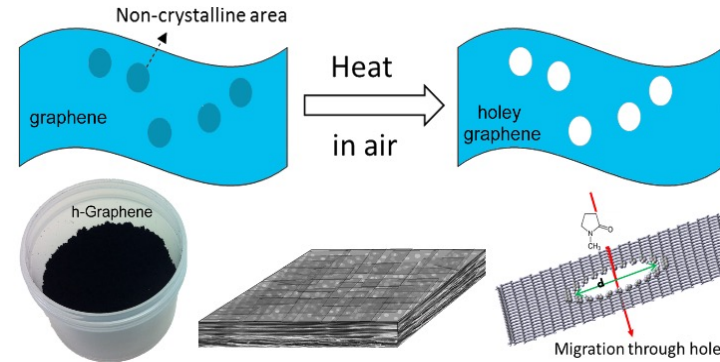
- ☐ Holey graphene is MATERIAL: *Graphene structural derivative*
- ☐ Porous graphene is ARCHITECTURE: *Graphene assembly*

“Porous holey graphene” would be ideal for energy storage applications.

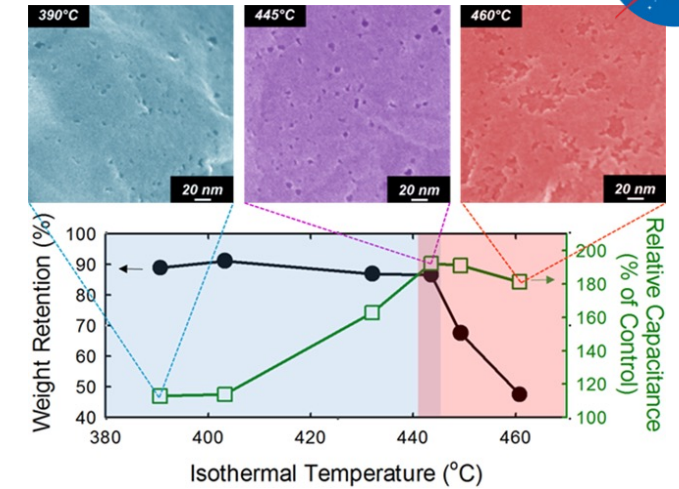
Holey Graphene: Synthesis



Nanoscale **2013**, 5, 7814.

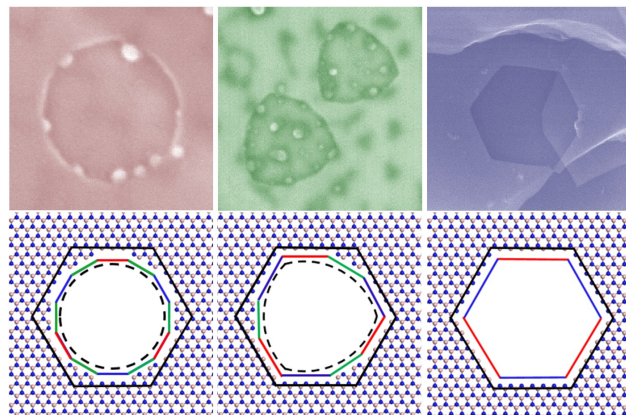


ACS Nano **2014**, 8, 8255.



Adv. Func. Mater. **2015**, 25, 2920.

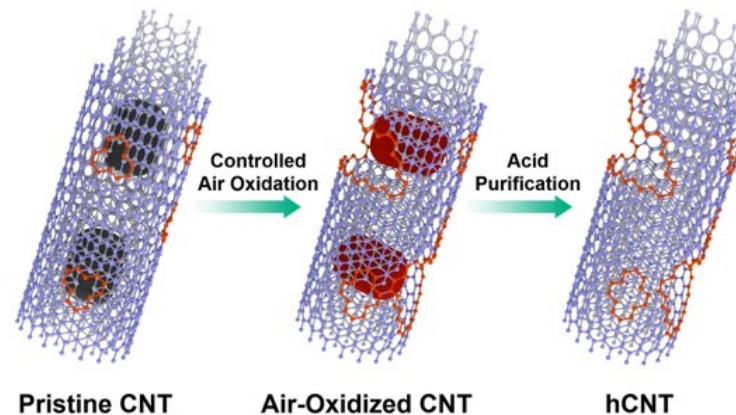
Synthesis from Catalytic Oxidation



Sci. Rep. **2015**, 5, 14510.

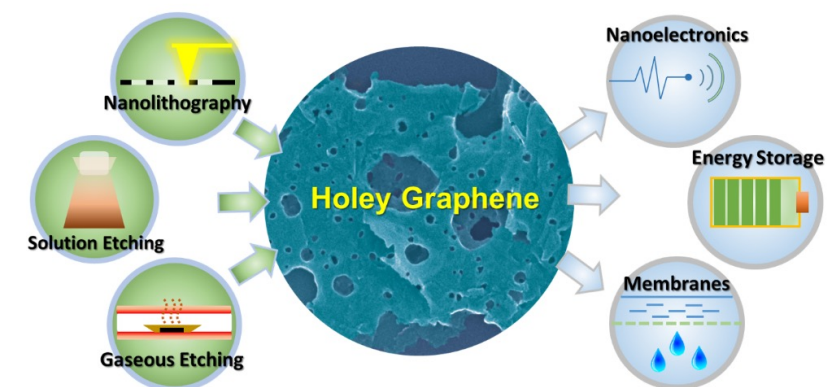
Holey Boron Nitride

Synthesis from Catalyst-Free Air Oxidation



Adv. Func. Mater. **2017**, 27, 1700762.

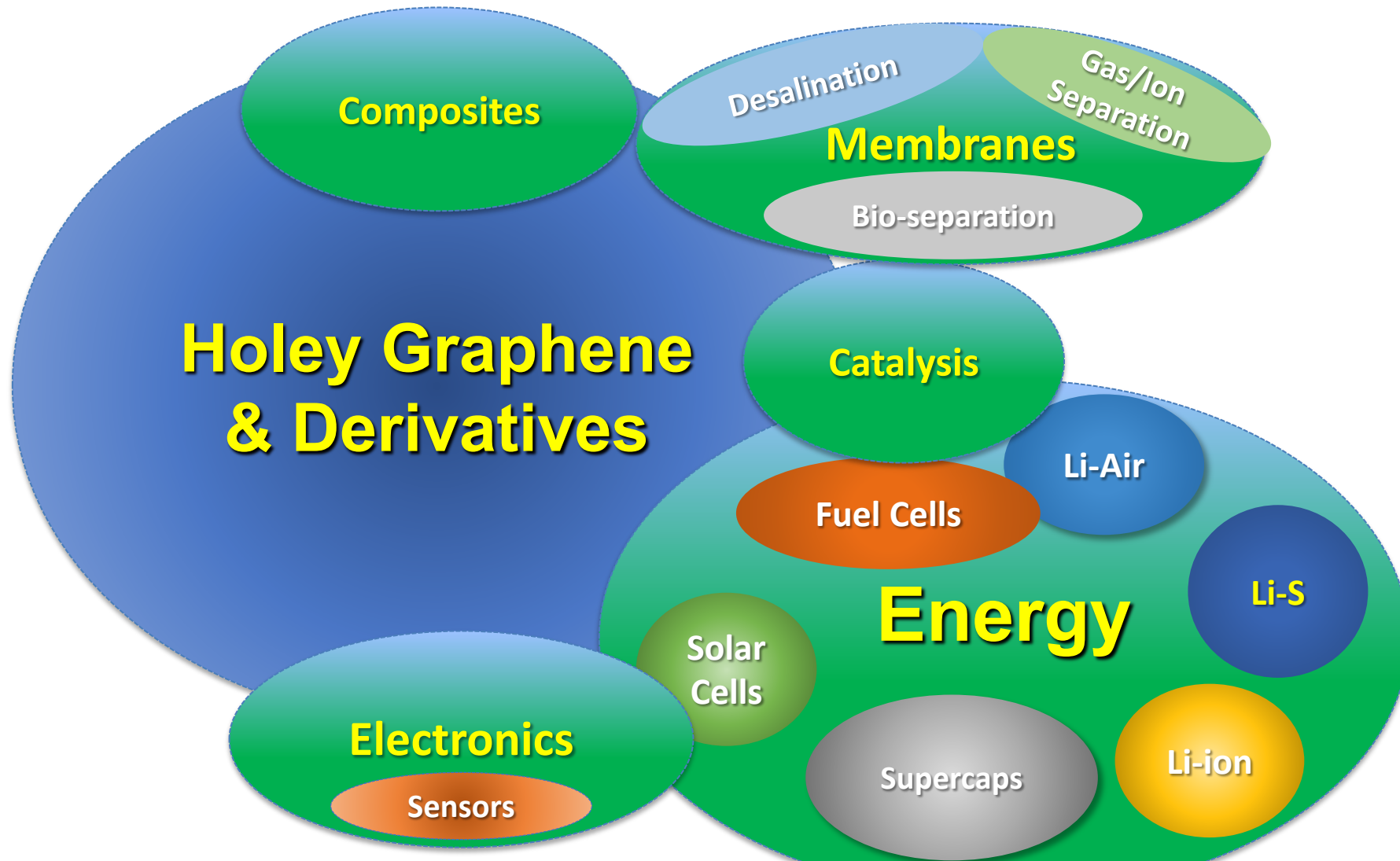
Holey Carbon Nanotubes



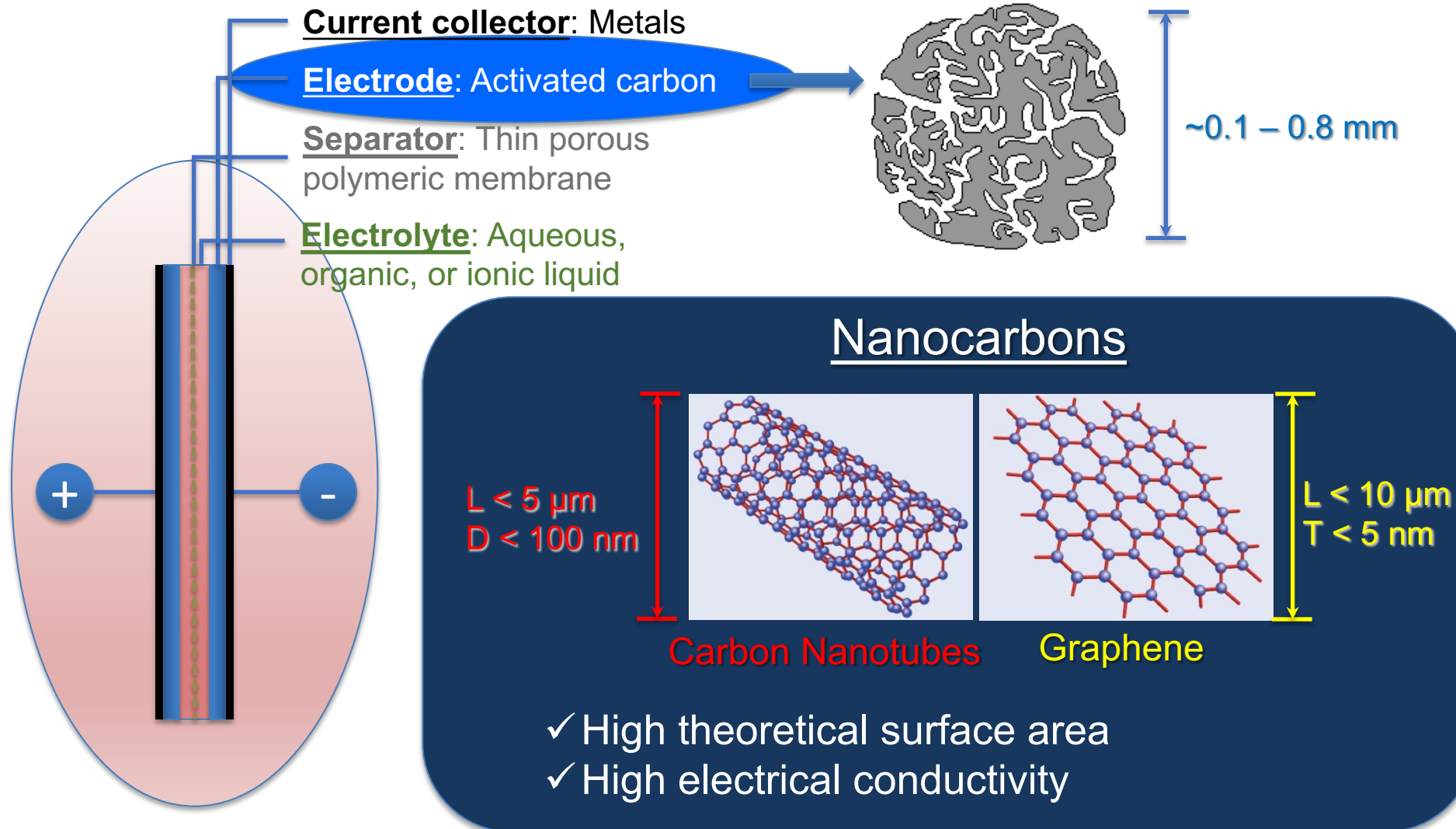
Mater. Res. Lett. **2017**, 5, 209-234.

Holey Graphene ≠ Porous Graphene

Holey Graphene Applications



Nanocarbon Electrodes for Supercapacitors



Foams and Aerogels?

Graphene/CNT
Foams/Aerogels:

- ✓ Lightweight
- ✓ Porous
- ✓ High Surface area

But with large volume



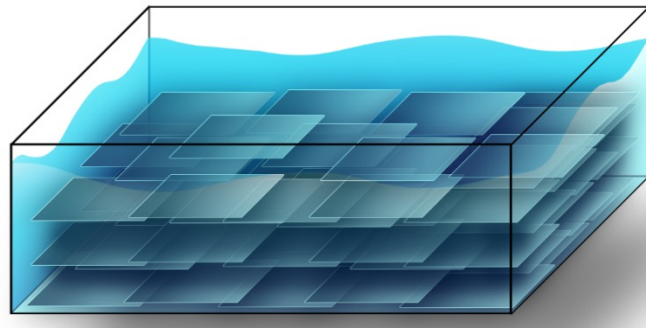
Small Footprint
Energy Storage Devices

Graphene vs. Holey Graphene

Improved ion transport path at high stacking density

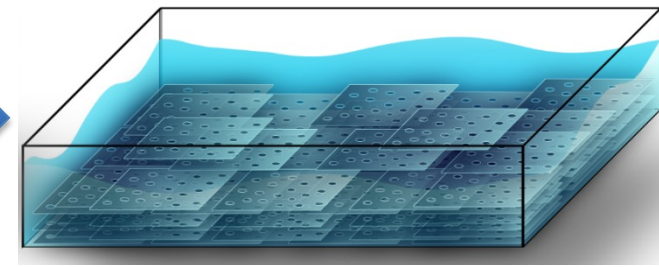


Raw graphene electrode



High volume

Holey graphene electrode



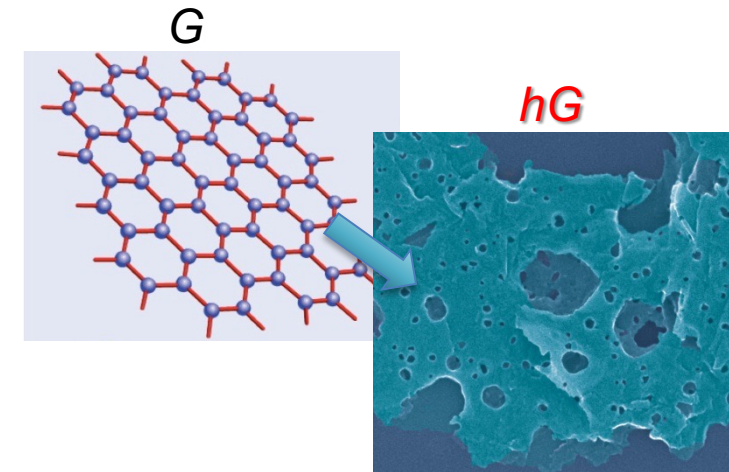
Low volume

**Equivalent
Capacitance**

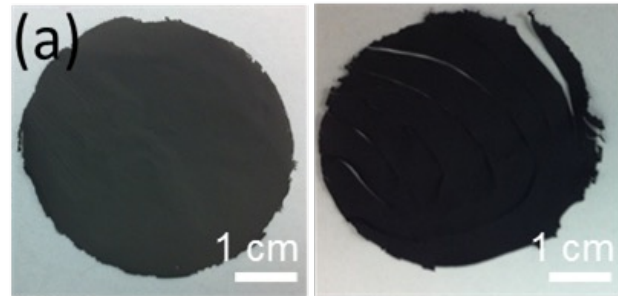
Collaboration: Prof. Liangbing Hu (University of Maryland)

Advantages of Holey Graphene

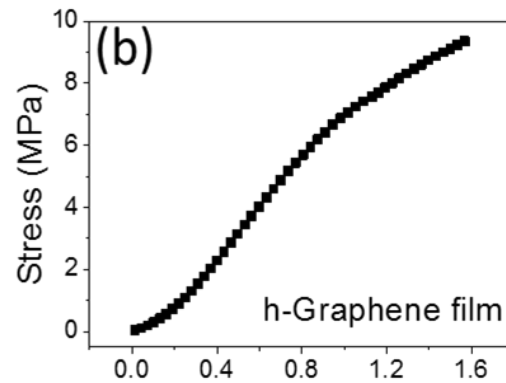
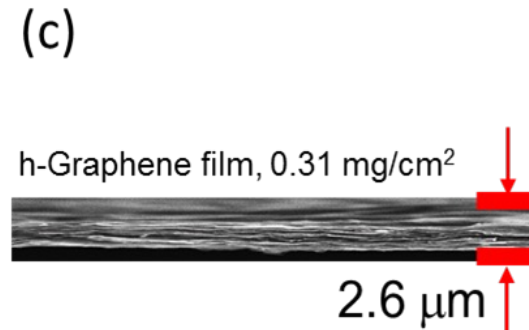
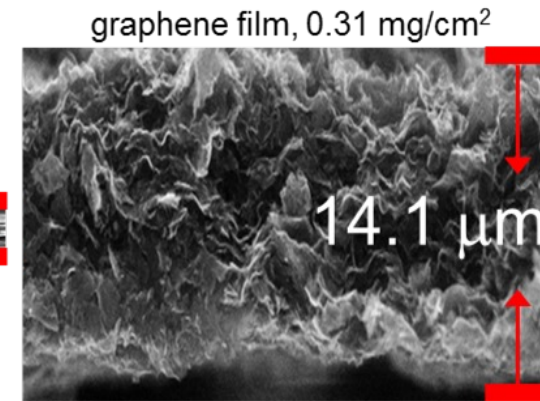
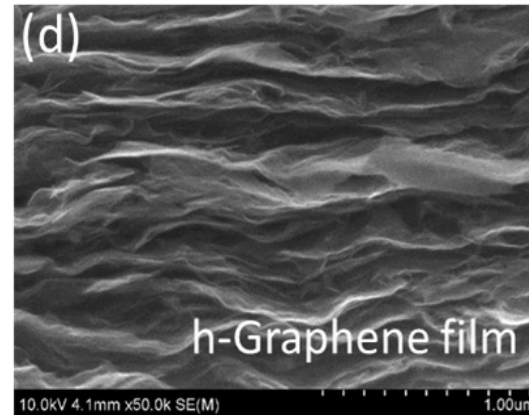
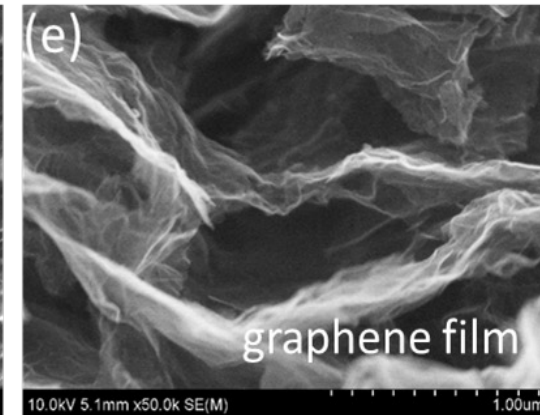
- ❑ In-plane porosity: Improve ion transport path
- ❑ Accessible surface area: Improve gravimetric capacitance
- ❑ Volume reduction: Mitigate need to create large pores/spacing
- ❑ Electrical conductivity: Retain graphitic crystallinity



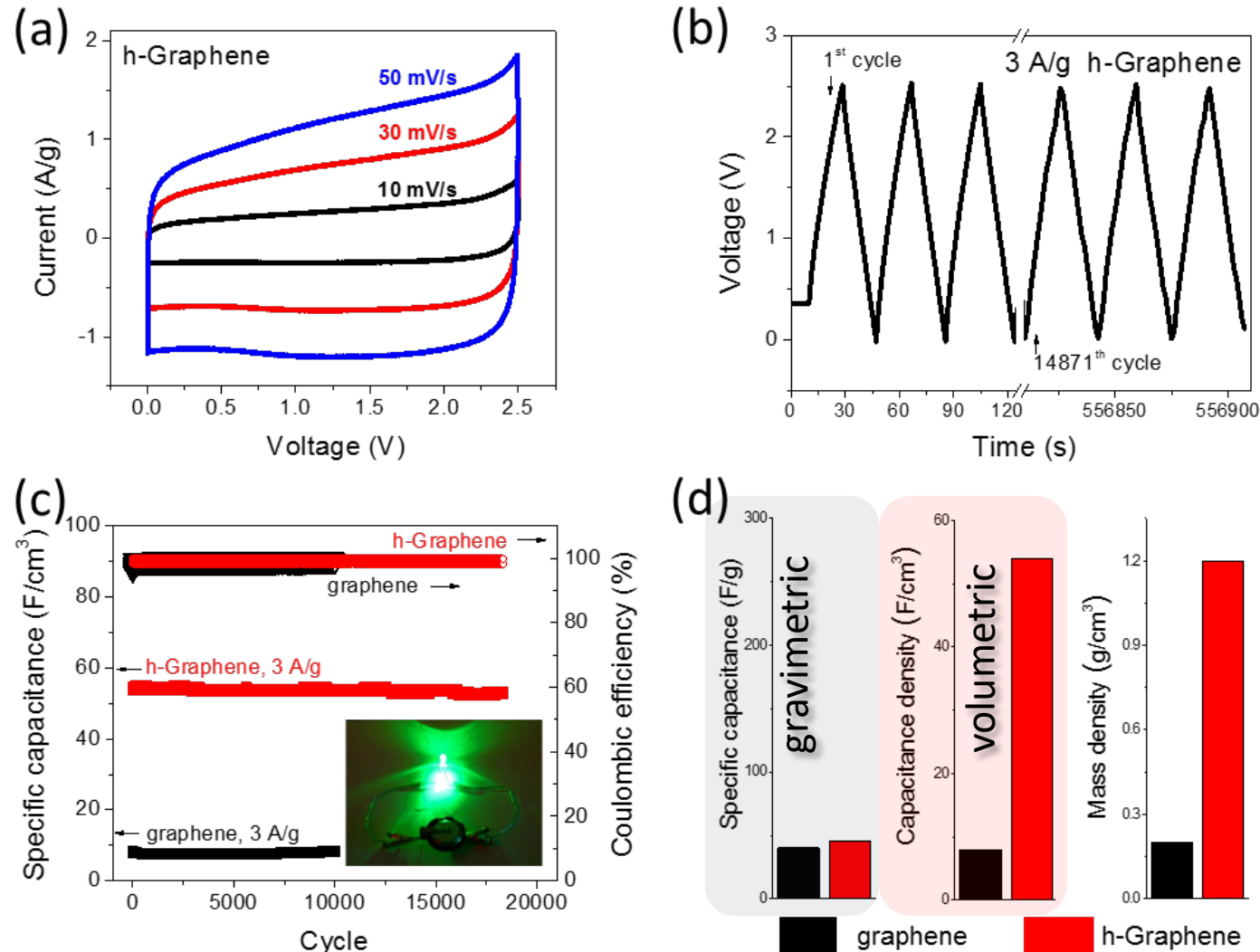
Holey Graphene Thin Film Electrodes



h-Graphene graphene
Filtration films



Enhanced Volumetric Performance

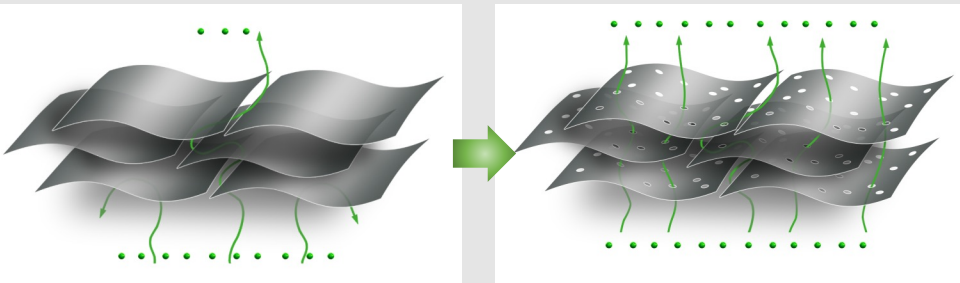


ACS Nano 2014, 8, 8255.

Holey Graphene: An Advanced Electrode Material



Supercapacitors



Intact Graphene

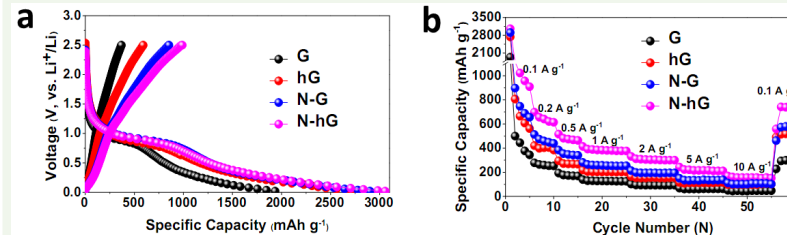
Holey Graphene

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

As-Prepared hG

Liangbing Hu
(U Maryland)

Li-Ion Battery (Anode)



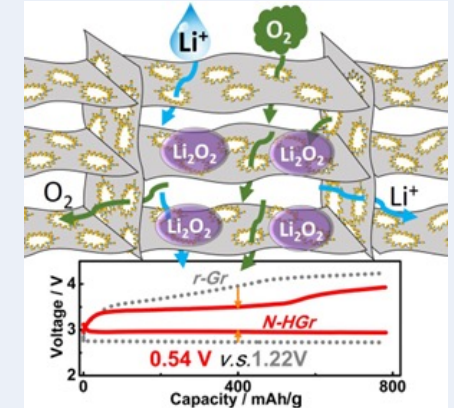
Small **2015**, 11, 6179.

N-doped hG

Liming Dai
(CWRU)

Li-O₂ Batteries

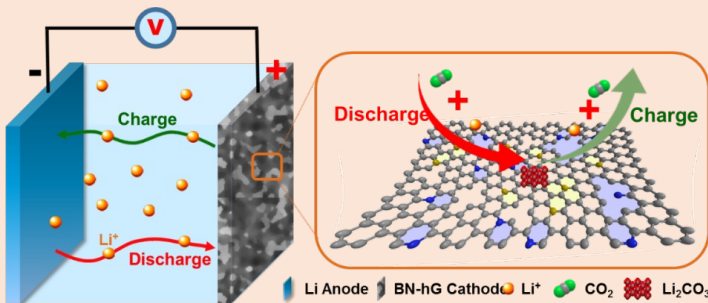
Liming Dai
(CWRU)



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

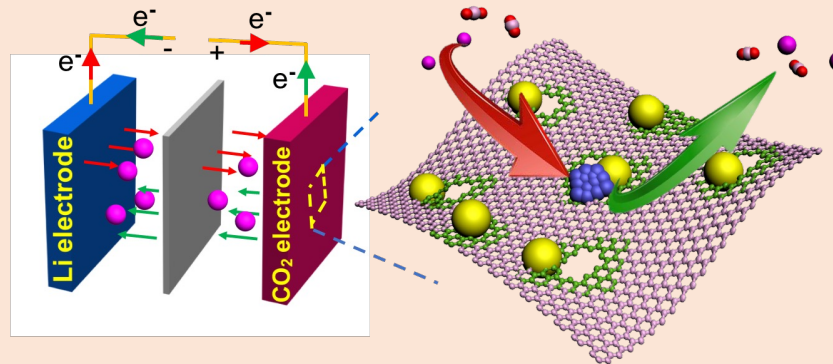
N-doped hG

Li-CO₂ Batteries



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

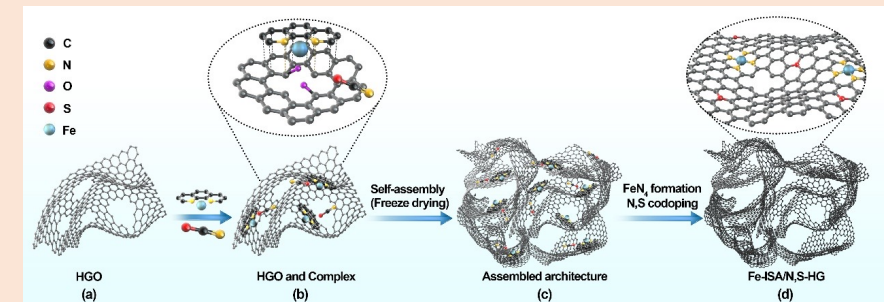
B,N-codoped hG



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

Carbon Dot-Supported on hG

Liming Dai
(CWRU)



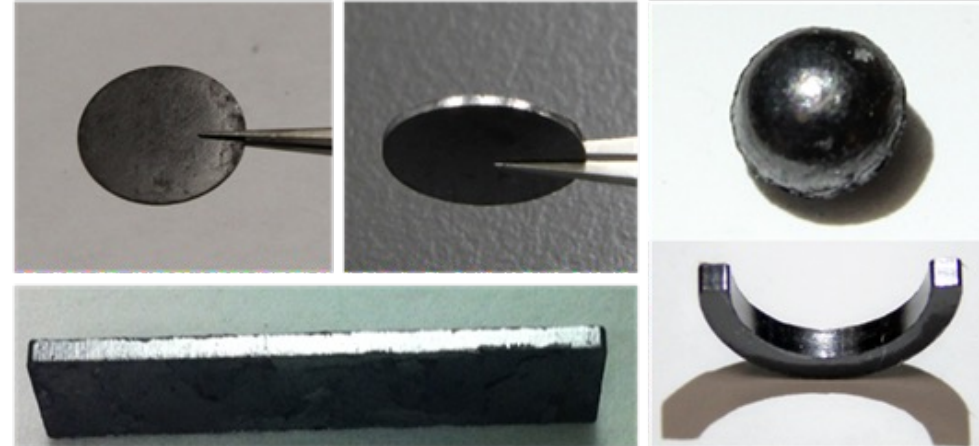
Adv. Mater. **2020**, 32, 1907436.

Single Fe Atom Catalysts Supported on hG

A New Narrative: Holey Graphene is Dry Compressible



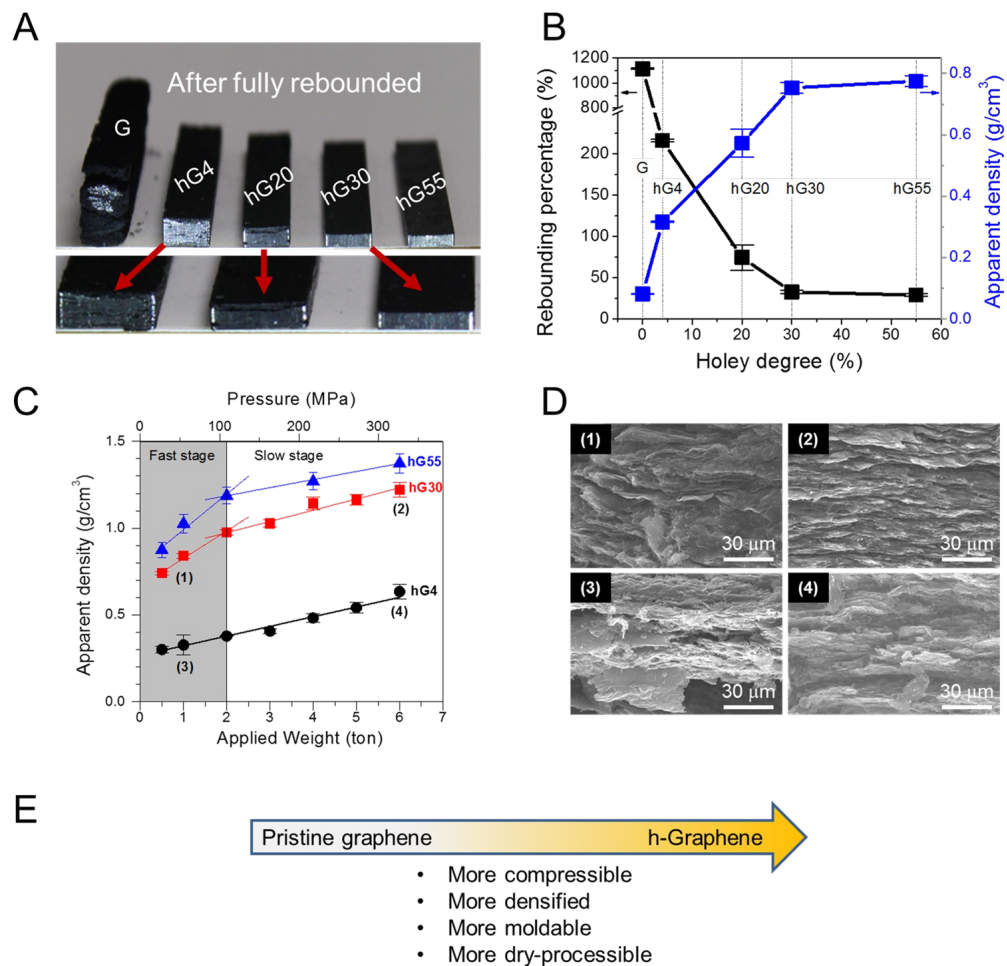
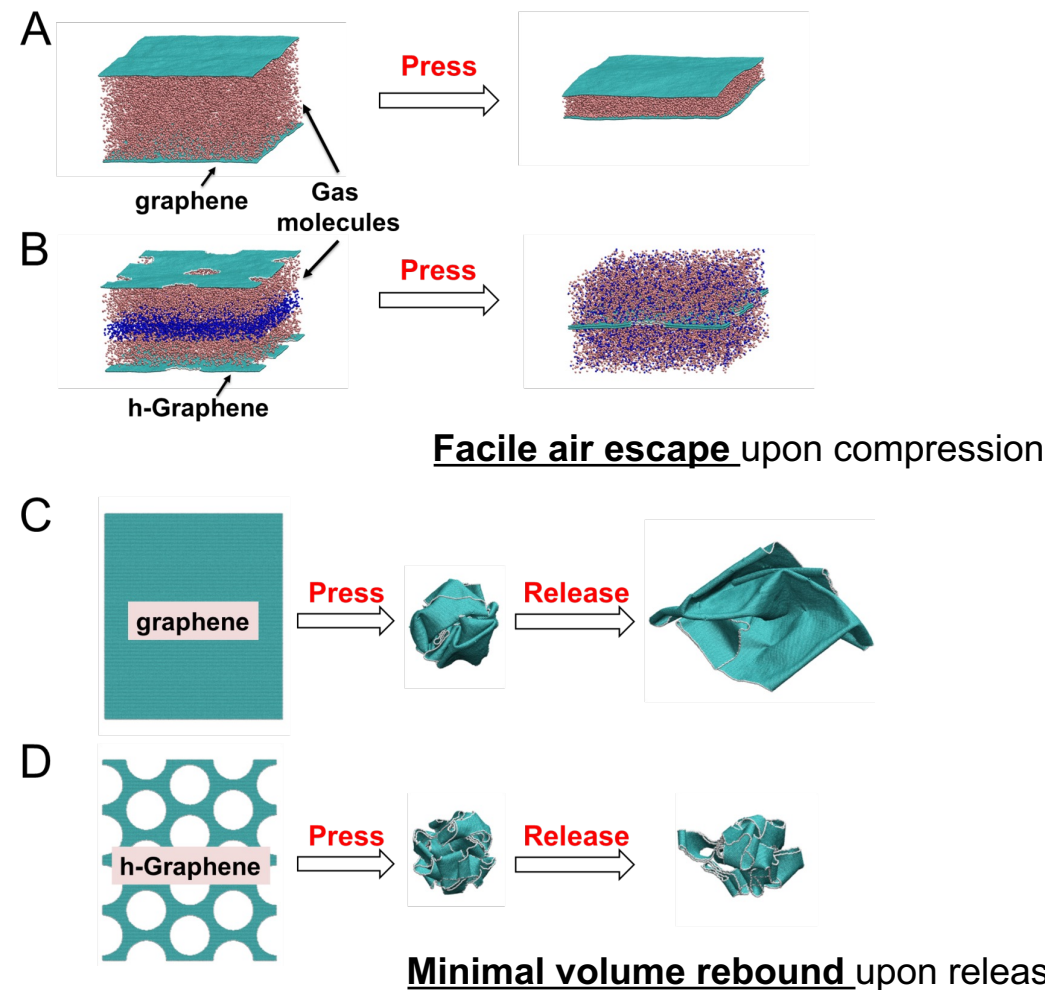
**Holey Graphene
Powder**



**Holey Graphene
Monolithic Architectures**

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

A New Narrative: Holey Graphene is Dry Compressible



Dry compressibility of hG is a game changer in thick electrode architecture fabrication.

ACS Nano **2017**, 11, 3189.

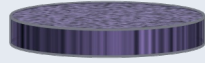
A Game Changer in Electrode Preparation I



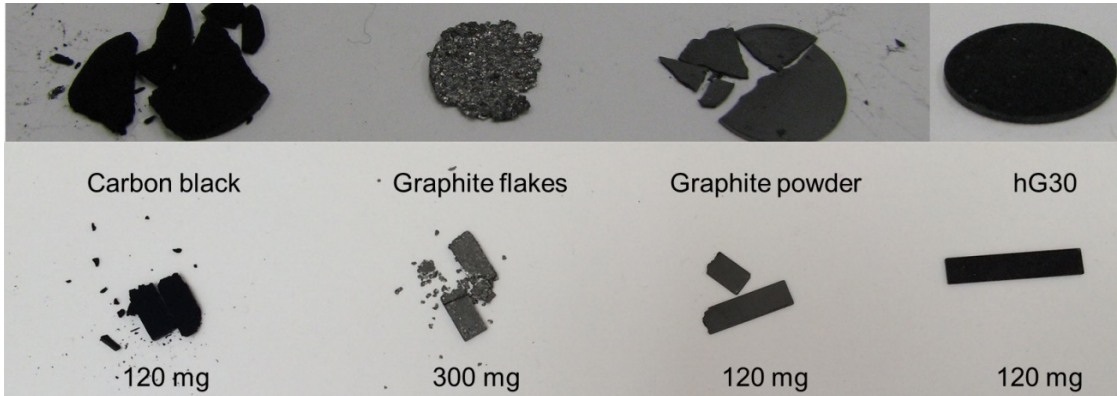
Monolithic Electrodes



hG



N-doped hG

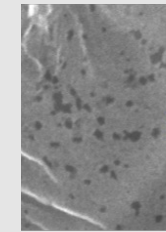


Drop from 36 cm

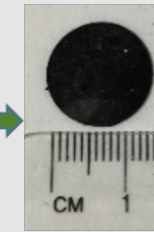
ACS Nano **2017**, 11, 3189.

Drop from 36 cm,
and then 110 cm

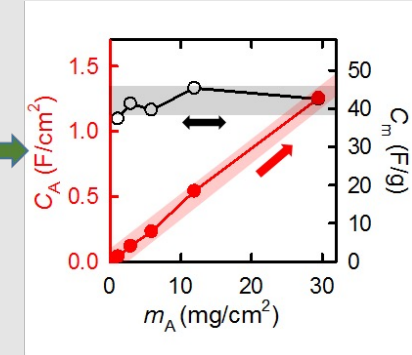
Supercapacitors



Holey Graphene



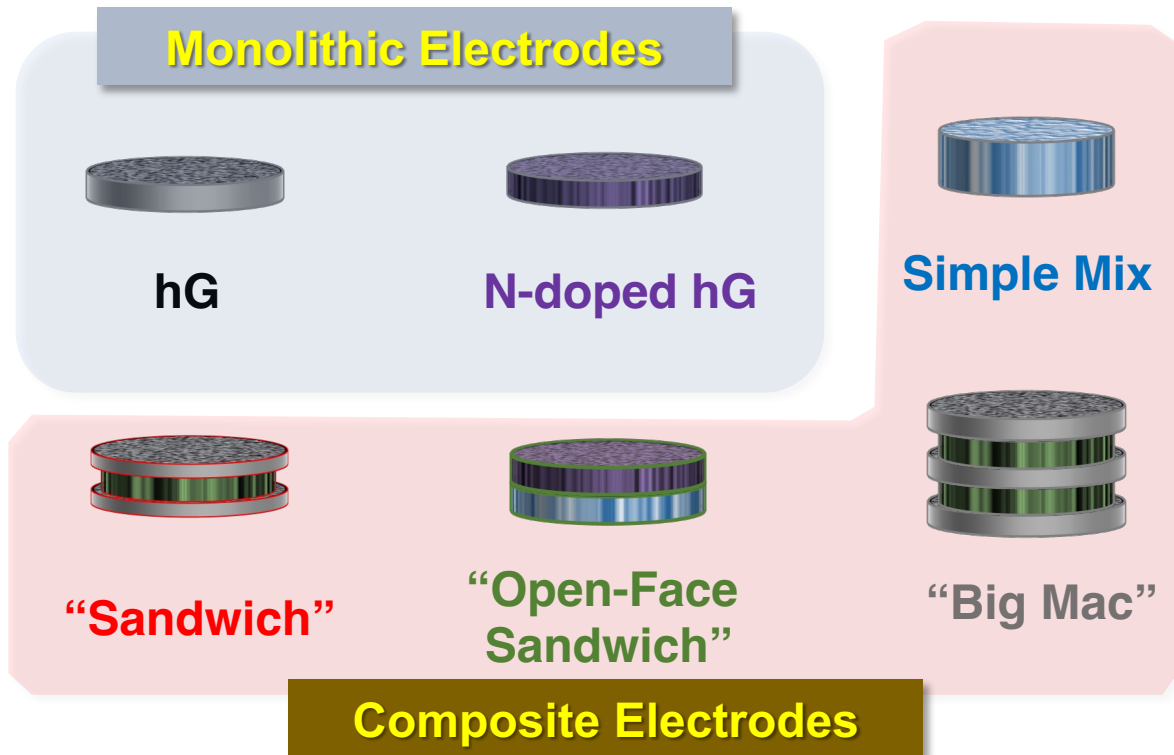
Dry Pressed Electrodes



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

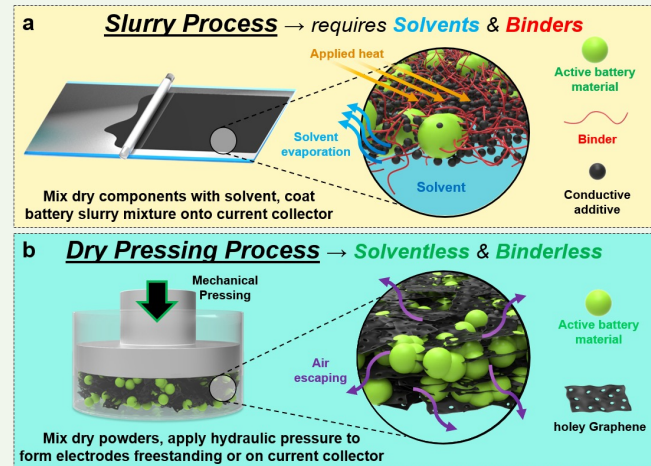
- Solvent-free
- Binder-free
- Completion within minutes
- Scalable: High mass loading

A Game Changer in Electrode Preparation I



- ❑ **Matrix (compressible):** Holey graphene
- ❑ **Filler (non-compressible):** Active or auxiliary components (e.g. catalysts, active electrode materials, other additives)

Li Ion Batteries (Cathode)



ACS Appl. Energy Mater. 2019, 2, 2990-2997.

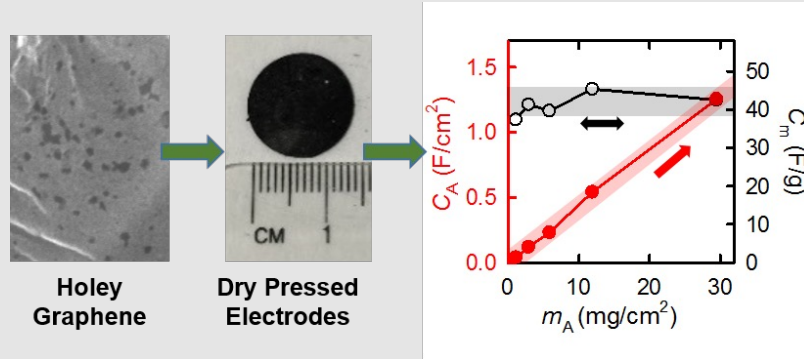
- Solvent-free
- Binder-free
- Completion within minutes
- Scalable: High mass loading
- Enable complex architectures

A Game Changer in Electrode Preparation



Versatile Applications

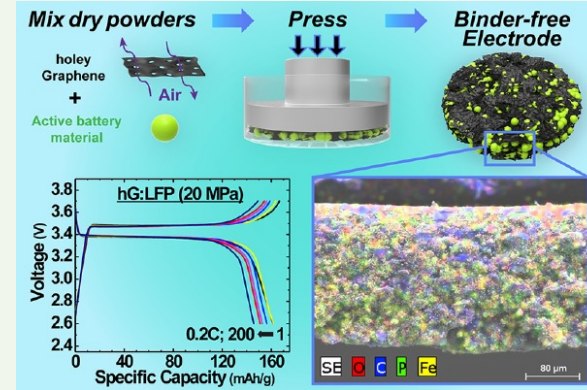
Supercapacitors



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

Li-Ion Batteries

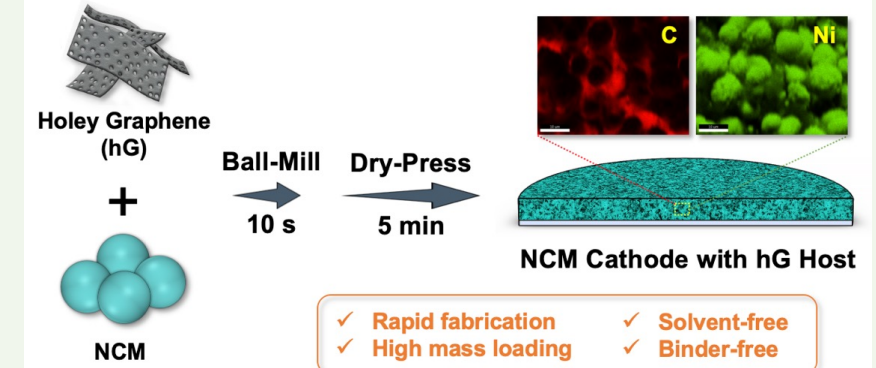
LFP



LFP: Lithium iron phosphate

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

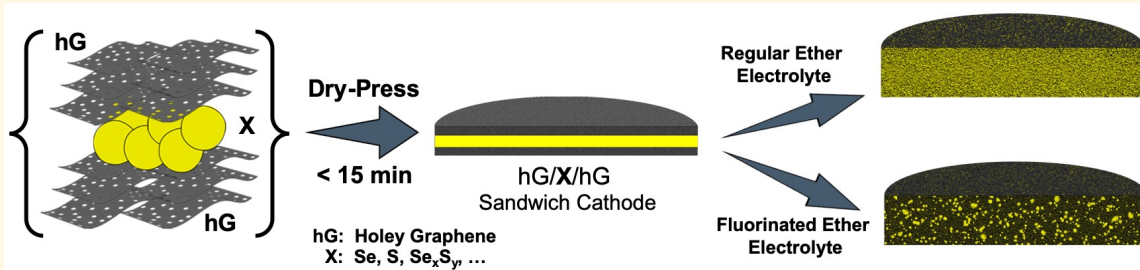
NCM



NCM: Lithium nickel cobalt manganese oxide

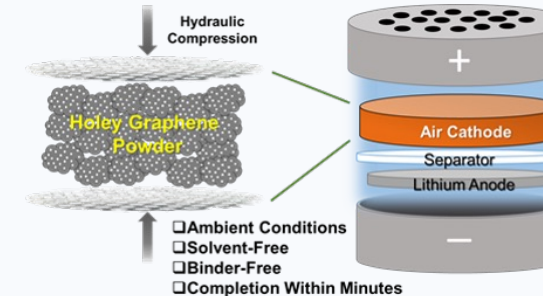
Electrochim. Acta **2020**, 362, 137129

Li-S/Se Batteries

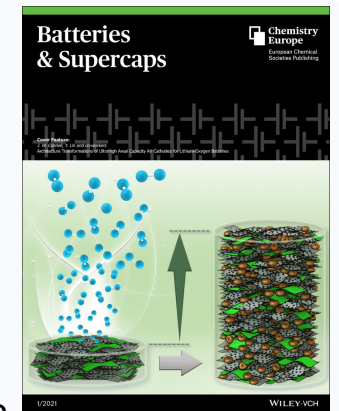


Batteries & Supercaps **2019**, 2, 774; ACS Appl. Energy Mater. **2020**, 3, 6374; Front. Energy Res. **2021**, 703676.

Li-O₂ Batteries



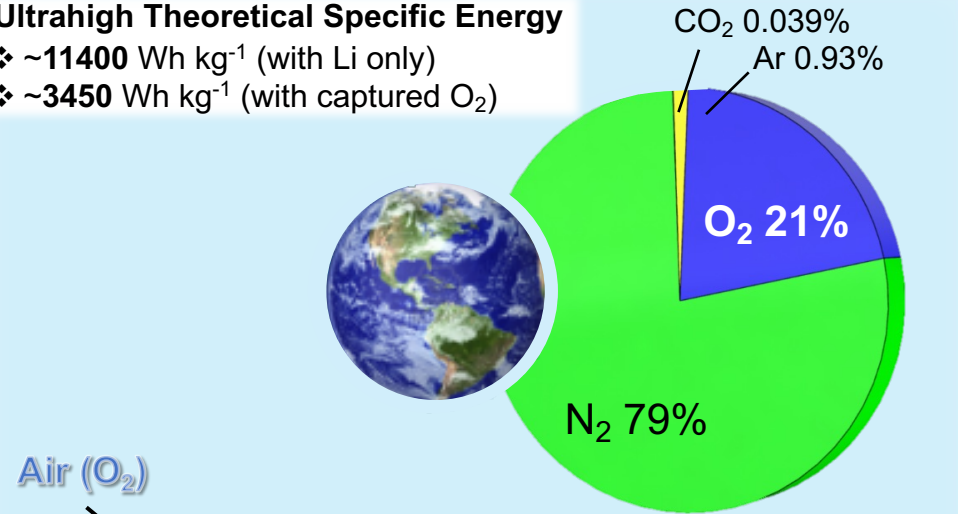
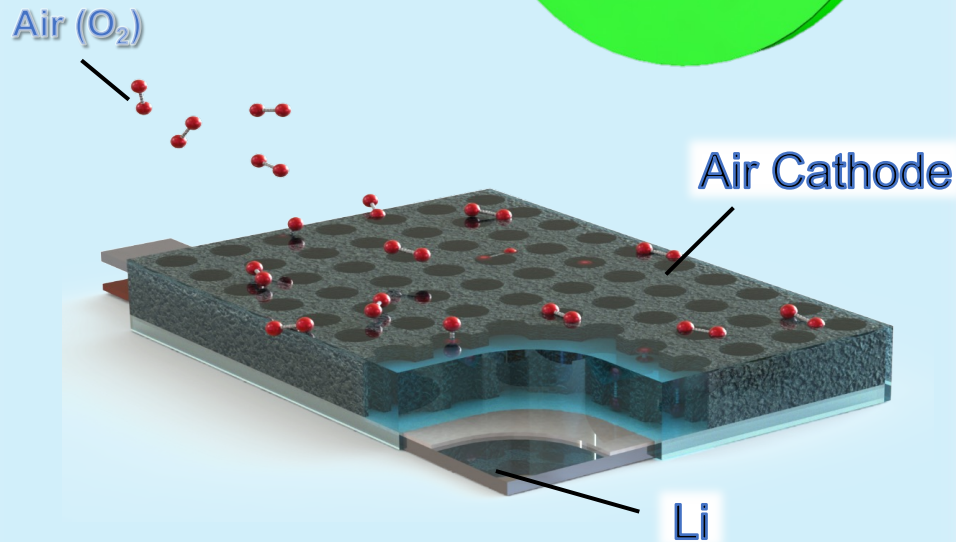
Nano Lett. **2017**, 17, 3252; Nano Energy **2017**, 31, 386; J. Electrochem. Soc. **2020**, 167, 080522; Batteries Supercaps **2021**, 4, 120.



Li-Air (O₂) Batteries

Ultrahigh Theoretical Specific Energy

- ❖ ~11400 Wh kg⁻¹ (with Li only)
- ❖ ~3450 Wh kg⁻¹ (with captured O₂)



- Porous
- Conductive
- Catalytic (ORR/OER)

Reactions at the Air Cathode

Oxygen Reduction Reaction (ORR):
 $\text{O}_2 + 2\text{e}^- + 2\text{Li}^+ \rightarrow \text{Li}_2\text{O}_2$ (discharge)

Oxygen Evolution Reaction (OER):
 $\text{Li}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{e}^- + 2\text{Li}^+$ (charge)

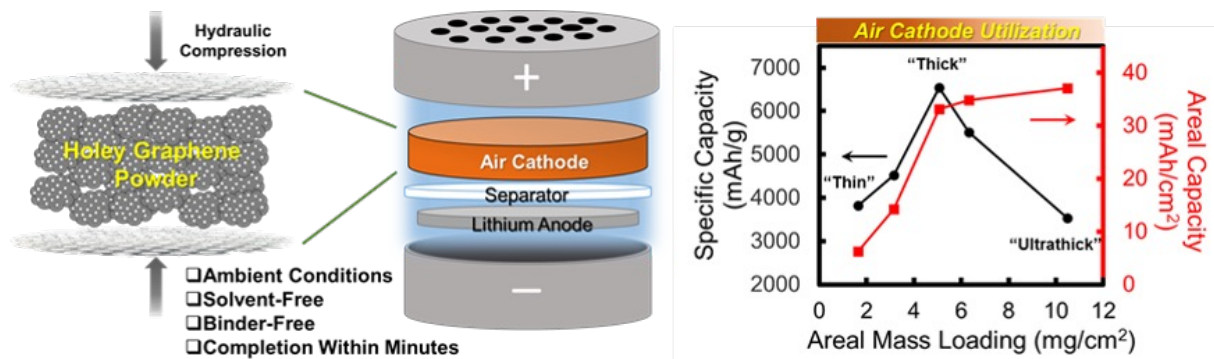
❖ Air cathode performance

- ❖ Capacity (discharge)
- ❖ Round-trip efficiency (charge)
- ❖ Rate performance
- ❖ Scalability

❖ Electrolyte decomposition

- ❖ Li anode deactivation
- ❖ Interference from air

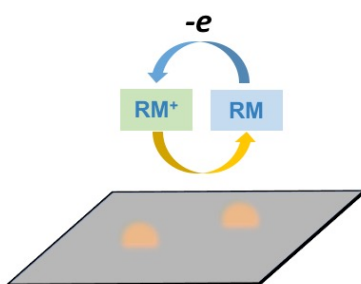
Ultrahigh Areal Capacity Holey Graphene Air Cathodes



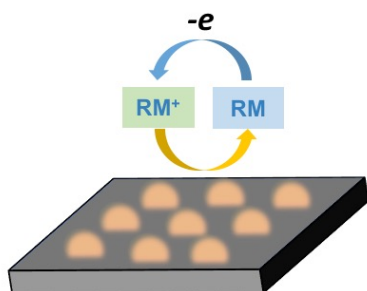
Nano Lett. **2017**, 17, 3252.

Research Li-O₂ Batteries

Practical Li-O₂ Batteries

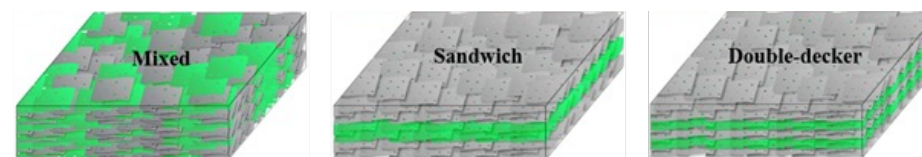


- ☐ Low Areal Capacity
- ☐ Thin, Low Mass Loading
- ☐ RM in Excess

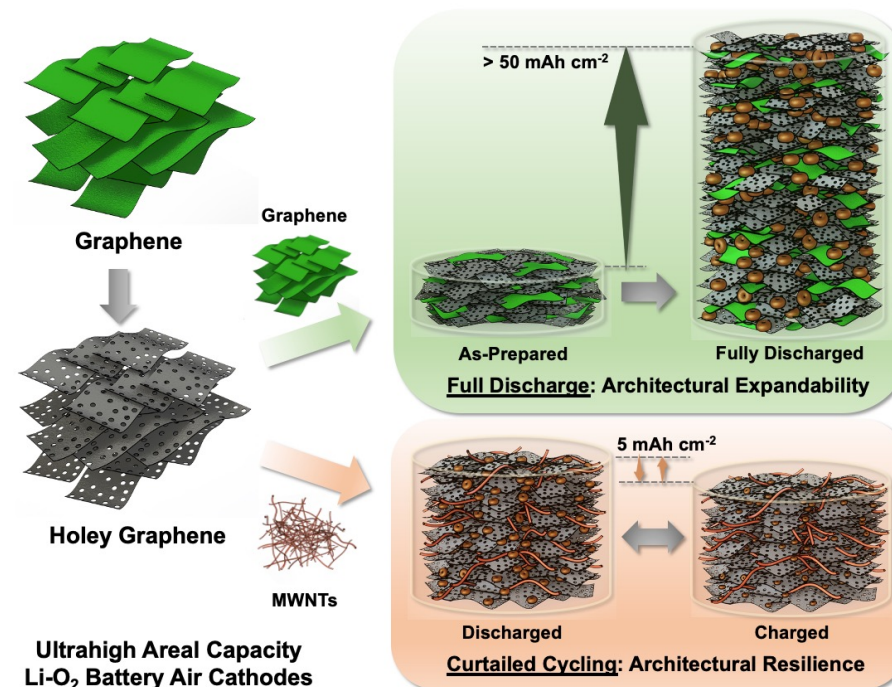


- ☐ High Areal Capacity
- ☐ Thick, High Mass Loading
- ☐ RM Starved

J. Electrochem. Soc. **2020**, 167, 080522.

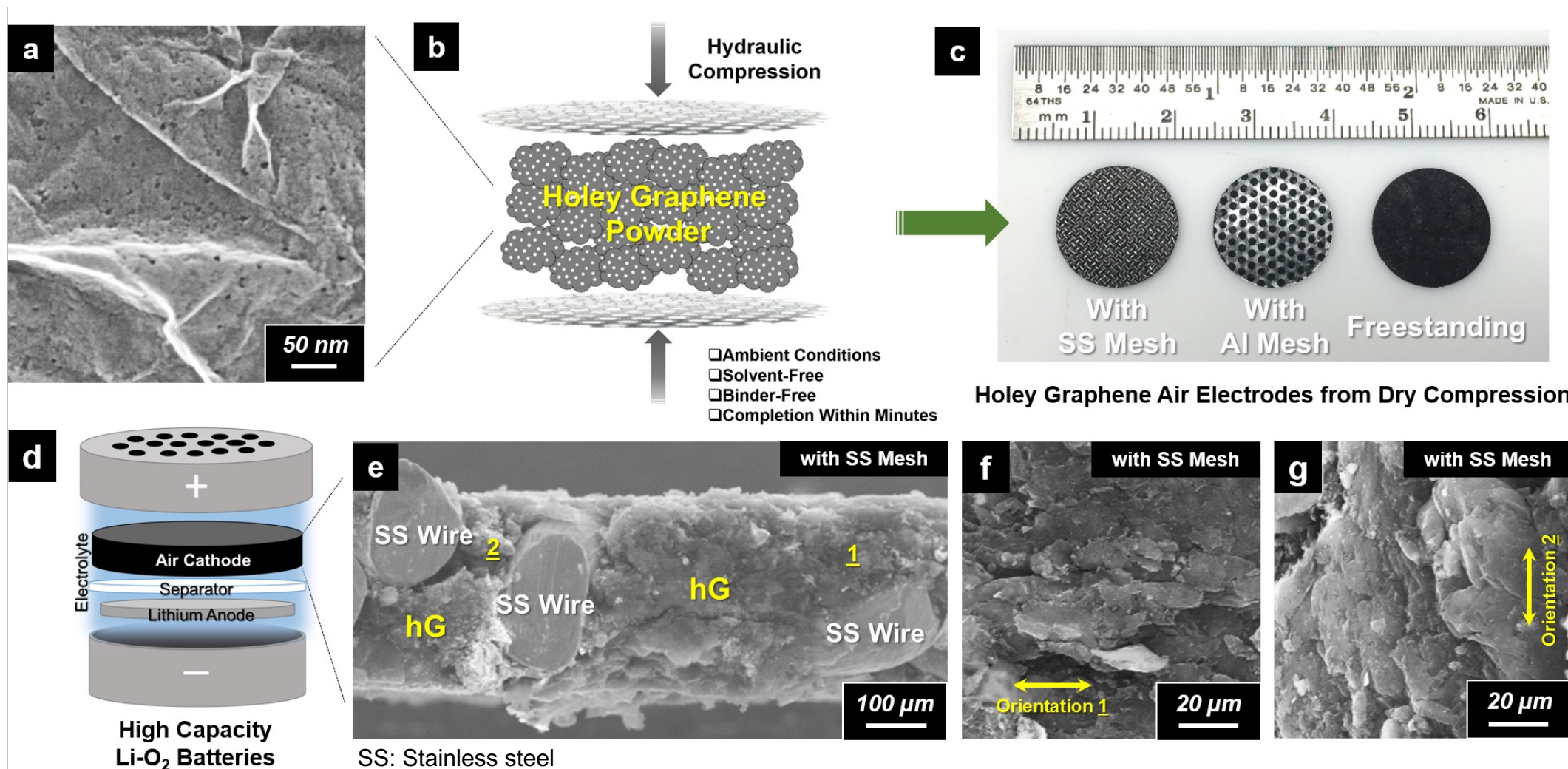


Nano Energy **2017**, 31, 386.



Batteries & Supercaps **2021**, 4, 120.

Dry Pressed Holey Graphene Air Cathode

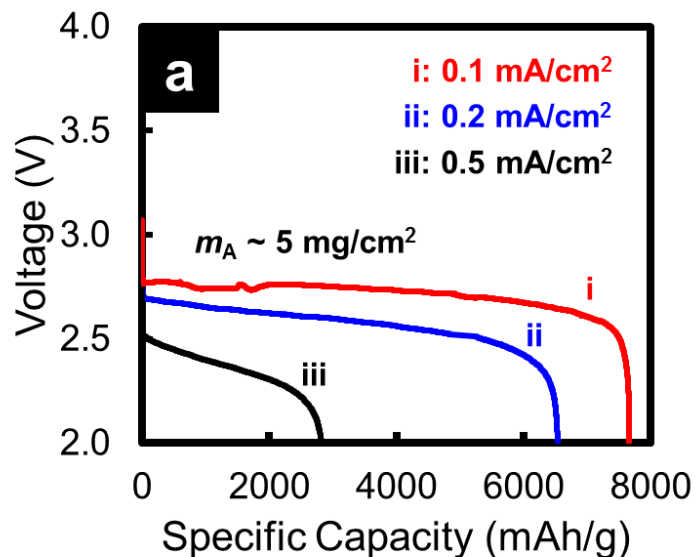
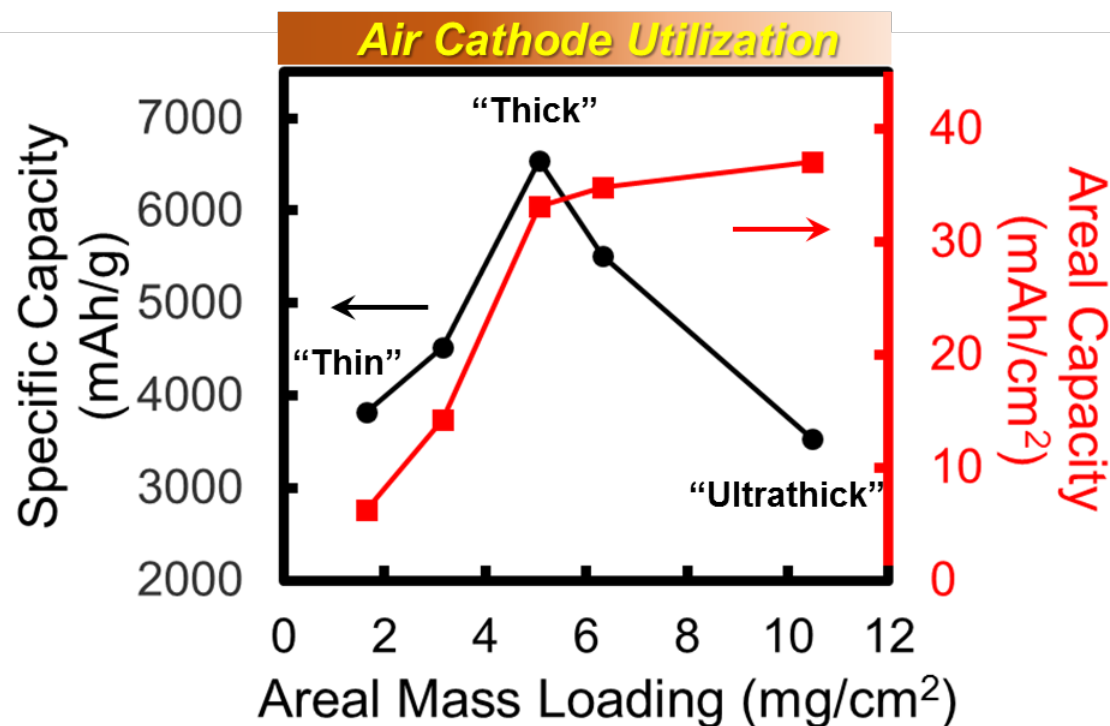


□ Facile fabrication of high carbon mass loading air cathodes.

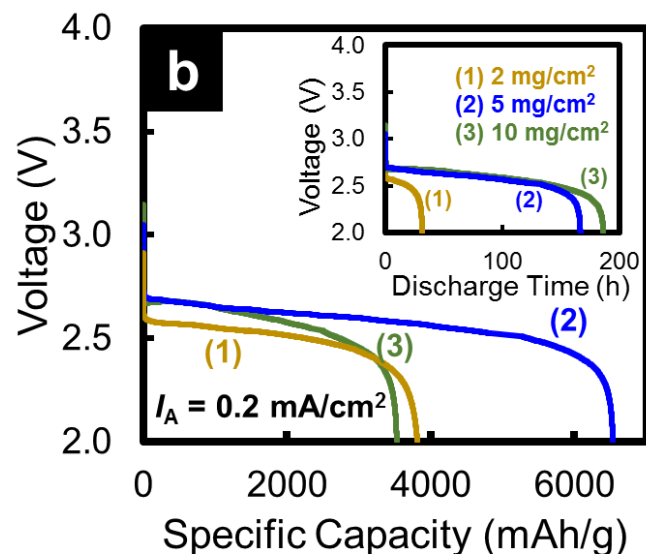
Nano Lett. **2017**, 17, 3252.

25

Dry Pressed Holey Graphene Air Cathode



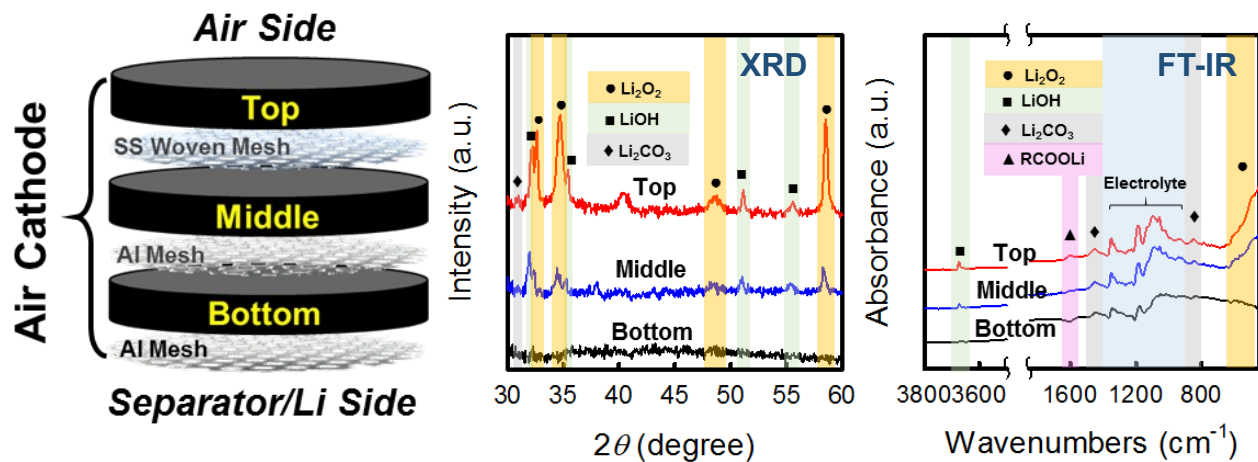
□ Specific capacity reaches peak with mass loading @ 5 mg/cm² while areal capacity plateaus



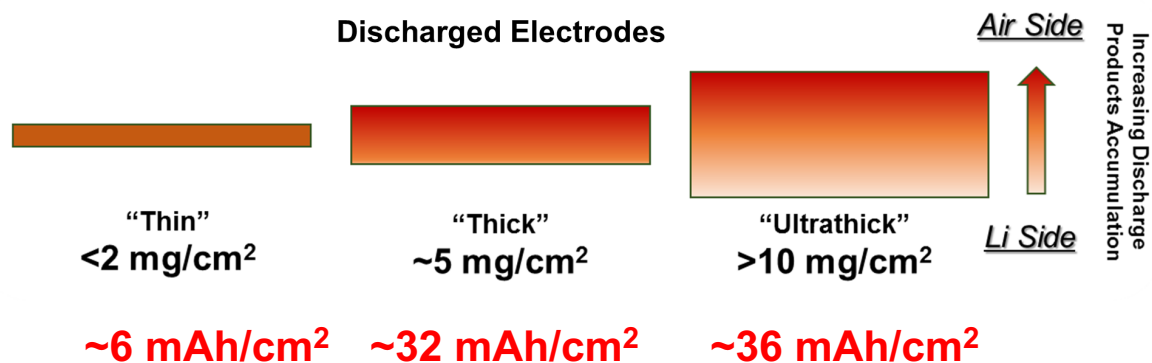
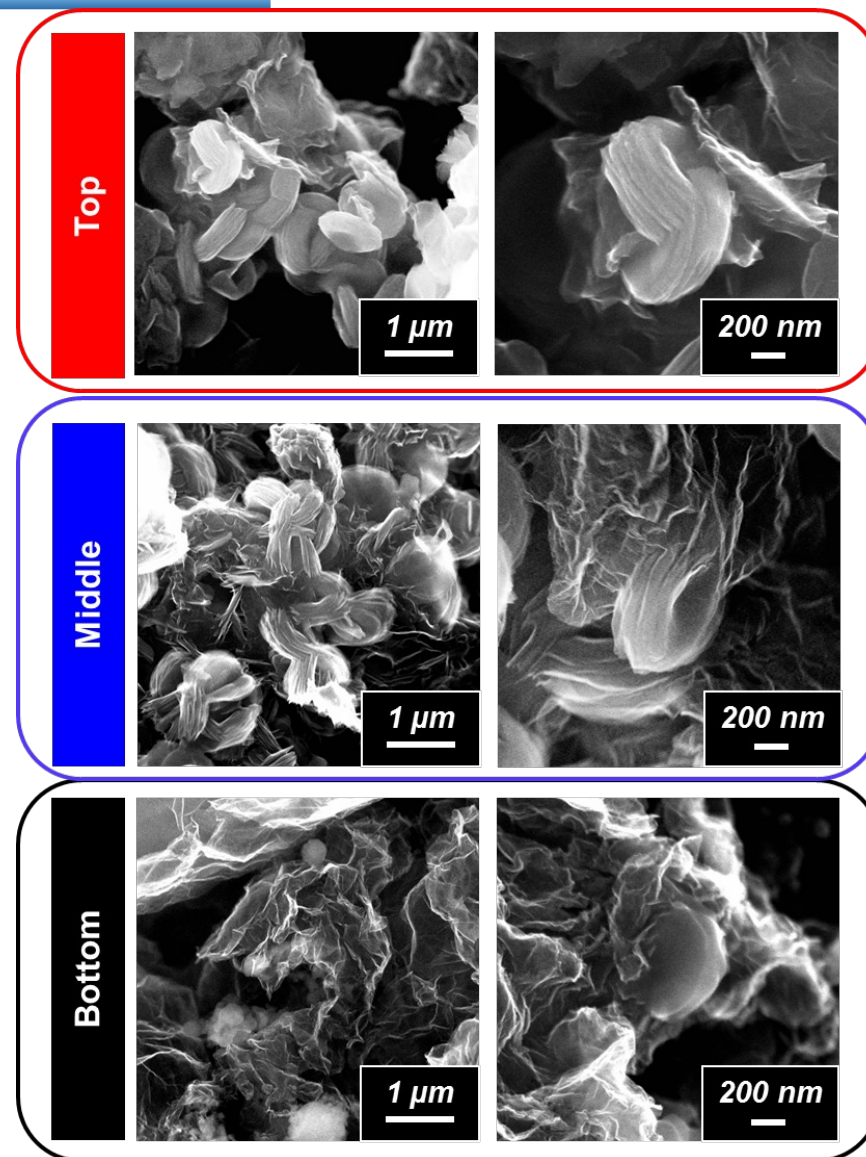
- Carbon mass loadings ~2 – 10 mg/cm²
- Specific capacity >6000 mAh/g @ 0.2 mA/cm²
- Areal capacity >30 mAh/cm² @ 0.2 mA/cm²

Nano Lett. **2017**, 17, 3252.

Dry Pressed Holey Graphene Air Cathode

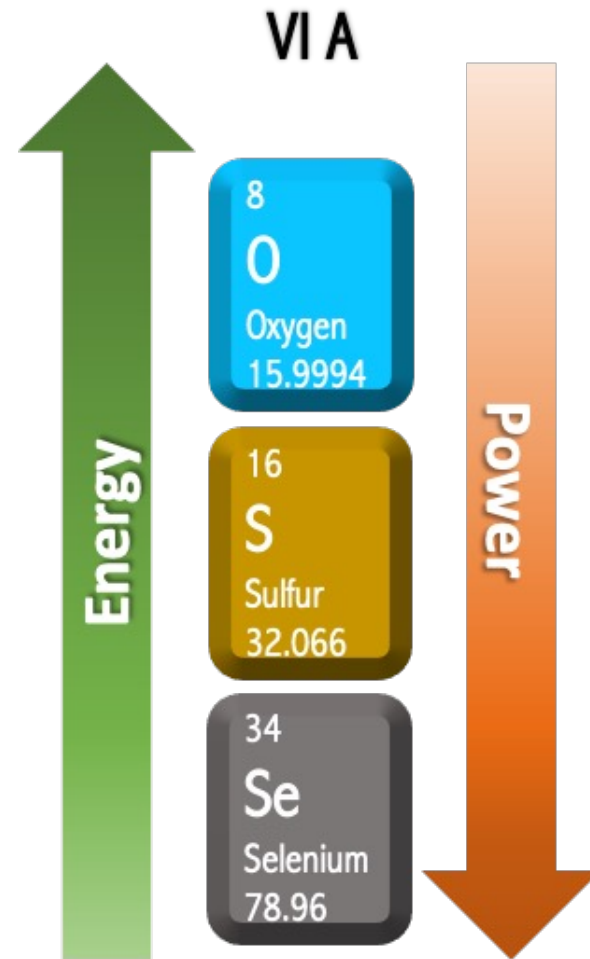


□ Dry-press technique allowed for convenient fabrication of multilayered “analytical” cathodes for post-mortem depth analysis.

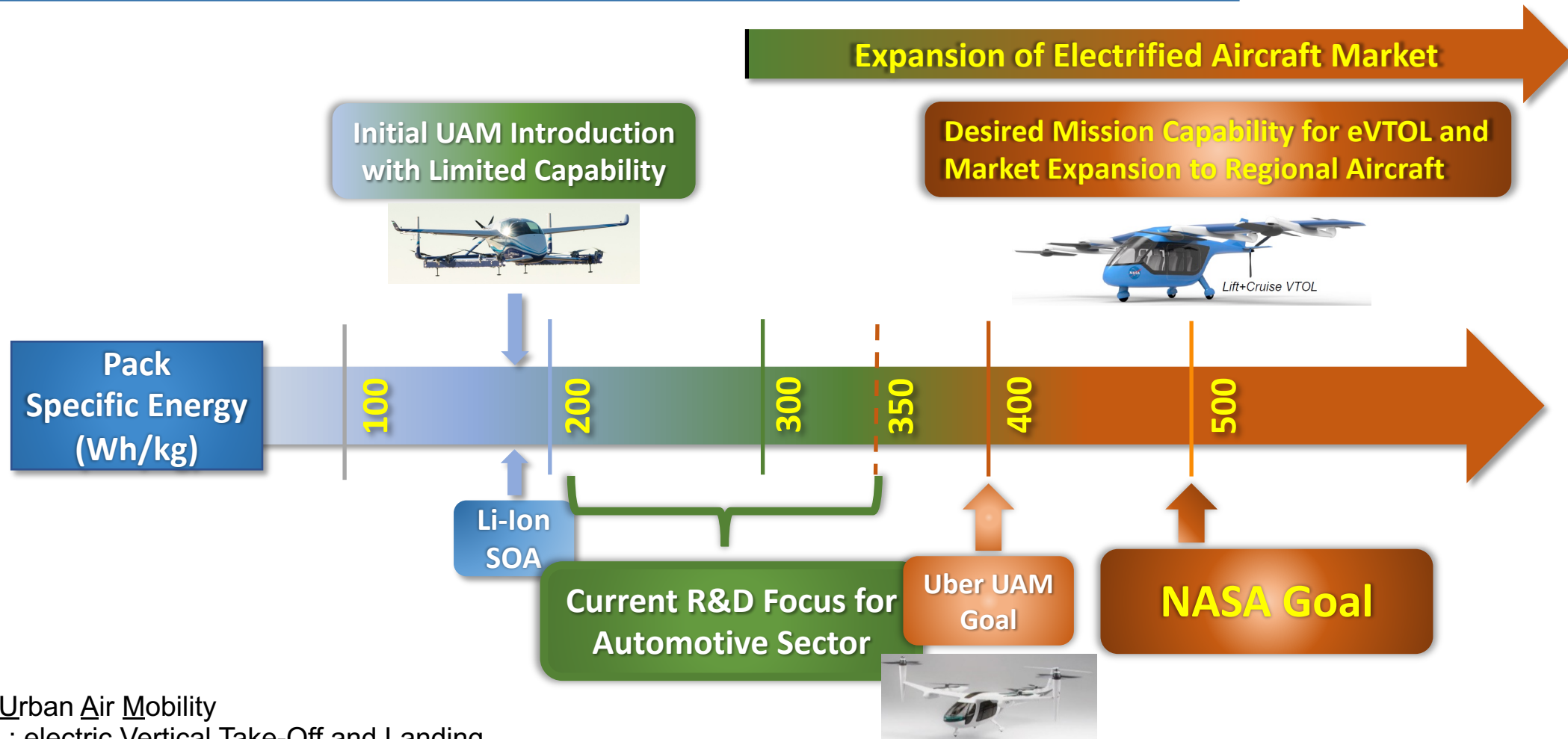


Nano Lett. 2017, 17, 3252.

Cathode Materials for Advanced Batteries

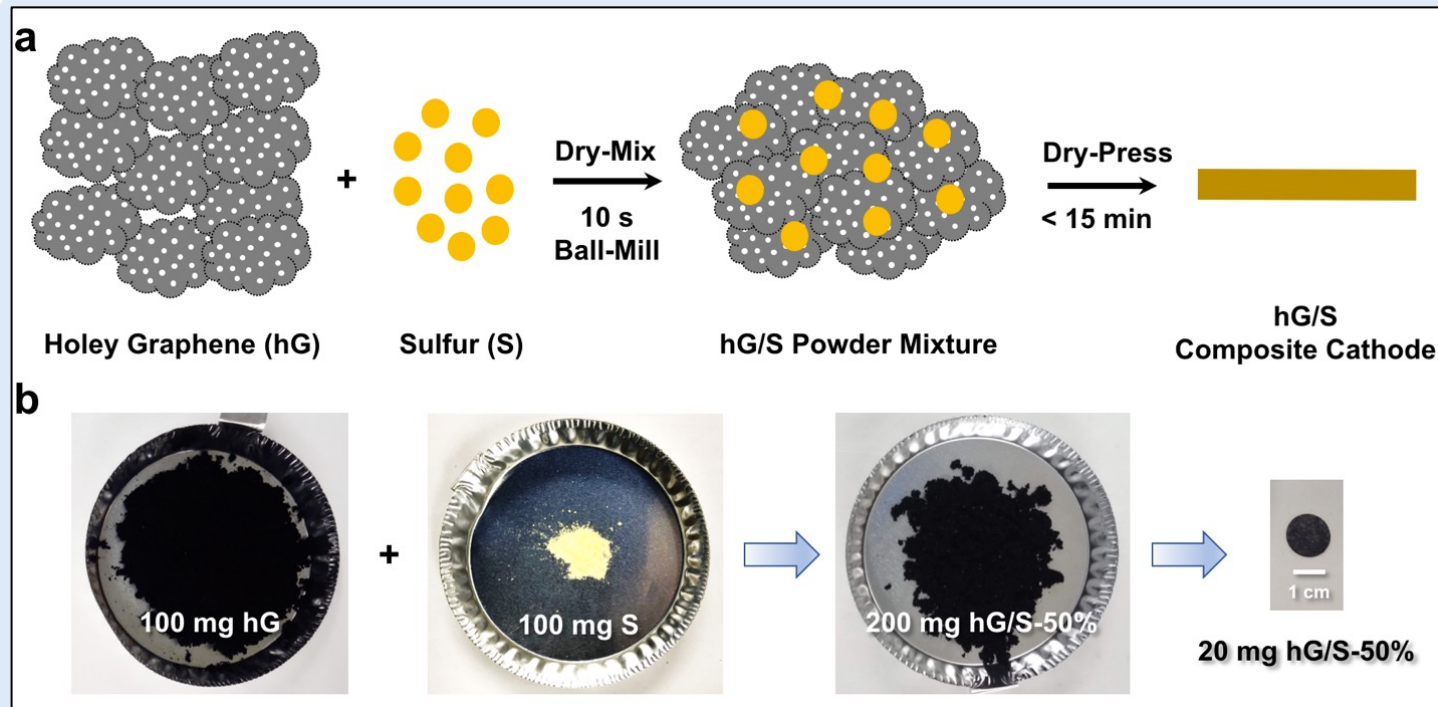
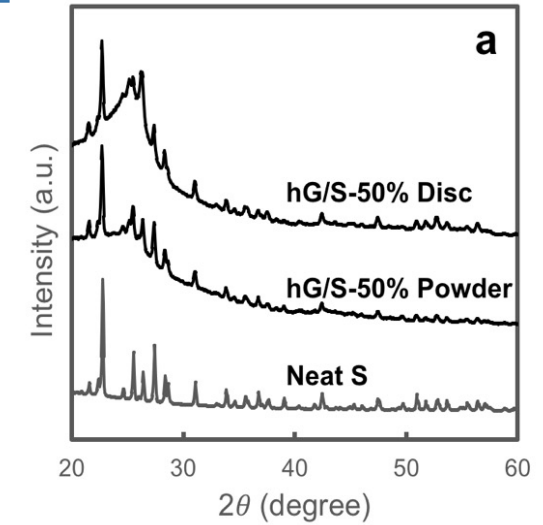
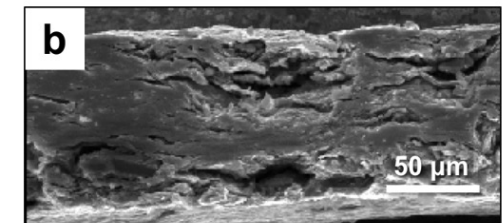
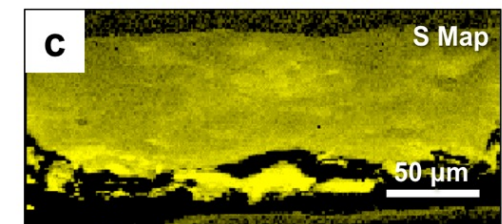


Batteries for Electric Aircraft



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

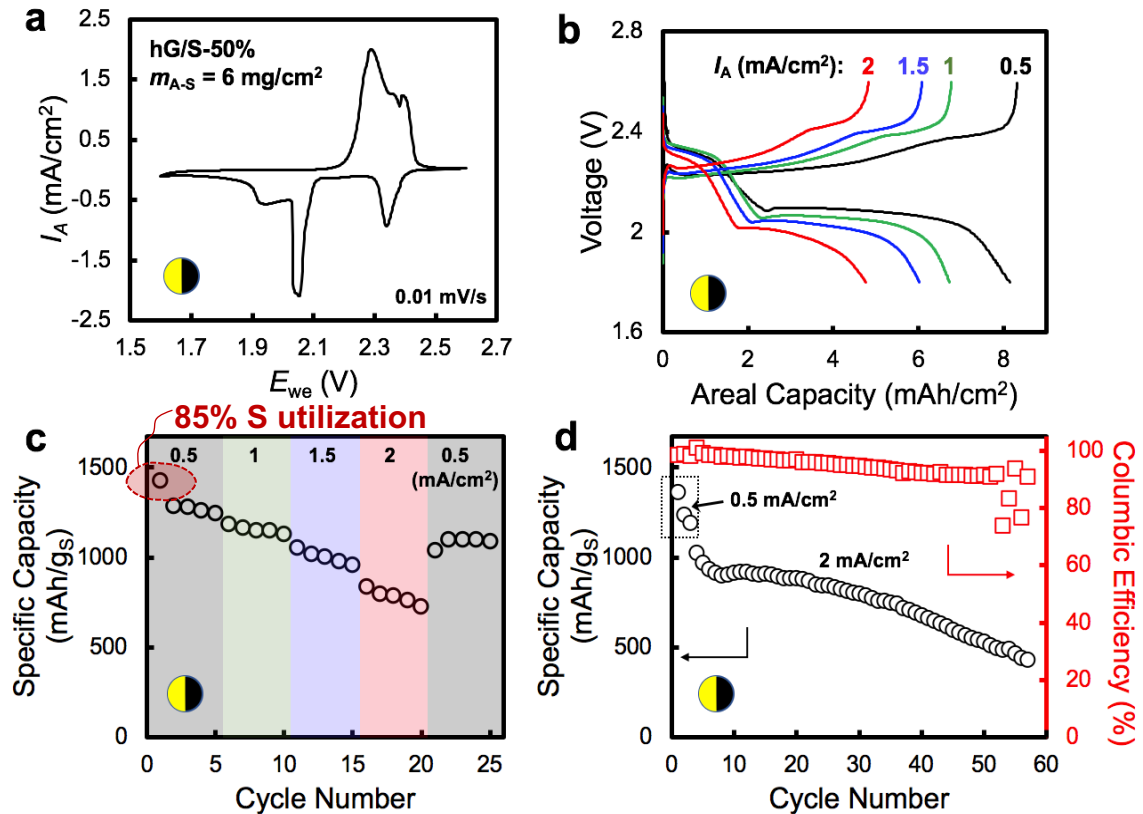
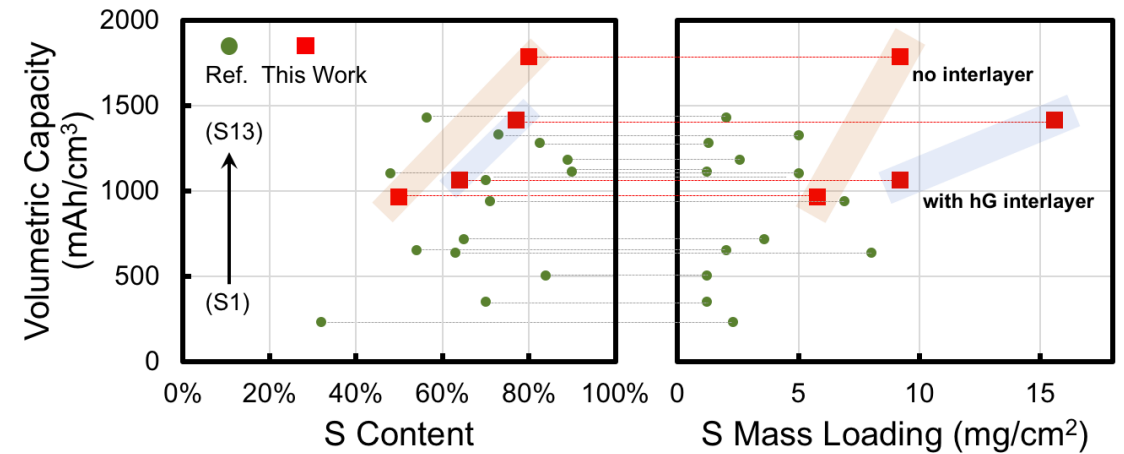
Dry Pressed S Cathodes Enabled by hG



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

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

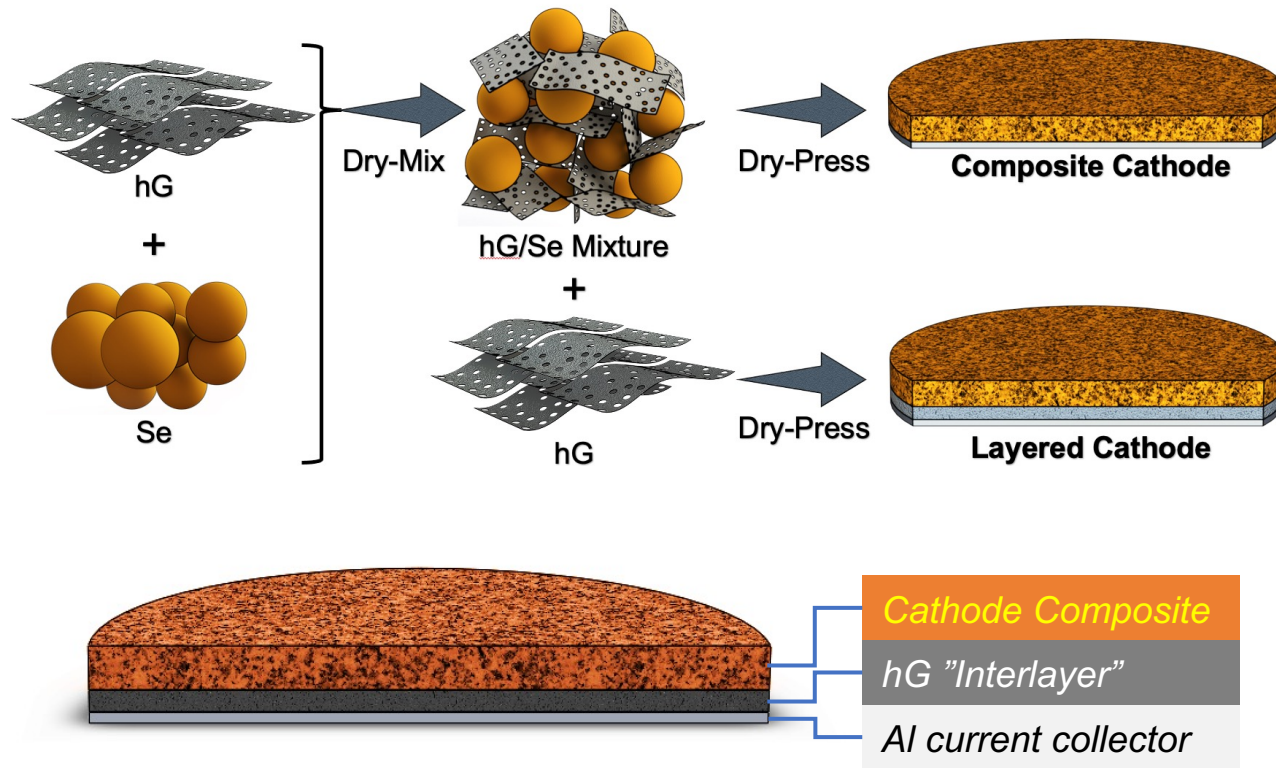
High Performance S/hG Composite Cathodes



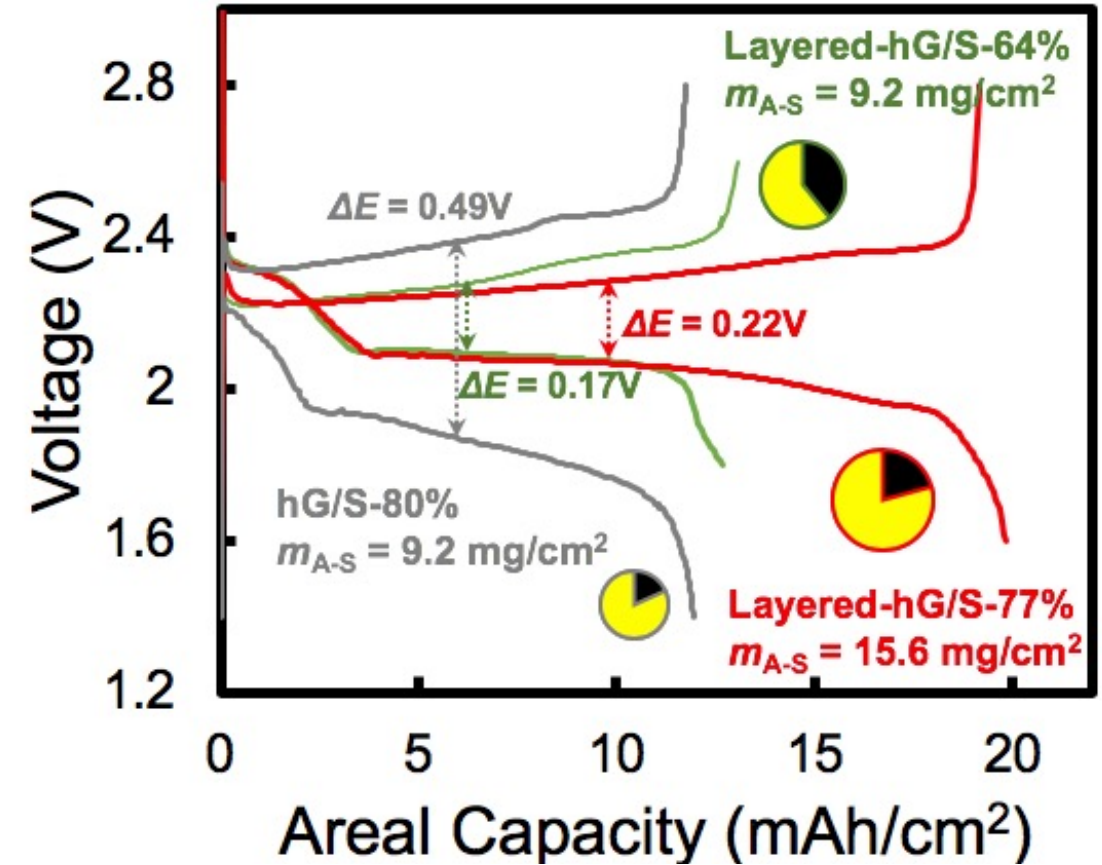
Batteries & Supercaps, **2019**, 2, 774-783.

- Dry-pressed S/hG composite cathodes exhibited **ultrahigh areal and volumetric performance** with **high S utilization efficiency**.

Layered S/Se Cathode Architecture Improves Performance

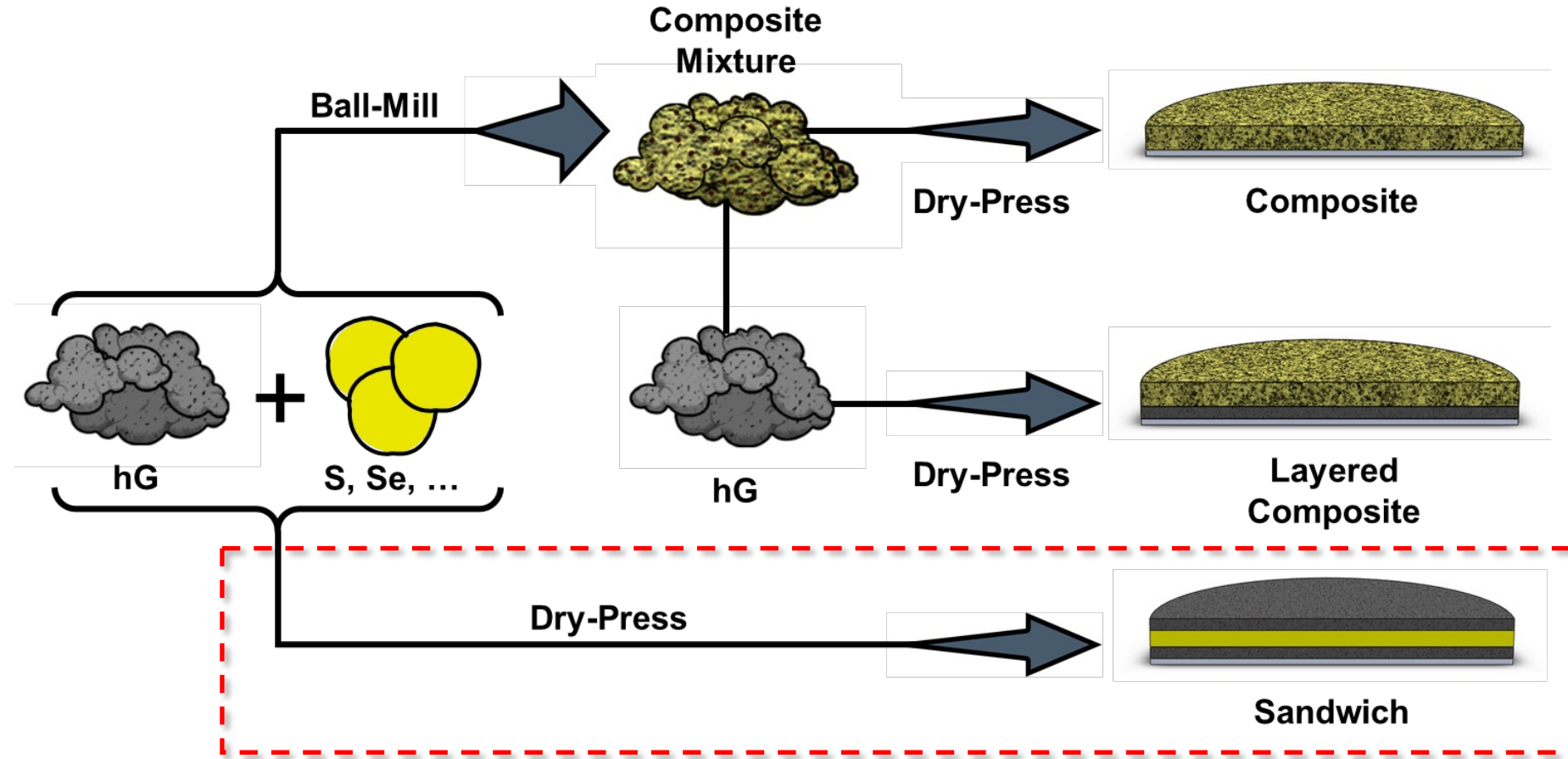


- ❑ Lightweight conductive interlayer (~10 wt%)
- ❑ Improves current collector– cathode contact
 - ✓ Electrochemistry kinetics
 - ✓ Overpotential



Batteries & Supercaps, **2019**, 2, 774-783.
Frontiers in Energy **2021**, 703676.

Composite, Layered, and Sandwich Electrodes

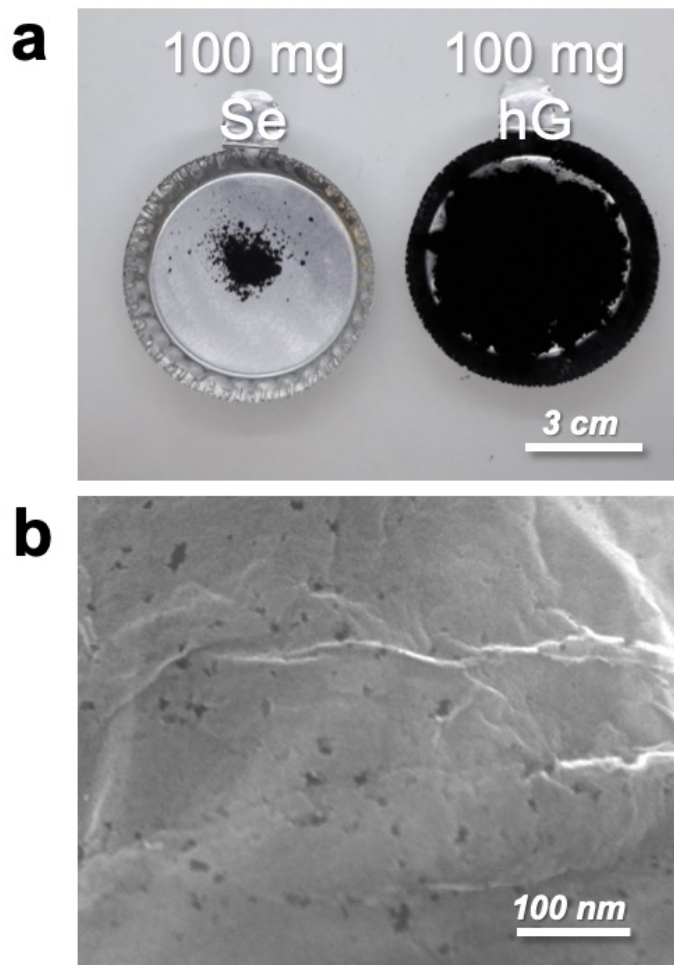


- ❑ High active material content (up to 90 wt%)
- ❑ High mass loading: high areal capacity
- ❑ Excellent current collector– cathode contact

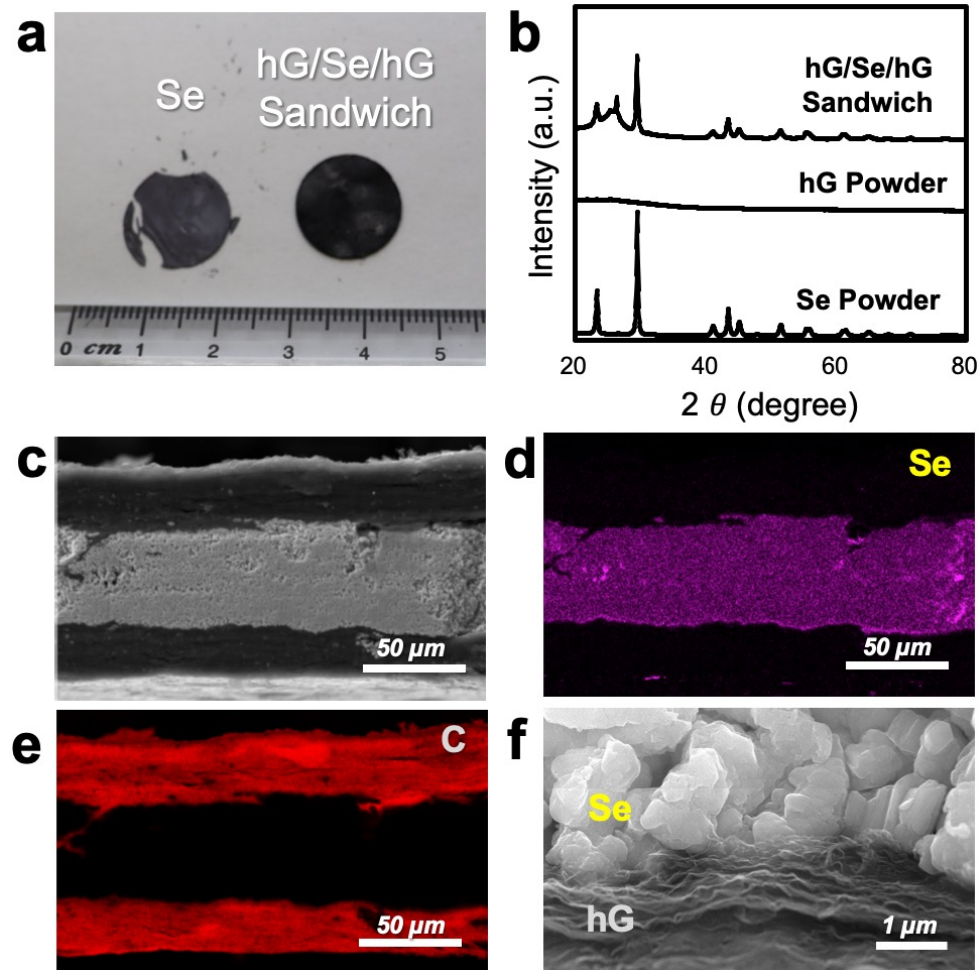
- ❑ **Extremely facile: single-step, no mixing needed**
- ❑ **Widely applicable: S, Se, Se_xS_y , Li_2S**

Starting Powders and Sandwich Discs

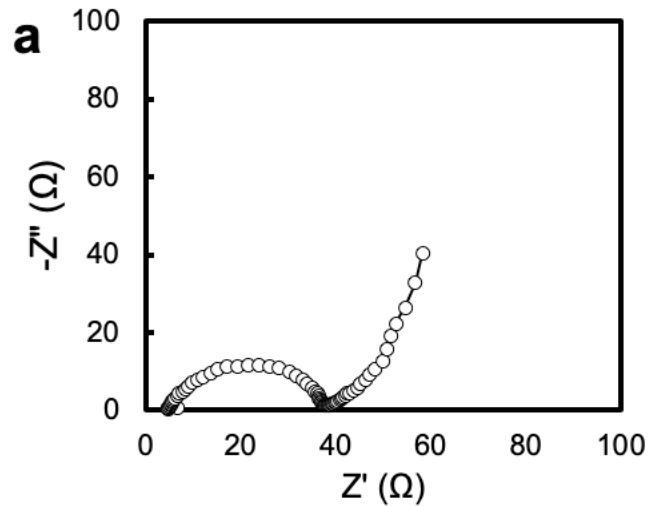
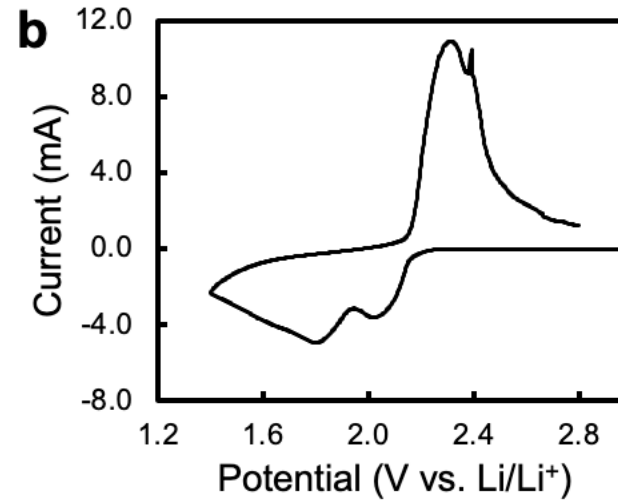
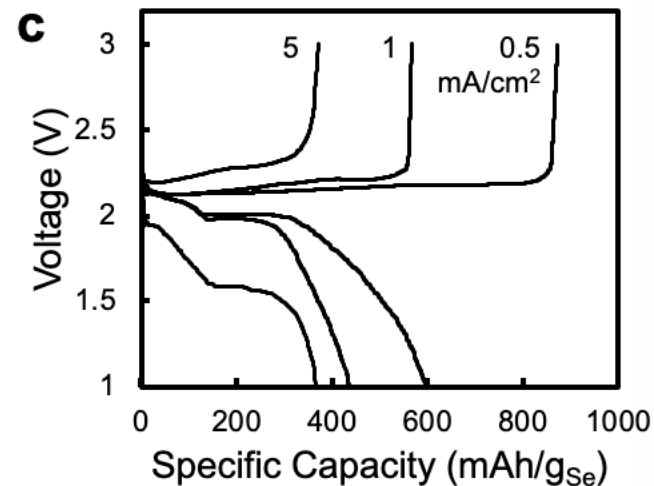
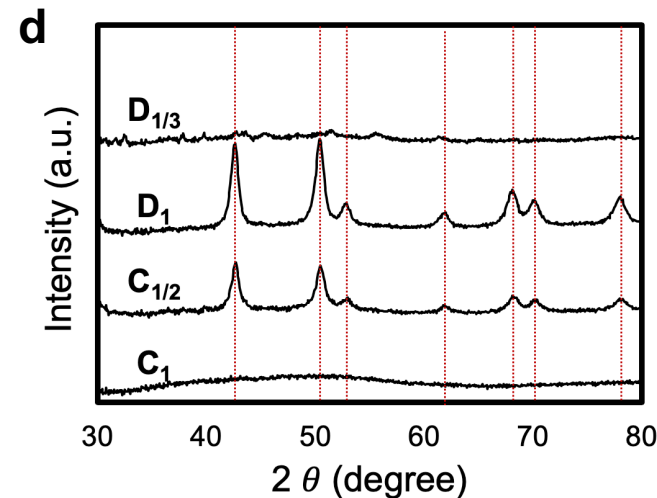
Se vs. hG Powder



hG/Se/hG Sandwich Electrode



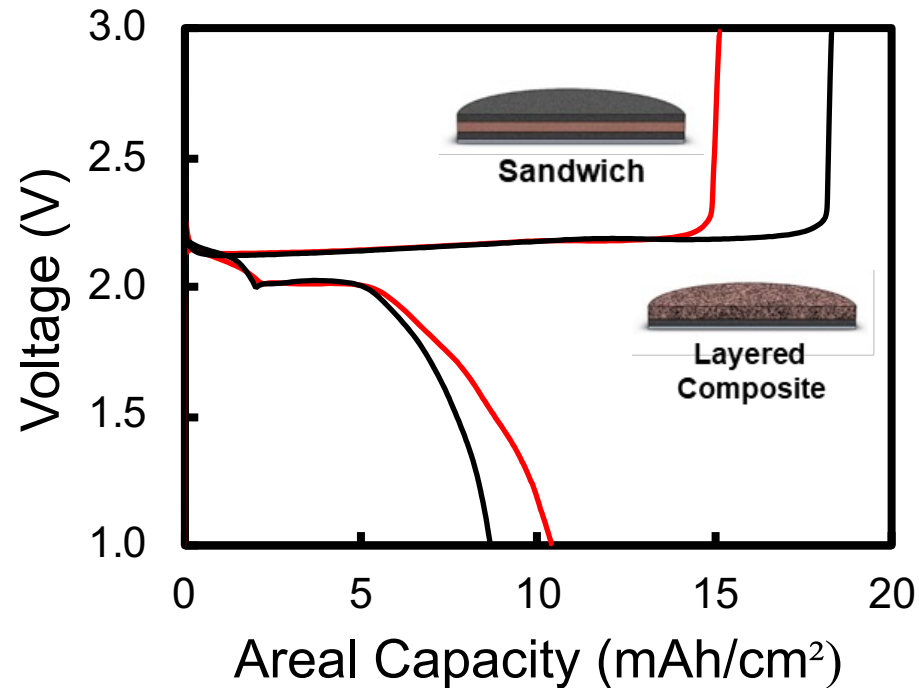
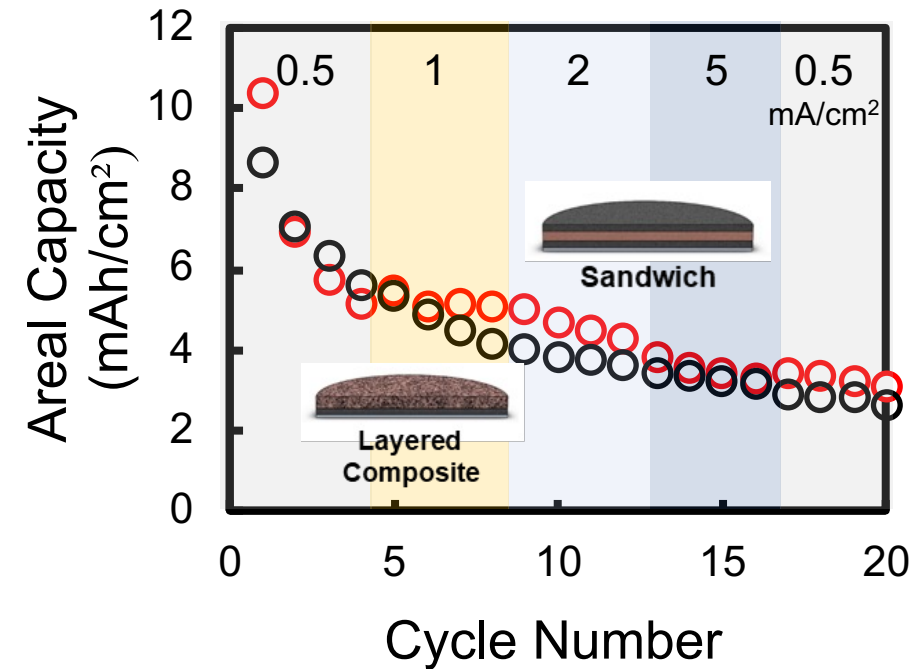
Sandwich Electrode Performance



- ❑ High mass loading: 17.3 mg/cm²
- ❑ High Se content: 75 wt%
- ❑ High Se utilization: 88%
- ❑ High specific capacity: 598 mAh/g_{Se}
- ❑ High areal capacity: 10.4 mAh/cm²
- ❑ Excellent rate performance: > 5 mA/cm²
- ❑ Excellent reversibility

ACS Appl. Energy Mater. **2020**, 3, 6374

Composite vs. Sandwich Electrode



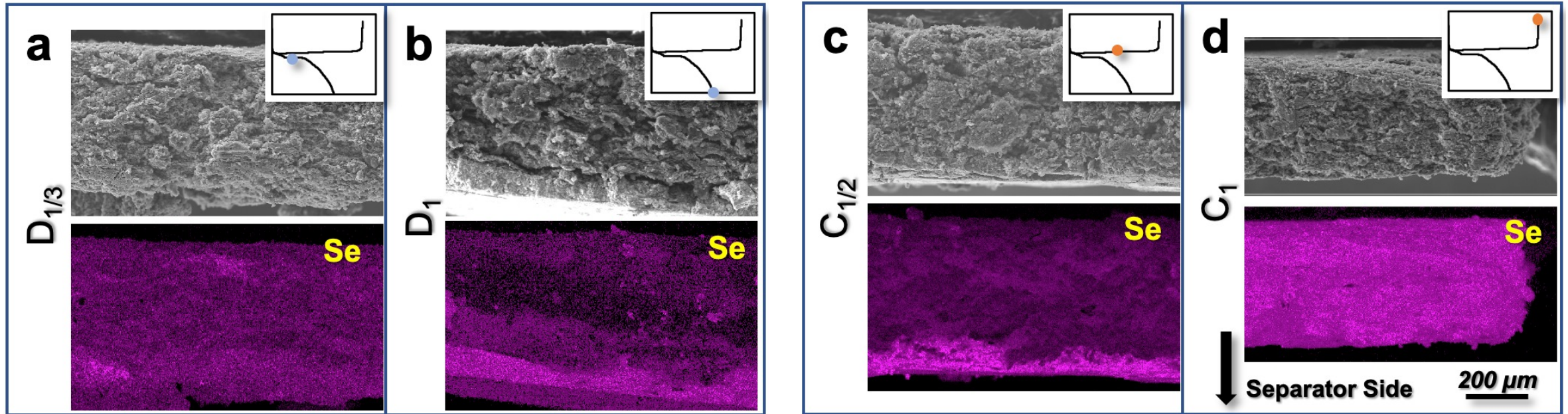
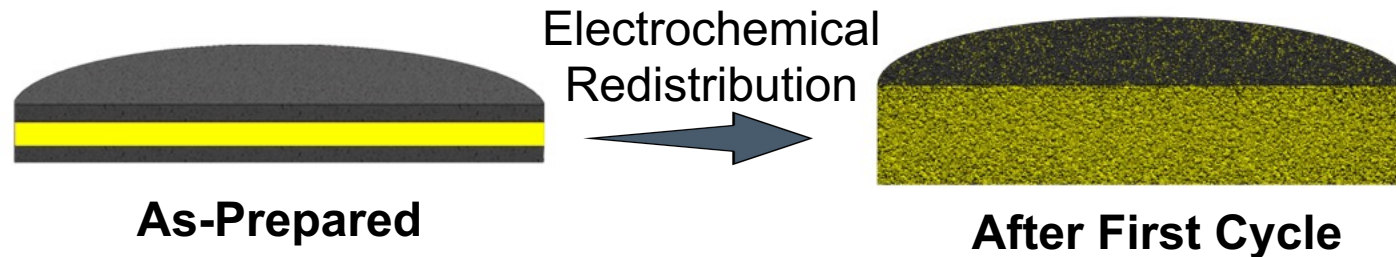
Sandwich vs. (layered) composite architectures:

- ❑ Similar performance: overpotential, utilization
- ❑ **Extremely facile preparation!**

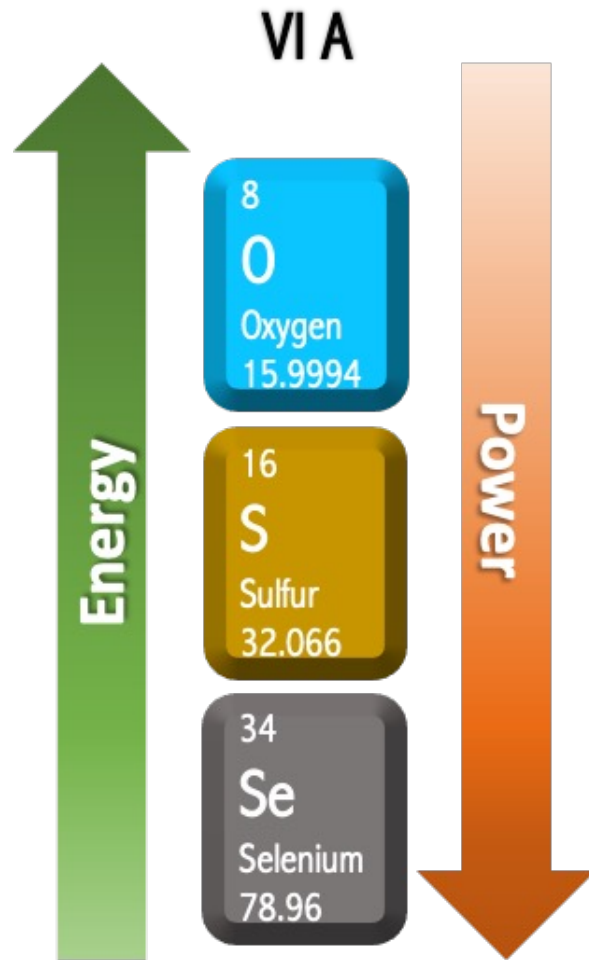
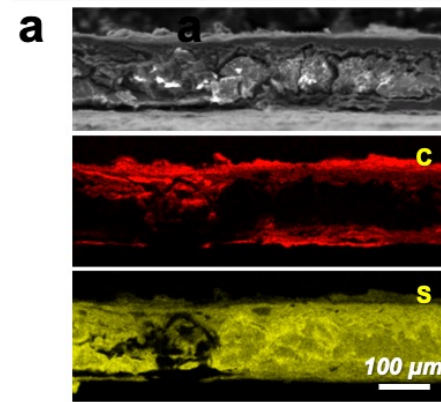
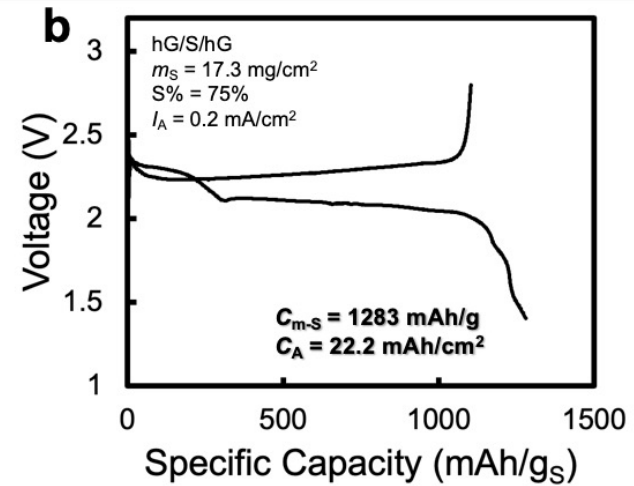
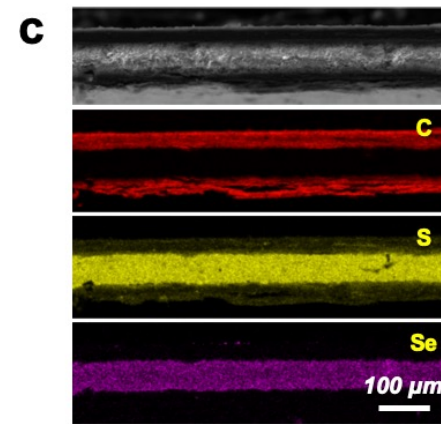
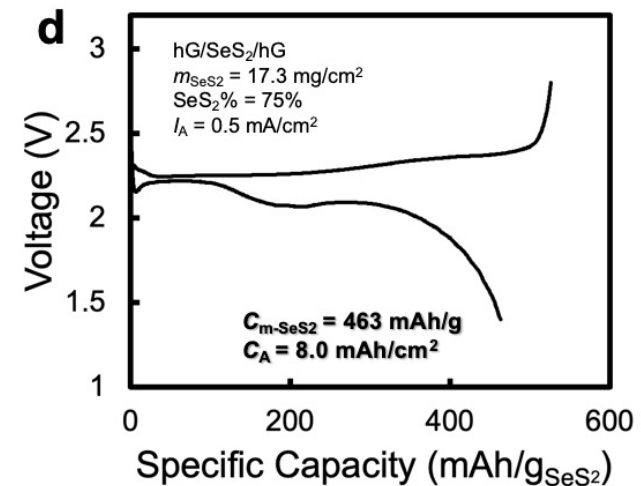
The Fate of Sandwiched Se

Discharge

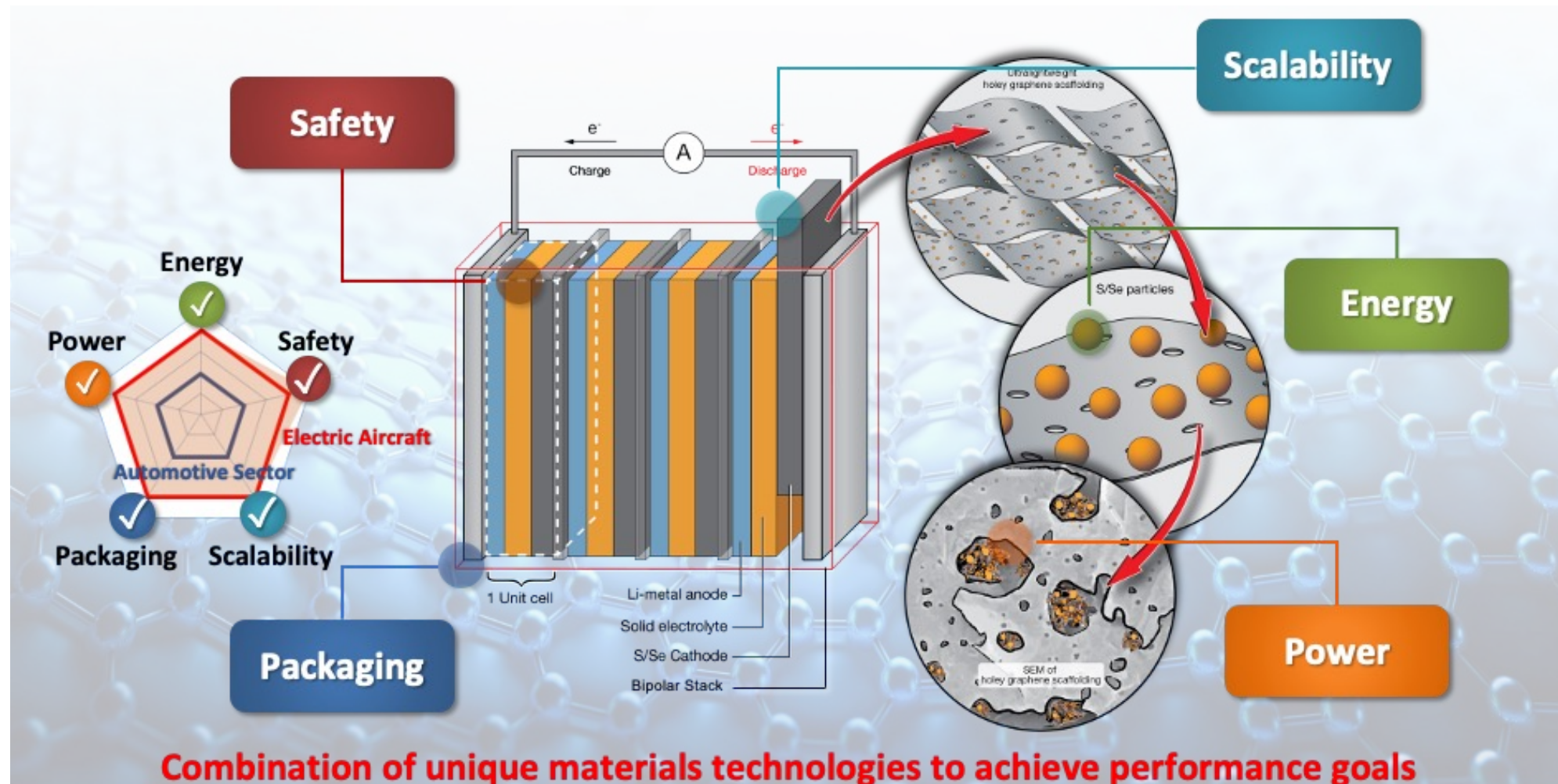
Charge



S and SeS₂ Sandwich Cathodes

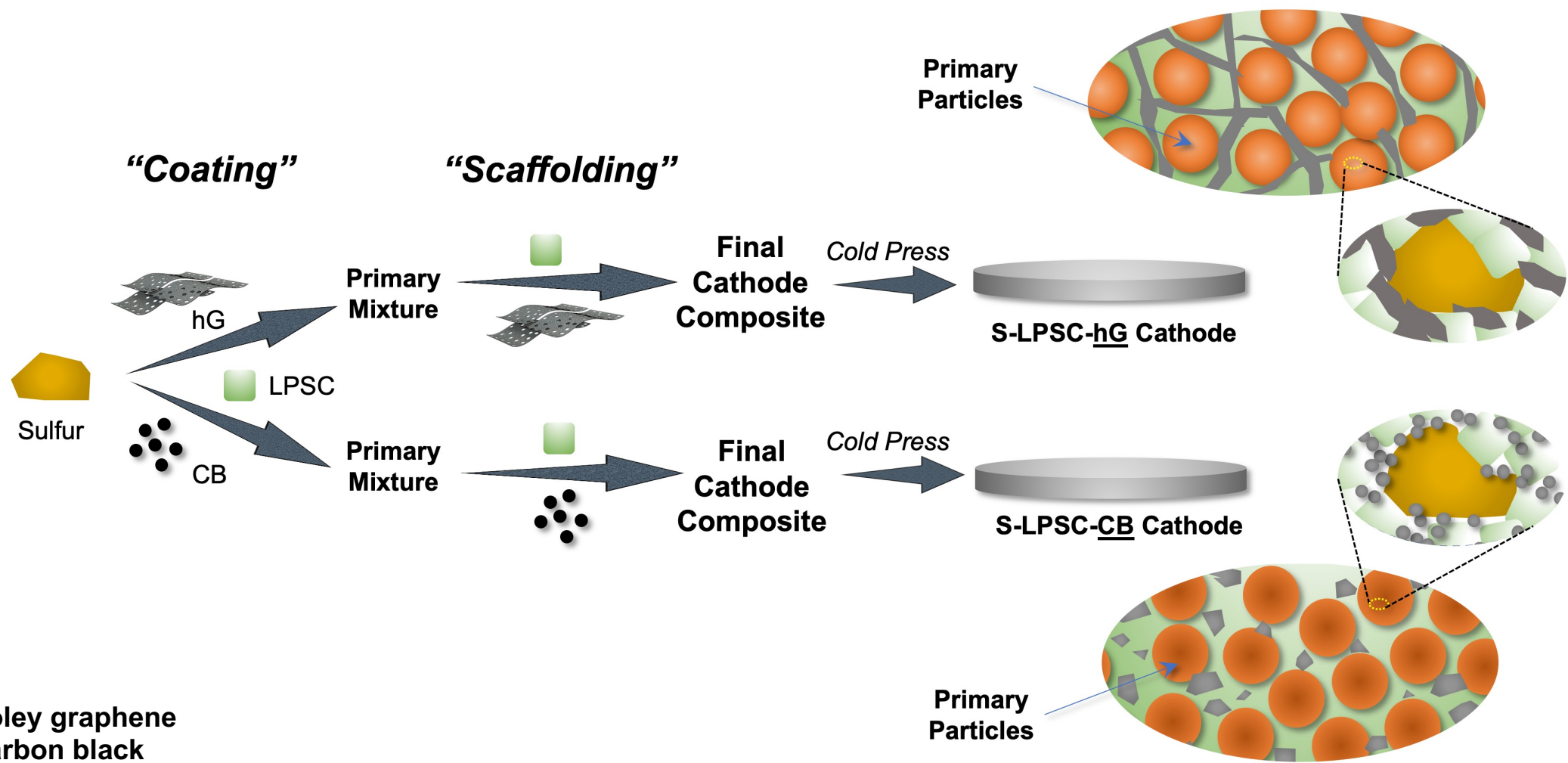


NASA's Interest in Solid-State Batteries

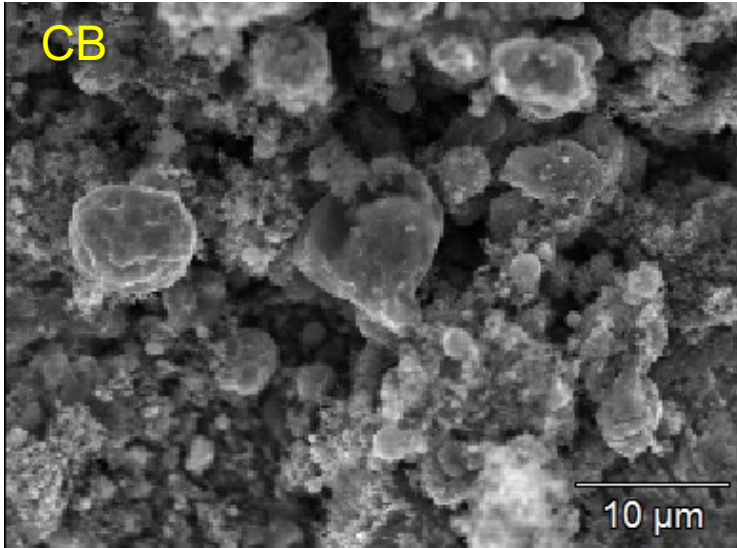
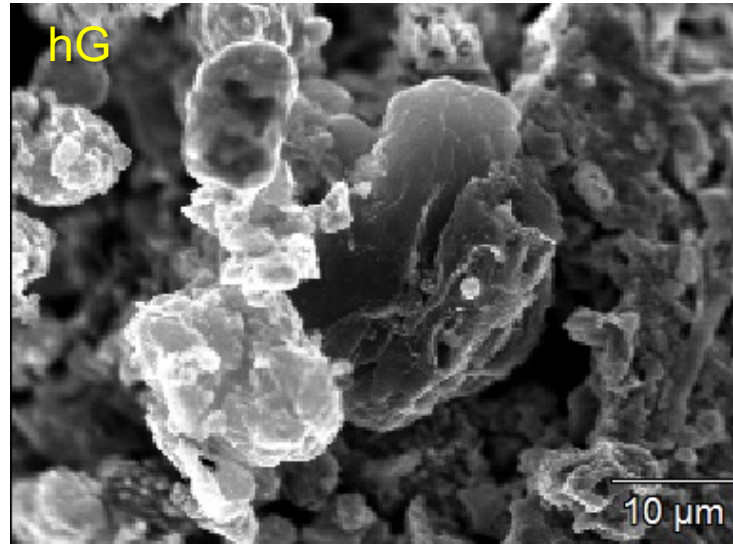


SABERS: Solid-state Architecture Batteries for Enhanced Rechargeability and Safety

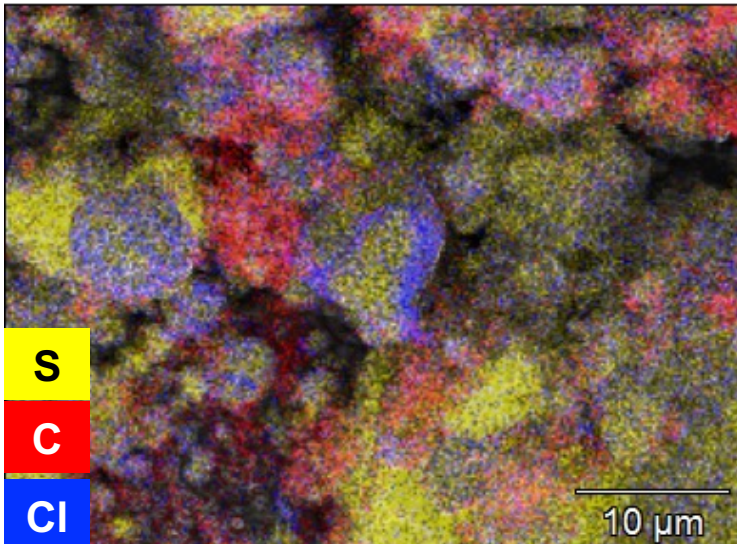
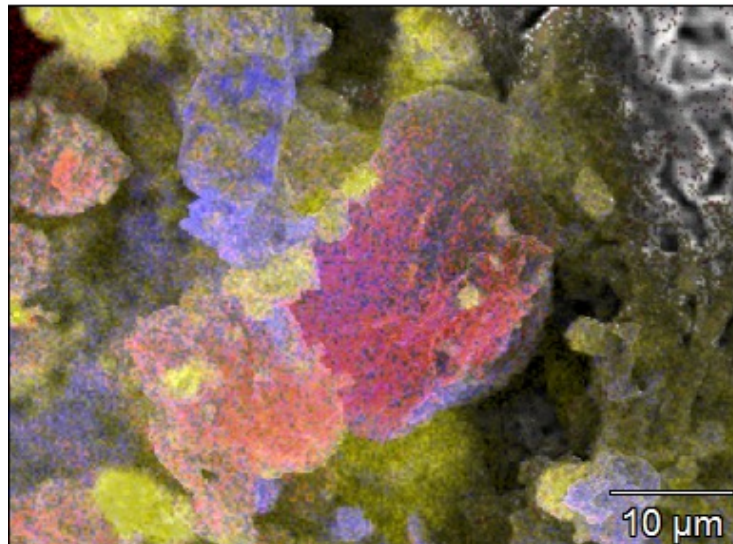
All-Solid-State S Cathodes



Composite Solid-State Cathode Powder



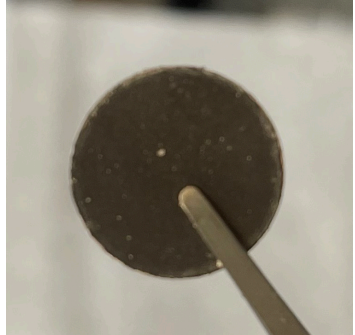
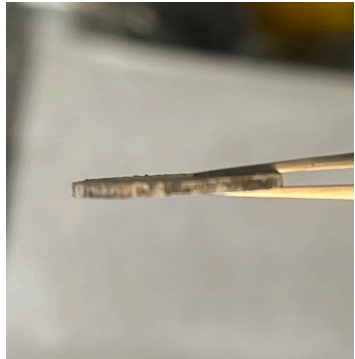
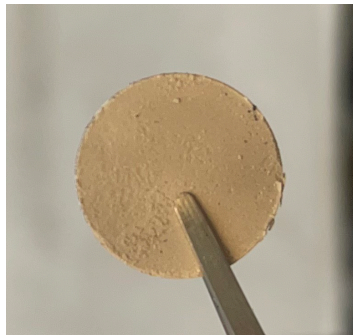
- ❑ Active material: **S**
- ❑ Solid electrolyte (SE): **$\text{Li}_6\text{PS}_5\text{Cl}$ (LPSCI)**
- ❑ Carbon: **CB (carbon black) vs hG (holey graphene)**
- ❑ Multistep mixing process



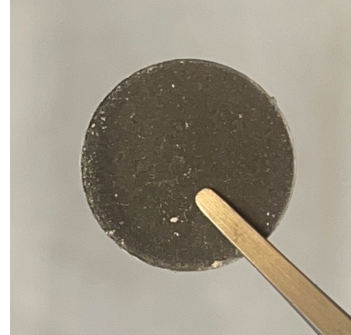
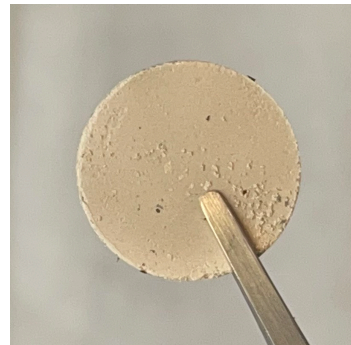
CB: Super C45

Dry-Pressed Cathode/SE Bilayer Discs

CB

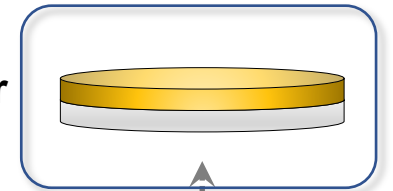


hG



- ❑ 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...?

Cathode/SE Bilayer

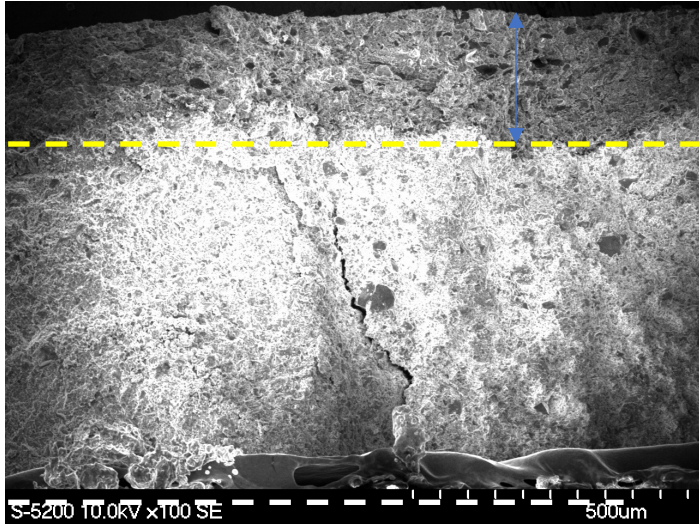
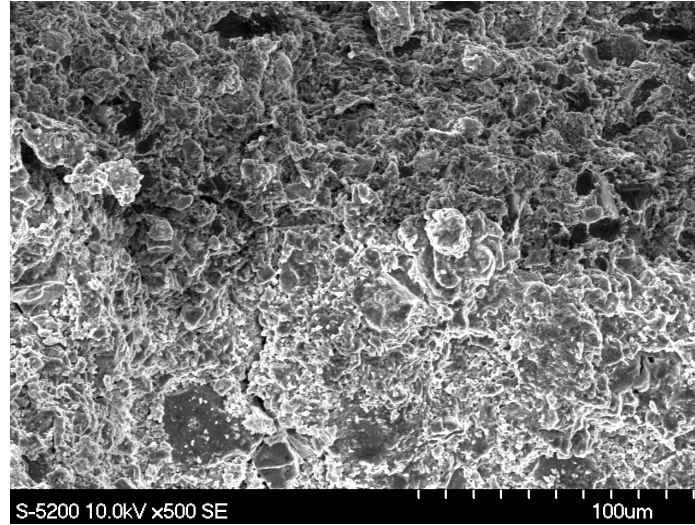
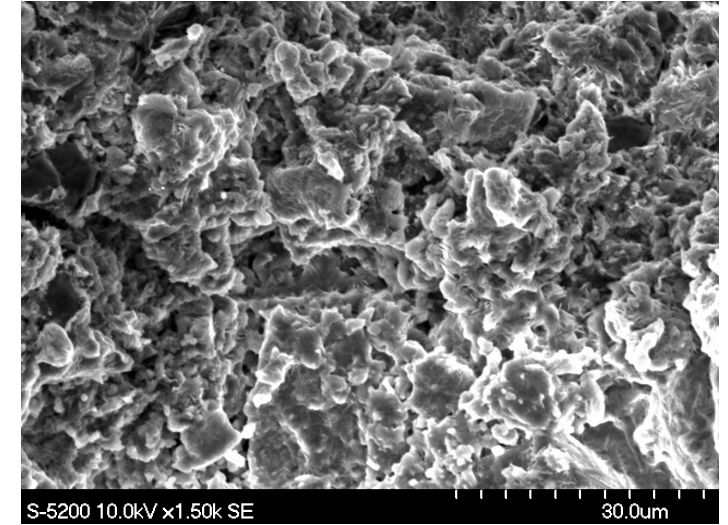


Li metal

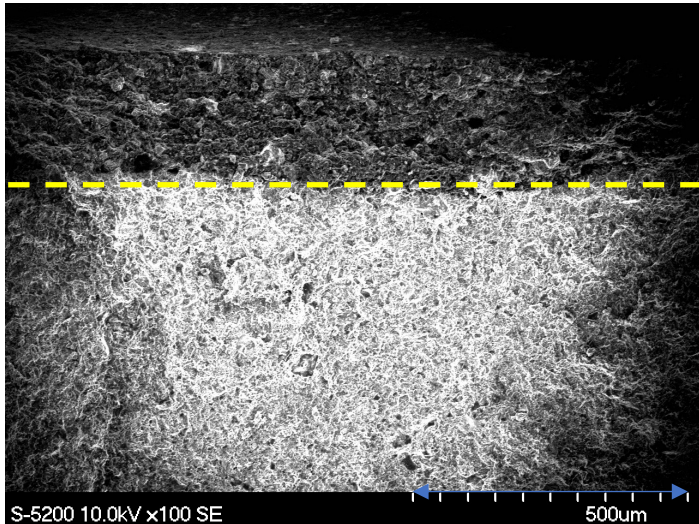
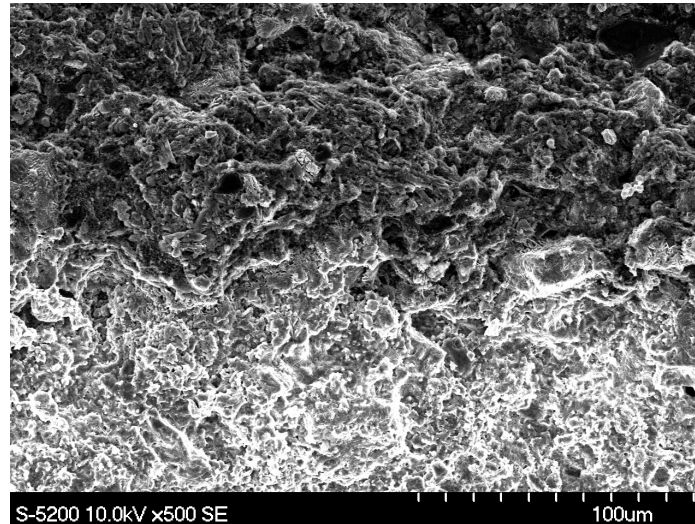
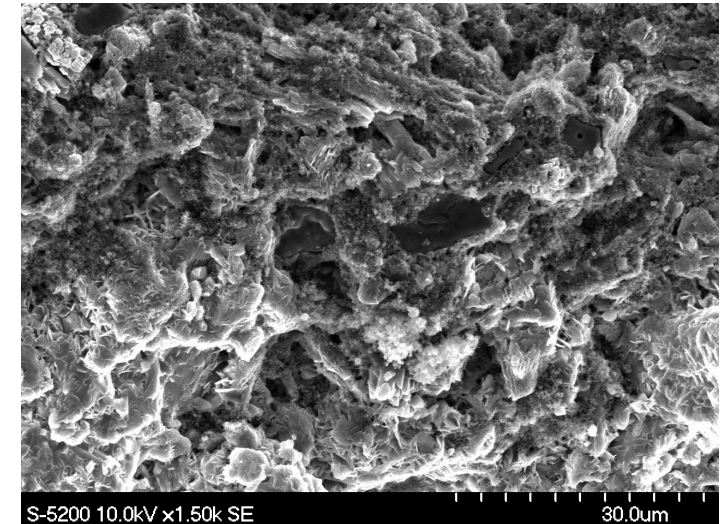


Dry-Pressed Cathode/SE Bilayers

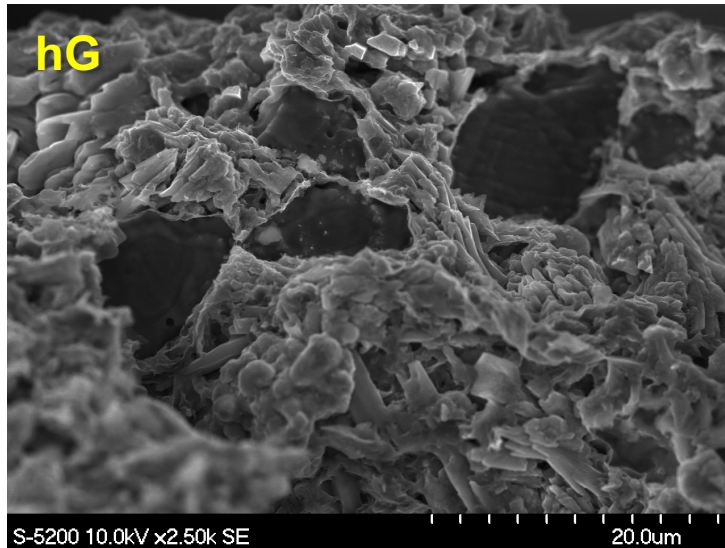
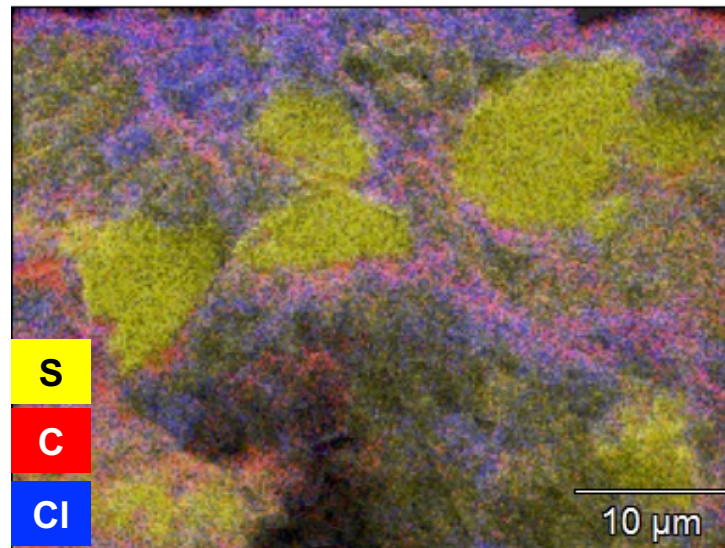
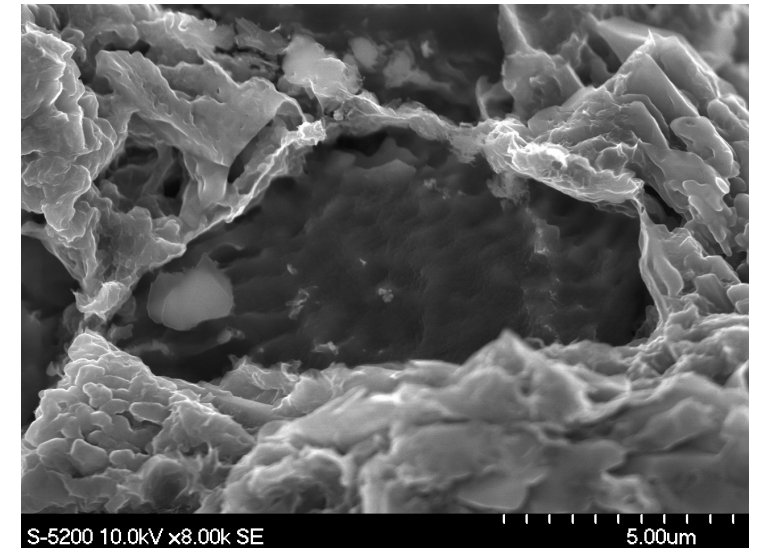
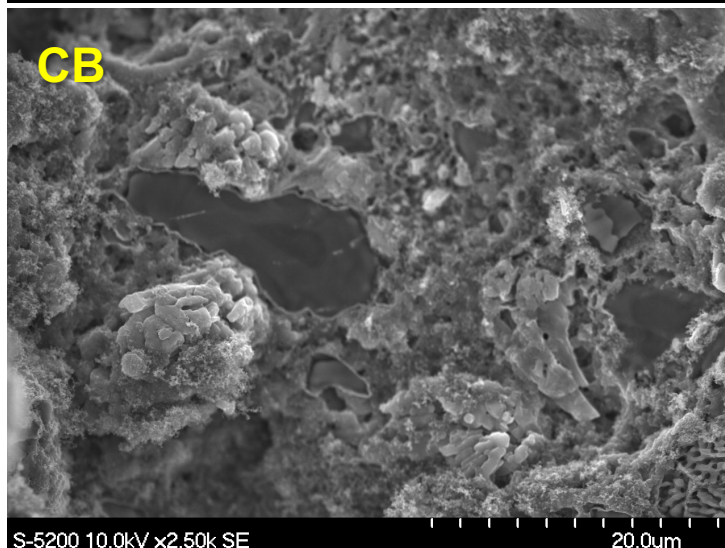
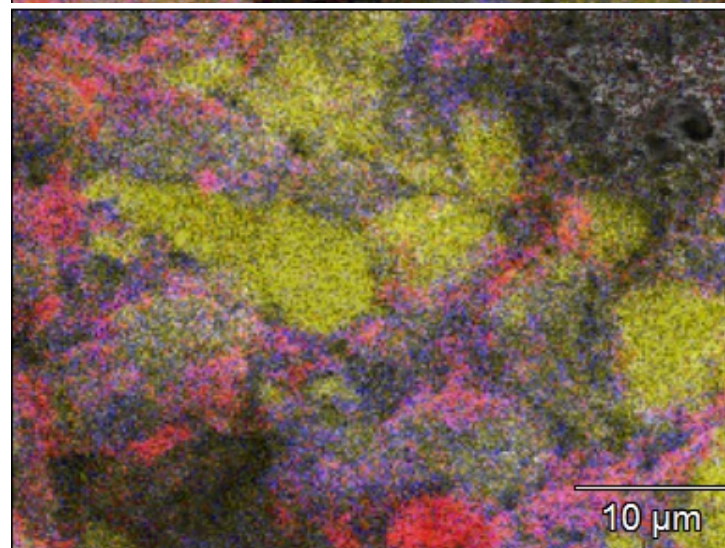
hG



CB

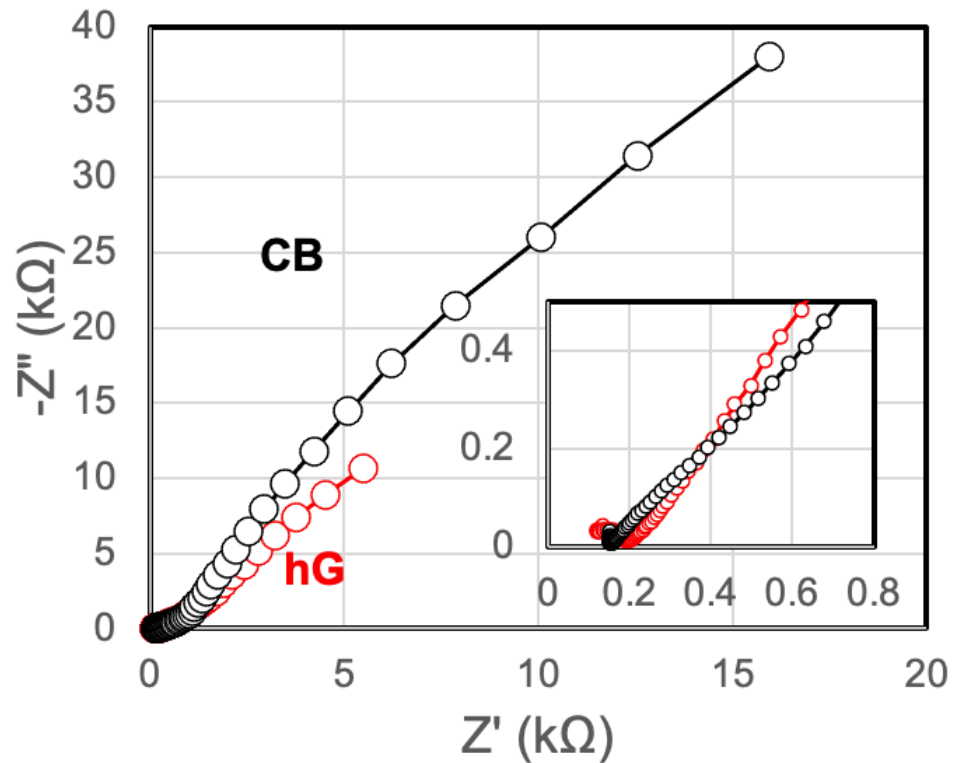


Cathode Microstructures

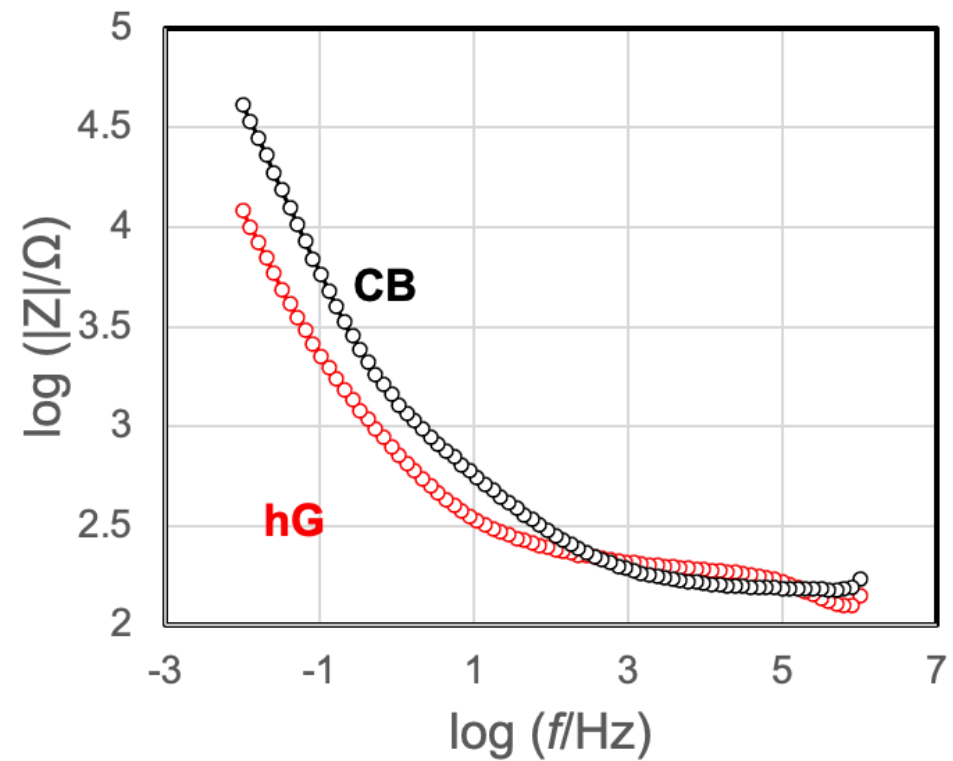


All-Solid-State Li-S Cell Impedance Characteristics

Nyquist Plot

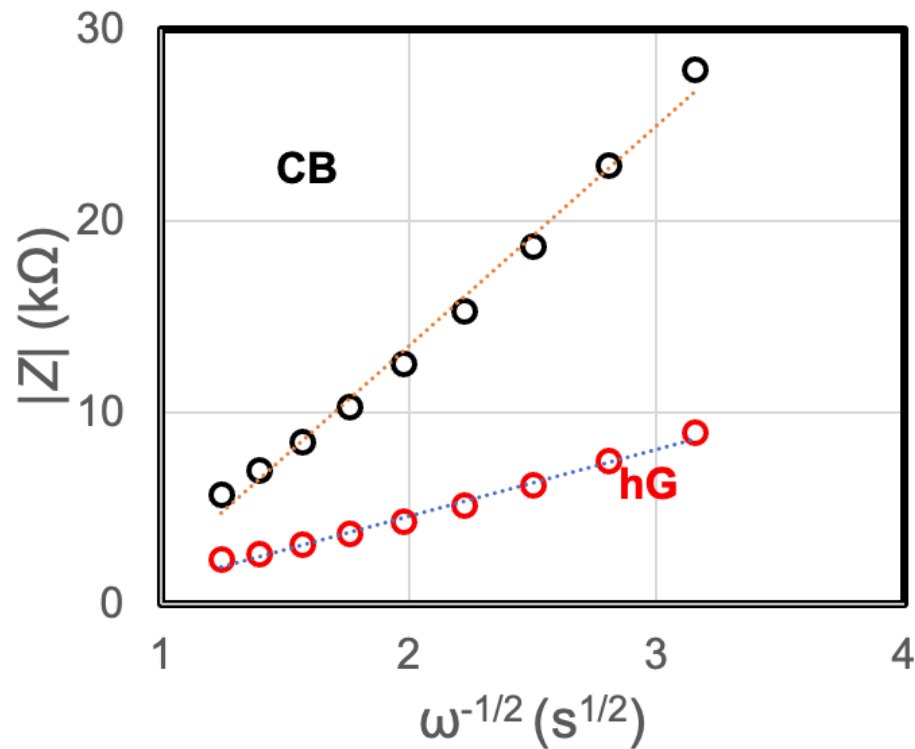


Bode Plot



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

Li Ion Diffusion Properties

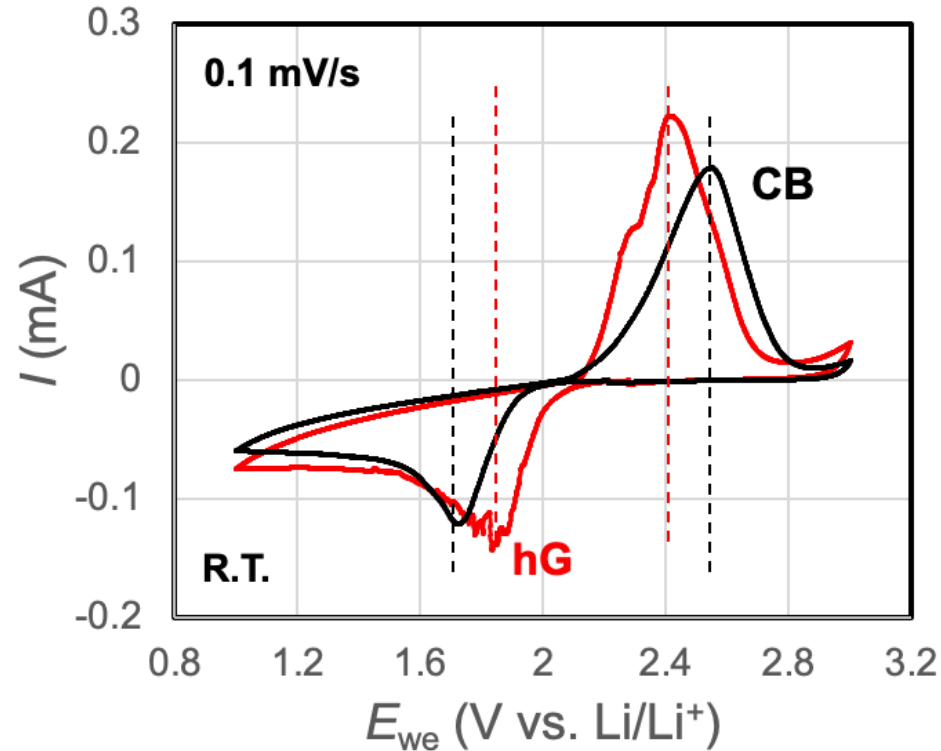
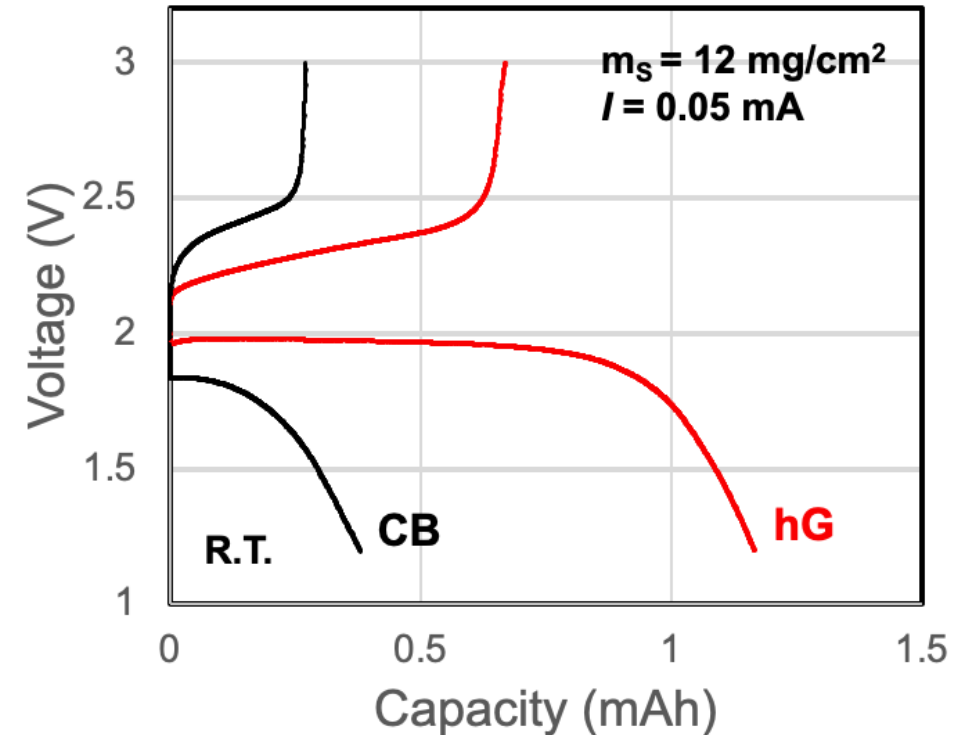


$$D_{Li^+} = \frac{R^2 T^2}{2 A^2 n^4 F^4 c^2 \sigma_w^2}$$

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

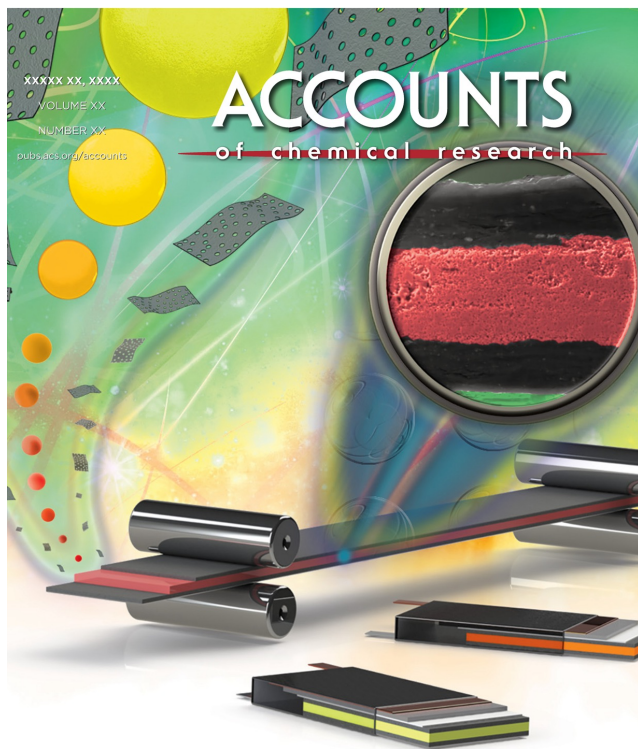
- The use of hG allows one magnitude higher of Li ion diffusion through the cathode.

All-Solid-State Li-S Cell Performance



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

Summary



ACS Publications
Most Trusted. Most Cited. Most Read.

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- ❑ Holey graphene is a structural derivative of graphene that can be prepared via catalytic or catalyst-free oxidation of graphene
- ❑ Holey graphene is an advanced electrode material due to the presence of holes through the nanosheet thickness
- ❑ Holey graphene powder is dry compressible and can be used for a variety of energy storage applications

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

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- ❑ Student Interns:
 - 2015: Evan Walsh; Steven Lacey
 - 2016: Brandon Moitoso; Chalynette Martinez-Martinez; Emily Hitz; Natalie Delumpa-Alexander
 - 2017: Sterling Baird; Kobi Jones; Marina Chang; Joshua Jack
 - 2018: Francisco Mendez Sosa; Louisa Greenburg
 - 2019: Christian Plaza-Rivera; Nam Tran; Bryson Clifford
 - 2020-2021: Brandon Walker; April Rains
 - 2022: Abigail Durgin; Bona Kim; Ashley Lam; Lucy Somervill; Rehan Rashid; Daniel Caicedo