

Solvent-Free Preparation of High Energy, Binder-Free Electrodes Enabled by Dry Compressible Holey Graphene

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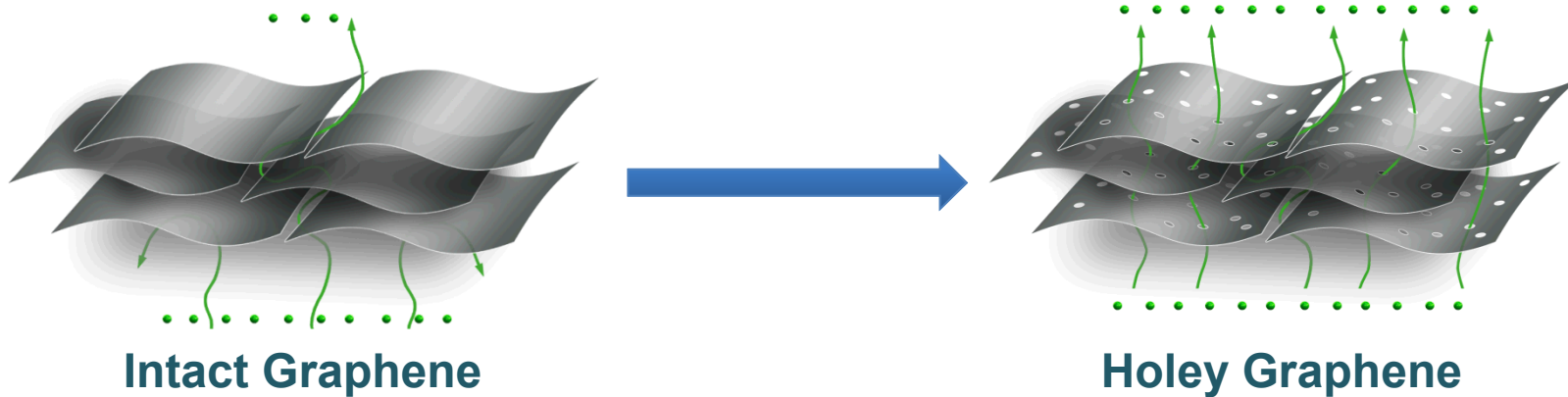
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44th International Conference and Expo on Advanced Ceramics and Composites

01/30/2020

Holey Graphene vs. Graphene

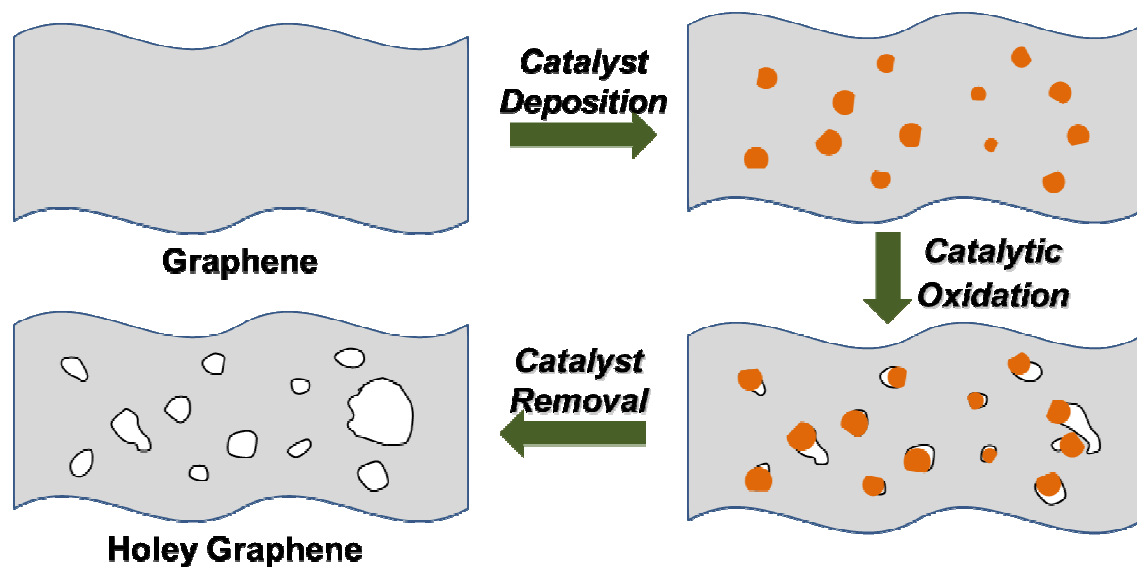
Improved ion transport path at high stacking density



- ☐ In-plane porosity: Improve ion transport path, reduce tortuosity
- ☐ Accessible surface area: Improve gravimetric capacitance
- ☐ Volume reduction: Mitigate need to create large pores/spacing
- ☐ Hole-edge functionalities: Improve mesoscale wetting
- ☐ Electrical Conductivity: Retain graphitic crystallinity

Bulk Preparation of Holey Graphene

"Generation I"



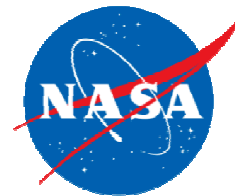
Controlled Catalytic Oxidation



Nanoscale **2013**, 5, 7814.

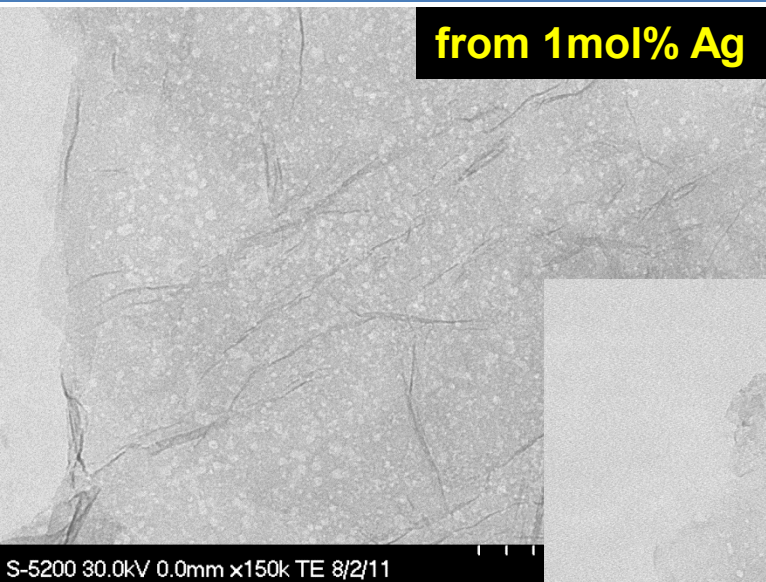
Holey Graphene = hG = h-Graphene

US 9120677 B2



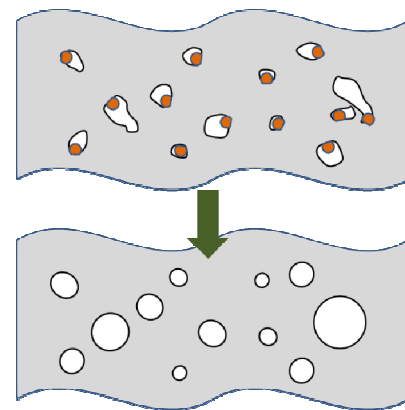
Holey Graphene from Catalytic Etching

from 1mol% Ag

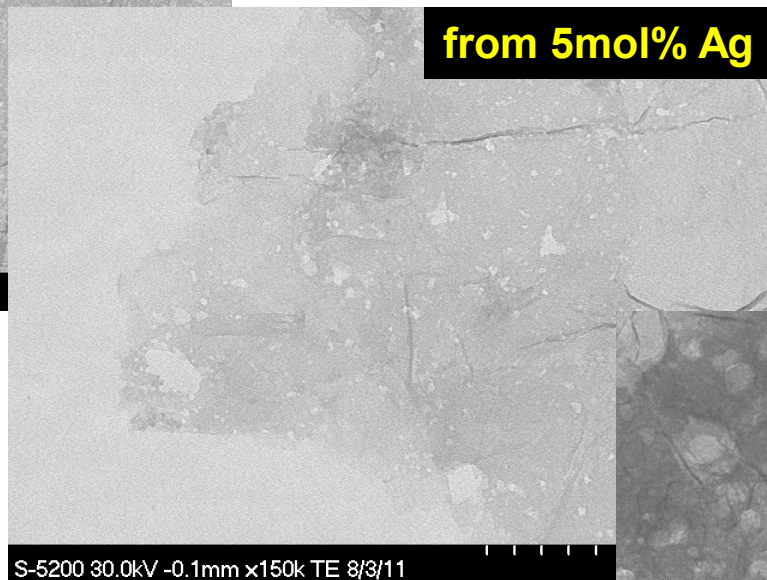


Oxidative acid wash

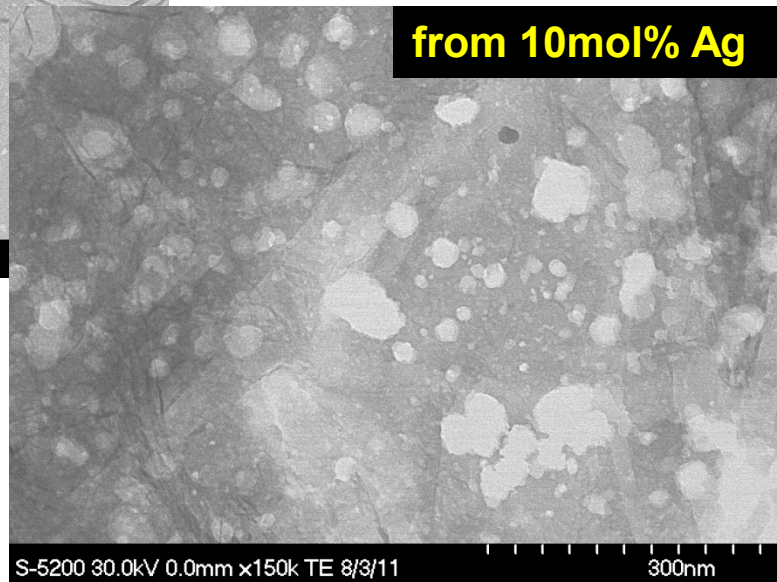
- ❖ Ag catalyst removal
- ❖ “Polish” hole/track edges



from 5mol% Ag

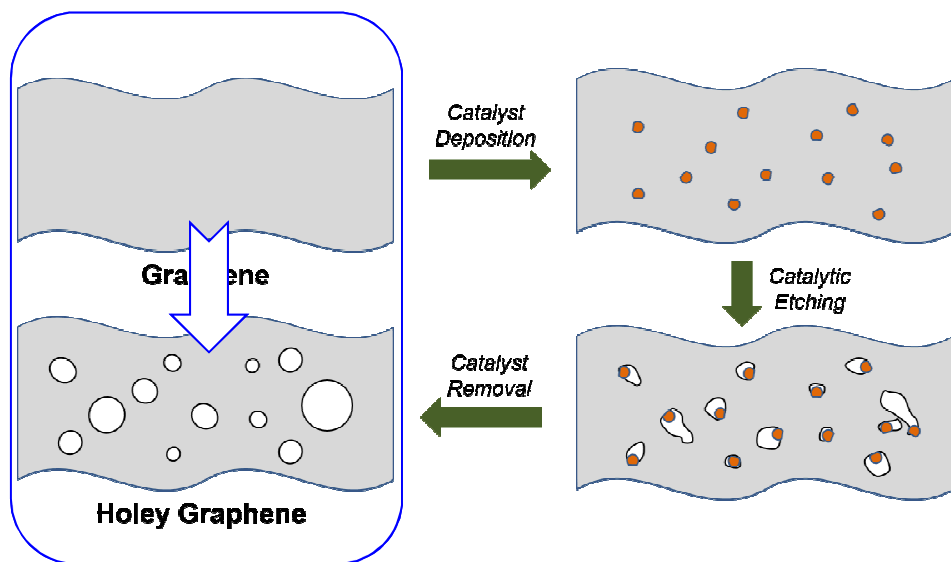


from 10mol% Ag

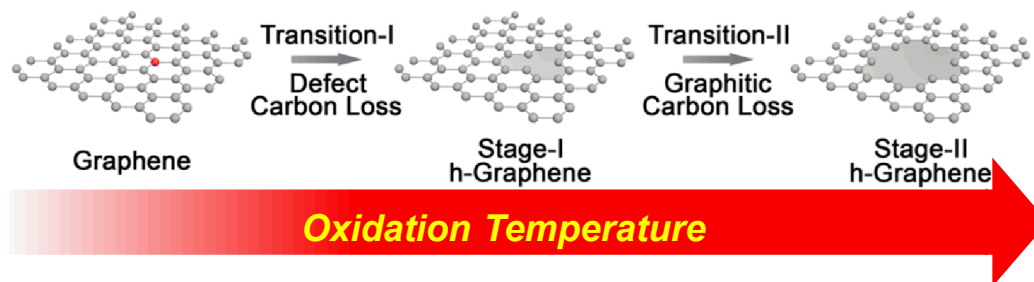


- ❑ Etching: 300 °C, 3h, Air
- ❑ Polishing: **HNO₃ (2.6 M)**, 2h reflux

Catalyst-Free Synthesis of hG



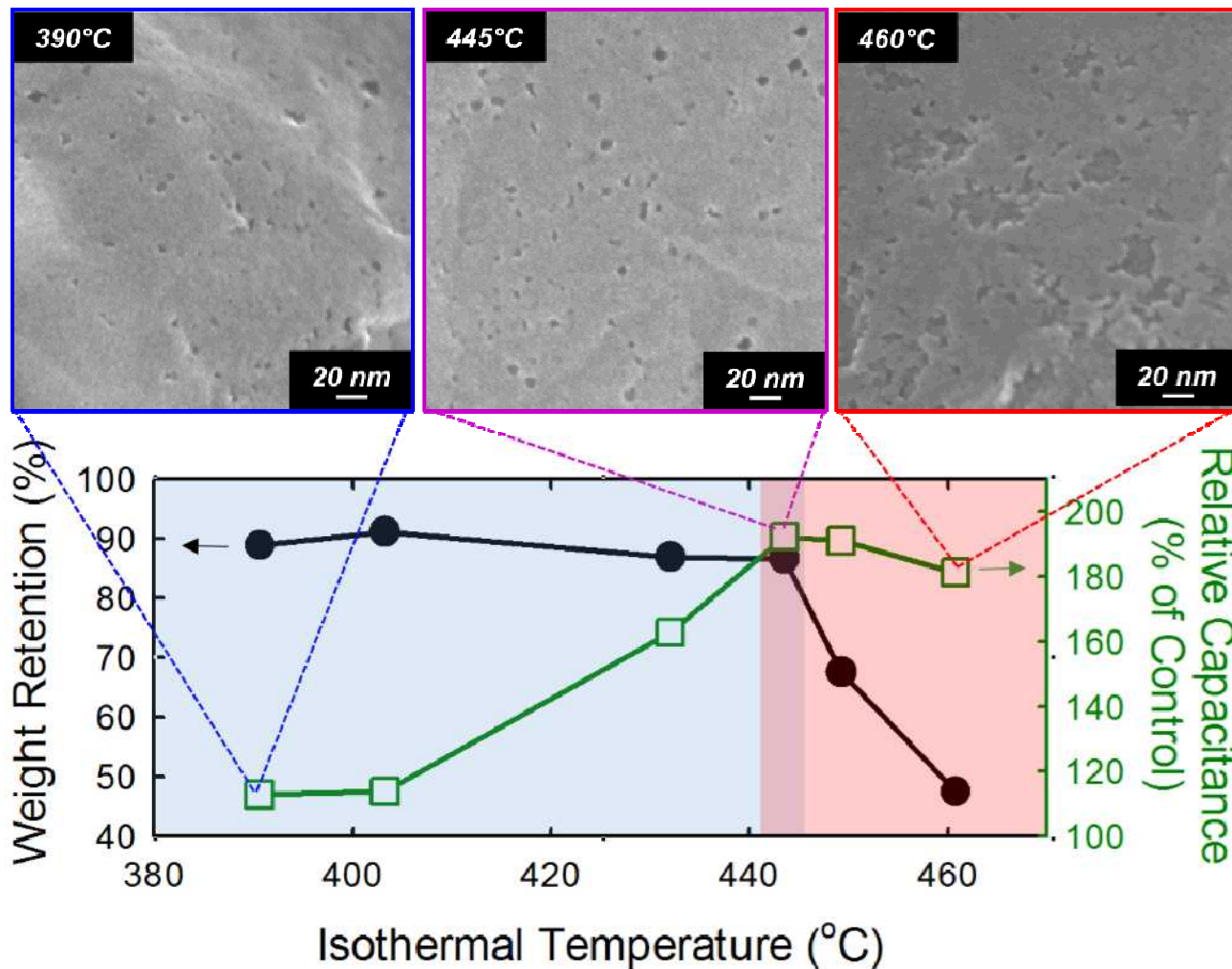
“Generation II”



Single Step + Catalyst-Free = Highly scalable!



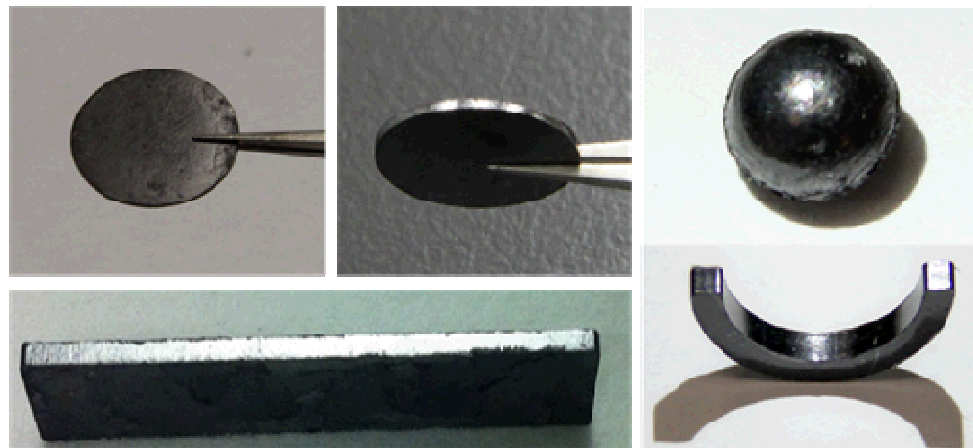
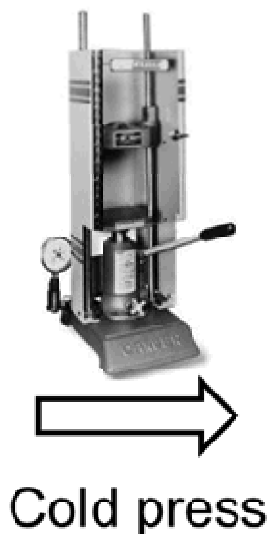
Catalyst-Free Synthesis of hG



Unique Dry Compressibility of hG



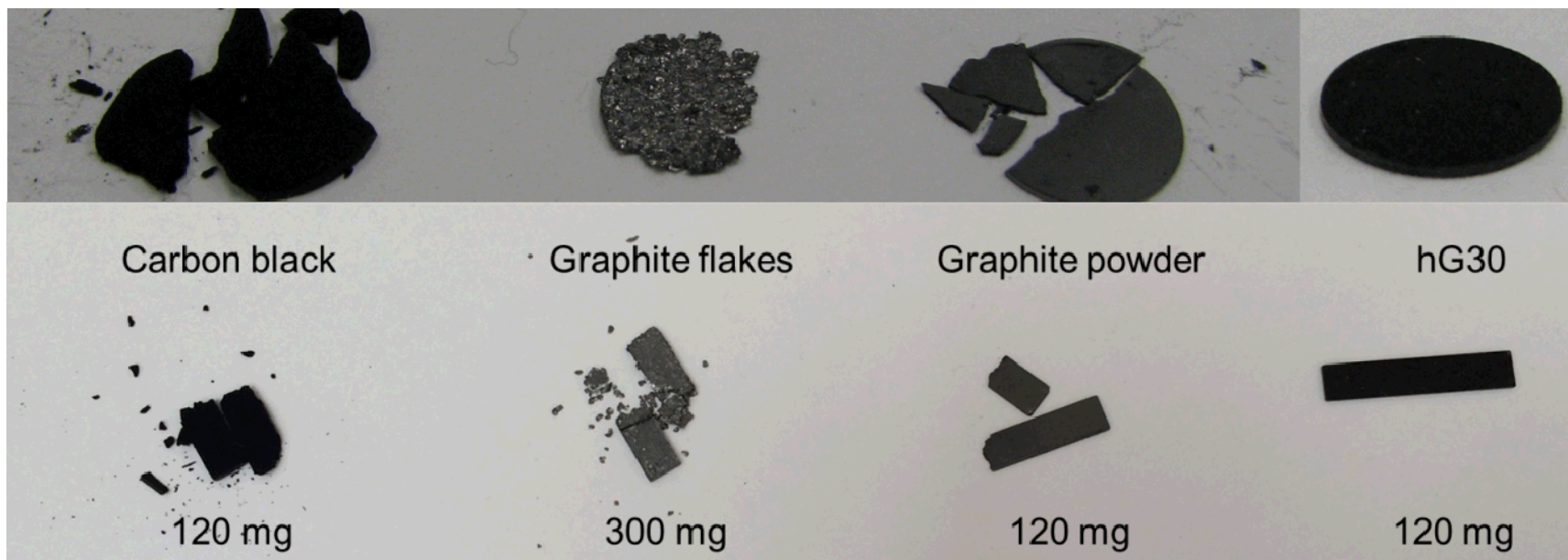
**Holey Graphene
Powder**



**Holey Graphene
Monolithic Architectures**

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

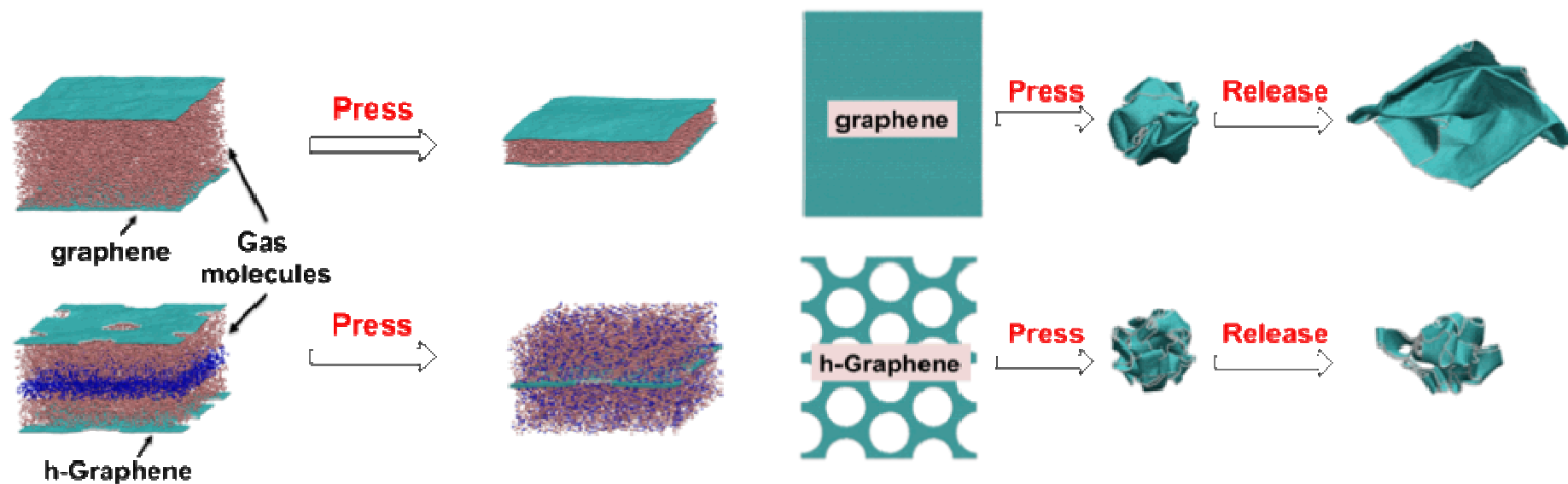
Other Common Carbon Materials Are Not Compressible



Drop from 36 cm

Drop from 36 cm,
and then 110 cm

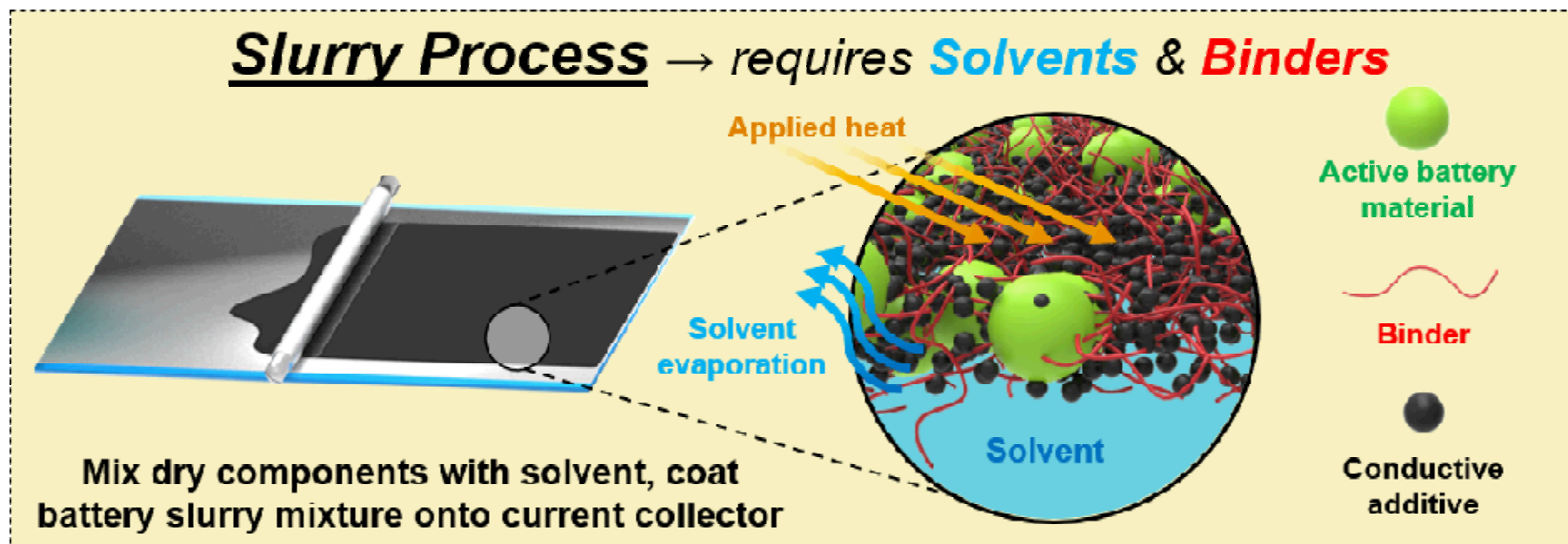
What Makes hG Compressible?



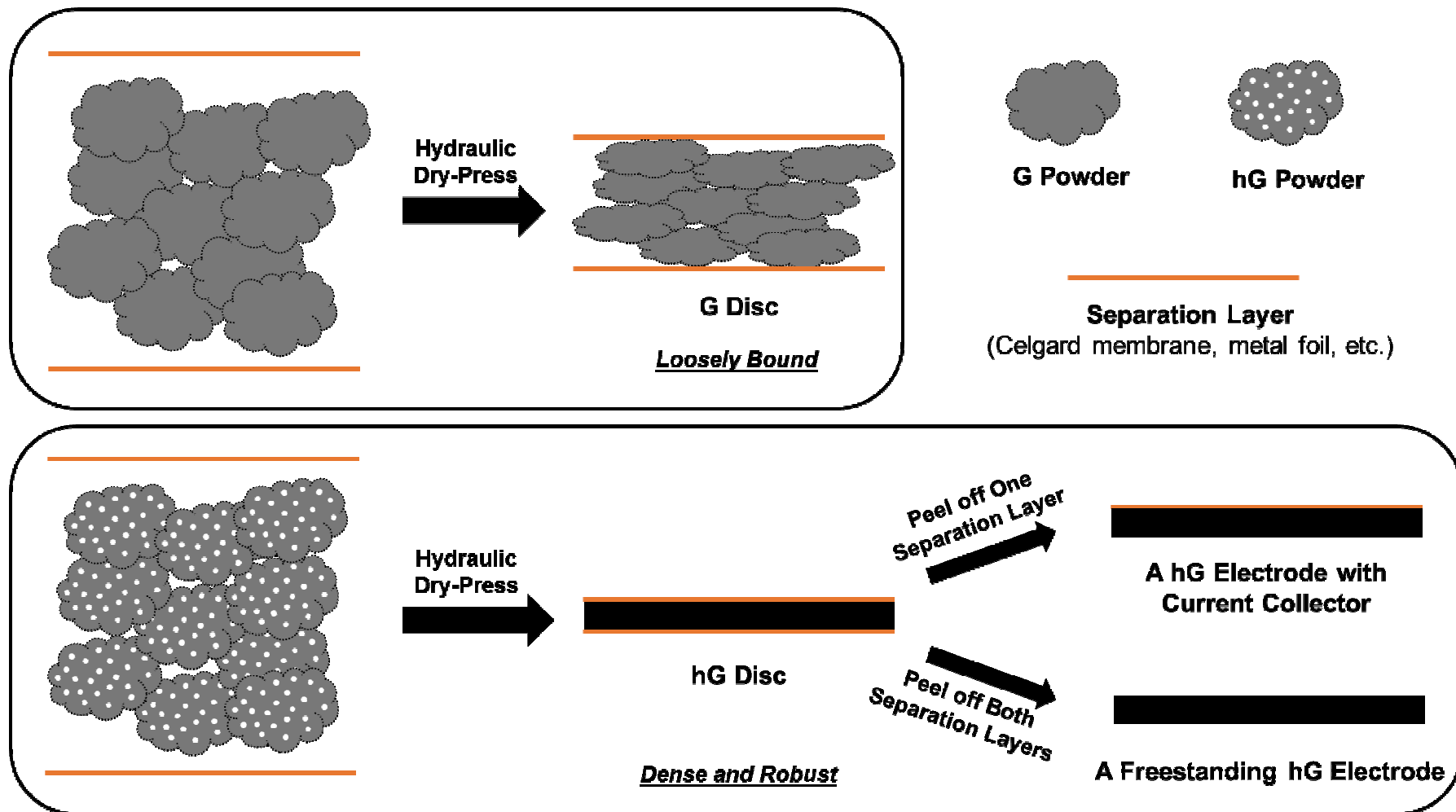
Facile air escape upon compression

Minimal volume rebound upon release

Conventional Electrode Preparation

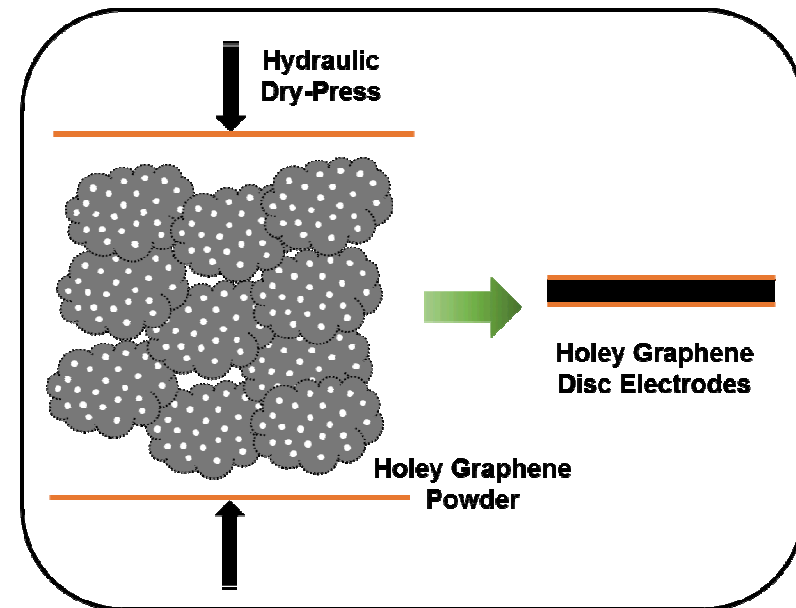


Dry Pressed hG Electrodes

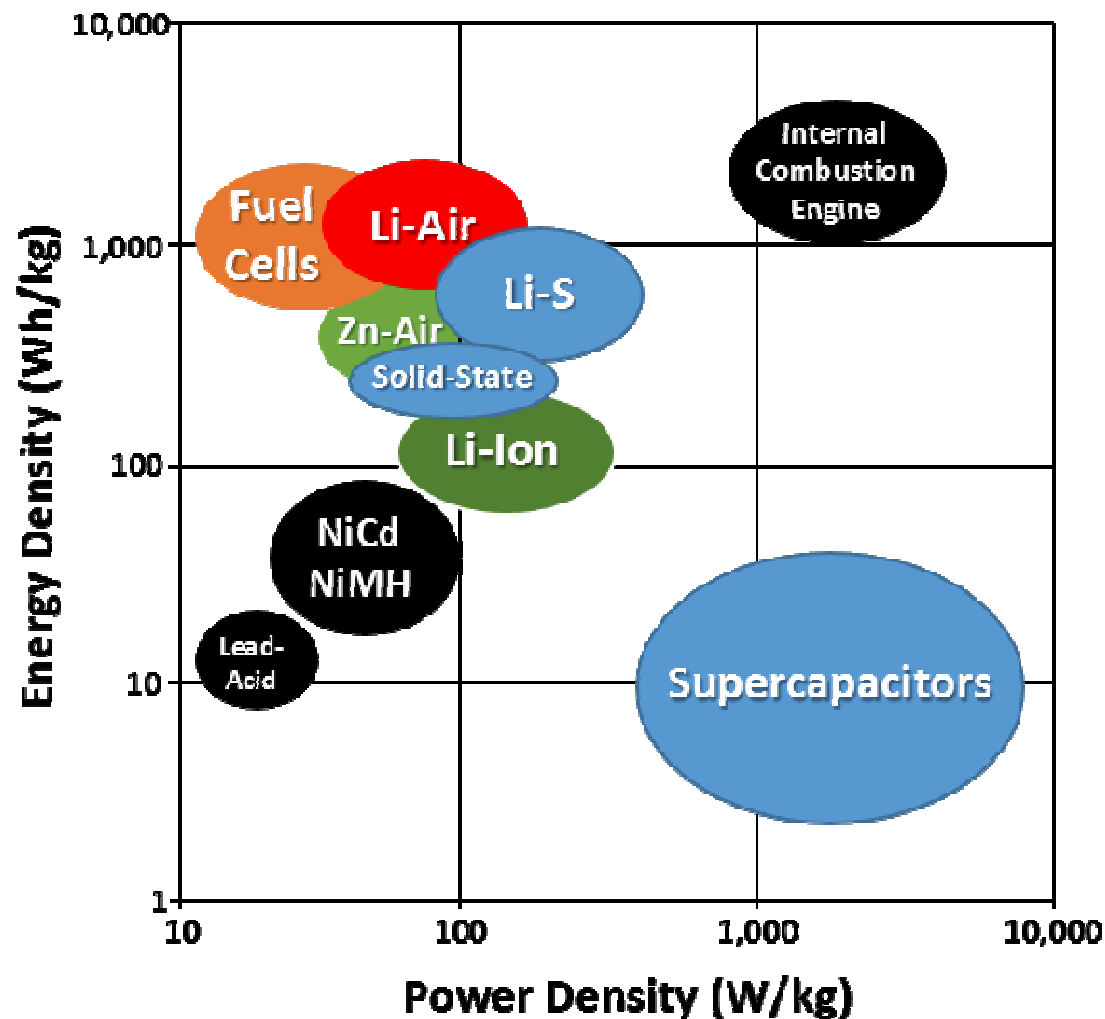


Key Advantages of Dry Pressed Electrodes

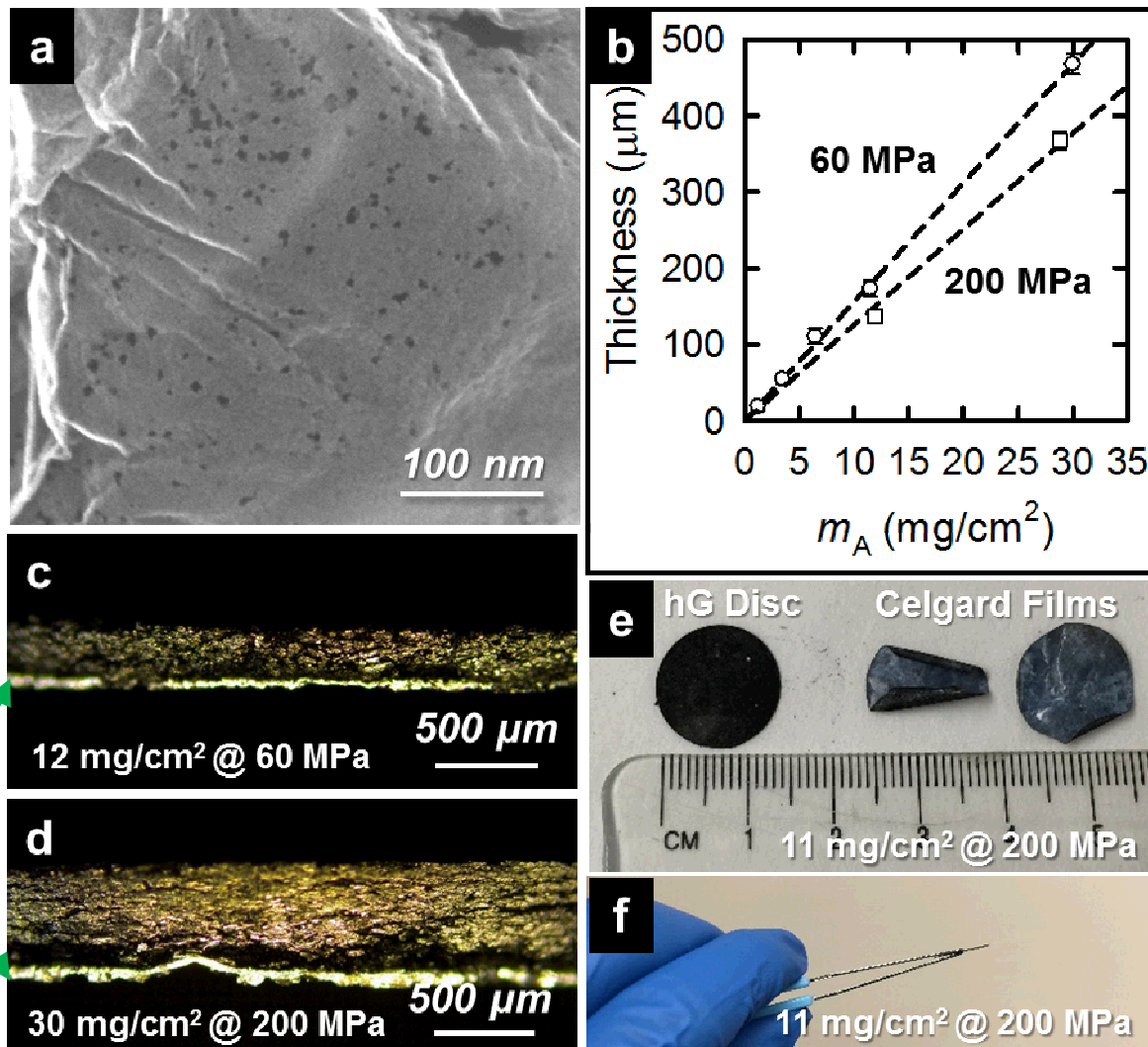
- ❑ Solvent-free
- ❑ Binder-free
- ❑ Completion within minutes
- ❑ Scalable: High Mass Loading



Energy Storage Platforms

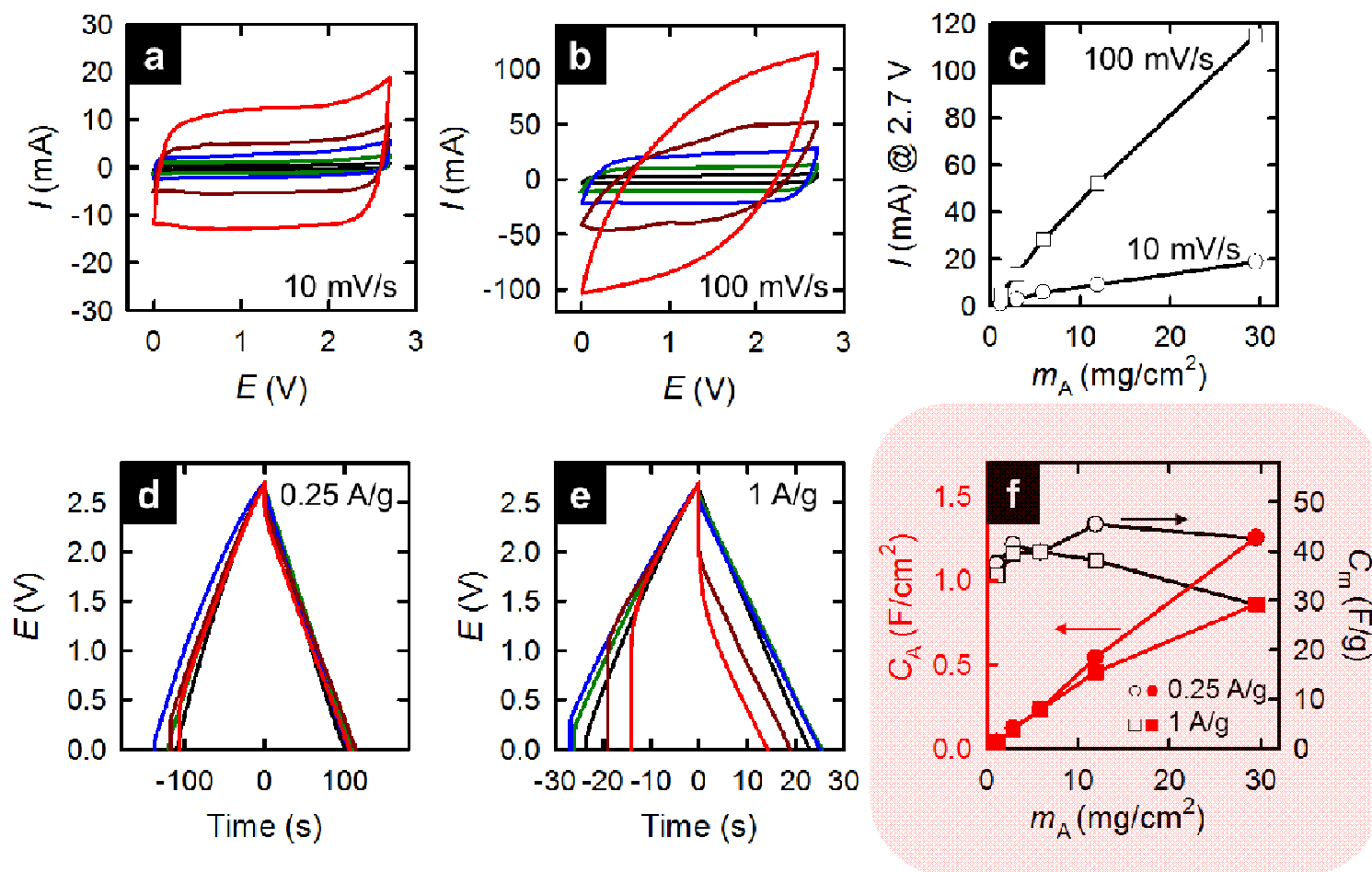


Ultrahigh Mass Loading Dry-Pressed Supercapacitor Electrodes



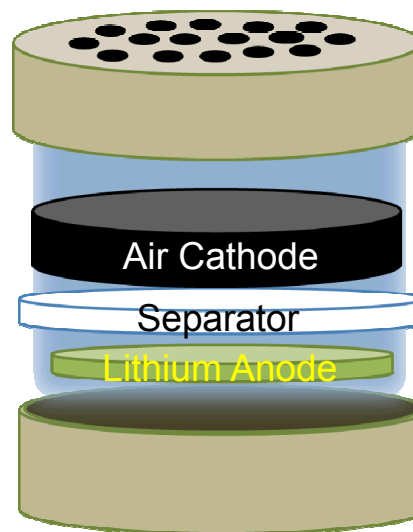
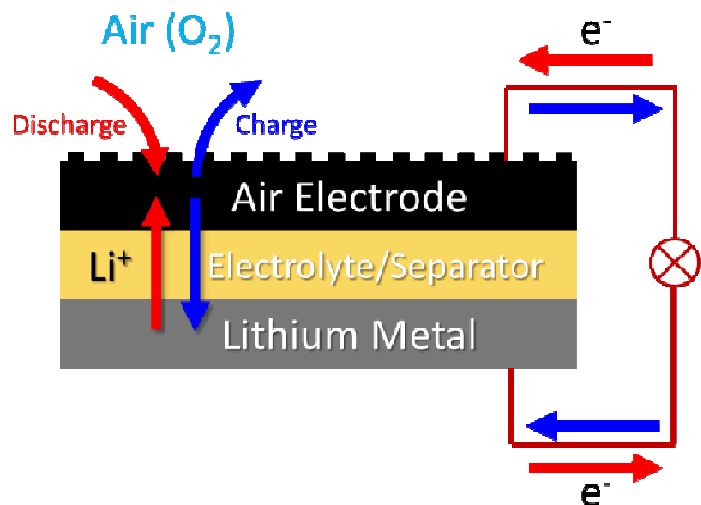
Freestanding
(no backing)

Supercapacitor Performance vs. Mass Loading



Superior areal performance at a mass loading as high as $30 \text{ mg}/\text{cm}^2$!

Key Challenges for Lithium-Air Batteries



- Porous
- Conductive
- Catalytic (ORR/OER)

Reactions at the Air Cathode

Oxygen Reduction Reaction (ORR):
 $O_2 + 2e^- + 2Li^+ \rightarrow Li_2O_2$ (discharge)

Oxygen Evolution Reaction (OER):
 $Li_2O_2 \rightarrow O_2 + 2e^- + 2Li^+$ (charge)

❖ Air cathode performance

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

❖ Electrolyte decomposition

❖ Li anode deactivation

❖ Interference from air

Building Criteria for Air Cathodes

Current Norm

*Air Cathode
Material*



Cathode Material Research

Is the cathode material effective in
facilitating discharge/charge reactions?

A New Direction

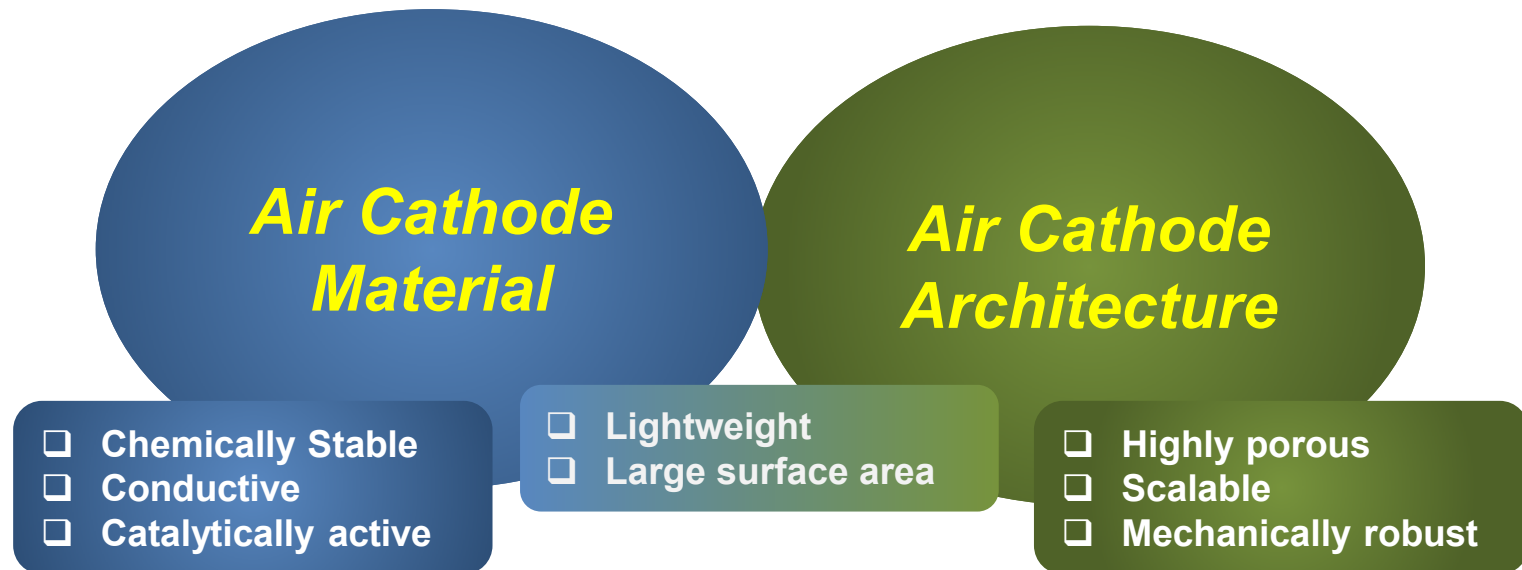
*Air Cathode
Architecture*



Cathode Architecture Research

Is the cathode architecture effective in
facilitating discharge/charge reactions
with competitive total/areal capacity?

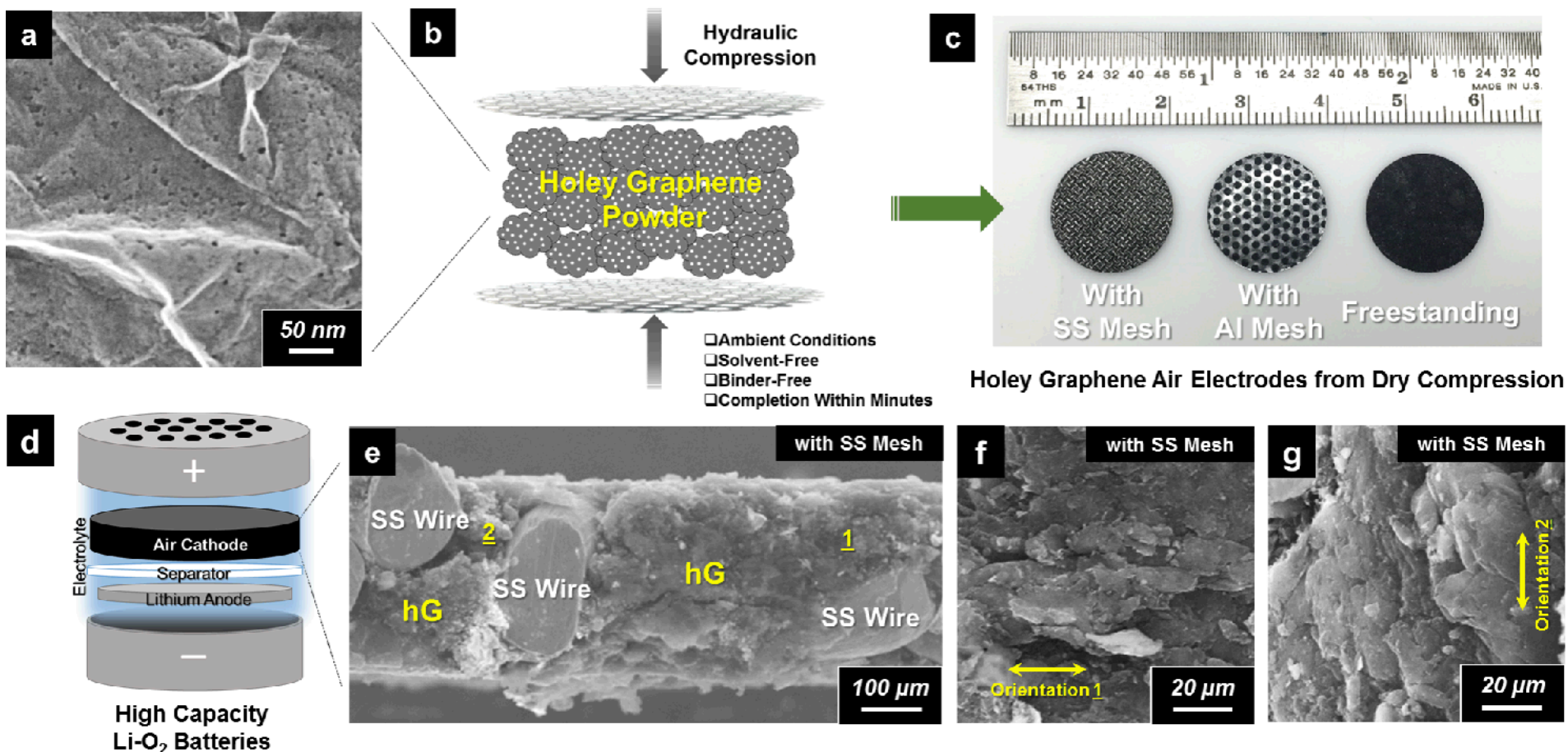
Building Criteria for Air Cathodes



- ☐ Carbon nanomaterials, including graphene and carbon nanotubes, are excellent air cathode material platforms.
- ☐ Highly porous nanocarbon electrodes are excellent air cathode architecture platforms.

Effective air cathode architectures are critical for practical Li-O₂ batteries.

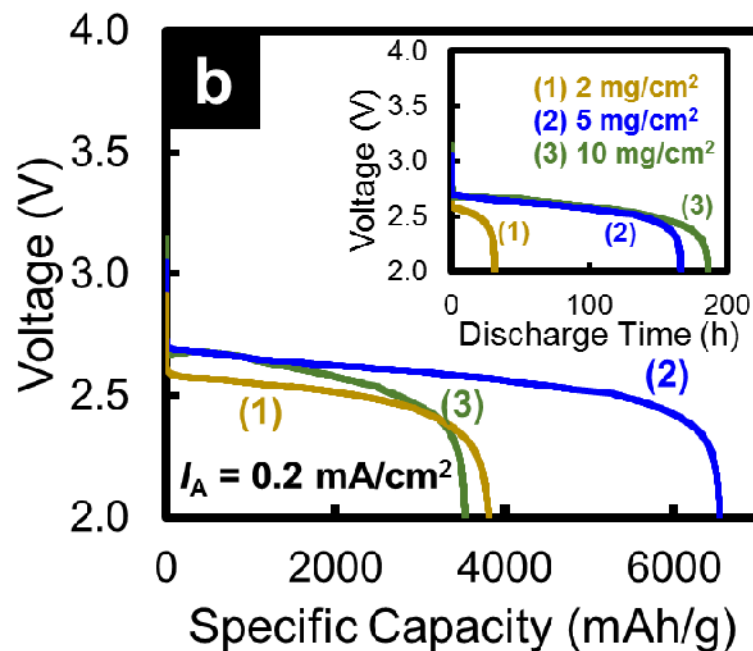
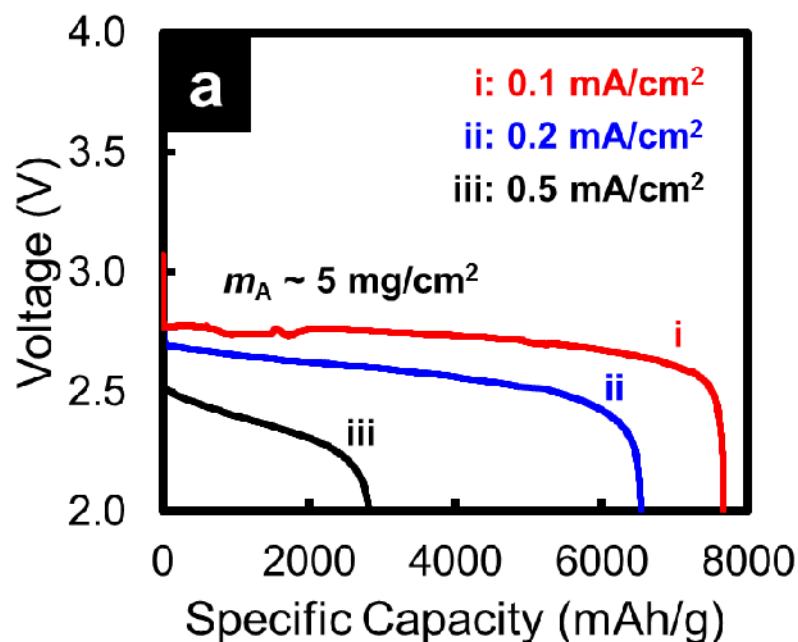
Dry-Pressed hG Air Cathodes



- SS woven mesh support enhanced preferable alignment of graphene sheets.
- Freestanding hG electrode also exhibited excellent performance.

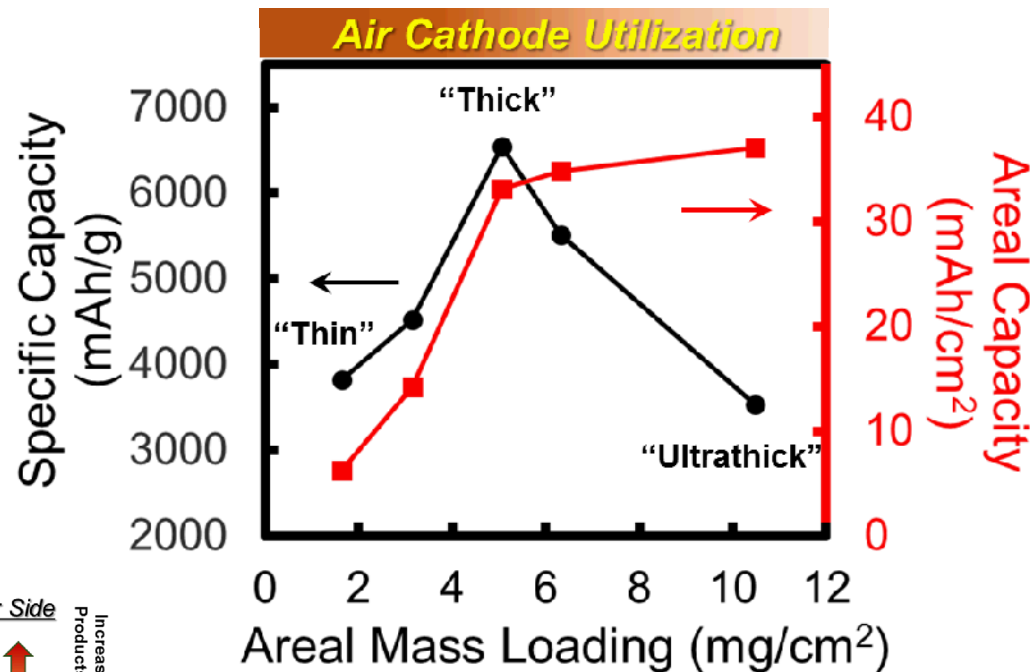
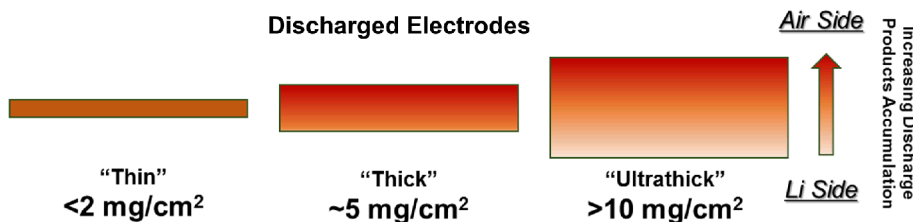
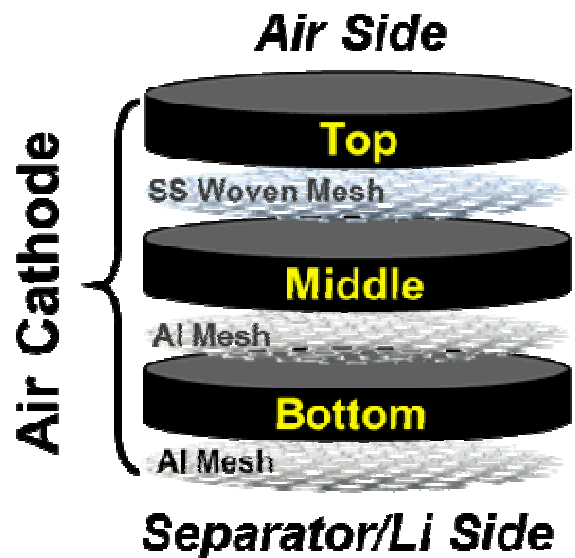


Ultrahigh Capacity Li-O₂ Batteries with Dry-Pressed hG Air Cathodes



- Excellent gravimetric performance on par with most carbon nanomaterial air cathodes at **ultrahigh mass loading**, which resulted in **ultrahigh areal capacity**.
- Routinely achieve **>40 mAh/cm²** at **10 mg/cm²**.

Material Utilization Efficiency in Ultrathick Air Cathodes



❑ Cathode material utilization efficiency reduces after an optimal mass loading (currently ~5 mg/cm²).

Neat & Composite Electrode Architectures Enabled by Dry-Pressible hG

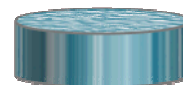
Neat Carbon Electrodes



hG



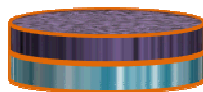
N-doped hG



Simple Mix



“Sandwich”



“Open-Face Sandwich”

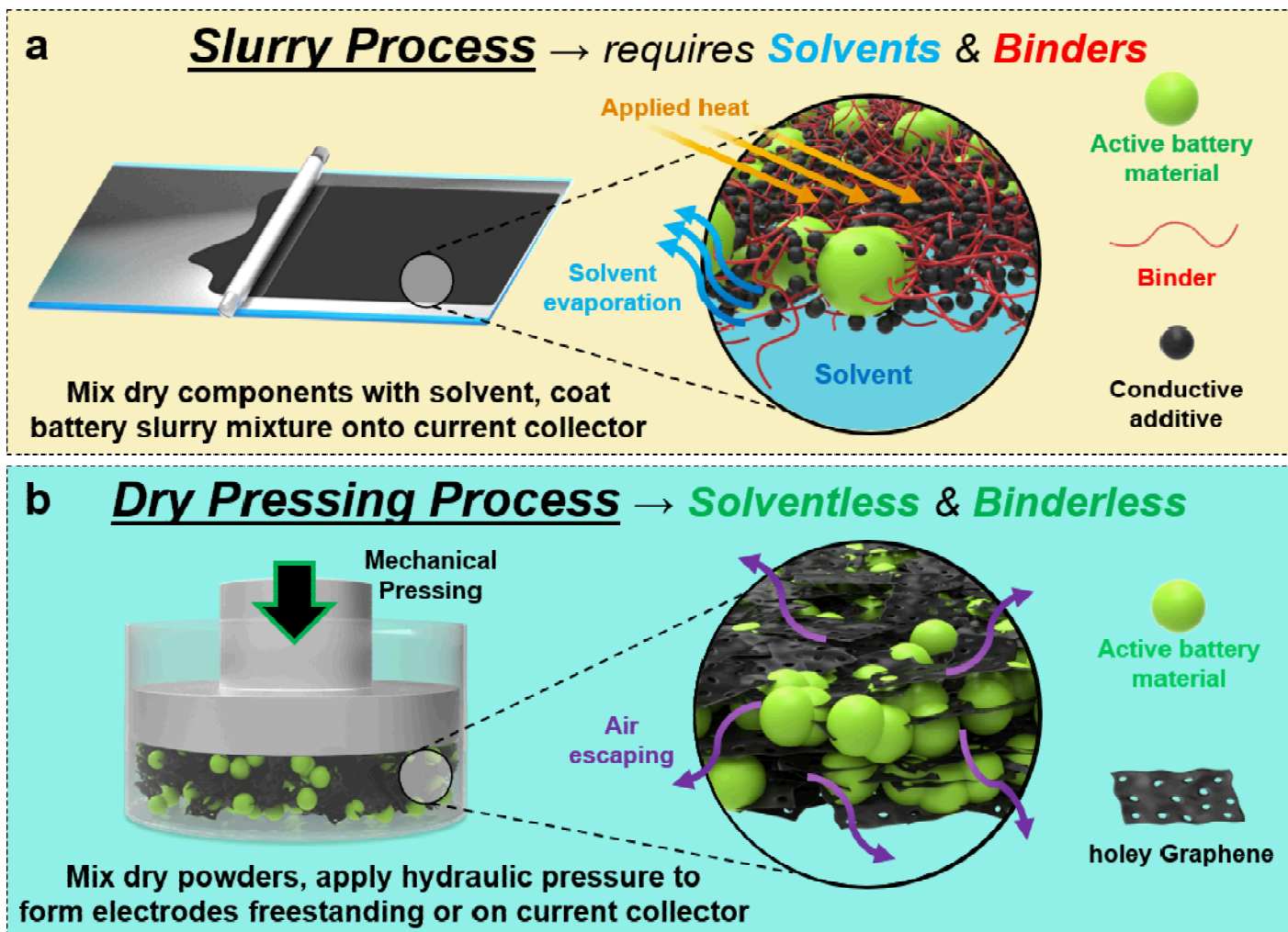


“Big Mac”

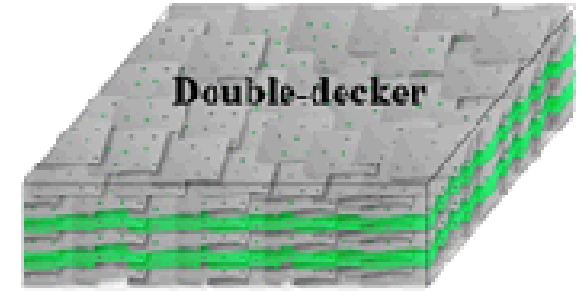
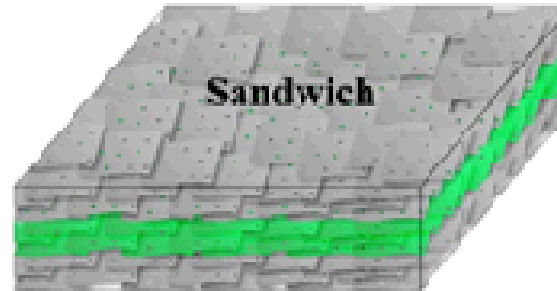
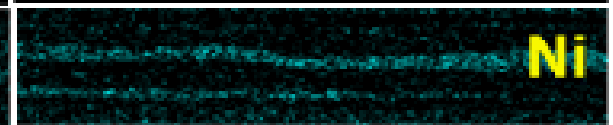
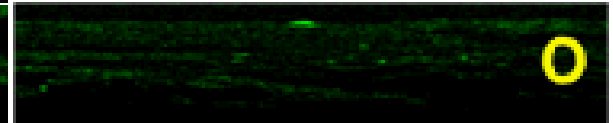
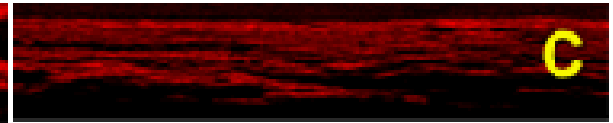
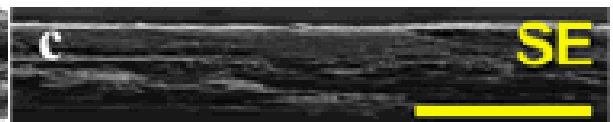
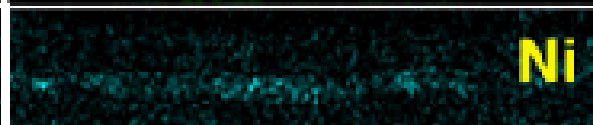
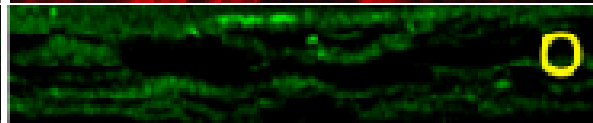
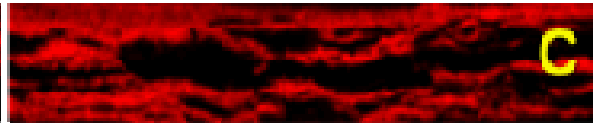
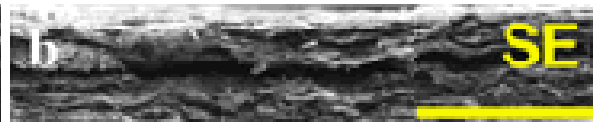
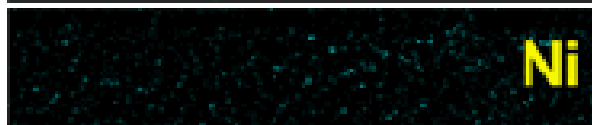
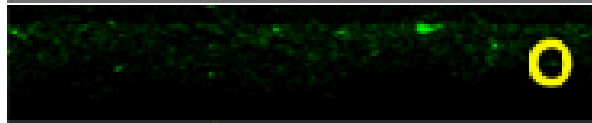
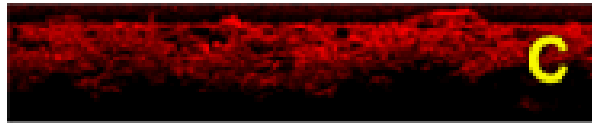
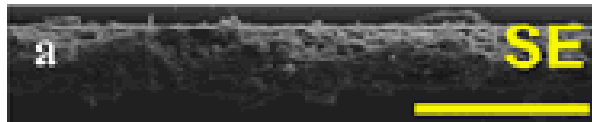
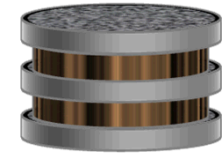
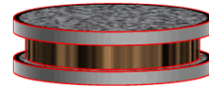
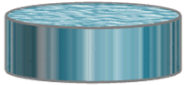
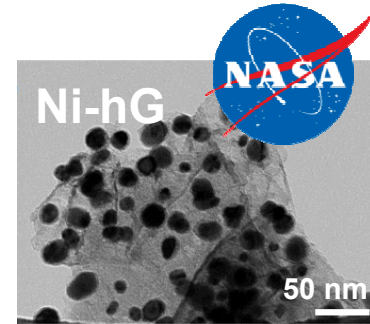
Composite Electrodes

- ❑ Neat Carbon Electrodes: hG is the active component
- ❑ Composite Electrodes: hG is an ultralightweight conductive matrix/scaffold

Dry-Pressed Composite Electrodes



Air Cathode Architecture Design



Building Criteria for Air Cathodes

Current Norm

*Air Cathode
Material*



Cathode Material Research

Is the cathode material effective in
facilitating discharge/charge reactions?

A New Direction

*Air Cathode
Architecture*



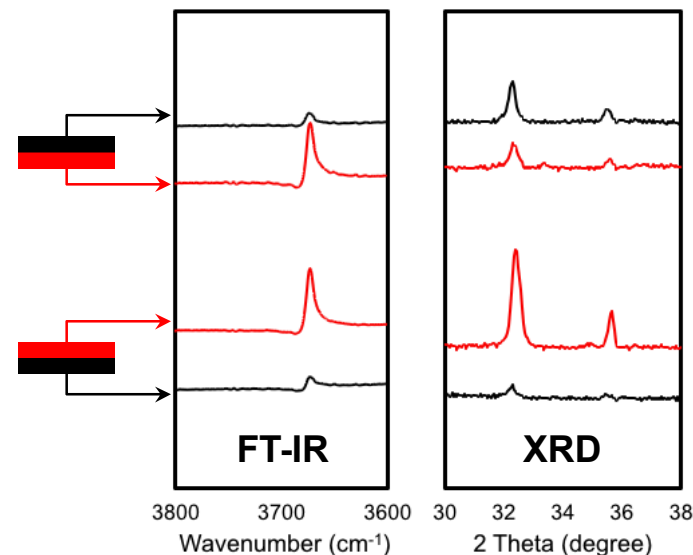
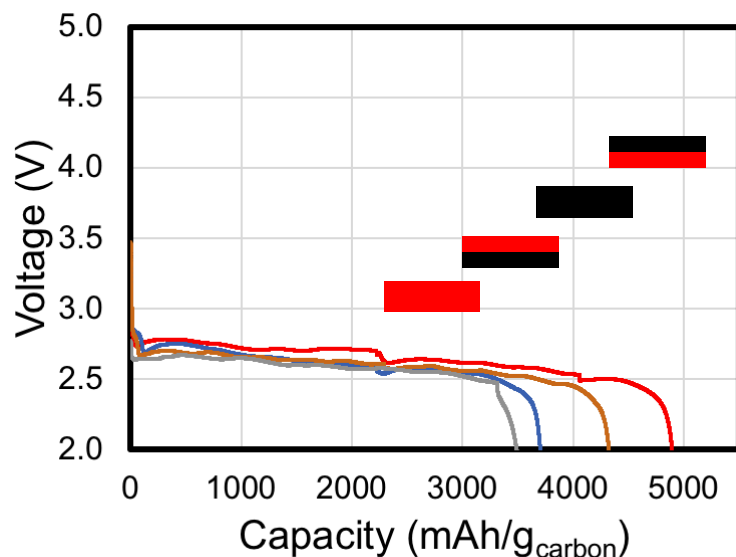
Cathode Architecture Research

Is the cathode architecture effective in
facilitating discharge/charge reactions
with competitive total/areal capacity?

Directing Discharge Reaction to Different Cathode Depths

■ hG: porosity layer – *host for discharge products*

■ Ru: catalysis layer (in a hG matrix) – *facilitate discharge (and charge) reaction(s)*



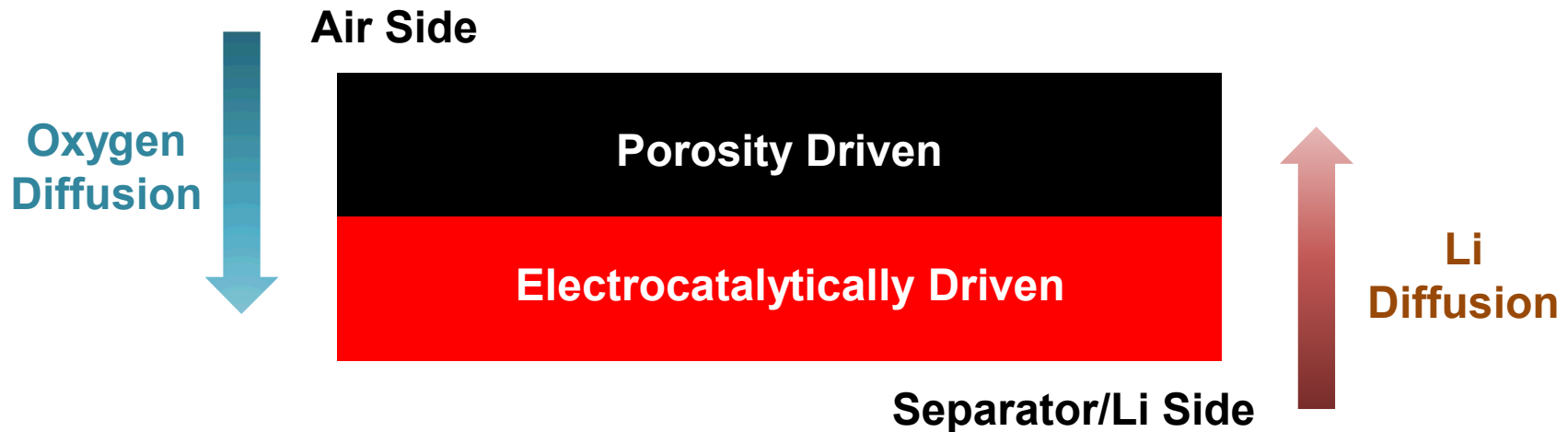
- ❑ Total air cathode mass loading ~ 9 - 11 mg/cm²
- ❑ Current density: 0.2 mA/cm²
- ❑ Unoptimized cell energy density (excluding packaging): ~ 700 Wh/kg

- ❑ Air cathode architecture manipulations allow optimization of cathode utilization.
- ❑ Need for a balance between porosity (hG) and catalytic efficiency (Ru).

Directing Discharge Reaction to Different Cathode Depths

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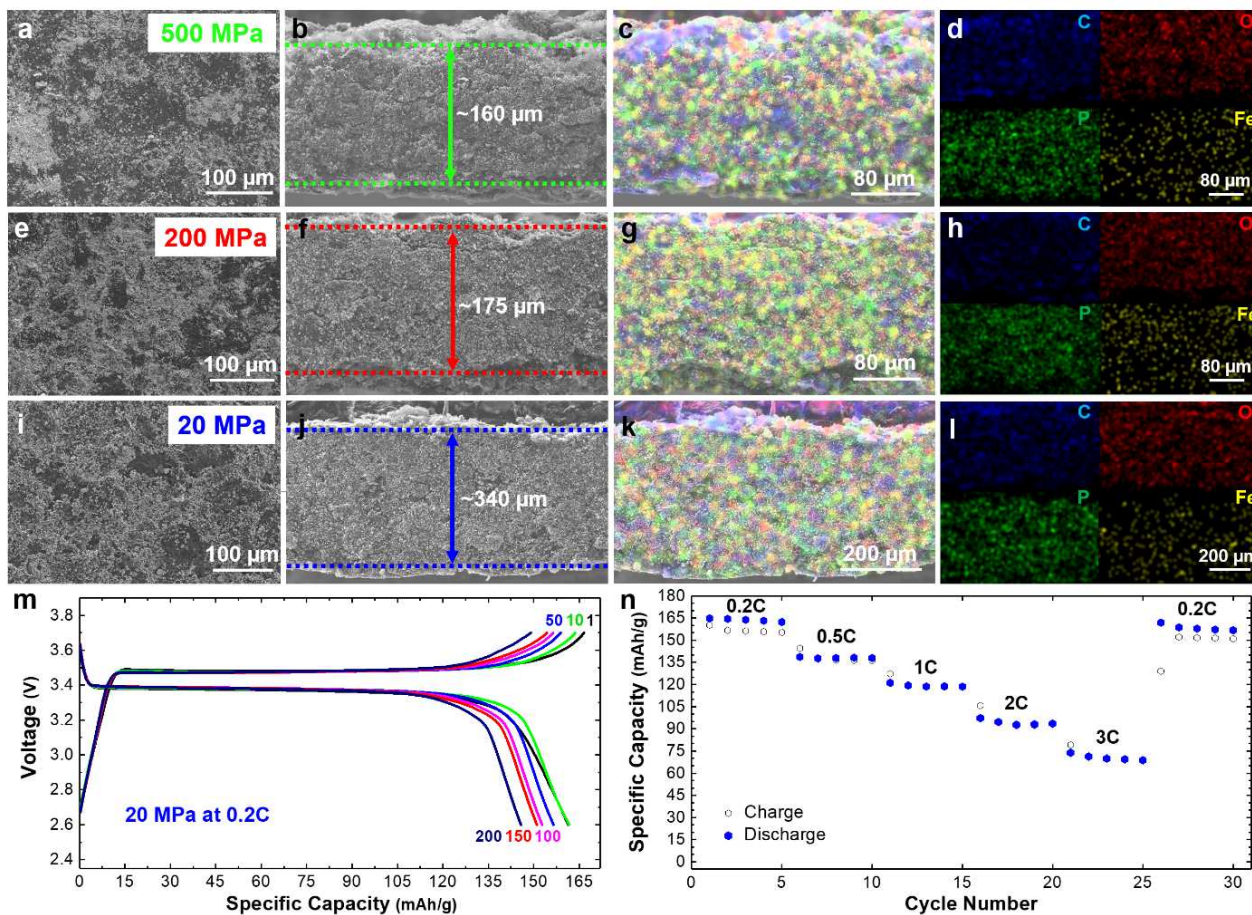
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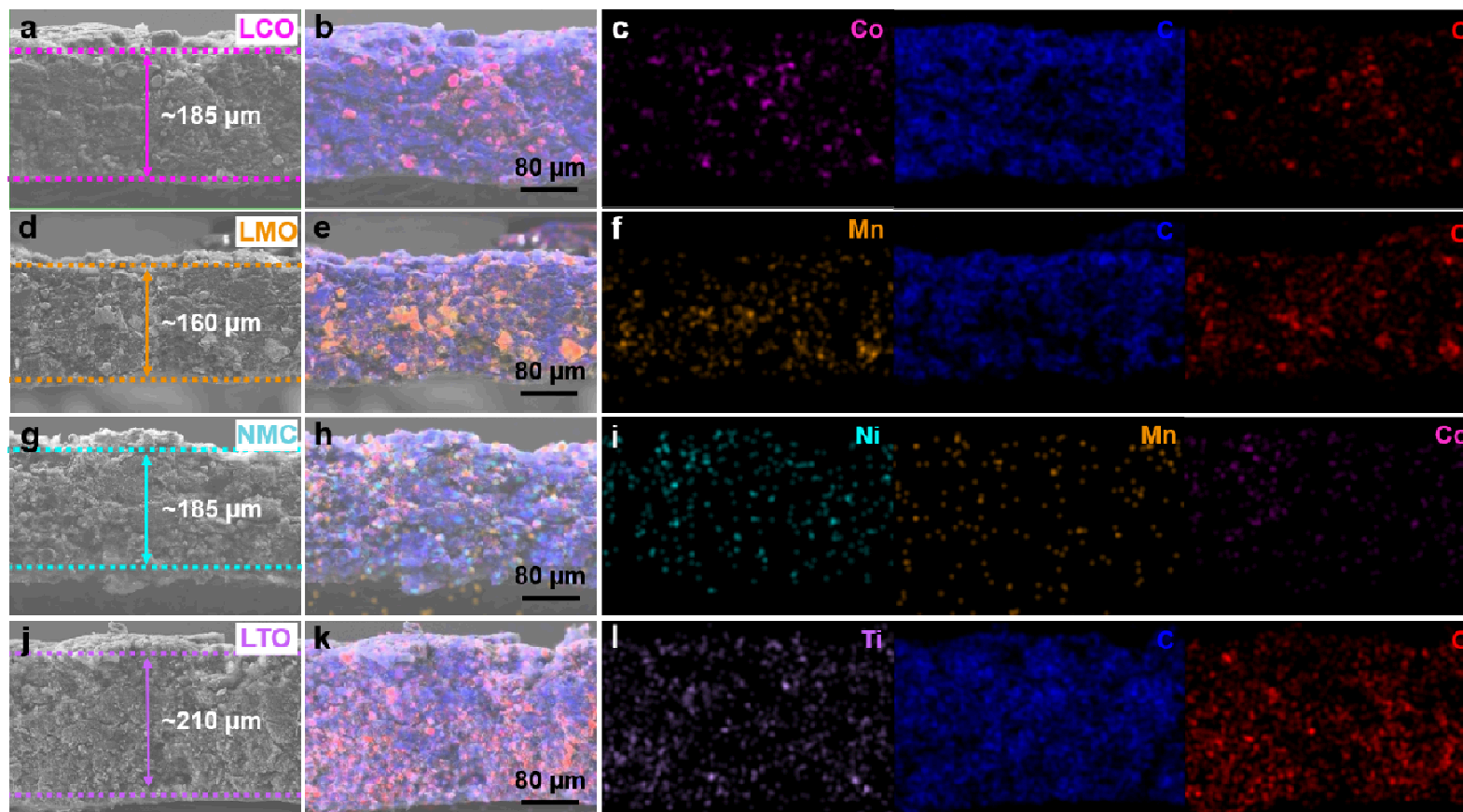
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Dry-Pressed Lithium Ion Battery Electrodes



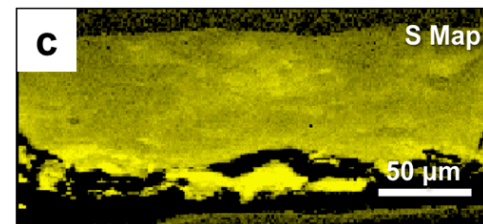
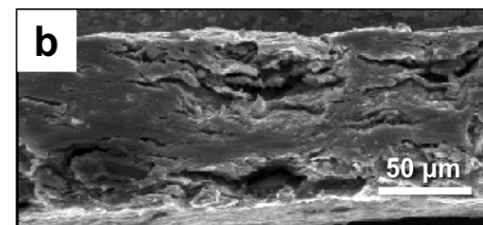
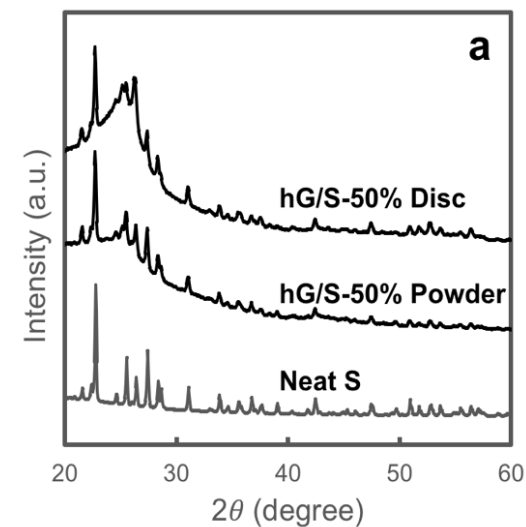
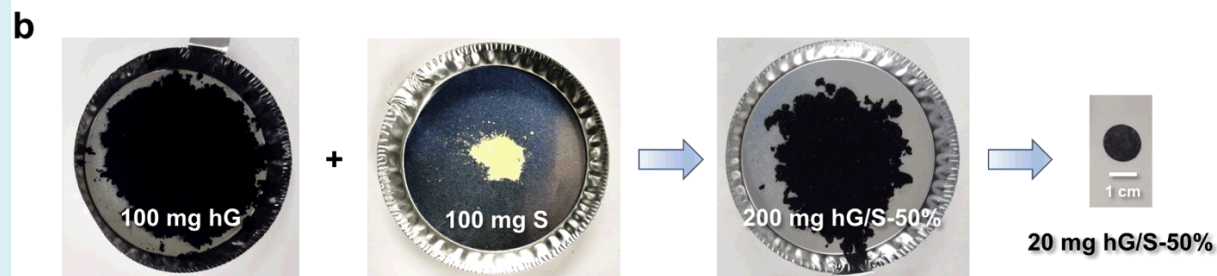
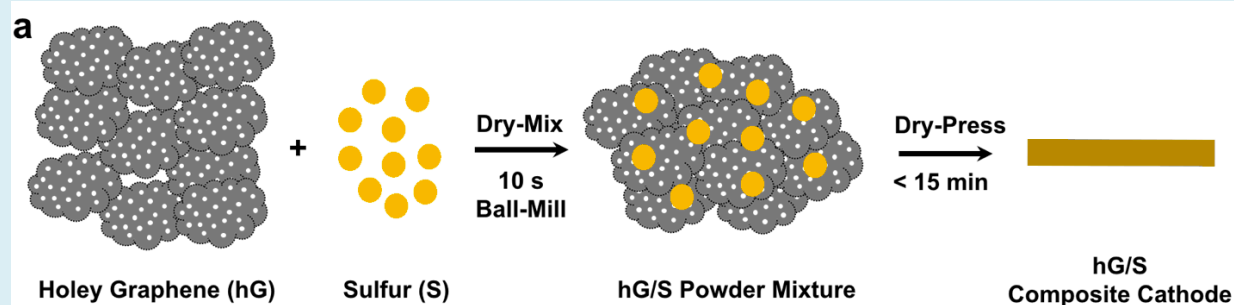
□ Dry-pressed hG/lithium iron phosphate (LFP) electrodes from various fabrication conditions exhibited excellent performance.

Dry-Pressed Lithium-Ion Battery Electrodes



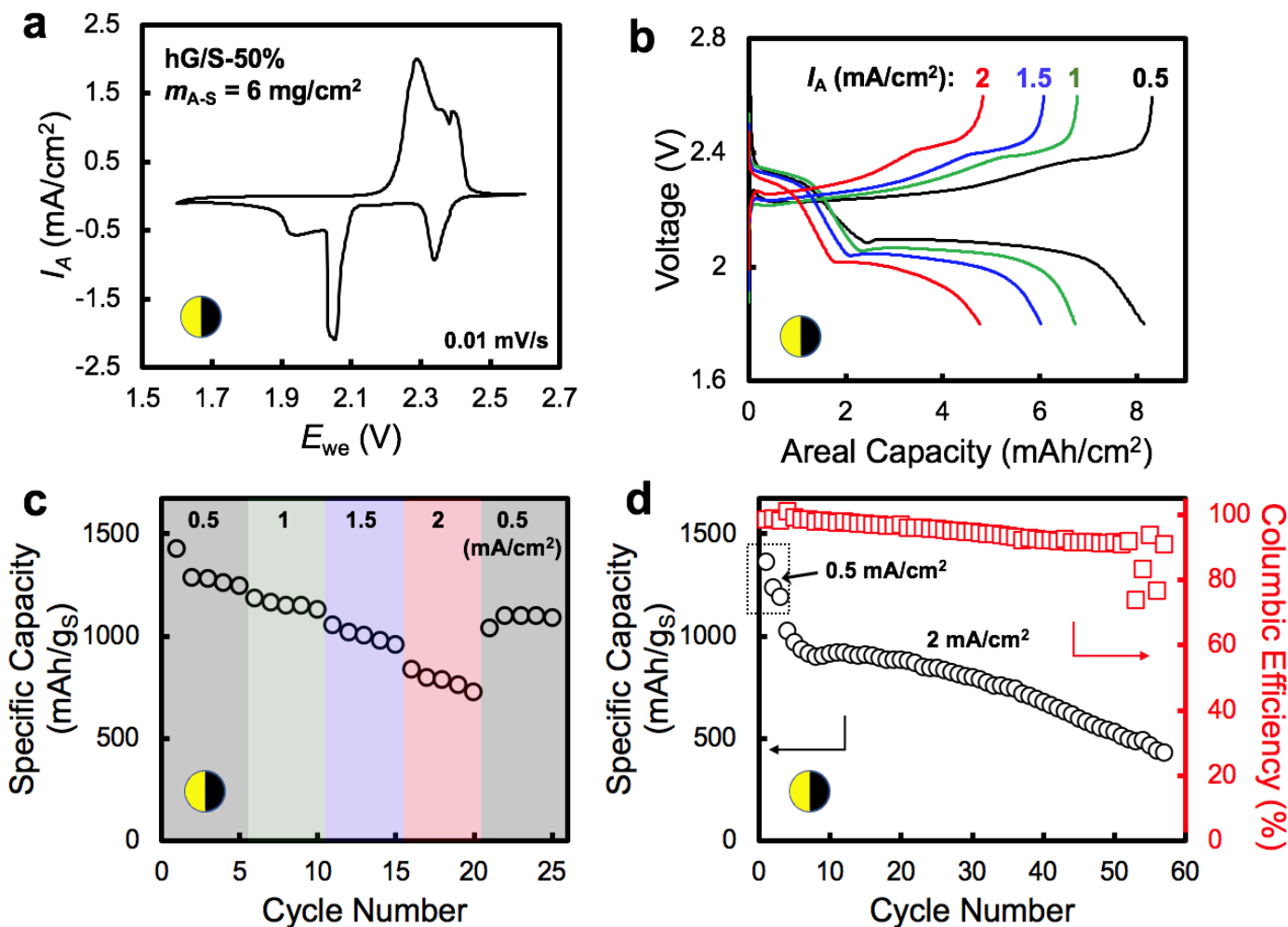
□ Dry compression can be similarly applied to various lithium-ion battery electrode materials (LCO, LMO, NMC, LTO, etc.)

Dry-Pressed hG/S Cathodes



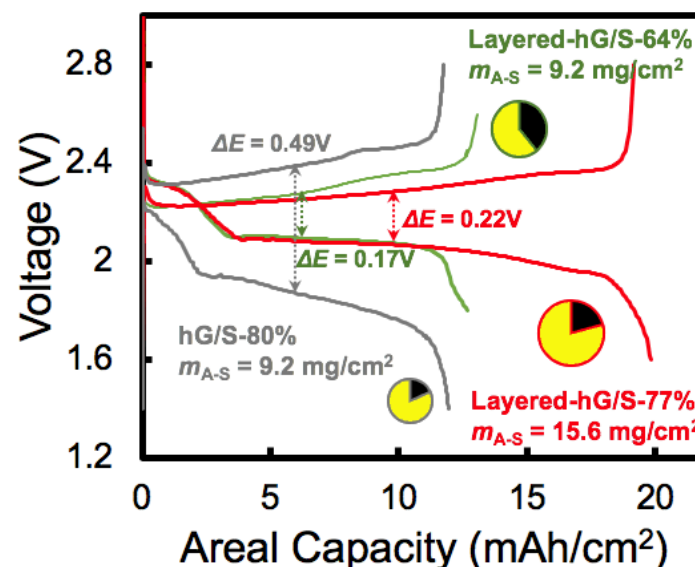
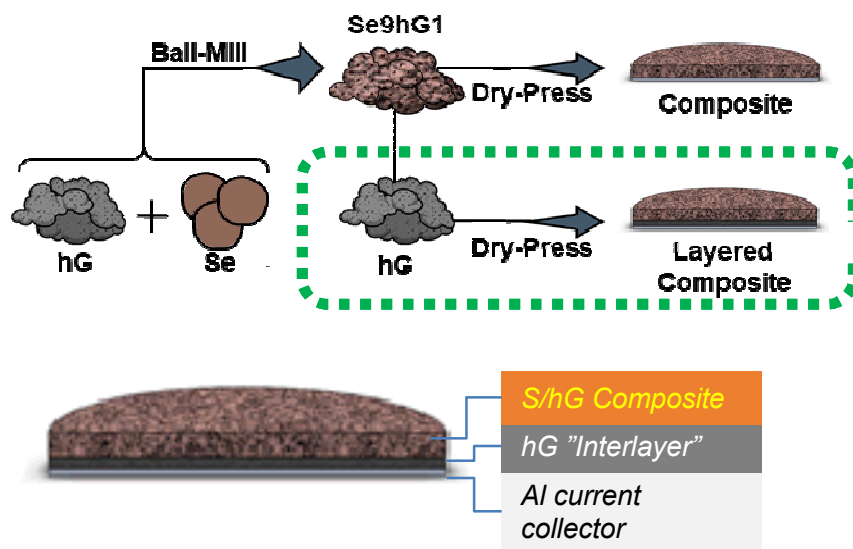
❑ Extremely facile preparation of high-performance, high S content, high mass loading S cathodes.

Dry-Pressed hG/S Cathodes



□ hG/S cathodes exhibit excellent S utilization and ultrahigh areal capacity.

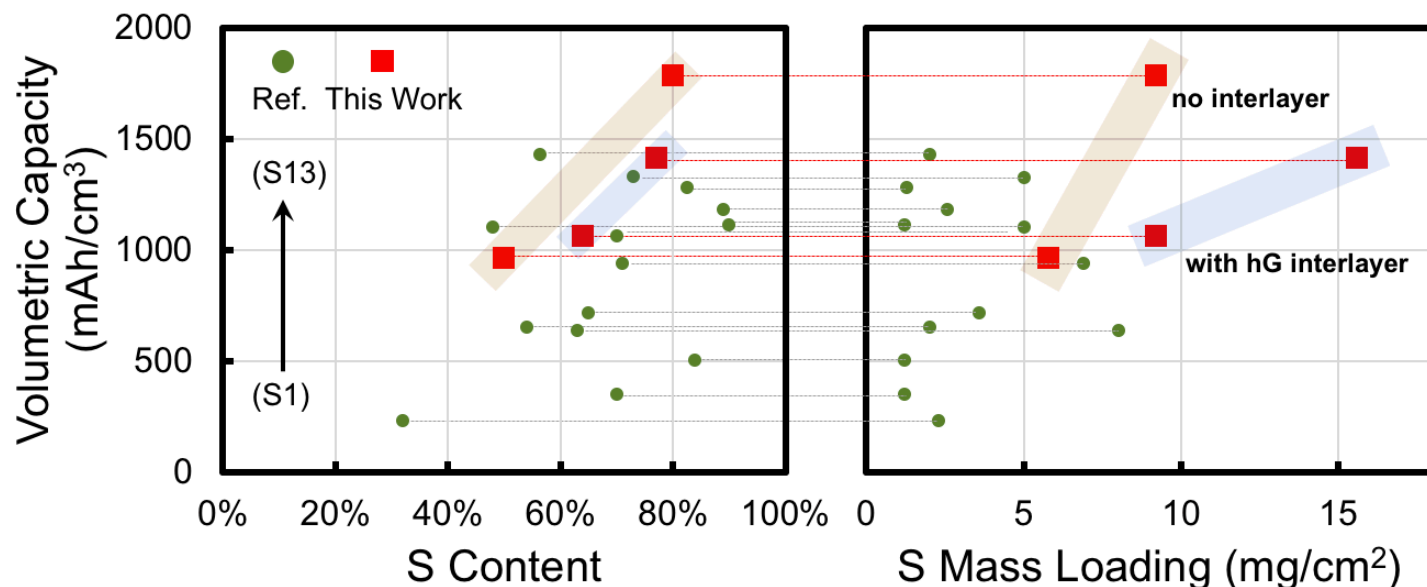
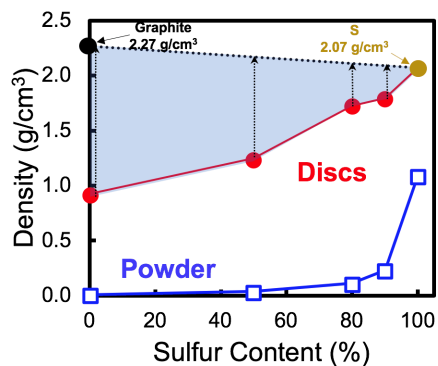
Cathode Architectures for Improved Performance



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

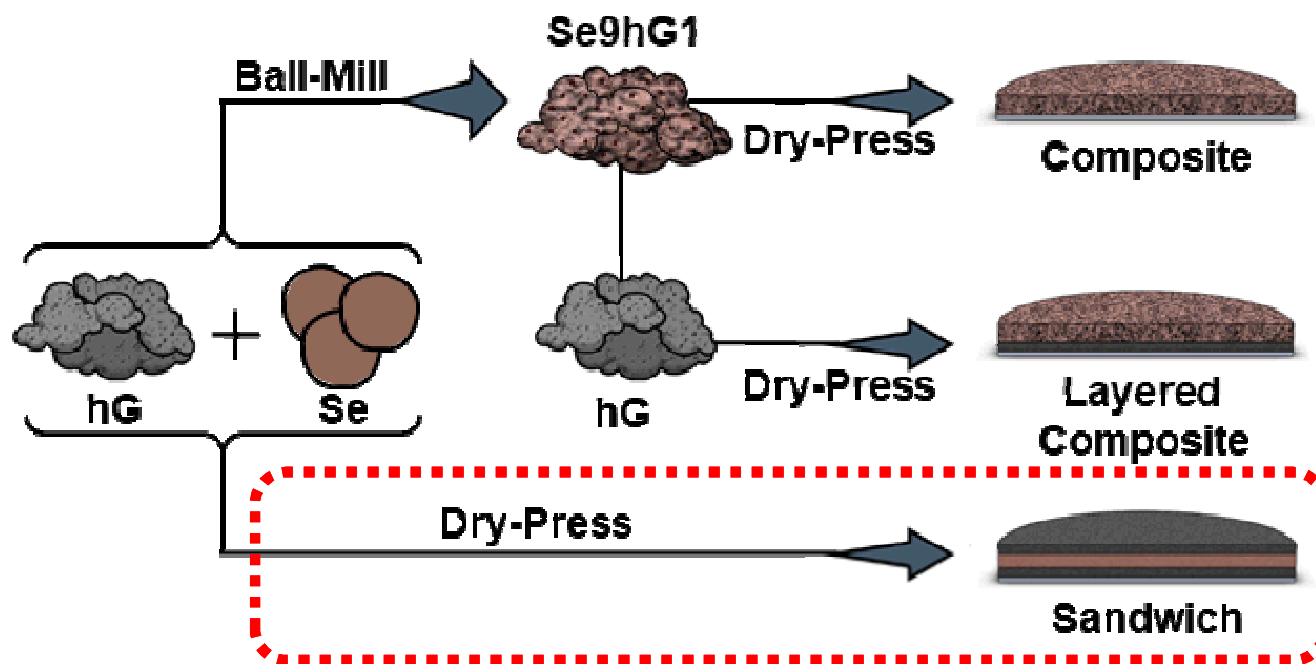
- ❑ Lightweight conductive interlayer (~10 wt.%)
- ❑ Improves current collector– cathode contact
 - ✓ Electrochemistry kinetics
 - ✓ Overpotential

Dense and Porous S Electrodes: High Volumetric Performance



□ High volumetric performance at both high S content and high S mass loading.

“Sandwich” Cathodes

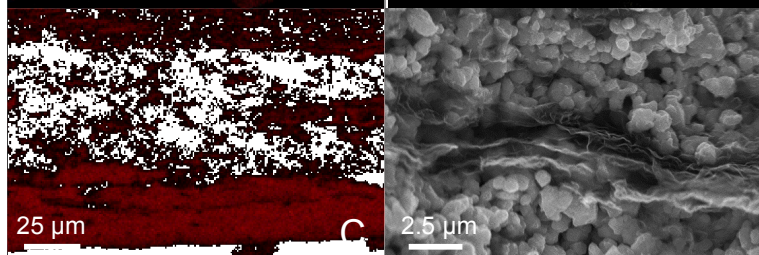
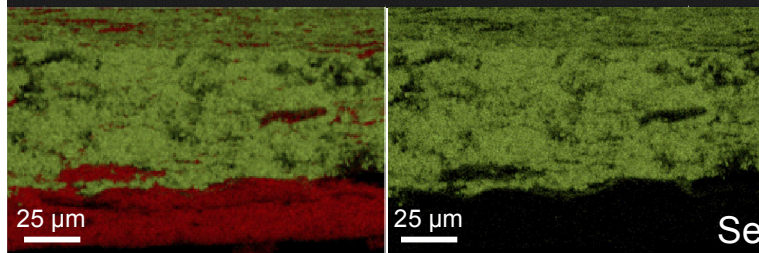
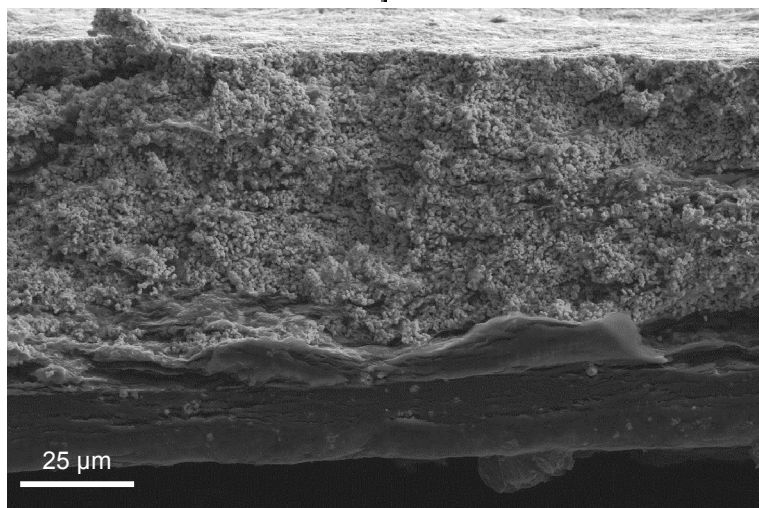


- ❑ High active material content (up to 90 wt.%)
- ❑ High mass loading: high areal capacity
- ❑ Excellent current collector– cathode contact
- ❑ Extremely facile: single-step, no mixing needed
- ❑ Widely applicable: S, Se, Se_xS_y , Li_2S

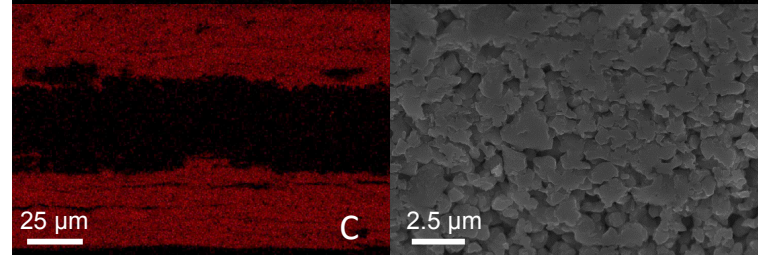
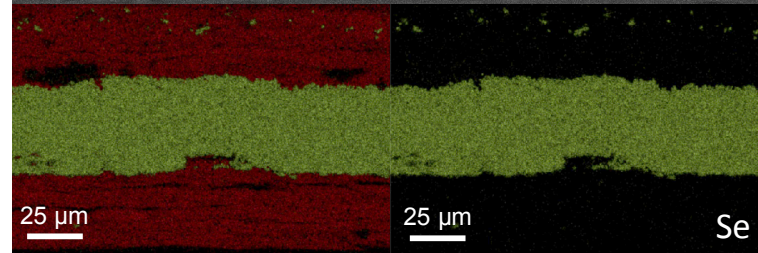
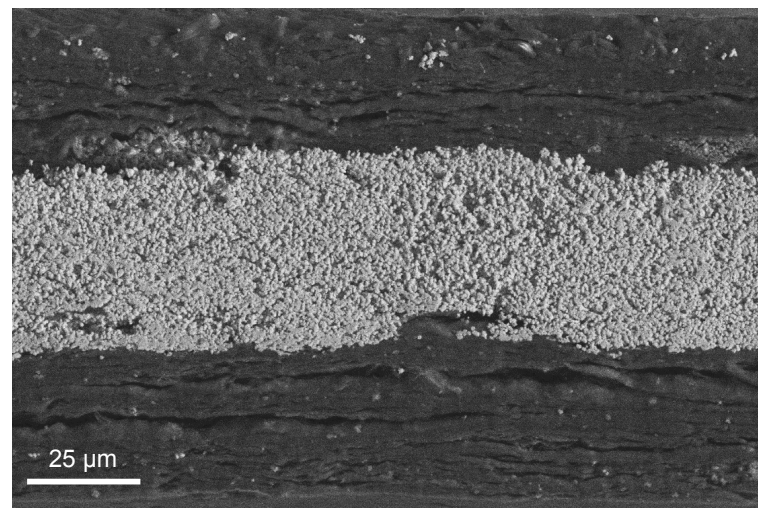
Morphology of Layered Cathode Architectures



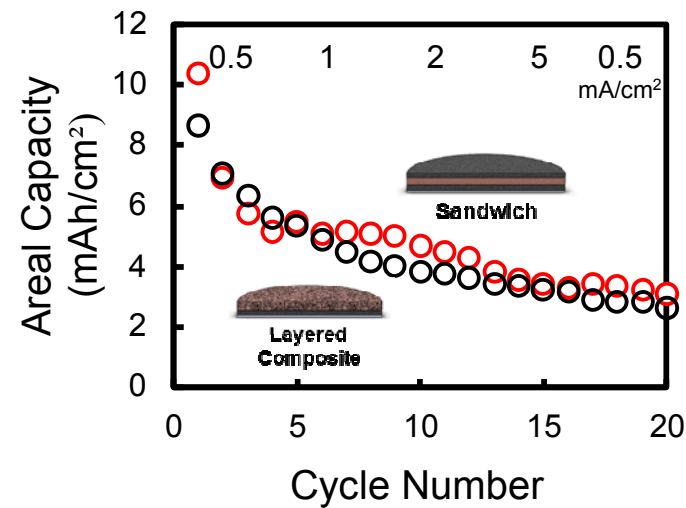
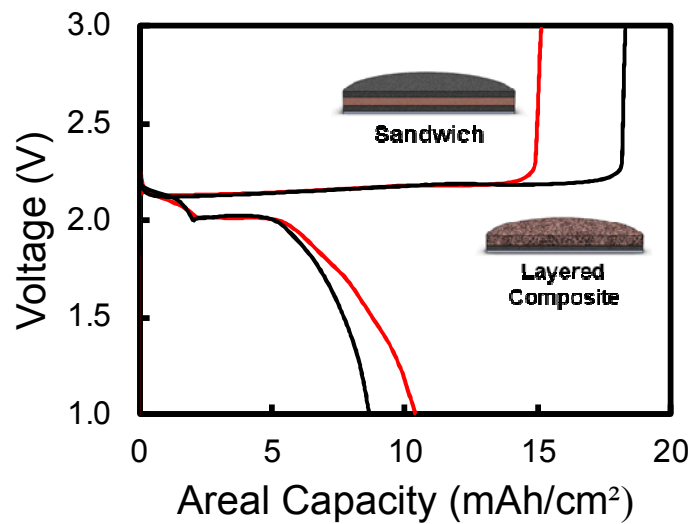
**Layered
Composite**



Sandwich



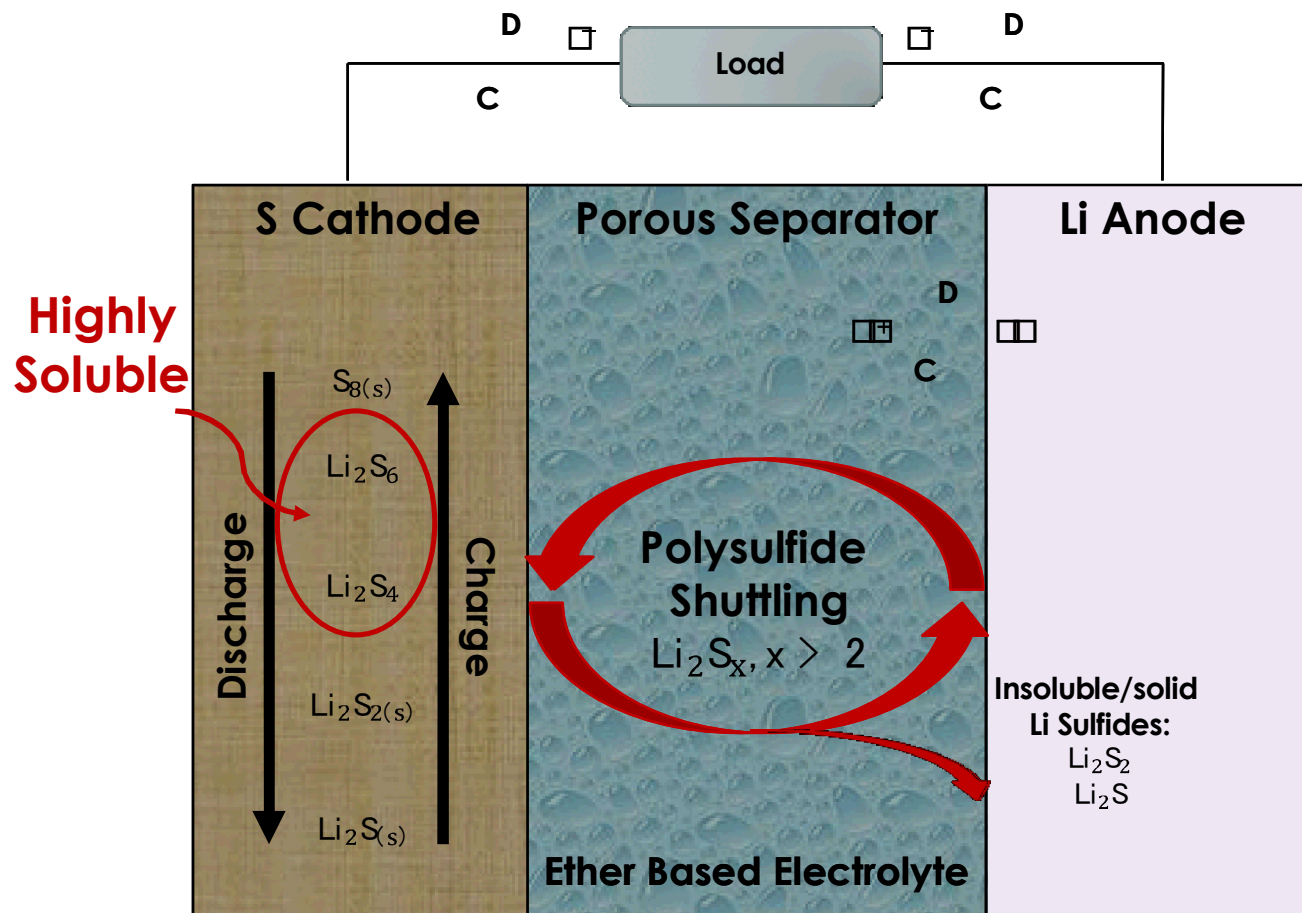
hG-Se-hG Sandwich Cathodes



Sandwich vs. (layered) composite architectures:

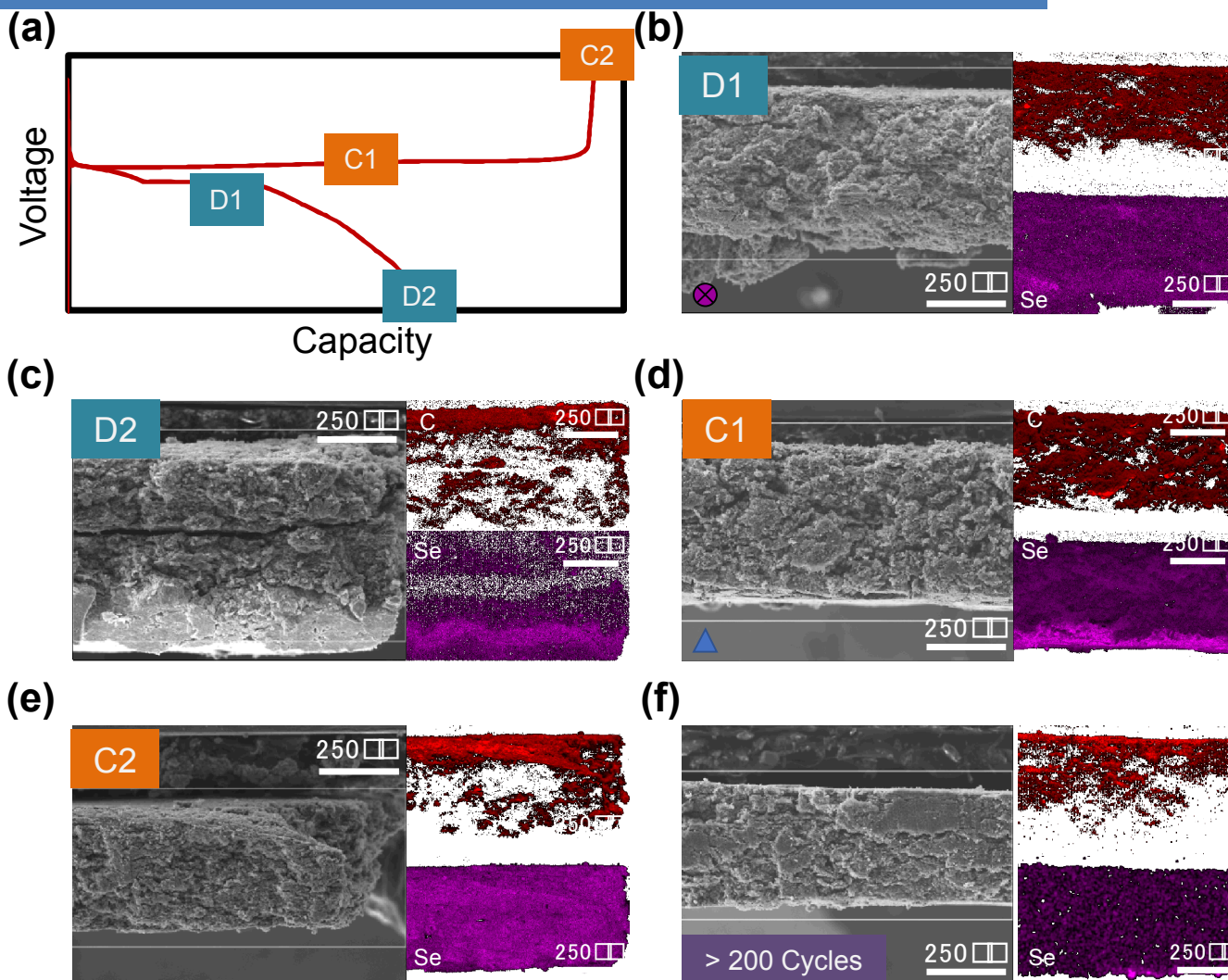
- ☐ Similar performance: overpotential, utilization
- ☐ Less harmful intermediate shuttling
- ☐ Extremely facile preparation!

Li-S/Se Batteries: Conversion Battery Chemistry



- Active materials are converted into soluble intermediate species during discharge and charge.

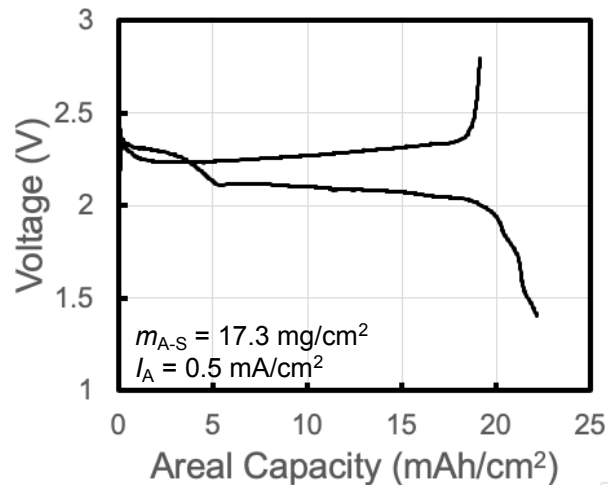
Evolution of Sandwich Cathode Architecture



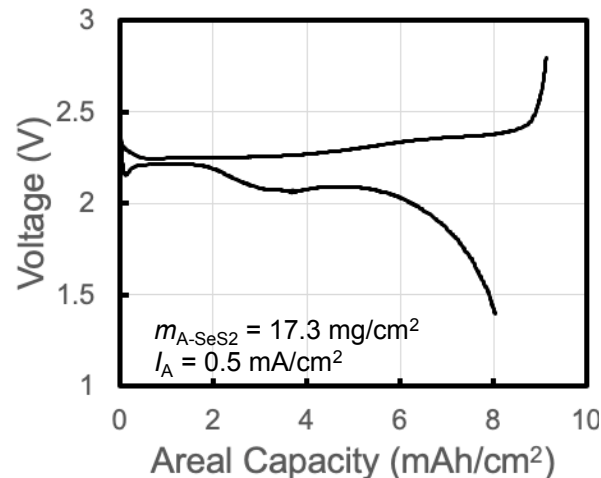
□ Neat active material layer electrochemically redistributed during the first cycle, while the entire electrode structure spontaneously self-densify.

hG-Enabled Sandwich Architectures with Various Active Materials

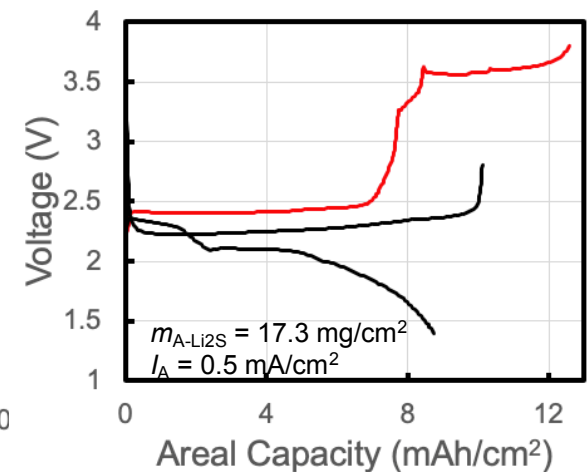
hG/S/hG



hG/SeS₂/hG



hG/Li₂S/hG



- ☐ S: High energy density
- ☐ Se: High power density, good energy density
- ☐ SeS_x: Tunable with requirements in both energy and power
- ☐ Li₂S: High energy density but no volume expansion

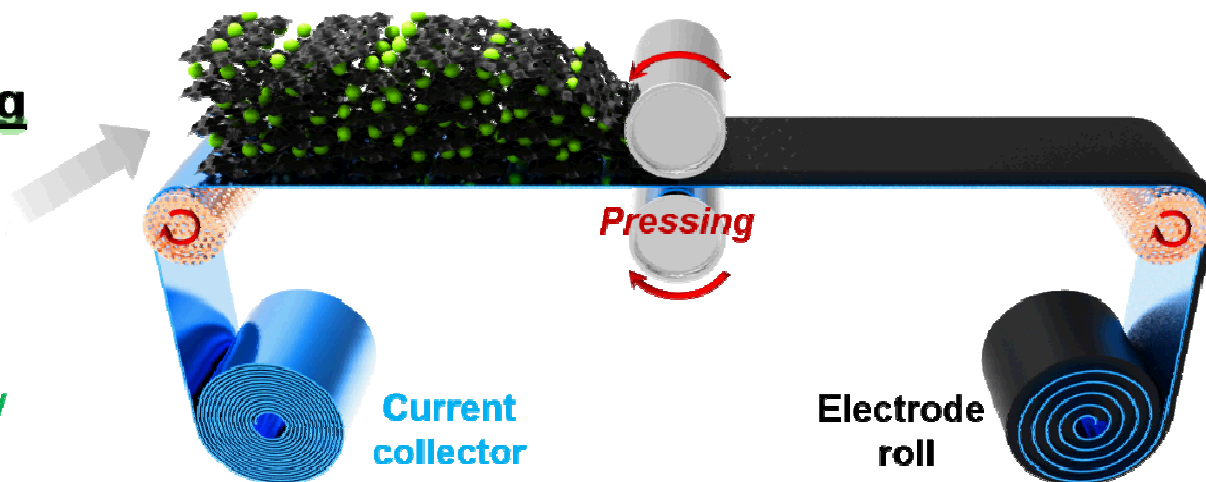
Scaling Up Concept: Roll-to-Roll

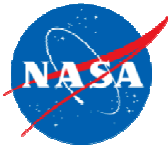
Dry Roll-to-Roll (DR2R) Manufacturing

Mix dry powders and dispense

holey Graphene

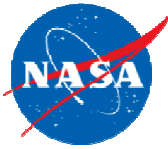
Active battery material





Summary

- ❑ Holey graphene enables facile and versatile dry-press electrode preparation
 - ✓ Solvent-free and binder-free
 - ✓ Both neat & composite electrodes
 - ✓ High mass loading electrodes
 - ✓ Electrodes with layered architectures
 - ✓ High energy density



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