

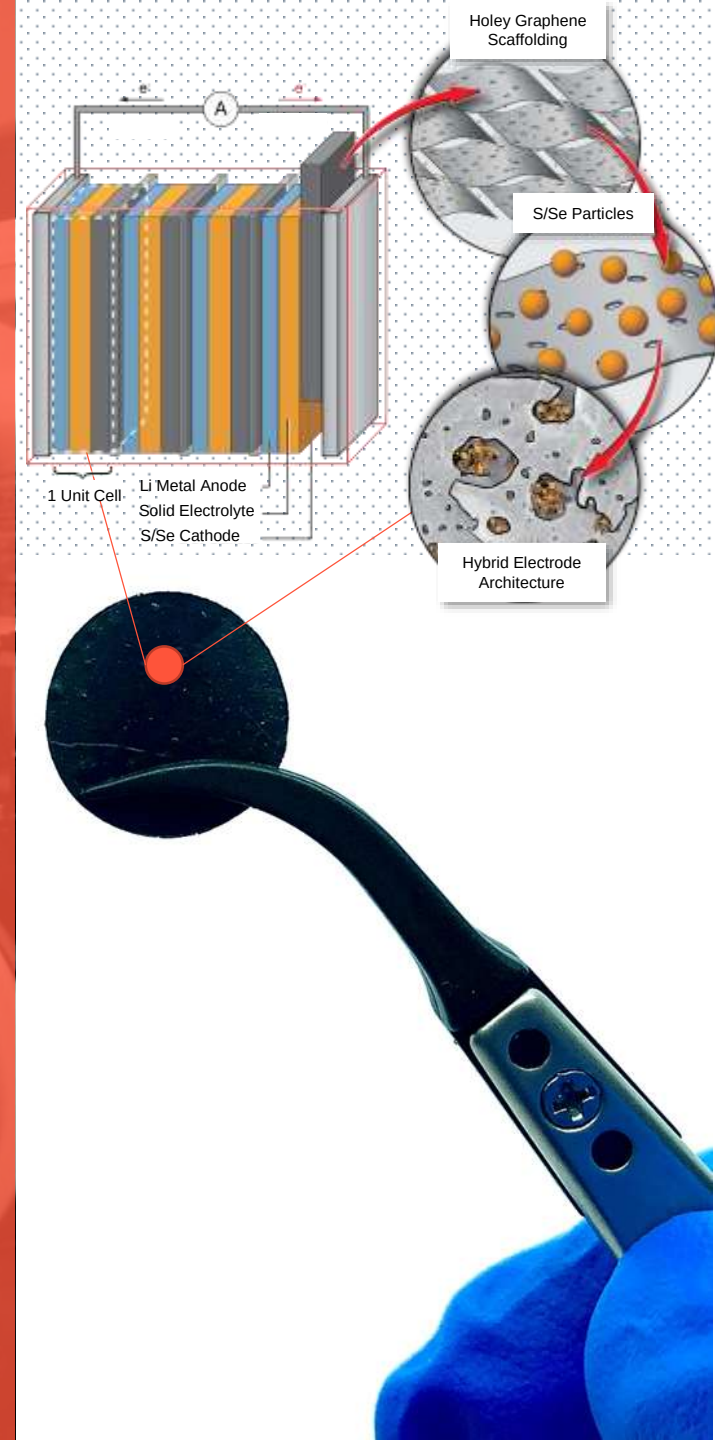
Toward SABERS: Feasibility of Holey Graphene Cathode Scaffold for Lithium- Sulfur/Selenium Batteries

Christian O. Plaza-Rivera,¹ Dr. Yi Lin,² Dr. John Connell³

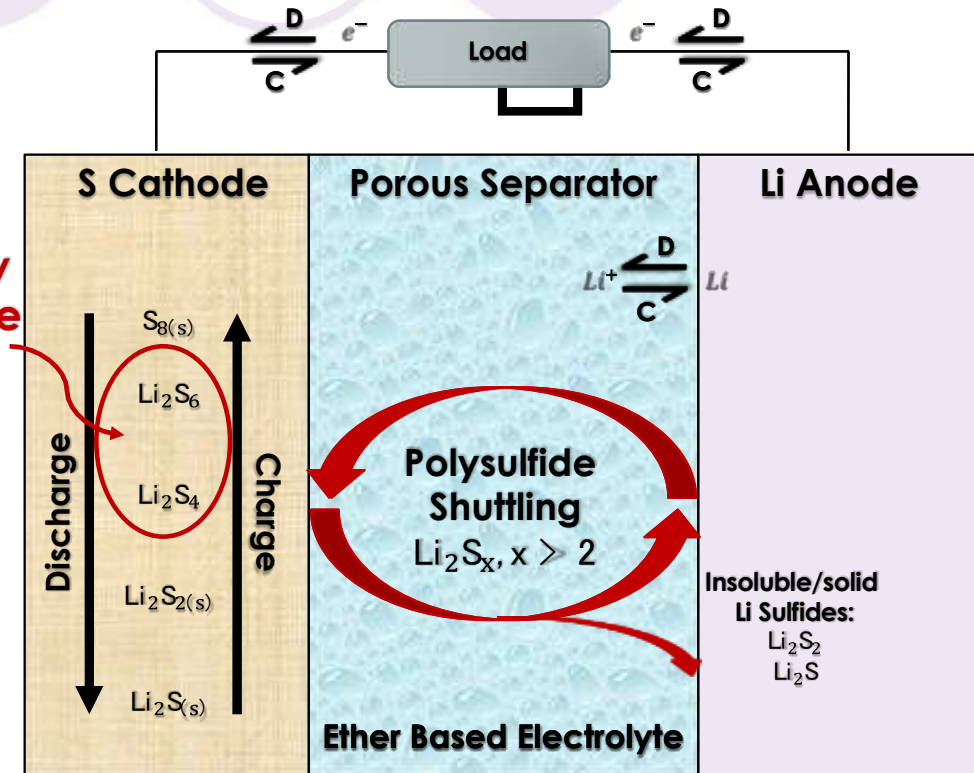
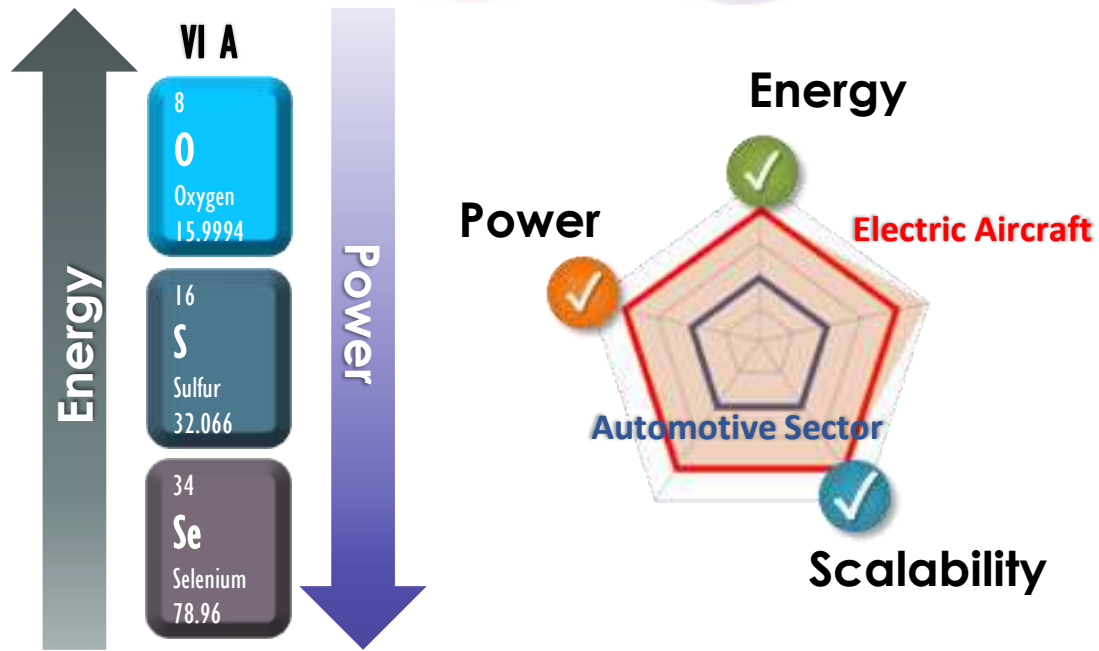
¹NASA Interns, Fellows, and Scholars (NIFS) Program

²National Institute of Aerospace

³Advanced Materials and Processing Branch, NASA Langley Research Center



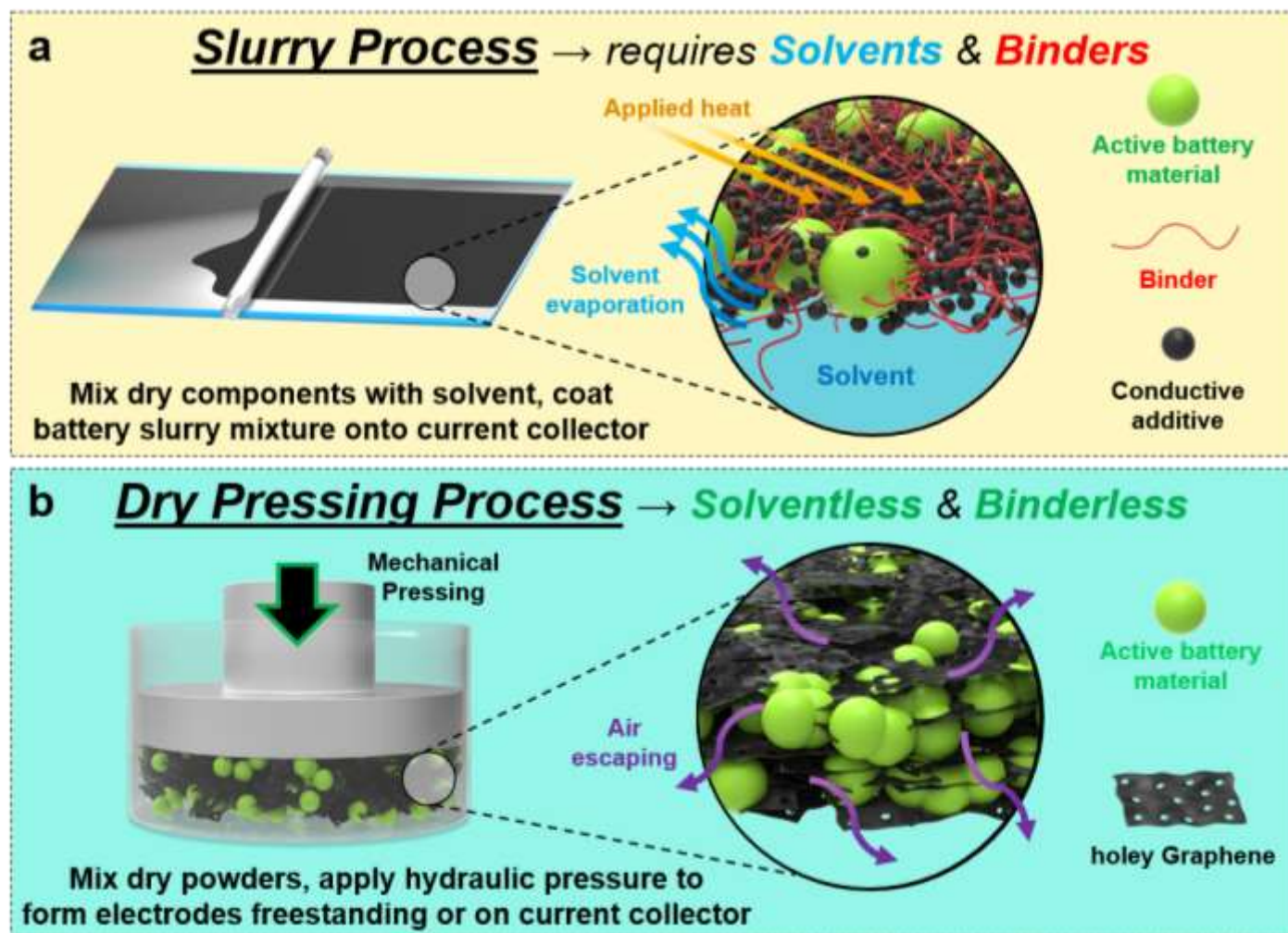
Li-S/Se Chemistry Overview



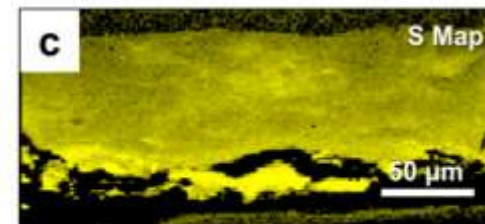
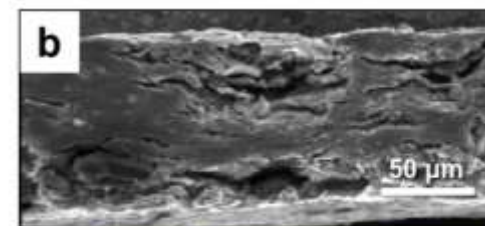
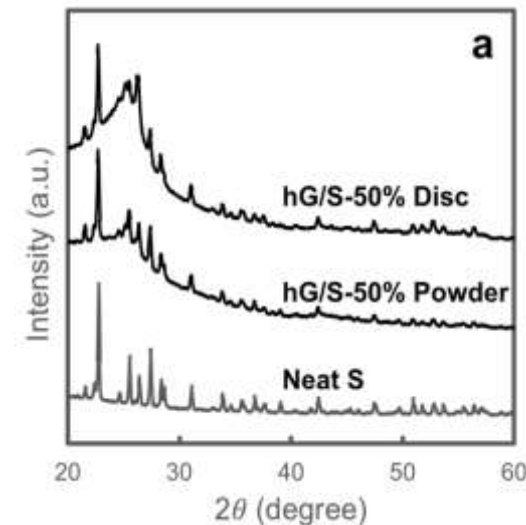
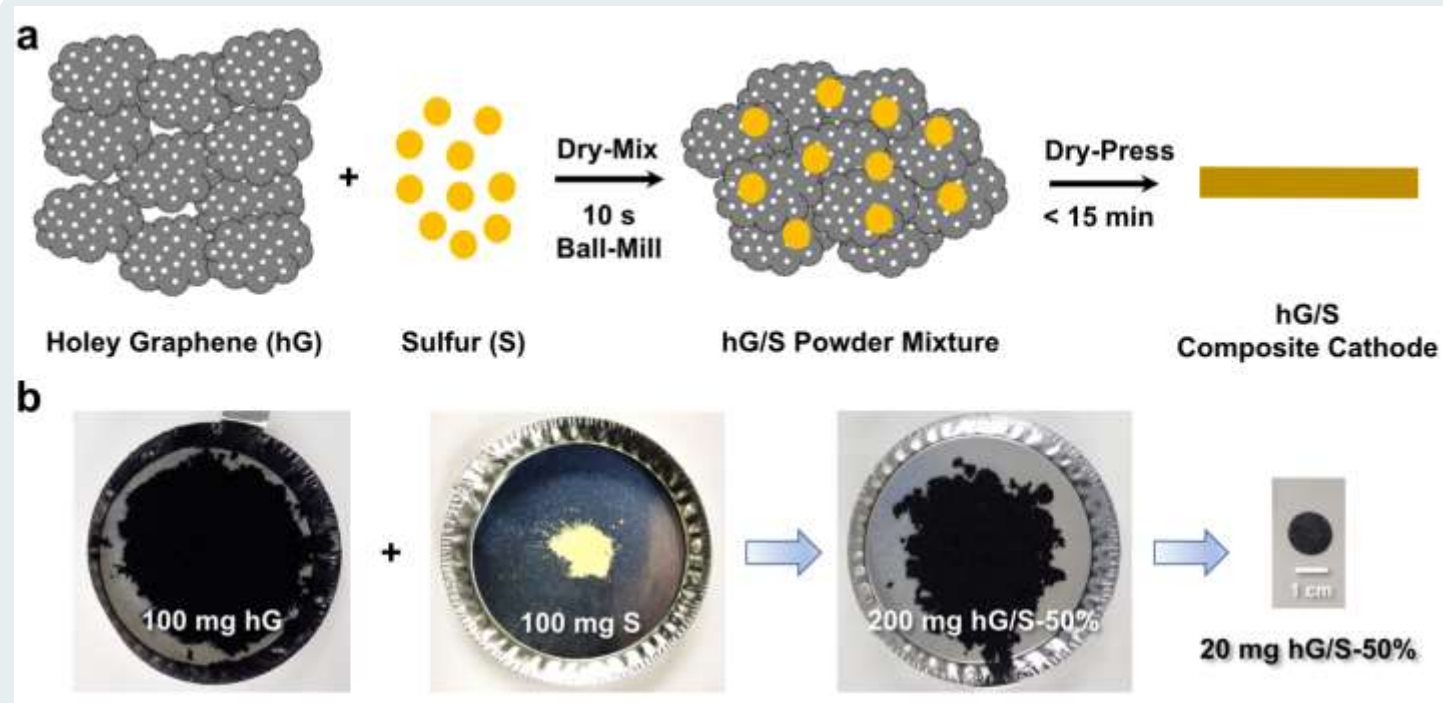
	Conductivity (S/cm)	Specific Capacity (mAh/g)
S	5×10^{-30}	1675
Se	10^{-5}	675

- ❑ Li-S and Li-Se pairs are similar in battery chemistry;
- ❑ S/Se compounds are intermediate species between S and Se;
- ❑ Lithiated S/Se, i.e., $\text{Li}_2\text{S}_x\text{Se}_{1-x}$ can also be used as active material;
- ❑ **SABERS** proposes the use of S/Se hybrid chemistry to achieve both energy (S) and power (Se).

Dry-Pressible Holey Graphene (hG) Electrode Scaffold

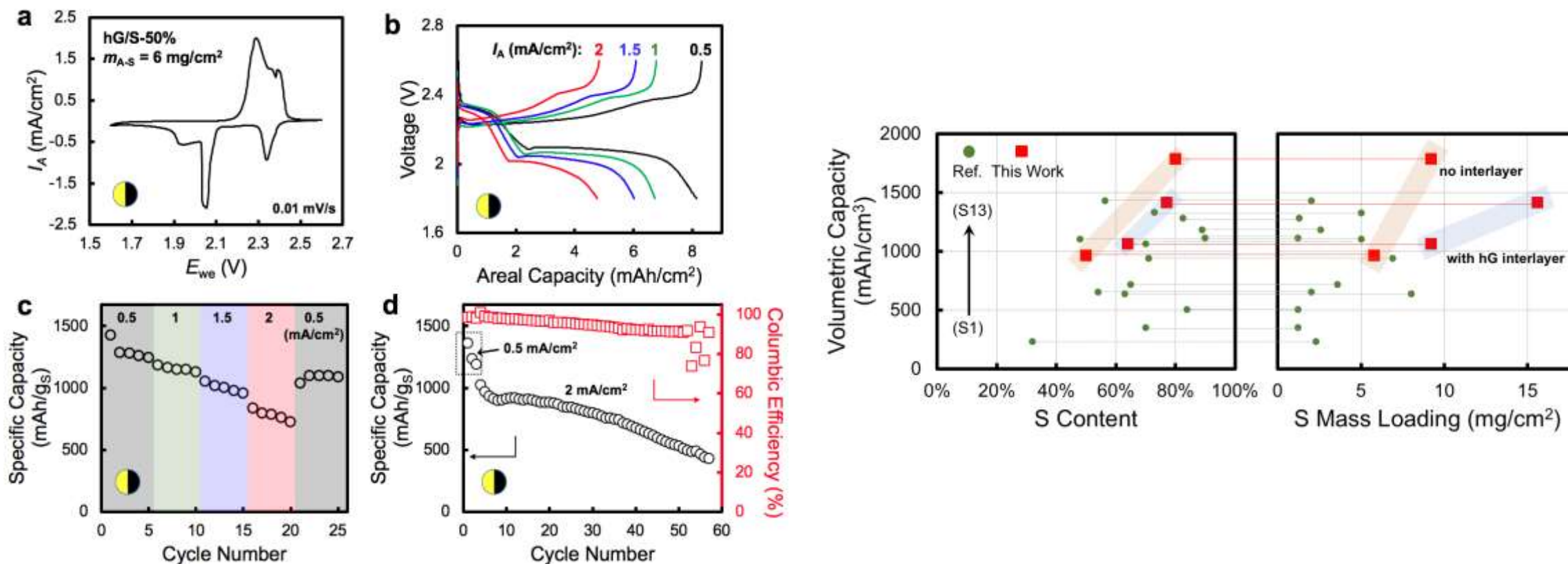


Dry Pressed S Cathodes Enabled by hG



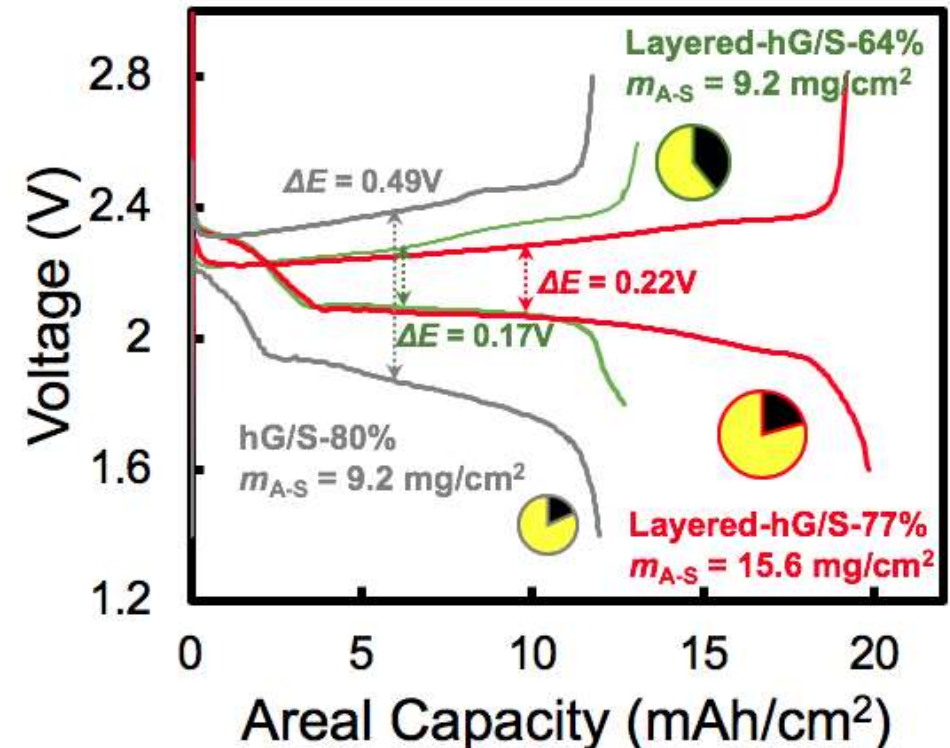
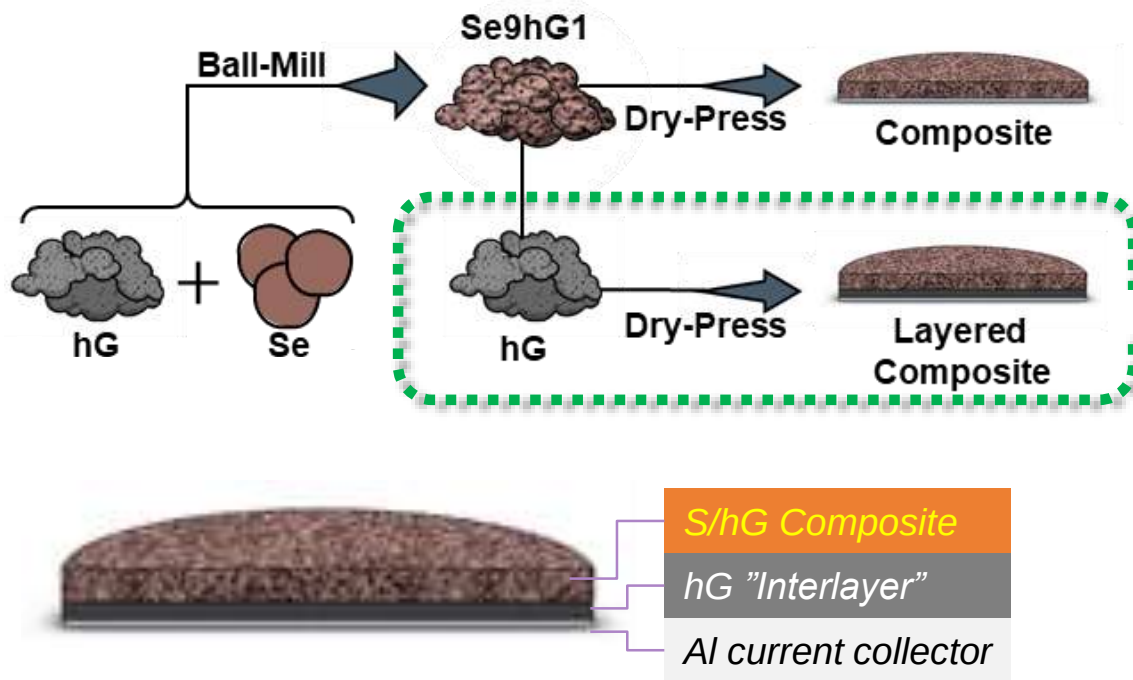
□ Facile solvent-free preparation of high S content, high mass loading S cathodes.

High Performance S/hG Cathodes



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

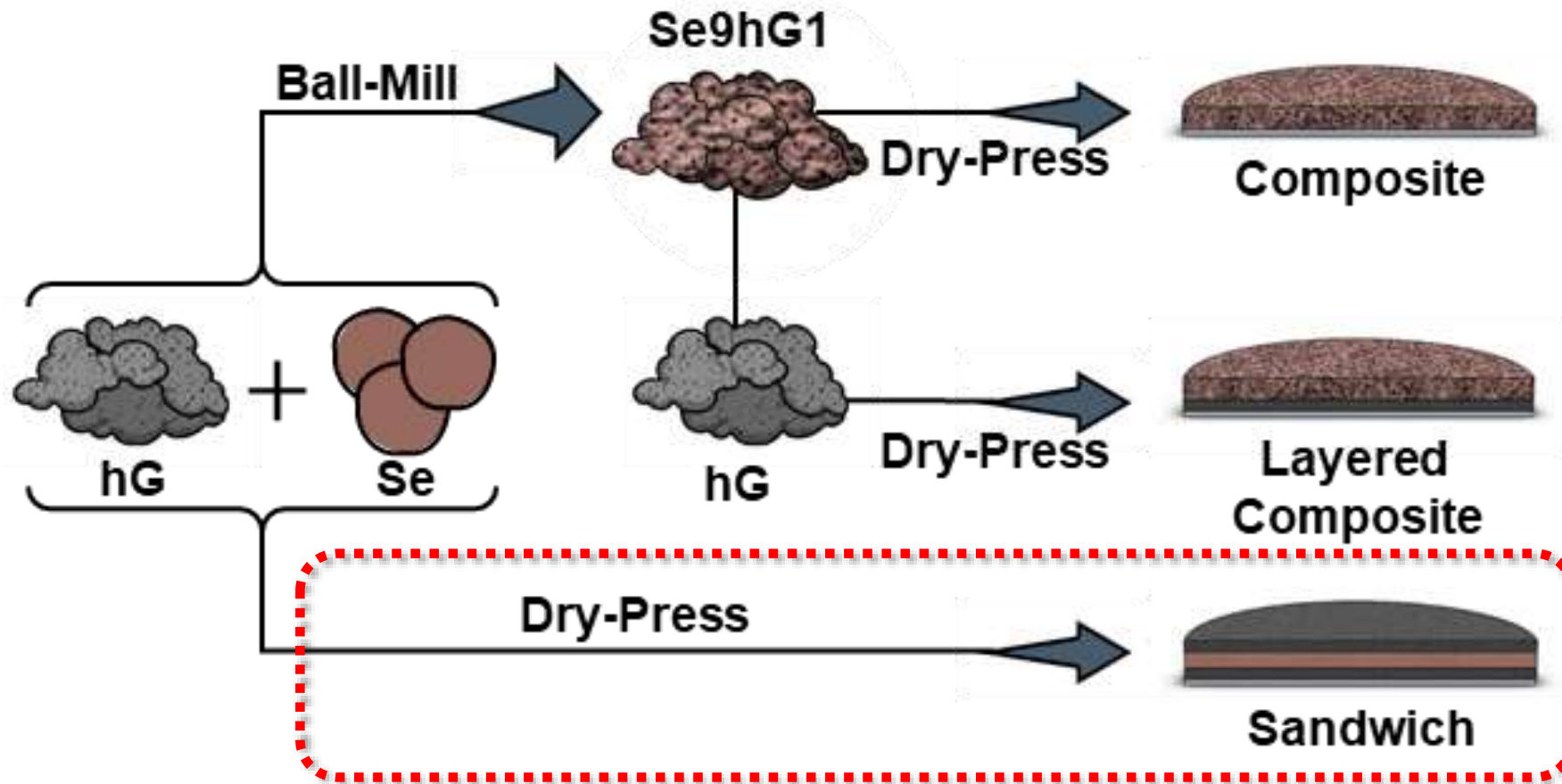
Cathode Architectures for Improved Performance



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

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

“Sandwich” Cathodes



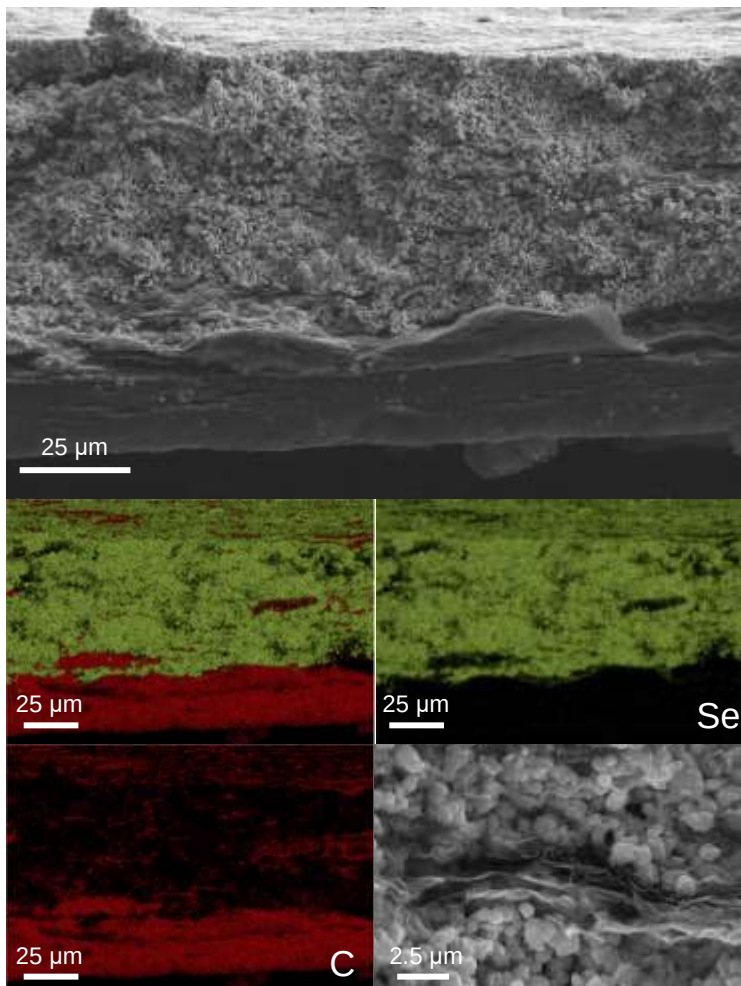
- ❑ High active material content (up to 90 wt.%)
- ❑ High mass loading: high areal capacity
- ❑ Excellent current collector– cathode contact

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

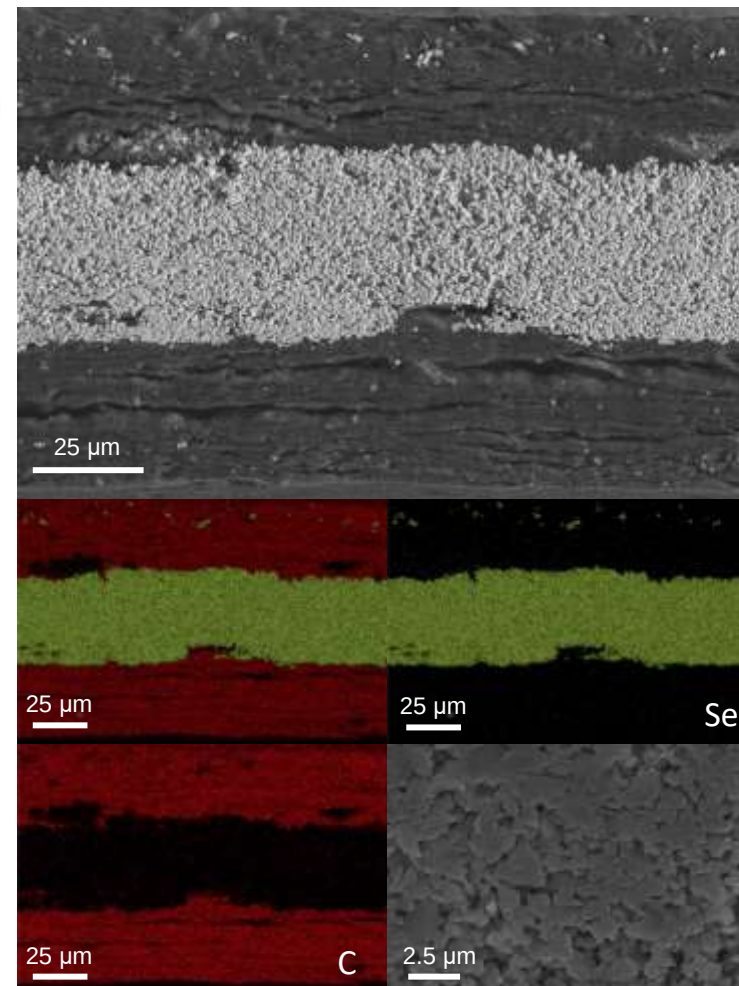
Morphology of Cathode Architectures



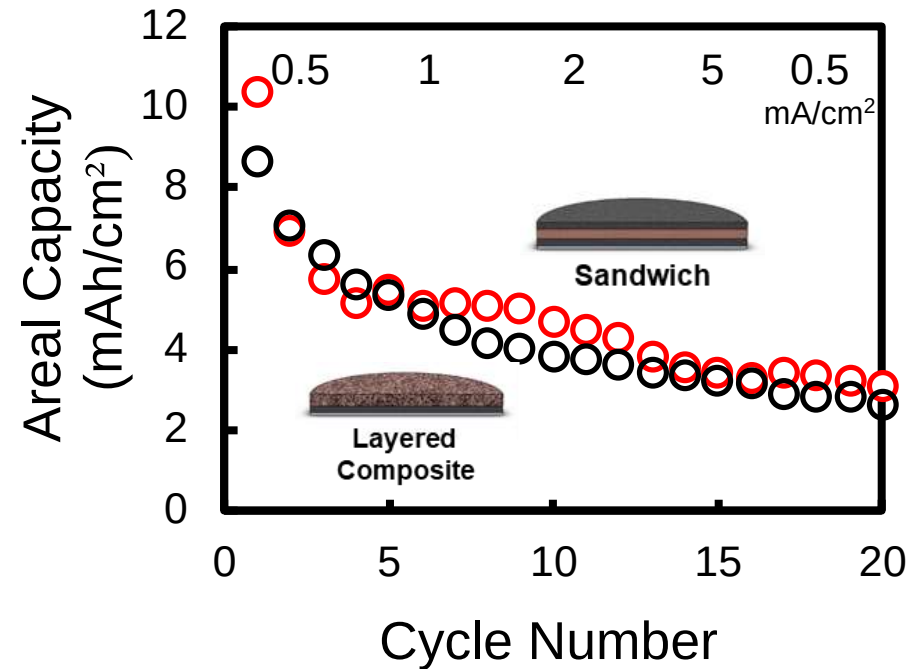
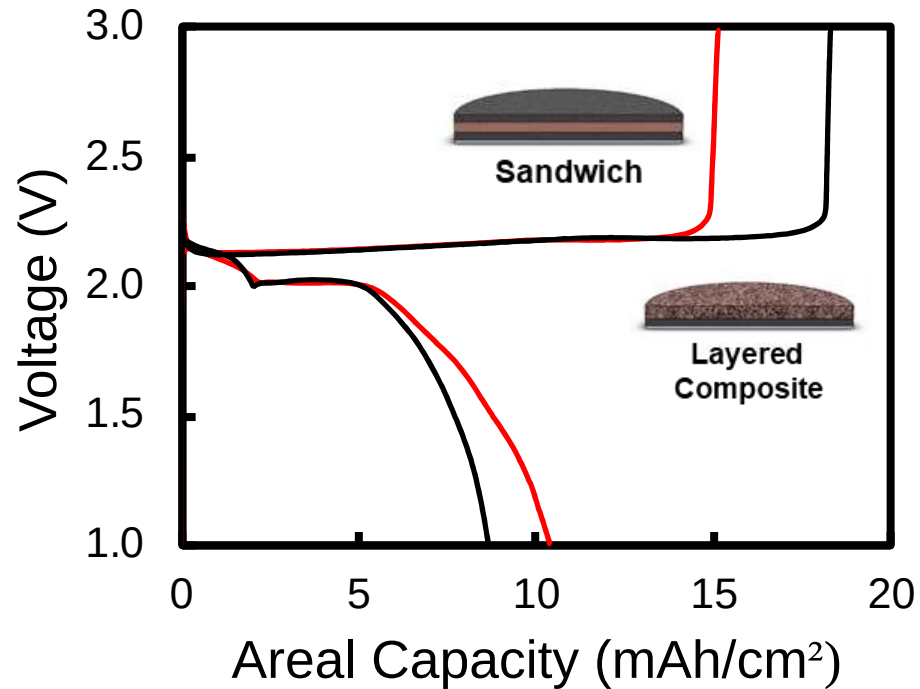
Layered Composite



Sandwich



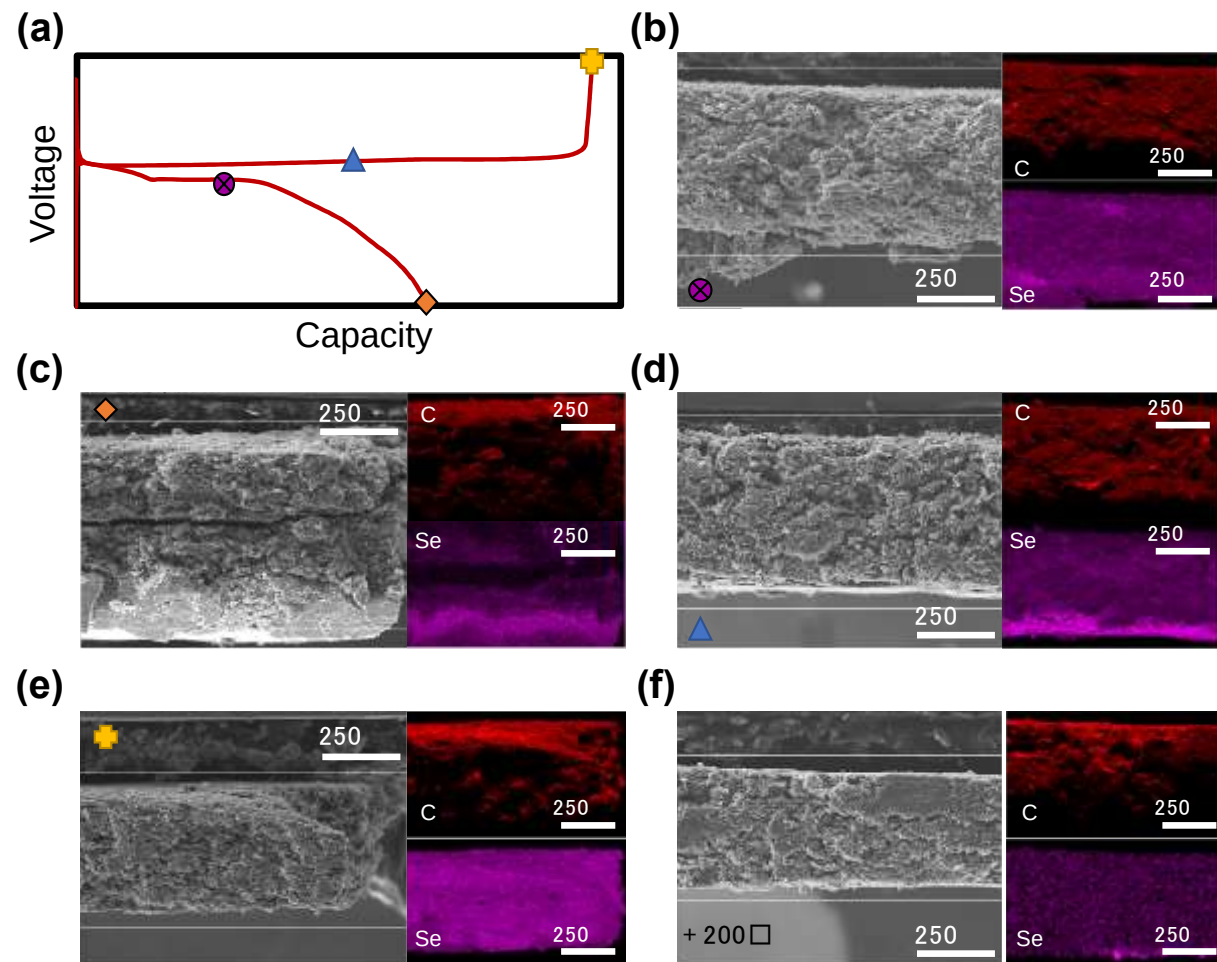
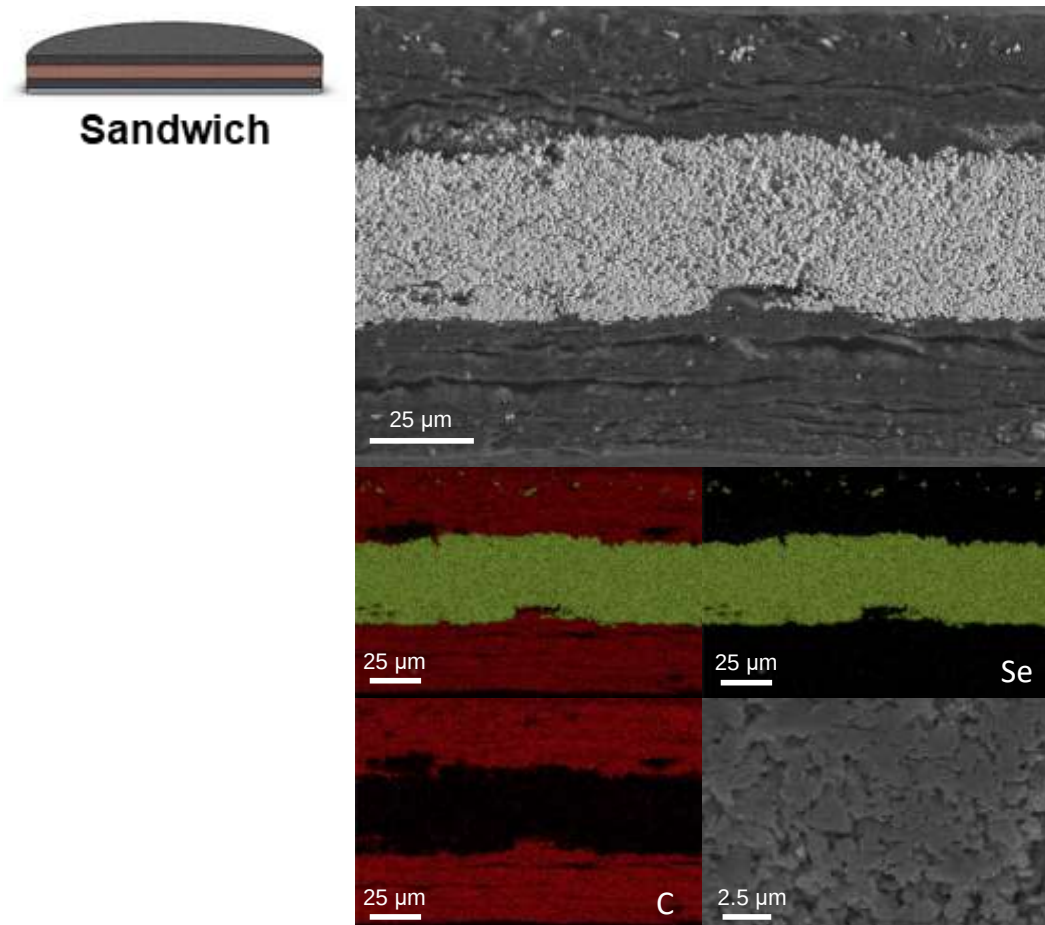
hG-Se-hG Sandwich Cathodes



Sandwich vs. (layered) composite architectures:

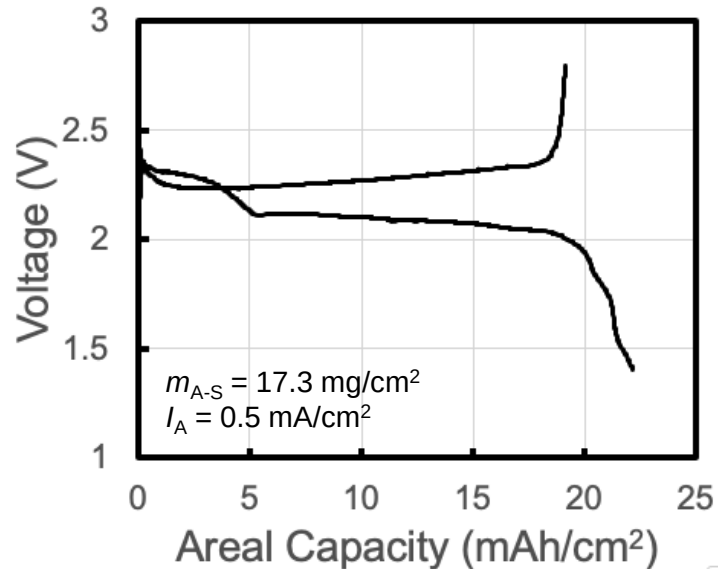
- ❑ Similar performance: overpotential, utilization
- ❑ Less harmful intermediate shuttling
- ❑ **Extremely facile preparation!**

Evolution of Sandwich Cathode Architecture

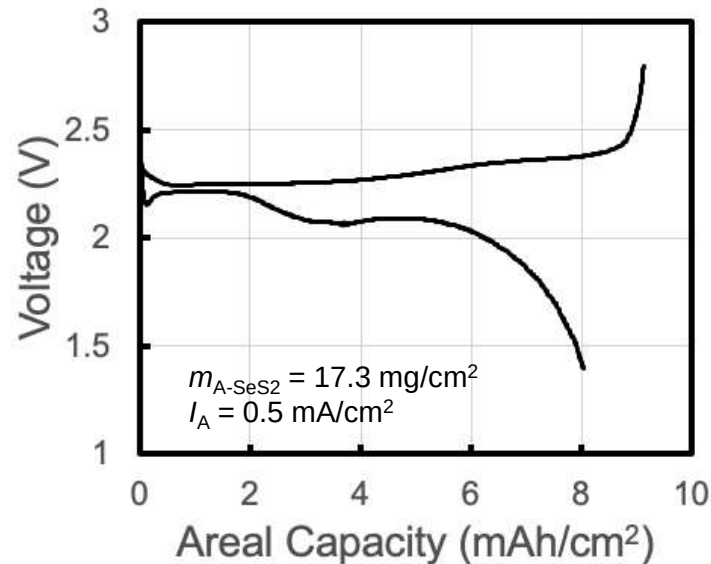


General Applicability of hG-Enabled Sandwich Architectures

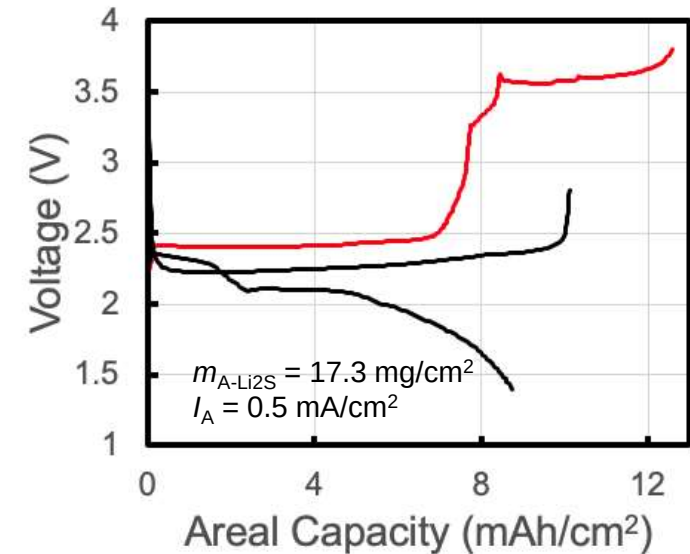
hG/S/hG



hG/SeS₂/hG



hG/Li₂S/hG

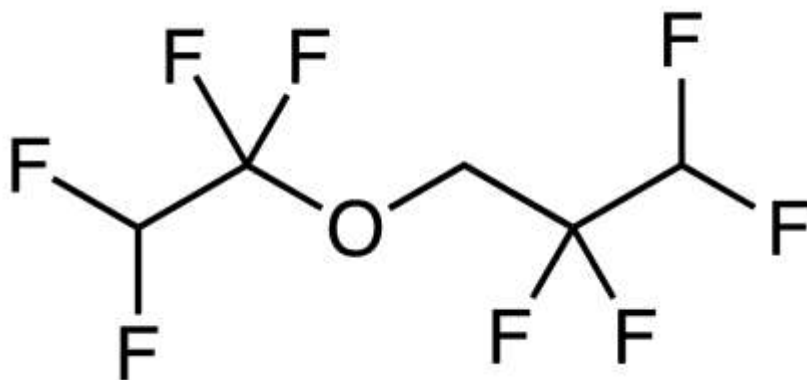


- ❑ Single-step, dry-pressed
- ❑ Neat active material layer

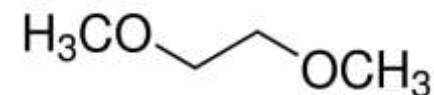
- ❑ High mass loading
- ❑ High areal capacity

Exploration of Perfluorinated Solvents

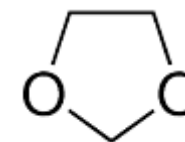
Common Electrolyte Solvents



1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (TTE)



1,2-dimethoxyethane (DME)

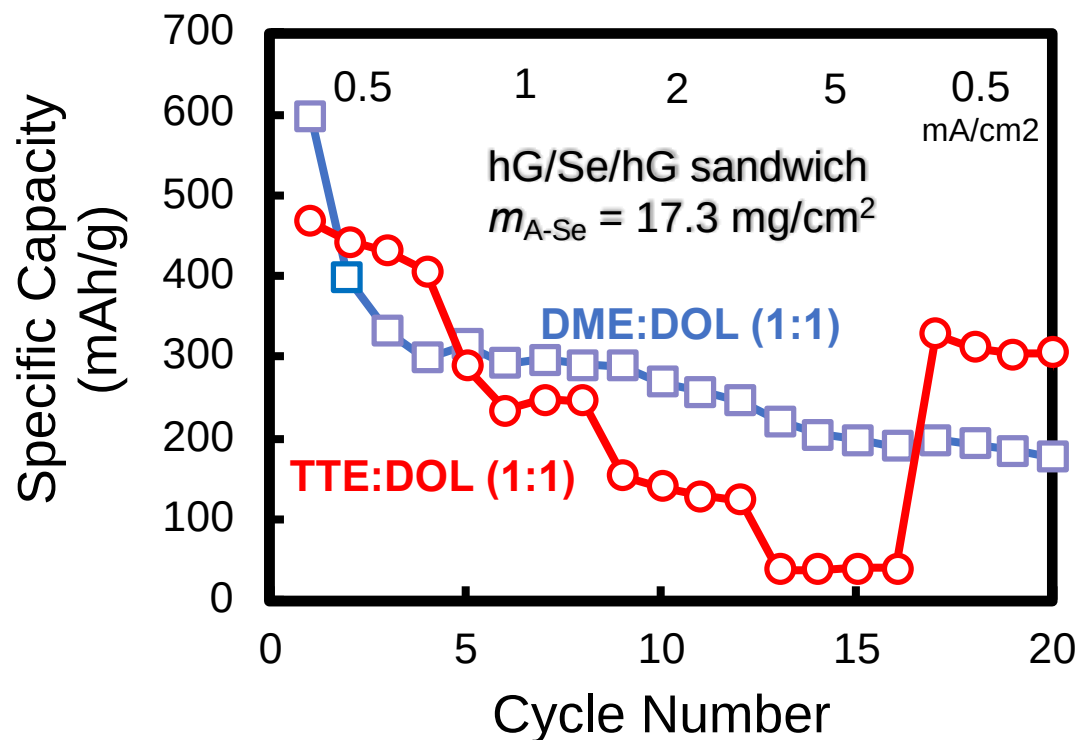


1,3-dioxolane (DOL)

Premises of using perfluorinated solvents:

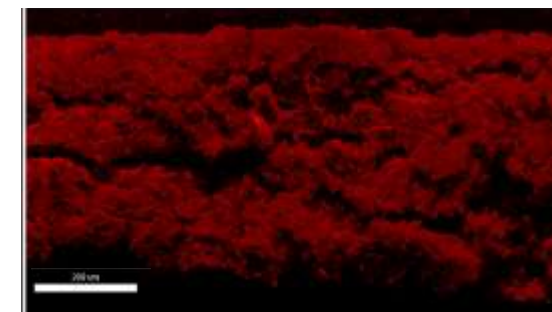
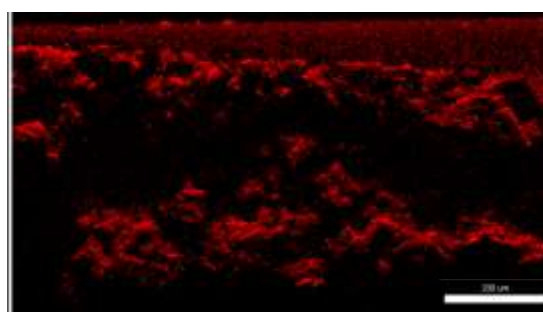
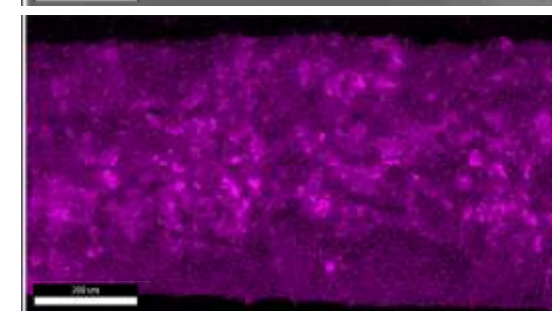
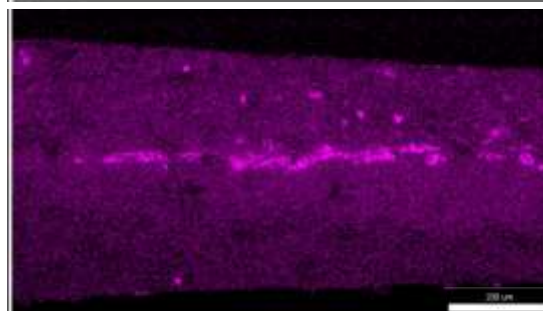
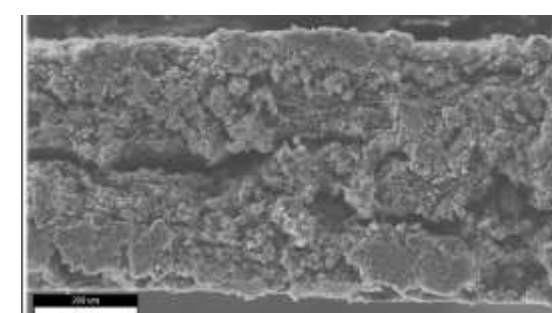
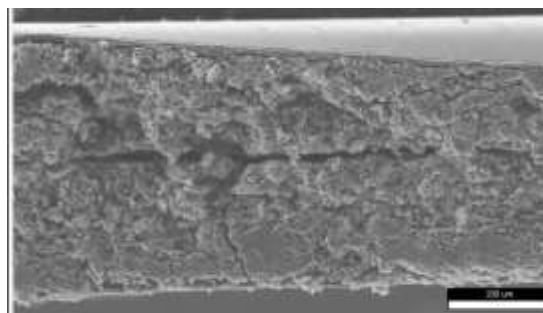
- ❑ **Non-flammable: Safe!**
- ❑ Low solubility of reaction intermediates: *Reduced shuttling, improved columbic efficiency, improved cyclability*

Exploration of Perfluorinated Solvents



First Discharge

First Charge

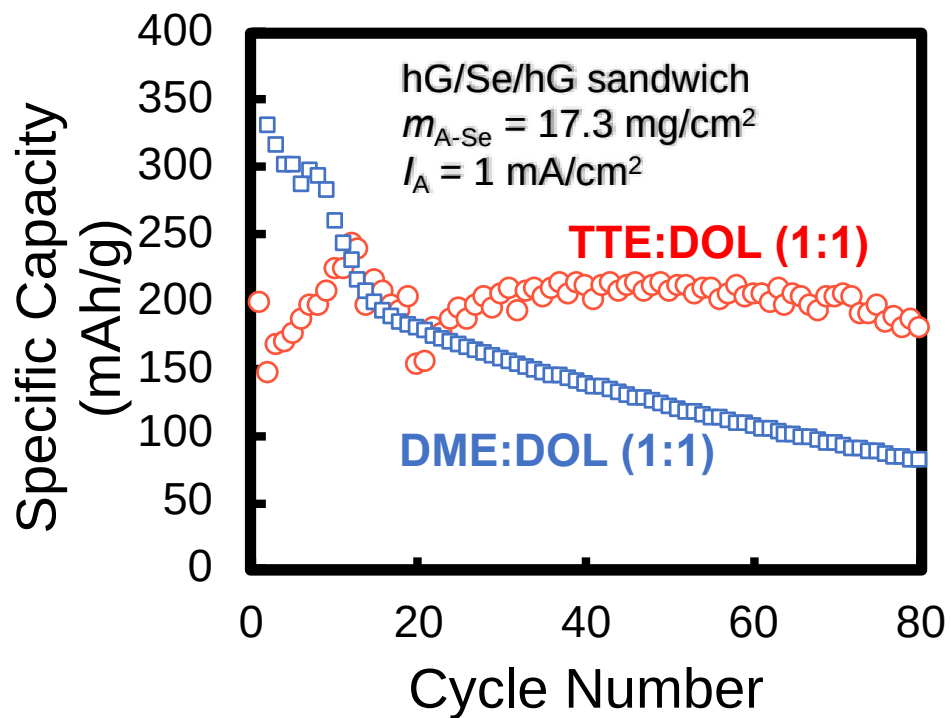


Fluorinated vs. conventional ether solvents:

- ❑ Little intermediate shuttling
- ❑ Higher columbic efficiency
- ❑ Better cyclability
- ❑ *Lower rate*

Scale bars = 200 nm

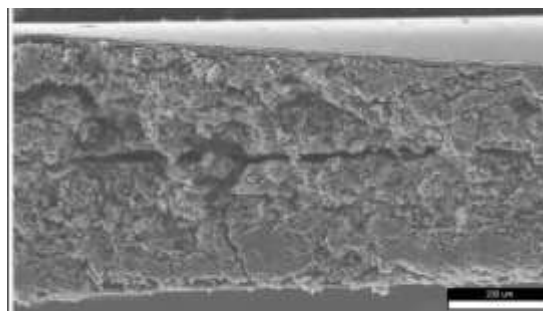
Exploration of Perfluorinated Solvents



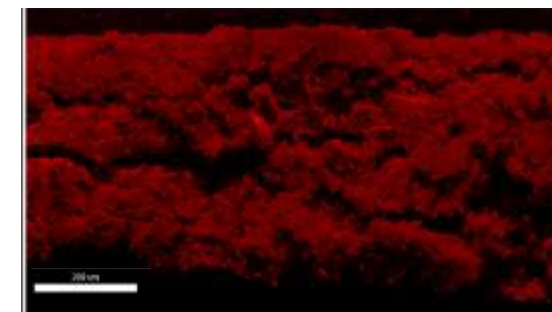
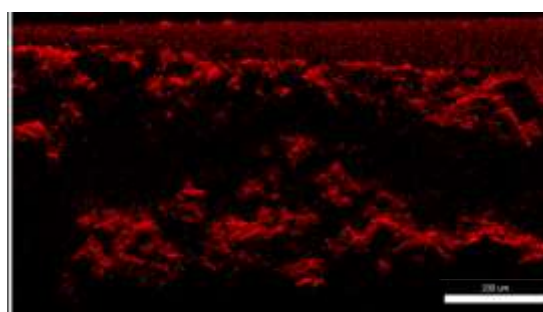
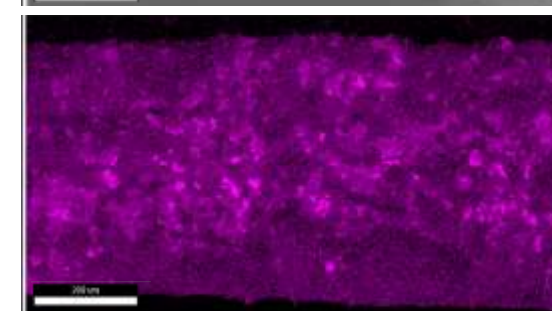
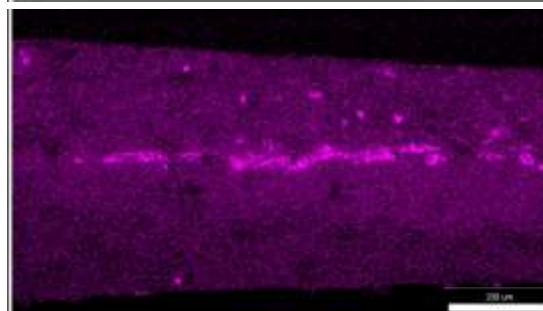
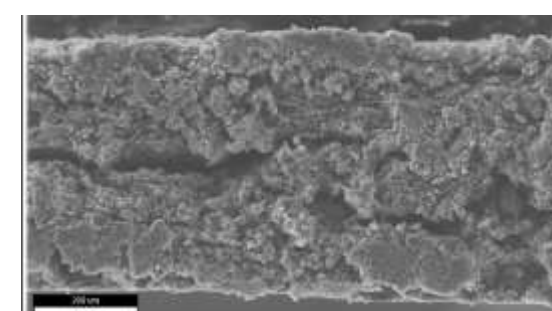
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First Discharge

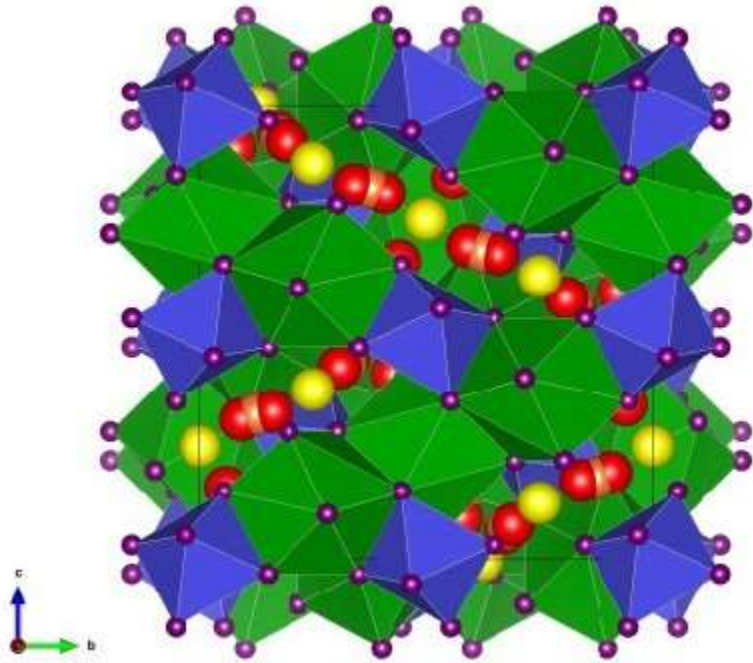


First Charge



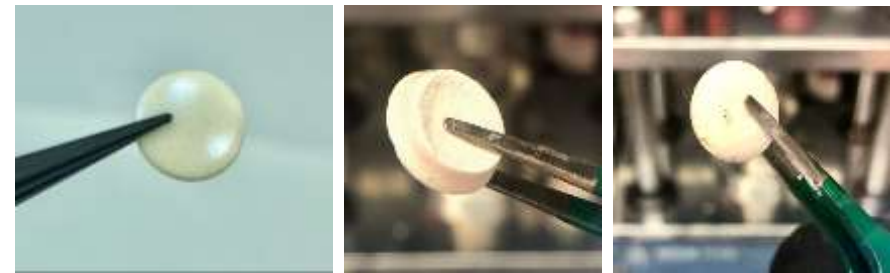
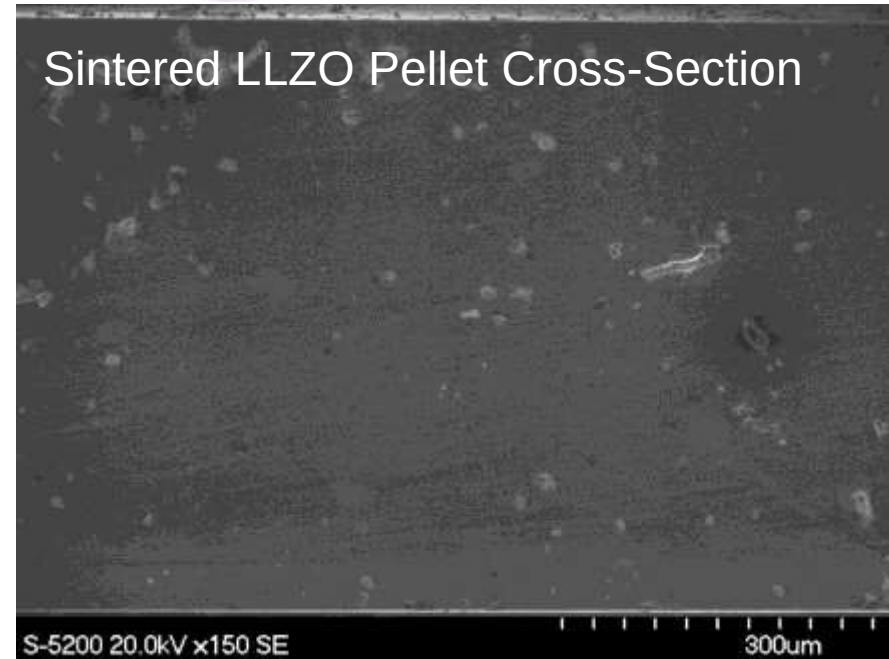
Scale bars = 200 nm

Garnet Solid State Electrolyte (SSE)



Lithium Lanthanum Zirconium Oxide (LLZO)

- ❑ High ionic conductivity ($\sim 10^{-4}$ S/cm)
- ❑ Relatively stable in air
- ❑ Poor electrode-electrolyte interface



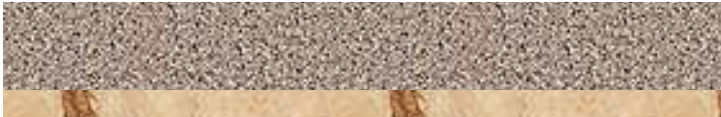
Sintered, Polished
Pellet

Sintered Powder

Garnet-Based Cathode Architectures



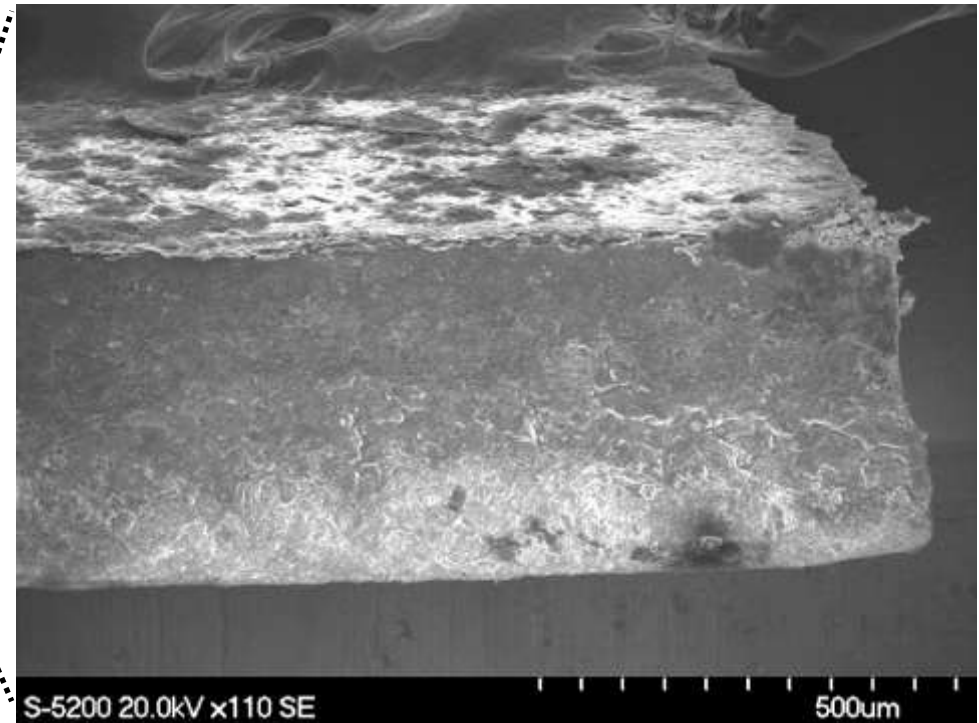
→ hG
→ LLZO|AM|hG
→ LLZO



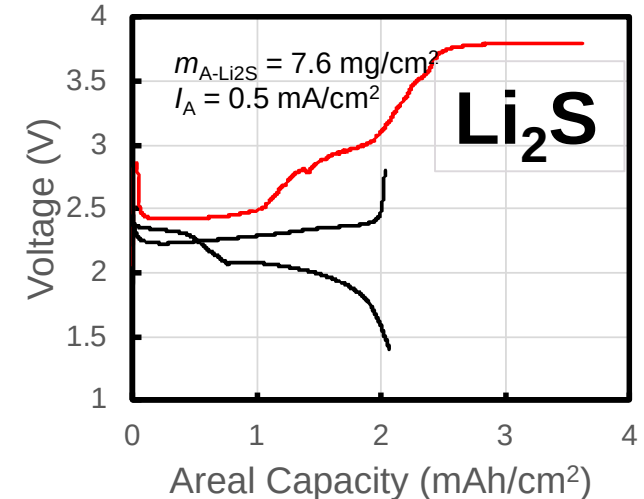
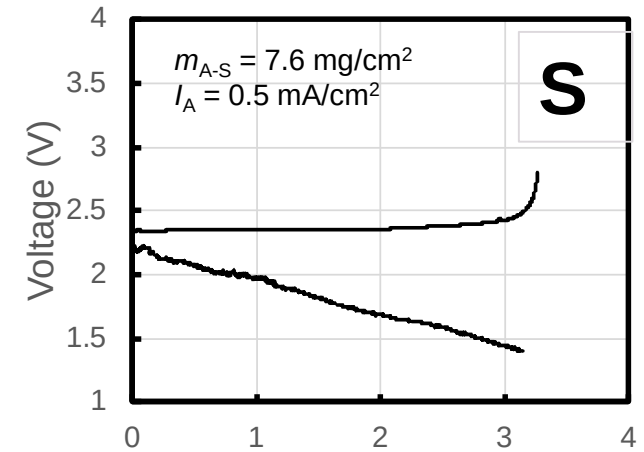
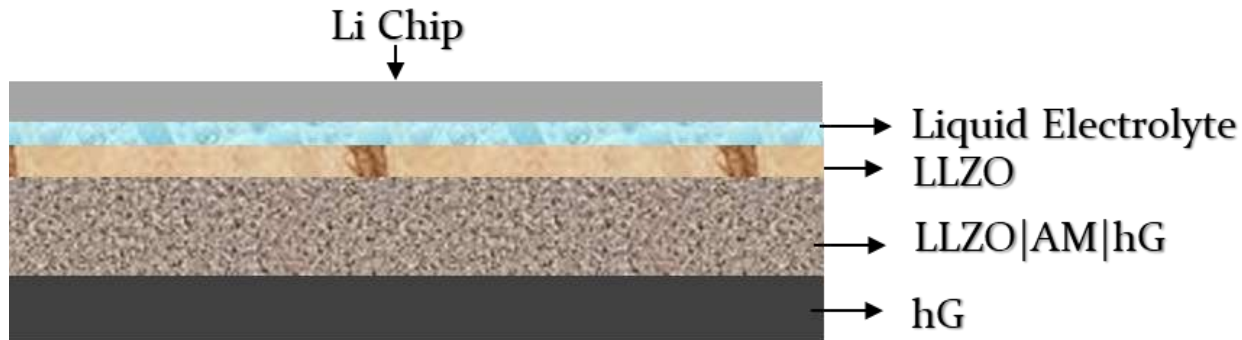
→ LLZO|AM|hG
→ LLZO



→ LLZO|AM|hG



Improving SSE-Electrode Interface



- ❑ Hybrid electrolytes: SSE + (non-flammable) liquid electrolyte
- ❑ Lithiated active material (e.g., Li₂S) as starting cathode to minimize unwanted volume expansion

Summary and Outlook

- ◉ hG is an effective scaffold that enables facile preparation of dry-pressed electrodes;
- ◉ hG-based dry compression approach can be used for various S/Se-based cathodes with unique, high performance cathode architectures;
- ◉ hG enables facile solid-state cell fabrication:
 - ◉ Various SSEs, including garnet, sulfide, and polymer electrolytes, will all be tested for feasibility.
 - ◉ Hybrid electrolyte systems will be studied