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OAK RIDGE National Laboratory

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Na-based Hybrid Flow Batteries for Low-Cost Energy Storage

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U.S. DEPARTMENT of ENERGY

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Project Overview (1/2)

Project Goal: Develop redox flow batteries (RFBs) containing earth-abundant elements (Na/S) for grid-storage applications.

Current Practice:

Grid-Storage Technology	Energy Density	Supply Chain	Affordability	Scalability
Lithium-ion Batteries	+++++	++	+++	++++
All-Vanadium Flow Batteries	++	++	++	+++++
Molten Sodium-Sulfur Batteries	+++	+++++	+++	+++

Why ORNL:

i. Strong track record on advanced battery materials, solid electrolytes, and electrochemical diagnostics
ii. Unique synergies across SMEs in materials science, computational modeling, and power electronics

Innovation:

i. Novel synthesis methods, interfacial engineering, and cell designs to improve performance of Na/S-based RFBs
ii. Advanced AC impedance methods to identify and mitigate performance bottlenecks

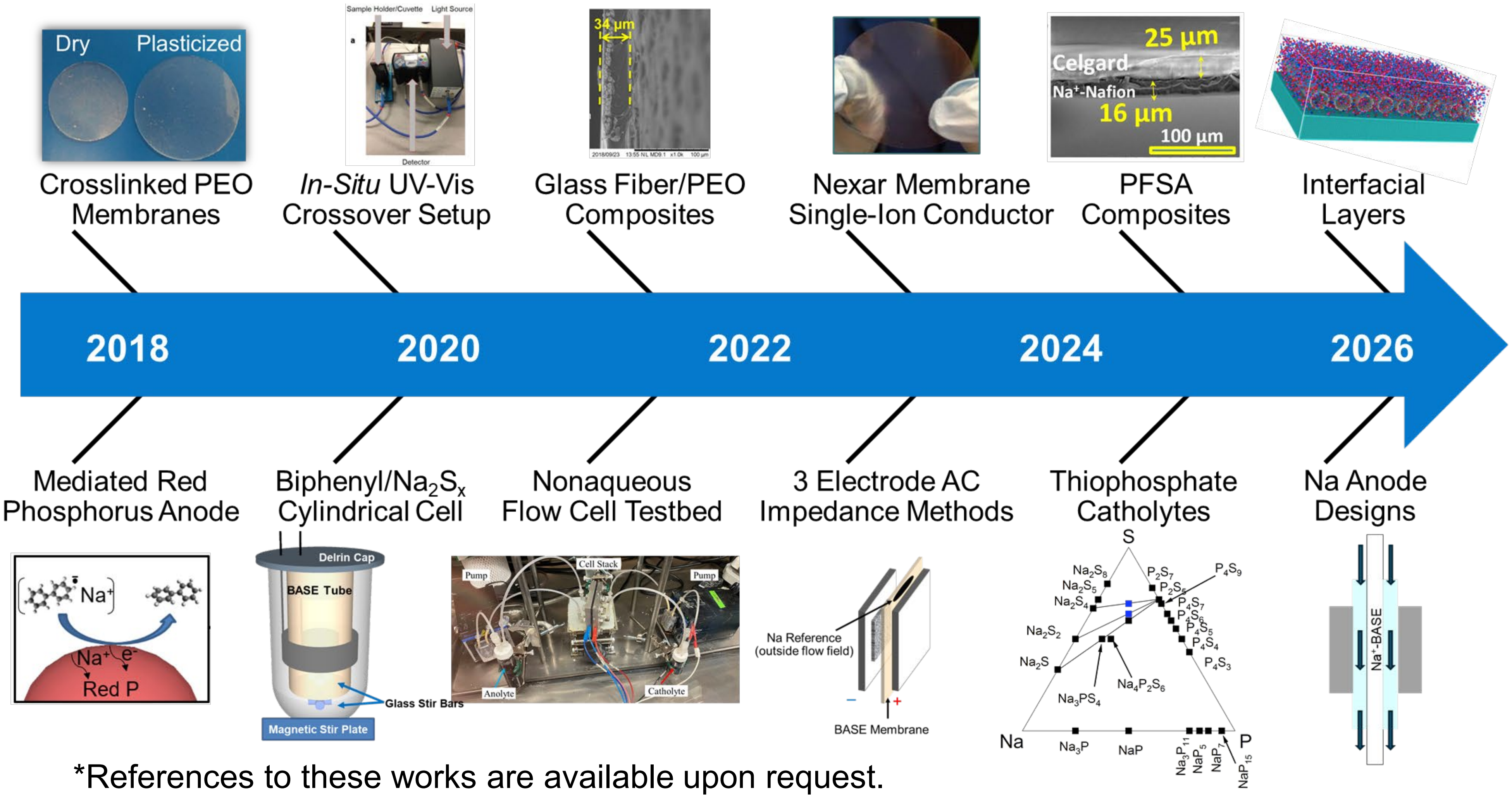
Duration: Since FY18, ORNL has developed novel electrolytes and membranes for nonaqueous RFBs, which has yielded numerous peer-reviewed manuscripts* and patents* and contributed to broader community engagement and workforce development.

Impact: Room-temperature hybrid RFBs will increase energy density and reduce cost compared to incumbent technologies. If successful, this approach will help enable a more robust electrical grid to meet the demands of emerging applications (e.g., AI datacenters).

Project Overview (2/2)

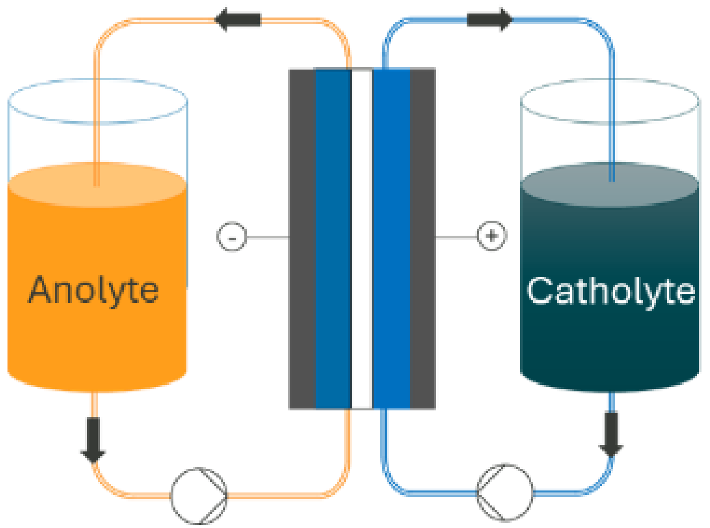
Vertical/Investment Area: Materials and Systems Innovation

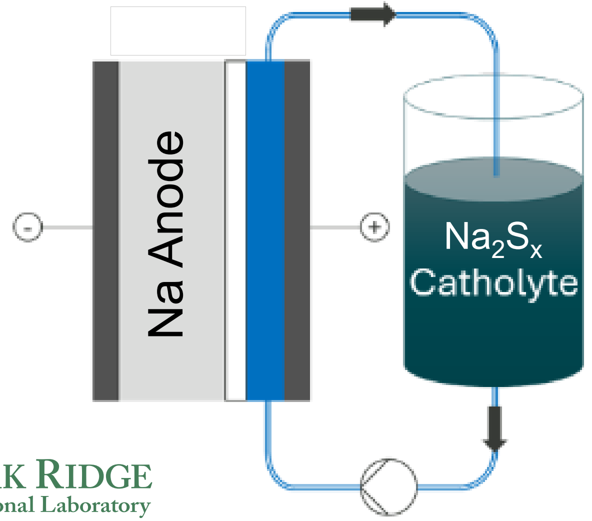
Alignment: This program is developing new materials for next-generation batteries, which will stabilize grid services. Furthermore, these systems utilize domestically available resources which have more robust supply chains compared to lithium-ion batteries.



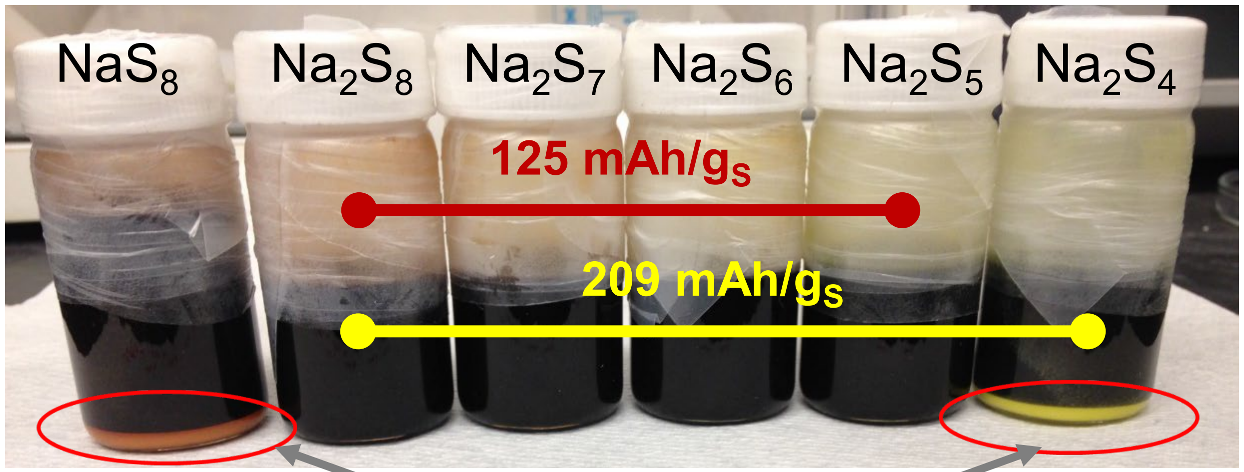
*References to these works are available upon request.

Hybrid flow batteries based on earth-abundant active materials (Na, S) provide opportunities to increase energy and decrease cost compared to traditional RFBs.





Baseline Catholyte: Na_2S_x in Diglyme (~2V vs. Na/Na^+)

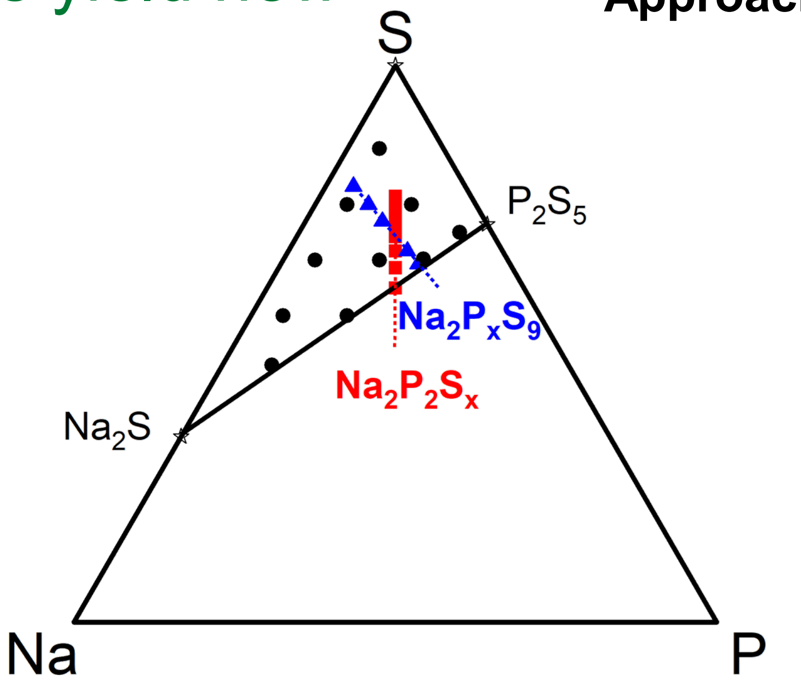


Insoluble Phases at high/low SOCs

Key Technical Challenges

1. Catholyte solubility and S utilization (affects cost and energy)
2. Reversible sodium metal anode (e.g., dendrites, passivation)
3. Membranes (see poster by Guang Yang, ORNL)

Complexing polysulfides with phosphorus and halides yield new classes of ternary/quaternary catholytes.



Thiophosphate Catholytes (FY24-25)

$$\underbrace{Na_2S + xS + yP_2S_5}_{\text{Insoluble}} \xrightarrow[\text{2EGDME}]{} \underbrace{Na_2P_{2y}S_{x+5y+1}}_{\text{Highly Soluble Complex}}$$

Halide-Substituted Catholytes (FY26)

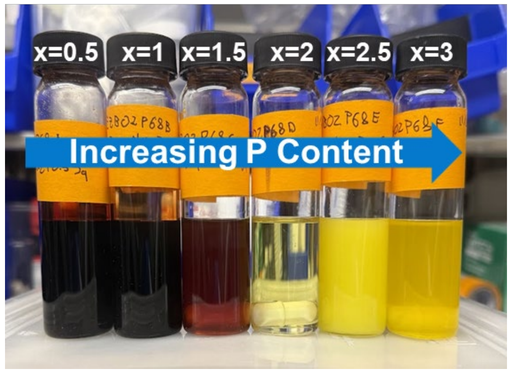
Route 1: $Na_2S + 2S + P_2S_5 + NaX \xrightarrow[\text{2EGDME}]{} Na_3P_2S_8X$

Route 2: Alternative halide precursors (P_2I_4, PBr_3, etc.)

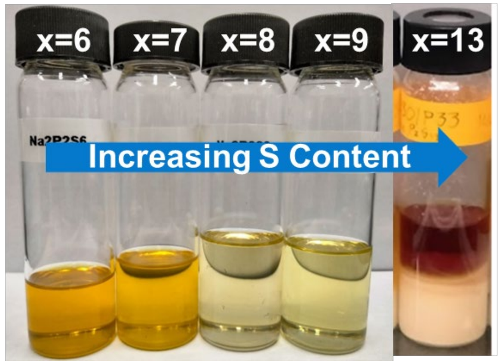
Guiding Questions for FY26

- What is opportunity space for quaternary Na-P-S-X catholytes?
- How does halide substitution impact structure, solubility, and redox properties?
- How does Na anode design influence RFB performance?

0.7m $Na_2P_xS_9$

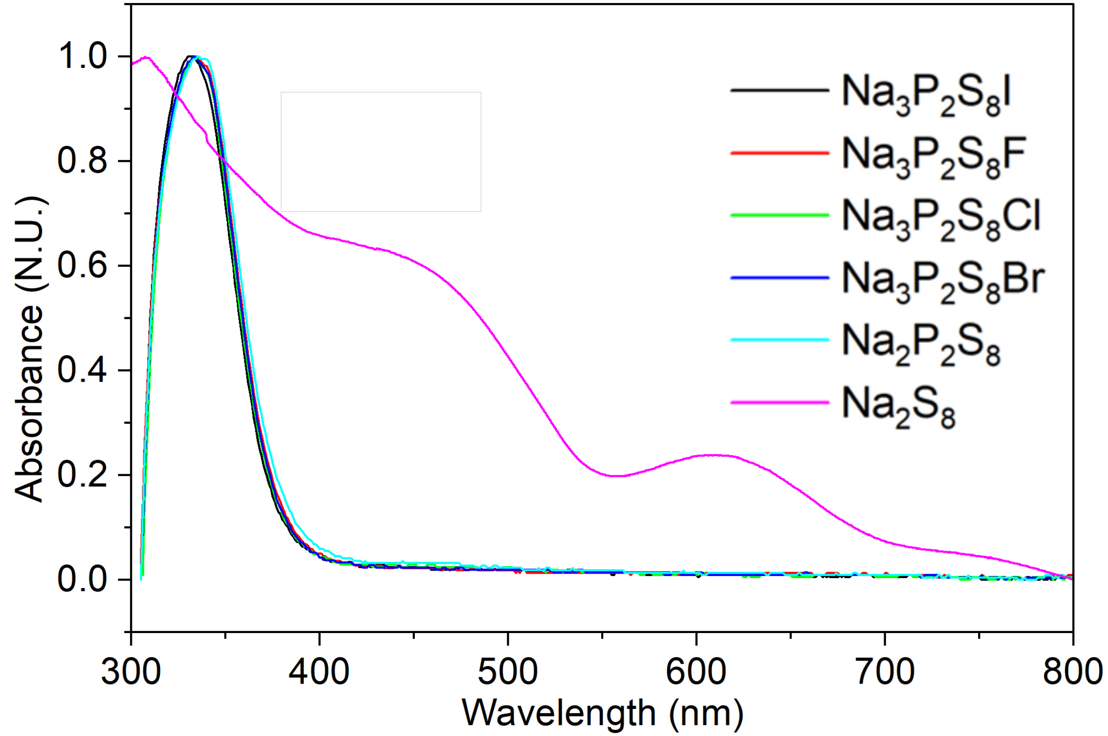


0.7m $Na_2P_2S_x$

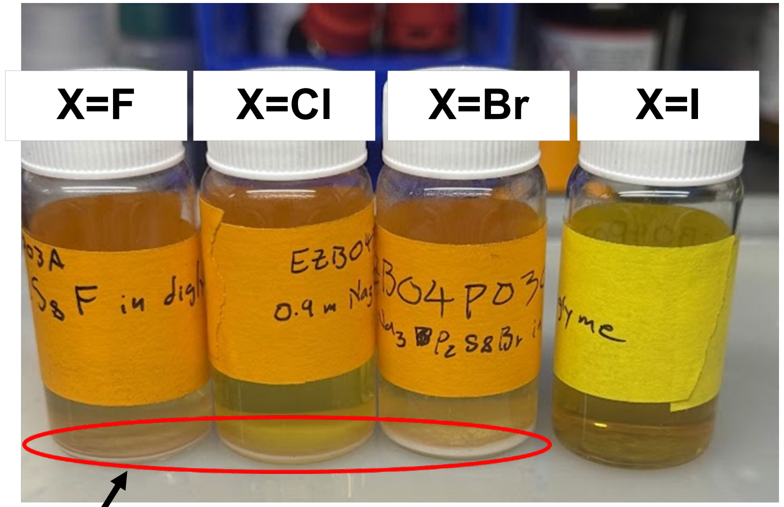


Sodium halide salts were incorporated in solvent-mediated reaction route to explore quaternary Na-P-S-X catholytes.

$$Na_2S + 2S + P_2S_5 + NaX \xrightarrow[\text{2EGDME}]{} Na_3P_2S_8X$$



$Na_3P_2S_8X$ in 2EGDME



Solid precipitates likely unreacted NaX

Baseline Materials for Comparison

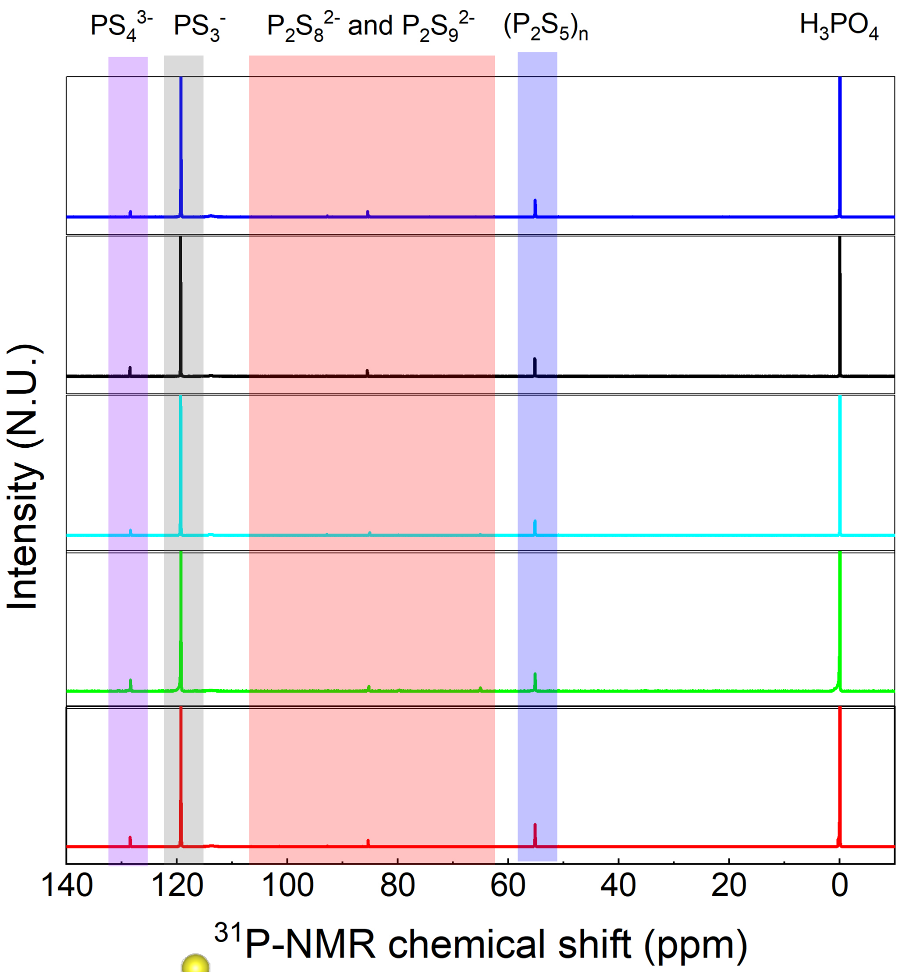
$Na_2P_2S_8$

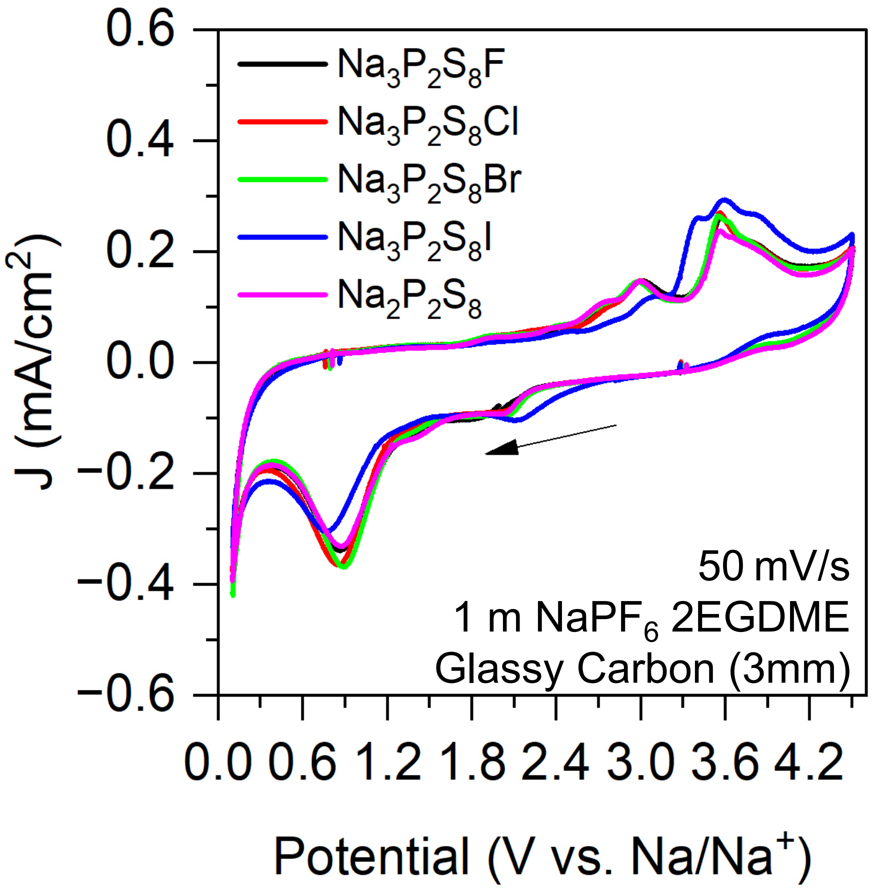
Na_2S_8

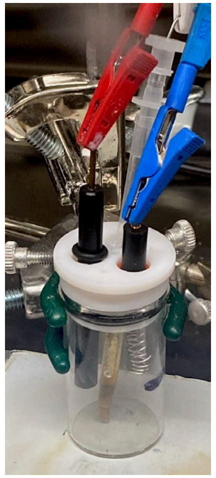
Key Findings

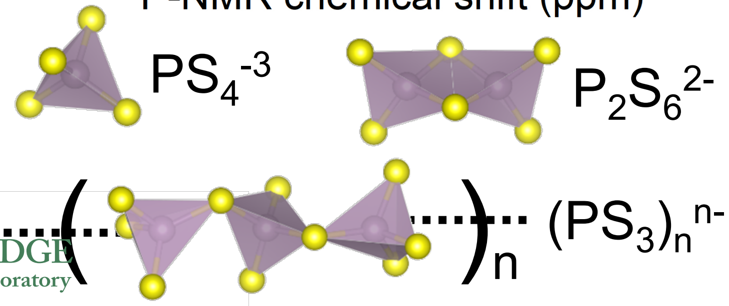
1. Most catholytes have lower-than-expected halide content due to precipitation
2. UV-vis demonstrates no free polysulfides (consistent with findings on Na-P-S)

^{31}P NMR and electrochemical analysis indicate halide substitution has minimal impact on catholyte structure and redox properties.









Key Findings

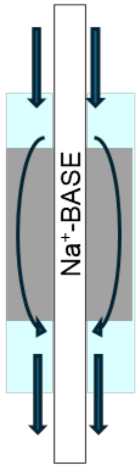
1. All compositions have similar distribution of thiophosphate polyanions (PS_4^{3-}, $(PS_3^-)_n$ chains, etc.)
2. Halide substitution has negligible impact on redox properties

Na plating/stripping was evaluated in symmetric cells containing various flow fields and electrode architectures.

Motivation

- FY25 work showed Na anode is major bottleneck for full cells (Na|BASE|Na-P-S)
- Introducing liquid gap between Na and BASE offers opportunity to tune electrode passivation

Design 1



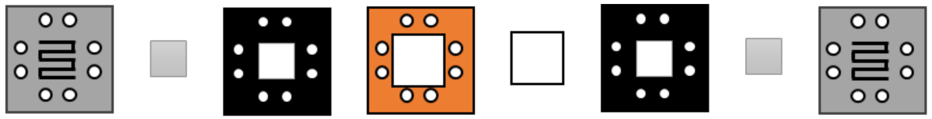
Na Metal

Liquid Electrolyte (1m $NaPF_6$, 2EGDME)

Ni Foam Current Collector

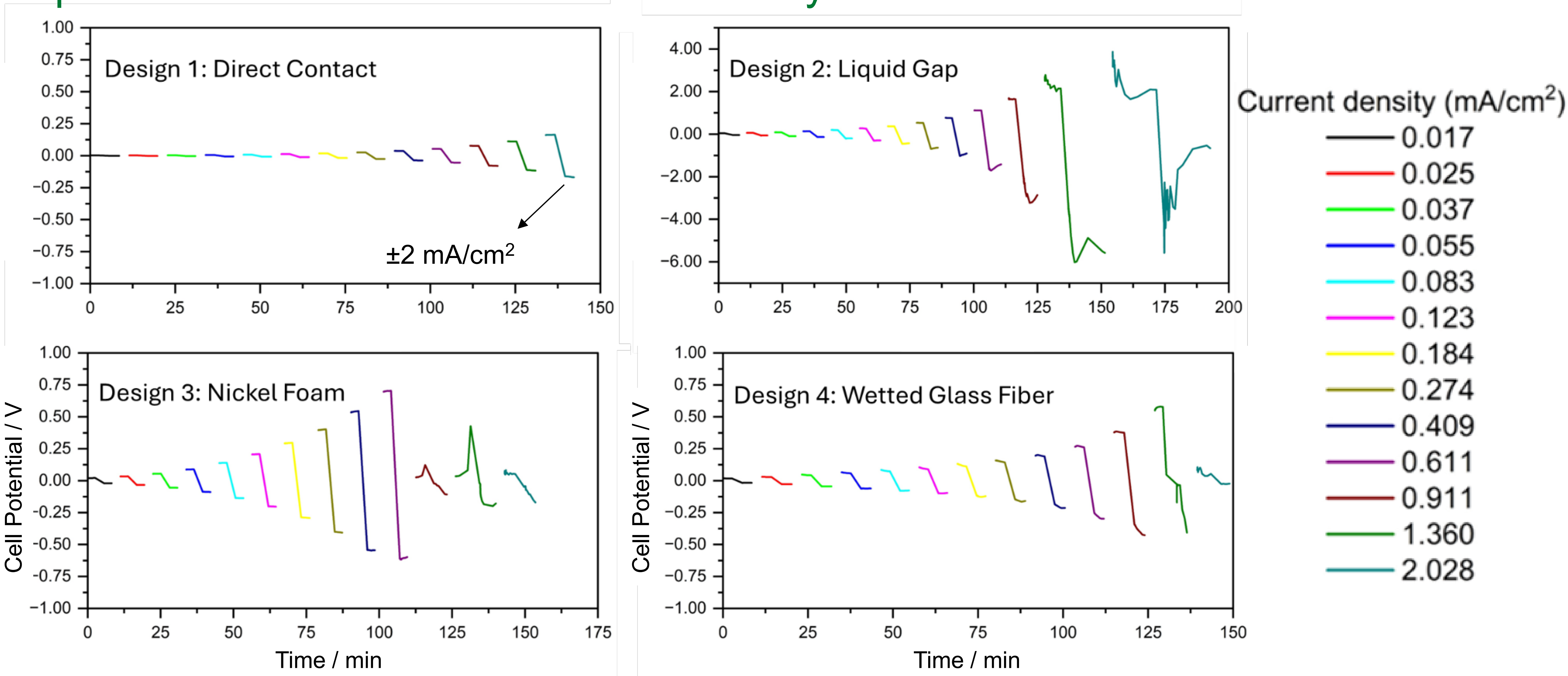
Glass Fiber Mat (soaked with electrolyte)

Na|BASE|Na Symmetric Cells

1 

Design	Liquid Gap?	Flow Field	Electrode Geometry
1	No	Serpentine	Planar
2	Yes	In-Plane	Planar
3	Yes	In-Plane	Porous
4	Yes	Stagnant	Planar

Na|Na cells exhibit large overvoltage when liquid electrolyte present between Na and BASE electrolyte.



Hypotheses for Large Overvoltage in Liquid-Containing Cells

1. Nonuniform electrode wetting yields lower-than-expected interfacial area
2. Large junction potential between liquid electrolyte and BASE

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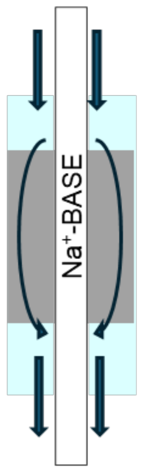
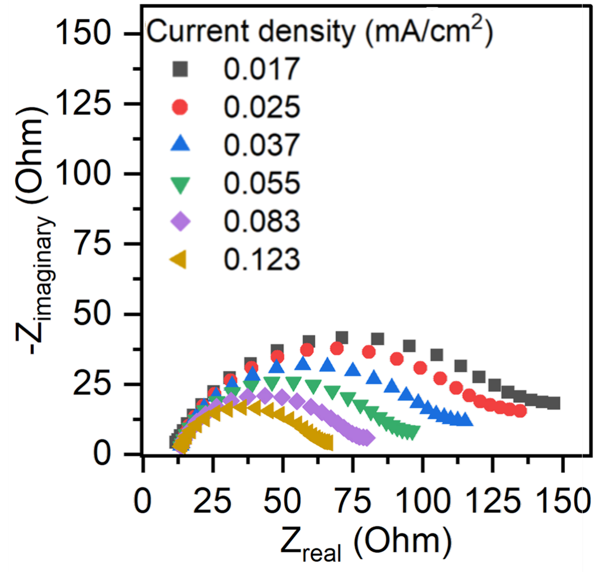
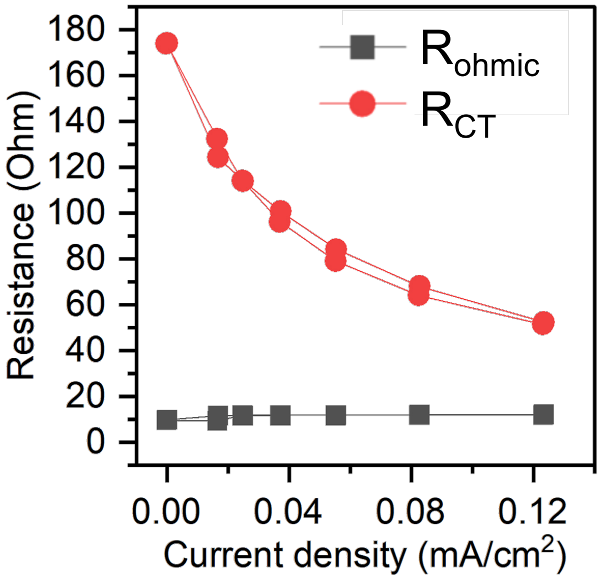
EIS measurements under non-zero loads were used to decouple overvoltage associated with different processes for Designs 1 and 4.

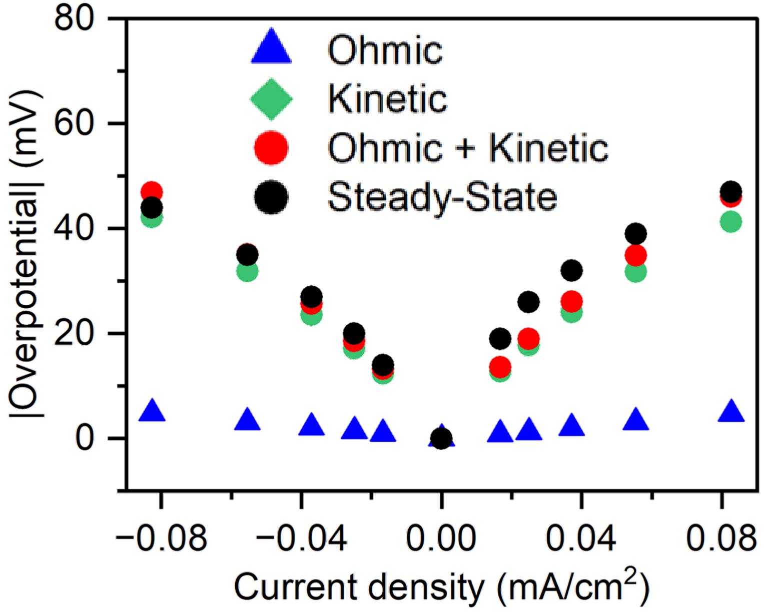
Design 1



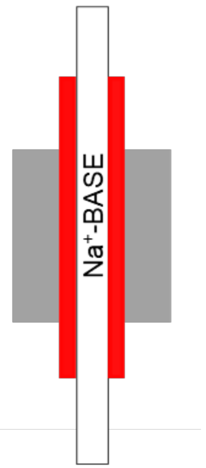


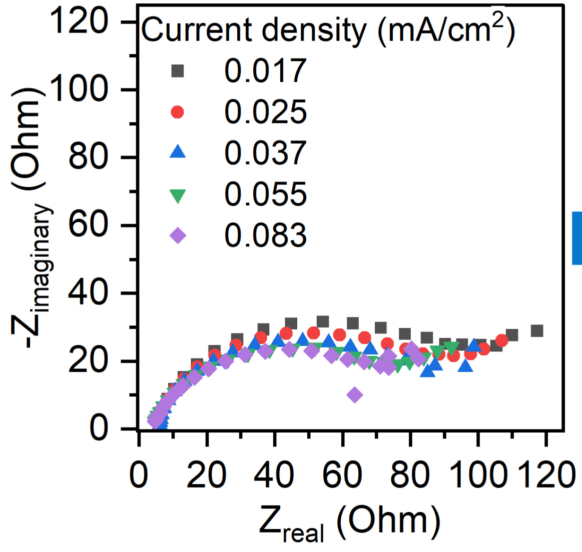


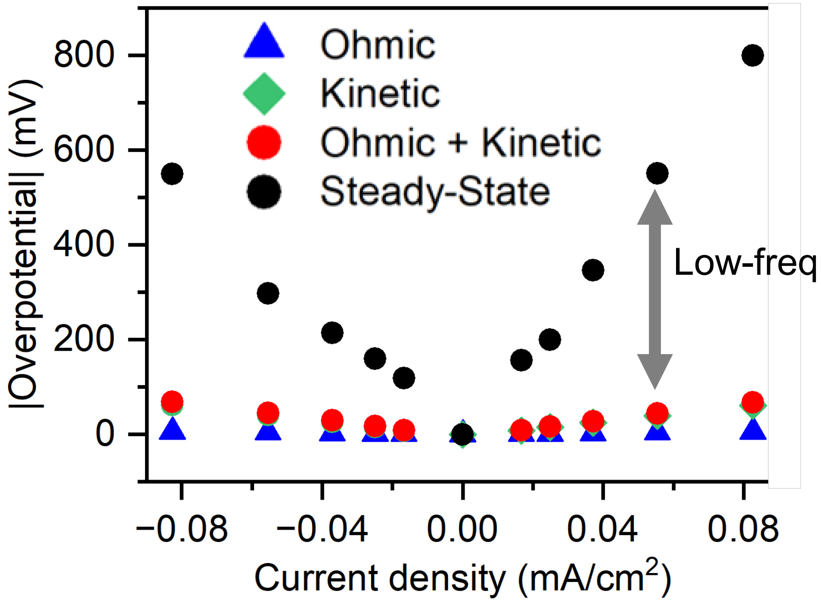
$$\eta_k = \int_0^i R_k \, di$$



Design 4







Low-frequency process

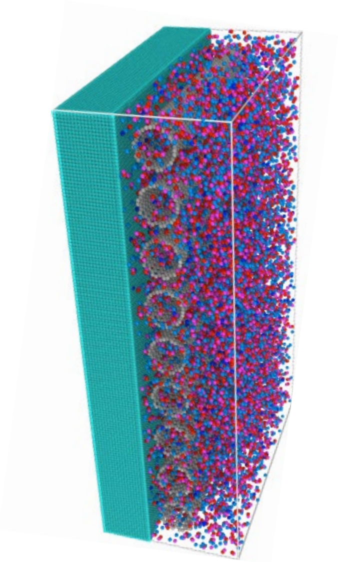
Key Findings

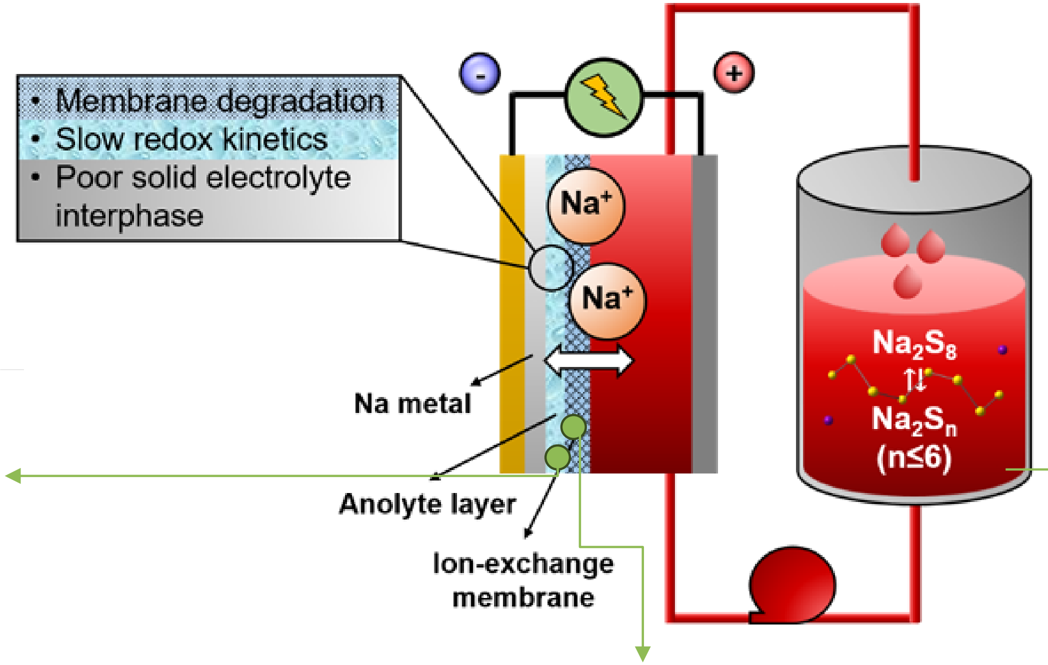
Design 1: Change in R_{CT} consistent with Butler-Volmer kinetics

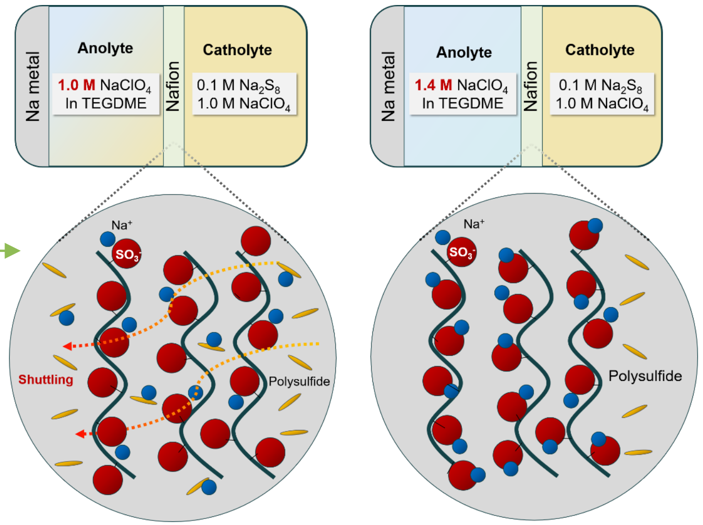
Design 4: Unresolved low-frequency process (liquid/BASE interface?) dominates overvoltage

Transport-Controlled Interfaces for Na Stabilization and Na_2S_x Crossover Reduction

Cost-Effective, Ion-Selective Membranes for Next-Generation Flow Batteries (PI: Guang Yang)







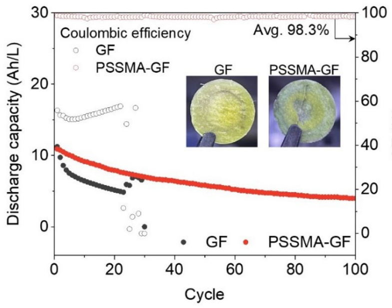
Cation-Diffusive Layers to Stabilize Na Metal Anodes

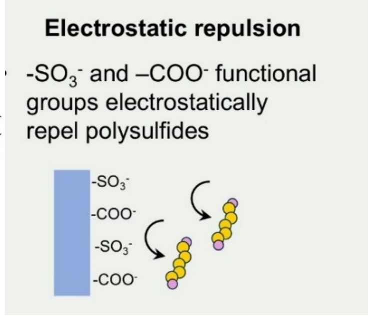
- >70% lower overpotential
- ~98% Na plating/stripping efficiency
- 2× higher current density
- Stable capacity and energy efficiency
- Lower resistance, smoother cycling

Wu, Goswami, Liu, Yang etc. ***Advanced Functional Materials*** (2026): e31310.

Non-PFAS Membrane Protection Layer

- Increased CE by 64%
- Suppressing polysulfide shuttle by electrostatic and steric repulsion





Kang, Liu, Yang etc. ***ACS Nano*** (2026) (just accepted)

Ionic-Strength Control to Suppress Polysulfide Crossover

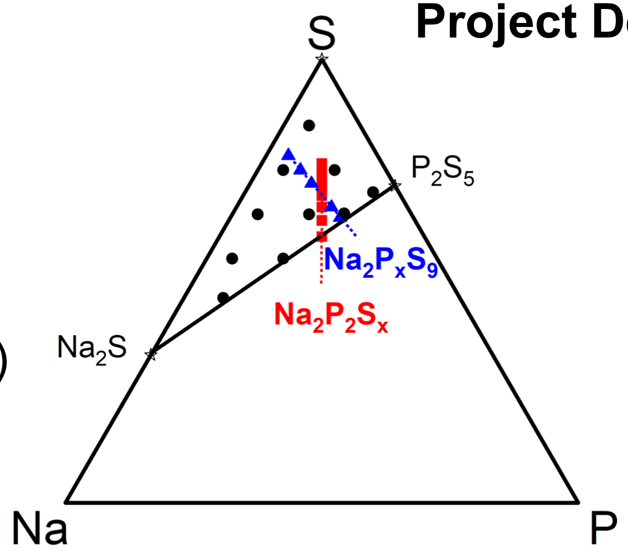
- ~2× higher deliverable capacity
- 14.3% higher energy efficiency
- Reduced polysulfide shuttling
- Less Na_2S buildup
- Lower resistance growth, better cyclability

Wu, Fuead, Yang etc. ***Energy Storage Materials*** (2026) (just accepted)

See Poster by Yang et al

Conclusion & Impact

Project Details

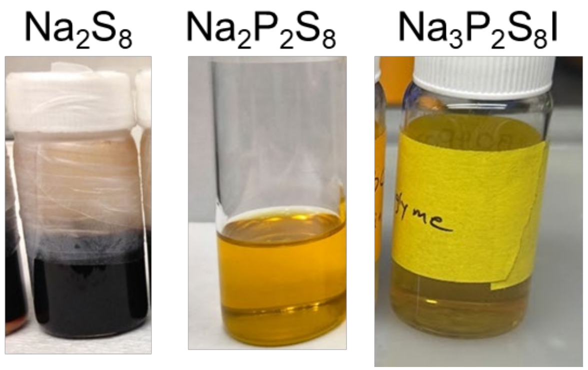


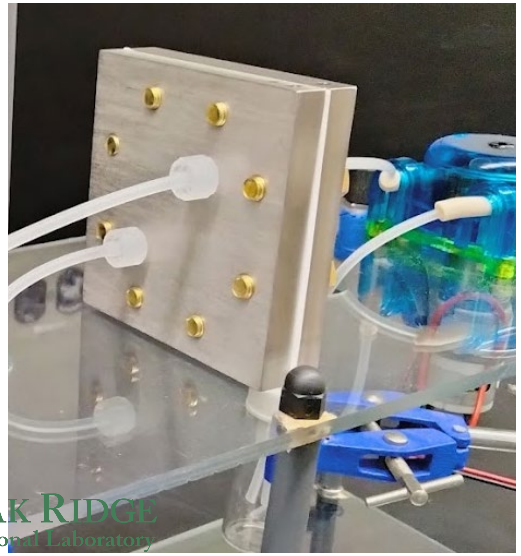
Na-(P)-S-(X) catholytes for redox flow batteries

- Traditional polysulfides (Na_2S_x) have limited practical capacity due to insoluble species at high/low SOCs
- Solvent-mediated reaction platform developed to incorporate P and halides (X) into catholyte

Hybrid RFBs containing Na metal anodes

- Anode architecture and flow field have major impact on overvoltage
- Junction potential between liquid electrolyte and ceramic membrane reduces round-trip efficiency compared to traditional liquid-only cells
- Interfacial engineering and membrane strategies improve cycling performance





Impact

- 5 peer-reviewed manuscripts, 3+ presentations
- External collaborations on RFBs
  - ORNL (S. Allu, EC Self) and SNL (R. Wittman, S. Macchi)
  - ORNL (G Yang) and GA Tech (N Liu)
  - RFB benchmarking activity (J. Bailey, Queen’s University Belfast)
- Meeting and symposia organization
  - Beyond Li-ion Batteries (Berkeley, CA June 23-25, 2026)
  - ACS Fall 2026 (Chicago, IL Aug. 23-27, 2026)

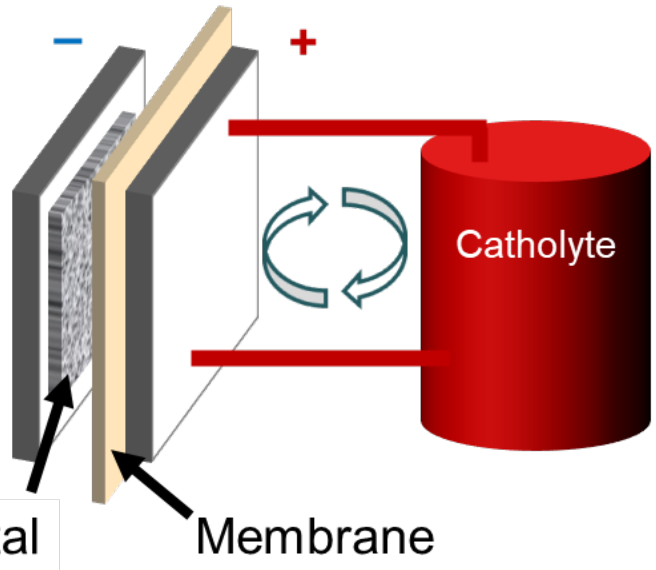
Future Direction/Next Steps

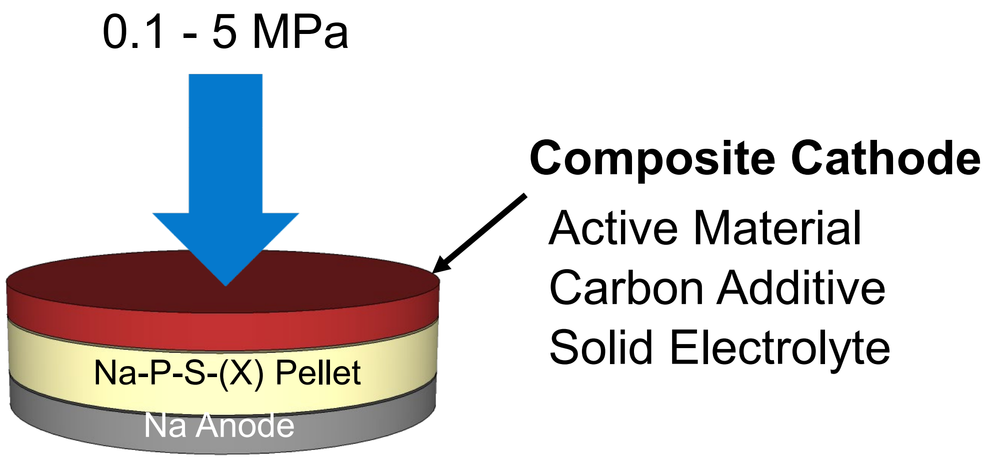
Topic 1: Na Metal Hybrid Redox Flow Batteries (PI: Guang Yang)

- <u>HPC-Guided Experiments</u>: Develop PFAS-free, low-cost binders and membranes
- <u>Dry Processing</u>: Solvent-free fabrication of thin membranes (<100 μm)
- <u>Scaleup</u>: Benchmark Na|Na_2S_x performance in cell formats of varying footprints (10-100 cm^2)

Topic 2: Sodium Metal Solid-State Batteries (PI: Ethan Self)

- <u>Synthesis</u>: Solvent-mediated reactions for thiophosphate solid electrolytes
- <u>Hardware</u>: Solid-state reference electrodes to decouple losses at anode vs. cathode
- <u>Electrochemistry</u>: Influence of stack pressure and cathode design on cycling performance





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