Na-based Redox Flow Batteries for Grid-Scale Energy Storage

Ernesto Camilo Zuleta S.[1], Vaidyanathan Sethuraman[1], Michelle L. Lehmann[1], Gabriel A. Goenaga-Jiménez[2], Wenda Wu[1], Guang Yang[1], Lei Cheng[1], Ethan C. Self[1] (PI)

[1] Energy Storage and Conversion Group, Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN, 37830

[2] Department of Chemical and Biomolecular Engineering, The University of Tennessee, Knoxville, TN, 37996

PROJECT PROFILE

Topic: Sodium Batteries | **Vertical**: Materials and Systems Innovation

Strategic Pathway: Grow: Long-term expansion by enabling innovation, advancing new technologies, and building capacity for a future-ready electricity system

Project Start and Finish: FY23-FY26

PROBLEM

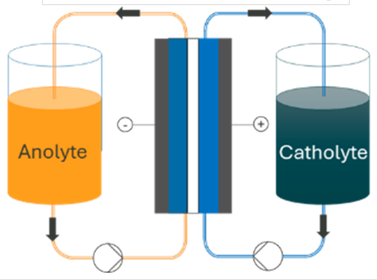
- Incumbent electrochemical energy storage technologies are unable to meet the cost, performance, and reliability requirements for grid-scale applications. In the past 5 years, the gap between energy supply and demand has grown significantly due to emerging applications such as datacenters for AI technologies.
- To address these challenges, this program is developing next-generation batteries containing low-cost, earth-abundant materials.

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

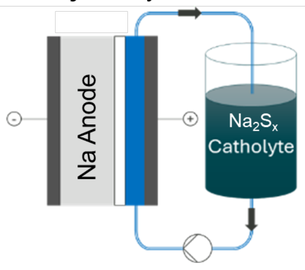
APPROACH

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

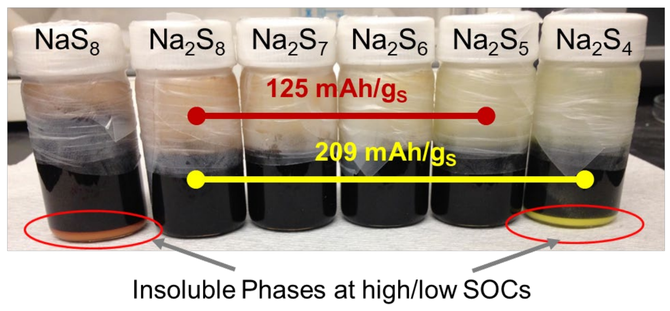
Traditional Flow Battery



This Project: Hybrid Flow Battery



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)

FY26 Milestones	Status
Catholyte Synthesis	Complete
Catholyte Structural and Electrochemical Evaluations	Complete
Optimize Reversible Na Metal Anode	On Track (due June 30, 2026)
Hybrid RFB Construction and Testing	On Track (due Sept. 30, 2025)

RESULTS: CATHOLYTE DEVELOPMENT

Solvent-Mediated Synthesis: A new class of catholytes are prepared by complexing polysulfides with phosphorus and halides.

Thiophosphate Catholytes (FY24-25)

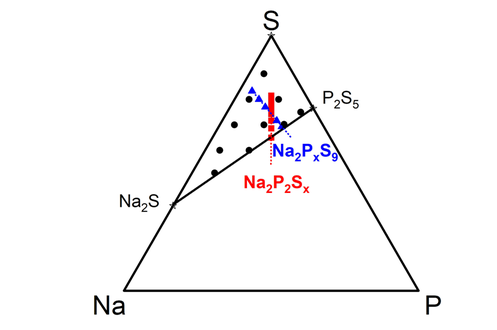
$$\underbrace{Na_2S + xS + yP_2S_5}_{\text{Insoluble}} \xrightarrow[2EGDME]{} \underbrace{Na_2P_{2y}S_{x+5y+1}}_{\text{Highly Soluble Complex}}$$

Halide-Substituted Catholytes (FY26)

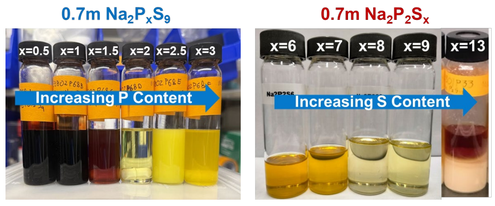
Motivation: Substituting halides (e^- withdrawing) is expected to increase catholyte's operating voltage

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

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



0.7m $Na_2P_xS_9$ | 0.7m $Na_2P_2S_x$

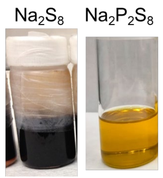


Guiding Questions for FY26
- What is opportunity space for quaternary Na-P-S-X catholytes?
- How does halide substitution impact catholyte's structure, solubility, and redox properties?
- How does Na anode design influence RFB performance?

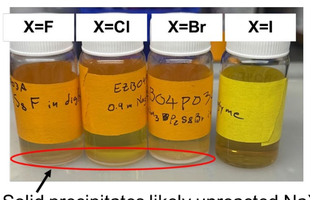
Sodium halide salts were incorporated in solvent-mediated reaction platform to synthesize quaternary Na-P-S-X catholytes.

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

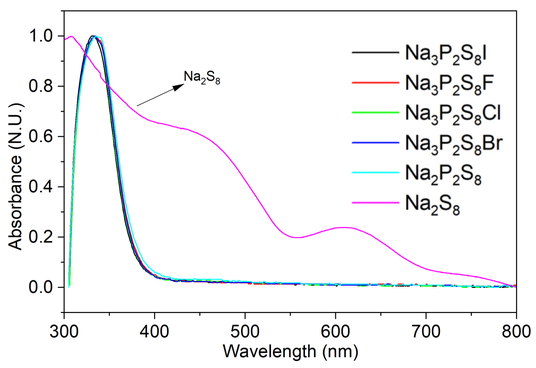
Baseline Materials

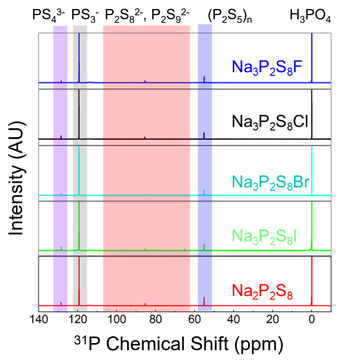


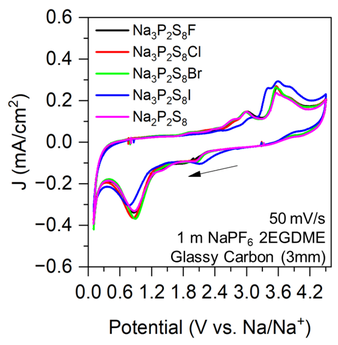
$Na_3P_2S_8X$ in 2EGDME



Solid precipitates likely unreacted NaX





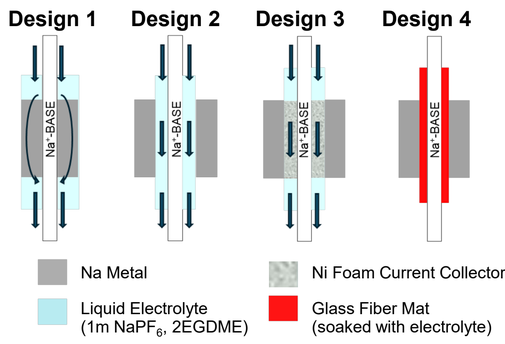


Key Findings
1. UV-vis demonstrates no free polysulfides due to complexation with P
2. Most catholytes have lower-than-expected halide content due to precipitation
3. All compositions have similar distribution of thiophosphate polyanions
4. Halide doping/substitution has negligible impact on redox properties

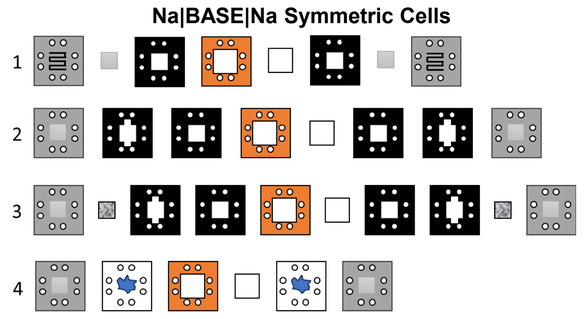
RESULTS: SODIUM ANODE DESIGN

Na plating/stripping was evaluated in Na|Na 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



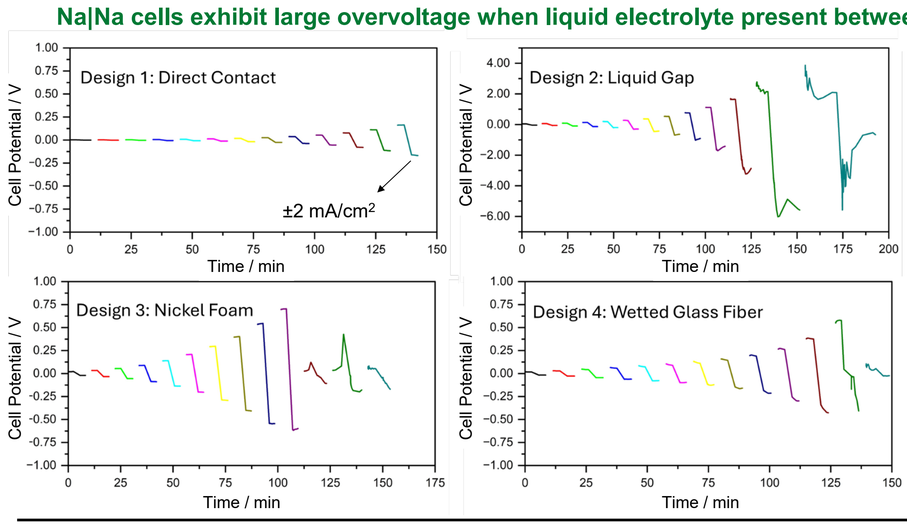
Na|BASE|Na Symmetric Cells



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

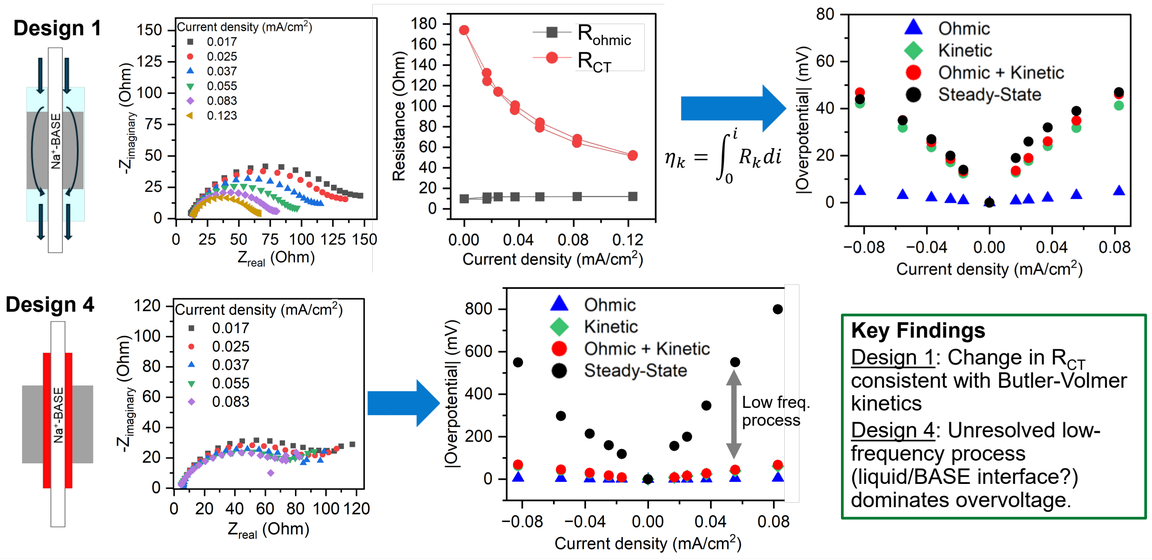
Collaboration with GA Goenaga-Jiménez and TA Zawodzinski (UT-Knoxville)

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



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

Galvanostatic EIS measurements were used to decouple overvoltages in different cell designs.



Key Findings

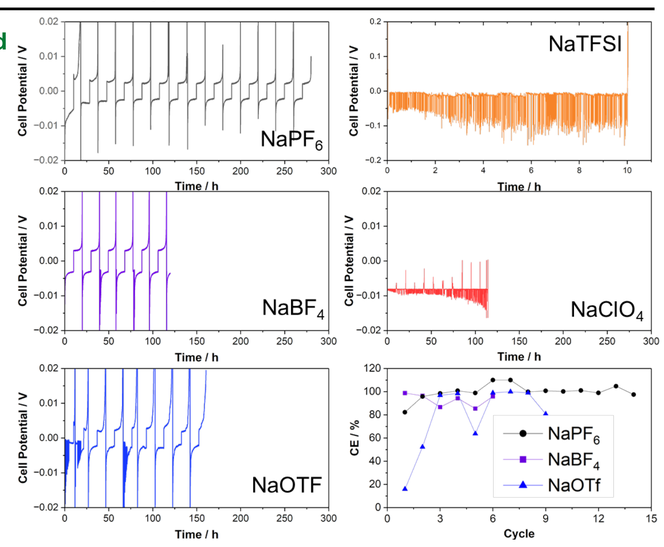
Design 1: Change in R_{CT} consistent with Butler-Volmer kinetics

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

Alternative electrolyte candidates were evaluated to stabilize Na plating/stripping

Experimental Details (R2032 Cells)
- WE: Al foil
- CE: Na foil
- Electrolyte: 0.9 m Na^+ Salt in 2EGDME
- Plate 1 mAh/cm^2 (-0.1 mA/cm^2)
- Strip until 0.5 V vs. Na/Na^+ (+0.1 mA/cm^2)

Key Findings
1. $NaPF_6$ and $NaBF_4$ are viable for sodium anodes
2. Dendrites present significant issues for NaOTF, NaTFSI, and $NaClO_4$-based electrolytes
3. Low overvoltage in these cells supports hypothesis of large junction potential at liquid/BASE interface in hybrid RFBs



CONCLUSIONS & IMPACT

Catholyte Design
- Traditional polysulfides (Na_2S_x) have limited practical capacity due to insoluble species at high/low SOCs
- Solvent-mediated reaction platform was developed to incorporate P and halides (X) into catholyte
- Ongoing Work: Alternative halide precursors (e.g., Na_2I_4, PBr_3, etc.)

Hybrid Na Metal RFBs
- Anode design has major impact on cell's overvoltage
- Junction potential between liquid electrolyte and ceramic membrane reduces round-trip efficiency compared to traditional liquid-only cells

FY26 Scientific Output

[1] EC Zuleta S, V Sethuraman, ML Lehmann, G Goenaga, G Yang, L Cheng, EC Self "Solvent-based Synthesis and Characterization of Sodium Thiophosphate Catholytes for Nonaqueous Redox Flow Batteries" *Chem. Eng. J.* **2026**, *531*, 173687.

[2] EC Self, V Sethuraman, RL Sacci "Evaluating Passivated Battery Electrodes using AC Impedance Spectroscopy" *J. Electrochem. Soc.* **2026**, *173*, 020516.

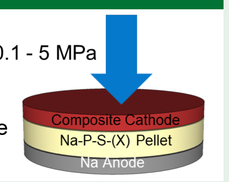
[3] EC Self "Assessing Nonlinear Polarization in Batteries using AC Impedance Spectroscopy" *249th Meeting of the Electrochemical Society*, Seattle, WA, May 24-28, 2026 (Oral Presentation)

[4] EC Self "Low-Cost, Earth-Abundant Catholytes for Redox Flow Batteries" *249th Meeting of the Electrochemical Society*, Seattle, WA, May 24-28, 2026 (Oral Presentation)

[5] EC Zuleta S, G Goenaga, EC Self "Evaluation of Anode Designs for Sodium Metal Hybrid Redox Flow Batteries" *249th Meeting of the Electrochemical Society*, Seattle, WA, May 24-28, 2026 (Oral Presentation)

FUTURE DIRECTIONS

Sodium Metal Solid-State Batteries
- Motivation: Na metal anode unable to support current densities needed for practical RFBs
- Synthesis: Solvent-mediated reactions for thiophosphate solid electrolytes
- Hardware Development: Solid-state reference electrodes to decouple losses at anode vs. cathode
- Electrochemistry: Influence of stack pressure and cathode design on cycling performance



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