Sodium Polysulfide and Thiophosphate Catholytes for Redox Flow Batteries

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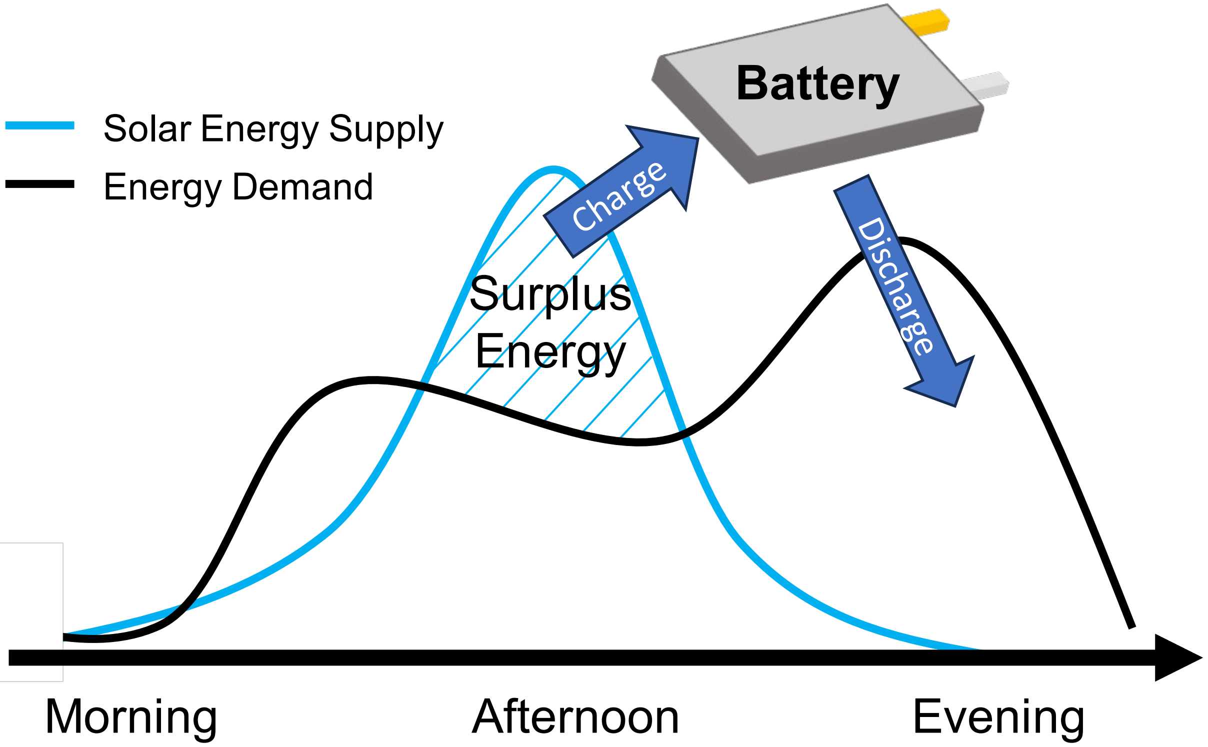
Presentation ID: 601
2024 DOE OE Energy Storage Peer Review
August 5-7, 2024

Long duration energy storage (LDES) systems will play an integral role in modernizing the electrical grid in the coming decades.



Metric	Target Value
Installed Capital Cost	$40/kWh (for 10 h storage)
Lifetime	20+ years
Storage Duration	10+ hours

Target Metrics from: Albertus et al. *Joule* **2020**, 4, 21.

DOE Energy Earthshots 2030 Goals

- Long duration energy storage > 10 hrs
- Reduce energy storage cost by 90%

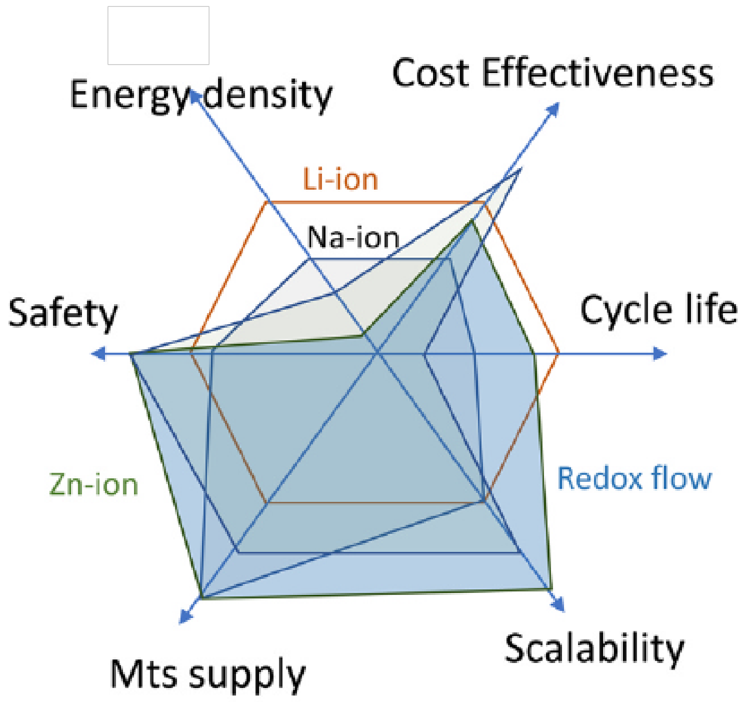


Figure from: J. Liu et al. *Next Energy* **2023**, *1*, 100015.

Redox Flow Batteries (RFBs) for LDES
Advantage: Decouple energy (tank) and power (stack).
Challenges: Cost and lifetime

Research Objective and Goals

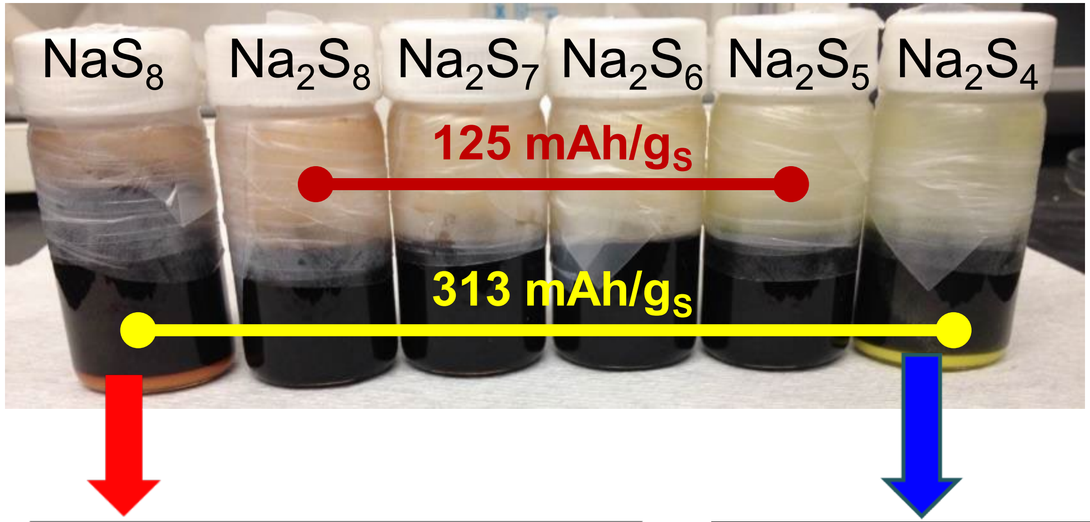
Milestone	Status
Map out the Na-P-S ternary phase space and evaluate the Na storage properties of sodium thiophosphate catholytes for high energy nonaqueous RFBs.	• Complete
Compare the reversible capacity and cycle life of RFBs containing various polymer and ceramic membranes. Correlate measured cell performance with key membrane properties (e.g., Na^+ conductivity, selectivity, and chemical stability).	• Complete
Optimize hardware design and component selection to maximize the energy/power density and cycling stability of nonaqueous lab-scale RFBs (~6 cm^2 electrode footprint). Compare the performance of and assess challenges/opportunities for Na metal hybrid RFBs vs. traditional RFB architectures.	• Complete
Evaluate the composition and thickness of passive films formed on Na metal anodes in nonaqueous electrolytes. Quantify how solvent/salt selection impacts the relative amounts of organic/inorganic decomposition products on the Na metal surface.	• On Track • To be completed by 9/30/24

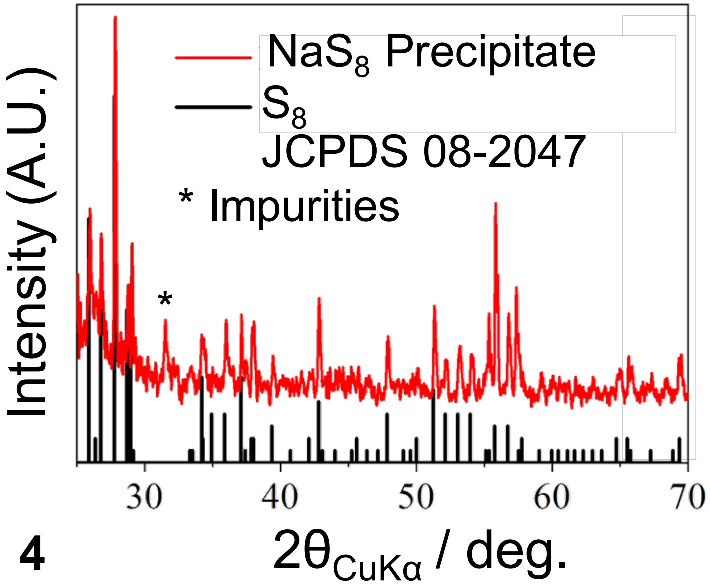
Summary of Research Activities

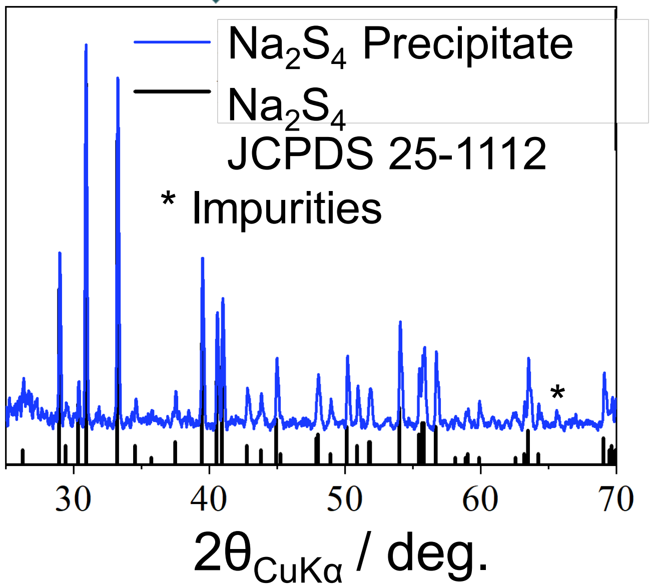
1. Design and synthesize Na-P-S catholytes using solvent-mediated route
2. Evaluate how P complexation impacts catholyte structure and electrochemical properties
3. Develop hardware for hybrid RFBs containing Na metal anodes

Background and Motivation: Na_2S_x is promising catholyte for nonaqueous RFBs but faces technical challenges for practical devices.

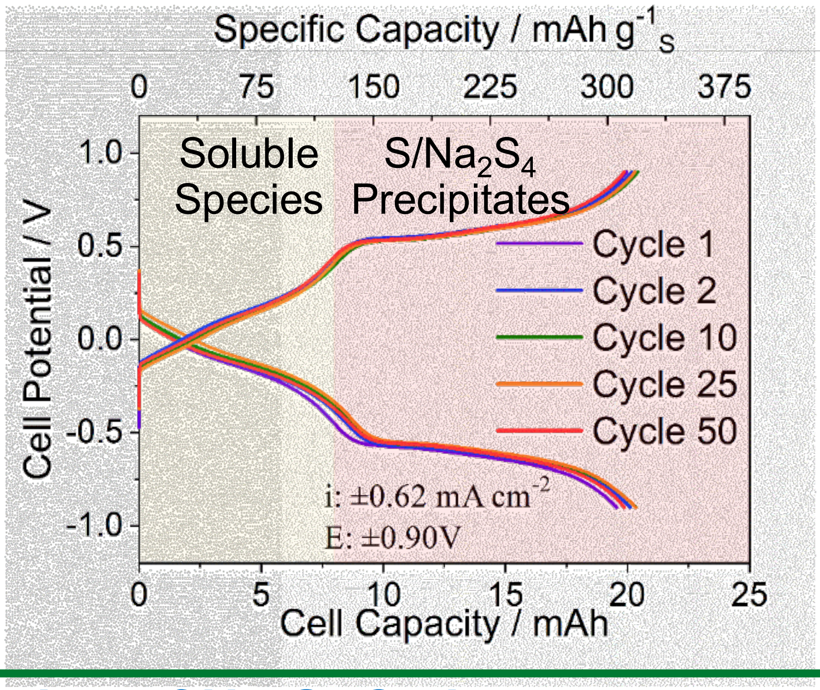
Na_2S_x in Diglyme (2EGDME)







Na_2S_x|BASE|Na_2S_x Symmetric Flow Cell



Overview of Na_2S_x Catholytes

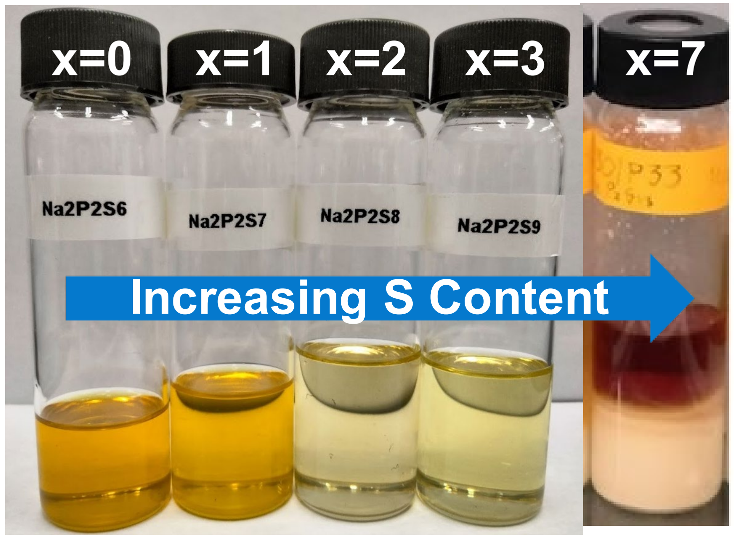
- ✓ Low cost, earth-abundant active material
- ✓ Outstanding reversibility and cycling stability (symmetric and full cells)
- ✗ Low solubility (<<0.1m) when x<5
- ✗ Low sulfur utilization (125 mAh/g) when only soluble Na_2S_x species are cycled.
- ✗ Cycling insoluble species (e.g., Na_2S_4, S) is only viable for small lab-scale prototypes.

E. C. Self et al. *J. Electrochem. Soc.* **2021**, 168, 080540.

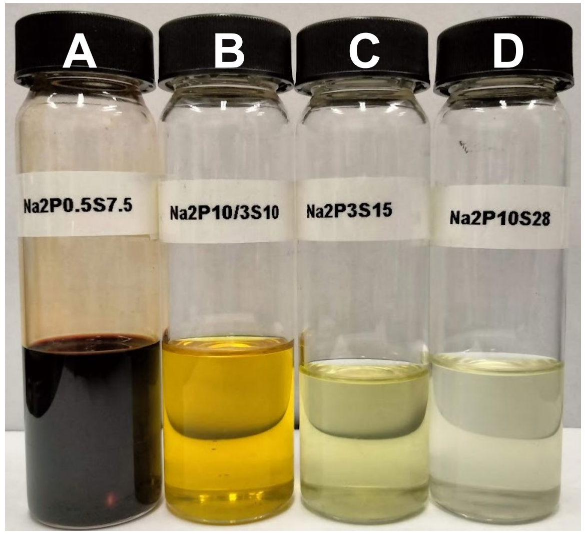
Complexing polysulfides with phosphorus yields new class of ternary Na-P-S catholytes.

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

$Na_2P_2S_{6+x}$ (FY23/24)

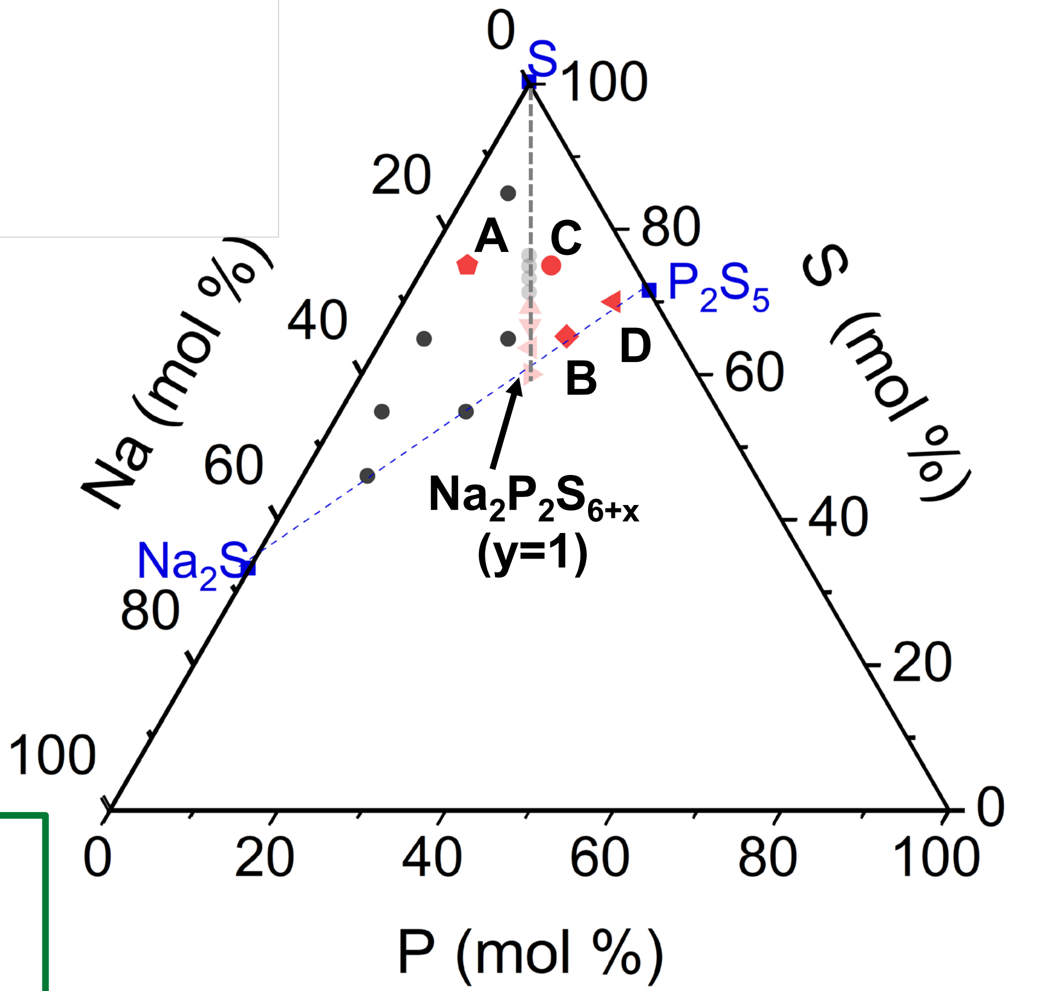


New Compositions (FY24)



Catholyte Stoichiometries

A: $Na_2P_{0.5}S_{7.5}$ C: $Na_2P_3S_{15}$
B: $Na_2P_{10/3}S_{28/3}$ D: $Na_2P_{10}S_{28}$

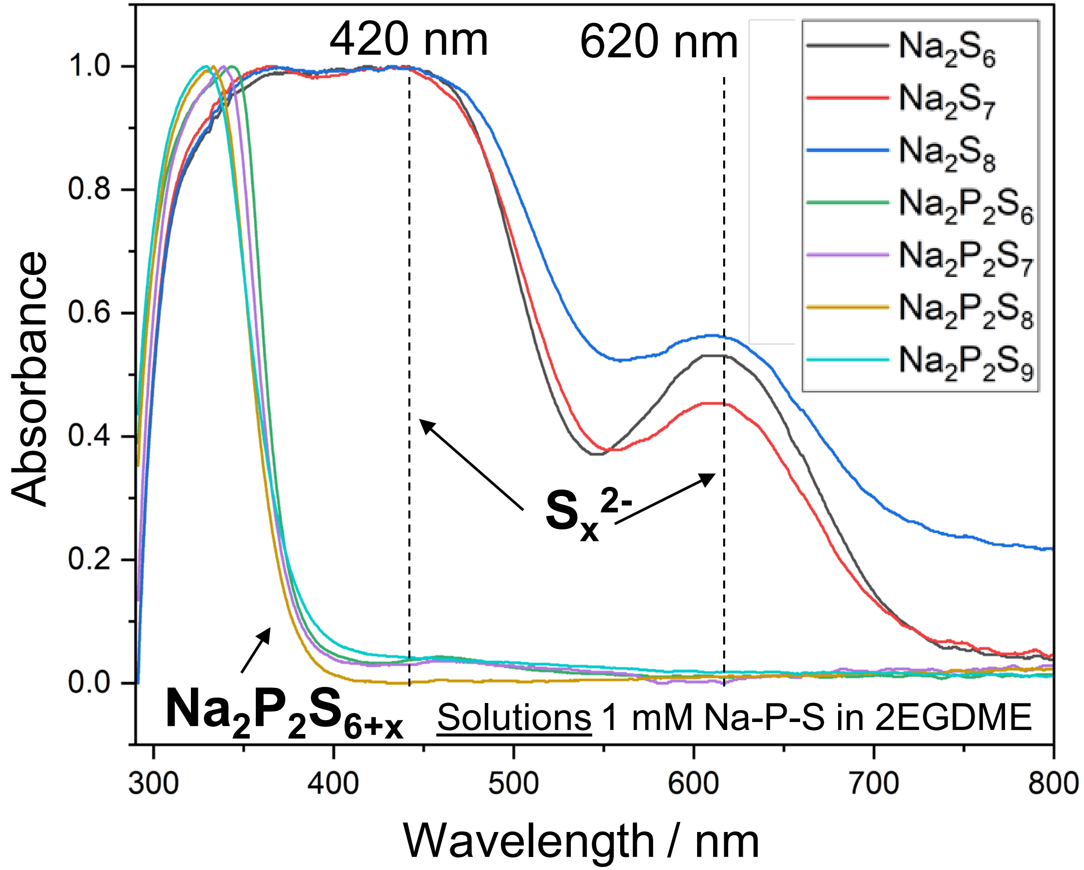


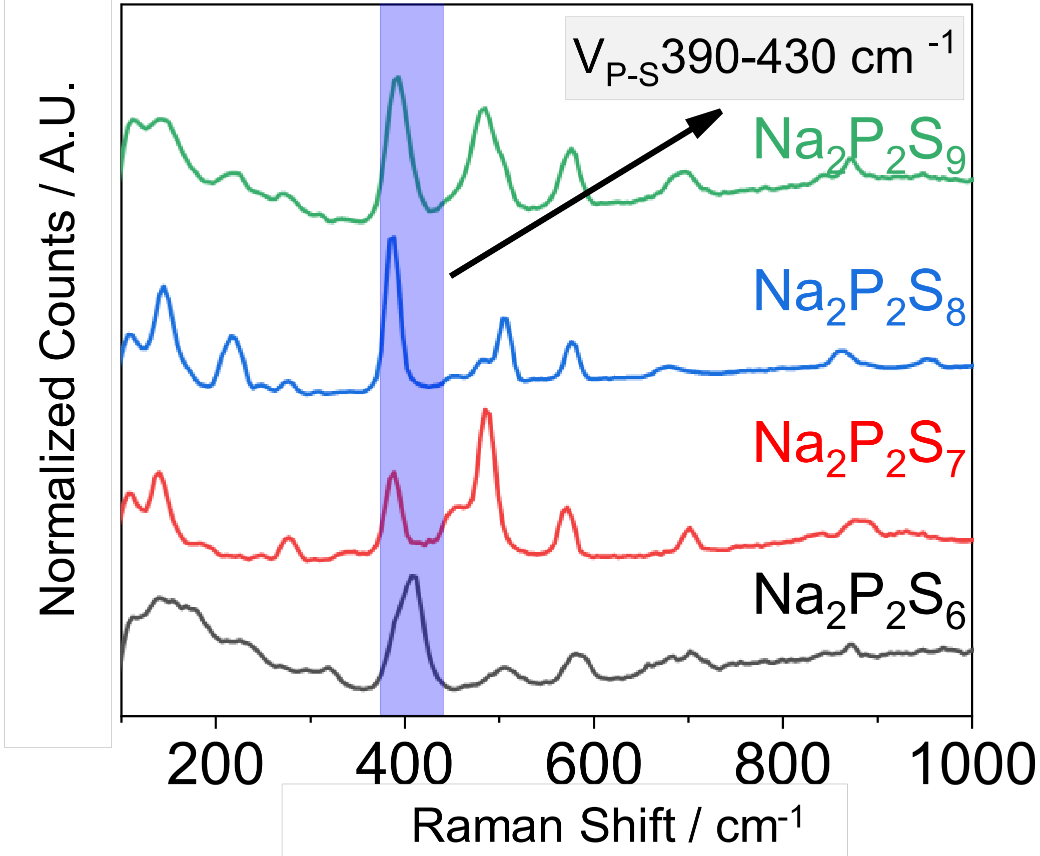
Red: Highly soluble complexes (>0.7m)
Black: Precipitate formation

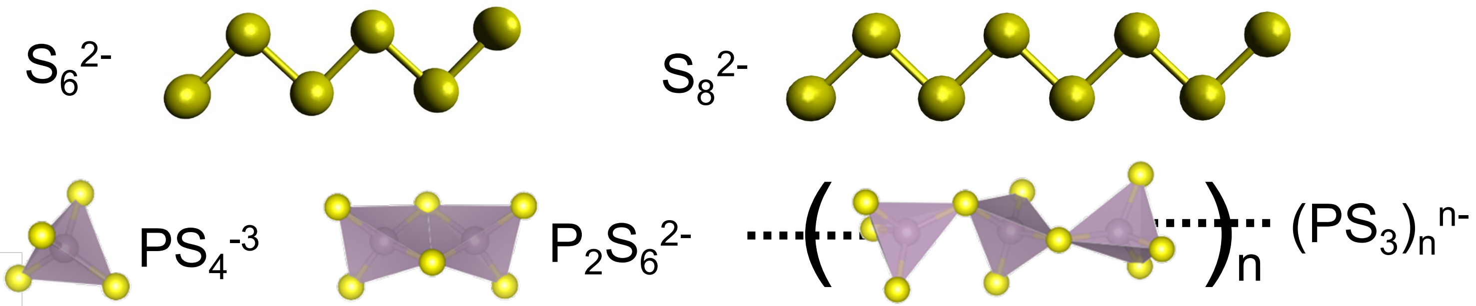
Key Findings
- Eighteen Na-P-S catholyte candidates were synthesized
- Eight compositions were downselected for further evaluation due to their high solubility in diglyme

E. C. Zuleta Suarez, M. L. Lehmann, et al (2024, Unpublished)

UV-vis and Raman spectroscopy were used to assess P complexation in Na-P-S catholytes.



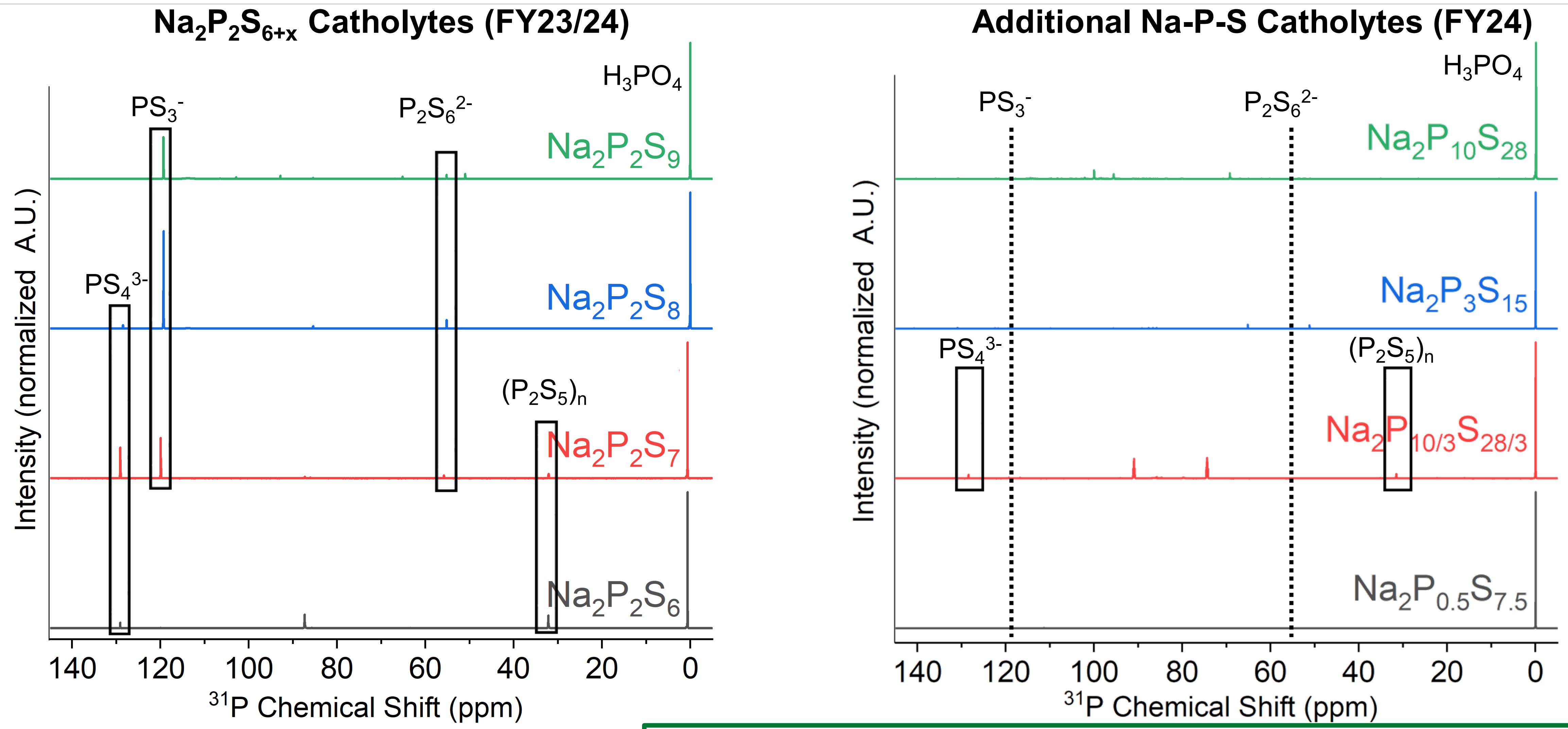




Key Finding

- Complexing with P yields Na-P-S structure which is fundamentally distinct from traditional polysulfides (Na_2S_x)

^{31}P NMR was used to identify P-S polyanions in catholyte candidates.



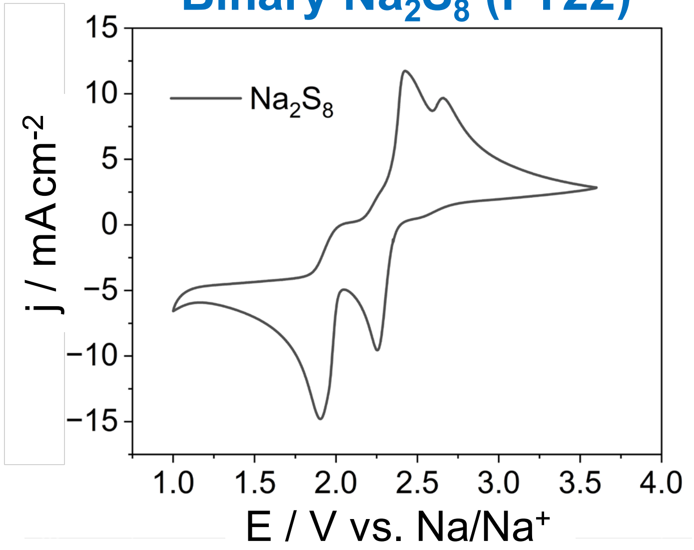
Key Findings

1. Polyanion structure varies widely across Na-P-S phase space.
2. Quantitative analysis of polyanion distribution is very difficult!

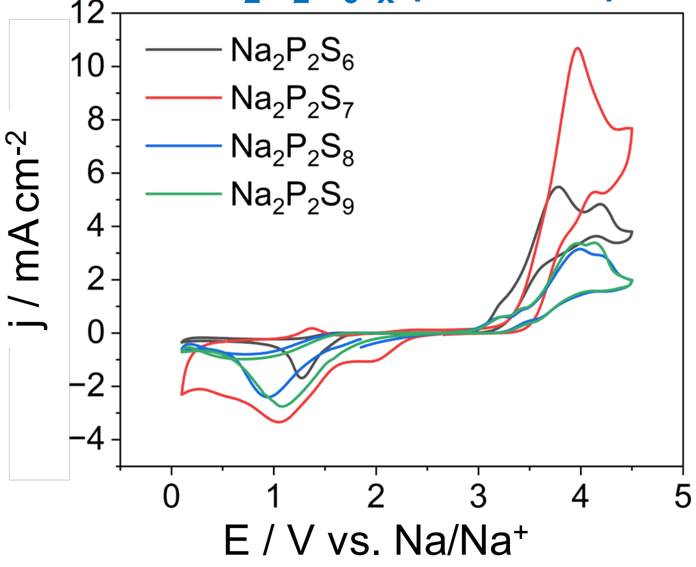
^{31}P peak assignments from *PNAS* **2021,** 118, e2116184118

Complexing with P yields highly soluble catholytes, but materials exhibit large voltage hysteresis during Na insertion/removal.

Binary Na_2S_8 (FY22)



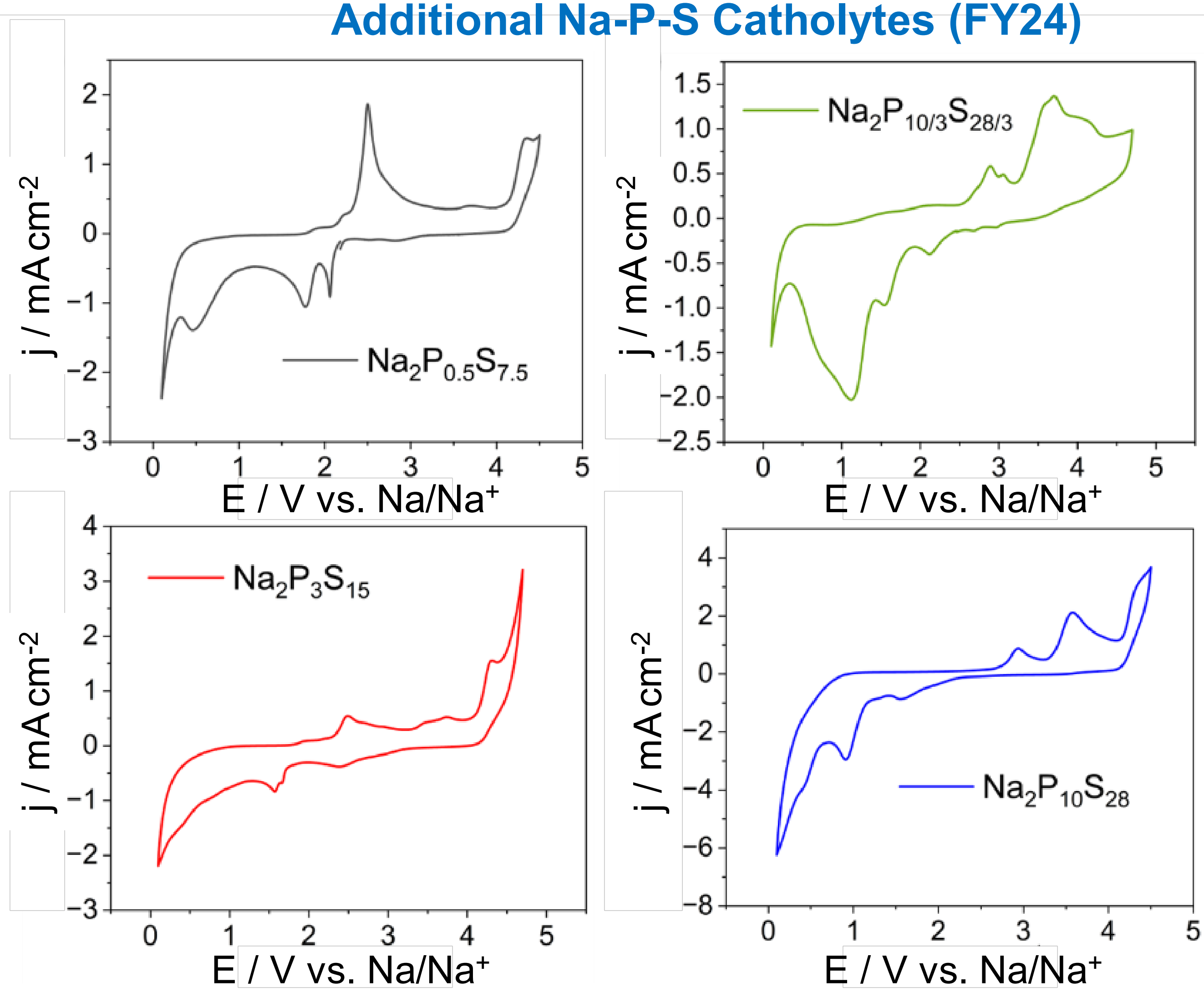
$Na_2P_2S_{6+x}$ (FY23/24)



Electrolyte: 1-2 mM catholyte in 1M $NaPF_6$/2EGDME

Scan Details: 50 mV/s, glassy carbon (3 mm)

Additional Na-P-S Catholytes (FY24)



Key Finding

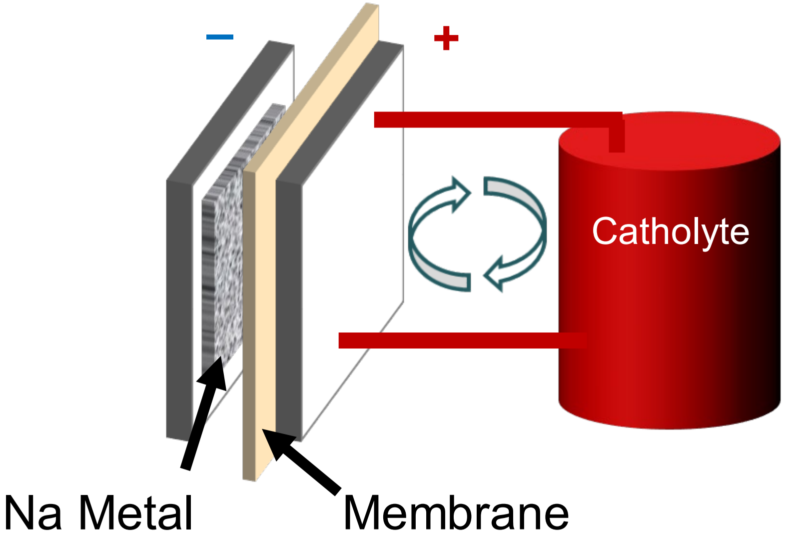
- Need to balance P content to increase solubility without hindering S^{2-}/S^0 redox

Hardware was developed for hybrid RFBs containing Na metal anodes

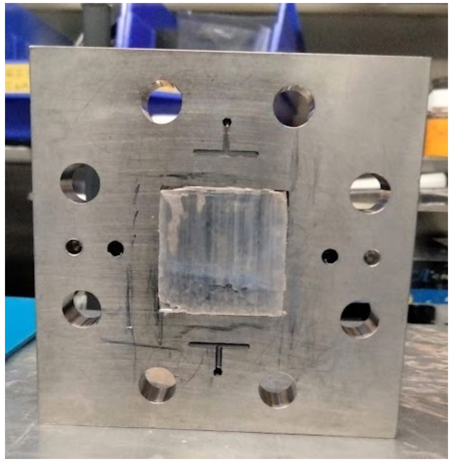
Traditional vs. Hybrid RFBs

- Most prior work has focused on cells containing biphenyl anolyte (+0.2 V vs. Na/Na^{+})
- Na metal anode will increase cell voltage by ~0.2 V but comes with additional interfacial challenges

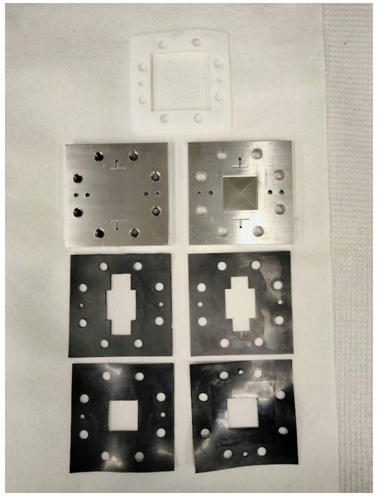
Na Metal Hybrid Flow Batteries



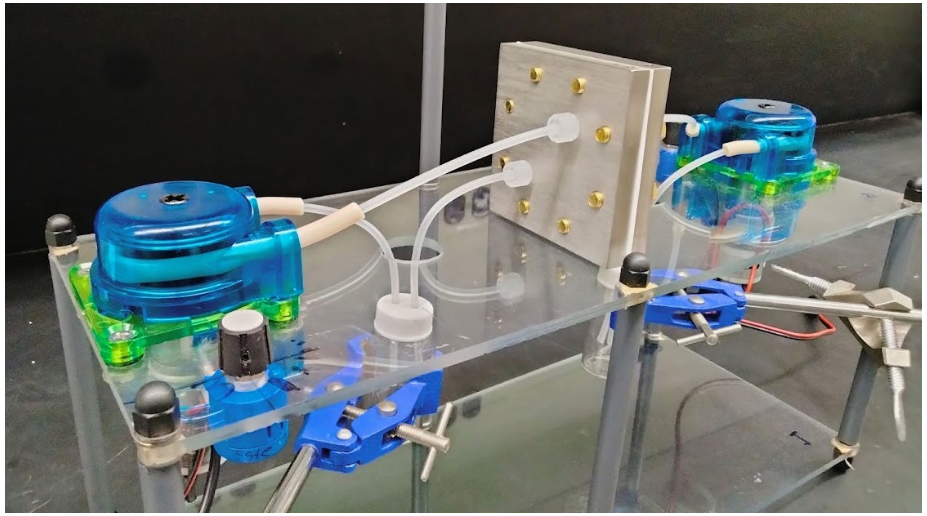
Anode Plate



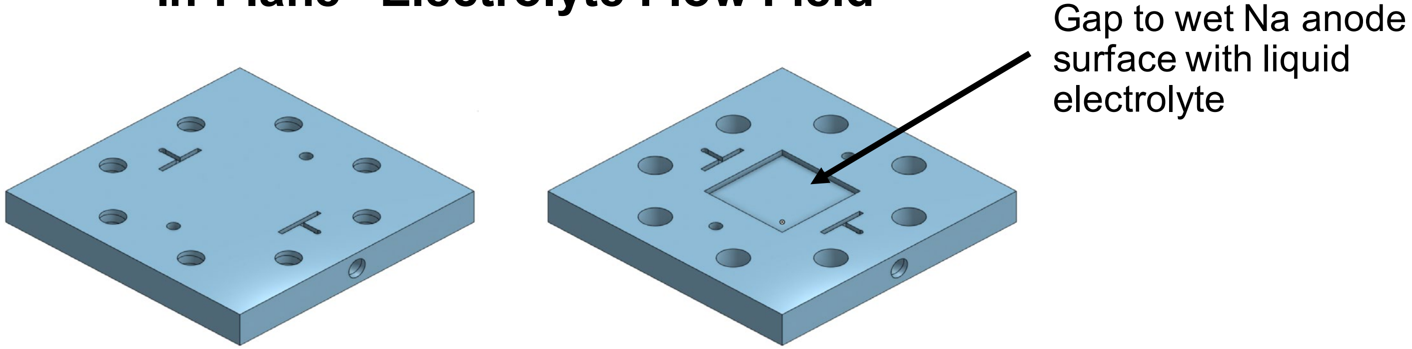
Gasket Design



Small-Footprint Testbed (increase throughput)



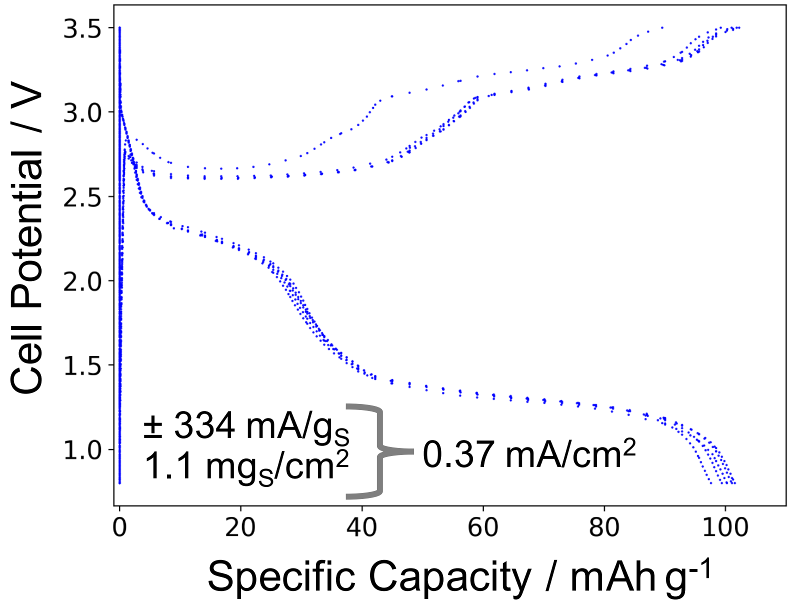
"In-Plane" Electrolyte Flow Field



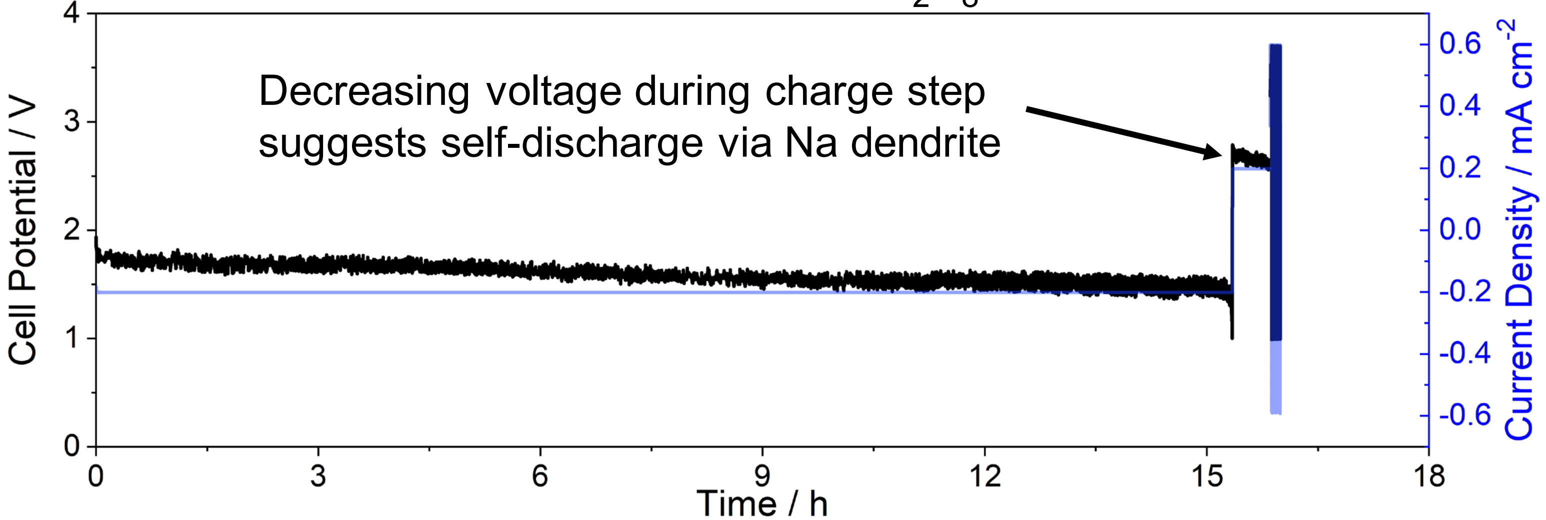
Collaboration with G. A. Goenaga-Jiménez (UT-Knoxville)

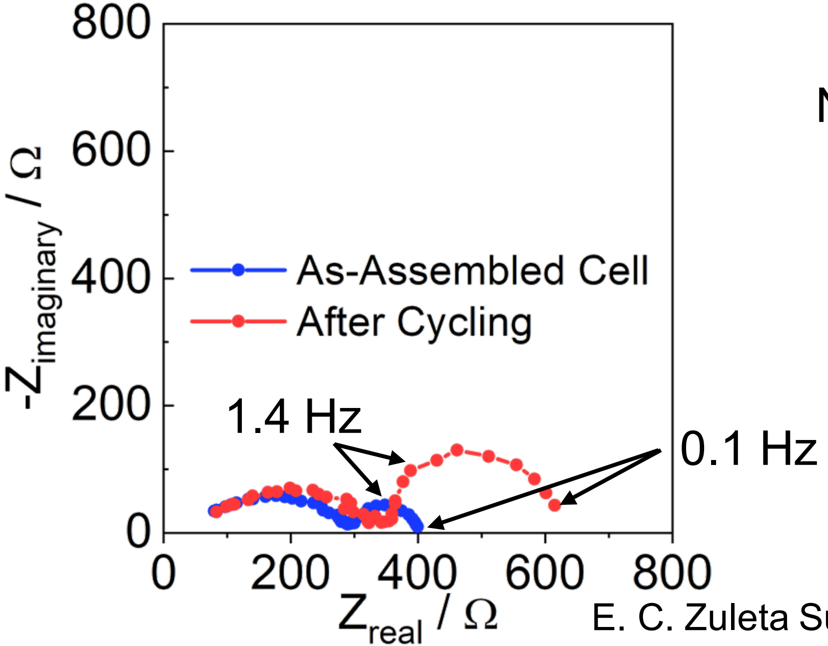
Low current density remains a bottleneck for hybrid RFBs

Coin Cell (R2032)
Na/Na^+ Nafion212/$Na_2P_2S_7$



Hybrid RFB (Preliminary Data with FY24 Hardware)
Na/BASE/Na_2S_8





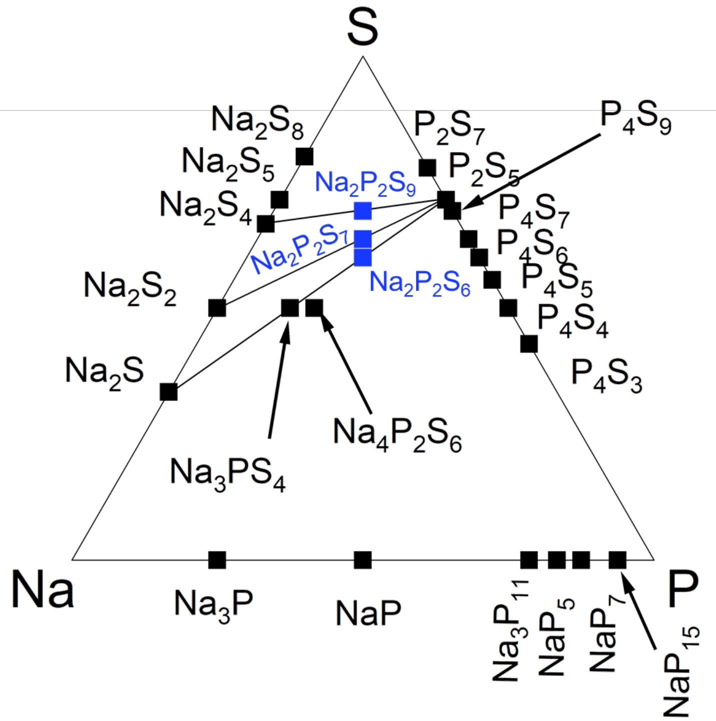
Na Surface after Cycling

- Na-P-S catholytes exhibit good cycling stability.
- Coin cells enable rapid material screening, but results don't always translate to RFB architecture

M. L. Lehmann et al. (2024, Unpublished)

E. C. Zuleta Suarez et al. (2024, Unpublished)

Summary and Ongoing/Future Work



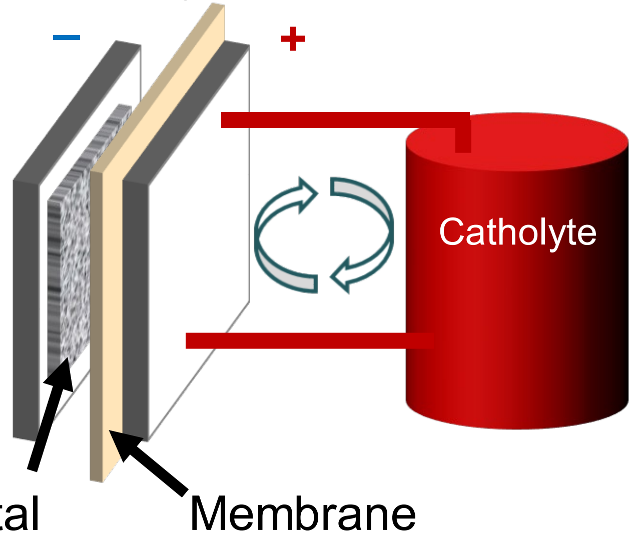
Na/S-based catholytes for redox flow batteries

- Na_2S_x has outstanding cycling stability but limited practical capacity
- Complexing with P greatly increases solubility of low order polysulfides
- New class of Na-P-S catholytes candidates developed and tested

Hybrid RFBs containing Na metal anodes and solid-state electrolyte

- Opportunities: Low-cost active materials, high cell voltage
- Challenges: Na dendrites and low current density at room temperature

Na Metal Hybrid Flow Batteries



Ongoing/Future Work

- New electrolyte formulations to suppress Na dendrites
- Halide substitution to increase catholyte operating voltage
- Integrate membranes with higher conductivity (power density) and selectivity (cycle life)

FY24 Manuscripts

[1] E. C. Self, F. M. Delnick, R. L. Sacci, J. Nanda "Assessing Nonlinear Polarization in Electrochemical Cells using AC Impedance Spectroscopy" *J. Electrochem. Soc.* **2024**, 171, 030513

[2] E. C. Zuleta Suarez, M. L. Lehmann, G. Yang, E. C. Self "Sodium Thiophosphate Catholytes for Nonaqueous Redox Flow Batteries" (Anticipated Submission Date: Dec. 1, 2024)

FY24 Presentations

[1] E. C. Self "Materials for Next-Generation Batteries: Li^+ Solid-State Conductors and Na-Based Catholytes" University of Houston, November 29, 2023 (Houston, TX) (Invited)

[2] E. C. Zuleta Suarez, M. Lehmann, G. Yang, E. Self "Sodium polysulfides as catholytes for redox flow batteries" 245th Meeting of the Electrochemical Society, Oral Presentation, May 26-30, 2024 (San Francisco, CA)

[3] E. C. Self, F. M. Delnick, R. L. Sacci, J. Nanda "Assessing Nonlinear Polarization in Electrochemical Cells using AC Impedance Spectroscopy" 245th Meeting of the Electrochemical Society, Oral Presentation, May 26-30, 2024 (San Francisco, CA)

[4] E. C. Self "Low-Cost, Earth-Abundant Catholytes for Redox Flow Batteries" Beyond Lithium XIV Meeting, July 23-25, 2024 (Knoxville, TN) (Invited)

Acknowledgments

This material is based upon work supported by the U.S. Department of Energy, Office of Electricity (OE), Energy Storage Division.

ORNL Core Research Team
Michelle Lehmann (Poster)
Wenda Wu (Poster)
Guang Yang (Presentation 301)
Ernesto Camilo Zuleta Suarez (Poster)

Additional Thanks
Mali Balasubramanian
Josh Damron
Frank M. Delnick
Gabriel A. Goenaga-Jiménez
Yuanshun Li
Jagjit Nanda
Tomonori Saito
Michael Starke
Jameson (Landon) Tyler
Thomas A. Zawodzinski

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Questions?

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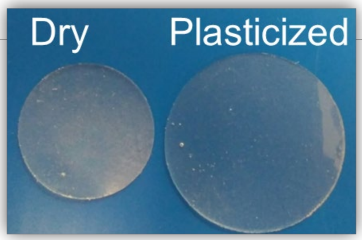
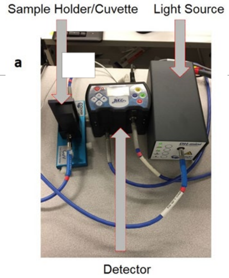
Backup Slides

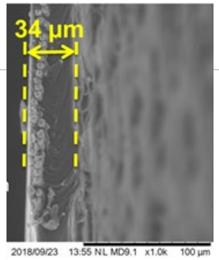
ORNL has developed advanced electrolyte and membranes for nonaqueous RFBs



Crosslinked PEO Membranes



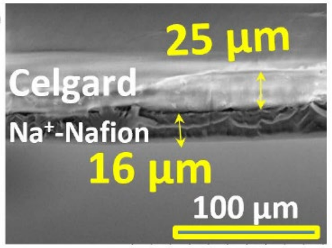
In-Situ UV-Vis Crossover Setup



Glass Fiber/PEO Composites

Nexar Membrane Single-Ion Conductor

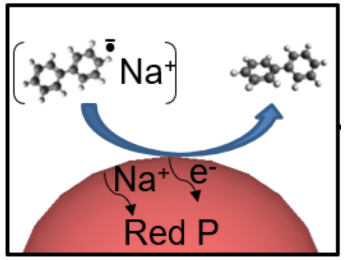
Bettergy Corp. Benchmarking



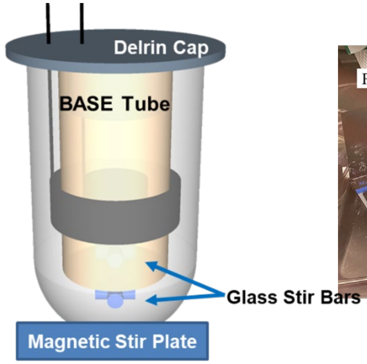
PFSA Composites

2018 **2019** **2020** **2021** **2022** **2023/4**

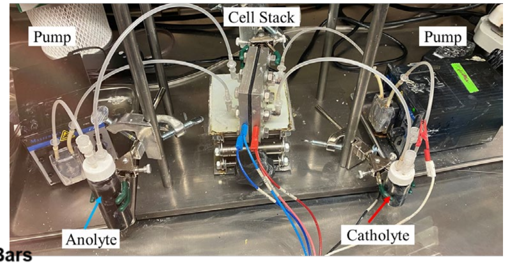
Mediated Red Phosphorus Anode



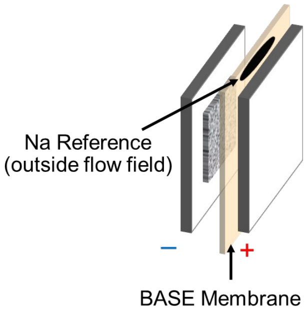
Biphenyl/Na_2S_x Cylindrical Cell



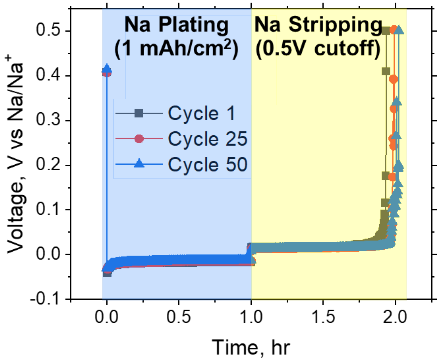
Nonaqueous Flow Cell Testbed



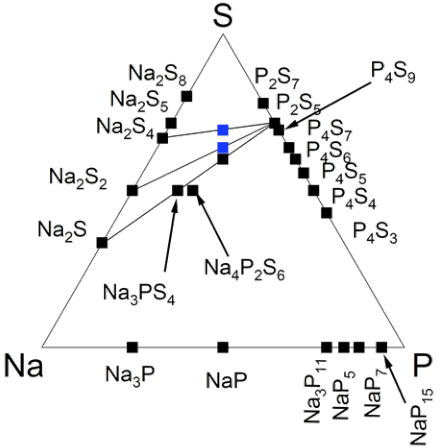
3 Electrode AC Impedance Methods



Reversible Na Metal Anodes

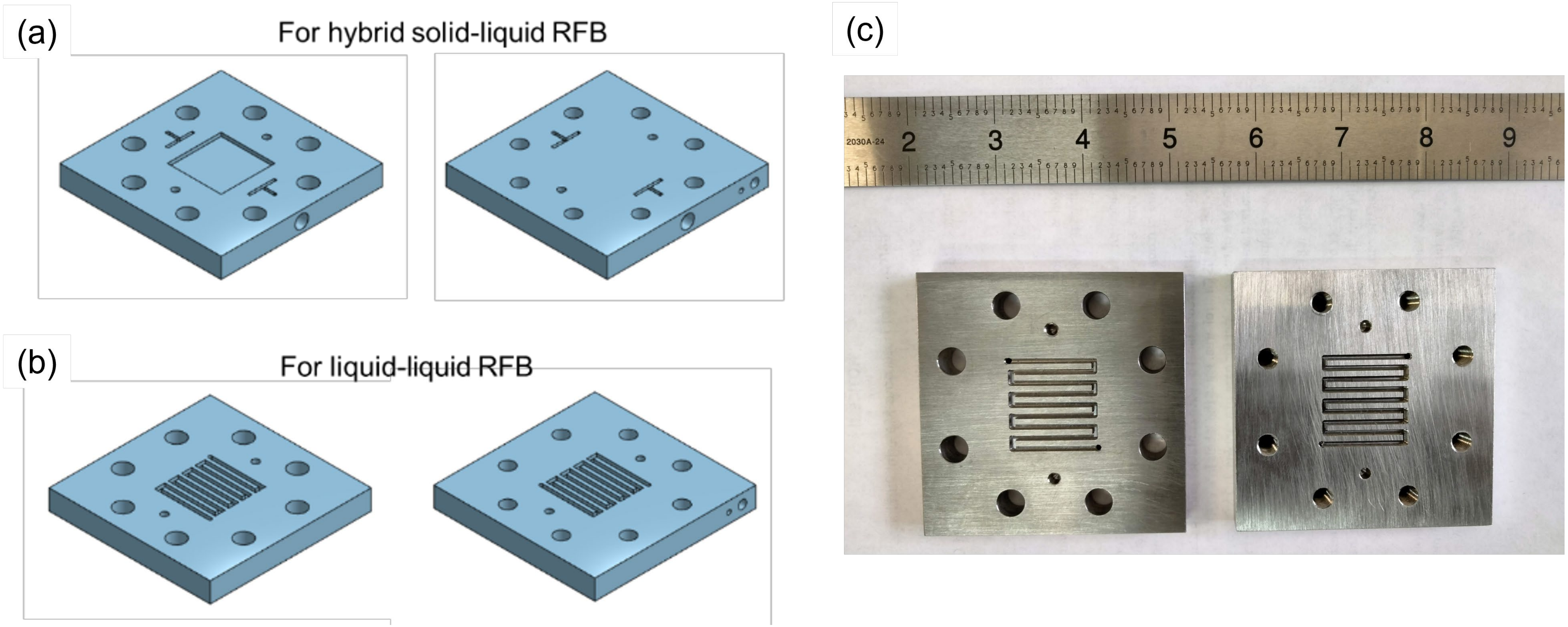


Thiophosphate Catholytes



 *references to these works are available upon request

Additional schematics and photographs of RFB cell hardware.



 Collaboration with G. A. Goenaga-Jiménez (UT-Knoxville)