Ambient Temperature Polysulfide-Based Redox Flow Batteries and Membrane Development

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Presentation #602
DOE OE Energy Storage Peer Review
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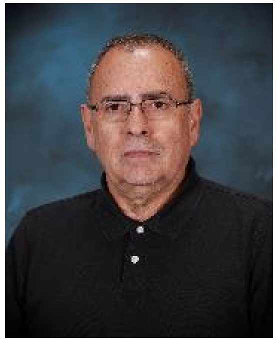

Frank Delnick
(Retired 6/22)


Landon Tyler
(Graduated 6/22)

Core Expertise and Focus Areas

- High energy flow battery chemistries based on earth-abundant active materials
- Ion-selective polymer electrolytes with high ionic conductivity for Na-based batteries
- Advanced characterization and device integration

Acknowledgment

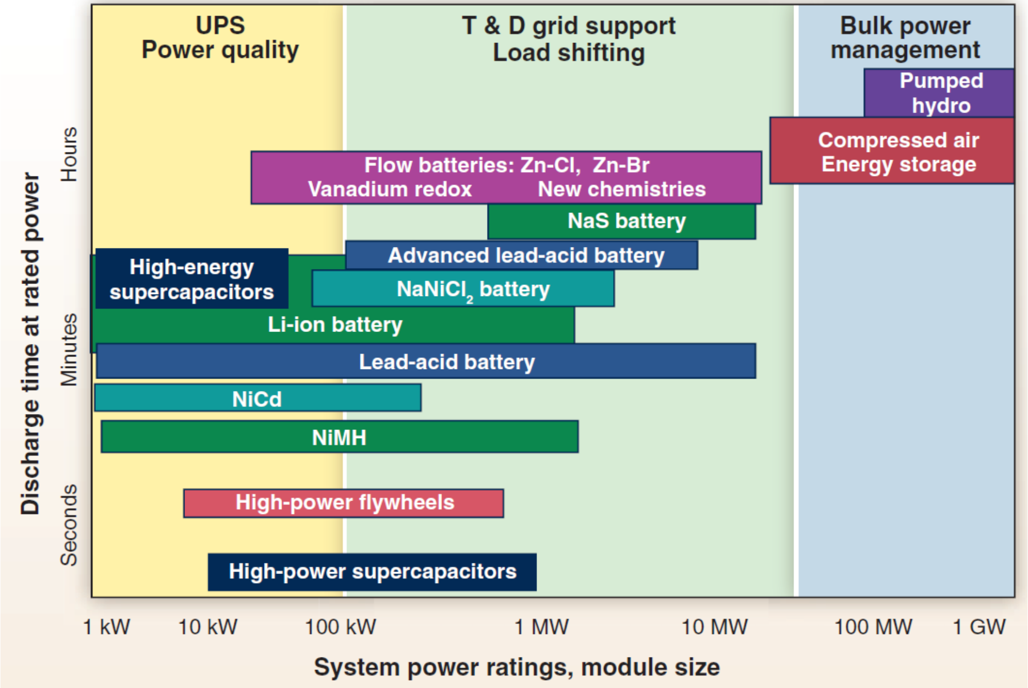
This work is supported by Dr. Imre Gyuk, Manager, Energy Storage Program, Office of Electricity, Department of Energy.

Thanks to Michael Starke, program manager, ORNL.

Long-duration energy storage (LDES) systems will play an integral role in achieving clean electricity from renewables to meet decarbonization goals.

DOE Energy Earthshots 2030 Goals

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



Dunn et al. *Science* **2011**, 334, 928.

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

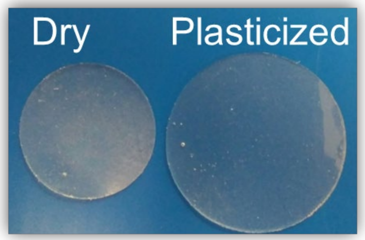
Albertus et al. *Joule* **2020**, 4, 21.

ORNL R&D focuses on next-generation redox flow batteries (RFBs) based on **earth-abundant active materials** and **advanced polymer electrolytes**.

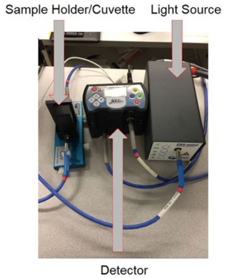
FY22 Technical Achievements

- Developed liquid electrolyte to stabilize Na metal anode
- Identified novel additives to increase solubility of low-order Na polysulfides
- Fabricated mechanically robust single-ion conducting membranes for $Na\text{-}Na_2S_x$ RFBs

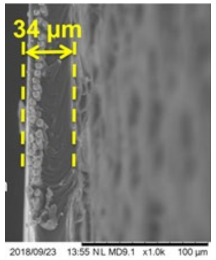
Timeline of ORNL Research on Nonaqueous Redox Flow Batteries



Crosslinked PEO Membranes



In-Situ UV-Vis Crossover Setup



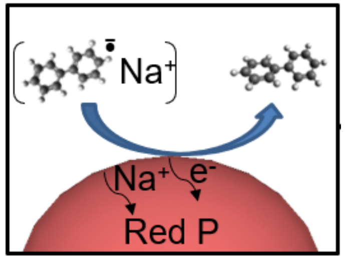
Glass Fiber/PEO Composites

Single-Ion Conductor Membranes

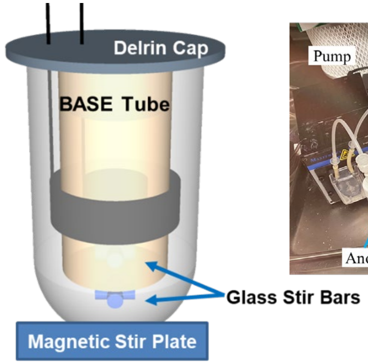
Bilayer Membrane Benchmarking

2018 **2019** **2020** **2021** **2022**

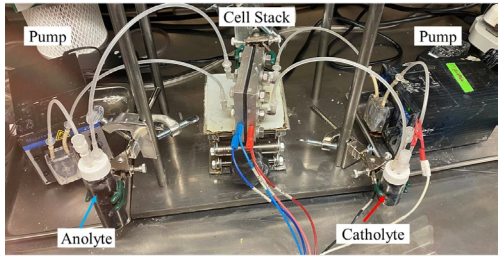
Mediated Red Phosphorus Anode



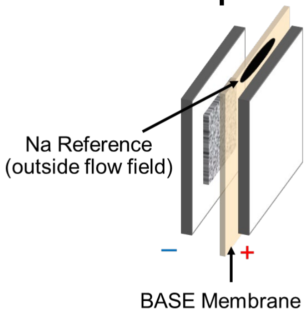
Biphenyl/Na_2S_x Cylindrical Cell



Nonaqueous Flow Cell Testbed

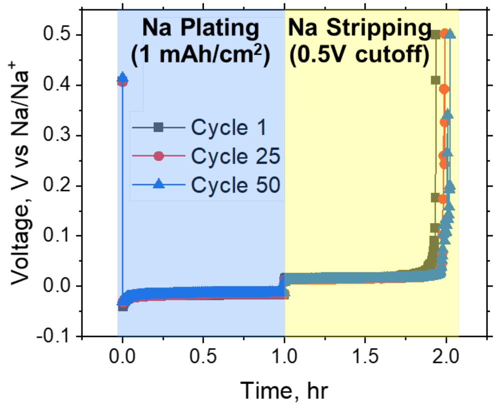


3 Electrode AC Impedance Method Development



$$E(i)-E^{eq}= \int_0^i Z(i')di'$$

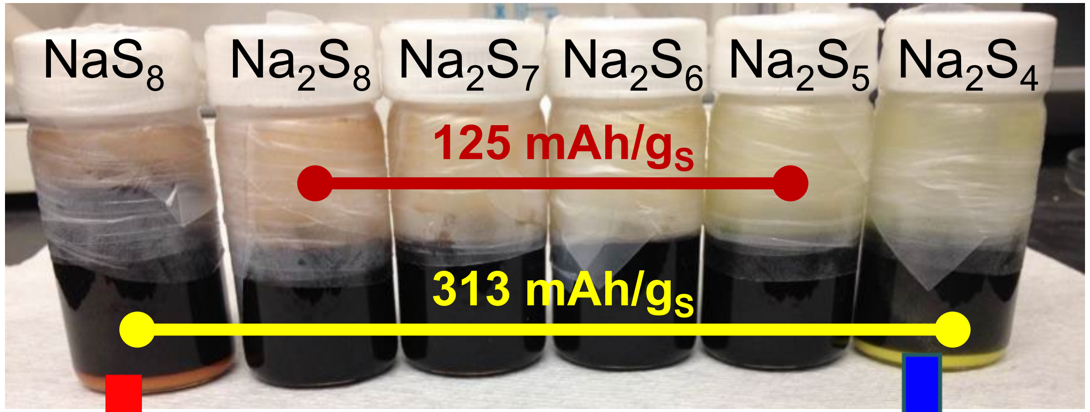
Reversible Na Metal Anodes

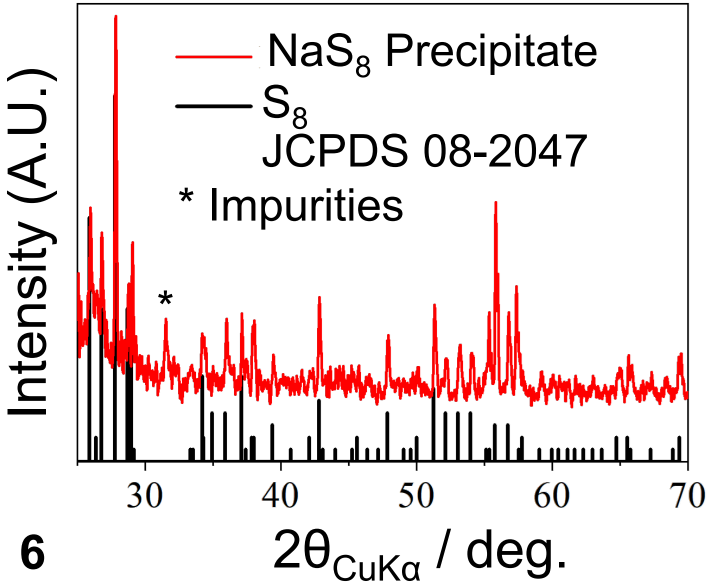


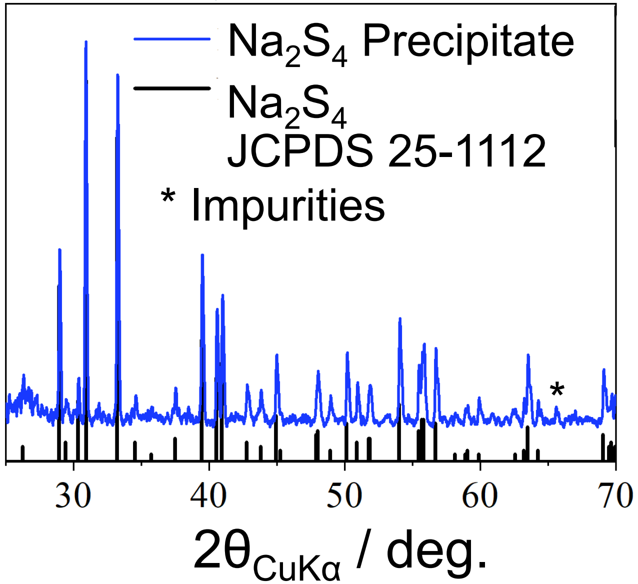
*references to these works are available upon request

Na_2S_x is promising catholyte for nonaqueous flow batteries due to low cost and outstanding cycling stability

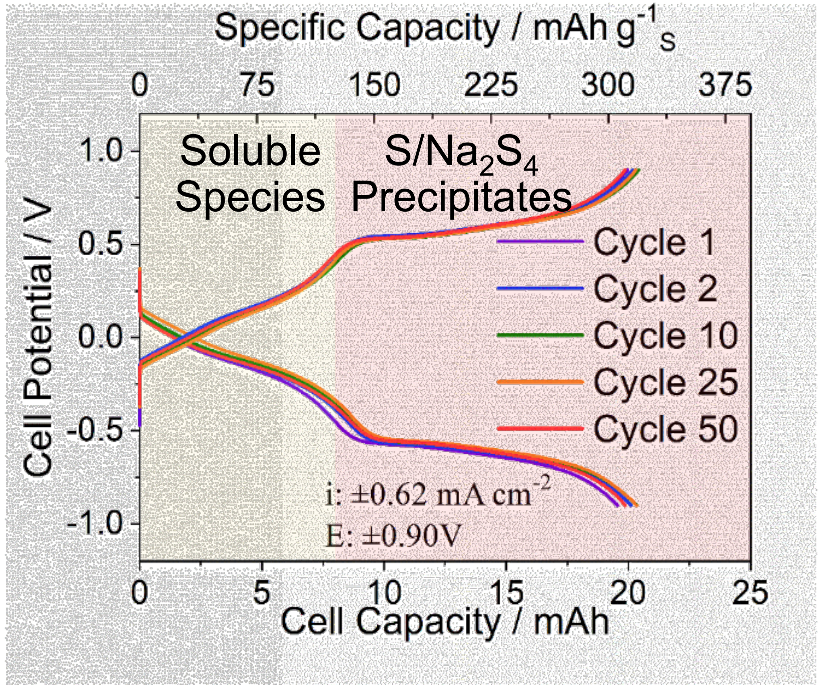
Na_2S_x in Diglyme (2EGDME)







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
- ✗ 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.

Adding P_2S_5 to low-order Na_2S_x yields high-capacity, highly soluble Na-P-S catholyte. FY23 will explore electrochemical properties of these new catholytes

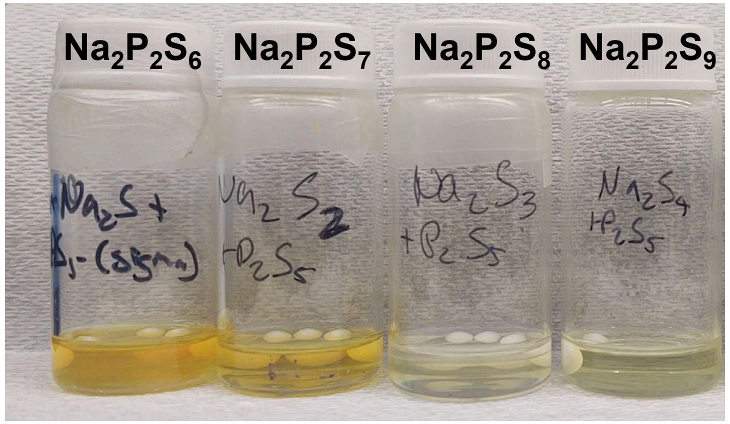
$$Na_2S_x + P_2S_5 \xrightarrow{\text{2EGDME}} \boxed{Na_2P_2S_{5+x}}$$

Na_2S_x: Insoluble when x<5

P_2S_5: Insoluble

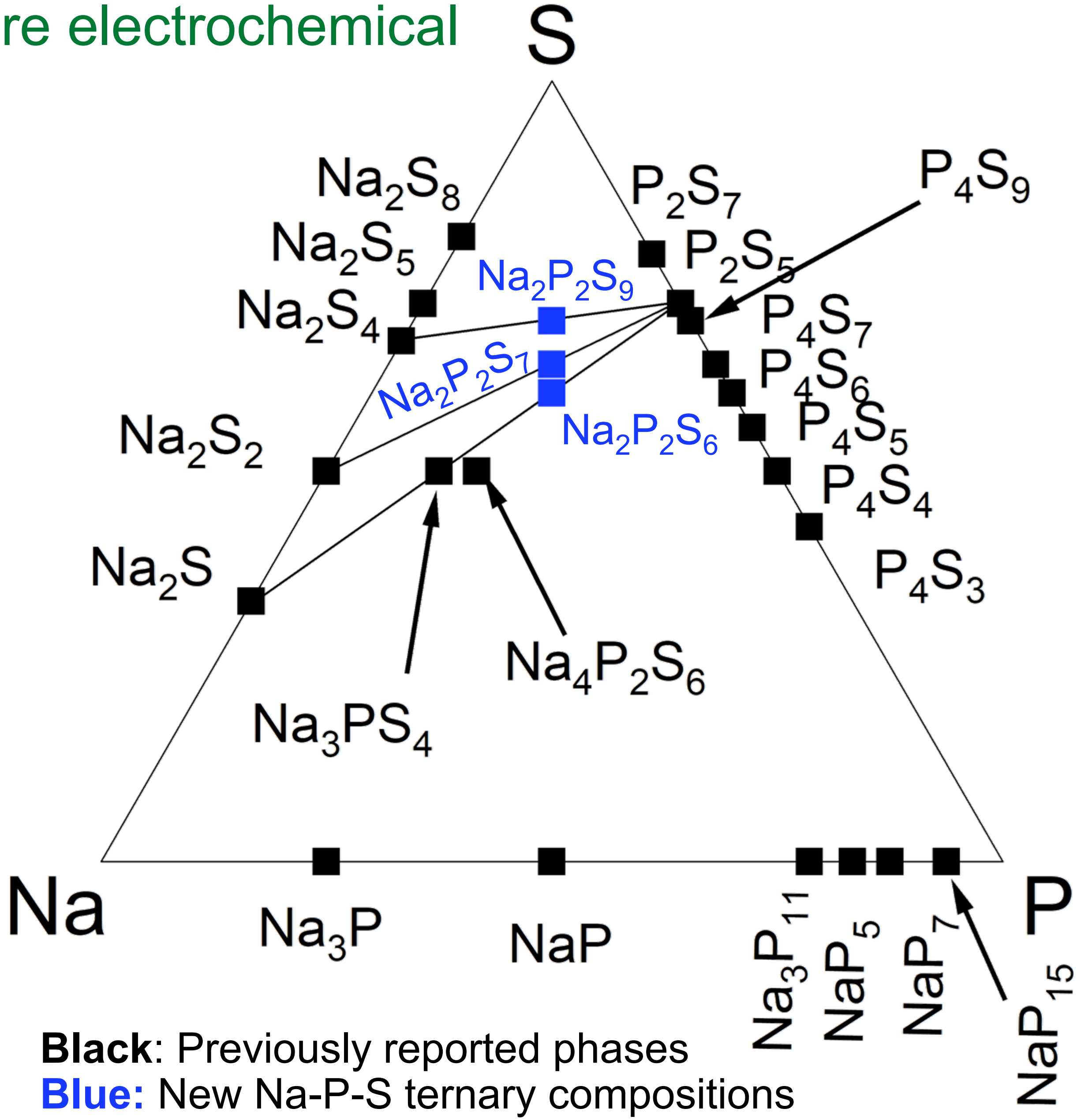
$Na_2P_2S_{5+x}$: High-capacity solvated complex

0.5m $Na_2P_2S_x$ in 2EGDME



Composition	Theoretical Capacity* (mAh/g_{AM})
$Na_2P_2S_6$	1,070
$Na_2P_2S_7$	1,130
$Na_2P_2S_8$	1,177
$Na_2P_2S_9$	1,220

* Assumes 2 electrons transferred per sulfur



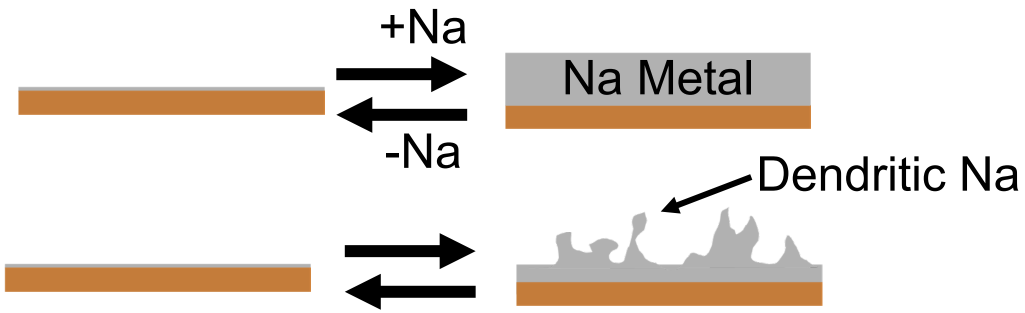
Black: Previously reported phases
Blue: New Na-P-S ternary compositions

ORNL Invention Disclosure 81939560 (Submitted Sept. 13, 2022)

$NaPF_6$-based glyme electrolytes enable highly reversible Na metal anodes which opens vast opportunities for Na metal hybrid flow batteries

Desired Na Anode Operation

Conventional Electrolytes

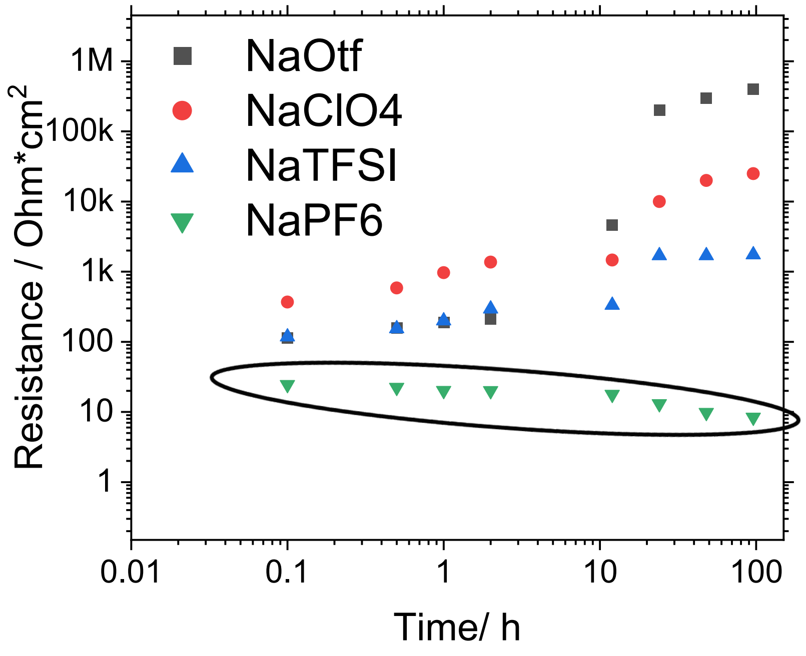


✗ Poor safety (internal shorting)
✗ Low reversibility (isolated Na)

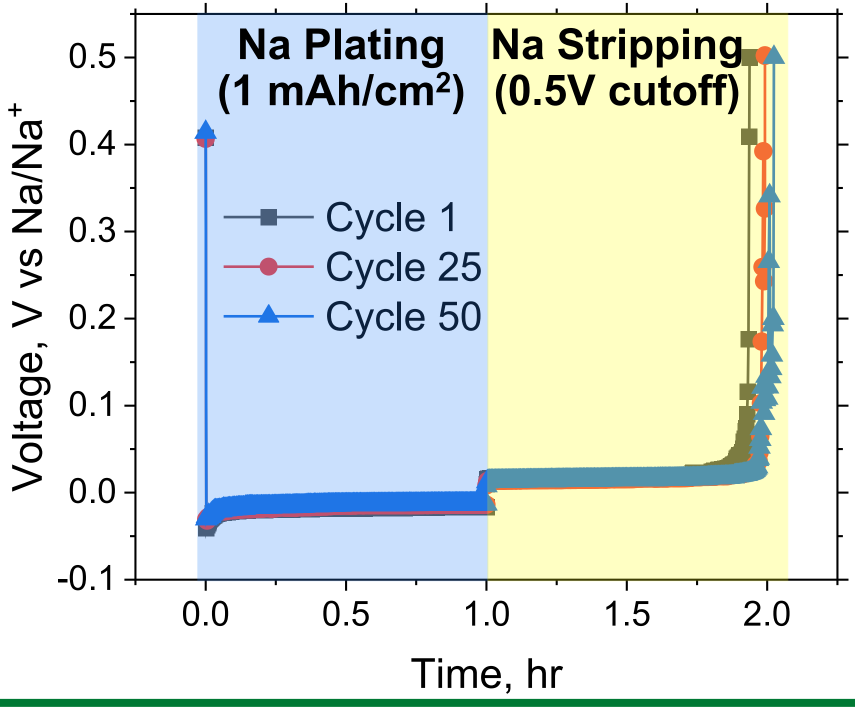
Electrolyte Formulations Investigated

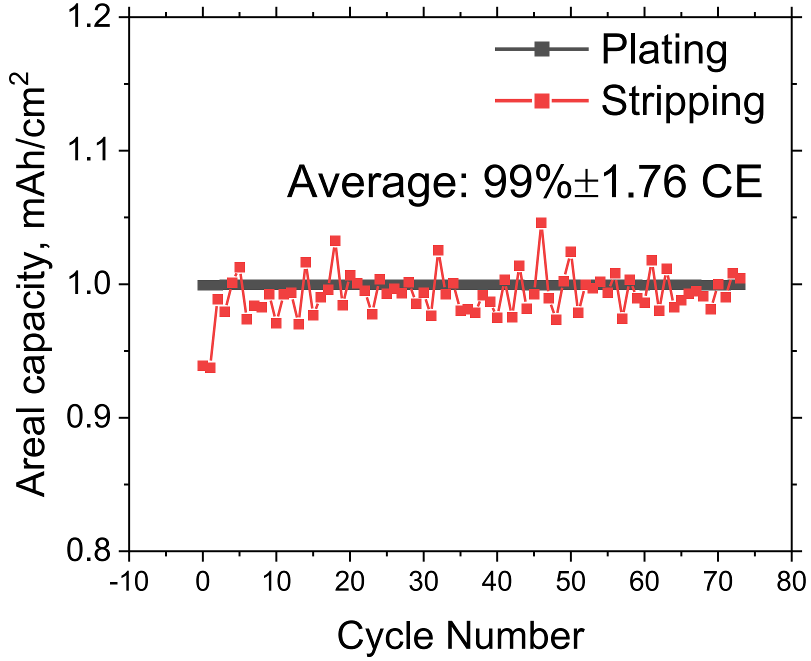
Solvents	Salts
Monoglyme	NaOTF
Diglyme	$NaClO_4$
Tetraglyme	NaTFSI
	$NaPF_6$

Na|Na Symmetric Cell



Na|Cu Asymmetric Cell

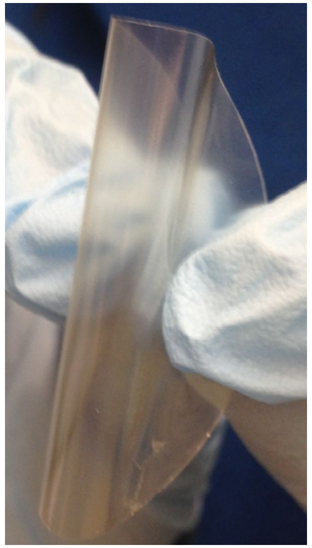




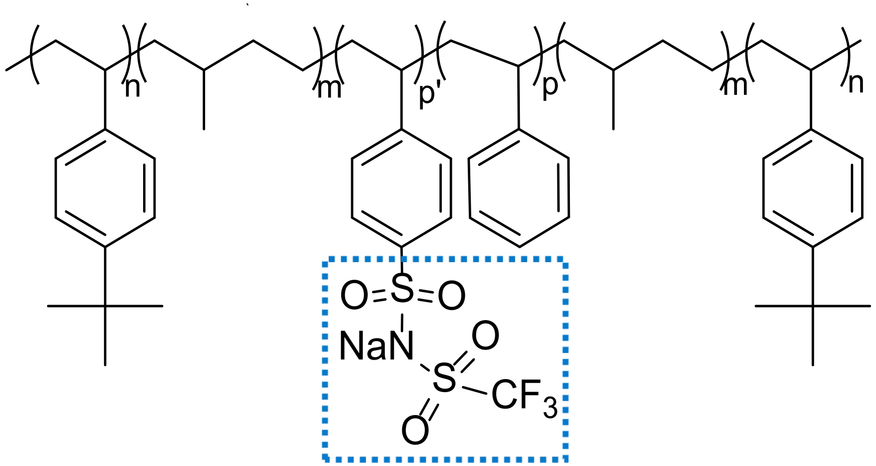
Stable Na passivation and plating/stripping behavior in $NaPF_6$/2EGDME electrolyte.

J. L. Tyler et al. **2022** (Unpublished)

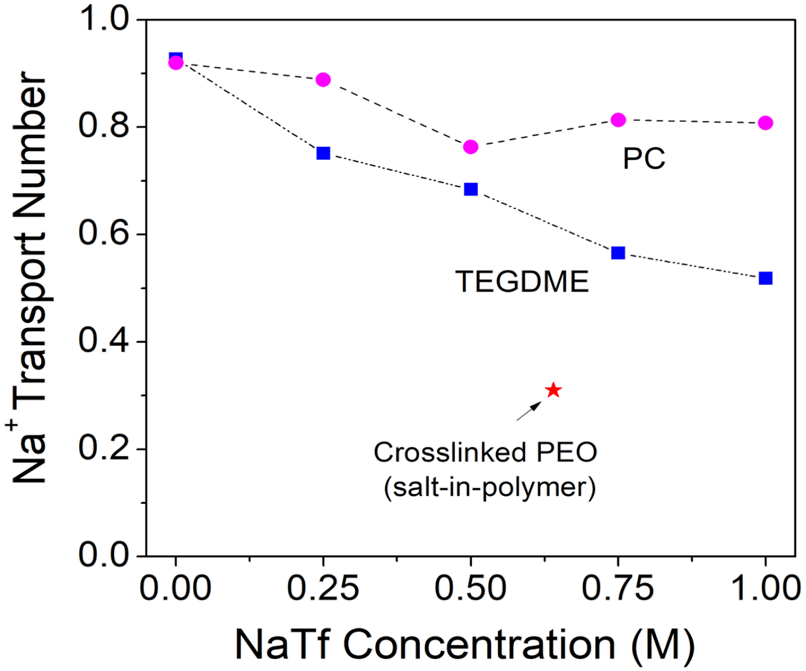
Next-Generation Membranes: ORNL's single-ion conducting polymers have outstanding properties compared to conventional polymers (e.g., PEO)

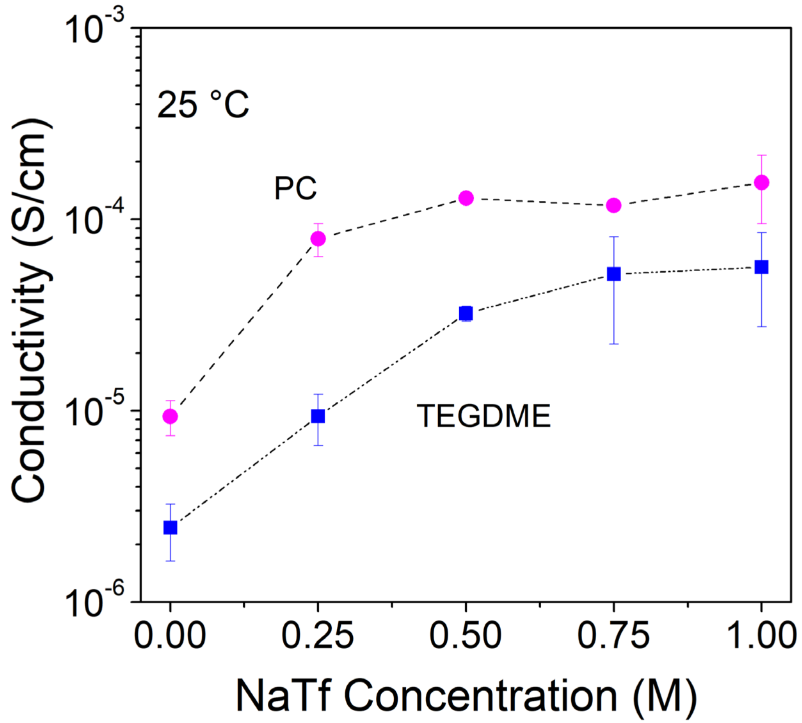


20-30 μm
>1 GPa modulus



Ion-selective sidechain



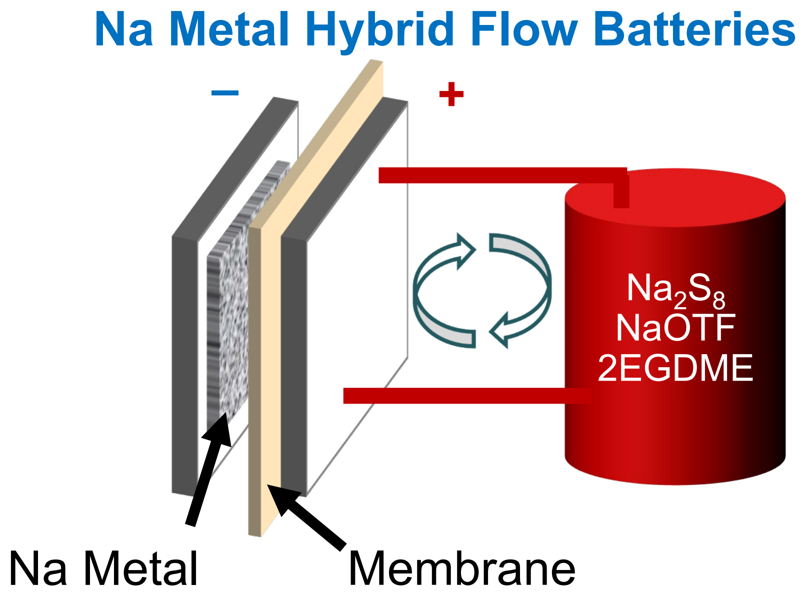


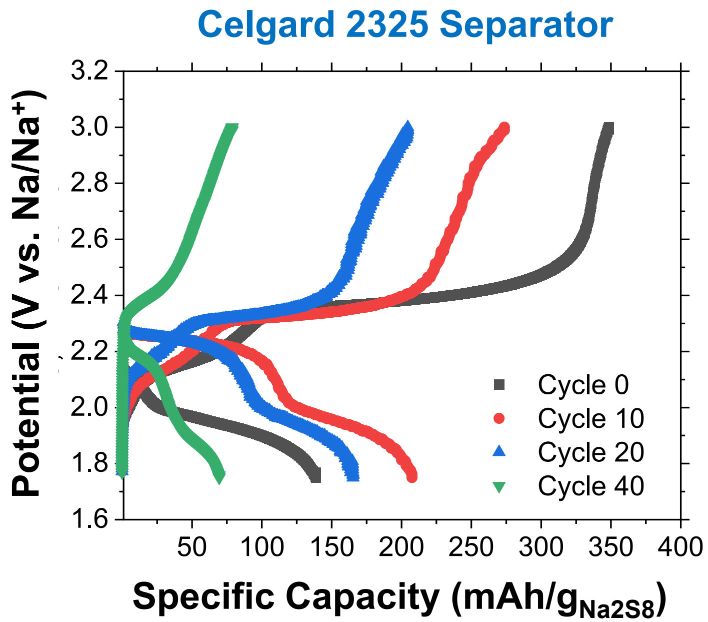
Advantages of ORNL's single-ion conducting membranes

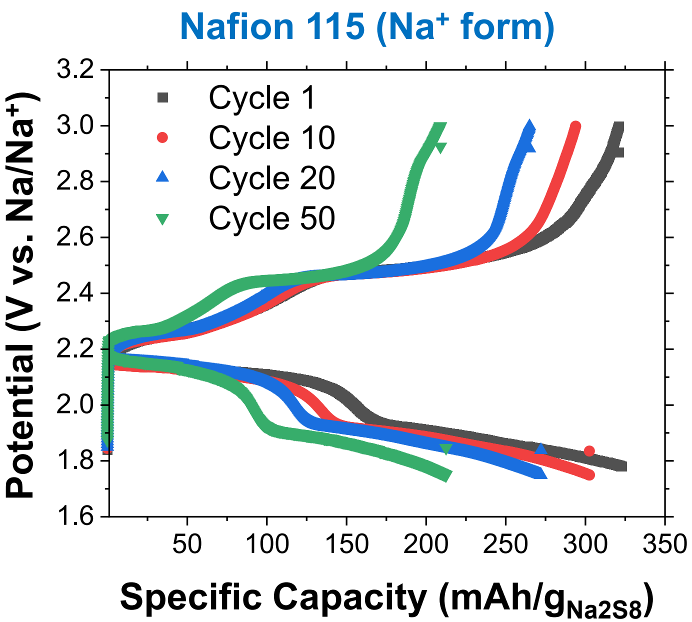
- ✓ Low cost (prepared from commercial polymer precursor)
- ✓ High Na^+ selectivity in concentrated electrolytes
- ✓ High Na^+ conductivity (~0.1 mS/cm at RT)
- ✓ Compatible with wide range of supporting electrolytes

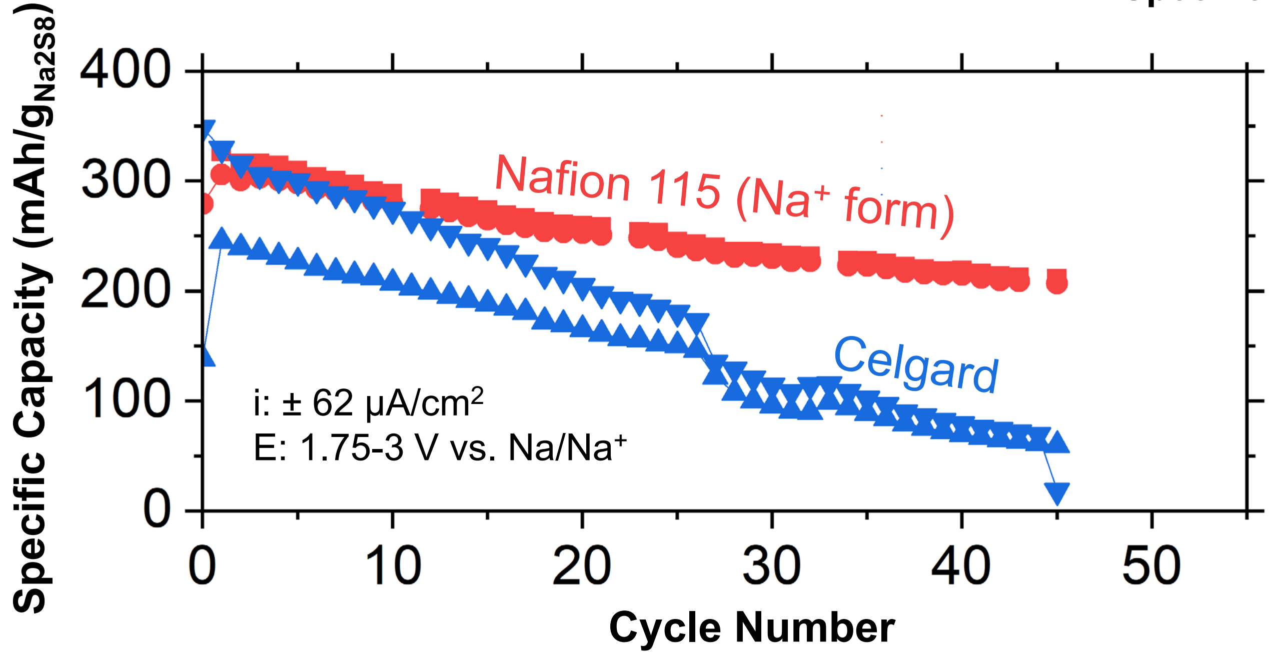
M. L. Lehmann et al. *Macromolecules* **2022**, *55*, 7740.

The performance of hybrid flow batteries containing Na metal anode and Na_2S_8 catholyte were benchmarked using commercial membranes.









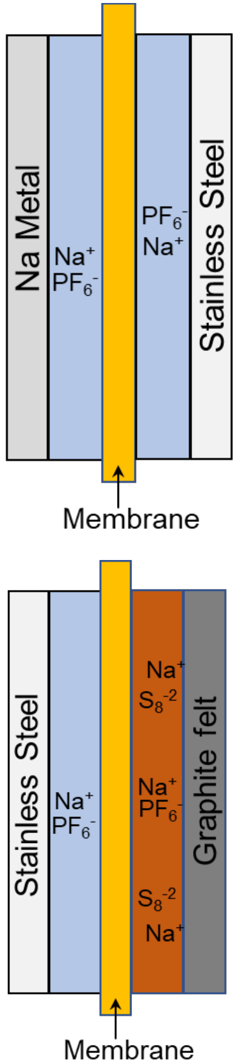
Key Findings:

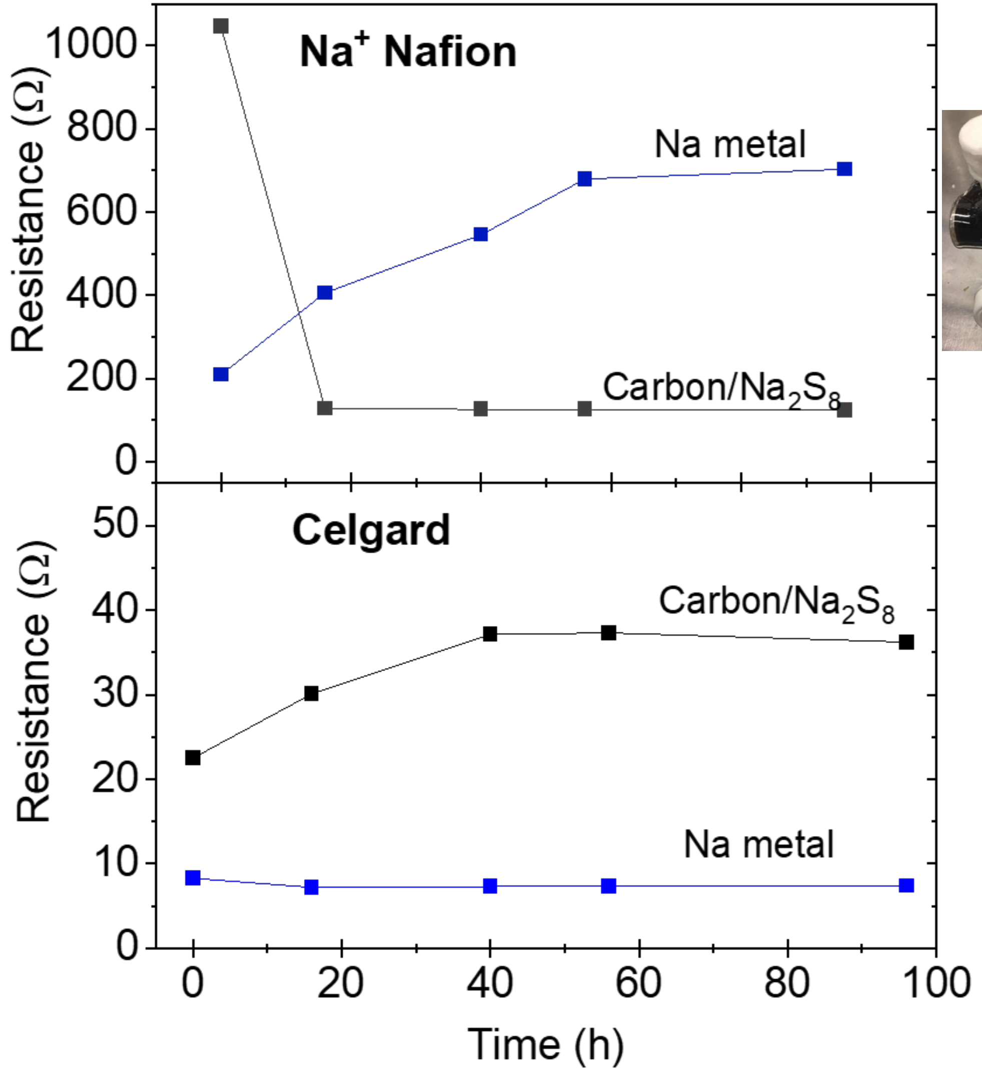
1. Hybrid Na|Nafion|Na_2S_8 hybrid flow cells exhibit high capacity and moderate cycling stability.
2. Strategies needed to stabilize Na metal anode
3. Membranes with improved selectivity (e.g., single ion conductors) needed.

J. L. Tyler et al. **2022** (Under Review)

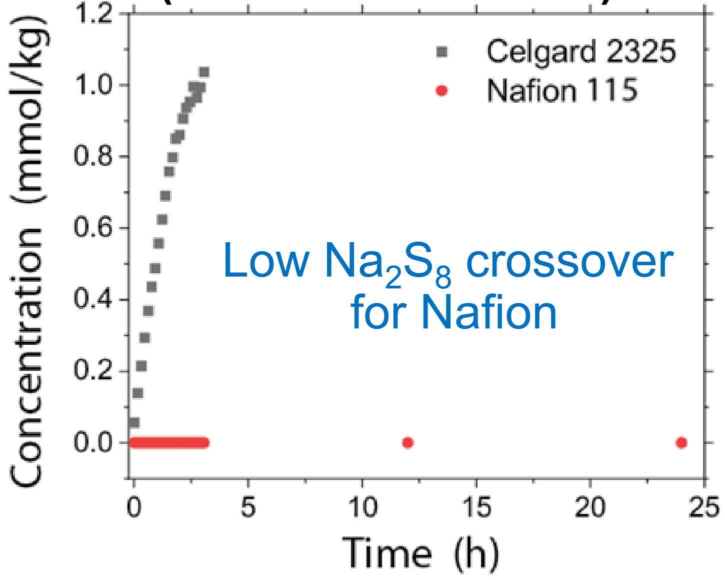
The chemical stability and Na_2S_8 crossover rates of commercial membranes were evaluated. A bilayer membrane (Celgard|Na^+ Nafion) will be tested in FY23 to improve cycling stability of Na metal/Na_2S_x hybrid flow cells.

Half Cell Configurations



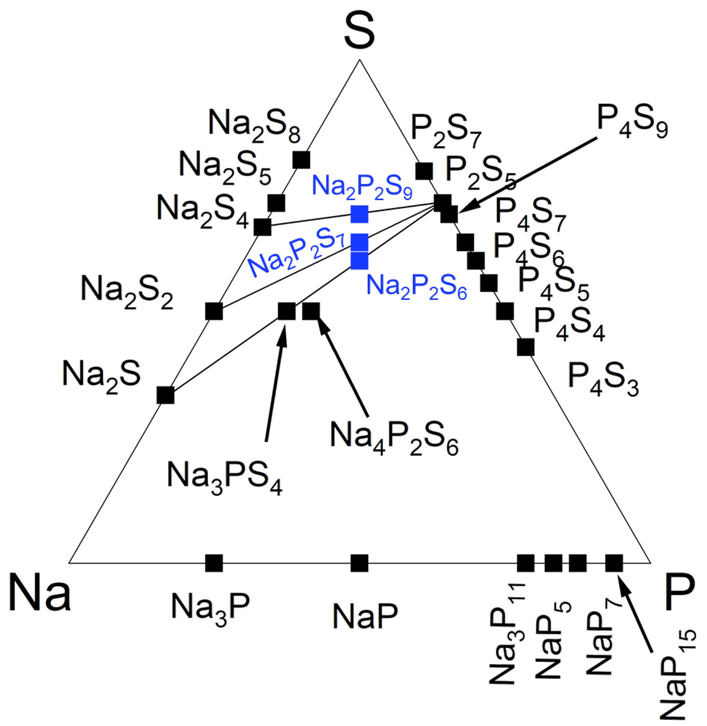


Na_2S_8 Crossover Evaluation (Concentration Cell)



Membrane	Chemical Stability		Na_2S_x Crossover
	Na Anode	Na_2S_x Catholyte	
Celgard	✓	✓	✗
Na^+ Nafion	✗	✓	✓
Bilayer membrane (FY23)	✓	✓	✓

Ongoing and Future Work



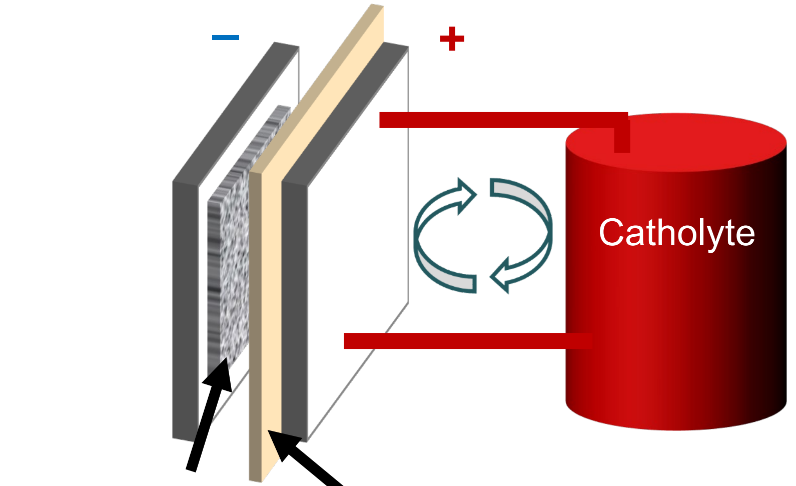
Nonaqueous Catholytes from Earth Abundant Materials

- Na_2S_x has outstanding cycling stability but limited practical capacity due to poor solubility when x≤4
- New class of Na-P-S catholytes prepared by formation of solvated Na_2S_x-P_2S_5 complexes

Na Metal Hybrid Flow Batteries

- $NaPF_6$/2EGDME electrolyte enables outstanding reversibility of Na metal anode
- Requires membrane with excellent reductive stability and low Na_2S_x crossover

Na Metal Hybrid Flow Batteries



Ion selective membranes for Na-based flow batteries

- Crosslinked polymers, single ion conductors, composites
- Benchmark performance of emerging polymers from startup companies (e.g., Bettergy Corp.)
- Investigate transport using *operando* FT-IR and UV-vis
- **Targets**: ASR < 50 Ω cm^2, no crossover

FY22 Manuscripts

[1] J. L. Tyler, R. L. Sacci, M. L. Lehmann, G. Yang, T. A. Zawodzinski, J. Nanda "Nafion inhibits polysulfide crossover in hybrid nonaqueous redox flow batteries" **2022** (Under Review)

[2] M. L. Lehmann, L. Tyler, E. C. Self, G. Yang, J. Nanda, T. Saito "Membrane design for non-aqueous redox flow batteries: current status and path forward" *Chem* **2022**, 8, 1611.

[3] M. L. Lehmann, G. Yang, J. Nanda, T. Saito, "Unraveling ion transport in trifluoromethanesulfonimide pentablock copolymer membranes in nonaqueous electrolytes" *Macromolecules* **2022**, *55*, 7740.

[4] H. Hao, Y. Wang, N. Katyal, G. Yang, H. Dong, P. Liu, S. Hwang, J. Mantha, G. Henkelman, Y. Xu, J. A. Boscoboinik, J. Nanda, D. Mitlin "Molybdenum carbide electrocatalyst in situ embedded in porous nitrogen-rich carbon nanotubes promote rapid kinetics in sodium-metal-sulfur batteries" *Advanced Materials* **2022**, *34*, 2106572.

[5] Y. Zhang, G. Yang, M. L. Lehmann, C. Wu, L. Zhao, T. Saito, Y. Liang, J. Nanda, Y. Yao, "Separator effect on zinc electrodeposition behavior and its implication for zinc battery lifetime" *Nano Letters* **2021**, *21*, 10446.

FY22 Intellectual Property

[1] E. C. Self, M. L. Lehmann, G. Yang, J. Nanda, "Na-P-S Catholytes for Nonaqueous Flow Batteries" ORNL Invention Disclosure 81939560 (submitted September 13, 2022).

[2] T. Saito, M. Lehmann, J. Nanda, "High Ionic Conductivity Polymer Electrolyte Compositions for Alkali and Beyond Alkali Metal Batteries", U.S. Patent Application 17/703,371 (filed March 25, 2022).

[3] J. Nanda, G. Yang, T. Saito, F. M. Delnick, "Mechanically robust solid electrolyte compositions for alkali and beyond alkali metal batteries" U.S. Patent Application 17/397,233 (filed February 10, 2022).

[4] F. M. Delnick, J. Nanda, E. C. Self "High capacity organic radical mediated phosphorus anode for redox flow batteries" US Patent No. US 11,145,885 B2 (published October 12, 2021)

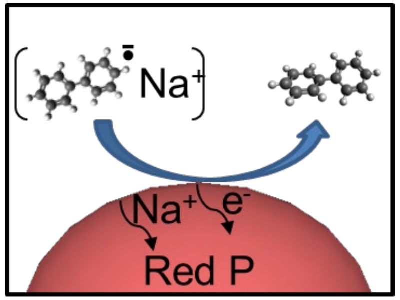
Questions?

Backup Slides

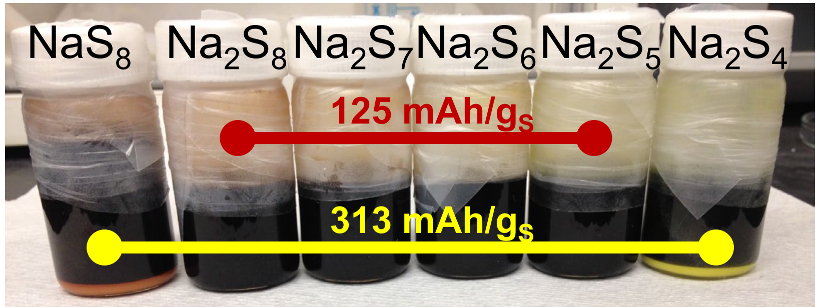
ORNL R&D: Next-Generation Flow Battery Materials for Low-Cost Grid Storage

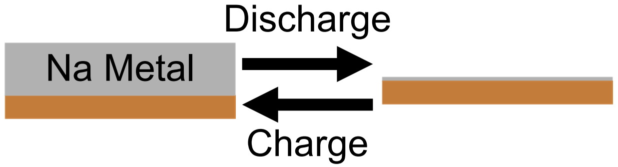
I. High Energy, Earth Abundant Electrolytes for RFBs

- Reversible Na metal anodes
- Room temperature sulfur catholytes
- Mediated anodes/cathodes



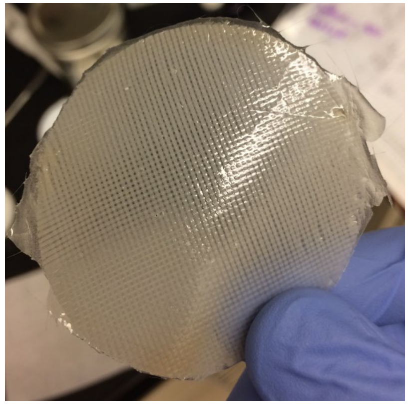
Na_2S_x Catholyte





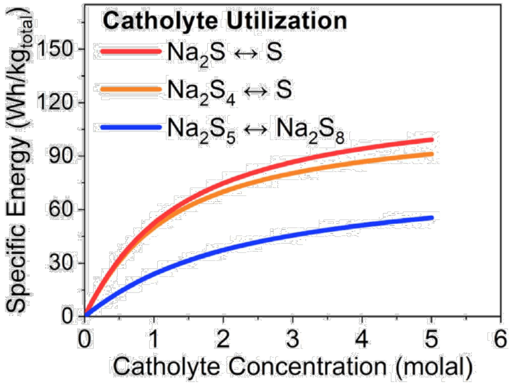
II. Cost-effective Membranes for RFBs

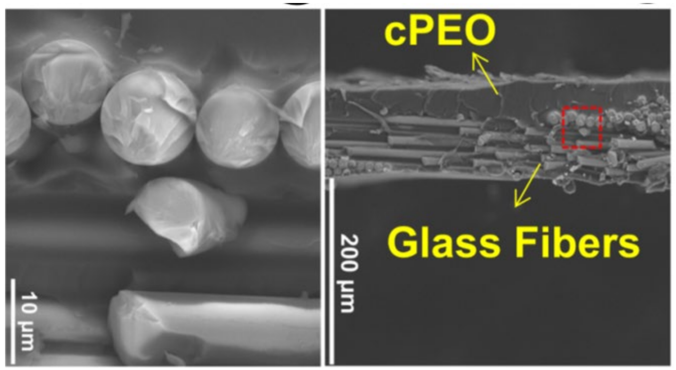
- Crosslinked polymer composite electrolytes
- Highly selective single ion conductors
- Scalable synthesis and processing routes

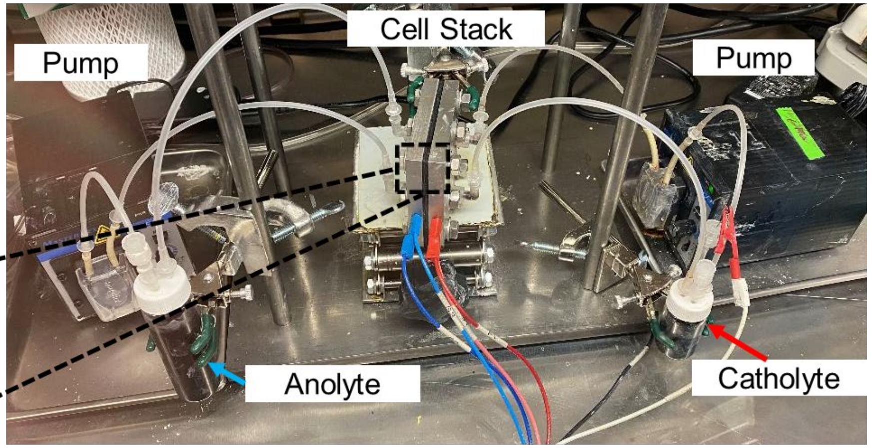


III. Advanced Characterization to Optimize Device Performance

- **Spectroscopy**: Identify polymer structure/transport correlations
- **Electrochemistry**: Probe parasitic reactions, assess long-term stability
- **AC Impedance**: Quantify energy loss mechanisms







$$E(i) - Eeq = \int_0^i Z(i')di'$$

Next-Generation Membranes: Address major bottlenecks of existing membranes which lack the necessary conductivity, selectivity, and mechanical properties.

Ceramic Separators
(e.g., Na^+ ß”-Al_2O_3)

- ✗ Thickness >0.5mm
- ✗ Brittle
- ✗ High manufacturing cost

ORNL’s Next-Generation Polymer Membranes

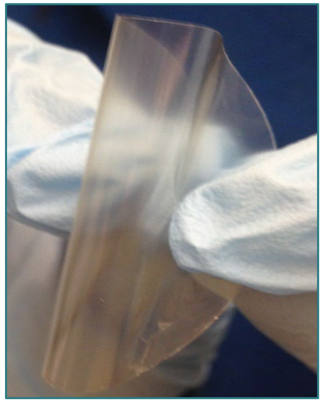
2018 → 2022

Gen I Polymer/Ceramic Filler Composites
ACS Energy Letters, *3*(7), pp.1640-1647

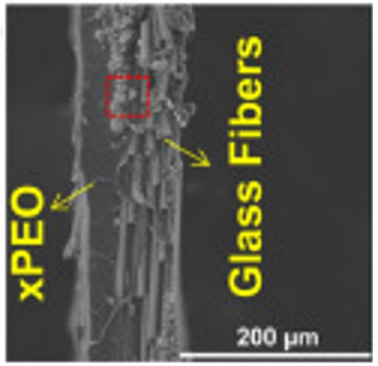
Gen II Crosslinked Polymers
Energy Storage Materials, *21*, pp.85-96.
Journal of The Electrochemical Society, *167*(7), p.070539.

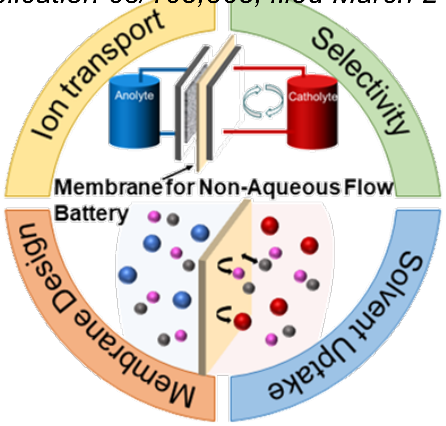
Gen III Polymer/Inorganic Scaffold Composites
Energy Storage Materials, *35*, pp.431-442.
U.S. Patent Application 17/397,233, filed February 10, 2022

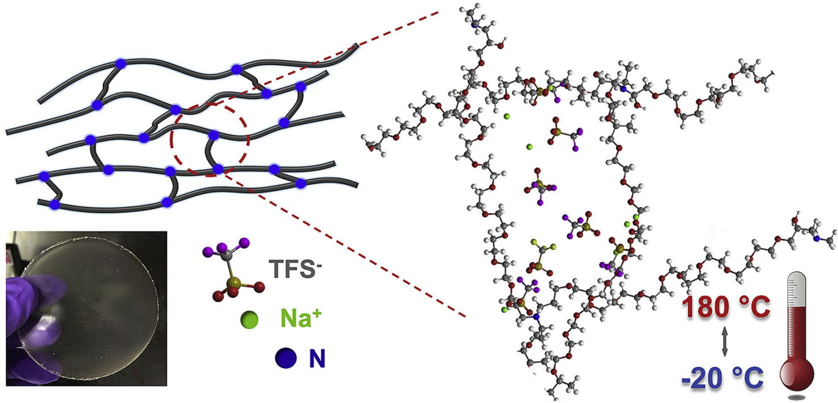
Gen IV Single ion Conducting Polymers
Chem 2022, 8(6), 1-22;
Macromolecules, 2022 (accepted)
U.S. Patent Application 63/165,865, filed March 24, 2022



20-30 µm

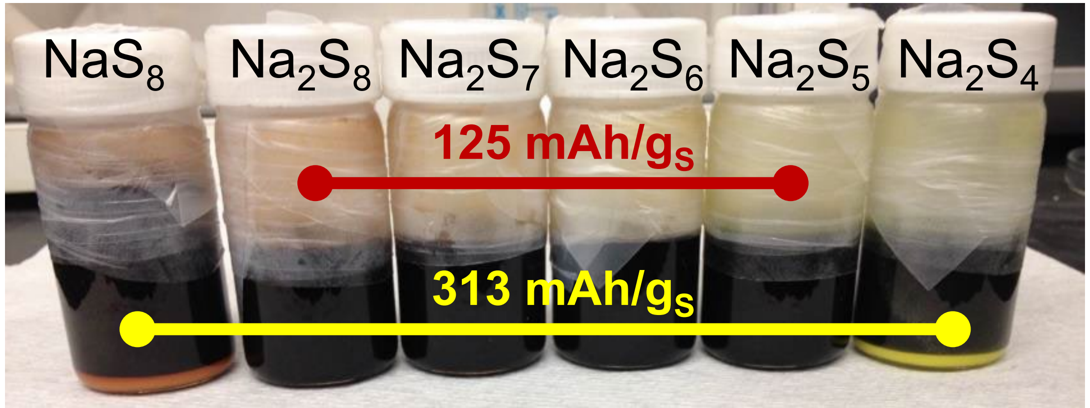






ORNL Membrane Technology
- ✓ Compatible with R2R processing (<50 µm)
- ✓ High mechanical strength (GPa)
- ✓ High Na^+ conductivity (>0.1 mS/cm at 25°)

Catholyte and Device Prototypes: ORNL developed custom hardware for nonaqueous biphenyl/sodium polysulfide flow batteries which operate at 25°C.

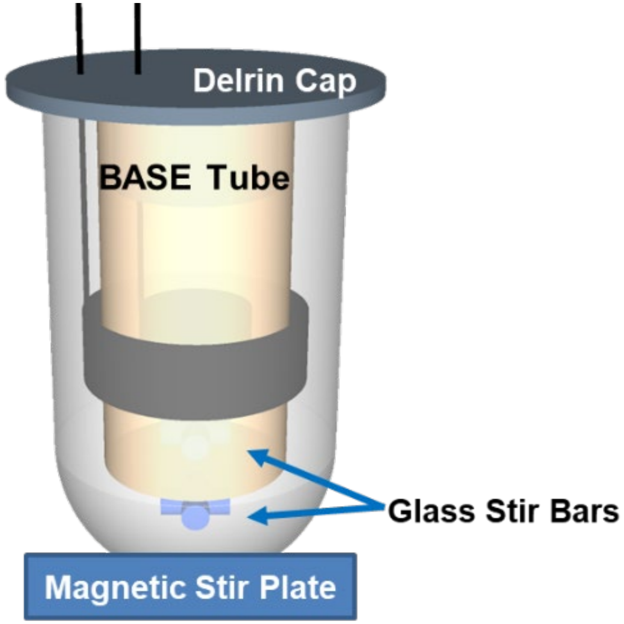


Cathode: $Na_2S_8 + 2\ Na^+ + 2\ e^- \leftrightarrow 2\ Na_2S_4$ $\quad E^0 = 2.3$ V vs. Na/Na$^+$

Anode: $Na^+ß^{\bullet-} \leftrightarrow ß^0 + Na^+ + e^-$ $\quad E^0 = 0.2$ V vs. Na/Na$^+$

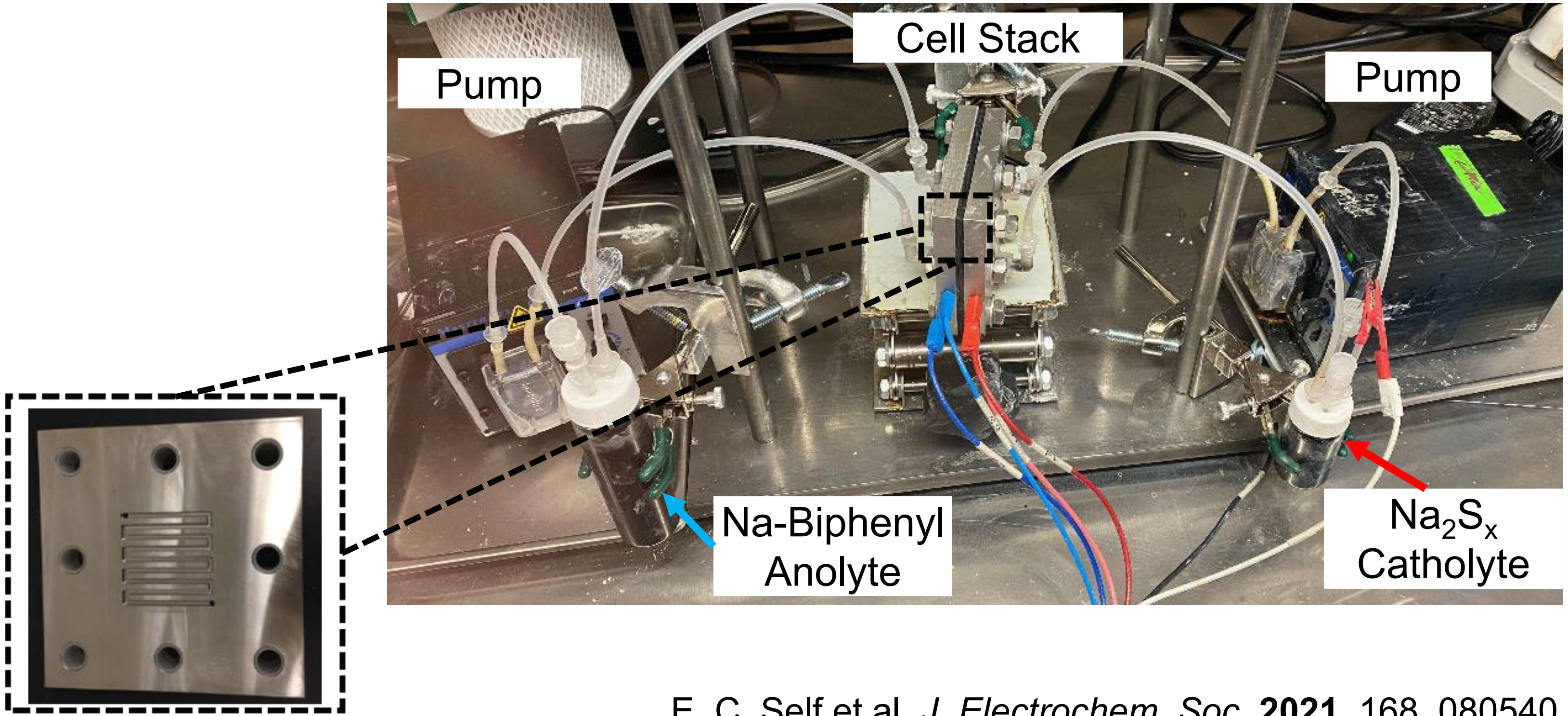
Full Cell: $Na_2S_8 + 2\ Na^+ß^{\bullet-} \leftrightarrow 2\ Na_2S_4 + 2\ ß^0$ $\quad E_{cell} = 2.1$ V

Cylindrical Cell Configuration



Inner: Na_2S_x Catholyte
Outer: Na-Biphenyl ($Na^+ß^{\bullet-}$) Anolyte

Flow Cell Configuration



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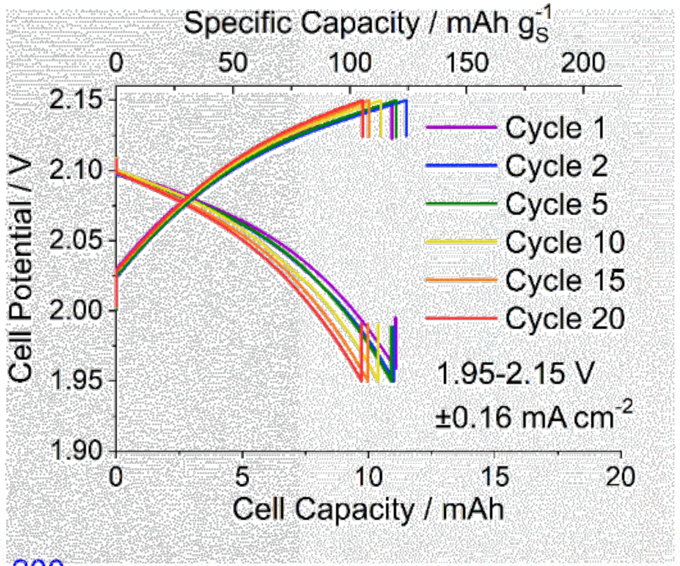
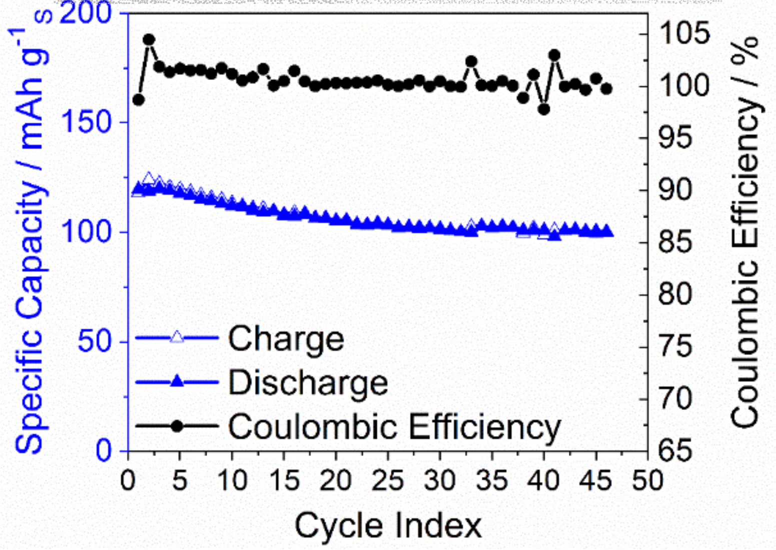
FY21 Recap: Biphenyl/Na_2S_x flow cells containing ceramic exhibit outstanding cycling stability (several months continuous testing).

Full Cell: Cycling Soluble Phases

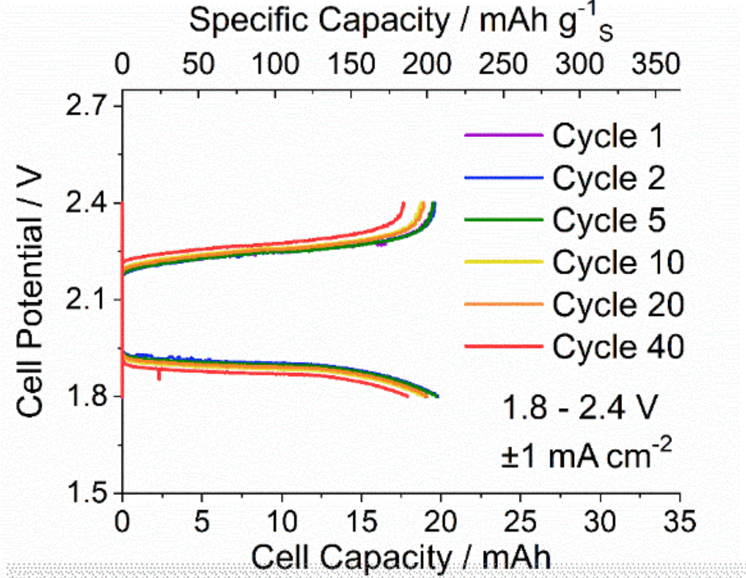
$Na_2S_5 \leftrightarrow Na_2S_8$ ($Q_{theoretical}$ = 125 mAh/g_S)

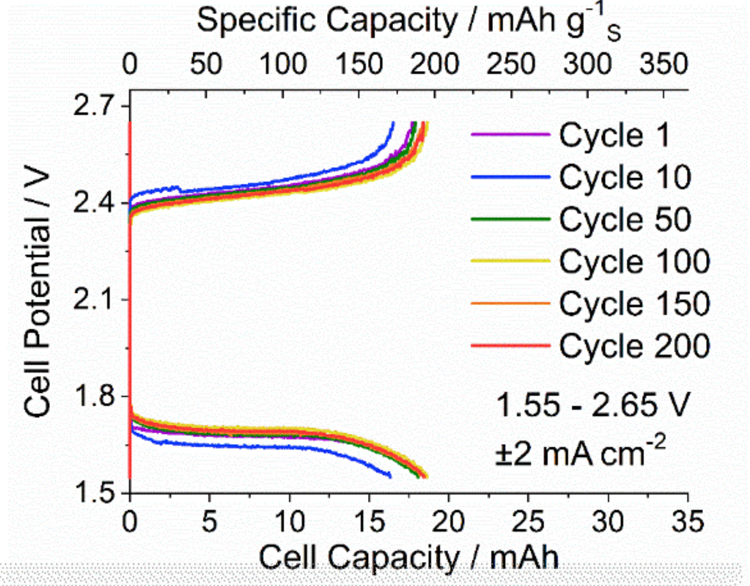


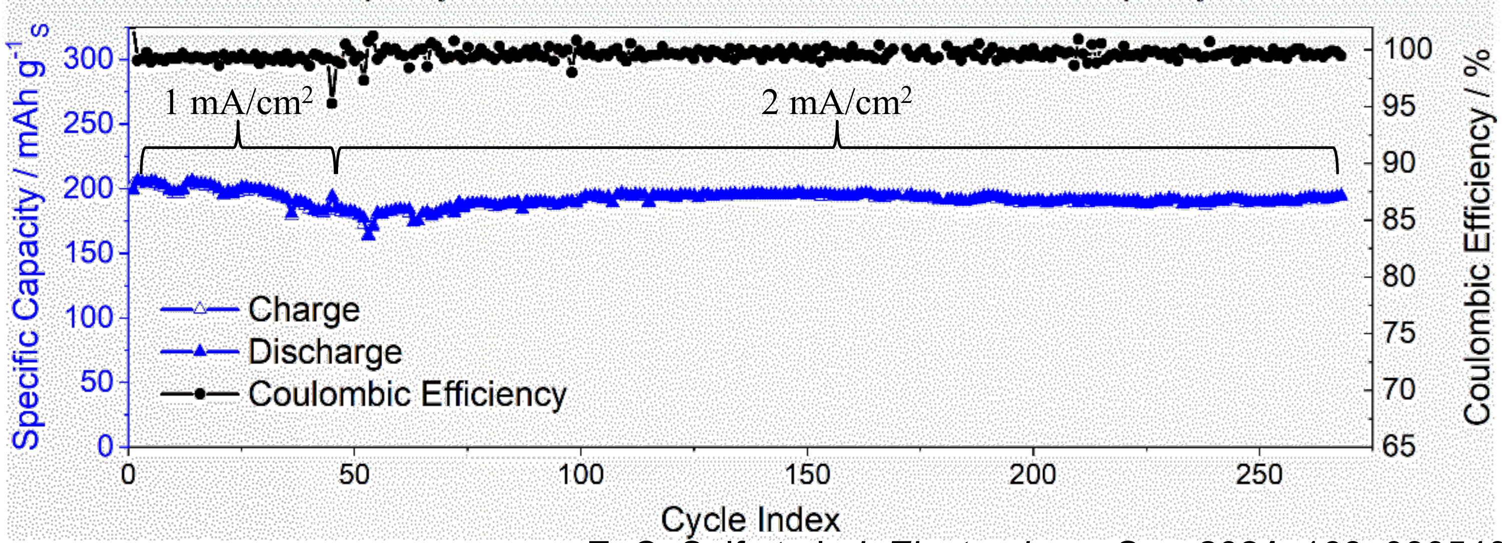


Full Cell: Cycling Insoluble Phases

$Na_2S_8 \leftrightarrow S_8$ ($Q_{theoretical}$ = 209 mAh/g_S)







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