Tailored Ion-selective Membranes for Low-cost Alkali Metal Redox-flow Batteries

Guang Yang

Presentation #604
DOE OE Energy Storage Peer Review
October 25, 2023

Energy Storage & Conversion Group
Chemical Sciences Division
yangg@ornl.gov
Office: 8655765252

Project Team

Guang Yang

Michelle Lehmann
(Poster 10/24)

Tomonori Saito

Ethan Self
(Presentation 404)

Camilo Suarez

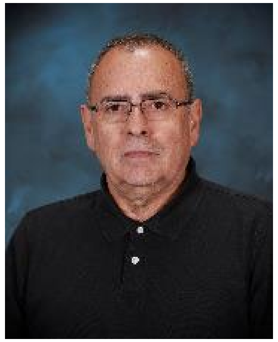
University Collaborators

Thomas Zawodzinski

David Mitlin
(UT-Austin)

Recent ORNL Team Members

Jagjit Nanda
(SLAC-Stanford)



Frank Delnick
(Retired 6/22)

Landon Tyler
(Graduated 6/22)

Team's Core Expertise and Focus Areas

- Advanced flow battery chemistries leveraging earth-abundant resources.
- Ion-selective polymer electrolytes optimized for high ionic conductivity in alkali metal-based batteries
- Advanced characterizations

Industrial Partners

KRATON

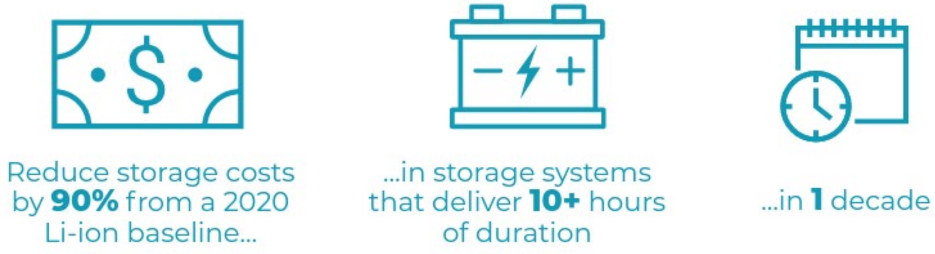
BETTERGY
Clean Energy for Better Life™

Acknowledgment

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

Additional thanks to Mali Balasubramanian and Michael Starke, program managers, and Gabriel Veith at ORNL.

Membranes: key enabler for redox flow batteries (RFBs) for long-duration energy storage (LDES)

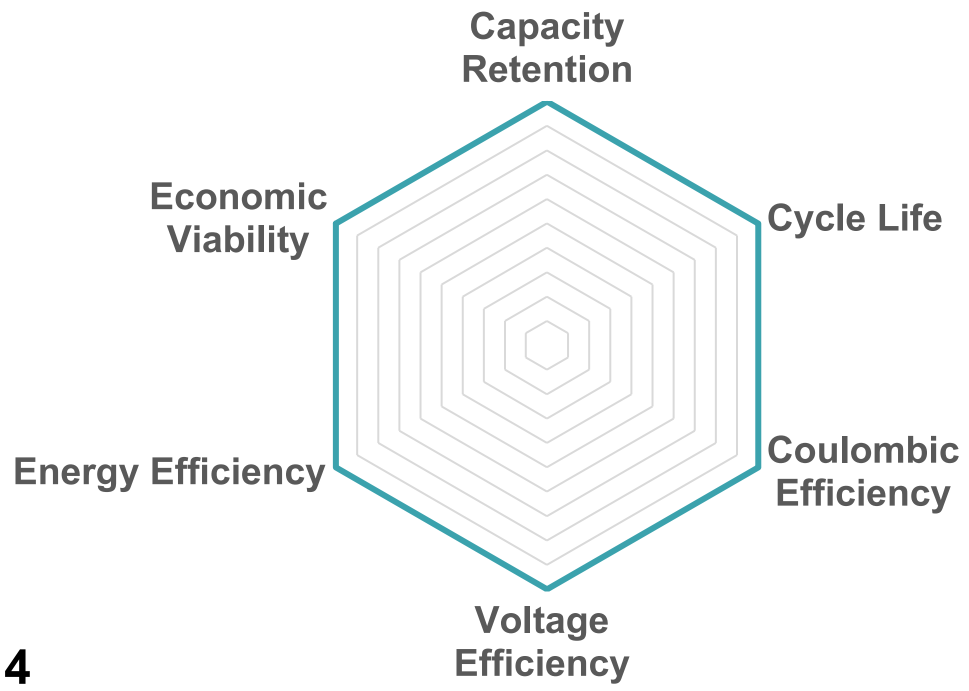


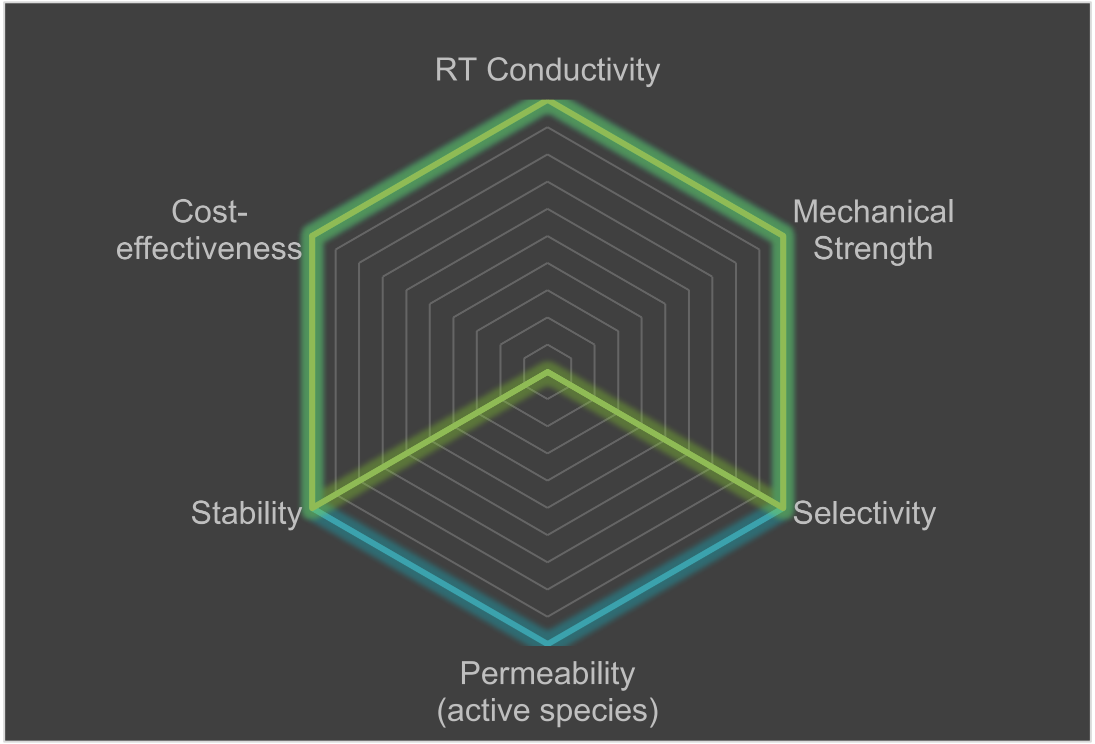
- Long duration energy storage > 10 hrs
- Reducing energy storage cost by 90%

The membrane is >40% of the total cost of the RFB

Successful membrane R&D ultimately leads to cheaper and more efficient storage solutions with RFB

RFB performance matrics





Goal: Address major bottlenecks of existing membranes which fail to balance conductivity, selectivity, and mechanical properties

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

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

ORNL Membrane Target:
- ✓ Compatible with R2R processing (<50 μm)
- ✓ High mechanical strength (GPa)
- ✓ High Na^+ conductivity (>0.1 mS/cm at 25°)
- ✓ High cation transport number (>0.7)
- ✓ Low redox active species crossover

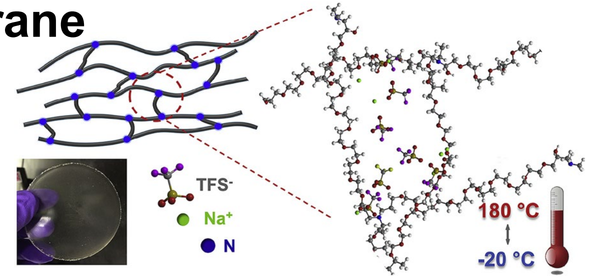
Gen I. Linear polymer electrolyte with hard additives
- ➢ Blocking Na dendrite
- ➢ Low selectivity

ACS Energy Letters, *3*(7), pp.1640-1647

Gen II. Cross-linked polymer membrane
- ➢ Increased strength
- ➢ Increased ionic conductivity
- ➢ Low selectivity

Energy Storage Materials, *21*, pp.85-96.

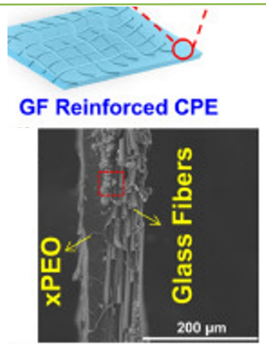
Journal of The Electrochemical Society, *167*(7), p.070539.



Gen III. Polymer membrane with inorganic scaffold
- ➢ GPa mechanical strength
- ➢ Reduced cell resistance
- ➢ Scalable
- ➢ Low selectivity

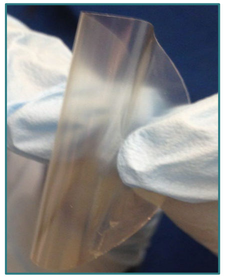
Energy Storage Materials, *35*, pp.431-442.

U.S. Patent Application 17/397,233, filed February 10, 2022



Gen IV. Ionic-selective membranes/single ion conductor
- ➢ GPa mechanical strength
- ➢ Reduced thickness and cell resistance
- ➢ High selectivity

Chem 2022, 8(6), 1-22;
Macromolecules, 2022, 55, 7740−7751
U.S. Patent Application 63/165,865, filed March 24, 2022



Salt in polymer

Selectivity, Strength ↑

Crossover ↓

Single-ion conductor

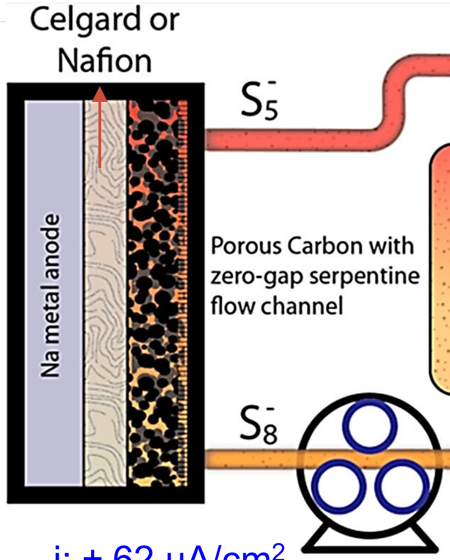
20-30μm, >1GPa modulus

Milestones and progress

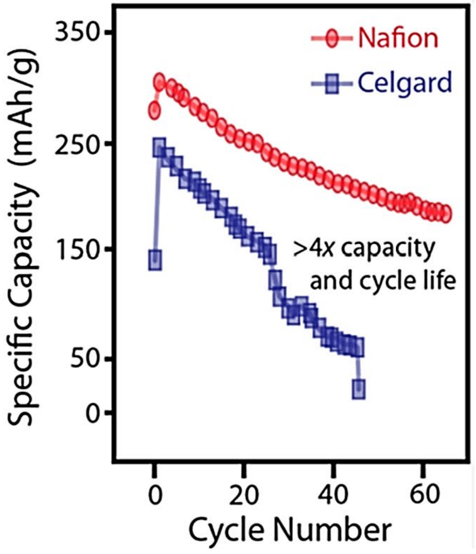
Goal: Develop pore-filled, single-ion conducting hybrid membranes to better stabilize both Na metal anode and Na_2S_x catholyte in a Na redox flow battery.

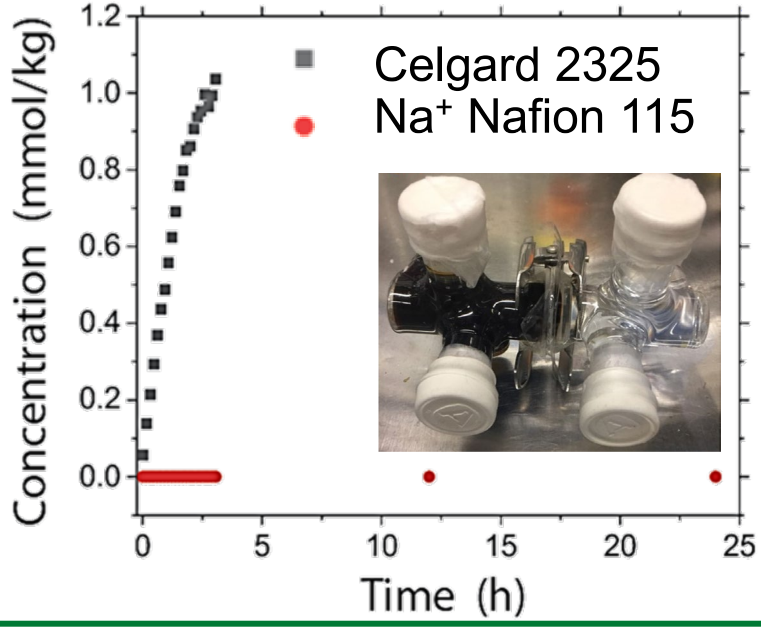
Milestone Description	Schedule	Progress toward Completion
Evaluate the thin (25 µm) perfluorinated Na^+ single ion conductor membrane crossover, stability versus Na anode and carbon felt cathode	Mar.2023	Complete
Design and synthesize porous polypropylene/Na^+ exchanged perfluorinated membrane hybrid separators and evaluate their ionic conductivity, thermal properties, mechanical strength, and electrochemical stability	Jun. 2023	Complete
Develop cross-linkable random block polymer membranes with 1-3 nm ion-conducting channels and evaluate their multiple properties	Aug. 2023	Complete
Down select promising membrane candidates, and integrate them with Na metal and supporting electrolyte to optimize cycling performance in a Na|Na_2S_x redox flow battery	Nov. 2023	In progress

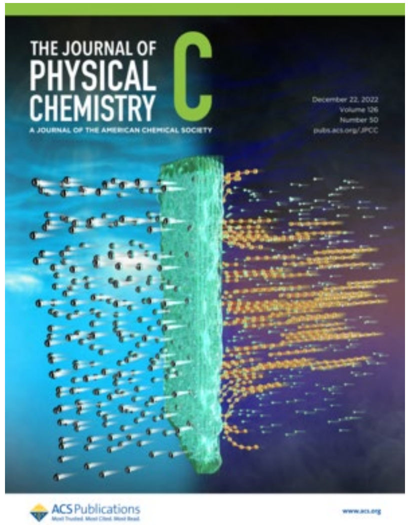
FY22 Q4/FY23 Q1 efforts recap

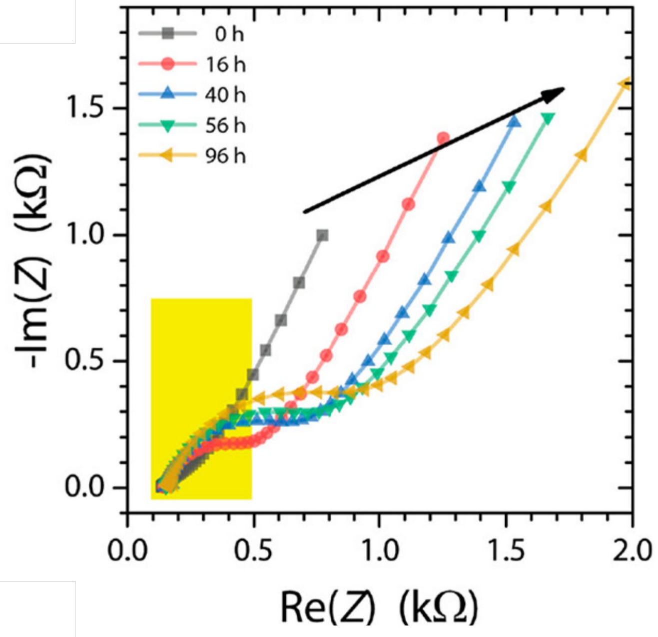


i: ± 62 μA/cm^2
E= 1.75-3 V vs. Na/Na$^+$









Key Findings:

- Na$^+$-Nafion effectively reduces the polysulfide shuttle and improve the capacity and cycle life benchmark to commercial porous membranes
- Na$^+$-Nafion continuously reacts with the Na metal anode, resulting in increased interfacial resistance

New polymer membranes are needed to mitigate capacity fade for long duration storage

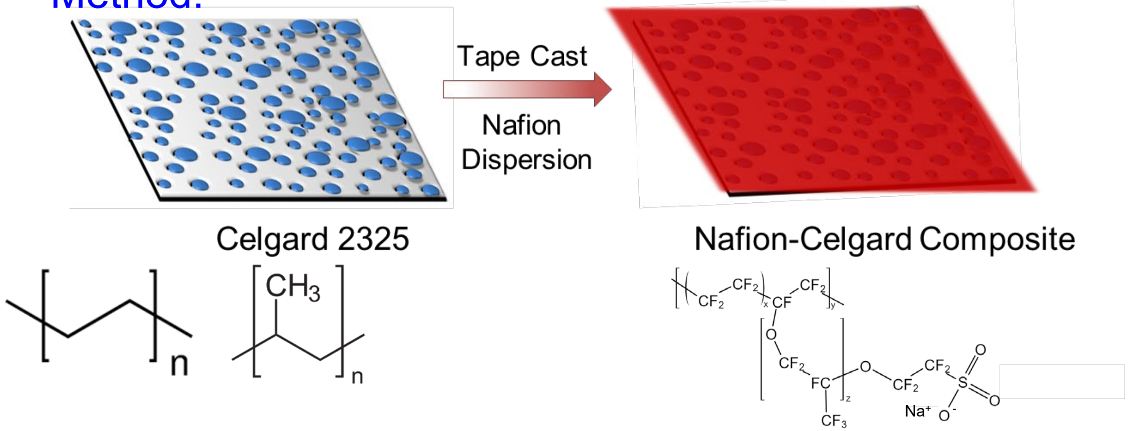
The Journal of Physical Chemistry C 126.50 (2022): 21188-21195.

FY23 Research Focus: Developing hybrid single-ion conducting membranes

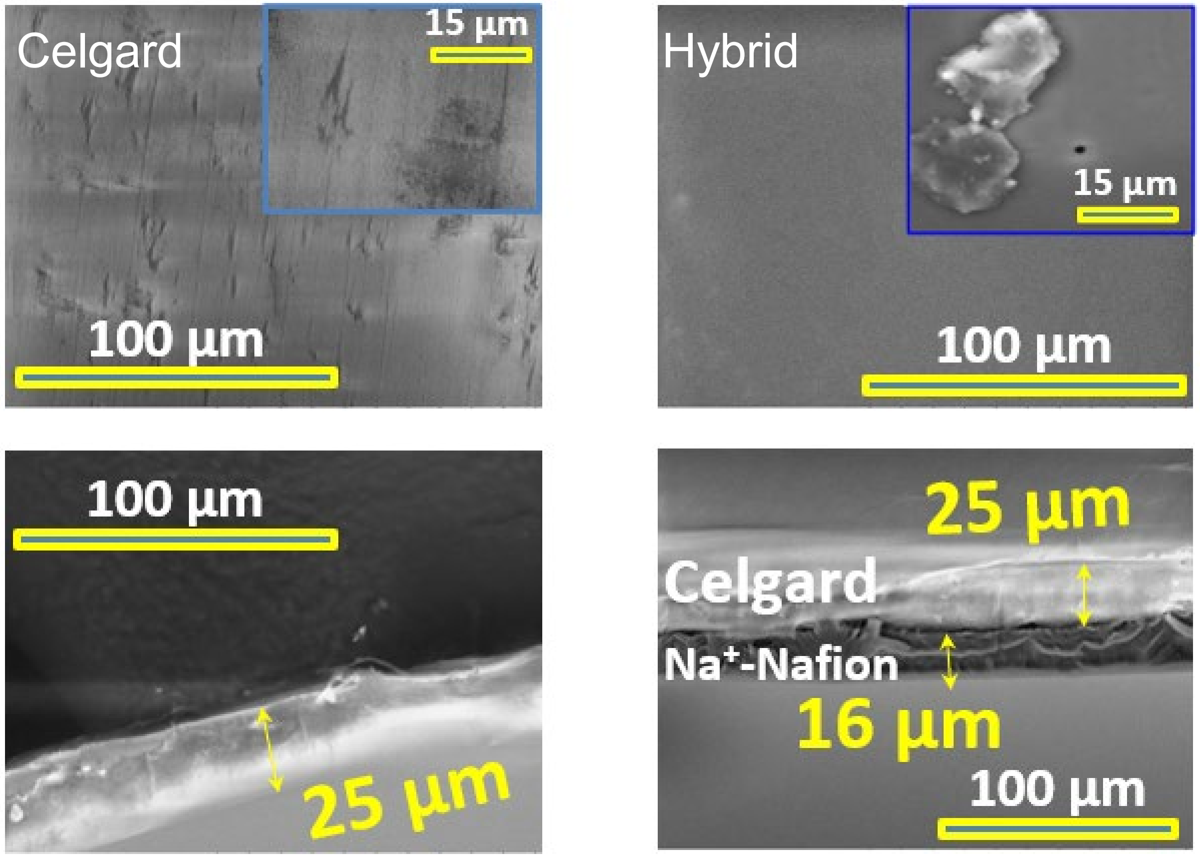
Achievements –

- ➢ Have developed a scalable method to synthesize hybrid single-ion conducting membranes
- ➢ Have established electrochemical and spectroscopic methods for membrane evaluations
- ➢ Have initiated efforts in developing low-cost hydrocarbon copolymer membranes

Method:



Film structure evaluation:



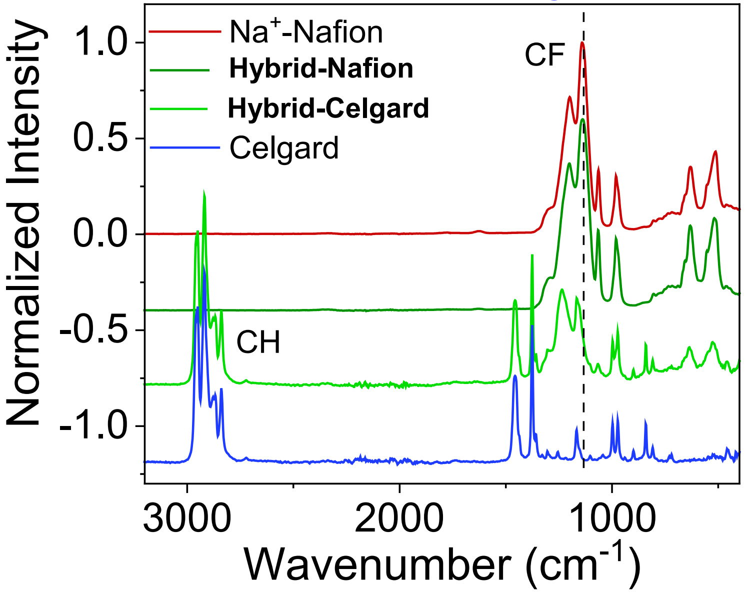
Key Findings:

1. A scalable tape casting method was developed to fabricate the hybrid single-ion polymer electrolyte
2. The thickness of the resulting hybrid membrane is customizable and remains thin.
3. The hybrid membrane display a "Janus" structure

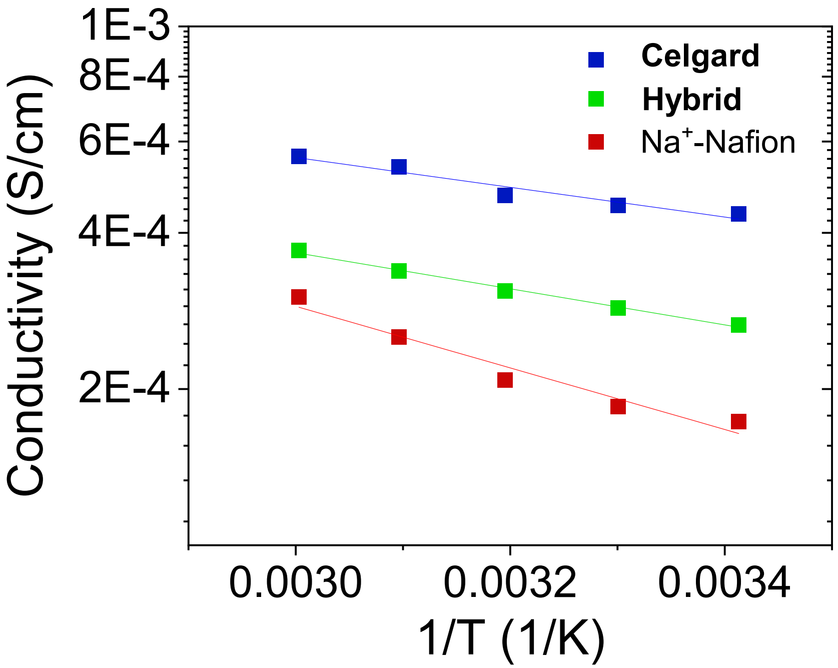
Also see Poster "Design of Mechanically Robust Membranes for Sodium Polysulfide Hybrid Redox Flow Battery" by Lehmann et al.

Evaluation of the hybrid membranes properties

"Janus" structure confirmed by IR spectroscopy



Ionic conductivity at RT comparable to liquid electrolyte



~GPa level storage modulus

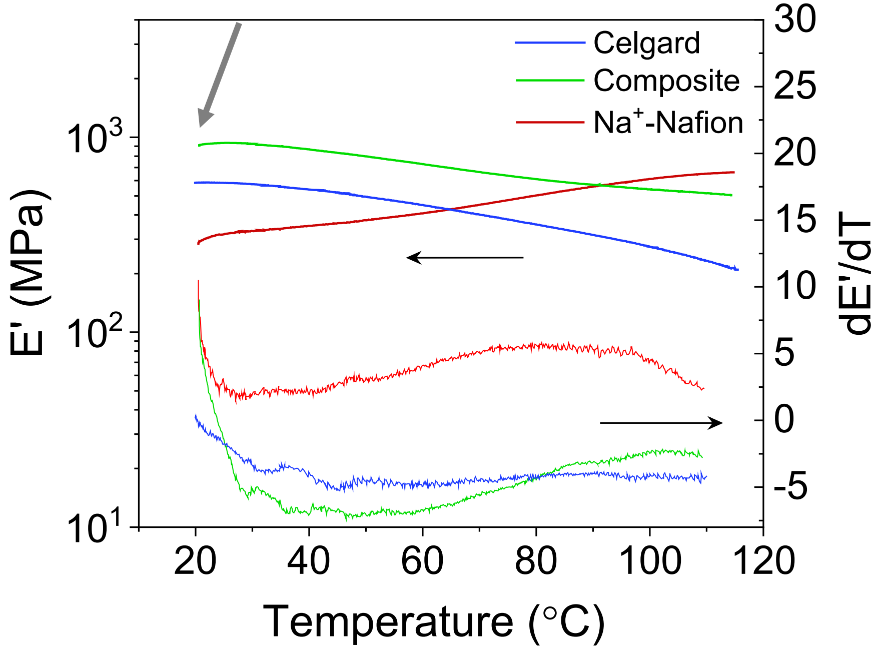


Table 1. Properties of the various membranes.

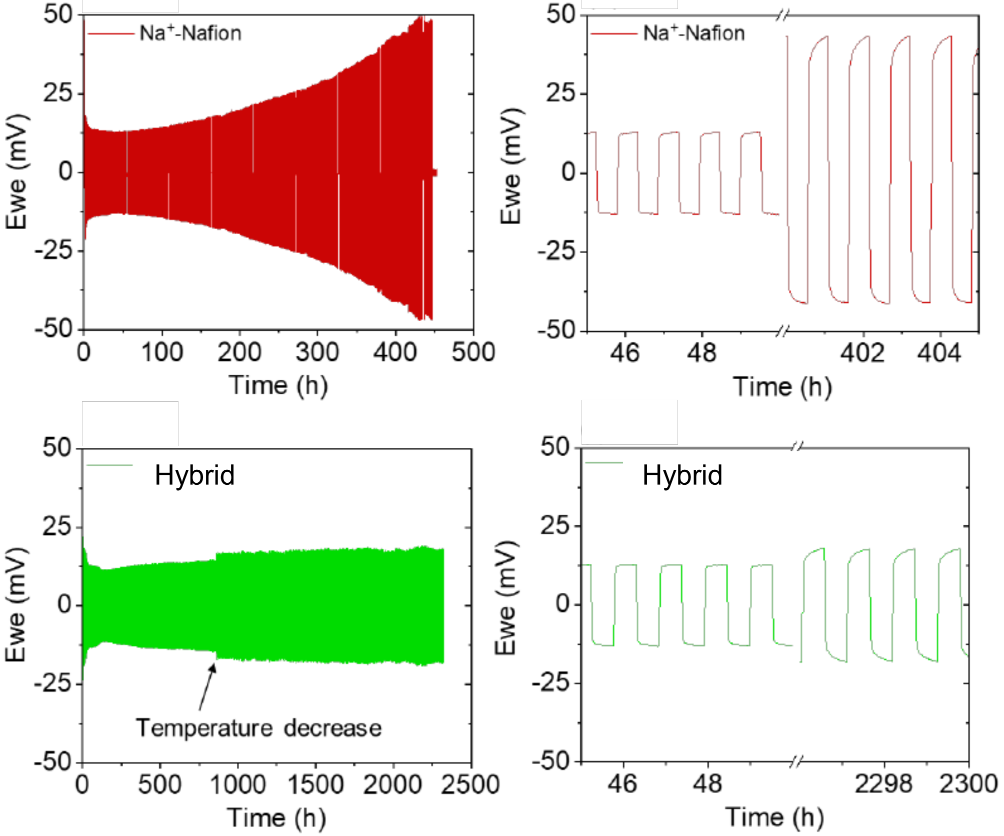
Sample	Na_2S_8 Permeability (cm^2/s)	Conductivity (mS/cm, 20 °C)	Area Specific Resistance (Ω cm^2, 20 °C)	Storage Modulus (MPa, 25 °C)
Celgard	2.2×10^{-6}	0.44	5.2	584
Na^+-Nafion	3.1×10^{-8}	0.17	19.5	318
Hybrid	1.4×10^{-7}	0.26	23.7	935

Key Findings:

1. Two sides of the hybrid membrane exhibit different chemistries – confirming its "Janus" structure
2. Hybrid membrane display RT ionic conductivity comparable to Celgard with liquid electrolyte
3. Hybrid membrane demonstrates a storage modulus close to the GPa level

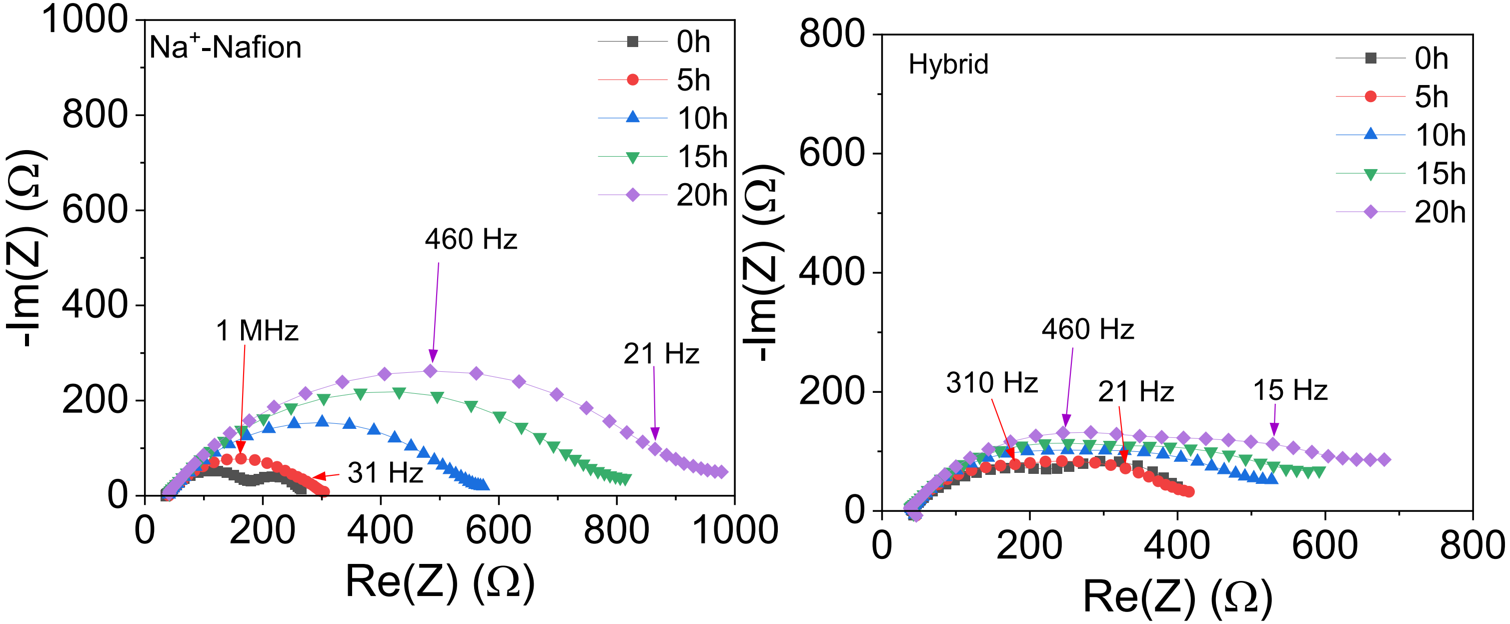
Enhanced stabilization of Na Metal Anode and Na_2S_x catholyte with hybrid membranes

Na|Membrane|Na symmetric cell striping/plating test



0.1 mA/cm^2 with 0.5 hr striping+0.5 hr plating

Na|Membrane|Na_2S_x time-resolved EIS

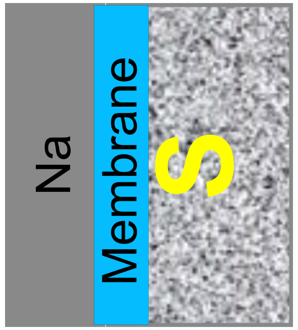


High frequency: electrolyte resistance
Low frequency: interfacial resistance

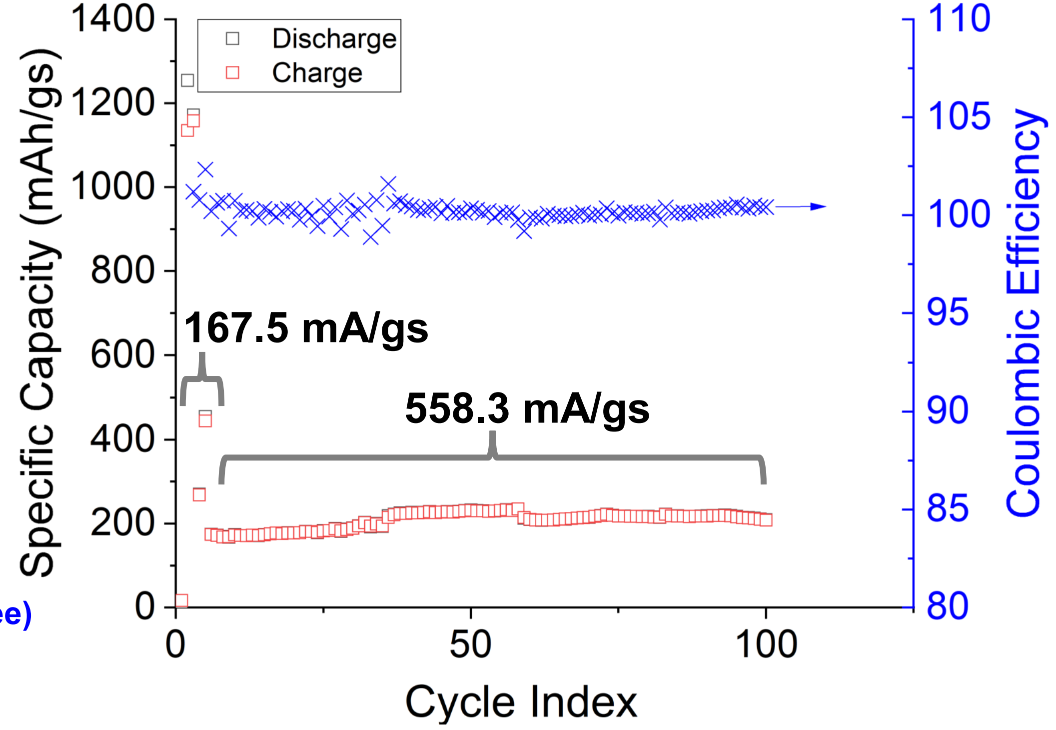
Key Findings:

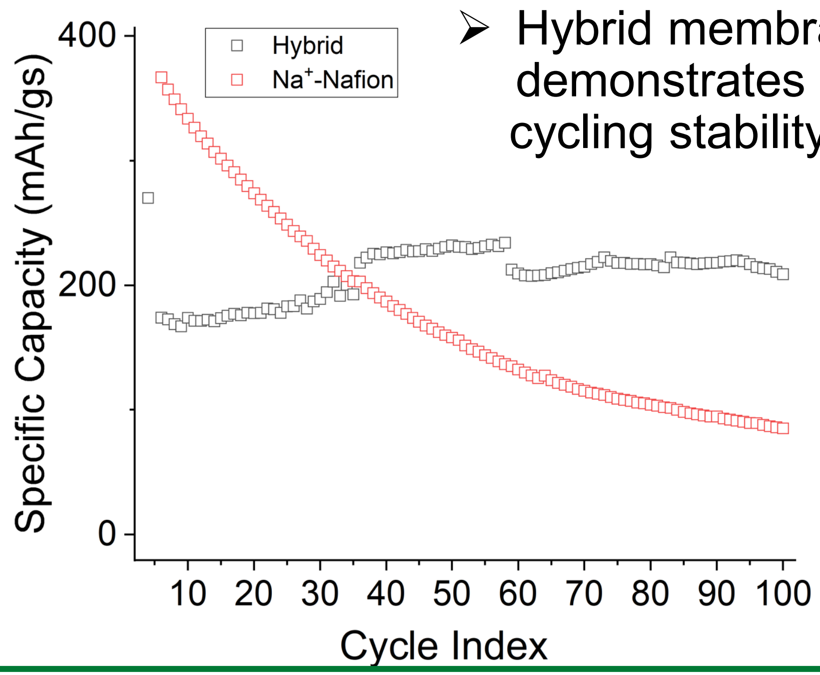
1. Hybrid membranes exhibit enhanced cycling stability against Na metal – capability of alleviating Na dendritic growth
2. Hybrid membranes stabilize the Na metal better with reduced interfacial resistance over time.

Hybrid membranes promote the cycling stability of the Na-Na_2S_x battery)

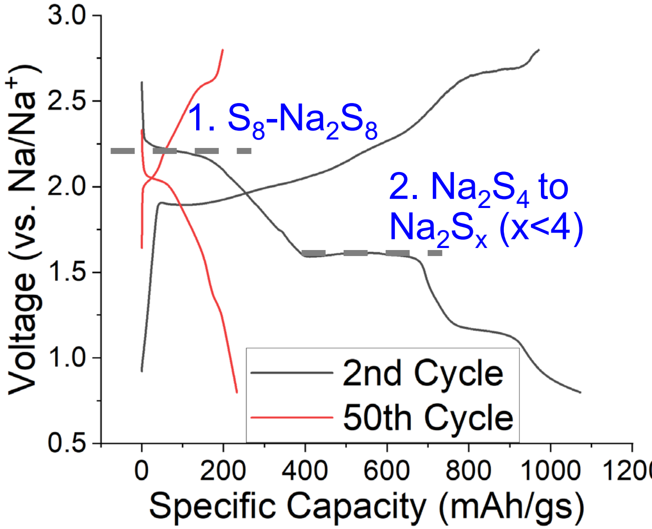


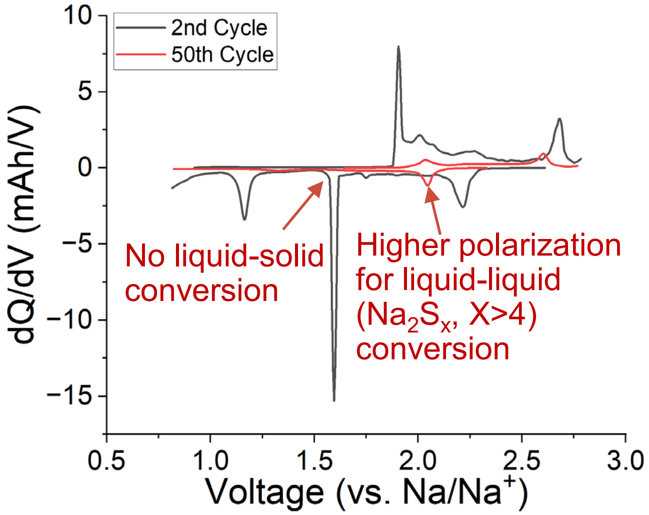
Electrolyte:
1M NaPF6 in 2EGDME
Anode: **Na metal**
Cathode:
1.2 mg/cm² S + porous carbon paper (binder free)





- Hybrid membrane demonstrates better cycling stability





Key Findings:

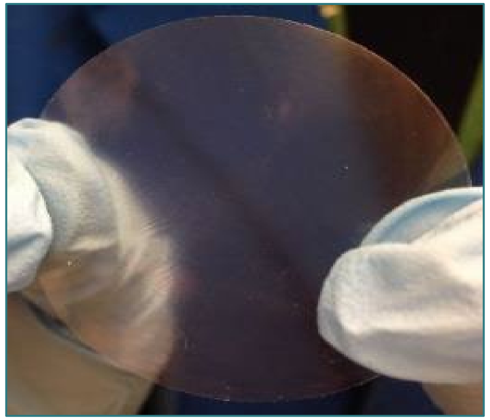
1. Hybrid single ion-conducting membrane exhibits better cycling stability and high Coulombic efficiency
2. Low capacity (~200 mAh/g) is likely due to the presence of insoluble low-order Na_2S_x (X<4)

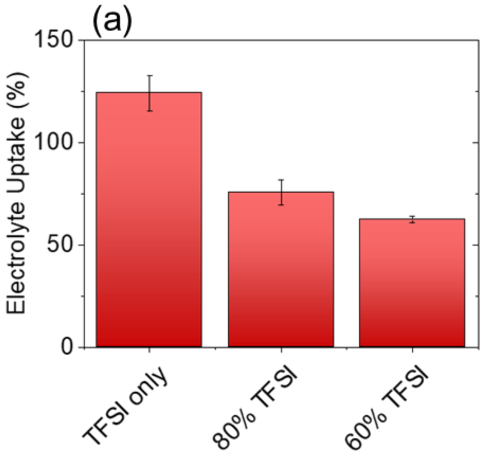
Possible solutions:

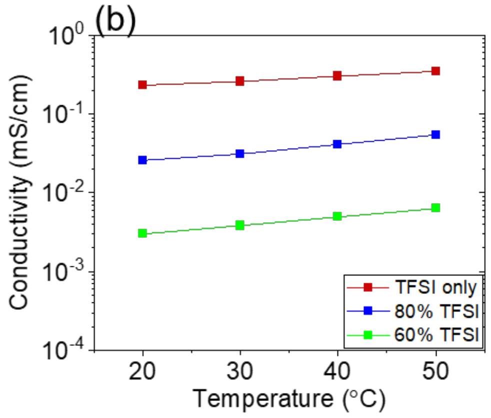
1. Develop new catholytes (Na-P-S) to dissolve low-order Na_2S_x (See presentation #404 PI: Ethan Self)
2. Develop electrochemical catalysts to promote low-order Na_2S_x conversion kinetics

Ongoing research

Develop low-cost hydrocarbon polymer electrolyte chemistries







Advantages of ORNL's Modified Nexar

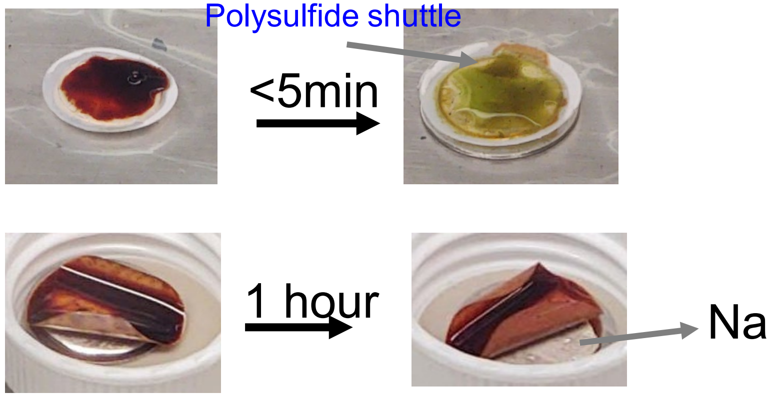
- ✓ Low cost (prepared from commercial hydrocarbon precursor)
- ✓ High selectivity for Na^+ cations (t^+ ~0.8)
- ✓ High Na^+ conductivity(0.1 mS/cm at RT)
- ✓ Tailored mechanical strength up to 1 GPa

- Modified chemistry to reduce brittleness for non-aqueous conditions

KRATON

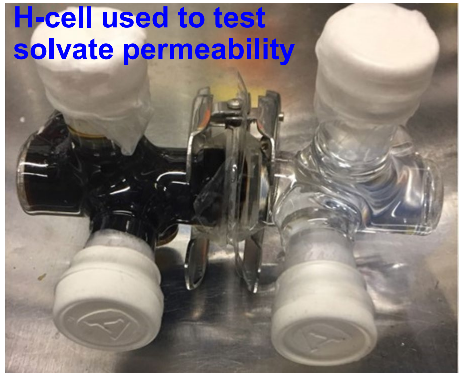
Benchmark to commercial and emerging membranes

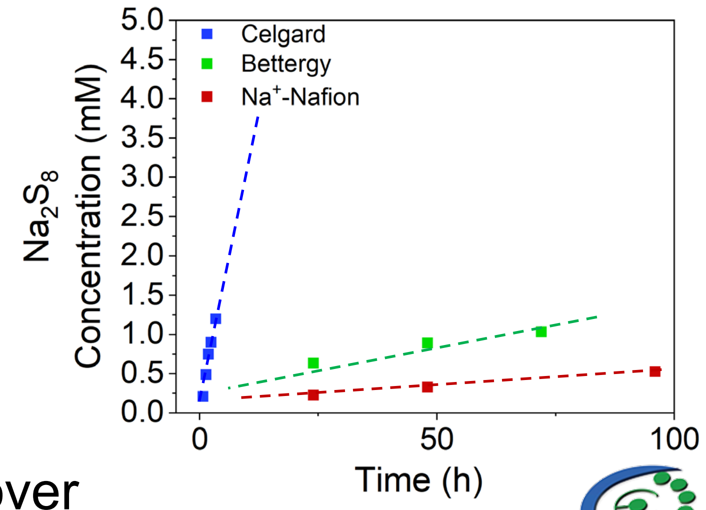
Discoloration due to Polysulfide shuttle



Bettergy: Ceramic composite membrane for Li-S batteries

H-cell used to test solvate permeability

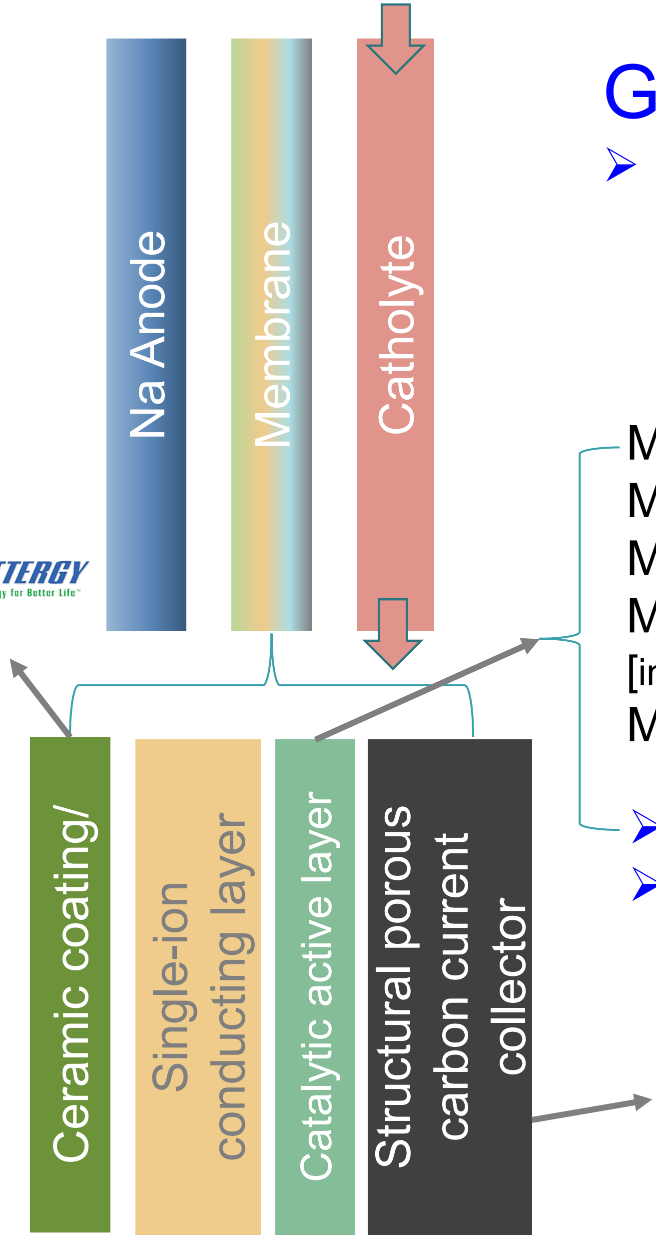




➢ Mitigated crossover

BETTERGY Clean Energy for Better Life™

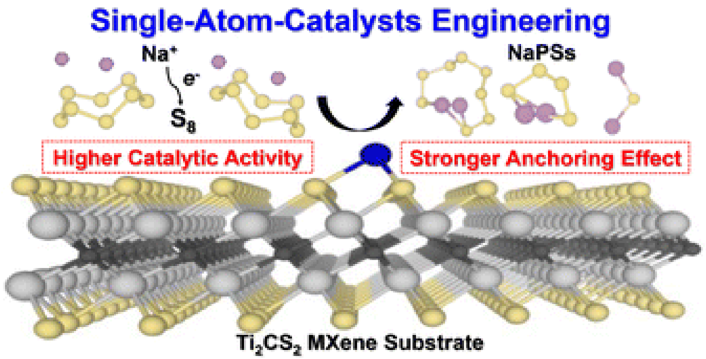
Proposed future research – Multifunctional Membrane Electrode Assembly (MEA)



Goal:

- Develop multifunctional MEA targeting: (i) alleviating alkali metal plating on the membrane surface; (ii) restricting metal anode dendrite growth; (iii) promoting polysulfide chemical/physical adsorption and enhancing redox kinetics.

Metallic catalysts (e.g. Cobalt vanadium)
Metal nitride catalysts (e.g. TiN; MoN; VN)
Metal oxide catalysts (e.g. TiO_2)
Metal carbide catalysts (e.g. MoC/MoC_2)
[in collaboration with **Mitlin Group@UT Austin**]
Metal sulfide catalysts (e.g. Mo_2S; FeS_2)

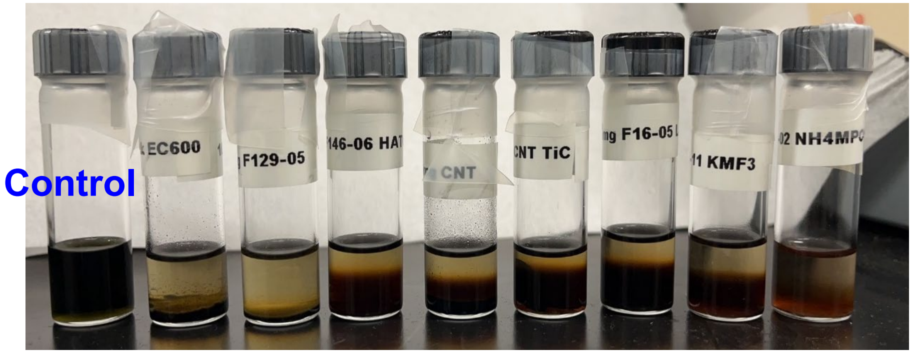


https://doi.org/10.1039/D2NR05930D

- Promote Na_2S_x redox kinetics
- Promote Na_2S_x adsorption

Porous carbon current collector
physical/chemical adsorption of polysulfide

Control



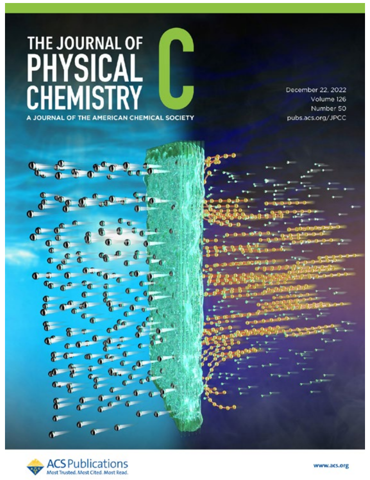
FY23 Achievements

Invention Disclosure/patents

1. Invention Disclosure ID#: 202305380, DOE S# , "Addressing Sodium Metal Anode Stability with a New Hybrid Membrane" (elected for patent protection)
2. ORNL patent, “Mechanically robust ion-conducting membranes for redox flow batteries” shortlisted for Chevron Studio Technology Partners Program (ORNL FY23 OE Interim Annual Report highlight)

Journal Publications

1. (Cover Article) Tyler, J.L., Sacci, R.L., Lehmann, M.L., Yang, G., Zawodzinski, T.A. and Nanda, J., 2022. Nafion Inhibits Polysulfide Crossover in Hybrid Nonaqueous Redox Flow Batteries. **The Journal of Physical Chemistry C**, 126(50), pp.21188-21195.
2. (Editor Invited) Lehmann, M. L., Self, E. C., Saito, T., & Yang, G. (2023). Composite Membrane for Sodium Polysulfide Hybrid Redox Flow Batteries. **Membranes,** 13(8), 700.
3. Rahman, Yang, Saito et al., “Tough and recyclable carbon-fiber composites with exceptional interfacial adhesion enabled by tailored vitrimer and carbon fiberinterface” **Cell Reports Physical Science** (under review)
4. Cao, Yang, Lin et al. “Unleashing the potential of graphite intercalation compounds for extreme-condition Li-ion batteries" (reference number: NENERGY-23061347-T)”, **Nature Energy (**under review)
5. Chen, Keum, Wang, Yang et al. "Interface-Enhanced Conductivities in Surfactant-Mediated Ion Complexes" **Frontiers in Nanotechnology** (under review)



Conference talks (4)

1. Yang, Lehmann, Self, Sacci, Saito, and Nanda. “Develop Low-cost Membranes for non-aqueous Redox-flow Batteries” TechConnect World 2023
2. **(*invited*)** Yang et al. “Unravel Structural and Chemical Heterogeneity of Polymer-based Solid Electrolytes” Industrial & Engineering Chemistry (I&EC) ACS FALL 2023 [CONTROL ID: 3928849]
3. Lehmann, Self, Saito, and Yang “Pentablock Copolymer Membranes for Non-Aqueous Redox Flow Batteries” The Electrochemical Society meeting, ECS243, Boston, 2023
4. Yang, Lehmann, Self, Sacci, Saito, and Nanda. “Development of Cost-effective Membranes for Redox-flow Batteries” The Electrochemical Society meeting, ECS243, Boston, 2023

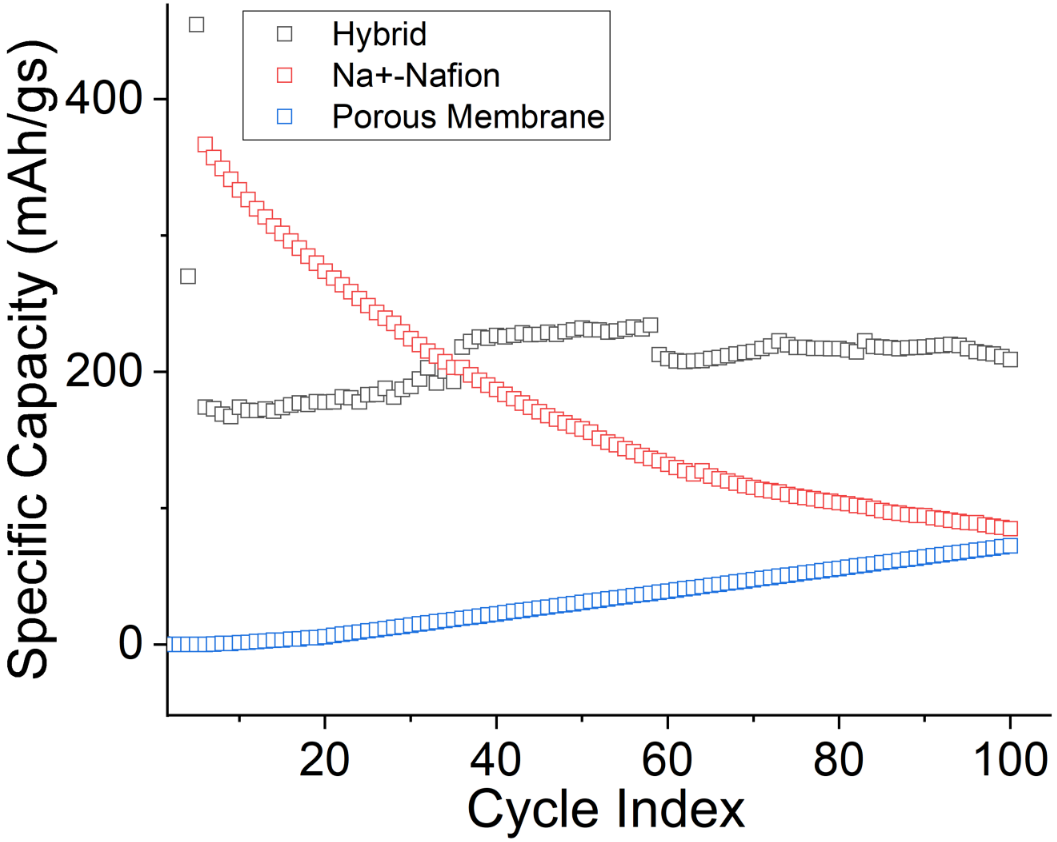
Partnership and opportunities with other DOE offices

1. Two industrial partners: Kraton Co. and Bettergy
2. AMMTO Redox Flow battery program led by ORNL on the new membrane architecture design

Thank you for your attention!

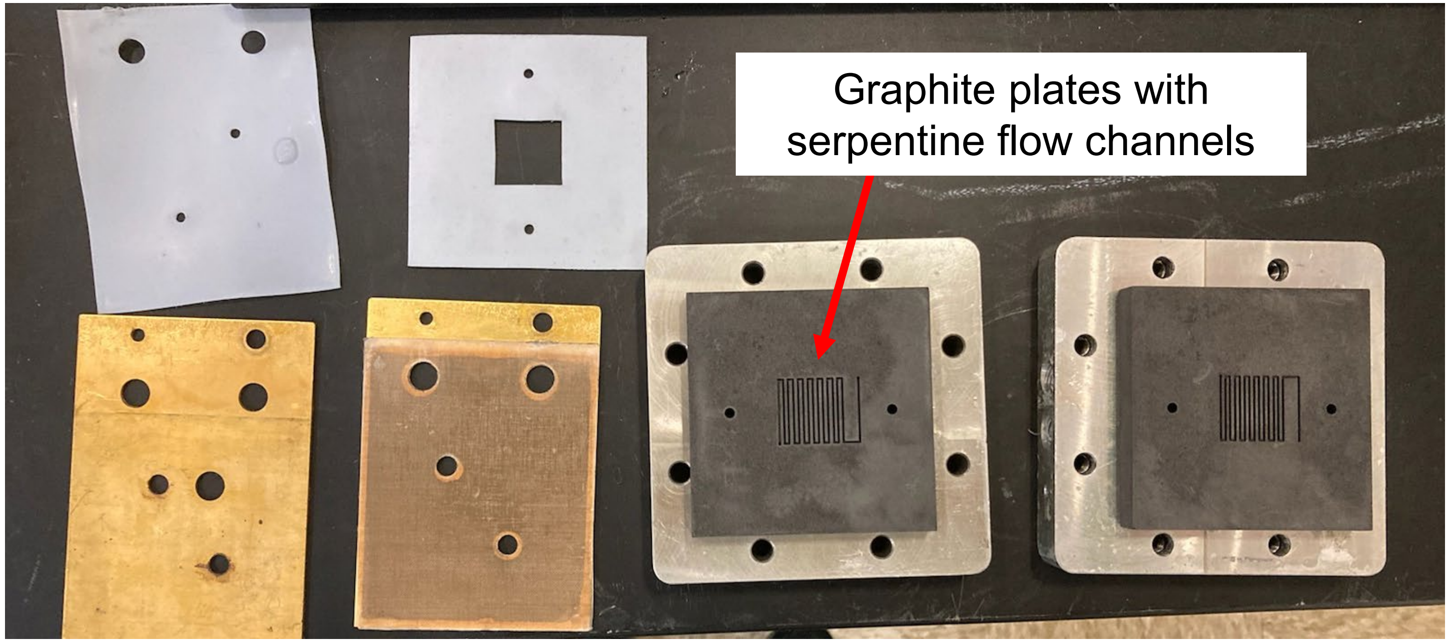
Technical Backup Slides

Comparison of the discharge capacity of the Na-Na2Sx batteries with various membranes



ORNL portfolio focuses on lab-scale prototypes for next-generation chemistries (TRL 1-3). Device optimization requires thorough investigations on all cell components.

Cell Hardware

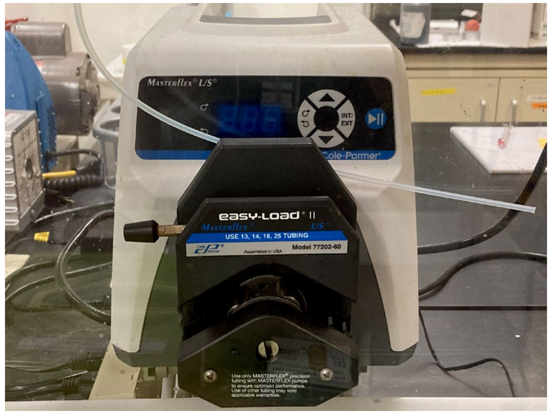


Porous Electrodes

1. Graphite felts (2-3 mm)
2. Carbon papers (200-400 μm)
3. Ni foam (1-2 mm)

Image: https://www.fuelcellstore.com/sigracet-36-aa

Peristaltic Pumps



Membranes

1. **Conventional** Nafion (211, 212, 117) in H^+/Na^+/K^+ forms
2. **Emerging** Composite membranes from industry (Bettergy Corp.)
3. **Next-Generation** Novel ionomers, crosslinked polymers, composites