Ambient Temperature Polysulfide-Based Redox Flow Batteries and Membrane Development

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ORNL is managed by UT-Battelle, LLC for the US Department of Energy

Thrust Area : Cost Competitive Energy Storage

(i) Development and demonstration of innovative battery and non-battery energy storage components

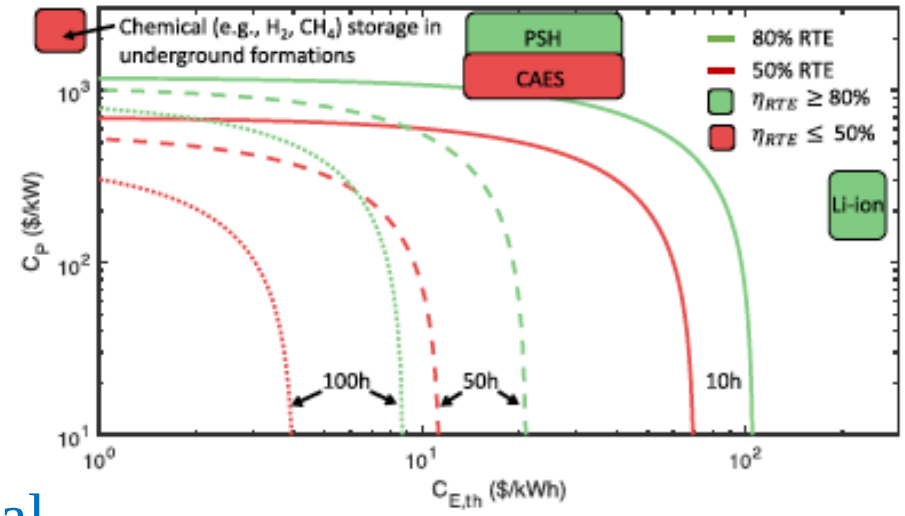
(ii) Research on novel materials and system components to resolve key cost and performance challenges for electrochemical energy storage systems based on earth abundant advanced chemistries.

Potential Use Case – Long Duration Energy Storage 10-100 Hrs at Rated Power

Key Requirements

- Low installed energy capital cost : 5-35 $/kWh
- Energy round trip efficiency (RTE) > 50%
- Provide multiple value streams : Enable several applications with a single, long operating-life asset

Requires low cost and high energy density chemical reactants



Relationship between power and energy capital cost for different RTE and chemistry

Albertus et.al. Joule, 4, 2020

PROJECT OBJECTIVE

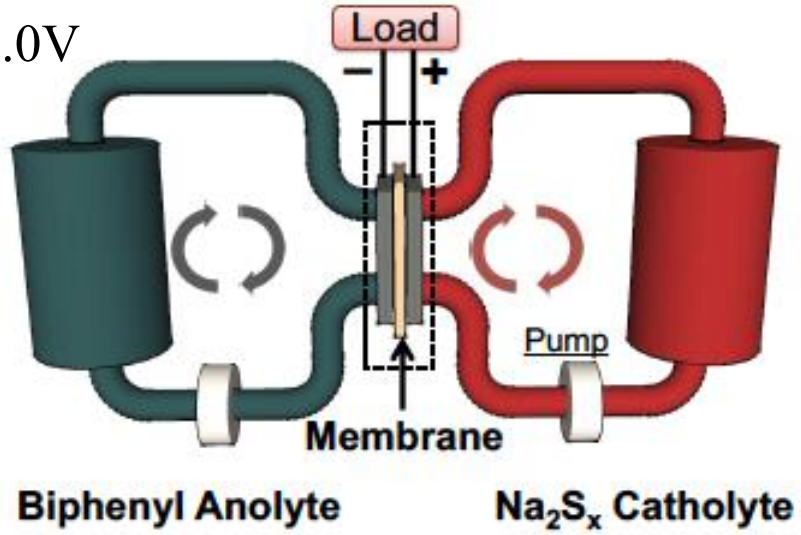
I. Demonstrate potential high energy density redox systems for long duration storage based on earth abundant materials.

II. Develop low cost and scalable approach membranes for non-aqueous redox flow batteries

We have developed a Na-polysulfide based redox flow cell as one of the viable low cost and high energy density systems

Na_2S_x Catholyte	$Na_2S_x \leftrightarrow Na_yS_x + (2-y)Na^+ + (2-y)e^-$	E_+ ~2.2V vs. Na/Na^+
Biphenyl Anolyte	$ß^0 + Na^+ + e^- \leftrightarrow Na^+ß^{\bullet -}$	E_- ~0.2V vs. Na/Na^+
Overall	$Na_2S_x + (2-y)ß^0 \leftrightarrow Na_yS_x + (2-y)Na^+ß^{\bullet -}$	E_{cell} ~ 2.0V

Supporting Electrolyte: 0.9m NaTFS in 2EGDME

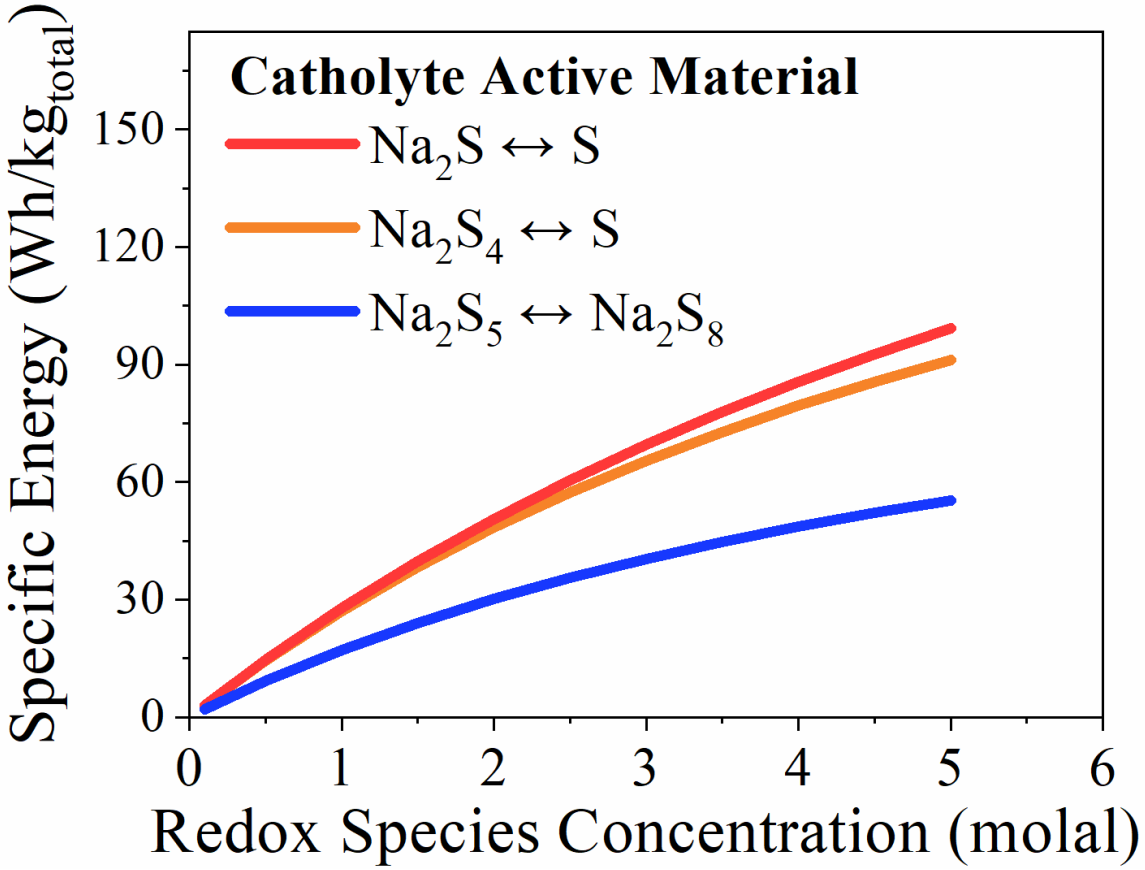


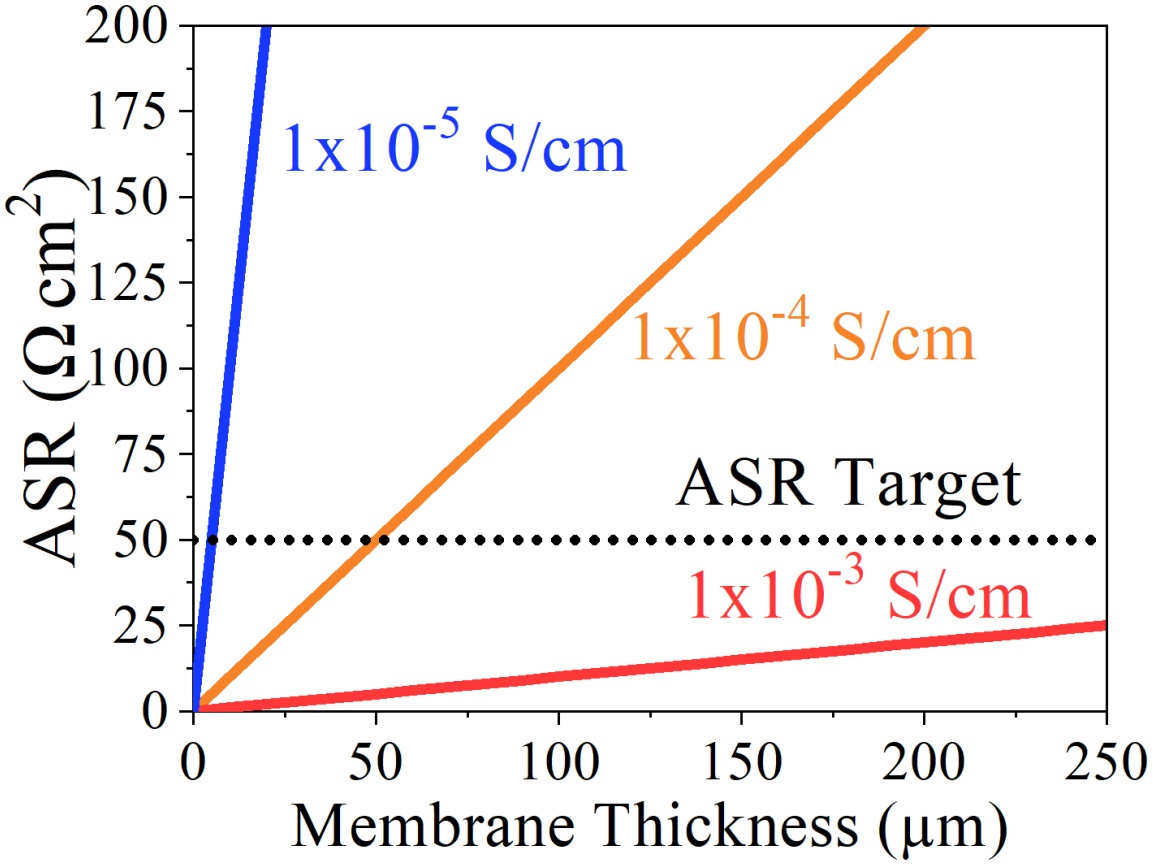
PROJECT METRICS AND MILESTONES

- Develop and test Na-polysulfide redox flow cell for long-duration energy storage
- Synthesize, fabricate, and optimize Na-ion based composite membranes
  - Targets: Na^+ conductivity > 10^{-4} S/cm; transference number t_+ > 0.7; Youngs modulus > 10 MPa
- Test membranes in redox flow system to study durability and mitigate degradation of membranes and redox species.
  - Target: Membrane area specific resistance (ASR) < 50 ohm-cm^2
- Test compatibility and chemical crossover of membrane separators for nonaqueous flow batteries

Metrics based on OE workshop organized by LANL-PNNL-ORNL-Sandia on Non-Aqueous Redox Flow Batteries, Santa Fe, NM-2019

Na_2S_x/biphenyl flow battery can achieve specific energies up to 100 Wh/kg (includes mass of redox species + salt + solvent). Power density can be improved by developing membranes with high Na^+ conductivity.

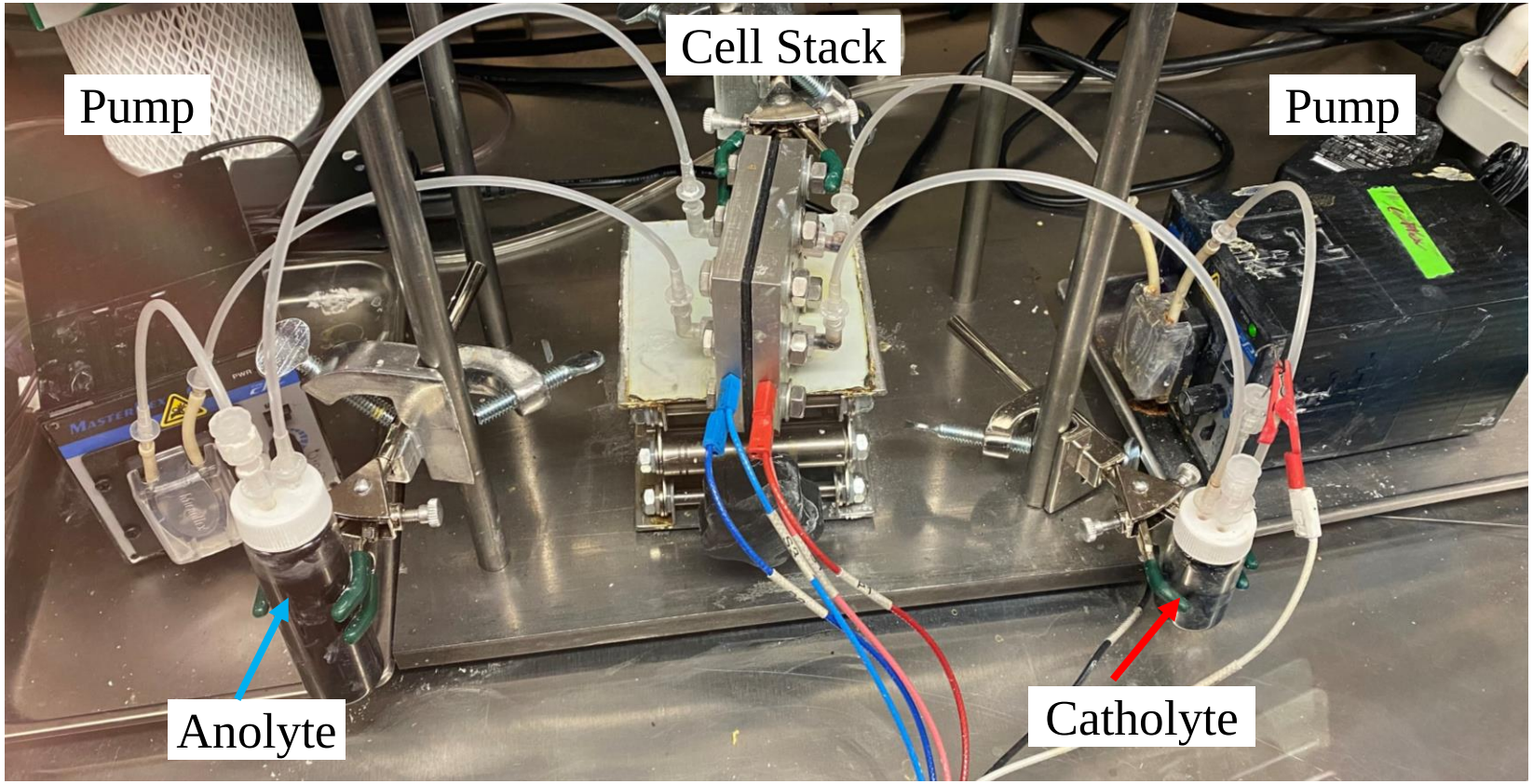




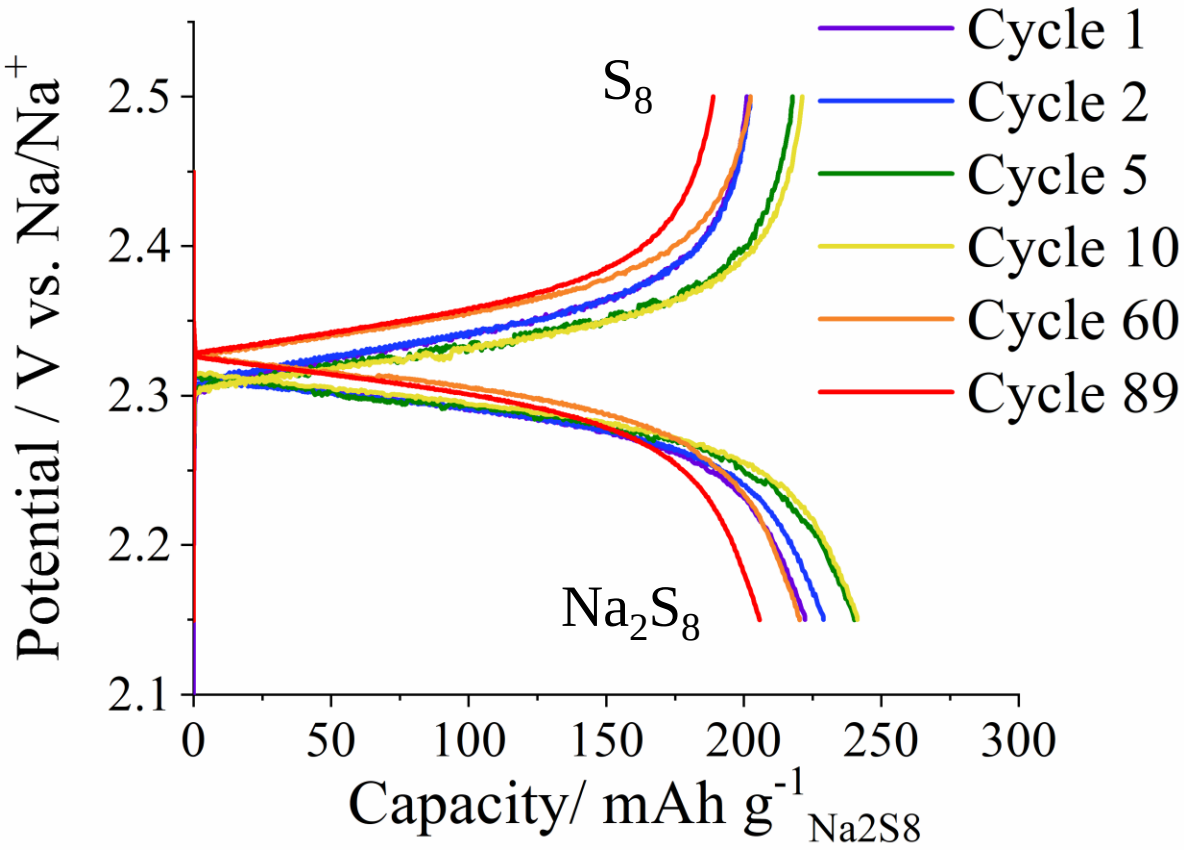
System's specific energy is highly dependent on redox species concentration and sulfur utilization.

Hardware was developed to benchmark the performance of polymer membranes and high energy anolytes/catholytes for nonaqueous redox flow batteries.

Nonaqueous Flow Cell Testbed

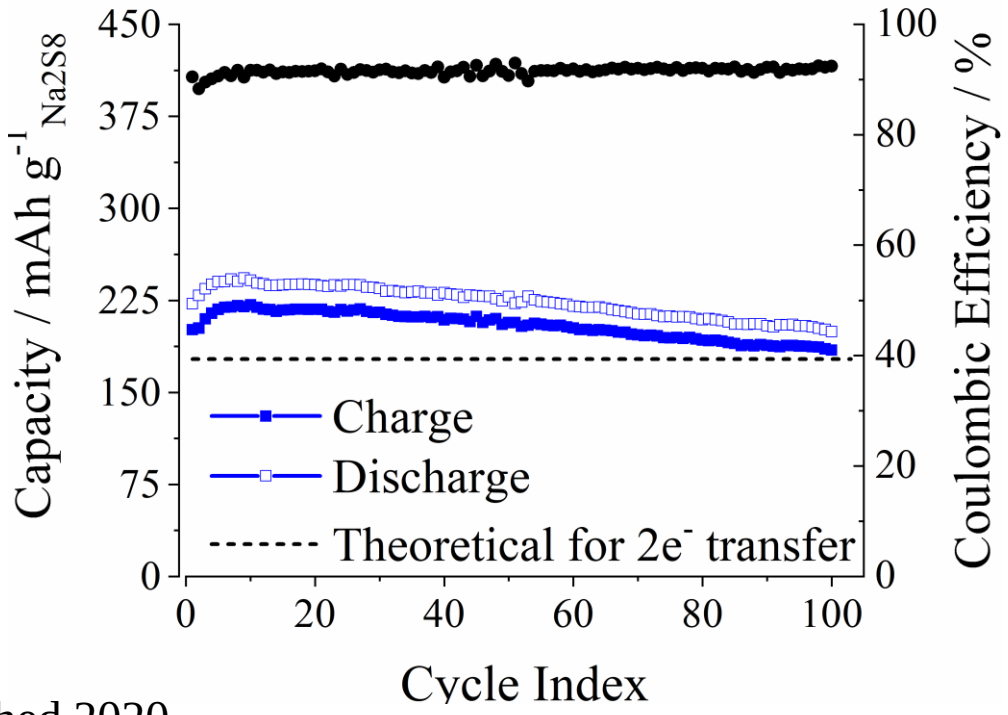


Sodium polysulfide/biphenyl RFB shows reversible capacity > 200 mAh/g_{Na2S8}. Ongoing work is focused on identifying irreversible reaction products during discharge.



Compartment	Redox Species*	Capacity (mAh)
Catholyte	Na_2S_8	2 (for 2 e^- process)
Anolyte	Biphenyl (ß)	100 (50-fold excess)

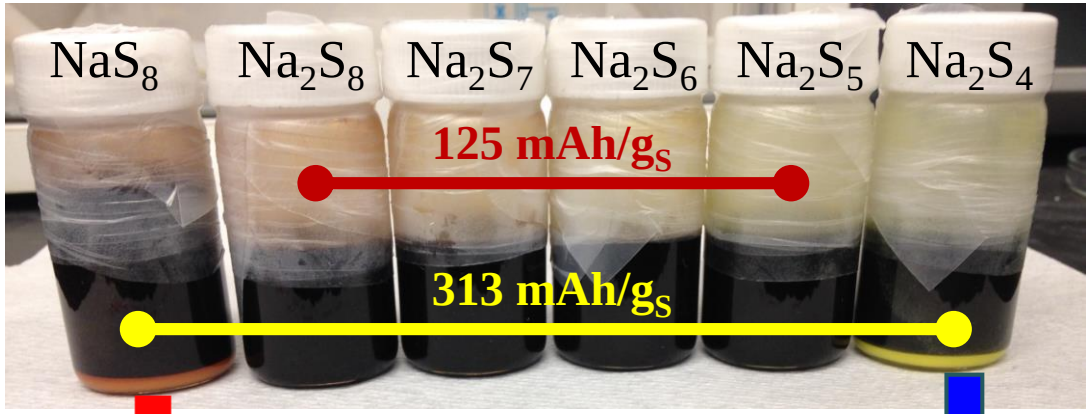
* Baseline Electrolyte = 0.9 m NaTFS in diglyme

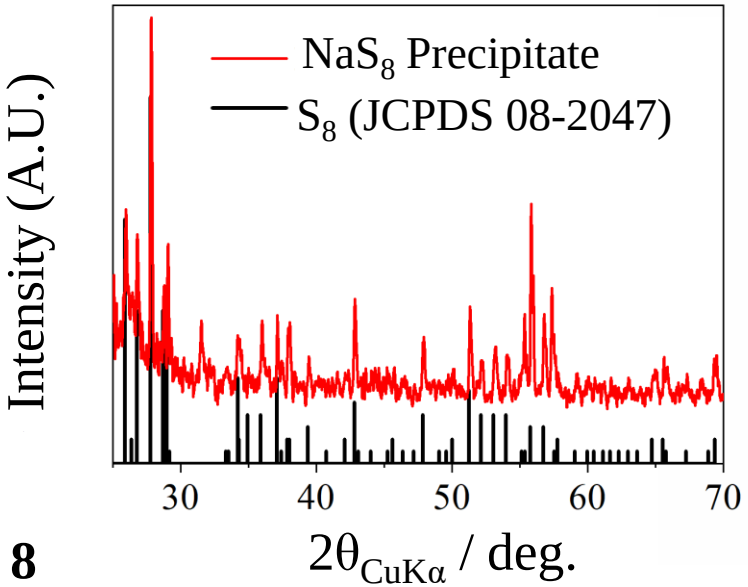


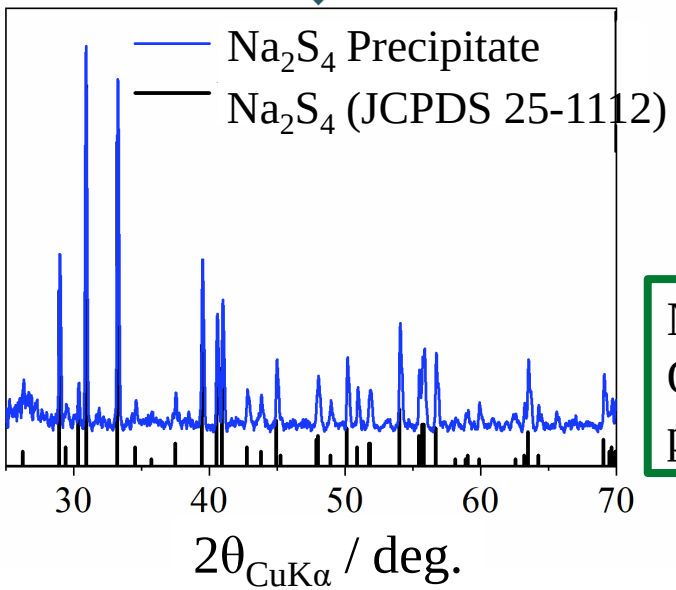
Unpublished 2020

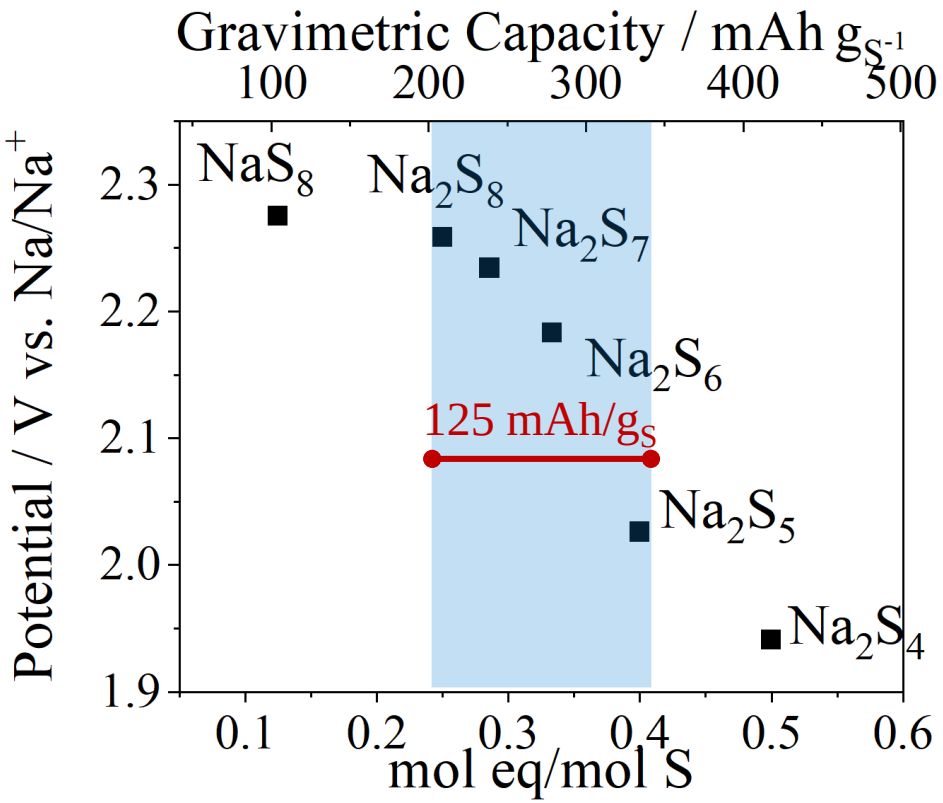
Energy density of sodium polysulfide (Na_2S_x) catholyte increases with sulfur utilization, but formation of insoluble phases during cycling (S/Na_2S_4) may inhibit flow cell performance.

Na_2S_x/2EGDME Polysulfide Solutions (0.2m)







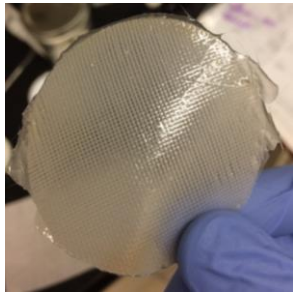


Na_2S_x is highly soluble in 2EGDME for $5 \leq x \leq 8$. Outside this window, formation of S and Na_2S_4 precipitates was confirmed using XRD.

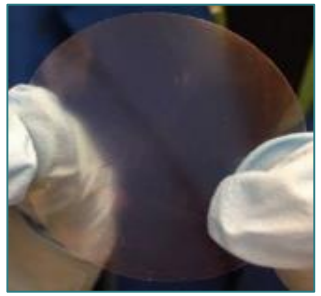
Several composite membranes have been fabricated for testing in nonaqueous flow batteries.

Membrane Type	Storage Modulus (MPa)	Max Tensile Stress (MPa)	Conductivity at 30°C (S/cm) with TEGDME	Transference Number
Crosslinked PEO-PEI	~1	1.34	1.76×10^{-4}	0.55
PEO Composite	1000	21	3.47×10^{-5}	<0.5
Nexar Ionomer	1800	20	1.25×10^{-4}	**>0.9**

Crosslinked PEO-PEI



PEO-Glass Fiber Composite



Nexar Ionomer (single-ion conductor)

PEO-based membranes

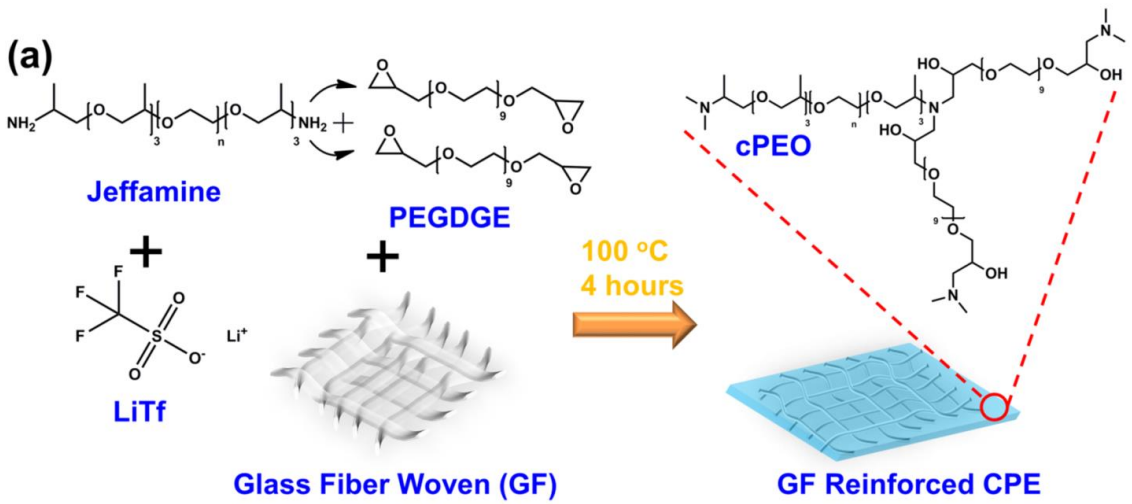
- ❖ Advantages
  - Low cost
  - Single step fabrication
  - Tailored mechanical strength (reinforced by glass fiber)
  - Good ionic room temp conductivity

Nexar Ionomer

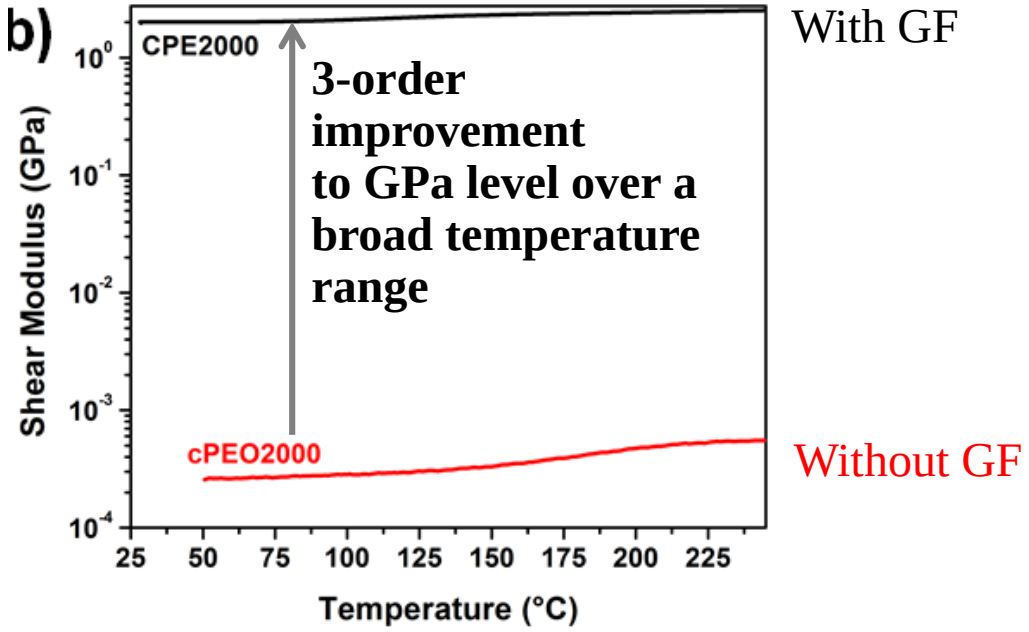
- ❖ Advantages
  - Commercially available (Kraton polymers)
  - High transference number (>0.9) **(improved ion selectivity)**
  - Excellent mechanical properties
  - Good room temp conductivity

Ultra-strong polymer inorganic membrane developed and tested in FY19/20.

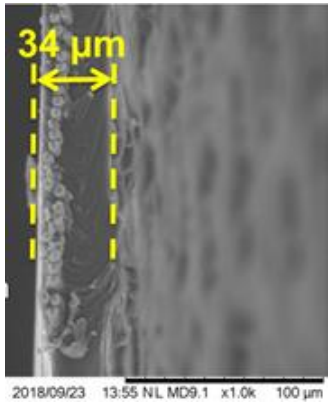
One-step crosslinking synthesis – glass fiber reinforced PEO



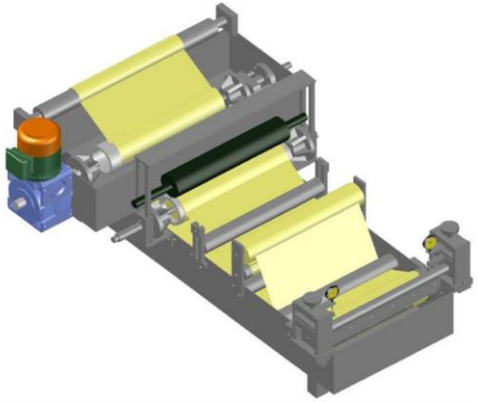
GPa level moduli



Reduced Thickness



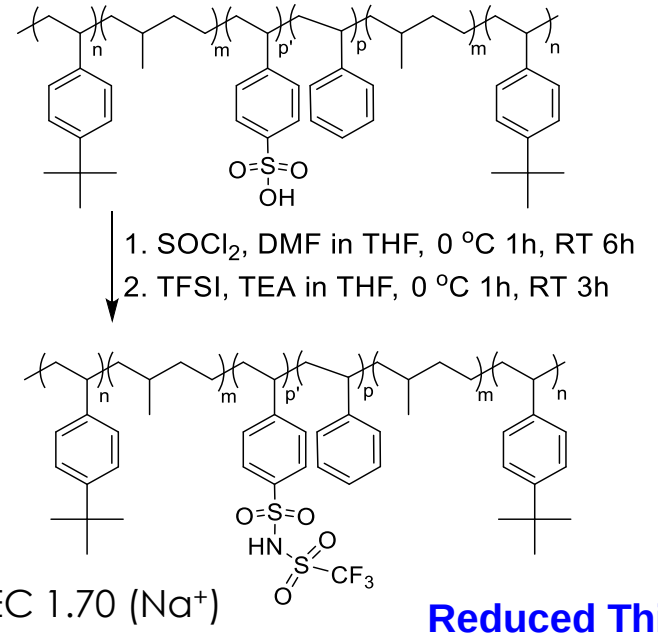
Compatible with Roll-2-Roll



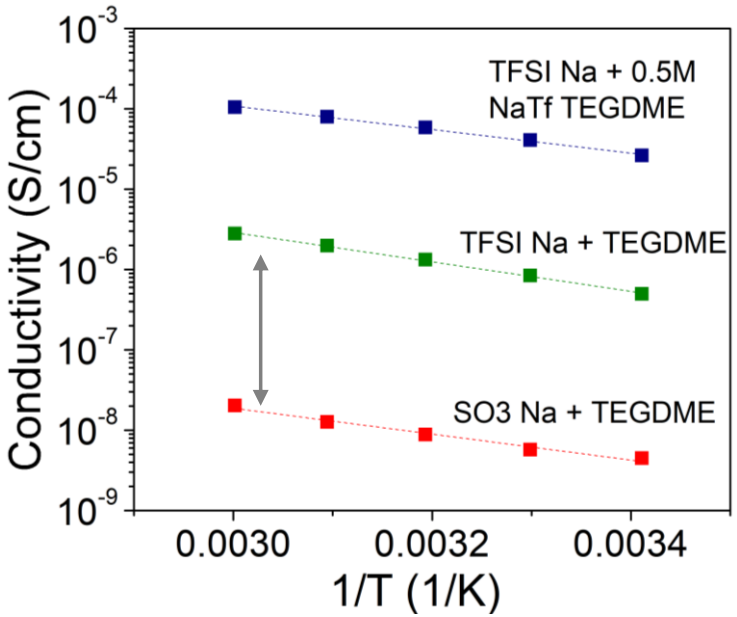
- Boosted storage moduli
- Reduced cell internal resistance due to reduced thickness
- Low-cost and scalable

Membrane Design- Improve ion selectivity by designing single-ion conductor membranes

Conversion to TFSI for increased conductivity



IEC 1.70 (Na^+)

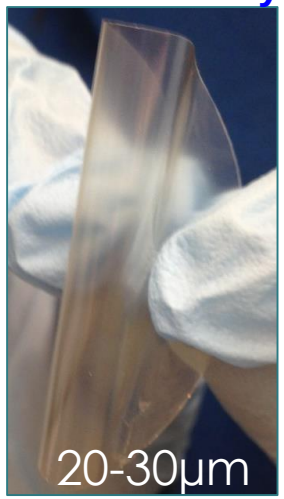


~10^{-4} S/cm ionic conductivity in electrolyte

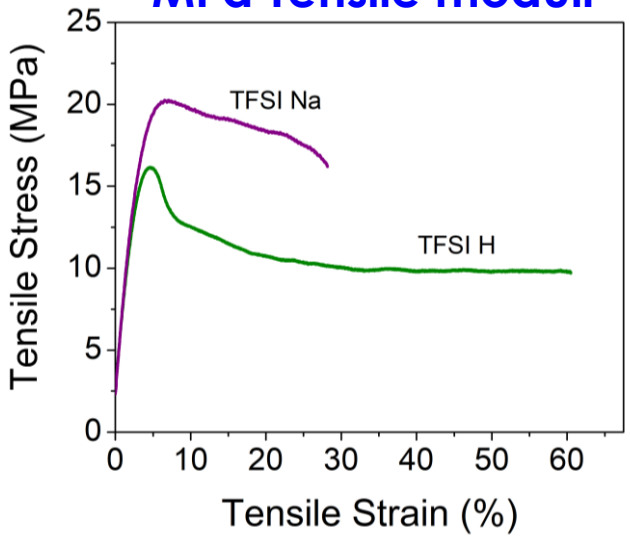
2-order conductivity increase with conversion to TFSI

Free Standing Film

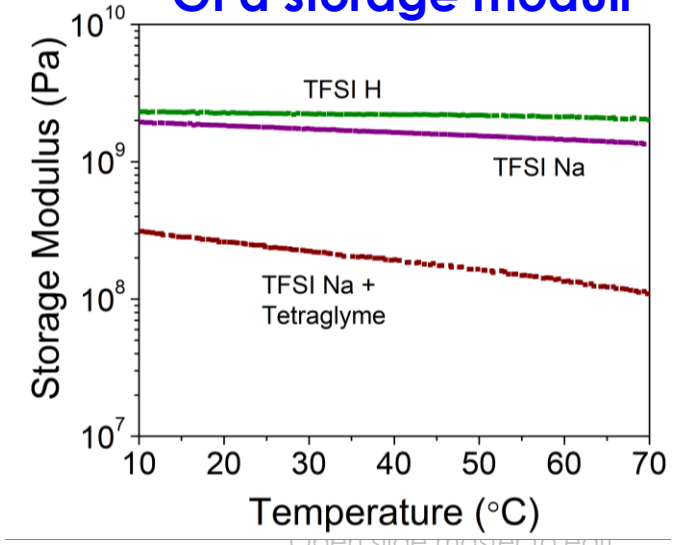
Reduced Thickness with Flexibility



~MPa Tensile moduli



~GPa storage moduli



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Lehmann, M.L., Nanda, et al. Electrolyte Concentration Dependence of Ion Transport in Pentablock Copolymer Ion Exchange Membranes. *In preparation*

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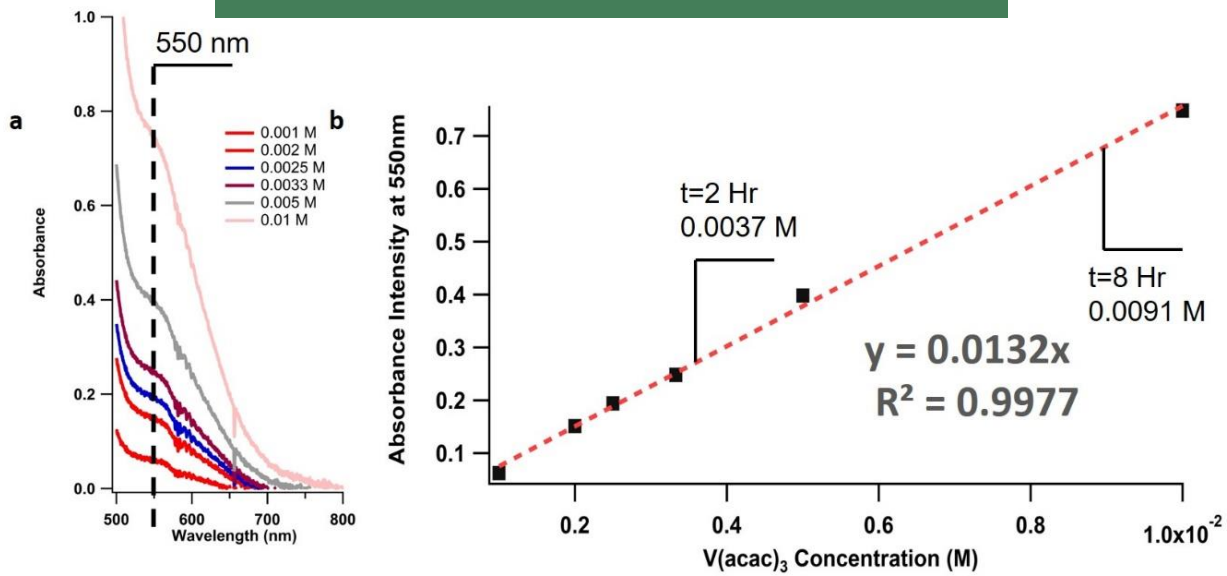
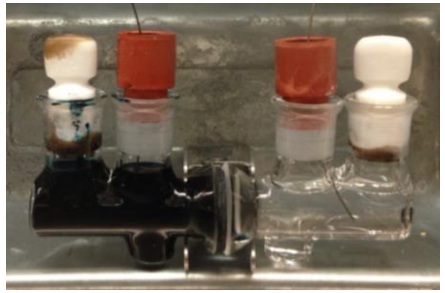
Based on the calibration methods developed in FY19, crossover testing for various membranes are in progress.

Concentration calibration curve

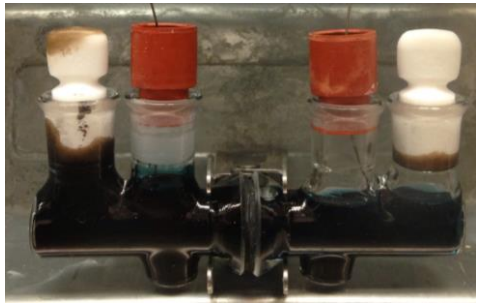


- The absorbance intensity at 550 nm increases linearly with TEA-V(acac)$_3$) concentration in acetonitrile
- The calibration curve correlates a measurable value (UV absorbance) to an unknown parameter (redox species concentration)

Membrane Permeability Measurements



Initial Configuration



Redox Species Crossover

Membranes for Testing (In Progress)

1. Commercial Na^+ ß" Al_2O_3 ceramic (Ionotec)
2. Crosslinked PEO and PEO/glass fiber composites
3. Na^+ conducting pentablock copolymer (Nexar®)
4. Thin ceramic membranes (<500 µm) from SNL (E. Spoerke) and PNNL (G. Liu)

Key Accomplishments – FY20

High Energy Anolytes and Catholytes for Nonaqueous Flow Batteries

- Na_2S_x/biphenyl RFB can achieve up to 100 Wh/kg depending on redox species concentration and S utilization.
- System exhibits outstanding cycling stability in a laboratory prototype cell
- Formation of insoluble phases (S and Na_2S_4) in cell stack does not compromise cycle life or reversibility under conditions investigated

Developed Mechanically Robust Polymer Composite Membranes with High Na^+ Conductivity

- Low cost and scalable membrane design approach
- Mechanical properties can be boosted by inorganic reinforcement (e.g., nonwoven glass fibers) > 10 MPa
- High room temperature ionic conductivity (e.g., $1x10^{-4}$ S/cm at room temperature)

Future Work –FY21

Na^+-Conducting Membrane Development

- Synthesize new ionomer materials (e.g., **Nexar Ionomer**) with an emphasis on mechanical strength, selectivity, and chemical stability with NRFB electrolytes
- Improve ionic conductivity and mitigate redox species crossover

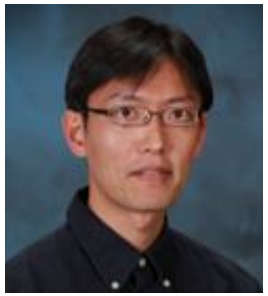
Nonaqueous Flow Battery Testing

- Crossover measurements will benchmark the performance of various polymer and ceramic membranes
  - **Targets**: ASR < 50 $\Omega\,cm^2$ with minimal crossover rates to enable balanced cell cycling for months/years
- Effect of higher concentrations on cell performance will be investigated
- Technoeconomic analysis will compare cost and energy density of various NRFB chemistries.

PROJECT TEAM

PI: Jagjit Nanda

Frank Delnick



Tomonori Saito

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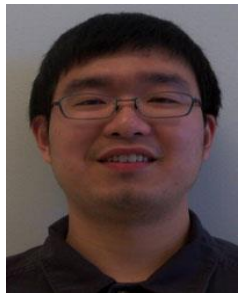

Kun Lou

External Collaborators FY19/20

- Vijay Murugesan and Wei Wang, PNNL – Membrane Characterization
- R. Mukundan, LANL – Ceramic composite membranes
- Vish Viswanathan and P. Balducci - Techno-economic Modeling
- Eric Spoerke and Cy Fujimoto, Sandia – Membranes for RFB's

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PROJECT RESULTS

Publications and Patents – FY20

1. E. C. Self, F. M. Delnick, R. E. Ruther, J. Nanda, High Capacity Organic Radical Mediated Phosphorus Anode for Sodium Based Redox Flow Batteries ACS Energy Lett. 4 (11), 2593-2600, 2019
2. M. Lehmann, G. Yang, J. Nanda and T. Saito, Well-designed Crosslinked Polymer Electrolyte Enables High Ionic Conductivity and Enhanced Salt Solvation, J. Electrochem. Soc. 167, 070539, 2020
3. G. Yang et. Al. Anomalously High Elastic Modulus of a Poly(ethylene oxide)-Based Composite Electrolyte, Energy Storage Materials. 2020 (under revision)
4. B. Lee, M. Kim, S. Kim, J. Nanda, S. J. Kwon, H. D. Jang, D. Mitlin, S. W. Lee, High Capacity Adsorption – Dominated Potassium and Sodium Ion Storage in Activated Crumpled Graphene, Advanced Energy Materials, 1903280, 2020
5. F. Perras, S. Hwang, Y. Wang, E. Self, P. Liu, R. Biswas, S. Nagarajan, V. H. Pham, Y. Xu, J. Boscoboinik, D. Su, J. Nanda, M. Prusik, D. Mitlin, Site-Specific Sodiation Mechanisms of Selenium in Microporous, Nano Letters, 20, 918, 2020
6. P. Liu, Y. Wang, Q. Gu, J. Nanda, J. D. Watt, D. Mitlin, Dendrite-Free Potassium Metal Anodes in a Carbonate Electrolyte Adv. Mater**.** 2019, 1906735
7. F. M. Delnick, J. Nanda, E. C. Self**,** High Capacity Organic Radical Mediated Phosphorus Anode for Redox Flow Batteries, US. Patent App. No. US 2020/0028197 A1, (Published Jan. 23, 2020)
8. J Nanda, G Yang, F M Delnick, T Saito, Mechanically Robust Ion Conducting Membranes For Redox Flow Batteries. (Invention Disclosure #:201804195 – ORNL- Feb 2020)

Acknowledgment

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

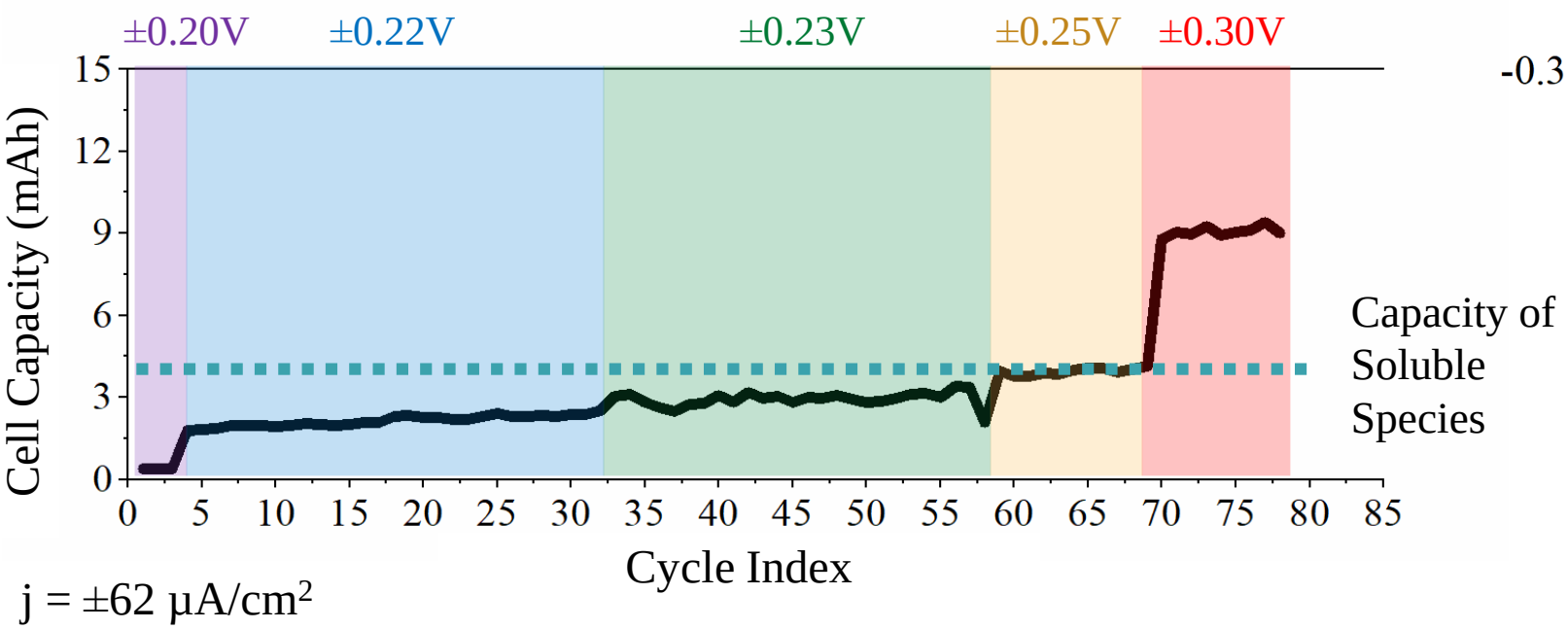
Michael Starke, Thomas King – ORNL
Vince Sprenkle – PNNL
Babu Chalamala – Sandia

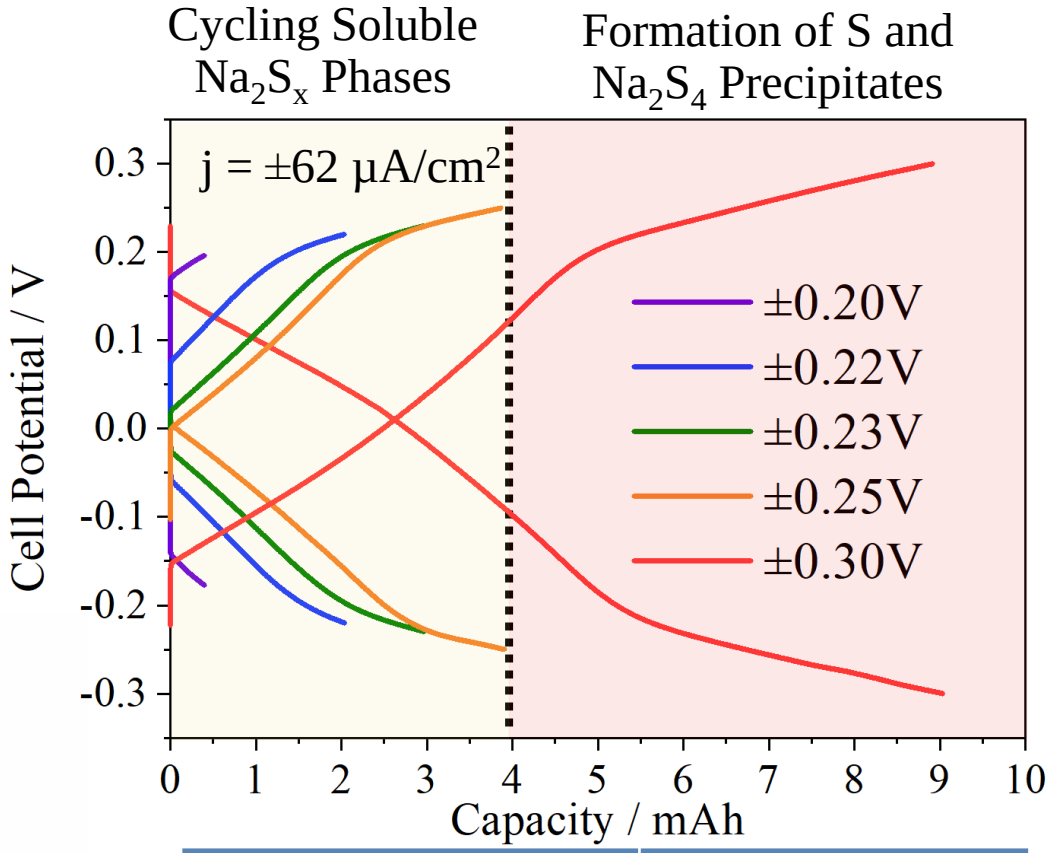
Additional Slides

A symmetric Na_2S_x/Na_2S_x RFB was tested to evaluate catholyte reversibility. System exhibits outstanding cycling stability even when insoluble phases (S and Na_2S_4) are formed in the cell stack.

Experimental Details (Symmetric Cell)

Redox Couple: 50% SOC Na_2S_x on each side **(N/P = 1.00)**
Supporting Electrolyte: 0.9 m NaTFS/2EGDME
Membrane: Na^+ß" Al_2O_3 (1 mm thick)





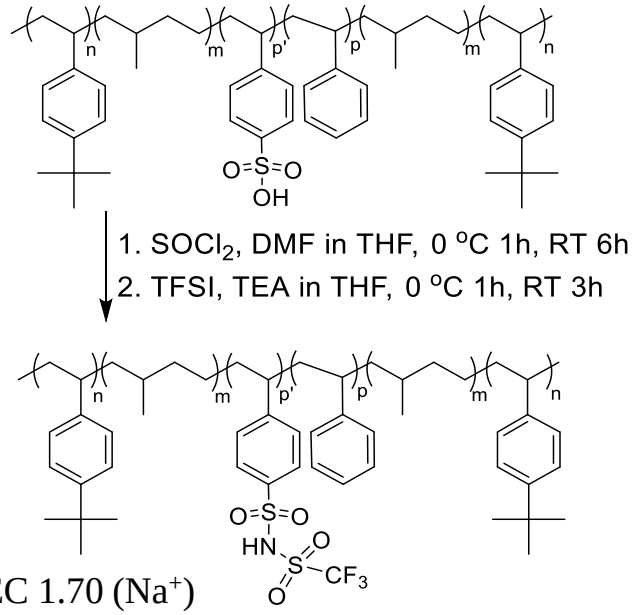
Cutoff Potential (V)	CE (avg ± stdev)
0.20	100.3 ± 0.01%
0.22	100.8 ± 2.7%
0.23	100.5 ± 1.8%
0.25	100.5 ± 1.8%
0.30	101.5 ± 3.9%

* Large standard deviation in CE is caused by cutoff potential falling on voltage plateau

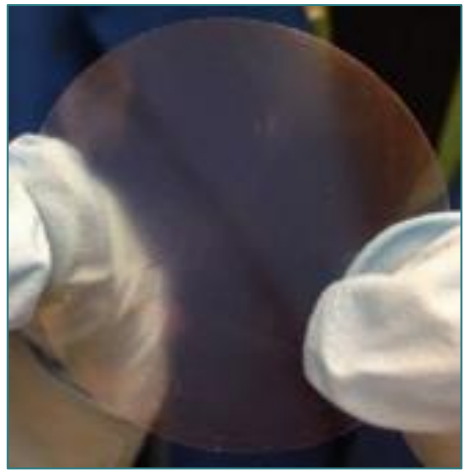
Stable capacity of a balanced Na_2S_x symmetric cell (N/P = 1.00) indicates irreversible reactions are minimal over the investigated cycling conditions.

Membrane Design- Improve ion selectivity by using single-ion conductors.

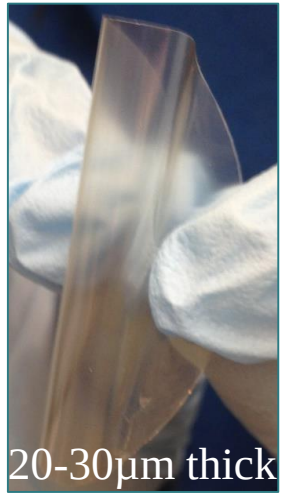
Conversion to TFSI for increased conductivity



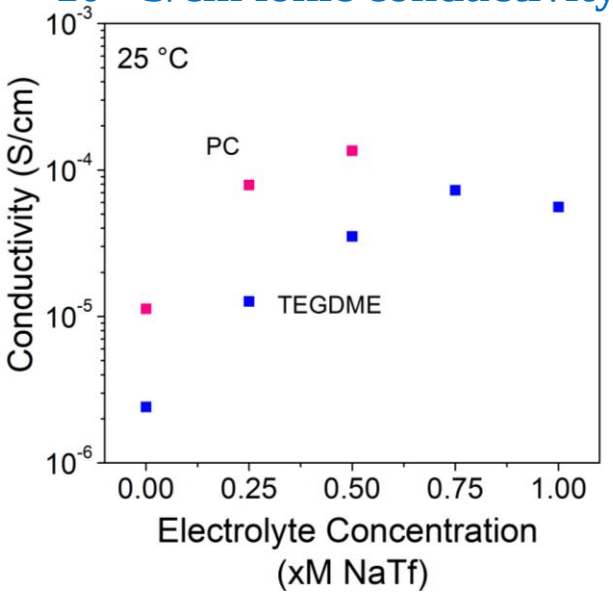
Freestanding Film



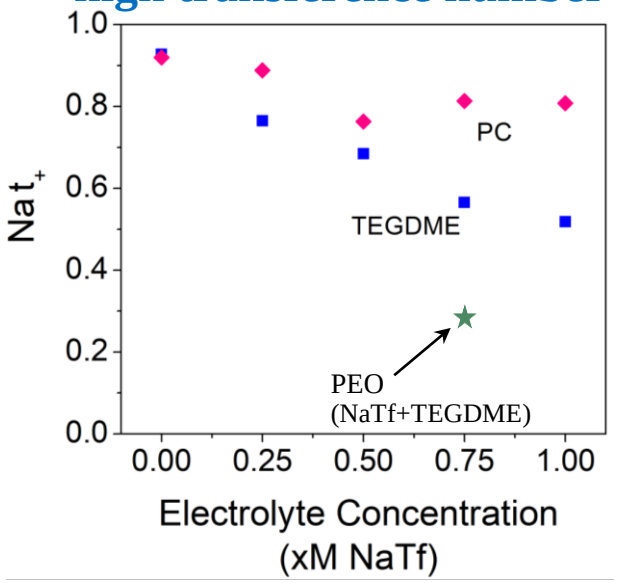
Flexible, Thin Membrane



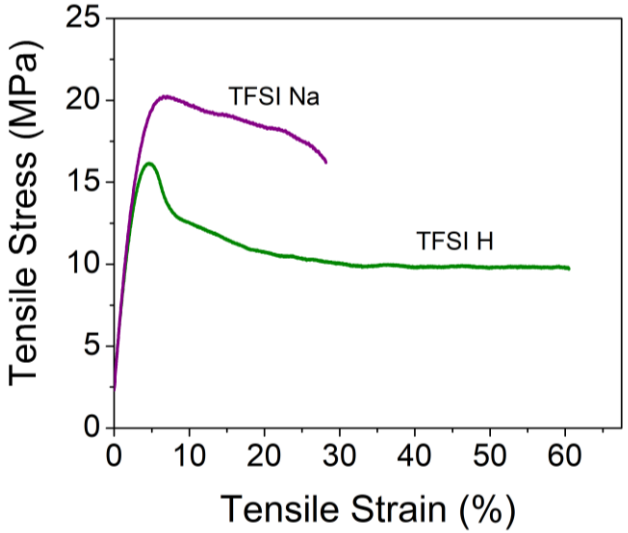
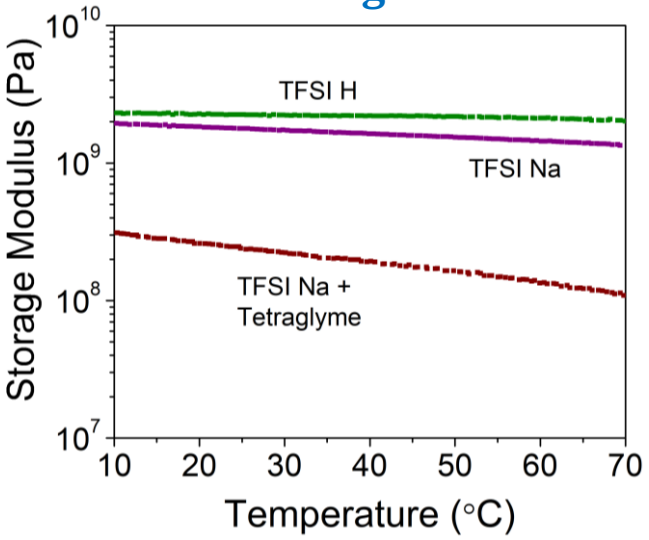
~10^{-4} S/cm ionic conductivity



high transference number



~GPa tensile moduli



~GPa storage moduli