OAK RIDGE National Laboratory

Low Cost Membranes for High Energy Density Non-aqueous Redox Flow Batteries

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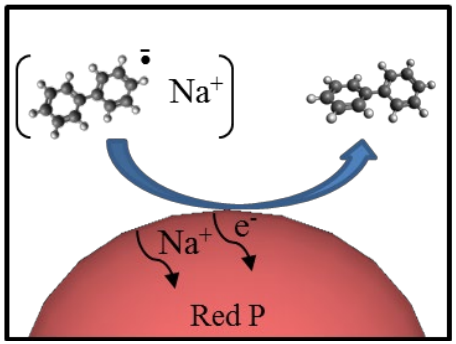
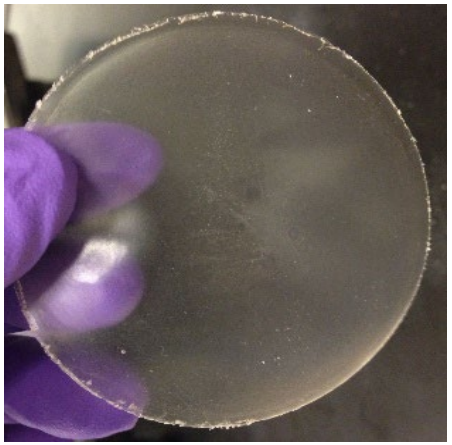
ORNL is managed by UT-Battelle, LLC
for the US Department of Energy

U.S. DEPARTMENT OF ENERGY

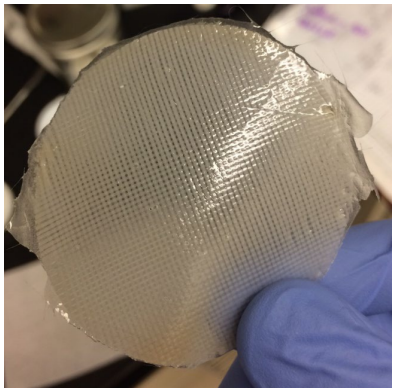
Summary of Accomplishments: FY18

- Demonstrated a high energy density anode for a nonaqueous redox flow battery
  - Arene anion radical mediators (< 1 V vs. Na/Na^+)
  - Red phosphorus (1,000+ mAh/g)
- Developed low cost membranes for non-aqueous RFBs
  - PEO-CMC plasticized with tetraglyme
  - Crosslinked PEO
  - PEO Reinforced with Glass Fiber Mat

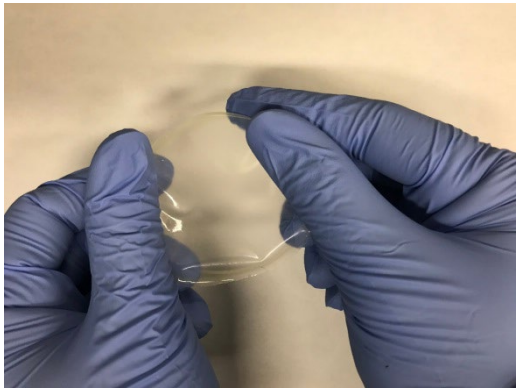




Crosslinked PEO



PEO-Glass Fiber Composite



Stretchable Ionomer

Arene anion radicals were identified to mediate reversible Na storage in P anode

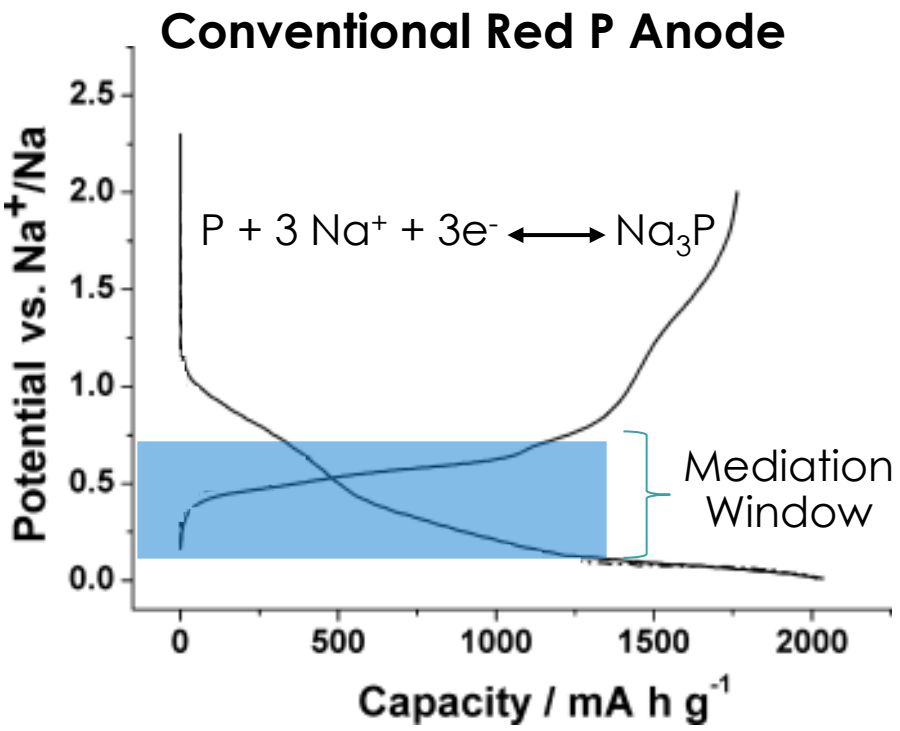
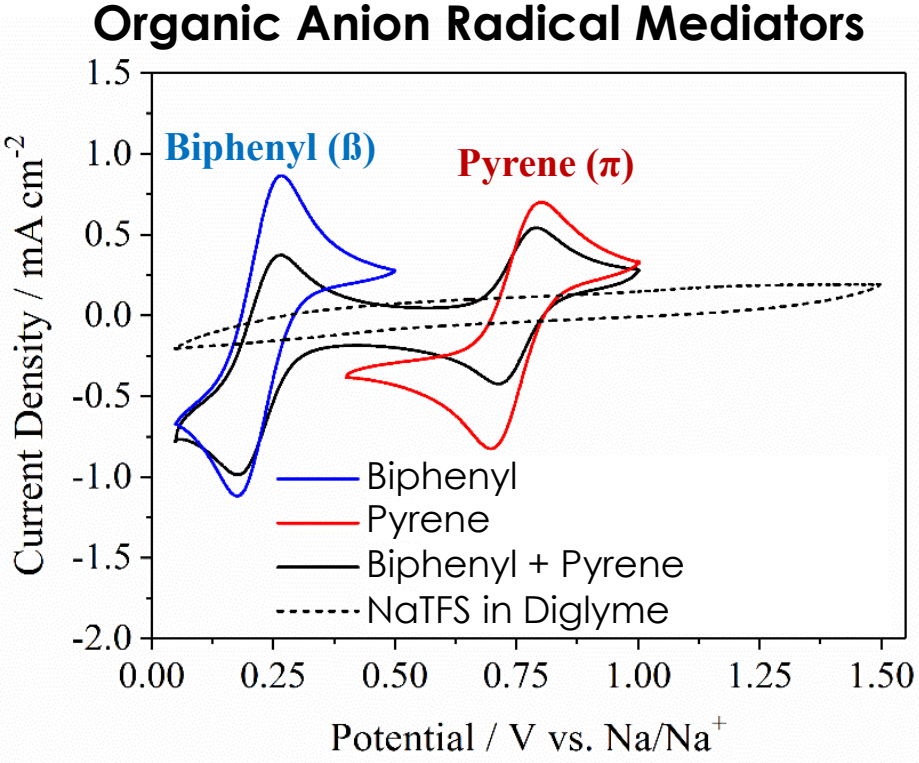


Image adapted with permission from *Angew. Chem.* **2013**, 125, 4731



Charge: $P + 3\ (Na^+ß^{\bullet-}) \longrightarrow Na_3P + 3\ ß^0$

Discharge: $Na_3P + x\ \pi^0 \longrightarrow Na_{3-x}P + x\ (Na^+\pi^{\bullet-})$

Theoretical Capacity: 2,596 mAh/g_P (Na_3P)

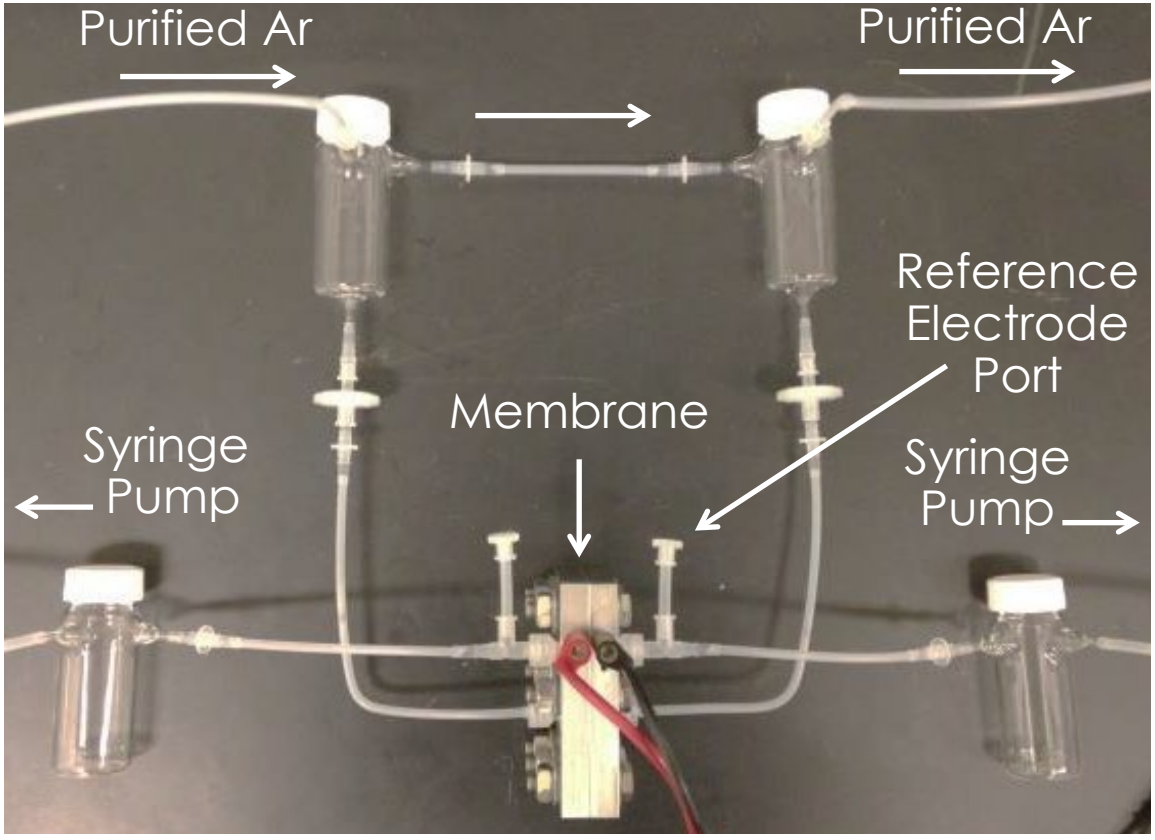
Self et al., Submitted, 2018

A custom redox flow cell was designed to demonstrate a mediated red phosphorus anode

Cell Components:

Working/Auxiliary Electrodes: Porous Ni foam
Reference Electrode: Na in 1 m NaTFS (TEGDME)
Membrane: Na^+ß" Al_2O_3 Ceramic (Ionotec, 45 x 45 x 1.5 mm^3)

Serpentine Flow Channels



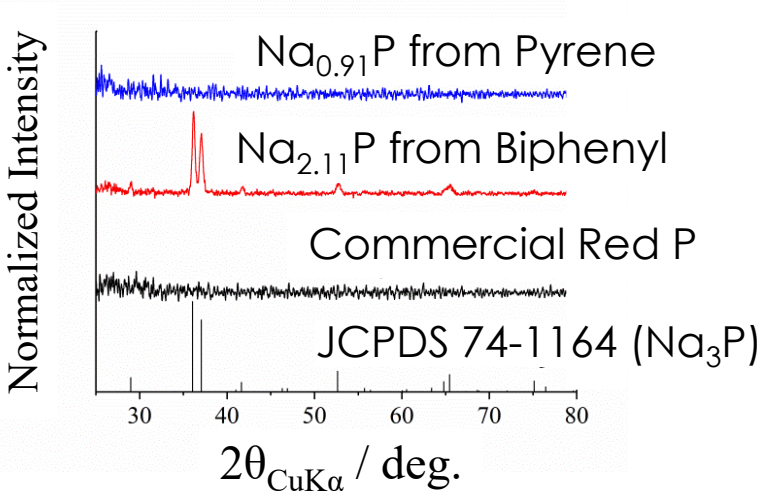
Flow Cell (connected to potentiostat)

ORNL IP filed August 2017

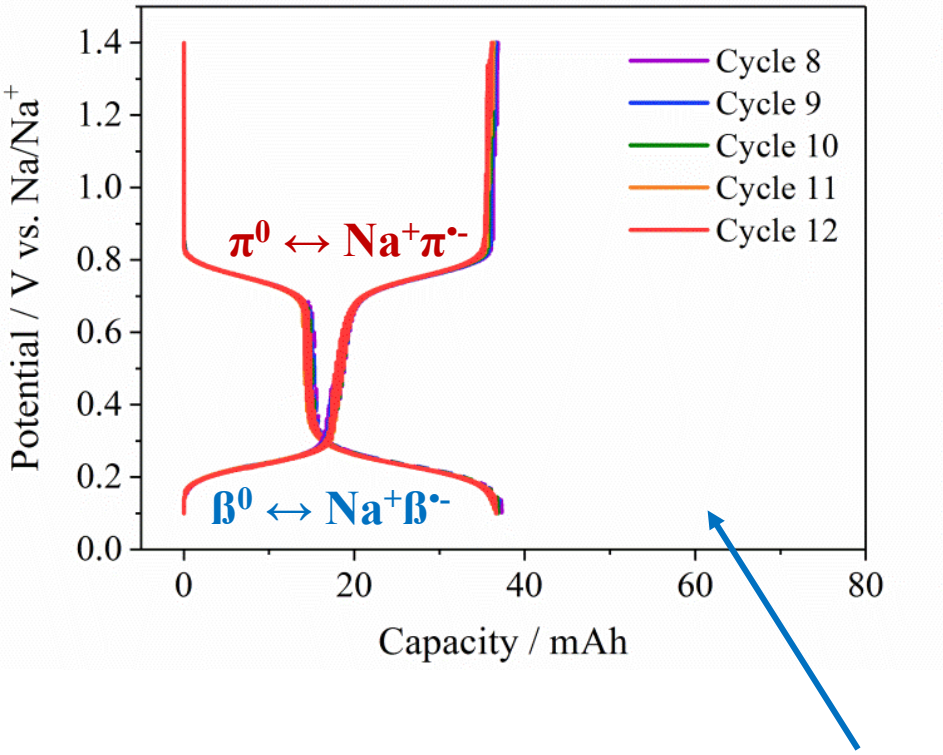
Reversible Na storage in a red phosphorus anode via electrochemical mediation was successfully demonstrated

Electrolyte: Sodium triflate in diglyme solvent
Biphenyl (charging mediator)
Pyrene (discharging mediator)
Red Phosphorus

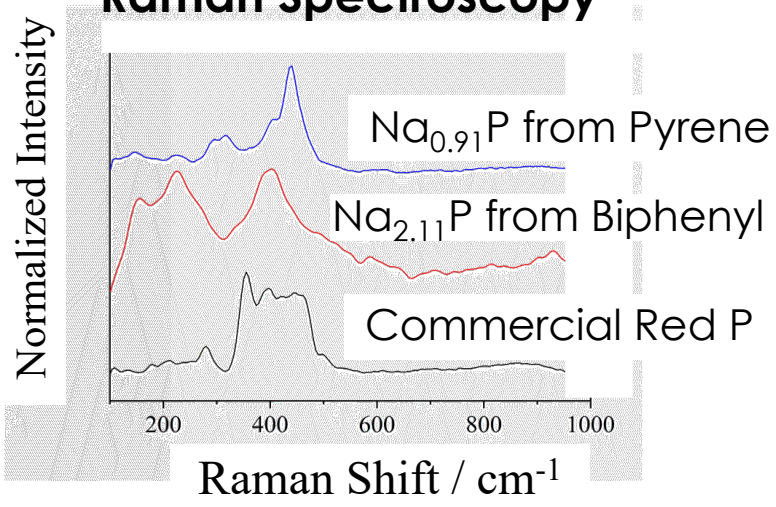
XRD



Cycling Mediators Only



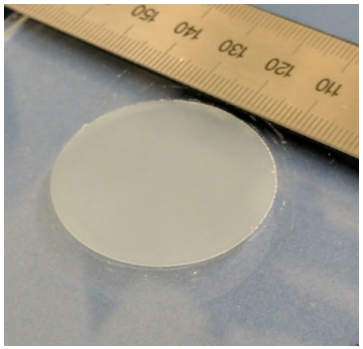
Raman Spectroscopy



Phosphorus Capacity ~ 1,800 mAh/g ($Na_{2.11}P$)

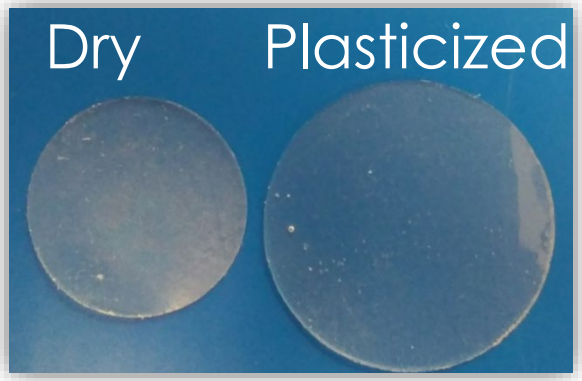
Several synthesis routes were developed to produce low cost polymer membranes for Na-based, nonaqueous flow batteries

Linear PEO + CMC[1]



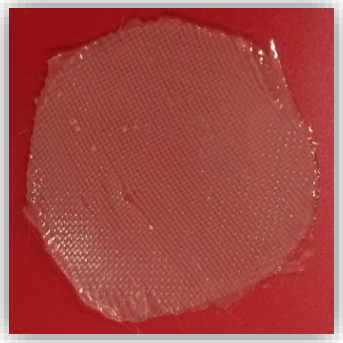
Blended CMC phase improves mechanical properties

Crosslinked PEO [2]



Plasticization with TEGDME yields high conductivity but limited mechanical integrity

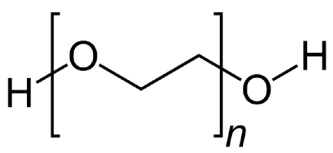
Crosslinked PEO + Glass Mat Reinforcement [3]



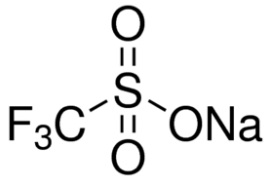
Reinforcing crosslinked PEO with a glass fiber mat provides unprecedented strength and high conductivity

[1] Ruther et al., *ACS Energy Lett.*, **2018**.
[2] Lehmann et al., *J. Mater. Chem. A*, **2018** (Under Review).
[3] Yang et al., Unpublished, **2018**

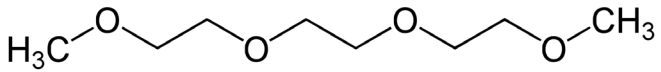
Adding 5 wt% CMC to a plasticized PEO membrane improves the mechanical properties without sacrificing conductivity



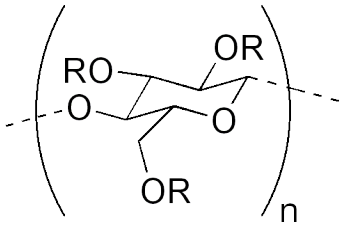
PEO



NaTFS



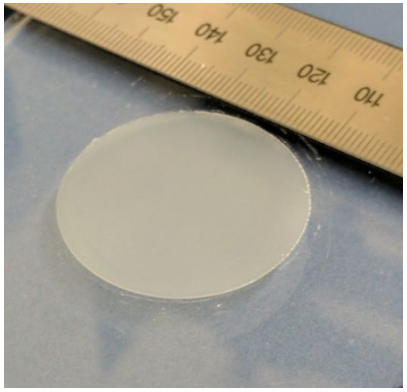
TEGDME

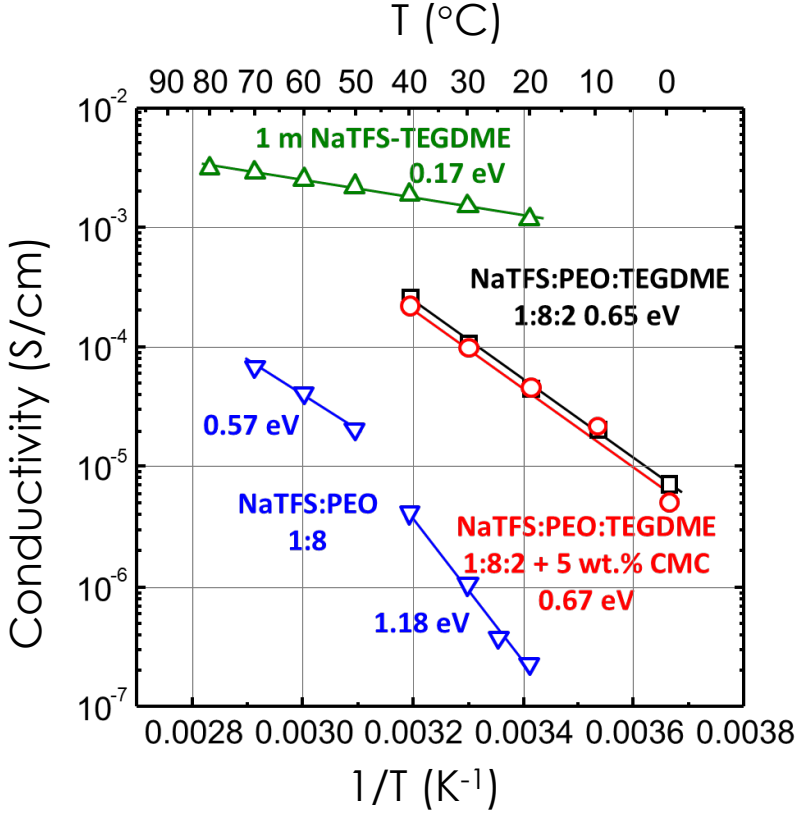


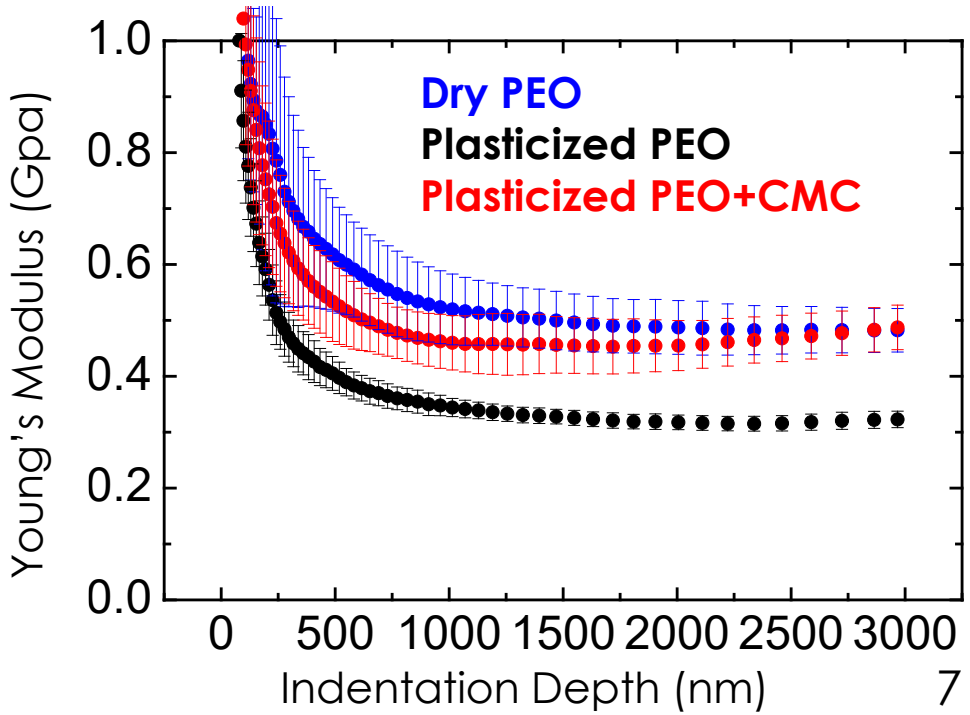
R = H or CH_2CO_2Na

CMC

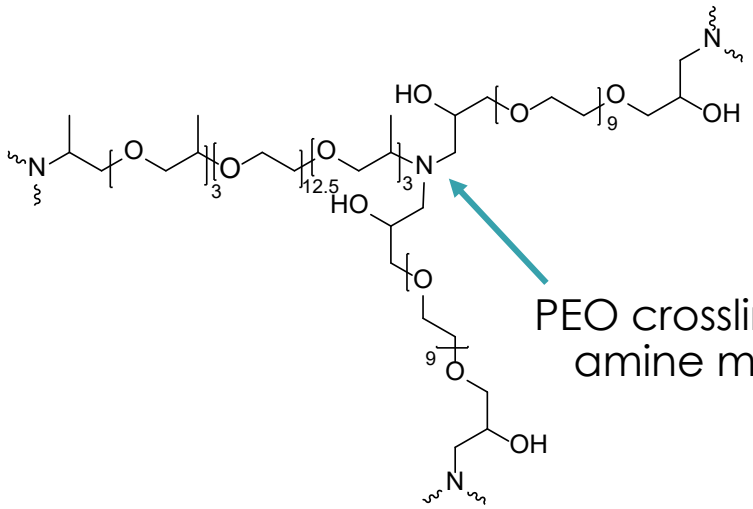
NaTFS-PEO-TEGDME

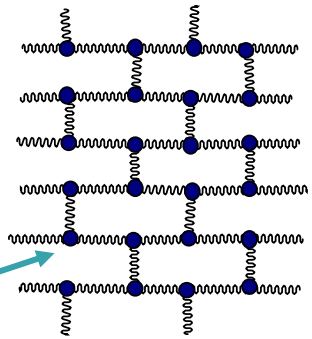


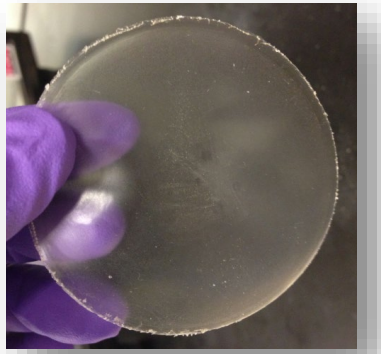


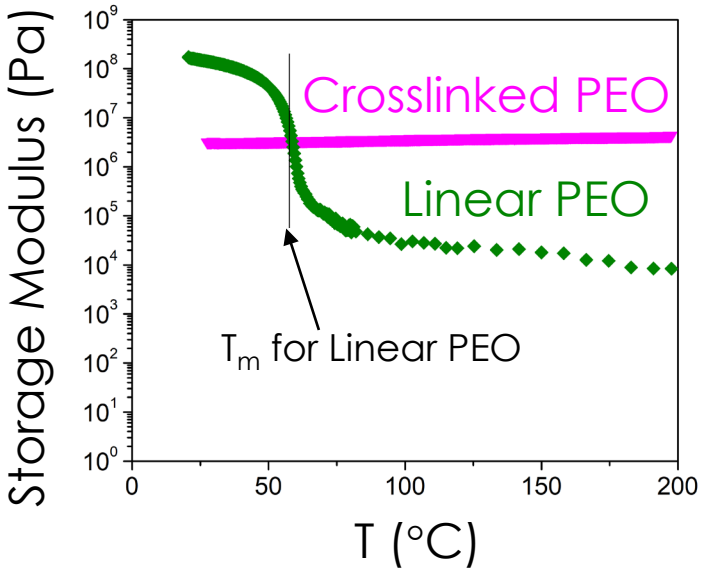


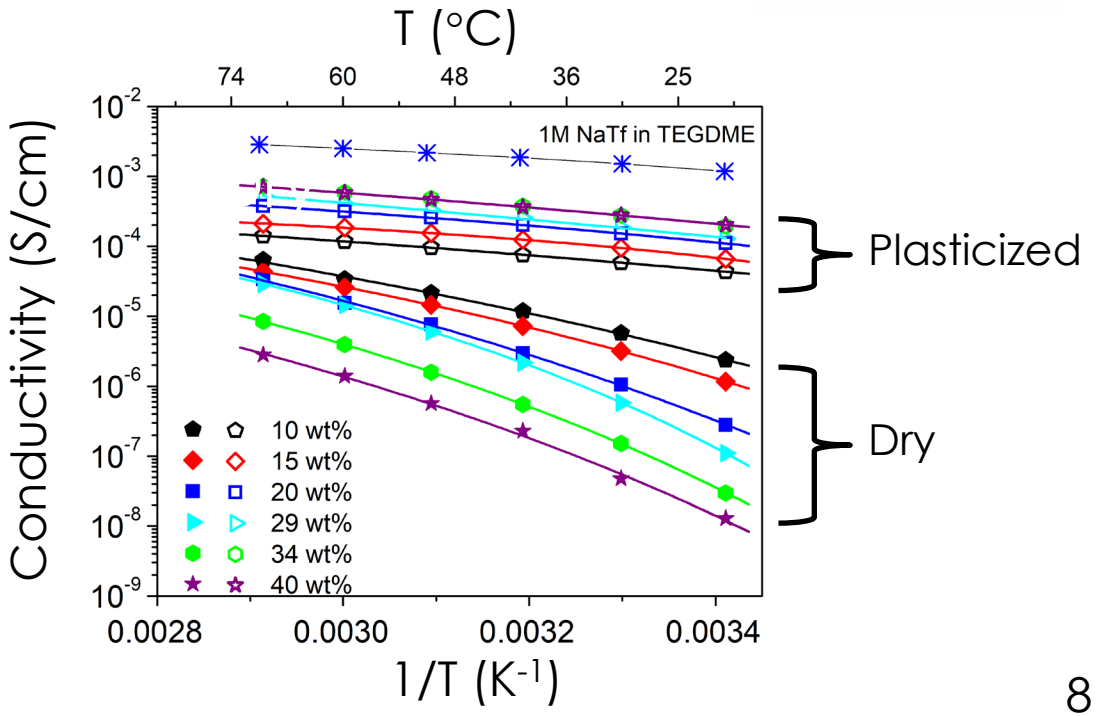
Plasticized, crosslinked PEO exhibits higher ionic conductivity and better mechanical properties compared to linear PEO



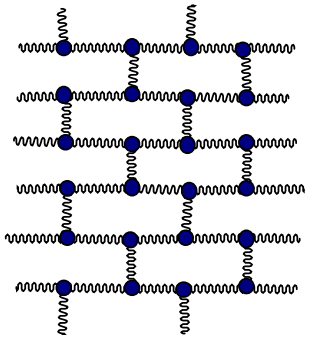




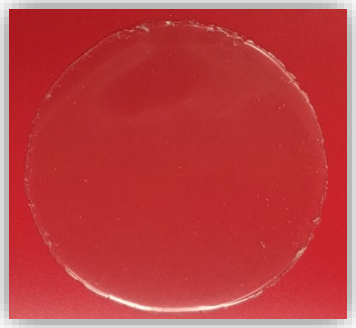




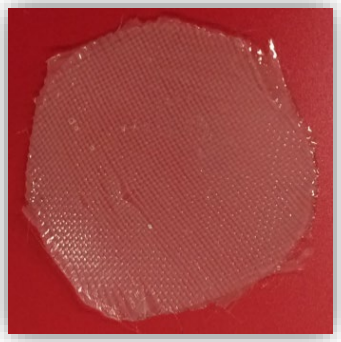
A crosslinked PEO/glass fiber mat membrane shows unprecedented conductivity and mechanical properties

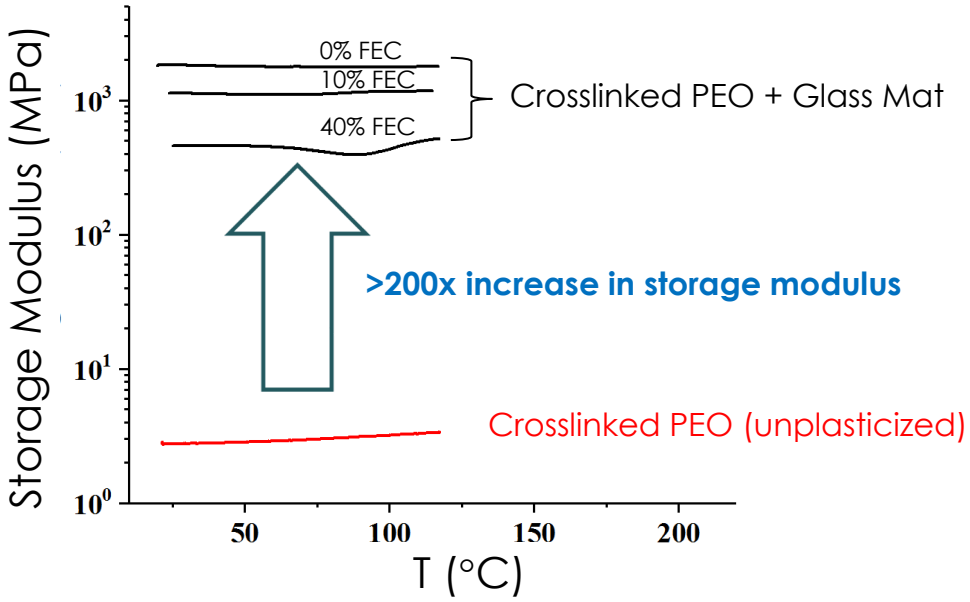


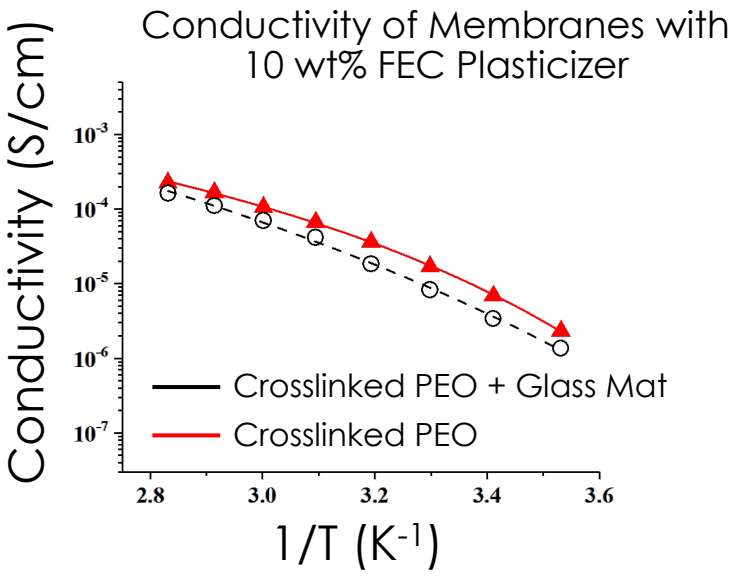
Crosslinked PEO



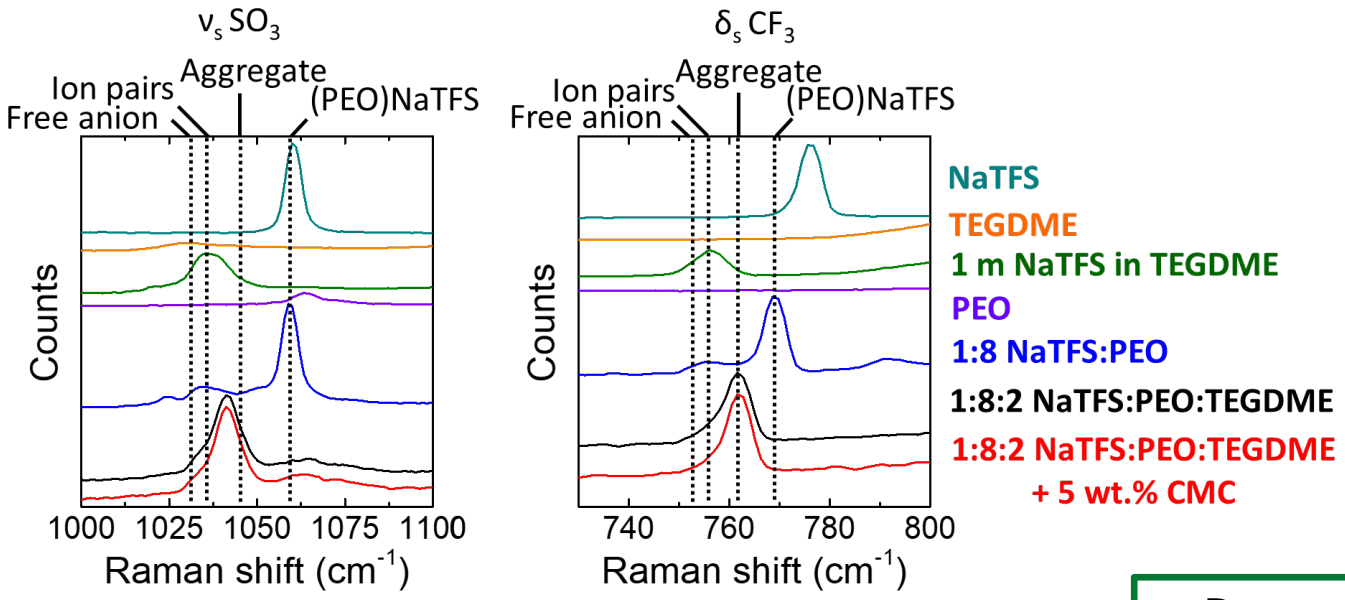
Crosslinked PEO + Glass Mat

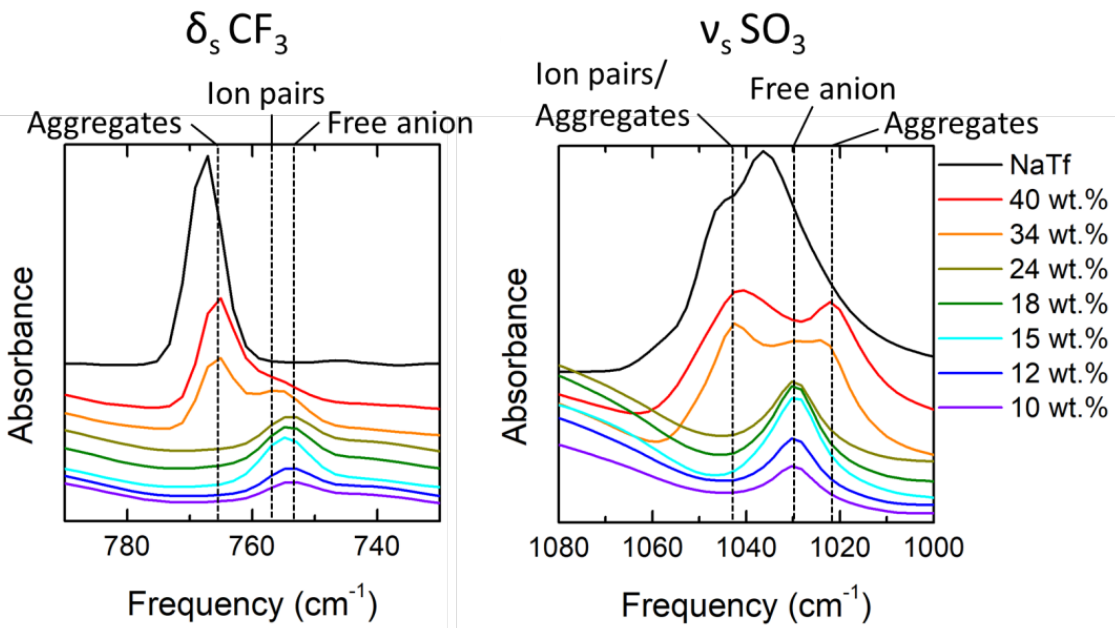






Raman/FTIR spectroscopy provide key insights into the cation solvation structure and mechanism for high conductivity





- Dry membranes contain ion aggregates → low conductivity
- Plasticization lowers the ion coordination number, yielding higher conductivity.

FY19 and Future Work

- **Optimize the ionic conductivity and mechanical strength of plasticized membranes for alkali batteries. Develop electrospun SiO_2 nanofiber matrices to further improve membrane mechanical properties.**

- **Test polymer membranes in mediated flow cell devices. Perform chemical compatibility and crossover experiments.**

- **Screen several low cost high capacity cathode materials to pair with red P anode for a mediated flow cell. Cathode candidates include sulfur and phosphorus-sulfides. Work with an industrial partner and Sandia National Laboratory for prototyping and scale up**

- **Technoeconomic modeling of Na-ion membranes for mediated redox flow energy storage with team at PNNL**

Acknowledgment and Collaboration

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

Tom King, Michael Starke - ORNL
Vince Sprenkle, Vish Viswanathan - PNNL
Babu Chalamala - Sandia

List of Invention Disclosures, Publications, and Presentations

Invention Disclosures

1. *Process for Energy Storage in a Mediated Redox Flow Cell* (ORNL Invention Disclosure No. 201703964)
2. Mechanically Robust Ion Conducting Membranes for Redox Flow Batteries **(**ORNL Invention Disclosure No. 201804195, DOE S-138,866)

Publications

1. R. E. Ruther, G. Yang, F. M. Delnick, Z. Tang, M. L. Lehmann, T. Saito, Y. Meng, T. A. Zawodzinski Jr., J. Nanda, Mechanically Robust, Sodium-Ion Conducting Membranes for Nonaqueous Redox Flow Batteries *ACS Energy Lett.* **2018**, 3, 1640.
2. M. L. Lehmann, G. Yang, D. Gilmer, E. C. Self, R. E. Ruther, S. Ge, B. Li, T. Hong, A. P. Sokolov, F. M. Delnick, J. Nanda, T. Saito, Tailored Crosslinking of Poly(Ethylene Oxide) Membranes Enables Mechanical Robustness and Improved Sodium-Ion Conductivity with Plasticization *J. Mater. Chem. A* **2018** (Under Review)
3. E. C. Self, F. M. Delnick, R. E. Ruther, J. Nanda, High Capacity Organic Radical Mediated Phosphorus Anode for Redox Flow Batteries **2018** (Submitted).

Conference Presentations

1. R. E. Ruther, G. Yang, E. C. Self, Z. Tang, M. L. Lehmann, T. Saito, Y. Meng, T. A. Zawodzinski Jr., F. M. Delnick, J. Nanda, *Robust, Sodium-Ion Conducting Membranes for Non-Aqueous Redox Flow Batteries*, Energy Storage Beyond Li-ion, July 24-26, 2018, Westlake, OH [Poster]
2. E. C. Self, F. M. Delnick. R. E. Ruther, J. Nanda, *A Mediated Anode for Non-Aqueous Redox Flow Batteries*, MRS Spring Meeting, April 2-6, 2018, Phoenix, AZ [Oral]
3. M. Lehmann, D. Gilmer, E. C. Self, R. Ruther, F. Delnick, T. Hong, J. Nanda, T. Saito, *Development of Sodium Ion Conductive Membranes for Organic Redox Flow Battery*, MRS Spring Meeting, April 2-6, 2018, Phoenix, AZ [Oral]