# Mediated Na-ion Based Redox Flow Chemistries

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# Megawatt scale energy storage provides a new value chain in battery industry and manufacturing

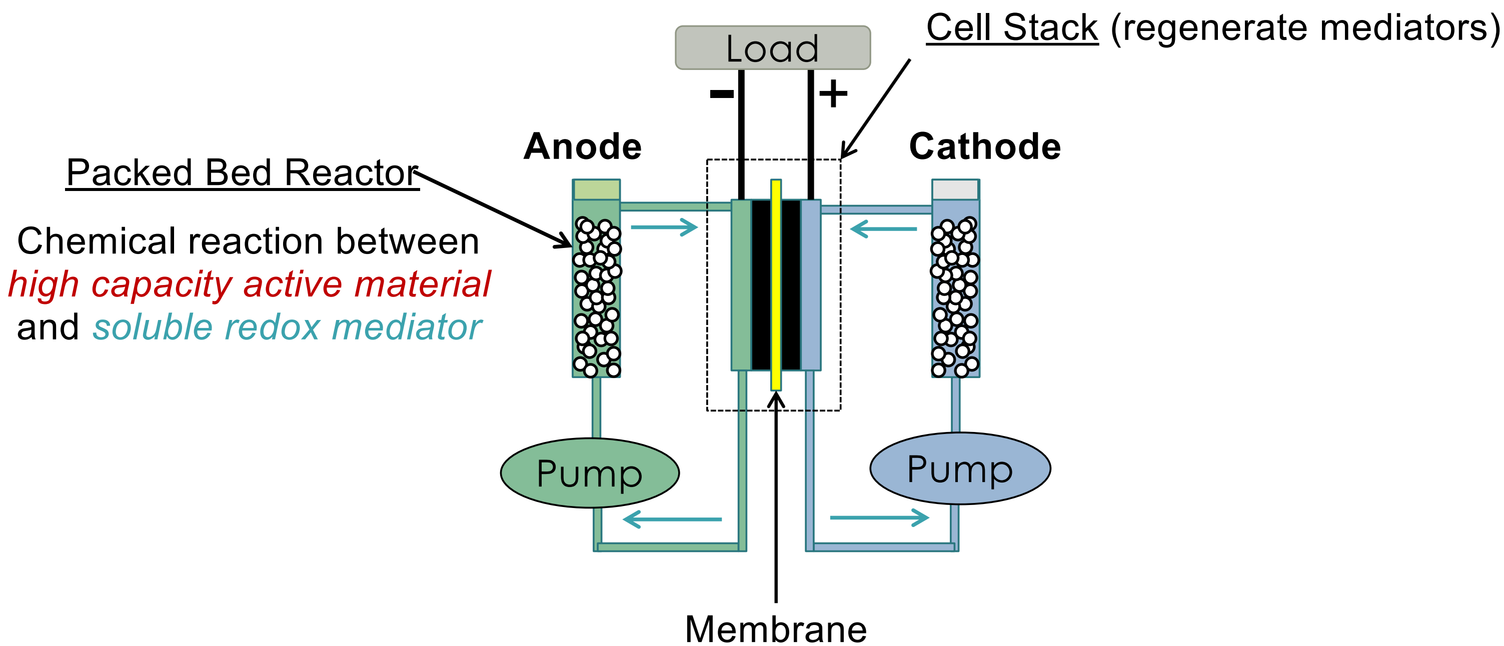
Military Bases

Remote Islands and Off-grid


Backup power for data center

Increased renewables (solar & wind) penetration to the grid

# Overview of ORNL's Mediated Redox Flow Battery Technology



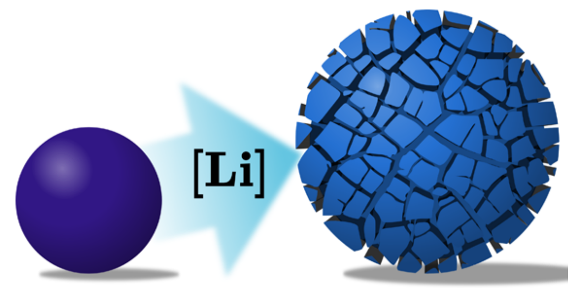

### Advantages of Mediated Flow Battery

- ✓ Extremely high energy density can be achieved (200 Wh/kg vs. 25 Wh/kg)
- ✓ Accommodate active materials with large volume changes
- ✓ Only ohmic losses in system are through the membrane
- ✓ Improved safety in event of short circuit
- ✓ Low cost (scales with physical size)

ORNL patent application 2015, 2017

# Low cost radical mediators enable new, high-capacity anodes and cathodes that are incompatible with conventional cell architectures.

Mediated redox flow batteries
- accomodate large volume changes
- eliminate costly electrode processing
- enable highly energetic materials to operate safely




| Anode Capacities (mAh/g) | | | | | | | Cathode Capacities (mAh/g) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $Li_3N$ | $Li_3Mg$ | $Li_3P$ | LiAl | $Li_{2.6}Sn$ | $LiC_6$ | $V^{2+/3+}$ | $V^{4+/5+}$ | $Li_2S_8$ $Li_2S_3$ | $LiFePO_4$ | Oxides | Organics | $O_2$ |
| 2,308 | 1,782 | 1,552 | 790 | 587 | 339 | 30 | 30 | 88 | 150 | 250 | 2,500 | 3,350 |

VRFB **1x**

Mediated RFB prototype **5x**

Mediated RFB – full cell

**23x energy density**

ORNL patent application 2015, 2017

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

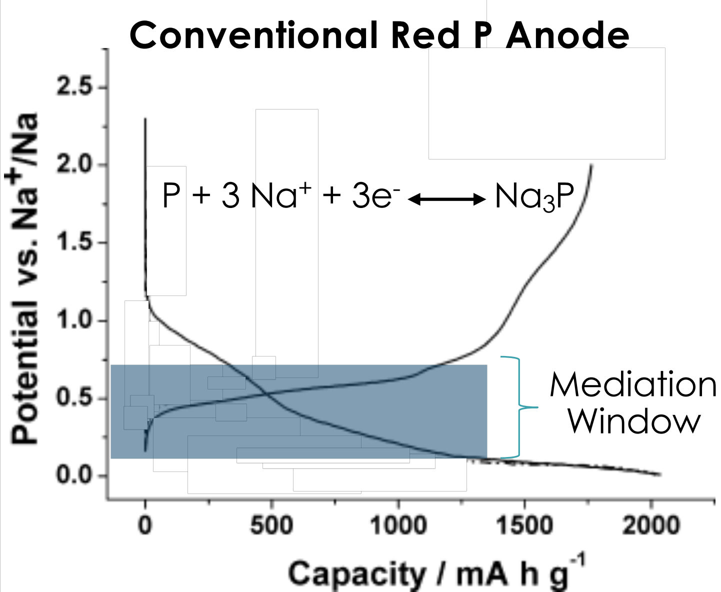
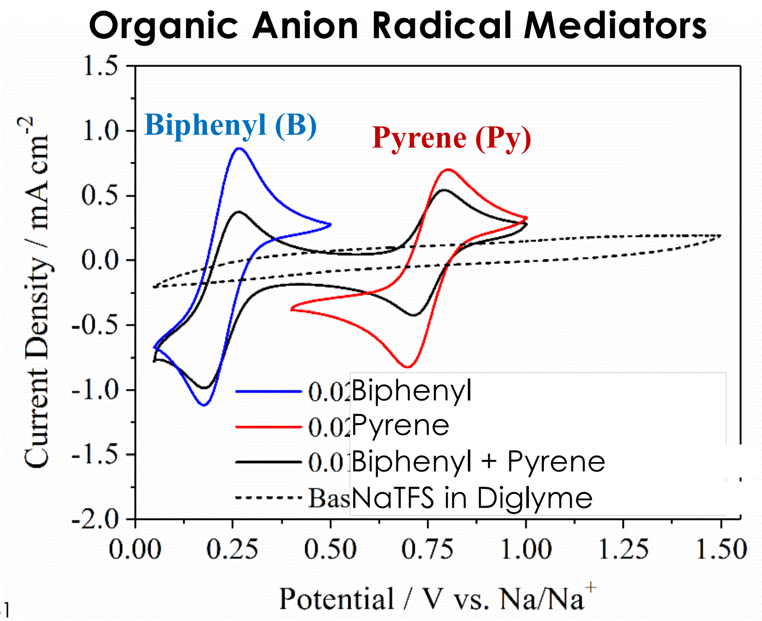



Image adapted with permission from *Angew. Chem.* **2013**, 125, 4731

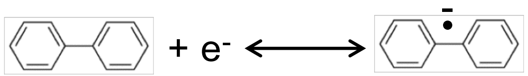



Self et al., Submitted, 2018

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

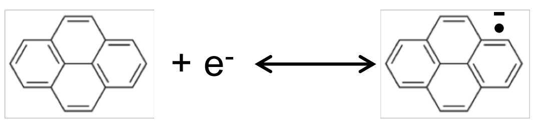
# Anion radical mediators were selected to take advantage of the high capacity of phosphorus.

## Anion Radical Mediators



$E^0$ ~ 0.2 V vs. Na/$Na^+$

**Biphenyl Anion Radical ($B^{\bullet -}$)**



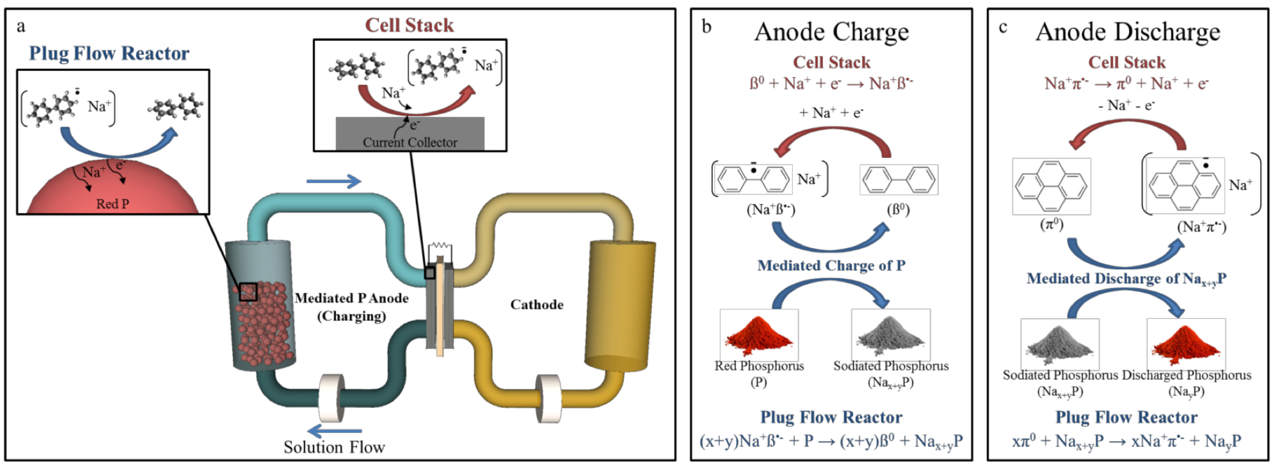
$E^0$ ~ 0.7 V vs. Na/$Na^+$

**Pyrene Anion Radical ($Py^{\bullet -}$)**

## Anion Radical Mediated Na Storage

$$P + 3Na^+ + 3\,B^{\bullet -} + Py^{\bullet -} \longrightarrow Na_3P + 3\,B + Py^{\bullet -}$$

$$Na_3P + 3\,Py + B \longrightarrow P + 3Na^+ + 3\,Py^{\bullet -} + B$$



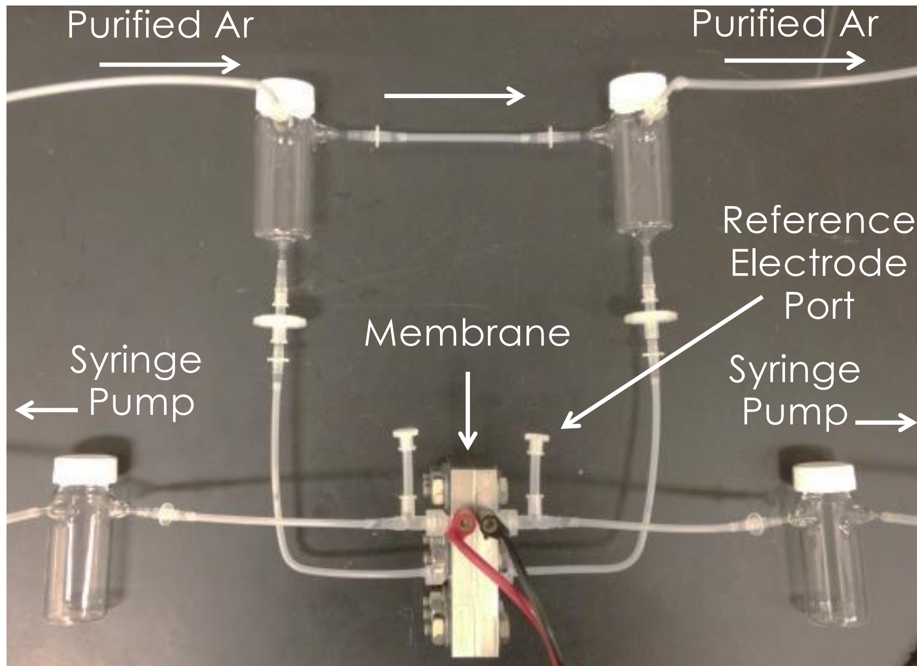

Self et al., Submitted, 2018

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

**Cell Components:**

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

**Serpentine Flow Channels**

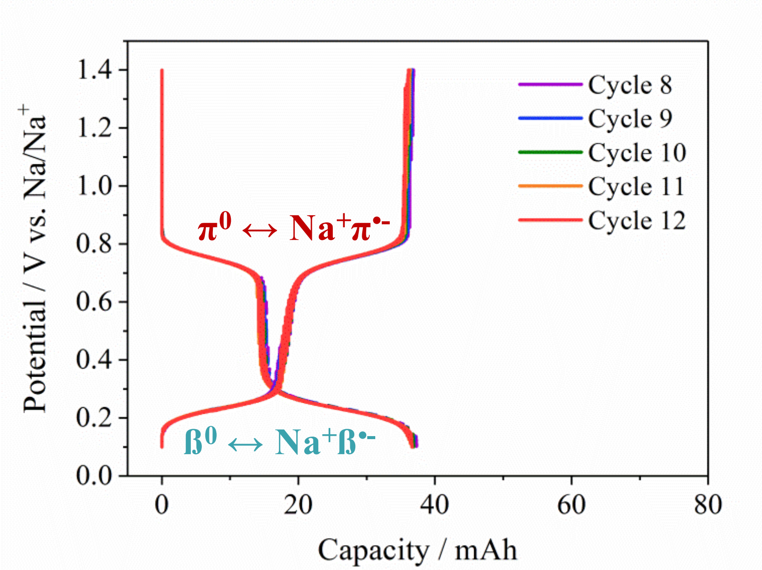


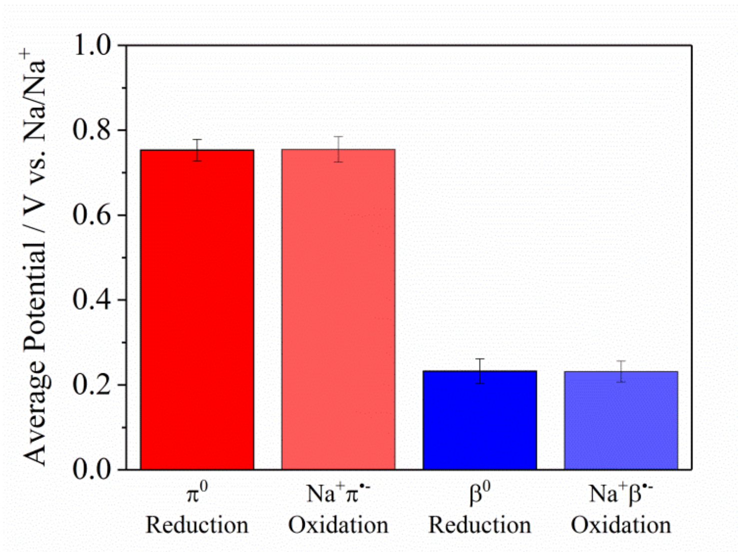

**Flow Cell (connected to potentiostat)**

# Symmetric Flow Cell Containing Only Mediators

**Electrolyte**: 0.7 m NaTFS in diglyme
Biphenyl (ß, 20 mAh)
Pyrene (π, 20 mAh)

**Cycling Protocol**: 5 mL/min solution flow rate (400 A)
Galvanostatic cycling (0.78 mA/cm$^2$)

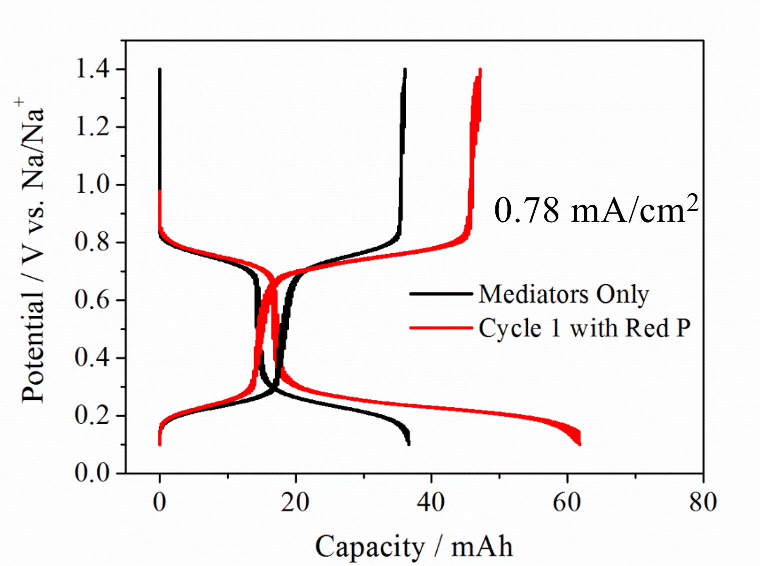


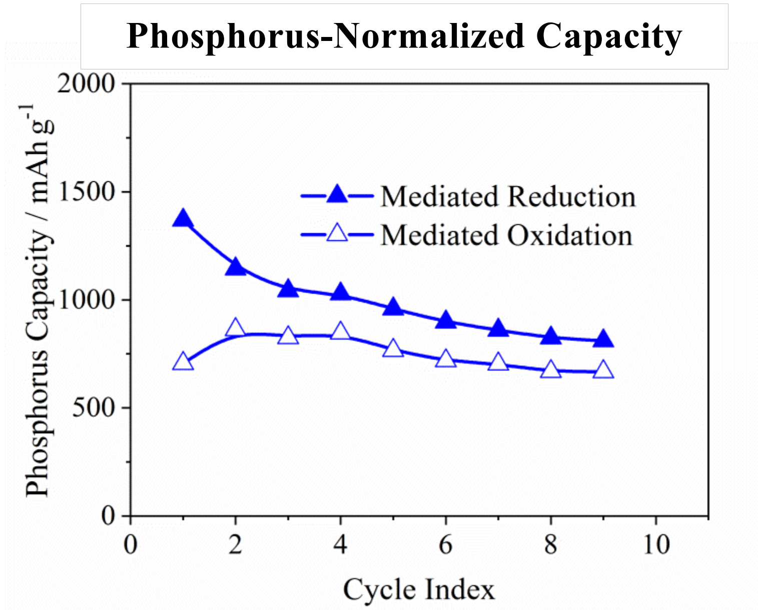




Biphenyl and pyrene mediators exhibit good cycling stability with very low overpotential.

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

**Electrolyte**: 0.7 m NaTFS in diglyme
20 mAh Biphenyl (mediator for sodiation of P)
20 mAh Pyrene (mediator for desodiation of $Na_xP$)
22 mg red P (ca. 20 mAh)



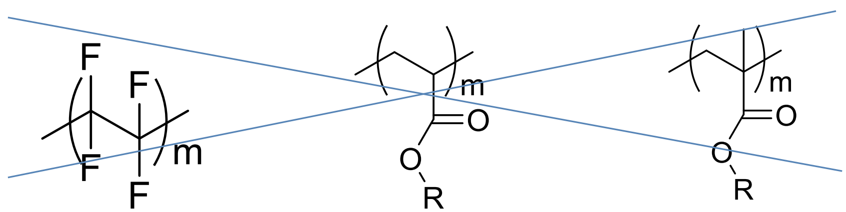




Membrane: Na-beta Alumina

Self et al., Submitted, 2018

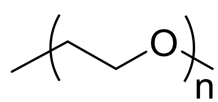
# Radical Anion Mediated Redox Flow Battery - Membrane Development

- Due to the highly reducing nature of the biphenyl radical the majority of polymers degrade under these conditions

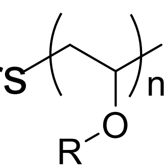



- Polymers that have been found to be stable against biphenyl radical:

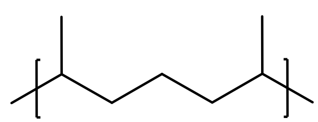
- Poly(ethylene oxide)




- Polyvinyl ethers

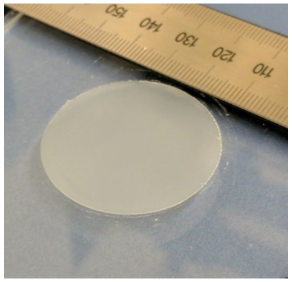



- Polyolefins



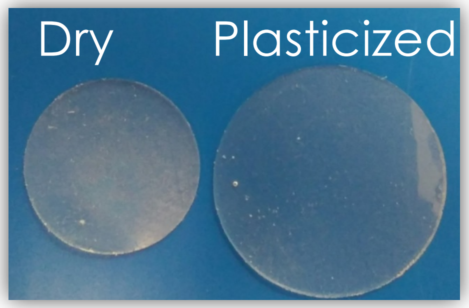
# Several synthesis routes were developed to produce low cost polymer membranes for Na-based, nonaqueous flow batteries

**Linear PEO + CMC[1]**



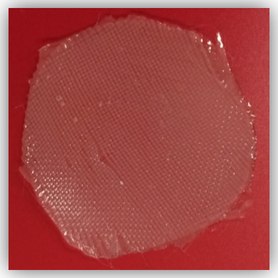
Blended CMC phase improves mechanical properties

**Crosslinked PEO [2]**




Plasticization with TEGDME yields high conductivity but limited mechanical integrity

**Crosslinked PEO + Glass Mat Reinforcement [3]**

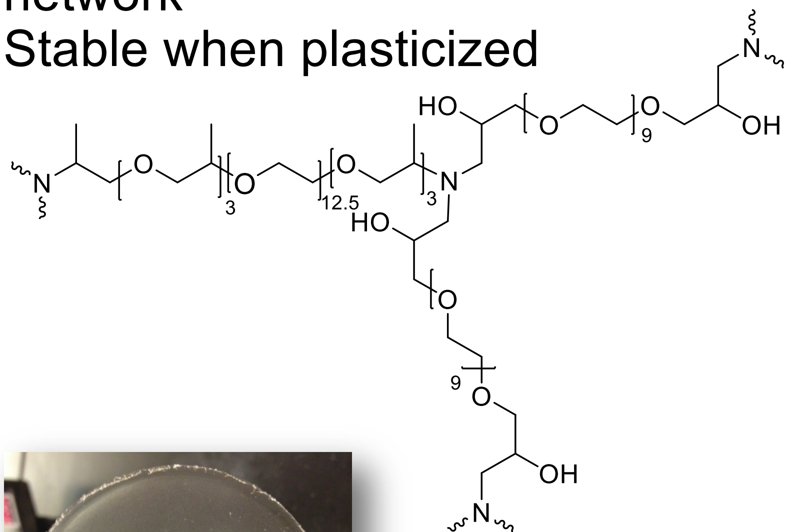


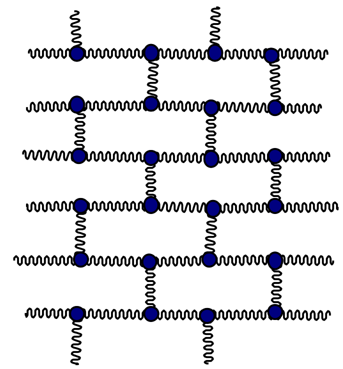
Reinforcing crosslinked PEO with a glass fiber mat provides unprecedented strength and high conductivity

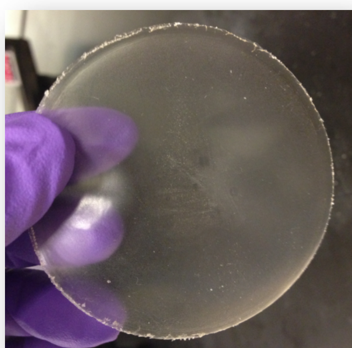
[1] Ruther et al., *ACS Energy Lett.*, **2018**.
[2] Lehmann et al., *Energy Storage Materials*, **2018** (Under Review).
[3] Yang et al., Unpublished, **2018**

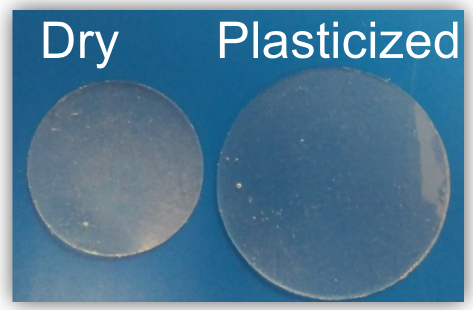
# Cross-linked PEO-based Membrane

- Created a robust cross-linked network
- Stable when plasticized










- Characterized membranes dry and plasticized with tetraglyme

Lehman et al Energy Storage Materials ( Under review)

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