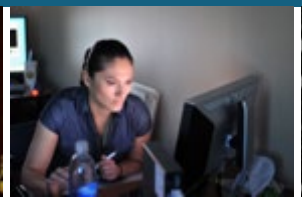
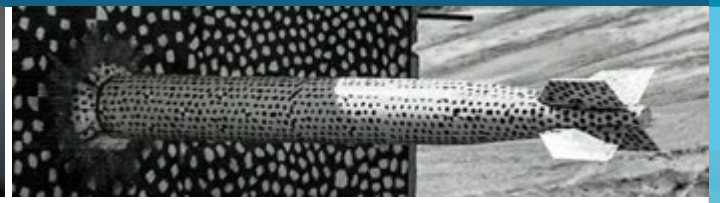
Advanced Membranes for Flow Batteries: Anion Exchange Membranes





PRESENTED BY

Cy Fujimoto

2019 Budget = $300k
SAND2019-10624 C

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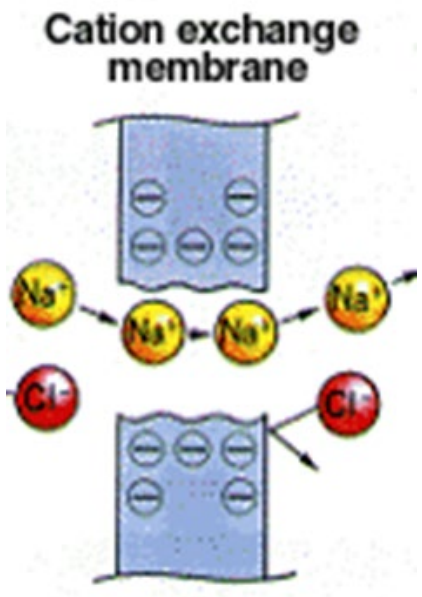
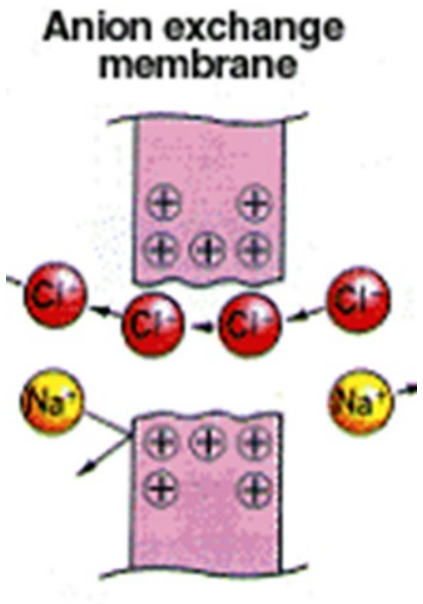
Membrane Basics

The performance of flow batteries are influenced by membrane properties. Membrane conductivity dictates battery round trip efficiency and membrane selectivity regulates capacity retention.

- Due to cost concerns of acidic vanadium flow batteries, this is driving R&D interest in pH neutral and high pH environments typically used in aqueous organic and non aqueous flow batteries.
- New flow battery chemistries being developed under a variety of pHs.

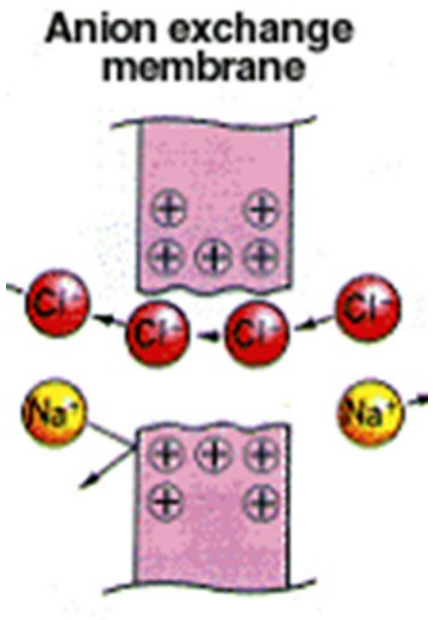


In acidic environments (VRFB)
CEM used pH < 7



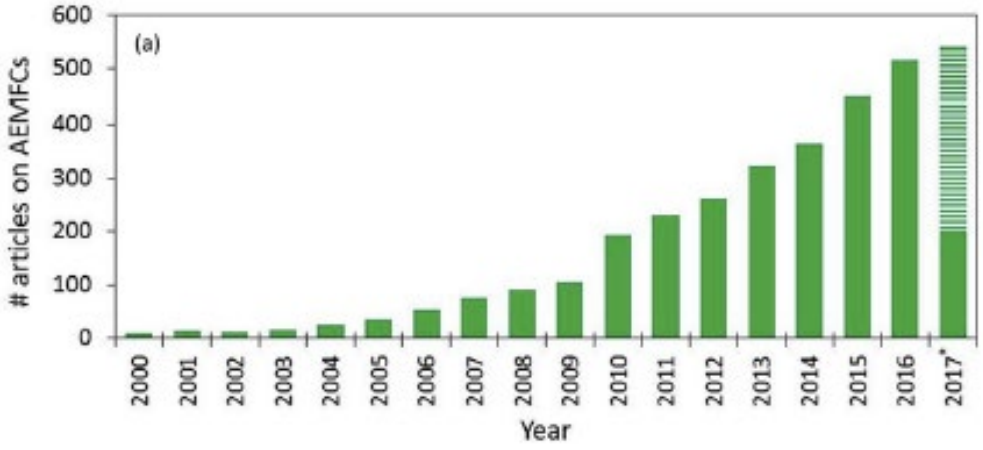
In alkaline environments
AEM used pH > 7

Anion Exchange Membrane (AEM) Basics:



1. Polymer that contains bound positive charges.
2. ***Alkaline stable*** AEM allows for new electrochemical applications.
3. There is no widely accepted ***alkaline stable*** "state of the art" AEM.

Growth of AEM interest 2001 - 2017



Handful of small AEM companies

ecolectro

Dioxide Materials™ The CO_2 Recycling Company™

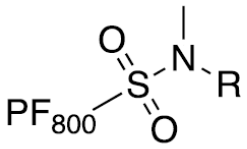
IONMR

ORION POLYMERS

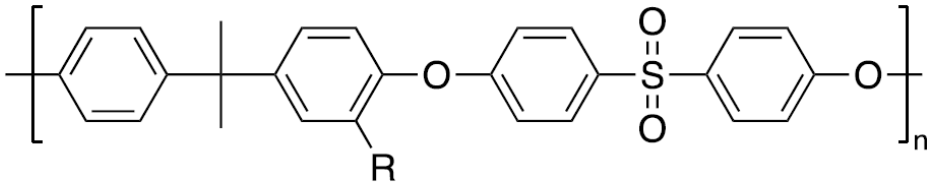
Recent independent stability survey of AEM

- Growth and interest in AEMs, but need to objectively determine best AEM candidates
- Third party lab investigated accelerated membrane durability under alkaline conditions by soaking films in 1 M KOH for 1000 hrs at 80 °C and monitoring any loss in 1. IEC 2. Conductivity 3. Mechanical

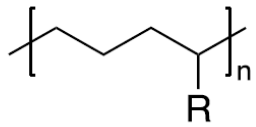
Perfluoro (PF)

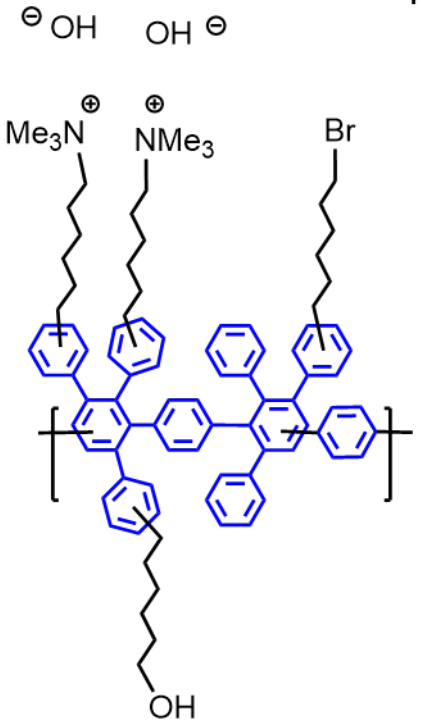


Poly(aryl ether sulfone) (PAES)



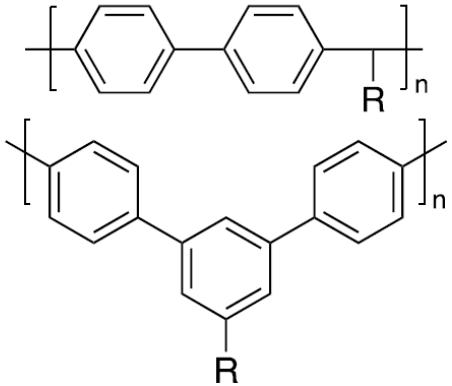
Polyethylene (PE)



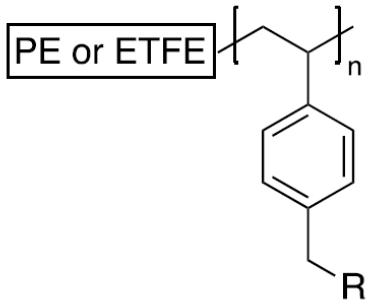


PPN6

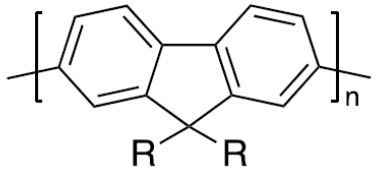
Polyphenylene (PPN)



Polystyrene (PS)



Polyfluorene (PFN)

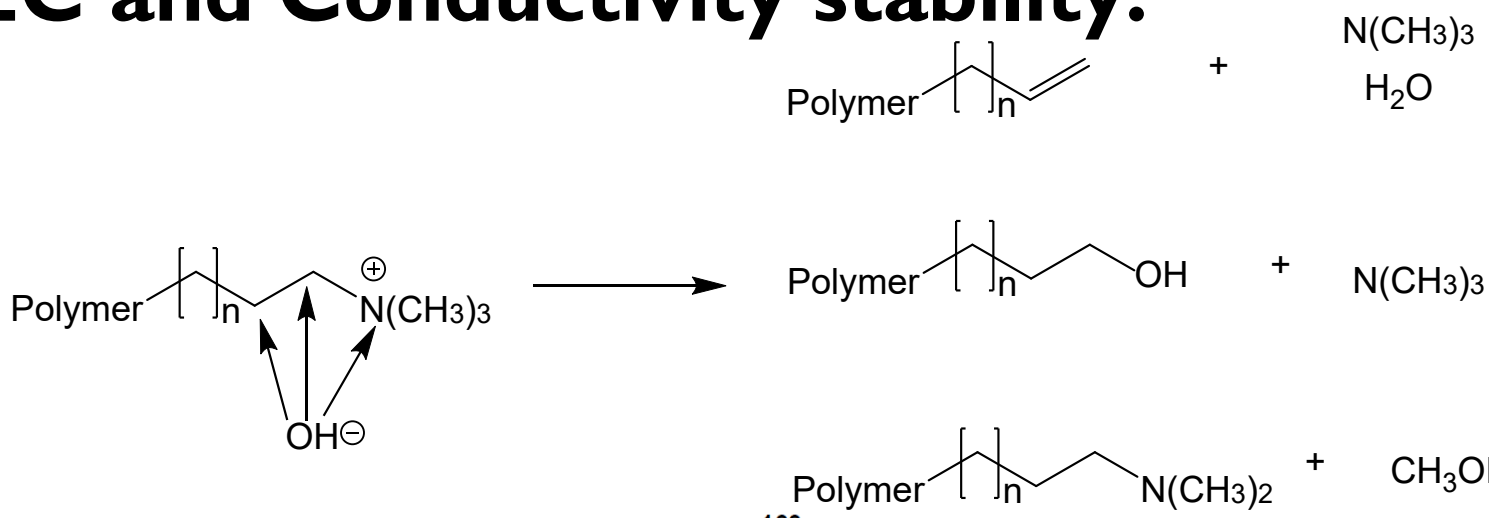


$R = (CH_2)_m X^+OH^-$

X = typically $N(CH_3)_3$

Credit: Kelly Meeks and Bryan Pivovar NREL

IEC and Conductivity stability:



- Hydroxide ion is a strong base and nucleophile.
- Three different mechanism that result in IEC and conductivity loss.

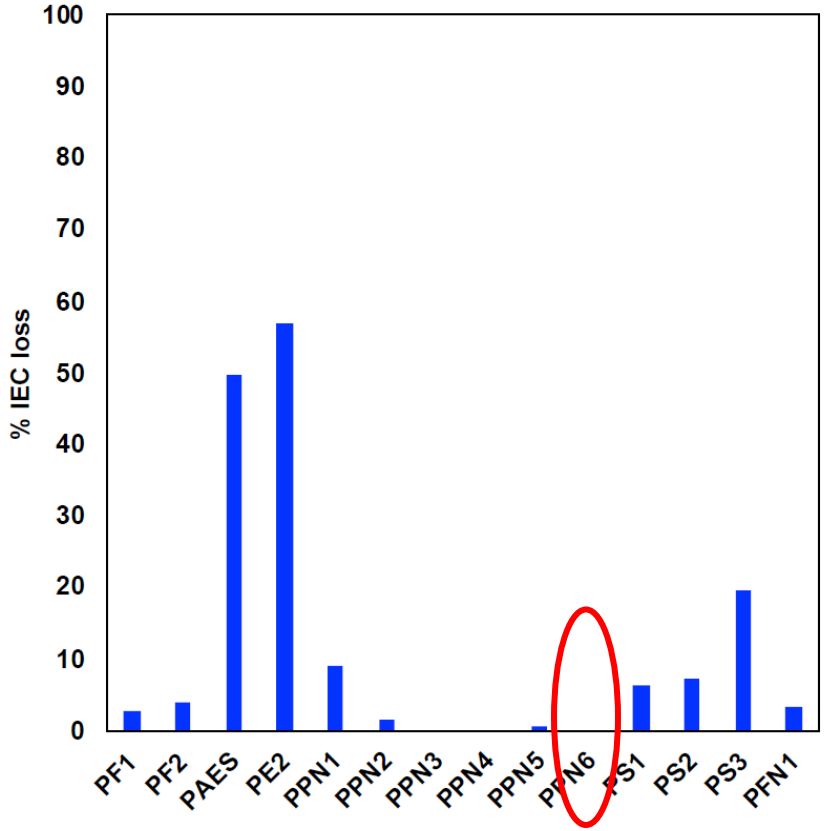
Acceptable loss < 5%

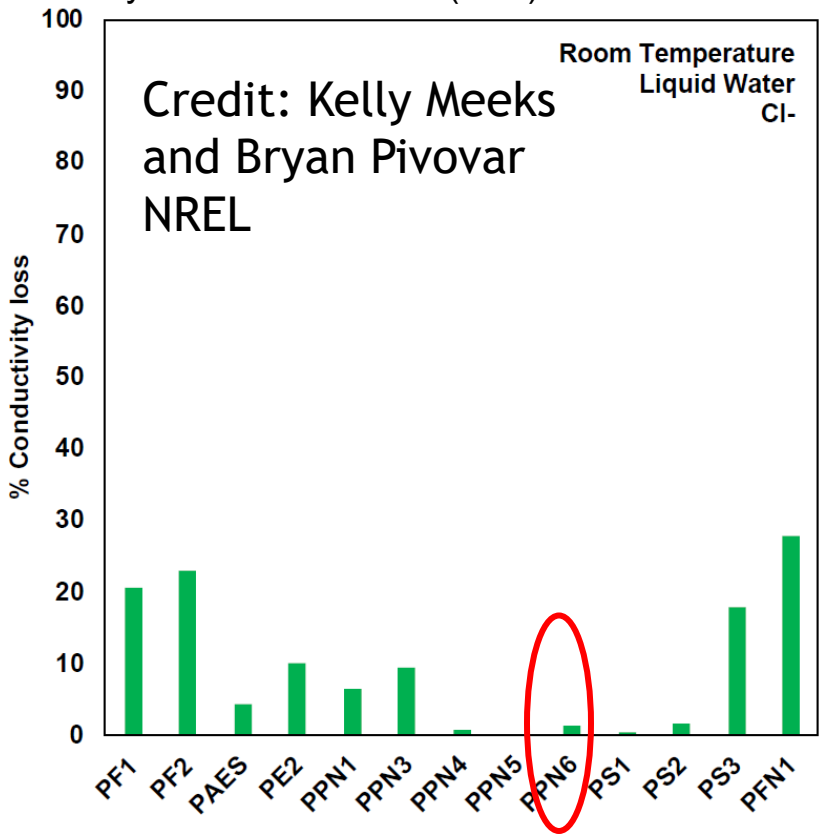
Sandia polymer, PPN6 passed this test!

64 % of surveyed polymers saw less than a 5% loss in IEC (Sandia polymer is PPN6).

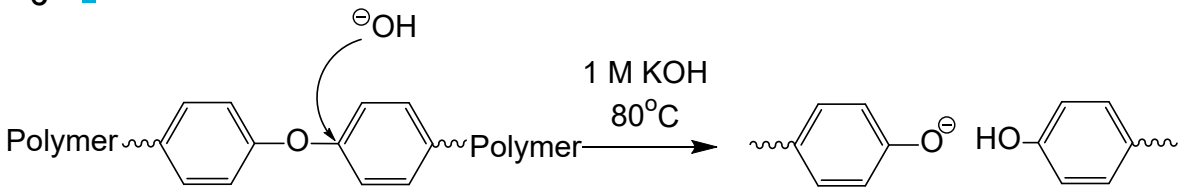
but

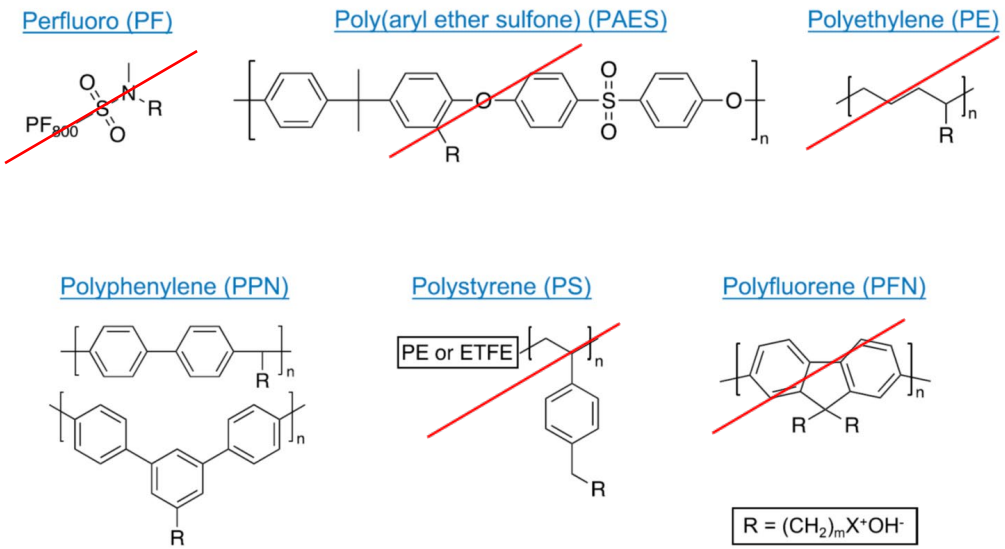
42 % of surveyed polymers saw less than a 5% loss in conductivity (Sandia polymer is PPN6).



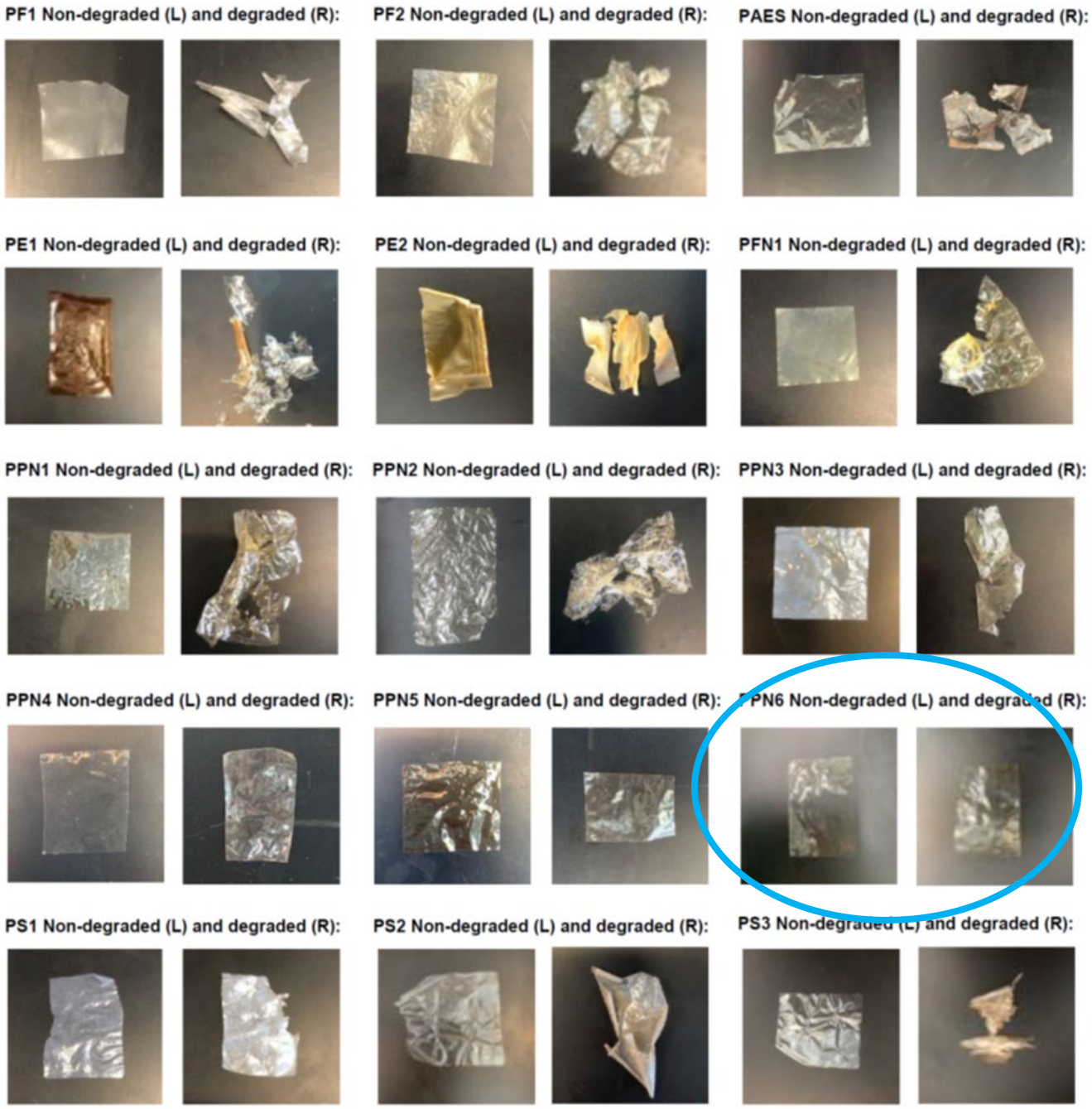


Mechanical stability:





Only 20% of films maintained mechanical properties.
Only three poly(phenylene) type structures survived (***PPN6 is the Sandia polymer***).
All other types of backbones look to degrade.
PPN6 showing encouraging durability.

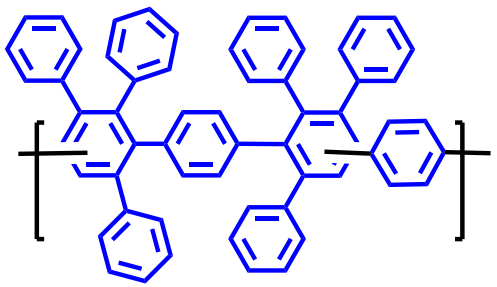


Credit: Kelly Meeks and Bryan Pivovar NREL

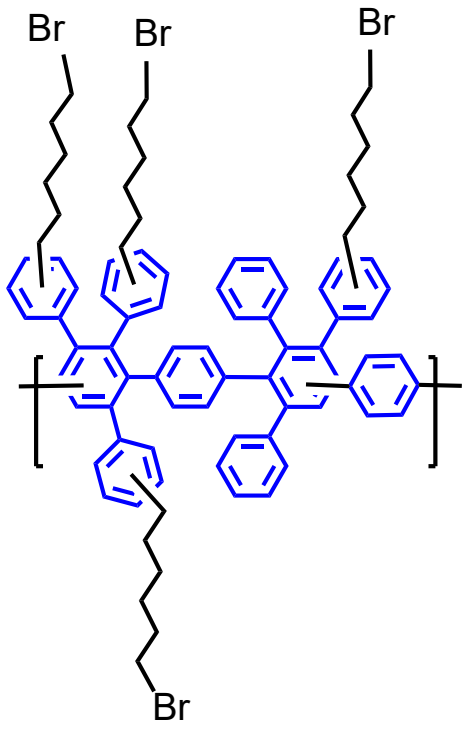
Membranes for Flow Batteries (FB)

- Membranes for flow batteries = precise control of IEC. Too High IEC = high crossover, capacity loss. Too Low IEC = low conductivity, low efficiency. Need to optimize polymer IEC which is dependent on polymer structure and battery chemistry.
- Recently discovered a processing issue that was affecting IEC control = performance in flow battery applications.

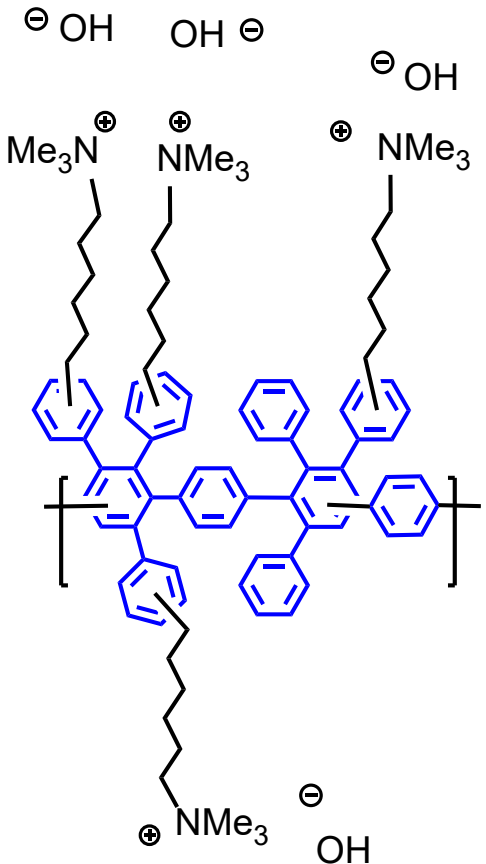
Starting Material



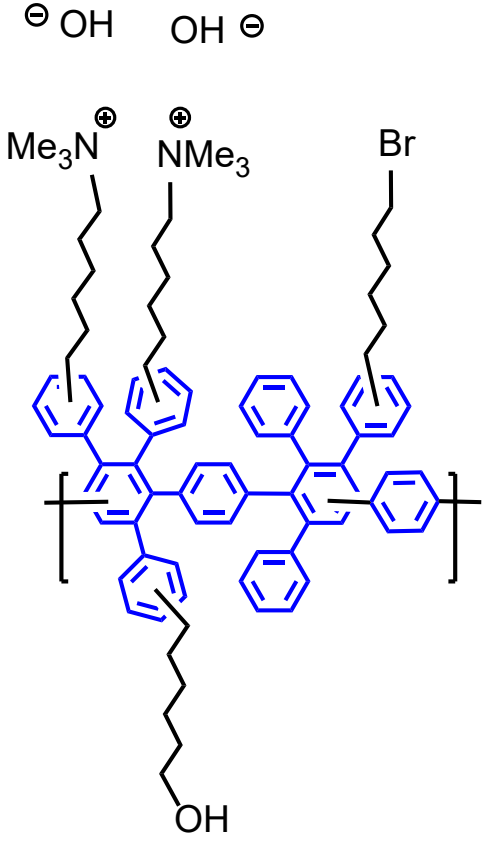
Intermediate



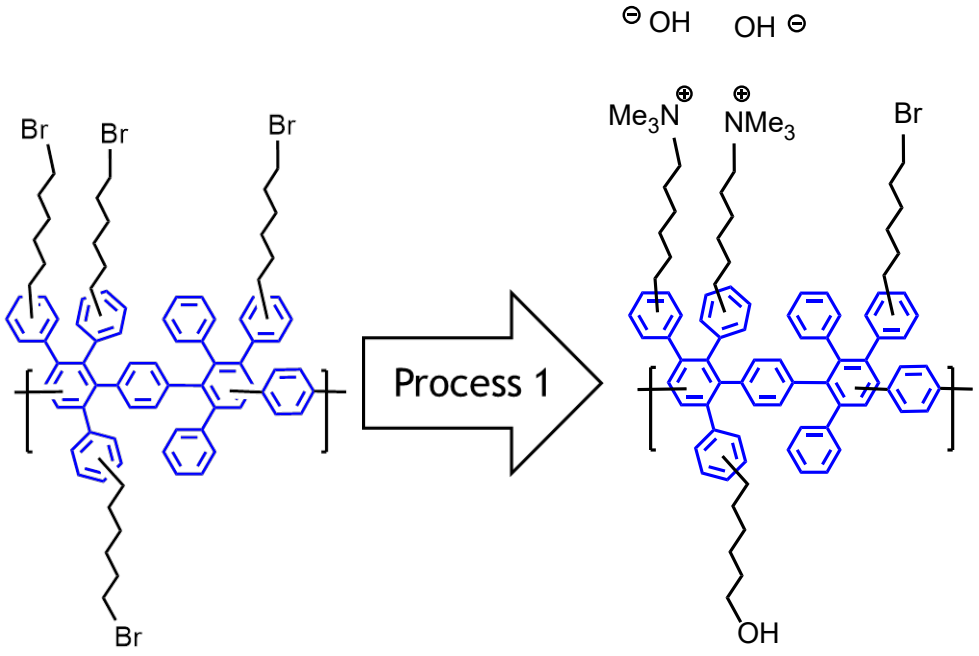
Desired product



Actual product

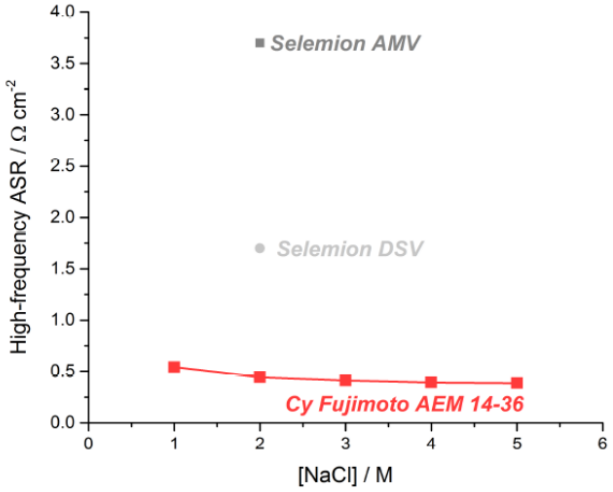


Aqueous Soluble Organic FB:



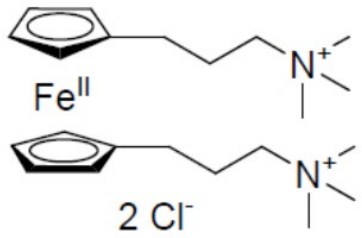
Polymer with large amount of alkyl bromide (4-5) Process 1 partial conversion.

SNL = Low resistance



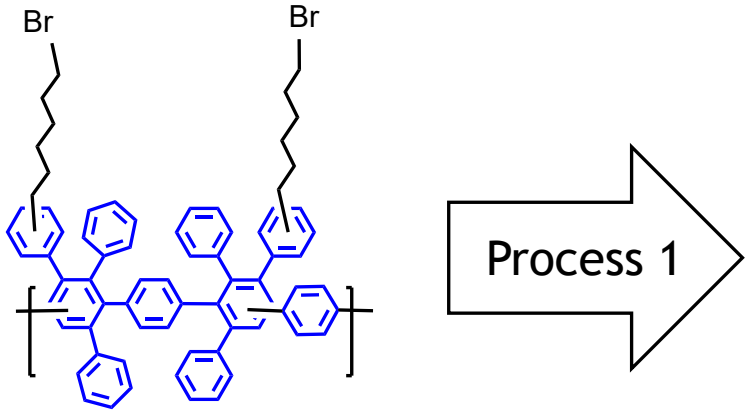
SNL 3.5 x lower resistance than Selemion DSV

SNL = Low selectivity



Target $1x10^{-10}$ cm^2/s
SNL 6×10^{-9} cm^2/s
Selemion DVS $1x10^{-12}$ cm^2/s

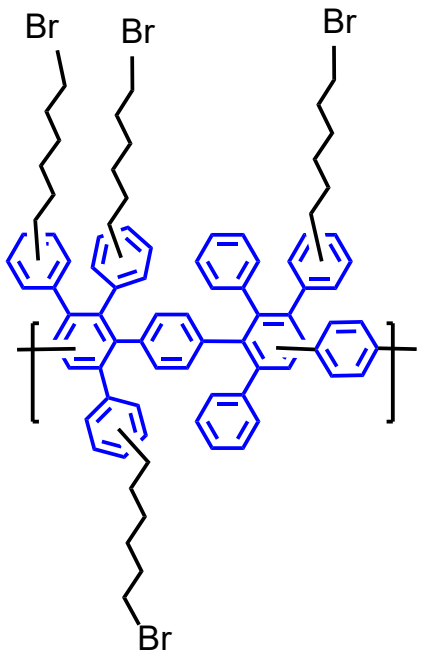
Unpublished work from Dr. Aziz labs

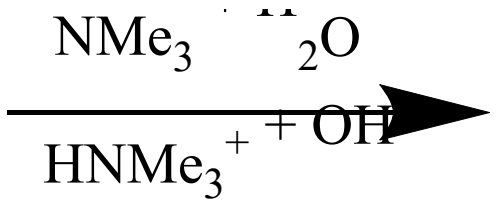


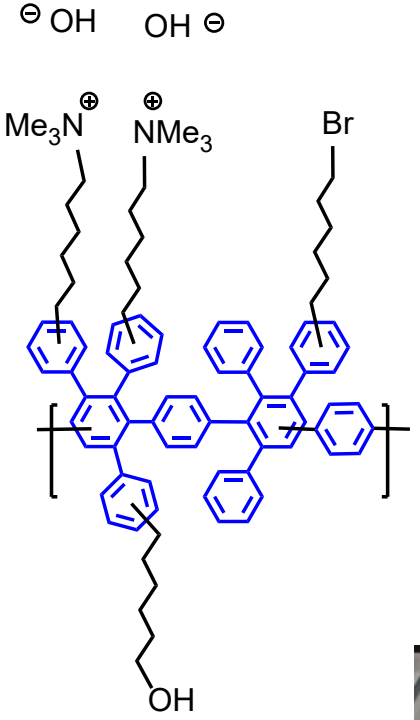
No reaction

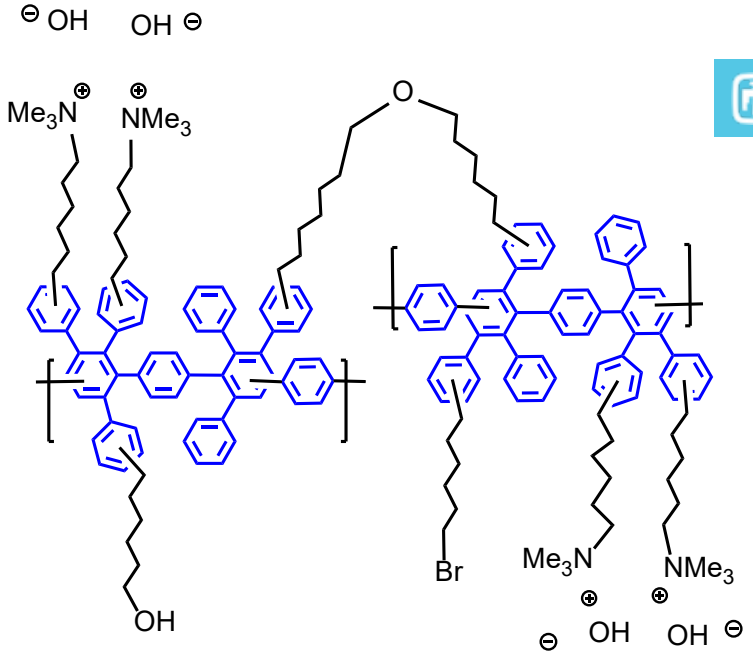
But polymers with low amount of alkyl bromide (1-2) Process 1 no reaction.

Polymer Process I:

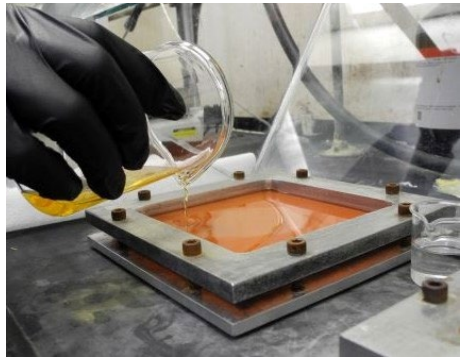


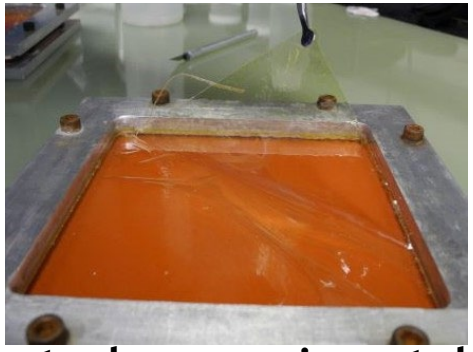






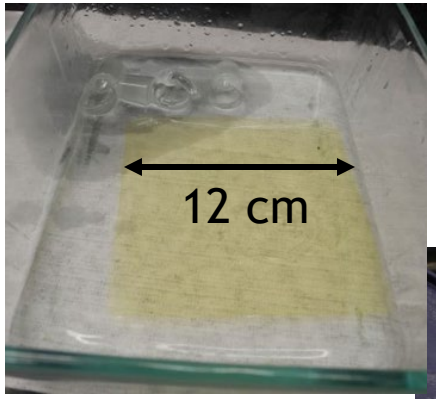
Dissolve in CCl_3H

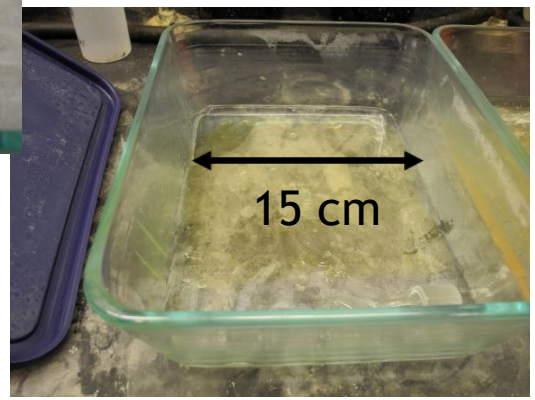




Heterogeneous reaction

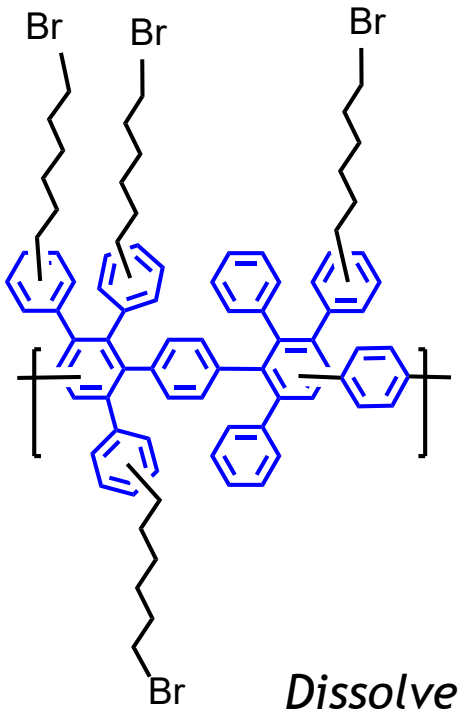
5 M $N(CH_3)_3$ in water





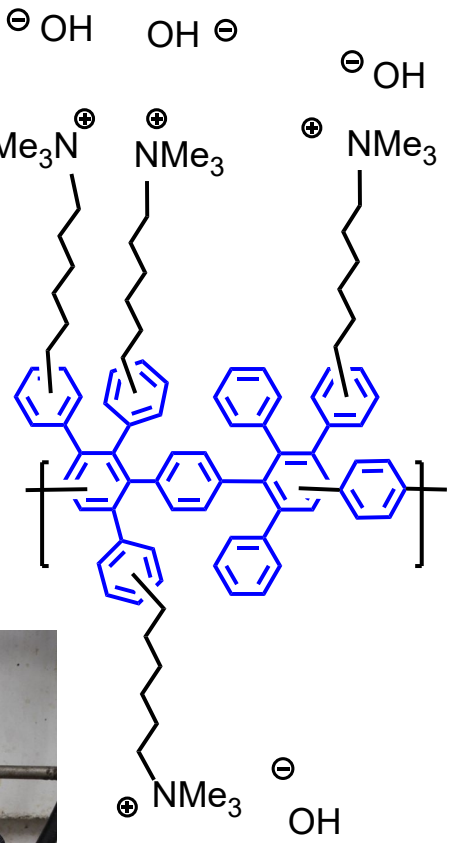
Using Process 1 poor IEC control: experimental IEC (2.3 eq/g) always lower than theoretical (2.7 meq/g). Heterogeneous reaction rate dependent on polarity of polymer.

Polymer Process 2:

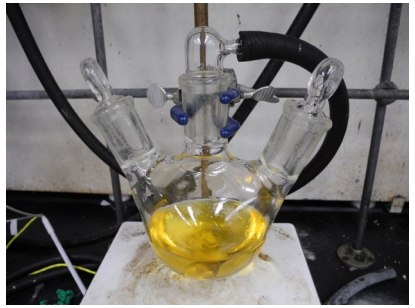


DMSO

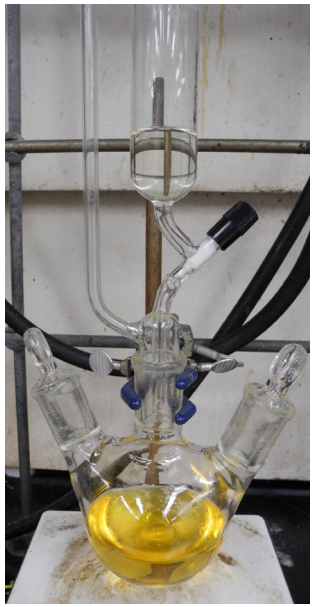
NMe_3 in EtOH

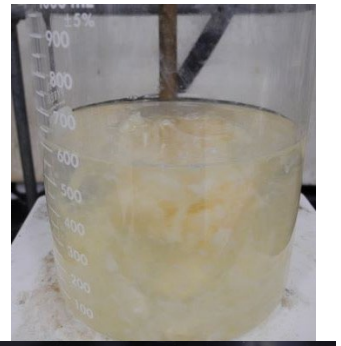


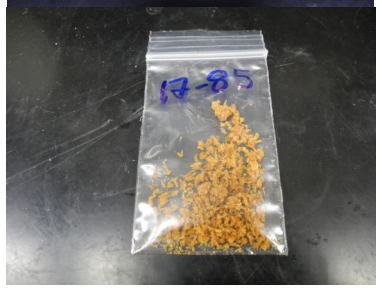
Dissolve in DMSO



Add amine to polymer







Process 2 improves control of IEC: Experimental IEC (2.68 eq/g) now matches theoretical (2.7 meq/g). Submitted non provisional patent SD15069.0.

Conclusions:

- High interest in alkaline stable anion exchange membranes.
- Various polymers are being investigated, but the SNL polymer has shown promising durability in comparison tests.
- Issues in controlling polymer IEC was due to processing conditions (Process 1).
- Developed Process 2 which has shown full conversion of alkyl bromide to ammonium; IEC control. Submitted non-provisional patent.

Future Tasks:

- Flow battery test of AEMs synthesized by Process 2
- Membrane commercialization

Patents/Papers:

- C. Fujimoto "Halo-Containing Anion Exchange Membranes and Methods Thereof" US Patent No. 10,294,325 B2, Issued May 21, 2019
- C. Fujimoto. "Functionalization of Diels-Alder Polyphenylene Polymers." Patent No. US 10,053,535 B2, November 2018
- Acid-catalyzed benzoylation reactions of Diels-Alder polyphenylenes in Polymer (December 2018), 158, 190-197. Fujimoto, Cy; Sorte, Eric; Bell, Nelson; Poirier, Cassandria; Park, Eun Joo; Maurya, Sandip; Lee, Kwan-Soo; Kim, Yu Seung.

Thank You

Thank You to the DOE Office of Electricity and especially Dr. Gyuk for his dedication and support to the Energy Storage industry and Sandia's Energy Storage Program.

Questions?

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