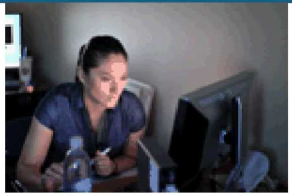
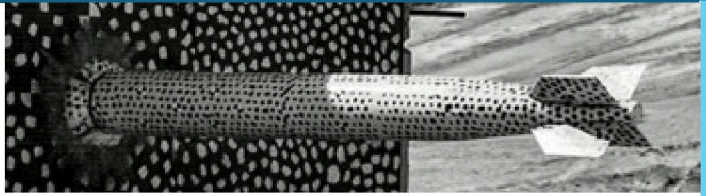
SAND2019-14447C

Advanced Membranes for Flow Batteries: Anion Exchange Membranes





PRESENTED BY

Cy Fujimoto

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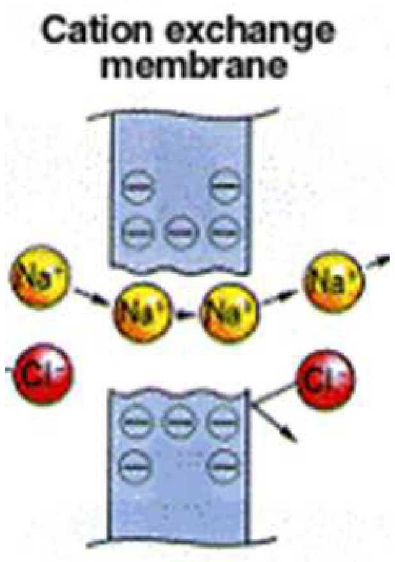
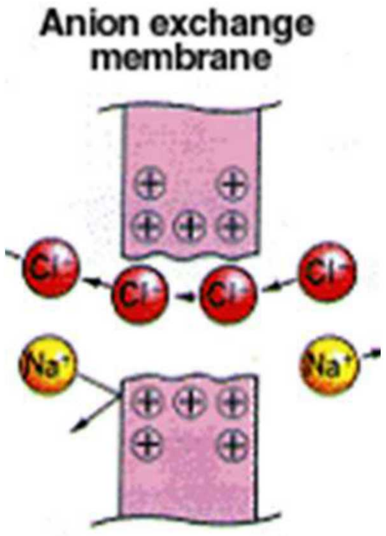
Membrane Basics

Flow battery performance is 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, driving R&D interest in pH neutral and high pH environments for aqueous organic and non aqueous flow batteries.



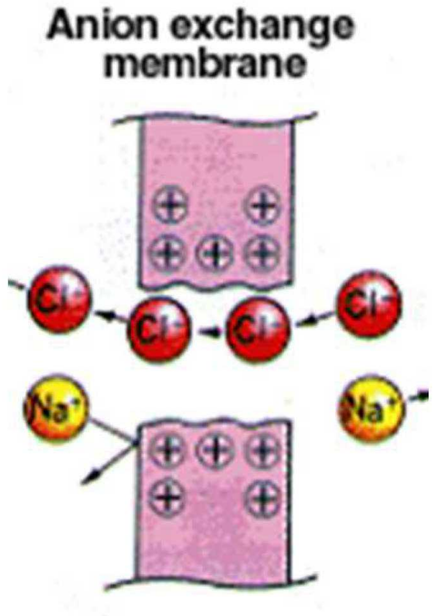
In acidic environments (VRFB)
CEM used pH < 7



In alkaline environments
CEM used pH > 7

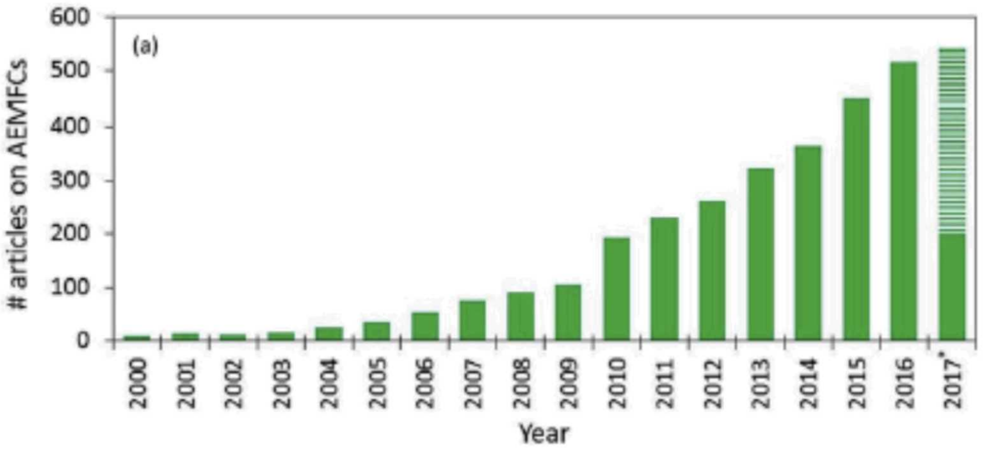
- In neutral and high pH, ideal membrane has high anion transport (high anion conductivity).

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 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

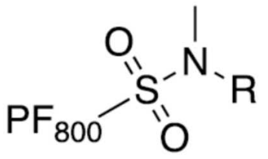
IONOMR

ORION POLYMERS

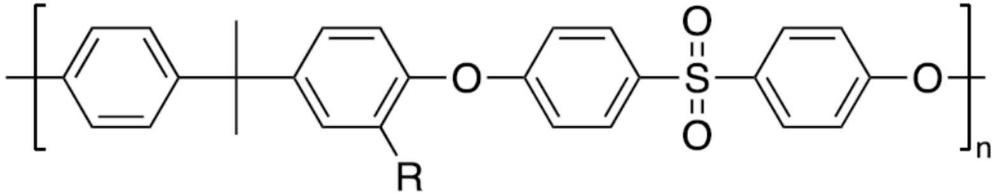
Recent independent stability survey of AEM

- Third party lab the most promising polymer candidates from research labs worldwide
- Probe membrane stability in alkaline by soaking films in 1 M KOH for 1000 hrs at 80 °C and monitoring any loss in
  1. IEC/Conductivity
  2. Mechanical

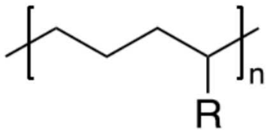
Perfluoro (PF)

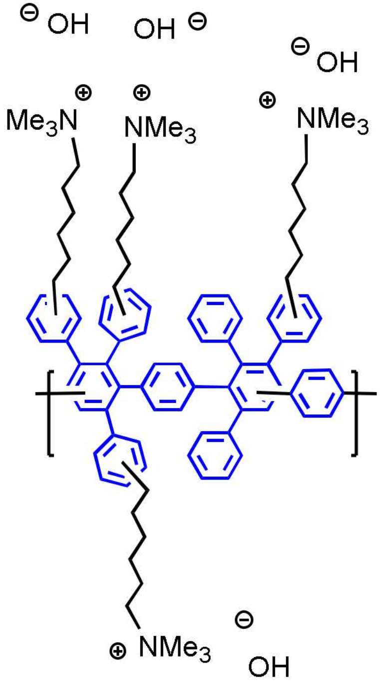


Poly(aryl ether sulfone) (PAES)



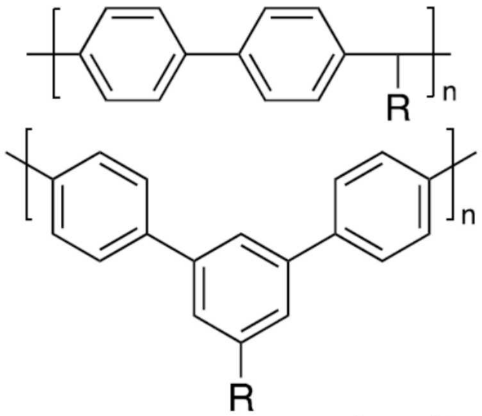
Polyethylene (PE)



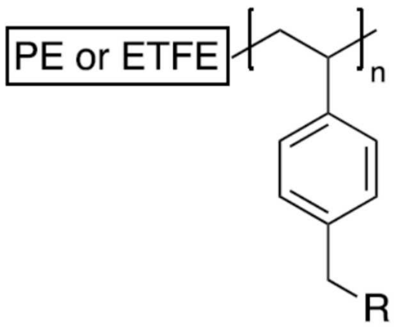


PPN6

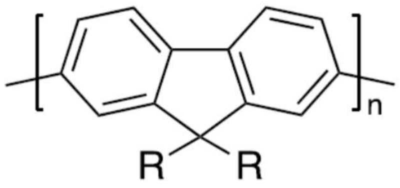
Polyphenylene (PPN)



Polystyrene (PS)



Polyfluorene (PFN)

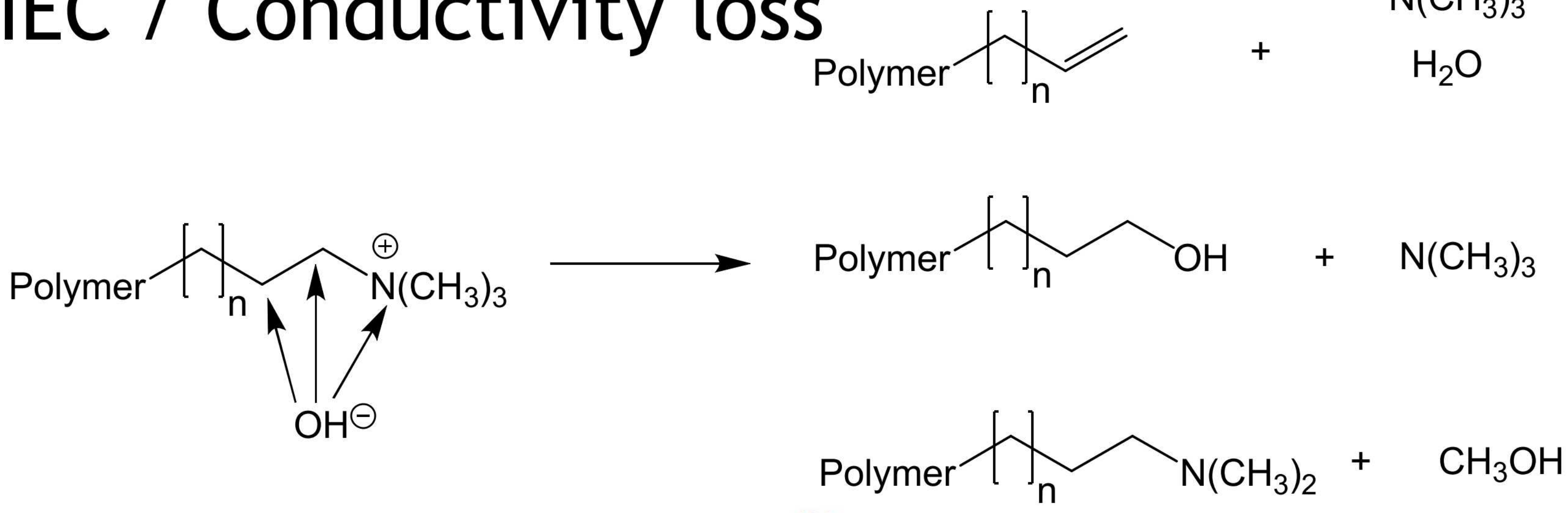


$R = (CH_2)_m X^+ OH^-$

X = typically $N(CH_3)_3$

Credit: Kelly Meeks and Bryan Pivovar NREL

IEC / Conductivity loss



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

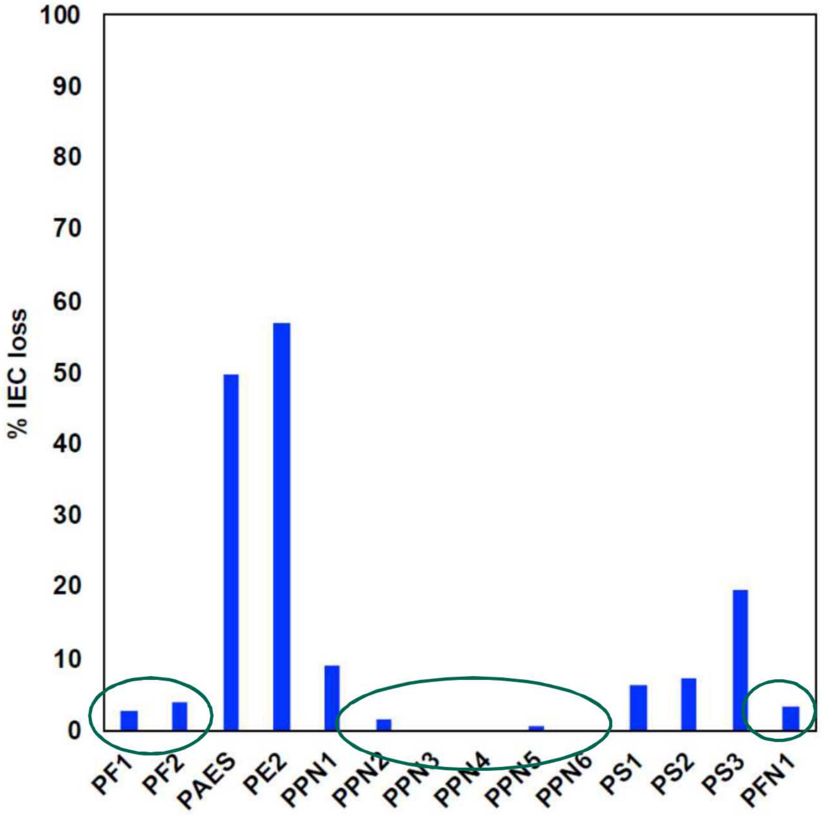
Acceptable loss < 5%

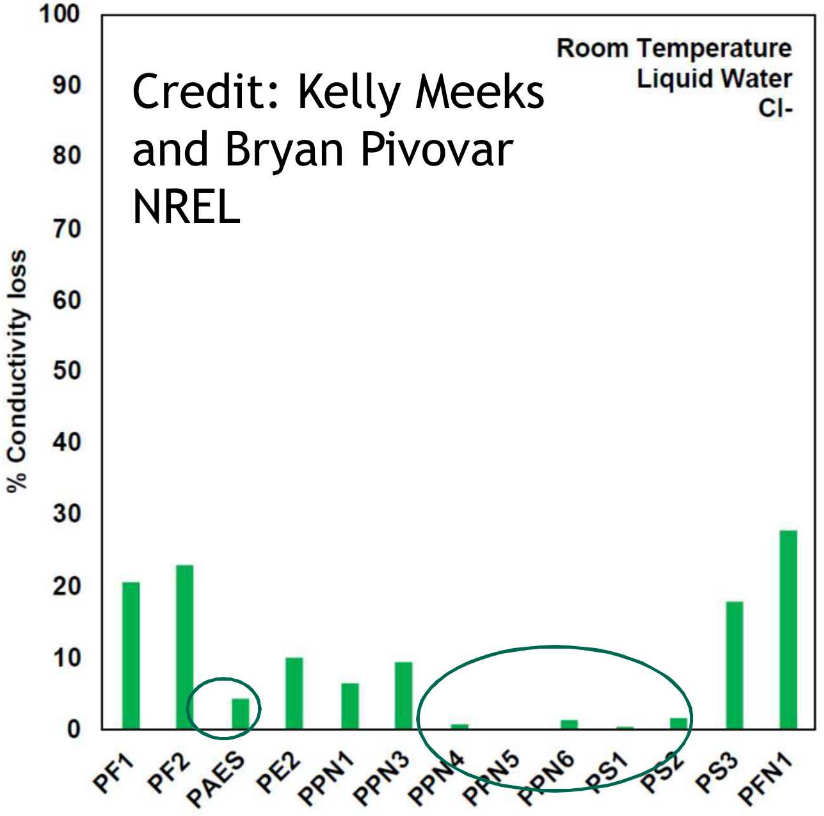
PPN6 passed this test!

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

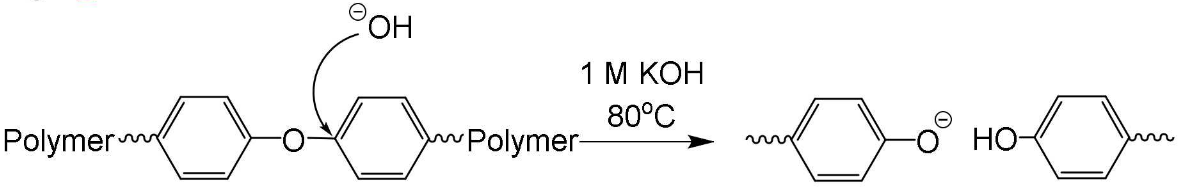
but

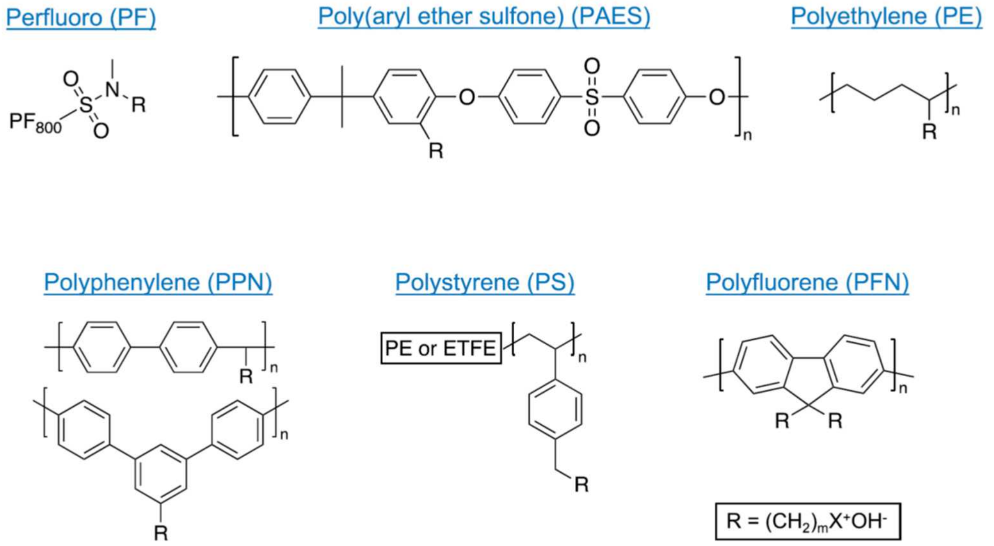
42 % of surveyed polymers saw less than a 5% loss in conductivity (Sandia polymer is PPN6).

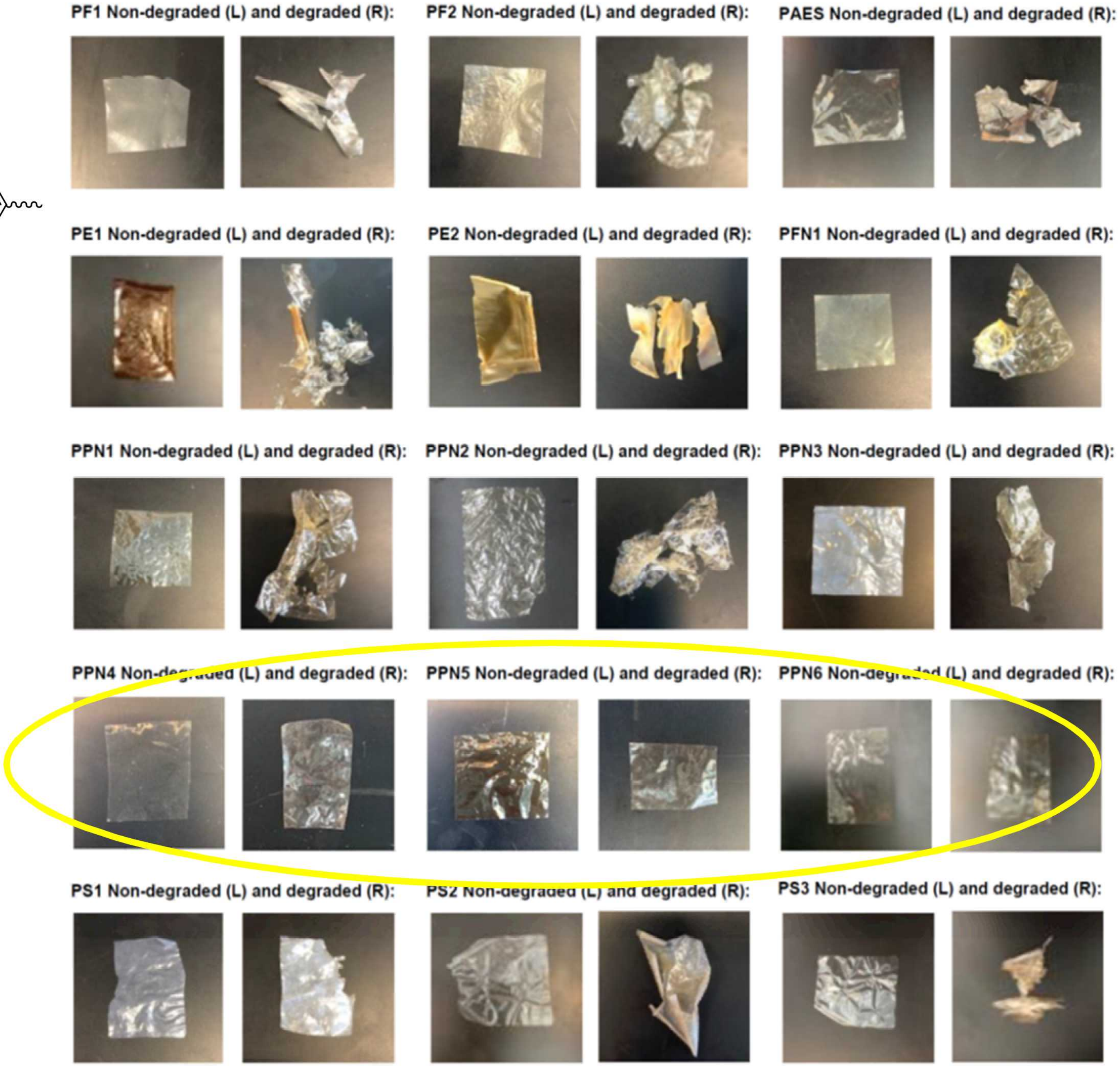




Mechanical stability







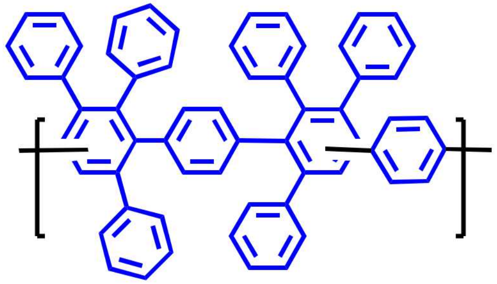
Credit: Kelly Meeks and Bryan Pivovar NREL

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

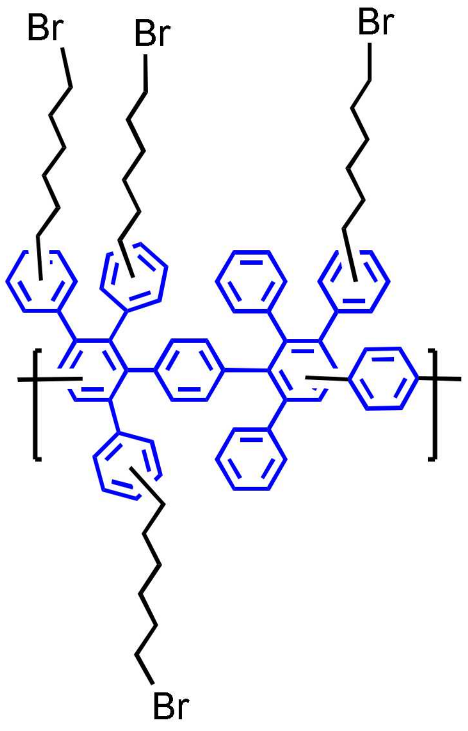
Membranes for Flow Batteries (FB)

- For FB, precise control of IEC. Too High IEC = high crossover, capacity loss. Too Low IEC = low conductivity, low efficiency.
- Recently discovered a synthetic issue that was affecting IEC control = performance in flow battery applications.
- Actual ICE were lower (15-20%) than expected and resultant film could not be processed.

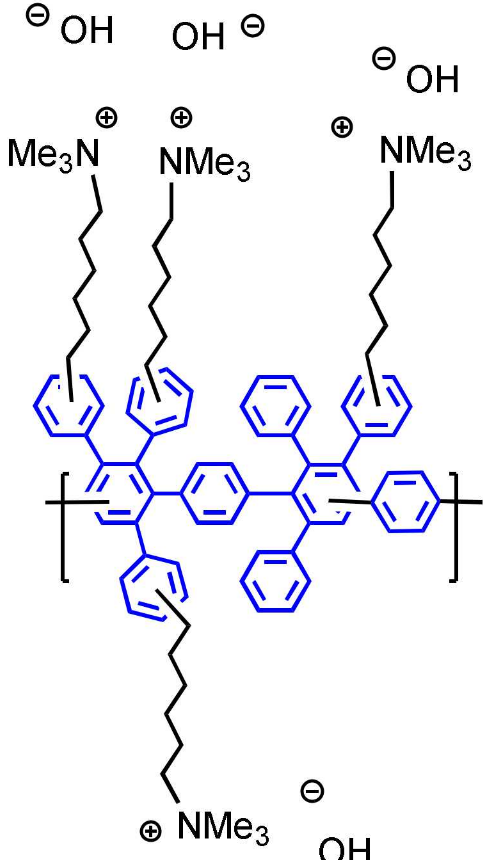
Starting Material



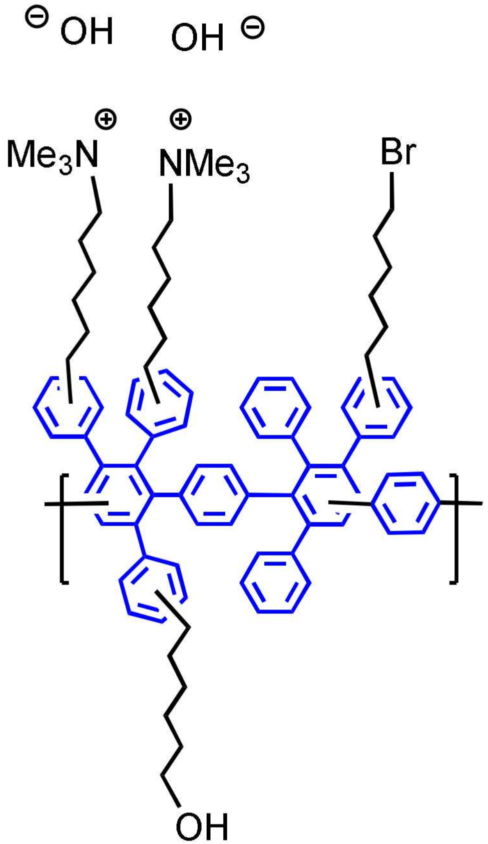
Intermediate



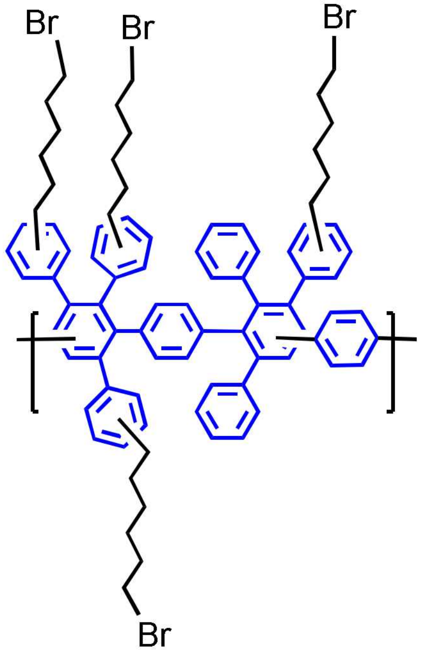
Desired product

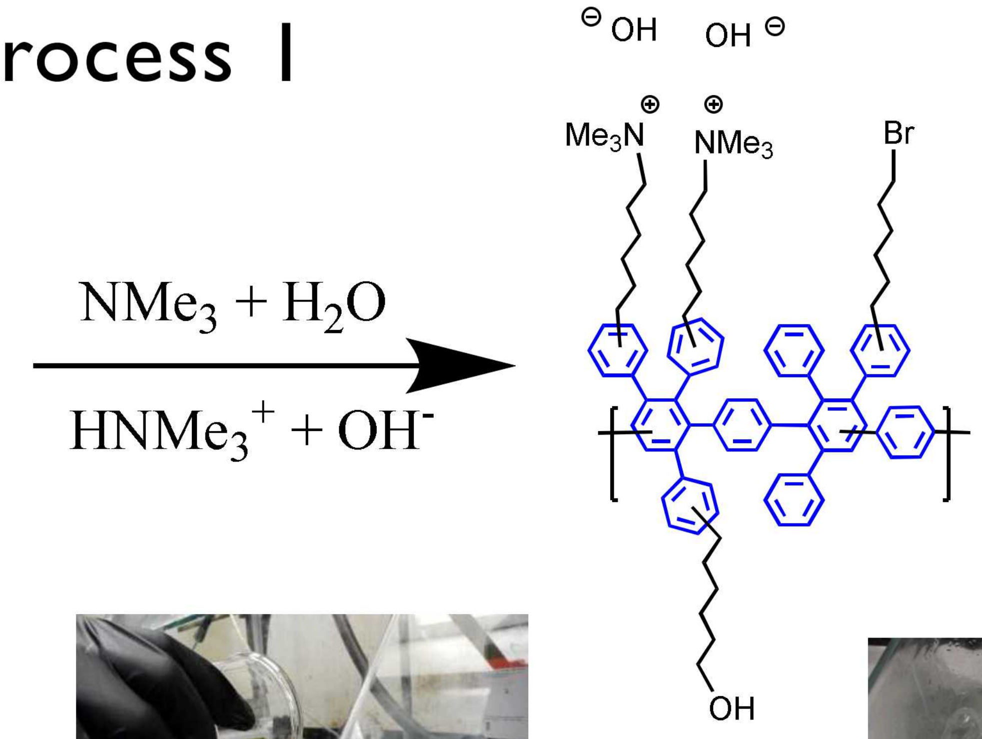


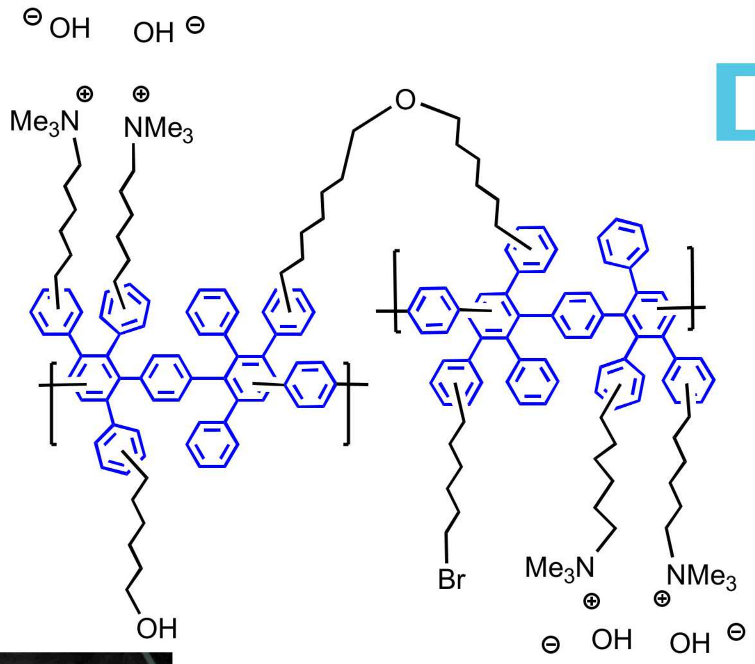
Actual product



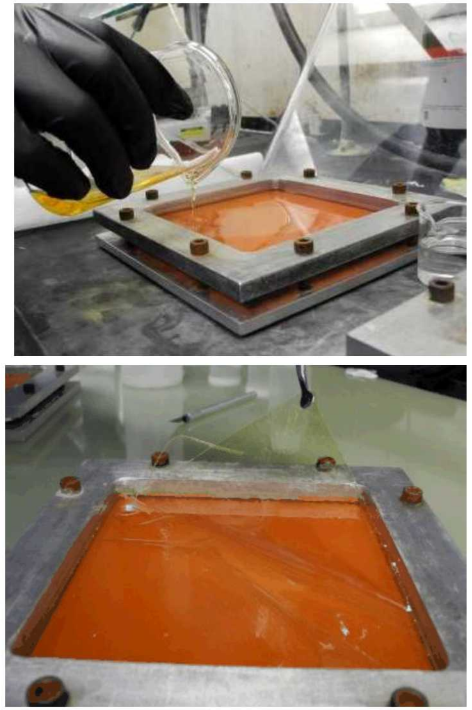
Polymer Process I





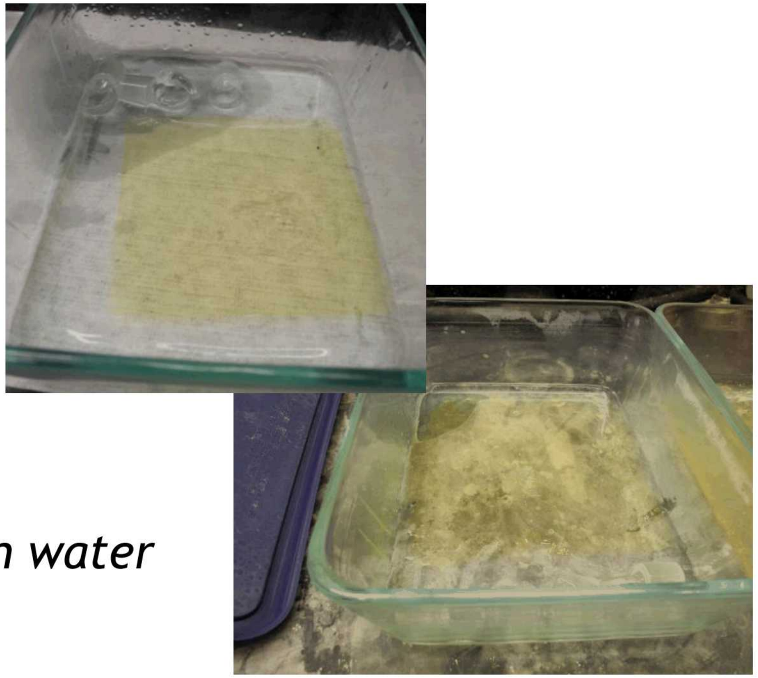


Dissolve in CCl_3H



Heterogenous reaction

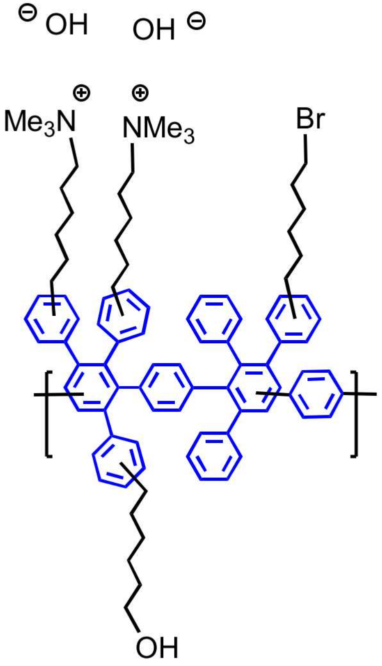
5 M $N(CH_3)_3$ in water



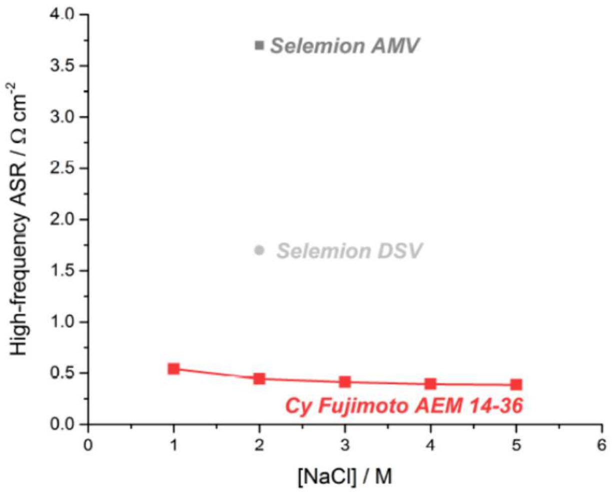
However, experimental IEC (2.3 eq/g) always lower than theoretical (2.7 meq/g)
Film after bath, could not be dissolved.

Aqueous Soluble Organic FB

Membranes made through Process 1 high conductivity but, high crossover issues.

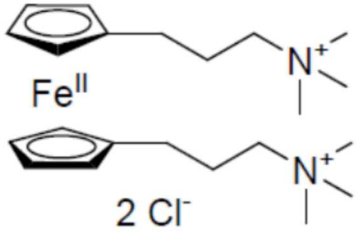


SNL = Low resistance



SNL 3.5 x lower resistance than Selemion DSV

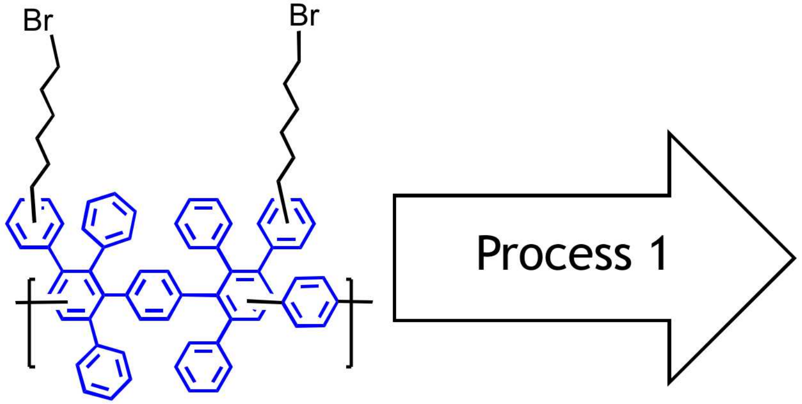
SNL = Low selectivity



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

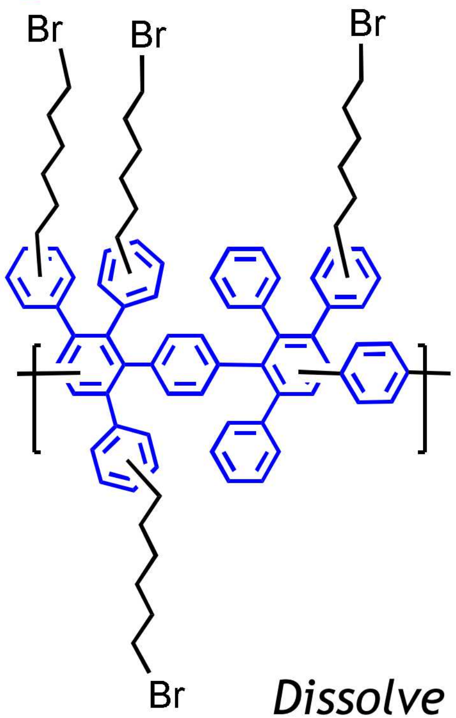
Unpublished work from Dr. Aziz labs

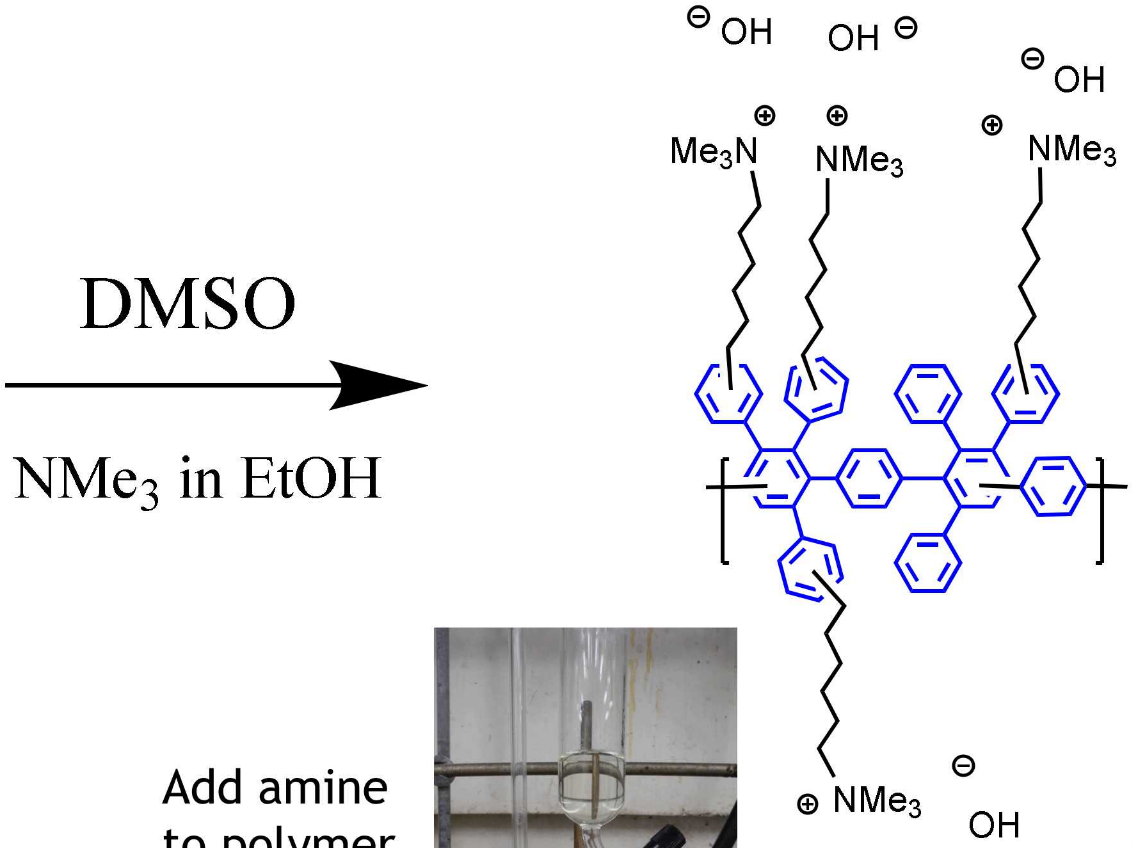
- Polymer with large amount of alkyl bromide (4-5) Process 1 would convert ¾.
- But polymers with low amount of alkyl bromide (1-2) Process 1 reaction slow.



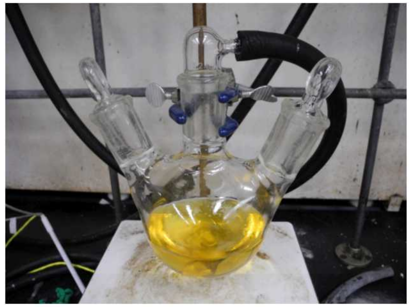
Amination very slow, after week poor conversation

Polymer Process 2

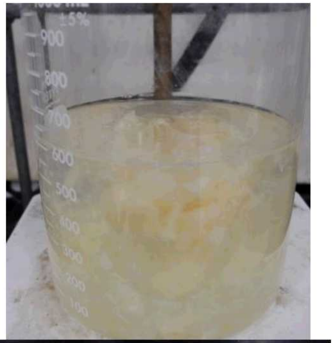




Dissolve in DMSO



Add amine to polymer



Experimental IEC (2.68 eq/g) now matches theoretical (2.7 meq/g)

Submitted provisional patent on process

Summary/Conclusions

- Interest in anion exchange membrane high.
- Various polymers are being investigated, but the SNL polymer has shown promising durability compared to other materials.
- Issues in controlling polymer IEC which was due to processing conditions.
- Developed processing procedure that has shown full conversion of alkyl bromide to ammonium; better IEC control.

Future Tasks

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

Thank You

Thank You to the DOE OE and especially Dr. Gyuk for his dedication and support to the ES industry and Sandia’s ES Program.

2019 budget = $300k

Questions?

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