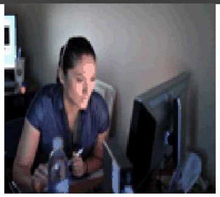
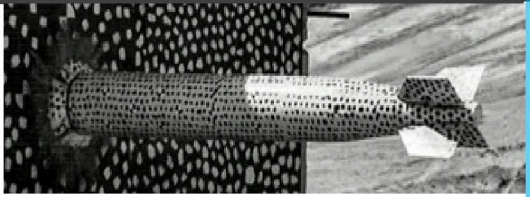
SAND2019-14448C

The Development of Diels Alder Poly(Phenylene) Membranes for Electrochemical Applications





PRESENTED BY

Cy Fujimoto

TOYOTA

GM

Automotive Fuel Cell Cooperation

WattJoule

Oak Ridge National Laboratory

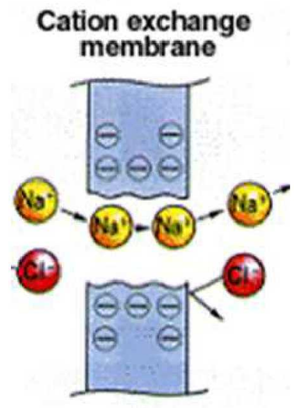
Pacific Northwest National Laboratory

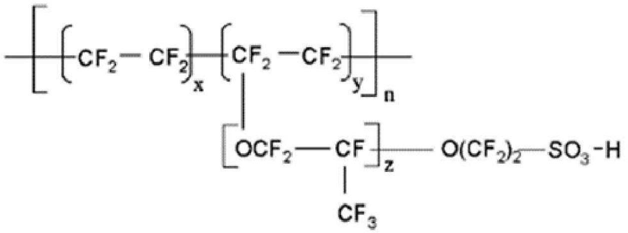
Los Alamos National Laboratory EST. 1943

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

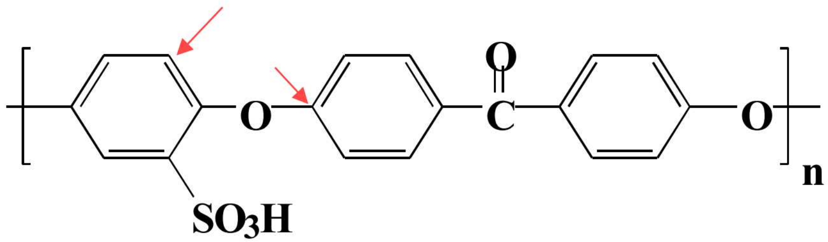
Why focus on Diels Alder poly(phenylene)?

- Membrane development program begin in 2001 through a SNL internally funded program to develop an alternative to Nafion.
- Shown are some common polymer backbones that have been investigated
- Polymers have long term stability issues
- Red arrows indicate “weak points”

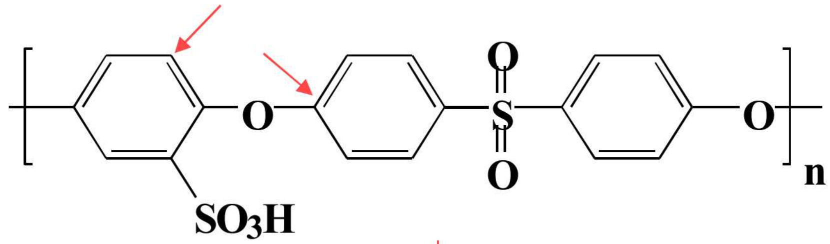




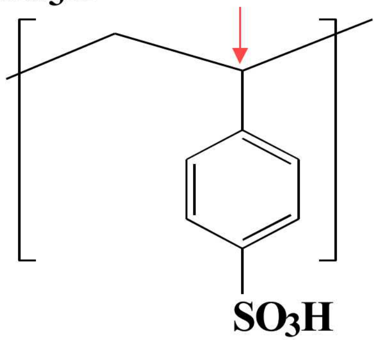
Nafion



SPEEK



SPES

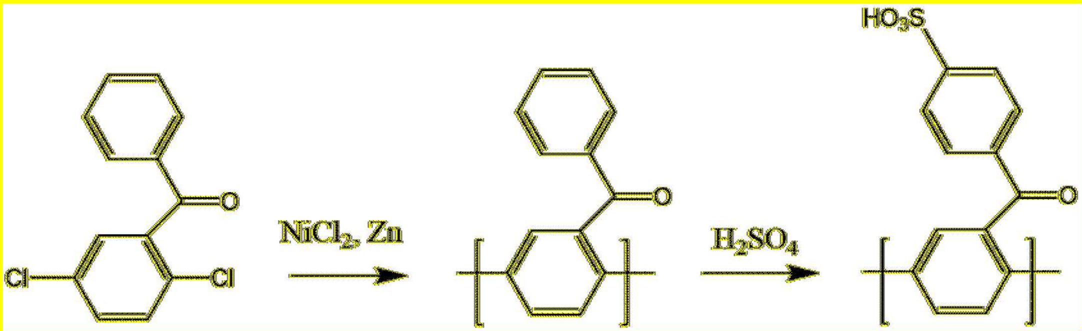


SPS

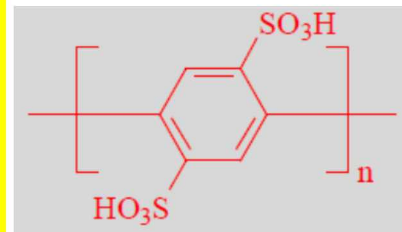
Hubner, G.; Roduner, E. *J. Mater. Chem.,* **1999**, 9, 409-418

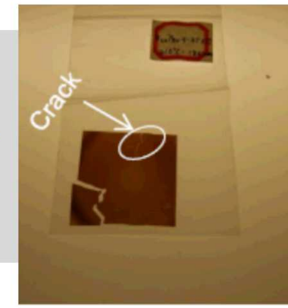
Why focus on Diels Alder poly(phenylene)?

Poly(phenylene)s offer higher chemical-thermal stability.



Eur. Pat. Appl. (2001), EP 1138712 A2 20011004.





Si, K; Dong, D; Wycisk, R; Litt, M.
J. Mater. Chem. (2012), 22(39), 20907-20917.

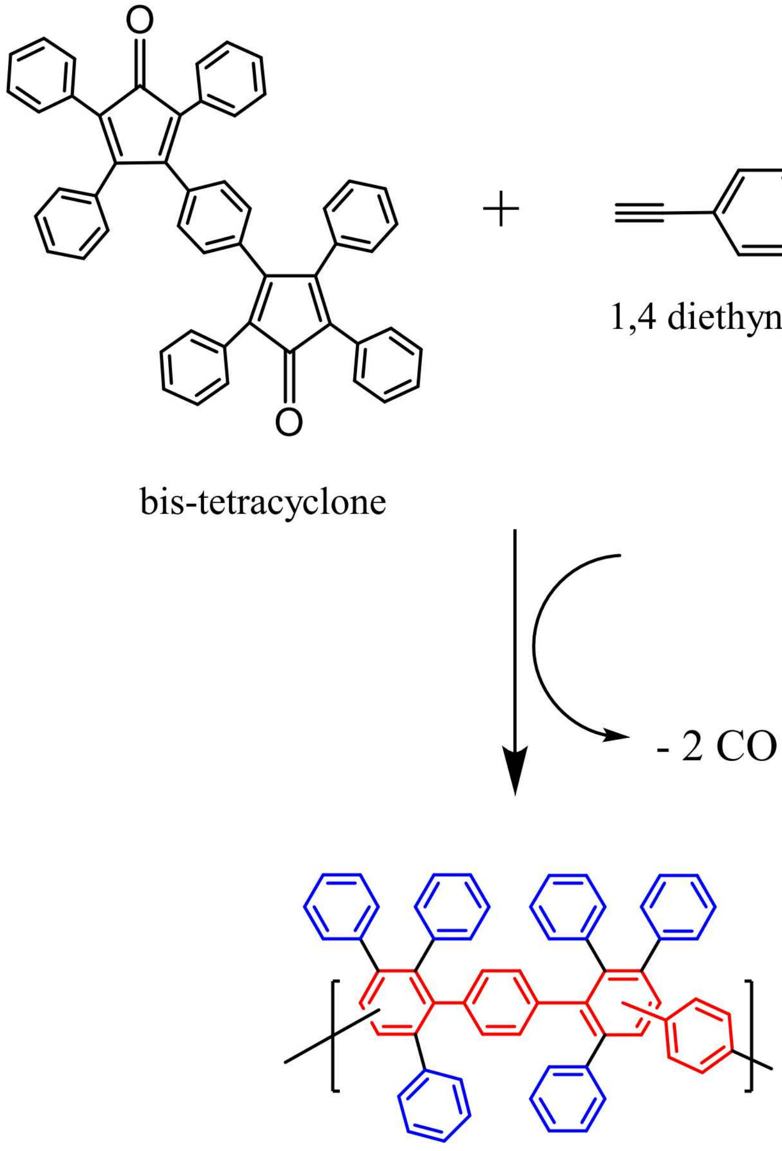
Disadvantages

1. Require use of metal catalysis: Reaction moisture sensitive and must remove catalysts after polymerization [increase costs]

2. Resultant polymers are a ridged rod (PPP), very difficult for chain entanglements = brittle mechanical properties even with high Mn

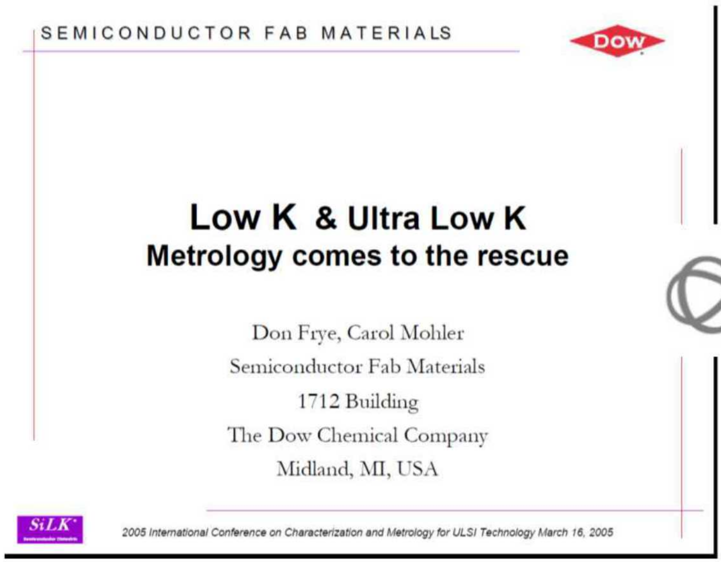
Why focus on Diels Alder poly(phenylene)?

- Diels Alder reaction no metal catalyst required, not moisture sensitive.
- The loss of CO drives the reaction – not reversible, can generate very high Mn.
- In reaction intermediate, two possible approaches the ethynyl group can approach ketone = both meta and para formed, polymer not ridged rod.
- Pendant phenyl groups (blue) are functionalized since sterically exposed.

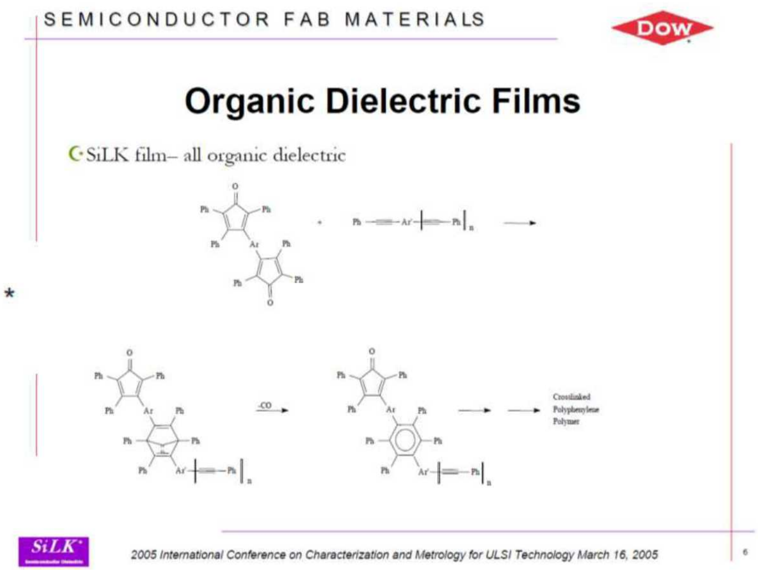


Stille, J; Harris, F; Rakutis, R; Mukamal, H. J. Polym. Sci., Polym. Lett. (1966), 4(10), 791-3

Why focus on Diels Alder poly(phenylene)?

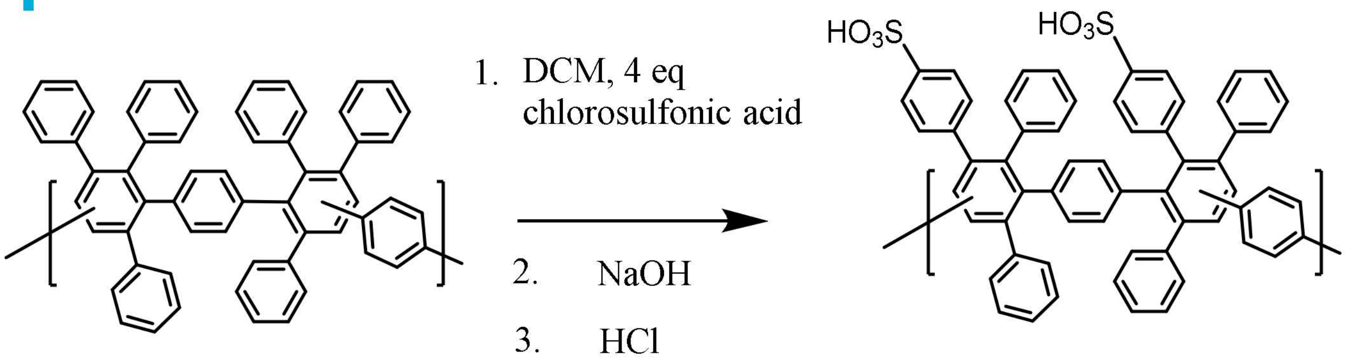


SiLKnet alliance *



- Possible – Feasible to scale chemistry? Yes
- Cost? Silicon dioxide (low volume pricing Sigma-Aldrich $64/kg) assume SiLk costs were not extremely far off from this value since cost was never an issue [Nafion $5000/kg approximately $250/$m^2$]

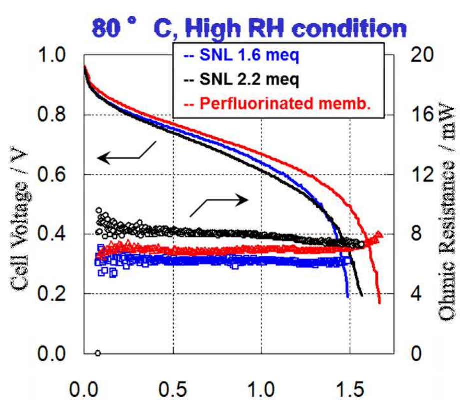
Cation exchange membrane for PEMFC

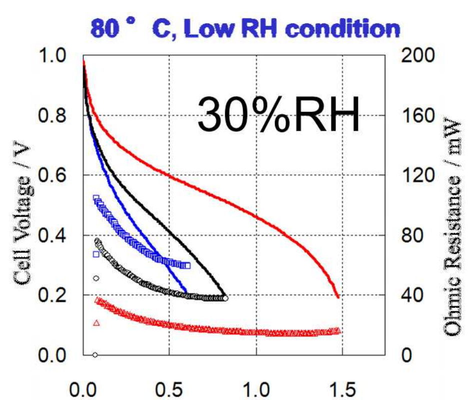


IEC > 2.5 meq/g, due to insolubility

SDAPP = Sulfonated Diels Alder Poly(phenylene)

Fujimoto, C; Hickner, M; Cornelius, C; Loy, D. Macromolecules (2005), 38(12), 5010-5016.
Cornelius, C; Fujimoto, C; Hickner, M. U.S. (2007), US 7301002 B1 20071127.





- Condition : 60 ° C, 2 Hrs (for HC membranes)
- Solution : 3 wt% H_2O_2, 4 ppm Fe^{2+}
- Result : 99 % remained (1.6 meq), 97 % remaind (2.2 meq)

- Membrane : 2.2 meq
- Solution : 1 wt% H_2O_2, 10 ppm $FeCl_2$
- Condition : 100 ° C, 2 Hrs
- Result : Completely destroyed
  A little amount of precipitations was remained in the solution.

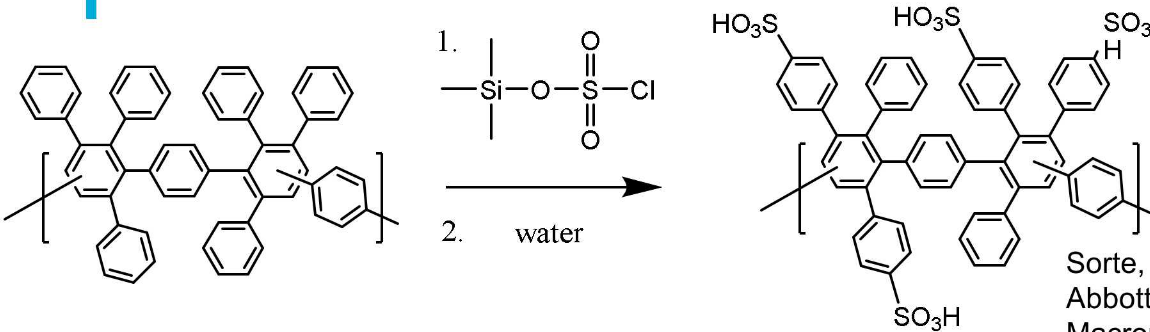
- Commercially available Nafion shows 2 ~ 4 % decrease in weight with standard condition for 8 Hrs.

Highly durable as a HC membrane, but desired to improve durability

TOYOTA

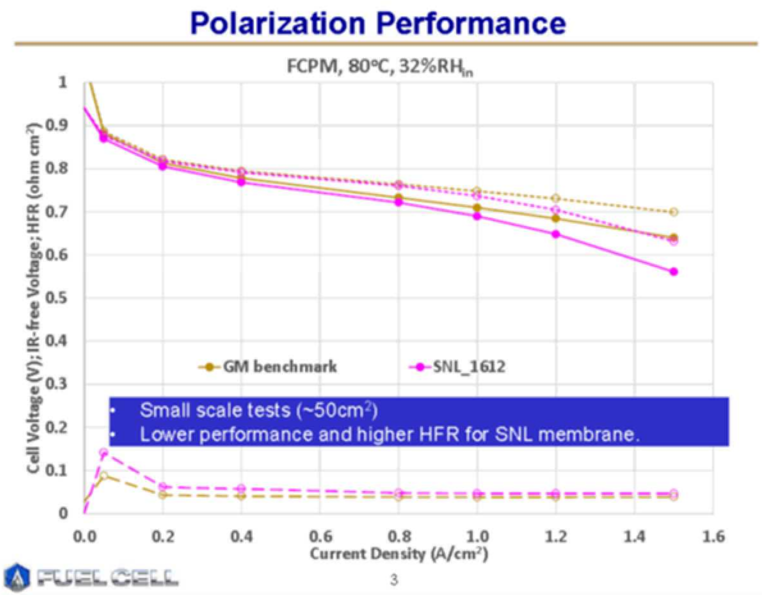
Very good humidified performance and good durability
Poor low RH performance and not as durable as PSFAs

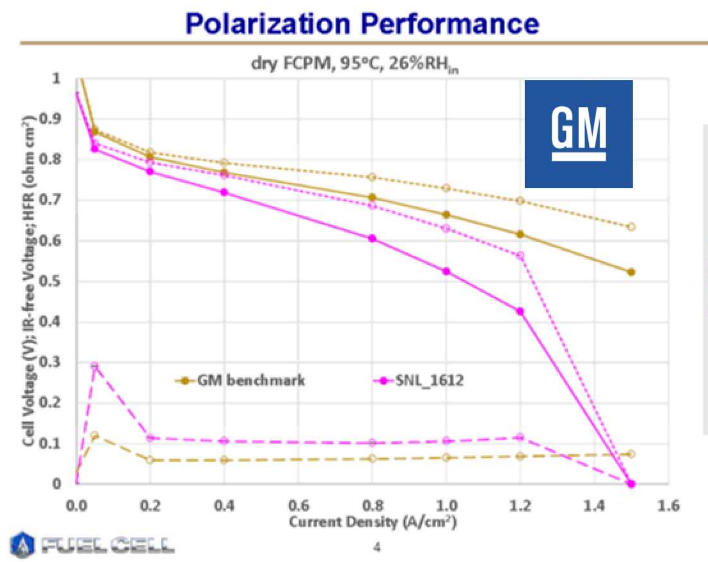
Cation exchange membrane for PEMFC



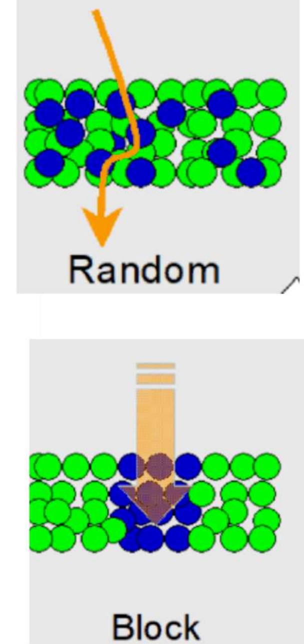
IECs up to 3.5 meq/g, higher values lead to water solubility

Sorte, E; Paren, B; Rodriguez, C; Fujimoto, C; Poirier, C; Abbott, L.; Lynd, N; Winey, K; Frischknecht, A; A. Macromolecules (2019)





Polymer microstructure model

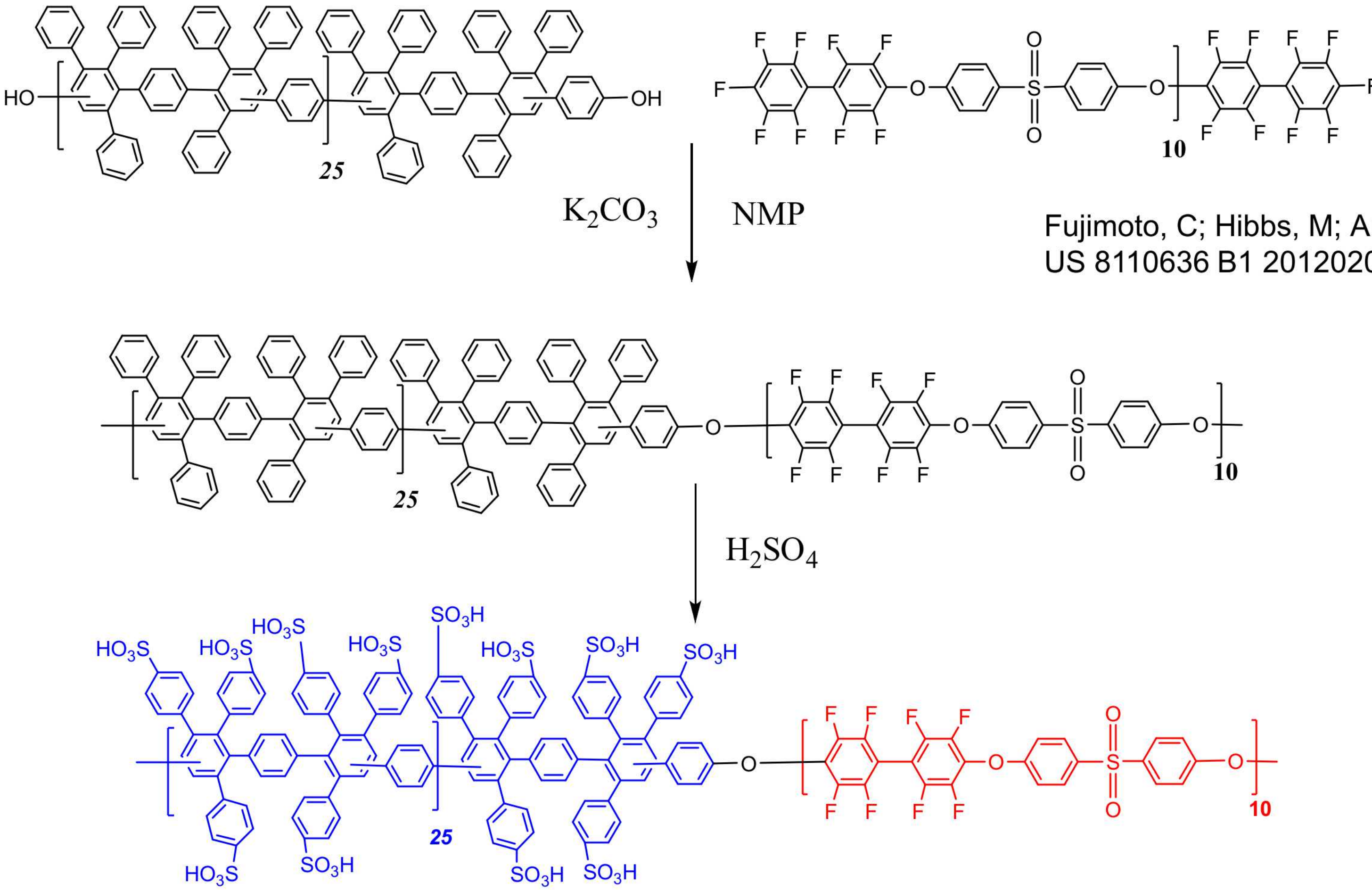


Much better low RH performance (30 %)

At very low RH (< 25 %) performance lags behind Nafion

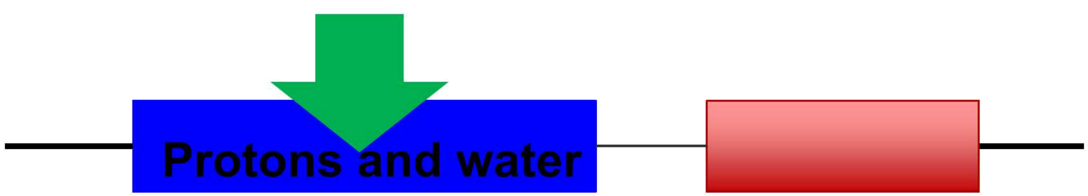
Reaching limits of randomly sulfonated polymer

Cation exchange membrane for PEMFC



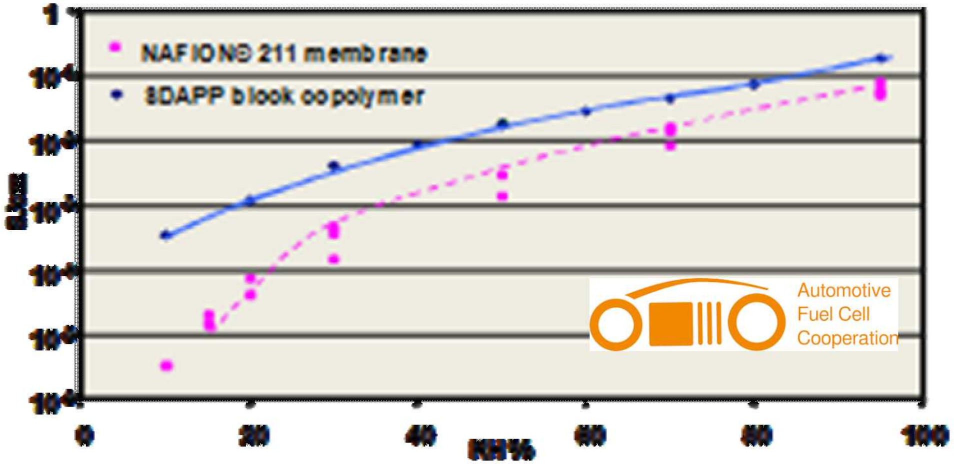
Fujimoto, C; Hibbs, M; Ambrosini, A. U.S. (2012), US 8110636 B1 20120207

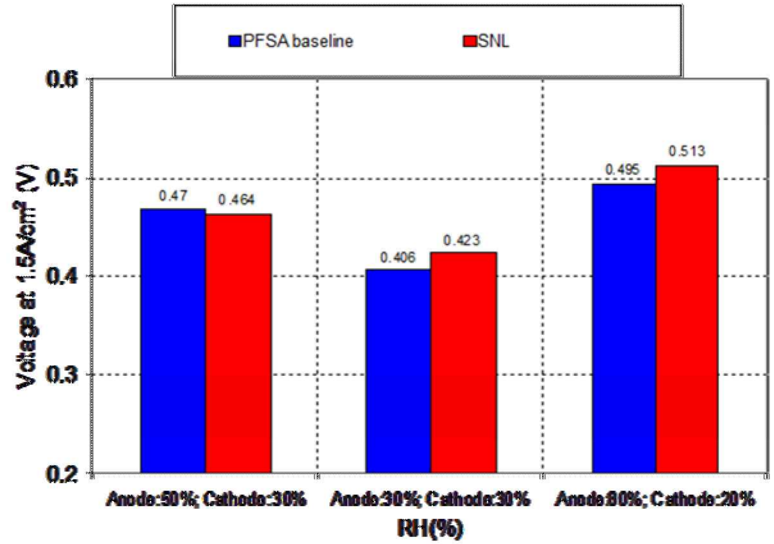
m = 25 n = 10
IEC = 2.7 eq/g

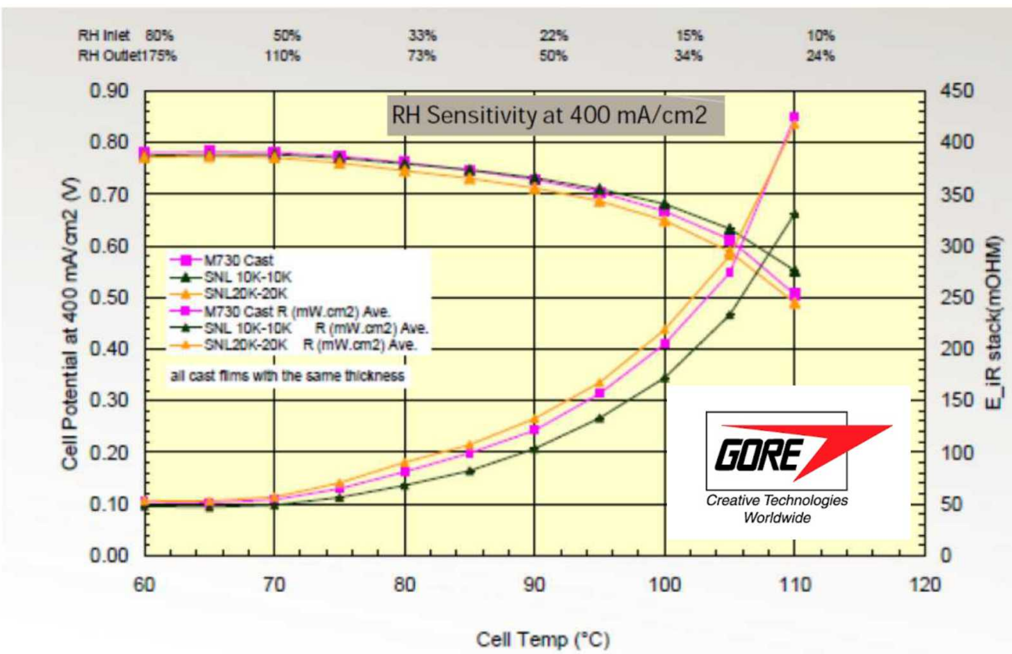


Block development was done in partnership with AFCC

Cation exchange membrane for PEMFC







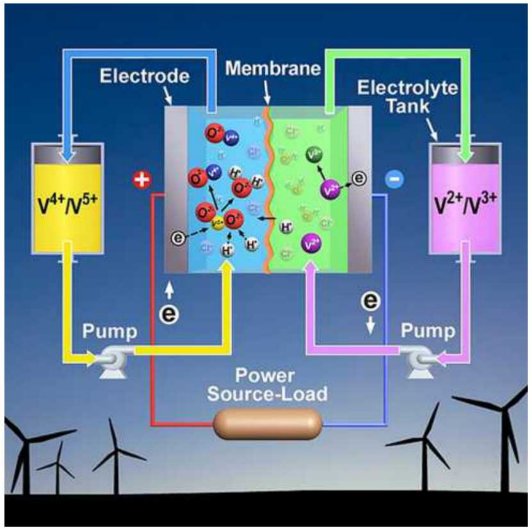
Block fuel cell performance on par with PFSA materials, even at very low RH.

Wet/Dry cycling durability needed to be improved.

Funding in the area begins to wane.

Cation exchange membrane for VRFB

- R&D interest in large scale energy storage program increased
- Flow batteries are an important in large scale storage; separation of energy and power.
- VRFB most mature; robust battery. Allows for deep discharge, long life cycles and little capacity fade.
- Several companies looking to commercialize the technology.



UniEnergy Technologies

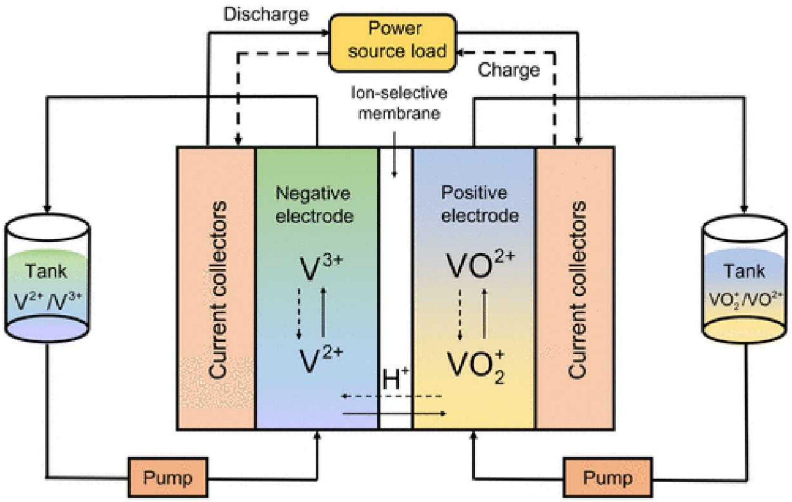
WattJoule

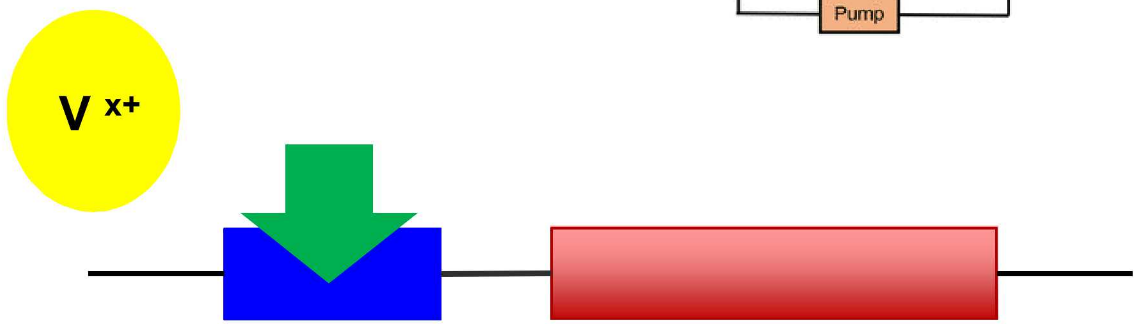
VIONX ENERGY

Cation exchange membrane for VRFB

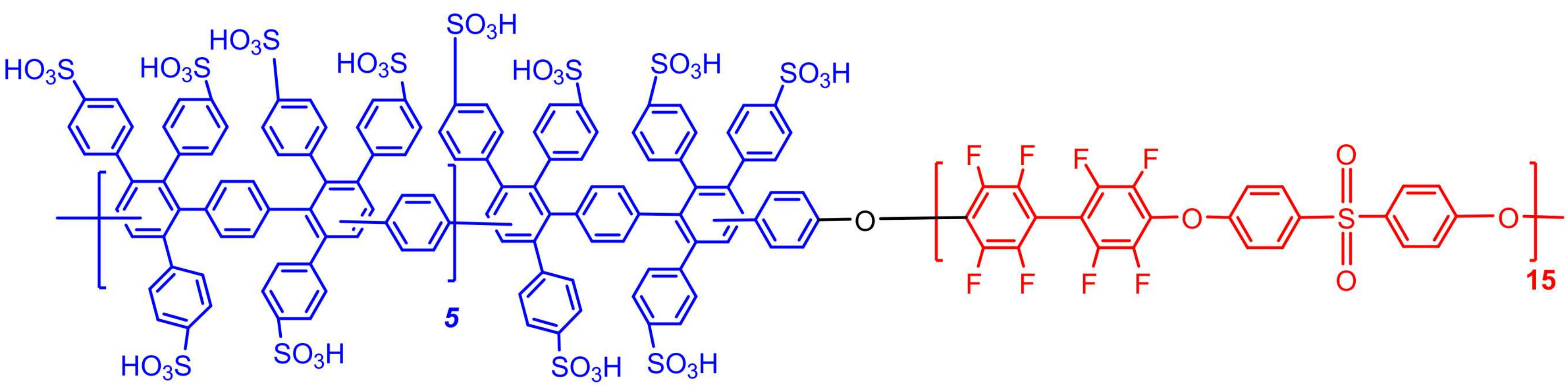
- Membrane selectivity is key, requires high proton over vanadium transport.

- Believed the blocks with an inverse morphology would be ideal.

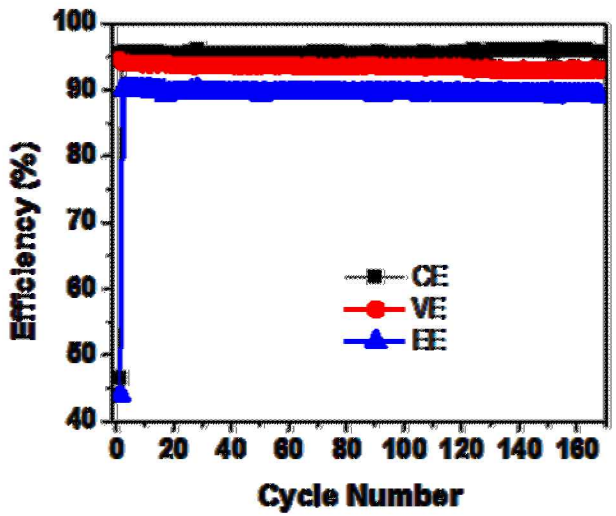


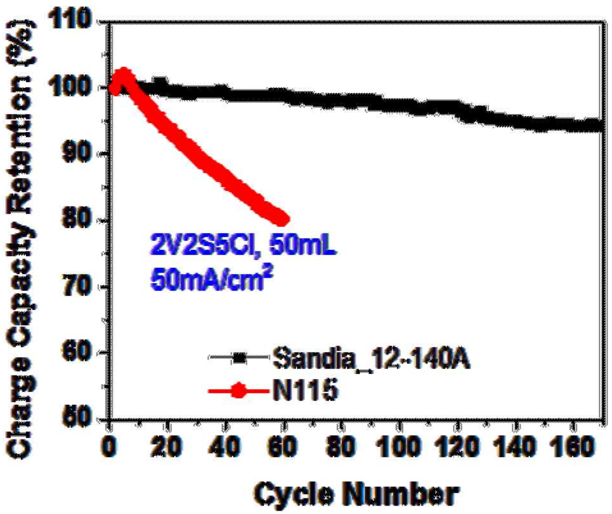


Protons and water



Cation exchange membranes for VRFB





Pacific Northwest
NATIONAL LABORATORY

Data by PNNL, SNL membrane has high efficiencies (90% EE, PFSA 75%) and high capacity retention; PFSA 75% EE

	Pmax, mW/cm²	Specific Resistance, Ωcm²
Sandia	1159	0.505
Fluorinated	946	0.610

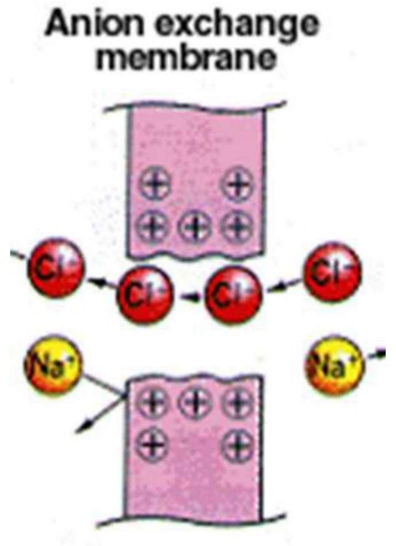
WattJoule

Membrane	Efficiency, Round Trip	Efficiency, Coulombic	Efficiency, Voltaic
Sandia	82.2%	96.2%	85.4%
Fluorinated	72.3%	92.5%	78.2%

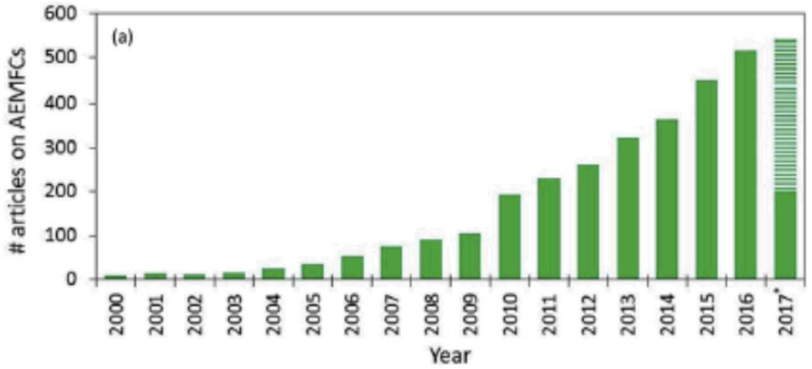
Blocks have better performance compared to PFSA, better capacity retention.
Durability still not as good as Nafion and looking to improve durability.

Anion Exchange Membrane (AEM)

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

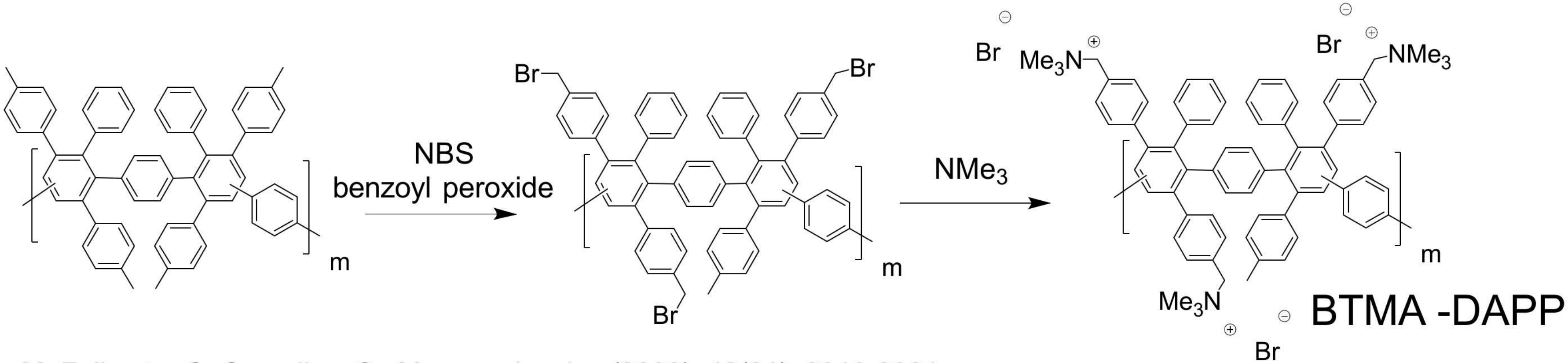
ecoLECTRO

Dioxide Materials
The CO_2 Recycling Company

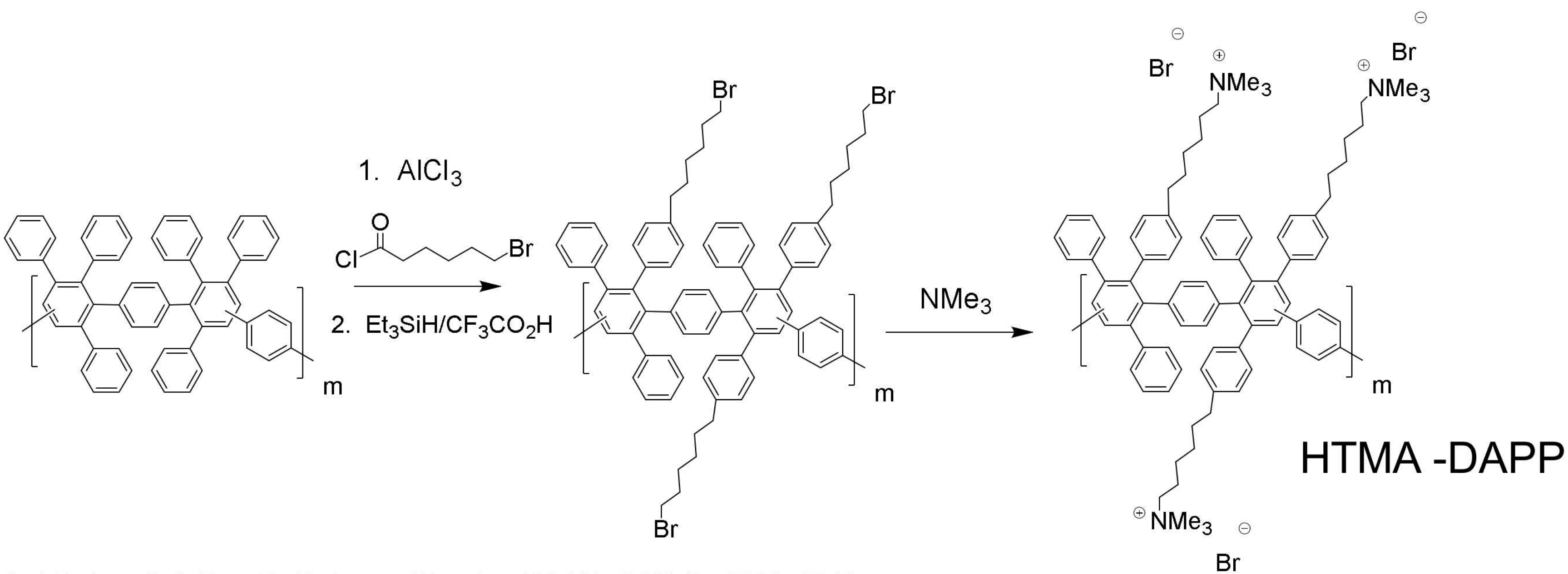
IONOMR

ORION POLYMERS

Anion exchange membrane structures



Hibbs, M; Fujimoto, C; Cornelius, C. Macromolecules (2009), 42(21), 8316-8321.
Hibbs, M; Cornelius, C Fujimoto, C. U.S. (2011), US 7888397 B1 20110215.

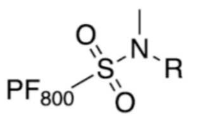


Hibbs, M. J Polym Sci, Part B: Polymer Physics (2013), 51(24), 1736-1742.
Hibbs, M. U.S. (2014), US 8809483 B1 20140819.

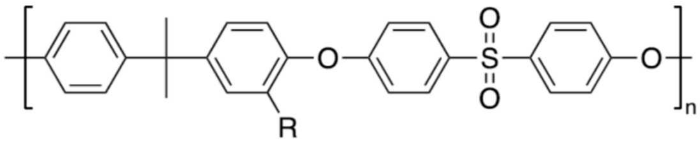
Recent independent stability survey of AEM

- 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 hr at 80 °C and monitoring any loss in 1. IEC 2. Conductivity 3. Mechanical

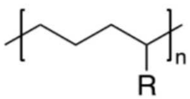
Perfluoro (PF)

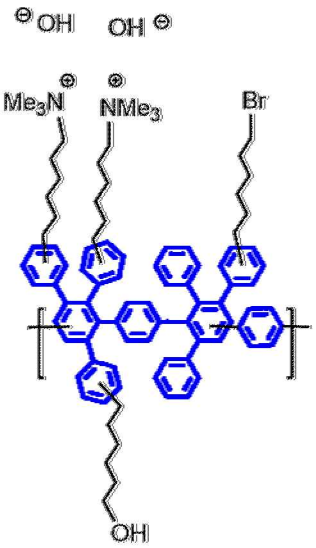


Poly(aryl ether sulfone) (PAES)



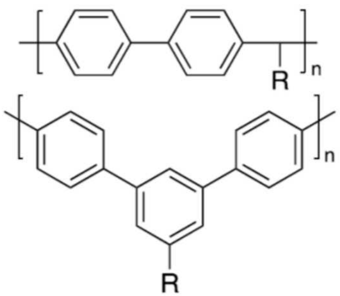
Polyethylene (PE)



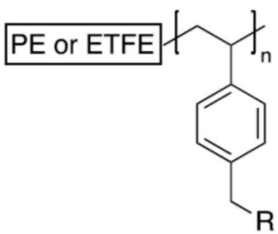


PPN6

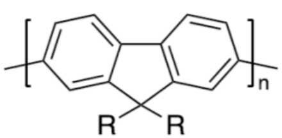
Polyphenylene (PPN)



Polystyrene (PS)



Polyfluorene (PFN)



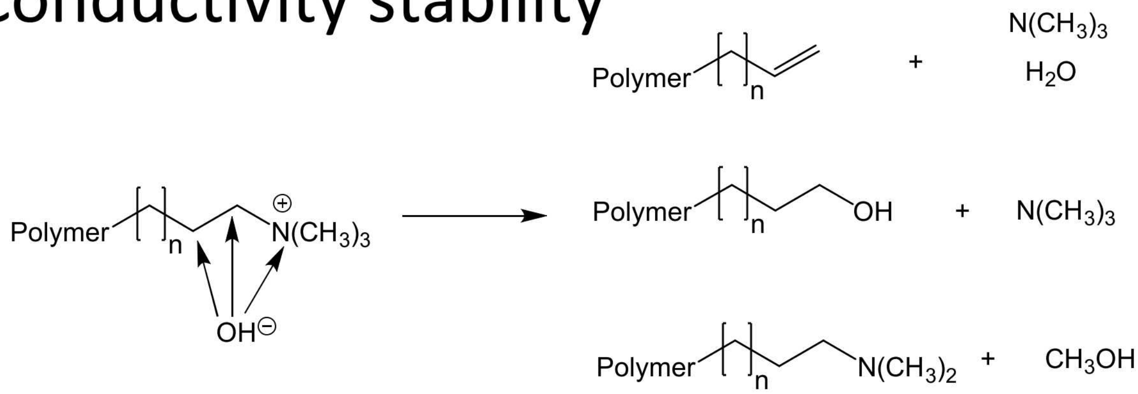
$R = (CH_2)_mX^+OH^-$

X = typically $N(CH_3)_3$

Credit: Kelly Meeks and Bryan Pivovar NREL
Presented at 236th ECS Meeting 2019

NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Anion exchange membrane IEC and Conductivity stability



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

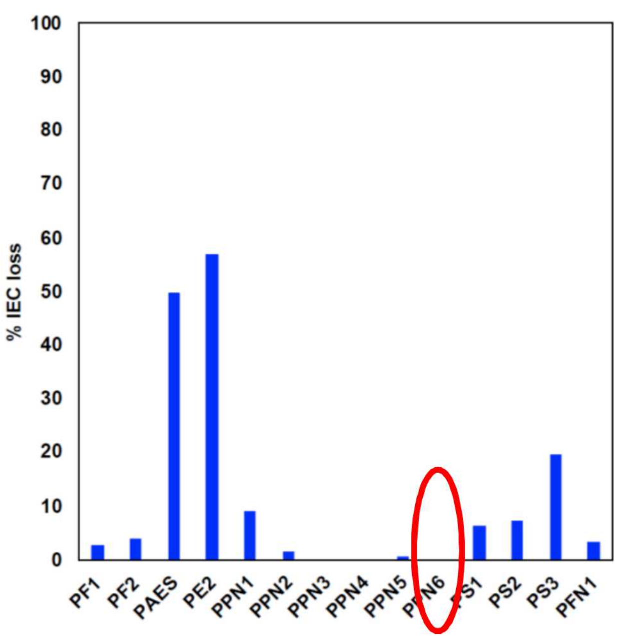
Acceptable loss < 5%

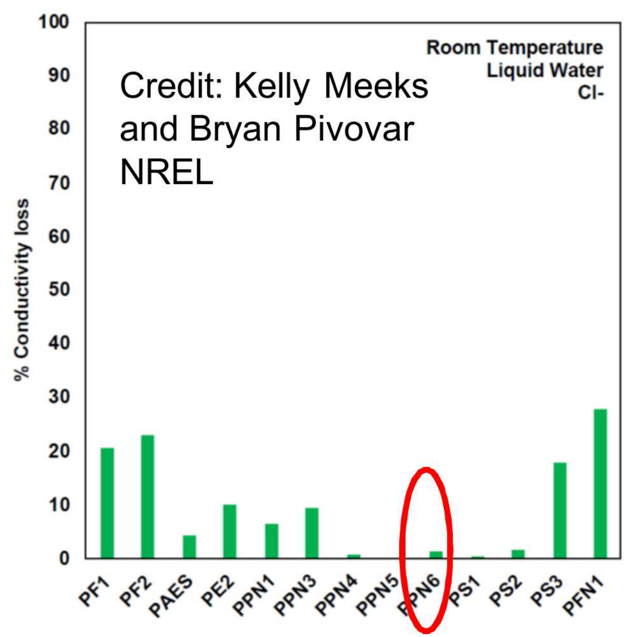
Sandia polymer, PPN6 passed this test!

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).





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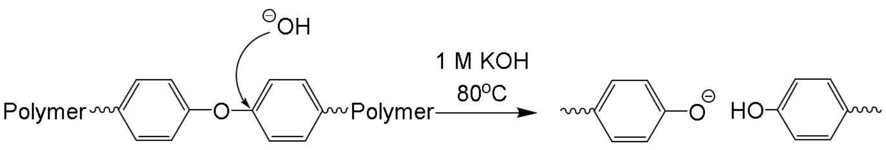
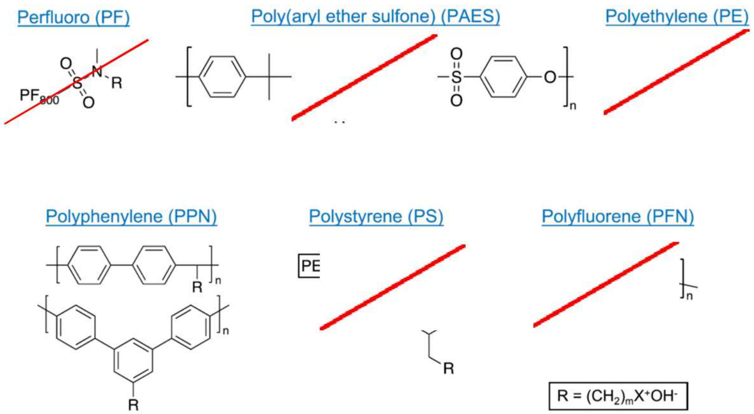
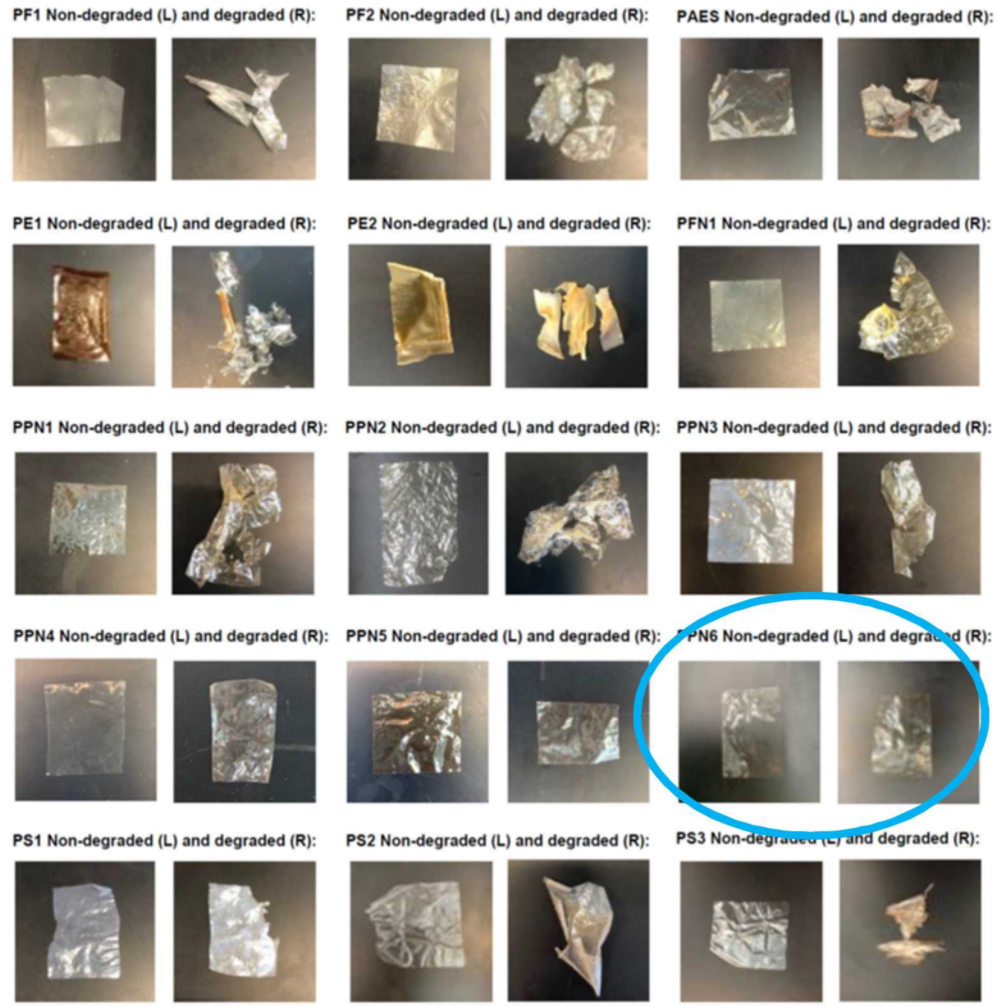
Anion exchange membrane Mechanical stability





- **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

NREL
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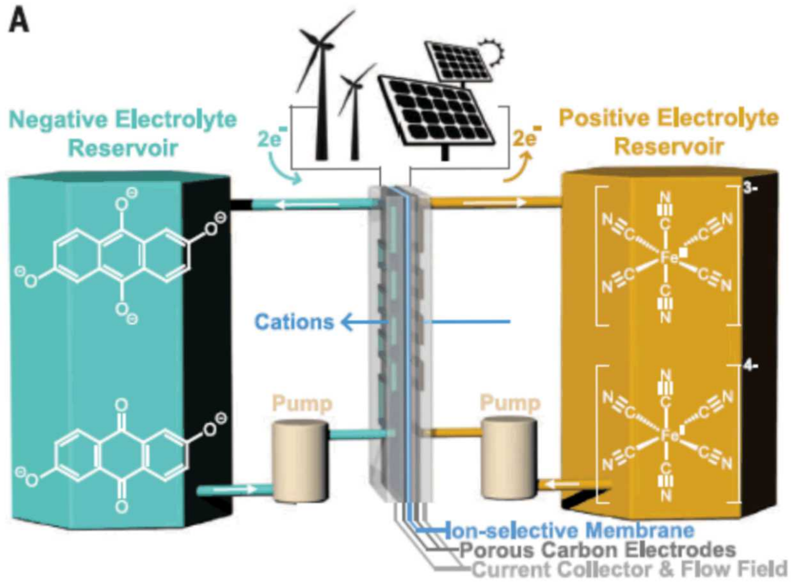
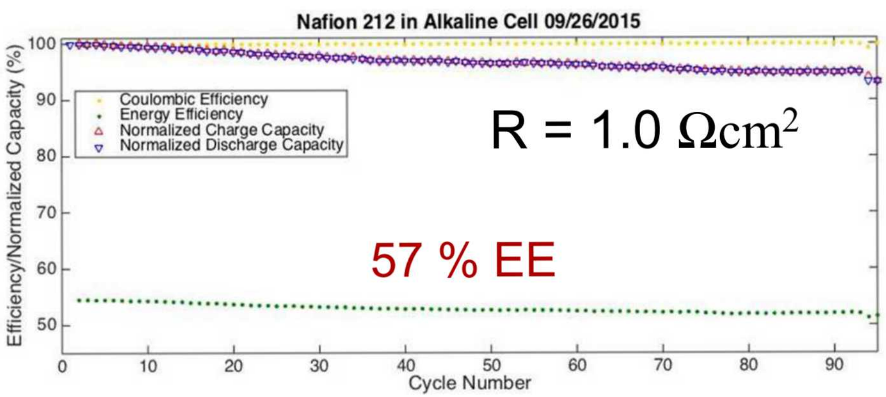
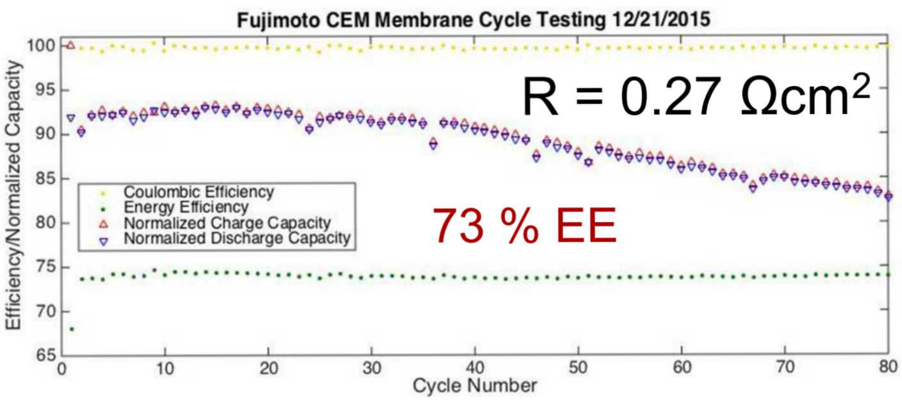
Anion exchange membrane in AOFB

Harvard professor, Michael Aziz developing aqueous flow battery with earth abundant materials

Using alkaline environment helps improve solubility quinone (increase energy density)





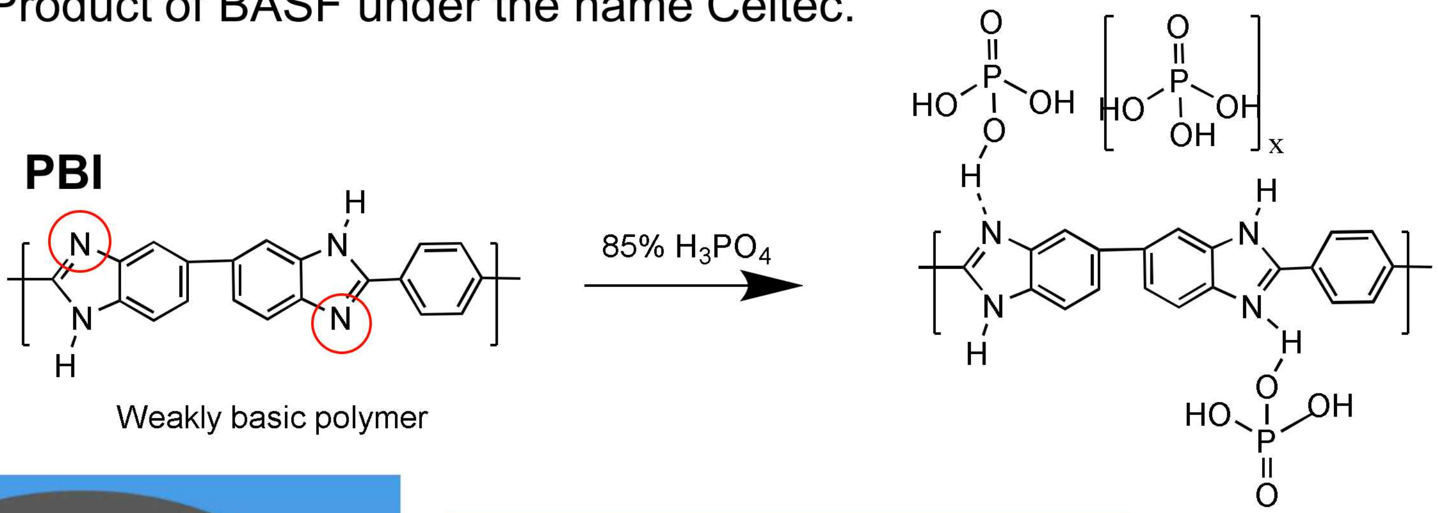


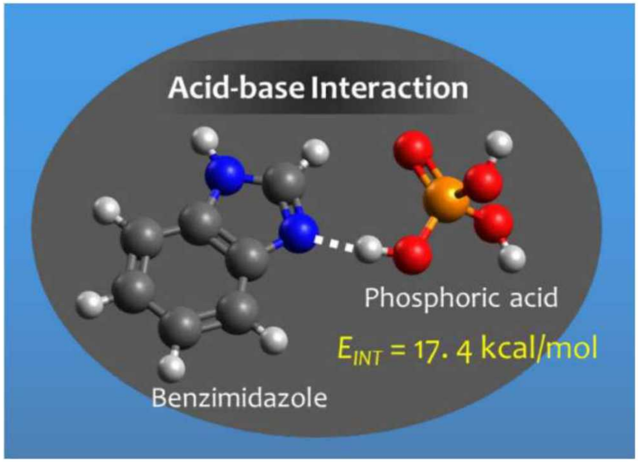
SNL polymer shows ¼ of the resistance of Nafion. Higher energy efficiencies than Nafion (+20%).

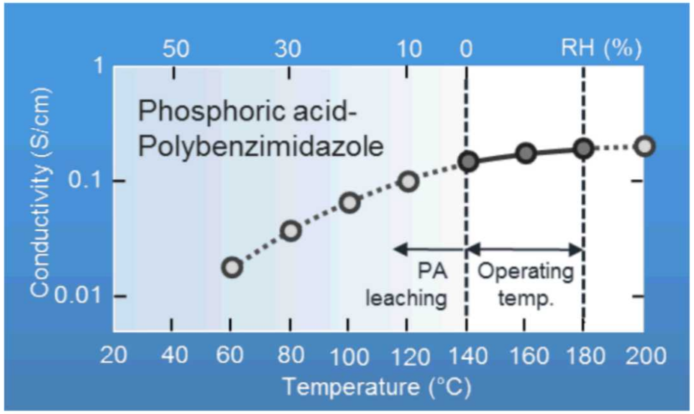
However, slightly higher capacity loss seen with SNL material.

Intermediate temperature fuel cell (ITFC)

PEM fuel cells temperature limitation is caused by the need of water (conducting medium). Phosphoric acid doped PBI, employs phosphoric acid as conducting medium. Product of BASF under the name Celtec.

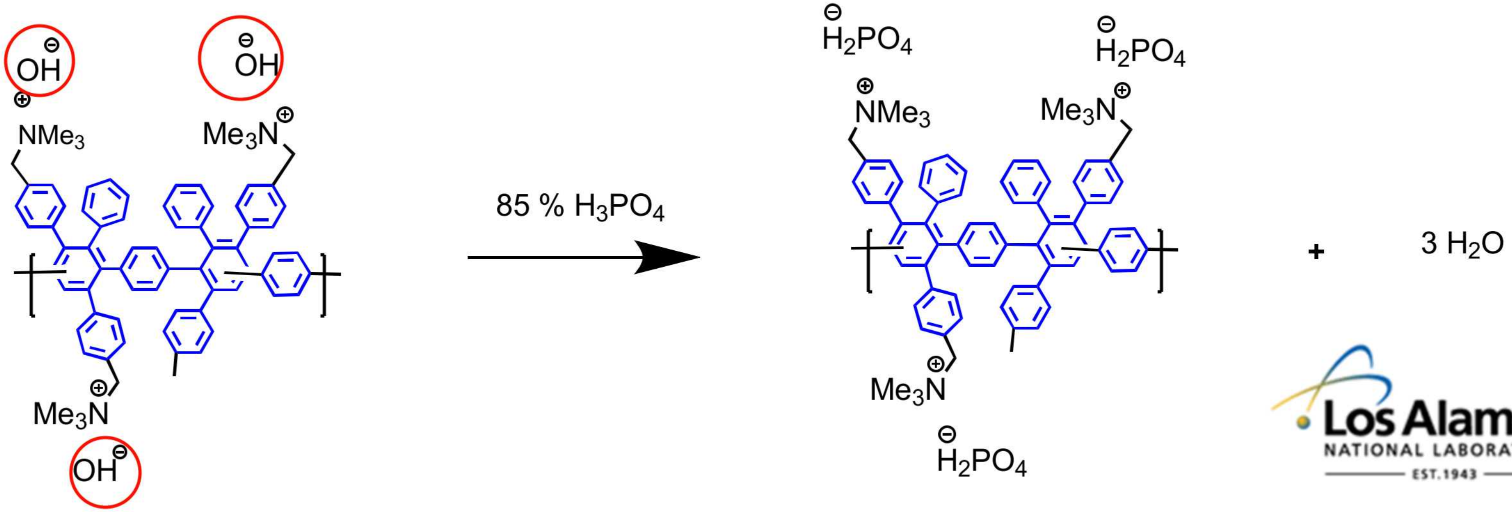




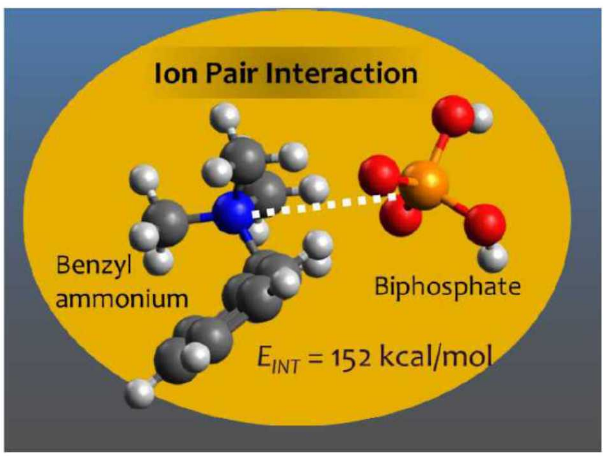


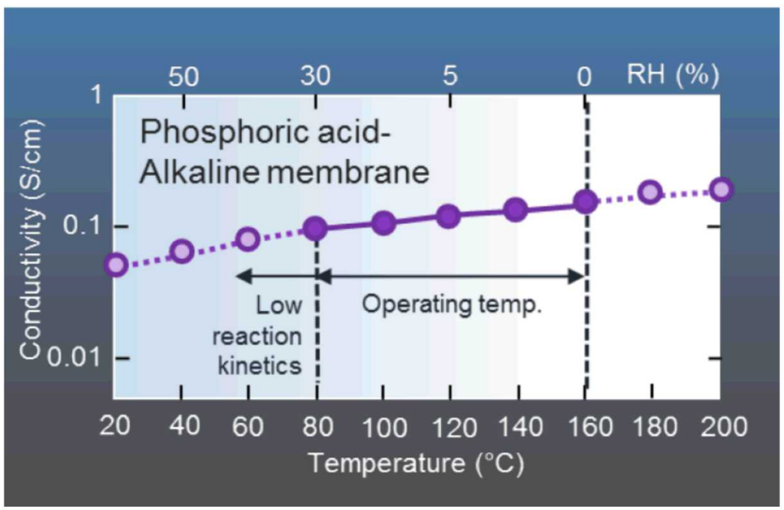
Phosphoric acid doped PBI can operate at temperatures (140 – 180^{o}C), but issue is phosphoric acid loss by leaching due to weak polymer-acid interaction.

Anion exchange membrane for ITFC



Strong base containg polymer



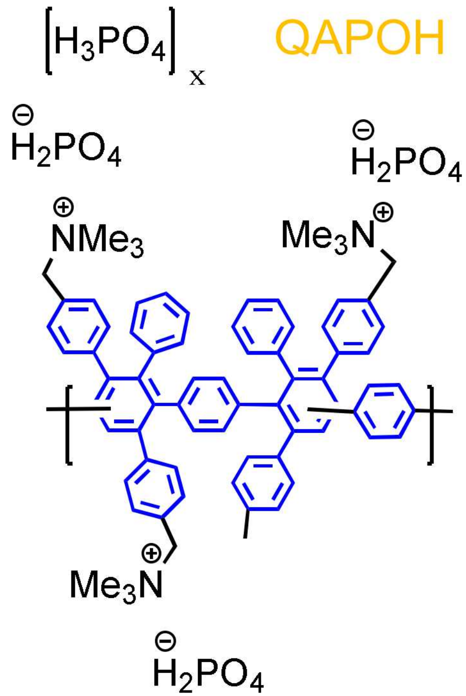


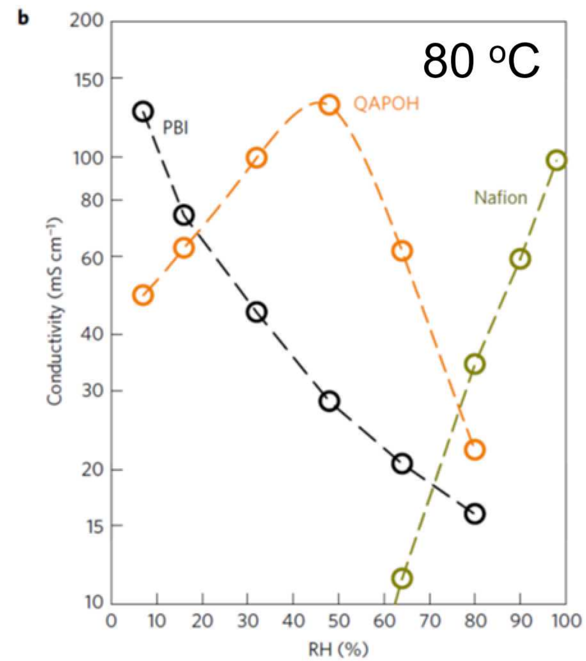
Anion exchange membrane doped with Phosphoric acid doped PBI have stronger polymer-acid interaction (ionic). Broadens operation temperatures.

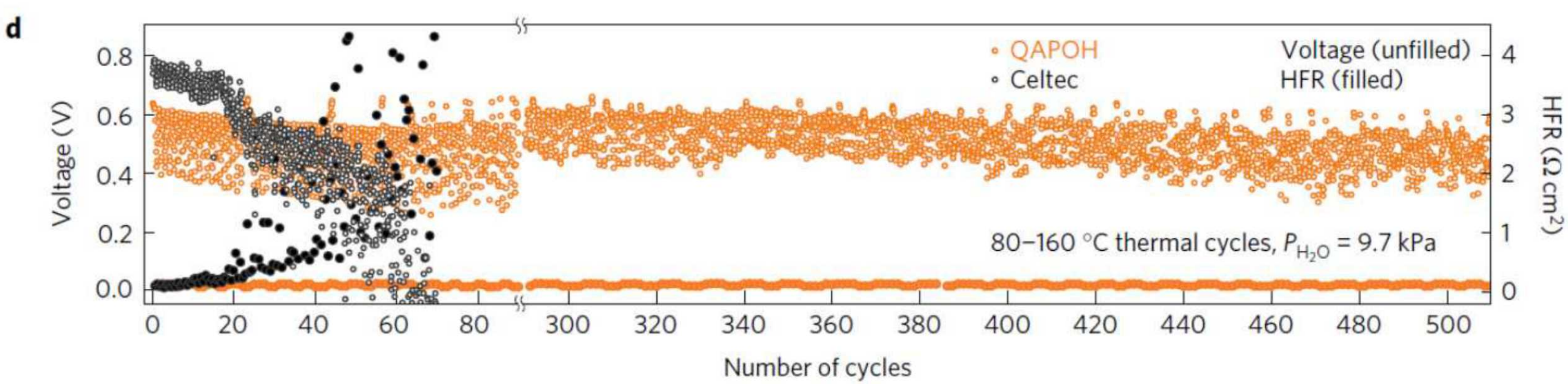
Lee, K; Spendelow, J; Choe, Y; Fujimoto, C; Kim, Y.S. Nature Energy (2016), 1(9), 16120.

Anion exchange membrane for ITFC

- QAPOH has high conductivity even in the presence of water (up to 50% RH)
- Long term fuel cell performance of QAPOH between 80 - 160 ^oC superior to Celtech







Lee, K; Spendelow, J; Choe, Y; Fujimoto, C; Kim, Y.S. Nature Energy (2016), 1(9), 16120.

Conclusions

- Sandia has developed a platform of materials based on Diels Alder poly(phenylene)s.
- Developing both cation and anion exchange membranes for electrochemical use.
- Acid block co-polymers have showed very good performance in PEM fuel cell and vanadium redox flow battery.
- Anion exchange membrane has very good durability.
- Employing the anion exchange membranes in a variety of applications and show promise.

Acknowledgments

Ehen Baca help making polymers and battery testing.

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