

Gordon Research Conference
August 8, 2016

SAND2016-7479C

HYDROCARBON-BASED MEMBRANES FOR ALKALINE MEMBRANE FUEL CELLS

Michael Hibbs

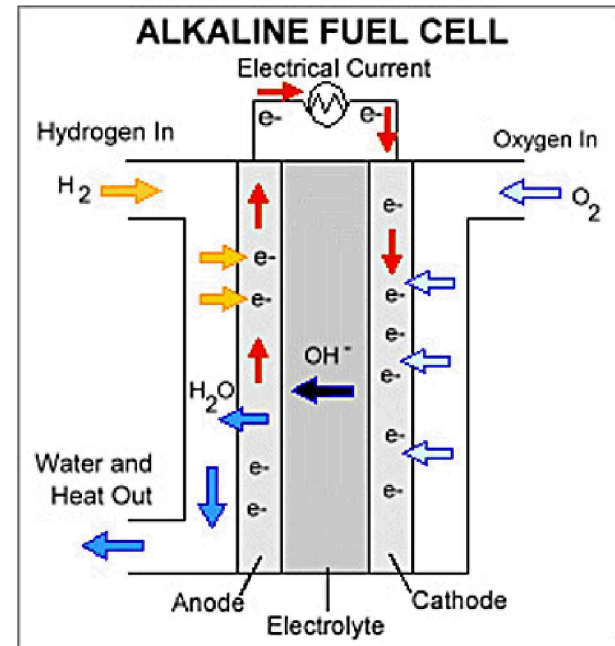
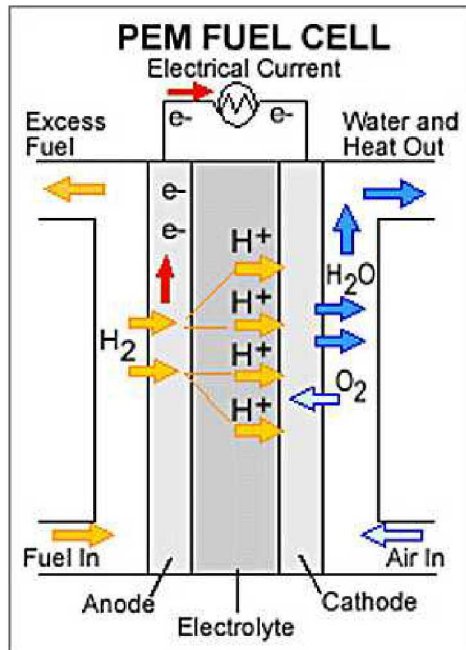
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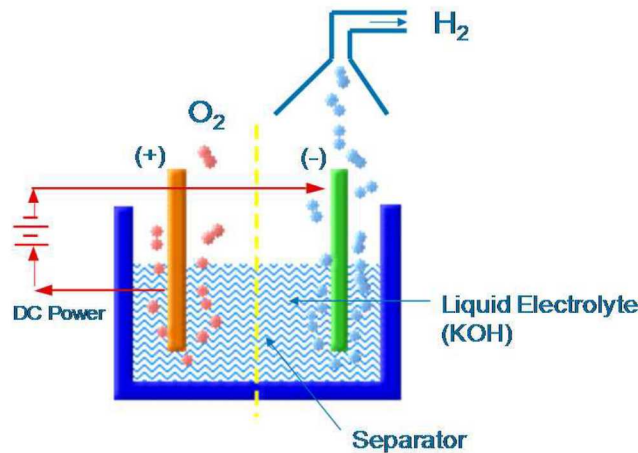


Alkaline Membrane Fuel Cells

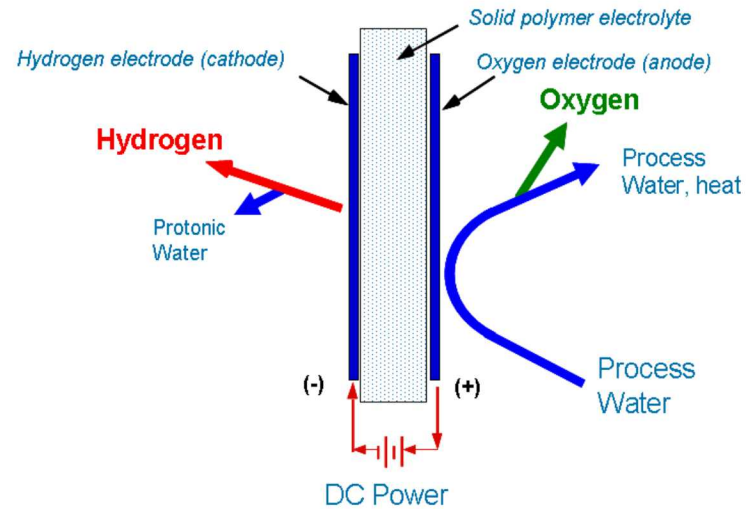


- Reaction kinetics at both electrodes are more facile at high pH
- Higher operating voltages are possible (due to lower overpotentials)
- Alternative fuels (alcohols) are easier to oxidize at high pH
- Non-noble metal catalysts can be used (significant cost reduction)
- Not a new concept - AFCs were used in the Apollo spacecraft and early space shuttle Orbiter vehicles.

Alkaline Electrolysis Cell Configurations



Liquid electrolyte Cell



Membrane-based cell (PEM or AEM)

- Commercialized systems are either liquid KOH or PEM-based.
- Liquid electrolyte systems contain corrosive solutions (handling and materials costs) and porous separators (gas crossover and high resistance across gap)
- PEM systems require platinum group metal catalyst such as iridium oxide, whereas alkaline systems electrolysis can be conducted with Ni or Ag.
- An anion-exchange membrane based system would provide the advantages of both alkaline liquid electrolyte and PEM systems.



Membrane Issues

There is no commercial standard AEM (such as Nafion[®] for PEM).

1. Backbone stability
 - Membrane must maintain mechanical integrity for up to 5000h at high pH.
 - Must be stable to MEA fabrication (hot and dry)
2. Stable cationic groups
 - Quaternary ammonium groups can be attacked by OH⁻.
3. Conductivity
 - OH⁻ inherently 2-3x less mobile than H⁺
 - Identity of anions (OH⁻/CO₃²⁻/HCO₃⁻)
 - Conductivity at low RH
4. Water swelling
 - Physical stress on cell hardware due to expansion/compression.
 - Delamination of electrodes from membrane.

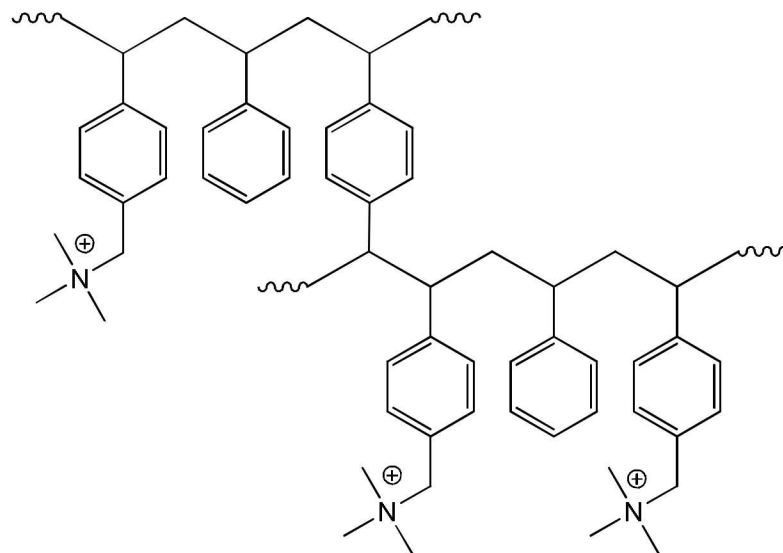
From DOE Alkaline Membrane Fuel Cell Workshops, May 8-9 2011

April 1, 2016

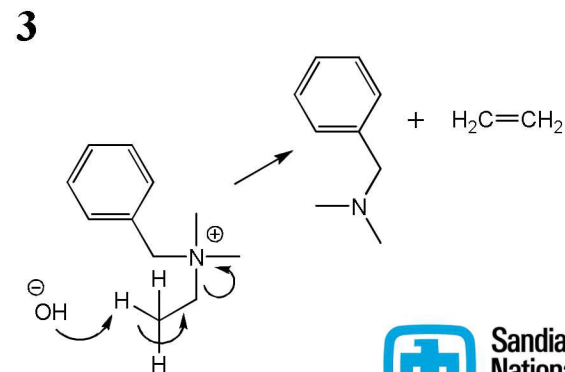
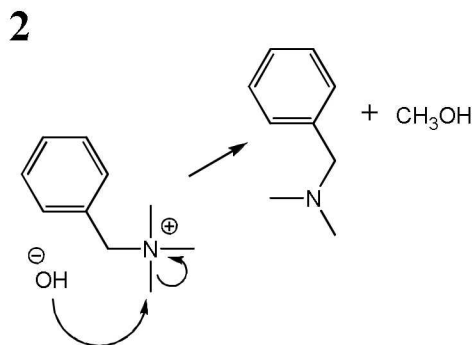
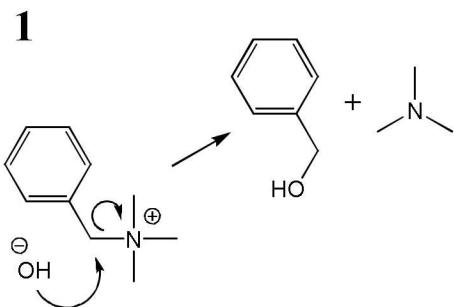
Cations on Anion Exchange Membranes (AEMs)

A Typical Commercially-available AEM:

- Crosslinked polystyrene with benzyl trimethylammonium groups (BTMA)
- Typically blended with PVC or a polyolefin
- Cast on fabric support
- Used for electrodialysis

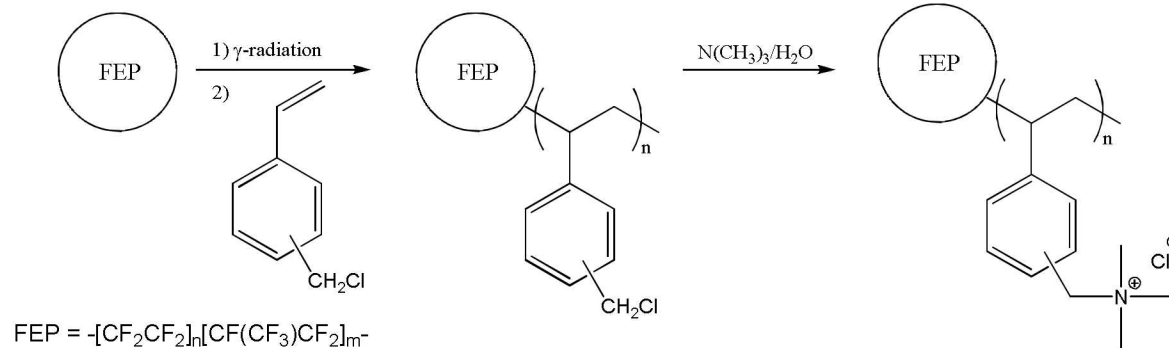


Three degradation pathways for quaternary ammonium groups:

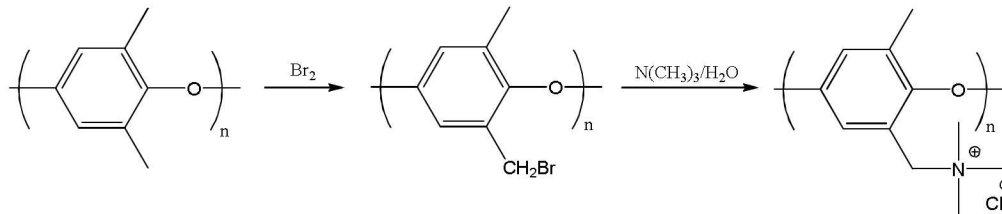


AEMs: The State of the Art

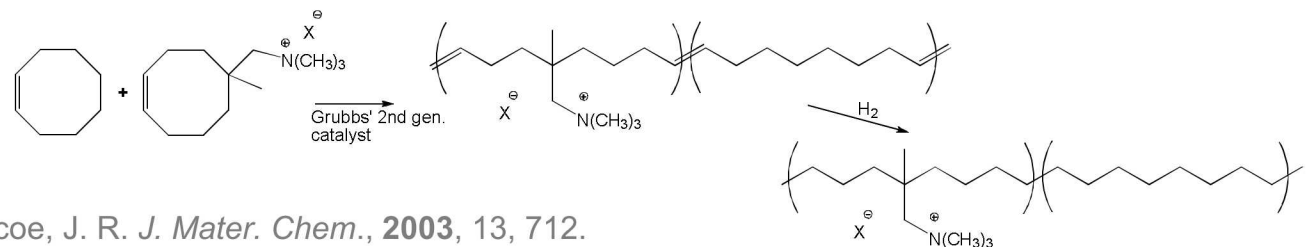
Radiation-grafting of functionalized poly(styrene) onto fluorinated polymers¹:



Bromination of poly(2,6-dimethyl-1,4-phenylene oxide)²:



Poly(ethylene)-based AEM from ROMP³:



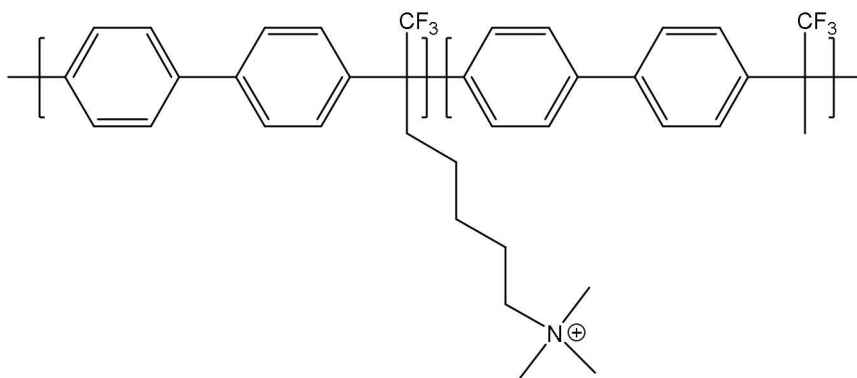
¹Danks, T. N.; Slade, R. T. C.; Varcoe, J. R. *J. Mater. Chem.*, **2003**, 13, 712.

²Wu, Y.; Wu, C.; Xu, T.; Lin, X.; Fu, Y. *J. Membr. Sci.*, **2009**, 338, 51.

³Kostalik, H. A.; Clark, T. J.; Robertson, N. J.; Mutolo, P. F.; Longo, J. M.; Abruna, H. D.; Coates, G. W. *Macromol.*, **2010**, 43, 7147.

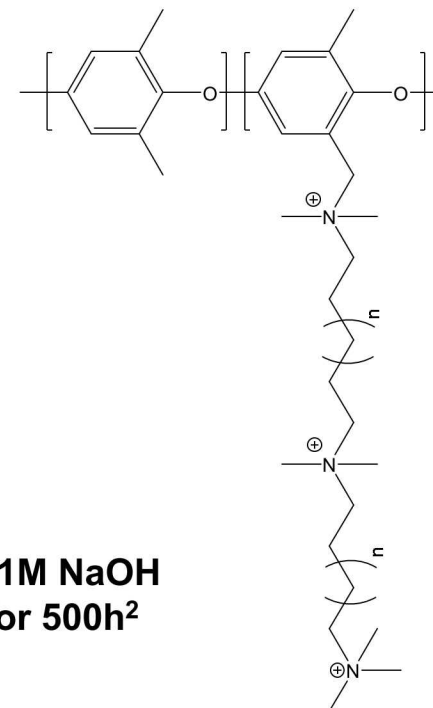
AEMs: The State of the Art

Poly(biphenylene alkylene) with tethered ammonium groups¹



Stable in 1M NaOH at 80 °C for 700h¹

Poly(phenylene oxide) with multication sidechains²



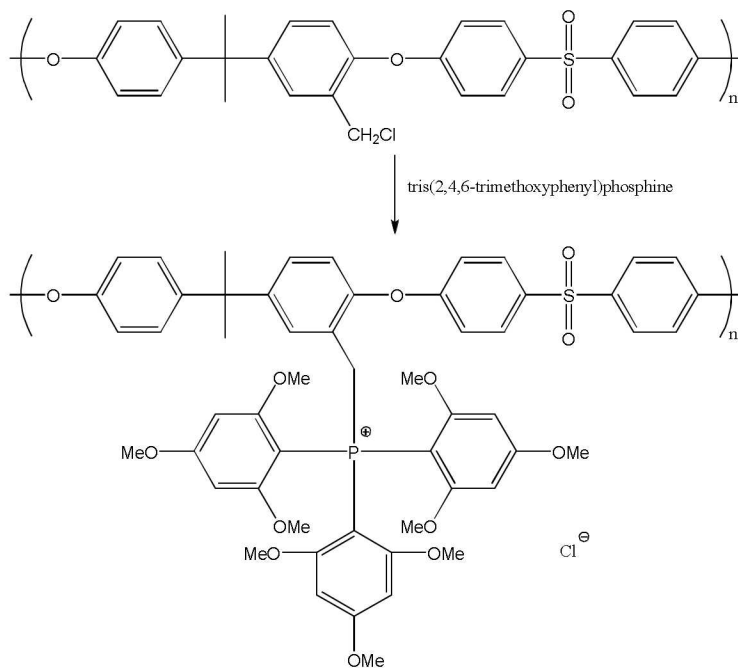
Stable in 1M NaOH at 80 °C for 500h²

¹Lee, W.-H.; Kim, Y.S.; Bae, C. *ACS Macro Lett.* **2015**, 4, 814.

²Zhu, L.; Pan, J.; Wang, Y.; Han, J.; Zhuang, L.; Hickner, M.A. *Macromol.* **2016**, 49, 815.

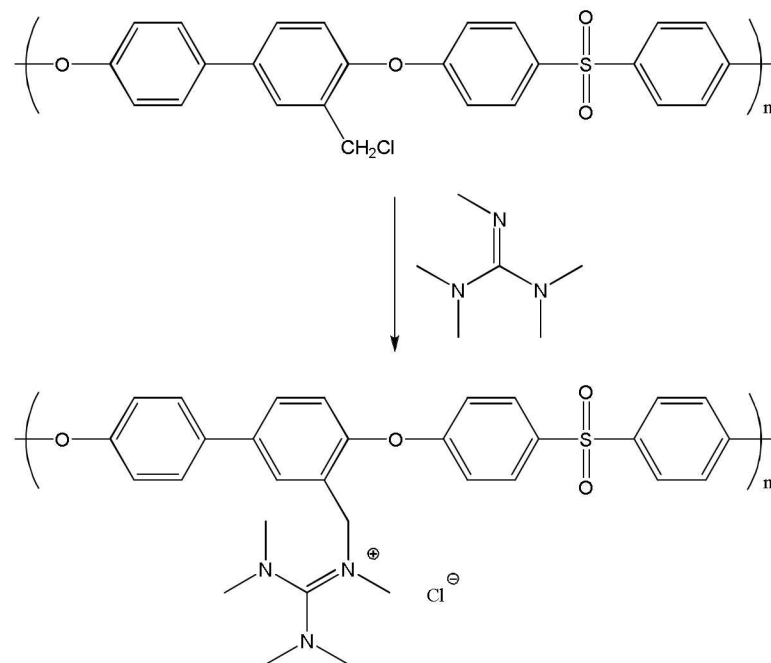
Alternative Cationic Groups

Poly(sulfone) with benzyltris(2,4,6-trimethoxyphenyl) phosphonium groups¹



Stable in 1M KOH at 60 °C for 48h¹

Poly(sulfone) with benzylpentamethyl guanadinium groups²

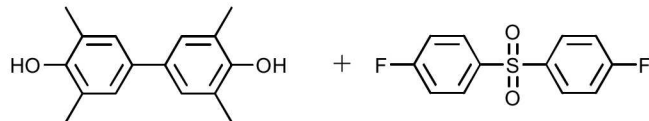


Stable in 1M KOH at 60 °C for 48h²

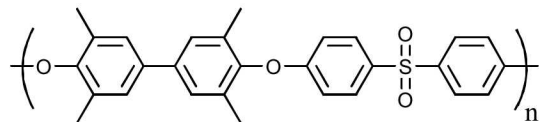
¹Gu, S.; Cai, R.; Luo, T.; Chen, Z.; Sun, M.; Liu, Y.; He, G.; Yan, Y. *Angew. Chem. Int. Ed.*, **2009**, 48, 1.

²Wang, J.; Li, S.; Zhang, S. *Macromol.* **2010**, 43, 3890.

AEMs made at Sandia: Poly(sulfone)-Based Membranes

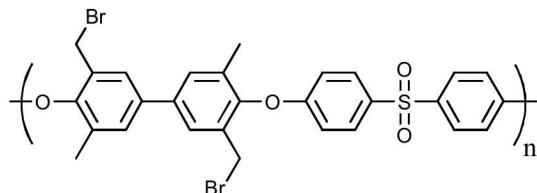


↓ K_2CO_3 , NMP
175 °C, 24 h

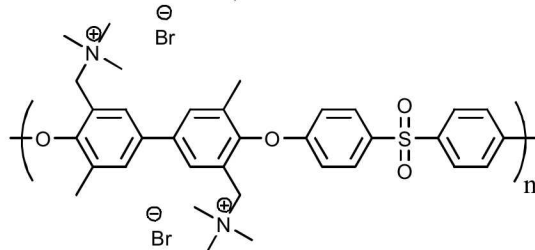


Radel-type polysulfone

↓ NBS, benzoyl peroxide
80 °C, 3h

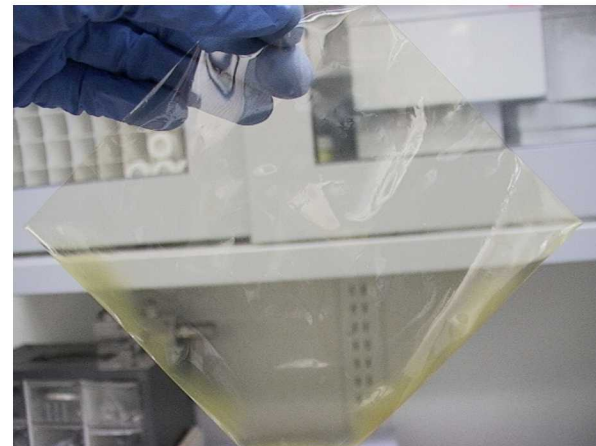


1) cast film
2) $N(CH_3)_3$, 25 °C

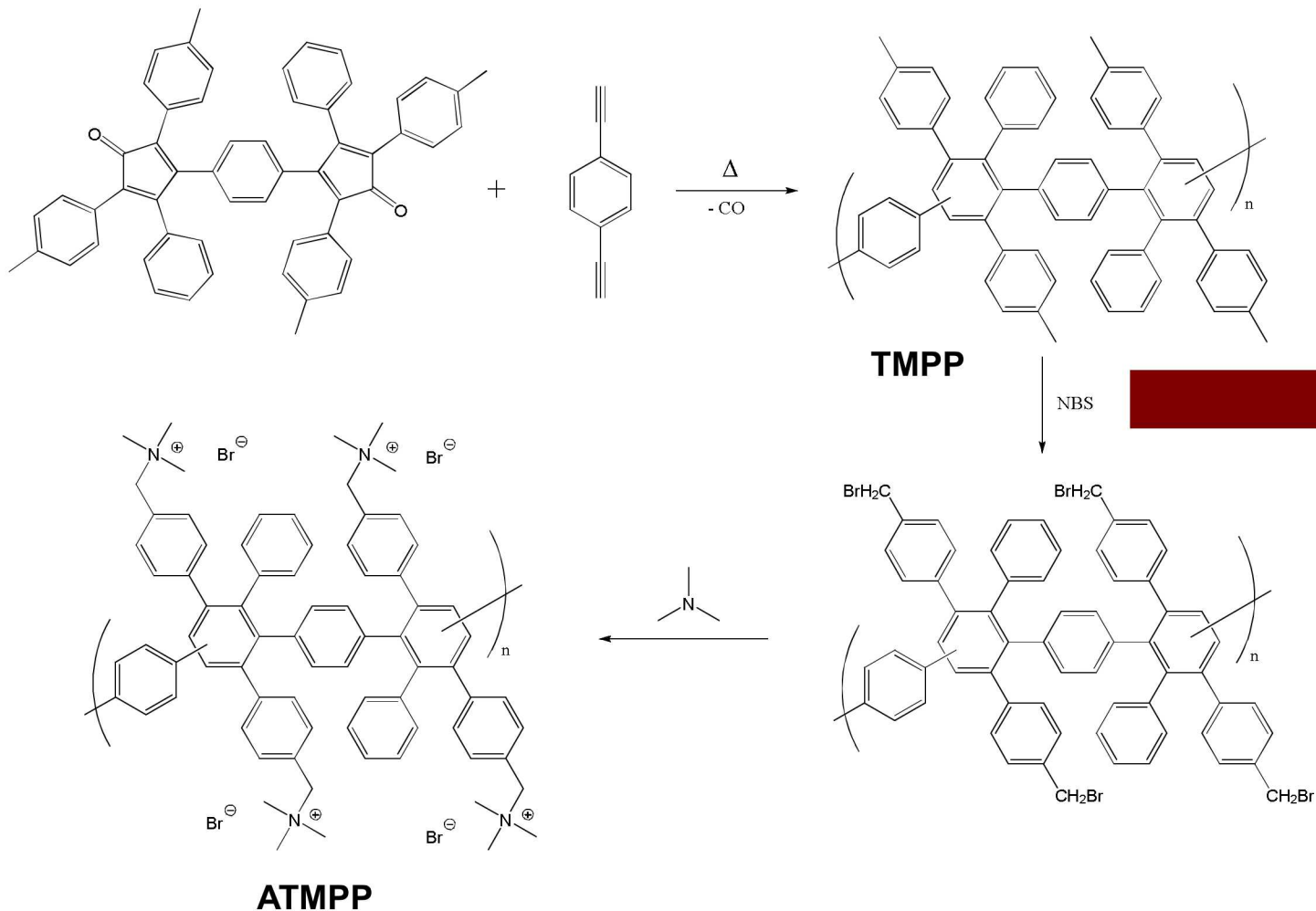


ATMPS

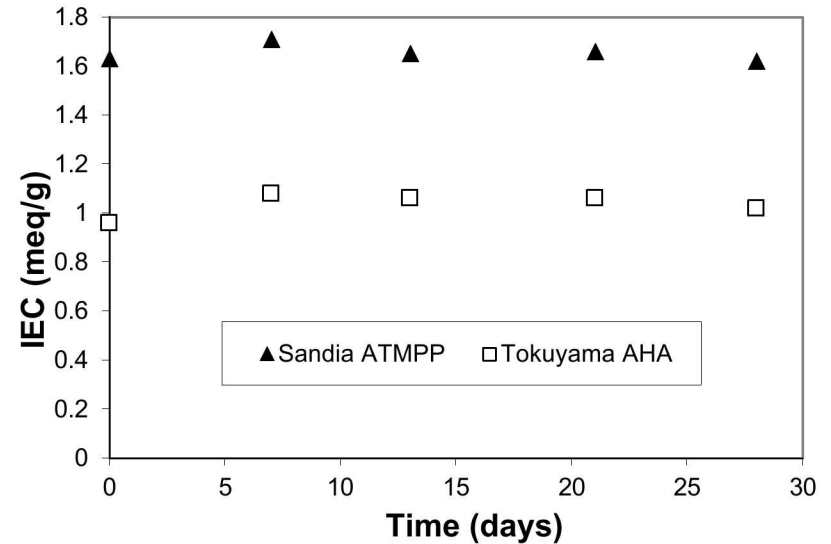
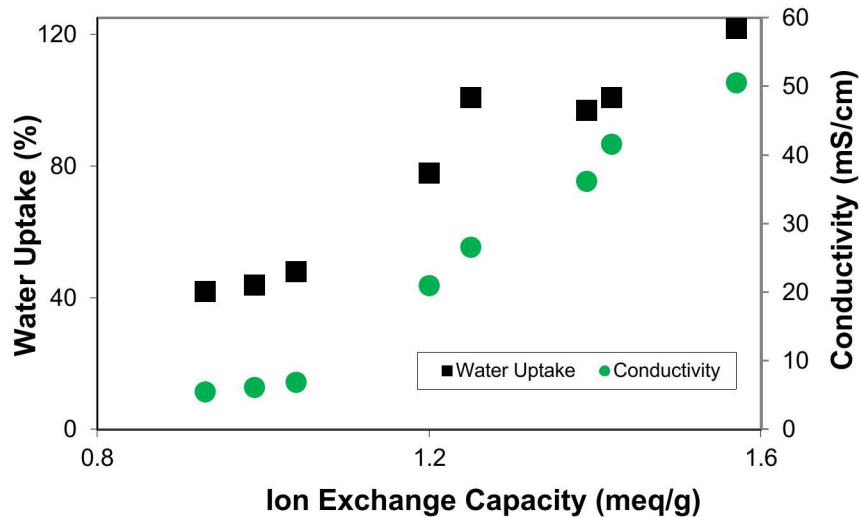
$M_w = 80-100k$



AEMs made at Sandia: Poly(phenylene)-Based Membranes

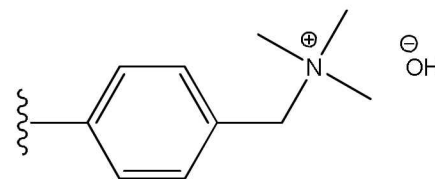
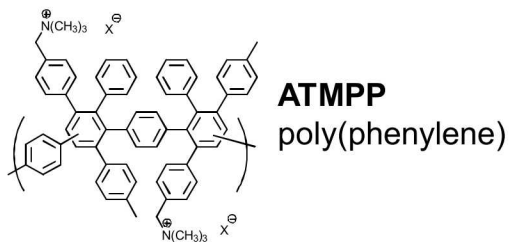


ATMPP Properties & Stability



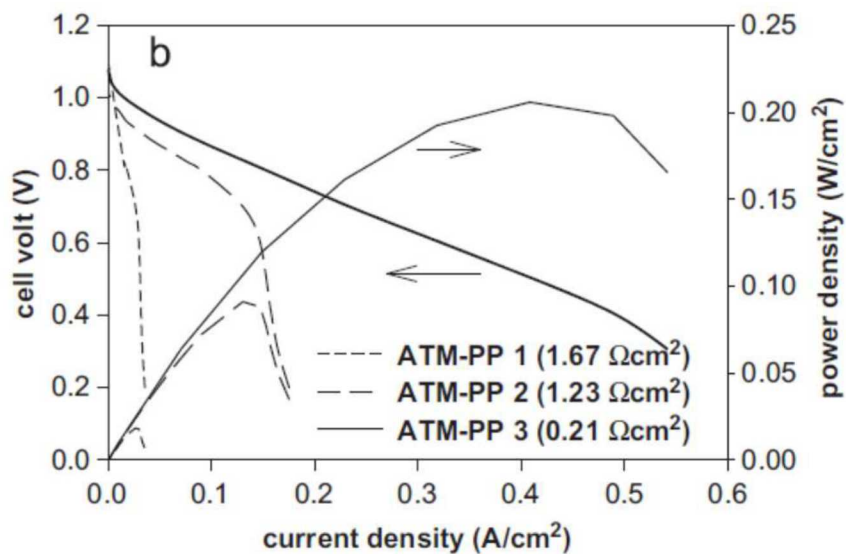
- Hydroxide conductivities were measured in liquid water at room temperature.
- SAXS indicated little or no microphase separation.

- Test conditions: 4M NaOH (aqueous), 60 °C, no stirring.
- AHA is “base stable” electro dialysis membrane – crosslinked polystyrene.
- Both membranes have BTMA cations.

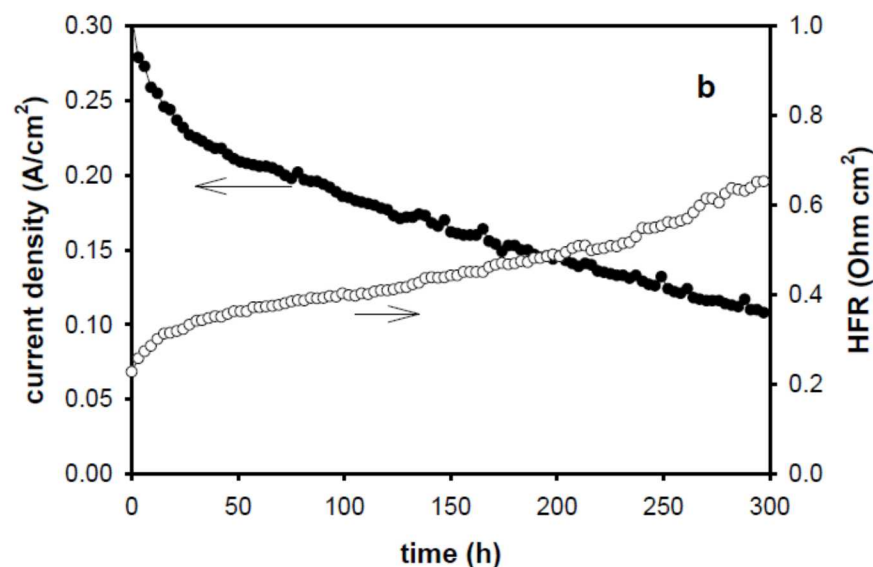


Fuel Cell Testing at LANL

H₂/O₂ Fuel Cell polarization curves



Durability in H₂/O₂ fuel cell



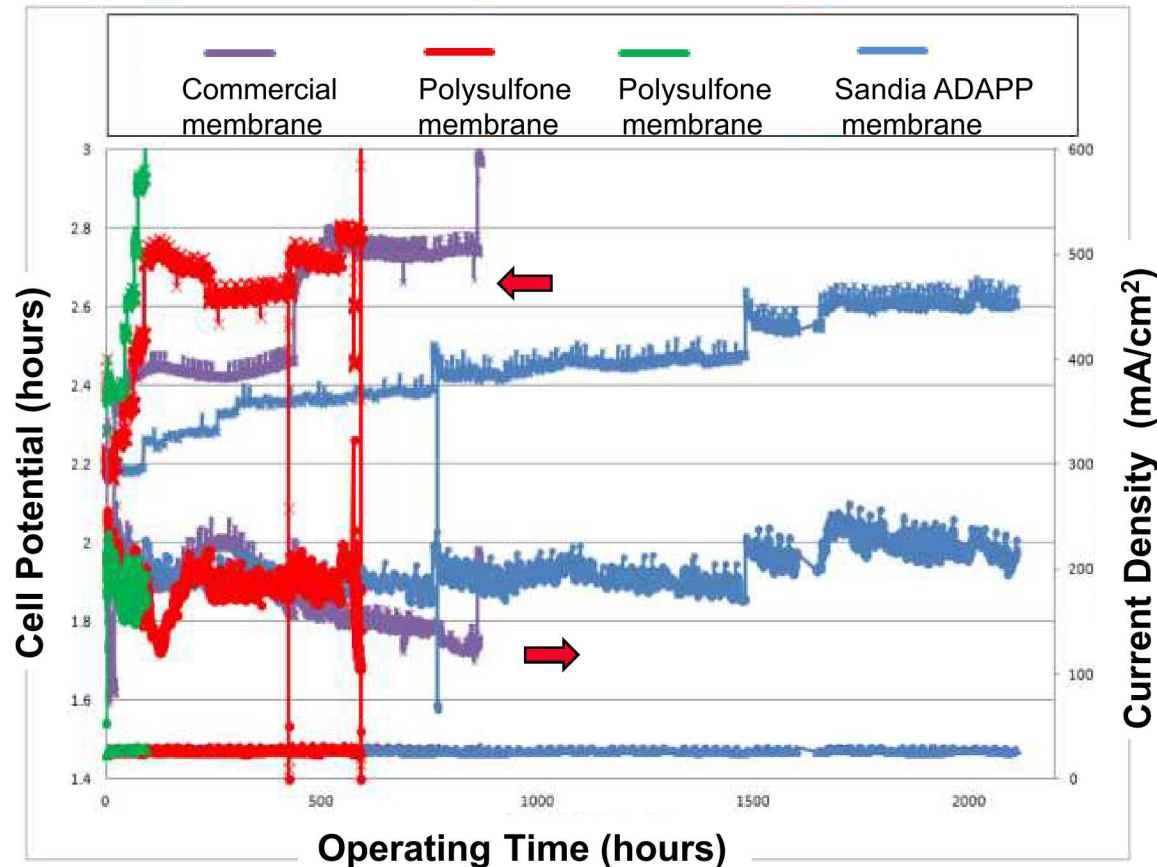
- ATMPP used as both membrane and ionomer/binder.
- ATMPP 1, 2, and 3 have increasing M_w (61, 77, 196 $\times 10^3$ g/mol) but similar IECs (1.7 meq/g).
- Fuel cell testing was done at 60 °C, 0.3 V, with Pt/C catalyst on both electrodes (3mg/cm²).
- Decline in current density is also presumably due to BTMA degradation.
- Testing performed by Yu Seung Kim at LANL.

Fujimoto, C.; Kim, D.-S.; Hibbs, M. R.; Wroblewski, D.; Kim, Y. S.
J. Membr. Sci. **2012**, 423-424, 438.

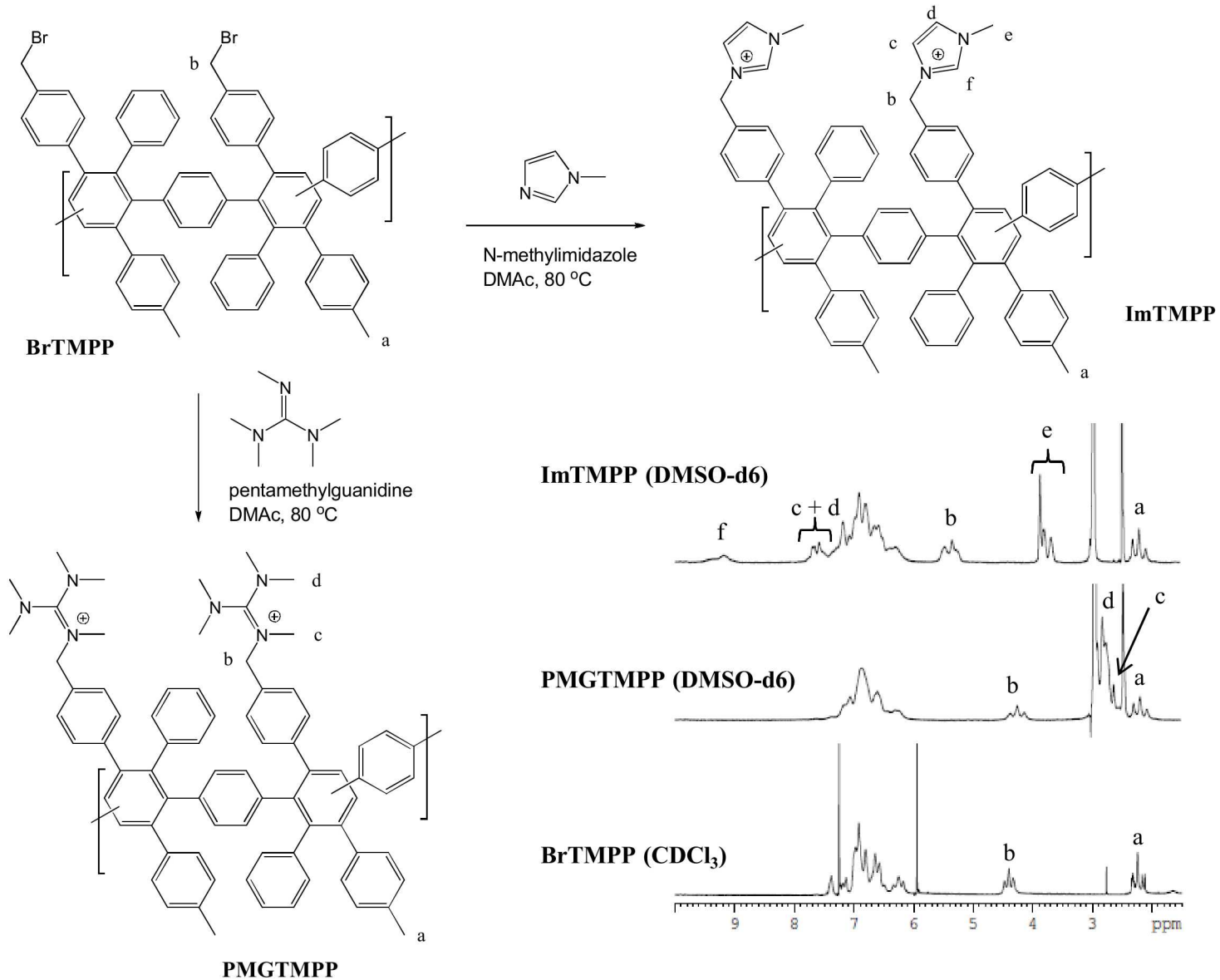
Electrolysis Testing at Proton OnSite

Durability test at 27 °C with PGM catalysts and no added electrolyte

- Established test bed for multiple materials collaborators
- Failure criterion = 3.0 V.
- Achieved 2000 hrs of stable operation using ADAPP membrane + ADAPP ionomer.
- Need to improve voltage stability.

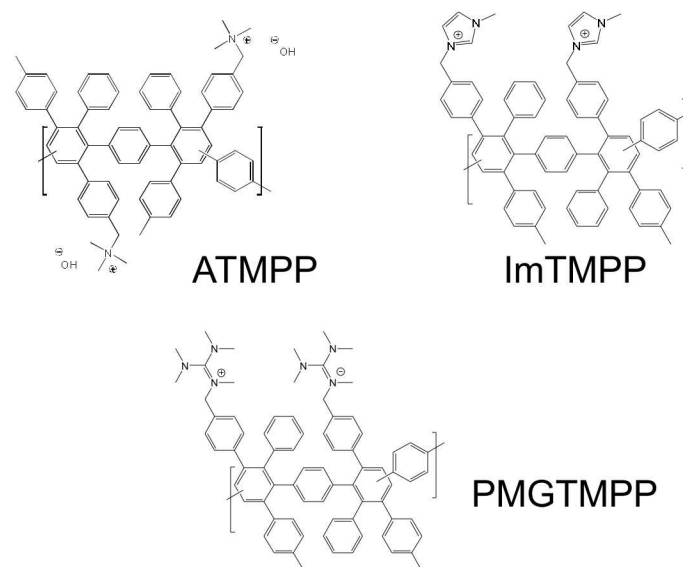
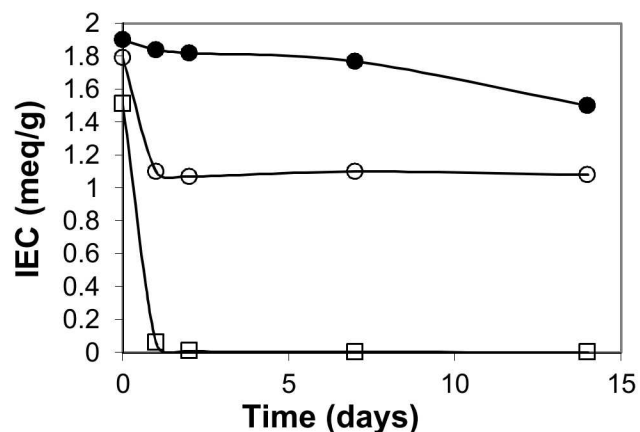
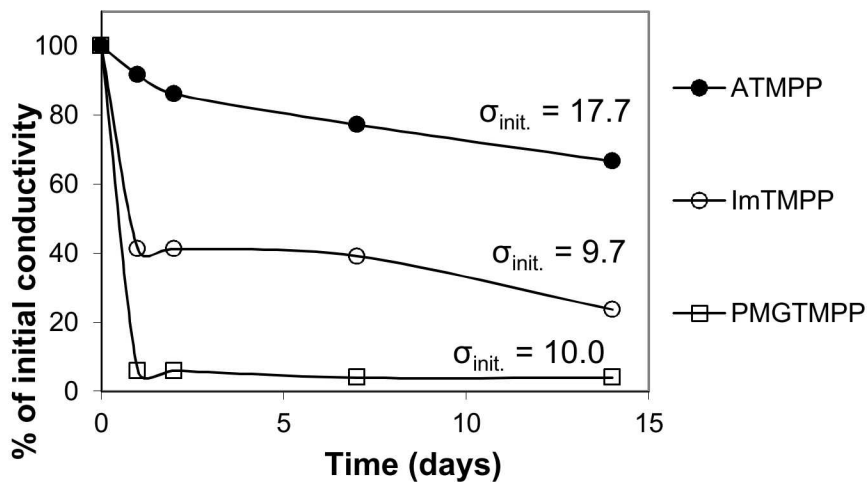


Resonance-Stabilized Cations



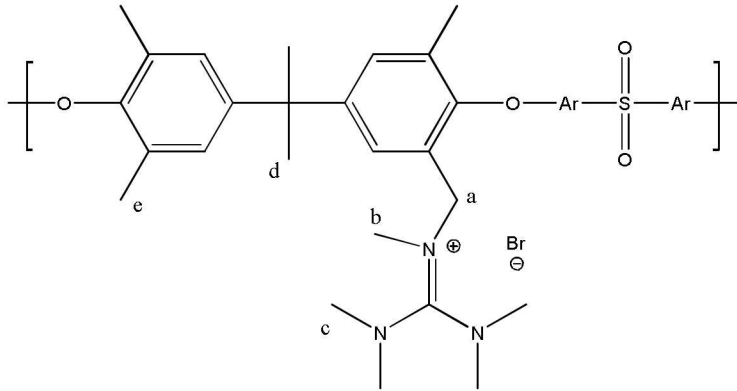
KOH Stability Test Resonance-Stabilized Cations

Test conditions: Membranes immersed in 4M KOH at 90 °C.

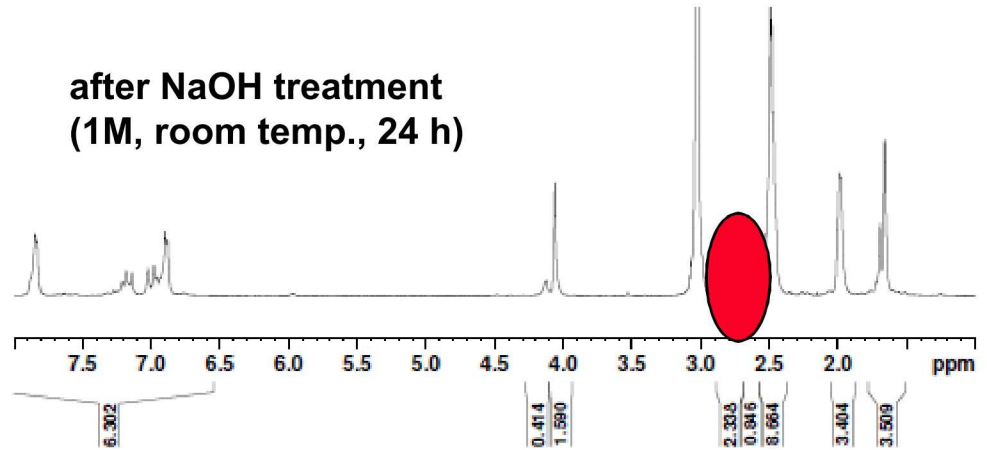


- Conductivities were measured with membranes in Cl⁻ form in 25 °C water.
- Hydroxide conductivity is generally 2-3x higher than chloride conductivity.
- Benzyl imidazolium and benzyl guanidinium cations are much less stable than BTMA.

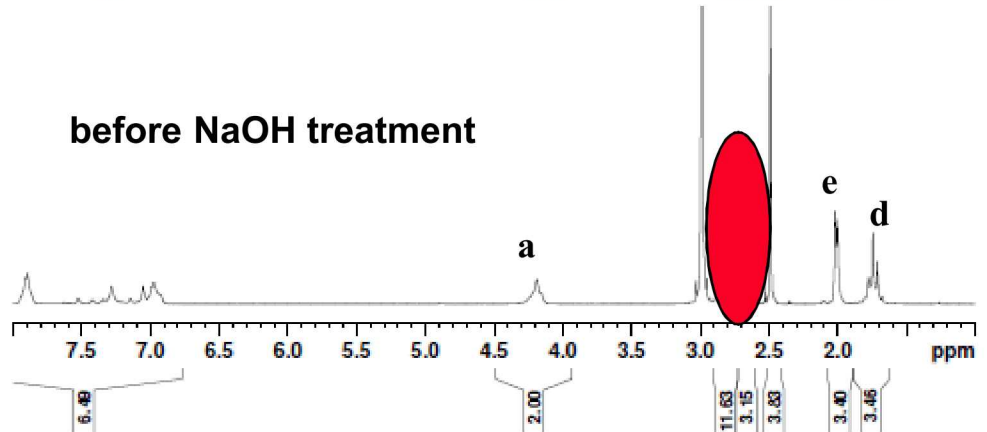
Decomposition of Benzyl PMG Cations



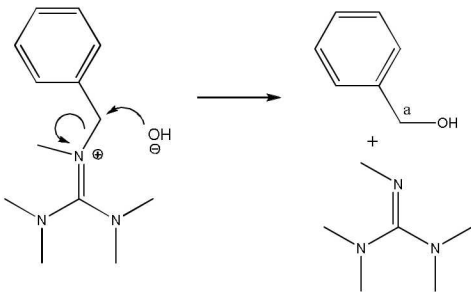
after NaOH treatment
(1M, room temp., 24 h)



before NaOH treatment

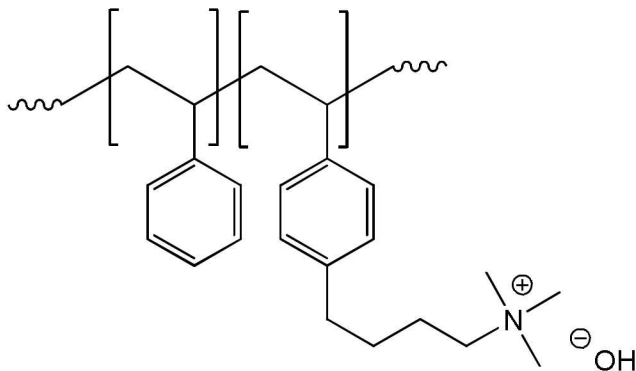


- The relative areas of b and c peaks decrease drastically after NaOH. But b:c area ratio does not change.
- The probable mechanism is nucleophilic attack by hydroxide ion at the benzylic carbon:



Improving the Stability of Quaternary Ammonium Groups

One study found that increasing the length of the alkyl tether on a BTMA cation increased alkaline stability¹

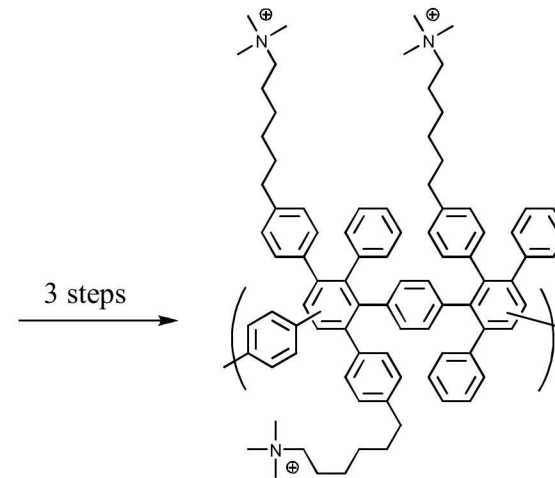
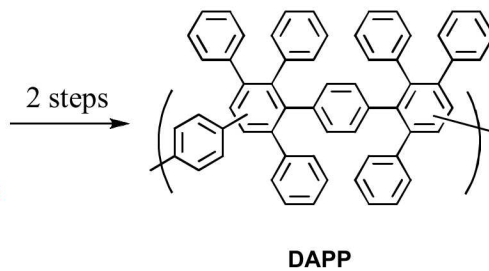
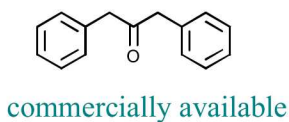
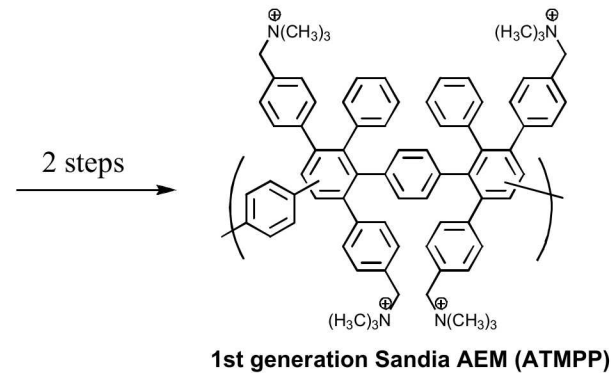
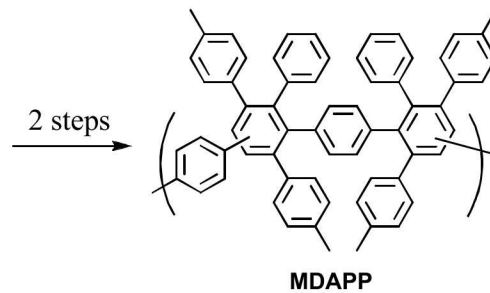
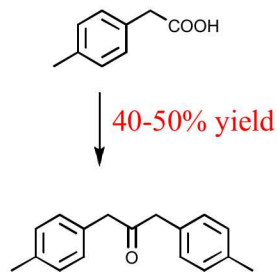


Tested for 30 days in 100 °C water (OH⁻ form):

	<u>IEC (after/before)</u>
Benzyltrimethylammonium	79 %
Tetramethylene spacer	92 %

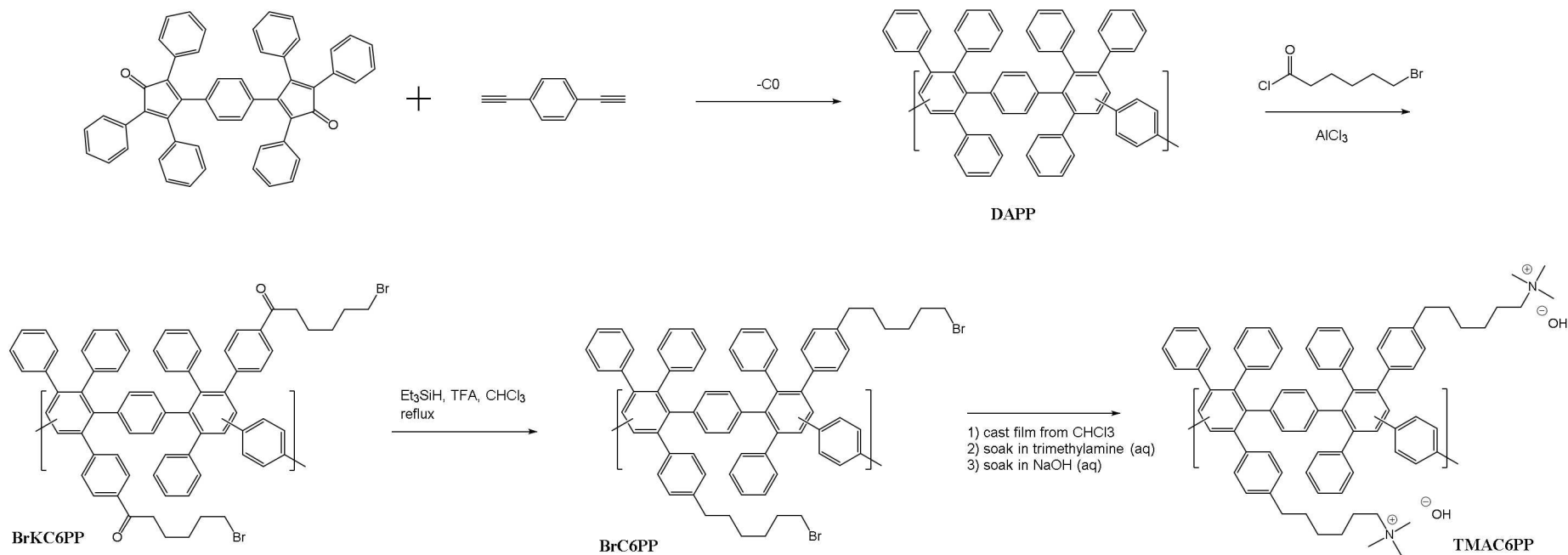
¹Tomoi, M.; Yamaguchi, K.; Ando, R.; Kantake, Y.; Aosaki, Y.; Kubota, H.
J. Appl. Polym. Sci. **1997**, *64*, 1161.

Poly(phenylene) AEM with Sidechains



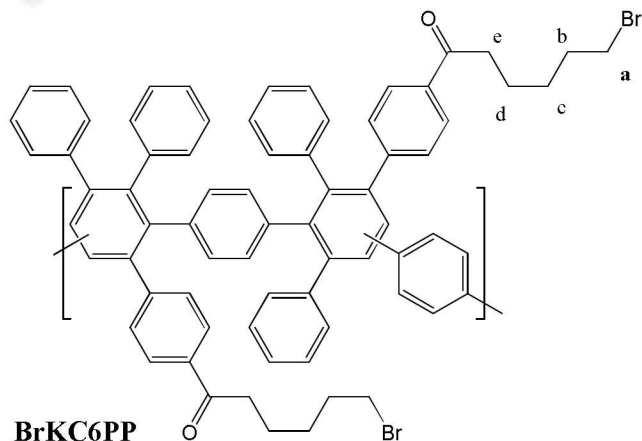
- **DAPP is easier to make than MDAPP, with higher molecular weights.**
- **Synthesis of DAPP has been scaled up to ~1kg.**

Poly(phenylene) AEM with Sidechains

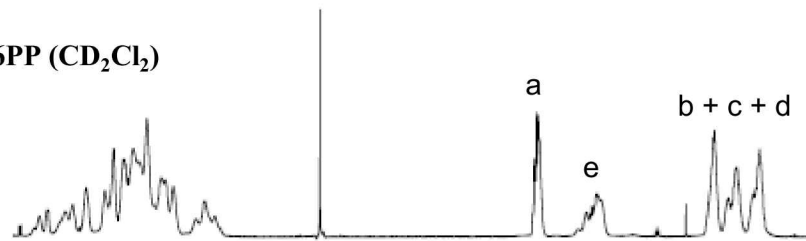


Hibbs, M. R. *J. Polym. Sci. Part B, Polym. Phys.* **2013**, 51, 1736.

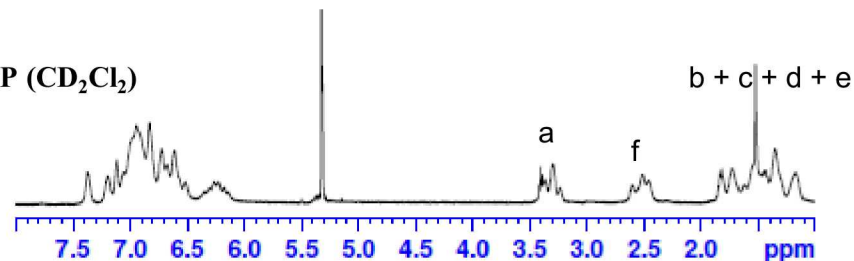
Poly(phenylene) with Alkyl Side Chains without Ketone



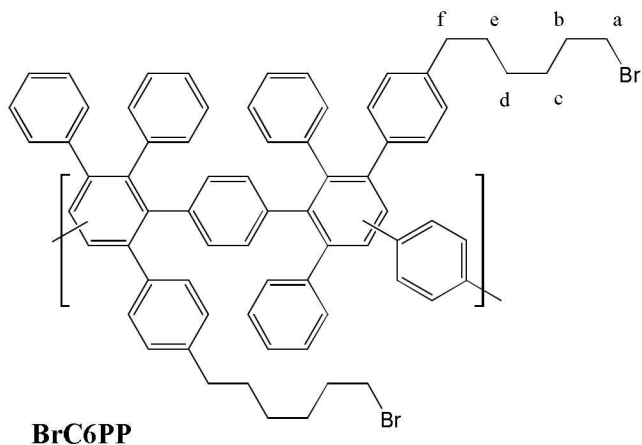
BrKC6PP (CD_2Cl_2)



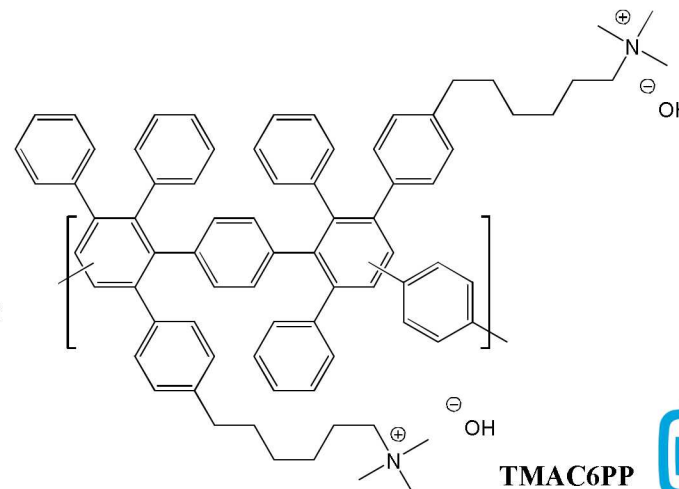
BrC6PP (CD_2Cl_2)



Et_3SiH , TFA, CHCl_3
reflux



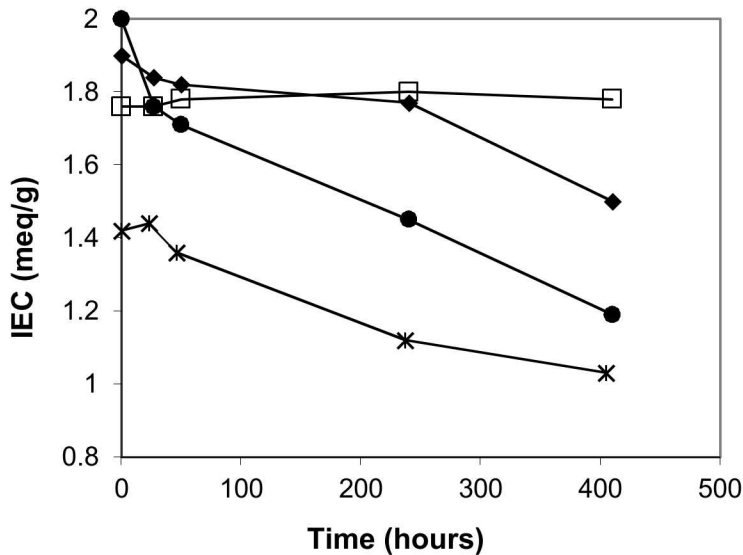
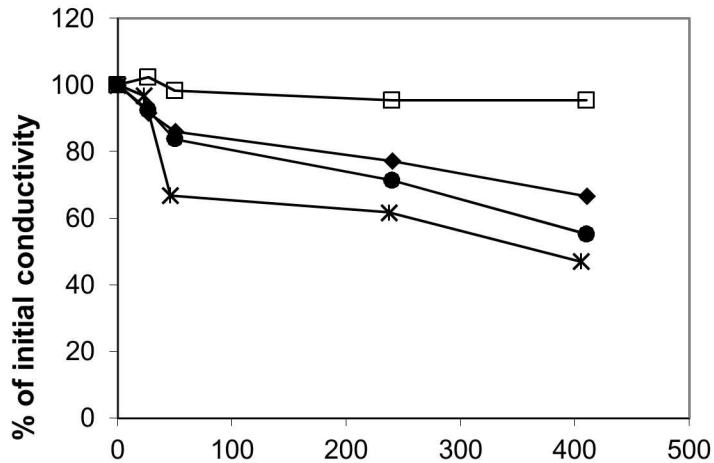
- 1) cast film from CHCl_3
- 2) soak in trimethylamine (aq)
- 3) soak in NaOH (aq)



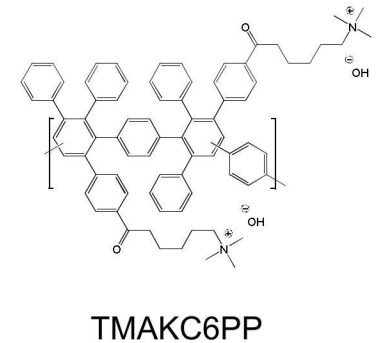
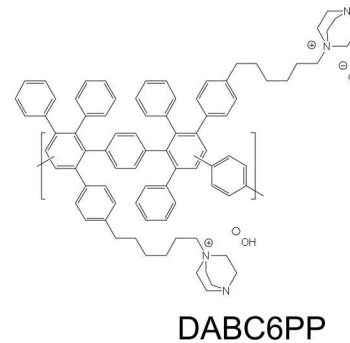
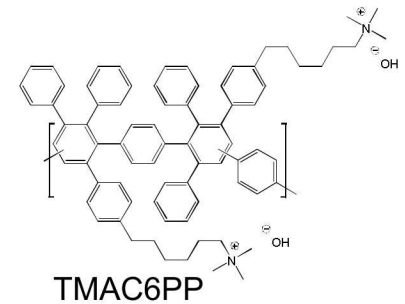
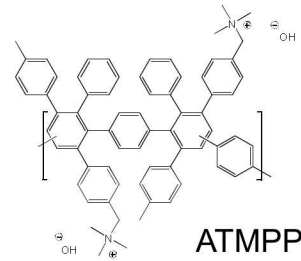
TMAC6PP

TMAC6PP Alkaline Stability

Test conditions: Membranes immersed in 4M KOH at 90 °C.



◆ ATMPP
 □ TMAC6PP
 ● DABC6PP
 * TMAKC6PP

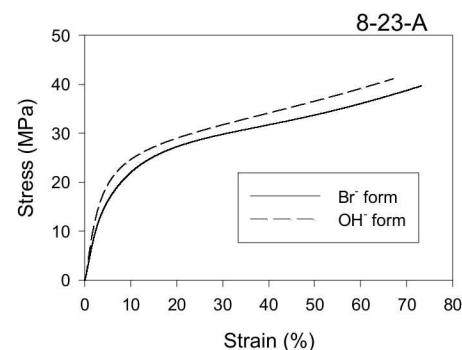
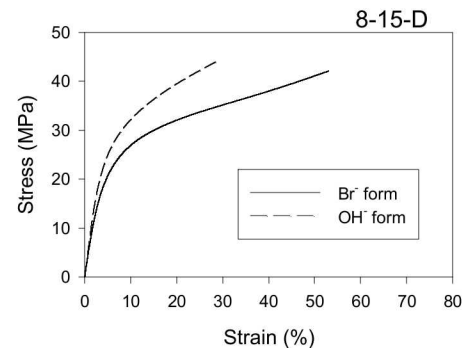
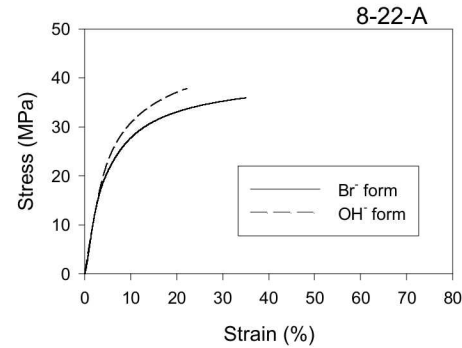


◆ ATMPP
 □ TMAC6PP
 ● DABC6PP
 * TMAKC6PP

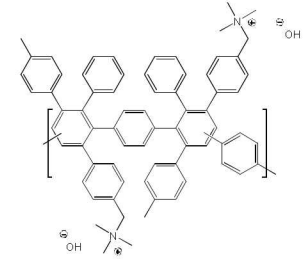
- TMAC6PP shows the greatest stability in high pH test.
- The ketone adjacent to the phenyl ring destabilizes the side chains.
- Quaternized DABCO on hexyl sidechains with no ketone are less stable than BTMA.

TMAC6PP Stress/Strain Testing

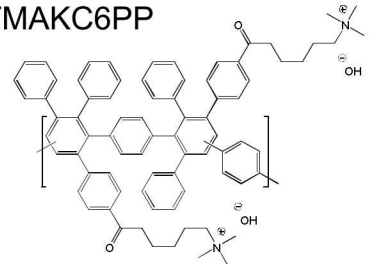
- AEMs with sidechains show better mechanical properties.
- With samples of similar molecular weights, TMAC6PP has over twice the elongation at break as ATMPP.
- Elasticity (lack of brittleness), especially when dry, is an important property for membrane-electrode assembly fabrication.
- This testing was performed at 50% relative humidity and 50 °C.



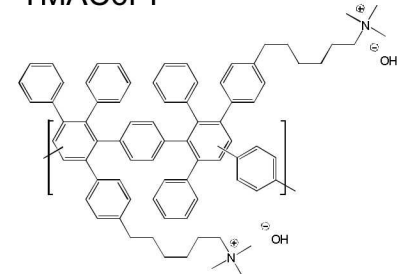
ATMPP



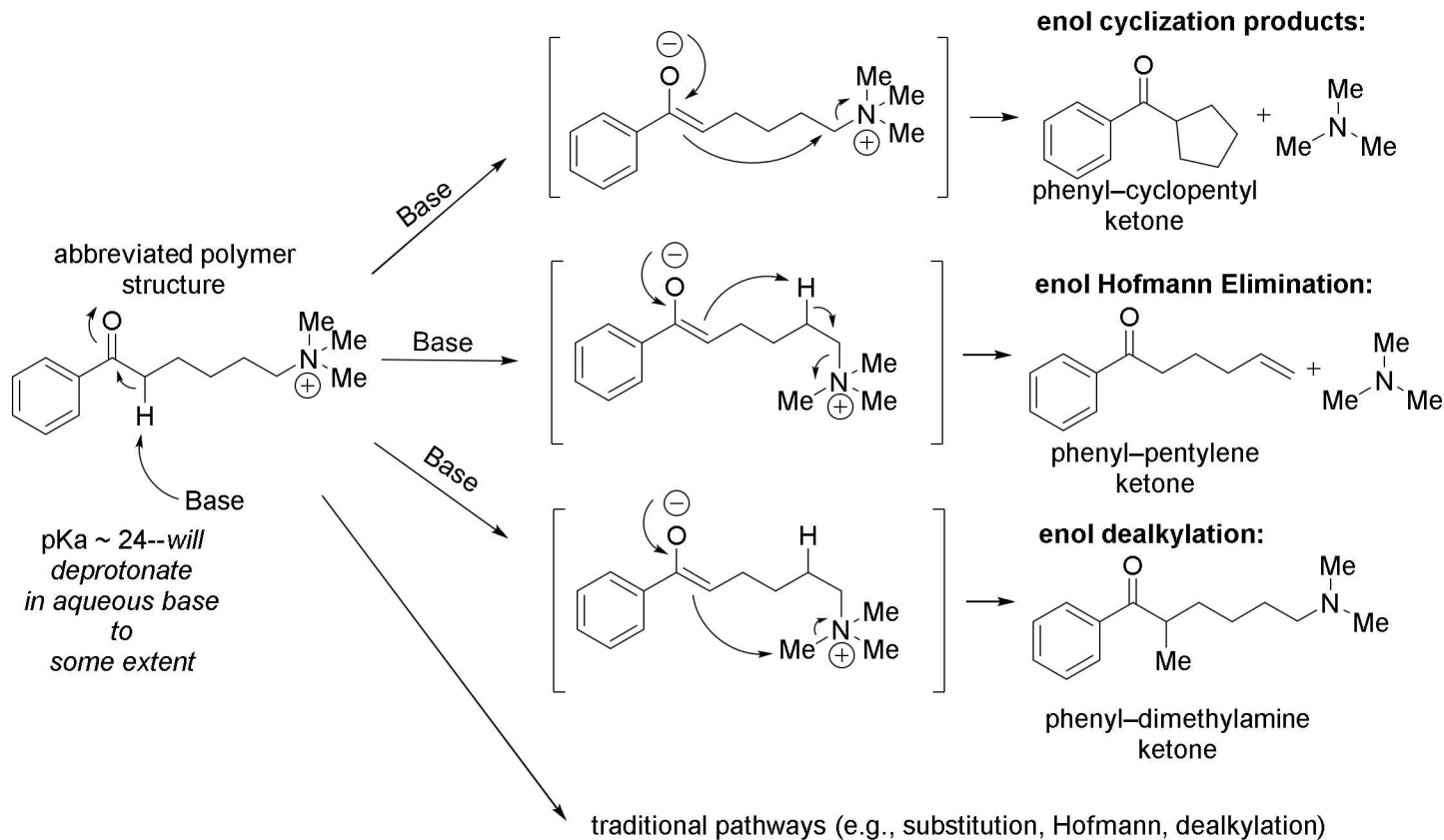
TMAKC6PP



TMAC6PP



Instability Due to Ketone

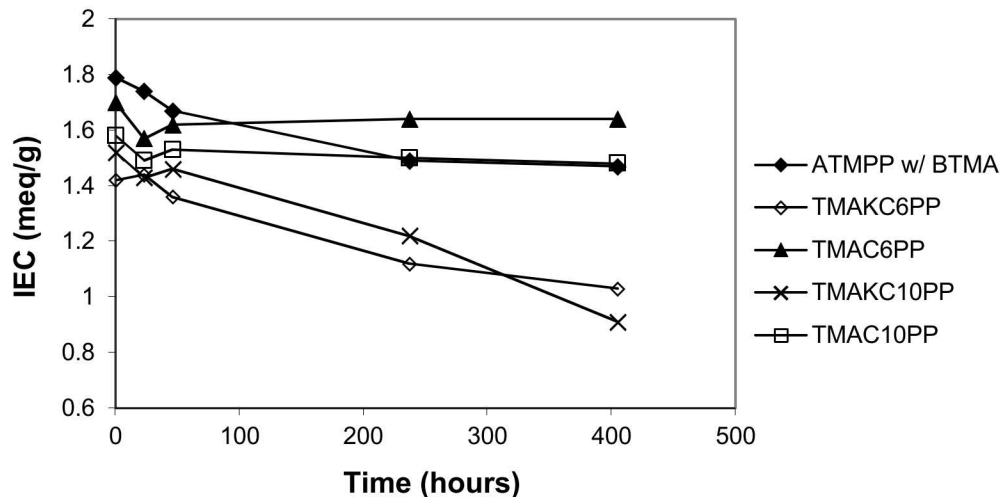
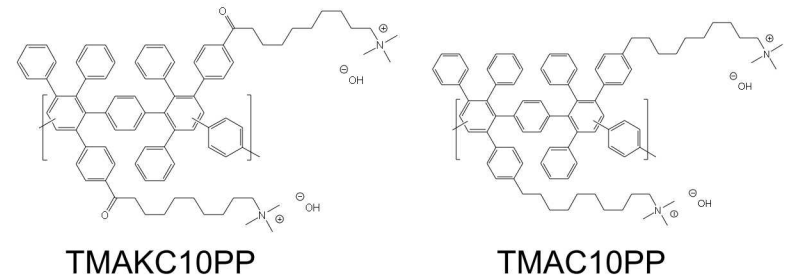
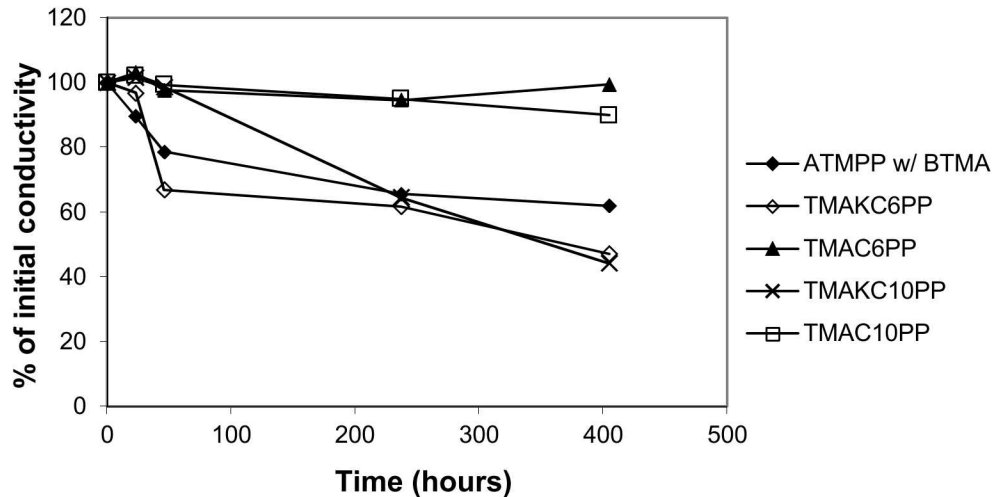


- Formation of enolate might begin pathway to cation degradation.
- Mechanisms that involve a 5- or 6-membered ring as an intermediate would be particularly likely.
- A longer sidechain would eliminate 5- and 6-membered ring intermediates.

Schemes drawn by Sean Nunez (PSU)

Stability of 10-Carbon Sidechain

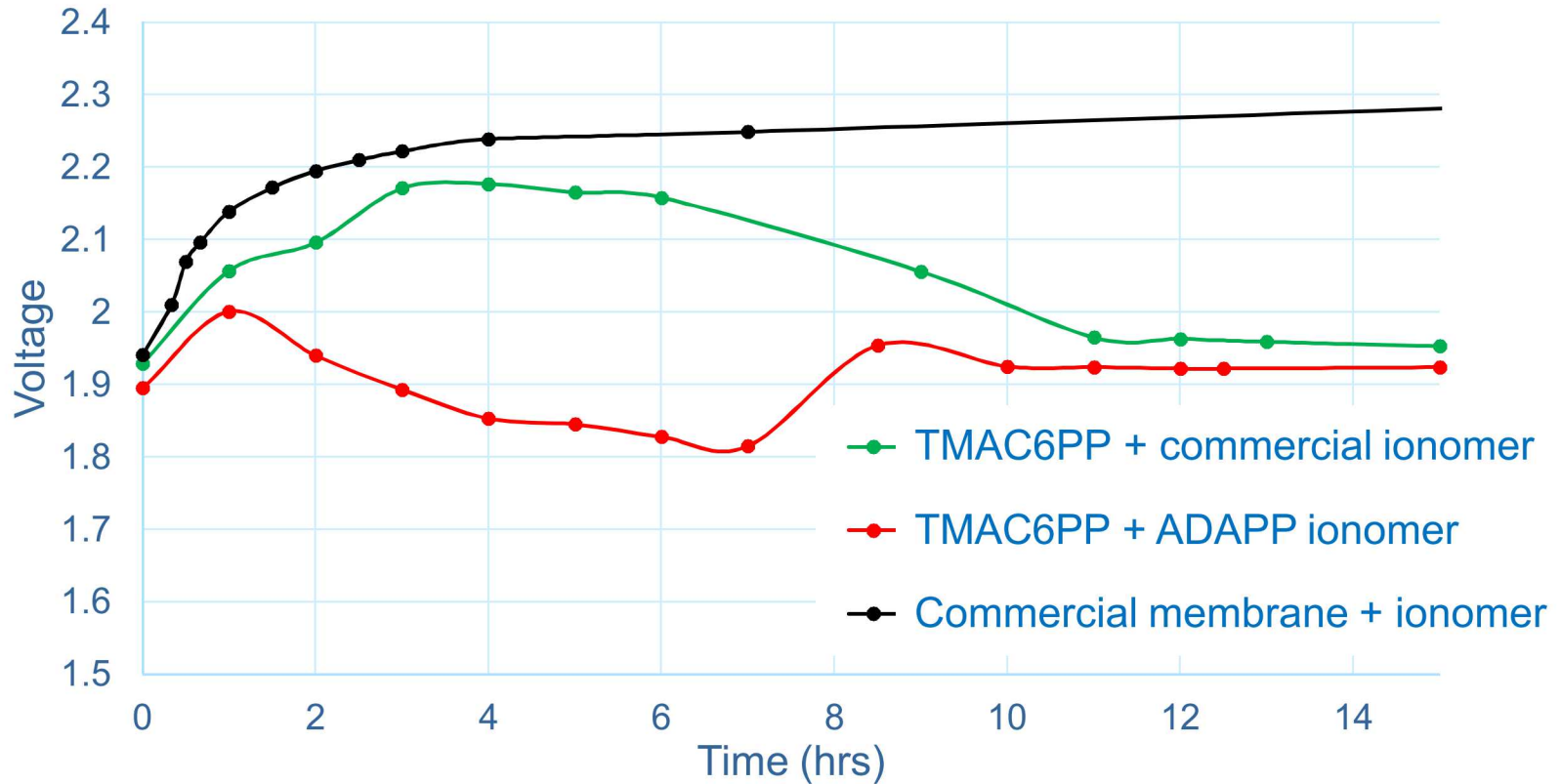
Test conditions: Membranes immersed in 4M KOH at 90 °C.



- 10-Carbon chain without ketone shows stability similar to TMAc6PP.
- 10-Carbon chain with ketone shows stability similar to TMAKC6PP.
- Enolate probably does play key role in degradation but not by intra-molecular attack at the terminal ammonium group.

Electrolysis Testing at Proton OnSite

200 mA/cm² steady state performance at 50 °C with PGM catalysts and no added electrolyte



Steady state performance indicated better stability versus commercial material.
Long-term testing TBD.



Conclusions

- Sandia's polysulfone-based AEMs have shown stable 1000-hour performance in electrolysis cell with 1 M KOH.
- Polysulfone-based AEMs lack chemical stability above room temperature or at higher KOH concentrations.
- Operational stability (>2000 hours) can be achieved in electrolysis cells using polyphenylene-based membranes without added electrolyte.
- Resonance-stabilized cations (imidazolium and pentamethyl guanidinium) are less stable to alkaline degradation than BTMA cations.
- Trimethylammonium cations on alkyl sidechains have better stability than BTMA despite the possibility of Hoffmann elimination reactions.
- Further work is needed to develop ionomers to integrate non-PGM catalysts with polyphenylene-based electrolysis systems.



Acknowledgements

Sandia National Laboratories

Cy Fujimoto
Jeff Nelson
Todd Alam
Janelle Jenkins

Proton OnSite

Kathy Ayers
Chris Capuano
Morgan George

Funding

US DOE EERE Fuel Cell Technologies Office
Sandia National Laboratories Laboratory Directed Research and Development
(LDRD) program

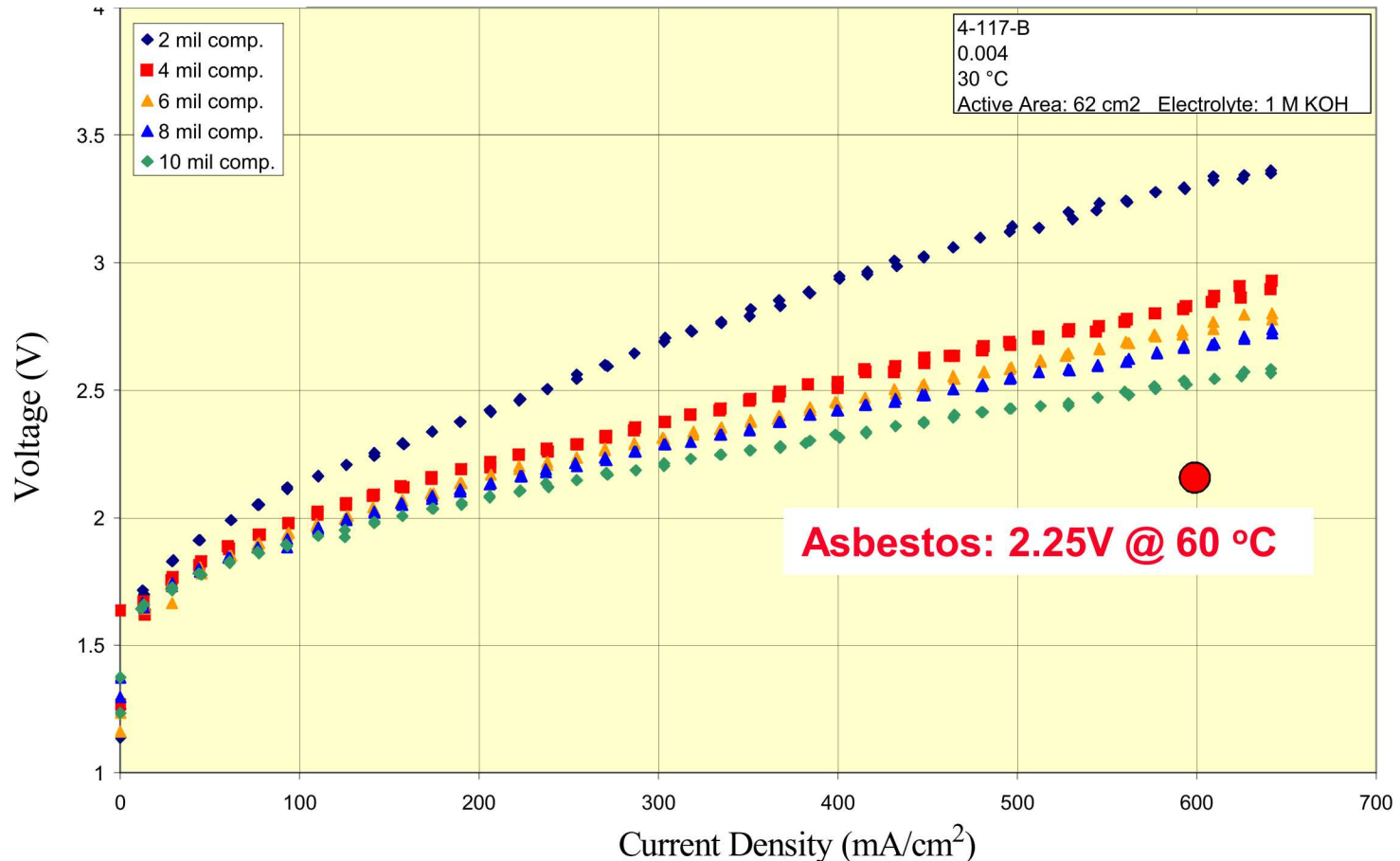
Los Alamos National Laboratory

Yu Seung Kim
Dae Sik Kim
Kwan-Soo Lee

Colorado School of Mines

Andy Herring
Rajeswari Janarthanan
Satyananda Kishore Pilli
James L. Horan
Daniel A. Gamarra

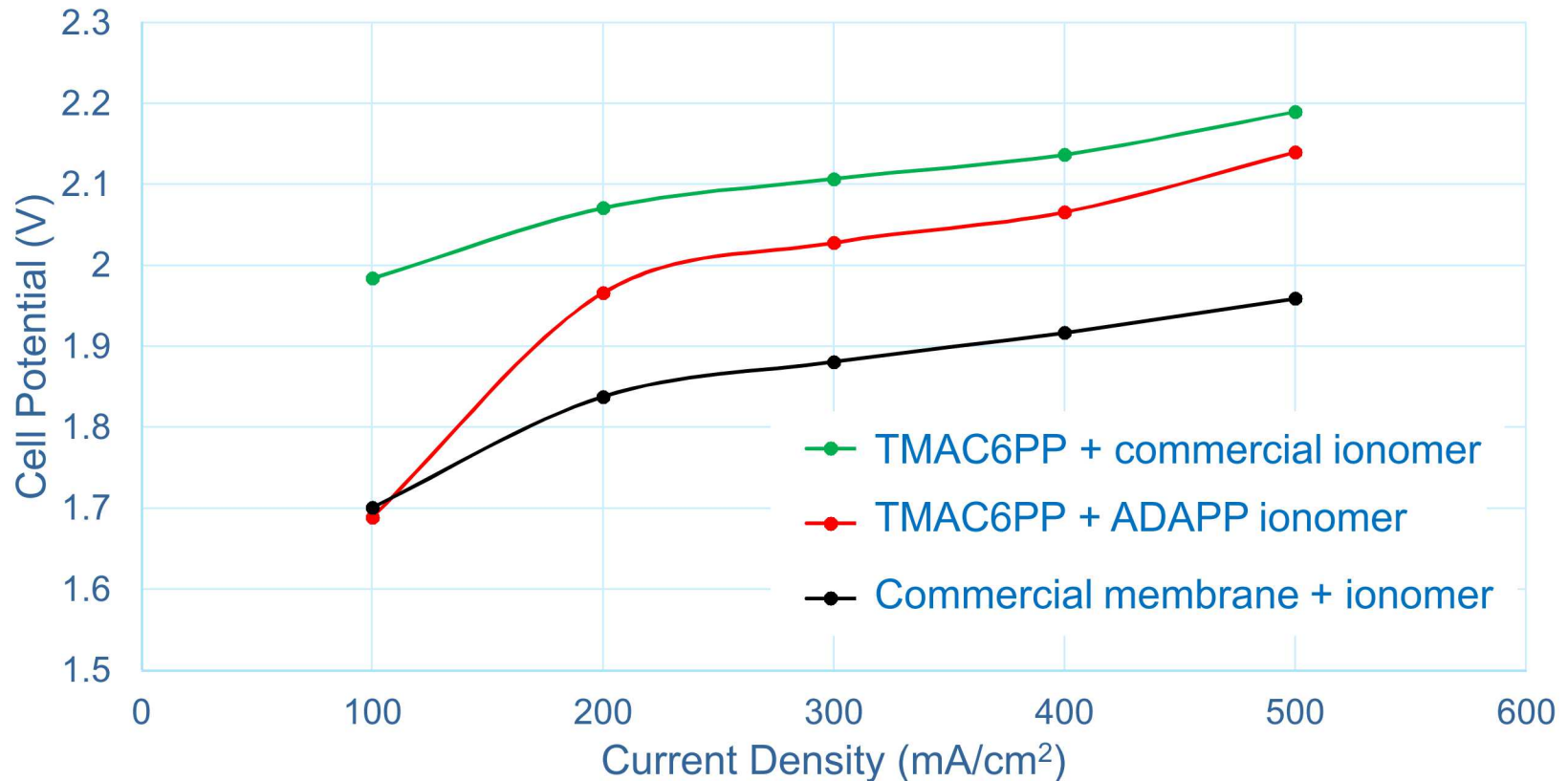
Electrolysis Data: Cell Compression



Cell conditions: 30 °C, 1M KOH, foam Ni electrodes, active area = 62 cm²
current swept from 0 – 40 Amps,

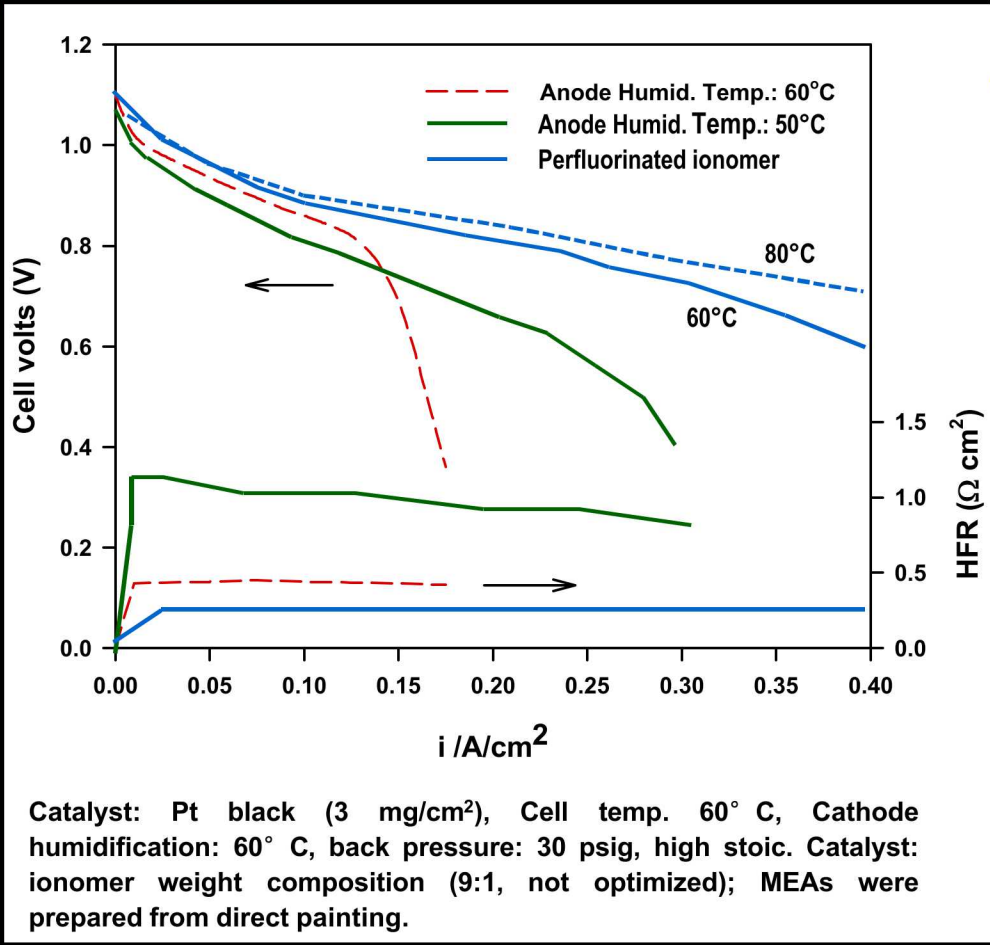
Electrolysis Testing at Proton OnSite

Initial polarization curves at 50 °C with PGM catalysts and no added electrolyte

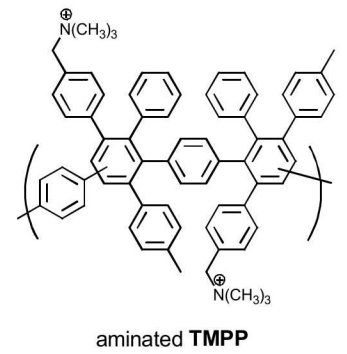


Polarization curve ~200 mV above commercially available membrane baseline for both ionomer tests

H₂/O₂ Performance of Alkaline Membrane Fuel Cells



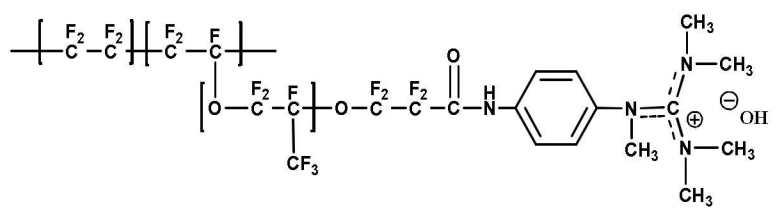
Membrane/ionomer
 IEC = 1.8 meq./g
 $\sigma = 55 \text{ mS/cm}$
 Thickness: 50 μm



Fully hydrated conditions (anode humid. temp.: 60°C)
 → Mass transport issue due to flooding
 → Possibly poor cation – catalyst structure

Partial hydrated conditions (anode humid. temp.: 50°C)
 → Improved performance with removing mass transport issue
 → Poor membrane hydration/remaining issue with cation

Ionomer (IEC = 0.74 meq./g, $\sigma = 20 \text{ mS/cm}$)

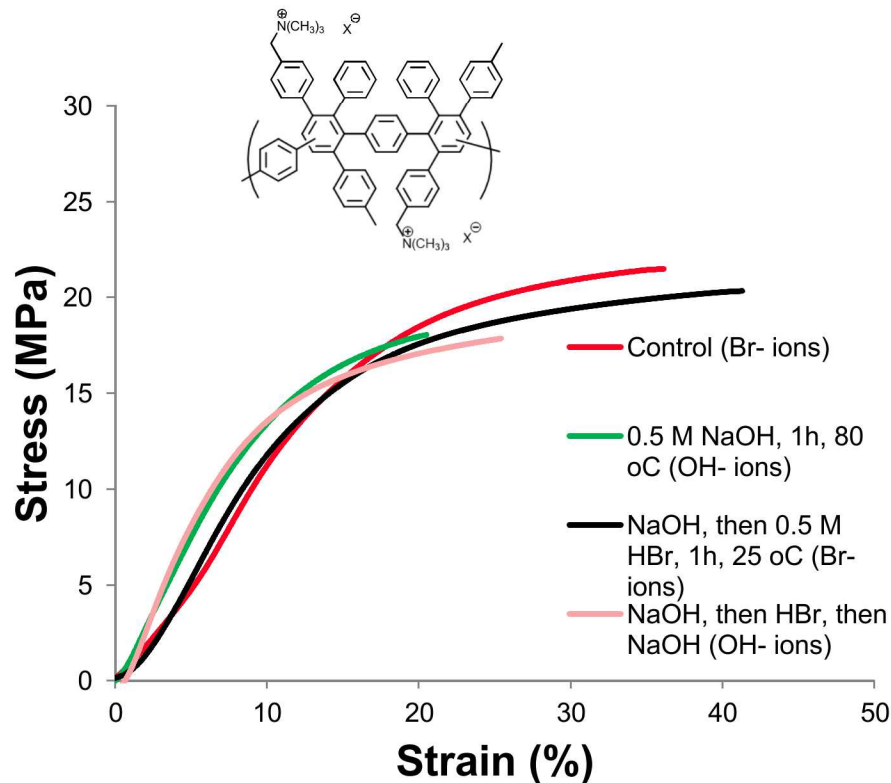
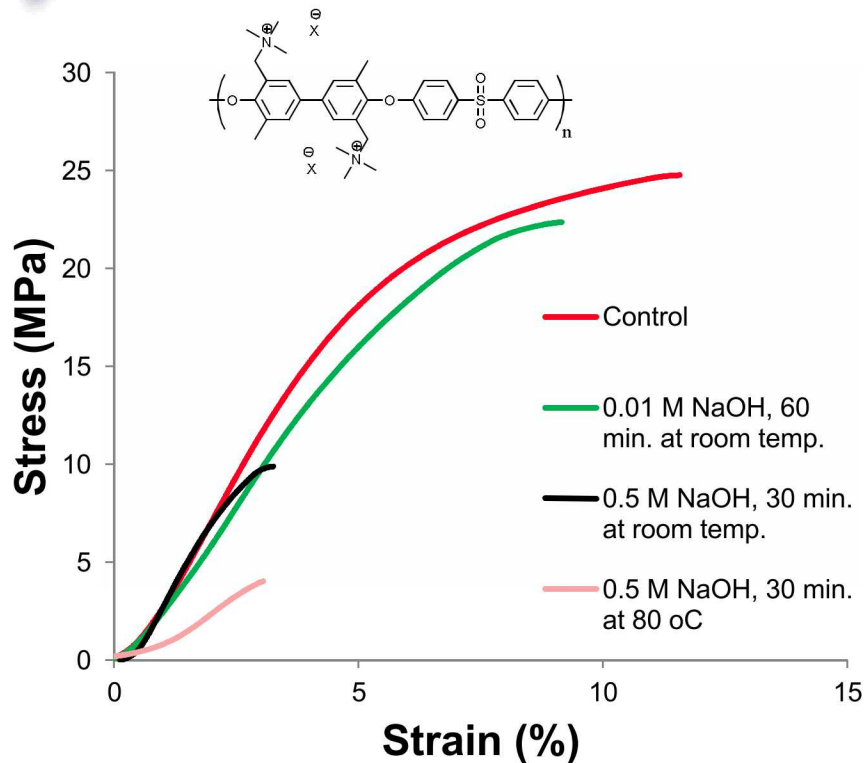


Perfluorinated ionomer (anode humid. temp.: 60°C)

→ Improved performance with removing mass transport issue
 → No membrane hydration problem
 → Maximum power density:
 236 (at 60°C) and 278 mW/cm² (at 80°C)

Data from Yu Seung Kim, LANL

Mechanical Stability



- Test conditions: 50 °C, 50% RH.
- Poly(arylene ether sulfone) shows significant degradation.
- Poly(phenylene) is weaker in OH⁻ form, but there is no sign of backbone degradation.

TMAC6PP Properties

- Water uptake and hydroxide conductivity values show very similar trends.
- No evidence that ion channel formation is any easier with cations on flexible tethers.
- TMAC6PP is not expected to change fuel cell performance relative to ATMPP, but the lifetime of the cell will be increased.
- Fuel cell testing with TMAC6PP membranes is in progress at UNM and CSM.

