5th Annual World Congress of Smart Materials
March 8, 2019

SAND2019-1712C

Development of Highly Stable Anion-Exchange Membranes for alkaline Electrochemical Cells

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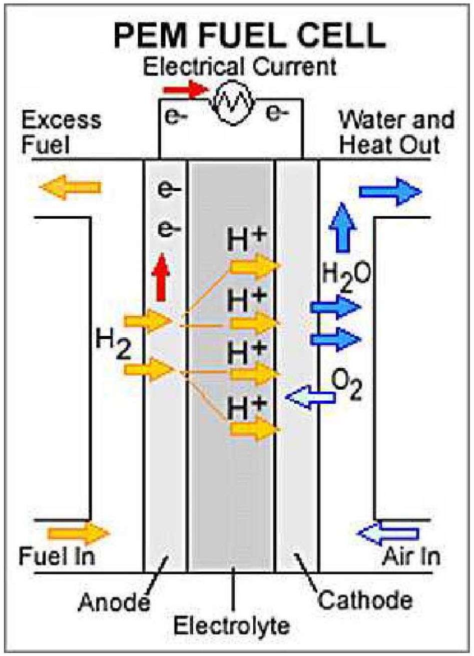
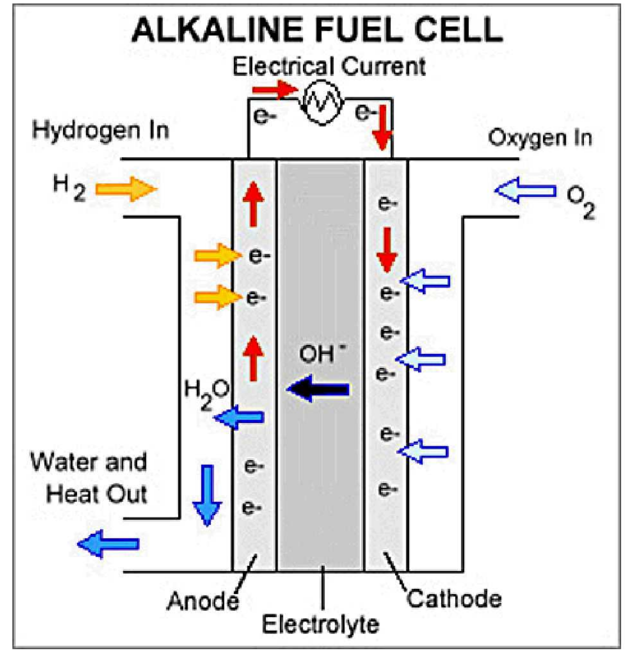
Alkaline Membrane Fuel Cells





$2H_2 \rightarrow 4H^+ + 4e^-$ $O_2 + 4e^- + 4H^+ \rightarrow 2H_2O$ $2H_2 + 4OH^- \rightarrow 4H_20 + 4e^-$ $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

- 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.

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Membrane Issues

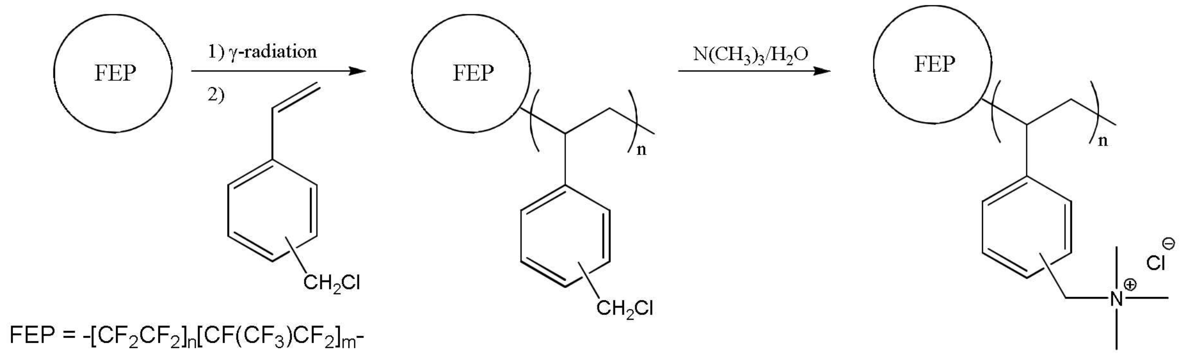
There is no commercial standard AEM (such as Nafion® for PEM).

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 ($OH^-/CO_3^{2-}/HCO_3^-$)
   - Conductivity at low RH
4. Water swelling
   - Physical stress on cell hardware due to expansion/compression.
   - Delamination of electrodes from membrane.

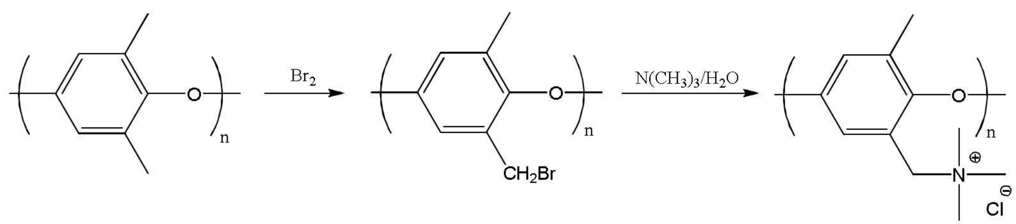
From DOE Alkaline Membrane Fuel Cell Workshops, May 8-9 2011

AEM Polymer Backbones

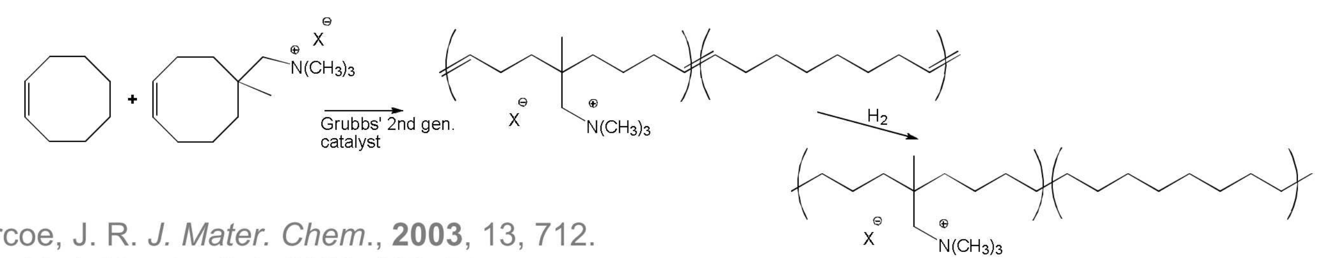
Radiation-grafting of functionalized poly(styrene) onto fluorinated polymers[1]:



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



Poly(ethylene)-based AEM from ROMP[3]:



[1]Danks, T. N.; Slade, R. T. C.; Varcoe, J. R. *J. Mater. Chem.*, **2003**, 13, 712.
[2]Wu, Y.; Wu, C.; Xu, T.; Lin, X.; Fu, Y. *J. Membr. Sci.*, **2009**, 338, 51.
[3]Kostalik, H. A.; Clark, T. J.; Robertson, N. J.; Mutolo, P. F.; Longo, J. M.; Abruna, H. D.; Coates, G. W. Macromol., **2010**, 43, 7147.

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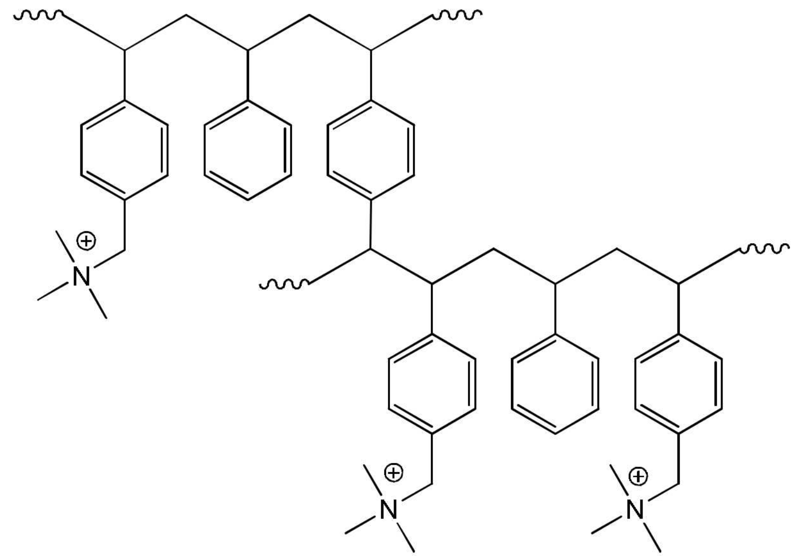
Cations on Anion Exchange Membranes (AEMs)

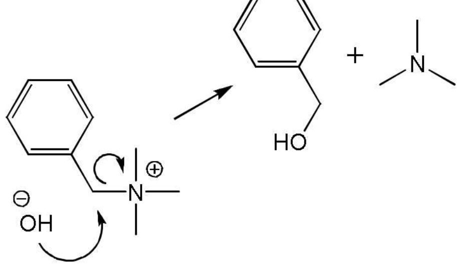
A Typical Commercially-available AEM:



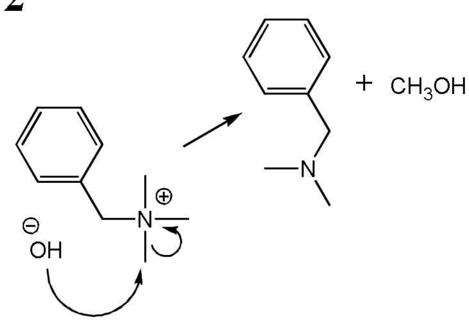
- Crosslinked polystyrene with benzyl trimethylammonium groups (BTMA)
- Typically blended with PVC or a polyolefin
- Cast on fabric support
- Used for electrodialysis

Three degradation pathways for quaternary ammonium groups:

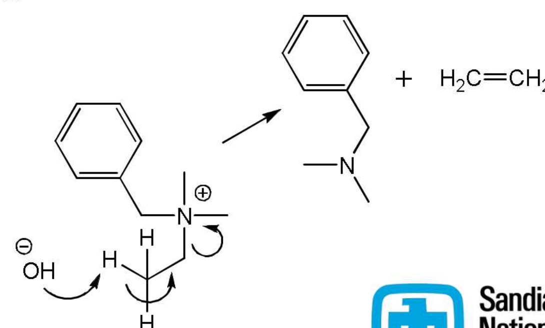
1



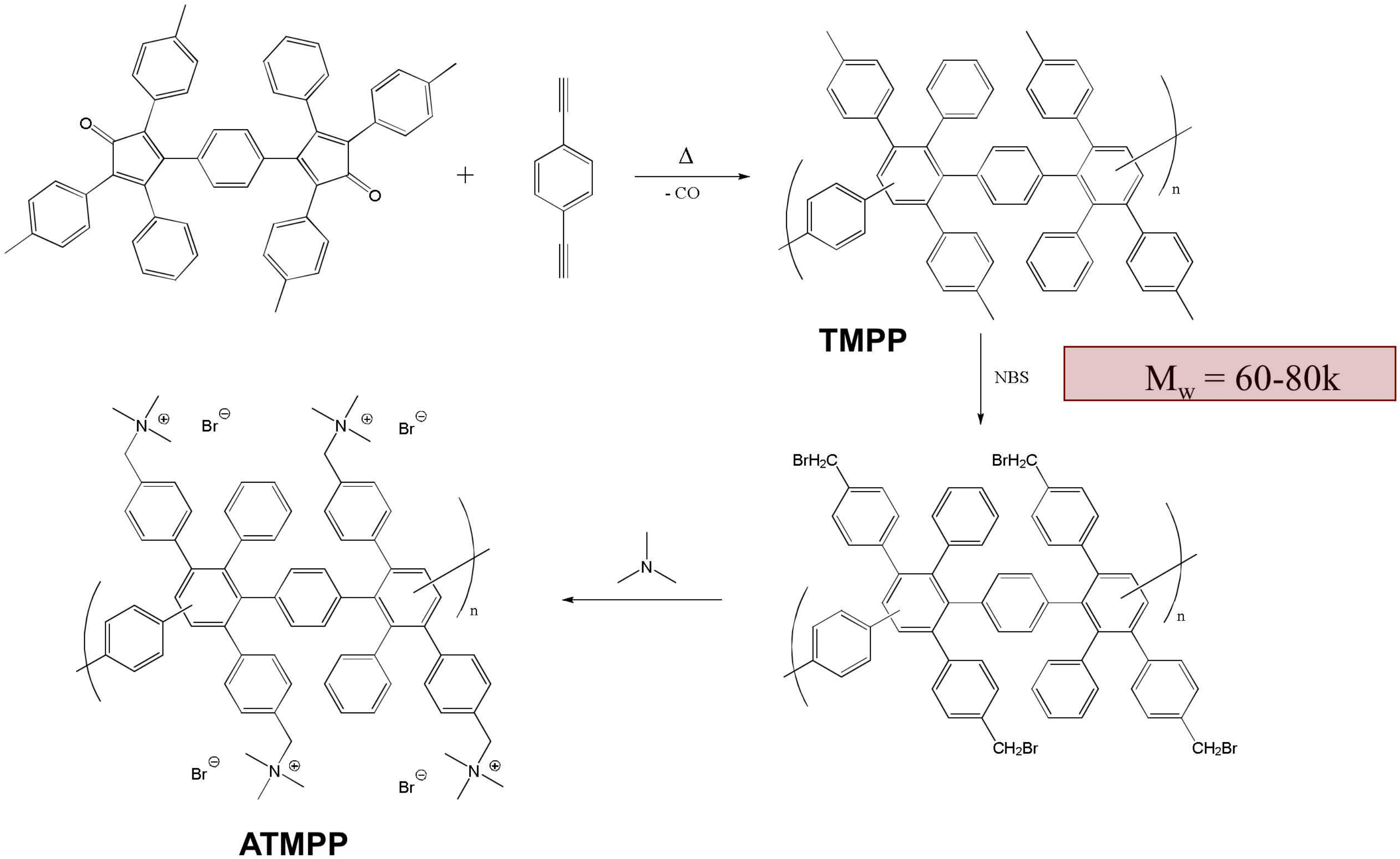
2



3



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



Hibbs, M. R.; Fujimoto, C. H.; Cornelius, C. J. *Macromol*. **2009**, 42, 8316.

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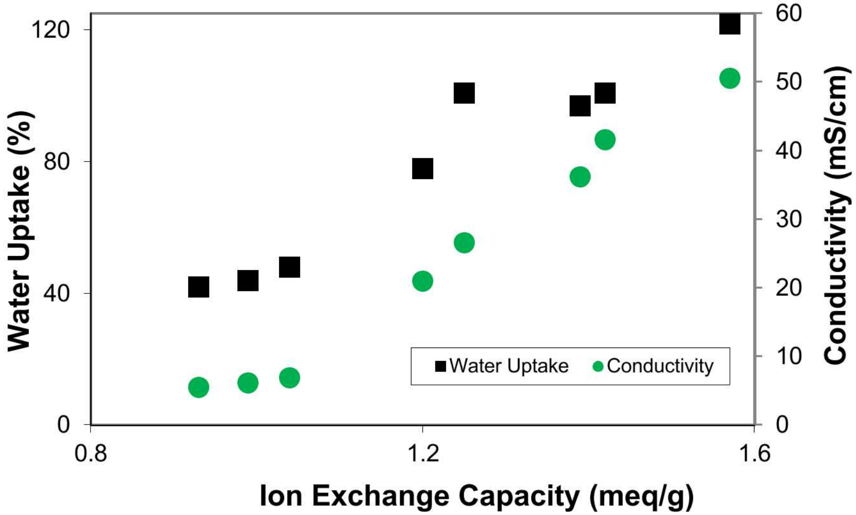
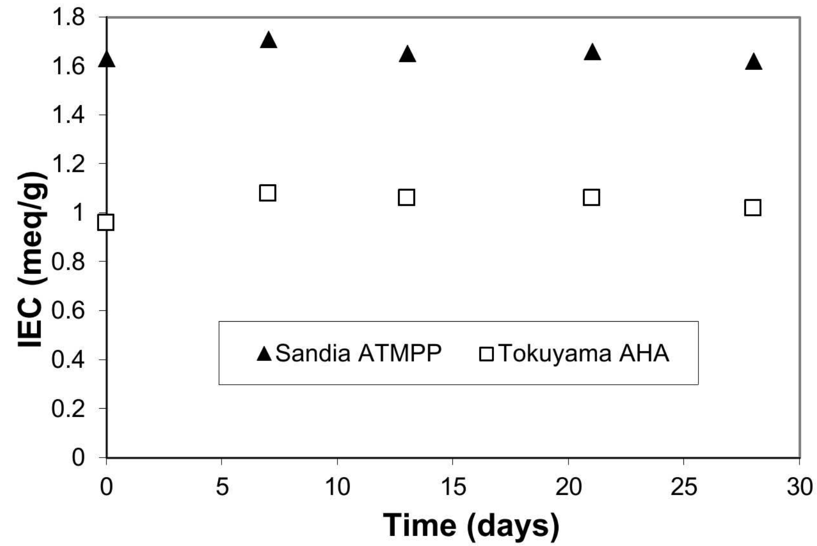
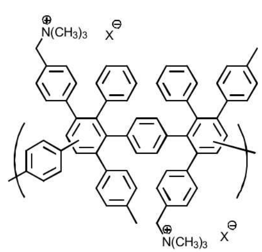
ATMPP Properties & Stability



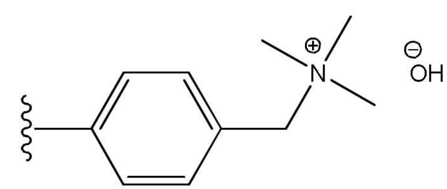


- Hydroxide conductivities were measured in liquid water at room temperature.
- SAXS indicated little or no microphase separation.



ATMPP
poly(phenylene)

- Test conditions: 4M NaOH (aqueous), 60 ^{o}C, no stirring.
- AHA is “base stable” electrodialysis membrane – crosslinked polystyrene.
- Both membranes have BTMA cations.



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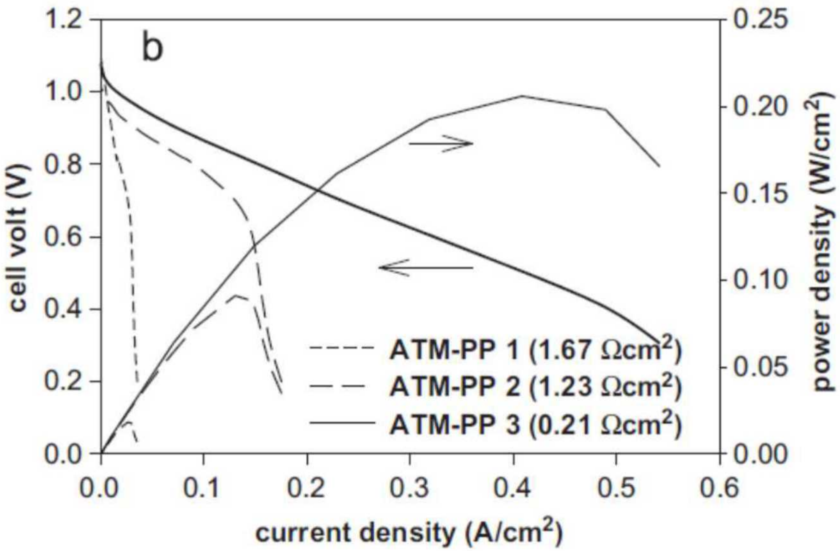
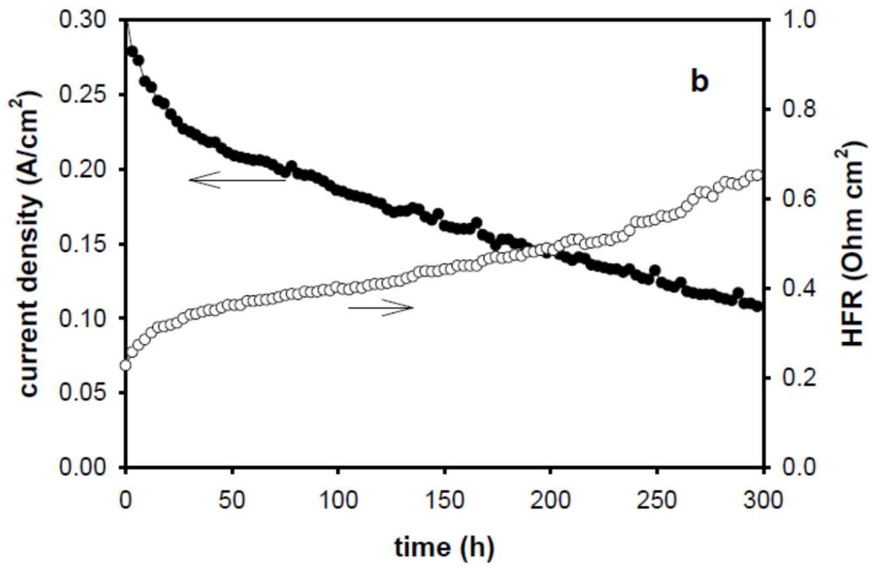
Fuel Cell Testing at LANL

H_2/O_2 Fuel Cell polarization curves



Durability in H_2/O_2 fuel cell



- ATMPP used as both membrane and ionomer/binder.
- ATMPP 1,2, and 3 have increasing M_w (61, 77, 196 x10^3 g/mol) but similar IECs (1.7 meq/g).
- Low Mw gives poor mechanical properties and poor membrane/electrode interface.
- Fuel cell testing was done at 60 ^oC, 0.3 V, with Pt/C catalyst on both electrodes (3 mg/cm^2).
- Decline in current density is also presumably due to BTMA degradation.
- Testing performed by Yu Seung Kim at LANL.

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

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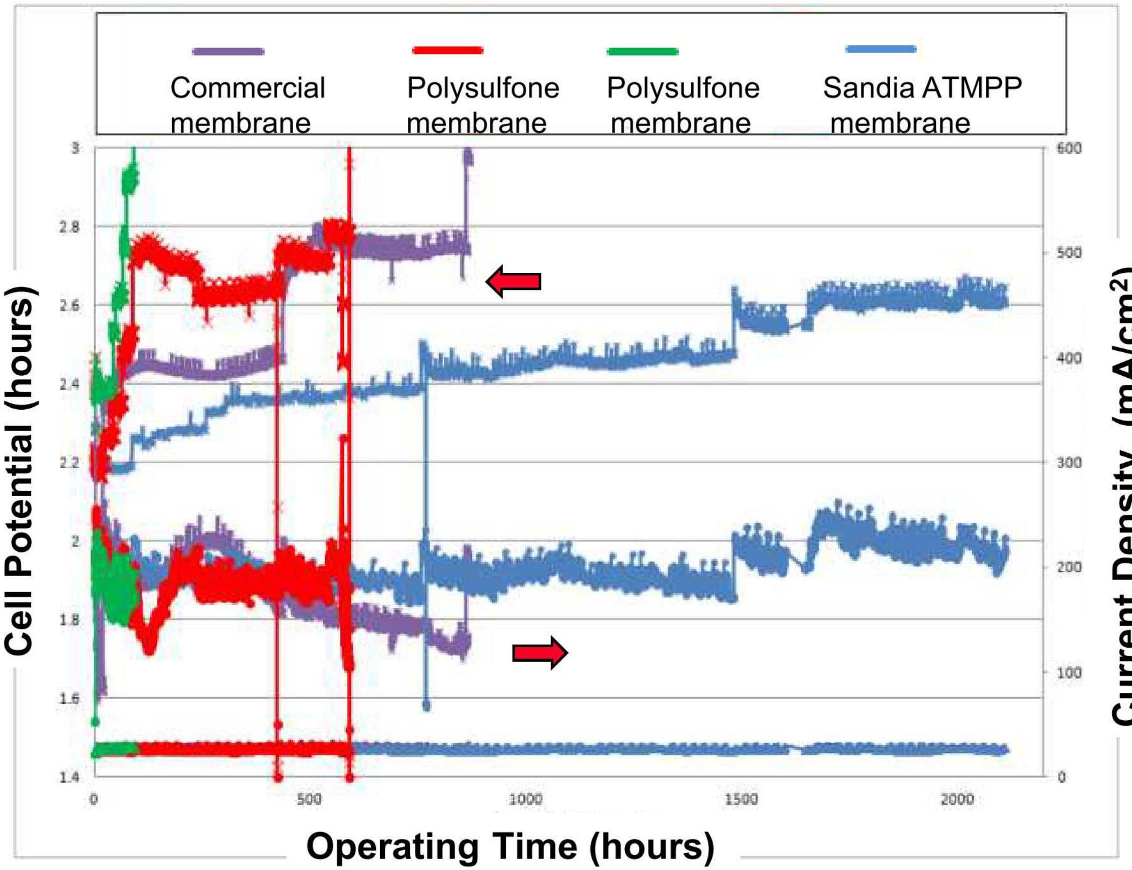
Electrolysis Testing at Proton OnSite

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 ATMPP membrane + ATMPP ionomer.
- Need to improve voltage stability.



PROTON ON SITE

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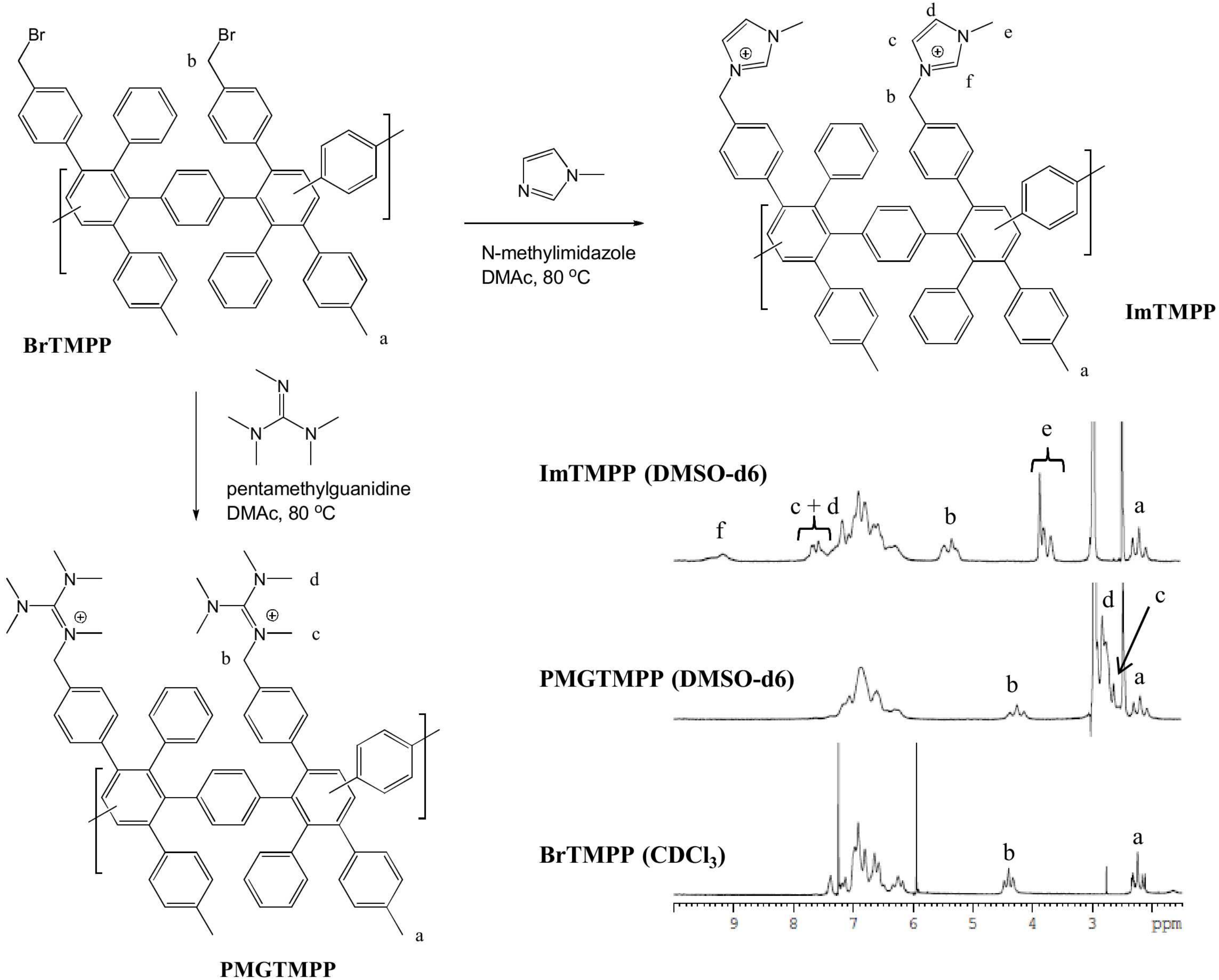
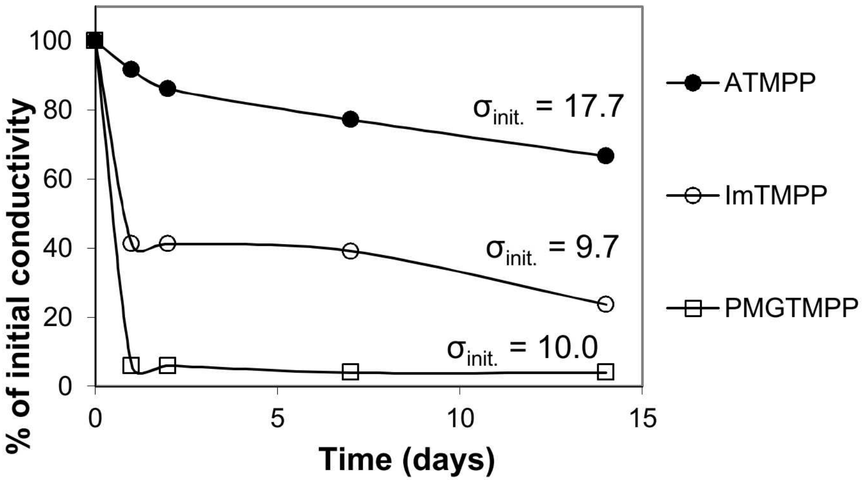
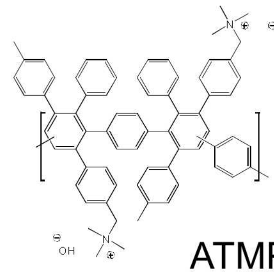
Resonance-Stabilized Cations



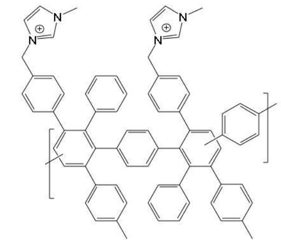
KOH Stability Test
Resonance-Stabilized Cations

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

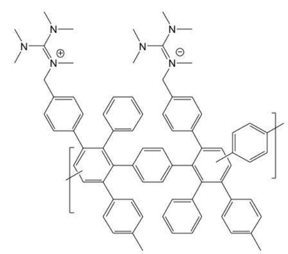




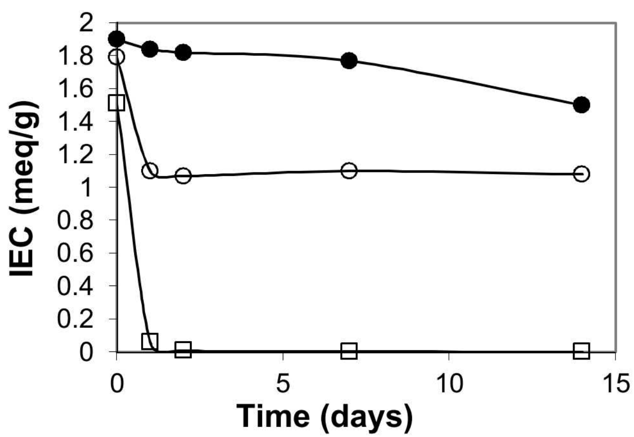
ATMPP



ImTMPP



PMGTMPP



- 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.

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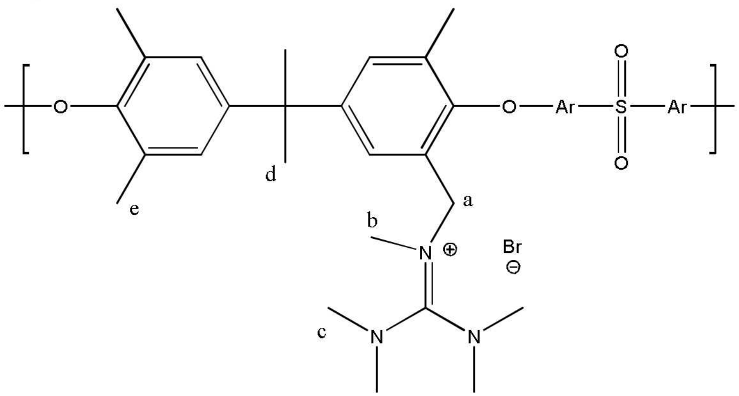
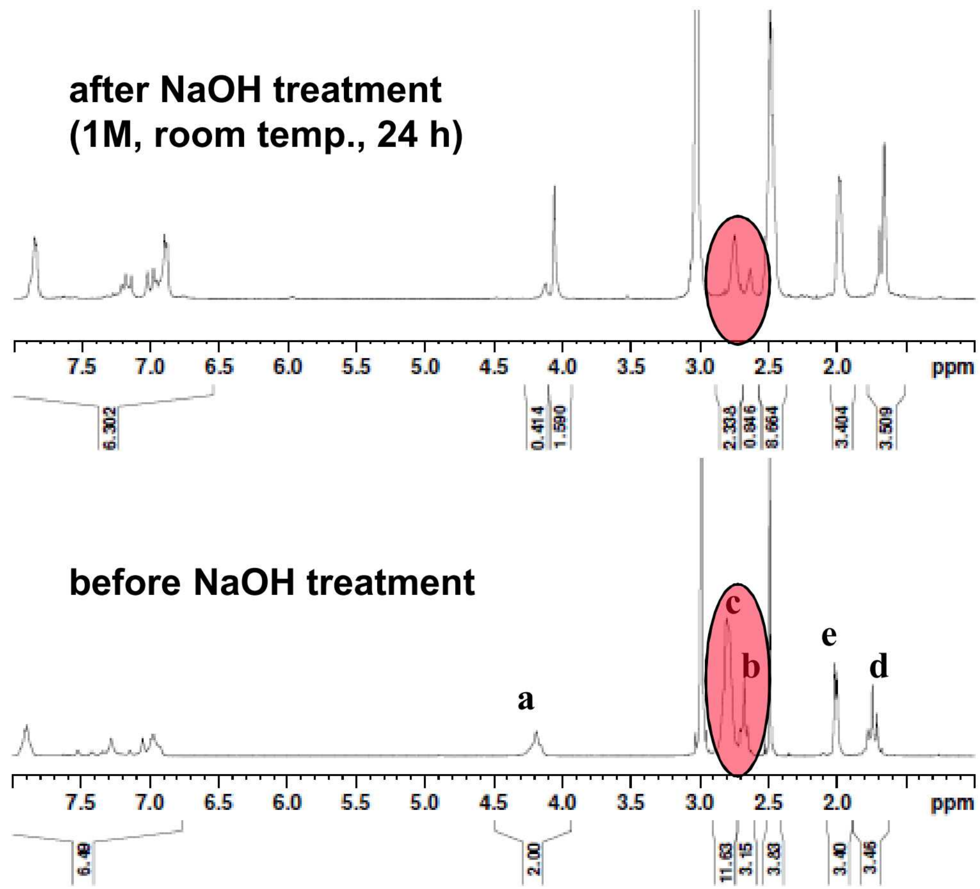
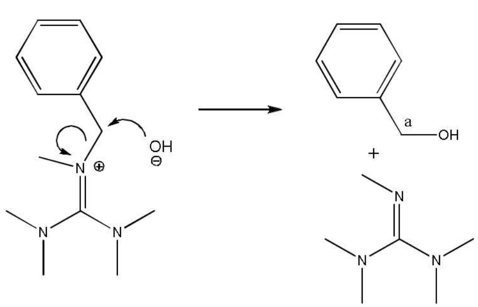
Decomposition of Benzyl PMG Cations





- 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:



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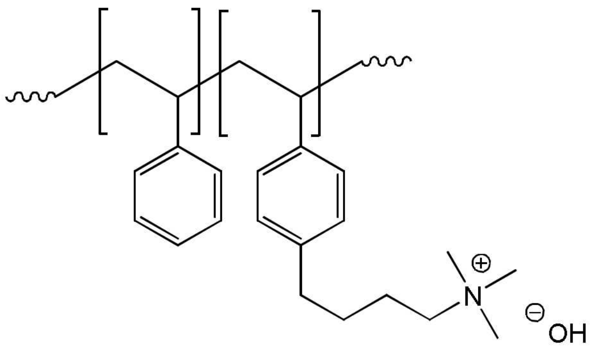
Improving the Stability of Quaternary Ammonium Groups

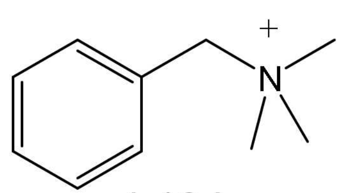
One early study found that increasing the length of the alkyl tether on a BTMA cation increased alkaline stability[1]

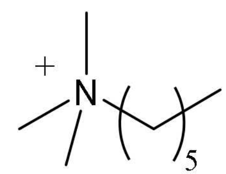


Tested for 30 days in 100 °C water (OH^- form):

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

Recent studies have confirmed the improved stability of model ammonium compounds with pendant alkyl groups[2]

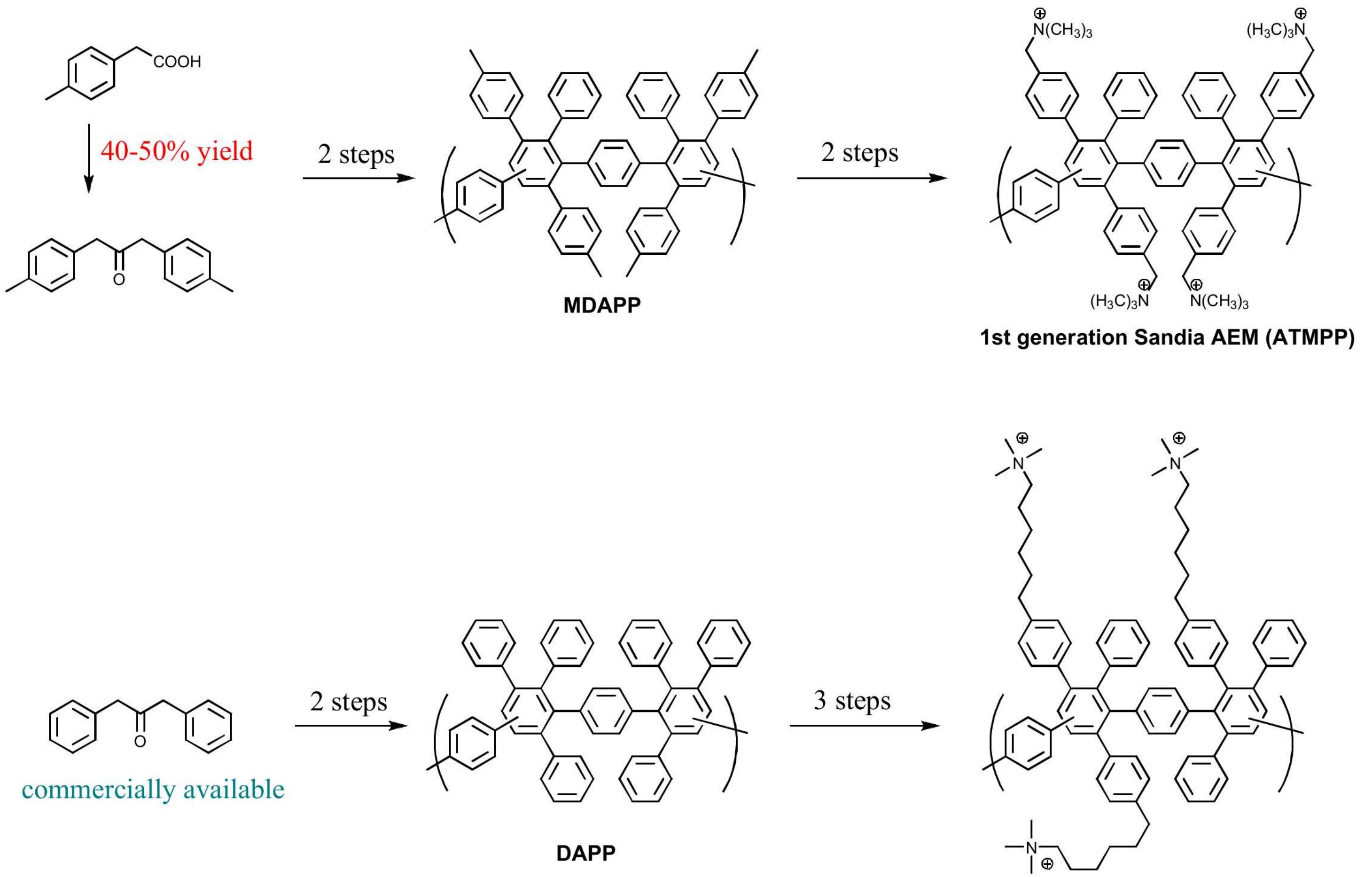




Half-life in 6M NaOH at 160°C:	4.18 h	31.9 h

[1]Tomoi, M.; Yamaguchi, K.; Ando, R.; Kantake, Y.; Aosaki, Y.; Kubota, H. *J. Appl. Polym. Sci*. 1**997**, *64*, 1161.
[2]Marino, M.G.; Kreuer, K.D. *ChemSusChem* **2015**, *8*, 513.

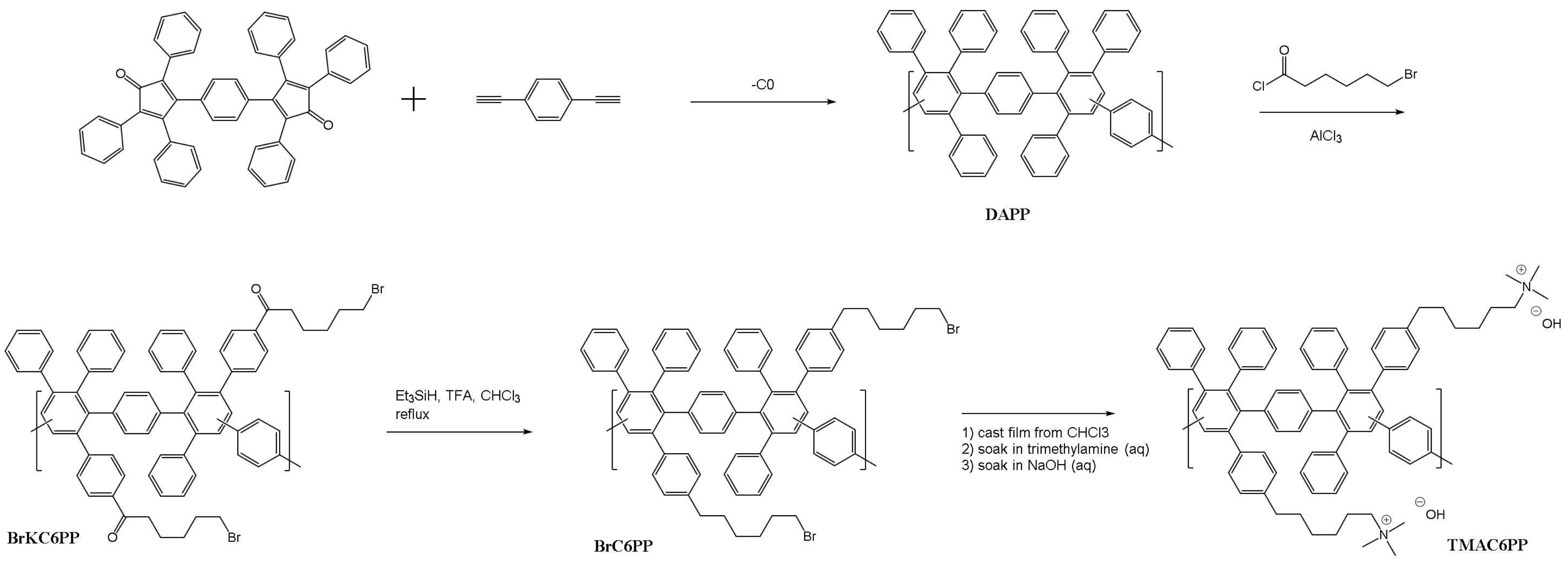
Poly(phenylene) AEM with Sidechains



2nd generation Sandia AEM (TMAC6PP)

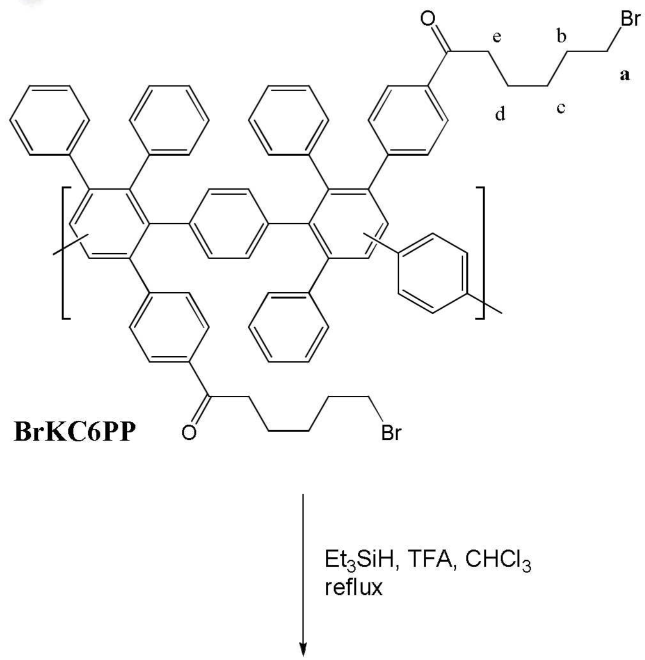
- **DAPP is easier to make than MDAPP, with higher molecular weights.**
- **Synthesis of DAPP has been scaled up to ~1kg.**

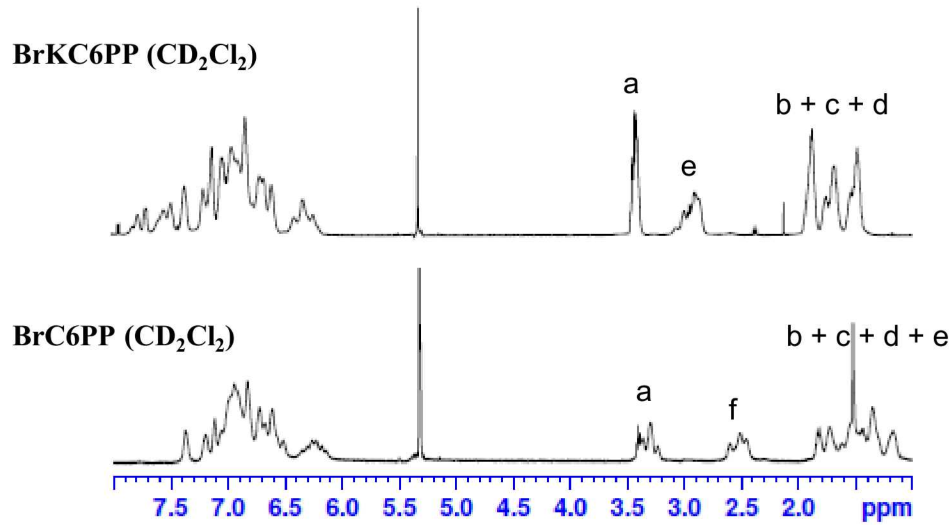
Poly(phenylene) AEM with Sidechains

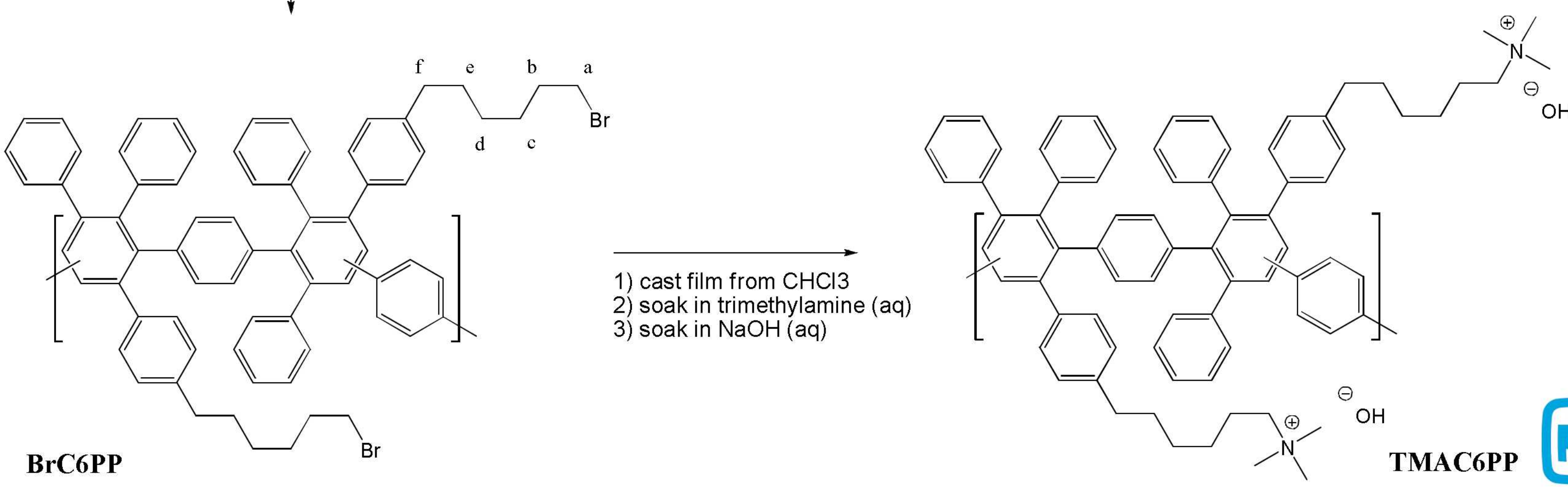


Hibbs, M. R. *J. Polym. Sci. Part B, Polym. Phys*. **2013**, 51, 1736.

Poly(phenylene) with Alkyl Side Chains without Ketone







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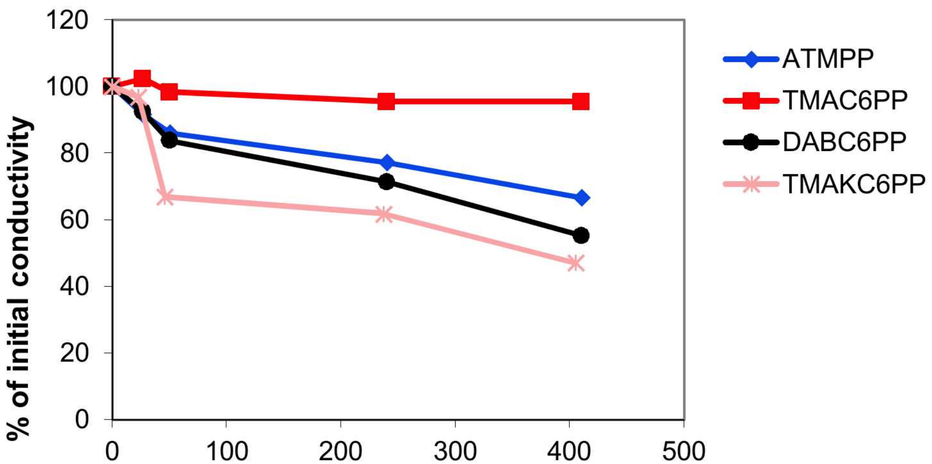
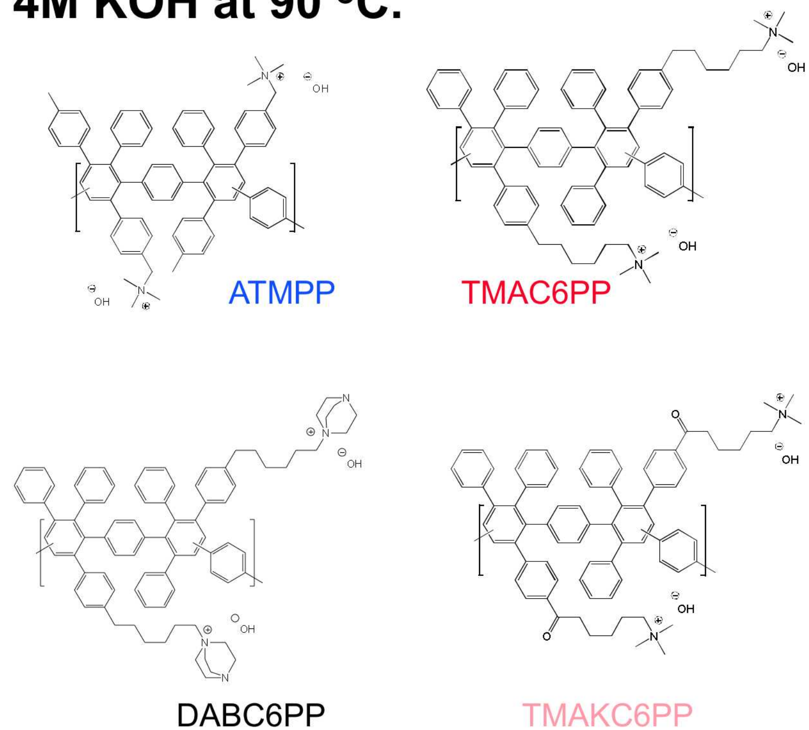
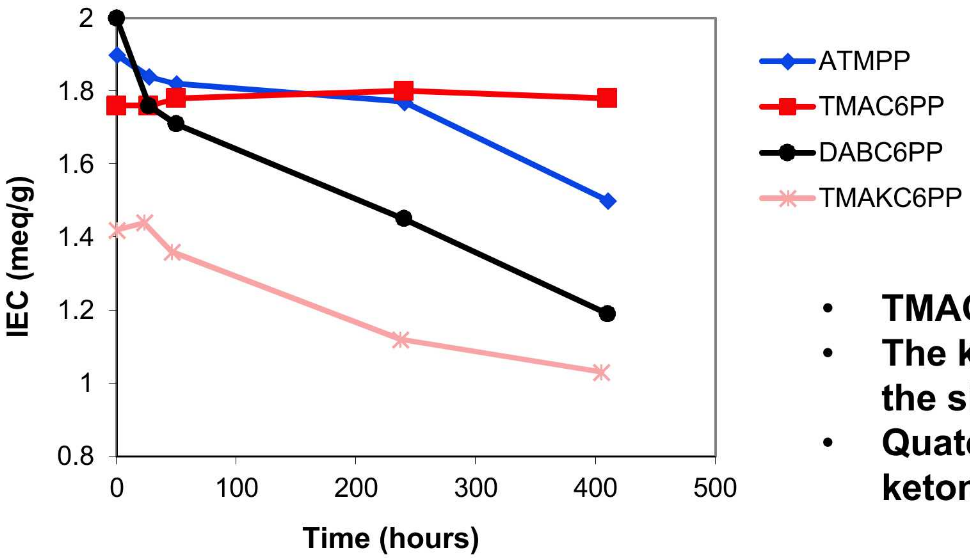
TMAC6PP Alkaline Stability

Test conditions: Membranes immersed in 4M KOH at 90 ^{o}C.



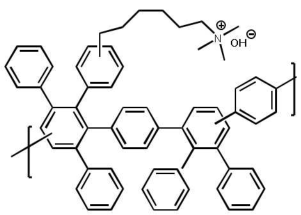




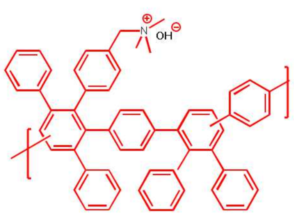
- **TMAC6PP shows the greatest stability in high pH test.**
- **The ketone adjacent to the phenyl ring destabilizes the side chains.**
- **Quaternized DABCO on hexyl sidechains with no ketone are less stable than BTMA.**

More Alkaline Stability Data

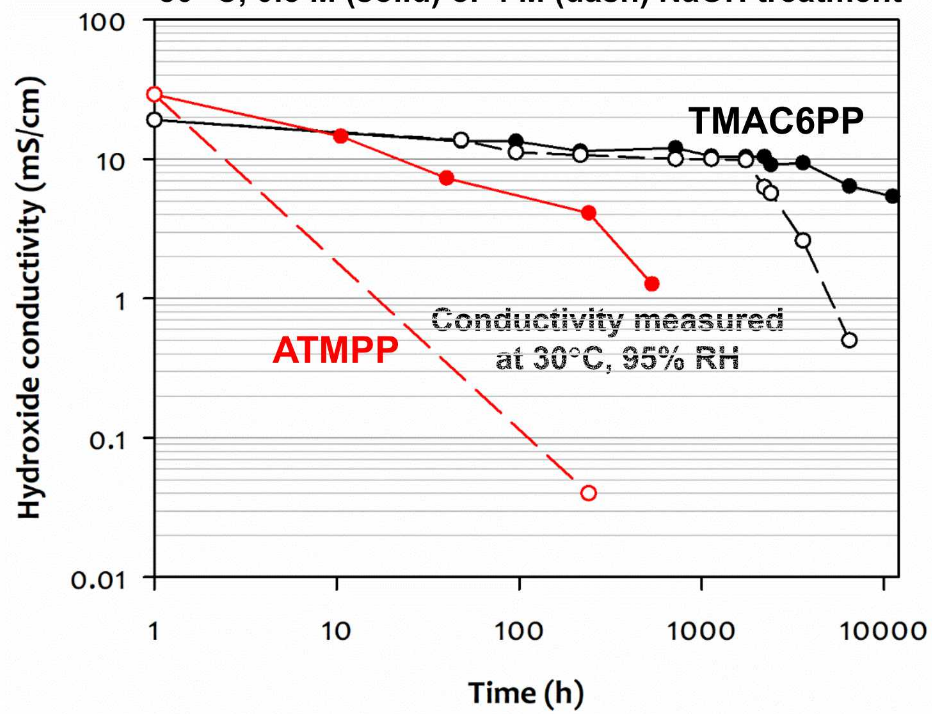
AEM stability test: Immerse AEMs in 0.5 M or 4 M NaOH at 80°C. Conductivity measured at 30°C/95% RH during the stability test.



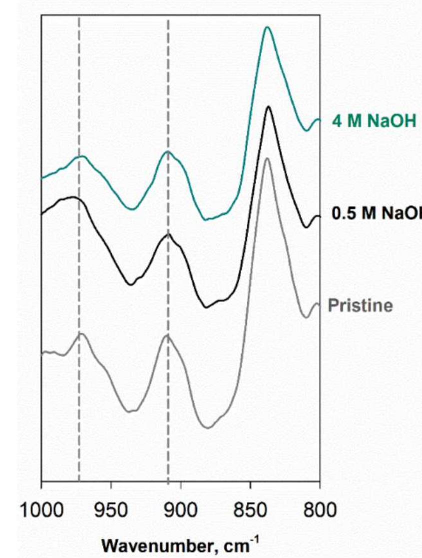
TMAC6PP



ATMPP (control)



FTIR of TMAC6PP after 3600 h NaOH treatment



Highlight: No conductivity & structural changes for TMAC6PP after 4 M NaOH treatment at 80°C for 2,200 h. → Most stable alkaline AEM reported

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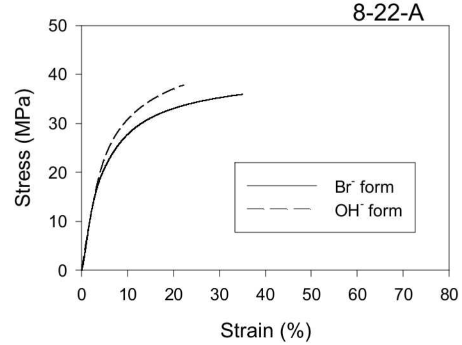
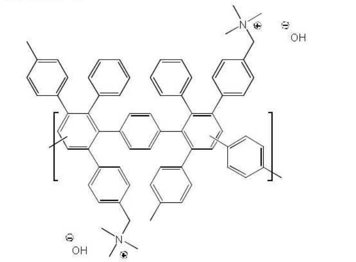
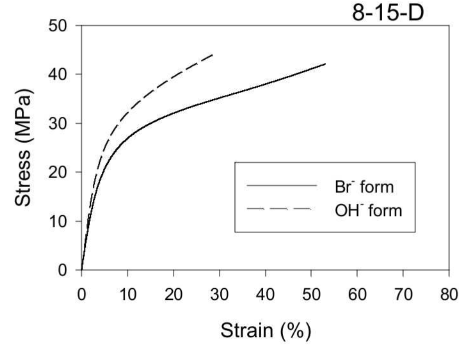
TMAC6PP Stress/Strain Testing

- 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.

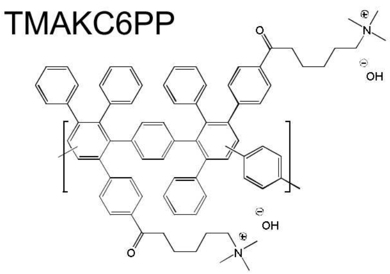


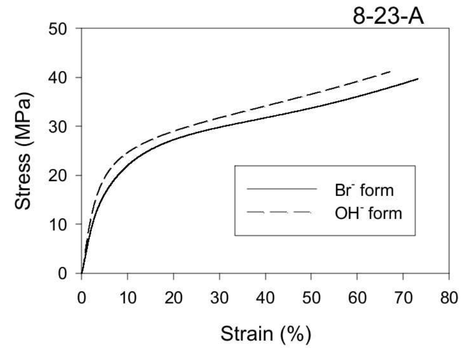
ATMPP



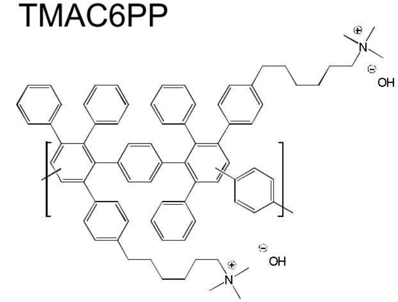


TMAKC6PP

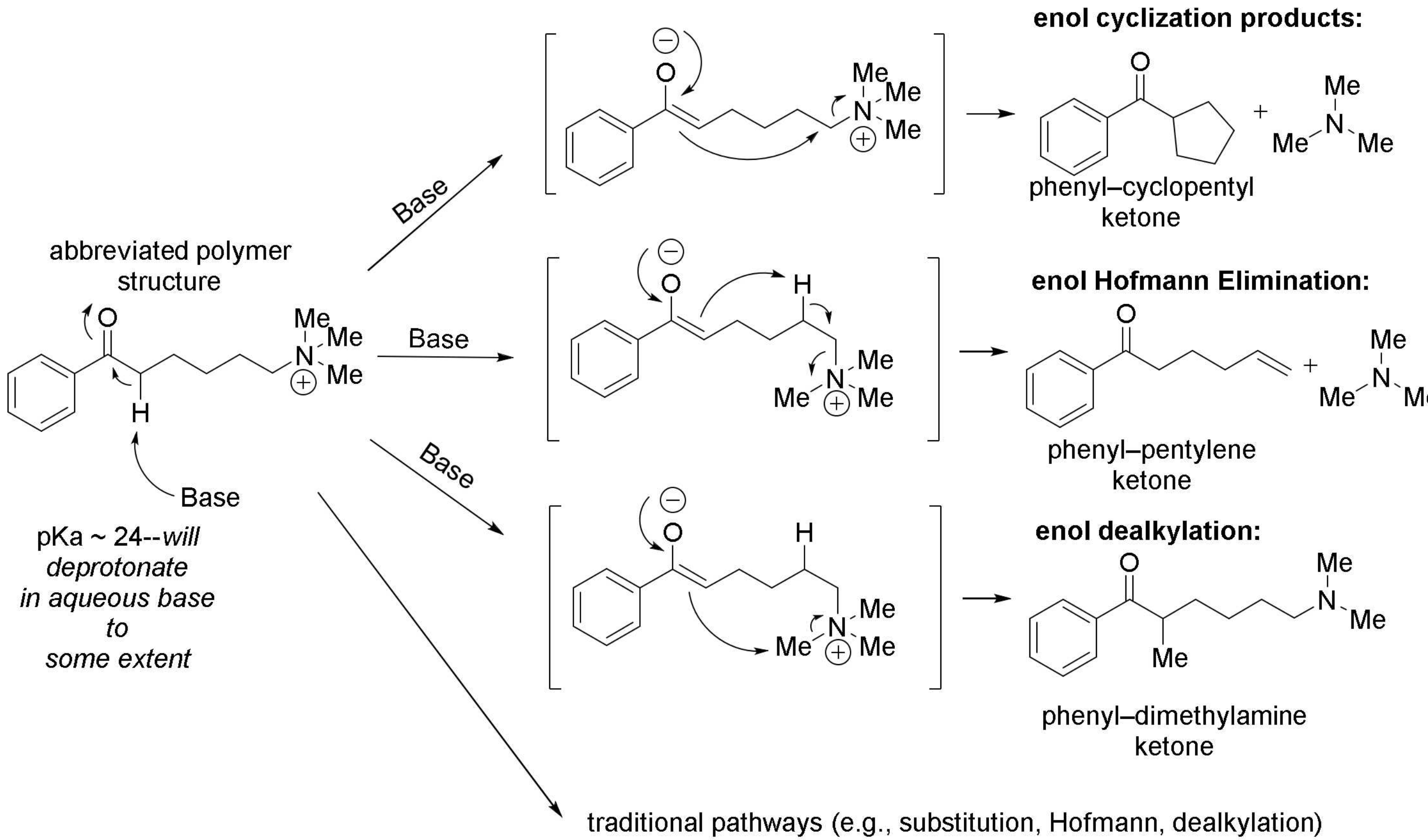




TMAC6PP



Instability Due to Ketone

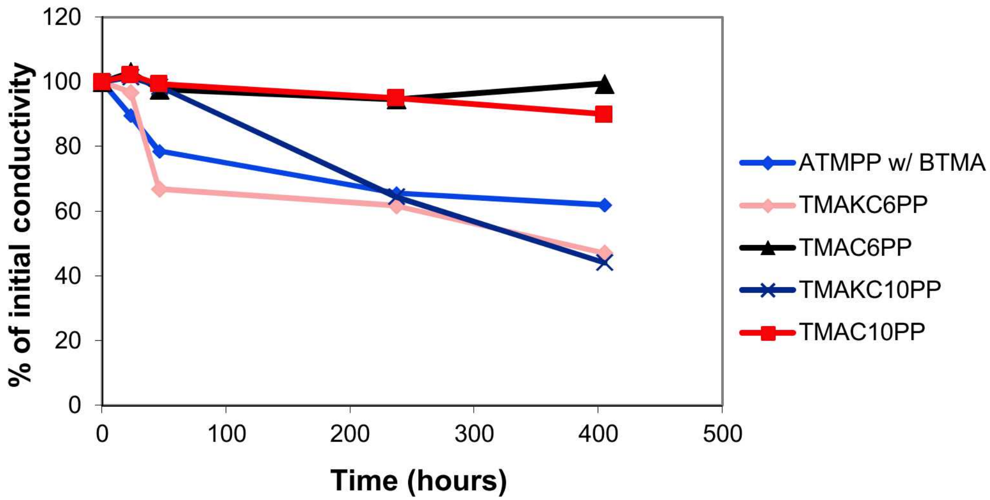


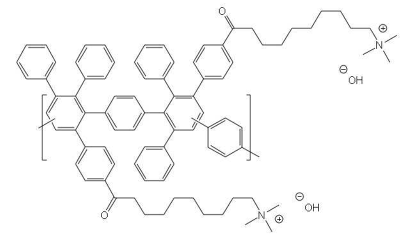
- Formation of enolate might begin pathway to cation degradation.
- Mechanisms that involve a 5- or 6-membered ring as an intermediate would be particularly likely.
- A longer sidechain would eliminate 5- and 6-membered ring intermediates.

Schemes drawn by Sean Nunez (PSU)

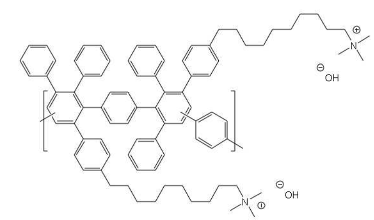
Stability of 10-Carbon Sidechain

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

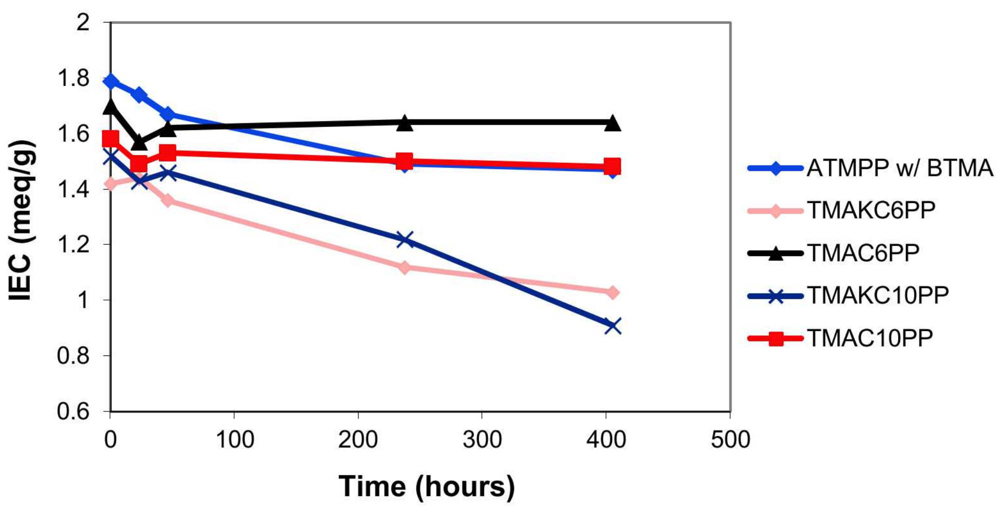




TMAKC10PP



TMAC10PP



- 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.

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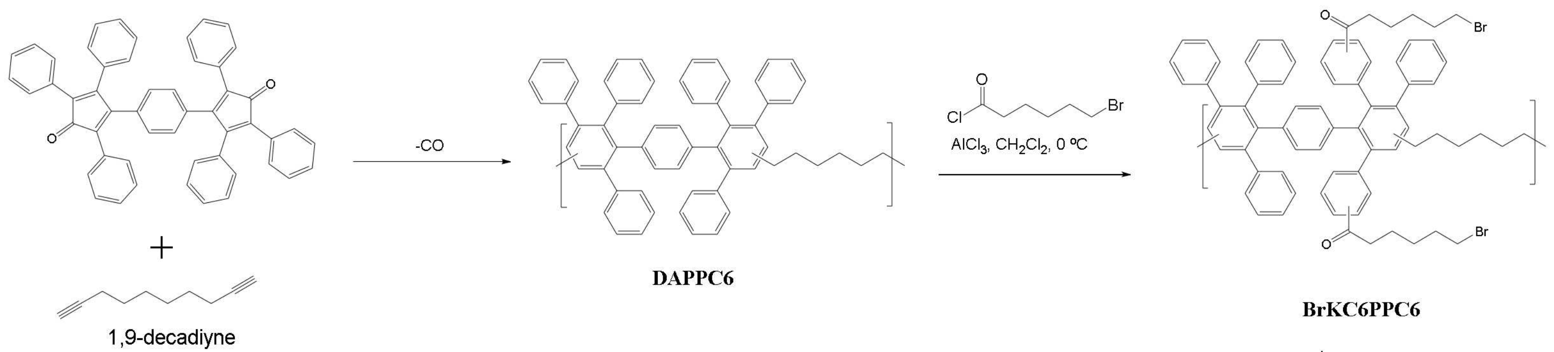
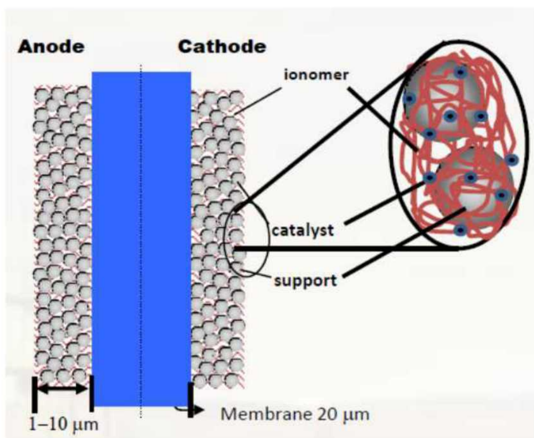
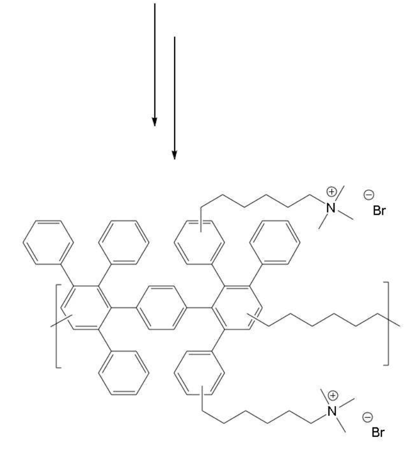
Poly(phenylene alkylene) Synthesis







- Flexible alkylene segments in backbone were intended to increase permeability of polymer.
- Typical M_w for DAPPC6 is 10K-15K, either due to low reactivity or purity of 1,9-decadiyne.
- TMAC6PPC6 films are brittle but polymer is still useful as electrode ionomer.

Alam, T.M.; Hibbs, M.R. *Macromol.* **2014**, 47, 1073.

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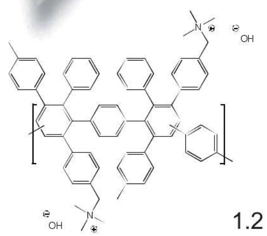
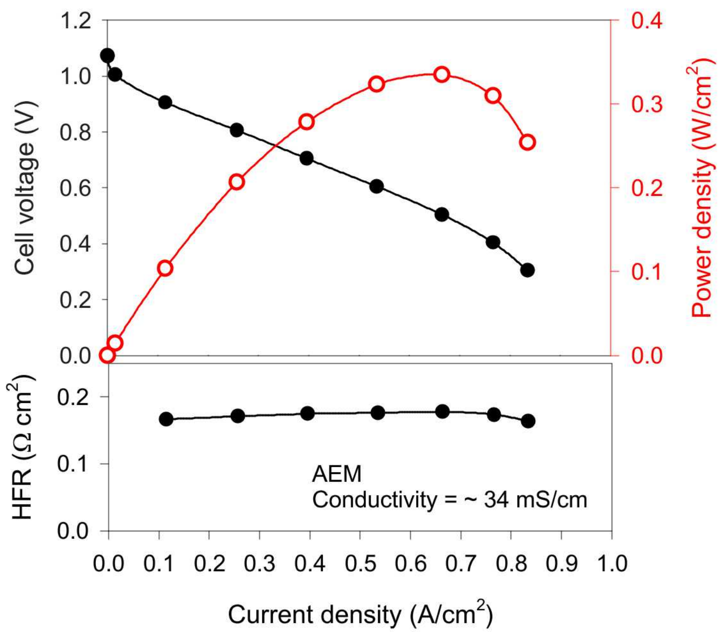
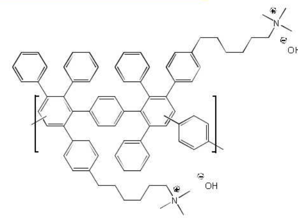
H_2/O_2 Fuel cell Performance of MEAs using ATMPP and TMAC6PP

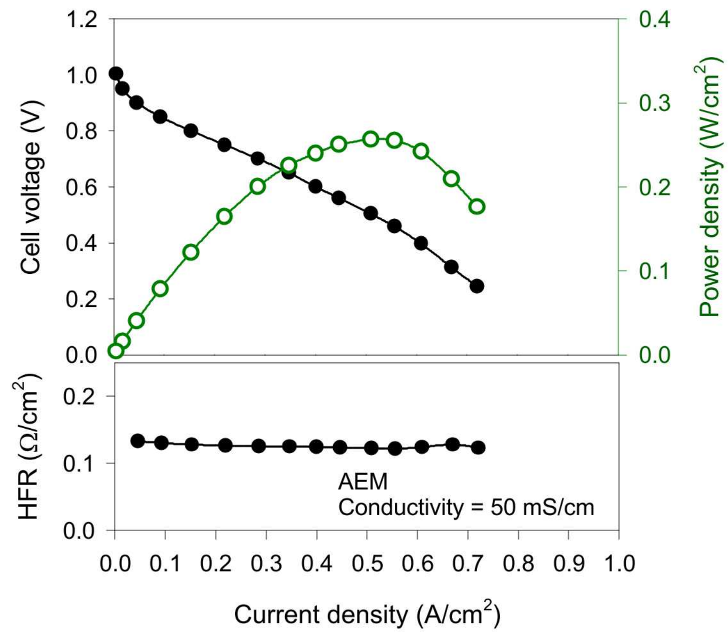


Membrane: ATMPP (50 μm thickness)
Ionomer: ATMPP IEC=1.7 mg/cm²
Anode: Pt black 3.4 mg_{Pt}/cm^2
Cathode: Pt black 6.5 mg_{Pt}/cm^2
Cell temperature: 80°C, Backpressure: 30 psig



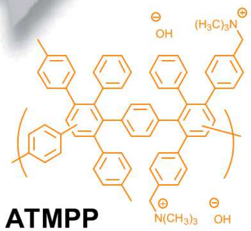
Membrane: TMAC6PP (48 μm thickness)
Ionomer: TMAC6PP IEC=2.0 mg/cm²
Anode: Pt black 0.2 mg_{Pt}/cm^2
Cathode: Pt black 0.2 mg_{Pt}/cm^2
Cell temperature: 80°C, Backpressure: 15 psig



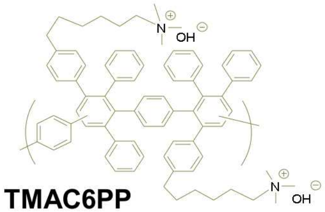


- Peak power density of the MEA using ATMPP: 340 mW/cm² at high Pt loading and higher back pressure.
- Peak power density of the MEA using TMAC6PP: 260 mW/cm² at low Pt loading and lower back pressure.
- Lower resistance of the TMAC6PP MEA is probably due to the fact that TMAC6PP membrane has slightly higher IEC and AEM thickness effect.

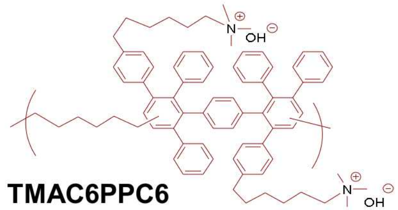
Improved Performance with Poly(phenylene alkylene) Ionomer



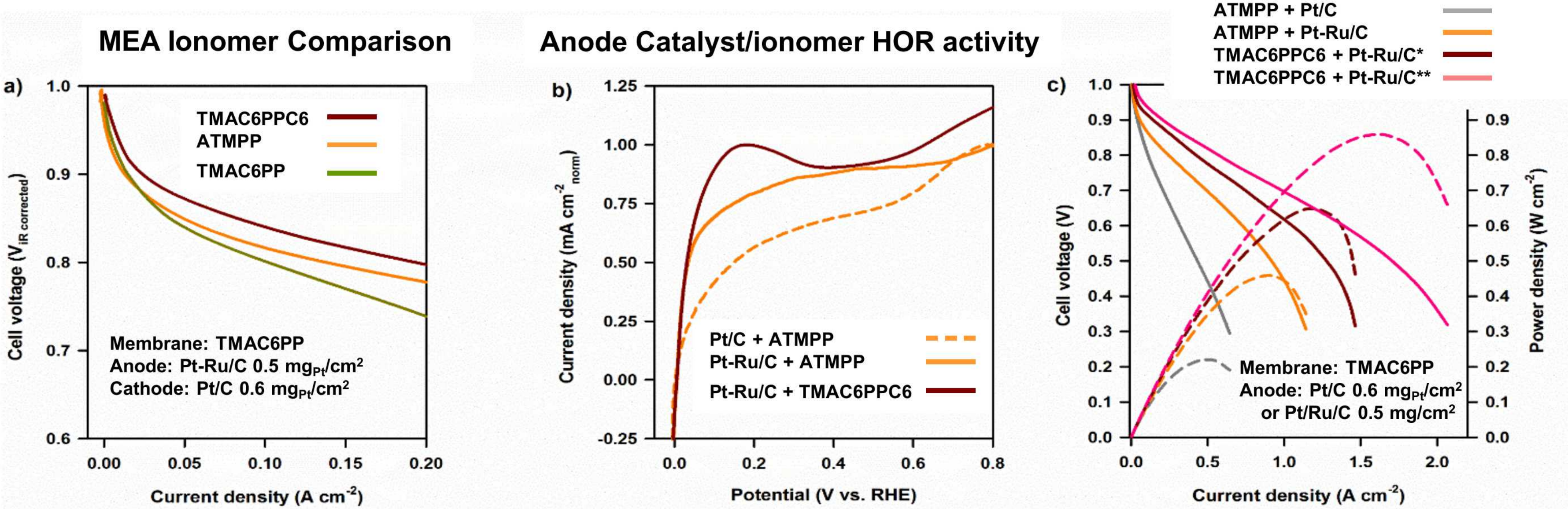
ATMPP



TMAC6PP



TMAC6PPC6



*H_2 flow rate = 500 sccm, O_2 flow rate = 300 sccm
**H_2 flow rate = 2000 sccm, O_2 flow rate = 1000 sccm

- **Poly(phenylene alkylene) ionomer has the lowest phenyl content (less adsorption on catalyst).**
- **Increasing flow rate greatly improves H_2 mass transport at the anode.**

Los Alamos NATIONAL LABORATORY

Maurya, S.; Fujimoto, C.H.; Hibbs, M.R.; Villarrubia, C.N.; Kim, Y.S. *Chem. Mater.* **2018**, 30, 2188.

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Conclusions

- The combination of Sandia's poly(phenylene) backbone with alkyltrimethyl ammonium cations gives the most stable hydrocarbon AEM available.

- Resonance-stabilized cations (imidazolium and pentamethyl guanidinium) are less stable to alkaline degradation than BTMA cations.

- Phenyl adsorption on the anode catalyst is a performance limiting factor.

- We are still working on the integration of non-PGM or low PGM catalysts into alkaline fuel cells.

Acknowledgements

Sandia National Laboratories

Jeff Nelson
Todd Alam
Janelle Jenkins

Proton OnSite
Kathy Ayers
Chris Capuano
Morgan George

Penn State University
Mike Hickner
Sean Nunez

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

University of New Mexico
Plamen Atanassov
Alexey Serov
Michael Robson
Kateryna Artyushkova
Wendy Patterson

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

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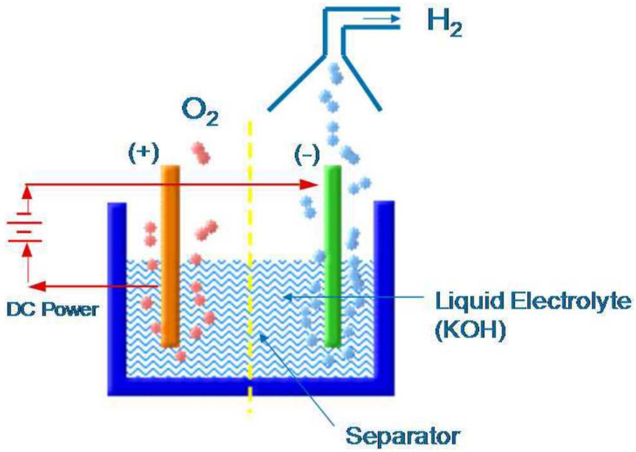
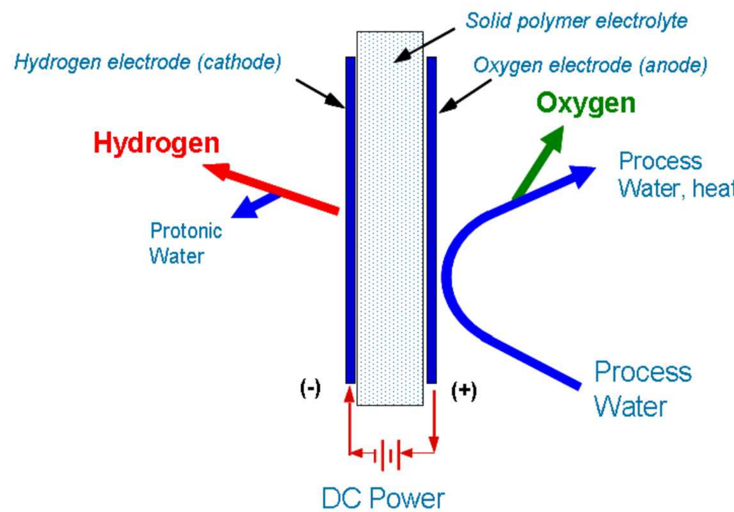
Back-up Slides

Alkaline Electrolysis Cell Configurations



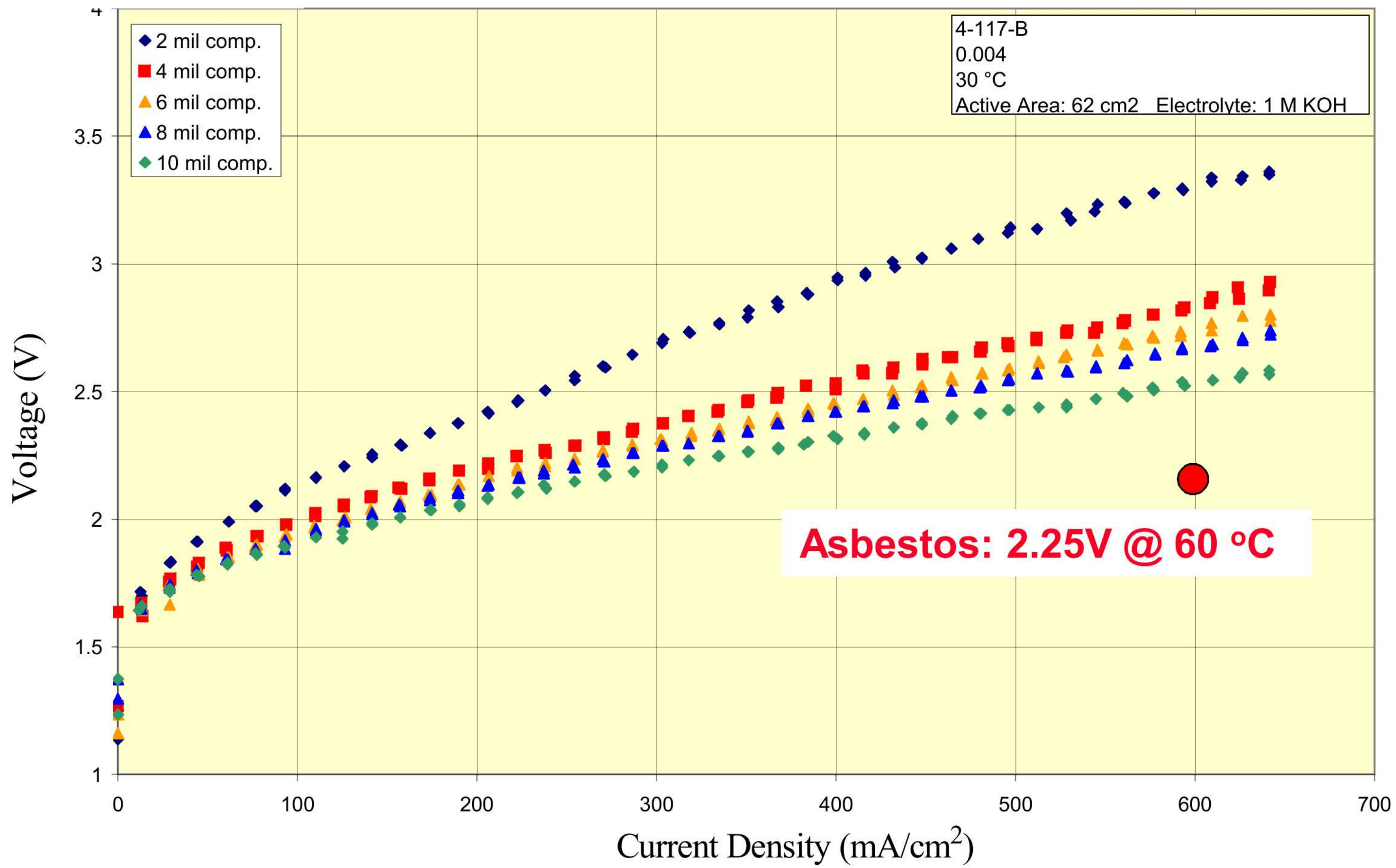
Liquid electrolyte Cell



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.

Electrolysis Data: Cell Compression



Cell conditions: 30 °C, 1M KOH, foam Ni electrodes, active area = 62 cm^2
current swept from 0 – 40 Amps,

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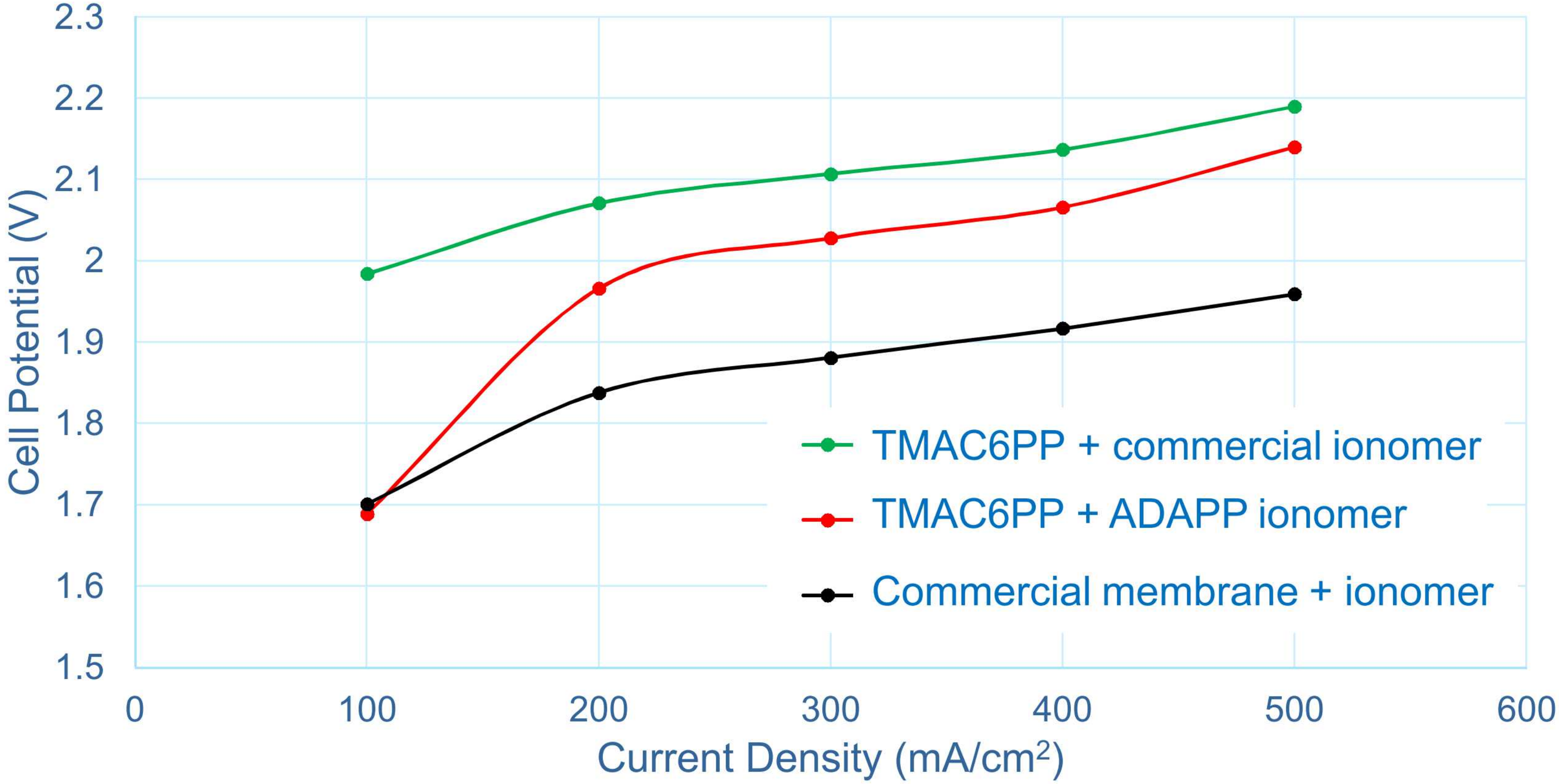
Electrolysis Testing at Proton OnSite

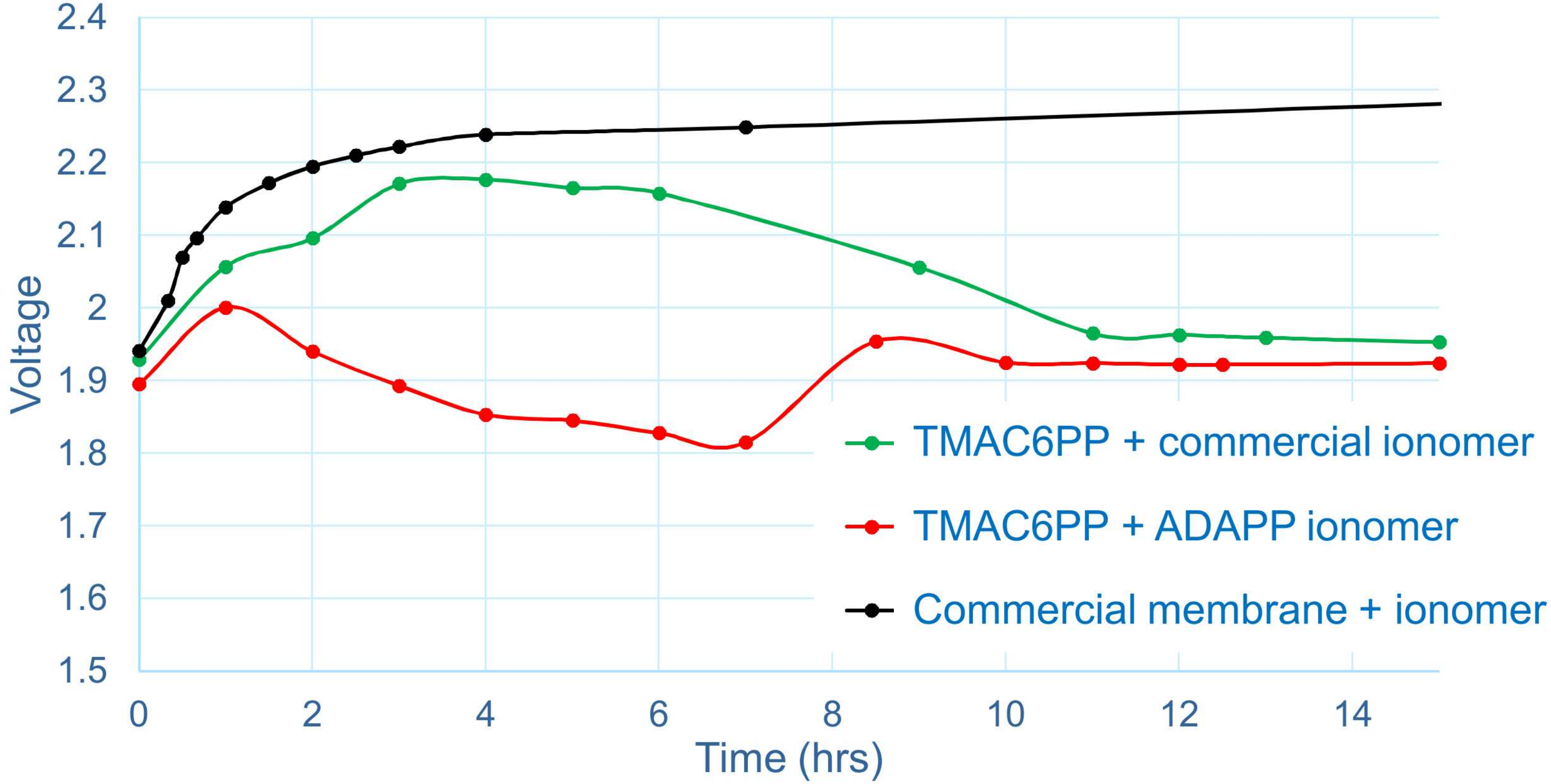
Initial polarization curves at 50 °C with PGM catalysts and no added electrolyte



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

Electrolysis Testing at Proton OnSite

200 mA/cm^2 steady state performance at 50 ^oC with PGM catalysts and no added electrolyte



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

PROTON ON SITE

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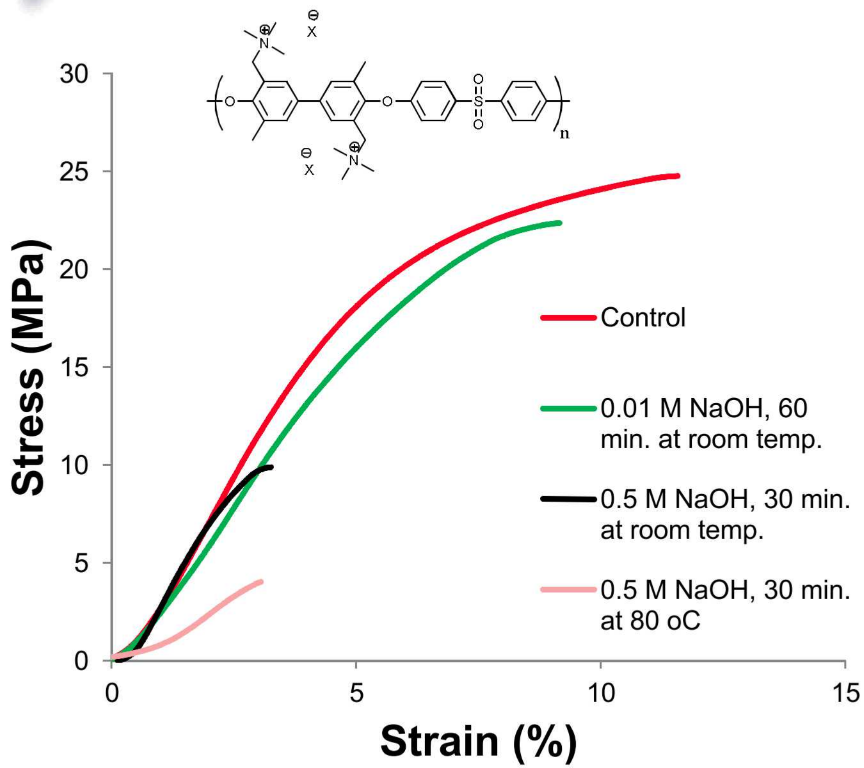
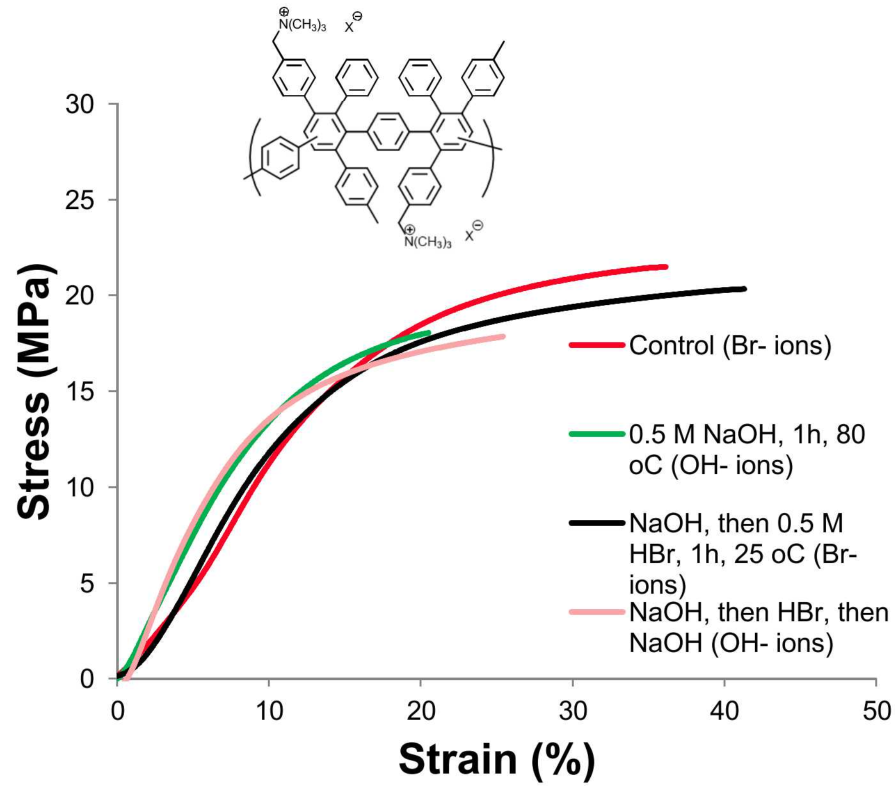
Mechanical Stability





- Test conditions: 50 ^{o}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.

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