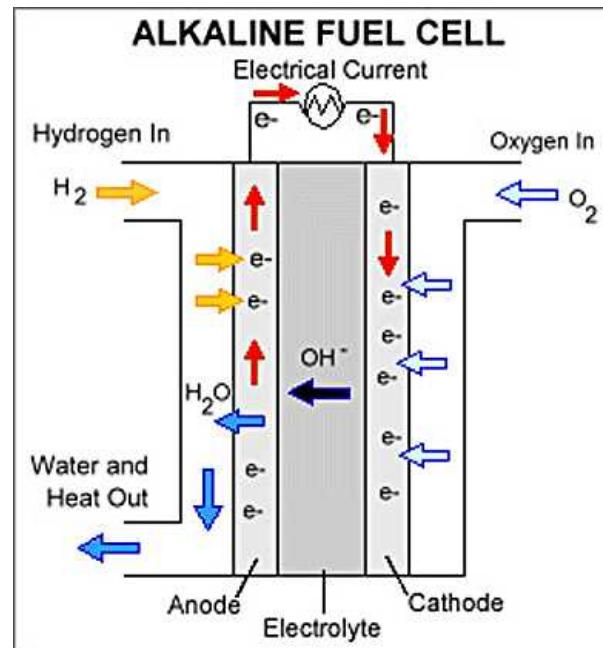
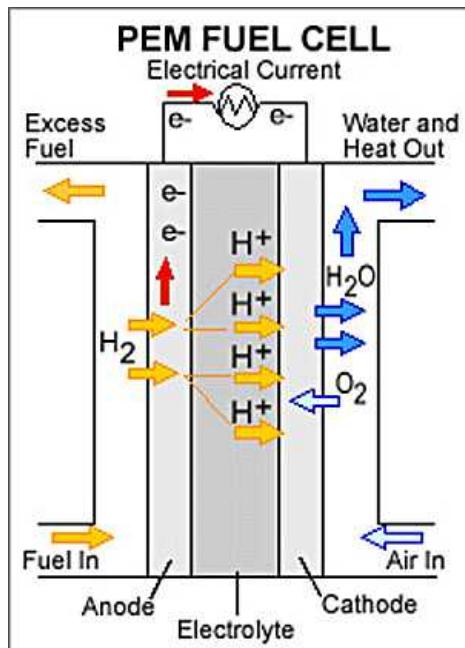


# DEVELOPMENT OF ANION-EXCHANGE MEMBRANES SANDIA

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Materials, Devices, and Energy Technologies, 6124  
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# Why Alkaline Fuel Cells (AFCs)?



- 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.



# Membrane Issues

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

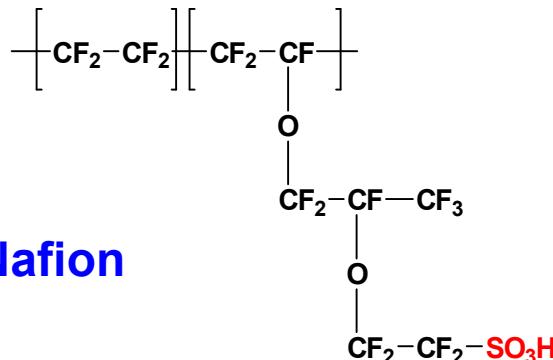
Membranes requirements<sup>1</sup>:

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<sup>-</sup>.
3. Conductivity
  - OH<sup>-</sup> inherently 2-3x less mobile than H<sup>+</sup>
  - Identity of anions (OH<sup>-</sup>/CO<sub>3</sub><sup>2-</sup>/HCO<sub>3</sub><sup>-</sup>)
  - Conductivity at low RH
4. Water swelling
  - Physical stress on cell hardware due to expansion/compression.
  - Delamination of electrodes from membrane.

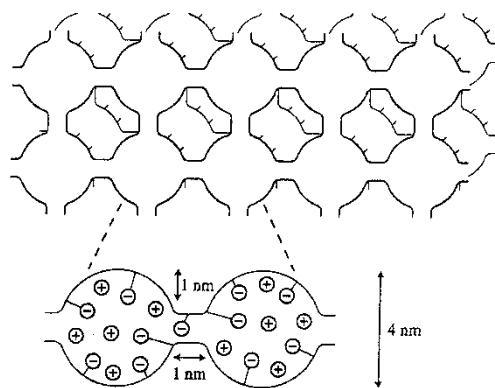
<sup>1</sup>From DOE Alkaline Membrane Fuel Cell Workshop, May 8-9 2011.

# PEM Materials

## The state of the art:

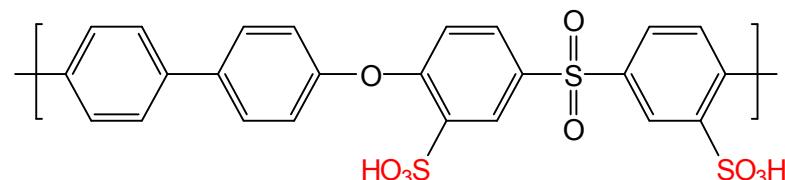


## Nafion

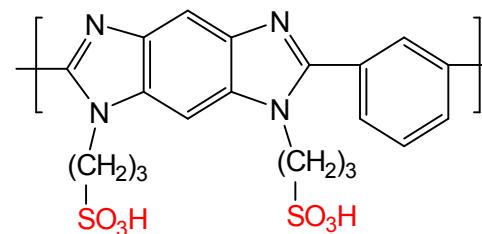


## Proposed pore structure in Nafion membranes<sup>1</sup>

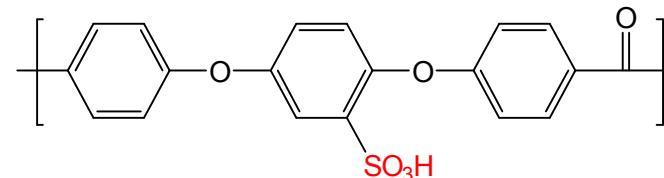
## Hydrocarbon membranes:



## Poly(ether sulfones)



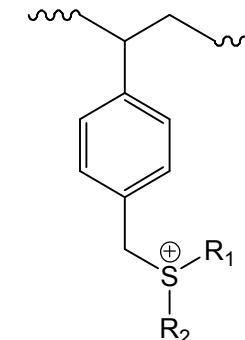
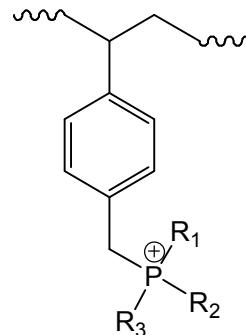
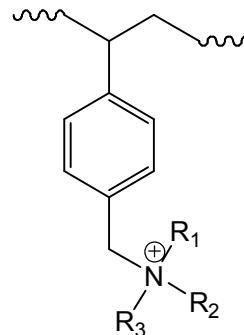
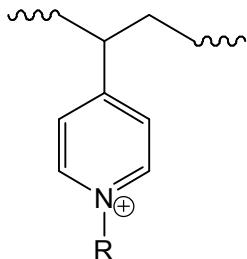
## Poly(benzimidazoles)



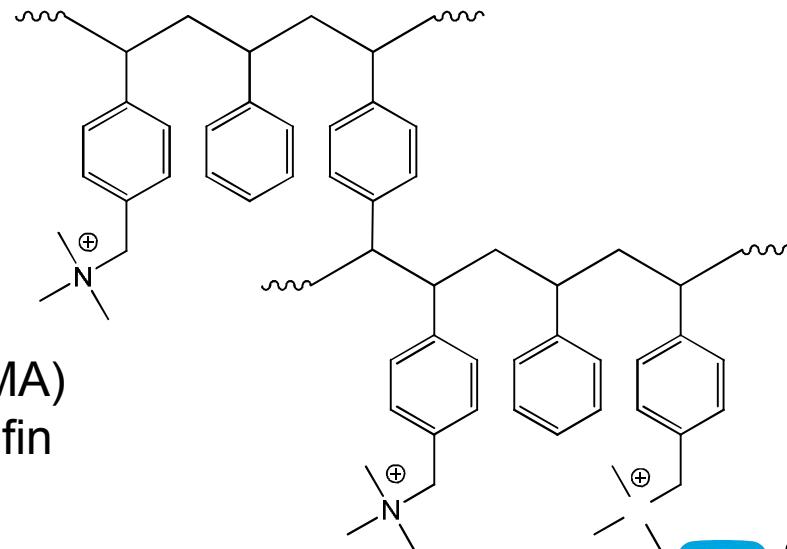
## Poly(ether ether ketone)

# Cations on Anion Exchange Membranes (AEMs)

Typical functional groups with fixed positive charges in AEMs:



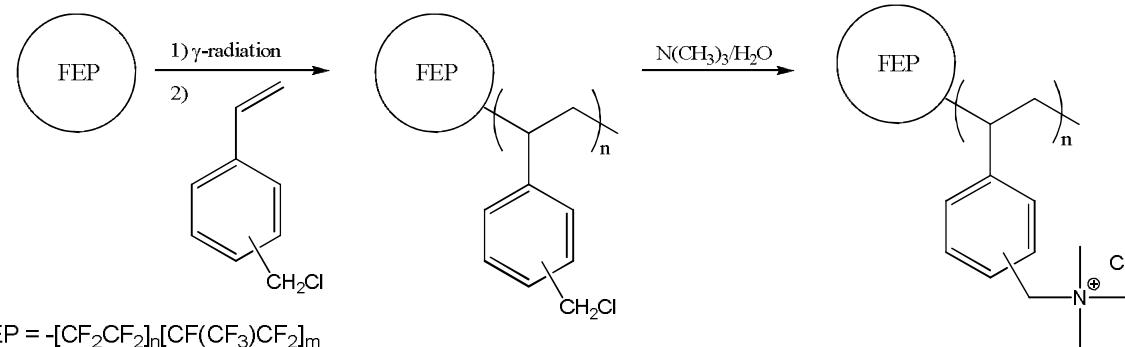
A Typical Commercially-available AEM:



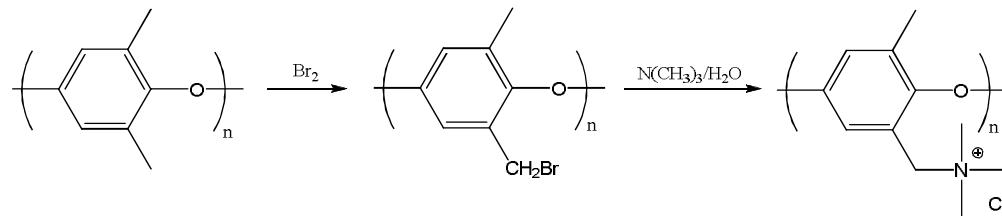
- Crosslinked polystyrene with benzyl trimethylammonium groups (BTMA)
- Typically blended with PVC or a polyolefin
- Cast on fabric support
- Used for electrodialysis

# AEMs: The State of the Art

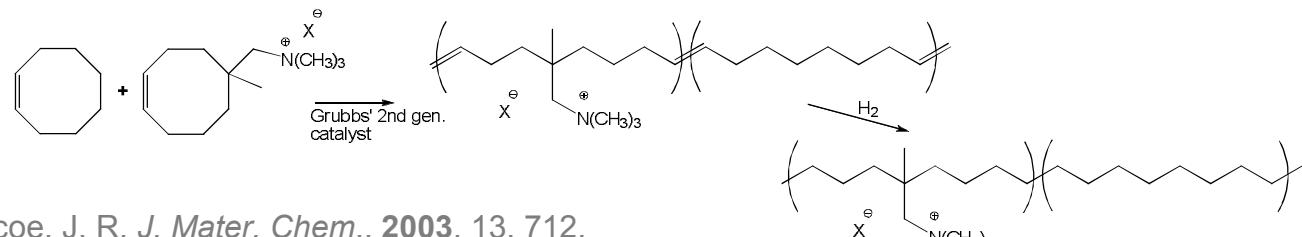
Radiation-grafting of functionalized poly(styrene) onto fluorinated polymers<sup>1</sup>:



Bromination of poly(2,6-dimethyl-1,4-phenylene oxide)<sup>2</sup>:



Poly(ethylene)-based AEM from ROMP<sup>3</sup>:



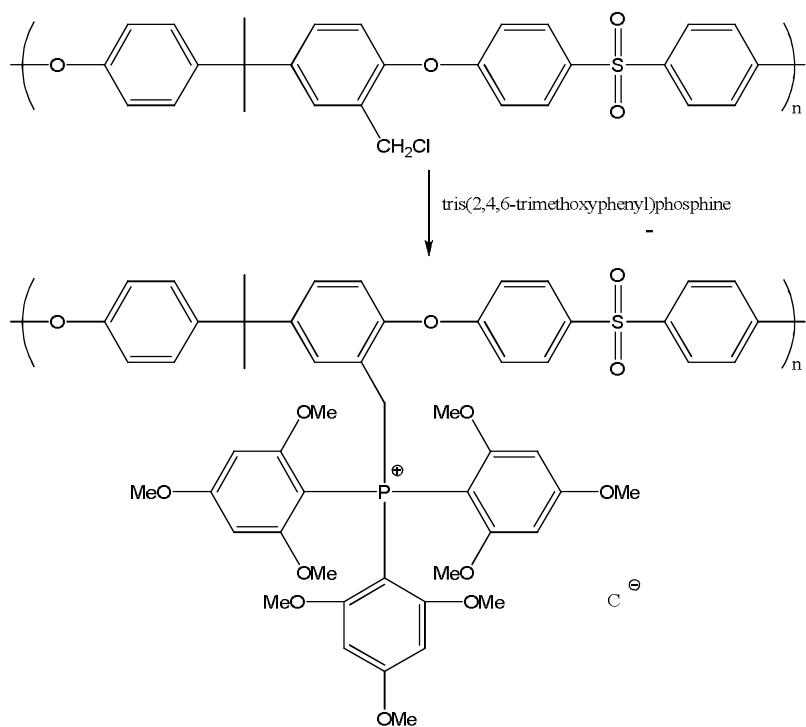
<sup>1</sup>Danks, T. N.; Slade, R. T. C.; Varcoe, J. R. *J. Mater. Chem.*, **2003**, 13, 712.

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

<sup>3</sup>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.

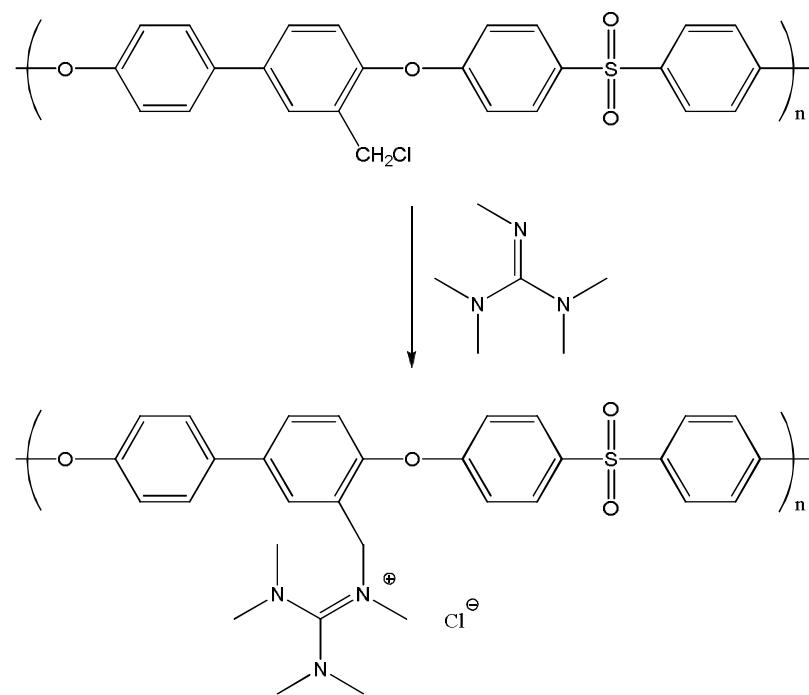
# Alternative Cationic Groups

## Poly(sulfone) with benzyltris(2,4,6-trimethoxyphenyl) phosphonium groups<sup>1</sup>



Stable in 1M KOH at 60 °C for 48h<sup>1</sup>

## Poly(sulfone) with benzylpentamethyl guanadinium groups<sup>2</sup>



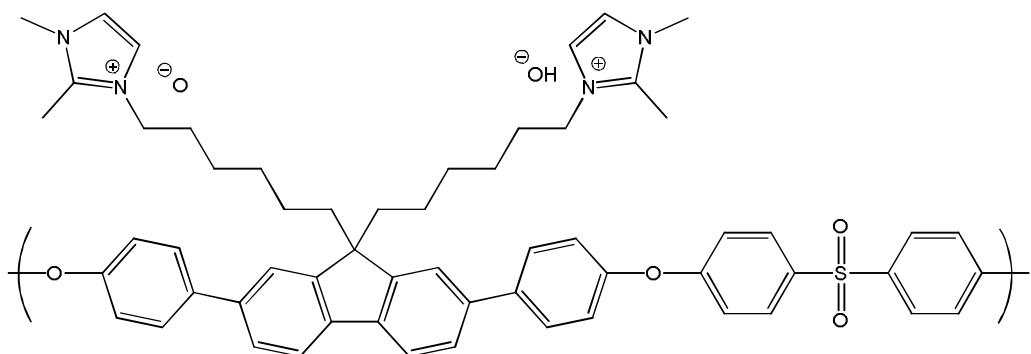
Stable in 1M KOH at 60 °C for 48h<sup>2</sup>

<sup>1</sup>Gu, S.; Cai, R.; Luo, T.; Chen, Z.; Sun, M.; Liu, Y.; He, G.; Yan, Y. *Angew. Chem.*, 2009, 121, 6621.

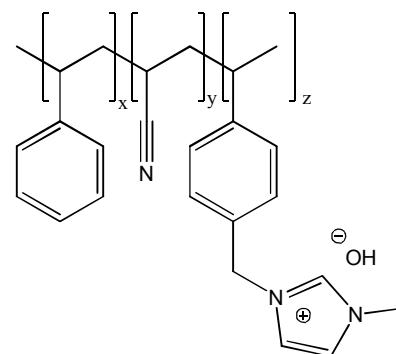
<sup>2</sup>Wang, J.; Li, S.; Zhang, S. *Macromol.* 2010, 43, 3890.

# Alternative Cationic Groups

Polyfluorene with pendant alkyl imidazolium groups<sup>1</sup>



Poly(styrene)-co-(acrylonitrile) with benzyl imidazolium groups<sup>2</sup>



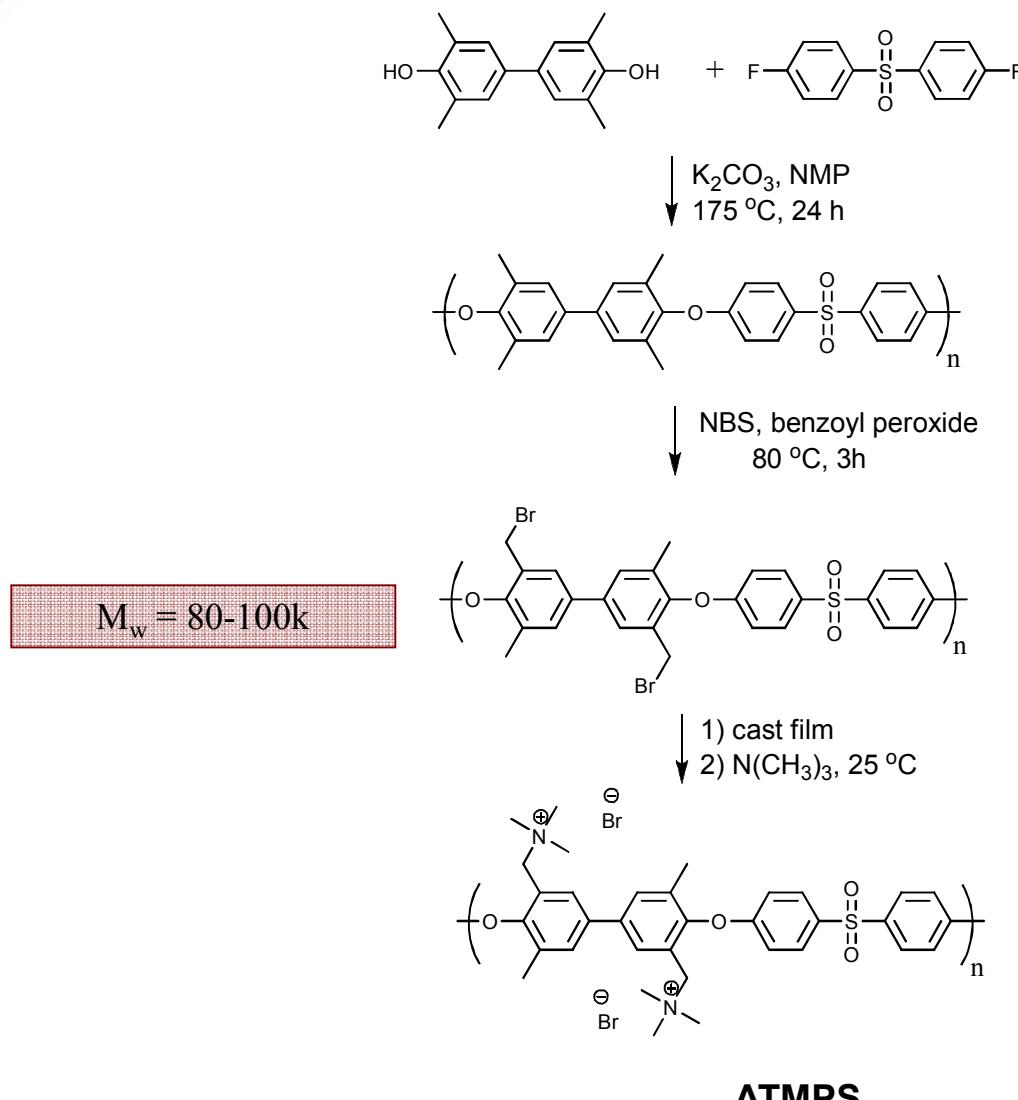
Stable in 1M KOH at 60 °C for 400h<sup>1</sup>

Stable in 1M KOH at 60 °C for 1000h<sup>2</sup>  
(BTMA version was not stable)

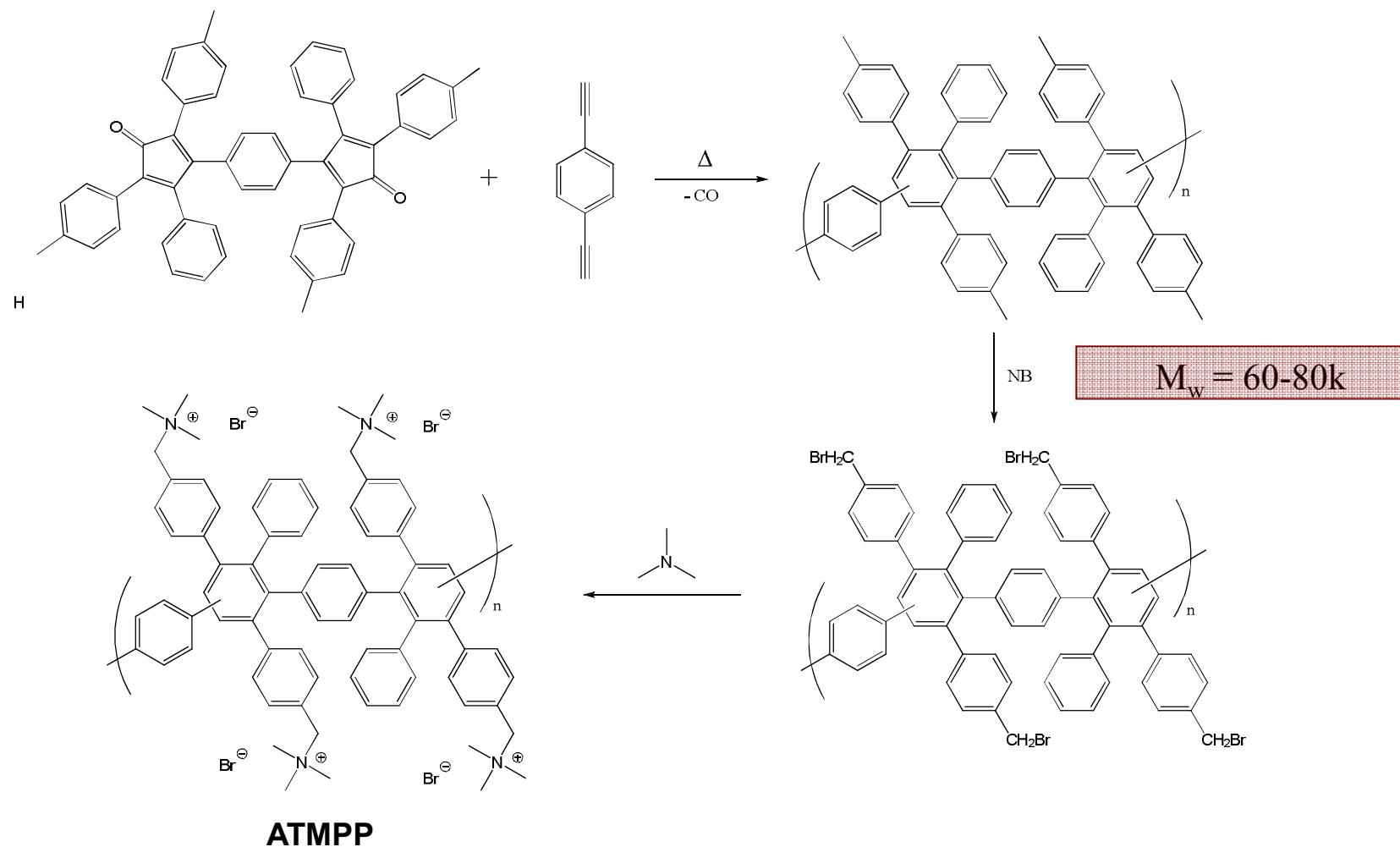
<sup>1</sup>Lin, B.; Qiu, L.; Qiu, B.; Peng, Y.; Yan, F. *Macromol.*, 2011, 44, 9642.

<sup>2</sup>Qiu, B.; Lin, B.; Qui, L.; Yan, F. *J. Mat. Chem.* 2012, 22, 1040.

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

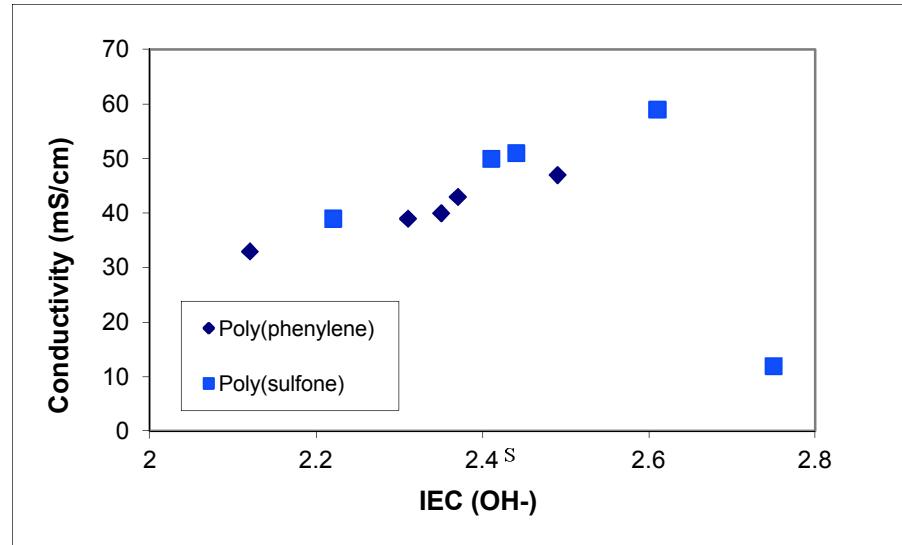
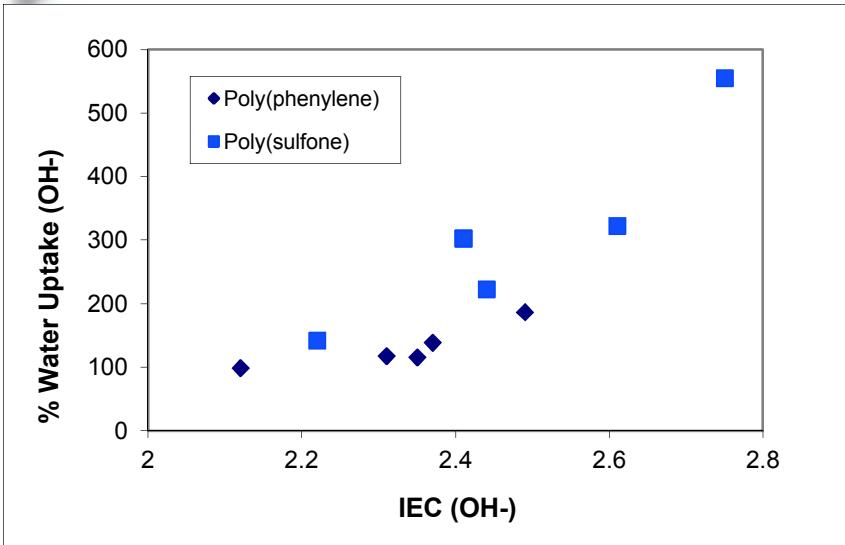


# AEMs made at Sandia: Poly(phenylene)-Based Membranes

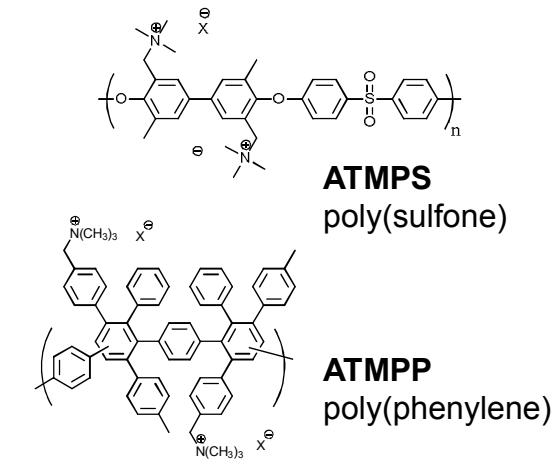


Hibbs, M. R.; Fujimoto, C. H.; Cornelius, C. J. *Macromol.* **2009**, *42*, 8316.

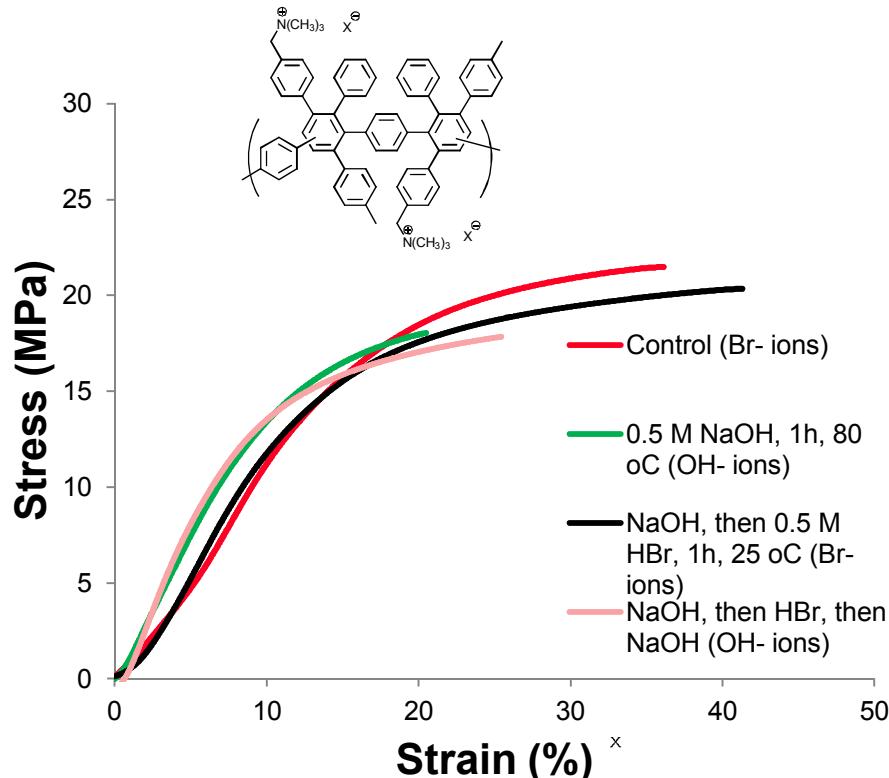
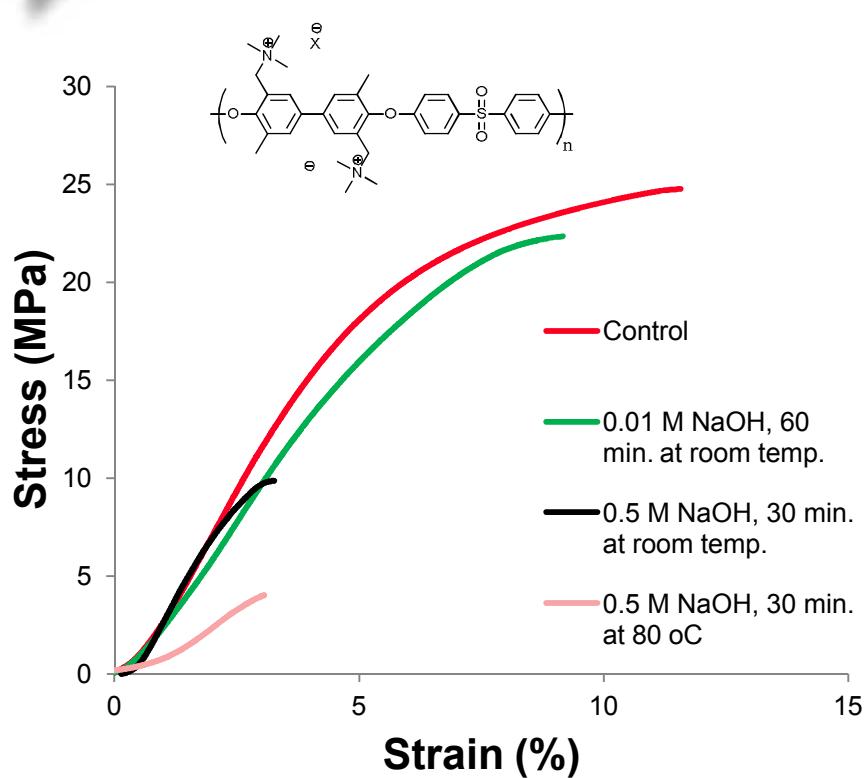
# ATMPS & ATMPP Properties



- ATMPS has larger water uptake than ATMPP at similar IECs.
- Both polymers have similar conductivity vs. IEC trends.
- At IEC > 2.6, ATMPS swells so much that the conductivity begins to decrease.
- ATMPP with IEC between 2.2 and 2.4 has been the most useful composition for fuel cell testing, as both membrane and ionomer in electrodes.

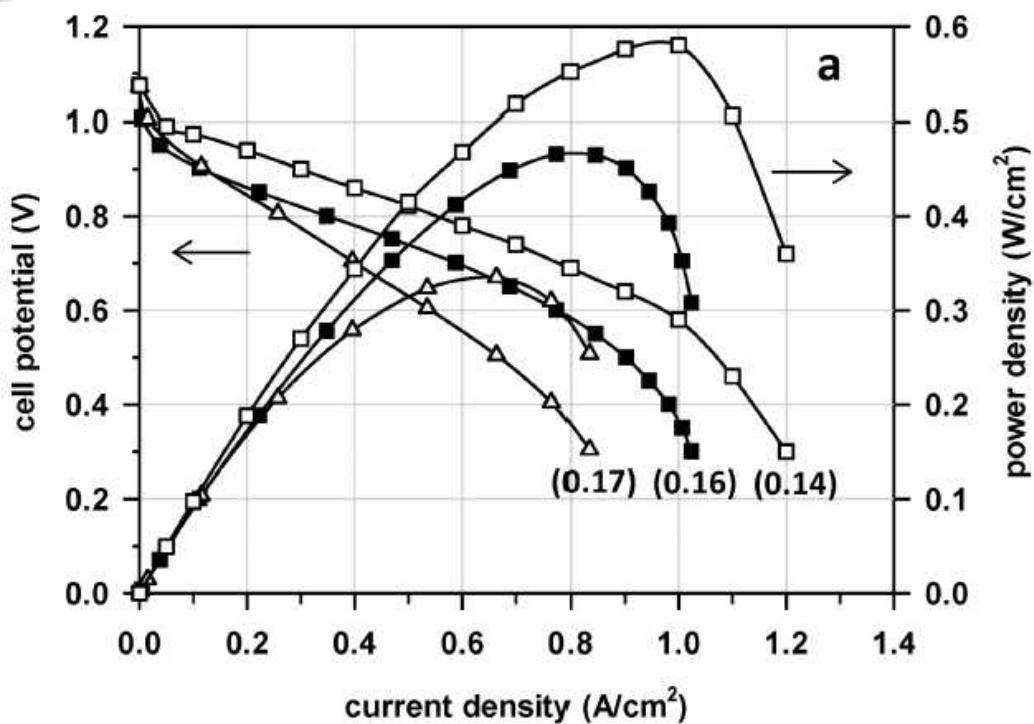


# Mechanical Stability



- Test conditions: 50 °C, 50% RH.
- Poly(arylene ether sulfone) shows significant degradation. It was too brittle to test after conversion back to Br<sup>-</sup> form.
- Poly(phenylene) is weaker in OH<sup>-</sup> form, but there is no sign of backbone degradation.

# H<sub>2</sub>/O<sub>2</sub> Performance of Alkaline Membrane Fuel Cells

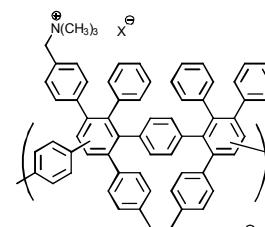


- H<sub>2</sub>/O<sub>2</sub> ATMPP membrane + Nafion-FA-TMG ionomer
- H<sub>2</sub>/air ATMPP membrane + Nafion-FA-TMG ionomer
- △ H<sub>2</sub>/O<sub>2</sub> ATMPP membrane + ATMPP ionomer

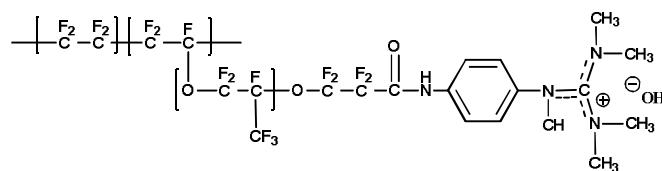
Catalyst: Pt black (3.4 mg/cm<sup>2</sup>) on anode, (6.5 mg/cm<sup>2</sup>) on cathode.  
 Cell temp. 80°C. Catalyst: ionomer weight composition (9:1, not optimized); MEAs were prepared from direct painting.

Kim, D. S.; Fujimoto, C. H.; Hibbs, M. R.; Labouriau, A.; Choe, Y.-K.; Kim, Y. S.  
*Macromol.*, 2013, 46, 7826-7833.

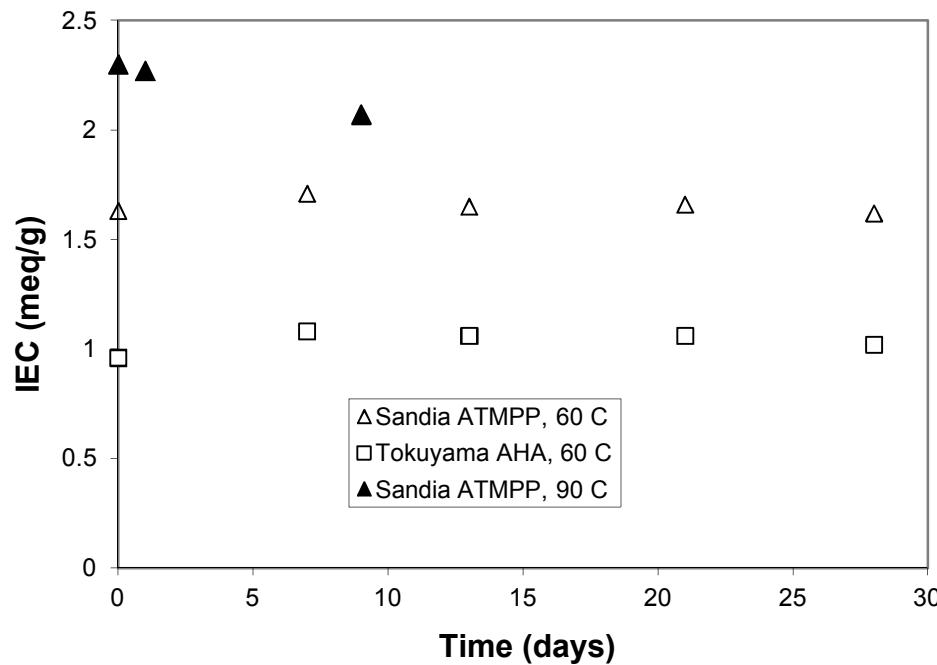
ATMPP  
 Membrane/ionomer  
 IEC = 1.8 meq./g  
 $\sigma$  = 120 mS/cm  
 Thickness: 50  $\mu$ m



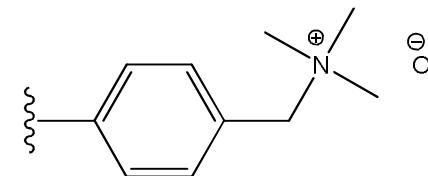
Nafion-FA-TMG  
 Ionomer (IEC = 0.74 meq./g,  $\sigma$  = 20 mS/cm)



# Cation Stability



Both membranes have benzyl trimethylammonium cations:

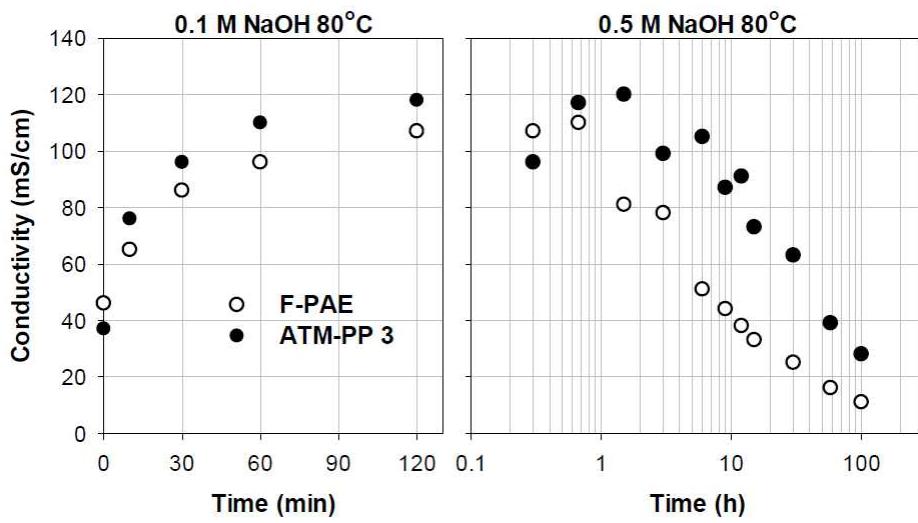


- Test conditions: 4M NaOH (aqueous), no stirring.
- AHA is “base stable” electrodialysis membrane – crosslinked polystyrene.
- A poly(sulfone) AEM (ATMPS) became too brittle to handle after 1-2 days.
- After 9 days at 90 °C, IEC of ATMPP decreased by 10%.
- Model studies indicate decreasing stability as hydration decreases.<sup>1</sup>

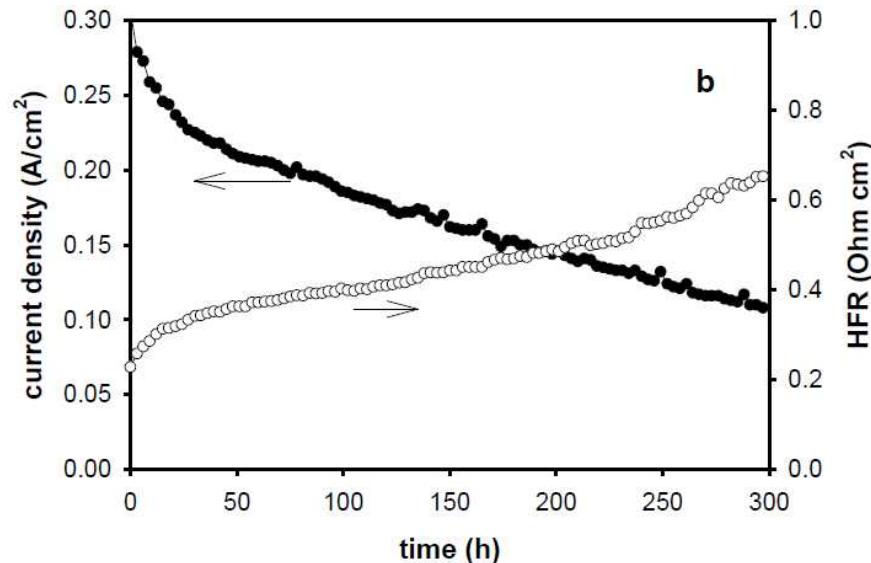
<sup>1</sup>Chempath, S.; Einsla, B. R.; Pratt, L. R.; Macomber, C. S.; Boncella, J. M.; Rau, J. A.; Pivovar, B. S. *J. Phys. Chem. C Lett.* 2008, 112, 3179.

# Cation Stability

Treatment in aqueous NaOH



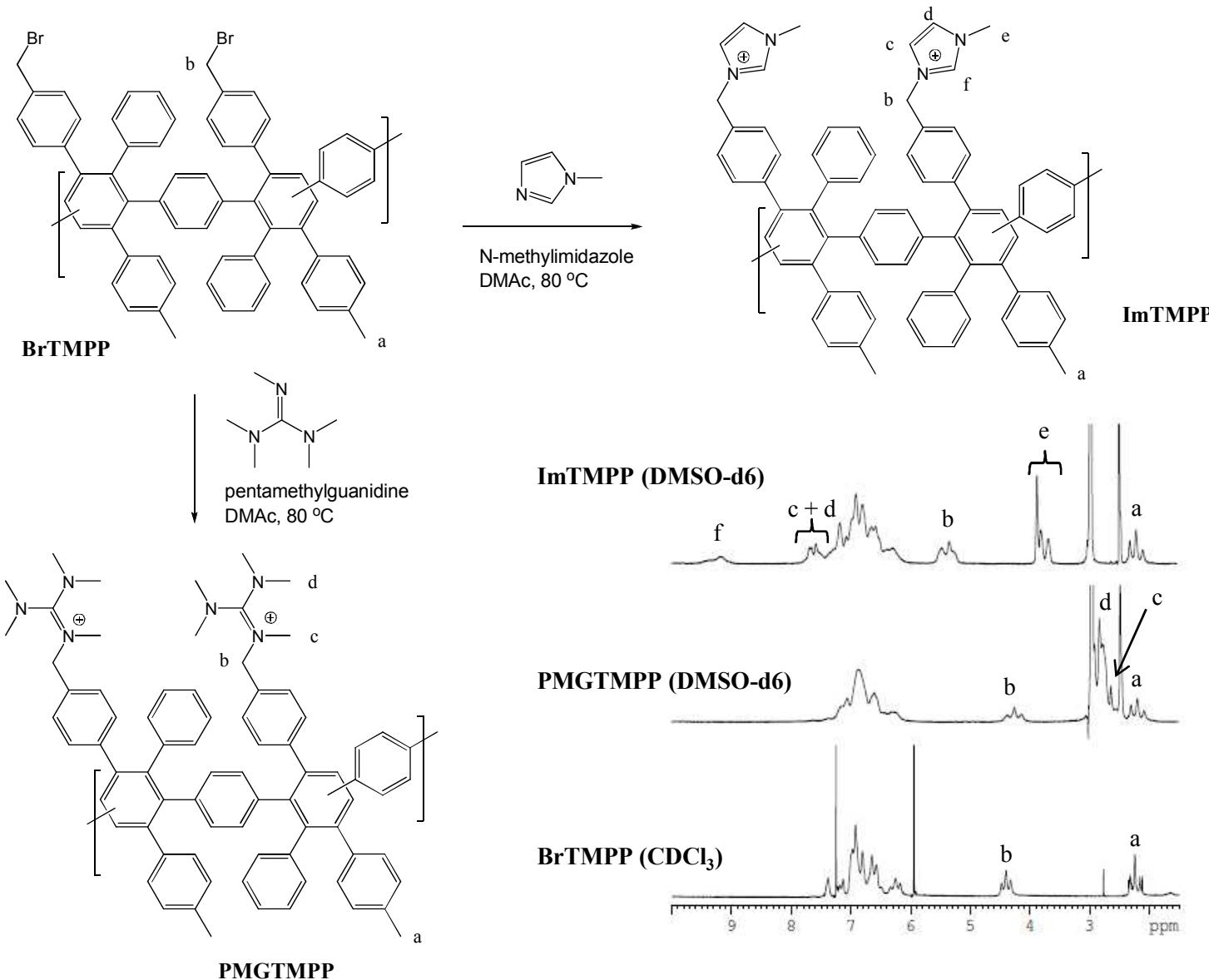
Durability in H<sub>2</sub>/O<sub>2</sub> fuel cell



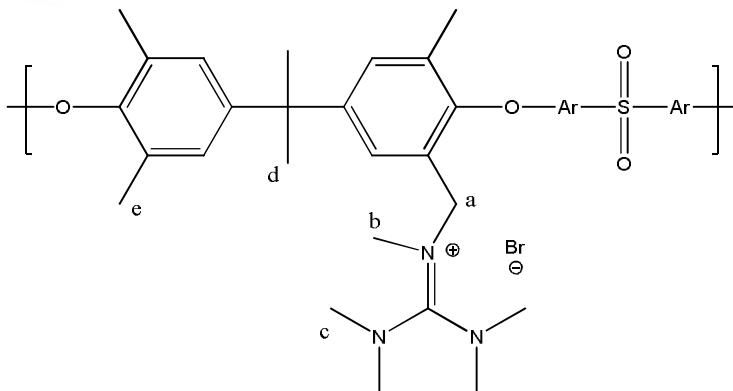
- In NaOH test, conductivity initially increases due to ion exchange and water uptake.
- Decline in conductivity over 100 h is due to degradation of BTMA cation.
- Fuel cell testing was done at 60 °C, 0.3 V, with Pt/C catalyst on both electrodes.
- Decline in current density is also presumably due to BTMA degradation.

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

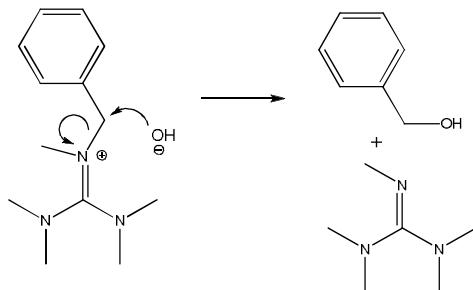
# Resonance-Stabilized Cations



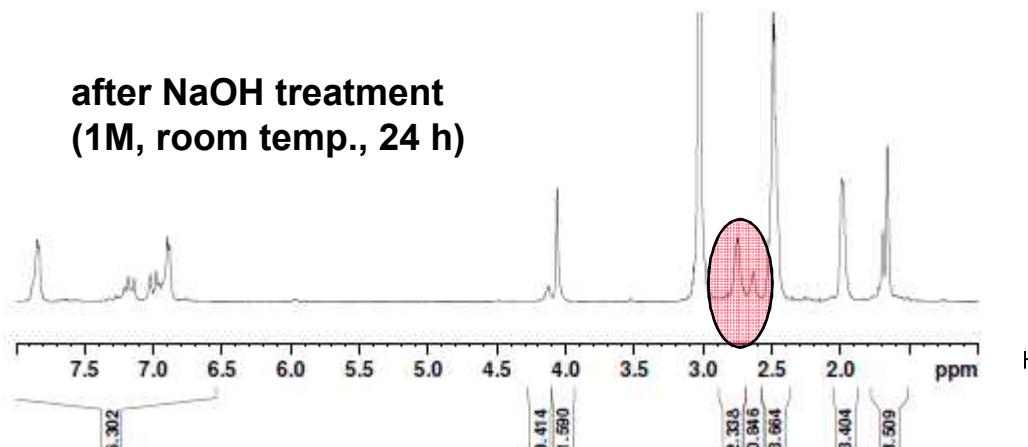
# Decomposition of Benzyl PMG Cations



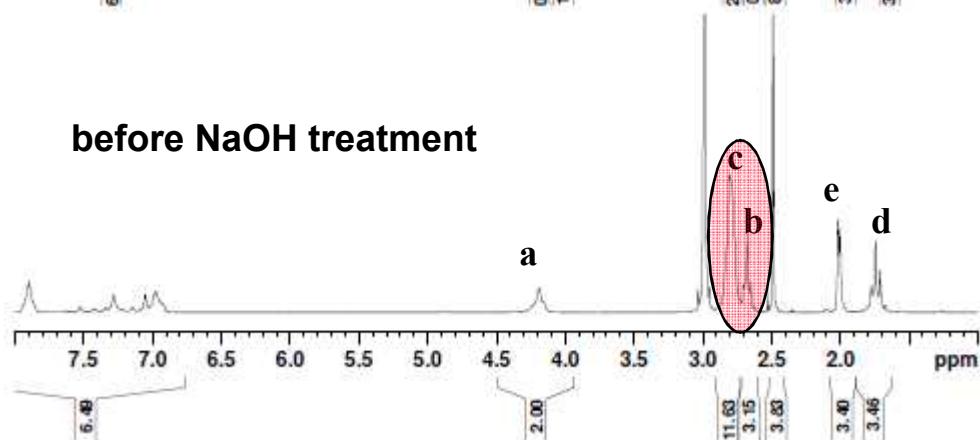
- The relative areas of b and c peaks decrease drastically after NaOH. But b:c area ratio does not change.
- The probable mechanism is nucleophilic attack by hydroxide ion at the benzylic carbon:



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



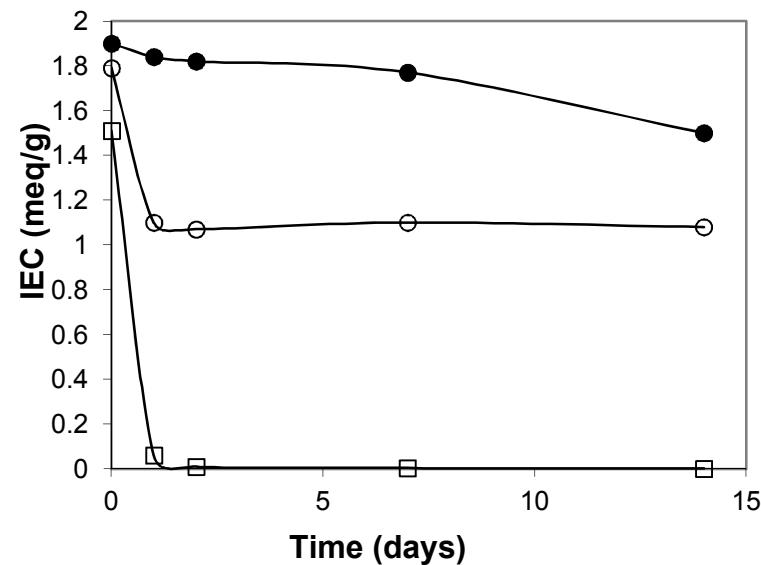
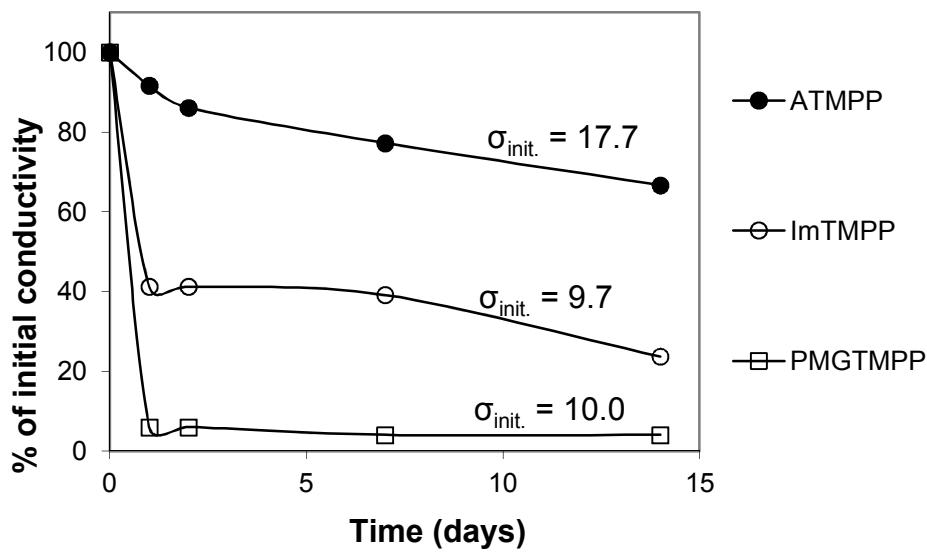
before NaOH treatment



# KOH Stability Test

## Resonance-Stabilized Cations

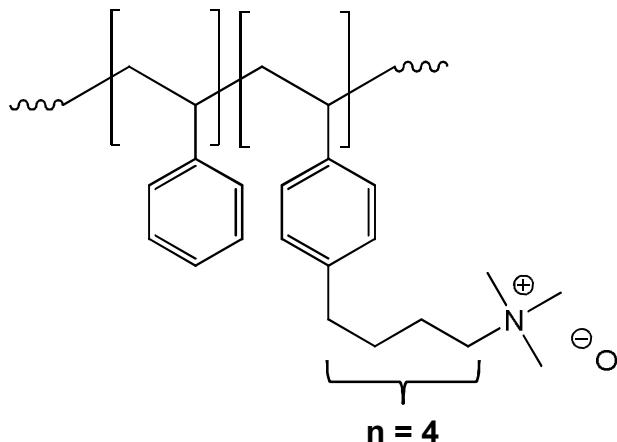
Test conditions: Membranes immersed in 4M KOH at 90 °C.



- Conductivities were measured with membranes in Cl<sup>-</sup> 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.

# Stability of Alkyl Trimethylammonium Groups

Alkylene spacers can increase stability<sup>1</sup>



Tested for 30 days in 100 °C water ( $\text{OH}^-$  form):

IEC (after/before)

Benzyltrimethylammonium ( $n = 1$ ) 79 %

Tetramethylene spacer ( $n = 4$ ) 92 %

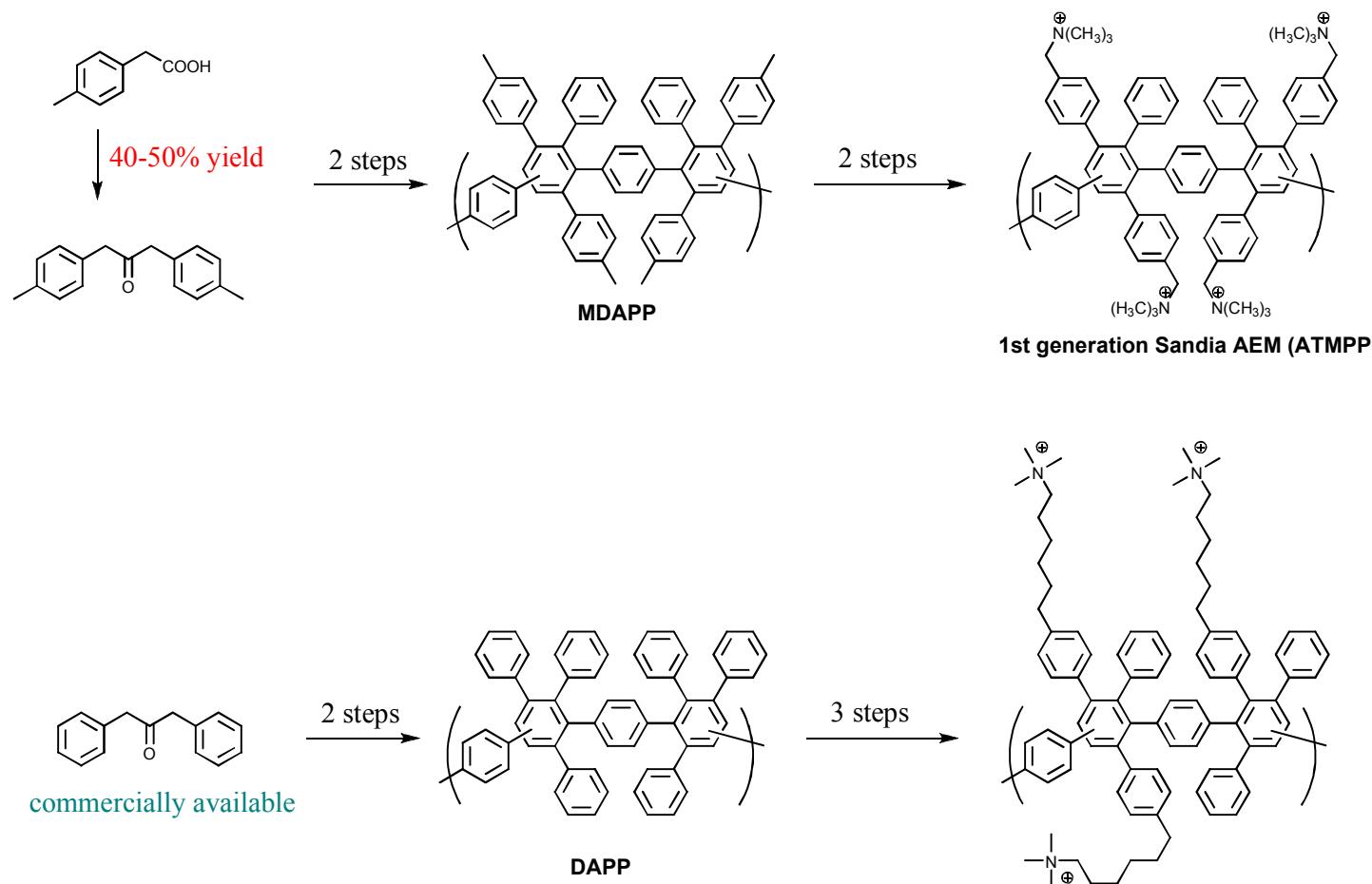
A recent computational study<sup>2</sup> by Pivovar at NREL concluded that  $n$ -alkyltrimethylammonium groups are more stable than BTMA when  $n > 3$ .

- Steric shielding of the  $\beta$ -hydrogens when  $n > 3$
- Increased susceptibility to  $\text{S}_{\text{N}}2$  attack at the methylene carbon in BTMA ( $n = 1$ ).

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

<sup>2</sup> Long, H.; Kim, K.; Pivovar, B. *S. J. Phys. Chem. C* 2012, 116, 9419.

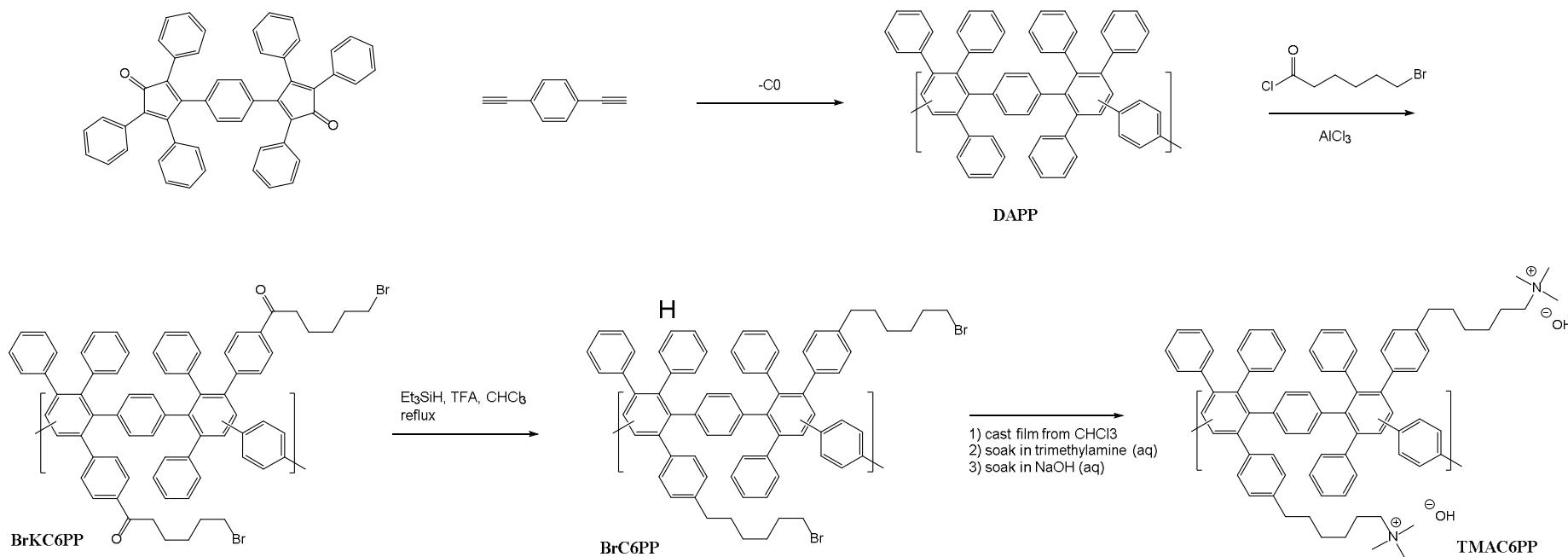
# Poly(phenylene) AEM with Sidechains



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

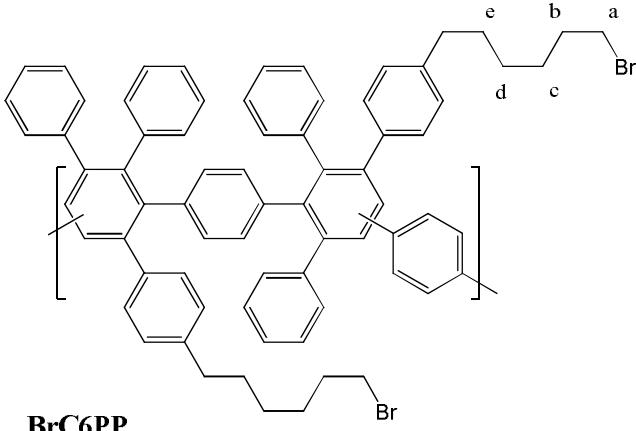
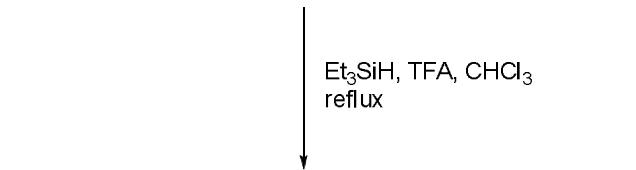
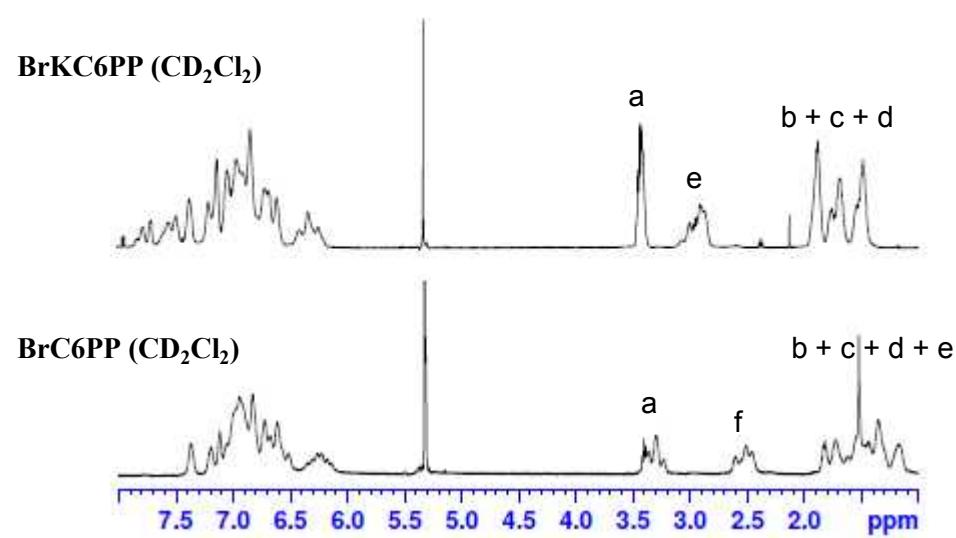
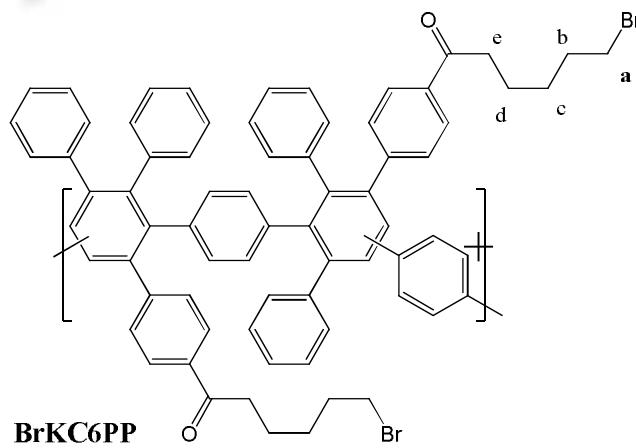
2nd generation Sandia AEM (TMAC6PP)

# Poly(phenylene) AEM with Sidechains

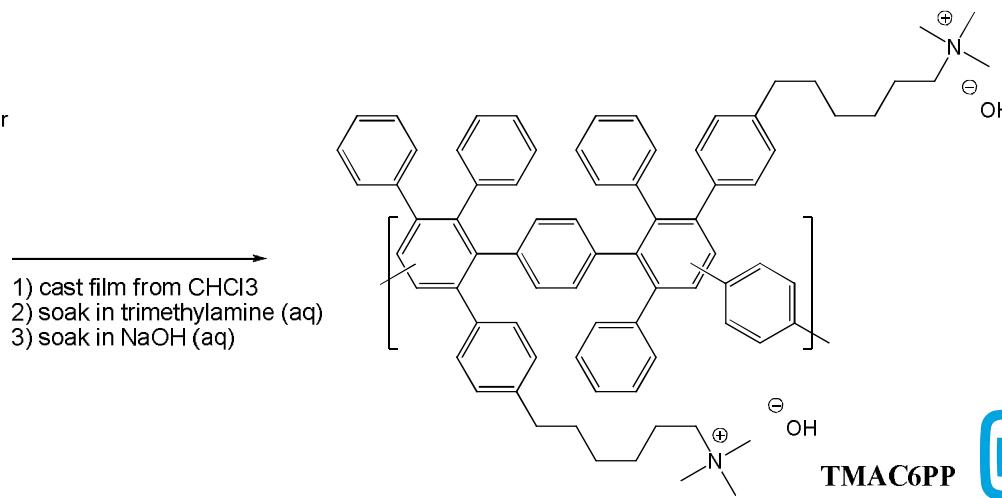


Hibbs, M. R. *J. Polym. Sci. B., Polym. Phys.* 2012, 000, 000–000

# Poly(phenylene) with Alkyl Side Chains without Ketone



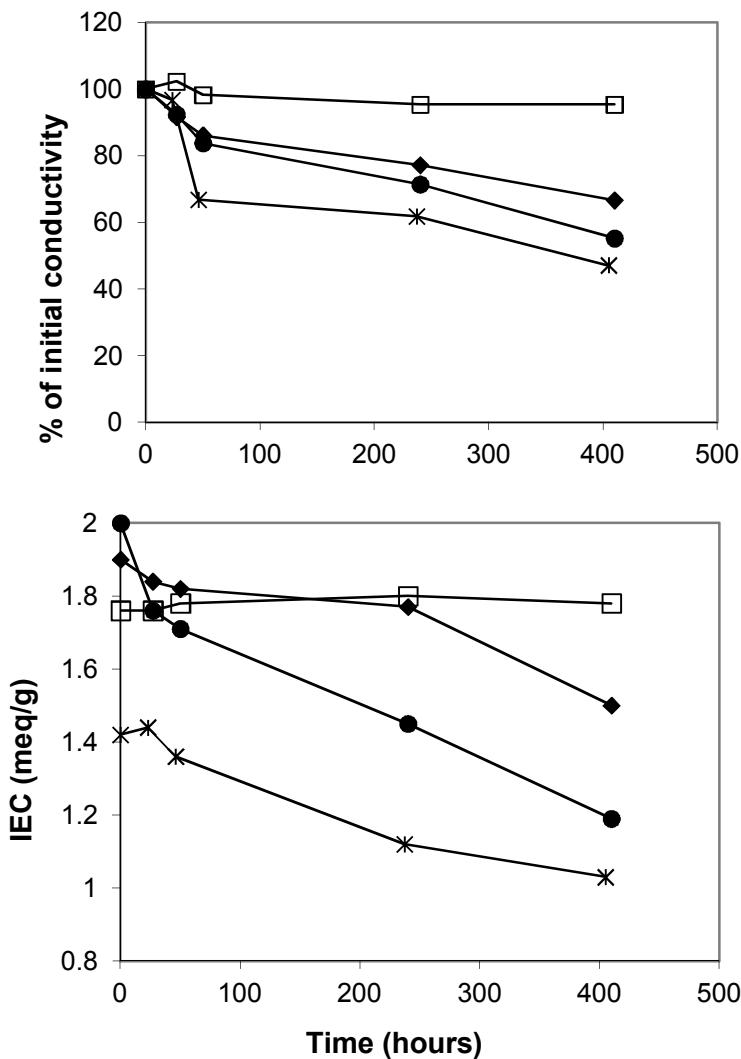
1) cast film from  $\text{CHCl}_3$   
2) soak in trimethylamine (aq)  
3) soak in  $\text{NaOH}$  (aq)



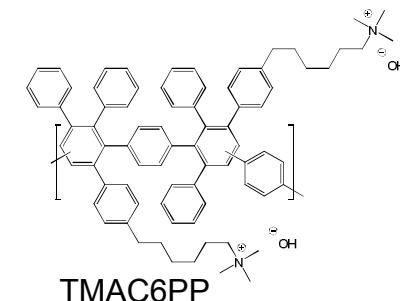
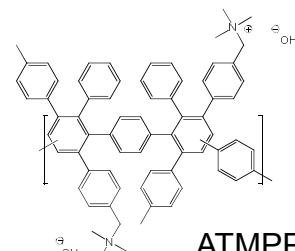
TMAC6PP

# TMAC6PP Attributes (1)

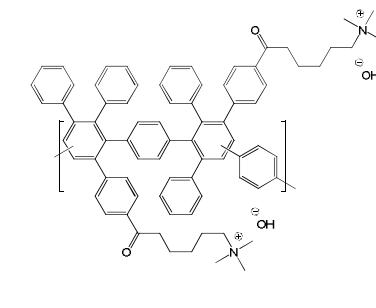
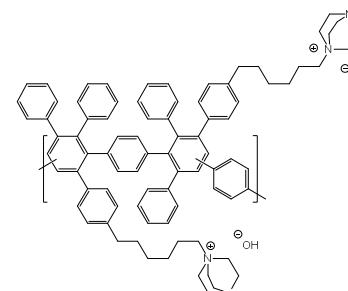
**Test conditions: Membranes immersed in 4M KOH at 90 °C.**



◆ ATMPP  
□ TMAC6PP  
● DABC6PP  
\* TMAKC6PP



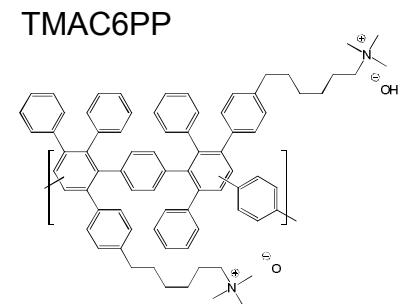
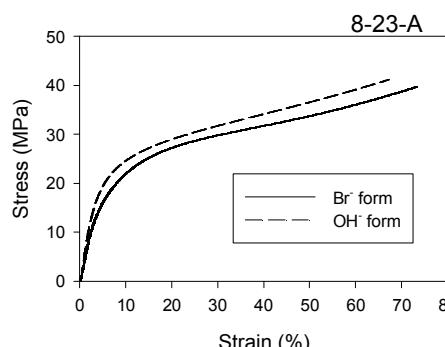
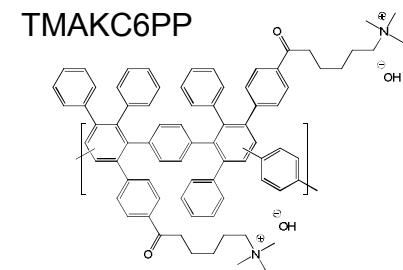
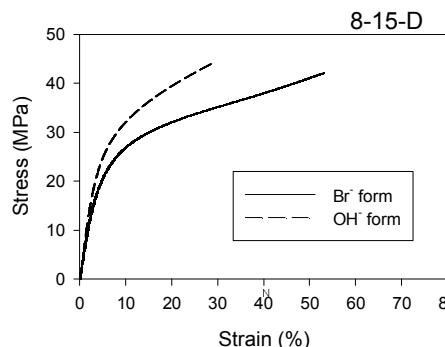
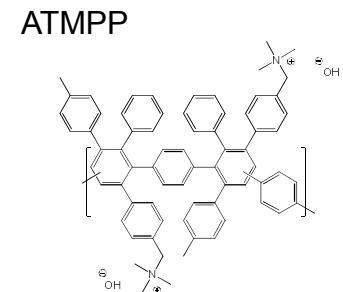
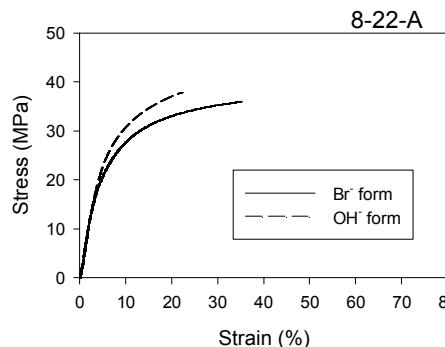
◆ ATMPP  
□ TMAC6PP  
● DABC6PP  
\* TMAKC6PP



- 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.

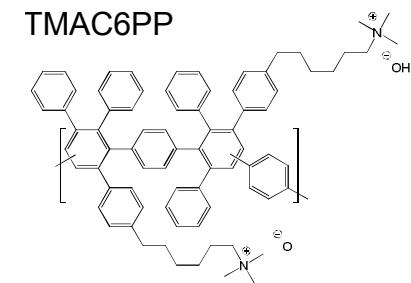
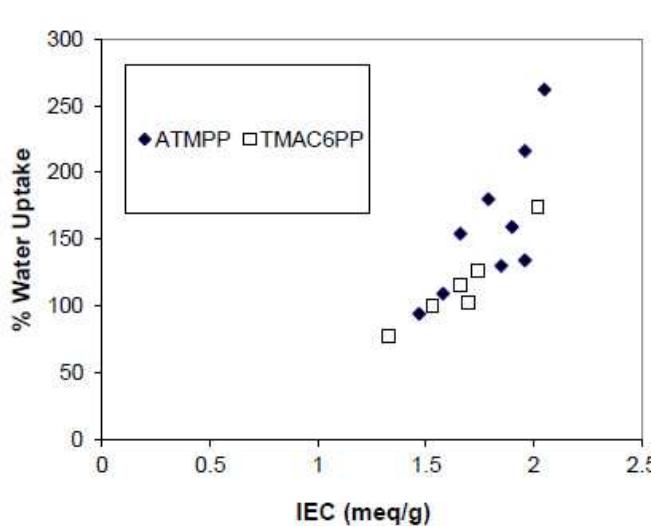
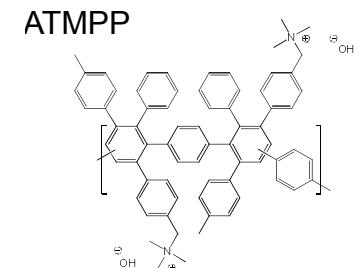
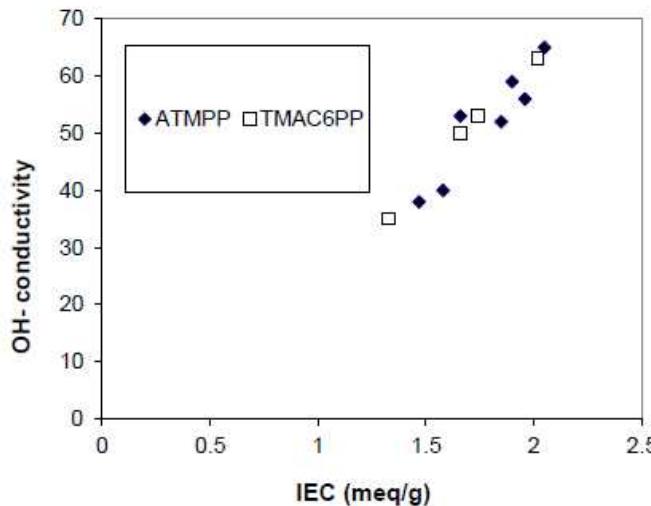
# TMAC6PP Attributes (2)

- 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.

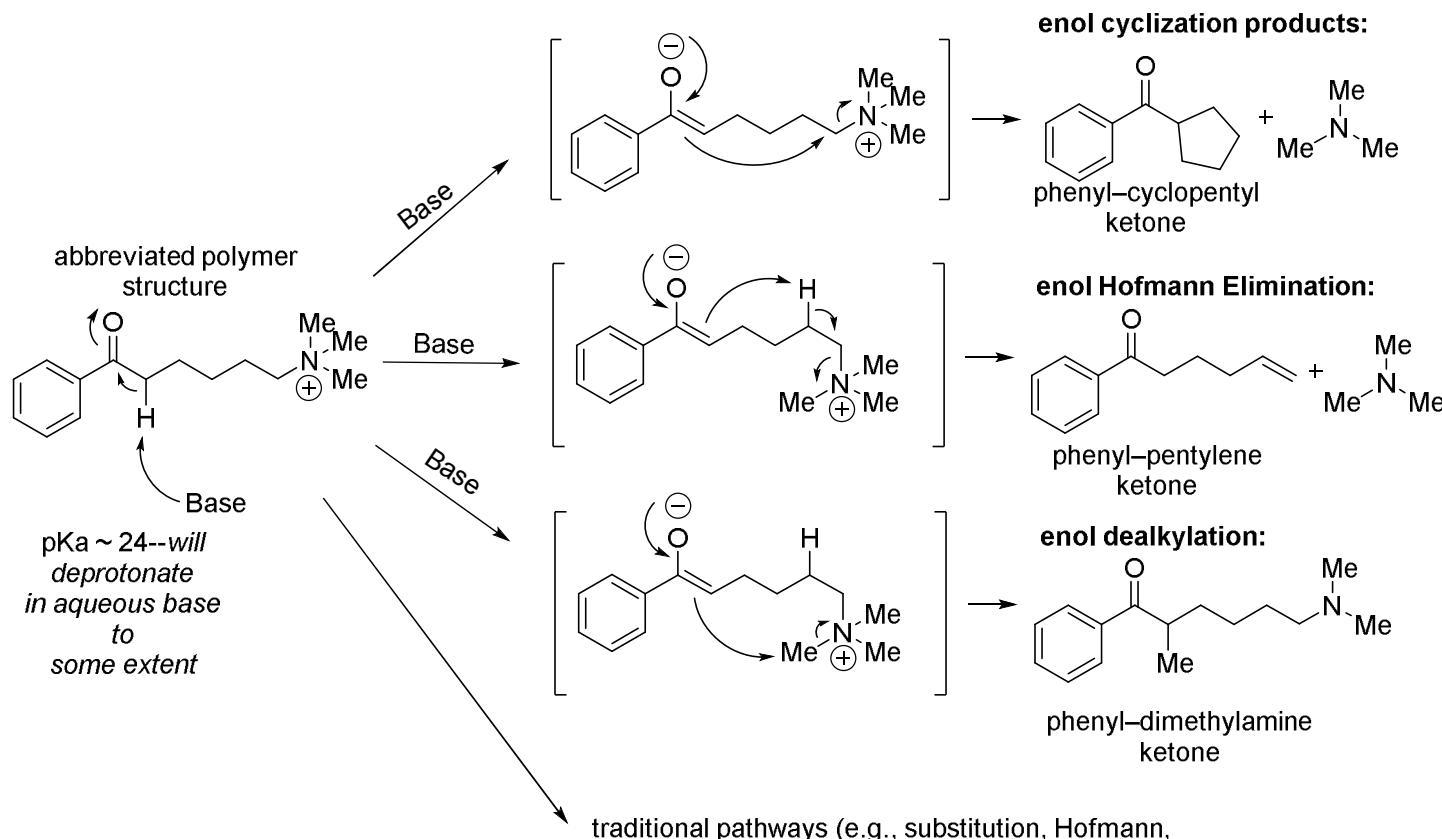


# TMAC6PP Attributes (3)

- 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.



# Instability Due to Ketone

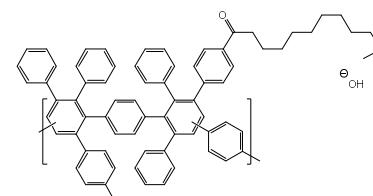
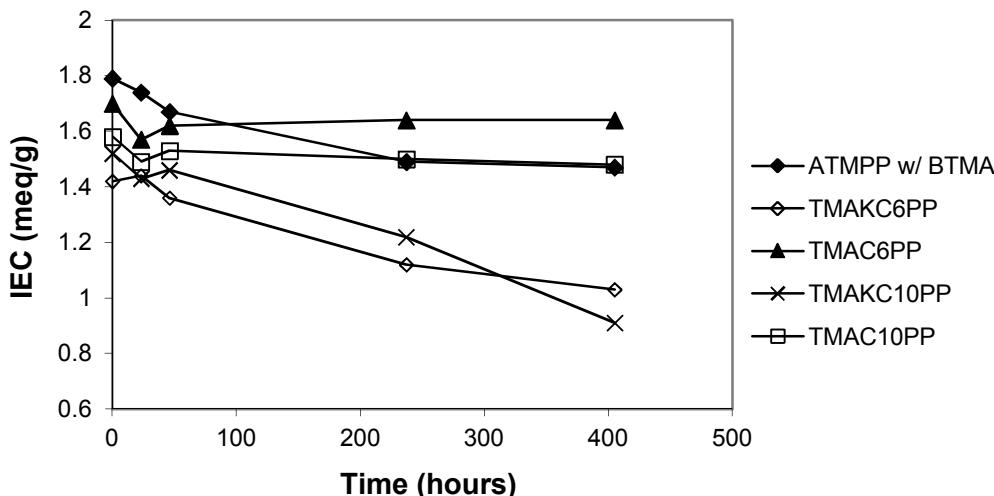
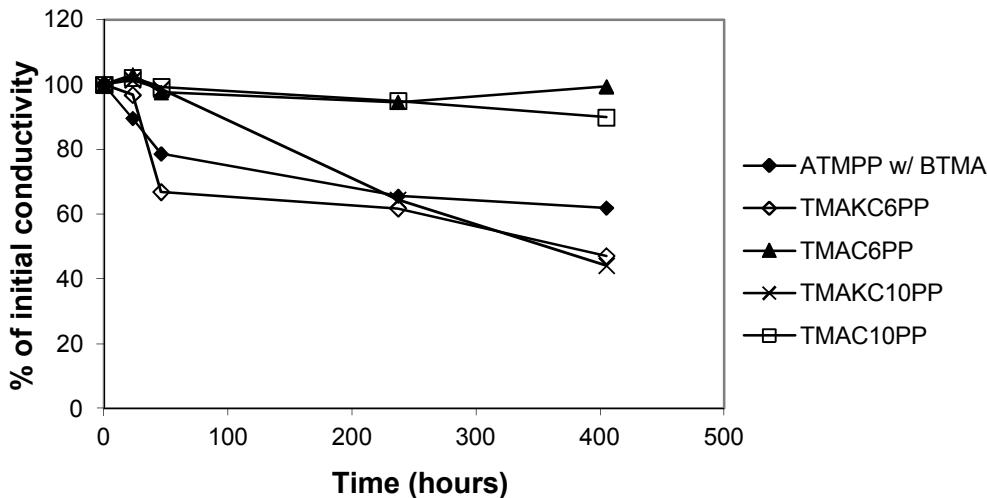


- Formation of enolate might begin pathway to cation degradation.
- Mechanisms that involve a 5- or 6-membered ring as an intermediate would be particularly likely.
- A longer sidechain would eliminate 5- and 6-membered ring intermediates.

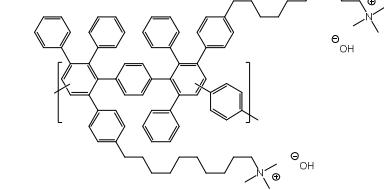
Schemes drawn by Sean Nunez (PSU)

# Stability of 10-Carbon Sidechain

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



TMAKC10PP

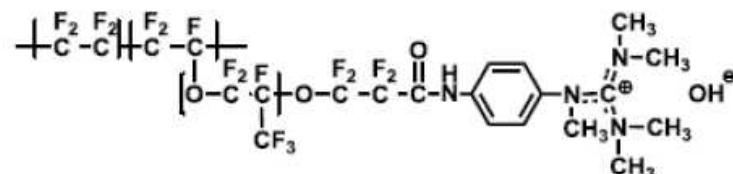
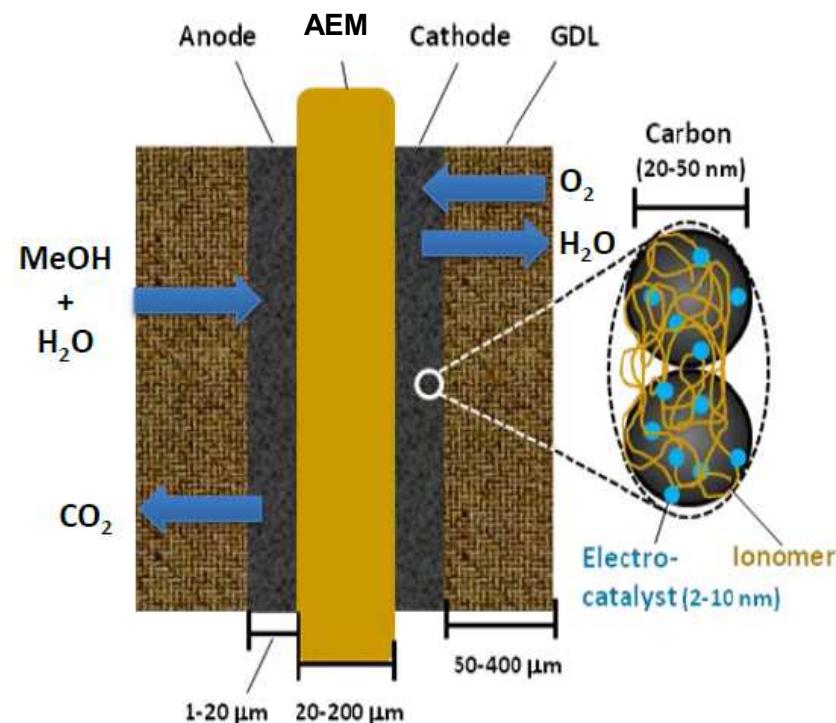


TMAC10PP

- 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. (dealkylation)

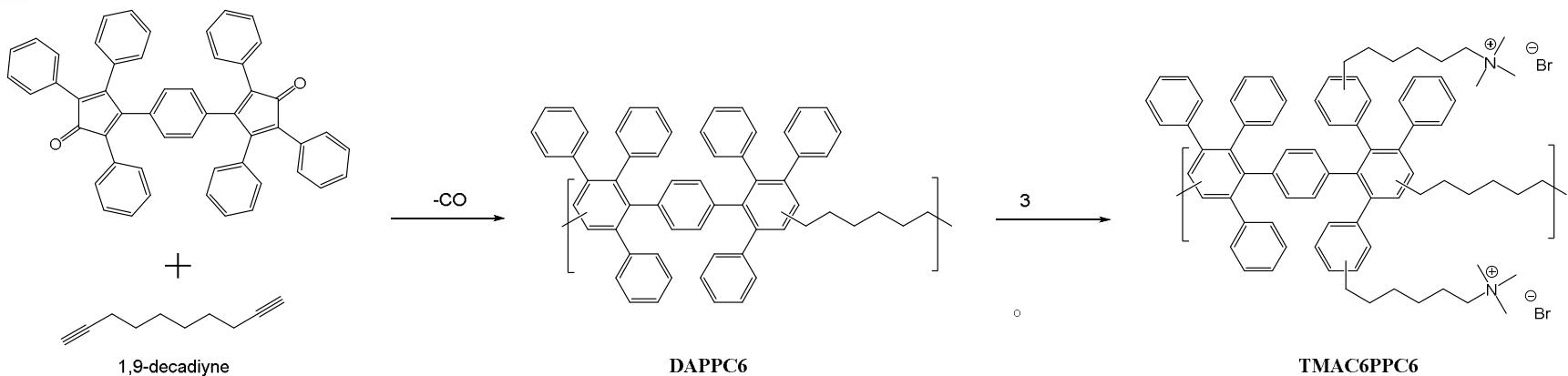
# Ionomers for Alkaline Fuel Cells

- Within the catalyst layer, we want to maximize transport of fuel, ions, and electrons (3-phase boundary).
- Usually the ionomer is the same as the membrane, although this isn't ideal.
- Yu Seung Kim at LANL developed an ionomer to pair with Sandia's ATMPP membranes to maximize power output (power density  $\sim 580$  mW/cm $^2$ , H $_2$ /O $_2$ ).
- The LANL ionomer is a perfluorinated backbone (from Nafion precursor) with pendant guanidinium groups.
- We want to develop a hydrocarbon-based ionomer to pair with TMAC6PP membranes.



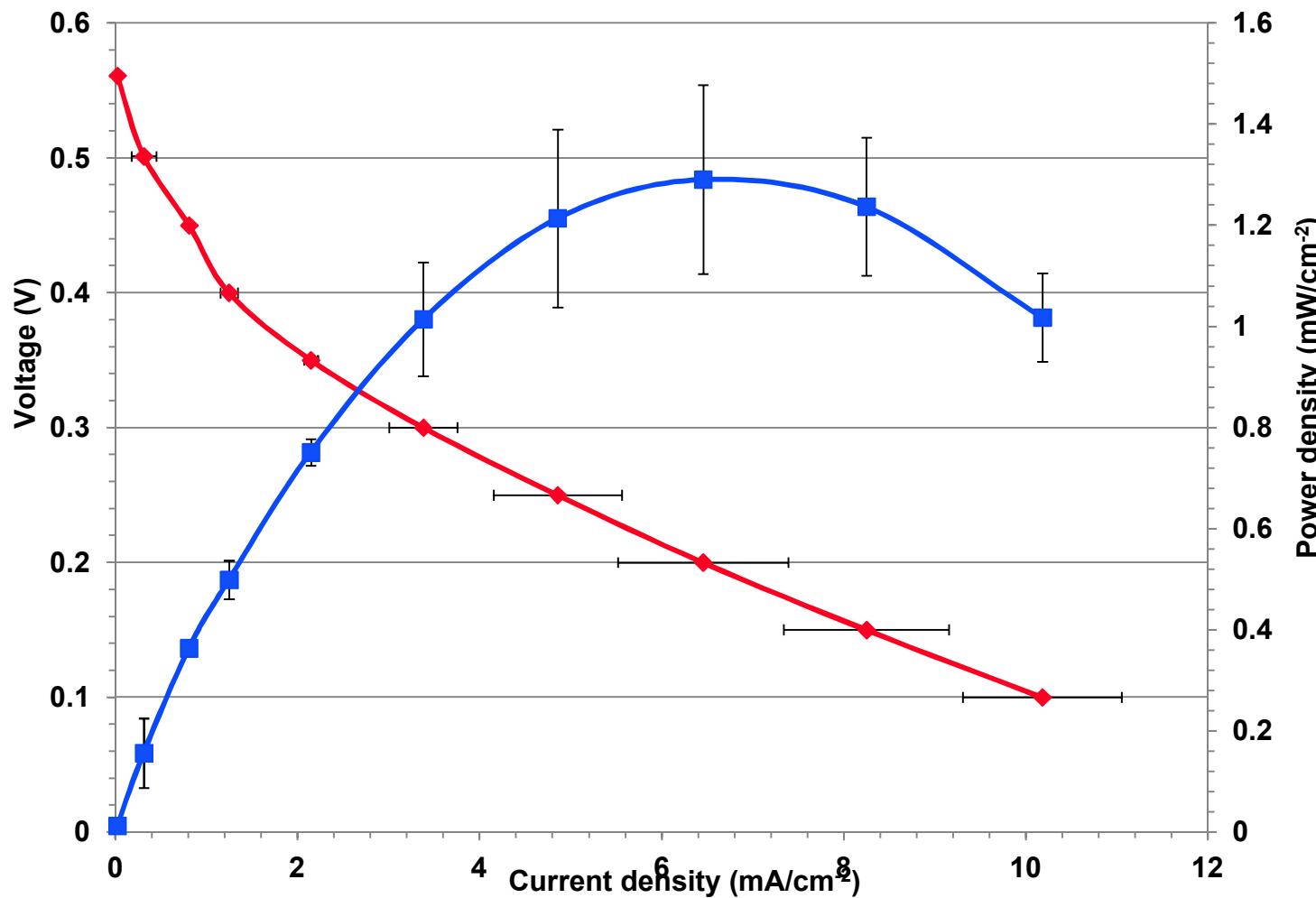
## LANL Ionomer

# New Ionomer for TMAC6PP



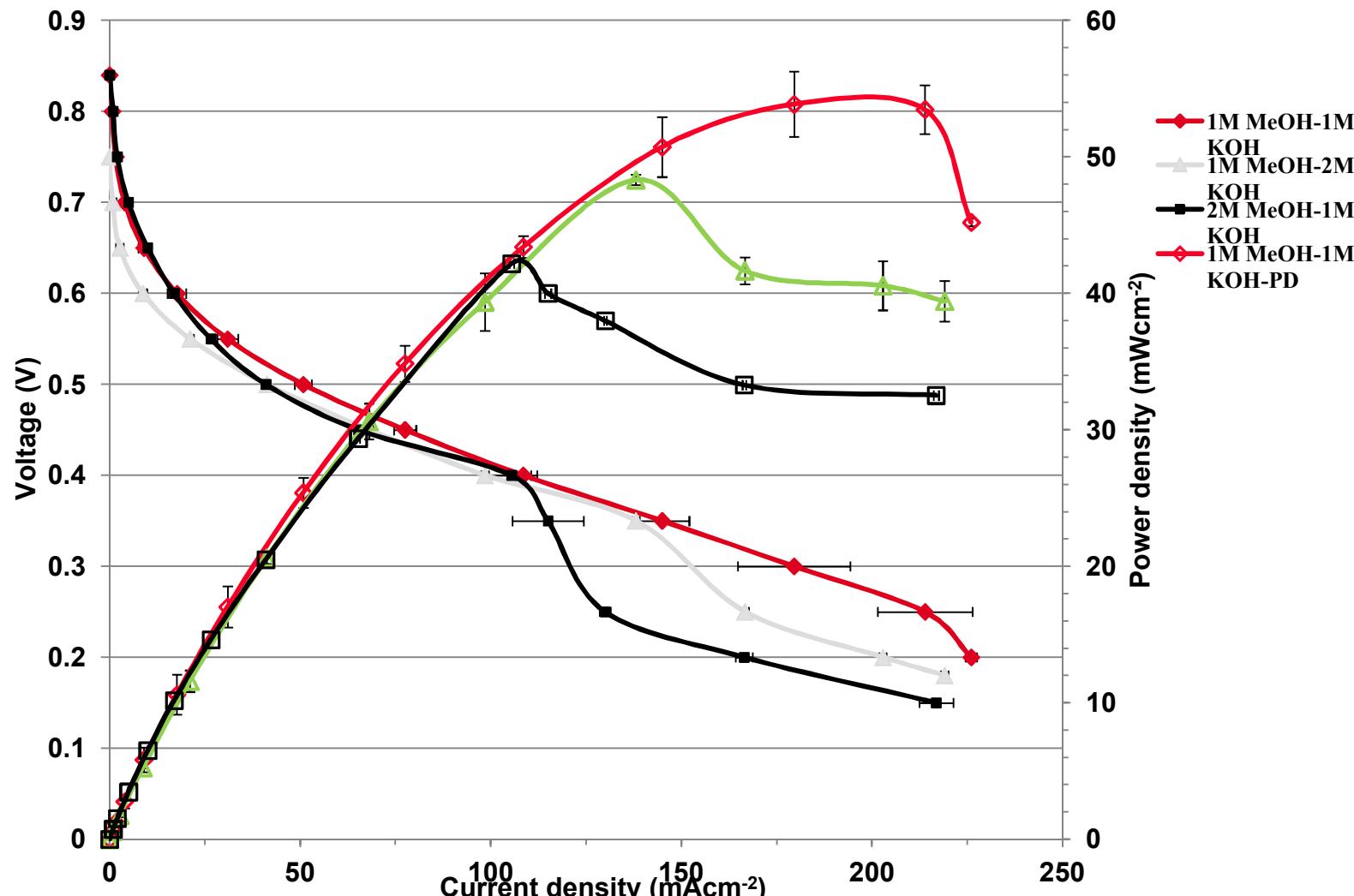
- Our new ionomer, TMAC6PPC6, is designed to be compatible with TMAC6PP while allowing for better transport properties.
- Flexibility of poly(phenylene alkylene) backbone is intended to improve permeability without sacrificing durability. (no permeability measurements yet)
- Dry DAPP  $T_g > 350$  °C  
Dry DAPPC6  $T_g \sim 200$  °C
- In hydrophilic ionomer form, water acts as a plasticizer to further reduce  $T_g$ .

# Alkaline DMFC Performance (CSM)



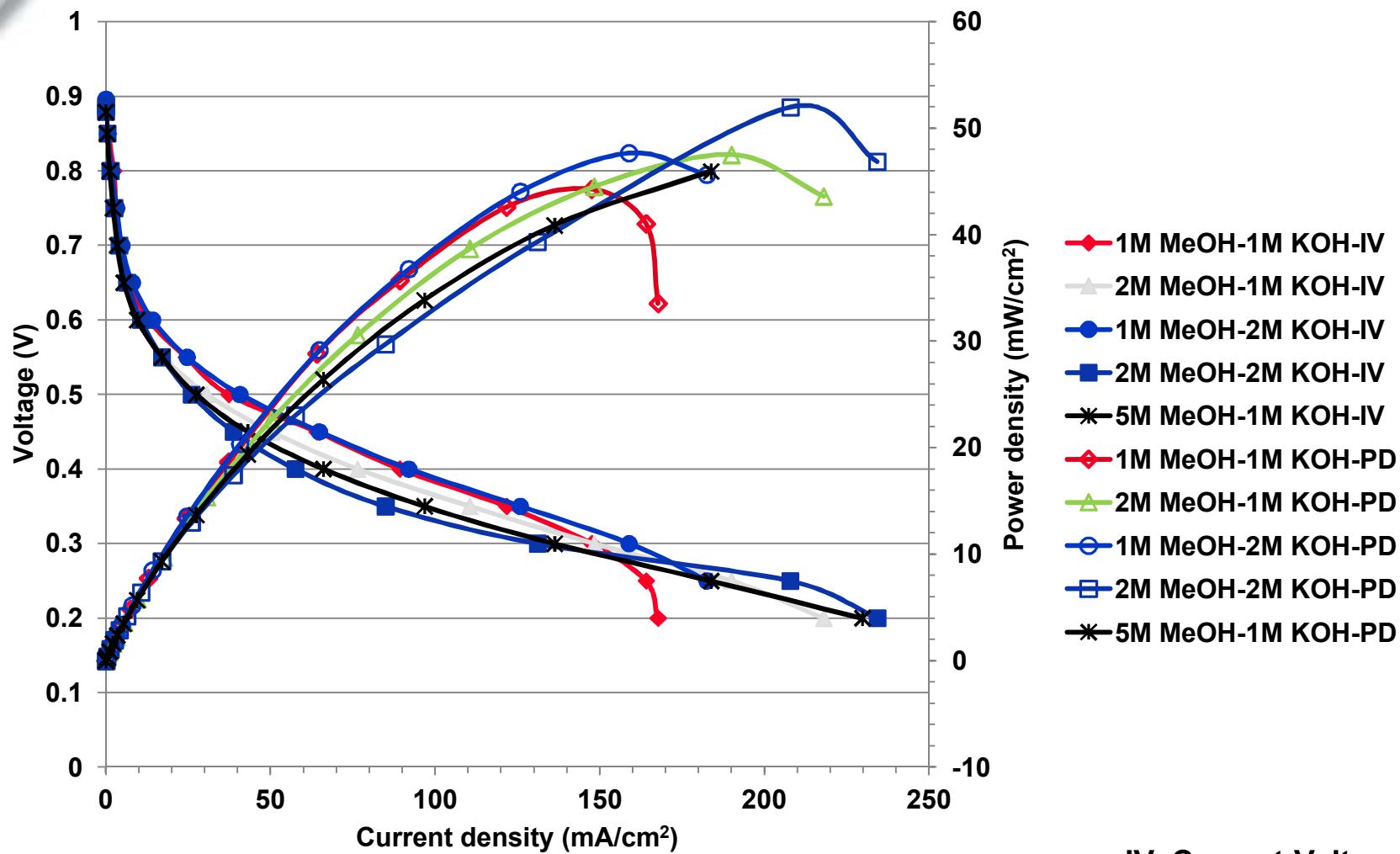
Pt/C/Zoltek, 1M  $\text{CH}_3\text{OH}$ ,  $80^\circ\text{C}$ , 0.5 ml/min – TMAC6PP – Pt/C/Etek,  $\text{O}_2$ ,  $80^\circ\text{C}$ , 0.2 L/min

# Alkaline DMFC Performance (CSM)



Pt/C/Zoltek,  $x\text{M CH}_3\text{OH} + x\text{M KOH}$ ,  $80^\circ\text{C}$ ,  $0.5 \text{ ml/min}$  – TMAC6PP – Pt/C/Etek,  
 $\text{O}_2$ ,  $80^\circ\text{C}$ ,  $0.2 \text{ L/min}$

# Alkaline DMFC Performance (CSM)



IV - Current-Voltage  
 PD - Power density

Pt/C/Zoltek, CH<sub>3</sub>OH + KOH, 80 °C, 0.5 ml/min – TMAC6PP – UNM-Gen-2/Etek, O<sub>2</sub>,  
 80 °C, 0.2 L/min



# CONCLUSIONS

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- Poly(phenylene)s are much more suitable for alkaline fuel cell membranes than poly(arylene ether sulfone)s.
- Resonance-stabilized cations are less stable on the poly(phenylene) than BTMA.
- Alkyl trimethyl ammonium sidechain-type cations offer the best alkaline stability to date.
- New ionomers allow easier MeOH transport at the anode and have led to DMFC power densities  $>50$  mW/cm<sup>2</sup>.
- Further improvements in cation stability and electrode design are critical to push the development of alkaline fuel cells.



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