ACS FUEL Division 2011

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POLY(PHENYLENE)-BASED ANION-EXCHANGE MEMBRANES AND IONOMERS FOR ALKALINE FUEL CELLS

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National Nuclear Security Administration

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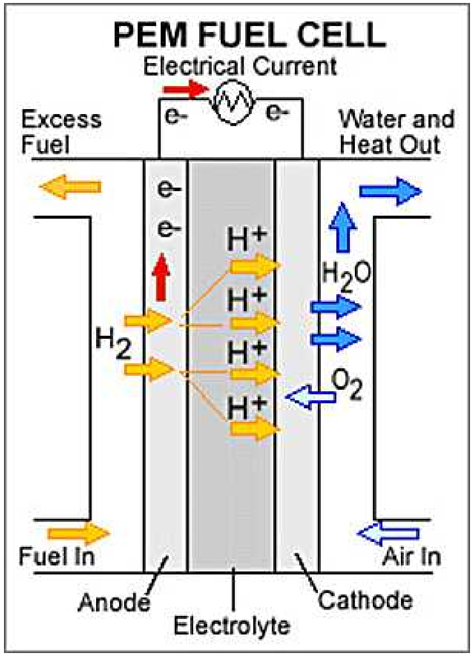
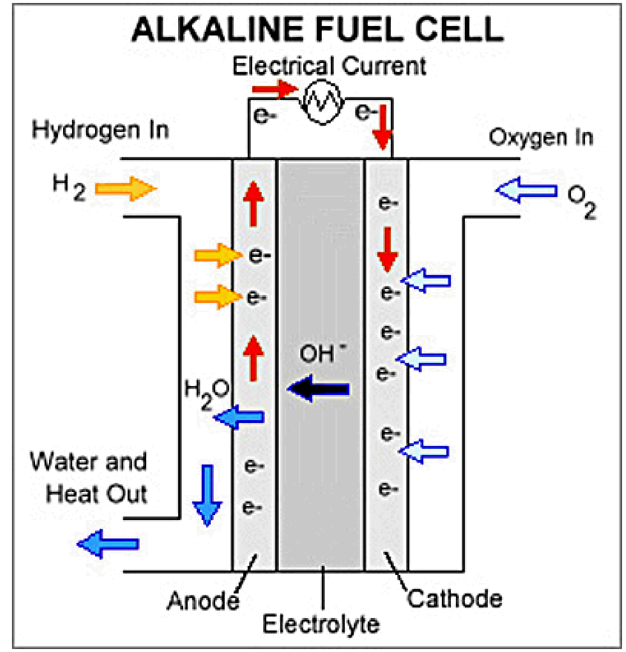
Why Alkaline Fuel Cells (AFCs)?





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

- 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).

Membranes requirements[1]:

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.

[1]From DOE Alkaline Membrane Fuel Cell Workshop, May 8-9 2011.

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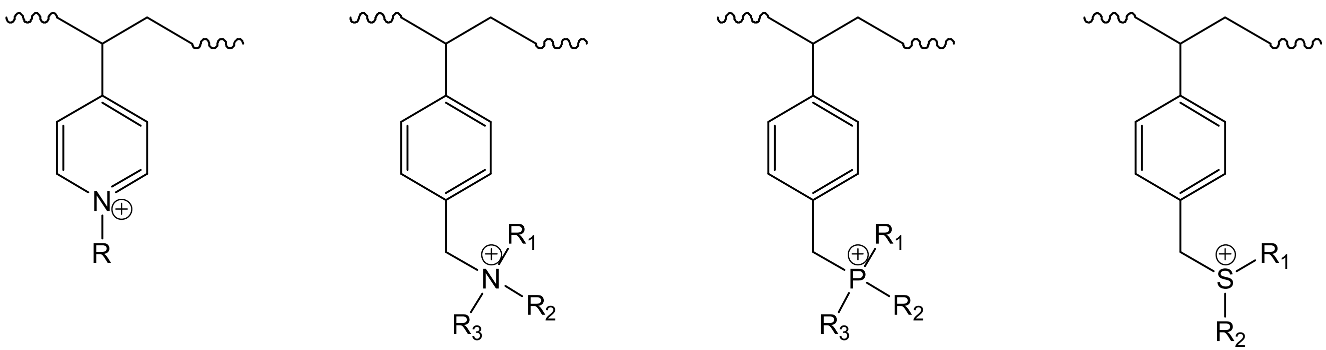
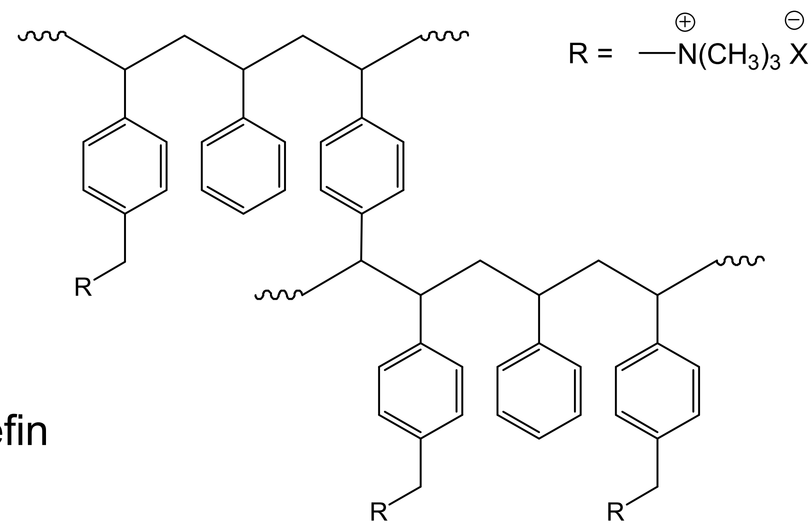
Anion Exchange Membranes (AEMs)

Typical functional groups with fixed positive charges in AEMs:



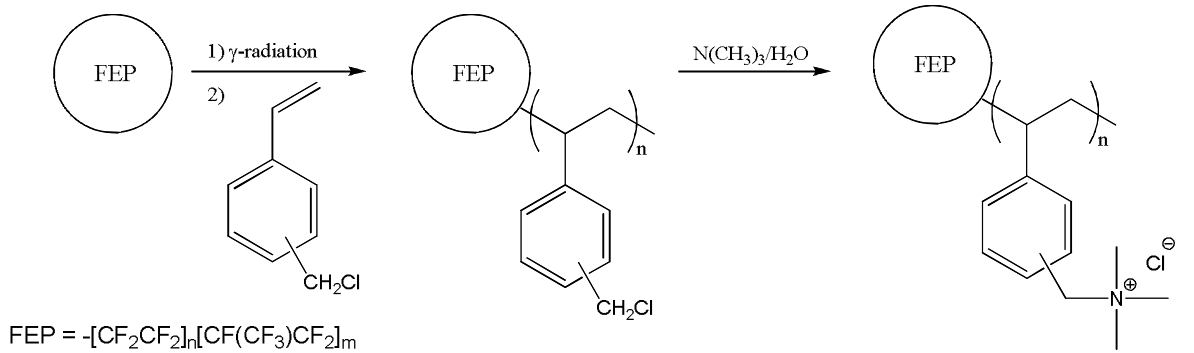
Commercially-available AEM:
(for electrodialysis, etc.)



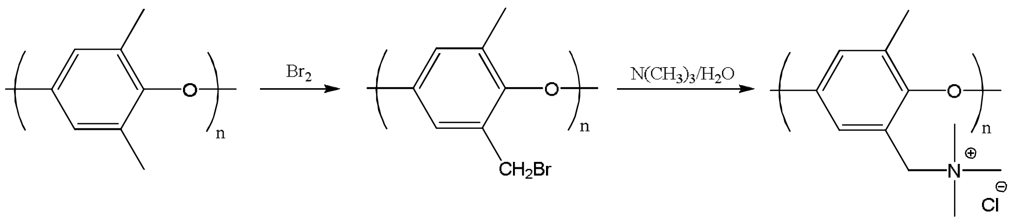
- Crosslinked polystyrene with benzyl trimethylammonium groups
- Typically blended with PVC or a polyolefin
- Cast on fabric support

AEMs: The State of the Art

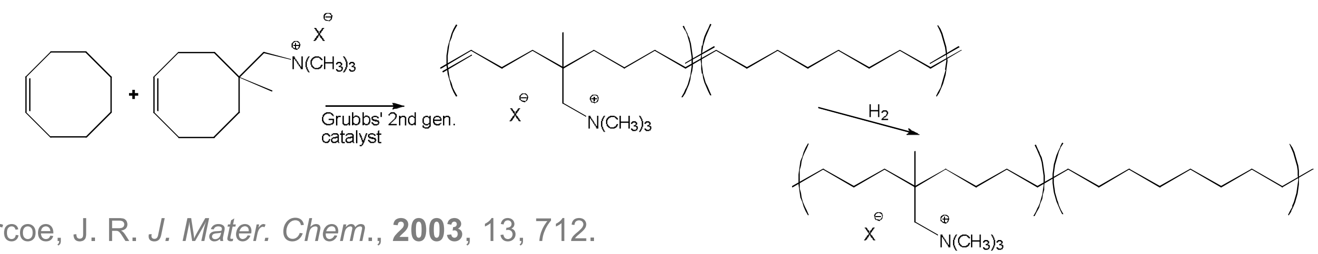
Radiation-grafting of functionalized poly(styrene) onto fluorinated polymers[1]:



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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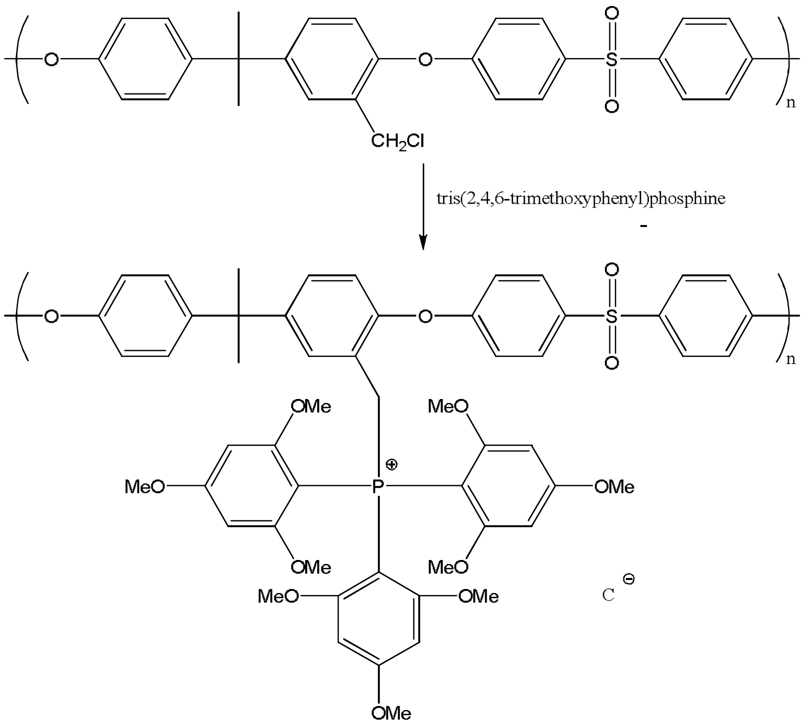
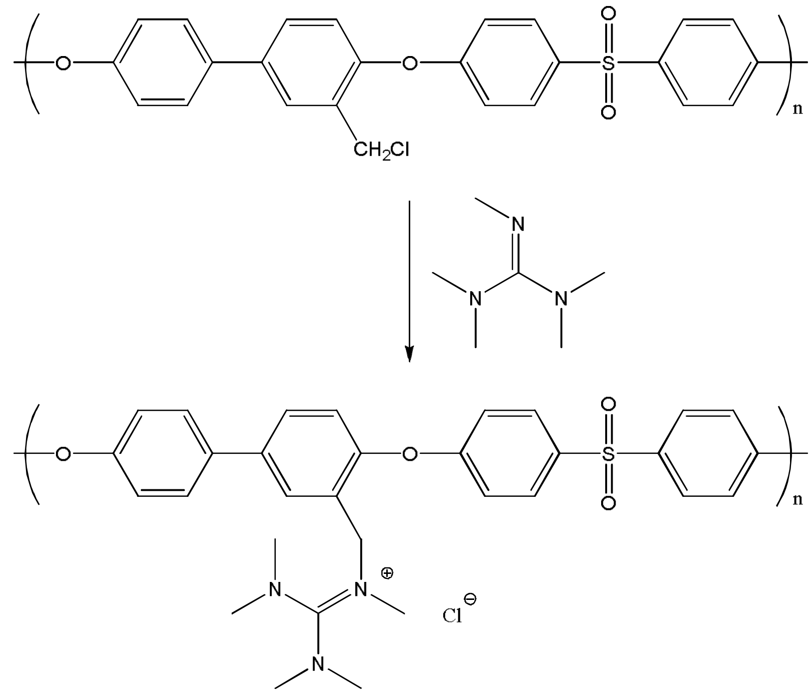
Alternative Cationic Groups

Poly(sulfone) with benzyltris(2,4,6-trimethoxyphenyl) phosphonium groups[1]

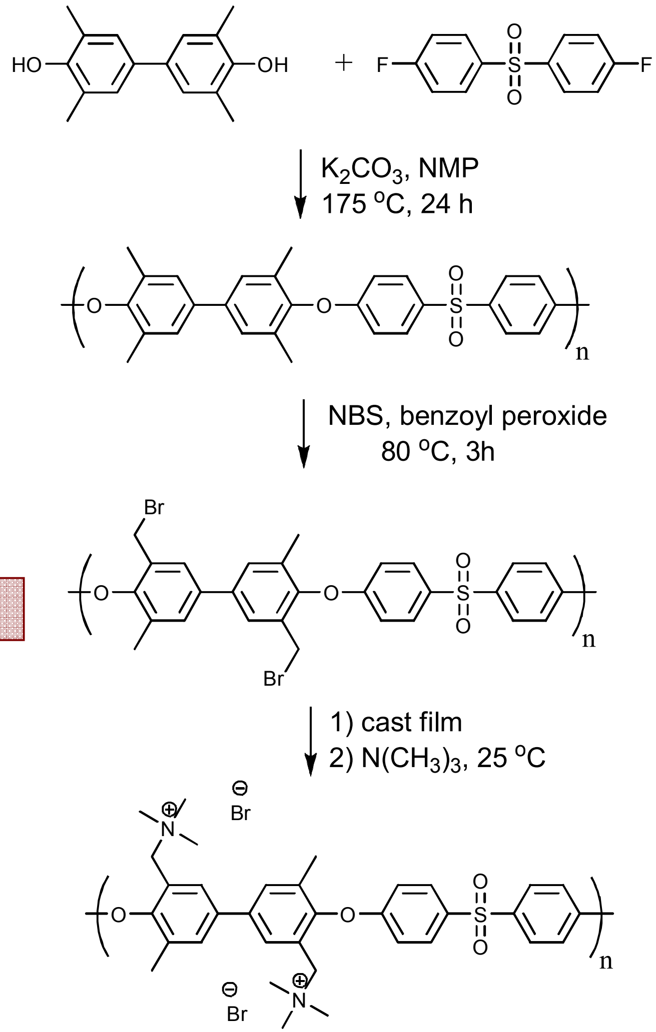


Poly(sulfone) with benzylpentamethyl guanadinium groups[2]



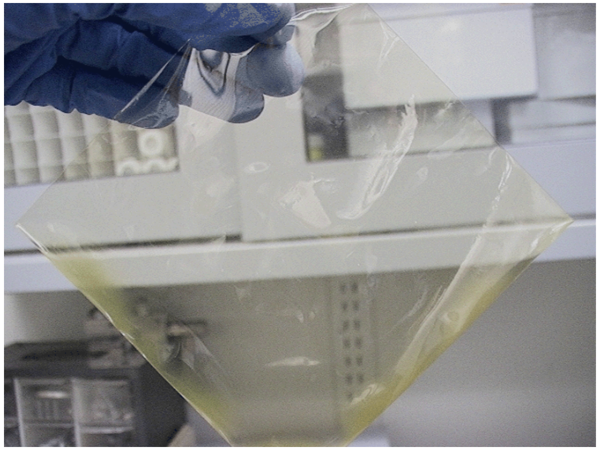
[1]Gu, S.; Cai, R.; Luo, T.; Chen, Z.; Sun, M.; Liu, Y.; He, G.; Yan, Y. *Angew. Chem. Int. Ed.*, **2009**, 48, 1.
[2]Wang, J.; Li, S.; Zhang, S. *Macromol*. **2010**, 43, 3890.

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

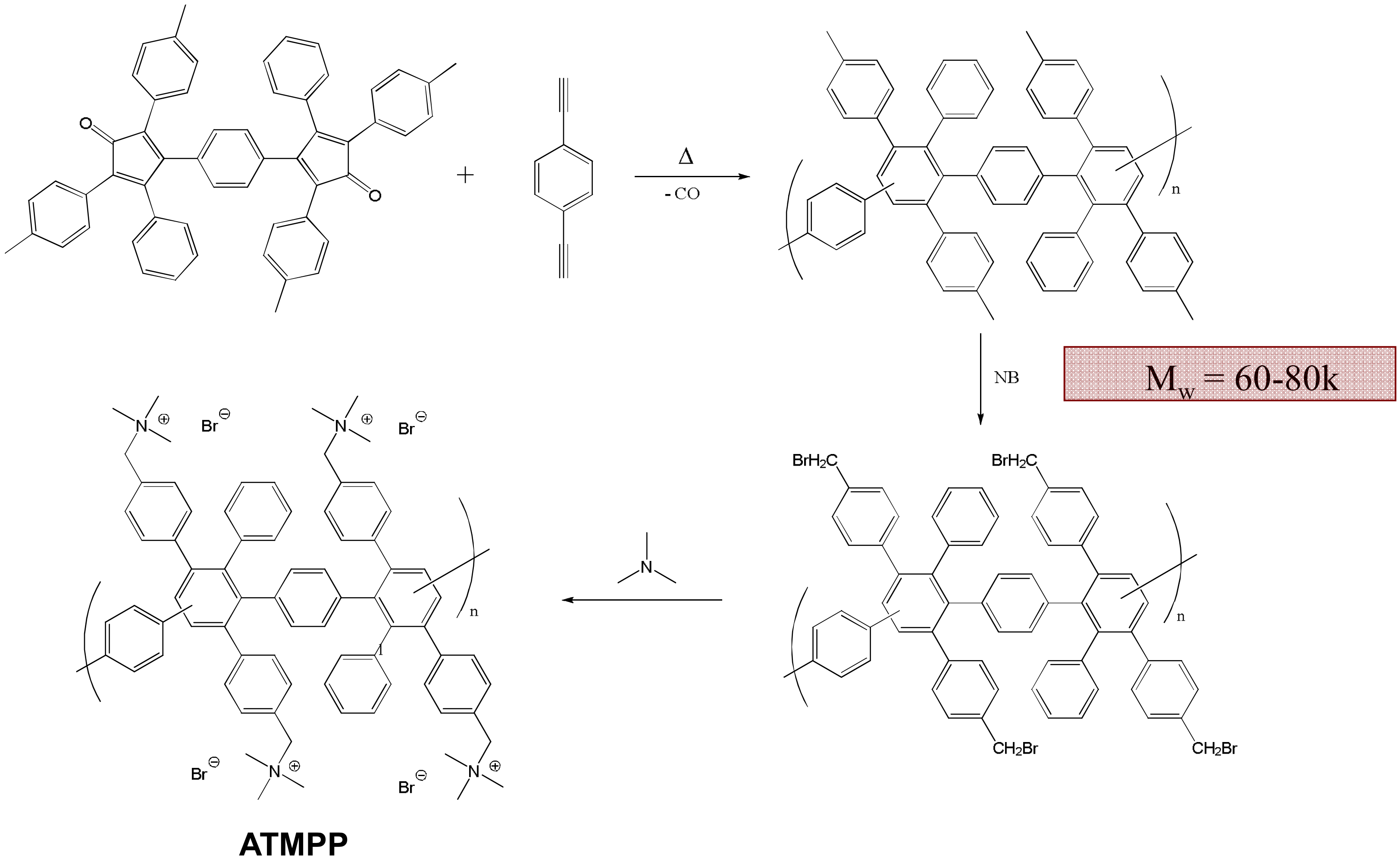


M_w = 80-100k

ATMPS



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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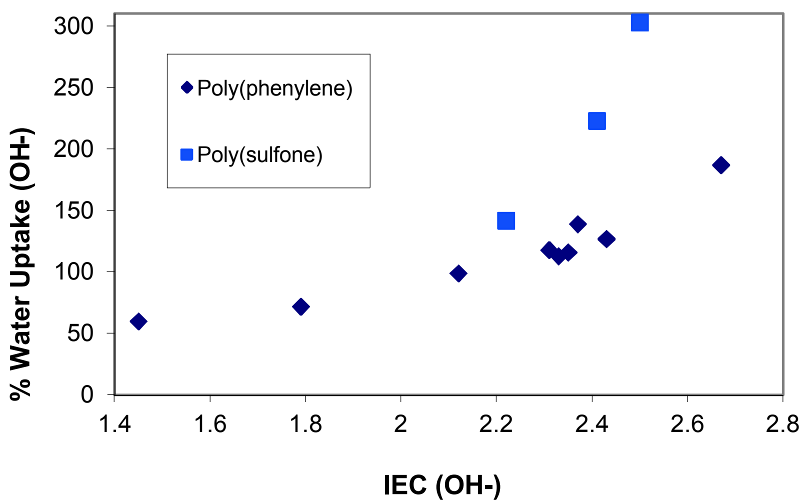
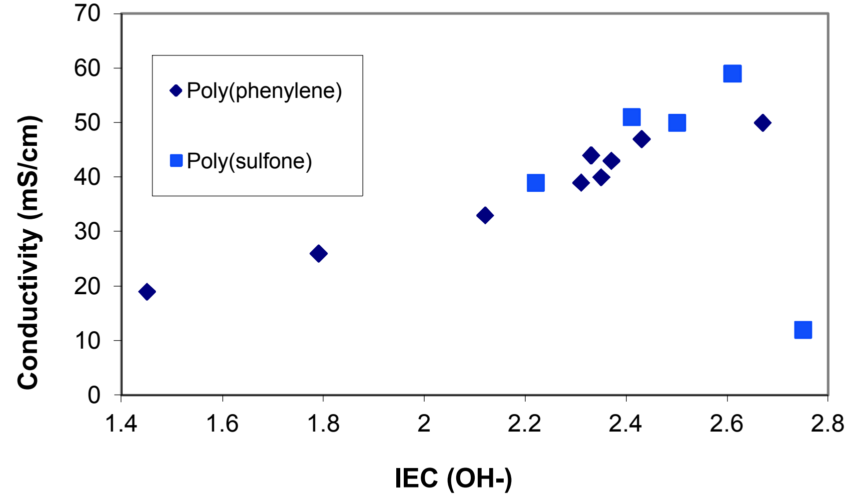
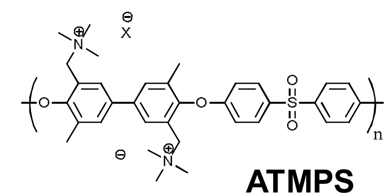
ATMPS & ATMPP Properties

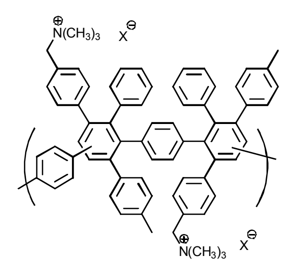




- Hydroxide conductivities were measured in liquid water at room temperature.
- ATMPS has larger water uptake than ATMPP at similar IECs.
- At IEC > 2.6, ATMPS swells so much that the conductivity begins to decrease.
- Fuel cell testing at LANL (H_2/O_2, 80 ^oC) has achieved power density of 278 mW/cm^2 with ATMPP membrane.



ATMPS
poly(sulfone)



ATMPP
poly(phenylene)

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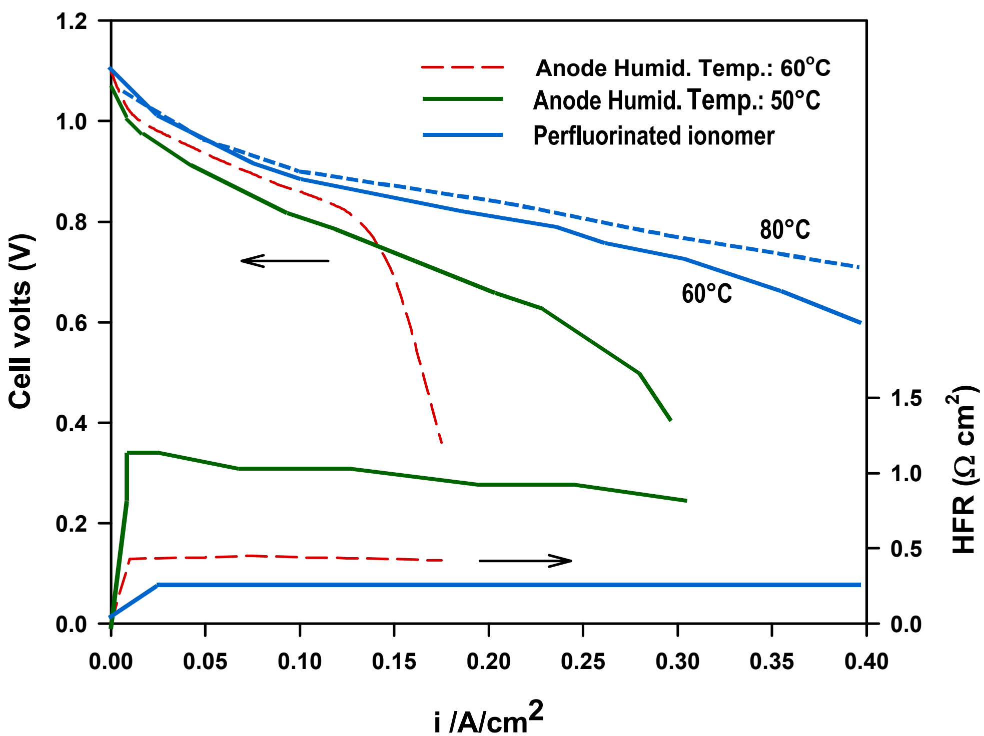
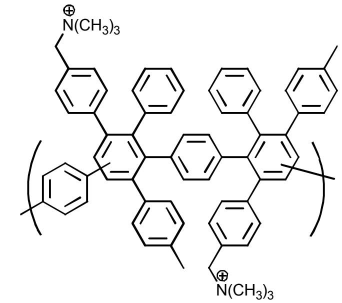
H_2/O_2 Performance of Alkaline Membrane Fuel Cells



Catalyst: Pt black (3 mg/cm²), Cell temp. 60°C, Cathode humidification: 60°C, back pressure: 30 psig, high stoic. Catalyst: ionomer weight composition (9:1, not optimized); MEAs were prepared from direct painting.

Membrane/ionomer
IEC = 1.8 meq./g
σ= 55 mS/cm
Thickness: 50 μm



aminated **TMPP**

Fully hydrated conditions (anode humid. temp.: 60°C)

→ Mass transport issue due to flooding

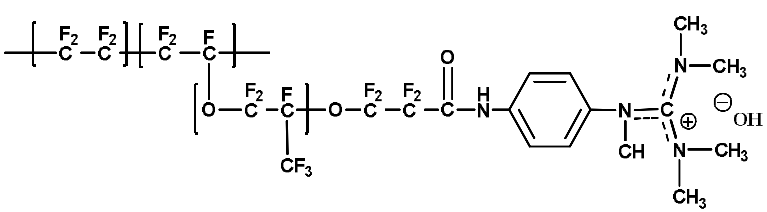
→ Possibly poor cation – catalyst structure

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, σ = 20 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 presented at 2011 DOE Hydrogen and Fuel Cells Program Review

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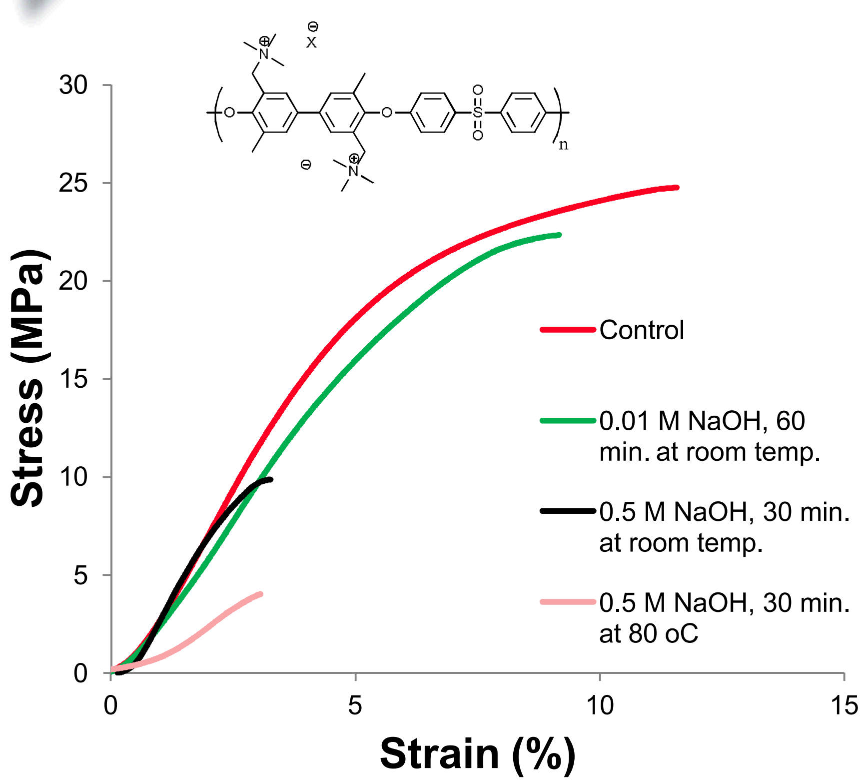
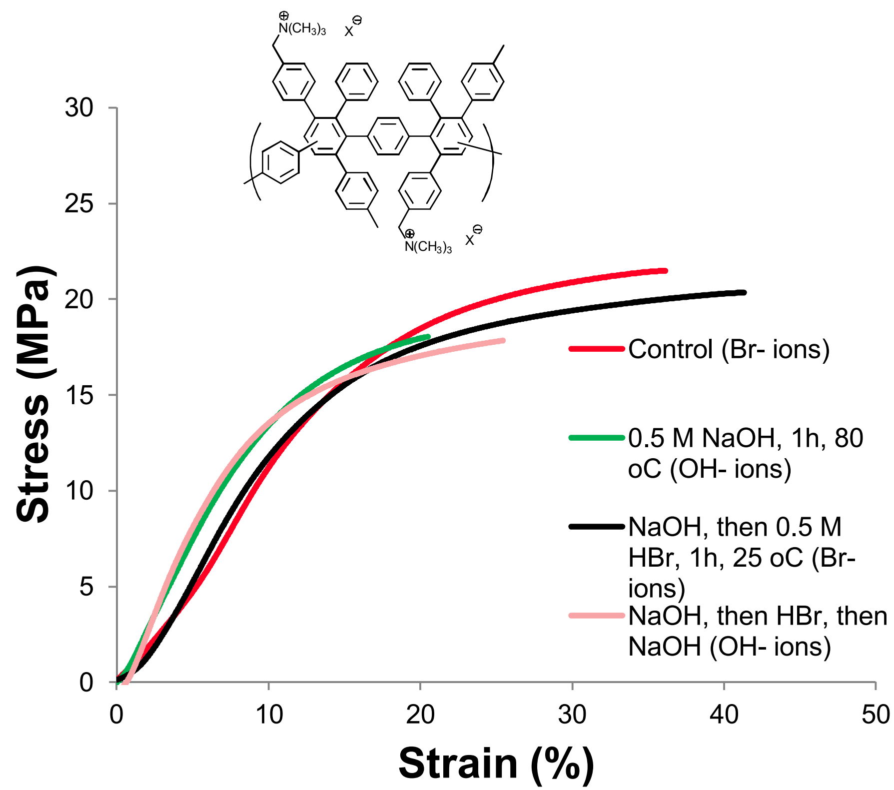
Mechanical Stability





- 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.

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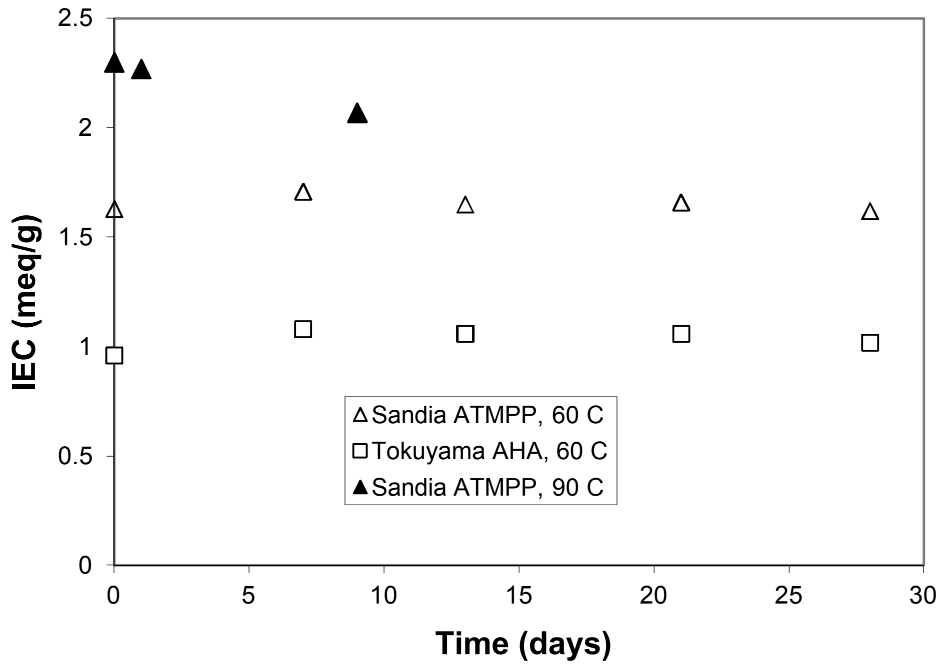
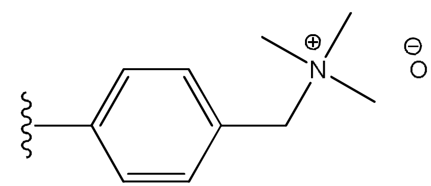
Cation Stability



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 ^{o}C, IEC of ATMPP decreased by 10%.
- Model studies indicate decreasing stability as hydration decreases.[1]

[1]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.

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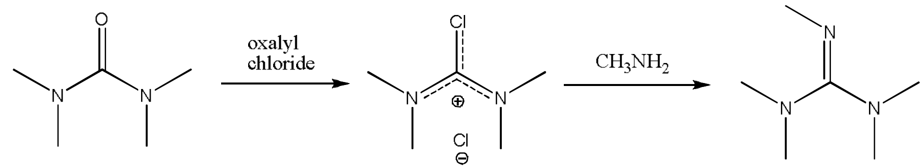
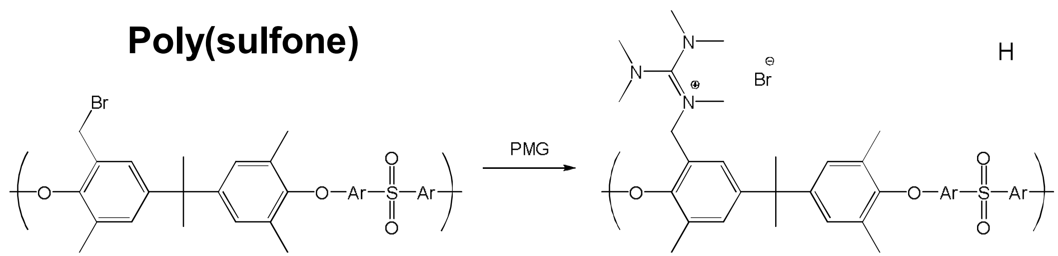
Resonance-stabilized Cations

- Delocalization of the positive charge should make the cations less susceptible to nucleophilic attack.
- Delocalization should also increase ion dissociation to get higher ionic conductivity.
- Poly(sulfone) and poly(phenylene) membranes with benzyl PMG groups were prepared according to the method of Wang et al.[1]
- Conductivities of both membranes were near zero after conversion to OH^- form.

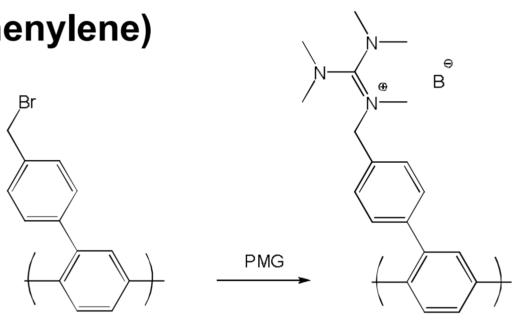


Pentamethylguanidine (PMG)[1]

Poly(sulfone)

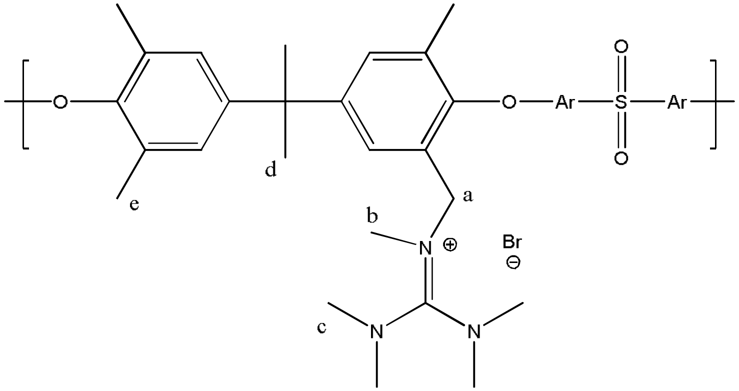


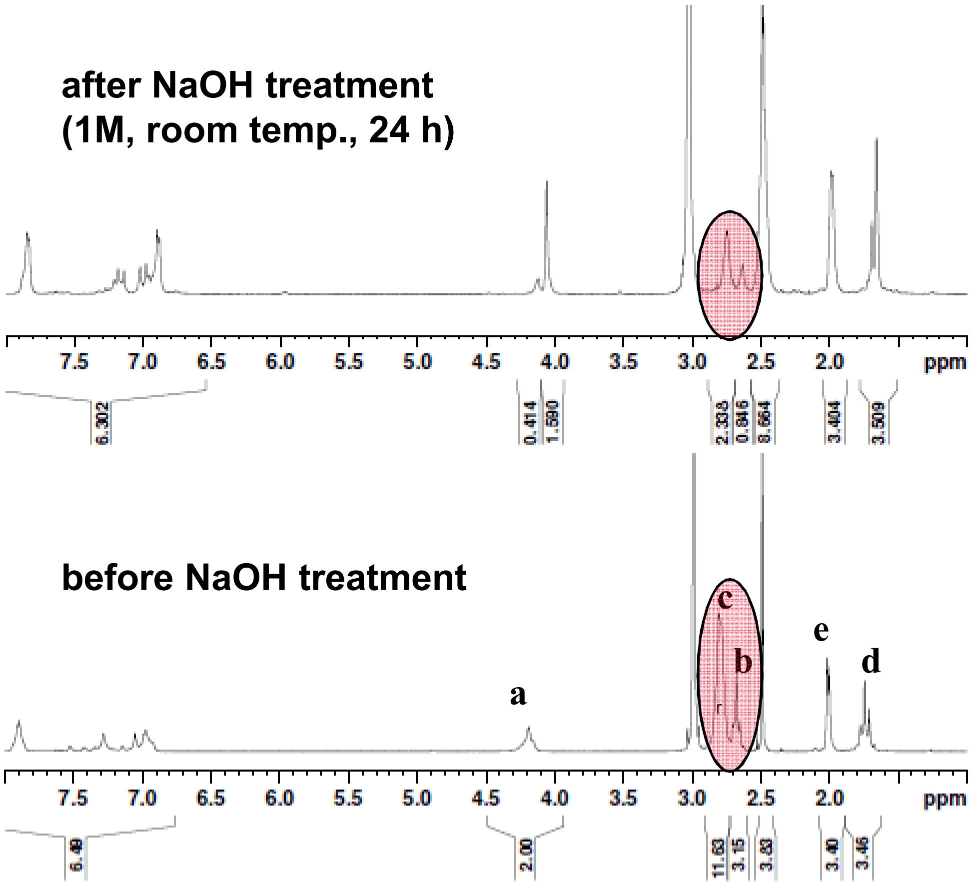
Poly(phenylene)



[1]Wang, J.; Li, S.; Zhang, S. Macromolecules **2009**, 42, 8711.

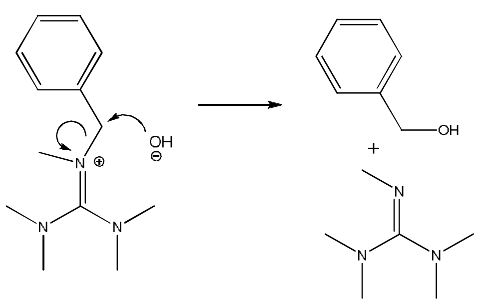
Decomposition of Benzyl PMG Cations





- 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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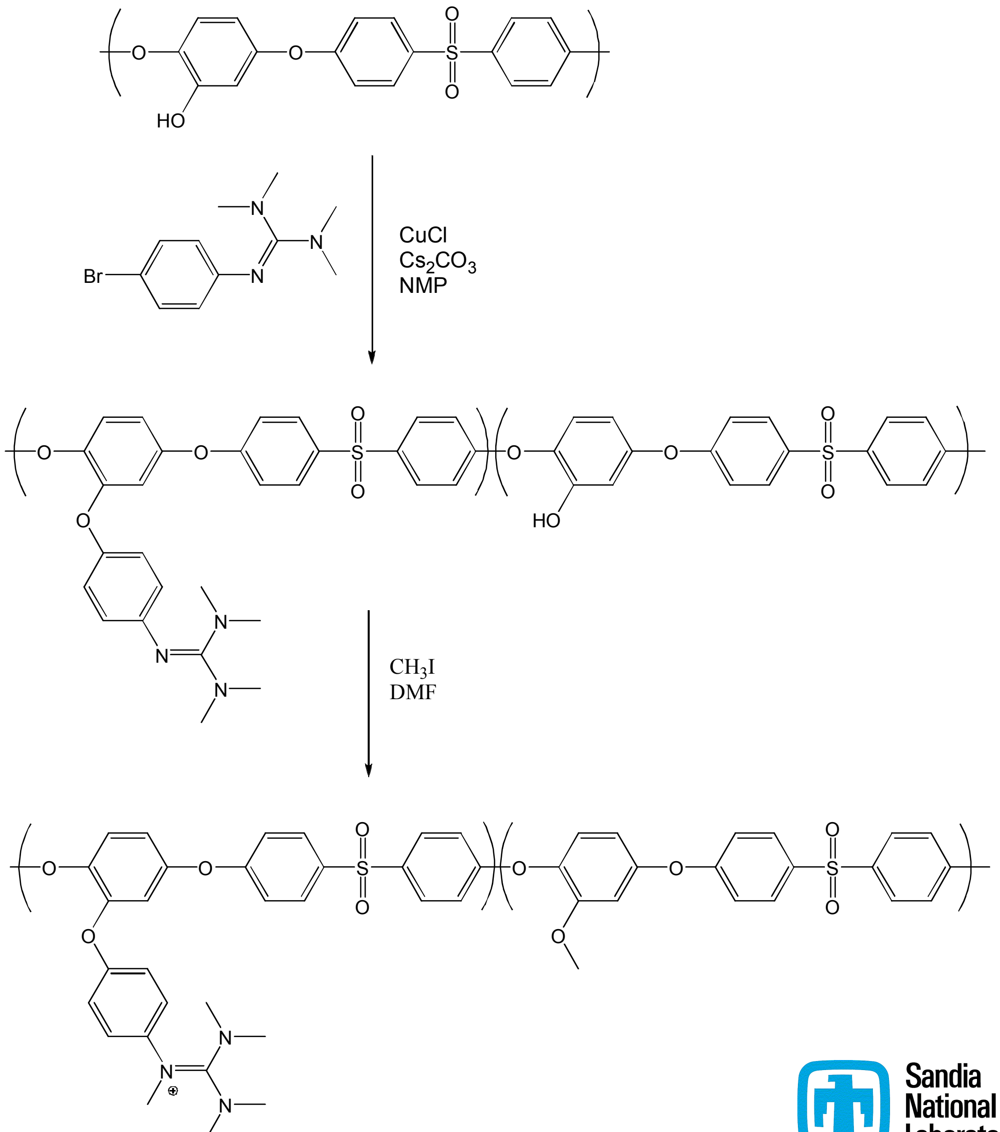
Polymer with Phenyl PMG Cations

- Parent polymer is poly(arylene ether sulfone) with phenol-type alcohols.
- 4-bromophenyl tetramethylguanidine is attached by Ullmann coupling.
- The uncoupled alcohols become methyl ethers during the methylation step.
- Electron donating para-phenyl ethers should further stabilize positive charge on guanidinium group.



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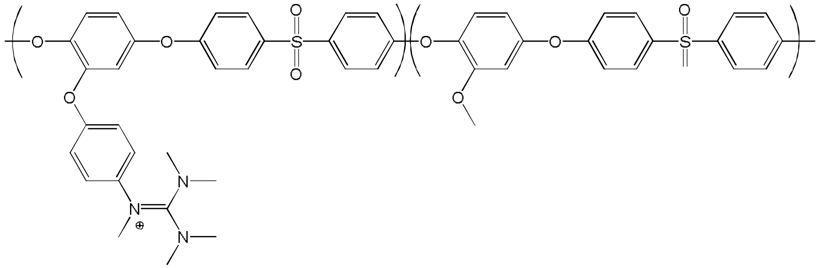
Phenyl PMG Membrane Properties



Batch #	Equivalents of TMG in coupling reaction	IEC (meg/g)	Water Uptake (wt. %)	OH^- Conductivity (mS/cm)
1	1.5	0.88	4	1
2	4	1.09	36	4
3	10	1.34	76	7

- The maximum possible IEC, 1.78, is difficult to achieve.
- With a 10x excess of 4-bromophenyl TMG, about 66% of repeat units undergo coupling reaction.
- Need a backbone with more alcohols/repeat unit (higher possible IEC) to get higher conductivities.
- Conductivities measured in liquid water (degassed) at room temperature.

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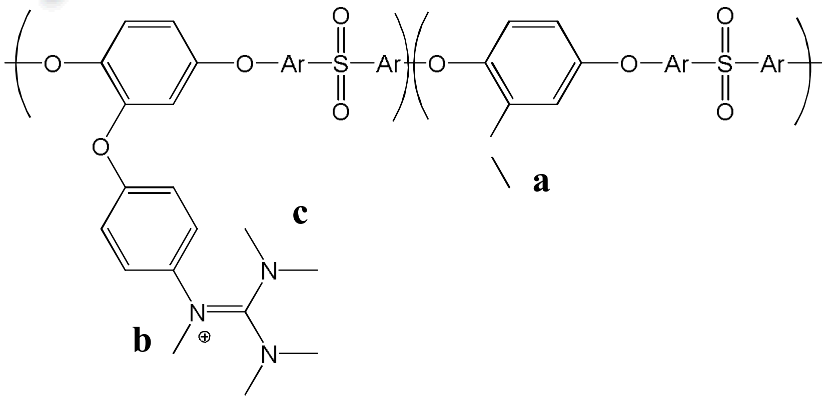
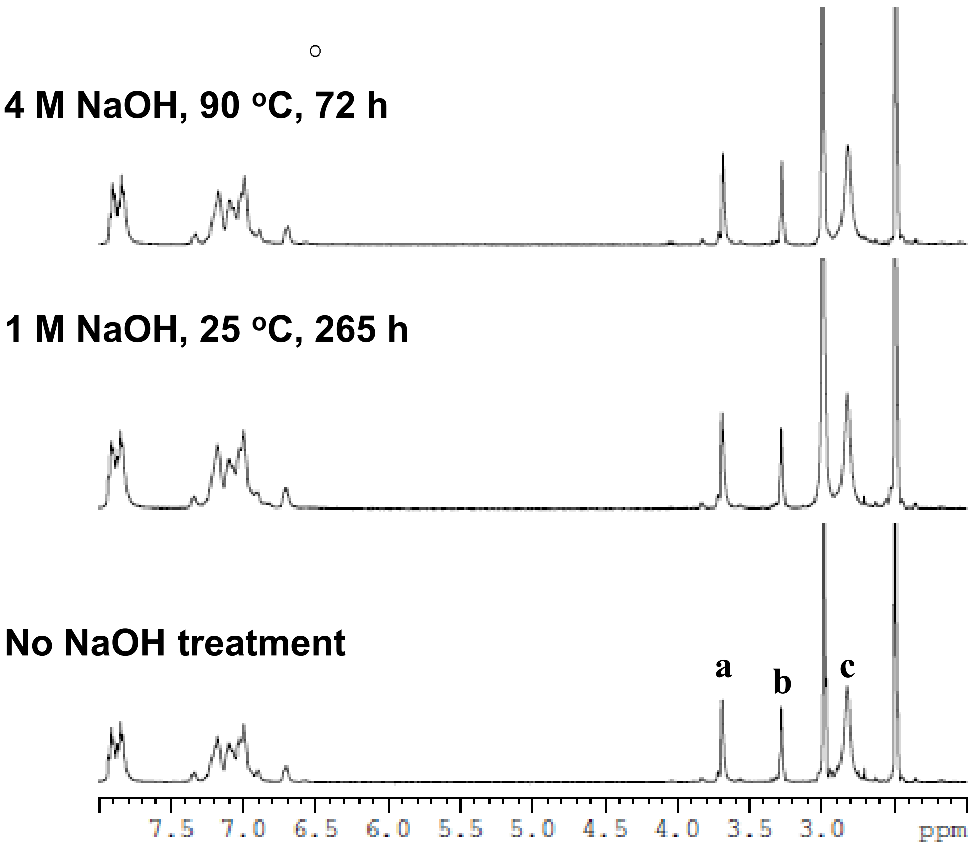
Stability of Phenyl PMG Cations





- Phenyl PMG groups are stable at high pH and elevated temparatures. (unlike benzyl PMG groups)
- Membranes became brittle after exposure to NaOH at 90 °C (probably backbone degradation).
- Need to attach phenyl PMG to a more stable backbone such as poly(phenylene).

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Conclusions

- New membranes and binders are needed to drive the development of alkaline fuel cells (AFC).
- Poly(arylene ether sulfone) backbones appear to be unstable at high pH conditions.
- Cations more stable than benzyl trimethylammonium groups are needed for operation at high temperature and/or low humidity.
- Guanidinium groups attached by a benzyl linkage are not stable at high pH.
- Our first attempt at making AEMs with phenyl guanidinium groups indicates a significant increase in stability to hydroxide attack.

Acknowledgements

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