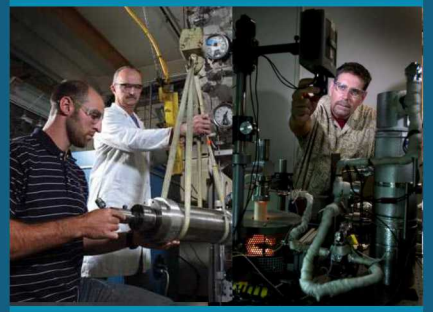
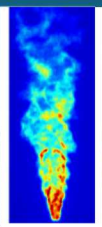
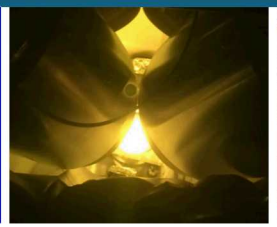
North American Membrane Society 28th Annual Meeting
May 15, 2019

SAND2019-5075C

High Temperature Fuel Cells with Ion-Pair Membranes and Phosphonated Ionomers







Michael Hibbs[1], Cy Fujimoto[1], Ehren Baca[1], Albert S. Lee[2], Yu Seung Kim[2]

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Los Alamos, NM

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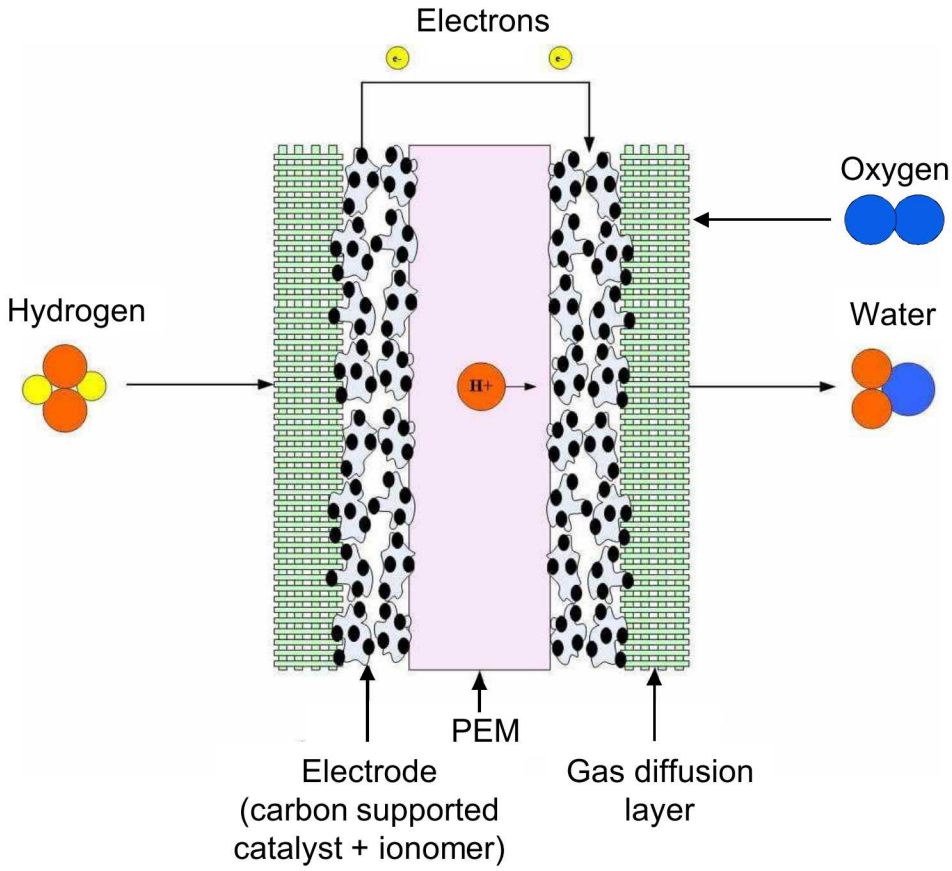
PEM Fuel Cells

Materials

- PEM (proton exchange membrane) conducts H^+ ions.
- Electrode contains catalyst particles and ion-conducting polymer.

Limitations

- Conduction typically requires water and temperatures <100 °C.
- Platinum or other precious metal catalyst is required.



Desired Improvements

- Reduce catalyst loading
- Simplify water management (humidity controls)
- Simplify temperature control (radiator)

Figure from fuelcellstore.com (modified)

High Temperature PEM Fuel Cells

Objective

Development of PEM fuel cells that can operate at temperatures between 200-300 °C.

Advantages of this technology

- Higher catalytic activity at higher temperatures (less catalyst needed).
- Easier thermal management (smaller radiators).
- No water needed (elimination of humidifiers).
- All of these lead to lower fuel cell costs.

Challenges

- Need durable membranes and ionomers that conduct protons without water.

Further cost reduction of fuel cells

Balance of Plant
- Humidifiers
- Large radiators
- Reactant quality control

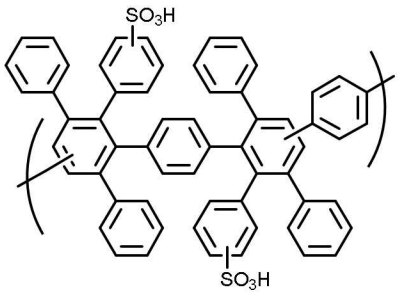
→ Simple Balance of Plant

High temperature and low RH fuel cell operation could enable fixed cost savings of \$7.5/kW_{net} by eliminating or reducing the size of BOP components such as humidifier and radiator.

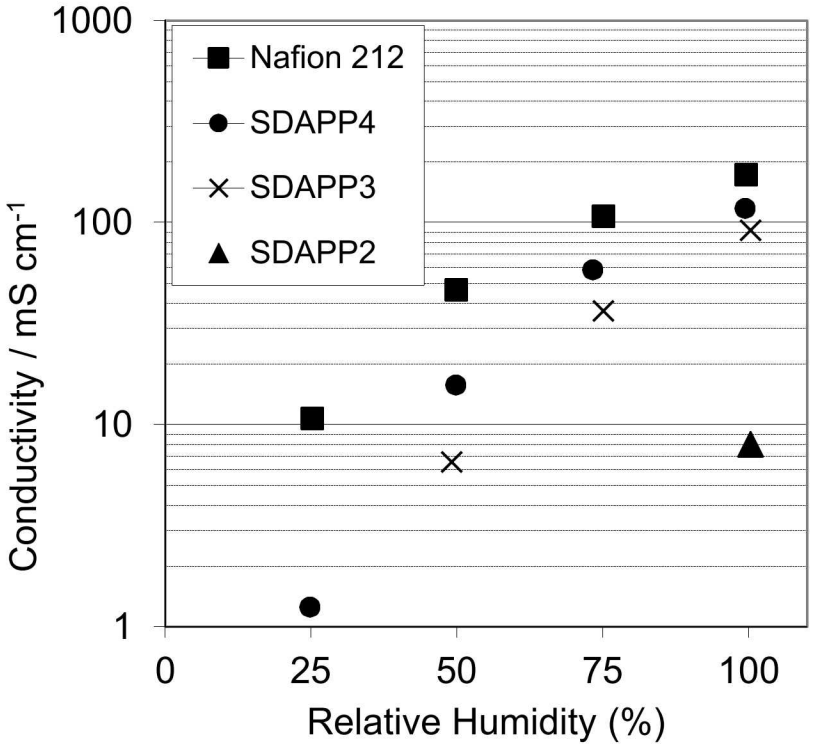
N. Dale, Nissan Motors

Background: Poly(phenylene)-based PEMs

Previous PEM fuel cell membrane from Sandia based on Diels-Alder polymerization



SDAPP

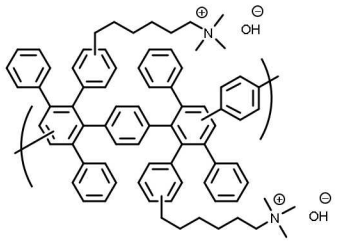


Highlight: Very stable hydrocarbon PEM but proton conductivity is strongly dependent on water content.

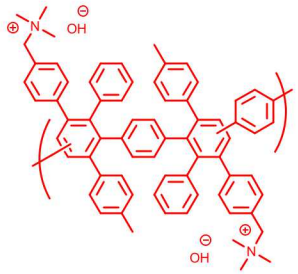
Stanis, R. J.; Yaklin, M. A.; Cornelius, C. J.; Takatera, T.; Umemoto, A.; Ambrosini, A.; Fujimoto, C. H. *J. Power Sources* 2010, 195, 104.

Background: Anion Exchange Membranes

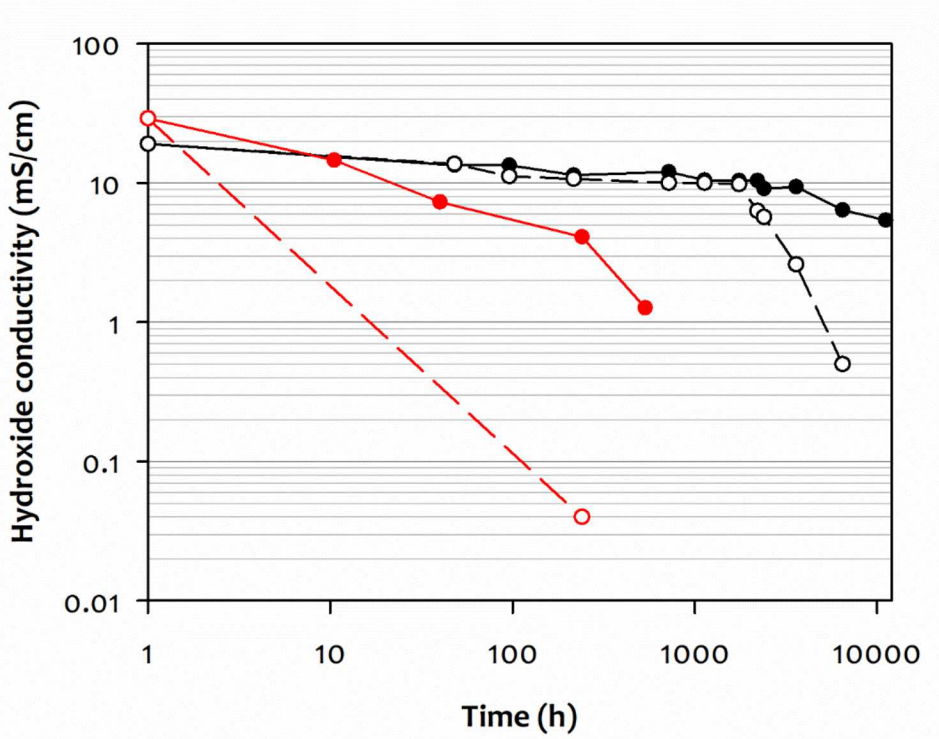
AEM stability test: Immerse AEMs in 0.5 M (solid) or 4 M (dashed) NaOH at 80°C. Conductivity measured at 30°C/95% RH during the stability test.



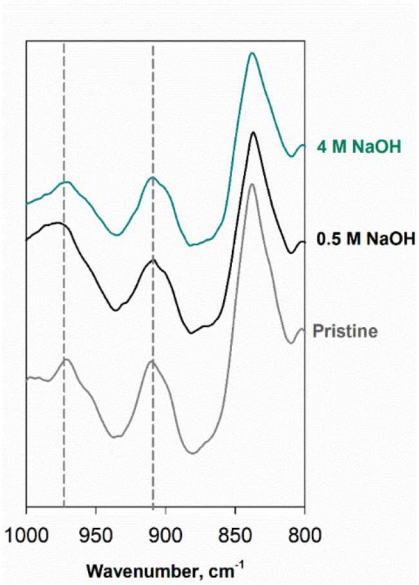
TMAC6PP



ATMPP



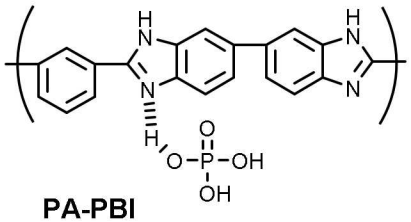
FTIR of TMAC6PP after 3600 h NaOH treatment



Highlight: No conductivity or structural changes for TMAC6PP after 4 M NaOH treatment at 80°C for 2,200 h. Among the most stable alkaline AEMs reported.

Ion-Pair Membranes

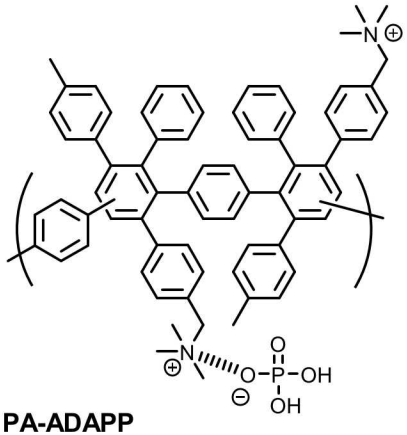
Previous high temperature fuel cell membrane with "shared" proton-type interaction[1]



PA-PBI

Acid-base interaction energy calculated for small molecule model = 17.4 kcal/mol

LANL/SNL-developed high temperature fuel cell membrane with purely ionic interaction



PA-ADAPP ion-pair

Ion-pair interaction energy calculated for small molecule model = 152 kcal/mol

Impact of strong ion-pair interaction:

- Better performance at low temperature/high RH because biphosphate doesn't leach out
- Better performance at high temperatures because biphosphate doesn't evaporate

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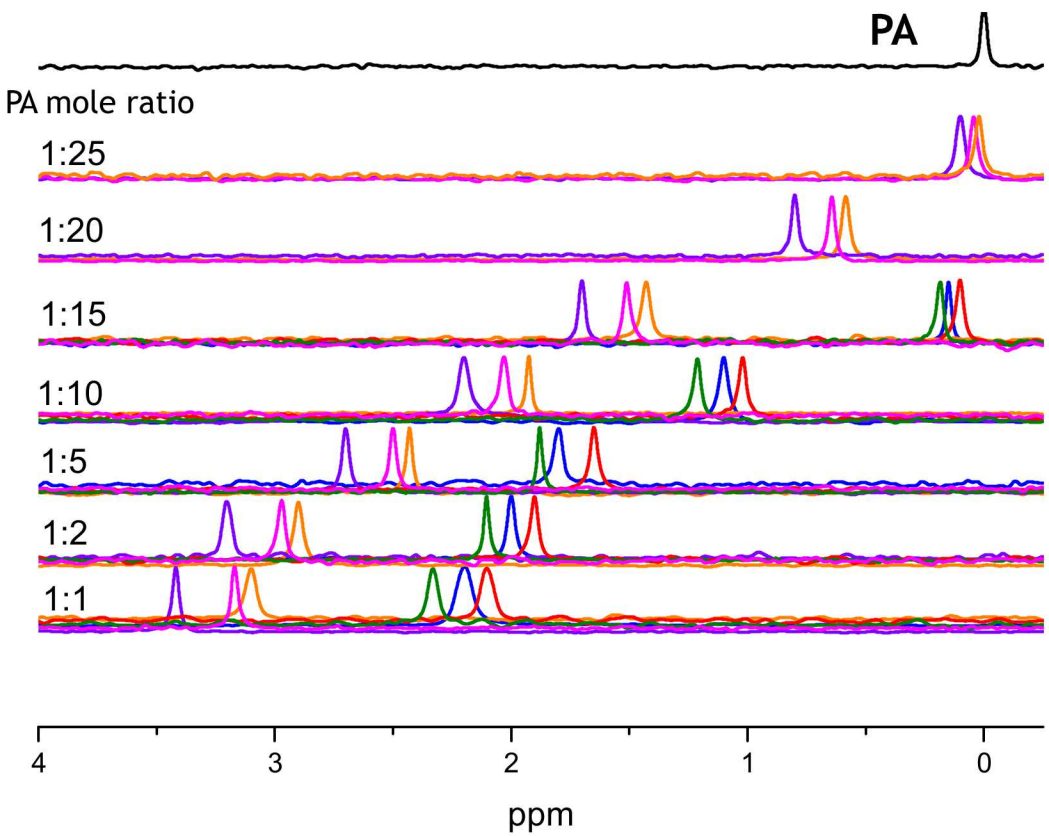
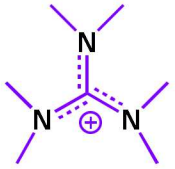
[1]Xiao, L.X.; Zhang, H.F.; Scanlon, E.; Ramanathan, L.S.; Choe, E.W.; Rogers, D.; Apple, T.; Benicewicz, B.C. *Chem. Mater.* 2005, 17, 5328.

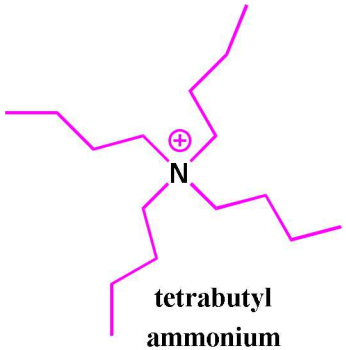
Interaction Measurement (^{31}P NMR)



Ion-pair



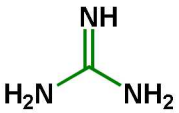
hexamethyl guanidinium (HMG^+)



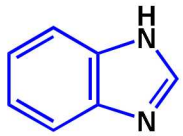
tetrabutyl ammonium (TBA^+)

tetramethyl ammonium (TMA^+)

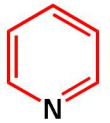
Acid-base



guanidine



benzimidazole



pyridine

- ^{31}P NMR shows a single peak, indicating exchanging electrons in the phosphate phase.
- Ion pair coordinated system has higher interaction energy – consistent with DFT study.
- Interaction energy HMG > TBA > TMA >> guanidine > benzimidazole > pyridine

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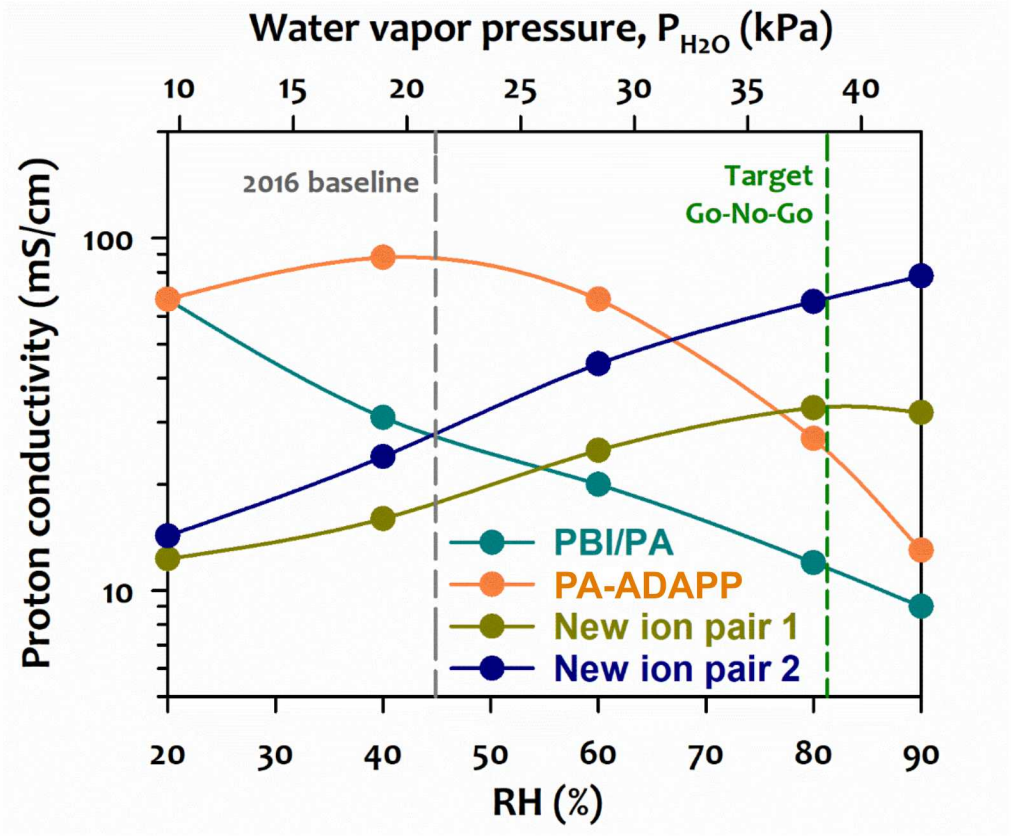
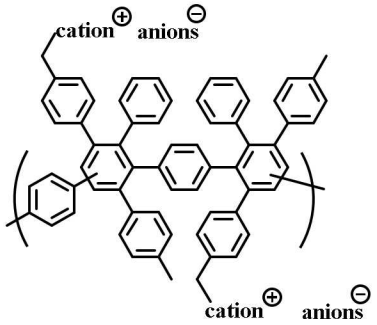
Water Tolerance

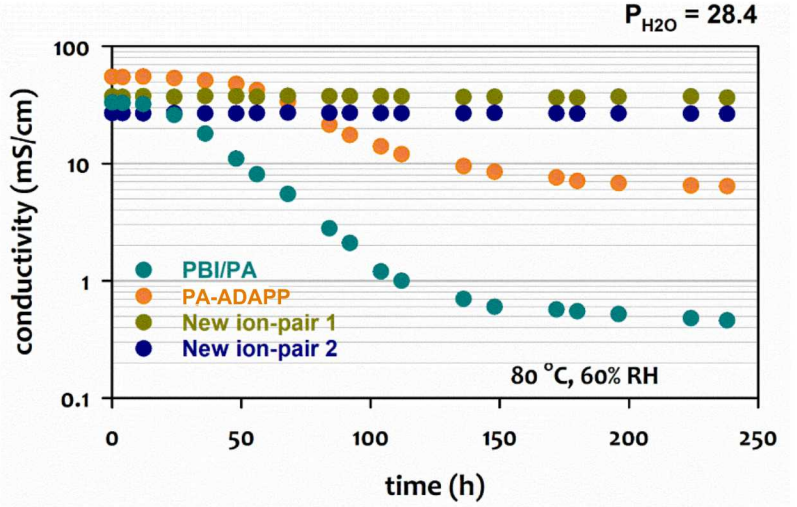


Chemical structure of ion-pair coordinated membrane



PA-ADAPP
cation/anion: TMAOH/PA

New ion pair 1, 2
cation/anion: proprietary info.



- PA-ADAPP ion pair membrane shows significant improvement in conductivity throughout RH test range but PA can leach out at RH > 50%.
- DAPP membrane reformulated with alternative ion pairs shows constant conductivity at all RH values.

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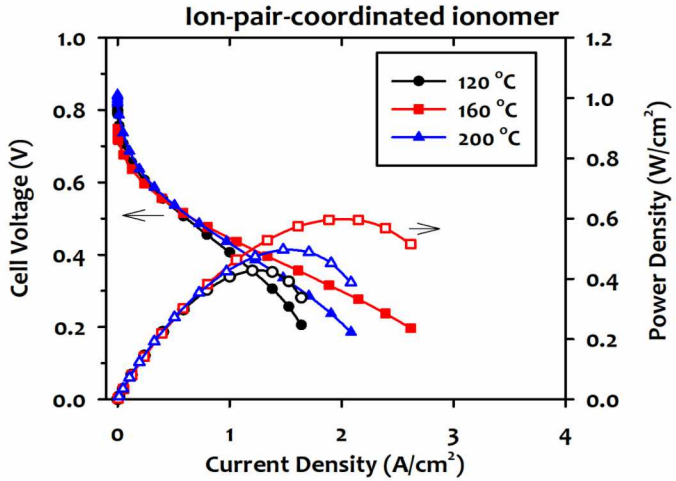
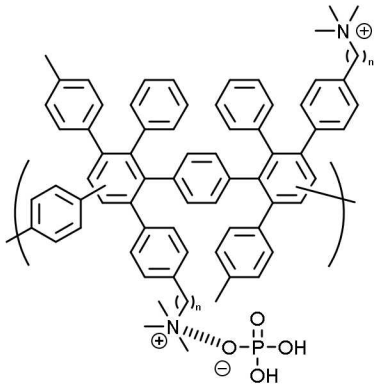
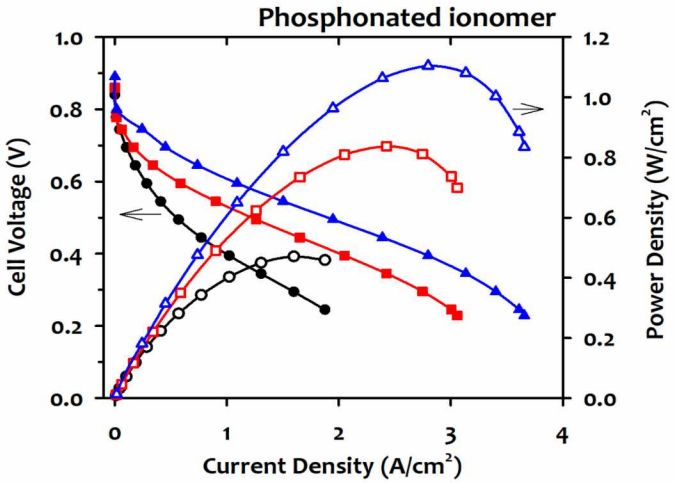
PA-ADAPP High Temperature Fuel Cell Performance

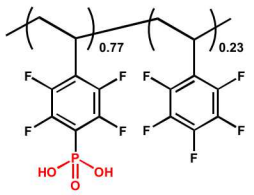
Membrane: PA-ADAPP
Ionomer: PA-ADAPP





Membrane: PA-ADAPP
Ionomer: PPFS





Measured in H_2/O_2, 147 kPa abs backpressure; Pt-Ru/C 0.75 mg_{Pt}/cm^2 for anode and Pt/C 0.6 mg/cm^2 for cathode

Better cell performance at 200 °C because phosphate can't evaporate or leach out of electrodes.

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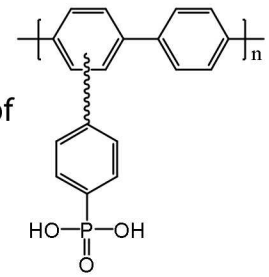
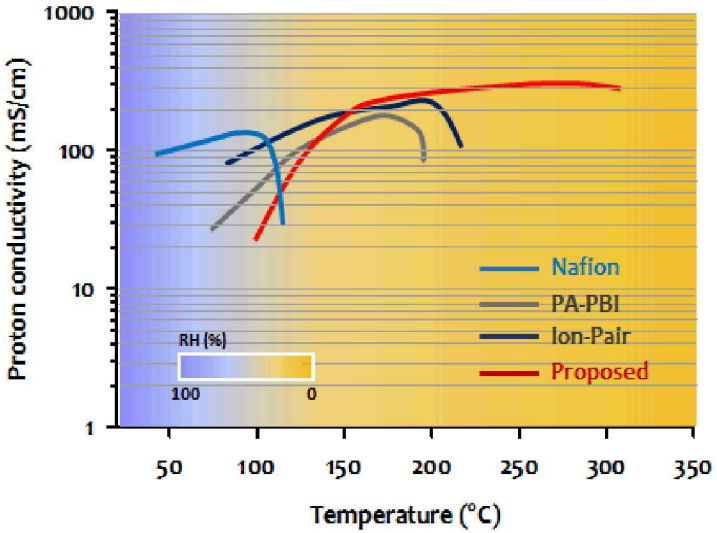
Universität Stuttgart

V. Atanasov & J. Kerres

New Ionomers with Covalently Bonded Phosphonic Acid Groups

General structure of proposed ionomers





Target characteristics

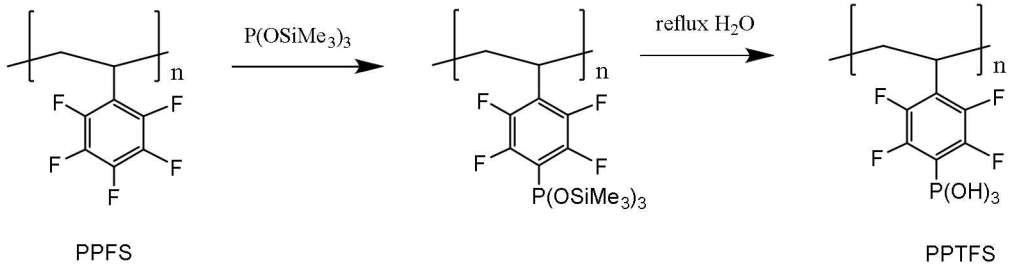
- H^+ conductivity > 100 mS/cm from 200-300 °C
- IEC between 1.5-3 meq/g
- M_w between 20-200K (low M_w to improve solubility)
- Solubility: 2-5 wt% in DMAc or DMSO
- Stability: <5% performance loss over 1000 hours

Features

- Diels-Alder polymerization forms poly(phenylene) without a catalyst and parent polymers are soluble in low-polarity organic solvents.
- Acid groups can't evaporate or leach out.
- Good interfacial compatibility with polyaromatic based ion-pair coordinated membrane.
- DOE-owned intellectual property

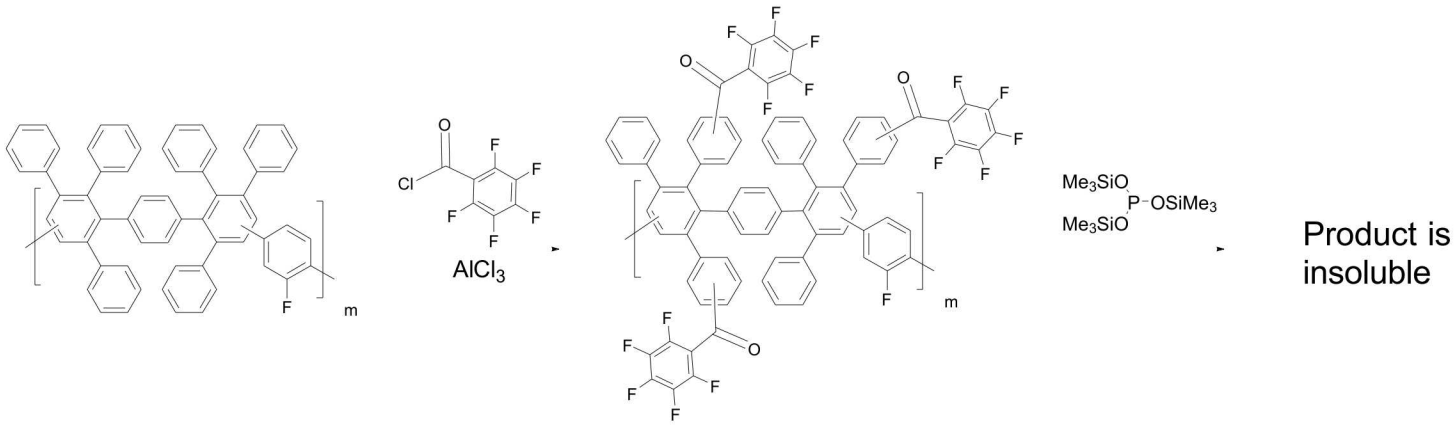
Synthesis: Pentafluoro DAPP

Previously published phosphonation method[1]



PPFS

PPTFS

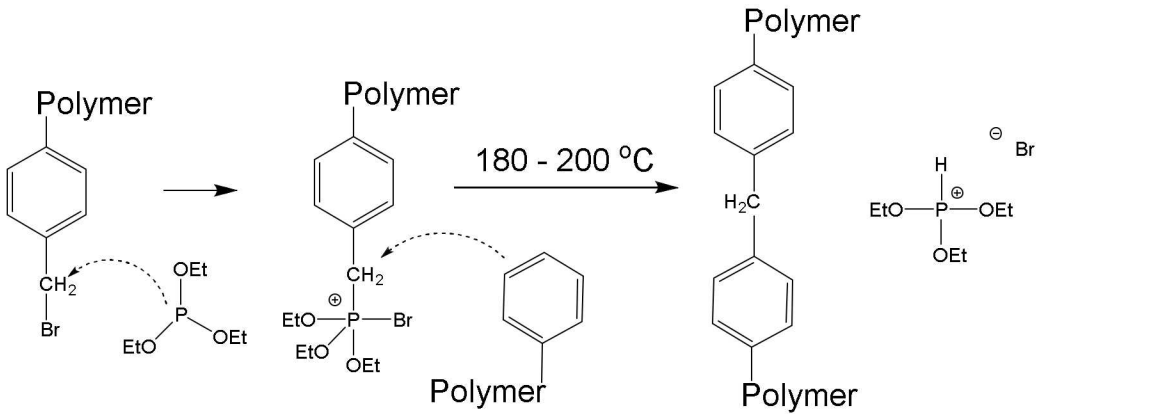


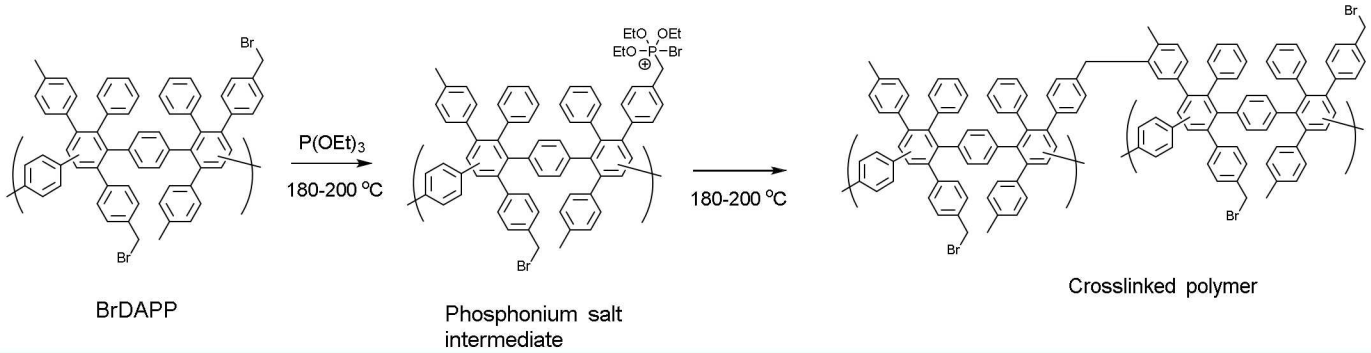
Product is insoluble

- Phosphonation of pentafluorophenyl groups on polystyrene has been reported.[1]
- Attempts to add trimethylsilylphosphite to pentafluorophenyl groups on DAPP have all led to insoluble products due to crosslinking or over-phosphonation.

[1]Atanasov, V.; Kerres, J. *Macromolecules* 2011, 44, 6416.

Synthesis: Possible Crosslinking Mechanism

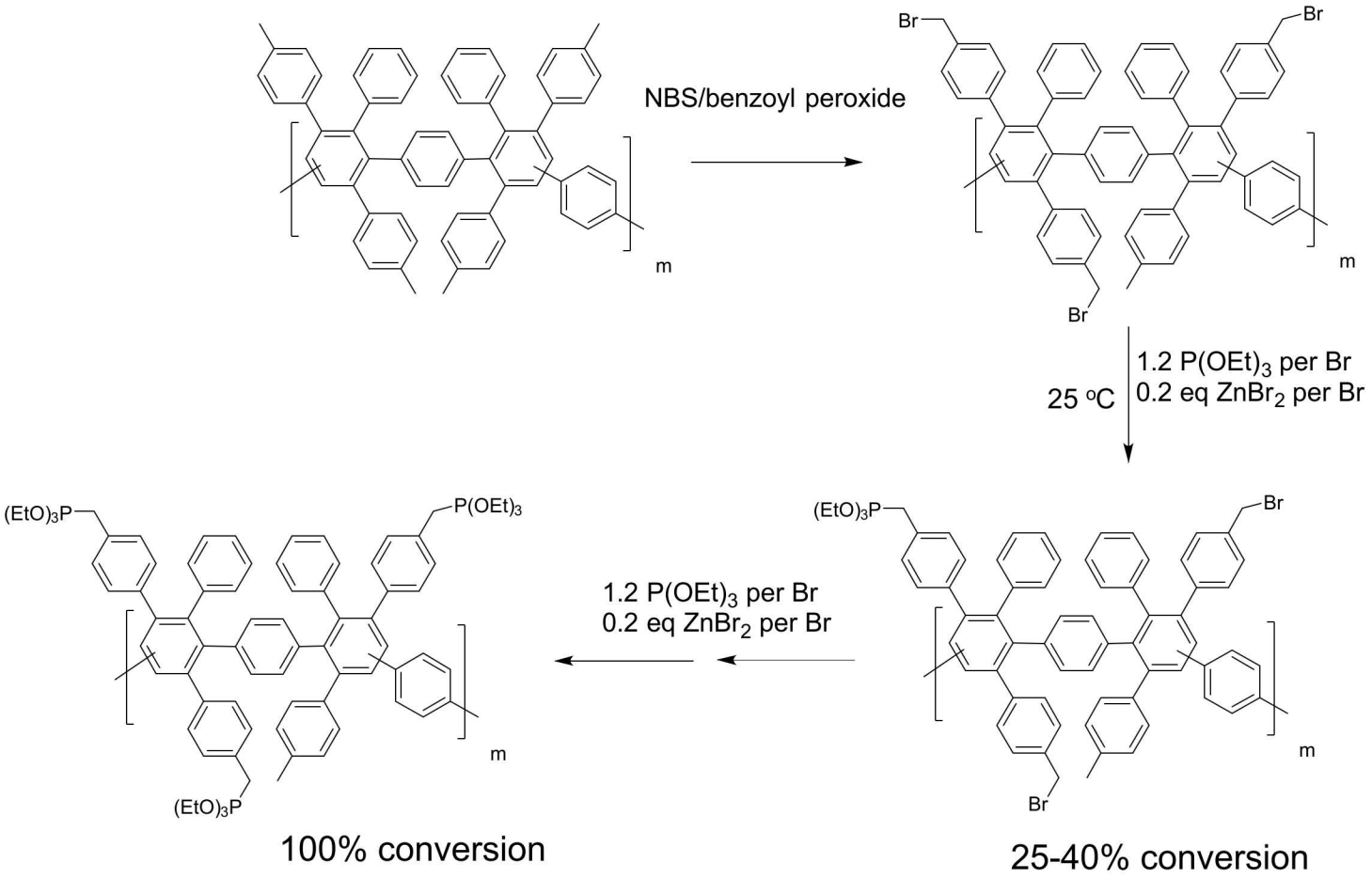




- The substitution reaction with triethylphosphite can lead to crosslinking.[1]
- BrTMPP can crosslink at elevated temperatures.
- Try to accomplish phosphonation under mild conditions to avoid crosslinking.

[1]Cabasso, I.; Jagur-Grodzinski, J.; Vofsi, D. *J. Appl. Polym. Sci.* 1974, 18, 1969.

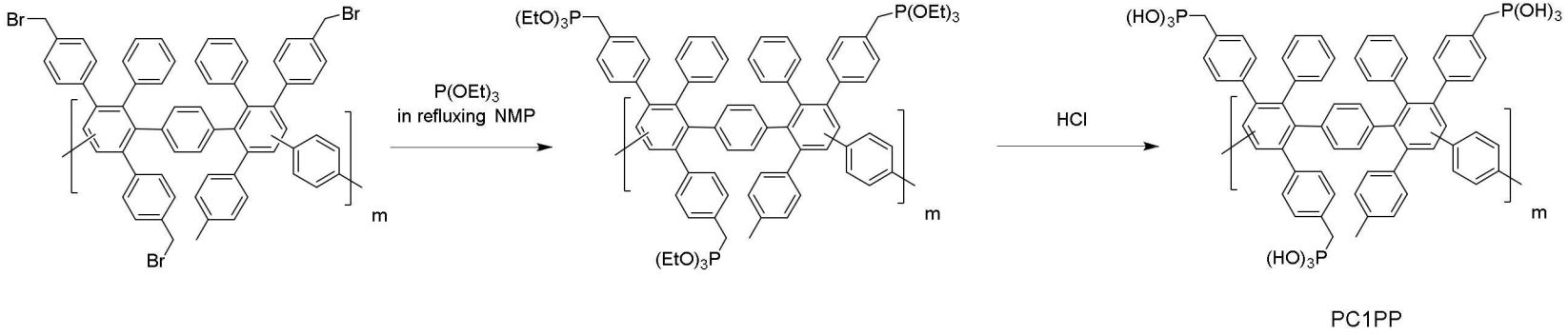
Synthesis: Low Temperature Phosphonation



- Low temperature phosphonation was successful but conversion was low.
- Complete conversion required many repeat steps.

[1]Rajeshwaren, G.G.; Nandakumar, M.; Sureshbabu, R.; Mohanakrishnan, A.K. *Org. Letters* 2011, 13, 1270.

Synthesis: Michaelis Arbuzov High Temperature Phosphonation



PC1PP

- High temperature reaction gives complete conversion with no evidence of crosslinking. The product is soluble in polar aprotic solvents.
- The deprotected product is ready to be tested as an ionomer.

Future Work

- Scale up synthesis of PC1PP ionomer.
- Synthesis of PC6PP and/or DAPP with pendant pentafluorophenyl groups.
- Measure membrane ASR in MEA with new ionomers.
- Measure catalytic activity with new ionomers.
- Optimize electrode structure using down-selected catalysts and ionomers.
- Low PGM fuel cell durability testing at 200 ^{o}C.

Acknowledgements

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