EFFECT OF BULKY CATIONS ON THE FUNCTION AND STABILITY OF ANION EXCHANGE MEMBRANES

by

Ye Liu
A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Chemical Engineering).

Golden, Colorado

Date _____________________

Signed: ___________________________

Ye Liu

Signed: ___________________________

Dr. Andrew M. Herring
Thesis Advisor

Golden, Colorado

Date _____________________

Signed: ___________________________

Dr. Matthew W. Liberatore
Thesis Advisor

Signed: ___________________________

Dr. David W.M. Marr
Professor and Head
Department of Chemical and Biological Engineering
ABSTRACT

A major advantage of alkaline fuel cells (AFCs), relative to well-established acidic fuel cells, is their enhanced reaction kinetics permitting the use of less costly, non-noble-metal catalysts. Developing anion exchange membranes (AEMs) for AFCs that are stable under high pH operating conditions is a significant challenge. Insufficient stability of the widely used quaternary ammonium (QA) cation is the main reason attenuate membranes lifetime. Ion conduction in AEMs is intrinsically slower than in proton exchange membranes is another factor impedes AEMs wide-scale application. Therefore, developing bulky cations with enhanced electronegativity and steric hindrance, and understanding the water/ion transport of the bulky cation functionalized AEMs were the focus of this thesis. In this work, three bulky cations attached to random copolymers were investigated in regard to OH\(^-\) stability, water absorption, morphology, ion conduction, and water transport.

A study of 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium functionalized polyphenylene oxide (PPO) indicated the attachment of 2,4,6-trimethoxyphenyl groups to unmodified imidazolium improved OH\(^-\) stability due to electron donating and bulk steric effect. Membranes with two ion exchange capacities (IECs) were studied showing high IEC sample (IEC=1.8 mmol/g) had a higher conductivity (23 mS/cm at 95% RH and 90°C) via increasing anion concentration. Different IECs also gave rise to membranes with different morphology and transport behavior.

Study on phosphonium cation attached by three hydrophobic 2,4,6-trimethoxyphenyl groups suggested a method to enhance chemical stability as well as reduce water uptake. In this section, different solvents selected by Hansen solubility parameter were used to maximize membrane phase separation. As expected, the optimal mixed solvent (DMSO: ethyl lactate by
41:59 vol%) cast membrane showed highest conductivity, and transports among membranes cast from different solvents are varied.

Cobaltocenium, with an 18 electron inert structure had highest chemical stability. By studying random and crosslinked membranes, we have obtained in-depth understanding of polymer configuration influence on membrane property. Crosslinked network impeded ion transport resulting in a smaller conductivity than random polymer. Also crosslinked membrane followed a water mediate transport instead of polymer chain movement dominated transport due to the crosslinked network hindered polymer chains movement.
# TABLE OF CONTENTS

ABSTRACT ................................................................................................................................ iii

LIST OF FIGURES ....................................................................................................................... ix

ACKNOWLEDGEMENTS .......................................................................................................... xv

CHAPTER 1 INTRODUCTION ................................................................................................ 17
  1.1 Alkaline Anion Exchange Membrane Fuel Cells (AAEMFCs) ........................................ 17
  1.2 Alkaline Stability of Anion Exchange Membranes (AEMs) ............................................. 19
    1.2.1 Backbone Stability .......................................................................................... 19
    1.2.2 Cation Stability ............................................................................................... 20
    1.2.3 Degradation Pathways for Quaternary Ammonium Cations ............................ 24
  1.3 Conductivity in Anion Exchange Membranes ............................................................... 26
  1.4 Thesis Statement ......................................................................................................... 27

CHAPTER 2 EXPERIMENTAL METHODS ........................................................................... 30
  2.1 Ion Exchange Capacity ............................................................................................... 30
  2.2 Water Uptake from Dynamic Vapor Sorption ............................................................ 30
  2.3 Morphology from Small Angle X-ray Scattering ....................................................... 31
  2.4 Free Diffusion from Pulse Gradient Stimulated Echo Nuclear Magnetic Resonance 32
  2.5 Conductivity from Electrochemical Impedance Spectroscopy ................................... 34

CHAPTER 3 ANION TRANSPORT IN A CHEMICALLY STABLE, STERICALLY BULKY α-C MODIFIED IMIDAZOLIUM FUNCTIONALIZED ANION EXCHANGE MEMBRANE ................................................................................ 37
  3.1 Abstract ....................................................................................................................... 37
  3.2 Introduction .................................................................................................................. 38
  3.3 Experimental ............................................................................................................... 41
    3.3.1 1,4,5-Trimethyl-2-(2,4,6-Trimethoxyphenyl) Imidazolium Functionalized PPO ................................................................. 41
3.3.2 Ion Exchange Capacity ................................................................. 42
3.3.3 Infrared Spectroscopy ................................................................. 42
3.3.4 Thermogravimetric Analysis ....................................................... 42
3.3.5 Dynamic Vapor Sorption ............................................................ 43
3.3.6 Small Angle X-ray Scattering ..................................................... 43
3.3.7 Microscopy ................................................................................. 44
3.3.8 Pulsed-Field Gradient Nuclear Magnetic Resonance ............... 44
3.3.9 Electrochemical Impedance Spectroscopy ................................. 45
3.3.10 Degradation Studies ................................................................. 46
3.3.11 Structural Modeling ................................................................. 46
3.4 Results and Discussion .................................................................. 46
3.4.1 Structure Verification ............................................................... 46
3.4.2 Chemical and Thermal Stability Studies ................................. 47
3.4.3 Water Sorption ........................................................................ 49
3.4.4 Morphological Studies ............................................................. 50
3.4.5 Water Self-Diffusion Inhibited in Polymer ............................... 54
3.4.6 Conductivity ............................................................................ 59
3.5 Conclusion ..................................................................................... 61
3.6 Acknowledgements ....................................................................... 62

CHAPTER 4  ANION EXCHANGE MEMBRANES COMPOSED OF A POLY(2,6-DIMETHYL-1,4-PHENYLENE OXIDE) RANDOM COPOLYMER FUNCTIONALIZED WITH A BULKY PHOSPHONIUM CATION ............ 63
4.1 Abstract ....................................................................................... 63
4.2 Introduction ................................................................................ 64
4.3 Experimental ............................................................................. 66
4.3.1 Materials .............................................................................. 66
4.3.2 Synthesis of Tris(2,4,6-trimethoxyphenyl) Phosphonium Functionalized Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO-TPQP) ........................................ 66

4.3.3 Membrane fabrication ..................................................................................... 67

4.3.4 Characterization .............................................................................................. 67

4.3.5 Structural modeling ........................................................................................ 69

4.4 Results and discussion ...................................................................................... 69

4.4.1 PPO-TPQP Synthesis and Structure ............................................................... 69

4.4.2 Chemical and Thermal Stability Studies ......................................................... 71

4.4.3 Solvent Selection Criteria ............................................................................... 73

4.4.4 Morphology and Water Uptake ...................................................................... 75

4.4.5 Self-Diffusion and Ionic Conductivity ........................................................... 81

4.4.6 Mechanical Property ....................................................................................... 89

4.5 Conclusions ....................................................................................................... 90

4.6 Acknowledgments .............................................................................................. 91

CHAPTER 5 PHYSICAL PROPERTIES OF RANDOM AND CROSSLINK PHENYLENE COBALTOCENIUM FUNCTIONALIZED ANION EXCHANGE MEMBRANES ............................................................. 93

5.1 Abstract ............................................................................................................. 93

5.2 Introduction ....................................................................................................... 93

5.3 Experimental .................................................................................................... 95

5.3.1 Materials ....................................................................................................... 95

5.3.2 Characterization .......................................................................................... 96

5.4 Results and Discussion .................................................................................... 97

5.4 Conclusion ....................................................................................................... 107

CHAPTER 6 SUMMARY AND CONCLUSIONS ..................................................... 108

CHAPTER 7 ONGOING AND FUTURE WORK ..................................................... 115
7.1.1 Materials ......................................................................................................................... 117

7.1.2 Synthesis of 1-hexyl-1-methylpiperidium Functionalized Triblock Copolymer ... 118

REFERENCES ........................................................................................................................... 123

COPYRIGHT PERMISSIONS ..................................................................................................... 139
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Schematic of an alkaline anion exchange membrane fuel cell</td>
<td>18</td>
</tr>
<tr>
<td>1.2</td>
<td>Cations have been used as the functional groups in anion exchange membrane electrolyte. (ammonium (a), pyridinium (b), phosphonium (c), sulfonium (d), guanidinium (e) imidazolium (f) and ruthenium (g))</td>
<td>20</td>
</tr>
<tr>
<td>1.3</td>
<td>Degradation routes of quaternization ammonium under alkaline condition [77]</td>
<td>25</td>
</tr>
<tr>
<td>2.1</td>
<td>Schematics of beams scattering against substance</td>
<td>31</td>
</tr>
<tr>
<td>2.2</td>
<td>Stimulated echo pulse sequence with the magnetic field gradient pulses</td>
<td>34</td>
</tr>
<tr>
<td>2.3</td>
<td>Schematic of four-electrode in-plane conductivity cell</td>
<td>34</td>
</tr>
<tr>
<td>2.4</td>
<td>Nyquist plot of an impedance loop with measured (blue) and fitting (red) data</td>
<td>35</td>
</tr>
<tr>
<td>3.1</td>
<td>Structure of 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium functionalized polyphenylene oxide</td>
<td>41</td>
</tr>
<tr>
<td>3.2</td>
<td>FTIR spectra of polyphenylene oxide and the 1,4,5-trimethyl-2-(2,4,6-trimethoxy phenyl) imidazolium functionalized polyphenylene oxides</td>
<td>46</td>
</tr>
<tr>
<td>3.3</td>
<td>IEC of 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium functionalized polyphenylene oxide (red) and unsubstituted imidazolium functionalized polyphenylene oxide (blue) during the alkaline stability test at 80°C in 1 M KOH</td>
<td>47</td>
</tr>
<tr>
<td>3.4</td>
<td>Thermal gravimetric analysis curve and derivative thermal gravimetric curve of 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium functionalized polyphenylene oxide</td>
<td>48</td>
</tr>
<tr>
<td>3.5</td>
<td>Water uptakes (solid) and hydration numbers (open) of 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium functionalized polyphenylene oxide. (PPO-TMIM-0.46, square; PPO-TMIM-0.33, diamond)</td>
<td>49</td>
</tr>
<tr>
<td>3.6</td>
<td>AFM tapping mode phase images of 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium functionalized polyphenylene oxide. (PPO-TMIM-0.46, (a) dry, phase scale=5° (b) wet, phase scale=20°; PPO-TMIM-0.33, (c) wet, phase scale=20°) Scan boxes are 500 nm × 500 nm</td>
<td>51</td>
</tr>
<tr>
<td>3.7</td>
<td>SAXS patterns of 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium functionalized polyphenylene oxide. (a) PPO-TMIM-0.33: dry, cross square; 25% RH, cross; 50% RH, diamond; 75% RH, triangle; 95% RH, square; soak,</td>
<td>47</td>
</tr>
</tbody>
</table>
Figure 3.8 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium optimized at the B3LYP /6-311G(2d,d,p) level of theory and basis set using the Gaussian 09 program.

Figure 3.9 Water self-diffusion coefficients of 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium functionalized polyphenylene oxide versus diffusion time. The measurement was taken under 80% RH at 25°C. (PPO-TMIM-0.33, square; PPO-TMIM-0.46, diamond)

Figure 3.10 Water self-diffusion coefficients of 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium functionalized polyphenylene oxide versus the square root of the diffusion time. (PPO-TMIM-0.33, square; PPO-TMIM-0.46, diamond)

Figure 3.11 Water self-diffusion coefficients of 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium functionalized polyphenylene oxide versus diffusion length. (PPO-TMIM-0.33, square; PPO-TMIM-0.46, diamond)

Figure 3.12 Visible microscope images of 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium functionalized polyphenylene oxide. ((a) PPO-TMIM-0.33, (b) PPO-TMIM-0.46)

Figure 3.13 Arrhenius plot of water self-diffusion coefficients under 80% RH. The measurements were performed at Δ=20 ms. (PPO-TMIM-0.33, square; PPO-TMIM-0.46, diamond)

Figure 3.14 Cl⁻ form conductivities of 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium functionalized polyphenylene oxide under 95% RH. (PPO-TMIM-0.33, square; PPO-TMIM-0.46, diamond)

Figure 4.1 Synthesis of tris(2,4,6-trimethoxyphenyl) phosphonium functionalized PPO

Figure 4.2 ¹H NMR spectrum of brominated poly(2,6-dimethyl-1,4-phenyloxide)

Figure 4.3 (a) ¹H NMR (b) ³¹P NMR: bottom, tris(2,4,6-trimethoxyphenyl) phosphine; top, the polymer after quaternization (c) ¹³C NMR (d) FTIR spectra of tris(2,4,6-trimethoxyphenyl) phosphonium functionalized PPO

Figure 4.4 Degradation study of benzyl tris(2,4,6-trimethoxyphenyl) phosphonium and benzyltrimethylammonium in 1 M KOD at 80°C

Figure 4.5 Thermal gravimetric analysis of tris(2,4,6-trimethoxyphenyl) phosphonium functionalized PPO
Figure 4.6   Images of membranes casted from DMSO (a), DMSO & ethyl lactate mix solvents (b) and ethyl lactate (c) ................................................................. 75

Figure 4.7   Light microscope images of PPO-TPQP-MIX. (Scale bar is 50 µm) ..................... 76

Figure 4.8   AFM tapping mode phase images of PPO-TPQP-DMSO (a), PPO-TPQP-MIX (b) and PPO-TPQP-Ethyl lactate (c). (Scan boxes are 500 nm × 500 nm) .......... 76

Figure 4.9   SAXS and zoom in SAXS spectra of PPO-TPQP-MIX (Figure 4.9 (a), (d)), PPO-TPQP-DMSO (Figure 4.9 (b), (e)) and PPO-TPQP-Ethyl lactate (Figure 4.9 (c), (f)). (0% RH, circle; 25% RH, square; 50% RH, triangle; 75% RH, inverted triangle; 95% RH, asterisk; soaked, diamond). ....................................................... 78

Figure 4.10  Tris(2,4,6-trimethoxyphenyl) phosphonium cation optimized at the B3LYP/ 6-311G(2d,d,p) level of theory and basis set using the Gaussian 09 program. .... 79

Figure 4.11  Water uptake (solid) and lambda value (open) of PPO-TPQP casted from different solvents. (PPO-TPQP-MIX, square; PPO-TPQP-DMSO, diamond; PPO-TPQP-Ethyl lactate, triangle). ........................................................................ 80

Figure 4.12  In-plane and through-plane swellings of PPO-TPQP casted from different solvents. ........................................................................................................ 81

Figure 4.13  Water self-diffusion coefficients of PPO-TPQP-DMSO, PPO-TPQP-MIX and PPO-TPQP-Ethyl lactate versus the square root of the diffusion time. (PPO-TPQP-DMSO, diamond; PPO-TPQP-MIX, square; PPO-TPQP-Ethyl lactate, triangle) ........................................................................ 82

Figure 4.14  Water diffusion coefficients of PPO-TPQP-DMSO (diamond), PPO-TPQP-MIX (square) and PPO-TPQP-Ethyl lactate (triangle) in terms of different temperature under 100% RH ......................................................................................... 84

Figure 4.15  Bromide conductivities of PPO-TPQP-DMSO (a), PPO-TPQP-MIX (b) and PPO-TPQP-Ethyl lactate (c) as a function of temperature under 95% RH (diamond) and 80% RH (square) ..................................................................................... 85

Figure 4.16  Comparison of conductivities between PPO-TPQP-MIX and random copolymer in reference papers (PPO-TPQP-MIX IEC=1.2 mmol/g, 95% RH, diamond; Poly (MMA-r-MEBIm-X) IEC=1.4 mmol/g, 90% RH [158], square; TMA functionalized random copolymer containing PPO and poly(2,6-diphenyl-1,4-phenylene oxide), IEC =0.9 (triangle), IEC=1.8 (circle), 95% RH [31]) ............... 85

Figure 4.17  Br⁻ diffusion coefficients of PPO-TPQP-DMSO (circle), PPO-TPQP-MIX (square) and PPO-TPQP-Ethyl lactate (triangle) under 95% RH as a function of temperature calculated from Nernst-Einstein equation. ........................................ 87
Figure 4.18 Conductivities of PPO-TPQP-DMSO (circle), PPO-TPQP-MIX (square) and PPO-TPQP-Ethyl lactate (triangle) as a function of humidity at 60°C. ...................... 89

Figure 4.19 Ratio of conductivity/lambda of PPO-TPQP-DMSO (diamond), PPO-TPQP-MIX (square) and PPO-TPQP-Ethyl lactate (triangle) in terms of relative humidity. ................................................................. 89

Figure 4.20 Tensile tests under both dry and hydrated conditions for tris(2,4,6-trimethoxyphenyl) phosphonium functionalized PPO. ........................................... 90

Figure 5.1 Structures of PNPCCI-r-PNBE (a) and PNPCCI-r-PDCPD (b). ......................... 96

Figure 5.2 Cyclic voltammetry of a phenylene cobaltocenium functionalized norbornene homopolymer solution (vs SHE)). .............................................................. 98

Figure 5.3 Thermal gravimetric analysis of phenylene cobaltocenium functionalized norbornene homopolymer. ................................................................................................................. 98

Figure 5.4 Water uptake (solid) and hydration number (open) of PNPCCI-r-PNBE (diamond) and PNPCCI-r-PDCPD (square) at different humidity levels. ................. 99

Figure 5.5 Conductivity of PNPCCI-r-PNBE (diamond) and PNPCCI-r-PDCPD (square) at 95% RH. ................................................................................................. 99

Figure 5.6 Water self-diffusion coefficients of PNPCCI-r-PNBE (diamond) and PNPCCI-r-PDCPD (square) versus the square root of the diffusion time......................... 101

Figure 5.7 Water diffusion coefficients of PNPCCI-r-PNBE (diamond) and PNPCCI-r-PDCPD (square) under 100% RH at different temperatures............................... 102

Figure 5.8 SAXS patterns of PNPCCI-r-PNBE (blue) and PNPCCI-r-PDCPD (red) at both dry (solid) and 95% RH (open). ................................................................. 103

Figure 5.9 Phenyl cobaltocenium cation optimized at the B3LYP/ 6-311G(2d,d,p) level of theory and basis set using the Gaussian 09 program................................. 104

Figure 5.10 TEM images of PNPCCI-r-PDCPD (a) and PNPCCI-r-PNBE (b). ..................... 104

Figure 5.11 Light microscope images of PNPCCI-r-PNBE (Scale bar is 50 µm) ............... 105

Figure 5.12 Alkaline stability of phenylene cobaltocenium (diamond) and trimethyl ammonium (square) cations at 80°C in 2 M KOH (CH₃OH:H₂O=9:1vol). ....... 105

Figure 5.13 OH⁻ conductivity of PNPCCI-r-PNBE (blue, diamond) at 90% RH and OH⁻ conductivity of PNPCCI-r-PDCPD (red, square) at 80% RH ....................... 106
Figure 6.1 Degradation studies performed at 80°C on 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium (solid diamond, 1 M KOH), tris(2,4,6-trimethoxyphenyl) phosphonium (solid square, 1 M KOH), phenylene cobaltocenium (solid triangle, 1 M NaOH/CH₃OH) and benzyl trimethyl ammonium (open square, 1 M KOH; open triangle, 1 M NaOH/CH₃OH). .......... 109

Figure 6.2 Thermal gravimetric analysis of 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium functionalized PPO (red), tris(2,4,6-trimethoxyphenyl) phosphonium functionalized PPO (green) and phenylene cobaltocenium functionalized norbornene (blue). .................................................................................................. 110

Figure 6.3 Water uptake (solid) and Lambda (open) of 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium functionalized PPO (blue, IEC=1.53, Cl⁻ form), tris(2,4,6-trimethoxyphenyl) phosphonium functionalized PPO (red, IEC=1.20, Br⁻ form), phenylene cobaltocenium functionalized norbornene (green, IEC=1.48, Cl⁻ form). ....................................................................................................... 111

Figure 6.4 Conductivity of 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium functionalized PPO (diamond, IEC=1.53, Cl⁻ form), tris(2,4,6-trimethoxyphenyl) phosphonium functionalized PPO (square, IEC=1.20, Br⁻ form), phenylene cobaltocenium functionalized norbornene (triangle, IEC=1.48, Cl⁻ form) and trimethyl ammonium functionalized AEMs (PPO-TMA[Br], IEC=1.84, asterisk; IEC=0.87, circle; ETFE-CMS-TMA [Cl], IEC=2.06, black circle; IEC=1.47, open circle) ............................................................................................................. 112

Figure 7.1 Synthesis of 6-piperidino-hexanol.......................................................................................................................... 118

Figure 7.2 Synthesis of 6-piperidino-hexoxy-PCMS-b-PCOE-b-PCMS. .......................................................... 119

Figure 7.3 Quaternization of 6-piperidino-hexoxy-PCMS-b-PCOE-b-PCMS into 1-methyl-1-hexoxypiperidium functionalized PCMS-b-PCOE-b-PCMS. ................................................. 120
LIST OF TABLES

Table 1.1  Diffusion coefficient for various monovalent ions in dilute aqueous solution at 25°C [79].

Table 3.1  Image J analysis of Feret diameters, SD of size distributions and RMS roughness of 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium functionalized polyphenylene oxide.

Table 3.2  Surface/volume ratio, $R_c$ and tortuosity for 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium functionalized polyphenylene oxides.

Table 3.3  Parameters of VTF regression of PPO-TMIM-0.46 on both conductivity and diffusion coefficients versus temperatures.

Table 4.1  Solubility of dissolving PPO-TPQl into different solvents.

Table 4.2  Hansen solubility parameters, $R_a$, RED of casting solvents (DMSO, Ethyl lactate, Mix solvent) and PPO-TPQl.

Table 4.4  Surface/volume ratio, $R_c$, tortuosity and $T_1$ of PPO-TPQP-DMSO, PPO-TPQP-MIX and PPO-TPQP-Ethyl lactate.

Table 4.5  Parameters of VTF regression of PPO-TPQP-DMSO and PPO-TPQP-Ethyl lactate on conductivity as well as diffusion coefficients versus temperatures.

Table 4.6  Parameters of Arrhenius fit of PPO-TPQP-MIX and PPO-TPQP-DMSO on conductivity as well as diffusion coefficients versus temperatures.

Table 5.1  Parameters of VTF regression on PNPCCl-r-PNBE from both conductivity and diffusion.

Table 5.2  Surface/volume ratio, $R_c$ and tortuosity for PNPCCl-r-PDCPD.
ACKNOWLEDGEMENTS

I’d like to express my gratitude to my thesis advisors, Dr. Andrew Herring and Dr. Matthew Liberatore. Thanks for your guidance and support during my research as well as the extra efforts and instructions on my writing. I would also like to thank Meichen Guo’s assistance on polymer synthesis and Jim Horan’s technical support on instrument maintenance, so that facilitate my research carrying out smoothly.

Many thanks go to PIs in the MURI team: Dr. Bryan Coughlin from University of Massachusetts Amherst, Dr. Yushan Yan from University of Delaware, Dr. Daniel M. Knauss from Colorado School of Mines, and Dr. Thomas A. Witten and Dr. Gregory A. Voth from University of Chicago for bringing out insightful questions and offering constructive suggestions in the teleconferences and annual meetings.

Many thanks also go to my group members, Ben Caire, Melissa Vandiver, Ashley Maes, Himanshu Sarode, Tara Pandey, Vinh Nguyen, Andrew Motz and Ashutosh Divekar for creating a pleasant atmosphere to work with. I thank my fellow MURI team members: Wenxu Zhang, Haomiao Yuan, Yifan Li, Yating Yang, Piril Ertem, Bingzi Zhang and Junhua Wang for their invaluable feedback and suggestions.

I would also like to thank my parents who have always supported, encouraged and believed in me. Special thanks go to my boyfriend for his gentle care on my daily living so that enables me to be focus on my research. I also would like to thank all my old and new friends stood by me through the good times and bad.

Finally, I want to thank the Army Research Office for support of this research under the MURI grant number #W911NF-10-1-0520 and the U.S. Department of Energy (DOE) Office for
support of the Argonne National Laboratory, Advanced Photon Source operation under Contract No. DE-AC02-06CH11357.
CHAPTER 1
INTRODUCTION

Fuel cells, directly convert chemical energy from a fuel into electrical energy with water and heat as by product. Fuel cells are primarily classified by the type of electrolyte as proton exchange membrane fuel cells (PEMFCs), alkaline fuel cells (AFCs), phosphoric acid fuel cells (PAFCs), molten carbonate fuel cells (MCFCs) and solid oxide fuel cells (SOFCs). PAFCs, SOFCs and MCFCs usually operate at high temperatures (PAFCs: 150~200°C; SOFCs and MCFCs: >500°C), while PEMFCs and AFCs operate below 100°C. PEMFCs as a low temperature fuel cell have been studied and developed due to their advantages of high conductivity and fast start-up time [1,2]. However, high manufacturing cost from using noble metal catalyst (typically platinum) in electrodes largely hampers their further commercialization.

1.1 Alkaline Anion Exchange Membrane Fuel Cells (AAEMFCs)

Reid invented AFCs in 1902 [3] and the National Aeronautics and Space Administration have employed them since mid-1960s in the U.S. space program. AFCs (Figure 1.1) may outperform all known low temperature fuel cells and are currently obtaining renewed attention [4]. In contrast to PEMFCs, with proton conducts along the polymer electrode, AFCs conduct hydroxide anions in a base electrolyte, which results in several advantages. (1) The oxygen reduction reaction (ORR) is much more facile in alkaline environments than in acidic environments, which enables the use of non noble metal catalysts [5]; (2) Improved oxygen reduction kinetics at cathode leads to a higher fuel cell efficiency up to 60%-70%; (3) The flexibility in terms of fuel and oxygen reduction reaction catalyst selection.
Figure 1.1 Schematic of an alkaline anion exchange membrane fuel cell.

The typical electrolyte used in AFC is concentrated alkaline aqueous solutions [3,6], which could react with CO$_2$ from the air [7,8]. Generated carbonate/bicarbonate solid would have lower ionic conductivity because the mobility of HCO$_3^-$ or CO$_3^{2-}$ is lower than that of OH$^-$; and also block the micro pores of the electrode and potentially damage the active layer [9]. An effective way to solve the carbonation issue is to replace the liquid alkaline electrolyte with a membrane-based alkaline electrolyte [10]. Anion exchange membranes (AEMs) are polymer electrolytes conducting OH$^-$ as they possess positively charged cationic groups covalently attached to a polymer backbone. These cationic groups can be inserted directly into the backbone or linked to the backbone via short or extended side chains. The application of AEMs not only keeps the advantage of liquid alkali electrolytes with high active reaction, but also helps to solve the problems of electrolyte leakage and component corrosion [11,12]. The primary requirements for AEM being used in AFC include: (1) excellent alkaline stability and thermal stability; (2) high hydroxide conductivity versus low electronic conductivity; (3) good mechanical strength

\[ \text{Anode: } H_2 + 2OH^- \rightarrow 2H_2O + 2e^- \]
\[ \text{Cathode: } O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \]
\[ \text{Overall reaction: } 2H_2 + O_2 \rightarrow 2H_2O + \text{electrical energy} + \text{heat} \]
and dimensional stability; (4) insoluble in fuel crossover [13]. Among all of these requirements, the major limitation of AEMs is the insufficient chemical stability under alkaline operating conditions [14,15]. According to the AFC-stack requirements, 8,000 operating hours without degradation or a decrease in efficiency should be fulfilled. For a large-scale steady-state application, an operating time of more than 40,000 hours is preferred when economically feasible. Another main limitation of AAEMFCs is the relative low conductivity compared with PEMFCs (70 mS/cm, 100% RH, 25°C) [16]. An efficient electrolyte transfer of the hydroxyl ions from cathode to anode needs to be developed in order to realize good fuel cell performance.

1.2 Alkaline Stability of Anion Exchange Membranes (AEMs)

A primary concern with the application of AEMs in electrochemical devices is their stabilities in alkaline medium. The membrane stability depends strongly on the nature of the backbone and the nature of functional groups.

1.2.1 Backbone Stability

Damage of the AEM backbone in OH\(^{-}\) is a critical issue, which would lead to a reduction of mechanical strength and conductivity. A wide range of chemistries is available to develop robust and alkaline stable polymer backbones. Backbones have been commonly used for AEMs include polyethylene [17,18], polyphenylenes [19-21], perfluorinated types [22-25] and those based on poly aromatic ethers, such as polysulfones [26-30], poly(phenylene oxides) [PPO] [31-39] and poly(ether ketones) [40-50]. Although polysulfones and fluorinated polymers have shown stability under basic conditions, recent studies revealed that aromatic ether-based backbones, such as polysulphone and PPO, functionalized with benzylic cations became brittle in base, which is due to the cation-triggered backbone degradation [20,51,52]. Backbone degradation has been reported for polyvinylidene fluoride (PVDF) and VDF containing
copolymers also. These polymers undergo a dehydrofluorination reaction in the basic medium, further leading to chain scission [53,54].

1.2.2 Cation Stability

Degradation of cationic groups is another main reason for the loss of functionality of AEMs. Most of the time, cationic groups are more vulnerable than the polymer backbone to OH\(^-\) attack. So far, in order to find out membranes with high stability, a number of different types of cations have been studied, including ammonium, pyridinium, phosphonium, sulfonium, guanidinium, imidazolium, ruthenium heterocycles (Figure 1.2).

![Cations](image)

Figure 1.2 Cations have been used as the functional groups in anion exchange membrane electrolyte. (ammonium (a), pyridinium (b), phosphonium (c), sulfonium (d), guanidinium (e) imidazolium (f) and ruthenium (g))

Quaternary ammonium is frequently used in AEMs due to the facile quaternization process. Investigation [55] of polysulfone based AEMs with diamines (\(N,N,N',N'\)-tetramethyl/metane/hexane/ethylene/butane/propane diammonium) showed that \(N,N,N',N'\)-tetramethyl hexanediammonium AEM had the highest stability and the longer the aliphatic chain length, the higher the membrane stability. A systematic stability study was performed on substitute (ethyl/n-
propyl/isobutyl/neopentyl) alkyltrimethylammonium cations in order to explore the effect of Hofmann elimination. Results indicated that the steric shielding of the β-hydrogen via the addition of methyl groups resulting in β-hydrogen reduction that largely improved the cation stability [56]. Stability study on the benchmark benzyl trimethylammonium (BTMA) cation revealed that BTMA has degraded 67% after soaking in 1 M NaOH/CH₃OH at 80°C for 20 days [57].

The stability of vinylpyridinium-co-divinylbenzene was compared to polyvinylbenzyltrimethyl ammonium. It was found that the IEC of vinylpyridinium-co-divinylbenzene decreased much faster than for poly-vinylbenzyltrimethyl ammonium after treatment in 5 M NaOH at room temperature for 12 days [14]. The study [58,59] of AEMs composed of various pyridinium derivative groups proved that pyridinium could be oxidized into pyridine in base and the chemical stability of pyridinium is too low to have application in AFCs [13].

A tris(2,4,6-trimethoxyphenyl) phosphonium functionalized AEM showed that the ionic conductivity could be maintained for 48 h when the membrane was immersed in either 10 M KOH at room temperature or in 1 M KOH at 60°C [60,61]. The stability of polysulfone functionalized with trimethyl phosphonium was compared to the polysulfone based trimethyl ammonium in KOH at 60°C [62]. The conductivities of the phosphonium functionalized AEMs decreased 49% and 67% in 1 M and 2 M KOH respectively, whereas the conductivities of the ammonium functionalized AEM only reduced 37% and 44% under the same conditions. More recently, a more stable tetrakis (dialkylamino) phosphonium, which could maintain stability for 20 days after soaking in 1 M NaOH at 80°C was developed [57]. Stability of AEMs with tetrakis
(dialkylamino) phosphonium was also studied. It was found the membrane could maintain stable for 22 days in 1 M KOH at 80°C or for 140 days in 15 M KOH at 22°C.

The sulfonium stability was investigated by Zhang et al. [63]. They claimed that even though trialkyl and arylalkyl functionalized sulfonium has been reported with lower chemical stability, it is still expected to have promising durability due to π-π conjugation, especially when these attached electron-donating groups help to delocalize the positive charge. They developed AEMs with diphenyl (3-methyl-4-methoxyphenyl) tertiary sulfonium and treated it in 1 M KOD at 60°C. The membrane still maintained its hydroxide conductivity after 10 days.

Guanidinium functionalized poly (arylene ether sulfone) [64] was put in 1 M NaOH at both 60°C for 48 h or at room temperature for 30 days, and there was no conductivity decrease under either condition.

A comparison between benzyltrimethylammonium and 1-benzyl-3-methylimidazolium with the same poly(ethylene-co-tetrafluoroethylene) (ETFE) backbone showed that imidazolium functionalized ETFE had lower chemical stability (1 M KOH solution under 60°C) compared with ammonium functionalized ETFE [65].

AEMs with ruthenium bis(terpyridine) complex cation, which was originally largely investigated in the photoelectronic field showed anion conductivities and mechanical properties comparable to traditional quaternary-ammonium-based AEMs. The ruthenium bis(terpyridine) complex cation exhibited excellent stability in 1 M NaOH solutions at room temperature over 6 months [66].

Besides varying the types of cations, modifying the cationic group structure is another method that has been shown to help improve the chemical stability of AEMs. Most recently,
typical cations bridged with long aliphatic chains have been shown to dramatically enhance the chemical stabilities of AEMs in base.

A poly(phenylene) tethered six-carbon spacer ammonium cationic polymer was compared to the stability of a similar AEM without the spacer chain [67]. Conductivities of the AEM without aliphatic chains decreased 33%, whereas the one with six-carbon spacers only decreased 5% after soaking the membrane in 4 M KOH solution at 90°C for 14 days.

Phosphonium bridged AEMs with different lengths of spacer chains were investigated in alkaline conditions at 90°C [68]. Three aliphatic chains ((CH₂)₇, (CH₂)₄ and (CH₂)) were compared. The result indicated that the longer the aliphatic chains, the higher the stabilities of the AEM. Therefore, (CH₂)₇ spacers phosphonium functionalized AEMs demonstrated the highest stability, while the one with (CH₂) spacer led to the lowest stability.

A poly(aryl ether sulfone) based hexaalkylguanidinium could maintain its ionic conductivity for 24 h after treated into 10 M NaOH solution at 25°C or 2 M NaOH solution at 80°C. In comparison, the commercially available membrane changed its color after merely 5 min by soaking in 1 M KOH [69].

The polyfluorene ionomers with two pendant (CH₂)₆ spacer imidazolium was treated in 1 M KOH solution under 60°C. Improved chemical stability was verified by NMR with no new peaks appear after 400 h [70].

Tomoi et al. [71] investigated on polyvinylbenzyl based ammonium polymer with two kinds of bridged spacer chains (alkylene, alkyleneoxy). They did a systematic work on spacer chain length influence by putting OH⁻ form of the polymer in demineralized water at 100°C for 30 days. For the alkylene spacer chain, the strong base capacity remaining ratio increased versus spacer chain length from CH₂ to (CH₂)₇, in which (CH₂)₆ exhibited highest remaining ratio. For
alkyleneoxy spacer chain (CH₂O(CH₂)n), the stability test was measured when n=3,4,6. When n=3, polymer stability was even less than polyvinyl benzyl trimethyl ammonium. When n=4 and n=6, the stability increased, however, n=6 had the highest remaining ratio of base capacity and, therefore, the highest stability.

Though many efforts have been made to increase AEM stability by varying cationic groups, it is difficult to make a solid comparison to the benchmark benzyl trimethylammonium (BTMA) since degradation tests have been performed under different conditions (different temperature, different base concentration). Also, selection of cationic groups need to consider from practical point of view like synthesis complexity, environmental effect and the cost. Generally, pyridinium, guanidinium, imidazolium and sulfonium did not show superiority or distinct superiority to BTMA. Tetrakis (dialkylamino) phosphonium cation [57] exhibited good durability under alkaline condition, but the complex synthesis process hinders its production into large scale. Similarly, the bis-terpyridine Ru complex [66], though showed promising OH⁻ stability, is expensive and harms environment. There is no further reports or publications either from the synthesis or from other groups. So far, long chain tethered cations have shown highly improved stability. The further work should aim at exploring stable cations and figuring out modification methods to increase cation stability, as well as manufacturing the stable cation into alkyl chain configuration.

1.2.3 Degradation Pathways for Quaternary Ammonium Cations

Figure 1.3 shows the main degradation routes of quaternary ammonium cation being attacked by OH⁻ groups. They are S_N2 reaction (nucleophilic substitution) [72], Hofmann elimination [73], Steven [74] and Sommelet-Hauser rearrangements [75], and ylide degradation [76].
Route (1) shows $S_N2$ reaction realized by $\text{OH}^-$ attack on $\alpha$-C position with final products of alcohol and amine. Possibility of $S_N2$ route compared with other degradation pathways is determined by both the stability of leaving groups and the polymer structure. Hofmann elimination is shown as Route (2). $\text{OH}^-$ attacks $\beta$ position hydrogen and quaternary ammonium group falls apart at the same time to generate amine and olefin. Hofmann elimination occurs when there is at least one $\beta$-hydrogen (the higher electron density at $\beta$-hydrogen, the more difficult of $\text{OH}^-$ to abstract the proton). For rearrangement reaction, the product of Steven
rearrangement of benzyltrimethylammonium is tertiary benzylamines that experienced by OH− attack on α proton. Only certain quaternary trimethylammonium cations follow Sommelet-Hauser rearrangement as shown in route (4). Steven rearrangement is more favored at the high temperature whereas Sommelet-Hauser rearrangement prefers to take place at the relative low temperature [77]. Besides the degradation routes mentioned above, there is another ylide intermediated process (route (5)) that leads to the same products with Sn2 reaction. A model study on tetramethylammonium hydroxide indicates that there are similar activation energy barriers between Sn2 and ylide routes [78].

### 1.3 Conductivity in Anion Exchange Membranes

The conductivity of anionic polymer electrolyte is a function of both concentration and mobility of OH− (equation (1.1)).

\[
\sigma_{\text{OH}^-} \propto \mu_{\text{OH}^-} C_{\text{OH}^-} \quad (1.1)
\]

where \(\sigma_{\text{OH}^-}\) is the OH− conductivity, \(\mu_{\text{OH}^-}\) is OH− mobility and \(C_{\text{OH}^-}\) is the OH− concentration. With fixed ion mobility, one strategy to increase the conductivity is to improve ion concentration by using AEMs with higher ion-exchange capacities (IECs, the number of cationic groups per unit mass of polymer). However, overly high IECs can cause excessive water uptake and dimensional swelling, damaging the AEMs mechanical strengths. Crosslinking is a commonly adopted solution to restrict membrane swelling. However, the intrinsic non-soluble nature of crosslinked polymer hinders the usage of the polymer as a soluble ionomer for polymer-impregnated porous electrodes in the membrane electrode assembly (MEA), which require a polymer solution with a low-boiling point water-miscible solvent. Therefore, another solution to improve conductivity is keeping the membrane with a moderate IEC, and increasing the effective mobility of OH−. OH− transport is intrinsically slower than H+ (Table 1.1). Diffusion coefficient
of OH\(^-\) in dilute aqueous solution at 25°C is about half of H\(^+\) diffusion since OH\(^-\) is larger. In AEMs, effective mobility of OH\(^-\) is even lower than that in dilute solutions due to OH\(^-\) transport have retarded by hydrophobic polymer framework resistance. Therefore, the development of phase-segregated AEMs containing hydrophobic phases interconnected with hydrophilic ionic clusters and channels is an efficient way to enhance the effective mobility of OH\(^-\). As mentioned above, the ionic conductivity is a comprehensive combination of different properties. Adequate water absorption facilitates anionic group transfer via sufficient anion hopping sites, but excess hydration level seriously decreases the membrane’s mechanical strength. Generation of phase separated AEMs still may have problem as to trade off with the other membrane properties as well as synthesis feasibility.

Table 1.1 Diffusion coefficient for various monovalent ions in dilute aqueous solution at 25°C [79].

<table>
<thead>
<tr>
<th>Ion</th>
<th>D (10(^{-5}) cm(^2) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(^+)</td>
<td>9.3</td>
</tr>
<tr>
<td>OH(^-)</td>
<td>5.3</td>
</tr>
<tr>
<td>HCO(_3)^-</td>
<td>1.2</td>
</tr>
<tr>
<td>NO(_3)^-</td>
<td>1.9</td>
</tr>
<tr>
<td>F(^-)</td>
<td>1.5</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>2.0</td>
</tr>
<tr>
<td>Br(^-)</td>
<td>2.1</td>
</tr>
</tbody>
</table>

1.4 Thesis Statement

Developing anion exchange membranes with stable cations is important. It is equally important to study morphological stability at different hydration levels and develop morphology-transport relationships. Central cations surrounded by electron donation functional groups are hypothesized to be more OH\(^-\) stable due to enhanced basicity and steric hindrance. Electron donating groups increase central cation electronegativity and prompt cation-anion dissociation.
Also, the physical size and proximity of the attached groups prevent OH$^-$ approaching to the central cation. Two models are commonly used in understanding the behavior of conductance in polymer electrolytes, they are Arrhenius behavior and Vogel-Tamman-Fulcher (VTF) behavior. Arrhenius behavior is explained by the dissociation of ionic pairs. VTF behavior has been explained on the basis of free volume theory. In this theory, the ionic transport mechanism in the membrane results from the polymer chain motion. Anion or water transport followed by the water mediated linear Arrhenius behavior is hypothesized would always faster than the transport followed by Vogel-Tammann-Fulcher (VTF) behavior.

This thesis focuses on the development of chemically durable AEMs with various bulky functional cations. Identifying the bulky cation’s influence via studying the interplay between polymer chemistry and water uptake, morphology, ionic conductivity and water transport. Specific objectives developed to understand bulky cation effect on stability and functions of anion exchange membranes are as follows. 1) Examine OH$^-$ stability by treating cations in hydroxide at elevated temperatures. 2) Study cation and polymer morphology across different length scales using experiments and simulations. 3) Understand ion and water transport in membranes by tuning the morphology cast from different solvents. 4) Study physical properties in terms of random and crosslink polymer configurations.

Chapter 2 explains characterization methods used for water absorption, morphology, conductivity and water transport studies. Chapter 3 describes a cation modification method as to improve the hydroxide stability by the attachment of electron donating trimethoxyphenyl as well as methyl groups on to imidazolium cation. Chapter 4 investigates properties of tris(2,4,6-trimethoxyphenyl) phosphonium functionalized PPO, focusing on casting by different solvents. Chapter 5 studies phenylene cobaltocenium functionalized AEMs exploring crosslinking effect
on membrane properties. Chapter 6 is the summary of studies on above bulky imidazolium,
phosphonium and cobaltocenium AEMs. Chapter 7 talks about our ongoing work that synthesis
of a hexylmethyl piperidium functionalized triblock AEM, which expects to exhibit improved
conductivity and chemical stability, and recommendations for future work.
CHAPTER 2

EXPERIMENTAL METHODS

2.1 Ion Exchange Capacity

Ion exchange capacity (IEC, in milli-mol per gram) is defined as the number of cationic groups per dry mass of polymer. Cl\(^-\) form membrane was titrated by using the Mohr method [80] using the following procedure: Cl\(^-\) form membrane was soaked in 1 M aqueous sodium nitrate for 24 h under room temperature to release Cl\(^-\) ions. The solution was titrated by standardized AgNO\(_3\) using K\(_2\)CrO\(_4\) as a colorimetric indicator. The weight of the membrane was recorded after dried in the vacuum oven at 60°C overnight. IEC was calculated as equation (2.1) since quantity of AgNO\(_3\) added is equal to the quantity of Cl\(^-\) after being ion exchanged by NO\(_3^-\).

\[
IEC = \frac{V_{AgNO_3} \times C_{AgNO_3}}{m_{dry}} \quad (2.1)
\]

where \(V_{AgNO_3}\) is the volume of standardized AgNO\(_3\) solution, \(C_{AgNO_3}\) is the concentration of standardized AgNO\(_3\) solution and \(m_{dry}\) is mass of the dry membrane.

2.2 Water Uptake from Dynamic Vapor Sorption

Water uptake of the membrane was tested by using of a SMS dynamic vapor sorption (DVS) instrument. Temperature and humidity are allowed to independently control in the sealed chamber, where an ultra sensitive microbalance was used to measure the sample weight as small amount as 1-30 mg. The sample after dried in the vacuum oven overnight was loaded in the glass sample pan. The gravimetric change in mass was measured under different humidity conditions. Relative humidity level was achieved by proportional mixture of dry nitrogen gas with and without water vapor controlled by mass flow meter. DVS measurement was performed at 60°C with two humidity cycles in the sequence of 0%, 20%, 40%, 60%, 80%, 95% then back to 0%. Each humidity stage stayed for 2 h and the equilibrium mass at end of each step was used to
calculate water uptake from the isotherm of mass variation versus relative humidity. Water uptake was calculated according to equation (2.2).

\[ WU(\%) = 100\% \times \frac{m_{RH} - m_{dry}}{m_{dry}} \]  \hspace{1cm} (2.2)

where \( m_{RH} \) is the mass of the sample under different relative humidities, \( m_{dry} \) is the mass of the sample under 0% RH.

Hydration number \( \lambda \), which indicates the number of water molecules per cationic group, was calculated as given by equation (2.3).

\[ \lambda = \frac{WU}{M_{H_2O} \times IEC} \]  \hspace{1cm} (2.3)

where \( M_{H_2O} \) is the molecular weight of water, IEC is the ion exchange capacity of the sample.

### 2.3 Morphology from Small Angle X-ray Scattering

Small angle X-ray Scattering (SAXS) is an analytical technique to determine the structure of organic/inorganic materials. It is non-destructive and usually requires only a small amount of sample preparation. SAXS is applied for structure detection with the dimension on the order of nm to 100 nm corresponding to scattering angle in the range of 0.1° to 10° [81]. When a beam of X-ray irradiates on the sample, part of the beam has been absorbed while the other part has been scattered by electrons. Scattering vector, \( q \), expressed as scattering beam, \( k_s \), minus incident beam, \( k_i \) (Figure 2.1 (a)) related to scattering angle, \( 2\theta \), as given in equation (2.4).

![Figure 2.1 Schematics of beams scattering against substance.](image)

\[ q = k_s - k_i \]  \hspace{1cm} (2.4)
\[ |q| = |k_s - k_i| = \frac{4\pi}{\lambda} \sin \theta \] (2.4)

where \( q \) is the scattering vector, \( k_s \) and \( k_i \) are scattering beam and incident beam, respectively, \( \lambda \) is the X-ray wavelength and \( 2\theta \) is the scattering angle. Bragg’s law (Figure 2.1 (b)), relates practical domain size (d spacing) to scattering angle as given in equation (2.5).

\[ \lambda = 2d \cdot \sin \theta \] (2.5)

Therefore, d spacing is inversely proportional to scattering vector as shown in equation (2.6) that larger scattering angle and larger q range correspond to small d spacing and vice versa.

\[ d = \frac{2\pi}{|q|} \] (2.6)

Small angle X-ray scattering (SAXS) experiment was performed at Advanced Photon Source (APS), Argonne National Laboratory on beamline 12ID-B. The beam wavelength is \( \lambda = 0.886 \) Å and beam exposure time were set for 1 seconds with an energy \( E = 14 \) keV. 2-dimensional scattering patterns were collected simultaneously with a 25×29 cm² area Pilatus 2M detector. The one dimension intensity versus q range plot was azimuth averaged from 2 D scattering pattern. The data were converted to a differential cross section.

A custom-made four-sample oven helped to control humidity and temperature. One slit was taken as the blank background while the other three slits were mounted with samples. Experiments were measured at 60°C with varied humidity levels. For each humidity step, at least 20 minutes were used to keep the sample to equilibrate after changing the humidity. The soaked sample was immersed in DI water for 24 h before the measurement.

2.4 Free Diffusion from Pulse Gradient Stimulated Echo Nuclear Magnetic Resonance

The self-diffusion coefficient was obtained by using of pulse gradient stimulated echo nuclear magnetic resonance (PGSE-NMR) technique. A pulse gradient stimulated echo (PGSTE) sequence, which composes of three \( \pi/2 \) radio frequency (rf) pulses with two rectangular gradient
pulses is shown in Figure 2.2. The $\pi/2$ rf pulse is applied to rotate the magnetization from z-axis into the x-y plane. During the first $\pi/2$ period, a gradient pulse with duration $\delta$ is applied so that generates a phase shift of the spins. The second $\pi/2$ rf pulse flips the transverse magnetization into the longitudinal direction. A second gradient pulse is further applied after the third $\pi/2$ rf. If the spins do not undergo any diffusion along with z direction, the effects of the two applied gradient pulses cancel and all spins refocus. On the contrary, if the spins have moved, the dephasing lead to an attenuation of spin echo signals, which is proportional to the displacement along the gradient [82]. Therefore, the position of the spin could be well defined so that further reveals the diffusion information. The diffusion coefficient could be expressed as Stejskal-Tanner equation [83,84] given in equation (2.7) when the transportation only related with z direction.

$$\frac{A(g)}{A(0)} = \exp(-\gamma^2 g^2 \delta^2 t_d D)$$

where $A(g)$ is echo amplitude, $A(0)$ is amplitude of the spin-echo signal in the absence of pulsed field gradient, $\gamma$ is gyromagnetic ratio, $g$ is amplitude of field gradient pulse, $\delta$ is duration of the field gradient pulse, $t_d$ is diffusion time ($t_d = \Delta - \delta/3$, where $\Delta$ is the time interval between the gradient pulses) and $D$ is self-diffusion coefficient.

Self-diffusion coefficient was obtained by using a Bruker AVANCEIII NMR spectrometer with a 5 mm Bruker single-axis DIFF60L Z-diffusion probe. Pulsed-field gradient varied into 16 steps. The NMR frequency was 400 MHz and data was analyzed by using of Bruker TopSpin software. NMR tube was prepared by rolling a piece of membrane into a 5 mm tube. On the bottom of the tube was filled with DI water or salt solution, which provide varied humidity level. Membrane was loaded isolated above the DI water in order to prevent free water influence when the membrane touching with DI water.
Figure 2.2 Stimulated echo pulse sequence with the magnetic field gradient pulses.

2.5 Conductivity from Electrochemical Impedance Spectroscopy

In-plane conductivity measurements were carried out by using a four-electrode cell, which composes two pieces of teflon blocks sandwiched platinium wires electrodes in the middle (Figure 2.3). Membrane was mounted perpendicularly in touch with the four electrodes, which connected to a VMP3 multichannel potentiostat.

Conductivity equals the reciprocal of resistivity, which is proportional to the resistance and cross section of the membrane, while inversely proportional to the length of the membrane.

Figure 2.3 Schematic of four-electrode in-plane conductivity cell.
From which relation, in-plane conductivity could be calculated from dimensions and resistance of the membrane as shown below.

\[
\sigma = \frac{L}{R \cdot W \cdot t}
\]  

(2.8)

where \(L\) is the distance between two electrodes, \(W\) and \(t\) are width and thickness of the membrane, respectively. \(R\) is the resistance that obtained from electrochemical impedance spectroscopy (EIS). The Nyquist plot (Figure 2.4) of imaginary impedance (capacitor) as a function of real impedance (resistor) shows the electrochemical impedance corresponding to frequency response over a range from \(0.4 \text{ to } 10^5\) Hz. Typical Nyquist impedance exhibits a regular semi circle with x axis indicating membrane and charge transfer resistance. Therefore, the intercept at lower frequency side was used to determine the total resistance.

![Figure 2.4 Nyquist plot of an impedance loop with measured (blue) and fitting (red) data.](image)

TestEquity oven is a well-insulated chamber enables independently control of humidity and temperature during data acquisition. Humidity level can be set in the range of 0% RH to 100% RH, while temperature can reach up to 120°C. The TestEquity oven maintains each test
condition for 16 loops (set 4 mins each loop), with the first 8 loops for membrane equilibration and the last 8 loops used to analyze resistance and averaged for conductivity.
CHAPTER 3

ANION TRANSPORT IN A CHEMICALLY STABLE, STERICALLY BULKY $\alpha$-C MODIFIED IMIDAZOLIUM FUNCTIONALIZED ANION EXCHANGE MEMBRANE

This chapter is modified from a paper published in

*Journal of Physical Chemistry C*

Ye Liu$^2$, Junhua Wang$^3$, Yuan Yang$^4$, Thomas M. Brenner$^5$, Sörenke Seifert$^6$, Yushan Yan$^7$, Matthew W. Liberatore$^8$, and Andrew M. Herring$^9$

3.1 Abstract

The morphology and anion transport of an $\alpha$-C modified imidazolium functionalized anion exchange membrane, 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium functionalized polyphenylene oxide (with ion exchange capacity = 1.53 or 1.82 mmol/g), were studied in detail. The novel cation is less susceptible to OH$^-$ attack (0% degradation) compared to unsubstituted imidazolium functionalized polyphenylene oxide (25% degradation) after 24 h at 80$^\circ$C in 1 M KOH. The two different IEC materials (with the same protected cation) show interesting differences in membrane performance. The lower IEC sample showed a smaller tortuosity and thus, needs a longer diffusion time for the water molecules to be fully hindered inside the hydrophobic clusters, which was confirmed by water self-diffusion measurements from pulsed field gradient NMR. From conductivity and diffusion measurements, the higher IEC sample exhibited Vogel-Tammann-Fulcher behavior, indicating the polymer chain’s movement

---

$^1$ Reprinted with permission of the Journal of Physical Chemistry C, 2014, 118(28), 15136-15145
$^2$ Primary author and researcher
$^3$ Co-author, postdoctoral scholar
$^4$ Co-author, NMR specialist
$^5$ Co-author, postdoctoral scholar
$^6$ Co-author, beamline scientist, Argonne National Laboratory
$^7$ Co-author, professor, University of Delaware
$^8$ Co-author, associate professor, University of Toledo
$^9$ Author for correspondence, professor, Colorado School of Mines
dominates the transport. However, the lower IEC sample exhibited the linear Arrhenius behavior signifying water-mediated transport. The maximum Cl\(^{-}\) conductivity observed was 23 mS/cm at 95\% RH and 90°C.

3.2 Introduction

Advanced anion exchange membranes (AEMs) have the potential to enable new electrochemical devices based on catalysis in alkaline media such as fuel cells or electrolyzers [85]. However, little is known about transport in these newer materials [86]. Alkaline fuel cells (AFCs) have been widely investigated since the 1960s [13]. The perceived advantages of alkaline electrolytes (e.g., KOH solution) used in AFCs include the applications of non precious metal catalysts and increased fuel flexibility [87,88]. However, the use of liquid alkaline electrolytes have disadvantages such as maintaining containment of the electrolyte, component corrosion, and reaction with CO\(_2\) to form insoluble carbonates that block the electrodes, which must be scrubbed, necessitating the use of pumps and dramatically lowering system power density [72]. There is currently great interest in using AEMs in electrochemical devices; the elimination of the liquid electrolyte increases system simplicity, and dramatically higher power densities can be achieved [11,12].

Two limitations of AEMs must be overcome to enable practical applications: their inherent low conductivity (compared to proton exchange membranes) and the chemical stability of the organic cations that are susceptible to nucleophile attack by hydroxide in the operating device [14,15]. A large number of new chemistries have been proposed to overcome the two issues of needing high ionic conductivity and chemical stability. However, in order to design next generation AEMs we must correlate the cation chemistry with other membrane properties, e.g. anion and water transport, morphology, water absorption, in order to better understand the
performance of the AEM [89-91]. Simple quaternary ammonium cations have been studied extensively as they provide good model systems and in certain membranes have been shown to have adequate stability, but they do not provide a route to the thousands of hours of transient operation required in many real devices [56,92]. Various 2nd generation cations have been proposed for enhanced chemical stability including phosphonium [57,60], pyridinium [93], sulfonium [63], imidazolium [65,94], guanidinium [64] and complex metal cations, e.g. (bis-terpyridine Ru) [66]. Of particular interest are the imidazolium functionalized AEMs, which provide the following potential benefits: 1) Conjugated structures generated from five heterocyclic rings help to delocalize positive charges, thus preventing nucleophilic attack by OH$^{-}$ through Hofmann or S$\text{N}_2$ elimination [95]. 2) Imidazolium functionalized membranes may more favorably generate phase-separated morphologies [96]. 3) Imidazolium chemistry avoids the negative environmental effects of using trimethylamine. 4) The imidazolium cation is thermally more stable than the ammonium cation [97].

To date studies on imidazolium functionalized AEMs have largely focused on conductivities, lifetime under alkaline conditions and the degradation mechanisms [65,94,98-101]. Zhang et al. [101] and Guo et al. [94] investigated AEMs with the same imidazolium cation but different polymer backbones (polysulfone, PSf-ImOH; poly(styrene-co-butyl methacrylate), PS-co-PBMA-Im). The chemical stabilities under alkaline conditions differ greatly. PSf-ImOH degrades in 3 M NaOH solution under 60°C after 24 h, whereas PS-co-PBMA-Im is stable even after 120 h in 6 M NaOH under 80°C. Thus, it has been proposed that imidazolium cation degradation is related to the membrane’s backbone structure. The conductivity of PSf-ImOH is 16.1 mS/cm in water at 20°C when IEC = 1.39 mmol/g, while the conductivity for PS-co-PBMA-ImOH is 33.3 mS/cm at 30°C with an IEC = 0.217 mmol/g. Also,
Deavin et al. [65] made a comparison of benzyltrimethylammonium and 1-benzyl-3-methylimidazolium cationic groups with the same poly(ethylene-co-tetrafluoroethylene) (ETFE) backbone. The imidazolium functionalized ETFE has similar conductivity (the $\text{HCO}_3^-$ conductivity increases from 16 mS/cm to 25 mS/cm from 30°C to 60°C respectively with an IEC = 1.8 mmol/g) and lower chemical stability (1 M KOH solution under 60°C) compared with the ammonium functionalized ETFE. More recently, Page et al. [100] modified the imidazolium cation by attaching a methyl group on the carbon in the middle of two nitrogen (α-C) with the same AEM membrane. The conductivity was similar to the unmodified material (the $\text{HCO}_3^-$ conductivity increases from 17.4 mS/cm to 27 mS/cm over the temperature range 30 - 60°C), but the chemical stability did improve, however it was still lower than the ammonium functionalized AEM. The degradation of the imidazolium cation under alkaline condition follows a ring-opening route by nucleophilic attack of OH$^-$ groups on the α-C [95,98]. Therefore, the α-C position on the imidazolium cation is considered to be an effective location for modification. More research is still needed on α-C functional group replacement [98,102].

To date, it is not known how a sterically bulky cation will affect the transport and morphological properties of an AEM. In this work we investigate a 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium functionalized PPO (PPO-TMIM) (Figure 3.1). This sterically bulky cation was chosen because it was expected to have greater stability based on the contribution of the electron donating methyl groups as well as the α-C increased steric effect. OH$^-$ has the highest intrinsic diffusion coefficient of the common anions used in AEMs. However, investigating the OH$^-$ form of an AEM is often inconvenient, as ambient carbon dioxide (at publication time, 400 ppm) will react with the OH$^-$ to form a mixture of $\text{CO}_3^{2-}$ and $\text{HCO}_3^-$ in the film. In this study, we investigated the films with Cl$^-$ anions, as a surrogate for
hydroxide as the films were supplied in the chloride form. We have recently shown that heavier halogen anions will enhance the transport of lighter halogen anions [103] and so we chose not to attempt to exchange the film for fluoride, which is more similar in size to hydroxide, as we did not want to risk studying a poorly characterized mixture of anions. However, we anticipate that the water-mediated transport of Cl\(^-\) in these films is still relevant to a general mechanism of anionic conductivity.

In this paper, the chemical stability of the substituted imidazolium cation functionalized polymer under alkaline conditions was compared to the unsubstituted imidazolium functionalized PPO (PPO-IM). We also studied the morphology of the materials under different humidity conditions and further correlated this with transport behavior. The water diffusion was rationalized in terms of the conductivity, and the potential of the material as an AEM was evaluated.

![Structure of 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium functionalized polyphenylene oxide.](image)

**Figure 3.1** Structure of 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium functionalized polyphenylene oxide.

### 3.3 Experimental

#### 3.3.1 1,4,5-Trimethyl-2-(2,4,6-Trimethoxyphenyl) Imidazolium Functionalized PPO

1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium functionalized polyphenylene oxide (PPO-TMIM) was synthesized according to the literature [104]. The materials were in two
imidazolium cation functionalization degrees, 33% and 46%, PPO-TMIM-0.33 and PPO-TMIM-0.46, with calculated IECs of 1.53 and 1.82 mmol/g respectively. An equivalent polymer with an unsubstituted imidazolium cation, PPO-IM, had a calculated IEC = 2.20 mmol/g.

3.3.2 Ion Exchange Capacity

The ion exchange capacity (IEC) was measured by titrating the Cl\(^-\) form of the membrane using the Mohr method [80]. IEC was calculated from equation (3.1). The quantity of AgNO\(_3\) added is equal to the quantity of Cl\(^-\) after being ion exchanged by NO\(_3^-\).

\[
\text{IEC} = \frac{V_{\text{AgNO}_3} \times C_{\text{AgNO}_3}}{m_{\text{dry}}} \quad (3.1)
\]

where \(V_{\text{AgNO}_3}\) is the volume of standard AgNO\(_3\) solution consumed, \(C_{\text{AgNO}_3}\) is the concentration of standard AgNO\(_3\) solution and \(m_{\text{dry}}\) is the mass of the dry membrane.

The theoretical IEC was calculated by using of the number of fixed ionic groups in a repeating unit divided by the molecular weight of a repeating unit [105].

3.3.3 Infrared Spectroscopy

Fourier transform infrared spectroscopy (FTIR) was recorded on a Nicolet Nexus 470 spectrometer with an attenuated total reflectance (ATR) accessory containing a diamond crystal. Spectra were obtained in the range of 500 cm\(^{-1}\) to 4000 cm\(^{-1}\), with 256 scans and a resolution of 8 cm\(^{-1}\).

3.3.4 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was carried out using a SSC/5200 SII analyzer controlled by a TGDTA Measure thermal analysis station. Typically 10 mg samples were loaded into a platinum pan. Measurements were performed at a heating rate of 10 °C /min from 25°C to 800°C under a nitrogen atmosphere.
3.3.5 Dynamic Vapor Sorption

Water uptake was measured at 60°C with different humidity levels. Samples were first kept at 0% RH for 8 h, then the humidity was increased in the sequence; 20%, 40%, 60%, 80%, 95% and then deceased to 0% with the same humidity steps. Each humidity condition was held for 2 h and the cycle was run twice. The equilibrium mass at the end of each step was used to calculate the water uptake from the isotherm of mass versus relative humidity. The water uptake was calculated according to equation (3.2).

\[ WU(\%) = 100\% \times \frac{m_{\text{RH}} - m_{\text{dry}}}{m_{\text{dry}}} \]  

(3.2)

where \(m_{\text{RH}}\) is the mass of the sample under different relative humidity and \(m_{\text{dry}}\) is the mass of the sample under 0% RH.

The hydration number, \(\lambda\), representing the number of water molecules per cationic group was calculated from equation (3.3).

\[ \lambda = \frac{WU}{M_{\text{H}_2\text{O}} \times \text{IEC}} \]  

(3.3)

where \(M_{\text{H}_2\text{O}}\) is molar mass of water.

3.3.6 Small Angle X-ray Scattering

Small angle X-ray scattering (SAXS) was performed at the Advanced Photon Source (APS), Argonne National Laboratory on beamline 12ID-B. The beam wavelength was \(\lambda = 0.886\) Å, with an exposure time of 1 s, and an energy of \(E = 14\) keV. Two-dimensional scattering patterns were collected simultaneously with a 25×29 cm² area Pilatus 2M detector. The one dimensional intensity versus q plot was azimuth averaged from the 2D scattering pattern for the SAXS in the range of 0.003 Å⁻¹ < q < 0.5 Å⁻¹, where \(Q=4\pi\lambda^{-1} \sin(\theta)\). The data were converted to a differential cross section.
A custom-made four-sample oven was used to control both humidity and temperature [106]. The oven had Kapton™ windows. One slot was left blank and used as the background, while the other three sample slots contained membrane samples. Experimental data was measured from 0% RH to 95% RH as well as soaked condition. For each humidity step, 20-40 minutes were used for equilibration and for soaked condition, membrane was immersed in DI water for 24 h before measurements.

### 3.3.7 Microscopy

Atomic Force Microscopy (AFM) images were taken in tapping mode using a Bruker Nanoscope III instrument with high-aspect ratio 225 µm cantilever tips (Nanoworld NCLR). Analysis was performed using Nanoscope 5.30r1 software. The dry sample was evacuated in a vacuum oven overnight at room temperature. The wet sample was treated in DI water for 24 h, and then imaged immediately under ambient conditions.

Micron scale morphologies of the membranes were acquired using a Thermo Fisher Nicolet iN10 microscope. The image was collected in transmission mode on the membrane soaked in DI water for 24 h under room temperature.

### 3.3.8 Pulsed-Field Gradient Nuclear Magnetic Resonance

$^1$H self-diffusion coefficients were obtained by use of pulse gradient stimulated echo nuclear magnetic resonance (PGSE-NMR) on an AVANCEIII NMR spectrometer with a 5 mm Bruker single-axis DIFF60L Z-diffusion probe. The pulsed field gradient at 25°C was varied from 0 G/cm to 128 G/cm over 16 randomized steps. The NMR frequency was 400 MHz and data was analyzed with Bruker TopSpin™ software. The decay of signal intensity could be expressed with the Stejskal-Tanner equation [83,84] given in equation (3.4) when the transport was only related within the z direction.
\[ \frac{A(g)}{A(0)} = \exp(-\gamma^2 g^2 \delta^2 t_d D) \]  

(3.4)

A(g) - echo amplitude  
A(0) - amplitude of the spin-echo signal in the absence of pulsed field gradient  
\( \gamma \) - gyromagnetic ration  
g - amplitude of field gradient pulse  
\( \delta \) - duration of the field gradient pulse  
t\(_d\) - diffusion time ( \( t_d = \Delta - \delta/3 \), where \( \Delta \) is the time interval between the gradient pulses)  
D - self-diffusion coefficient

The membrane sample was wound into a complete sealed 5 mm tube above a salt solution at the bottom providing 80% RH. Experiment was performed at 80% RH from 26°C to 45°C.

### 3.3.9 Electrochemical Impedance Spectroscopy

In-plane anionic conductivity was calculated by use of electrochemical impedance spectroscopy (EIS) based on the measurement of the ionic resistance [107]. The Randle’s equivalent electrical circuit was used to fit measured Nyquist Plot. The intercept at the lower frequency was used to determine the total ionic resistance. The frequency range was from 0.4 to \( 10^5 \) Hz with a fixed voltage magnitude of 10 mV. The membrane was mounted in a four-electrode cell connected to a BioLogic VMP3 multichannel potentiostat. The conductivity was calculated from the equation shown below.

\[ \sigma = \frac{1}{RS} \]  

(3.5)

where \( \sigma \) is conductivity (S/cm), \( R \) is resistance (\( \Omega \)), \( S \) is cross section area of the membrane (cm\(^2\)) and \( l \) is length of the membrane tested between two electrodes (cm).

An environmental chamber (TestEquity) was used to control both humidity and temperature during the experiment. The measurements were performed from 50°C to 90°C under 95% RH. Each testing condition ran for 16 loops with the first 8 loops for membrane equilibration and the last 8 loops for data analysis.
3.3.10 Degradation Studies

Chemical stability measurements were performed by treating PPO-TMIM and PPO-IM in 1 M potassium hydroxide solution at 80°C. The degradation of cationic groups were determined in terms of the IEC based on the titration of Cl⁻ form membranes as described above in section 3.3.2.

3.3.11 Structural Modeling

1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium cation structure was optimized by using density functional theory (DFT) at the B3LYP/6-311G(2d,d,p) level of theory and basis set using the Gaussian 09 program [108].

3.4 Results and Discussion

3.4.1 Structure Verification

Figure 3.2 FTIR spectra of polyphenylene oxide and the 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium functionalized polyphenylene oxides.

Comparison of FTIR spectra of polyphenylene oxide (PPO), PPO-TMIM-0.33 and PPO-TMIM-0.46 are shown in Figure 3.2. Both PPO-TMIM-0.33 and PPO-TMIM-0.46 display additional peaks at 1584 cm⁻¹, 1410 cm⁻¹, 1159 cm⁻¹ and 1126 cm⁻¹ when compared to the base
PPO. The 1584 cm$^{-1}$ and 1126 cm$^{-1}$ peaks are ascribed to C=N and C-N stretching, respectively, while the peaks at 1410 cm$^{-1}$ and 1159 cm$^{-1}$ are assigned to the imidazole ring asymmetric stretch and C-H vibrations [65,109].

3.4.2 Chemical and Thermal Stability Studies

![Figure 3.3 IEC of 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium functionalized polyphenylene oxide (red) and unsubstituted imidazolium functionalized polyphenylene oxide (blue) during the alkaline stability test at 80°C in 1 M KOH.](image)

We compare the chemical stability of the modified and unsubstituted imidazolium functionalized PPO polymers shown in Figure 3.3. Initial measured IECs of PPO-TMIM-0.46 and PPO-IM were 2.0 and 1.9 mmol/g. After 24 h of hydroxide treatment at 80°C, the IEC of PPO-TMIM was unchanged from the initial value, whereas the IEC of PPO-IM had decreased by 25%. It is possible that the minimum value of the IEC is the true value for the degraded film and that the gradual recovery of the IEC is due to entrapped salt that can not be easily washed from the film, nethertheless the PPO-IM polymer is clearly quite unstable under the test conditions. Other AEMs recently reported also display this degradation phenomenon [62]. The enhanced basicity of the modified imidazolium due to the electron donating methyl and trimethoxyphenyl
groups as well as the static effect from the large trimethoxyphenyl group efficiently prevent nucleophilic OH$^-$ attack on the α-C position as compared to the unsubstituted imidazolium cation. This improved long term stability of PPO-TMIM was also demonstrated by Wang [104] under the same degradation conditions.

Figure 3.4 Thermal gravimetric analysis curve and derivative thermal gravimetric curve of 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium functionalized polyphenylene oxide.

Thermal gravimetric analysis and derivative of the thermal gravimetric curves for PPO-TMIM-0.33 are shown in Figure 3.4. The TGA measurements have three weight loss regions corresponding to the highest weight loss rates at ca. 50°C, 240°C and 392°C. The first mass loss stage corresponds to water losses of ca. 5%. The second weight loss with the onset decomposition temperature at 217°C attributes to the nucleophilic attack of chloride anions through a $S_N2$ reaction to the 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium cation [97,110]. This onset decomposition temperature is higher than quaternary ammonium or the unmodified imidazolium cation [101]. The third region of mass loss results from the
decomposition of the PPO aromatic chains [96]. Both the chemical and thermal stabilities of this AEM, PPO-TMIM, confirm a promising application in AFCs.

3.4.3 Water Sorption

Water sorption of PPO-TMIM-0.33 and PPO-TMIM-0.46 are 17% and 22%, respectively, corresponding to $\lambda$ of 6 and 7 measured at 60°C and 95% RH (Figure 3.5). $\lambda$ for PPO-TMIM-0.33 and PPO-TMIM-0.46 are almost the same at 40% RH while only with 10% different at 95% RH. Water sorption of both PPO-TMIM-0.33 and PPO-TMIM-0.46 at ambient humidity are slightly lower than the TGA weight losses (PPO-TMIM-0.33 and PPO-TMIM-0.46 weight losses are 5% and 6%) from bound water. The reason is due to the small amount of bound water left when drying the sample in the DVS at low temperature for the purpose of preventing sample damage.

![Figure 3.5 Water uptakes (solid) and hydration numbers (open) of 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium functionalized polyphenylene oxide. (PPO-TMIM-0.46, square; PPO-TMIM-0.33, diamond)](image-url)
3.4.4 Morphological Studies

The DVS data, discussed above, reveals water sorption of PPO-TMIM-0.46 is 5% higher in absolute value and 30% higher in relative value than PPO-TMIM-0.33 at 95% RH. This leads to observable differences in the membrane morphologies. The effects of water sorption on the morphology are exhibited in AFM phase-contrast images in Figure 3.6. Figure 3.6 (a) shows that membrane is homogeneous when dry. After absorbing water, the membrane clearly shows the formation of clusters, which are likely due to hydrophilic and hydrophobic groups aggregation as shown in Figure 3.6 (b, c). Care must be taken in the interpretation of the phase contrast in these images. Previous reports on related AEMs have suggested that regions of lower phase (dark regions) correspond to hydrophilic domains, while regions with higher phase (bright regions) correspond to hydrophobic domains [96,111]. However, the slope of any morphological features contributes directly to the phase, due to the finite response time of the instrument feedback loop [112]. Thus, the dark regions at the cluster boundaries have been significantly influenced by the abrupt changes in morphology observed in the height images. The data is therefore used in conjunction with the SAXS data described below to confirm the cluster size.

The Root Mean Square (RMS) roughness of wet PPO-TMIM-0.46 is 3.53 nm while that of wet PPO-TMIM-0.33 is 2.21 nm, indicating that the clusters are taller in PPO-TMIM-0.46. Both wet films are significantly rougher than the dry PPO-TMIM-0.46 film, which has an RMS roughness of 1.37 nm. By using Image J to analyze the bright domain sizes (Table 3.1), it was found that PPO-TMIM-0.46 embraces a more even distribution with 30 (SD, 10) nm average Feret diameter compared to a smaller 25 (SD, 13) nm average Feret diameter of PPO-TMIM-0.33. Thus, the wet PPO-TMIM-0.46 material forms larger volume clusters than the wet PPO-TMIM-0.33 material.
Figure 3.6 AFM tapping mode phase images of 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium functionalized polyphenylene oxide. (PPO-TMIM-0.46, (a) dry, phase scale=5° (b) wet, phase scale=20°; PPO-TMIM-0.33, (c) wet, phase scale=20°) Scan boxes are 500 nm × 500 nm.

Table 3.1 Image J analysis of Feret diameters, SD of size distributions and RMS roughness of 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium functionalized polyphenylene oxide.

<table>
<thead>
<tr>
<th>sample designation</th>
<th>average of Feret diameters (nm)</th>
<th>standard deviations (SD) of size distribution (nm)</th>
<th>RMS roughness</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPO-TMIM-0.33</td>
<td>25</td>
<td>13</td>
<td>2.21</td>
</tr>
<tr>
<td>PPO-TMIM-0.46</td>
<td>30</td>
<td>10</td>
<td>3.53</td>
</tr>
</tbody>
</table>

SAXS (Figure 3.7) was used as a method for detecting the average phase morphology of the bulk materials [113,114]. Based on monitoring bulk morphology variations along with humidity, it is noticed that there is no long range ordered configuration (e.g. lamellae) exhibited owing to the random copolymer structure, unlike a typical block copolymer, which embraces long regular alternating junctions that probably enable a highly ordered configuration from the hydrophobic and hydrophilic domain arrangement [90,115]. However, some ionomer patterns designated from the q range around 0.2 Å\(^{-1}\) are exhibited. The large full width at half maximum (FWHM) of the ionomer peaks again indicates a weak long-range order of the structure.
Figure 3.7 SAXS patterns of 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium functionalized polyphenylene oxide. ((a) PPO-TMIM-0.33: dry, cross square; 25% RH, cross; 50% RH, diamond; 75% RH, triangle; 95% RH, square; soak, circle. (b) PPO-TMIM-0.46: dry, circle; 25% RH, triangle; 95% RH, square; soak, cross).

This ionomer pattern becomes more irregular when the humidity increases from 0% RH to 95% RH but is rearranged into a more ordered configuration again by soaking the membrane in water. The new ionomer peak with an improved scattering intensity moves towards a smaller q range after soaking the membrane in water because of the expanded ionomer domain sizes. The 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium cation size was calculated by the Gaussian 09 program (Figure 3.8). Dimensions from different configurations are between 6-12 Å, which is smaller than the d-spacing of ionomer peaks (31 Å in SAXS), which composes of ionic group as well as water molecules.
The differences between PPO-TMIM-0.33 and PPO-TMIM-0.46 are illustrated by the scattering slope variation at the q range of 0.003-0.02 Å⁻¹ from dry to wet condition. For the low IEC sample, the Porod slope increases from 3.1 to 3.6 when the humidity changes from 0 to 95% RH indicating an increase in symmetry; while the observation for the high IEC sample is contrary, with a scattering slope decreases from 3.6 to 3.0 as the particle configuration loses its symmetry. Moreover, comparing SAXS patterns between PPO-TMIM-0.46 and PPO-TMIM-0.33 under high humidity conditions, a new shoulder can be seen with the d spacing in the range of 10 nm - 32 nm, which corresponds to the uniformly distributed clusters of PPO-TMIM-0.46 observed in AFM (Figure 3.6 (b)). Both the shoulder and ionomer domain-length scales from SAXS are consistent with the bright and dark dimensions shown in AFM as quantified by Image J.
3.4.5 Water Self-Diffusion Inhibited in Polymer

The PGSE-NMR technique was used to add further insight into the overall transport properties and relate this to the membrane morphology. In restricted diffusion, the time-dependent region engages interactions of water molecules with membrane walls, while in the time-independent region all the diffusion is fully hindered inside the membrane walls and achieves $D_\infty$ [116]. Therefore, diffusion at different time intervals between gradient pulses are determined by the complexity of the membrane and it in turn reflects the anisotropy of the membrane.

Figure 3.9 Water self-diffusion coefficients of 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium functionalized polyphenylene oxide versus diffusion time. The measurement was taken under 80% RH at 25°C. (PPO-TMIM-0.33, square; PPO-TMIM-0.46, diamond)

Figure 3.9 shows the diffusion coefficient as a function of the evolution time in the PFG NMR experiment. Diffusion coefficients of both PPO-TMIM-0.33 and PPO-TMIM-0.46 decline along with the diffusion time indicating a restricted diffusion. The nano-scale morphology shown in AFM and SAXS gives rise to a weak diffusion dependence (slopes are $-2E-06$ cm$^2$/s$^2$ for PPO-TMIM-0.33, $-5E-06$ cm$^2$/s$^2$ for PPO-TMIM-0.46) as a result of the tortuosity of the membrane.
D\textsubscript{\infty} of PPO-TMIM-0.33 and PPO-TMIM-0.46 are 1.3 \times 10^{-6} \text{ cm}^2/\text{s} and 1.0 \times 10^{-6} \text{ cm}^2/\text{s}, respectively, when full geometrical restriction is achieved.

The Mitra equation \cite{19, 116} shown in equation (3.6) is used to further analyze the influence of the membrane morphology on the diffusion properties. This provides insights into phase complexities such as the overall size under which water molecules move freely or the tortuous ion conducting pathways in the membrane. Furthermore, the diffusion coefficient D\textsubscript{0}, when only Brownian motion occurs, can be obtained from extrapolation of D to t\textsubscript{d}=0.

\[
D = D_0\left[1 - \frac{4}{9\sqrt{\pi}} \cdot \frac{S}{V} \cdot \sqrt{D_0 \cdot t_d}\right] \tag{3.6}
\]
where S/V is the surface-to-volume ratio of the porous material.

![Figure 3.10](image)

Figure 3.10 Water self-diffusion coefficients of 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium functionalized polyphenylene oxide versus the square root of the diffusion time. (PPO-TMIM-0.33, square; PPO-TMIM-0.46, diamond)

From Figure 3.10, D\textsubscript{0} of PPO-TMIM-0.46 and PPO-TMIM-0.33 calculated according to equation (3.6) are 1.4 \times 10^{-6} \text{ cm}^2/\text{s} and 1.6 \times 10^{-6} \text{ cm}^2/\text{s}, respectively, which are lower than the bulk water diffusion coefficient of 2.3 \times 10^{-5} \text{ cm}^2/\text{s} at 25°C \cite{89}. The nanometer-scale clusters
observed in SAXS and AFM make water transport in the hydrophilic domains at $t_d=0$ much slower than the bulk water transport, which is due to the effect from the hydrated polymeric environment inside the channels [117].

S/V in the Mitra equation can be obtained from the slope in Figure 3.10. $R_c$, the reciprocal of S/V, is a critical parameter that designates the structure length scale within which intra-domain transport is dominant [118,119]. From Table 3.2, we observed that $R_c$ of both PPO-TMIM-0.46 and PPO-TMIM-0.33 are much larger than cluster sizes shown in AFM and SAXS. By comparing $R_c$ values between PPO-TMIM-0.46 and PPO-TMIM-0.33, it is noticed that even though PPO-TMIM-0.33 embraces a lower water uptake, $R_c$ of PPO-TMIM-0.33 is still larger than that of PPO-TMIM-0.46. The tortuosity of the membrane is calculated from equation (3.7) [120].

$$D_\infty = D_0 \alpha^{-1}$$  \hspace{1cm} (3.7)

where $\alpha$ is the tortuosity. From Table 3.2, the tortuosity of PPO-TMIM-0.33, calculated by equation (3.7), is smaller than that of PPO-TMIM-0.46. Smaller tortuosity designates a less morphological barrier for transport. The smaller cluster sizes of PPO-TMIM-0.33 observed in AFM give rise to more junctions of dark domains so that promote transport pathway connections. Hence, PPO-TMIM-0.33, which embraces a smaller tortuosity, makes itself into a larger critical length scale and possesses a weaker dependence on diffusion time, even though it has a lower water uptake.

The diffusion length, which relates the diffusion coefficient, $D$, to the diffusion time, $t_d$, is calculated according to equation (3.8) [121].

$$<a^2>^{1/2} = \sqrt{2Dt_d}$$  \hspace{1cm} (3.8)
where \(<a^2>^{1/2}\) is the diffusion length. By plotting the diffusion coefficient versus diffusion length (Figure 3.11), the fully restricted domain size is observed when the diffusion coefficient levels off. We noticed that fully restricted length scales of PPO-TMIM-0.33 and PPO-TMIM-0.46 are 6.3 \(\mu\text{m}\) and 3.4 \(\mu\text{m}\), respectively, which are in line with the \(R_c\) values, 6.7 \(\mu\text{m}\) of PPO-TMIM-0.33 and 2.6 \(\mu\text{m}\) of PPO-TMIM-0.46, obtained from Mitra equation. Thus, the length scale of intra-domain transport of water molecules extends into the micron scale.

![Figure 3.11: Water self-diffusion coefficients of 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium functionalized polyphenylene oxide versus diffusion length. (PPO-TMIM-0.33, square; PPO-TMIM-0.46, diamond)](image)

Table 3.2: Surface/volume ratio, \(R_c\) and tortuosity for 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium functionalized polyphenylene oxides.

<table>
<thead>
<tr>
<th>sample designation</th>
<th>S/V ((\mu\text{m}^{-1}))</th>
<th>(R_c) ((\mu\text{m}))</th>
<th>tortuosity ((\alpha))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPO-TMIM-0.33</td>
<td>0.15</td>
<td>6.7</td>
<td>1.18</td>
</tr>
<tr>
<td>PPO-TMIM-0.46</td>
<td>0.39</td>
<td>2.6</td>
<td>1.47</td>
</tr>
</tbody>
</table>
We used visible microscopy to verify that the membrane had morphological features on the micron scale (Figure 3.12). Both PPO-TMIM-0.33 and PPO-TMIM-0.46 display small circular patterns ca. 5 µm and larger black dots at ca. 10-15 µm. These micron order of magnitude lengths and nanoscale domains shown in SAXS and AFM compose a hierarchical structure. Thus, the interconnected hydrophilic channels facilitate water-molecule transport into a larger length scale (on the micron scale, Figure 3.12) beyond the dimensions observed in SAXS and AFM (on the nanometer scale).

The self-diffusion coefficients of water for the two polymers as a function of temperature are shown in Figure 3.13. Both PPO-TMIM-0.46 and PPO-TMIM-0.33 diffusion coefficients increase along with temperature. The low IEC sample shows a linear relationship with an $E_a$ of $7±0.3$ kJ/mol, while the high IEC sample displays a non-linear, convex, super-Arrhenius behavior. The membrane with higher water uptake, PPO-TMIM-0.46, shows a larger diffusion coefficient at higher temperature (above 40°C), which is in line with the conductivity result in Figure 3.14, even though the water diffusion does not necessarily exhibit a linear relation or proportionality to conductivity [89].
Figure 3.13 Arrhenius plot of water self-diffusion coefficients under 80% RH. The measurements were performed at $\Delta=20$ ms. (PPO-TMIM-0.33, square; PPO-TMIM-0.46, diamond)

### 3.4.6 Conductivity

The Cl$^-$ form conductivities of PPO-TMIM-0.46 and PPO-TMIM-0.33, under 95% RH at 90°C, are 23 mS/cm and 16 mS/cm respectively (Figure 3.14) and are comparable with other imidazolium functionalized AEMs [65,94,100,101]. The Arrhenius plot of PPO-TMIM-0.33 exhibits a linear behavior from 50°C to 90°C, indicating a water mediated vehicle mechanism. $E_a$ of PPO-TMIM-0.33 is $15 \pm 2$ kJ/mol which is slightly lower than other imidazolium AEMs [94],[122]. The Nernst-Einstein equation [123] (equation (3.9)) is used to distinguish the conducting mechanism through the comparison of water diffusion coefficients from PFG NMR with calculated Cl$^-$ diffusion coefficients.

$$D = RT \frac{\kappa}{cz^2F^2} \quad (3.9)$$

where $D$ is the diffusion coefficient, $\kappa$ is the conductivity, $c$ is the concentration of anionic groups in the membrane, $z$ is the ionic charge, $F$ is the Faraday constant, $R$ is the gas constant and $T$ is the temperature. The Cl$^-$ diffusion coefficient of PPO-TMIM-0.33, calculated based on
equation (3.9) is $1.55 \times 10^{-6}$ cm$^2$/s, which is smaller than the water diffusion coefficient, $1.77 \times 10^{-6}$ cm$^2$/s, under 45°C and 80% RH. Therefore, the Cl$^-$ diffuses slower than water via the vehicle mechanism, because solvated Cl$^-$ is larger than the water molecules. Applying the same calculation on PPO-TMIM-0.46, the Cl$^-$ diffusion coefficient is $1.56 \times 10^{-6}$ cm$^2$/s, which is also smaller than the water diffusion coefficient, $1.82 \times 10^{-6}$ cm$^2$/s. However, the conductivity of PPO-TMIM-0.46 membrane, exhibits a super Arrhenius behavior similar to that of the water diffusion.

We can fit both the ionic conductivity and water diffusion data for the high IEC polymer to the Vogel-Tammann-Fulcher (VTF) equation shown below [124-127].

$$
\sigma(T) = \sigma_0 \exp \left(-\frac{b}{T-T_0}\right), \quad D(T) = D_0 \exp \left(-\frac{b}{T-T_0}\right)
$$

(10)

where $\sigma_0$ and $D_0$ are the conductivity and diffusion coefficients at infinite temperature, $b$ is a constant related to the entropic barrier to free volume creation, $T_0$ is the temperature at which the mobility of ions and the conductivity drop to zero. Based on the three-parameter fit by using of Mathematica (Table 3.3), $T_0$ fit from PFG NMR water diffusion coefficient and EIS Cl$^-$ conductivity are similar, ca. 240 K which is nominally considered 50K lower than the $T_g$ of the material [128,129]. We assign this to the $T_b$, 290K, of the hydrophilic phase. $b$ value obtained from conductivity of 132K is higher than that obtained from water diffusion of 100K, indicating Cl$^-$ is energetically less mobile than H$_2$O in the channel. The maximum conductivity, $\sigma_0$, is calculated to be 0.075 S/cm; and water diffusion coefficient, $D_0$, calculated to be $7.1 \times 10^{-6}$ cm$^2$/s which is an order of magnitude smaller than for free water at room temperature, $2.3 \times 10^{-5}$ cm$^2$/s, again indicative of the highly hindered transport in these polymers.
Figure 3.14 CI⁻ form conductivities of 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium functionalized polyphenylene oxide under 95% RH. (PPO-TMIM-0.33, square; PPO-TMIM-0.46, diamond)

Table 3.3 Parameters of VTF regression of PPO-TMIM-0.46 on both conductivity and diffusion coefficients versus temperatures.

<table>
<thead>
<tr>
<th>VTF regression</th>
<th>$\sigma_0$ (S/cm), $D_0$ (cm$^2$/s)</th>
<th>b (K)</th>
<th>$T_0$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>conductivity</td>
<td>0.075</td>
<td>132</td>
<td>238</td>
</tr>
<tr>
<td>diffusion coefficient</td>
<td>$7.1 \times 10^{-6}$</td>
<td>100</td>
<td>244</td>
</tr>
</tbody>
</table>

3.5 Conclusion

In this study, a novel 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium functionalized PPO polymer was studied. The increased electron donating and steric hindrance of the cation enhanced the chemical durability compared to the unsubstituted imidazolium functionalized PPO. In addition, the PPO-TMIM polymers have good thermal stabilities. From AFM, the membrane exhibited a homogeneous morphology under dry conditions, compared to a phase separation in the humidified films. The average Feret diameters of clusters of PPO-TMIM-0.33 and PPO-TMIM-0.46 were 25 nm and 30 nm, respectively, analyzed by Image J. The domain sizes in AFM corresponded to the d spacing (3 nm and 10-32 nm) displayed in the SAXS.
patterns. Transport studies showed a high dependency on the morphology of the membrane. Free water diffusion coefficients in the polymers were ca. $1.5 \times 10^{-6}$ cm$^2$/s that is, smaller than the diffusion in bulk water due to restrictions from hydrophobic framework.

Larger IEC membrane (PPO-TMIM-0.46) displayed a higher conductivity of 23 mS/cm in Cl$^-$ form at 95% RH and 90°C. Interestingly the lower IEC membrane (PPO-TMIM-0.33) exhibited Arrhenius behavior following a vehicle mechanism in its transport properties, whereas the high IEC polymer showed super Arrenhius behavior, which could be fit to a VTF model as the ion transport was facilitated by the movement of the cationic side chains in the hydrophilic phase. As the content of the large cation is increased in the hydrophilic channels the ions clearly do not move in a fully dissociated manner un-influenced by the cation chemistry.

3.6 Acknowledgements

The authors thank the Army Research Office for support of this research under the MURI grant number #W911NF-10-1-0520. The Advanced Photon Source operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory, was support by the U. S. DOE under Contract No. DE-AC02-06CH11357. We also thank James L. Horan and Tara P. Pandey for the help with visible microscopy measurement.
CHAPTER 4

ANION EXCHANGE MEMBRANES COMPOSED OF A POLY(2,6-DIMETHYL-1,4-PHENYLENE OXIDE) RANDOM COPOLYMER FUNCTIONALIZED WITH A BULKY PHOSPHONIUM CATION

This chapter is modified from a paper published in

*Journal of membrane science*

Ye Liu², Bingzi Zhang³, Corey L. Kinsinger⁴, Yuan Yang⁵, Soenke Seifert⁶, Yushan Yan⁷, C. Mark Maupin⁸, Matthew W. Liberatore⁹, and Andrew M. Herring¹⁰

4.1 Abstract

A random copolymer, tris(2,4,6-trimethoxyphenyl) phosphonium functionalized poly(2,6-dimethyl-1,4-phenylene oxide) (PPO-TPQP) was cast from three different solvents: dimethyl sulfoxide (DMSO), ethyl lactate and 41:59 vol% mixture of DMSO and ethyl lactate. Solvents were selected via analysis of Hansen solubility parameters. An optimized mixture of DMSO and ethyl lactate chosen for film fabrication, which was contrasted with films cast from the neat constituent solvents. Atomic force microscopy identified more domains from nanometer to tens of nanometer sizes, while the light microscope show patterns on the order of micron. SAXS spectra revealed a cation scattering peak with a d-spacing from 7 to 15 Å. Trends in conductivity and water diffusion for the membranes cast from different solvents are different.

---

¹ Reprinted with permission of the Journal of Membrane Science, 2016, 506, 50-59
² Primary author and researcher
³ Co-author, Ph.D. researcher
⁴ Co-author, Ph.D. candidate
⁵ Co-author, NMR specialist
⁶ Co-author, beamline scientist, Argonne National Laboratory
⁷ Co-author, professor, University of Delaware
⁸ Co-author, assistant professor, Colorado School of Mines
⁹ Co-author, associate professor, University of Toledo
¹⁰ Author for correspondence, professor, Colorado School of Mines
The mix solvent cast membrane shows a linear Arrhenius behavior implicating a fully dissociated cation/anion groups, and has the highest conductivity of 3 mS/cm at 95% RH, 90°C. The ethyl lactate cast membrane follows the linear Arrhenius relation in conductivity, while showing VTF behavior in water self-diffusion. While water increases bromide dissociation, water and bromide transport in these films seems to be decoupled. This is particularly true for the film cast from ethyl lactate.

4.2 Introduction

Anion exchange membranes (AEMs) exhibit potential for a large variety of processes, such as mass separation (electrodialysis, filtration, water purification) [58,130], chemical synthesis (electrolysis) [131], and energy conversion and storage (fuel cells and advanced batteries) [12,13,132]. In all of these processes, the cationic groups attached to the polymer backbone control the transport of the anionic species [133]. However, many AEMs are not chemically stable to hydroxide, which is essential to some applications especially under drier and hotter conditions. High hydroxide concentrations decompose cationic groups via S_N2, Hofmann elimination, or other degradation processes [72,73]. Therefore, durable AEMs with efficient, selective transport are desired, and so new stable cations and polymer backbones must be developed.

Recently, bulky cations have shown improved chemical stability. Zhang et al. designed a new diphenyl (3-methyl-4-methoxyphenyl) tertiary sulfonium cationic group [134]. This sulfonium cation remained stable in 1 M KOD solution at 60 °C for 10 days. A 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium cation [104,135] demonstrated that attaching the 2,4,6-trimethoxyphenyl group to the cation improves stability. In Gu et al.’s work [60], a tris(2,4,6-trimethoxyphenyl) phosphonium functionalized polysulfone membrane survived for 48 h when
immersed either in 10 M KOH at room temperature or in 1 M KOH at 60°C. Jiang et al. [136] investigated a tris(2,4,6-trimethoxyphenyl) phosphonium functionalized bromomethylated poly(2,6-dimethyl-1,4-phenylene oxide) that maintains stability in 1 M NaOH at 60°C for 75 h. Zha et al. [137] first reported AEMs with a ruthenium bis(terpyridine) complex cation. This membrane exhibited excellent stability in 1 M NaOH solution at room temperature over 6 months. Promising chemical stability of these bulky cations results from the contributions of the electron donating function as well as increased steric effects from the attached side groups. It has also been recently realized that the polymer backbone stability is also a crucial factor towards durable polymers for AEM applications. In particular, residual bromide from incomplete quaternization is a site for hydroxyl attack and so should be avoided [138].

The polymer morphology, ionic nanostructure, and degree of ionic dissociation all affect transport properties in AEMs [139,140]. Solvents can alter the polymeric configuration and properties due to distinct interactions between the polymer chain and the solvent. Effects of the casting solvent on the phase behavior of the diblock [141,142] or triblock [143] copolymers have been well studied. The conductivities of AEMs can also be influenced by changing solvents during the casting process. Elabd et al. [144] investigated the conductivity of sulfonated poly(styrene-b-isobutylene-b-styrene) triblock copolymers applied in proton exchange membrane fuel cells. The proton conductivities of these triblock copolymers varied by 3 orders of magnitude, ranging from $1.07 \times 10^{-2}$ mS/cm cast from a toluene/ethanol mixture (85/15 w/w) to 5.95 mS/cm cast from toluene. Ong et al. [38] developed a random poly(2,6-dimethyl-1,4-phenylene oxide) AEM with a hydroxide conductivity of 17 mS/cm at 60°C in water when cast from NMP, while the conductivity of a membrane cast from a chlorobenzene/DMF mixture solvents was 8 mS/cm.
Little work has investigated the casting solvents’ influence on water and ionic group transport in AEMs. In this study, we report the synthesis of a new polymer with a bulky phosphonium cation attached to a polyphenylene oxide polymer via a selective bromination method used to avoid the large amount of excess bromide present in a previously synthesized similar AEM [138]. By studying the random copolymer, instead of a block copolymer, the intrinsic transport properties can be examined in a system with more random phase separation and structuring. By varying the solvent used for casting, the impact of polymer morphology with transport and conductivity is established. Insights into the anionic conductivity are gained from a study of the water self-diffusion coefficients from NMR measurements.

4.3 Experimental

4.3.1 Materials

Poly(2,6-dimethyl-1,4-phenylene oxide), N-bromosuccinimide, chlorobenzene, 2,2-azobis(2-methylpropionitrile), ethanol, 1-methyl-2-pyrrolidone, tetrahydrofuran and tris(2,4,6-trimethoxyphenyl)phosphine were purchased from Sigma-Aldrich. The molecular weight of poly(2,6-dimethyl-1,4-phenyloxide) was reported as Mw=35000, Mn=16000 (Sigma-Aldrich).

4.3.2 Synthesis of Tris(2,4,6-trimethoxyphenyl) Phosphonium Functionalized Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO-TPQP)

A solution of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) (6 g, 50 mmol in 60 mL chlorobenzene) was heated to 140°C, followed by addition of N-bromosuccinimide (5.34 g, 30 mmol) and 2,2-azobis(2-methylpropionitrile) (0.246 g, 1.5 mmol). After mechanically stirring at 140°C for 1 h, the reaction mixture was poured into ethanol to precipitate the product. The brominated polyphenylene oxide (BPPO) precipitate was filtered, washed with ethanol, and dried in vacuum at room temperature for 12 h.
The BPPO (3.03 g, 20 mmol) was dissolved in 1-methyl-2-pyrrolidone (NMP, 80 mL), followed by addition of tris(2,4,6-trimethoxyphenyl)phosphine (6.39 g, 12 mmol). The mixture was stirred at 80°C for 12 h and then precipitated in tetrahydrofuran. The precipitate was filtered and thoroughly washed with excess tetrahydrofuran in order to remove unreacted tris(2,4,6-trimethoxyphenyl)phosphine.

4.3.3 Membrane Fabrication

10 wt% PPO-TPQP was dissolved in DMSO, ethyl lactate, or a mixture of DMSO and Ethyl lactate (41:59 vol%) respectively at 60°C for 2 h. The polymer solution was drop cast on a pre-cleaned glass substrate and heated in a vacuum oven at 80°C for 24 h. After removal from the substrate, the membrane was soaked in DI water to completely remove the solvent.

4.3.4 Characterization

\( ^1 \text{H} \) nuclear magnetic resonance (NMR) was recorded on a JEOL 500 MHz spectrometer. The methods for Fourier transform infrared spectroscopy (FTIR), water vapor sorption and calculations of hydration numbers (\( \lambda \)) were reported previously [135]. The liquid water uptake mass was obtained by first weighing a vacuum dried membrane (oven at 60°C for 48 h) and then soaking the membrane in DI water for 48 h at 60°C, followed by measuring the weight of the membrane quickly after removing the surface water.

In-plane and through-plane swelling were determined by dimensional changes (X and Y) from dry to liquid water soaked conditions. The swelling of the membranes was calculated from equation (4.1) and equation (4.2).

\[
\text{In-plane swelling} = \frac{X_w - X_d}{X_d}, \frac{Y_w - Y_d}{Y_d}
\]

(4.1)

where \( X_w \) and \( Y_w \) are width and length at wet condition; \( X_d \) and \( Y_d \) are width and length when the membrane is dry.
Through-plane swelling = \frac{L_w - L_d}{L_d} \quad (4.2)

where $L_w$ is the thickness at wet condition and $L_d$ is the thickness when the membrane is dry.

Atomic force microscopy (AFM) images were taken in tapping mode using a Bruker Nanoscope III instrument with high-aspect ratio 225 μm cantilever tips (Nanoworld NCLR). Phase images analysis used Nanoscope 5.30r1 software and domain size quantification used Image J. Micron scale morphologies of the membranes were acquired using a Thermo Fisher Nicolet iN10 microscope. The image was collected in reflection mode.

Small angle X-ray scattering (SAXS) was performed at the Advanced Photon Source (APS), Argonne National Laboratory on beamline 12ID-B. Two-dimensional scattering patterns were collected simultaneously with a Pilatus 2M detector. The one-dimensional intensity versus $q$ employed azimuth averaging from the 2D scattering pattern in the range of $0.005 \text{ Å}^{-1} < q < 1 \text{ Å}^{-1}$ where $q=4\pi\lambda^{-1}\sin(\theta)$. Experiments were carried out from 0% RH to 95% RH as well as liquid soaked conditions. For each water vapor humidity step, membranes were equilibrated for 20 to 40 minutes before scattering patterns were collected. The soaked sample was immersed in DI water at room temperature for 24 h before measurements.

Measurements of $^1$H self-diffusion coefficients were carried out from pulsed-field gradient nuclear magnetic resonance (PFG NMR) as described before [135]. Membranes were cut into strips and loaded into a 5 mm NMR tube with DI water at the bottom. The open tube was then moved into a Test Equity oven set at 95% RH, 25°C. The tube was sealed after 24 h when membranes were fully equilibrated. Experiments were performed at 100% RH from 25°C to 50°C. The inversion recovery sequence, 180°-τ-90°, was used for $T_1$ measurement.
In-plane anionic conductivity was measured using electrochemical impedance spectroscopy (EIS) using a biologic VMP 3 multichannel potentiostat [135]. Measurements were performed from 50°C to 90°C under 95% RH and from 65% RH to 95% RH at 60°C.

Mechanical tests were performed using a Sentmanat Extensional Rheometer (SER) fixture (Xpansion Instruments) on an ARES G2 rheometer platform (TA Instruments) [145]. The SER fixture has two counter rotating drums that uniaxially stretch the polymer film suspended between the drums. Membranes were cut into strips of about 5 mm (W) × 25 mm (L).

4.3.5 Structural Modeling

The tris(2,4,6-trimethoxyphenyl) phosphonium cation structure was optimized by using density functional theory (DFT) at the B3LYP/6-311G(2d,p) level of theory and basis set using the Gaussian 09 program [108].

4.4 Results and Discussion

4.4.1 PPO-TPQP Synthesis and Structure

Tris(2,4,6-trimethoxyphenyl) phosphonium functionalized poly(2,6-dimethyl-1,4-phenylene oxide) (PPO-TPQP) was successfully synthesized by bromination of poly(2,6-dimethyl-1,4-phenylene oxide), followed by quaternization with tris(2,4,6-trimethoxyphenyl) phosphine (Figure 4.1).

Figure 4.1 Synthesis of tris(2,4,6-trimethoxyphenyl) phosphonium functionalized PPO.
The synthesis of the intermediate BPPO was validated by $^1$H NMR spectroscopy (Figure 4.2). The methyl and methylene protons of the brominated polymer were seen at 2.1 and 4.3 ppm, respectively. Integration of these two peaks gave the bromination level as 40%. The aromatic protons were observed ca. 6.6 ppm.

![Figure 4.2 $^1$H NMR spectrum of brominated poly(2,6-dimethyl-1,4-phenyloxide).](image)

Structure of PPO-TPQP was validated by elemental analysis, $^1$H NMR (Figure 4.3(a)), $^{31}$P NMR (Figure 4.3(b)), $^{13}$C NMR (Figure 4.3(c) and FTIR (Figure 4.3(d)). The elemental analysis (of the vacuum oven dried sample, 80°C, 24 h) was in good agreement with the calculated values, Anal. Calcd (C$_{188}$H$_{208}$O$_{46}$P$_4$Br$_4$ 3,651): C 62.00, H 5.70, O 20.16, Br 8.75, P 3.39. Found: C 59.56, H 5.81, O 20.68, P 3.62. In the $^1$H NMR (Figure 4.3(a)), signals at 6.37-6.55 ppm and 6.25 ppm are assigned to aromatic protons from the PPO backbone and the phosphonium cation, respectively. The signals at 3.87 ppm and 3.59 ppm are attributed to the methoxy groups at the para- and ortho- positions. The group of peaks at 1.67-2.08 ppm indicates protons on methyl groups on the PPO backbone. In the $^{31}$P NMR (Figure 4.3(b)), after quaternization (top), there is no peak from the starting phosphine, -65.9 ppm (bottom), while a
new phosphonium peak at 5.2-5.5 ppm is present, indicating the attachment of the bulky phosphonium cation. The FTIR spectra (Figure 4.3(d)) of PPO-TPQP display peaks at 1229 cm$^{-1}$, which are not observed for PPO and are assigned to the C-O-C stretching from methoxylphenyl groups [146].

![Diagram of NMR spectra](image)

Figure 4.3 (a) $^1$H NMR (b) $^{31}$P NMR: bottom, tris(2,4,6-trimethoxyphenyl) phosphine; top, the polymer after quaternization (c) $^{13}$C NMR (d) FTIR spectra of tris(2,4,6-trimethoxyphenyl) phosphonium functionalized PPO.

4.4.2 Chemical and Thermal Stability Studies

Degradation of benzyl tris(2,4,6-trimethoxyphenyl) phosphonium and benzyltrimethyl ammonium cations were tested by using $^1$H NMR (from University of Delaware). The number of cation remaining versus degradation time was calculated as shown in Figure 4.4. After treated in
1M KOD at 80°C for 20 days, benzyl tris(2,4,6-trimethoxyphenyl) phosphonium showed better chemical stability compared to benzyl trimethyl ammonium that benzyl tris(2,4,6-trimethoxyphenyl) phosphonium degraded ca. 41%, while benzyl trimethyl ammonium degraded ca. 41%.

Figure 4.4 Degradation study of benzyl tris(2,4,6-trimethoxyphenyl) phosphonium and benzyltrimethylammonium in 1 M KOD at 80°C.

Figure 4.5 Thermal gravimetric analysis of tris(2,4,6-trimethoxyphenyl) phosphonium functionalized PPO.
The thermal stability of PPO-TPQP was evaluated by TGA in a nitrogen atmosphere at a heating rate of 10 °C/min (Figure 4.5). The slight mass loss at 50°C are from the absorption water from the hydrophilic quaternary groups. The second weight loss with the onset decomposition temperature at 200°C result in the loss of the quaternary phosphonium groups, implying initial deterioration of membranes [136]. The following weight loss region starting from ca. 330°C was mainly attributed to the decomposition of polymer chains.

4.4.3 Solvent Selection Criteria

The Hansen Solubility Parameter (HSP) was used to select the solvent for polymer casting. In Hansen space, the sphere is defined by 3 Hansen parameters, which are the energy from dispersion forces, dipolar forces and hydrogen bonds between molecules. The relative energy difference (RED) shown in equation (4.3), measures the mutual compatibility between solvent and polymer. When RED is larger than 1, the solvent does not dissolve the polymer. When RED is less then 1, the polymer and solvent are compatible and predicted to be mutually soluble, the closer of RED to 0, the less energy difference between the polymer and solvent. When RED =1, the polymer will partially dissolve [147,148].

\[ \text{RED} = \frac{R_a}{R_0} \]  
(4.3)

\( R_a \)-distance between Hansen parameters, which is calculated by equation (4.4)

\( R_0 \)-interaction radius (radius of Hansen sphere)

\[ (R_a)^2 = 4(\delta d_s - \delta d_p)^2 + (\delta p_s - \delta p_p)^2 + (\delta h_s - \delta h_p)^2 \]  
(4.4)

\( \delta d_s \)- energy from dispersion forces between solvent molecules

\( \delta d_p \)- energy from dispersion forces between polymer molecules

\( \delta p_s \)- energy from dipolar intermolecular force between solvent molecules

\( \delta p_p \)- energy from dipolar intermolecular force between polymer molecules
\( \delta h_s \) - energy from hydrogen bonds between solvent molecules

\( \delta h_p \) - energy from hydrogen bonds between polymer molecules

The units of all parameters are MPa\(^{\frac{1}{2}}\).

The determination of HSPs for PPO-TPQP began with dissolving the polymer in a set of 12 different common solvents of known HSP chosen to vary \( \delta d \), \( \delta p \) and \( \delta h \) (Table 4.1). Generally the polymer did not dissolve when \( \delta p \) was < 5.7 and \( \delta h \) was < 7.0. From this HSP of \( \delta d \), \( \delta p \) and \( \delta h \) for PPO-TPQP was calculated as 17.5, 10.7 and 11.6, and \( R_0 \) was 6.2 (Table 4.2). This information was used to calculate the \( R_a \) and RED for a number of solvents with appropriate cost, safety, and odor over a range of volatilities.

DMSO was shown to give a RED of almost 1 (Table 4.2), and represented the limit of solvents that the PPO-TPQP would dissolve in. Ethyl lactate was chosen as being a good solvent for the polymer with much higher volatility than DMSO with RED = 0.7. The HSPiP package [149] was then used to find the ethyl lactate : DMSO ratio with the minimum RED which was at 59:41 vol\% with a RED of 0.2, even closer to 0.

Table 4.1 Solubility of dissolving PPO-TPQP into different solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( \delta d )</th>
<th>( \delta h )</th>
<th>( \delta p )</th>
<th>Solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>18.4</td>
<td>2.0</td>
<td>0</td>
<td>Not</td>
</tr>
<tr>
<td>Toluene</td>
<td>18.0</td>
<td>2.0</td>
<td>1.4</td>
<td>Not</td>
</tr>
<tr>
<td>Xylene</td>
<td>17.8</td>
<td>3.1</td>
<td>1.0</td>
<td>Not</td>
</tr>
<tr>
<td>Chloroform</td>
<td>17.8</td>
<td>5.7</td>
<td>3.1</td>
<td>Not</td>
</tr>
<tr>
<td>THF</td>
<td>16.8</td>
<td>8.0</td>
<td>5.7</td>
<td>Not</td>
</tr>
<tr>
<td>Acetone</td>
<td>15.5</td>
<td>7.0</td>
<td>10.4</td>
<td>Dissolve</td>
</tr>
<tr>
<td>DMSO</td>
<td>18.4</td>
<td>10.2</td>
<td>16.4</td>
<td>Dissolve</td>
</tr>
<tr>
<td>DMAC</td>
<td>16.8</td>
<td>9.4</td>
<td>11.5</td>
<td>Dissolve</td>
</tr>
<tr>
<td>DCM</td>
<td>17.0</td>
<td>7.1</td>
<td>7.3</td>
<td>Dissolve</td>
</tr>
<tr>
<td>NMP</td>
<td>18.0</td>
<td>7.2</td>
<td>12.3</td>
<td>Dissolve</td>
</tr>
<tr>
<td>Methanol</td>
<td>14.7</td>
<td>22.3</td>
<td>12.3</td>
<td>Dissolve</td>
</tr>
<tr>
<td>Phenol</td>
<td>18.5</td>
<td>14.9</td>
<td>5.9</td>
<td>Dissolve</td>
</tr>
</tbody>
</table>
Table 4.2 Hansen solubility parameters, Ra, RED of casting solvents (DMSO, Ethyl lactate, Mix solvent) and PPO-TPQP.

<table>
<thead>
<tr>
<th>sample designation</th>
<th>δd (MPa ½)</th>
<th>δp (MPa ½)</th>
<th>δh (MPa ½)</th>
<th>Rₐ (MPa ½)</th>
<th>R₀ (MPa ½)</th>
<th>RED</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPO-TPQP</td>
<td>17.5</td>
<td>10.7</td>
<td>11.6</td>
<td>6.20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DMSO</td>
<td>18.4</td>
<td>16.4</td>
<td>10.2</td>
<td>6.17</td>
<td>0.998</td>
<td></td>
</tr>
<tr>
<td>Ethyl lactate</td>
<td>16.0</td>
<td>7.6</td>
<td>12.5</td>
<td>4.38</td>
<td>0.709</td>
<td></td>
</tr>
<tr>
<td>Mix solvent</td>
<td>17.0</td>
<td>11.2</td>
<td>11.6</td>
<td>1.13</td>
<td>0.183</td>
<td></td>
</tr>
</tbody>
</table>

As the ethyl lactate evaporates, the solubility of the PPO-TPQP will, therefore, get worse and the more hydrophilic parts of the polymer will tend to phase separate. Hence solvent casting PPO-TPQP from DMSO, ethyl lactate, and the optimized mixture of the two solvent should give us AEMs with differing morphologies and properties.

### 4.4.4 Morphology and Water Uptake

All three films were formed as visibly transparent yellow/orange materials (Figure 4.6). Thicknesses of PPO-TPQP-DMSO, PPO-TPQP-MIX and PPO-TPQP-Ethyl lactate are 60 µm, 40 µm and 20 µm respectively. Light microscopy revealed all films to have dark circular features ranging in size from 2 - 10 mm (Figure 4.7).

![Figure 4.6 Images of membranes casted from DMSO (a), DMSO & ethyl lactate mix solvents (b) and ethyl lactate (c).](image-url)
The influences of the 3 solvent systems on the membranes morphology at smaller scale were observed by AFM tapping mode phase images (Figure 4.8). All of them have a more hydrophilic and hydrophobic phase separation at ambient conditions, where the dark regions have been shown to be the ionic aggregates and the light regions to be the hydrophobic polymer backbone [150]. Thus, microscopies of PPO-TPQP-DMSO, PPO-TPQP-MIX and PPO-TPQP-Ethyl lactate suggest a hierarchical domain structure with morphology on both micron and nanometer scales.

Figure 4.8 AFM tapping mode phase images of PPO-TPQP-DMSO (a), PPO-TPQP-MIX (b) and PPO-TPQP-Ethyl lactate (c). (Scan boxes are 500 nm × 500 nm)
The ionic and hydrophobic domain sizes are different among the three different membranes in a length scale from nanometers to tens of nanometers (Table 4.3). The PPO-TPQP-DMSO membrane shows larger hydrophilic (FD = 22 ± 12 nm) and hydrophobic (FD = 31 ± 17 nm) domains than the PPO-TPQP-MIX and PPO-TPQP-Ethyl lactate membranes (hydrophilic FD = 16 ± 8, 15 ± 9 nm, hydrophobic FD = 19 ± 10, 21 ± 12 nm, respectively), which have similar domain sizes. Clearly the DMSO in which the hydrophobic part of the polymer is more soluble created large domains while the ethyl lactate in which the more hydrophilic part is more soluble created smaller domains.

Table 4.3 Image J analysis of Feret diameters (FD) and standard deviations (SD) of PPO-TPQP-DMSO, PPO-TPQP-MIX and PPO-TPQP-Ethyl lactate.

<table>
<thead>
<tr>
<th>sample designation</th>
<th>average of FD (nm)</th>
<th>SD of size distribution (nm)</th>
<th>average of FD (nm)</th>
<th>SD of size distribution (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bright domain</td>
<td>Dark domain</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PPO-TPQP-DMSO</td>
<td>31</td>
<td>17</td>
<td>22</td>
<td>12</td>
</tr>
<tr>
<td>PPO-TPQP-MIX</td>
<td>19</td>
<td>10</td>
<td>16</td>
<td>8</td>
</tr>
<tr>
<td>PPO-TPQP-Ethyl lactate</td>
<td>21</td>
<td>12</td>
<td>15</td>
<td>9</td>
</tr>
</tbody>
</table>

SAXS patterns of PPO-TPQP-DMSO, PPO-TPQP-MIX and PPO-TPQP-Ethyl lactate membranes (Figure 4.9), were measured from dry to 95% RH at 60°C. No distinct peaks were observed in the low q range of 0.005 - 0.1 Å⁻¹ (Figure 4.9(a)-(c)), but in all cases, upturn was observed at q = 0.02 Å⁻¹, designating poorly organized long-range order, which is not surprising for the random PPO-TPQP copolymer.
By examining the slope variation from 0 to 95% RH, the slope of the PPO-TPQP-DMSO membrane has a relative large drop from 2.9 to 2.0, while the slope for the PPO-TPQP-MIX membrane increases from 2.4 to 2.6 and the slope for the PPO-TPQP-Ethyl lactate membrane remained constant at 3.2. The large change for the PPO-TPQP-DMSO membrane is not surprising considering the film was cast from the hydrophobic DMSO. On absorbing water at 60°C the water strongly influences the polymer morphology by swelling the hydrophilic regions decreasing their symmetry. For the films cast from mixed solvents or ethyl lactate, which influenced the more hydrophilic domains, less changes or even no changes are observed on
symmetry variation. At large q range at 0.1-1 Å\(^{-1}\), a small peak was found at a d-spacing of 7-15 Å (Figure 4.9(d)-(f)) and the peak positions did not shift from dry to 95% RH. However, the size of the observed d-spacing is smaller than that of ionomer peaks in other AEMs, where d = 3 nm - 6 nm for 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium functionalized PPO [135] or d = 3 nm - 5 nm for trimethyl ammonium functionalized perfluorinated material based on the 3M perfluorinated sulfonyl fluoride [22]. Because the peak does not move versus humidity and we know that in two of the films the symmetry of the scattering objects in the more hydrophilic domains is changing, a hypothesis that the 7-15 Å feature was due to scattering from the large phosphonium cation was tested by calculating the cation structure using the Gaussian 09 program (Figure 4.10).

The dimensions of the cation size from different configurations are between 7-13 Å, which has excellent agreement to the d-spacing shown in SAXS spectra. This is in contrast to the polymer we studied with the bulky 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium
cation [135], where the cation size obtained is in the range of 6-12 Å, the d-spacing of the corresponding peaks in SAXS is between 31-62 Å and shows a definite dependence on humidity. These results indicate that the peaks in the SAXS patterns, Figure 4.9 (d)-(f) are attributed to the scattering between cations, whereas in the polymer with the bulky imidazolium, the peaks are due to interference between ionic aggregates, similar to the ionomer peaks observed in perfluorosulfonic acid polymers such as in Nafion® [151,152].

The influence of polymer morphology on water uptake is shown in Figure 4.11. The PPO-TPQP-MIX membrane has the highest water uptake and hydration number (WU=28%, \( \lambda =12.8 \), liquid water) while the PPO-TPQP-Ethyl lactate membrane has the smallest (WU=10%, \( \lambda =4.6 \), liquid water). Water uptake generally matches the swelling behavior (Figure 4.12). Overall, modest water uptakes are observed in the range of 10%-28% when all the films are soaked in liquid water corresponded to an in-plane-X swelling of 4%-7%, in-plane-Y swelling of 4%-6% and a through-plane swelling of 6%-10%.

![Figure 4.11 Water uptake (solid) and lambda value (open) of PPO-TPQP casted from different solvents. (PPO-TPQP-MIX, square; PPO-TPQP-DMSO, diamond; PPO-TPQP-Ethyl lactate, triangle).](image)

80
4.4.5 Self-Diffusion and Ionic Conductivity

To probe the molecular motions of the water in the polymer, spin-lattice ($T_1$) relaxation time was used to correlate morphological structures. Since $T_1$ probes molecule motions on a time scale of 2.5 ns ($1/\omega_0$, $\omega_0$ is the $^1$H Larmor frequency, 400 MHz in our experiment) [153], diffusion coefficients of PPO-TPQP-DMSO, PPO-TPQP-MIX and PPO-TPQP-Ethyl lactate are calculated as $2.13 \times 10^{-6}$ cm$^2$/s, $2.04 \times 10^{-6}$ cm$^2$/s and $2.08 \times 10^{-6}$ cm$^2$/s, respectively. Therefore, from equation (4.5) the diffusion lengths [117,154] of PPO-TPQP-DMSO, PPO-TPQP-MIX and PPO-TPQP-Ethyl lactate are 1.03 nm, 1.01nm and 1.02 nm.

$$<a^2>^{1/2} = \sqrt{2Dt_d}$$

where $<a^2>^{1/2}$ is the diffusion length, $t_d$ is the diffusion time and D is the diffusion coefficient.

Dependence of water self-diffusion coefficient upon diffusion time was recorded at 25°C (Figure 4.13) by PFGSE NMR. The PPO-TPQP-DMSO, PPO-TPQP-MIX and PPO-TPQP-Ethyl lactate membranes all display restricted diffusion behavior where the self-diffusion coefficients decrease and then level off with increasing diffusion evolution time [116,155]. Restricted
diffusion implies that water diffuses in a heterogeneous network, which corresponding to the phase separation as observed in the AFM and light microscope images. When full geometrical restriction is achieved, the water self-diffusion coefficient ($D_\infty$) of PPO-TPQP-Ethyl lactate is higher, $6.3 \times 10^{-7}$ cm$^2$/s, while those of PPO-TPQP-DMSO and PPO-TPQP-Ethyl lactate are both ca. $4.6 \times 10^{-7}$ cm$^2$/s. These values are one order of magnitude smaller than diffusion coefficients of 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium functionalized PPO ($1.0 \times 10^{-6}$ cm$^2$/s) [135] and Nafion® 117 ($5.6 \times 10^{-6}$ cm$^2$/s) [156] where ionomer peaks that swell are observed, and two order of magnitude smaller than the bulk water diffusion coefficient ($2.3 \times 10^{-5}$ cm$^2$/s at 25°C) [89].

The same diffusion experiments also revealed the membrane heterogeneity via a theory developed by Mitra (equation (4.6)) [19,119].

$$D = D_0 \left[ 1 - \frac{4}{9 \sqrt{\pi}} \cdot \frac{S}{V} \cdot \sqrt{D_0 \cdot t_d} \right]$$ (4.6)
where $D_0$ is diffusion coefficient at $t=0$, and $S/V$ is the surface-to-volume ratio of the porous material. By fitting the slope of the diffusion data from Figure 4.13 into equation (4.6), evidence of morphological complexity is quantified by the critical length scale, $R_c$, the reciprocal of $S/V$ and the tortuosity $\alpha$ ($\alpha=D_0/D_\infty$) [118,135] (Table 4.4).

Table 4.4 Surface/volume ratio, $R_c$, tortuosity and $T_1$ of PPO-TPQP-DMSO, PPO-TPQP-MIX and PPO-TPQP-Ethyl lactate.

<table>
<thead>
<tr>
<th>sample designation</th>
<th>S/V (μm$^{-1}$)</th>
<th>$R_c$ (μm)</th>
<th>Tortuosity ($\alpha$)</th>
<th>$T_1$ (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPO-TPQP-DMSO</td>
<td>2.58</td>
<td>0.39</td>
<td>4.50</td>
<td>596</td>
</tr>
<tr>
<td>PPO-TPQP-MIX</td>
<td>2.57</td>
<td>0.39</td>
<td>4.35</td>
<td>535</td>
</tr>
<tr>
<td>PPO-TPQP-Ethyl lactate</td>
<td>2.33</td>
<td>0.43</td>
<td>3.32</td>
<td>478</td>
</tr>
</tbody>
</table>

$R_c$ is on the order of hundreds of nanometers, which is larger than the domain sizes shown in AFM images and so must extend into the domains observed in the light microscope. $R_c$ is the same (0.39 μm) for PPO-TPQP-DMSO and PPO-TPQP-MIX, but larger for the ethyl lactate cast film (0.43 μm). The tortuosity decreases in the order PPO-TPQP-DMSO>PPO-TPQP-MIX>PPO-TPQP-Ethyl lactate with values of 4.50, 4.35 and 3.32, respectively.

The Arrhenius plots of the water self-diffusion coefficients as a function of temperature (Figure 4.14) implicate that the solvent from which the membrane was cast also impacts the mechanism of water transportation. In Figure 4.14, diffusion coefficients with non-linear trends, which can be fitted into Vogel-Tamman-Fulcher (VTF) equation, are observed for PPO-TPQP-DMSO and PPO-TPQP-Ethyl lactate. The VTF [157] equation (equation (4.7)) is used to represent the ion transport facilitated by the movement of the cationic side chains. The results of the VTF fitting of the self-diffusion coefficients are given in Table 4.5. The water self-diffusion of PPO-TPQP-MIX shows a linear Arrhenius behavior (Table 4.6).

\[
D(T) = AT^{-1/2}e^{-E_i/R(T-T_0)}
\]  

(4.7)
where A is a constant, R is the gas constant, $E_i$ is the pseudo-activation energy and $T_0$ is the temperature at which the mobility of ions and the conductivity drop to zero.

Figure 4.14 Water diffusion coefficients of PPO-TPQP-DMSO (diamond), PPO-TPQP-MIX (square) and PPO-TPQP-Ethyl lactate (triangle) in terms of different temperature under 100% RH.

Table 4.5 Parameters of VTF regression of PPO-TPQP-DMSO and PPO-TPQP-Ethyl lactate on conductivity as well as diffusion coefficients versus temperatures.

<table>
<thead>
<tr>
<th>sample designation</th>
<th>relative humidity</th>
<th>A</th>
<th>$E_i$ (kJ/mol)</th>
<th>$T_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPO-TPQP-DMSO (D)</td>
<td>100%</td>
<td>1.3±0.5×10^{-8}</td>
<td>1.6±0.6</td>
<td>227±14</td>
</tr>
<tr>
<td>PPO-TPQP-DMSO (σ)</td>
<td>95%</td>
<td>0.8±0.3</td>
<td>2.4±0.3</td>
<td>256±4</td>
</tr>
<tr>
<td>PPO-TPQP-DMSO (σ)</td>
<td>80%</td>
<td>0.08±0.03</td>
<td>1.2±0.8</td>
<td>278±9</td>
</tr>
<tr>
<td>PPO-TPQP-Ethyl lactate (D)</td>
<td>100%</td>
<td>8.9±0.9×10^{-9}</td>
<td>1.0±0.1</td>
<td>242±6</td>
</tr>
</tbody>
</table>

Conductivity versus temperature of PPO-TPQP-DMSO, PPO-TPQP-MIX and PPO-TPQP-Ethyl lactate measured at both 95% RH and 80% RH are shown in Figure 4.15. PPO-TPQP-MIX has highest conductivity of 3 mS/cm\(^{-1}\) at 90°C, 95% RH. A comparison to literature values for bromide conductivities reported previously is shown in Figure 4.16 [158,159]. There are surprisingly few good comparative studies in the literatures. These two polymers were selected, because they are random copolymer structures with a bromide counter ion and PPO backbone, measured under water vapor, which have a true comparison to PPO-TPQP. The
bromide conductivities of PPO-TPQP-MIX comparable to and intermediate to the values from IEC of 0.9 and 1.8 mmol/g membranes with trimethyl ammonium cations at identical temperature and humidity level, indicating the bulky phosphonium cation does not negatively impact bromide transport.

Figure 4.15 Bromide conductivities of PPO-TPQP-DMSO (a), PPO-TPQP-MIX (b) and PPO-TPQP-Ethyl lactate (c) as a function of temperature under 95% RH (diamond) and 80% RH (square).

Figure 4.16 Comparison of conductivities between PPO-TPQP-MIX and random copolymer in reference papers (PPO-TPQP-MIX IEC=1.2 mmol/g, 95% RH, diamond; Poly(MMA-r-MEBIm-X) IEC=1.4 mmol/g, 90% RH [158], square; TMA functionalized random copolymer containing PPO and poly(2,6-diphenyl-1,4-phenylene oxide), IEC =0.9 (triangle), IEC=1.8 (circle), 95% RH [31])
Also, we noticed that the plot of PPO-TPQP-MIX exhibits a linear trend, the same as small
cation (imidazolium and ammonium) random copolymers. The Arrhenius plot for PPO-TPQP-
DMSO is curved so fit to the VTF equation (equation (4.8)) under both 95% RH and 80% RH
(Table 4.5), similar to its water diffusion behavior in Figure 4.14.

\[
\sigma(T) = A T^{-1/2} e^{-E_{i}/RT} (T - T_0)
\]  

where \( A \) is a constant proportional to the number of mobile charge carriers, \( R \) is the gas constant,
\( E_i \) is the pseudo-activation energy and \( T_0 \) is the temperature at which the mobility of ions and the
conductivity drop to zero. Constant \( A \) at 95% RH is ca. one order of magnitude larger than that
of 80% RH since more bromide is dissociated and so contributes more to the ionic conductivity.
A thermal transition is indicated in the region of all the conductivity measurements (VTF \( T_0 \) is
50°C lower than measured transitions). However, the plot of PPO-TPQP-Ethyl lactate displays a
linear Arrhenius relation (Table 4.6), which is in contrast to the water self-diffusion curve trend
in Figure 4.14. The Arrhenius plots of PPO-TPQP-MIX indicate that the cation anion pairs are
always dissociated probably because it exhibits the highest water uptake. Even so there is never
enough water in these films to fully hydrate the bromide anion that typically needs 6 waters
[160], where as at 95% RH, PPO-TPQP-MIX film approaches 5. Increasing the water content of
the films increases the conductivity values for bromide. However increasing RH also increases
the \( E_a \) for bromide transport, \( E_a \) doubles from 36 ± 5 kJ/mol at 80% RH to 70 ± 6 kJ/mol at 95% RH,
whereas the water self-diffusion exhibits a \( E_a \) of 21 ± 1 kJ/mol at 100% RH indicating that
water transport is decoupled from bromide transport. This seems to be consistent as we also
noticed another trend for PPO-TPQP-Ethyl lactate, which has the lowest conductivity but has the
highest water diffusion coefficient among the three membranes.
Table 4.6 Parameters of Arrhenius fit of PPO-TPQP-MIX and PPO-TPQP-DMSO on conductivity as well as diffusion coefficients versus temperatures.

<table>
<thead>
<tr>
<th>sample designation</th>
<th>relative humidity</th>
<th>$E_a$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPO-TPQP-MIX (D)</td>
<td>100%</td>
<td>21±1</td>
</tr>
<tr>
<td>PPO-TPQP-MIX (σ)</td>
<td>95%</td>
<td>70±6</td>
</tr>
<tr>
<td>PPO-TPQP-MIX (σ)</td>
<td>80%</td>
<td>36±5</td>
</tr>
<tr>
<td>PPO-TPQP-Ethyl lactate (σ)</td>
<td>95%</td>
<td>73±4</td>
</tr>
<tr>
<td>PPO-TPQP-Ethyl lactate (σ)</td>
<td>80%</td>
<td>45±8</td>
</tr>
</tbody>
</table>

Figure 4.17 Br$^-$ diffusion coefficients of PPO-TPQP-DMSO (circle), PPO-TPQP-MIX (square) and PPO-TPQP-Ethyl lactate (triangle) under 95% RH as a function of temperature calculated from Nernst-Einstein equation.

To further illustrate this point we consider an approach where impact of ion concentration on conductivity is eliminated. A solution is performed by calculating bromide diffusion coefficients from bromide conductivities by Nernst-Einstein equation (equation (4.9))
[123], from which enable a direct comparison between the measured water self-diffusion and bromide diffusion.

\[ D = \frac{RT \kappa}{cz^2F^2} \]  

(4.9)

where \( \kappa \) is the conductivity, \( c \) is the concentration of anionic groups in the membrane, \( z \) is the ionic charge, \( F \) is the Faraday constant, \( R \) is the gas constant and \( T \) is the temperature. Figure 4.17 shows bromide diffusion coefficients of PPO-TPQP-DMSO, PPO-TPQP-MIX and PPO-TPQP-Ethyl lactate as a function of temperature calculated from Nernst-Einstein equation. We observe PPO-TPQP-Ethyl lactate has a conflicting behavior towards water and bromide diffusion when compared with the other two membranes. Exploring why PPO-TPQP-Ethyl lactate has such a different behavior, we study the water contributions to the diffusion process by calculating hydration number normalized conductivity. We use conductivity measured under 60% RH to 95% RH (Figure 4.18) divide by hydration number under the same humidity level as shown in Figure 4.19. We observed as the RH increases, conductivity/\( \lambda \) ratio of PPO-TPQP-Ethyl lactate increases more slowly than that of PPO-TPQP-MIX and PPO-TPQP-DMSO. When relative humidity is 95% RH, conductivity/\( \lambda \) ratio of PPO-TPQP-Ethyl lactate is less than half of PPO-TPQP-DMSO and PPO-TPQP-MIX. These findings indicate that single water molecule in PPO-TPQP-Ethyl lactate make the smallest contribution to conductivity. In other words, PPO-TPQP-Ethyl lactate has a weakest correlation between water and conductivity, therefore exhibit a discrepancy between water and bromide diffusion.
Figure 4.18 Conductivities of PPO-TPQP-DMSO (circle), PPO-TPQP-MIX (square) and PPO-TPQP-Ethyl lactate (triangle) as a function of humidity at 60°C.

Figure 4.19 Ratio of conductivity/lambda of PPO-TPQP-DMSO (diamond), PPO-TPQP-MIX (square) and PPO-TPQP-Ethyl lactate (triangle) in terms of relative humidity.

4.4.6 Mechanical Property

Tensile tests were measured at 60°C under both dry and hydrated conditions to determine the effect of water on mechanical properties (Figure 4.20).
Figure 4.20 Tensile tests under both dry and hydrated conditions for tris(2,4,6-trimethoxyphenyl) phosphonium functionalized PPO.

After absorbing water, stress at break, Young’s modulus decreases and elongation increases, indicating water in hydrated membranes acts as plasticizer. PPO-TPQP has a much higher Young’s modulus and smaller stress at break, elongation compared to the commercially available Nafion® 115 membrane (PPO-TPQP: 388-560 MPa Young’s modulus from wet to dry, 11-14 Mpa Stress at break from wet to dry, 3-8% elongation from dry to wet; Nafion® 115, 75-130 MPa Young’s modulus, 37-46 Mpa stress at break and 190-240% elongation from wet to dry [161]). Therefore, we know that PPO-TPQP is brittle when dry compared to wet; and membranes with better flexibility and elasticity that can be achieved by replacing the backbone with rubbery (low Tg) polymers is required for further commercial applications.

4.5 Conclusions

In this study, DMSO, Ethyl lactate and DMSO & Ethyl lactate mix solvents were selected based on Hansen solubility parameter to drop cast PPO-TPQP containing the large phosphonium cation. All three membranes have modest water uptake in the range of 10-28 wt% after being soaked in DI water at 60 °C. From SAXS measurements, the membranes’ nanoscale morphology was shown to be invariant with humidity. The peak at about d-spacing of 7-15 Å was consistent with the optimized cation size calculated by DFT from the Gaussian program. The casting
solvents influence on the more hydrophilic and hydrophobic domain distributions were observed by SAXS. Both SAXS and AFM demonstrate a poorly organized long-range order structure in the membranes. The membrane cast from the optimized solvent mixture, PPO-TPQP-MIX, did have the highest conductivity among the three membranes with 3 mS/cm at 95% RH, 90°C, while PPO-TPQP-Ethyl lactate has highest water diffusion coefficient of $6.3 \times 10^{-7}$ cm$^2$/s at 100% RH, 25°C. The PPO-TPQP-MIX material always showed Arrhenius behavior in bromide conductivity and water diffusion. Conductivity follows PPO-TPQP-MIX > PPO-TPQP-DMSO > PPO-TPQP-Ethyl lactate which are in the same order as water uptake. However, Water diffusion coefficient follows PPO-TPQP-Ethyl lactate > PPO-TPQP-MIX ≈ PPO-TPQP-DMSO since PPO-TPQP-Ethyl lactate has smallest tortuosity. Furthermore, PPO-TPQP-MIX and PPO-TPQP-DMSO have similar trends in both conductivity and water diffusion versus temperature. Yet, PPO-TPQP-Ethyl lactate shows a linear Arrhenius relation in conductivity, while exhibits a VTF non-linear in water diffusion coefficient. Such a different conductivity and diffusion behavior of PPO-TPQP-Ethyl lactate is due to its strongest bromide water decoupling. First, the activation energy at 95% RH doubles to that at 80% RH indicating water molecules contribute to dissociate ionic groups instead of improving the conductivity. Second, hydration number normalized conductivity confirms PPO-TPQP-Ethyl lactate does have the weakest water/bromide transport correlation. Reducing Young’s modulus and enhancing the elongation of PPO-TPQP would generate a flexible and mechanically strong membrane.

### 4.6 Acknowledgments

The authors thank the Army Research Office for support of this research under the MURI grant number #W911NF-10-1-0520. The Advanced Photon Source operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory, was support
by the U. S. DOE under Contract No. DE-AC02-06CH11357. We also thank Dr. Steven Abbott for the HSP calculation on PPO-TPQP by using the HSPiP package.
CHAPTER 5

PHYSICAL PROPERTIES OF RANDOM AND CROSSLINK PHENYLENE COBALTOCENIUM FUNCTIONALIZED ANION EXCHANGE MEMBRANES

5.1 Abstract

Phenylene cobaltocenium was functionalized into random (Poly (norbornene phenylene cobaltocenium chloride)-random-polynorbornene, PNPCCl-r-PNBE) and crosslinked (Poly (norbornene phenylene cobaltocenium chloride)-random-polydicyclopentadiene, PNPCCl-r-PDCPD) anion exchange membranes with ion exchange capacity of 1.48 and 1.39 mmol/g, respectively. By creating a crosslinked membrane, lower water uptake (WU=15% at 95% RH and 60°C) and conductivity (27 mS/cm at 95% RH and 90°C) were measured compared to the random copolymer membrane (WU=17% at 95% RH and 60°C; 41 mS/cm at 95% RH and 90°C). The Cl\(^-\) conductivity of PNPCCl-r-PNBE is higher than imidazolium [135] and ammonium cation functionalized random AEMs [162] with similar IECs. Water and ion transport inside random and crosslink membranes are different also. PNPCCl-r-PNBE has relative movable norbornene segments, which give rise to a polymer chain dominated transport, while water play a more important role for the ion transport inside PNPCCl-r-PDCPD since crosslinked network restricts flexibility of the polymer chain motion.

5.2 Introduction

Anion exchange membranes (AEMs) are polymer electrolyte with potential use in the alkaline fuel cell (AFC) since (1) AEMs have improved CO\(_2\) tolerance compared to liquid electrolytes, and (2) the intrinsic enhanced electrode kinetics of oxygen reduction in alkaline medium enables the usage of non precious metal catalyst [163,164]. AEMs consist of cation groups covalently linked to a polymer backbone. Cationic functional groups form hydrophilic
domains where counter ions can transport across the membrane, while the polymer matrix primarily determines mechanical strength and membrane morphology.

Several functional requirements must be met to move AEMs to wide spread use. First, an AEM should remain stable at the working temperature over long timescales (e.g., stationary systems: 40000 h durability, vehicles: 5000 h durability) [165]. Second, an efficient transfer of the hydroxyl ions from one electrode to the other should occur. Also, water swelling should be minimized; excess water in membrane seriously decreases the membrane’s mechanical strength [166].

Chemical stability of the membrane is determined from both polymer matrix and cation properties [51,52,77]. Cations are central to chemical degradation via \( \text{OH}^- \) groups attack through \( \text{S}_{\text{N}}2 \) substitution and/or Hofmann elimination pathways [167]. In order to rival the chemical stability of trimethyl ammonium cations [56,168,169], a series of novel, bulky cations have been developed, including sulfonium [134], phosphonium [57,170,171], imidazolium [65,94,100,101], and ruthenium [66] to enhance the electrolyte durability through improving basicity and steric hindrance of cationic groups. However, these bulky cations are expected to weaken the membrane’s flexibility as well as mechanical strength since polymer chains are set apart from tight alignment.

Metallocene containing polymers have inorganic metal centers and organic frameworks, which combine to be a good electrolyte candidate due to the highly stable 18-electron structure. One example is cobaltocenium (18-electron), oxidized from 19-electron cobaltocene, which has higher stability toward further oxidation. Zhang et al. [172] synthesized cobaltocenium-containing methacrylate homopolymer by reversible addition-fragmentation chain transfer polymerization (RAFT). Ren et al. [173] prepared side-chain cationic cobaltocenium-containing
polymers via ring-opening metathesis polymerization (ROMP). One cobaltocenium cation has been applied in AEM alkaline fuel cell area [174], in which work an AEM with permethyl cobaltocenium cation bridged to the polysulfone backbone by a 6 carbon diamine linkage was studied. Membrane with IEC of 1.20 showed a hydroxide conductivity of 22 mS/cm measured in deionized water at room temperature. IEC have lost 18% and 27%, respectively, after 1000 and 2000 hours treatment in 1 M KOH at 80°C.

The introduction of cross-linking configuration into polymer structures is one way to improve AEM properties - suppressing excess water uptake and swelling [175,176] as well as enhance mechanical and chemical stability [177]. However, cross-linking may reduce the size of the ionic channels; increased cross-linking density may impede conductivity, which is a commonly observed trend [178,179]. Here, we study a crosslink poly(norbornene phenylene cobaltocenium chloride)-random-polydicyclopentadiene membrane (PNPCCI-r-PDCPD). The overall performance including chemical stability, conductivity, and mechanical property are evaluated. By comparison to the poly(norbornene phenylene cobaltocenium chloride)-random-polybornene (PNPCCI-r-PNBE), cation as well as the crosslinked framework’s influence on the water/anion transport and correlations between membrane morphology and transport are investigated.

5.3 Experimental

5.3.1 Materials

Poly(norbornene phenylene cobaltocenium chloride)-random-polybornene (PNPCCI-r-PNBE, Figure 5.1(a)) and Poly(norbornene phenylene cobaltocenium chloride)-random-polydicyclopentadiene (PNPCCI-r-PDCPD, Figure 5.1(b)) were provided from University of Massachusetts, Amherst with titrated IECs of 1.48 and 1.39 mmol/g, respectively.
5.3.2 Characterization

Thermogravimetric analysis (TGA) was carried out using a SSC/5200 SII analyzer controlled by a TGDTA Measure thermal analysis station. 20 mg samples were loaded into a platinum pan. Measurements were performed at a heating rate of 10 °C/min from 20°C to 700°C under a nitrogen atmosphere.

Water uptake and hydration number was measured by a SMS dynamic vapor sorption (DVS) instrument [171].

Small angle X-ray scattering (SAXS) was performed at the Advanced Photon Source (APS), Argonne National Laboratory on beamline 12ID-B [171].

Measurements of $^1$H self-diffusion coefficients were carried out from pulsed gradient stimulated echo nuclear magnetic resonance (PGSE-NMR) on an AVANCEIII spectrometer [171]. Experiments were performed at 100% RH from 25°C to 50°C.

In-plane anionic conductivity was measured using electrochemical impedance spectroscopy (EIS) using a biologic VMP 3 multichannel potentiostat [171]. OH conductivity was measured in an air isolated Bekktech conductivity cell, which is purged with UHP nitrogen.
gas. Cl− form membrane was soaking in 1 M KOH for 20 h followed by rinsing with degassed deionized water until the rinsed water had a neutral pH to ion exchange into OH−.

Cyclic voltammetry measurements of the polymer were done using a three-electrode configuration consisting of a glassy carbon working electrode, an Ag/AgNO3 (0.01 M in acetonitrile) reference electrode, and a Pt wire counter electrode in tetrabutylammonium hexafluorophosphate electrolyte solution (0.1M) in DMF. Measurements were calibrated to the ferrocene/ferrocenium redox couple (Fc/Fc+) as an external reference. Voltage scans from 0.25 V to -2.75 V at scanning rate of 200 mV/s.

The phenyl cobaltocenium cation structure was optimized by using density functional theory (DFT) at the B3LYP/6-311G(2d,d,p) level of theory and basis set using the Gaussian 09 program.

5.4 Results and Discussion

In cyclic voltammetry measurements (Figure 5.2), two reversible peaks were observed, corresponding to Co(III/II) and Co(II/I) redox couples. In an AEM fuel cell, the oxidation potential of hydrogen at the anode versus standard hydrogen electrode (SHE) is +0.83 V, and the reduction potential of oxygen at the cathode versus SHE is +0.40 V [66]. In comparison, the Co(III/II) reduction potential was measured as -0.65 V which fall outside of the operating range. Therefore, cobaltocenium is electrochemically stable and could be used as an electrolyte in the range of AEM fuel cell operational potentials.
Figure 5.2 Cyclic voltammetry of a phenylene cobaltocenium functionalized norbornene homopolymer solution (vs SHE).

Figure 5.3 Thermal gravimetric analysis of phenylene cobaltocenium functionalized norbornene homopolymer.

Thermal gravimetric analysis of PNPCCl-r-PNBE (Figure 5.3) reveals only one significant stage of weight loss staring at 440°C, which results from the decomposition of the backbone [180]. The degradation of Cp rings (C₅H₅, abbreviated as Cp) has been reported at 850°C [181]. PNPCCl-r-PNBE shows a better thermal stability than 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium (degrade at ca. 220°C) and tris(2,4,6-trimethoxyphenyl)
phosphonium (degrade at ca. 200°C) PPO studied in chapter 3 and 4, respectively. Also, Cp rings are more stable than trimethyl ammonium, which degrades at around 140°C [182].

Water uptake and hydration number of PNPCCl-r-PNBE and PNPCCl-r-PDCPD (Figure 5.4) are similar from dry to 80% RH, while PNPCCl-r-PNBE has 2% higher water uptake and 0.4 higher hydration number than PNPCCl-r-PDCPD at 95% RH. The crosslinked membrane does not prevent water molecules from penetrating into the membrane at low humidity level while slightly suppresses water absorption when humidity increases.

![Figure 5.4 Water uptake (solid) and hydration number (open) of PNPCCl-r-PNBE (diamond) and PNPCCl-r-PDCPD (square) at different humidity levels.](image)

Figure 5.4 Water uptake (solid) and hydration number (open) of PNPCCl-r-PNBE (diamond) and PNPCCl-r-PDCPD (square) at different humidity levels.

![Figure 5.5 Conductivity of PNPCCl-r-PNBE (diamond) and PNPCCl-r-PDCPD (square) at 95% RH.](image)

Figure 5.5 Conductivity of PNPCCl-r-PNBE (diamond) and PNPCCl-r-PDCPD (square) at 95% RH.
Conductivity measurements were performed from 30°C to 90°C under 95% RH (Figure 5.5). PNPCCl-r-PNBE shows higher conductivity of 42 mS/cm at 90°C, 95% RH compared to 27 mS/cm of PNPCCl-r-PDCPD at the same condition. From Figure 5.4, hydration number of PNPCCl-r-PNBE is 6.6, approaching a fully hydrated state (solvation number of Cl⁻ in water is about 6 [183]). Transport supposes to be water dominated. However, the polynorbornene segments in PNPCCl-r-PNBE have very low glass transition temperature (ca. 40°C), which promotes the polymer chain rearrangement. From Figure 5.5 we notice PNPCCl-r-PNBE exhibits a non-linear behavior, which can be fit into Vogel-Tamman-Fulcher (VTF) (Table 5.1). Therefore, polymer chain movement dominates transport in PNPCCl-r-PNBE, instead of water-dominated transport. For PNPCCl-r-PDCPD, water uptake and hydration number are slight smaller, and crosslinking has confined the polymer chain movement that further restrict free volume generation. Therefore, conductivity versus temperature of PNPCCl-r-PDCPD shows a linear Arrhenius trend designating water-dominated transport. Activation energy is 29±1 kJ/mol, which is larger than the Cl form bulky imidazolium PPO (15±2 kJ/mol) as shown in chapter 3 [135].

<table>
<thead>
<tr>
<th>VTF regression</th>
<th>σ₀ or D₀</th>
<th>b (K)</th>
<th>T₀(K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>conductivity</td>
<td>σ₀ = 0.088 S/cm</td>
<td>57</td>
<td>285</td>
</tr>
<tr>
<td>diffusion coefficient</td>
<td>D₀ = 1.07×10⁻⁹ m²/s</td>
<td>20</td>
<td>281</td>
</tr>
</tbody>
</table>

Water self-diffusion is important to understand transport mechanism and morphological property of membranes. Water self-diffusion was measured at 100% RH and room temperature in terms of diffusion time (Figure 5.6). D∞ of PNPCCl-r-PNBE is 3.3×10⁻⁶ cm²/s, while that of PNPCCl-r-PDCPD is 0.9×10⁻⁶ cm²/s when diffusion fully restricted. Diffusion coefficient of
PNPCCl-r-PNBE is higher than PNPCCl-r-PDCPD at 100% RH and 25°C, which is consistent with conductivity, again showing the crosslinked membrane has restricted water transport. However, the diffusion coefficient of PNPCCl-r-PNBE and PNPCCl-r-PDCPD in terms of diffusion time does not exhibit a distinct decrease. Therefore, PNPCCl-r-PNBE and PNPCCl-r-PDCPD are expected to be less hydrophilic and hydrophobic phase separation compared to the phosphonium and imidazolium AEMs studied before. Applying the Mitra equation, a linear fit of diffusion coefficient as a function of small diffusion time can be made, and S/V, Rc, and tortuosity are obtained (Table 5.2). Rc is larger than that of imidazolium (2.6 µm -6.7 µm) and phosphonium (0.39 µm -0.43 µm) functionalized PPO, and α is comparable across the same three systems (imidazolium 1.18-1.47, phosphonium 3.32-4.50). Tortuosity value is more related with hydrophilic/hydrophobic domain arrangement, rather than directly reflection of the phase separation; therefore, SAXS and TEM are needed to formulate a more complete understanding of the different phases.

Figure 5.6 Water self-diffusion coefficients of PNPCCl-r-PNBE (diamond) and PNPCCl-r-PDCPD (square) versus the square root of the diffusion time.
Table 5.2 Surface/volume ratio, $R_c$ and tortuosity for PNPCCl-r-PDCPD

<table>
<thead>
<tr>
<th>sample designation</th>
<th>$S/V$ (µm$^{-1}$)</th>
<th>$R_c$ (µm)</th>
<th>tortuosity ($\alpha$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PNPCCl-r-PDCPD</td>
<td>0.55</td>
<td>18.1</td>
<td>2.42</td>
</tr>
</tbody>
</table>

Water diffusion coefficients of PNPCCl-r-PNBE and PNPCCl-r-PDCPD have also been taken as a function of temperature from 25°C to 50°C (Figure 5.7). Diffusion coefficient of PNPCCl-r-PNBE, which achieves $6.2 \times 10^{-10}$ m$^2$/s at 45°C, is always higher than that of PNPCCl-r-PDCPD with shows $2.4 \times 10^{-10}$ m$^2$/s at 50°C. Similar to conductivity-temperature relation, PNPCCl-r-PNBE also shows a linear Arrhenius trend and PNPCCl-r-PDCPD display the curved behavior, which can be fit into VTF mechanism (Table 5.1). Therefore, the crosslinked membrane has restricted water molecule and anion transport, and transport mechanism has dominated by water mediate instead of polymer chain movement since polymer chains are immobilized via crosslinking.

![Figure 5.7 Water diffusion coefficients of PNPCCl-r-PNBE (diamond) and PNPCCl-r-PDCPD (square) under 100% RH at different temperatures.](image-url)
SAXS measurements were taken under both dry and 95% RH (Figure 5.8). PNPCCl-r-PDCPD shows the ionomer peak with d spacing ca. 3 nm, while PNPCCl-r-PNBE has the scattering pattern with a larger d spacing ca. 9 nm. The dimensions of a single cation are between 4-12 Å (Figure 5.9) based on density function theory calculation from Gaussian program. Thus, the SAXS scattering patterns are attributed larger structures instead of single cations. The PNPCCl-r-PDCPD peak ascribes to ionomer peak, which composes of water and anionic groups. Therefore, the domain size swell and the peak shift towards low q range at high humidity level. Since crosslink confine the polymer configuration, the peak position only shift a very small amount from q of 0.21 Å⁻¹ at dry conditions to 0.18 Å⁻¹ at 95% RH. In contrast, PNPCCl-r-PNBE does not show the peak shift between dry and 95% RH humidity levels indicating the scattering pattern may account for some hydrophobic aggregation.
Figure 5.9 Phenyl cobaltocenium cation optimized at the B3LYP/6-311G(2d,d,p) level of theory and basis set using the Gaussian 09 program.

Figure 5.10 TEM images of PNPCCl-r-PDCPD (a) and PNPCCl-r-PNBE (b).

TEM images of PNPCCl-r-PDCPD and PNPCCl-r-PNBE show hydrophilic (dark) and hydrophobic domains (bright) in Figure 5.10, and both membranes have similar hydrophilic domain sizes of ca. 4 nm (Figure 5.10). This size is much smaller than those from 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium functionalized PPO (10 nm-13 nm) and tris(2,4,6-trimethoxyphenyl) phosphonium functionalized PPO (15 nm-22 nm). Thus, the PNPCCl-r-PDCPD and PNPCCl-r-PNBE membranes are less phase separated, which agrees with the diffusion behavior (Figure 5.6), which does not show restricted diffusion. Moreover, the
hydrophilic domain size is consistent with the scattering pattern size in SAXS of PNPCCI-r-PDCPD, but smaller than that of PNPCCI-r-PNBE further help to indicate that scattering peak in PNPCCI-r-PNBE might due to some hydrophobic aggregation that does not change between dry to wet conditions observed by SAXS. From the light microscope image (Figure 5.11), there is no clear phase separation on the order of micron, which is different to the light microscope images of PPO-TPQP (Figure 4.7) and PPO-TMIM (Figure 3.12).

Figure 5.11 Light microscope images of PNPCCI-r-PNBE (Scale bar is 50 µm)

Figure 5.12 Alkaline stability of phenylene cobaltocenium (diamond) and trimethyl ammonium (square) cations at 80°C in 2 M KOH (CH₃OH:H₂O=9:1vol).
Degradation study (Figure 5.12) was performed by the University of Massachusetts, Amherst by soaking the phenyl cobaltocenium and trimethyl ammonium cation in 2 M KOH (CH\textsubscript{3}OH:H\textsubscript{2}O=9:1vol) at 80°C. The cobalcocenium cation shows an extremely good stability that with only 8% degradation after 650 h compared to a 62% degradation of trimethyl ammonium after 500 h. However, OH\textsuperscript{-} conductivity measurement (Figure 5.13) shows a less stability of the membrane compared to the cation. In Figure 5.13, OH\textsuperscript{-} conductivity of PNPCCI-r-PNBE increases from 30°C to 45°C and then decreases at higher temperatures (50°C and 55°C), which indicates membrane degradation in the OH\textsuperscript{-} form. For PNPCCI-r-PDCPD, conductivity increases continuously from 30°C (0.011 S/cm) to 60°C (0.016 S/cm) and follows a linear Arrhenius relation versus 1/T with activation energy of 11 kJ/mol. PNPCCI-r-PDCPD is more stable than PNPCCI-r-PNBE due to crosslinked structure that shields cationic groups from OH\textsuperscript{-} proximity. Our future work will focus on figuring out the mechanism of the polymer degradation under OH\textsuperscript{-} condition.

![Graph showing conductivity vs. inverse temperature](image)

Figure 5.13 OH\textsuperscript{-} conductivity of PNPCCI-r-PNBE (blue, diamond) at 90% RH and OH\textsuperscript{-} conductivity of PNPCCI-r-PDCPD (red, square) at 80% RH
5.4 Conclusion

We have studied cobaltocenium-functionalized, norbornene-based polymers and compared properties between random and crosslinked membranes. Cyclic voltammetry and thermogravimetric analysis indicate cobaltocenium has sufficient electrochemical and thermal stability to be used as the electrolyte in alkaline fuel cells. Comparing random and crosslinked membranes, TEM images indicated similar hydrophilic domain sizes of ca. 4 nm, which corresponds to the d spacing (ca. 3 nm) from scattering peak for the crosslink membrane, while the random copolymer membrane exhibited scattering peak with larger d spacing of ca. 9 nm. Crosslinking suppresses water uptake (15%, 60°C and 95% RH) and hinders anion transport (conductivity=27 mS/cm, 90°C and 95% RH) compared to the random copolymer (WU=17%, 60°C and 95% RH; conductivity=41 mS/cm, 90°C and 95% RH). Polymer chains in a crosslink network has enhanced rotation barrier, therefore water and anion transport dominated by water mediate transportation instead of chains movement.

However, stability testing on PNPCCl-r-PNBE (OH−conductivity drop off at 50°C) is discouraging compared to the cobaltocenium cation alone (stable in 1 M NaOH/CH3OH at 80°C for 100 h), which demonstrates that a polymer functionalized with cobaltocenium cations may extremely vulnerable in a hydroxide environment. Further investigation will focus on deciphering the mechanism of degradation in cobaltocenium-functionalized membranes.
CHAPTER 6
SUMMARY AND CONCLUSIONS

Alkaline anion exchange membrane fuel cells are widely investigated as a promising alternative to the well-established proton exchange membrane fuel cells. Anion exchange membranes require thermally, chemically, and mechanically stability in a basic environment at the operating temperature and humidity as well as efficient OH\textsuperscript{-} transport across the membrane. Optimization of membrane properties is closely related to the nature of cationic groups, polymer chemistry, and the polymer morphology. This thesis studied AEMs functionalized with three different bulky cations. Bulky cations influenced polymer chemical stability, thermal stability, water uptake, and conductivity. Interplay between chemistry-correlated morphology and transport was explored also.

Degradation studies (Figure 6.1) on 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium functionalize PPO and unsubstituted imidazolium PPO (soaked both two membranes into 1 M KOH at 80°C) indicated attachment of 2,4,6-trimethoxyphenyl group efficiently improve OH\textsuperscript{-} stability due to the enhanced steric and basicity of the central cation. We further investigated a super hydrophobic and bulky phosphonium cation attached by three 2,4,6-trimethoxyphenyl groups. The chemical stability of tris(2,4,6-trimethoxyphenyl) phosphonium surpassed benzyl trimethyl ammonium by 30% after degrading in 1 M KOH at 80°C for 20 days. Cobaltocenium cation, which has 18 valance electrons occupying 9 molecular orbitals achieved the same electron configuration as a noble gas in the same period. By soaking in 1 M NaOH/CH\textsubscript{3}OH at 80°C for 20 days, phenylene cobaltocenium had almost no mass loss and showed 60% higher cation remaining than trimethyl ammonium [57].
Figure 6.1 Degradation studies performed at 80°C on 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium (solid diamond, 1 M KOH), tris(2,4,6-trimethoxyphenyl) phosphonium (solid square, 1 M KOH), phenylene cobaltocenium (solid triangle, 1 M NaOH/CH\textsubscript{3}OH) and benzyl trimethyl ammonium (open square, 1 M KOH; open triangle, 1 M NaOH/CH\textsubscript{3}OH).

Three membranes - 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium, tris(2,4,6-trimethoxyphenyl) phosphonium, and phenylene cobaltocenium - had sufficient thermal stability for use in alkaline anion exchange membrane fuel cells, which operate at 80°C (Figure 6.2). Onset degradation temperature of 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium and tris(2,4,6-trimethoxyphenyl) phosphonium were ca. 220°C and 200°C, respectively. Cobaltocenium functionalized norbornene had the highest thermal stability with the main degradation begins at ca. 400°C. All these three bulky cations were more thermally stable than benchmark trimethyl ammonium, which has a degradation temperature commencing around 140°C [182].
Three bulky cation functionalized AEMs had moderate water uptake in the range of 10%-18% (60°C, 95% RH) (Figure 6.3). Water uptake and hydration number of 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium functionalized PPO and phenylene cobaltocenium functionalized norbornene were similar and both are larger (WU ca. 70% higher at 95% RH, hydration number ca. 30% higher at 95% RH) than water uptake of tris(2,4,6-trimethoxyphenyl) phosphonium functionalized PPO, which is likely due to tris(2,4,6-trimethoxyphenyl) phosphonium being more tightly surrounded by hydrophobic side groups.

![Figure 6.2](image)

Figure 6.2 Thermal gravimetric analysis of 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium functionalized PPO (red), tris(2,4,6-trimethoxyphenyl) phosphonium functionalized PPO (green) and phenylene cobaltocenium functionalized norbornene (blue).
Figure 6.3 Water uptake (solid) and Lambda (open) of 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium functionalized PPO (blue, IEC=1.53, Cl\textsuperscript{-} form), tris(2,4,6-trimethoxyphenyl) phosphonium functionalized PPO (red, IEC=1.20, Br\textsuperscript{-} form), phenylene cobaltocenium functionalized norbornene (green, IEC=1.48, Cl\textsuperscript{-} form).

Figure 6.4 summarized conductivities conducted at 95% RH. Br\textsuperscript{-} conductivity of tris(2,4,6-trimethoxyphenyl) phosphonium functionalized PPO with IEC=1.20 was in between conductivities of trimethyl ammonium AEMs [159], which also in Br\textsuperscript{-} form with IEC=0.87 and 1.84, respectively. 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium functionalized PPO in Cl\textsuperscript{-} form (IEC=1.53 mmol/g) also had comparable conductivity to the poly(ethylene-co-tetrafluoroethylene) grafted vinylbenzyl quaternary ammonium AEMs [162] (IEC=2.06 mmol/g and 1.47 mmol/g) with the same anionic groups measured in liquid water. Among all the membranes, Cl\textsuperscript{-} form phenylene cobaltocenium functionalized norbornene had highest conductivity, which achieved 41 mS/cm at 95% RH and 90\degree C.
To summarize, bulky cations surrounded by electron donation functional groups or with 18-electron inert structure can effectively increase the cation OH⁻ stability. Tris(2,4,6-trimethoxyphenyl) phosphonium and phenylene cobaltocenium are more chemically stable than trimethyl ammonium. Also, these three bulky cations have higher degradation temperature than trimethyl ammonium and are thermally stable used as membrane electrolyte in alkaline fuel cells. Tris(2,4,6-trimethoxyphenyl) phosphonium attached with three 2,4,6-trimethoxyphenyl hydrophobic groups hindered water absorption and did not show obvious evidence of conductivity loss. Among all the membranes, phenylene cobaltocenium functionalized norbornene exhibited a very promising conductivity (41 mS/cm at 95% RH and 90°C, Cl⁻ form),
which is higher than conductivities of the imidazolium and trimethyl ammonium AEMs. However, polymer functionalized with phenylene cobaltocenium was not as stable as phenylene cobaltocenium cation alone in hydroxide form, which reason needs to be further investigated.

This thesis also developed a method to improve membrane conductivity by changing the solvent used for casting, which was selected using Hansen solubility parameters. The optimal solvent (41:59 vol% mixture of DMSO and ethyl lactate) generated morphology featured hydrophilic and hydrophobic domain separation with highly connected hydrophilic pathways. Also, membrane cast by the mixture solvent has more water sorption than the pure solvent (DMSO along and ethyl lactate along) cast membranes. Therefore, mixture solvent cast membrane enhanced the conductivity by 34% compared to DMSO cast membrane and about doubled the conductivity compared to ethyl lactate cast membrane. Besides, solvents also affected water and anion transport mechanism. Ethyl lactate cast membrane showed a linear relation in conductivity, while a VTF non-linear relation in diffusion from Arrhenius plots, which further have been demonstrated that ethyl lactate cast membrane has the strongest cation-anion dissociation.

Comparing random and crosslink cobaltocenium AEMs showed that crosslink membrane had lower water sorption (WU=15% at 95% RH) at high humidity level (95% RH and 60°C), and lower conductivity (27 mS/cm at 95% RH and 90°C) compared to the random membrane (WU=17% at 95% RH, conductivity=41 mS/cm at 95% RH and 90°C). Conductivity of the phenylene cobaltocenium functionalized norbornene in Cl⁻ form was also higher than other random AEMs (imidazolium and ammonium functionalized AEMs) with the same anionic group. Water and anion transport mechanisms were altered in terms of random and crosslink polymer configurations. As to OH⁻ stability, phenylene cobaltocenium cation was much more
stable than cobaltocenium-based polymer. The reason for such large differences between cation and polymer durability should be further investigated.

We found that varied IECs, different solvents used to cast membranes and different polymer structures alter ion and water transport behaviors. Both bulky imidazolium and cobaltocenium functionalized AEMs showed that conductivities, which followed by the VTF mechanism were higher than conductivities followed by linear Arrhenius mechanism. On the contrary, conductivities of phosphonium functionalized PPO membrane followed by VTF mechanism surpassed conductivities followed by Arrhenius mechanism. There lacks of straightforward correlations between transport mechanisms to conductivity/water diffusion data.
CHAPTER 7
ONGOING AND FUTURE WORK

7.1 Work on Progress: Synthesis of 1-methyl-1-hexoxypiperidinium Functionalized AEM

Based on our above studies on 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium, tris(2,4,6-trimethoxyphenyl) phosphonium and phenylene cobaltocenium, these bulky cations functionazlied AEMs have efficiently increased OH\(^-\) stability compared to small cations (imidazolium and trimethyl ammonium) functionalized AEMs, while have comparable conductivities (except for phenylene cobaltocenium) to trimethyl ammonium functionalized AEMs that with the same IEC level and conducting groups. Increasing membrane IEC is able to enhance conductivity but at sacrificing mechanical strength, while crosslink function in the opposite way that benefits mechanical property and deteriorate conductivity.

Establishing AEMs tethered with a long hydrophobic alkyl chain have been reported to enhance conductivity via enhancing transport efficiency [184-186]. It is believed that the added hydrophobic groups promote the microscopic phase separation between hydrophilic and hydrophobic domains and produce enlarged and clustered ionic channels [187,188]. Besides, a number of peer works show that long spacer chains also efficiently improve OH\(^-\) stability. There are three ways to incorporate the hydrophobic side chains. 1) side chains are inserted in between the cation groups and backbones as the linkage which generate a pendent type membrane [189-191]; 2) side chain are attached to the end of cation groups that form a tadpole structure [138,186,192-194] 3) the side chain attach to the backbone that apart from the cation groups. Degradation study [189] on the alkyl spacer chain linked trimethyl ammonium functionalized PPO (PPO-7Q-1.5) showed that PPO-7Q-1.5 can maintain stable after immersion in 1 M NaOH at 80°C for 200 h, while trimethyl ammonium functionalized PPO degraded 80% at the same
condition. Quaternary ammonium with an alky tail chain (C6D40) functionalized PPO [186] have been found degraded 21% after 2000 h by soaking in 1 M NaOH at 80°C compared to a 54% degradation from the membrane without alkyl chain at the same condition. Rao et al [185] have compared the stabilities between alkyl imidazolium-functionalized poly(arylene ether sulfone) block copolymers with alkyl chains length of C2 (Al-PES-2) and C6(Al-PES-6). After soaking in 2 M NaOH at 60°C for 500 h, conductivity of Al-PES-2 decreases 50% while conductivity of Al-PES-6 only decreased 13%. Study on a trimethyl ammonium functionlized polysulfone with separate alkyl side chains (aQAPS-S6) [187] showed that by soaking the membrane in 1 M KOH at 60°C for 300 h, aQAPS-S6 only had a 5% weight loss, while trimethyl ammonium functionlized polysulfone without side chains showed 30% weight loss.

Degradation of AEMs with long said chains in base also follows direct nucleophilic substitution and Hofmann elimination pathways. Yet, the reason for the long chains to improve OH⁻ stability is still less clear. Potential explanations on the said chains preventing cations to be attacked include 1) hydrophobic side chains provide steric shielding around cation groups [186]; 2) due to the alkyl said chain create enlarged and aggregated ionic channels, cations are able to be fully solvated, so as to be OH⁻ resistant [138]. Aromatic ether-based backbones functionalized with benzylic cations undergo cation-triggered backbone degradation via quaternary carbon hydrolysis and ether hydrolysis [184]. Attaching side chains between backbone and cation group have been proved by Arges et al [138] to be an effective approach to alleviating cation induced degradation of aromatic ether-based backbones due to the induced distance in between.

A systematic degradation study on a group of alkytrimethylammonium cations with alkyl chain length from C1 to C16 were developed by soaking cations into 6 M NaOH at 160 °C [195]. Ethyltrimethylammonium had the lowest stability since the degradation is dominated by fast
Hofmann elimination. Stability achieved maximum from propyltrimethylammonium to hexyltrimethylammonium and then dropped off dramatically when the alkyl chain length grows beyond C6, which probably owing to a micelle-induced decomposition. However, investigations on AEMs with C16 length of side chains [185,194] did exhibit a largely improved OH\(^-\) stability compared to AEMs with benzyl trimethyl ammonium. The contrast behavior towards OH\(^-\) stability between hexadecyltrimethylammonium and hexadecyltrimethylammonium functionalized AEM might due to the restriction of polymer backbones to micelle chain stretch out. In considering the influence of poor compatibility between long alkyl side chains and polymer backbone onto the membrane mechanical strength, C6 was chosen as an optimal alkyl chain length to study. Marino et al [195] also showed that dimethylpiperidinium has a super high OH\(^-\) stability with half-life degradation time of 87 h when soaking in 6 M NaOH at 160°C, while the half-life degradation time of benzyl trimethyl ammonium at the same condition is only 4 h. So in our work, we will develop and investigate 1-hexyl-1-methylpiperidium functionalized triblock copolymer, which expects to have high chemical stability as well as promising conductivity.

7.1.1 Materials

Piperidine, C\(_5\)H\(_{11}\)N, (Aldrich, 411027, ≥99.5%); 1-Chloro-6-hydroxyhexane, Cl(CH\(_2\))\(_6\)OH, (Acros, 109281000, 95%); Potassium carbonate, K\(_2\)CO\(_3\), (J. T. Baker, anhydrous, 5-3012, 99.9%); N,N-Dimethylformamide, C\(_3\)H\(_7\)NO, (Sigma-Aldrich, anhydrous, 227056, ≥99.8%); Sodium sulfate, Na\(_2\)SO\(_4\), (Fisher Scientific, S421-500, anhydrous); Ethyl acetate, CH\(_3\)COOC\(_2\)H\(_5\), (EtOAc, Macron, UN1173, 99.9%); Tetrahydrofuran, C\(_4\)H\(_8\)O, (Sigma-Aldrich, anhydrous, 401757, ≥99.9%); Sodium hydride, NaH, (Sigma-Aldrich, 452912, 60% dispersion in
mineral oil); Methanol, CH$_3$OH, (Sigma-Aldrich, 34860, ≥99.9%); Methyl iodide, ICH$_3$, (Sigma-Aldrich, 18504, ≥99.9%).

Poly(chloromethylstyrene)$_{107}$-b-polycyclooctene$_{344}$-b-poly(chloromethylstyrene)$_{107}$ (PCMS-b-PCOE-b-PCMS) was provided by University of Massachusetts Amherst. Molecular weight of the triblock copolymer is 72000 and polydispersity index is 1.51.

7.1.2 Synthesis of 1-hexyl-1-methylpiperidium Functionalized Triblock Copolymer

6-piperidino-hexanol

To a 250 mL round bottom flask, piperidine (10 mL, 100.16 mmol, 1.00 eq) was dissolved in 100 mL DMF, followed by slowly addition of K$_2$CO$_3$ (26.3 g, 0.19 mol, 1.87 eq), and 1-chloro-6-hydroxyhexane (20.5 mL, 0.148 mol, 1.48 eq). The reaction mixture was stirred at 95°C for 20 h and cooled down to room temperature, then it was filtered and washed with EtoAc (100 mL). The product was diluted with DI water to dissolve potassium carbonate and DMF followed addition of aqueous sat. sodium bicarbonate solution. The organic layer was collected and the aqueous layer was extracted with EtOAc (3 x 100 mL). The combined organic layers were washed with brine (3 x 150 mL), and then dried over anhydrous sodium sulfate. The solvent was evaporated, dried in the oven at 50°C overnight and gave a yield of 18.33 g (orange oil, 97.2%).

![Figure 7.1 Synthesis of 6-piperidino-hexanol.](image)

6-piperidino-hexoxy-PCMS-b-PCOE-b-PCMS 3 g polymer was dissolved in 15ml anhydrous THF. 3 ml 6-(piperidin-1-yl)hexan-1-ol was added in 15 ml anhydrous THF under Ar, 0°C. 0.4312 g NaH was cautiously added and reaction was stirred for further 70 min. Solution 1
then added dropwise and mixture was reacted at room T for 24 h. The product was dissolve in DMP to make 20% solution. The polymer solution was drop cast on a pre-cleaned glass substrate and heated in a vacuum oven at 60°C for 24 h. After removal from the substrate, the membrane was soaked in DI water to completely remove the solvent.

![Reaction diagram]

**Figure 7.2** Synthesis of 6-piperidino-hexoxy-PCMS-b-PCOE-b-PCMS.

**1-methyl-1-hexoxypiperidium functionalized PCMS-b-PCOE-b-PCMS** The cast 6-piperidino-hexoxy-PCMS-b-PCOE-b-PCMS membrane was soaked in 35 ml methanol added with 3 ml methyl iodide. The solution was stirred for 24 h at 30°C, then thoroughly washed by excess methanol and DI water, obtained membrane was in $\Gamma^-$ form. Ion exchange the membrane into $\text{Cl}^-$ form was performed by soaking the membrane into 1 M NaCl solution for 48 h at room temperature followed by completely wash and soak the membrane in DI water for another 5 days. Then the membrane was dried in vacuum oven overnight at 60°C.
In the second step synthesizing 1-methyl-1-hexoxypiperidium functionalized triblock copolymer, 6-piperidino-hexanol was reacted with vinyl benzyl chloride and both amine and hydroxyl group are able to react with benzyl chloride. The polymer solution used to cast membrane still had a small amount of crosslinking since the solution was cloudy, though a membrane could be created. In the future work, more reaction conditions will be tried out, like adjusting solvent concentration (very dilute solution) as well as polymer monomer ratio (excess 6-piperidino-hexanol) to keep crosslink to the minimum. With the non-crosslink product, structure of the polymer could be well defined from NMR. Also polymer could be well dissolved in solvents to get mechanically stronger membrane. Moreover, chemical stability will be studied by soaking the membrane in 1 M KOH at 80°C. Membrane degradation will be defined by the
loss of IEC based on titration. Also, morphology as well as transport property of the long spacer chain AEM will also be investigated.

7.2 Recommendations for Future Work

As discussed in Chapter 4, in order to increase the alkaline stabilities of phosphonium cation, the selection criteria of the phosphine precursor should combine both steric and electronic attributes. Methyl group has a larger steric hindrance than the methoxy group since methyl group has a more negative steric substituent constant ($E_s$) than the methoxy group ($E_s$(Me) = -1.24, $E_s$(MeO) = -0.55) [196]. Even though methoxy is volumetric larger than methyl group, C-O bond rotation allows more free volume to minimize steric repulsion. In the future work, developing more stable tris(2,4,6-trimethylphenyl) phosphonium instead of tris(2,4,6-trimethoxyphenyl) phosphonium could take advantage of a methyl group’s larger steric hindrance.

Phenylene cobaltocenium functionalized norbornene has comparable water uptake and hydration number, while higher conductivity compared to 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium functionalized PPO, indicating the high conductivity of cobaltocenium membrane does not mainly on account of water promoted transport. Moreover, there is no evidence from TEM that phenylene cobaltocenium functionalized norbornene has a highly ordered hydrophilic domains, which are able to facilitate anion transport. Figuring out why the cobaltocenium cation highly conducts is able to help to modify cation structure. With this advantage, we can generate highly conduct membrane with moderate IEC that reduces risk of damaging mechanical property, also avoids synthesis of block copolymer.

Backbone degradation in OH⁻ has not been investigated as extensively as cation degradation. Fluorinated polymers have been reported was among the most base-resistant
backbone, and polyvinylidene fluoride was not found to be stable [166]. Though polysulfone was shown to be stable even after exposure to 40% NaOH at 70-80°C for 300 h [197], after quaternization, the membrane easily went brittle due to cation triggered backbone degradation. Similarly, in our durability study, we found single cobaltocene cation and its functionalized polymer were not equally stable. Soaking in 2 M KOH at 80°C, the phenylene cobaltocene cation only showed 8% degradation after 650 h, while the polymer degraded at 50°C observed from \( \text{OH}^- \) conductivity measurement. The result raises a new question as to backbone cation interaction that has not been largely investigated so far.
REFERENCES


[38] A.L. Ong, S. Saad, R. Lan, R.J. Goodfellow, S. Tao, Anionic membrane and ionomer based on poly (2, 6-dimethyl-1, 4-phenylene oxide) for alkaline membrane fuel cells, J. Power Sources 196 (2011) 8272-8279.


[75] S.W. Kantor, C.R. Hauser, Rearrangements of benzyltrimethylammonium ion and related quaternary ammonium ions by sodium amide involving migration into the ring1, 2, 3, J. Am. Chem. Soc. 73 (1951) 4122-4131.


COPYRIGHT PERMISSIONS

This Appendix includes expressed, written permission from the copyright holders granting permission for republication of the material contained in Chapter 3 and Chapter 4. Written consent for republication from all Co-authors is also included.
Thesis-Permission to reproduce

Yuan Yang <yuanyang@mines.edu>  
To: Ye Liu <yeliu@mymail.mines.edu>  

Hi Ye,

I hereby permit Ye Liu to reproduce the following works as part of her thesis:

"Anion exchange membranes composed of a poly(2,6-dimethyl-1,4-phenylene oxide) random copolymer functionalized with a bulky phosphonium cation" published in the J. Membrane Sci. 2016, 506, 50-59.


Good luck!  
Best,  
Yuan Yang
Hi Ye,

Congrats and best of luck in your defense!

I hereby permit Ye Liu to reproduce the following works as part of her thesis:


Tom

Thomas Brenner
AERI Post-Doctoral Fellow
Dept. of Materials and Interfaces
Weizmann Institute of Science
Title: Anion exchange membranes composed of a poly(2,6-dimethyl-1,4-phenylene oxide) random copolymer functionalized with a bulky phosphonium cation

Author: Ye Liu, Bingzi Zhang, Corey L. Kinsinger, Yuan Yang, Soenke Seifert, Yushan Yan, C. Mark Maupin, Matthew W. Liberatore, Andrew M. Herring

Publication: Journal of Membrane Science
Publisher: Elsevier
Date: Dec 31, 1969
Copyright © 1969, Elsevier

Order Completed

Thank you for your order.

This Agreement between ("You") and Elsevier ("Elsevier") consists of your order details and the terms and conditions provided by Elsevier and Copyright Clearance Center.

**License number**
Reference confirmation email for license number

**License date**
Jun 20, 2016

**Licensed Content Publisher**
Elsevier

**Licensed Content Publication**
Journal of Membrane Science

**Licensed Content Title**
Anion exchange membranes composed of a poly(2,6-dimethyl-1,4-phenylene oxide) random copolymer functionalized with a bulky phosphonium cation

**Licensed Content Author**
Ye Liu, Bingzi Zhang, Corey L. Kinsinger, Yuan Yang, Soenke Seifert, Yushan Yan, C. Mark Maupin, Matthew W. Liberatore, Andrew M. Herring

**Licensed Content Date**
Available online 22 January 2016

**Licensed Content Volume**
n/a

**Licensed Content Issue**
n/a

**Licensed Content Pages**
1

**Type of Use**
reuse in a thesis/dissertation

**Portion**
full article

**Format**
both print and electronic

**Are you the author of this Elsevier article?**
Yes

**Will you be translating?**
No

**Order reference number**

**Title of your thesis/dissertation**
Effect of bulky cations on the function and stability of anion exchange membranes

**Expected completion date**
Aug 2016

**Estimated size (number of pages)**
160

**Elsevier VAT number**
GB 494 6272 12

**Requestor Location**
Ye Liu
615 Water Street
408 Apt
<table>
<thead>
<tr>
<th>Billing Type</th>
<th>Invoice</th>
</tr>
</thead>
</table>
| Billing address | Ye Liu  
615 Water Street  
408 Apt  
GOLDEN, CO 80401  
United States  
Attn: Ye Liu |
| Total         | 0.00 USD        |
I hereby permit Ye Liu to reproduce the following works as part of her thesis:

"Anion exchange membranes composed of a poly(2,6-dimethyl-1,4-phenylene oxide) random copolymer functionalized with a bulky phosphonium cation" published in the *J. Membrane Sci.* 2016, 506, 50-59.

[Quoted text hidden]
Thesis-Permission to reproduce

Christopher Maupin <cmmaupin@mines.edu>  
To: Ye Liu <yeliu@mymail.mines.edu>  

Mon, Jun 20, 2016 at 12:37 PM

Dear Ye,

Yes, I give you permission to use the from our co-authored paper.

I hereby permit Ye Liu to reproduce the following works as part of her thesis:

"Anion exchange membranes composed of a poly(2,6-dimethyl-1,4-phenylene oxide) random copolymer functionalized with a bulky phosphonium cation" published in the *J. Membrane Sci.* 2016, 506, 50-59.

Best wishes,

Mark

************************************************
C. Mark Maupin, Ph.D.
Council Member, Pacific Division of AAAS
AAAS-PD Information Sciences Section Chair
Senior Editor AIMS Molecular Science
Assistant Professor
Chemical and Biological Engineering Department
Colorado School of Mines
Alderson Hall, Rm 437
Golden, CO 80401
Phone: 303-273-3197
Fax: 303-273-3730
Web page: http://biofuels.mines.edu/
************************************************

From: Ye Liu [yeliu@mymail.mines.edu]
Sent: Monday, June 20, 2016 12:23 PM
To: Christopher Maupin
Subject: Thesis-Permission to reproduce

[Quoted text hidden]
I hereby permit Ye Liu to reproduce the following works as part of her thesis:

"Anion exchange membranes composed of a poly(2,6-dimethyl-1,4-phenylene oxide) random copolymer functionalized with a bulky phosphonium cation" published in the J. Membrane Sci. 2016, 506, 50-59.


Sincerely,

Soenke Seifert, Ph.D

Argonne National Laboratory,
APS/ANL 433E008
9700 South Cass Avenue,
Argonne Illinois 60439
office: 6302520391