

REPORT DOCUMENTATION PAGE			Form Approved OMB NO. 0704-0188		
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1. REPORT DATE (DD-MM-YYYY)		2. REPORT TYPE		3. DATES COVERED (From - To)	
		New Reprint		-	
4. TITLE AND SUBTITLE (Invited) Thin Robust Anion Exchange Membranes for Fuel Cell Applications			5a. CONTRACT NUMBER		
			W911NF-10-1-0520		
			5b. GRANT NUMBER		
6. AUTHORS H. N. Sarode, M. A. Vandiver, Y. Liu, A. Maes, T. P. Pandey, S. P. Ertem, T. Tsai, B. Zhang, D. Herbst, G. Linberg, Y.-L. S. Tse, S. Seifert, V. Di Noto, E. B. Coughlin, Y. Yan, G. Voth, T. Witten, D. M. Knauss, M. V. ...			5c. PROGRAM ELEMENT NUMBER		
			611103		
			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAMES AND ADDRESSES			8. PERFORMING ORGANIZATION REPORT NUMBER		
Colorado School of Mines 1500 Illinois Street Golden, CO 80401 -1887					
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211			10. SPONSOR/MONITOR'S ACRONYM(S) ARO		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S) 58161-CH-MUR.58		
12. DISTRIBUTION AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.					
13. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.					
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15. SUBJECT TERMS Anion Exchange Membranes, Ionic Conductivity, Polymer Morphology, Polymer Stability					
16. SECURITY CLASSIFICATION OF:		17. LIMITATION OF ABSTRACT		15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Andrew Herring
UU	UU	UU	UU		19b. TELEPHONE NUMBER
					303-384-2082

Report Title

(Invited) Thin Robust Anion Exchange Membranes for Fuel Cell Applications

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REPORT DOCUMENTATION PAGE (SF298)
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Continuation for Block 13

ARO Report Number 58161.58-CH-MUR
(Invited) Thin Robust Anion Exchange Membrar...

Block 13: Supplementary Note

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Thin Robust Anion Exchange Membranes for Fuel Cell Applications

Himanshu Sarode,^a Melissa A. Vandiver,^a Ye Liu,^a Ashley M. Maes,^a Tara P. Pandey,^a
S. Piril Ertem,^c Tsunghan Tsai,^c Bingzi Zhang,^d Daniel C. Herbst,^f
Gerrick E. Lindberg,^e Ying-Lung Steven Tse,^e Sönke Seifert,^g Vito Di Noto,^h
E. Bryan Coughlin,^c Yushan Yan,^d Gregory A. Voth,^e Thomas A. Witten,^f
Daniel Knauss,^b Matthew W. Liberatore,^a and Andrew M. Herring.^a

^aDepartment of Chemical and Biological Engineering and

^bDepartment of Chemistry and Geochemistry, Colorado School of Mines, Golden, CO
80401, USA

^cDepartment of Polymer Science and Engineering, Conte Research Center, University of
Massachusetts, Amherst, MA 01003, USA

^dDepartment of Chemical Engineering, University of Delaware, Newark, DE 19716, USA

^eDepartment of Chemistry and ^fDepartment of Physics, James Franck Institute and
Computation Institute, University of Chicago, Chicago, IL 60637, USA

^gAdvanced Photon Source, Argonne National Laboratory, Argonne, Illinois, 60439, USA

^hDipartimento di Scienze Chimiche, Università di Padova, 35131 Padova, Italy

Extensive transport and modeling studies have been performed on a series of polymers based on the benzyltrimethylammonium cations. We have created a realistic reactive model of solvated hydroxide that has interesting properties in the polymer matrix. In ordered diblock polymers we have strong theoretical evidence for a heterogeneous distribution of water across the channel. Fluoride is used as a non-reactive surrogate for hydroxide to increase the computational efficiency of transport calculations that can be performed. In addition to these studies we are discovering new base stable processable robust polymer backbones and cations. These bulky cations seem to dramatically affect the transport properties of the anions showing a VTF rather than an Arrhenius behavior with temperature.

Introduction

The potential of anion exchange membrane (AEM) fuel cells to provide inexpensive compact power from a wider variety of fuels than is possible with a proton exchange membrane (PEM) fuel cell, has continued to drive research interest in this area. Alkaline catalysis in fuel cells has been demonstrated with non-precious metal catalysts (1), and with a variety of fuels beyond H₂ and methanol. Alkaline fuel cells (AFCs), based on aqueous solutions of KOH, have serious drawbacks associated with system complexity and carbonate formation. Anion exchange membrane (AEMs) fuel cells have a number of advantages over both PEM fuel cells and traditional AFCs; however, ionic conductivity in AEMs is still lower than PEMs and chemical stability of membrane attached cations in hydroxide is still not sufficient for practical applications (2).

Fuel cell electrolyte membranes must be designed to balance, among other things, ionic conductivity vs. structural integrity. These goals are often at odds with each other when it comes to water absorption. Ions require wet pathways to traverse the membrane. Too much water, however, and the polymer can become a gel and lose integrity. One way to satisfy both requirements is by having a di-block co-polymer with a hydrophilic block purposed to absorb water, while a hydrophobic block retains the membrane structure. To gain a fundamental understanding of water absorption at the nanoscale level, we have studied in depth a relatively simple di-block system, poly(methylbutylene)-block-poly(vinylbenzyl trimethylamine), or PMB-PVBTMA. This was chosen for its relative ease of study in experiment, theory, and simulation, allowing a multi-pronged approach. The material anneals to form alternating lamellae of the two blocks, PMB and PVBTMA. PMB is a well-studied hydrocarbon that is rubbery at operating temperature. It was selected to be strong enough to hold together the membrane, but flexible enough to allow the other block to swell with water. PVBTMA is a positively-charged polyelectrolyte, so it absorbs water and facilitates anion transport. In this paper we report our progress in modeling this material, the synthesis of AEMs with optimized properties, studies to understand anion transport, and the consequences of using bulkier but more stable cations in AEMs.

Atomistic Modeling

Computational simulations of the atomistic origins of hydroxide transport in anion exchange membranes rely on having an accurate and efficient description of hydroxide. Many details of hydroxide transport and solvation in water have been characterized with sophisticated experiments and high-level quantum calculations. Experiments cannot currently provide the needed resolution to understand the atomic details of AEM performance, so theoretical methods are required. Unfortunately quantum calculations are not able to consider the required large system sizes and long time scales because of the computational expense, so approximate but accurate methods must be developed. The multistate reactive molecular dynamics (MS-RMD) method has been found to be the best compromise between accuracy and cost (1). A model was parameterized for the simulation of hydroxide in water. An important finding of this model was the crucial importance of water as a transient hydrogen bond acceptor for hydroxide. While molecular arrangements with water accepting a hydrogen bond from hydroxide are relatively rare, these arrangements are important for proton transfer events. Using *ab initio* molecular dynamics simulations of aqueous KOH, we parameterized an MS-RMD hydroxide model for use in concentrated basic systems like anion exchange membranes that samples the correct solvation structures of hydroxide. In addition to describing the correct solvation structures, we found that this model yields a proton transfer free energy barrier and proton hop frequencies similar to those of *ab initio* molecular dynamics simulations.

We are now simulating this MS-RMD hydroxide model in the homopolymer polyvinyl benzyltrimethylammonium (PVBTMA) (see a typical snapshot in Figure 1). The membrane environment is found to have interesting effects on the structure and transport of hydroxide. The coordination number of water molecules is found to be higher than the bulk water number of 4.3. The free energy barrier for proton transfer is found to be slightly reduced from the value in aqueous solution. Interestingly though, while the proton transfer events in the anion exchange membrane are more frequent as would be

expected from the increased hydration and reduced free energy barrier, these tend to be “rattling” events, where newly formed hydroxide ions tend to be short-lived and the chemical identity of the hydroxide ion oscillates between two water centers. While it appears that the anion exchange membrane environment promotes the solvation of hydroxide by more water molecules and reduces the free energy barrier for proton transfer when compared to aqueous solution, the likelihood of hydroxide migration is actually reduced. Therefore the balance between standard vehicular and “Grotthuss” hopping transport mechanisms will be different than is observed for hydroxide in aqueous solution. We are continuing our efforts to investigate these effects.

During the synthesis of anion exchange membranes, the counterion must be exchanged from a halide to hydroxide. The ion exchange is usually not complete and so it is important to understand this mixing of two different kinds of anions. We previously reported that this co-ion effect could lead to an observation in which chloride enhances the self-diffusion constant of fluoride in the homopolymer PVBTMA (2). We hypothesized the origin of this effect is from the fact that chloride loses some of its solvation water as it approaches a cation, and this effectively increases the hydration level for the medium. We proposed that this effect should be more general and should also happen in any aqueous system in which there are two different anions that have different ionic radii. With our new hydroxide model, it will be interesting to see how this co-ion effect can affect hydroxide transport when Grotthuss hopping mechanism is present.

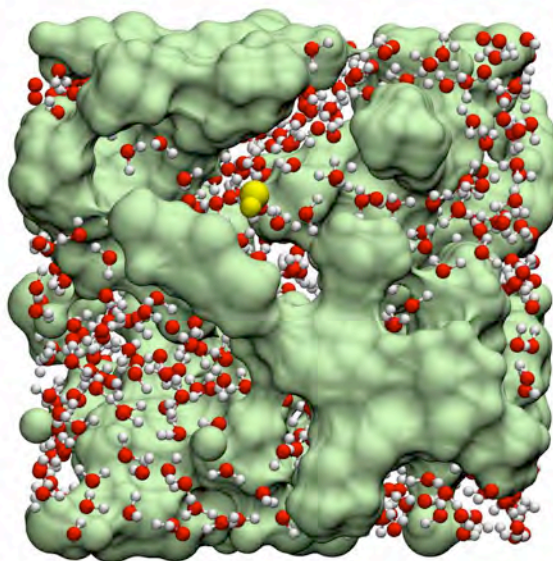


Figure 1: A typical configuration of the new hydroxide model in PVBTMA. The ball and stick atoms are water molecules, the amorphous volume represents polymer atoms, and the hydroxide ion is shown towards the top center of the atom as the space filling atoms.

Morphology

In previous reports, we compared the swelling seen in x-ray scattering (SAXS), water mass uptake (DVS), and Scheutjens-Fleer mean-field theory. On first inspection there was no quantitative agreement between any of the three. This was assuming that the

hydrophobic PMB lamellae remain at a fixed width, independent of water absorption. It turns out that this is not the case, and the hydrophobic lamellae indirectly react to changing water levels, as pointed out by Winey *et al.* (3). When the membrane absorbs water, the water molecules penetrate the PVBTMA, tending to spread apart the chains. This can happen in one of two ways. The PVBTMA can fan out away from the block interface, tending to form a polymer brush and causing the PVBTMA lamellae to widen. This is the behavior that we can predict from the mean-field model. Alternatively, the interface can expand in area, spacing the polymers out laterally. By itself, the latter effect causes the combined lamellar spacing to narrow. In reality, both effects happen concurrently and compete in a complex manner.

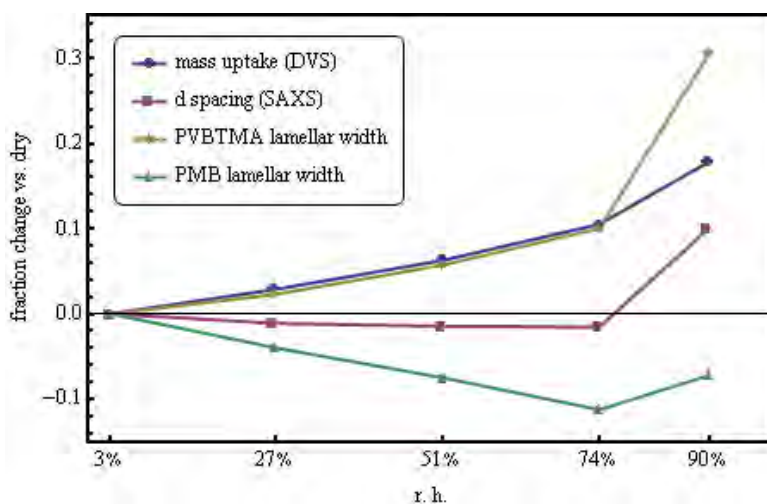


Figure 2: A comparison of fractional change vs. relative humidity of: mass change of the total membrane measured in DVS (circles); d-spacing from SAXS (squares); the inferred width of the PVBTMA lamellae (diamonds); and the inferred width of the PMB lamellae (triangles). The thickening vs thinning of the two blocks is due to competition between brush swelling and lateral swelling.

We have recently been able to quantify these effects and have used the results to improve the mean-field calculation. To measure how the thickness of both blocks varies with water uptake, we combined SAXS and DVS data taken under identical conditions. From the SAXS, we collected the primary q peak which determines the d -spacing, the sum of the hydrophilic and hydrophobic lamellar widths. The d -spacing actually decreases slightly with increasing water absorption up to 74% relative humidity before increasing (see Figure 2). This is indicative of lateral chain swelling, where the PMB lamellae narrow. The DVS experiment determines how much water the membrane absorbs. Assuming ideal mixture, this gives the increase in volume of the hydrophilic block. Therefore, taken together the two experiments give the width of each lamella as a function of humidity (see Figure 2). This can be used to calculate the grafting density, σ , of the hydrophilic polymers, a quantity that feeds into the mean-field calculation.

The Scheutjens-Fleer mean-field model is used to calculate the spatial water distribution within a hydrophilic lamella. Similar methods have been used to calculate the water distribution within a polymer brush, where polymers are attached to a rigid surface (4). With slight modifications, the calculation handles the variable grafting density,

σ (humidity), calculated from the experiments. As we have shown previously (5), the water distribution strongly favors a near-uniform osmotic pressure throughout. This permits two types of water distributions: either a uniform water distribution, or one where the polymer concentration jumps between two co-existing phases. In the latter case, the dilute phase usually arranges into a slab centered around the lamellar midplane, which we have termed a “water channel”. With the new σ (humidity) input, as well as improvements to other inputs, the predicted swelling is now within 10% of the experimental measurements. This adds confidence to the ability of mean-field theory to describe solvent uptake in di-block lamellar membranes in general, and to the possibility of water channels in the hydrophilic phase.

Polymer Synthesis

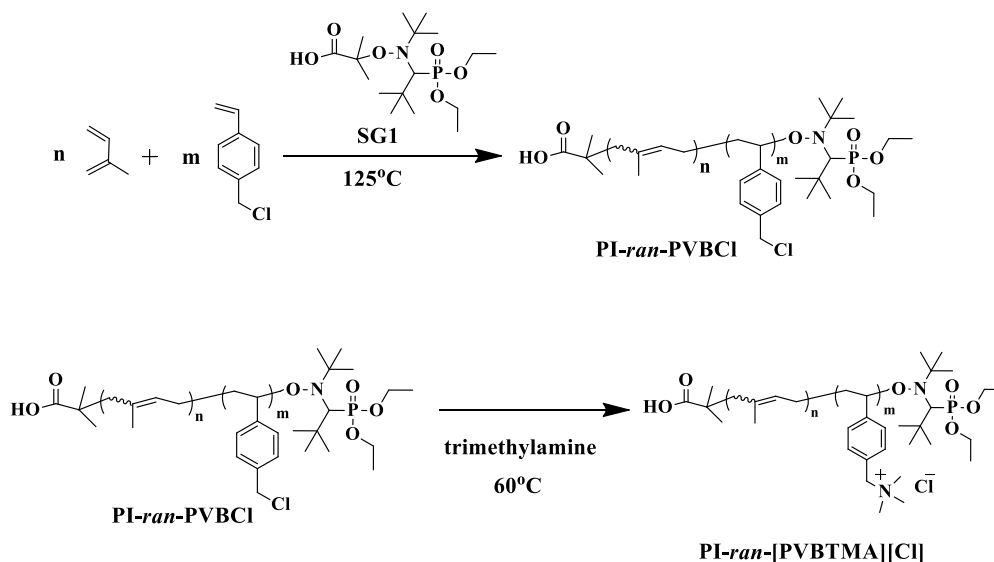
Here we present a versatile synthetic approach to obtain solvent processable, crosslinkable copolymers that form robust membranes suitable to use as anion exchange membranes (AEMs). Vinylbenzyl chloride (VBCl), and isoprene were used as building blocks to synthesize polyisoprene-*ran*-poly(vinylbenzyl chloride) (PI-*ran*-PVBCl) copolymers. Robust, flexible and ion conducting membranes were obtained through a simple thermal treatment without addition of any extra crosslinkers. The conductivity properties of the resulting membranes were investigated by impedance spectroscopy. Small angle X-Ray scattering (SAXS) experiments under controlled humidity and temperature was employed to correlate morphology with conductivity properties.

Random copolymers of isoprene and vinylbenzyl chloride (VBCl) were synthesized via nitroxide mediated polymerization, a versatile synthetic technique suitable for polymerization of a wide range of monomers. The versatility of this synthetic technique allowed synthesis of a series of copolymers with varying copolymer compositions through bulk polymerization of isoprene and VBCl monomers. Desired copolymer compositions were achieved by tuning the monomer ratio in the copolymerization reaction. Copolymer compositions were determined from ^1H -NMR by comparing the corresponding chemical shifts for allylic protons of isoprene units and benzylic protons of VBCl units: δ 4.7 - 6.0 ppm and at δ 4.5 ppm, respectively. The random character of the PI-*ran*-PVBCl copolymers was confirmed from the matching values of copolymer composition and monomer feed ratio. Reactivity ratios of isoprene and VBCl (1.30 and 0.75, respectively) analyzed from their Q-e values support this result (6). A broad dispersity is indicative of possible chain transfer reactions during polymerization, and has also been observed for homopolymerization of isoprene under similar temperature and reaction time conditions (7). Despite their broad dispersity the isolated polymers were soluble in organic solvents. These copolymers were designed to form a covalently crosslinked network structures; therefore, for the purposes of this work a well-controlled molecular weight is not crucial.

Through a simple quaternization reaction of the copolymers in aqueous trimethylamine (TMA) solution, benzyl chloride units were converted to benzyltrimethylammonium (BTMA) cations, with chloride as the counter ion, with a range of ion exchange capacities between 0.77 and 2.34 mmol/g. Quantitative conversion to BTMA was confirmed by FTIR spectroscopy by monitoring the complete disappearance of the carbon chloride bond vibration band at 1260 cm^{-1} . A qualitative confirmation of complete quaternization is the change in solubility properties of the

copolymers. During the quaternization process water insoluble PI-*ran*-PVBCl copolymers became water soluble polyisoprene-*ran*-poly(vinyl benzyl trimethylammonium chloride) (PI-*ran*-P[VBTMA][Cl]) copolymers. This is a strong indication of formation of a hydrophilic polycation. Besides being soluble in water, all of the quaternized copolymers showed excellent solubility in methanol, regardless of their IECs, providing solvent processability and ease of membrane fabrication.

In present work, we have demonstrated the transport behaviors of the AEMs with different IECs and crosslink densities including water diffusion coefficients and anion exchange constants by using time-resolved FTIR-ATR spectroscopy. The data quantitatively show the water diffusion coefficient increases with increasing IEC and decreasing crosslink density. The transport properties are similar to that of Nafion™. The water diffusivities in terms of the hydration level have also been obtained. The results suggest the diffusion coefficient increases with increasing water content. Finally, the transportation of various single anions and mixed anionic pairs within these AEMs were performed. The ranking of ion transport rate for a series of different anions is $\text{NO}_3^- > \text{BF}_4^- > \text{CO}_3^{2-} \approx \text{HCO}_3^-$. Therefore, within these cross-linked membranes we have explored fundamental transport properties in real-time enabling the investigation of the water and anion transport mechanisms in AEMs and the correlation of property- to-structure relationships. From these results we are able to have a better understanding on how to further design AEMs access desired optimum performances for AAEMFCs.



Scheme 1: Polymerization of PI-*ran*-PVBCl (Top), quaternization to PI-*ran*-P[VBTMA][Cl] (bottom)

Transport Studies

Benzyl Trimethyl Ammonium Cations.

As the standard benzyltrimethyl ammonium (BTMA) cation is not stable to hydroxide, but is synthetically convenient we study transport using fluoride anions. This

is because Fluoride is approximately the size of the hydroxide anion and modeling these system is facile because Fluoride can only move via a vehicle mechanism and so can be modeled using classical molecular dynamics methods, it also has the advantage that it has a spin $\frac{1}{2}$ nucleus, ^{19}F and so NMR studies (2) can probe anionic diffusion and differentiate it from water diffusion. Here we use a Polyphenylene Oxide diblock polymer co-polymerized with polyvinyl benzyl trimethyl ammonium blocks (PPO-b-PVBTMA[F⁻]), Figure 3, for PFGSE NMR and ionic conductivity studies under humidified conditions in this work.

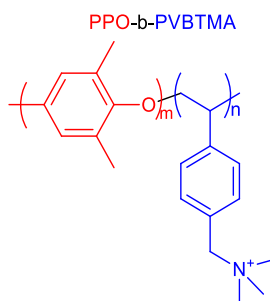


Figure 3: Polyphenylene Oxide –b- Polyvinyl Benzyl Trimethyl ammonium polymer membrane, IEC = 2.7 meq/g dry polymer

Figure 4 shows fluoride diffusion as a function of diffusion time and temperature. It can be seen in the figure that as we increase the diffusion time, that the diffusion of fluoride ions is restricted and lowers the diffusion of fluoride ions, showing the presence of tortuous anionic pathways in the membrane. We can characterize the sub micron feature size using Mitra's equation for this AEM (8). The size of the features inside of the membrane was found to be between 30 nm to 43 nm thus proving the presence of nanometer size channels in the membrane for water and ion transport. Even though the IEC of the membrane is 2.7 meq/g, λ was found to be 4.7 waters/charge carrier at 60 °C from Dynamic Vapor Sorption experiments, showing that the membrane does not swell much even at such high IEC.

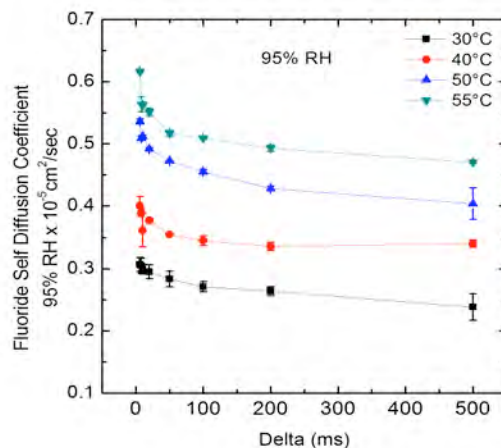


Figure 4: Fluoride diffusion in PPO-b-PVBTMA[F⁻] AEM under saturated humidity environment

Conductivity of this membrane was measured under 95% relative humidity condition using electrochemical impedance spectroscopy as shown in Figure 5. The fluoride conductivity was 30.5 mS/cm at 60 °C. The conductivity as well as fluoride diffusion follows Arrhenius behavior with an E_a of 15.6 and 20.5 kJ/mol respectively, showing lower temperature dependence of these two transport properties. Thus low water uptake, low activation energy and high conductivity of this membrane makes it a promising material for applications in anion exchange membrane fuel cells.

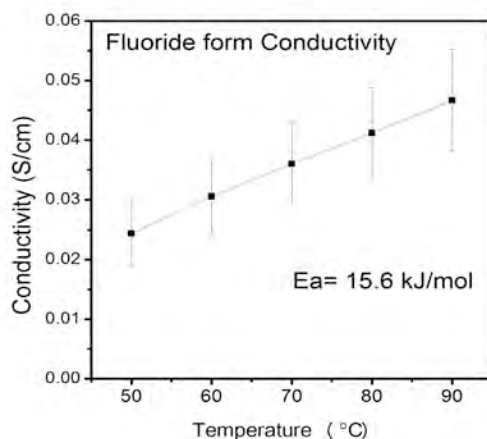


Figure 5: Conductivity of PPO-b-PVBTMA[F] under 95% Relative Humidity

Stable Cations

Novel cations are emerging to be more chemically stable based on cation-structures modification. We showed in our previous work using 1,4,5-trimethyl-2-(2,4,6-trimethoxy phenyl) imidazolium functionalized polyphenylene oxide (PPO-TMIM), that attachment of 2,4,6-trimethoxy phenyl groups onto imidazole ring (α -C) enhances the chemical stability due to electron donating function as well as steric effect (9). Hence, we expect a more encouraging durability in the alkaline condition by adding three 2,4,6-trimethoxyphenyl groups on a high basicity phosphine. The structure of the tris(2,4,6-trimethoxyphenyl) phosphonium functionalized polyphenylene oxide (PPO-TPQP-40) polymer we are studying on is shown in Figure 6. The calculated theoretical IEC is 1.18 mmol/g.

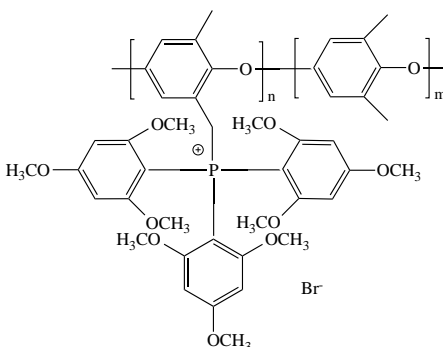


Figure 6. Structure of tris(2,4,6-trimethoxyphenyl) phosphonium functionalized PPO.

Besides the chemical stability benefits, these large novel cations are expected to effect the properties of the polymer and anion transport as compared to simple benzyltrimethyl ammonium cations. For example, the bulky cations probably influence a tight entanglement between polymer chains during the membrane fabrication process, or affect the water molecules distribution under humidified conditions. Figure 2 shows the membrane image by drop casting from DMSO solution. This shows that an intact, transparent membrane can be formed with the bigger cations. The bromide conductivity data at both 95% RH and 80% RH is shown in Figure 3. We noticed that both of them do not exhibit a linear Arrhenius behavior. From 30 to 50 °C conductivities increase faster than in the temperature range between 50 to 90 °C. The inflection point at around 50 °C indicates either a super Arrhenius transport behavior or two Arrhenius transport combinations. The highest conductivity of the Br⁻ form membrane is 3.0 mS/cm. We are currently studying this material using a variety of techniques in the hydroxide form.



Figure 7. Image of a PPO-TPQP-40 film from drop casting from DMSO.

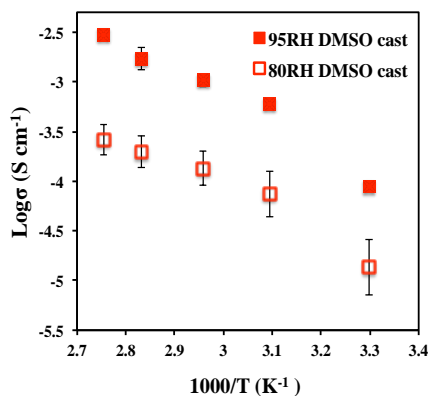


Figure 8. Conductivities of the PPO-TPQP-40 polymer under 95% RH and 80% RH.

Conclusions

Using benzyltrimethyl ammonium (BTMA) cations as a model cation, we have developed a model of hydroxide that is shedding new light on how hydroxide moves through anion exchange membranes. Interestingly initial results suggest that the hydroxide is more hydrated in the polymer matrix than in bulk water. Modeling also

suggests that the distribution of water in a channel in the polymer is not heterogeneous. High mobility of these cations is required in processable cross-linkable materials and so we have developed polymer systems that can achieve these properties. Transport studies indicate that most AEMs have considerable restriction in their diffusion path lengths, but ionic conductivities using the smaller BTMA cations show Arrhenius behavior indicating that the anions are fully dissociated. For larger cations that are much more stable to hydroxide nucleophilic attack, ionic conductivity often does not show Arrhenius behavior, and so a VTF or similar model must be used to describe the behavior of the anion that is much more associated with the cation.

Acknowledgments

The authors would like to thank the Army Research Office for support of this research under the MURI program, grant number W911NF-10-1-0520. Use of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory, was supported by the U.S. DOE under Contract No. DE-AC02-06CH11357.

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