Poly(arylene ether) Ionomers with Pendant Quinuclidium Groups and Varying Molecular Weight for Alkaline Electrodes

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The properties of the ionomer used to construct electrodes for direct methanol anionic fuel cells are critically important to the fuel cell performance. In this study, a new polymer backbone with a higher degree of fluorination for increased hydrophobicity has been shown to improve both the alkaline anode and cathode performance. It was also shown that decreasing the molecular weight of the ionomer improves fuel cell performance. Finally, higher fuel cell performance was observed with quinuclidinium head groups on the anionic ionomer, in comparison to the more traditional trimethyl ammonium cation. The improvements in performance appear to be due to improved mass transport of reactants and products through the electrode as a result of increased free volume within the electrode and a more efficient construction of the electrical double layer at the ionomer/catalyst interface.
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Direct methanol and hydrogen anion exchange membrane (AEM) fuel cells are of interest as an alternative to proton exchange membrane (PEM) fuel cells. Methanol has a high volumetric energy density, and is easy to transport and handle. Methanol also does not require a reformer as with other liquid fuels. Direct methanol alkaline fuel cells have the potential to address many of the problems with PEM cells. AEM fuel cells provide enhanced methanol oxidation kinetics[1] and allow the use of non-noble metal catalyst such as nickel and silver.[2–4] The direction of ion migration from cathode to anode provides a mechanism for reduced fuel crossover which could lead to thinner membranes and reduced ionic resistance.[3,4] In an AEM fuel cell, oxygen is reduced to hydroxide consuming water at the cathode and water is generated at the anode. Thus, the creation of an efficient three-phase boundary and managing the water content within the electrodes is a critical issue.[5]

At this time, alkaline fuel cells have not been as successful as their acid counterparts. One of the reasons for the poor performance of AEM cells is the lack of anion conducting membranes and ionomers with performance comparable to Nafion. Alkaline anion exchange materials are not as highly developed as Nafion and improvements are needed including higher conductivity, stability, and ion transport properties. A direct methanol alkaline fuel cell using a radiation grafted poly (ethylene co-tetrafluoroethylene) (ETFE) membrane with platinum catalysts and pure oxygen at the cathode at 2.5 bar back pressure at 80°C was reported to have a peak power density of 8.5 mWcm^{-2}.[6] Advances in AEM ionomers for electrode fabrication are especially important because the catalyst utilization in direct methanol AEM cells is generally lower than the utilization in acid fuel cells using Nafion as an ionomer.
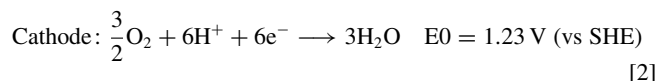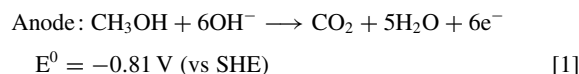
Anion exchange membranes (AEMs) have been synthesized by attachment of a cationic functional group onto the polymer backbone in a two-step process.[7] The first step involved the chloromethylation of the polymer backbone followed by amination with trimethyl amine creating the quaternary ammonium cation. Benzyl trimethyl ammonium cations are commonly used because there are no β-hydrogens and thus they do not undergo Hofmann elimination.

Several groups have reported the synthesis of AEMs using poly(aryl ether sulfone). AEMs based on polysulfone (e.g. Udel 1700, Amoco), was initially reported by Zschocke and Quellmalz.[8] Stable electrodialysis was observed under alkaline conditions. The AEM was prepared by chloromethylation of polysulfone followed by amination with trimethylamine to form the benzyltrimethylammonium groups. Bauer et al. prepared AEMs from the same chloromethylated polysulfone by amination with a bis-tertiary amine, 4,4′-diazabicyclo-[2.2.2]-octane (DABCO). It was concluded that the resulting membranes were

more stable under alkaline conditions than membranes with benzyl-trialkylammonium groups.[9] Kohl et al. prepared AEMs from polysulfone containing partially fluorinated monomers by amination with trimethylamine. The membranes exhibited conductivities between 10 mS/cm and 60 mS/cm at temperatures between 25°C and 80°C when fully hydrated in 1M sodium carbonate.[10] Such poly(sulfone)-based ionomers have also been evaluated as potential ionomers in the catalyst layers of alkaline fuel cells.

In our previous studies, copoly(arylene ether) with octafluoro biphenyl groups and pendant quaternary ammonium cations was synthesized for use as an ionomer in alkaline electrodes.[11,12] The partially fluorinated backbone provided low water uptake, and high thermal and chemical stability. A hydrogen/oxygen hybrid fuel cell fabricated with this ionomer in the membrane electrode assembly (MEA) showed a maximum power density of 315 mWcm^{-2} at 60°C. This was superior to the previous value the 215 mWcm^{-2} for the poly(aryl) ether based ionomer with a similar ion exchange capacity (IEC).[11,3] Quaternary alkyl ammonium cations are the most common head groups for AEM ionomers. Several different cationic head groups have been evaluated as ionomers including phosphonium,[13] guanidinium,[14] and imidazolium.[15,16] In this study, we report the first investigation of a polycyclic amine aza bicyclo (2,2,2) octante alkylated as a quaternary ammonium cation, quinuclidinium, as the ionomer for alkaline electrodes in fuel cells. Quinuclidinium has a larger van der Waals volume than the trimethyl ammonium head group.[17] The size of the head group and its effect on the ionomer packing has a significant impact on anion mobility. Quinuclidinium may have greater free volume for enhanced reactant transport.

A hybrid PEM/AEM direct methanol fuel cell has been used as a tool in investigating electrode changes because one electrode at a time can be changed. In addition, the hybrid configuration may lead to simpler water management.[13] In the hybrid fuel cell configuration, both AEM and PEM materials are used to form a junction within the cell. The direct methanol hybrid fuel cell can be constructed in two ways: (i) AEM anode and PEM cathode, or (ii) PEM anode and AEM cathode.[18] The reactions for case (i), AEM/PEM are shown in Equations 1 and 2.
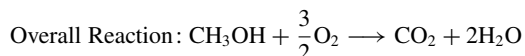
$$\text{Anode}: CH_3OH + 6OH^- \longrightarrow CO_2 + 5H_2O + 6e^-$$

$$E^0 = -0.81 \text{ V (vs SHE)} \qquad [1]$$

$$\text{Cathode}: \frac{3}{2}O_2 + 6H^+ + 6e^- \longrightarrow 3H_2O \quad E0 = 1.23 \text{ V (vs SHE)} \qquad [2]$$

Water is split at the AEM/PEM interface, Equation 3. The overall cell reaction is given in Equation 4.

$$\text{AEM/PEM Interface}: 6H_2O \longrightarrow 6OH^- + 6H^+ \qquad [3]$$
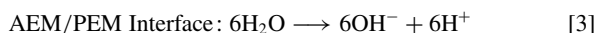
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$$\text{Overall Reaction}: CH_3OH + \frac{3}{2}O_2 \longrightarrow CO_2 + 2H_2O$$
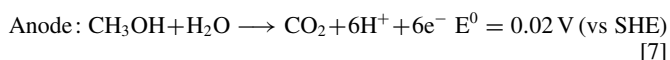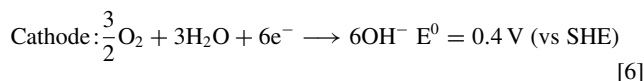
$$E^0 = 1.21 \text{ V (vs SHE)} \qquad [4]$$

The charge separation at the AEM/PEM interface creates a junction potential, E_j, Equation 5.[13]

$$E_j = \varphi^{AEM} - \varphi^{PEM} = \frac{RT}{F}\ln\left(a_{H^+}^{PEM}a_{OH^-}^{AEM}\right) - \frac{RT}{F}\ln(K_w) \qquad [5]$$

Where, E_j is the contact potential between the AEM, φ^{AEM}, and PEM, φ^{PEM}, $a_{OH^-}^{AEM}$ is the activity of hydroxide in the AEM, $a_{H^+}^{PEM}$ is the activity of protons in the PEM, K_w is the water equilibrium constant, R is the ideal gas constant, T is the temperature, and F is Faraday's constant.

The second hybrid case has a PEM anode and AEM cathode, Equations 6 and 7. Water is created at the PEM/AEM junction.

$$\text{Cathode}: \frac{3}{2}O_2 + 3H_2O + 6e^- \longrightarrow 6OH^- \ E^0 = 0.4 \text{ V (vs SHE)}$$
$$[6]$$

$$\text{Anode}: CH_3OH + H_2O \longrightarrow CO_2 + 6H^+ + 6e^- \ E^0 = 0.02 \text{ V (vs SHE)}$$
$$[7]$$

This has the advantage that the anode is operated at high pH and can use non-platinum catalysts. It also has the advantage that water is created near the cathode, close to where it is consumed. The overall reaction for the cell and junction relationship is the same as in AEM/PEM case, Equations 4 and 5. However, the sign of the junction potential in the AEM/PEM case is opposite to that of the PEM/AEM case.

In either case, the pure AEM fuel cell or the hybrid PEM/AEM fuel cell, there is a critical need for improved ionomers to increase the catalyst utilization within the electrode structures. The goal is to achieve greater hydrophobicity, chemical stability, and better transport properties within the three dimensional electrode structure to increase the electrode performance. In this study, new AEM ionomers, poly(arylene ether) functionalized with quinuclidinium groups were synthesized and tested in hybrid fuel cells. The hybrid fuel cell configuration was used as a diagnostic tool in evaluating progress at the AEM electrode using an established PEM electrode as the opposite electrode. The ionomers were evaluated as the AEM anode and cathode using the two hybrid configurations.

Experimental

Materials.— Decafluorobiphenyl (DFBP) (Aldrich), 1,1,2,2-tetrachloroethane (Alfa Aesar), toluene (Alfa Aesar), N-bromosuccinimide (NBS), N,N-dimethylacetamide (DMAc) (Alfa Aesar), 2,2,2-trifluoro-1-(4-methylphenyl)ethanone (DuPont), benzoyl peroxide (BPO), quinuclidine, and trimethylamine (Alfa Aesar) were used as-received. Potassium carbonate (Aldrich) was dried at 120°C for 24 h before use. Other chemicals were obtained as reagent grade and used as-received.

Synthesis of 1,1-bis(4-hydroxyphenyl)-1-(4-methylphenyl)-2,2,2-trifluoroethane (BHMP3F).— [19] 2,2,2-trifluoro-1-(4-methylphenyl)ethanone (9.4075 g) and phenol (18.8021 g) were added to a three-neck, 250 mL round-bottom flask equipped with a stirring bar, gas inlet and dropping funnel. The mixture was stirred at 45°C for 10 min to form a homogeneous solution. The triflic acid (1.15 mL) was added, and the mixture was heated at 60°C for 3 h under N_2 atmosphere until a pale yellowish solid formed. The product was washed with boiling water three times and re-crystallized from toluene to give a white solid.

Polymerization of Poly(arylene ether) (PAE).— [11] In a typical polycondensation reaction, a 250 mL three-necked round-bottomed flask equipped with a magnetic stirring bar, a N_2 inlet, and an addition funnel, was charged with *BHMP3F* (10.8015 g), DFBP (10.0233 g), potassium carbonate (4.8024 g), toluene (48 mL) and DMAc

(132 mL). The mixture was stirred at room temperature for 20 min and then heated to 90°C for 5 h under N_2 atmosphere. After reaction, the solution was poured dropwise into deionized water (2 L) and a white product precipitated from solution. After washing with hot, deionized water and ethanol several times, the polymer, denoted PAE, was dried under vacuum at 60°C for 15 h.

Bromination of Poly(arylene ether) (BPAE).— [21] The bromination of the PAE was carried out in 1,1,2,2-tetrachloroethane, using N-bromosuccinimide (NBS) as the bromination agent and BPO to initiate the radial reaction. PAE (5.8431 g), NBS (2.3855 g), BPO (0.1622 g) and 100 mL of 1,1,2,2-tetrachloroethane were introduced into a 250 mL, three-necked, round-bottomed flask. The mixture was heated to 85°C and reacted for 12 h in an N_2 atmosphere. After reaction, the mixture was poured into 500 mL of ethanol, and collected by filtration. After washing with ethanol several times, the BPAE polymer was dried under vacuum at 60°C for 15 h.

Quaternization of BPAE.— PAE with pendant quinuclidium groups was synthesized by quaternization reation of BPAE with quinuclidine. Specifically, BPAE (0.200 g CH_2Br) and quiniclidine (0.02774 g) were dissolved in 3 mL of DMF. The reaction mixture was stirred at 60°C for 48 h in an N_2 atmosphere. After reaction, the solvent was removed by pouring the mixture into an evaporating dish to dry at room temperature.

The ^{1}H-NMR spectra of the synthesized polymers were recorded for structural characterization. The data were collected with a Model DMX400 spectrometer using $CDCl_3$ as the solvent.

Electrochemical characterization.— Two different catalysts, both obtained from Electrochem Inc., were used in this study to fabricate the fuel cell electrodes. The anode used Pt/Ru(60 wt%) on C and the cathode used Pt(40 wt%)/C. The anode catalyst loading was 4 mg/cm^2 and the cathode loading was 2 mg/cm^2. The Nafion 117 membranes used in the experiments were obtained from Ion Power Inc. The Nafion was pretreated by boiling in 3% H_2O_2, followed by treating with 1M H_2SO_4 and then H_2O, both at 80°C. Each step was followed by rinsing with distilled water several times. The membranes were stored in distilled water until used in the MEA fabrication. High purity solvents (99.9%), including dimethyl formamide (DMF), isopropyl alchol (IPA), methanol (MeOH), and sodium hydroxide were obtained from VWR. Hydrophilic gas diffusion layer (GDL) 2050 L and hydrophobic TGPH 90 obtained from Toray Industries were used for the anode and cathode, respectively.

The electrode fabrication consisted of the following sequence. For the AEM cathode, the alkaline ionomer (1 wt% in DMF) was mixed with the Pt/C catalyst (40 wt%) so that the ionomer content was 10 wt% with respect to the catalyst. A DMF and ethanol mixture (3:2 by weight) was added in order to prepare the catalyst slurry. The prepared mixture was then sonicated for 30 minutes at room temperature. The mixture was sprayed on to the GDL until the desired loading was achieved. A small amount of the ionomer was sprayed on to the top surface of the catalyst layer to prevent the direct contact of the catalyst with the membrane. The electrodes were then dried at room temperature and immersed in 0.1 M NaOH solution overnight in order to exchange the Cl$^-$ to OH$^-$ ions. Finally, the electrodes were soaked in distilled water to remove the excess OH$^-$ ions.

Pt/C (40 wt%) was mixed with a 5 wt% Nafion solution in alcohol so that the Nafion consisted of 15 wt% with respect to the catalyst for the preparation of the low pH electrodes. Water and isopropyl alcohol (IPA) (1:3 by weight) were used to prepare the catalyst slurry. The slurry was sprayed onto the Toray TGPH 90 carbon paper and dried at room temperature.

A 5 wt% Nafion/ IPA mixture (1:2 by volume) was sprayed directly onto the surface electrode immediately before assembly. The low pH electrodes were first pressed onto the Nafion 117 membrane at 135°C and 2 MPa gauge pressure for 5 minutes. The AEM electrode was later assembled onto the half-cell by pressing at 50°C and 2 MPa pressure for 5 minutes to form the MEA.
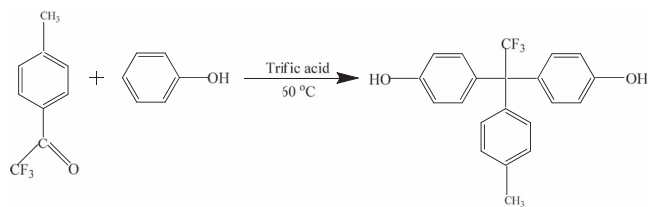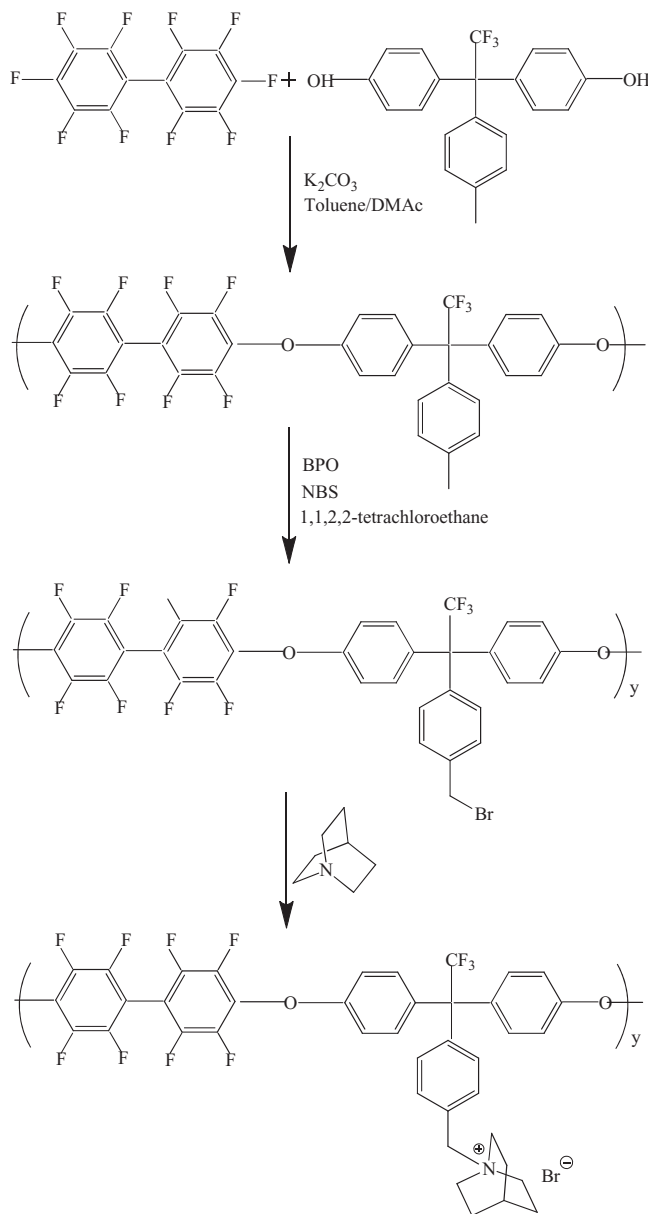
Scheme 1. Synthesis of 1,1-bis(4-hydroxyphenyl)-1-(4-methylphenyl)-2,2,2-trifluoroethane.

The fuel cell hardware was obtained from Fuel Cell Technologies. The Poco graphite blocks were machined with a single serpentine pattern for the fuel and gas flow. Stainless steel plates were used as the current collectors. Preheated methanol (55°C) was circulated at 5 mL/min with a peristaltic pump. Oxygen (Airgas Inc.) gas flowed counter current to the methanol flow at the cathode at 50 sccm in all tests at ambient pressure. The equilibration of the MEA was carried out by operating the cell at a constant load of 250 mV for 10 hours before the electrochemical data were recorded. The polarization curves for the MEAs were obtained by using a Princeton PAR 2273 potentiostat.

Results and Discussion

The fluorine-containing bisphenol monomer *BHMP3F* was synthesized by the superacid-catalyzed condensation of 2,2,2-trifluoro-1-(4-methylphenyl)ethanone with excess phenol, as shown in Scheme 1. The overall yield of the reaction was above 90%, and the structure was confirmed by ^{1}H NMR, as shown in Figure 1. This bisphenol monomer contains a trifluoroethylidene group as the linkage for the two phenolic moieties, which have been shown to be stable in the monomer form.[19] The polymer is hydrophobic in nature which helps control the water uptake during fuel cell operation.

The synthetic mechanism for the preparation of the partially fluorinated poly(arylene ether) with pendant quinuclidium groups is shown in Scheme 2. The first step in the synthesis of the polymer backbone is a polycondensation reaction. The copolymerization of *BHMP3F* and DFBP was carried out in a DMAc/toluene cosolvent under nitrogen at ambient temperature for 20 min followed by reaction at 90°C for 5 h. Bromination of the methyl groups in the PAE was performed under anhydrous conditions at 85°C using PAE as the starting material, 1,1,2,2-tetrachloroethane as the solvent, NBS as the bro-

Figure 1. ^{1}H NMR spectrum of 1,1-bis(4-hydroxyphenyl)-1-(4-methylphenyl)-2,2,2-trifluoroethane.

Scheme 2. The synthetic route for partially fluorinated copoly(arylene ether) ionomer with pendant quaternary quinuclidium groups.

momethyl reagent, and benzoyl peroxide as the initiator. Finally, the bromomethyl moiety was converted into the quinuclidium cation by the quaternization reaction of BPAE with quinuclidine at 60°C for two days.

The chemical structure and composition of neat PAE and BPAE were investigated by liquid phase ^{1}H-NMR spectroscopy with CDCl$_3$ as the solvent and reference. As shown in lower half of Figure 2, the methyl protons attached to aromatic rings are assigned to the peak at 2.34 ppm and the aromatic protons of PAE are divided into two regions: a high-field (6.93–7.06 ppm) and low-field (7.08–7.17 ppm) region.[11] Integration of the peaks in the high and low field regions each correspond to 12 hydrogens, reflecting the chemical structure of the PAE repeat units. The 1H-NMR result is consistent with the structure of the PAE copolymer. The high-field NMR response has the characteristic chemical shift of the main-chain, ortho-oxygen aromatic protons which reflect shielding from the electron-donating ether linkage. The low-field signals are attributed to the aromatic hydrogens from the strongly electron-withdrawing groups. As shown in the upper half of Figure 2, a new peak, f', appeared in the brominated polymer.
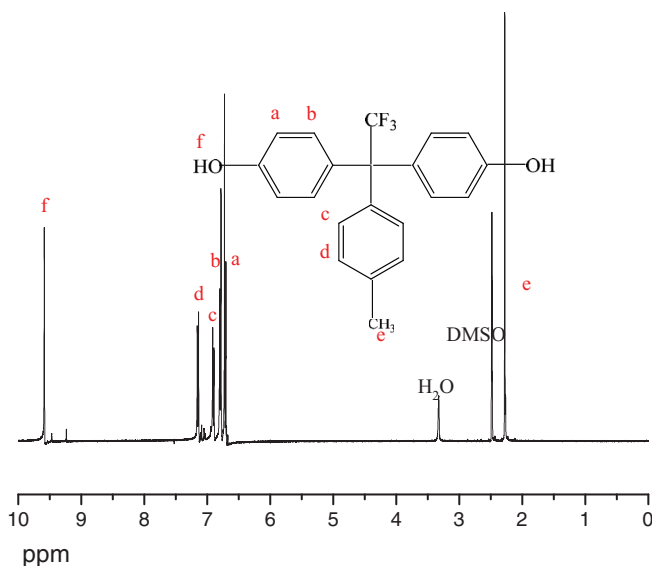
Figure 2. ^{1}H NMR spectra of PAE and BPAE.

Figure 4. Polarization and Power density curves of anode hybrid fuel cell operated with different ionomers at the anode 2M MeOH at 5 mL/min on the anode and 50 sccm O_2 on the cathode at 55°C.
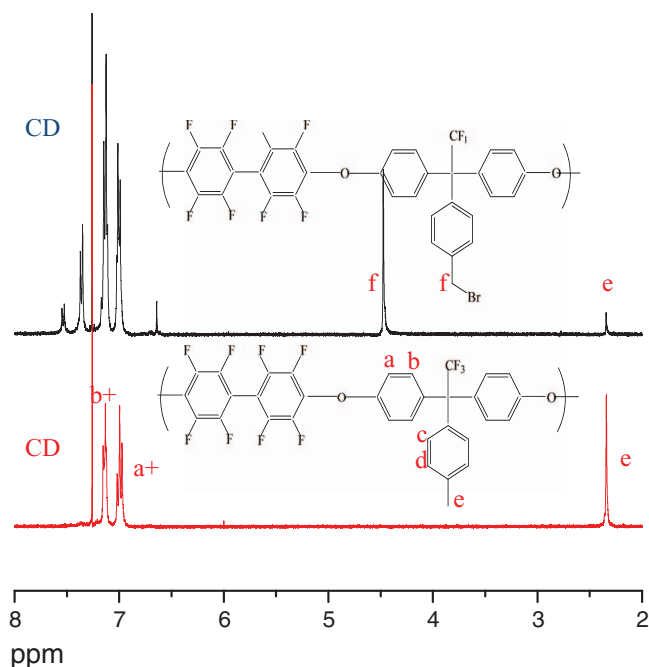
The appearance of the f' peak in the brominated structure coincides with a decrease in the e' peak in the unbrominated form, as shown in the lower half of Figure 2. The peak near 4.47 ppm was assigned to the bromomethyl protons, and the degree of bromination was determined by comparing f' and e' peak intergals. The bromination reaction was essentially complete based on the magnitude of the decrease in the methyl signals. The final products were stable in 1N KOH at 60°C for at least 10 days.

In this study, the performance of the two anion conducting polymers, identified as ionomer I and ionomer II, as shown in Figure 3,
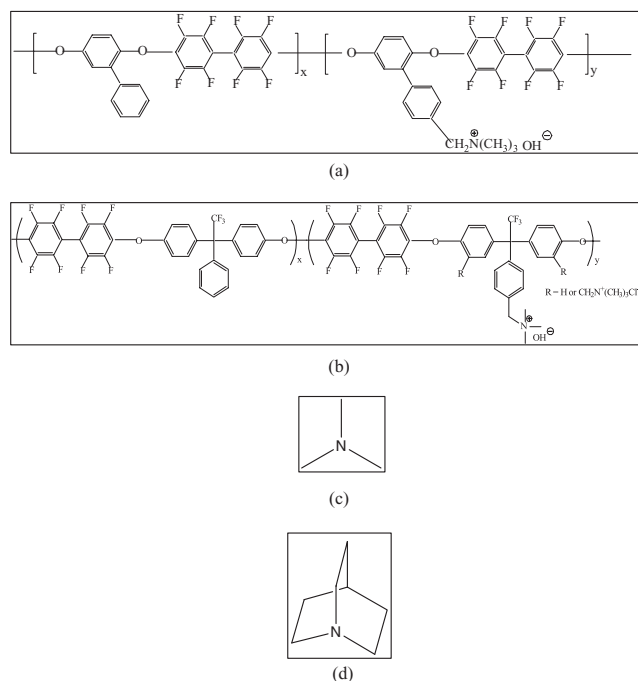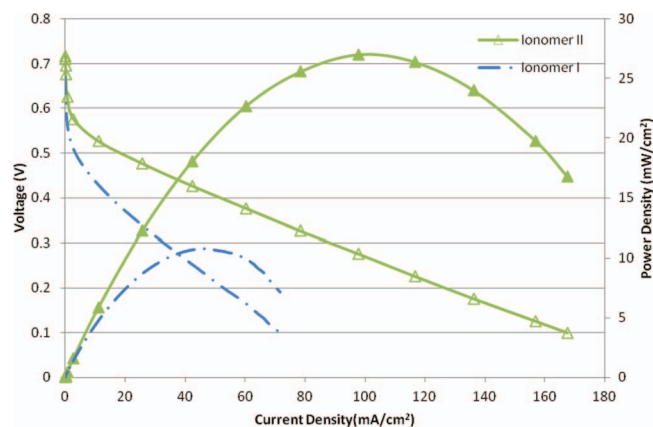

Figure 3. (a) Structure of ionomer I and (b) structure of ionomer II with head groups (c) quaternary ammonium and (d) quinuclidine.

were investigated as the anode and cathode in a hybrid direct methanol fuel cell. The IEC value for ionomers I and II were found to be 1.21 and 1.30 meq/g, respectively. The water uptake at 25°C for ionomer I was 55% and 25 wt% for ionomer II. The relatively low water uptake value for ionomer II is a result of the two additional trifluoromethyl groups of the polymer backbone. The conductivity values of ionomers I and II could not be obtained since they were prepared at low molecular weight polymers and freestanding membranes could not be formed.

The fuel cell performance of ionomers I and II in the trimethyl ammonium form were first tested as the anode in a hybrid fuel cell. Figure 4 shows the current-voltage and current-power curves for ionomers I and II used as the alkaline anode in a hybrid fuel cell. The cathode was a traditional Nafion, PEM cathode. The cell was operated at 55°C with 2M MeOH (5 mL/min) at the anode and 50 sccm O_2 on the cathode. The peak power obtained with ionomer I was 12 mW/cm^2 compared to 26 mW/cm^2 for ionomer II. The higher performance for ionomer II is attributed to the increased hydrophobicity due to the presence of the trifluoromethyl groups. The higher hydrophobicity of ionomer II contributes to the enhanced dimensional stability in the presence of excess water which likely maintains the mass transport pathways during hydration for reactants and products. Also, it was previously shown through modeling that a lower water content resulted in OH$^-$ ions that were not as well solvated and therefore were more reactive.[20] Since the hydrophobic ionomers have reduced water content compared to polyether sulfones, they likely result in greater reactivity owing to reduced solvation of the OH$^-$ ions.

The performance of ionomors I and II in the benzyl trimethyl ammonium form was also studied as the cathode in a hybrid fuel cell. In this configuration, hydroxide is produced at the cathode and protons are produced at the anode, both of which migrated to the PEM/AEM junction where they combine to form water. Since water is a reactant at the AEM cathode, unlike the PEM cathode where it is a product, hydration is needed at the alkaline cathode. Excess water at the cathode created at the PEM/AEM junction can diffuse to either electrode. This is a significant advantage over the hybrid configuration with an AEM anode, where water splitting occurs at the PEM/AEM junction. Figure 5 shows the current-voltage and current-power curves for ionomers I and II as the cathode (Nafion PEM anode) at 55°C using 2M MeOH at 5 mL/min at the anode and 50 sccm O_2 at the cathode. The peak power obtained with ionomer I was 15 mW/cm^2 compared to 25 mW/cm^2 for ionomer II. The lower water uptake at the cathode is critical for catalyst utilization because oxygen transport can be inhibited by excess water swelling within the AEM cathode. A similar study with half cells being constructed from ionomer I and a more hydrophilic ionomer showed a similar result.[12]

The effect of molecular weight of ionomer II on the performance of the hybrid fuel cell has been studied. Ionomer II samples with the
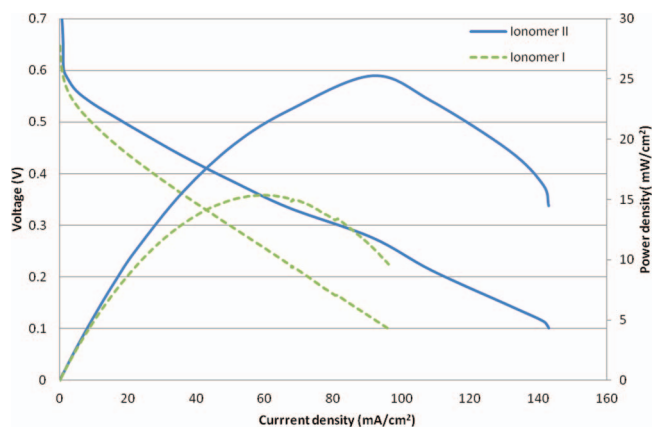
Figure 5. Polarization and Power density curves of cathode hybrid fuel cell operated with different ionomers at the cathode 2M MeOH at 5 mL/min on the anode and 50 sccm O_2 on the cathode at 55°C.
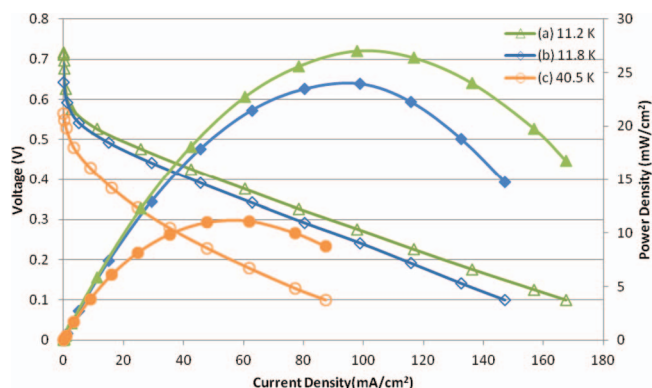

Figure 6. Polarization (open symbols) and Power density (solid symbols) for the anode hybrid fuel cell with different molecular weight ionomers: 11.2 k, 11.8 k, 40.5 k operated with 2M MeOH at a flow rate of 5 mL/min and oxygen flow rate 50 sccm at 55°C.

same polymer backbone and essentially the same IEC values with the trimethylammonium cation were synthesized with different molecular weights ranging from 11 k to 40 k, as shown in Table I. The ionomers were first studied in the anode hybrid fuel cell configuration. The highest power (26 mW/cm^2) was observed with the lowest molecular weight ionomer, as shown in Figure 6.

The performance of the different molecular weight ionomers (ionomer II) on the performance of the cathode in the hybrid configuration is shown in Figure 7. Just as in the case of the anode, the lower molecular weight ionomer showed better performance and higher power density. As stated previously, it is difficult to form free-standing membranes from low molecular weight ionomers because the molecular weight is well below the value normally expected for chain entanglement. The increased mobility of the low molecular weight ionomer appears to allow easier transport of reactants and products within the electrodes due to greater free-volume. The higher molecular weight ionomers are believed to restrict reactant and product transport. In addition, higher chain segment mobility can assist in forming
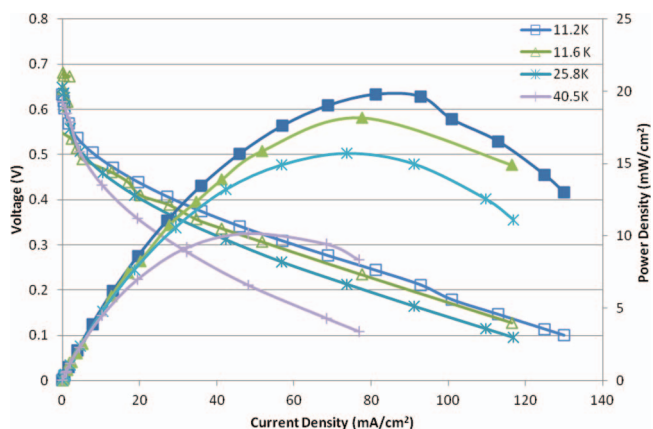
Table I. Properties of ionomers with different molecular weights with same backbone used in anode hybrid fuel cell.

Ionomer	Mn	PDI	IEC (meq/g)
(a) Ionomer II–1	11.1 k	2.67	1.3
(b) Ionomer II–2	11.8 k	2.27	1.3
(c) Ionomer II–3	25.8 k	2.60	1.3
(d) Ionomer II–4	40.5 k	5.08	1.3

Figure 7. Polarization and Power density curves for cathode hybrid fuel cells with different molecular weight ionomers 11.2 k, 11.8 k, 25.8 k, 40.5 k operated with 2M MeOH at mL/min and 50 sccm O_2 at 55°C.

an efficient double layer structure at the polymer/catalyst interface.[21] Polymer chain mobility of polystyrene was found to decrease with the increase in molecular weight.[22] Thus, it appears that the lower molecular weight ionomer leads to higher mass transport and/or catalyst utilization.

The type of head group was investigated using low molecular weight ionomer II as the basis for comparison. A sample of ionomer II was extracted before formation of the benzyl trimethyl ammonium cation (before reaction with trymethyl amine) and used to prepare an ionomer with the quinuclidinium head group. Figure 8 shows the current-voltage and power-voltage curves for ionomer II with trimethyl amine and quinuclidinuium head groups when used as the anode in a hybrid methanol fuel cell. Figure 9 shows the quaternary ammonium and quinuclidinium based ionomers used as the cathode. In both cases, the quinuclidinium cation was superior to the quaternary ammonium cation. In addition, the lower methanol recirculation rate (0.6 mL/min vs 5 mL/min) in Fig. 9, showed that the higher performance most likely due to less methanol cross-over. The spent methanol within the anode electrode structure is most likely not replenished as quickly at lower recirculation rate resulting in a larger gradient in methanol concentration and less cross-over through the membrane. Lastly, the hybrid cell using the alkaline cathode outperformed the cell using the alkaline anode regardless of head group. It was previously shown that in ionic liquids that the van der Waals volume of quinuclidine is slightly larger than the trimethyl ammonium cation.[17] This may provide slightly greater free-volume within the electrode structure leading to better mass transport properties.
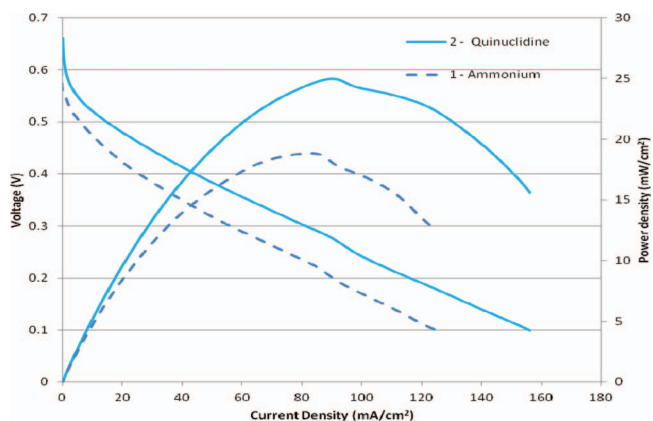

Figure 8. Polarization and power density curves of anode hybrid fuel cell operated with trimethyl ammonium and quinuclidinium cation ionomers at the anode using 2M MeOH at 5 mL/min on the anode and 50 sccm O_2 on the cathode at 55°C.
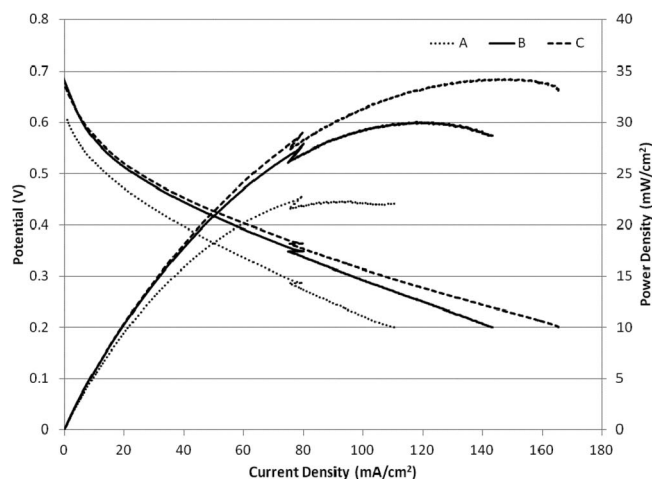
Figure 9. Polarization and power density curves for cathode hybrid fuel cells with trimethyl ammonium and quinuclidinium ionomers at the cathode using 2M MeOH and 50 sccm O_2 at 55°C. Curve A is for the quaternary ammonium ionomer with a methanol recirculation rate of 5 mL/min, Curve B for quaternary ammonium ionomer with a methanol recirculation rate of 0.6 mL/min, and Curve C is for quinuclidinium ionomer with a methanol recirculation rate of 0.6 mL/min.

Conclusions

Fuel cells involving a combination of acid and alkaline electrodes with PEM membranes have been used for direct methanol fuel cells to characterize a newly developed ionomer, the effect of the ionomer molecular weight, and two cation head groups. Ionomer II had a higher degree of hydrophobicity than ionomer I because it included additional trifluoromethyl groups. The impact of the ionomer molecular weight was also studied. It was found that molecular weight can significantly affect the fuel cell performance. Lower molecular weights are preferred most likely due to increased free volume leading to higher mass transport and easier assembly at the catalyst/ionomer interface. Finally, the cationic quinuclidinium head group was shown to be su-

perior to the trimethyl ammonium cationic head group for both the anode and cathode electrode. Additionally, the hybrid configuring using the AEM cathode and PEM anode shows higher performance than the PEM cathode/AEM anode configuration in all trials.

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