3-Methyltrimethylammonium poly(2,6-dimethyl-1,4-phenylene oxide) based anion exchange membrane for alkaline polymer electrolyte fuel cells

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Abstract. Hydroxyl ion (OH⁻) conducting anion exchange membranes based on modified poly (phenylene oxide) are fabricated for their application in alkaline polymer electrolyte fuel cells (APEFCs). In the present study, chloromethylation of poly(phenylene oxide) (PPO) is performed by aryl substitution rather than benzyl substitution and homogeneously quaternized to form an anion exchange membrane (AEM). ^{1}H NMR and FT–IR studies reveal successful incorporation of the above groups in the polymer backbone. The membrane is characterized for its ion exchange capacity and water uptake. The membrane formed by these processes show good ionic conductivity and when used in fuel cell exhibited an enhanced performance in comparison with the state-of-the-art commercial AHA membrane. A peak power density of 111 mW/cm² at a load current density of 250 mA/cm² is obtained for PPO based membrane in APEFCs at 30 °C.

Keywords. Alkaline polymer electrolyte fuel cell; anion exchange membrane; PPO; homogeneous quaternization.

1. Introduction

Presently, alkaline polymer electrolyte fuel cells (APEFCs) using anion exchange membranes have received an immense interest among researchers (Varcoe and Slade 2005). The advantages of APEFCs lie in their low activation loss, fast cathode kinetics that permits the use of non-precious metal catalysts (Lin *et al* 2006) and reduced oxidant reduction over-potential at high pH with increased efficiency (Gu *et al* 2009). Issues in alkaline fuel cells (AFCs) are the formation of carbonate salts when KOH or NaOH solution reacts with CO_2 at the cathode (McLean *et al* 2002) and the pH change in the catalyst region due to carbonation causing voltage loss (Wang *et al* 2003). These problems are addressed by the use of solid electrolyte in APEFCs.

Recently, there have been several attempts to develop solid polymer electrolytes (SPE) for alkaline fuel cell (Merle *et al* 2011). Earlier reports on anion exchange membrane (AEM) focused on using polymers like polyvinyl alcohol (PVA) and poly(ethylene oxide) (PEO) as solid support to hold alkaline solution for its OH⁻ conductivity (Wu *et al* 2008; Xiong *et al* 2008;). SPE comprising conducting polymers are the polyelectrolytes which have ionic sites (usually quaternary ammonium or quaternary phosphonium type) grafted on the polymer backbone. To preserve the polymer electroneutrality, a mobile counter-ion is attached to each ionic functional group (Agel *et al* 2001).

Many studies have been devoted to develop quaternized polymers by introducing reactive chloromethyl group followed by its reaction with tertiary phosphine, tertiary amine and pentamethylguanidine (Li *et al* 2006; Wang J *et al* 2010; Arges *et al* 2012). Several AEMs were prepared using the aromatic moiety of a variety of polymers like poly(ether-imide) (PEI), polysulfone (PS), poly (arylene ether sulfone) (PESF), etc (Fang and Shen 2006; Zhou *et al* 2009; Yan and Hickner 2010; Wang G *et al* 2010). Also Varcoe and Slade (2006) prepared AEMs by radiation grafting of monomers onto the polymer films using γ-ray source.

Poly(phenylene oxide) (PPO) has emerged as one of the most promising polymer for the fabrication of anion exchange membrane due to its excellent physicochemical properties. Wu *et al* (2010) prepared AEMs by incorporating silica into PPO which exhibited high tensile strength and good conductivity. Recently, membranes with imidazolium groups (attached to benzyl position) have been developed from brominated PPO (BPPO) with good ionic conductivities (Ran *et al* 2012). But imidazolium cation is not advantageous over the benchmark quaternary ammonium cation due to its poor stability (Deavin *et al* 2012). The present study reports the introduction of quaternary ammonium cation on the aryl carbon rather than benzyl carbon in the preparation of anion exchange membrane from engineering plastics, viz.

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poly(2,6-dimethyl-1,4-phenylene oxide) via chloromethylation followed by a pre-functionalization methodology for quaternization.

2. Experimental

2.1 *Chloromethylation of PPO*

The chloromethylation of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) was carried out as reported in the literature (Wang *et al* 2010). Required amount of PPO was dissolved in chlorobenzene (15 wt% solution) in a three-neck round-bottom flask equipped with reflux condenser and a mechanical stirrer. Calculated amount of zinc chloride catalyst with respect to the weight of polymer was dissolved in chloromethyl ethyl ether (twice the molar quantity of the polymer) and then added drop-wise into the flask containing PPO solution. The reaction mixture was allowed to stir for 5 h at 50 °C under reflux condition. After cooling, the mixture was precipitated using methanol, washed with distilled water and dried in an oven at 70 °C for 24 h to form whitish-chloromethylated PPO (CPPO).

2.2 *Membrane fabrication*

Anion exchange membrane was formed by quaternization through homogeneous amination. Homogeneous amination was carried out by dissolving the dried CPPO in 1-methyl-2-pyrrolidone (NMP) to prepare 3 wt% solution. To this, trimethylamine solution (30 wt% in water) was added and the reaction mixture was stirred for 24 h at room temperature. The solution was poured onto a flat glass plate and dried at 75 °C in a vacuum oven to form QPPO membrane. The obtained membrane was soaked in 2 mol L^{-1} KOH solution for 24 h to convert from chloride to hydroxide form. Finally, the membrane was repeatedly washed with deionized water to remove residual KOH and stored in deionized water prior to use.

2.3 *Structural characterization*

Proton (^{1}H) NMR spectra were recorded on a Bruker instrument at 300 MHz using deuterated chloroform (CDCl$_3$) as the solvent and tetramethylsilane as an internal standard. The chemical modification of the polymers was further confirmed by Fourier transform infrared spectrophotometer (FT–IR–ATR) (Thermo Electron Corporation, Model Nexus 670) within the spectral range of 4000–400 cm^{-1}.

2.4 *Ion exchange capacity, water uptake and ionic conductivity*

Ion exchange capacity (IEC, in mmol/g) was determined using the Mohr's titration method (Li *et al* 2006). Water uptake measurements were carried out by sorption method (Mohanapriya *et al* 2009). The conductivity of the membranes was measured using a two-probe a.c. impedance spectroscopy with AUTOLAB PGSTAT 30 over the frequency range from 1 MHz to 10 Hz with 10 mV amplitude at varying temperatures ranging from 30 to 70 °C as reported earlier in the literature (Mohanapriya *et al* 2009). Before testing, the membranes were equilibrated in deionized water for 24 h.

2.5 *Membrane-electrode assembly (MEA) fabrication and APEFC performance evaluation*

Teflonized Toray-TGP-H-120 carbon papers were coated with the slurry of Vulcan XC-72R carbon suspended in cyclohexane along with 15 wt% polytetrafluroethylene (PTFE) to form the gas diffusion layer. The catalyst ink was prepared by taking the required amount of 40% Pt/C in deionized water followed by the addition of ethanol solution containing Fumion (FAA-3) ionomer and ultra-sonication for 30 min. The electrodes (both anode and cathode) were prepared by coating the catalyst ink on the gas diffusion layer until the desired Pt loading of 0·5 mg/cm^2 was reached. The electrodes were dipped in KOH solution (1 mol L^{-1}) to exchange the binder from Cl$^-$ to OH$^-$ form. MEA was formed by sandwiching QPPO membrane between the above two electrodes and then placed in a single-cell fixture with parallel serpentine flow-field machined on graphite plates. The active electrode area was 4 cm^2 with humidified H$_2$ and O$_2$ flowing at 200 mL min^{-1}. Cell polarization studies were carried out galvanostatically using electronic load Model-LCN4-25-24/LCN 50-24 from Bitrode Instruments (US).

3. Results and discussion

The preparation of anion exchange membrane (AEMs) involves chemical reactions such as chloromethylation and quaternization followed by ion exchange. Among them, chloromethylation and quaternization are the two key reactions that influence the conductivity. Chloromethylation is the crucial step in the synthesis of functionalized polymers because of its high reactivity that determines the subsequent degree of quaternization, in turn influencing the anion conductivity. In the present study, chloromethylation is done on the aromatic ring of the polymer making it less susceptible to steric hindrance unlike the conventional method of benzyl substitution wherein the electronegative nature of oxygen presumably tend to withdraw electrons towards itself thus, reducing the electropositive character of nitrogen. Chloromethylated PPO was further quaternized by homogeneous amination, in which PPO is directly converted to ionic form and is equally distributed over the polymer matrix because of strong ionic interactions when compared with

heterogeneous amination (Yan and Hickner 2010). Scheme 1 provides synthetic protocol for the preparation of alkaline membrane from PPO.

3.1 *NMR and FT–IR studies*

The chloromethylation reaction was confirmed by ^{1}H NMR spectra. Figure 1 shows proton resonance signals of both PPO and chloromethylated PPO (CPPO). The peak at 6·4–6·5 ppm is assigned to the aryl protons of PPO.
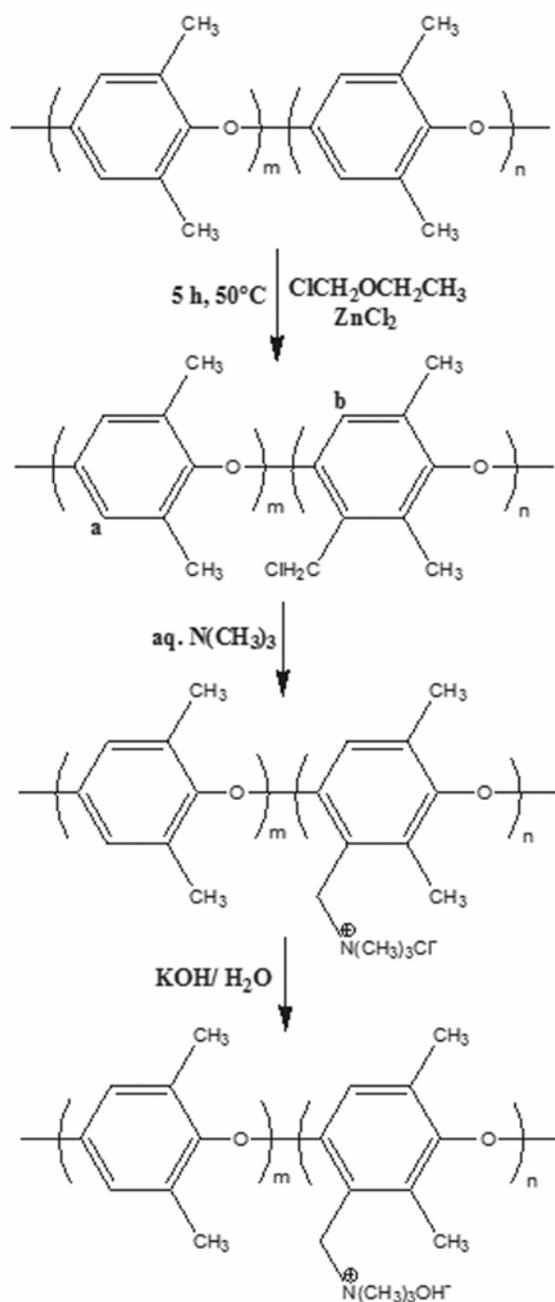
Scheme 1. Synthetic procedure for preparation of quaternized PPO membrane.

The protons due to the benzyl group appear at 2·0–2·1 ppm as a multiplet. Two prominent peaks appear in the spectra of CPPO. The peak at 4·9 ppm is attributed to the protons of chloromethyl group, and because of electrophilic substitution, aryl protons are shifted to a new position at 6·1 ppm. The percentage of substitution of chloromethyl group was calculated using the following relation (Wu *et al* 2006):

$$DS\ (\%) = \frac{100 * b}{0 \cdot 5a + b},$$

where *a* and *b* are the integrals of protons represented in the spectra. The maximum degree of substitution observed for CPPO is represented in table 1.

The chemical structures of the functionalized polymers were further investigated by FT–IR. Figure 2 shows FT–IR spectra of PPO, CPPO and QPPO. The peak at 1600 cm^{-1} corresponds to C=C bond stretching and the band at 1190 cm^{-1} is due to C–O–C stretching (Wu *et al* 2010) of PPO. In CPPO, the peak at 720 cm^{-1} is assigned to the stretching vibration of C–Cl bond and the band at 1410 cm^{-1} is the characteristic bending vibration of CH_2 group (Lu *et al* 2008). Since ^{1}H-NMR spectra were not recorded for QPPO due to its insolubility in $CDCl_3$; the introduction of quaternary ammonium group was confirmed by FT–IR. In QPPO, a new absorption peak at 930 cm^{-1} due to C–N stretching indicates the characteristic peak of quaternary ammonium group (Wu *et al* 2006). In addition, the absence of peak at 720 cm^{-1} (C–Cl bond) also confirms conversion of the chloromethyl group to quaternary ammonium group. Also the band at 1410 cm^{-1} (CH_2 group) is shifted to a higher wavenumber at 1440 cm^{-1} due to quaternization.

3.2 *Membrane conductivity and APEFC performance studies*

Ionic conductivity is a vital property that influences the performance of a fuel cell. Membrane conductivity is influenced by ion concentration, ion mobility and level of hydration. Figure 3 represents anionic conductivity of QPPO membrane in comparison with AHA membrane at varying temperatures from 30 to 70 °C. In general, the anion conductivity increases with increase in temperature due to the enhanced mobility of anion. Under fully hydrated conditions, the conductivity of QPPO membrane was in the range of 0·004–0·008 S/cm. Among the two membranes, QPPO reached a maximum conductivity of 8·3 × 10^{-3} S/cm at 70 °C due to higher IEC and water uptake in comparison with AHA. The ionic conductivity data for QPPO and AHA membranes and its corresponding IEC and water uptake values are shown in table 1.

Figure 4 shows cell polarization curves for MEAs containing QPPO and commercial AHA membranes at 30 °C. A higher peak power density of 111 mW/cm^2 at a load
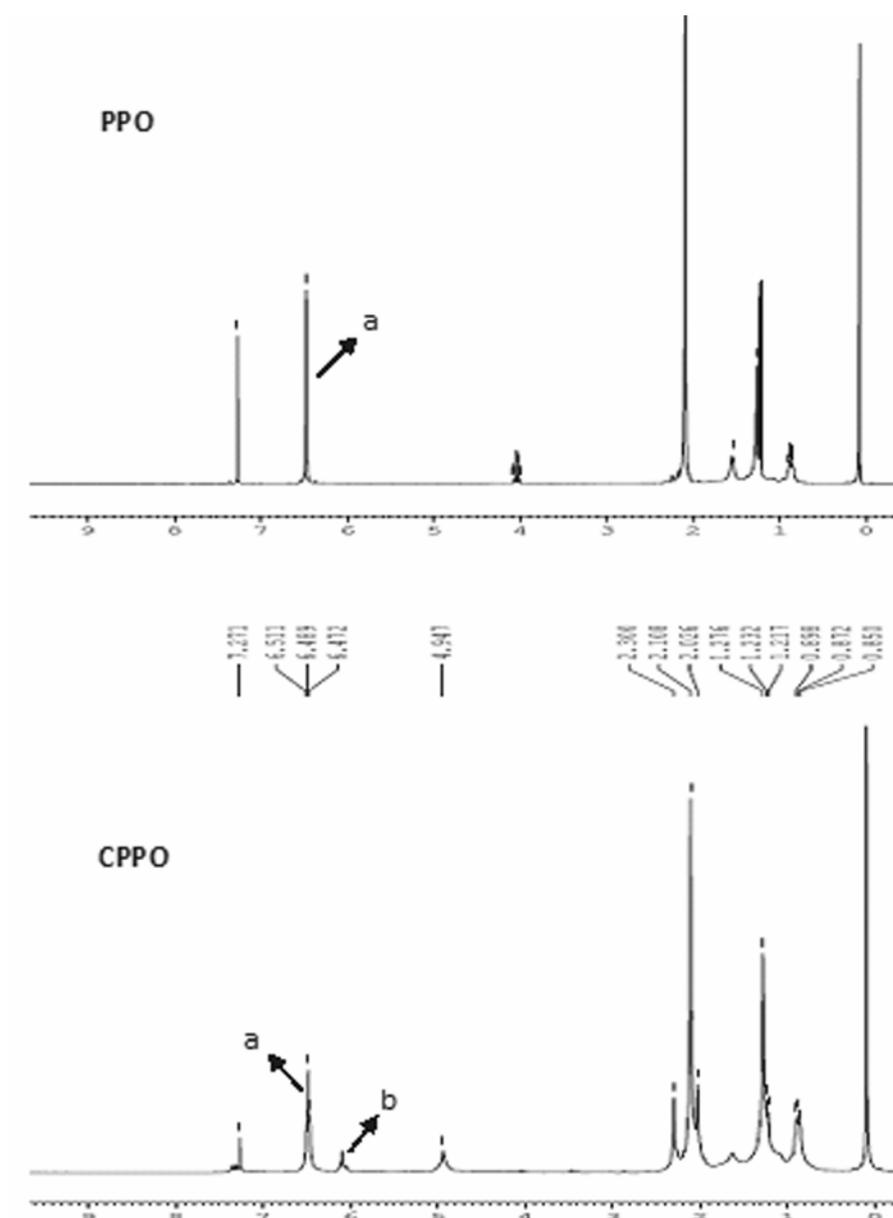
Figure 1. ^{1}H NMR spectra of PPO and CPPO.

Table 1. Characteristic properties of PPO and its membrane.

| Sample type | Degree of substitution[a] (%) | Nitrogen content[b] (wt%) | Conductivity (mS/cm) | | IEC (mmol/g) | Water uptake (%) |
			30°C	70°C		
CPPO	40	–	–	–	–	–
QPPO membrane	–	2·33	4·36	8·3	0·70	25
AHA membrane	–	–	1·7	2·7	0·35	15

[a]Calculated from NMR spectra. [b]Determined from CHNS analysis.

current density of 250 mA/cm^2 is observed for QPPO based MEAs in comparison with a peak power density of 58 mW/cm^2 at a load current density of 125 mA/cm^2 for AHA based MEAs. The higher performance is due to the substitution of chloromethyl groups in aryl position of polymer which increases the distance of interaction between the quaternary ammonium group and oxygen atom of polymer thus inhibiting the steric hindrance. However,
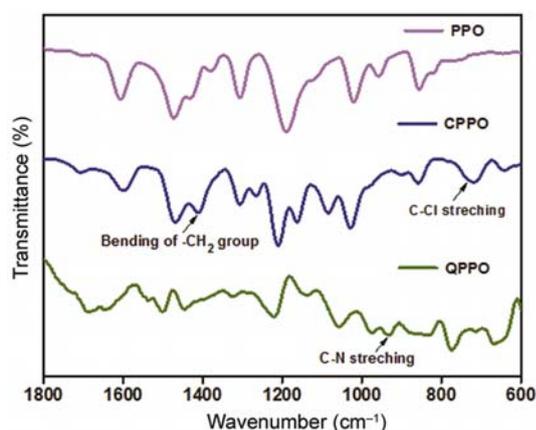
Figure 2. FT–IR spectra of PPO, CPPO and quaternized PPO.
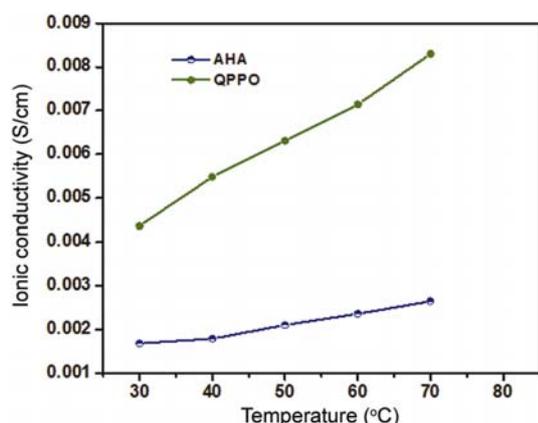
Figure 3. Conductivity for QPPO and AHA membranes as a function of temperature.
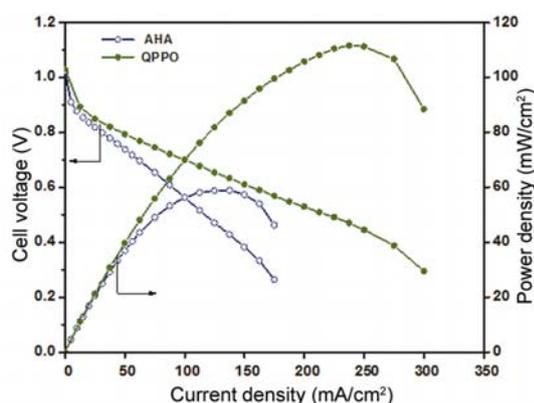
Figure 4. Cell performance curves of APEFCs comprising AHA and QPPO membranes.

at higher temperatures, performance of the membrane decreased probably due to a possible degradation because of nucleophilic attack of OH^- on the polymer backbone by S_N2 nucleophilic displacement (Fang and Shen 2006). The above performance needs to be further optimized by varying the ionomer content in the catalyst layer and by improving the membrane stability at higher temperatures. Further studies on these issues are in progress.

4. Conclusions

An anion exchange membrane was prepared by chloromethylation and quaternization of PPO. Chloromethylation of aromatic ring and homogeneous quaternization have resulted in the enhanced ionic conductivity of anion exchange membrane. The membrane in alkaline fuel cell showed higher performance in comparison with the commercial AHA membrane.

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