Anionic membrane and ionomer based on poly(2,6-dimethyl-1,4-phenylene oxide) for alkaline membrane fuel cells

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ABSTRACT

Hydroxyl-ion conductive poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) membranes with different characteristics were prepared via relatively simple bromination/amination serial reactions with reduced number of involved chemicals and shorter reaction time. The effects of reactants ratio, reaction atmosphere, polymer concentration, casting solvent, and hydroxylation treatment on reaction were investigated in details. The microstructure, water uptake, swelling ratio, ion-exchange capacity and ionic conductivity of the membranes were also studied. The obtained results demonstrate that, the ionic conductivity of the membrane is dependent on casting solvent. The N-methyl-2-pyrrolidonecast membrane exhibits the highest conductivity with the thinnest film. Although the membrane was prepared via a relatively simple preparation route with least toxic chemicals, a competitive ionic conductivity value of 1.64×10^{-2} S cm^{-1} was achieved at 60 °C. A power density of 19.5 mW cm^{-2} has been demonstrated from the alkaline membrane fuel cell operated at 70 °C, assembled from the entirely homemade membrane electrode assembly without any hot-pressing.

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1. Introduction

Alkaline membrane fuel cells (AMFCs) have recently attracts attention of many researchers worldwide [1–11]. A boost in the research regarding AMFCs is due to the development of alkaline anion-exchange membranes (AEM), which have highly potential in eliminating the problem of the progressive carbonation of alkaline electrolyte [12], and also as an alternative approach to the challenges in Nafion-based proton exchange membrane fuel cells (PEMFCs) [13–15], such as high cost membranes [16] and platinum-based catalyst [17]. Analogous to PEMFCs [18,19], a continuous development of AEM for AMFC technology is therefore apparently essential.

Postpolymerization modification is an important method for obtaining new chemical and physical properties for an existing polymer to be tailored for specific applications [20]. A series of methods for preparing diverse AEM have been developed for AMFC applications, ranging from radiation–grafting [21], halogenation–quaternization reactions [22] to quaternization–sol gel reactions [23]. The most commonly utilized method for

synthesizing strongly basic AEM is halogenation–quaternization reactions, usually comprising chloromethylation and quaternary amination.

With the increasing use of toxic chemicals in industry, simple and rapid methods for membranes preparation with least toxic materials are becoming more and more important. Although the use of chloromethylmethyl ether in chloromethylation provides excellent conversions and high yields, however this material is a carcinogen and rather expensive [24]. In addition, to improve mechanical stability, the membranes will suffer cross-linking and resulting in limitation of membrane molding with intricate shape [25]. In order to avoid the use of carcinogen materials, Wu and co-workers have developed a new series of AEMs directly from engineering polymer, poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) through sequence processes of bromination–hydroxylation–quaternization–sol–gel reaction–heat treatment [26]. In their works, molar ratio of bromine to PPO of 1.5:1 was used for bromination; hydroxylation treatment was employed; quaternization step was conducted for 13 h in a medium, comprising triethylamine, chlorobenzene, dimethylformamide and ethanol; additional used of monophenyltriethoxysilane and tetraethoxysilane for 24 h sol–gel reaction was involved; and the synthesis route was ended with heat treatment at 130 °C for 5 h.

To further simplify the membranes preparation procedure with least toxic materials, PPO-based AEMs were prepared via a

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simple bromination–quaternization route. In this work, the use of nitrogen atmosphere was eliminated in bromination reaction; quaternization reaction was conducted for only 5 min with solo trimethylamine gas; and sol–gel reaction with heat treatment was also eliminated. The prepared brominated/quaternizedAEMs were examined by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and AMFC test. The microstructure, water content, swelling ratio, ion exchange capacity, ionic conductivity and polarization of membranes were determined. The effects of reactants ratio, reaction atmosphere, polymer concentration, type of casting solvent, and hydroxylation treatment were discussed. To the best of our knowledge, the microstructure, ionic conductivity, water content, swelling ratio and ion exchange capacity of the membrane cast from different solvents were first investigated.

2. Experimental

2.1. Materials

Poly(2,6-dimethyl-1,4-phrnylene oxide) (PPO) of $Mw = 30,000 \, g \, mol^{-1}$ (Aldrich, 99.5% GC) was used as received. Bromine, chlorobenzene, N,N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP), potassium hydroxide (KOH), hydrochloric acid (HCl) and phenolphthalein reagent were of analytical grade (Alda-Aesar) and used as received.

2.2. PPO-based anion-exchange membranes preparation

2.2.1. Bromination

Appropriate amount of bromine and 1.5 g of PPO were added into a 2-neck round bottom reaction flask with chlorobenzene (30 mL) as solvent. The reaction mixture was subjected to reflux in oil bath at the controlled temperature of 135 °C for 10 h. The resulted solution was then cast into a thin film and dried in oven overnight at the controlled temperature of 60 °C.

2.2.2. Hydroxylation

For hydroxylation treatment, brominated PPO film was submerged in 1 M KOH bath at controlled temperature of 60 °C for 24 h. After the hydroxylation treatment, the resulted film was then rinse generously with distillate water and dried in oven overnight at 60 °C.

2.2.3. Quaternization

The dried films with and without hydroxylation treatment were dissolved in an investigated solvent to yield 10 wt% polymer solution. The homogeneous solution was then bubbled with trimethylamine gas for 1 h at room temperature. The quaternized polymer solution was then cast to thin film over a smooth glass Petri disc. The resulted film was subsequently being dried in oven overnight at controlled temperature of 60 °C.

2.3. Membrane characterizations

2.3.1. Scanning electron microscopy (SEM)

A Hitach S-2700 scanning electron microscope (SEM) was used at accelerating voltage of 5 kV. Dried membrane samples were fractured at liquid nitrogen temperature and fixed to a SEM spin stub with a conductive adhesive. Membranes images were taken at different magnifications for microstructure characterization.

2.3.2. Fourier transform infrared spectroscopy (FTIR)

The functional groups of prepared membranes were examined using Perkin Elmer Spectrum 100 FT-IR spectrometer. The solid samples were analyzed in transmission mode within the scanning wavelength of 4000–550 cm^{-1}.

2.3.3. Water content and swelling ratio

The membranes were soaked in large volume of 0.1 M KOH solution for 24 h to convert membranes from chloride-form to hydroxide form. The resulted membranes were rinsed intensively with distillate water to remove excess KOH. The water uptake and swelling of membrane were evaluated by first drying the prepared membranes in desiccators over anhydrous calcium chloride at room temperature until constant dry weight (W_d) and length (L_d) were obtained. The dry membranes were immersed in distillate water at room temperature for 24 h. The excess water was swabbed away by using tissue paper before weighing. The weight and length were measured several times until constant weight (W_w) and length (L_w) were achieved. The water uptake of membranes was calculated using Eq. (1) [22]:

$$Water \; uptake \, (\%) = \left[\frac{W_w - W_d}{W_d} \right] \times 100\% \tag{1}$$

The swelling ratio of membranes was calculated using Eq. (2) [27]:

$$Swelling \; ratio \, (\%) = \left[\frac{L_w - L_d}{L_d} \right] \times 100\% \tag{2}$$

2.3.4. Ion exchange capacity (IEC)

The ion exchange capacity (IEC) of prepared membranes was measured using classical acid–base titration method. The hydroxide of membranes was neutralized by immersing the samples in 50 mL of 0.1 M HCl solution for 24 h. The IEC was determinated by titration of the HCl solution with 0.1 M KOH solution to measure the amount of acid being neutralized by the hydroxide of membrane at the presence of phenolphthalein reagent as pH indicator. The IEC was calculated from the titration result via the following Eq. (3):

$$IEC \, (m \; mol \; g^{-1}) = \left[\frac{Consumed \; 1 \, M \, KOH \times molarity \, KOH}{Weight \; of \; dried \; membrane} \right] \tag{3}$$

2.3.5. Ionic conductivity

The hydroxyl ion (OH$^-$) conductivity of prepared membranes was measured using normal standard four-point probe technique. Before conductivity measurement, membranes were first transformed to OH$^-$-form through immersing the solid membranes in 1 M KOH solution for 24 h. The resulted membranes were then washed intensively with deionized water until a neutral pH of residual water was obtained. The membranes were respectively sandwiched between two pieces of conductive wet-proofed carbon papers with the active surface dimension of 1 cm^2. The membrane samples were then assembled into Teflon measuring cell and were tightened to a constant torque for ensuring good membrane-electrodes contact with reproducible results. The assembled cell was soaked in deionized water medium to start the conductivity measurement. Electrochemical impedance spectroscopy was performed using a Solartron Analytical SI 1260 impedance/gain-phase analyzer under galvanostatic mode with ac perturbation current amplitude of 0.1 mA over a frequency range 1 MHz to 100 mHz. The impedance data were recorded with Solartron Impedance Measurement software, SMaRT^{TM}. The resistance was obtained from the associated Nyquist plot. The OH$^-$ ionic conductivity (σ) was calculated according to Eq. (4):

$$\sigma = \left[\frac{L}{R \times S} \right] \tag{4}$$

where R is the measured membrane resistance, L and S are the thickness area of the membrane respectively.
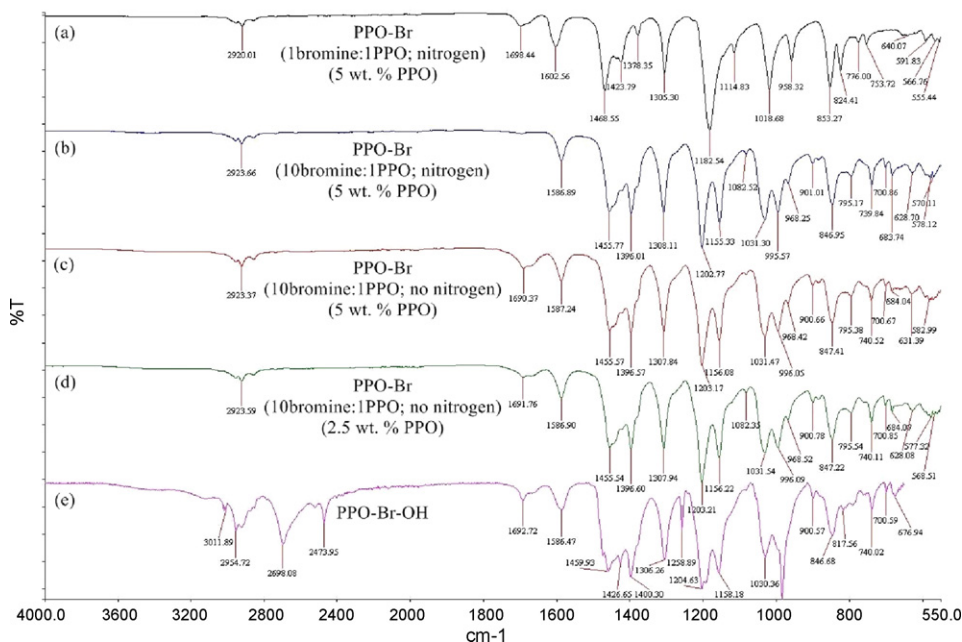
Fig. 1. The FTIR spectra of brominated PPO at different reaction conditions.

2.4. Performance of alkaline membrane fuel cell

2.4.1. Membrane electrode assembly

Ionomer binder was homemade using the quaternized PPO dissolved in NMP to yield 5 wt% ionomer suspension. The catalyst ink was prepared by mixing 30 wt% Pt/C (Vulcan XC-72R supported platinum, BASF), deionized water, NMP and the PPO ionomer suspension. The mixture was sonicated for 15 min in ultrasonic bath. After the sonication, the ink was deposited on wet-proofed carbon paper (E-TEK) until the desired metal loading of 0.65 mg cm^{-2} Pt was achieved. The synthesized PPO AEM sample was sandwiched in between two homemade electrodes with catalyst layer facing the AEM without hot-pressing, forming membrane electrode assembly (MEA) for fuel cell test.

2.5. Fuel cell test

A homemade test cell with the active area of 1 cm^2 was used to investigate the fuel cell performance. The test cell composes of a pair of graphite bipolar plates, machined with simple parallel flow fields, and two stainless steel end plates for holding the bipolar plates in place. Rod heaters were inserted into the end plates to control cell temperature. A Solartron 1287A electrochemical interface coupled with CorrWare/CorrView software was used to measure the polarization curves of alkaline membrane fuel cell at ambient pressure. The input flow rate of anode hydrogen (H$_2$) was 5 mL min^{-1} and cathode oxygen (O$_2$) was 10 mL min^{-1}. The external humidification temperatures of H$_2$ and O$_2$ were constantly kept at 90 °C and 85 °C, respectively. Prior to the polarization curves recording, the assembled cells were activated by operating unit cell at constant current until a stable performance was obtained.

3. Results and discussion

3.1. Reactions mechanism

In this work, PPO-based anion-exchange membranes were prepared via simple routes of bromination – with and without hydroxylation treatment quaternization reactions. During the bromination reaction at 135 °C, heat causes the weak Br$_2$ bond to undergo homolytic cleavage to generate two bromine radicals and starting the chain process. When PPO is treated with bromine (Br$_2$), a bromine radical abstracts a hydrogen from benzyl group of PPO to form HBr, and the benzyl radical abstracts a bromine atom from another molecule of Br$_2$ to form the benzyl bromide product and another bromine radical. This cycle of radical substitution repeats until the conditions of reaction, such as reactants concentration and/or heat are altered. During the hydroxylation treatment, partial benzyl bromides of PPO undergo nucleophilic substitution reaction very readily in 1 M KOH solution at 60 °C. The electron rich species hydroxyl ion (OH$^-$) of KOH reacts at an electrophilic saturated carbon atom, attached with an electronegative substituent of bromine (the leaving group). During the quaternization reaction with trimethylamine, the amine as nucleophile reacts with the non-hydrolyzed benzyl bromides of PPO via substitution reaction. New carbon–amine (C–N) bond is created after the electrophilic carbon of the benzyl bromide is attacked by nucleophile amine then the bromide is displaced.

3.2. FTIR spectra

The FTIR spectra of brominated PPO membrane at different preparation conditions are shown in Fig. 1. The benzyl bromides (C–Br) stretches band at approximately 1155 cm^{-1} and in the 680–750 cm^{-1} region, while the C–H bends and the aromatic C–C stretches how up in the 1370–1470 cm^{-1} region. The band in the 1585–1600 cm^{-1} is attributed to the C=C stretches and the band near 2900 cm^{-1} belongs to C–H stretches of phenyl groups. The bands in the 1000–1150 cm^{-1} region are ascribed to the stretching vibration of ether (C–O), while the peak near 1690 cm^{-1} implies the presence of unexpected aromatic carbonyl functionalities (C=O). As shown in Fig. 1(e), a growth of wide absorption occurred from about 3600 to 3100 cm^{-1}, accompanied with the appearance of 2698 cm^{-1} band, indicate that hydroxyl groups (O–H) were involved in the substitution reaction. Distinct bands due to quaternization were detected in the 2500–2400 cm^{-1} region and intense band at 1258 cm^{-1}. The results indicate that surface bromide groups were rapidly quaternized with trimethylamine.
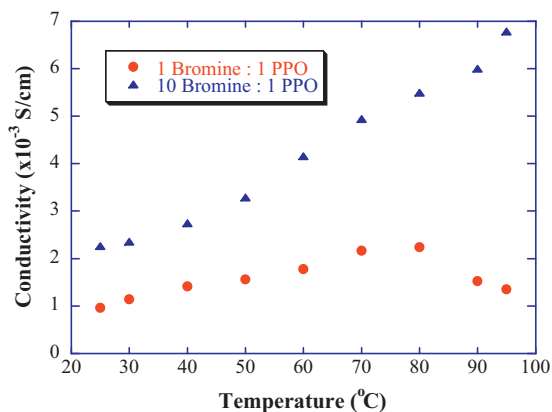
Fig. 2. Effect of bromine/PPO loading ratio on the ionic conductivity of PPO AEM.

Fig. 4. Effect of PPO concentration on the ionic conductivity of PPO AEM.

3.3. Effects of reactants ratio

The effect of bromine/PPO molar ratio on the bromination reaction of PPO was conducted at two different bromine loadings, by holding all other preparation parameters unchanged at 5 wt% PPO concentration, under nitrogen atmosphere, with hydroxylation treatment and NMP as membrane casting solvent. The resulted ionic conductivities of final brominated/quaternized membrane are shown in Fig. 2. One can see that with the increase of bromine/PPO loading ratio from equimolar to bromine in excess (bromine/PPO molar ratio at 10), the conductivity of membrane is enhanced to at least twofold. The conductivity of membrane increased with increasing temperature in the studied range from 25 to 95 °C for equimolar bromine/PPO, while the membrane conductivity dropped at temperature higher than 80 °C was observed for that with bromine/PPO ratio at 10. Thus, one can conclude that the ionic conductivity of brominated/quaternized membrane is strongly dependent on the reactant ratio of bromine/PPO.

3.4. Effects of reaction atmosphere

The effect of reaction atmosphere with and without nitrogen gas environment was investigated at preparation condition of 5 wt% PPO, 10 bromine/PPO ratio, with hydroxylation treatment and NMP as membrane casting solvent. Fig. 3 shows the resulted membranes conductivity versus temperature. With the increase of temperature from 25 to 60 °C, the conductivity of brominated membrane in nitrogen-free atmosphere increased. The conductivity dropped at temperature higher than 80 °C. For the ionic conductive membrane that was brominated under nitrogen atmosphere, conductivity increased with increasing temperature in the
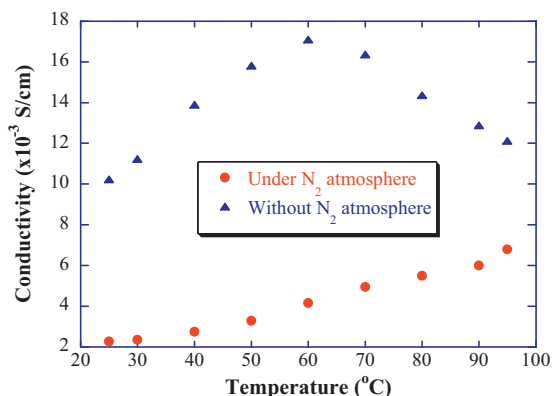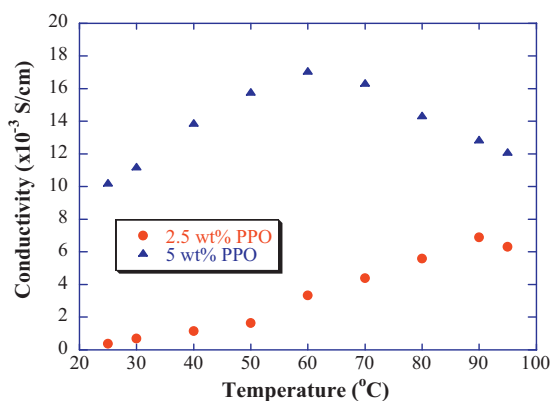
studied range 25–95 °C. However, the bromination reaction with nitrogen-free atmosphere enhances the ionic conductivity of membrane to at least twofolds higher in value. These studies indicate that the reaction atmosphere of bromination reaction has a strong influence on the quality of the final membrane. The reasons for using nitrogen environment are obviously to reduce defects, impurity and/or side reaction, where the phenomenon may due to oxygen, oxidization and/or water vapor. Our experiment indicates that nitrogen protection is not required in this reaction.

3.5. Effect of polymer concentration

The PPO concentration was prepared from 2.5 wt% and 5 wt%, while the other preparation parameters were maintained at bromine/PPO molar ratio of 10, nitrogen-free atmosphere, with hydroxylation treatment and NMP as membrane casting solvent. The effect of PPO concentration on the ionic conductivity of the resulted membranes is shown in Fig. 4. By doubling the PPO concentration from 2.5 to 5 wt% in bromination reaction medium, the ionic conductivity of final PPO membrane is enhanced to at least twofold. For the reaction medium with 5 wt% PPO, an optimum conductivity of 1.64×10^{-2} S cm^{-1} of the synthesized PPO membrane at 60 °C was obtained, while an optimum conductivity of 6.88×10^{-3} S cm^{-1} at 90 °C was recorded for the membrane synthesized from 2.5 wt% PPO. As expected, the results indicate that appropriate polymer concentration provides better reactant availability for effective bromination reaction.

3.6. Effect of casting solvent

Brominated/quaternized PPO membranes synthesized from 5 wt% PPO, bromine/PPO molar ratio of 10, nitrogen-free atmosphere and with hydroxylation treatment were prepared using three different combinations of selected casting solvents: chlorobenzene/DMF, chlorobenzene/DMAs and NMP. The ionic conductivities of the resulted membranes varies with increasing temperature which are shown in Fig. 5. Thus, plots in three different magnitudes with about the same trend are observed. Brominated/quaternized PPO membrane with the highest ionic conductivity values was prepared from NMP, while the lowest conductivity was recorded from chlorobenzene/DMF-cast PPO membrane. The NMP-cast membrane reaches the optimum conductivity value at 60 °C, and the chlorobenzene/DMF-cast membrane achieves its highest conductivity value at 70 °C, while at 50 °C was recorded for chlorobenzene/DMAs-cast membrane.

Fig. 6 shows the stability of ionic conductivity of the prepared membranes in 16 h duration. All the three membranes have a stable ionic conductivity reading in three different magnitudes via

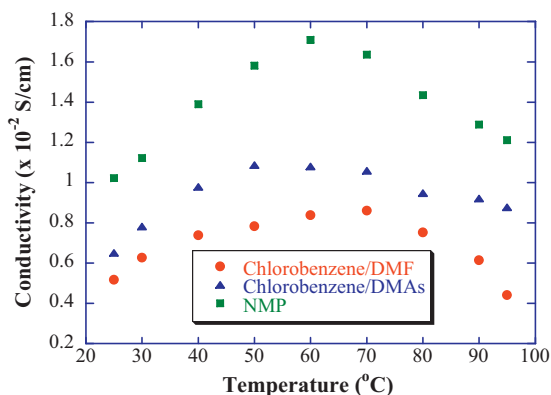**Fig. 3.** Effect of reaction atmosphere on the ionic conductivity of PPO AEM.

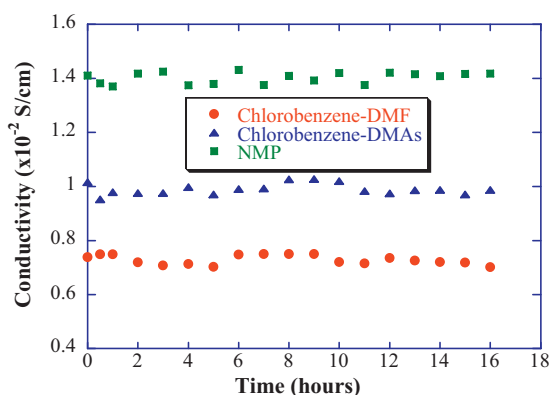**Fig. 5.** Effect of casting solvent on the ionic conductivity of PPO AEM.

Fig. 6. Effect of casting solvent on the stability of ionic-conductivity of PPO AEM at 40 °C.

an increase order from NMP, chlorobenzene/DMAs to chlorobenzene/DMF in the studied duration.

The behaviors of different solvent-combination-cast brominated/quaternized PPO membranes on water uptake, swelling ratio and ion exchange capacity are compared in Fig. 7. The NMP-cast PPO membrane possesses the highest water uptake ability and ion exchange capacity with the lowest membrane swelling ratio. In the reverse, chlorobenzene/DMF-cast membrane gives the lowest water uptake ability and ion exchange capacity with higher swelling ratio. With an increasing order of dielectric constant of sol-
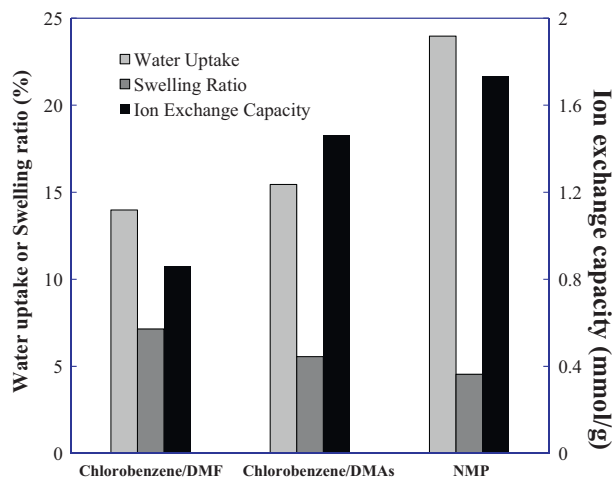

Fig. 7. Effect of casting solvent on the water uptake, swelling ratio and ion exchange capacity of PPO AEM.

vents: NMP (32) < DMAc (37.8) < DMF (38.3), the water uptake and ion exchange capacity of membrane decreased while the swelling ratio increased were observed.

Among the solvents used, NMP appeared to be the most suitable as casting solvent in terms of conductivity, stability, water uptake, swelling ratio and ion exchange capacity. It can be explained according to the microstructures observed in the three membranes, due to the differences in the solvent volatility and the PPO–solvents interaction. Fig. 8 illustrates the microstructure of the investigated solvents-cast membranes. It was reported that faster evaporation rates resulting from the use of more volatile solvent, results in preserving more of the polymer structure present in the casting solution [28]. Thus, matrix of PPO membrane entraps more free-volume via more volatile casting solvents. This can be confirmed by the formation of larger dimension nodules observed in the chlorobenzene/DMF-cast and chlorobenzene/DMAs-cast membranes, compared to the membrane produced from PPO that was dissolved in less volatile NMP casting solvent (Fig. 8). Among the three solvents, DMF and DMAs are more volatile than NMP. The brominated PPO does not and/or hardly soluble in DMF and DMAs alone. In order to enhance polymer solubility, chlorobenzene was added to the casting solutions in equivalent. The presence of chlorobenzene as one of the casting solvent again accelerates the solution volatility. Formation of larger grains in chlorbenzene/DMF-cast and chlorobenzene/DMAs-cast membranes than the NMP-cast membrane was observed as shown in Fig. 8. Dielectric constant of solvent is an important factor in determining the occurrence of ion-association. According to Coulomb's law, ion association will increase as the magnitude of dielectric constant decreases. Decrease in solvents' dielectric constant, would also enhance the hydrogen bonding among the donor and acceptor groups to reduce swelling [29]. Better polymer–solvent interaction between PPO and NMP also results to a thinner membrane with more uniform polymer network and smooth membrane surface. Higher membrane hydrophilicity with higher water uptake – ion exchange capacity and low swelling ratio were also obtained. A thin membrane with continuous hydrophilic ionic polymer matrix facilitates the transport of hydroxyl anion and therefore, the ionic conductivity of membrane was enhanced.

3.7. Effect of hydroxylation treatment

The effect of hydroxylation treatment was investigated from the membrane that was prepared via 5 wt% PPO, bromine/PPO molar ratio of 10, nitrogen-free atmosphere and NMP as membrane casting solvent. Fig. 9 shows the effect of hydroxylation treatment on the ionic conductivity of PPO membrane against temperature. The highest conductivity of the membrane with hydroxylation treatment occurred at 60 °C, while the peak of conductivity for the membrane without hydroxylation treatment fell at 70 °C. The membrane without hydroxylation treatment reaches competitive conductivity values to the membrane with hydroxylation treatment only at the temperature above 80 °C.

The behaviors of brominated/quaternized PPO membranes, prepared with and without hydroxylation treatment on water uptake, swelling ratio and ion exchange capacity are compared in Fig. 10. The PPO membrane with hydroxylation treatment possesses higher water uptake ability and ion exchange capacity with lower membrane swelling ratio. In contrary, the reserve trends are observed from the preparation route of PPO membrane without hydroxylation treatment.

As previously discussed in Section 3.1, part of benzyl bromides of PPO were displaced with hydroxyl group through hydroxylation treatment. The hydrophilicity of PPO membrane was then enhanced. This can be confirmed via the increase of water uptake and ion exchange capacity of the membrane after hydroxylation
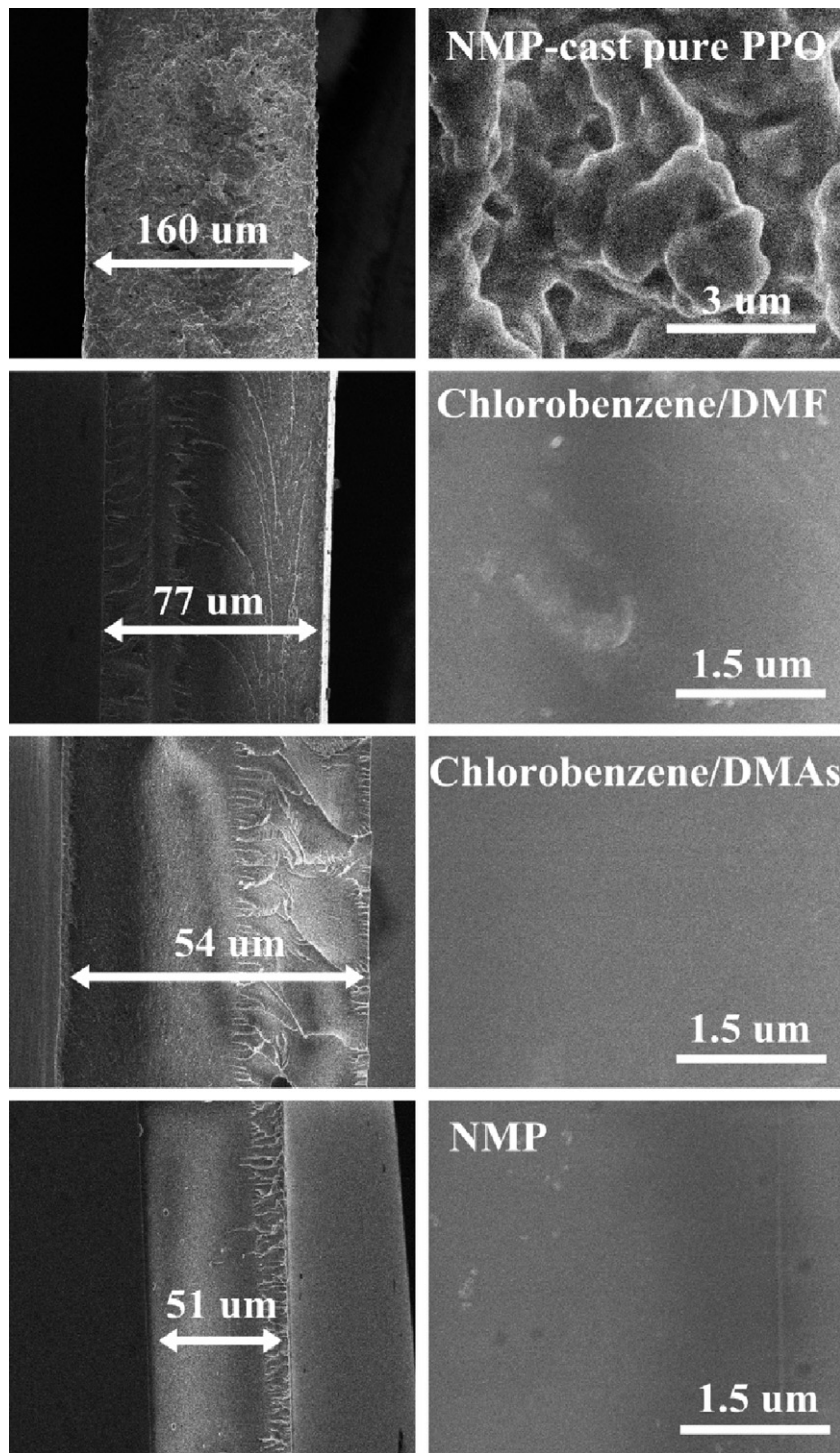
Fig. 8. SEM images of different solvents-cast PPO AEM. First column: membrane cross-section and second column: membrane surface.

treatment as shown in Fig. 10. The presence of more hydrogen bonding from hydroxyl group results to stronger polymer matrix and therefore lowers the membrane swelling ratio. It is also clear that ionic conductivity always follows the same trend as the water uptake and ion exchange capacity. Higher ionic conductivity values for the hydroxylation treated membrane were obtained. However, higher temperatures produce more anion vacancies that allow ionic motion in the direction of an applied electric field [30]. The membrane without hydroxylation treatment shows competitive conductivity values to the membrane with hydroxylation treatment at higher temperature were as observed (Fig. 9).

3.8. Polarization curves of alkaline membrane fuel cell

Fig. 11 shows the polarization curves of AMFC assembled with PPO AEM, prepared from the bromination reaction of 5 wt% PPO under the nitrogen-free condition and cast with NMP solvent after hydroxylation treatment. The performances were recorded at different cell temperatures in the range of 25–80 °C, by keeping the humidification temperature of H_2 and O_2 constant at 90 °C and 85 °C, respectively. Homemade ionomer suspension prepared from the quaternized PPO was utilized in the electrodes fabrication. As shown in Fig. 11(a), the highest open circuit voltage (OCV) of 1.02 V
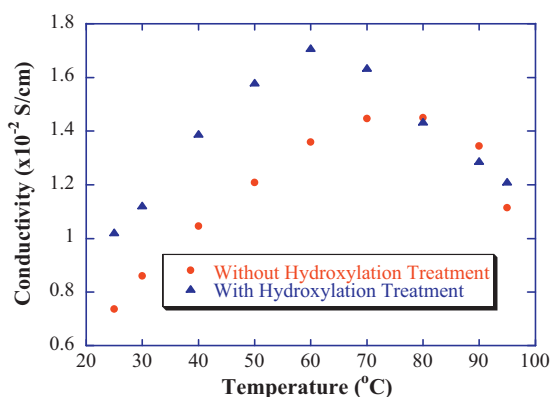
Fig. 9. Effect of hydroxylation treatment on the ionic conductivity of PPO AEM.

Fig. 11. Polarization curves of alkaline membrane fuel cell with PPO AEM recorded at different cell temperatures.

was achieved from the entirely homemade MEA. The polarization curves increase with the increasing temperature up to 70 °C, and then decrease at higher temperature of 80 °C. The highest power density of 19.5 mW cm^{-2} was also recorded at the cell temperature of 70 °C as illustrated in Fig. 11(b) by using the fuel cell test system without back pressure. The obtained results demonstrate that the prepared PPO AEM has the potential for AMFC applications although further improvement on power density is required.

The increase of cell temperature can directly increases the activity of the catalyst and boosts the rate of electro-chemical reactions. Thus, more water was being consumed at the cathode side from the electrochemical reaction with oxygen to produce OH$^-$ before the ion can be conducted through the AEM to the anode side. The OH$^-$ ions will then react with hydrogen to yield water and electricity. In addition, water is easily condensed at lower temperature. By increasing the cell temperature, more water being evaporated and induces more stable vapor composition for reactions then liquid water phase. This promotes water management and reaction kinetic via ease reactant reduction and water vapor exhaustion. Water flooding problem inside the electrodes can be minimized and improves local reactants diffusion toward the catalyst layers. The performance of fuel cell therefore was enhanced from 25 to 70 °C. However at cell temperature higher than 70 °C, thermal degradation of quaternized PPO AEM via N–C$_2$ bonds decomposition is expected. This is a common drawback of AMFC that requires significant technical solution.
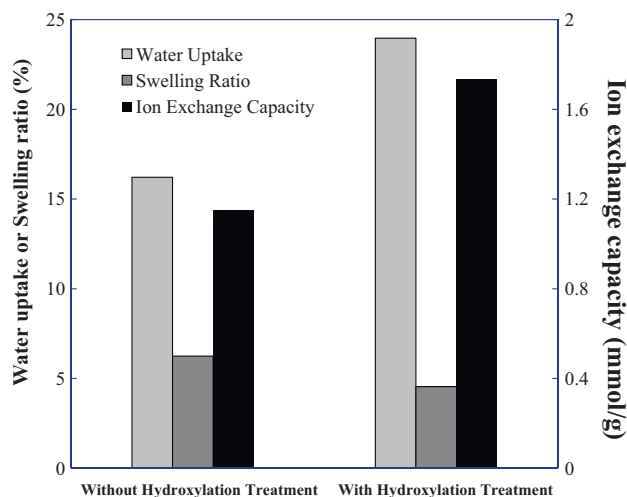

Fig. 10. Effect of hydroxylation treatment on the water uptake, swelling ratio and ion exchange capacity of PPO AEM.
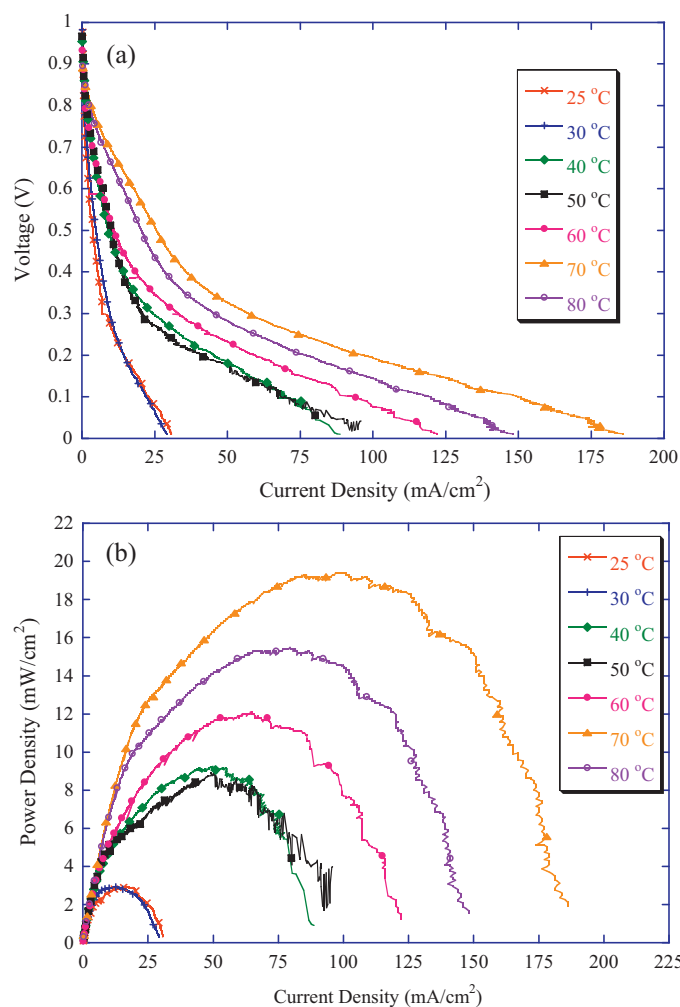
4. Conclusions

PPO-based AEMs were prepared via simple bromination–quaternary amination reactions, by shortening its synthesis route and also by reducing the use of toxic materials. The results show that the characteristics of prepared membranes have a great dependence on the investigated preparation parameters: the effects of molar ratio of reactants, reaction atmosphere, polymer concentration, type of casting solvent, and hydroxylation treatment. Proper controling on the preparation parameters with the right reaction conditions can enhance the performance of PPO AEM for AMFC applications. The obtained results demonstrate that, although with simple preparation route and least toxic chemicals, a competitive ionic conductivity value of 1.64 × 10^{-2} S cm^{-1} was achieved at 60 °C from the synthesized PPO membrane which was prepared from 5 wt% PPO, bromine/PPO molar ratio at 10, nitrogen-free atmosphere, with hydroxylation treatment and NMP as the membrane casting solvent. Thinner membrane was achieved by using the NMP as casting solvent. The membrane possesses the highest water uptake value of 24% and ion exchange capacity value of 1.74 m mol g^{-1} with the lowest swelling ratio of 4.5%. For the operation at temperature above 80 °C, the hydroxylation treatment in the preparation route of PPO-based AEM can be omitted. Homemade ionomer suspension prepared from the quaternized PPO has been utilized in the electrodes fabrication. The highest power density of 19.5 mW cm^{-2} was recorded at the optimum

temperature of 70 °C. The obtained results demonstrate that the prepared PPO AEM has the potential for AMFC applications.

Acknowledgements

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