



Short communication

The synthesis and characteristic of an anion conductive polymer membrane for alkaline anion exchange fuel cells

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ABSTRACT

An alkaline anion exchange membrane has been developed from poly (methyl vinyl ether-alt-maleic anhydride) (PMVMA) by grafting quaternary ammonium groups through a maleic anhydride ring-open reaction. FT-IR spectra showed successful grafting of quaternary ammonium groups on this cheap raw material. TGA showed that the degradation temperature was 150 °C which was due to the loss of the quaternary ammonium groups. The tensile stress of the resultant membrane after ion exchange was 9.0 MPa, and the Young's modulus was 0.14 GPa with a fractured elongation 11%. The through plane, anion conductivity varied from 1.9×10^{-2} to 2.7×10^{-2} S cm⁻² in the temperature range of 25–65 °C. The power density of a fuel cell with the membrane increased with the operation temperature in the range from 15 °C to 35 °C. With an ionomer loading of 15% in membrane electrode assemblies (MEA), the power density in the fuel cell was 115 mW cm⁻² and 40 mW cm⁻² for O₂ (35 °C) and air (30 °C), respectively.

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1. Introduction

Fuel cell technologies have the potential to provide a unique combination of features and benefits including efficiency and low pollution level [1–5]. During decades of development, various types of fuel cell have been designed which have attracted attention for the residential, portable and vehicle applications [3,6,7]. Among all these fuel cells, polymer electrolyte membrane fuel cells are the most promising technology which typically includes proton exchange membrane fuel cells (PEMFCs) and alkaline anion exchange membrane fuel cells (AAEMFC) [2,7–9]. Nafion (Dupont) based proton exchange membranes (PEMs) are the state-of-the-art polymer electrolyte membranes for the fuel cells with excellent chemical, mechanical and thermal stabilities, and high performance with Pt as the catalyst. However, the high cost of the membrane and Pt group catalyst is the main obstacle that impedes commercialisation [2,10,11]. These limitations can be linked directly to the materials used [7–9].

On the other hand, alkaline fuel cells (AFCs) with several important advantages over conventional PEMFCs such as cheaper non-noble metal can be used as the catalyst to reduce the cost and improved kinetics at the cathode as well as at the anode [2,8–11], are recognized as one of the most promising technologies. In recent

years, interest has grown in the development of alkaline anion exchange membranes (AAEMs) which is aimed to replace the liquid KOH in the catalyst electrolyte interface with soluble ionomeric materials with acceptable OH⁻ conductivity [11–14]. However, compared to the research on membranes for PEMFCs, there are very few readily available anion exchange membranes that serve as a commercial standard for electrochemical applications in the way that Nafion does in the field of PEMFC.

There are number of reports on synthesis of new polymers for AAEMs based on quaternary ammonium groups (QAG) or quaternary phosphonium groups (QPG) through either monomer or polymer modifications [10–15]. For example, quaternary ammonium modified polysulphone was reported as alkaline electrolyte and nonprecious metals as the catalyst for the negative and positive electrodes, showed a decent performance with a maximum power density of 50 mW cm⁻² at 60 °C under not well-optimized conditions [11]; A random copolymer of poly(methyl methacrylate-co-butyl acrylate-co-vinylbenzyl chloride) was reported with the peak power density 59 mW cm⁻² at 80 °C [12]; a perfluorinated anion exchange membrane with a 1,4-dimethylpiperazinium cation was reported with peak power density of 77 mW cm⁻² at 60 °C [13]; and most recently, anion conductive aromatic multiblock copolymers poly(arylene ether)s containing quaternized ammonio-substituted fluorene groups was reported with the maximum power density 297 mW cm⁻² at 80 °C [14]. These reports pave the way to the development of alkaline anion exchange membranes for the alkaline fuel cells (AFCs) and some promising results have been achieved. However, while the

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AAEM fuel cell holds great promise, the low cost high performance AAEM is still the main challenge for the development of AAEMFCs [2,8–11].

In this work, low cost polymer, namely poly (methyl vinyl ether-alt-maleic anhydride) was used to synthesize a quaternary ammonium grafted polymer material with potential application in AAEMFCs. The obtained quaternized poly (methyl vinyl ether-alt-maleic anhydride) was evaluated as the AAEM in terms of its ion conductivity, mechanic property and fuel cell application.

2. Experimental

2.1. Chemicals and reagents

Poly (methyl vinyl ether-alt-maleic anhydride) (molecular weight 216 kDa), 3-chloropropanol, hexanol, and N,N-dimethyl formamide, toluene, were obtained from Sigma–Aldrich (UK), trimethylamine was ordered from Fisher (UK); carbon-supported catalysts (60 wt.% Pt/C) was ordered from Alfa Aesar (UK, catalogue no. 44171). Carbon cloth with gas diffusion layer was supplied by Freudenberg Inc (Germany, catalogue no. H2315 T10A C1). Iso-propanol and potassium dihydrogen phosphate were purchased from Fisher Scientific (UK). All other chemicals were used as received and the water used was distilled water.

2.2. The membrane synthesis

First, 5 g of poly (methyl vinyl ether-alt-maleic anhydride) (PMVMA) was dissolved in 50 ml of toluene in a conical flask. Then 1 ml of 3-chloropropanol and 1 ml of N,N-dimethyl formamide was added to the solution in turn. The mixture was kept at 100 °C overnight under continuous stirring. Afterwards, 2 ml of hexanol was introduced through the condenser in order to block the unreacted anhydride units. The reaction mixture was kept at 100 °C for another 24-h under reflux. Then the rotary vacuum evaporator was applied to obtain the esterified PMVMA at 90 °C. The residue was dissolved in 100 ml of iso-propanol at room temperature. 20 ml of trimethylamine was added to the solution of esterified PMVMA and the reaction of the quaternisation was carried out under continuous stirring at 70 °C overnight in a flask which was followed by the vacuum evaporation at 70 °C. The resultant quaternized poly (methyl vinyl ether-alt-maleic anhydride) (qPMVMA) was dissolved in iso-propanol for the membrane preparation and directly used as ionomer in the preparation of membrane electrode assembly (MEA).

2.3. Anion conductive membrane preparation

5 mL of the qPMVMA iso-propanol solution was injected into the glass slide mould which was 10 cm × 10 cm × 0.5 cm and the mould was kept in the fume cupboard overnight to solidify the membrane. Then 5 mL of distilled water (deH₂O) was added into the mould to wet the membrane before peeling off the membrane from the mould. The membrane was immersed into 1 M KOH solution to obtain the ion exchanged membrane (qPMVMA/OH⁻).

2.4. Water uptake measurements

The membranes (Length × Wide × Thickness = 5 cm × 1 cm × 100 μm) were immersed in the N₂ saturated deionized water at room temperature (25 °C) overnight. Then the samples were taken out to remove the surface water by wiping with the clean tissue paper and weighted immediately. The wet membranes then were dried under vacuum at 80 °C until the constant weight was obtained. Five repeats were carried out.

2.5. Conductivity measurement

A four-point probe technique was used for membrane conductivity measurement. The membrane was contacted with platinum foils and connected to a frequency response analyser (FRA, Voltech TF2000, UK). All samples were cut into 1 cm wide, 5 cm long strips and placed on the platinum foil with 0.5 cm gap between them. AC impedance measurements were carried out at frequencies between 1 and 20 kHz. The humidity was provided by the steamer in N₂ flow. The polymer membranes were held at the desired conditions of temperature for 30 min to reach steady state.

2.6. Membrane electrode assemblies and fuel cell tests

Membrane electrode assemblies (MEA) were prepared as follows. Briefly, catalyst inks were prepared by blending carbon-supported catalysts (60 wt.% Pt/C) and ionomer (18 wt.% ionomer/catalyst) in iso-propanol under ultrasonic vibration for 30 min. The inks were sprayed onto a carbon-supporting cloth paper covered with a gas diffusion layer at 70 °C, and then the electrodes were held at 70 °C for 2 h. The Pt loading was 0.8 mg cm⁻² (both cathode and anode). Membrane electrode assemblies were made by pressing the anode and cathode onto the membranes at room temperature 0.2 ton cm⁻² pressure for 2 min.

The MEA was set between two high-density graphite blocks impregnated with phenolic resin, and the active electrode area was covered the parallel gas flow channels area (1 cm²). Electric cartridge heaters were mounted at the rear of the graphite blocks to maintain the desired temperature, which was monitored by imbedded thermocouples and controlled with a temperature controller. Gold-plated steel bolts were screwed into the blocks to allow electrical contact. H₂ and O₂ were fed to the cell at flow rates of 40 and 70 ml³ min⁻¹, respectively. The anode and cathode potentials were recorded with a scan rate of 5 mV s⁻¹ during the fuel cell tests.

2.7. Characterizations

The polymer samples were tested by FT-IR with PerkinElmer Universal STR Sampling PerkinElmer Spectrum 100 Series. The samples for Differential Scanning Calorimetry (TGA) were determined by PerkinElmer TGA with 5 °C min⁻¹ heat rate and air cooling, in the range of 30–700 °C. Differential Scanning Calorimetry (SDC) were determined by PerkinElmer PYRIS Diamond DSC with 5 °C min⁻¹ heat rate and air cooling, in the range of 40–220 °C. Ion conductivity was measured by frequency response analyser (FRA, Voltech TF2000, UK) and fuel cell test was operated using an Autolab potentiostat.

3. Results and discussion

The typical approach in developing AAEMs is introducing quaternary ammonium groups in the polymer backbones. In this work, cheap raw material poly (methyl vinyl ether-alt-maleic anhydride) (PMVMA) was used as the starter polymer to synthesize anionic conductive membrane by chemical modification through ring-open reactions. The synthesis routine is shown in Fig. 1. The resultant material, after the synthesis, contained quaternary ammonium salts (qPMVMA/Cl⁻) which could be ion exchanged into anionic polymer material (qPMVMA/OH⁻) by treatment with 1.0 M KOH.

FT-IR characterization was carried out to further confirm the synthesized polymer material qPMVMA/Cl⁻ and the start polymer PMVMA was used as comparison (Fig. 2). From these spectra, we can see that the start polymer PMVMA (Fig. 2, a) has several typical vibration bands around 2800 cm⁻¹ to 2950 cm⁻¹ for the C–H from alkyl groups and –CH₃, –CH₂; and vibration around 1730 cm⁻¹

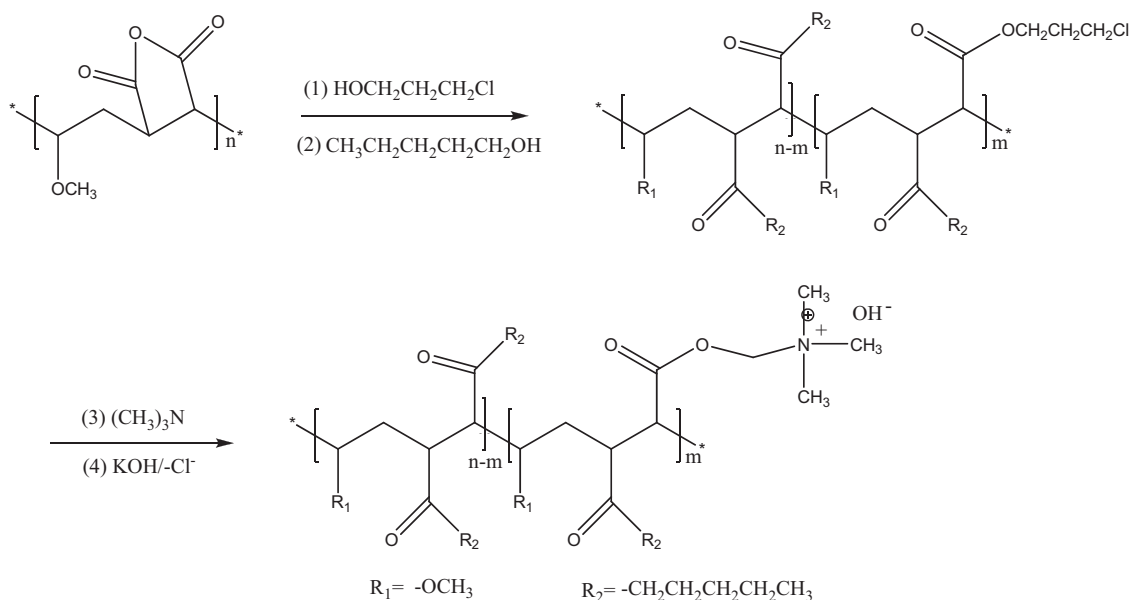


Fig. 1. The synthesis routine for the qPMVMA anion conductive polymer membrane.

for the typical $\text{C}=\text{O}$ from anhydride groups; while in the spectrum for qPMVMA/ Cl^- (Fig. 2b), the typical vibration near 955 cm^{-1} for $-(\text{CH}_3)_2\text{N}^+$ groups appears [15,16]. The characteristic absorption peaks indicate that the ring-open reactions were successfully carried out during the synthesis and the quaternary ammonium groups were successfully introduced onto the backbone polymer.

Thermogravimetric analysis (TGA) was applied to characterize the qPMVMA/ Cl^- polymer, and data are shown in Fig. 3. The TGA curve for the starter polymer PMVMA (Fig. 3) showed three steps of weight loss: first starts at 200°C which was due to the anhydride group degradation; second starts at 400°C due to polymer chains degradation; and third starts at 500°C due to carbonization.

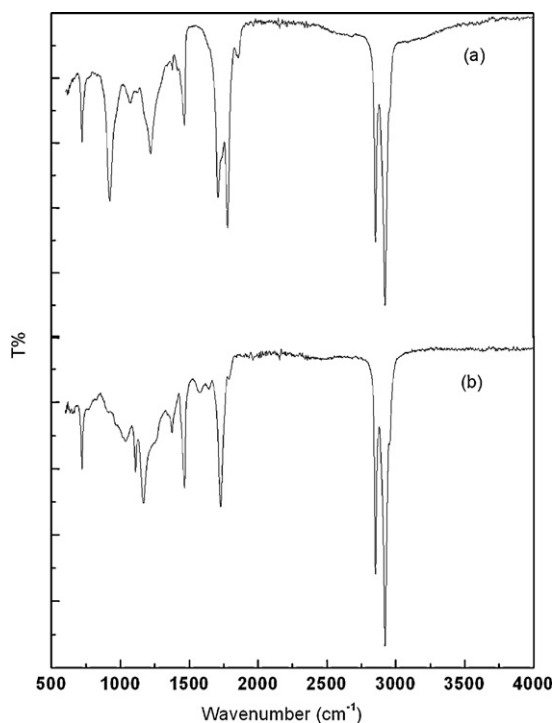


Fig. 2. FT-IR spectra of the anion conductive polymer membrane qPMVMA/ Cl^- (a) and the start polymer PMVMA (b).

While for the qPMVMA/ Cl^- polymer (Fig. 3b), the data also showed three main steps of weight loss: first starts at 150°C due to the quaternary ammonium group and anhydride groups degradations; second starts at 350°C due to the polymer chain degradation and third starts at 450°C due to carbonization. From the results, we can see that for the qPMVMA/ Cl^- polymer the degradation temperatures were much lower than for the starter polymer, which may be due to the ring-open reactions on the backbone polymer. Also the quaternary ammonium groups may contribute to the low thermostability of qPMVMA/ Cl^- polymer.

Mechanical properties were studied using tensile tests for both the qPMVMA/ Cl^- membrane and qPMVMA/ OH^- membrane and results are shown in Fig. 4. The stress-strain curve for the qPMVMA/ Cl^- membrane showed that the tensile strength was 15.2 MPa and Young's modulus was around 0.2 GPa , and the fractured elongation was 14% . For the qPMVMA/ OH^- membrane, the tensile stress was 9.0 MPa , and the Young's Modulus was 0.14 GPa , and the fractured elongation was 11% . These results show that the chloride form membrane was stiffer and brittle than the ion exchanged membrane, and both the tensile strength and the Young's modulus decrease after the ion exchange. This

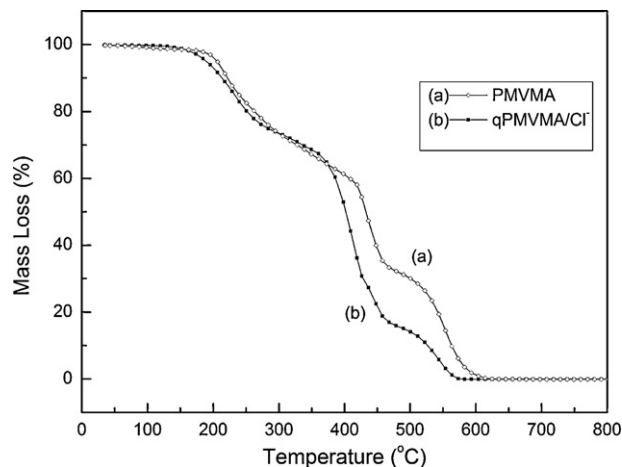


Fig. 3. Thermogravimetric analysis curves for the start polymer PMVMA (a) and the qPMVMA/ Cl^- (b).

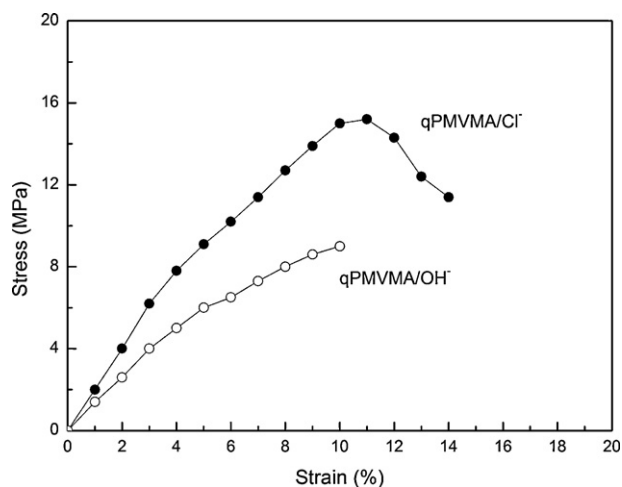


Fig. 4. Stress–strain curves of the qPMVMA/Cl⁻ membrane and qPMVMA/OH⁻ membrane.

trend is consistent with the literature report by Luo et al. [12]. The modulus was comparable to Nafion membranes with reported modulus of 0.3 GPa [17]. The mechanical properties were affected by various factors but the main reason for the resultant membrane characteristics was that there was no cross-linking between the polymer chains or thermal stable groups, such as benzyl group, and the ring-open grafting also sacrificed mechanic properties. Overall, the resultant membranes with this mechanic property can still be used for fuel cells.

Four-point probe through plane conductivity measurement was carried out at different temperatures at 100% relative humidity, to determine the anionic conductivity for the exchanged membrane and the results are shown in Fig. 5. The through plane conductivity increased from 1.9×10^{-2} to 2.7×10^{-2} S cm⁻¹ when the temperature increased from room temperature 25–65 °C. During the tests, the maximum conductivity near 60 °C reached 2.7×10^{-2} S cm⁻¹. Tests showed that the conductivity decreased when the temperature was higher than 60 °C. Although the high degree of quaternisation can increase ionic conductivity, it also has a detrimental effect on the mechanical property.

As using ionomer in the fuel cell catalyst layer electrodes can enhance the catalyst utilization, the qPMVMA/OH⁻ ionomer in isopropanol solution was used to prepare the MEA and Fig. 6 shows the SEM of the MEA prepared for the fuel cell tests. The SEM image of the carbon cloth (Fig. 6a) showed the porous structure of the gas

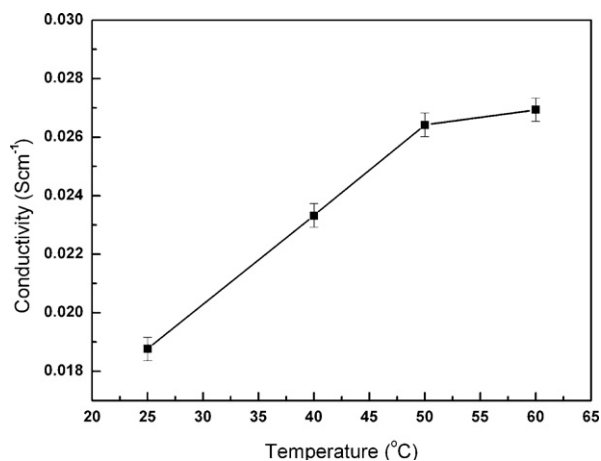


Fig. 5. Ion conductivity at different temperatures under 100% RH, 100 μm membrane thickness.

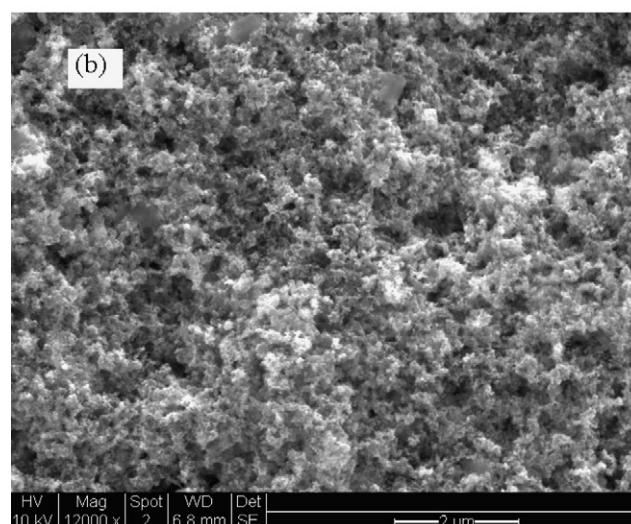
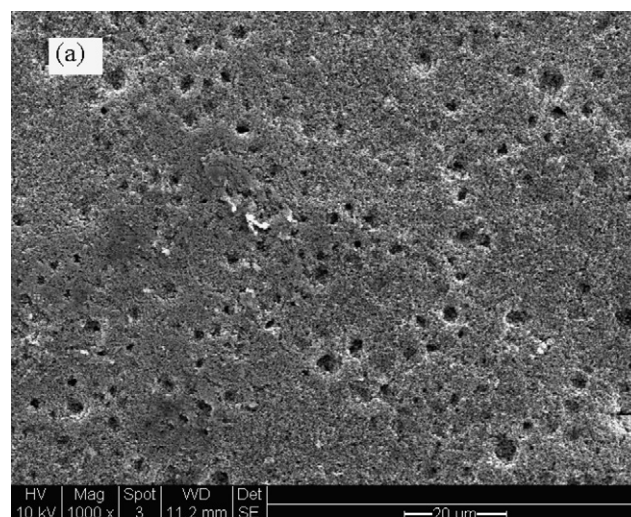


Fig. 6. SEM images of the MEA for the fuel cell performance tests. (a) The blank carbon cloth surface and (b) catalyst coated carbon cloth with 15% ionomer and 0.8 mg cm^{-2} Pt/C.

diffusion layer, while in the SEM image of the catalyst coated carbon cloth, with 15% ionomer loading and 0.8 mg cm^{-2} Pt/C (Fig. 6b), shows the structure of the porous carbon surface covered by the catalyst particles and ionomer. The porous morphology of the surface and ionomer in the MEA facilitate OH⁻ conduction and lower ionic resistance in the electrode during the fuel cell tests [18–20].

The fuel cell performance of the OH⁻ exchanged electrolyte membrane qPMVMA/OH⁻ was measured at atmospheric pressure and the polarization/power density curves are shown in Fig. 7. With O₂ in cathode and H₂ in anode, the peak power densities were 27 mW cm^{-2} , 56 mW cm^{-2} and 115 mW cm^{-2} for temperatures of 15 °C, 25 °C and 35 °C, respectively. The maximum fuel cell performance was comparable to some of the reported results [11–13] under the not well-optimized conditions, though it was lower than M. Tanaka et al. reported power density of 297 mW cm^{-2} at 80 °C [14]. The limiting current density (at 0 V) reached 430 mA cm^{-2} at the temperature of 35 °C (Fig. 7A). From the results we can see that the fuel cell performance increased with the temperature in the low range from 15 °C to 35 °C. The OCV was around 1.0 V and showed no change with the operating temperature. However, these results showed a large difference in the slopes of the I–V curve in the IR region (Ohmic resistance). Considering the membrane thickness of 100 μm, the ion conductivities of the MEAs were

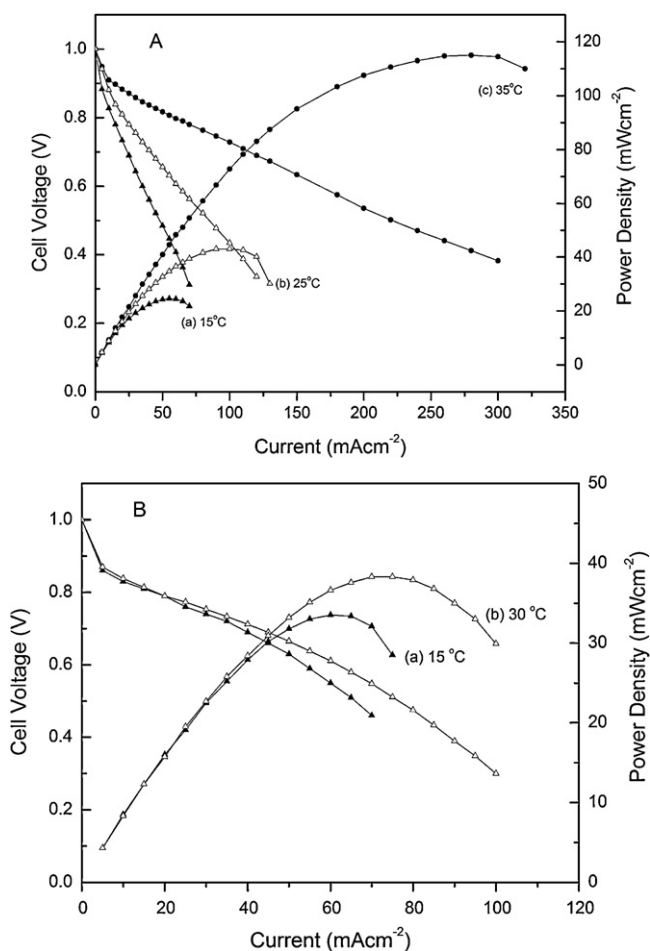


Fig. 7. Alkaline fuel cell polarization curves with H₂/O₂ (A) and H₂/air (CO₂ free) (B) at atmospheric pressure. Membrane thickness 100 μm ; ionomer loading 15 wt%; Pt loading (both cathode and anode) 0.8 mg cm⁻²; 100% RH on cathode.

$0.122 \times 10^{-2} \text{ S cm}^{-1}$, $0.21 \times 10^{-2} \text{ S cm}^{-1}$ and $0.56 \times 10^{-2} \text{ S cm}^{-1}$ for the corresponding operation temperature 15 °C, 25 °C and 35 °C, respectively. These values are much lower than the membrane conductivities of $1.9 \times 10^{-2} \text{ S cm}^{-1}$ and $2.2 \times 10^{-2} \text{ S cm}^{-1}$ from the conductivity test of the membrane in Fig. 5 at temperature of 25 °C and 35 °C, respectively. The additional voltage loss with the MEAs will be in part due to resistivities caused by the electrodes in the MEA as well as contributions from activation losses in the electrodes.

Fig. 7B shows the performance of the fuel cell with H₂ and air (CO₂ free). The power density increased from 33 mW cm⁻² to 40 mW cm⁻² and limit current increased from 118 mA cm⁻² to 127 mA cm⁻² when the operating temperature increased from 15 °C to 30 °C. Compared to the H₂/O₂ fuel cell data in Fig. 7A, the power density was much lower. This decrease was probably due to poorer fuel utilization due to lower partial pressure of oxygen in air compared to pure oxygen.

4. Conclusions

Alkaline anion exchange membranes for fuel cell were developed from poly (methyl vinyl ether-alt-maleic anhydride) (PMVMA) by grafting quaternary ammonium groups through maleic anhydride ring-open reactions. Ion conductivity increases with the operation temperature in the range from room temperature to 60 °C. Thermal stability decreased after the quaternisation reactions and polymer degradation began at 150 °C which was mainly associated with the quaternary ammonium groups. Although the mechanical property of the membrane decreased after OH⁻ exchange, it was still acceptable for the fuel cell. The grafting reactions had a significant effect on the membrane ion conductivity and mechanic property. Operating temperature significantly affected the fuel cell performance significantly in the range of 15–35 °C when H₂ and O₂ were used. The Ohmic resistance was greatly reduced when the temperature was increased in this range. Future efforts should be focused on the thermal resistance and mechanical property improvements either by the introducing of cross-linking or thermal stable groups into the polymer chain.

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References

- [1] S.M. Haile, *Acta Mater.* 51 (2003) 5981–6000.
- [2] G.F. McLean, T. Niet, S. Prince-Richard, N. Djilali, *Int. J. Hydrogen Energy* 27 (2002) 507–526.
- [3] A. Kirubakaran, S. Jain, R.K. Nema, *Renew. Sust. Energ. Rev.* 13 (2009) 2430–2440.
- [4] M. Tanak, M. Koike, K. Miyatake, M. Watanabe, *Polym. Chem.* 2 (2011) 99–106.
- [5] L. Gubler, G.G. Scherer, *Desalination* 250 (2010) 1034–1037.
- [6] G.C. Abuin, P. Nonjola, E.A. Franceschini, F.H. Izraelevitch, M.K. Mathe, H.R. Corti, *Int. J. Hydrogen Energy* 35 (2010) 5849–5854.
- [7] R. Devanathan, *Energy Environ. Sci.* 1 (2008) 101–119.
- [8] F. Bidault, D.J.L. Brett, P.H. Middleton, N. Abson, N.P. Brandon, *Int. J. Hydrogen Energy* 34 (2009) 6799–6808.
- [9] E. Gulzow, *J. Power Sources* 61 (1996) 99–104.
- [10] S. Gu, R. Cai, T. Luo, Z. Chen, M. Sun, Y. Liu, G. He, Y. Yan, *Angew. Chem. Int. Ed.* 48 (2009) 6499–6502.
- [11] S. Lu, J. Pan, A. Huang, L. Zhuang, J. Lu, *PNAS* 105 (2008) 20611–20614.
- [12] Y. Luo, J. Guo, C. Wang, D. Chu, *J. Power Sources* 195 (2010) 3765–3771.
- [13] M.J. Jung, C.G. Arges, V. Ramani, *J. Mater. Chem.* 21 (2011) 6158–6160.
- [14] M. Tanaka, K. Fukasawa, E. Nishino, S. Yamaguchi, K. Yamada, H. Tanaka, B. Bae, K. Miyatake, M. Watanabe, *J. Am. Chem. Soc.* 133 (2011) 10646–10654.
- [15] B.P. Tripathi, M. Kumar, V.K. Shahi, *J. Membr. Sci.* 360 (2010) 90–101.
- [16] M. Kozak, L. Domka, *J. Phys. Chem. Solids* 65 (2004) 441–445.
- [17] F. Bidault, D.J.L. Brett, P.H. Middleton, N.P. Brandon, *J. Power Sources* 187 (2009) 39–48.
- [18] R. Zeng, S.D. Poynton, J.P. Kizewski, R.C.T. Slade, J.R. Varcoe, *Electrochem. Commun.* 12 (2010) 823–825.
- [19] R. Zeng, R.C.T. Slade, J.R. Varcoe, *Electrochim. Acta* 56 (2010) 607–619.
- [20] M.B. Satterfield, P.W. Majsztrik, H. Ota, J.B. Benziger, A.B. Bocarsly, *J. Polym. Sci. B* 44 (2006) 2327–2345.