



Multifunctional composite membrane based on a highly porous polyimide matrix for direct methanol fuel cells

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ARTICLE INFO

Article history:

Received 19 May 2009

Received in revised form 7 July 2009

Accepted 6 August 2009

Available online 25 August 2009

Keywords:

Porous polyimide

Composite membrane

Methanol crossover

Proton conductivity

Direct methanol fuel cell

ABSTRACT

A highly porous polyimide film with tunable pore size, porosity and thickness is synthesized and used as a matrix to construct a Nafion-infiltrated composite membrane. A very efficient way for an easy and complete infiltration of the proton-conducting polymer into this substrate is developed, which is usually a major problem for composite membranes. Due to the complete inertness to methanol and the very high mechanical strength of the polyimide matrix, the swelling of the composite membrane is greatly suppressed and the methanol crossover is also significantly reduced (80 times), where as while high proton conductivity (comparable with Nafion) and mechanical strength (4 times stronger than Nafion) is still maintained. This membrane demonstrates significantly improved cell performance compared with the Nafion membrane and is a promising candidate for use in direct methanol fuel cells.

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1. Introduction

Direct methanol fuel cells (DMFCs) are promising power sources for various portable applications, such as laptop computers and mobile phones, because of their advantages of low weight and high specific energy compared with batteries. As a key component in a DMFC, the membrane must fulfill the following requirements simultaneously before successful commercialization can be realized: high proton conductivity, low methanol crossover and high mechanical strength [1–3]. Numerous efforts have been made to modify Nafion-based polymers [4–8] or synthesize alternative polymer-based membranes [9–11], with the aim of developing membranes with reduced methanol crossover while still maintaining high proton conductivity and mechanical strength. Most of the results show a certain level of reduction in methanol crossover. On the other hand, the proton conductivity and mechanical strength are also sacrificed to certain degree, which limits their use in real situations. To date, there have been no reports of the successful application of new membranes in practical DMFC applications.

One possible solution to this problem is to fabricate a polymer matrix and then fill it with a proton-conducting polymer [12–15]. The rigid structure of the matrix will limit the swelling of the added electrolyte and consequently will reduce the methanol crossover. The high mechanical strength of the matrix also offers

the possibility of fabricating a very thin structure to reduce the resistance of the membrane in operation. The choice and synthesis of the porous matrix film is critical and are the main objectives of this paper. Various substrates have been attempted, e.g., polytetrafluoroethylene (PTFE) [12,16], porous silica [14,17], crosslinked polyethylene (CLPE) [13,18], and commercial porous polyimide (PI) [19,20]. Unfortunately, the reported performance of DMFCs based on this type of membrane is either lacking or not satisfactory, mainly because of the difficulty to fill completely the porous substrate to form a workable membrane with sufficient proton conductivity and mechanical strength.

It is believed that porous polyimide is a suitable candidate because of its high mechanical strength, compatibility with Nafion and inertness towards methanol. A commercial porous PI film has been investigated by Yamaguchi et al. [19,20]. The commercial PI film is not, however, tailor made to suit its use in fuel cell applications and may not possess optimum properties. For example, the porous polyimide in the work has a porosity of only 55 vol.% and there by severely limits the proton conductivity of the composite membrane. Yamamoto et al. [21] also synthesized a porous polyimide by means of a hard template method. Unfortunately, the removal of the template involves the use of hydrofluoric acid which is not environmentally friendly and the mechanical strength of the membrane may be sacrificed. Increasing the porosity while maintain high mechanical strength might be challenging. On the other hand, the complete infiltration of electrolytes into the substrate to avoid the formation of pores inside the resulting composite membrane is not a trivial thing.

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In the present study, a highly porous PI film with tunable porosity, thickness and pore size a fabricated by chemical imidization of a poly(amic acid) solution synthesized from 1,4-phenylenediamine (PPDA), 4,4'-oxydianiline (ODA), and benzophenone-3,3',4,4'-tetracarboxylic dianhydride (BTDA) in N,N-dimethylformamide (DMF). A wet phase inversion method is applied to develop such porous structure by coagulating PI precursor film in non-solvent baths contained a mixture of DMF and 1-butanol at different volume ratios. Then, the porous PI film is filled with polyperfluorosulfonic acid (Nafion). Different from our previous work, [22,23], the protocol developed allows easy infiltration of the Nafion ionomer and thus the resulting membrane is free from pore defects. The composite membrane has outstanding properties such as high mechanical strength, low methanol crossover, high proton conductivity, and less dimensional change between dry and swollen states. Improved fuel cell performance is also demonstrated with this composite membrane.

2. Experimental

2.1. Preparation of porous PI film

A poly(amic acid) solution of 18.0 wt.% co-polymer in DMF was synthesized in a glass flask with a mechanical stirrer and nitrogen inlet and outlet. PPDA (99.9 wt.%, Sigma–Aldrich) and ODA (97.0 wt.%, Sigma–Aldrich) were completely dissolved in DMF, then BTDA (96.0 wt.%, Sigma–Aldrich) was added at a molar ratio of BTDA:PPDA:ODA (1:0.75:0.25). The reaction was carried out for 24 h at room temperature under a nitrogen atmosphere [24,25]. A mixture of acetic anhydride and pyridine (volume ratio 2:1) was added slowly to the obtained poly(amic acid) and the resulting solution was held at room temperature for 24 h to obtain a polyimide precursor solution with a 16.0 wt.% solid content [26,27].

The porous PI film was fabricated by a wet phase inversion technique [28,29]. First, the PI precursor was cast on glass plates by a spin coating machine (SCS G3, Cookson Electronics) at a speed of 900 rpm and a spin time of 30 s. Then, the casting film was coagulated immediately in a non-solvent bath at room temperature for 15 min to develop a porous structure, followed by ageing for 5 min in methanol and 5 min in water. The non-solvent solutions were mixtures of 1-butanol and DMF at various ratios. Finally, the porous PI film was dried in air for 12 h. The thickness of films can be easily controlled by varying the spin speed during the polymer casting.

2.2. Preparation of composite membrane

The filling polymer Nafion/ethanol suspension was prepared from commercial Nafion solution (5 wt.%, GasHub, Singapore). It was obtained by drying the commercial 5 wt.% Nafion solution at 60 °C until the solvent was evaporated completely. The dry Nafion was then treated with 25 wt.% nitric acid in water at 80 °C for 1 h, following by repeated rinsing with double deionized (DDI) water and further drying [30]. After that, the Nafion was put into ethanol and ultrasonicated to facilitate re-dispersion. The formed Nafion/ethanol solution had a Nafion weight ratio of 5 wt.%.

The porous PI substrate was extended over a round glass plate by a membrane caster; after that, the Nafion/ethanol solution was poured on the surface of the porous film [31]. The glass plate was put in an oven at 60 °C for 24 h and then dried in a vacuum oven at 120 °C for 12 h and 150 °C for 1 h. After that, the obtained composite membrane was treated with a common pretreatment procedure using H₂O₂ and H₂SO₄ solutions [32].

2.3. Porous film and composite membrane characterization

2.3.1. Fourier transform infrared (FT-IR)

The IR spectrum of the thin film was obtained by means of a FT-IR Spectrometer-PerkinElmer to identify the structure of the poly(amic acid), polyimide, and composite membrane.

2.3.2. Field-emission scanning electron microscope (FESEM)

The morphologies of the surfaces and cross-sections of the porous substrates and composite membranes were observed with a JEOL Field-Emission Electron Microscope (JSM-6700F). For cross-section observation, samples were fractured under cryogenic conditions using liquid nitrogen. All samples were coated with gold by an Auto Fine Coater before images were taken.

2.3.3. Substrate porosity, water content, and dimensional stability

The substrate porosity, ϕ_p (vol.%), was estimated using the following relationship Eq. (1) [12]:

$$\phi_p = \left\{ 1 - \frac{w_{\text{sub}}}{\rho_{\text{sub}} \cdot V_{\text{sub}}} \right\} \times 100 \quad (1)$$

where w_{sub} , ρ_{sub} , and V_{sub} are the weight, density and volume of the porous PI substrate, respectively.

Samples of the membranes were weighed (W_1) after immersion in DDI water at 80 °C for 24 h [33]. Then samples were weighed (W_2) after drying in a vacuum oven at 80 °C for 24 h. The water content (ΔW) was calculated as (2):

$$\Delta W (\%) = \frac{W_1 - W_2}{W_2} \times 100 \quad (2)$$

Dimensional stability was tested as follows [33]. Membranes, each of around 2.5 cm in diameter were stored in a vacuum oven at 80 °C for 24 h and the dimension was measured before (L_1) and after (L_2) soaking in DDI water at 80 °C for 24 h. The dimensional change (ΔL) was calculated as (3):

$$\Delta L (\%) = \frac{L_2 - L_1}{L_1} \times 100 \quad (3)$$

2.3.4. Mechanical strength testing

Mechanical strength was determined with a testing machine (Instron 5543) according to the standard test method for tensile properties of thin plastic sheeting, i.e., ASTM D 882-02. The samples were prepared in 5 mm width and 100 mm lengths with five test specimens for each membrane. The testing speed was 10 mm min⁻¹ and the initial gauge length was 50 mm.

2.3.5. Methanol permeability and proton conductivity measurement

The methanol permeability of the membranes was determined using the two-compartment diffusion cell technique, as reported elsewhere [5,34].

The proton conductivity of the membrane in the through-plane direction was measured using a potentiostat with a built-in frequency response analyzer (Autolab, Netherlands) in a home-made cell [35,36]. The cell consisted of two Teflon blocks attached with a platinum foil electrode (1.2 cm × 1.2 cm) and a platinum lead. The pretreated membrane (1.5 cm × 1.5 cm) was sandwiched between these two Teflon blocks that were held in place with Teflon screws. The impedance measurements were carried out on fully hydrated membranes at different temperatures (room temperature (RT), 50 °C, and 80 °C) over a frequency range of 250–150 kHz. The proton conductivity of the membrane was calculated according to $\sigma = L/RS$, where σ , L , R , and S denote the ionic conductivity, the thickness of the membrane, the resistance of the membrane, and the surface area of the electrode, respectively.

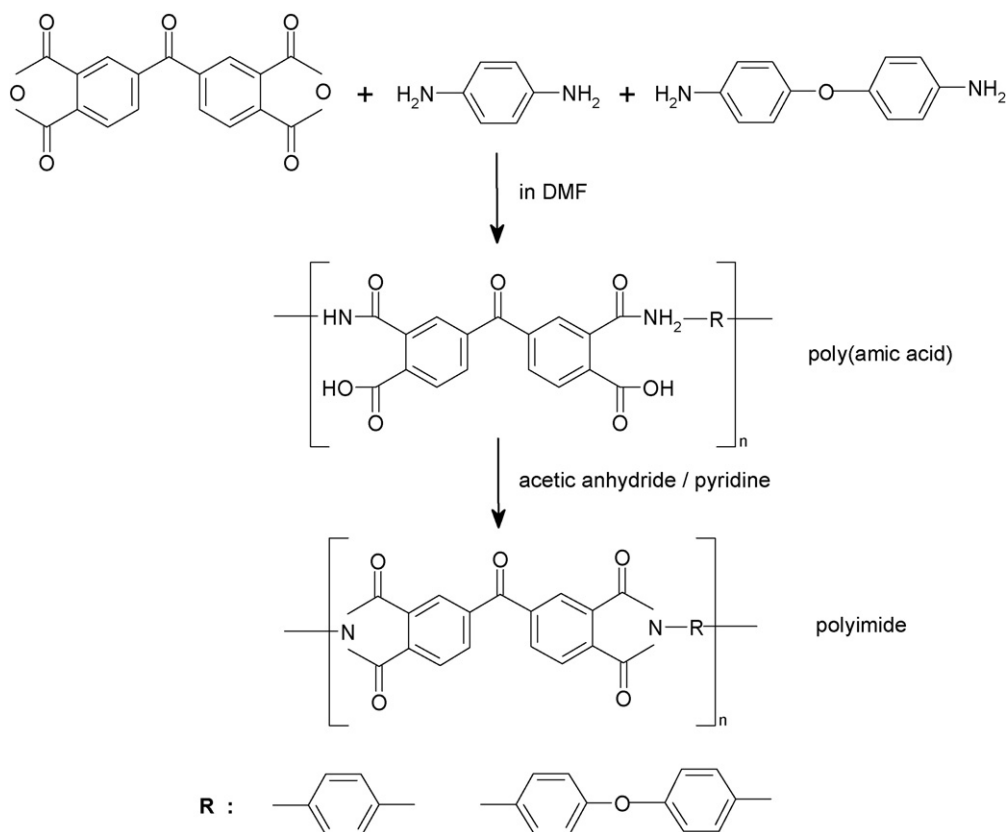


Fig. 1. Co-polyimide synthesis scheme based on BTDA–PPDA/ODA.

2.3.6. Fuel cell testing

Single fuel cell performances tests were conducted with an Arbin fuel cell test station. To minimize influence from electrode variation, commercial electrodes (Gashub, Singapore) were used for the membrane electrode assembly (MEA) fabrication and performance test. The electrode consisted of a PTFE-treated (20 wt.%) carbon paper substrate, a microporous layer with a carbon loading of 1.2 mg cm^{-2} , and a catalyst layer. The catalyst layer in the anode contained 40 wt.% PtRu/C and Nafion, with a total metal loading of 2.0 mg cm^{-2} (Pt:Ru = 1:1), while that in the cathode contained 40 wt.% Pt/C and Nafion, with a Pt loading of 2.0 mg cm^{-2} . A MEA with an active electrode area of 5 cm^2 was obtained by pressing the cathode and anode on to each side of a pretreated Nafion 112 membrane or composite membrane at 140°C and 2.0 MPa for 1 min (Hydraulic 3912, Carver, Inc.). The MEA was then assembled into a DMFC single-cell. The operation conditions were as follows: anode fuel 1.0 M or 5.0 M MeOH; flow rate, 1.0 mL min^{-1} ; oxygen pressure, 0.4 MPa; flow rate, 0.25 L min^{-1} . The temperature of the cell was maintained at 70°C . All single-cell tests were conducted in triplicate, and the results presented here are the average data.

3. Results and discussion

Polyimide is obtained by a two-step chemical imidization method, with the synthesis route shown in Fig. 1. In the first step, poly(amic acid) is formed from the reaction of aromatic dianhydride (BTDA) with aromatic diamine (PPDA and ODA). In the second step, the poly(amic acid) is chemically converted to a polyimide with the presence of acetic anhydride and pyridine [37]. The structure of the polyimide was confirmed by FT-IR. As can be seen in Fig. 2, the major peaks at 1660 cm^{-1} assigned to amide disappear completely after the chemical imidization. Instead, an imide ring absorption peak appears at 1775 cm^{-1} ; it is attributed to stretch-

ing of the carbonyl group of imide [24,26]. According to these FT-IR spectra results, it can be concluded that the chemical imidization process is completed by promoting agents at room temperature for 24 h, followed by vacuum heating at 150°C for 1 h.

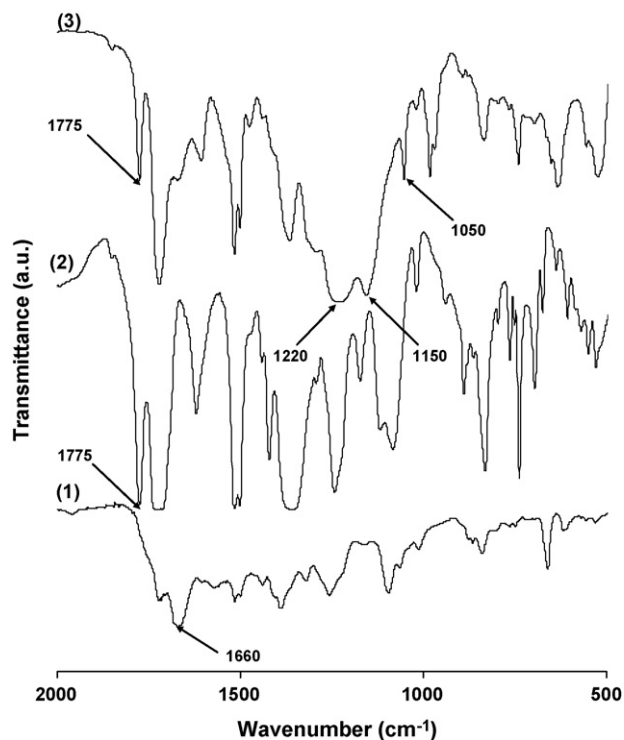


Fig. 2. FT-IR spectra of (1) poly(amic acid), (2) polyimide, and (3) PI/Nafion composite membrane.

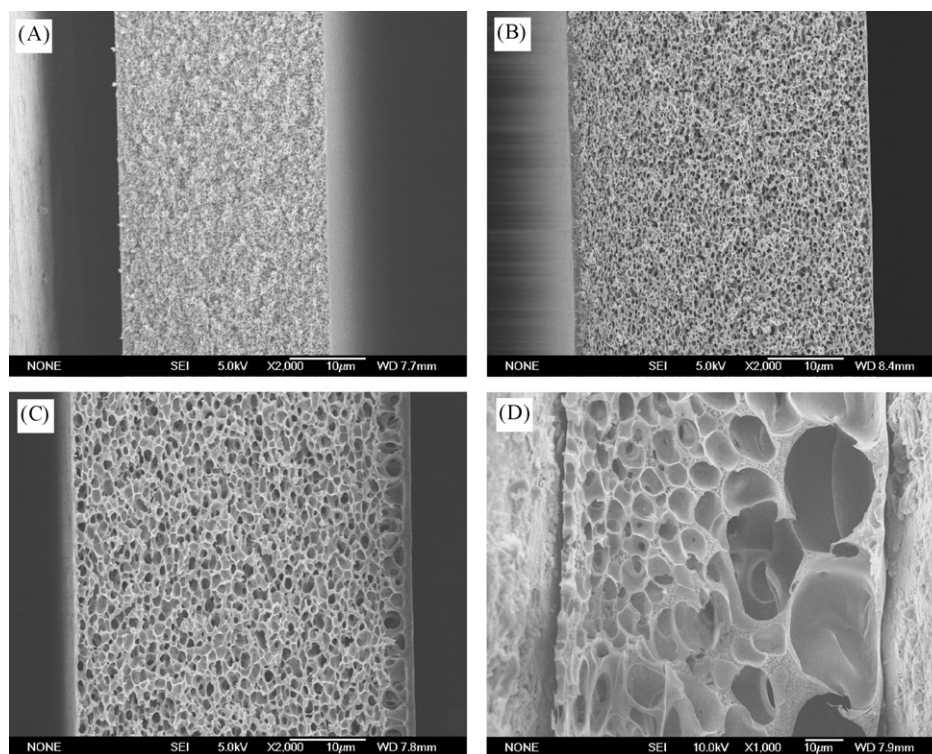


Fig. 3. FESEM images of cross-section of porous PI films prepared with different 1-butanol content in non-solvent bath with 1-butanol:DMF (vol.:%:vol.%) (A) 80:20, (B) 70:30, (C) 60:40, and (D) 50:50.

To function as a good matrix for a composite membrane, the porous PI film must have high porosity and remain mechanically strong and stiff at high porosity. Experimentally, the morphology of the porous film can be tuned by the solvent and non-solvent used during the pore-forming period [28,29]. A low compatibility between solvent and non-solvent will cause a delayed de-mixing so that the resulted film will consist of a porous top layer and a sponge-type sub-structure. Alternatively, a high affinity between them will cause an instantaneous de-mixing so that the formed membrane will consist of a porous top layer and finger type sub-structure, commonly called macrovoids. Macrovoid-containing films are mechanically weak and easily lose their integrity under high pressure operation [38].

In this study, an attempt is made to make porous PI film with high porosity and high mechanical strength. Since preliminary results showed that a sponge-type structure possesses higher mechanical strength than a finger-type at high porosity, DMF was selected as the solvent and 1-butanol as the non-solvent to develop such sponge type structure. Here the pore size can be controlled by changing the solvent/non-solvent ratio, as shown in Fig. 3. The pore size of porous films increases with decrease of the 1-butanol content in a coagulation bath. The pores can grow until the matrix phase, polymer-rich phase, is solidified. With lower 1-butanol contents, the polymer concentration of the polymer-rich phase is lower. Therefore, there is a longer time before the membrane solidifies and larger pores can develop [28]. To fabricate successfully a pore-filling composite membrane with a high performance, the porous PI matrix preferentially should have pore sizes on the sub-micrometer scale, or less, to suppress efficiently membrane swelling and maintain high mechanical strength [39]. If the pores are too large the blocking of methanol crossover will be less efficient and the mechanical strength of the substrate will usually be lower. If the pores are too small, however, infiltration can be difficult, as can be seen in Fig. 4, where a separate Nafion layer is formed at a 1-butanol:DMF ratio of 80 vol.:%:20 vol.:%, where

as a composite membrane is successfully prepared from porous matrixes at a 1-butanol:DMF ratio (vol.:%:vol.%) of 70:30, 60:40, and 50:50. Therefore, the porous matrix with the smallest size while still allowing complete Nafion infiltration i.e., synthesized at a 1-butanol:DMF ratio of 70 vol.:%:30 vol.:%, is chosen as the porous matrix to fabricate and characterize the composite membrane. As shown in Figs. 3B and 5A, the substrate exhibits a highly porous structure that contains a sponge-type sub-layer with a pore size of $\sim 0.3 \mu\text{m}$ and a top porous surface. The thickness of the porous film is increased as many as five times compared with a non-porous film ($40 \mu\text{m}$ vs. $8 \mu\text{m}$), from which the porosity of the porous PI film is estimated at $\sim 80 \text{ vol.}\%$. This result is also in agreement with the measured porosity based on Eq. (1). The overall porosity of a porous PI film can be easily controlled by the polymer content of the casting solution, as well as by the relative rates at which non-solvent enters and solvent leaves the casting solution. Moreover, from a thermodynamic standpoint, any additive in the casting solution will be expected to increase the rate of non-solvent entry and decrease the rate of solvent removal, which favours the formation of a film with high porosity. Therefore, the presence of the chemical imidization agents (acetic anhydride and pyridine) in the polyimide precursor as additives further increases the film porosity.

Other than the pore size effect, for a polymer electrolyte to successfully fill the pores of a host substrate, the viscosity and contact angle on the host substrate of the polymer solution must be low [33]. In this study, to facilitate Nafion filling, commercial 5 wt.% Nafion was re-dispersed in ethanol to reduce the viscosity and the contact angle with the porous PI film. In addition, a wet porous PI film was used as it has high affinity towards the filling polymer because of the presence of residual acetic anhydride in the matrix that makes the wet porous film more hydrophilic. During the process of filling Nafion into the pores of the porous substrate, the gravity force dragged Nafion solution into the wetted pores of the porous PI film and after evaporating the solvent, Nafion can completely plug the pores. This use of a wet porous PI film is found to

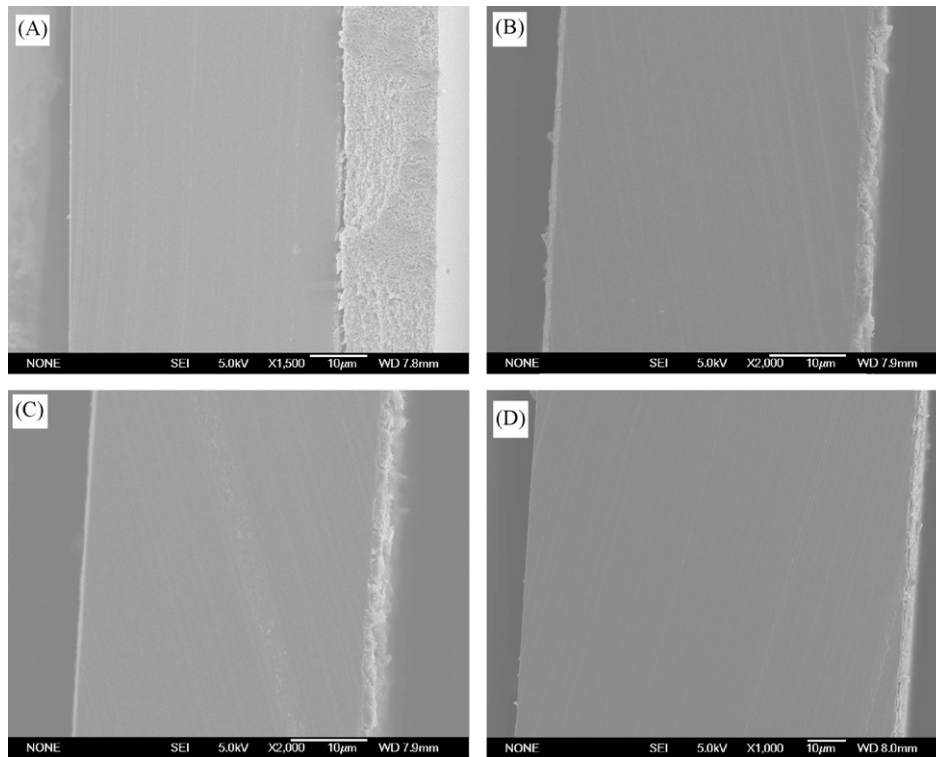


Fig. 4. FESEM images of cross-sections of PI/Nafion composite membranes based on porous PI films prepared with different 1-butanol content in non-solvent bath with 1-butanol:DMF (vol.%,vol.%): (A) 80:20, (B) 70:30, (C) 60:40, and (D) 50:50.

be critical to the formation of a composite membrane. If the porous polyimide is completely dried, with all the residual acetic anhydride in the small pores removed, pores will be observed in the composite membrane even if the porous PI is treated again with acetic anhy-

dride before Nafion infiltration. It is believed that, when the fully dried porous substrate is subject to this post-treatment with acetic anhydride, air will usually be trapped in some of the small pores and make them inaccessible to acetic anhydride. Subsequently, the

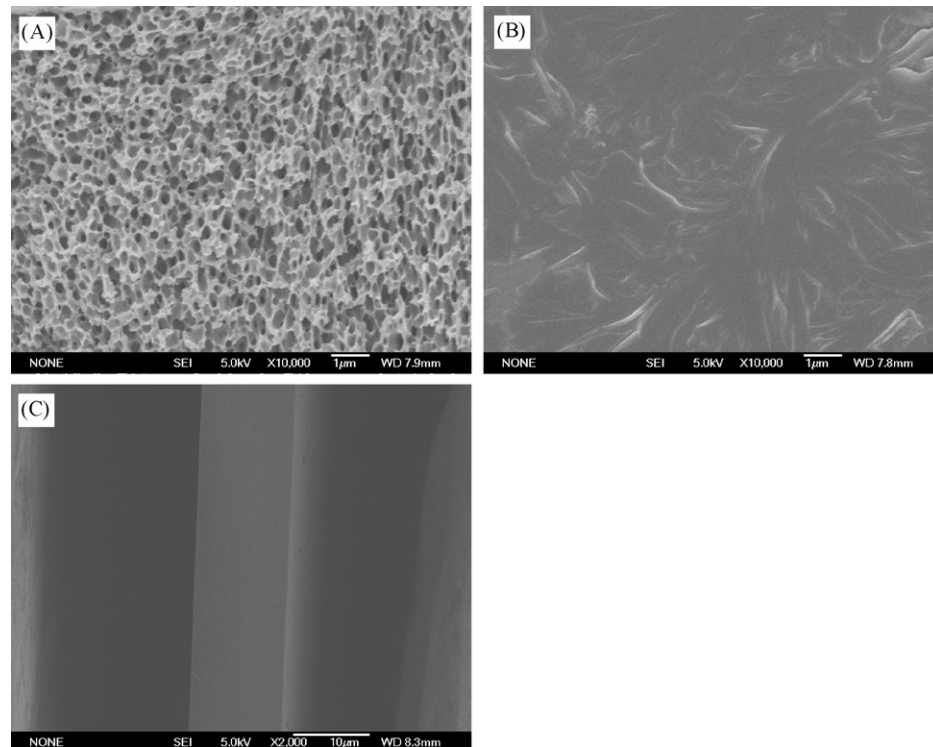


Fig. 5. FESEM images of (A) top surface of porous PI film prepared with 1-butanol:DMF = 70 vol.%,30 vol.%, (B) top surface of PI/Nafion composite membrane, and (C) cross section of non-porous PI film.

Table 1
Physical properties of membranes.

Membrane	Thickness (μm)	Water content (%)	Dimensional change (%)	Mechanical strength (MPa)
Nafion 112	64	15.67	11.85	26.4
PI/Nafion composite	46	5.92	4.75	104.5

Nafion ionomer will not be able to infiltrate these unwetted pores. Our previous work on the porous substrate synthesis used thermal imidization. [22,23] It involved drying of the porous PI substrate at high temperature, and this explained why Nafion cannot fully fill all the pores in that structure. Instead, as shown in Fig. 4B, no pore is observed for the composite membrane fabricated with the wet porous PI film and the filling polymer. A smooth morphology is also observed on the top surface (Fig. 5B), indicating that Nafion is distributed uniformly in the composite membrane. In addition, the FT-IR spectra PI/Nafion composite membrane (Fig. 2) shows an absorption peak at 1775 cm^{-1} , indicating the presence of PI in the composite membrane. In the range $1400\text{--}1100\text{ cm}^{-1}$, two very strong vibration bands are present. The band at 1150 cm^{-1} is due to symmetric C–F stretching, while the band at 1220 cm^{-1} is attributed to asymmetric C–F stretching. Moreover, a band at 1050 cm^{-1} attributed to S–O stretching of the SO_3 group of Nafion structure can also be identified [40,41].

The mechanical strength of membranes affects the manufacturing condition and durability of the MEA. Higher mechanical strength allows fabrication of thinner membranes with smaller resistance. The porous PI film in this work is BTDA–PPDA/ODA copolyimide with a combination of a flexible ODA monomeric unit and a rigid PPDA monomer. It is reported that the ultimate strength and tensile modulus of copolyimide is greater than those of the reference polyimides of BTDA–PPDA and BTDA–ODA [24]. As shown in Table 1, the composite membrane possesses much higher mechanical strength compared with the Nafion 112 membrane (104.5 MPa vs. 26.4 MPa), because of the reinforcing effect of the strong porous PI matrix.

The dimensional stability of the membrane is an important property for practical operation of a fuel cell. Since carbon electrodes do not swell and change in dimension from any water uptake, less damage to the structure integrity of the MEA and improved durability can be expected for those membranes with smaller changes in dimension [18]. Table 1 shows a comparison of the PI/Nafion composite membrane and Nafion 112 membrane. After being soaked in water at 80°C for 24 h, the PI/Nafion composite membrane Experiences a much lower dimensional change ($\sim 1/3$ of Nafion 112) and water uptake ($\sim 1/3$ of Nafion 112). It can be concluded that the strong PI matrix in the composite membrane can effectively suppress the membrane from swelling and prevent the membrane from absorbing excess water, although the volumetric ratio of PI is only 20 vol.%. Methanol crossover usually occurs in the hydrophilic region of the Nafion polymer, which expands with the adsorption of more water. The suppressed water adsorption or less dimensional change in the membrane indicates less expansion of the hydrophilic portion (smaller methanol passage). On the other hand, it is concluded that, in the pore-filling electrolyte

membrane, the host matrix is totally inert to methanol and that methanol crossover is mainly through the polymer electrolyte filler, or more specifically, the hydrophilic portion of the Nafion. The fact that the composite membrane mechanically prevents Nafion from swelling is expected to lower the methanol crossover. Indeed, as shown in Table 2, the measured methanol permeability of the composite membrane is ~ 80 times lower than that of the Nafion 112 membrane ($2.76 \times 10^{-6}\text{ cm}^2\text{ s}^{-1}$ vs. $3.36 \times 10^{-8}\text{ cm}^2\text{ s}^{-1}$), although 80 vol.% of the membrane is still Nafion polymer.

Two types of conductivity measurements have been reported in the literature, namely, in-plane [42,43] and through-plane [35,36] measurements. The in-plane conductivity measurements are known to be relatively insensitive to the contact resistance at the current carrying electrodes, but do not reflect the real conductivity of ionic motion through a membrane in a fuel cell. When the membrane is isotropic, the difference between the in-plane and the through-plane conductivity will be small. When the membrane is anisotropic, however, such as multilayer membranes, or composite membranes as in this work, the difference is expected to be large and the through-plane one is more representative. In this study, the through-plane conductivity for fully hydrated membranes is determined at various temperatures. As shown in Table 2, the proton conductivity of the membranes increases with increase in temperature as a result of higher proton mobility at higher temperature. At room temperature, the proton conductivity of the PI/Nafion composite membrane is only slightly lower than the Nafion 112 membrane (0.056 S cm^{-1} vs. 0.059 S cm^{-1}). The high porosity of the PI support matrix (80 vol.%) minimizes the adverse effect of the non-conducting PI on the conductivity of the resulting PI/Nafion composite membrane. Given that the thinner composite membrane is used as a result of the improved mechanical strength, the overall membrane resistance of the PI/Nafion composite membrane is actually smaller than that of the Nafion 112 ($0.082\ \Omega\text{ cm}^2$ vs. $0.108\ \Omega\text{ cm}^2$). The data in Table 2 also show the selectivity factor (Φ), a commonly used quantity to describe a membrane the performance of in a DMFC, and that is defined as the ratio between the proton conductivity and the methanol permeability. The selectivity (Φ) of the composite membrane is significantly higher than that of the Nafion 112 membrane ($1.67 \times 10^6\text{ S s cm}^{-3}$ vs. $2.14 \times 10^4\text{ S s cm}^{-3}$).

The single-cell performance of the MEAs based on the commercial Nafion 112, 117 and PI/Nafion composite membrane using 1 M methanol is presented in Fig. 6. As expected, the MEA with the PI/Nafion composite membrane shows considerably higher performance in comparison with those using a Nafion 112 or a 117 membrane, because of its lower membrane resistance and reduced methanol crossover. Particularly, the PI/Nafion membrane shows much higher open-circuit voltage (OCV) than Nafion 117 and 112 (0.77 V vs. 0.67 V and 0.55 V), although the composite membrane has a smaller thickness. The OCV of a MEA is closely related to the methanol crossover, i.e., higher methanol crossover leads to a lower OCV. The higher OCV for the PI/Nafion membrane then confirms that the PI/Nafion composite membrane in the MEA suppresses methanol crossover. This finding is consistent with the ex situ methanol permeability measurement. The advantage of significantly reduced methanol crossover with the composite membrane can be clearly seen from the performance test when feeding 5 M

Table 2
Proton conductivity and methanol permeability of membranes.

Membrane	Proton conductivity σ (S cm^{-1})			Methanol permeability (RT), P ($\text{cm}^2\text{ s}^{-1}$)	Selectivity (RT) $\Phi = \sigma/P$ (S s cm^{-3})
	RT	50°C	80°C		
Nafion 112	0.059	0.071	0.079	2.76×10^{-6}	2.14×10^4
PI/Nafion composite	0.056	0.068	0.077	3.36×10^{-8}	1.67×10^6

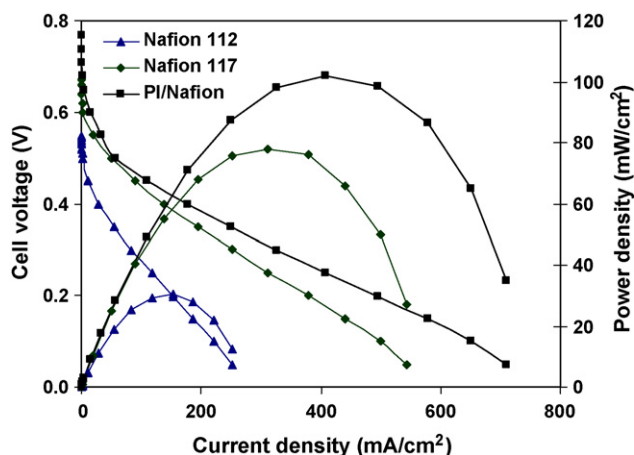


Fig. 6. DMFC single-cell performance of PI/Nafion composite membrane, Nafion 112, and Nafion 117 at 70 °C with 1 M CH₃OH.

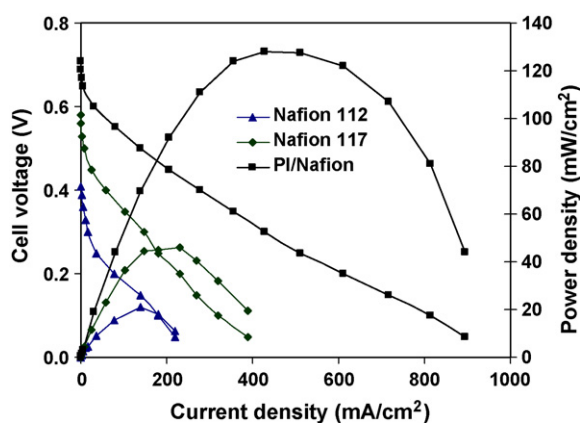


Fig. 7. DMFC single-cell performance of PI/Nafion composite membrane, Nafion 112, and Nafion 117 at 70 °C with 5 M CH₃OH.

methanol (Fig. 7). A high fuel concentration is preferred from an application point of view, as it indicates higher specific energy from the power source. At such a high concentration, the maximum power density of the MEA with the pure Nafion 112 and 117 membrane is only 21 mW cm⁻² and 40 mW cm⁻², while the maximum power density of the MEA with the PI/Nafion composite membrane still reaches 128 mW cm⁻² and the OCV of the composite membrane is much higher than Nafion 117 and 112 (0.71 V vs. 0.58 V and 0.41 V).

4. Conclusions

A highly porous PI film with a tunable pore size, thickness and porosity has been synthesized by means of a wet phase inversion process. With a pore size of around 0.3 μm and a porosity of 80 vol.%, this porous sponge-type PI film is used as a support matrix for the fabrication of a novel PI/Nafion composite membrane by infiltration of Nafion in all the pores. A very efficient way for an easy and complete infiltration of the proton-conducting polymer into this matrix has been found. It is realized by using a wet porous PI film with the presence of residual acetic anhydride. The PI/Nafion composite membrane has excellent properties compared with a Nafion 112 membrane, such as three times lower in dimensional change, four times higher in mechanical strength, eighty times lower in methanol crossover, and significantly higher

in selectivity factor. The improved performance of a DMFC with a PI/Nafion composite membrane is also demonstrated. Allowing the use of a very thin membrane and a high methanol concentration, the PI/Nafion composite membrane is very promising as a proton-exchange membrane for DMFCs. Not limited to Nafion, this approach can be extended to other proton conductors, for which even higher proton conductivity can be expected.

Acknowledgements

This work is supported by the Academic Research Fund AcRF/RG40/05 and ARC11/06, Ministry of Education, Singapore.

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