

Short communication

Nafion–Nafion/polyvinylidene fluoride–Nafion laminated polymer membrane for direct methanol fuel cells

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Abstract

The laminated composite polymer electrolyte membrane is prepared as a sandwich structure, i.e., Nafion–Nafion/polyvinylene difluoride (PVdF)–Nafion. The conductivity of the laminated membrane is $1.1 \times 10^{-2} \text{ S cm}^{-1}$. The middle layer of PVdF/Nafion successfully blocks methanol cross-over. In tests in a direct methanol fuel cell (DMFC), all of the Nafion–Nafion/PVdF–Nafion membranes give higher power densities than with a Nafion membrane. The highest current density using a blend membrane with 20% PVdF at a constant cell voltage of 0.3 V is $217.64 \text{ mA cm}^{-2}$ at 110°C . It is noteworthy that the Nafion–Nafion/PVdF–Nafion laminated membrane sustains high performance at temperatures above 130°C , whereas the performance of a Nafion membrane is drastically decreased.

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Keywords: Polymer electrolyte; Polyvinylidene fluoride; Direct methanol fuel cell; Conductivity; Membrane; Cross-over

1. Introduction

Today, when protecting global environment appears to be an important matter of concern and interest to mankind, research on fuel cells as emission-free energy sources has gained an importance. The fuel cell is an electrochemical device that converts the chemical energy of a fuel directly into electrical energy. Direct methanol fuel cells (DMFCs) using polymer electrolytes are currently being considered as candidate power sources for vehicular and portable applications.

Despite active research, the use of Nafion membranes in DMFCs have certain drawbacks. One of the difficulties is that small amounts of methanol can move across the polymer electrolyte membrane. This effect is called ‘methanol cross-over’ and causes overpotential losses at the negative electrode (cathode) of the fuel cell. This is the main reason for the observed decrease in the efficiency of the fuel cell [1,2]. Thus, it is important to prevent methanol cross-over.

In recent years, a wide variety of polymer blends have been developed to produce an effective solid electrolyte for DMFCs [3–7]. It is generally accepted that the intermediate physical properties of such blends can be more readily controlled and optimized if the components are miscible. More-

over, in research conducted on polymer electrolyte membranes for DMFCs, many attempts to improve performance have taken advantage of the blend structure of the polymer. A key factor in acquiring polymer electrolyte membranes via blending therefore relies on finding an optimum combination of thermal, chemical, mechanical properties with hydrophilicity in the polymers employed; so that, in turn, a membrane with adequate proton conductivity can be attained with good stability at high temperatures and resistance against methanol permeation.

In this study, the Nafion solution is blended with polyvinylidene fluoride (PVdF). The latter is considered as the structural component by virtue of its good methanol resistance as well as its excellent thermal stability. Nevertheless, the blended membrane has a serious drawback, namely, its poor contact with the electrodes in the membrane electrode assembly (MEA) process. To reduce the interfacial resistance of the MEA, a laminated structure of the blended polymer electrolyte membrane (Fig. 1) is investigated.

2. Experimental

2.1. Preparation of membrane

A 5% solution of Nafion perfluorinated ion-exchange resin was supplied by E.I. Du Pont de Nemours & Co. and

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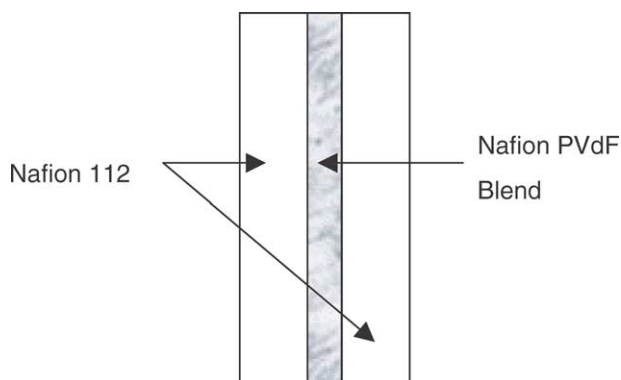


Fig. 1. Laminated structure of Nafion–Nafion/PVdF–Nafion membrane.

polyvinylidene fluoride (MW 534,000) in powder form was supplied by Sigma Aldrich. The original solvent of Nafion solution was replaced with dimethylformamide (DMF, from Yakuri Chemical, Japan) [8]. The latter was added to Nafion solution and stirred vigorously. The majority of the aliphatic alcohol and water was then removed by evaporation at 100 °C for 24 h. Polyvinylidene fluoride was dissolved by DMF to make a 10% PVdF solution. A quantity of that solution was added to the Nafion solution and stirred at 100 °C for 12 h. The Nafion and PVdF blended solution was obtained at the desired ratio. The blend membrane was cast and dried under vacuum at 120 °C for 24 h.

A laminated polymer electrolyte membrane was prepared from Nafion/PVdF blend and Nafion 112 membranes, namely: Nafion 112 | Nafion–PVdF blend membrane | Nafion 112. The lamination was hot pressed at 3 t and 160 °C.

2.2. Characterization of membrane

The ion-exchange capacity of the membranes was determined by titration. The sulfonic acid group in the membrane was brought to the proton form by immersion in 1.0 M HCl. The membrane was then washed thoroughly with deionized water until the solution became neutral and then immersed in a 2.0 M NaCl solution to replace the protons by sodium ions. The membrane was rinsed with deionized water until the Cl[−] ions in the membrane was not precipitated with AgNO₃. The used NaCl solution and rinsed water was then titrated with 0.01 N NaOH. The ion-exchange capacity was expressed as meq. of sulfonic groups/g of dry membrane (meq. = milliequivalents).

Water uptake was carried out by drying the membrane in a vacuum oven at 90 °C for 5 h. Then the membrane was immersed in deionized water and equilibrated for 3 days. The water uptake was calculated as the ratio of the weight of the swollen membrane and the dried one. The weight of the swollen membrane was measured carefully after removing the water from both surfaces.

The proton conductivity was measured by means of a.c. impedance spectroscopy. The samples were equilibrated overnight in 0.1 M HCl solution at room temperature. A

sample of the membrane was placed between two platinum electrodes. The proton conductivity of the membrane was calculated by the following equation:

$$\rho = \frac{L}{RS} \quad (1)$$

where S represents the effective membrane area of the cell, 1.5 cm × 1.5 cm, which is the same size as platinum electrode; and ρ , L and R denote the proton conductivity, membrane thickness and resistance of the membrane, respectively.

2.3. Measurement of methanol cross-over

The membrane was embedded in a single cell and one side of the membrane was fed with a 2 M methanol solution. The solution was injected continuously by a pump (1.8 ml per min). The other side of the membrane was purified with a continuous flow of oxygen at a fixed 300 sccm per min flow rate. The rate of methanol cross-over was determined by gas chromatography equipped with FID.

2.4. Measurement of single-cell performance

A thin layer (diffusion layer) of active carbon fiber and electrocatalyst was spread on a Teflonized carbon cloth support (E-Tek). The anode catalyst was platinum–ruthenium (Pt:Ru:C = 2:1:2) and the cathode catalyst was platinum (Pt:C = 3:2). The catalysts were loaded at 4.0 mg cm^{−2}.

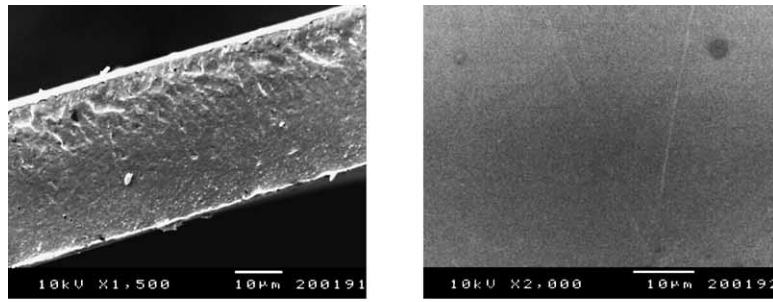
The membrane electrode assembly was fabricated by a hot pressing method for 10 min at 125 °C and 3 t (2000 psi). Performance tests were carried out using a small-scale laboratory DMFC with an external electrode area of 1 cm². The cell was electrically heated to enable isothermal operation at a fixed temperature. The anode feed was a methanol/water solution under ambient pressure and had been preheated to the desired operating temperature of the cell. The cathode feed was oxygen at elevated pressure (2 kgf cm^{−2}) and ambient temperature.

3. Results and discussion

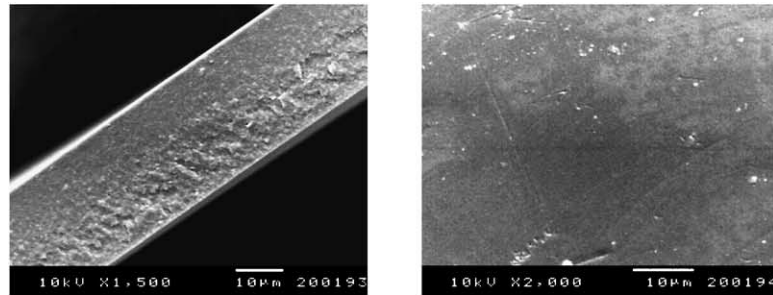
3.1. Characterization of blended membrane

Scanning electron microscopical (SEM) observation of the surface and fracture surface is a qualitative way of determining the phase morphology of polymer blends. Some SEM images of the surfaces and fracture surfaces of the Nafion/PVdF membrane are shown in Fig. 2. All of the membranes have featurelessly, smooth and homogeneous surfaces. As the PVdF content is increased, the fracture surfaces of the membranes have sponge-like structures.

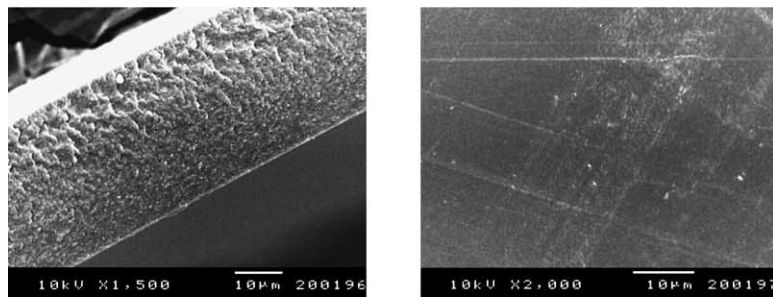
The ion-exchange capacity of the Nafion/PVdF membrane system is presented in Fig. 3. As increasing the content of PVdF, the ion-exchange capacity of the blend membrane is decreased linearly. The data show that the number of sul-



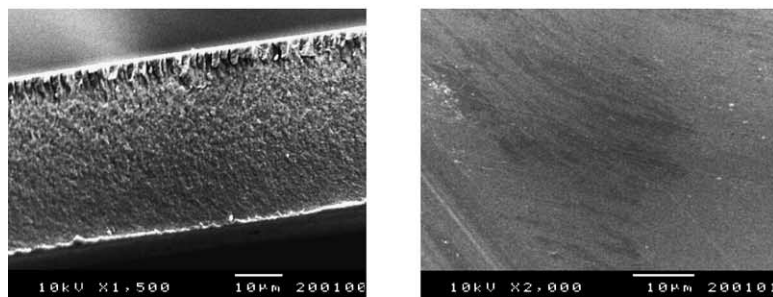
(1) Nafion 95% + PVdF 5% blend membrane



(2) Nafion 90% + PVdF 10% blend membrane



(3) Nafion 80% + PVdF 20% blend membrane



(4) Nafion 70% + PVdF 30% blend membrane

Fig. 2. Scanning electron micrographs of blended membranes.

fonic groups to transport protons becomes smaller with decrease in the proportion of Nafion. Water uptake decreases with increasing content of PVdF, see Fig. 4. Some of the hydrophobic part of PVdF suppresses swelling of the hydrophilic part of Nafion.

The fixed ion concentration of Nafion/PVdF membranes is shown in Fig. 5. PVdF has no fixed ions and is used as a methanol barrier; it only exists in Nafion. The concentration of fixed ions is a function of water content and ion-exchange capacity. The fixed ion concentration of Nafion/PVdF and

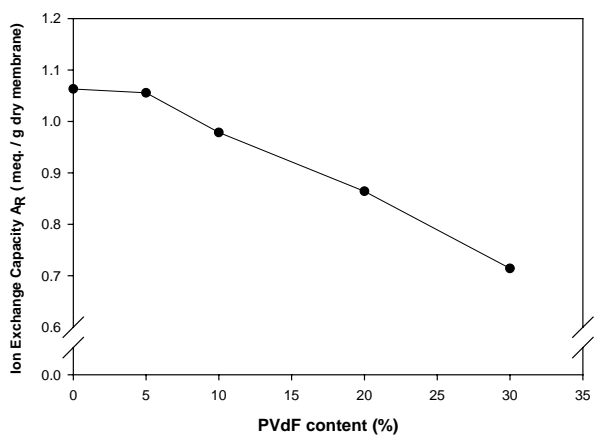


Fig. 3. Effect of PVdF content on ion-exchange capacity.

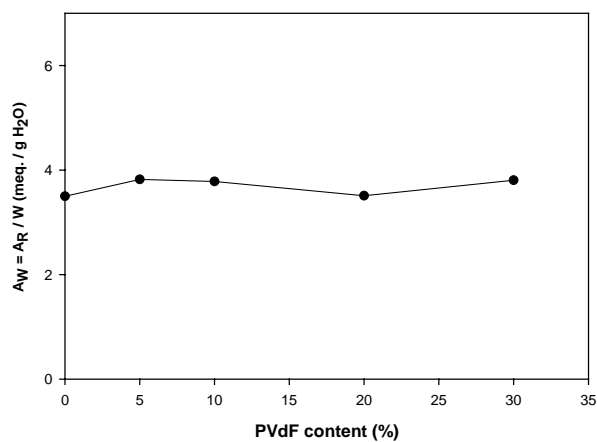


Fig. 5. Effect of PVdF content on fixed ion concentration.

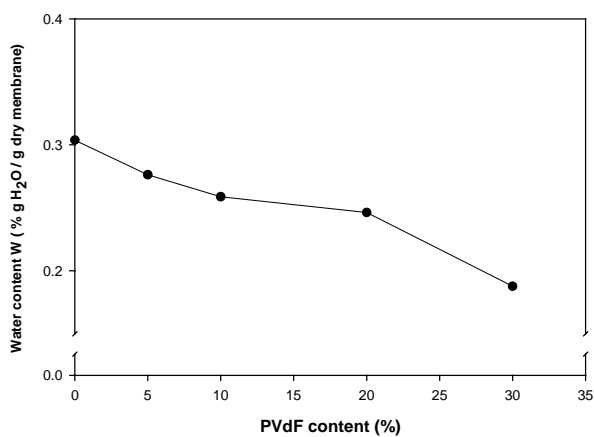


Fig. 4. Effect of PVdF content on water uptake.

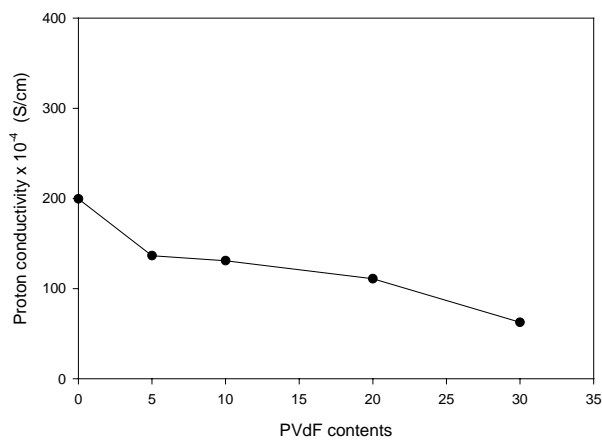
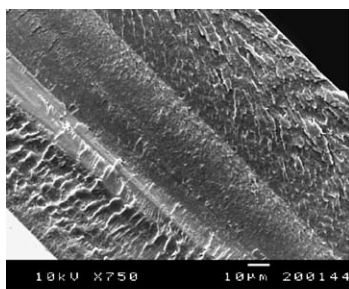
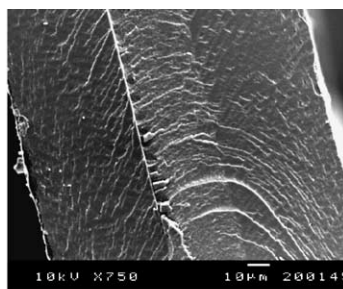


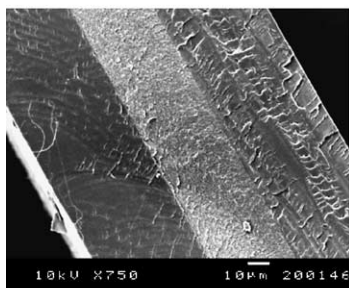
Fig. 6. Relationship between PVdF content and proton conductivity.



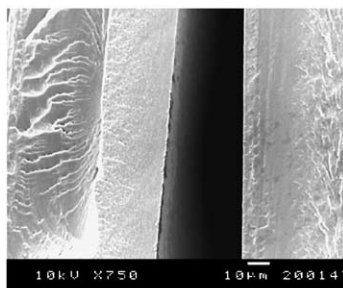
(1) Nafion 95% + PVdF 5%



(2) Nafion 90% + PVdF 10%



(3) Nafion 80% + PVdF 20%



(4) Nafion 70% + PVdF 30%

Fig. 7. Scanning electron micrographs image of fracture surface.

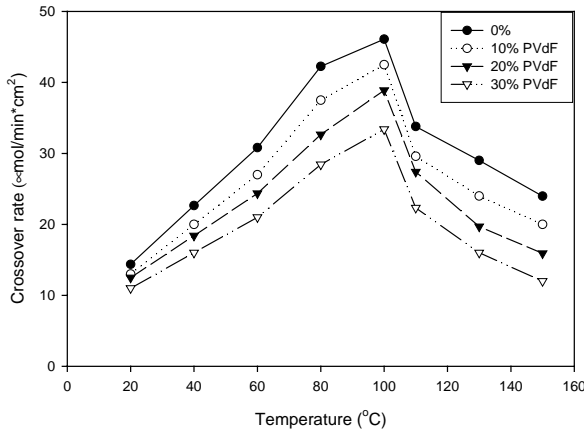


Fig. 8. Effect of cell temperature on methanol cross-over rate in membranes; 2 M MeOH at 1.8 ml per min, O₂ at 300 ml per min.

Nafion membrane was maintained steadily. Therefore, PVdF does not affect the fixed ions of Nafion in the blended membrane.

The proton conductivity of a Nafion/PVdF blended membrane as a function of PVdF content is presented in Fig. 6.

The proton conductivity is retained at a significant value in spite of an increase in the content of PVdF. The Nafion/PVdF blended membrane with 30% PVdF displays a drastic decrease in proton conductivity. This behavior is comparable with the change in water uptake, as shown in Fig. 4. When Nafion is blended with a low concentration of PVdF, Nafion should possess a continuous conducting and swelling network with a small amount of PVdF phase.

3.2. Characterization of Laminated membrane

The laminated structure of Nafion–Nafion/PVdF–Nafion is shown in Fig. 7. All the membranes, except that with a PVdF content of 30%, are laminated successfully. At 30% PVdF, when the fracture surface of laminated membrane is prepared as the sample of SEM, the laminated structure was separated because of the poor adherence between Nafion 112 and the Nafion/PVdF blended membrane.

The methanol cross-over rate is the crucial factor in a DMFC. In general, the transport of methanol and water through a conducting polymer membrane is a complex process. The relationship between methanol cross-over and the

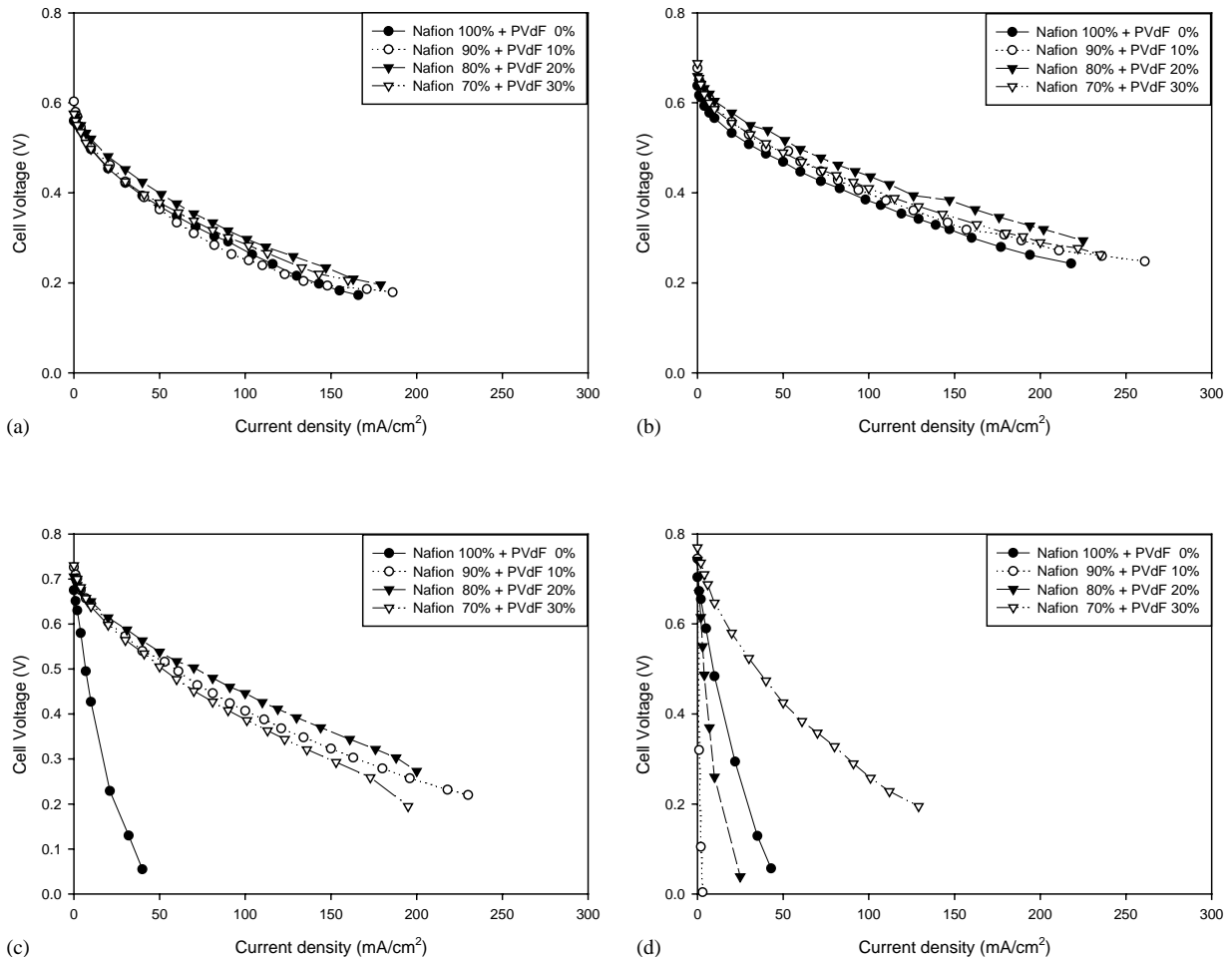


Fig. 9. Voltage–current density relation of single cell at: (a) 80°C, (b) 110°C, (c) 130°C, (d) 150°C.

cell operating temperature is shown in Fig. 8. At a temperature of 80 °C, the methanol cross-over in Nafion membrane and Nafion–Nafion/PVdF–Nafion laminated membranes increases. Above 80 °C, however, methanol cross-over is decreased. This trend is observed for all types of proton conducting membrane. The decrease in methanol cross-over above 80 °C is due to a decrease in methanol solubility [9]. Over the whole range of temperature, the methanol cross-over in the Nafion–Nafion/PVdF–Nafion membranes is lower than that in the Nafion membrane. As the PVdF content is increased, the cross-over rate in the laminated membrane decreases. Thus, hydrophobicity of PVdF successfully hinders methanol cross-over.

The Nafion membrane and the laminated membranes were applied in DMFCs. The *I*–*V* characteristics of a single cell using the Nafion–Nafion/PVdF–Nafion laminated membrane with different PVdF contents are presented in Fig. 9. The performance of the single cell was measured at various cell temperatures. Over the range of operating temperature, the Nafion–Nafion/PVdF–Nafion laminated membrane exhibits higher performance than the Nafion membrane. The thickness of the membranes was same, viz., 100 μm as shown in Fig. 7. Although the conductivity of the Nafion/PVdF membrane is lower than that of the Nafion membrane, the performance of the former membrane is enhanced. Therefore, due to the reduction in methanol cross-over, DMFC performance can be improved.

It is noteworthy that the Nafion–Nafion/PVdF–Nafion membrane shows good performance at high temperatures. Above 130 °C, the performance of Nafion is drastically decreased. By contrast, Nafion–Nafion/PVdF–Nafion membranes display good performance. Hydrophobic PVdF can prevent the evaporation of water from the proton-conducting channels of Nafion.

4. Conclusions

A laminated Nafion–Nafion/PVdF–Nafion membrane is prepared by blending and hot pressing. The blended mem-

branes are successfully prepared by substitution of the aliphatic solvent of Nafion with dimethylformamide. The laminated structure of the blended membrane is fabricated as a sandwich structure viz., Nafion–Nafion/PVdF–Nafion. The conductivity of the blended membrane is similar to that of the Nafion membrane. The laminated structure of the blended membrane overcomes the problem of reducing the interfacial resistance of the MEA interface. The Nafion–Nafion/PVdF–Nafion laminated membrane is also effective in hindering methanol permeability. Due to providing a barrier to methanol cross-over, the performance of the blended membranes is superior to that of the Nafion membrane. Moreover, the performance of the laminated membrane is maintained at high temperatures up to 130 °C.

Acknowledgements

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