

Short communication

Direct methanol fuel cell performance of Nafion[®]/poly(vinyl alcohol) blend membranes

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Abstract

In this study, the direct methanol fuel cell performance of Nafion[®]/poly(vinyl alcohol) (PVA) blend membranes at 5, 10, and 20 wt% PVA (annealed at 230 °C) was investigated at various methanol feed concentrations (2, 4, 8, and 16 M) and compared to the performance of Nafion[®] 117 at similar membrane thicknesses and fuel cell conditions. For Nafion[®] 117, the maximum power density decreased three-fold when the methanol feed concentration increased from 2 to 16 M. The Nafion[®]/PVA (5 wt% PVA) blend membrane reveals a similar trend, however the decrease in power is only 26% compared to 47% when methanol concentration is increased from 2 to 8 M. Furthermore, the maximum power density of the blend membrane (5 wt% PVA) is higher than Nafion[®] 117 at 2, 4, and 8 M methanol feed concentrations, while the maximum power density at 16 M is comparable between the two membranes. Specifically, at 8 M methanol, the maximum power density of the blend at 5 wt% PVA is 33% higher than Nafion[®] 117. Blend membranes at higher PVA concentrations are noticeably lower in performance compared to Nafion[®] 117. Overall, fuel cell performance trends match observed transport property (proton conductivity and methanol permeability) trends.

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1. Introduction

The direct methanol fuel cell (DMFC) provides an attractive alternative to the rechargeable battery in portable electronic devices. Current DMFCs operate at overall efficiencies of ~20–25%, which corresponds to power densities double that of the lithium-ion rechargeable battery [1]. However, several factors limit the DMFC from achieving its maximum theoretical efficiency (100%). One main factor is high methanol crossover (permeability) in polymer electrolyte membranes (PEMs) currently used in DMFCs. When excessive methanol permeates across the PEM, this results in oxidation of methanol, carbon monoxide catalyst poisoning (an intermediate of the methanol oxidation reaction), and flooding all at the cathode. All of these phenomena negatively impact the oxygen reduction reaction at the cathode and therefore leads to overall losses in DMFC power and efficiency [2–6]. As a result, DMFCs operate at low methanol feed concentrations (~2 M) to minimize these

effects. However, the equimolar methanol concentration coinciding with the anode half cell reaction is ~17 M. In other words, if PEMs with lower methanol crossover were developed and used in DMFCs, higher methanol feed concentrations could be used, which would result in higher power densities and fuel efficiencies.

The current standard PEM used in the DMFC is Nafion[®] 117 (DuPont), where 117 refers to 1100 equiv. weight (EW) and 0.007 inches in thickness. Nafion[®] membranes possess high proton conductivities at optimal water contents and are thermally, chemically, and oxidatively stable. However, Nafion[®] 117 also has a high methanol permeability: $\sim 2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ at 25 °C and 2 M methanol feed [7]. Recent research has focused on the development of new PEMs that will be as conductive as Nafion[®], but more resistant to methanol. There are numerous publications documenting membrane development for the DMFC, where design strategies include the synthesis of new ionic (sulfonic acid) random and block copolymers, graft copolymerization of ionic polymers onto hydrophobic membranes, blending ionic and non-ionic polymers, the synthesis of interpenetrating networks of ionic and non-ionic polymers, incorporating fillers (e.g., silica, montmorillonite) into ionic polymer membranes,

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and coating ionic polymer membranes with thin barrier coatings. A summary of these findings has recently been reviewed by DeLuca and Elabd [2]. Overall, few PEMs that have been developed possess both a similar proton conductivity and higher selectivity (proton conductivity/methanol crossover) compared to Nafion[®], where measuring proton conductivity and methanol permeability in PEMs are the standard prescreening experiments conducted before DMFC testing. Furthermore, only ~40% of the PEMs developed for the DMFC have actually been tested in a DMFC [2]. In the end, comparing DMFC test results on new PEMs and Nafion[®] side by side is the optimal experiment to gauge whether Nafion[®] can be outperformed.

This present study investigates the DMFC performance of Nafion[®]/poly(vinyl alcohol) (PVA) blend membranes at various methanol concentrations (2–16 M). In a previous study [7], these blend membranes were developed at various compositions and annealing temperatures and their transport properties (proton conductivity and methanol permeability) were measured. The rationale for this work is based on blending polymers with Nafion[®] that are selective for water over methanol. The water and methanol uptakes of Nafion[®] 117 were measured as 29 and 61 wt%, respectively [7]. In contrast, PVA has a higher affinity for water compared to methanol – 55 and 10 wt%, respectively, when annealed at 230 °C [7]. A key result from this study is that a Nafion[®]/PVA blend membrane at 5 wt% PVA (annealed at 230 °C) resulted in a similar proton conductivity to Nafion[®] 117 and a methanol permeability three times lower than Nafion[®] 117. As PVA content increased in the blend membranes, the proton conductivity decreased to values lower than Nafion[®] 117. However, an unusual trend was observed in a Nafion[®]/PVA blend membrane at 50 wt% PVA, where proton conductivity remained relatively constant, but methanol permeability decreased by one order of magnitude with increasing annealing temperature. This trend differs from most investigations, where proton and methanol transport usually increase or decrease simultaneously in sulfonic acid containing PEMs with changes in polymer properties (e.g., ion content, water content, morphology). Results from this study suggest that these two phenomena, proton and methanol transport, can be decoupled. It was also suggested that this unusual trend occurs due to changes in the blend phase behavior at different annealing temperatures, which was supported by infrared spectroscopy. In this study, the DMFC performance of Nafion[®]/PVA blend membranes at 5, 10, and 20 wt% PVA (annealed at 230 °C) was investigated at various methanol feed concentrations and compared to the performance of Nafion[®] 117 at similar membrane thicknesses and fuel cell conditions.

2. Experimental

2.1. Materials

Nafion[®] solutions were purchased from Ion Power, Inc. (1100 EW, 5 wt% in a mixture of water and alcohols, Liquion[®]) and Sigma–Aldrich (5 wt% in a mixture of 15–20 wt% water and 80–85% lower aliphatic alcohols). Poly(vinyl alcohol) (PVA) (99% hydrolyzed, average molecular weight = 86,000 g mol⁻¹)

was purchased from Scientific Polymer Products. Both Nafion[®] solutions and PVA were used as received. Nafion[®] 117 (1100 EW, 178 μm (0.007 in.) thick, commercially extruded film, DuPont) was purchased from Aldrich and purified. The purification procedure entailed boiling in 3 wt% hydrogen peroxide (Aldrich) for 1 h, washing in deionized (DI) water, boiling in DI water for 1 h, boiling in 1 M sulfuric acid (Aldrich, 99.999% purity), and washing in DI water. Platinum/ruthenium (Pt/Ru) black (50/50 by atomic wt%, HiSPEC[™] 6000) and platinum (Pt) black (HiSPEC[™] 1000) were purchased from Alfa Aesar[®]. Teflon[®]-coated Fiberglass tape with silicone adhesive (CS Hyde Company) was used as a decal for catalyst transfer, and poly(tetrafluoroethylene) (PTFE) films (McMaster Carr) were used as barriers in the heat pressing procedure. Ethylene propylene diene monomer (EPDM) gaskets (794 μm (1/32 in.) thick) were purchased from www.fuelcellstore.com[™] and used in the fuel cell assembly. Other chemicals used include methanol (Aldrich, 99.8+% purity, A.C.S. reagent), 2-propanol (Aldrich, ≥99% purity, ReagentPlus[™]) and ultra-pure reverse osmosis, DI water (resistivity ~16 MΩ cm).

2.2. Membrane electrode assembly (MEA)

Solution-cast Nafion[®] and Nafion[®]/PVA blend membranes were prepared in a previous study and are described in more detail elsewhere [7]. Membrane electrode assemblies (MEAs) were prepared by using a standard hand painting/decal transfer method [8]. Two inks were prepared for the anode and cathode electrode layers. The anode ink consisted of a 17:3 wt ratio of Pt/Ru black and Nafion[®] solution mixed with water and 2-propanol, while the cathode ink consisted of a 9:1 wt ratio of Pt black and Nafion[®] solution (Aldrich) mixed with water and 2-propanol. Both inks were sonicated for 30 min at 30 °C and subsequently painted repeatedly onto 5–7 cm² adhesive Teflon[®]-coated Fiberglass decals until a catalyst loading of ~4–6.5 mg cm⁻² was achieved. Each membrane was sandwiched between catalyst-coated decals: a Pt/Ru decal on the anode side and a Pt decal on the cathode side. The assembly was placed between two sheets of PTFE film and heat pressed (Laboratory Press, Model C, Carver) at 150 °C and 2268 kg (5000 lbs) for 30 s. After heat pressing, the decals were removed and the catalyst layer was completely transferred onto each side of the membrane.

2.3. Direct methanol fuel cell test

DMFC tests were performed on a Scribner 850C Compact Fuel Cell Test Station. An MEA was sandwiched between two graphite blocks (with EPDM gasket(s)) with 5 cm² serpentine single flow patterns and two temperature controlled current collectors. 115.2 cm kg (100 in. lbs) of torque was applied to each of the eight bolts to assemble the entire fuel cell assembly. After assembly, a gas leak test was performed with nitrogen to ensure a proper seal and that there were no defects with the MEA or membrane. After the leak test, the fuel cell assembly was connected to the fuel cell test station. The cathode (air) outlet was connected to

a backpressure regulator and the anode (methanol/water) outlet was configured to flow into a waste container. DMFC tests were conducted at a cathode backpressure of 1.76 kg cm^{-2} (25 psig). Other DMFC operating conditions, cell and cathode temperature and anode and cathode flow rate, are detailed in the results and discussion section. Cells had an open circuit voltage (OCV) of $\sim 0.6 \text{ V}$ or lower depending on the membrane, and DMFC tests were conducted by sweeping potential from OCV to 0.1 V by increments of 0.01 V every 10 s and recording current. Voltage, current density, and power density were monitored using Fuel Cell for Windows™ software supplied by Scribner and at least five consecutive voltage sweeps were taken to ensure operation at equilibrium. Inlet and outlet anode methanol concentrations were measured as a function of time at all methanol concentrations used in this study at a 4 ml min^{-1} feed rate and the results showed no change in methanol concentration.

3. Results and discussion

DMFC tests were performed on Nafion® 117 at various operating conditions: cell and cathode temperature ($40\text{--}80^\circ\text{C}$), anode (methanol) flow rate ($4\text{--}10 \text{ ml min}^{-1}$), and cathode (air) flow rate ($50\text{--}1000 \text{ ml min}^{-1}$). Performance improved with increasing cell and cathode temperature with the highest performance at 80°C . Fuel cell performance decreased with increasing methanol flow rate with the highest performance at 4 ml min^{-1} . DMFC performance increased with increasing air flow rate from 50 to 500 ml min^{-1} , but no noticeable improvement was observed at flow rates greater than 500 ml min^{-1} . Similar parametric results have been observed by other investigators [9]. Based on the experiments described above, DMFC operating conditions of 80°C for both the cell and cathode temperatures, 4 ml min^{-1} methanol flow rate, and 500 ml min^{-1} air flow rate were used in the remaining DMFC experiments in this study.

Fig. 1 shows the effect of methanol feed concentration on the DMFC performance of Nafion® 117. As the methanol concentration increases from 2 to 16 M , the DMFC performance

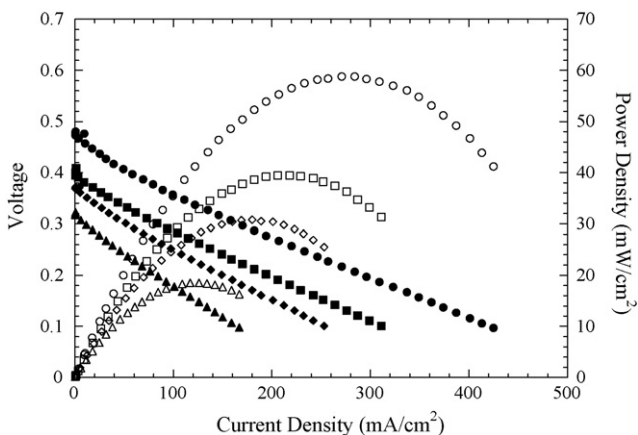


Fig. 1. Power (open) and polarization (filled) curves of Nafion® 117 at 2 M (\circ , \bullet), 4 M (\square , \blacksquare), 8 M (\diamond , \blacklozenge), and 16 M (\triangle , \blacktriangle) methanol feed concentrations. DMFC experimental conditions—cathode and cell temperature: 80°C ; anode temperature: $23\text{--}26^\circ\text{C}$; cathode backpressure: 1.76 kg cm^{-2} (25 psig); methanol flow rate: 4 mL min^{-1} .

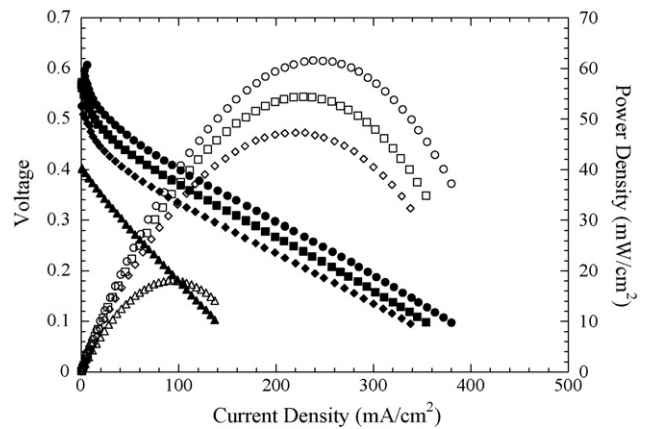


Fig. 2. Power (open) and polarization (filled) curves of Nafion®/PVA (5 wt% PVA) blend membrane at 2 M (\circ , \bullet), 4 M (\square , \blacksquare), 8 M (\diamond , \blacklozenge), and 16 M (\triangle , \blacktriangle) methanol feed concentrations. DMFC experimental conditions—cathode and cell temperature: 80°C ; anode temperature: $23\text{--}26^\circ\text{C}$; cathode backpressure: 1.76 kg cm^{-2} (25 psig); methanol flow rate: 4 mL min^{-1} .

decreases significantly. More specifically, the maximum power density decreases from 59 mW cm^{-2} at $\sim 280 \text{ mA cm}^{-2}$ (2 M) to 18 mW cm^{-2} at $\sim 120 \text{ mA cm}^{-2}$ (16 M)—a three-fold decrease in the maximum power density. Ge and Liu [9] have shown similar results in DMFC performance of Nafion® with a 66% reduction in voltage at an optimal operating current density and a decrease in open circuit voltage when the methanol feed concentration was increased from 2 to 6 M . These results clearly demonstrate the effect of methanol crossover (high methanol permeability in Nafion® membranes) and why low methanol feed concentrations ($\sim 1\text{--}2 \text{ M}$) are typically used in DMFCs. Note that $\sim 17 \text{ M}$ corresponds to the equimolar concentration corresponding to the anode half cell reaction [2]. Therefore, the DMFC performance should increase with increasing methanol feed concentration with membranes with a higher selectivity (high proton conductivity and low methanol permeability).

Figs. 2 and 3 show the DMFC performance of Nafion®/PVA blends (5 wt% PVA and 20 wt% PVA, respectively). These mem-

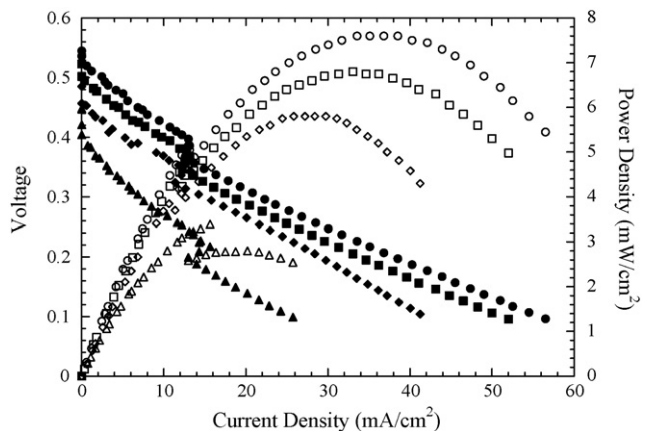


Fig. 3. Power (open) and polarization (filled) curves of Nafion®/PVA (20 wt% PVA) blend membrane at 2 M (\circ , \bullet), 4 M (\square , \blacksquare), 8 M (\diamond , \blacklozenge), and 16 M (\triangle , \blacktriangle) methanol feed concentrations. DMFC experimental conditions—cathode and cell temperature: 80°C ; anode temperature: $23\text{--}26^\circ\text{C}$; cathode backpressure: 1.76 kg cm^{-2} (25 psig), methanol flow rate: 4 mL min^{-1} .

branes were solution cast from a water/alcohol mixture and annealed at 230 °C. Details regarding the membrane fabrication can be found elsewhere [7]. Similar to Fig. 1, these performance curves (both polarization and power curves) are shown as a function of methanol feed concentration ranging from 2 to 16 M. The Nafion®/PVA (5 wt% PVA) blend membrane (Fig. 2) reveals a similar trend to Nafion® 117 in that the voltage and power decrease with increasing methanol feed concentration. However, it is interesting to note that the decrease in maximum power density from 2 to 8 M is less in the blend membrane compared to Nafion® 117, where the blend membrane decreases from 62 to 46 mW cm⁻², while the Nafion® 117 membrane decreases from 59 to 31 mW cm⁻². Respectively, this is a 26% decrease compared to a 47% decrease in maximum power density. In addition, the maximum power density of the blend membrane (5 wt% PVA) is higher than Nafion® 117 at 2, 4, and 8 M methanol feed concentrations, while the maximum power density at 16 M is comparable between the two membranes.

The Nafion®/PVA (20 wt% PVA) blend membrane (Fig. 3) also shows a decrease in voltage and power density with increasing methanol feed concentration. Overall, the voltage and power of the Nafion®/PVA blend (20 wt% PVA) are noticeably lower when compared to Nafion® 117 and the Nafion®/PVA blend (5 wt%). These results show the influence of two important transport properties: proton conductivity and methanol permeability. In general, the poor DMFC performance can be attributed to a low proton conductivity, where the conductivity of the Nafion®/PVA blend (20 wt% PVA) is ~30 times lower than Nafion® 117 (see Table 1). Conversely, the rise in DMFC performance of the Nafion®/PVA blend (5 wt% PVA) can be attributed to a lower methanol permeability, where the methanol permeability of the Nafion®/PVA blend (5 wt% PVA) is approximately four times lower than Nafion® 117.

A comparison of power curves for Nafion® 117 and Nafion®/PVA blend membranes at 5, 10, and 20 wt% PVA at a methanol feed concentration of 2 M is shown in Fig. 4. The power profiles for Nafion® 117 and Nafion®/PVA (5 wt% PVA) are similar. The Nafion®/PVA blend membrane at 5 wt% PVA has a slightly higher maximum power density, but the profile for Nafion® 117 extends to slightly higher currents. This comparison in Fig. 4 clearly shows that the Nafion®/PVA blend membranes at 10 and 20 wt% PVA results in a DMFC performance that is approximately an order of magnitude lower than Nafion® 117 and the blend containing 5 wt% PVA. These trends coincide with the proton conductivity data shown in Table 1,

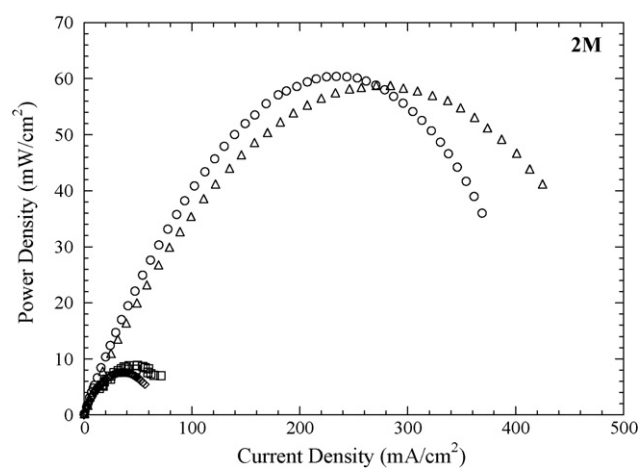


Fig. 4. Power curves of Nafion® 117 (Δ) and Nafion®/PVA blend membranes at 5 (\circ), 10 (\square), and 20 wt% PVA (\diamond) at a 2 M methanol feed concentration. DMFC experimental conditions—cathode and cell temperature: 80 °C; anode temperature: 23–26 °C; cathode backpressure: 1.76 kg cm⁻² (25 psig); methanol flow rate: 4 mL min⁻¹.

where the proton conductivity of Nafion® 117 is similar to the Nafion®/PVA blend membrane at 5 wt% PVA, but the proton conductivity of the Nafion®/PVA blend membranes at 10 and 20 wt% PVA is significantly lower.

It is important to note that a number of parameters, such as membrane thickness and cathode loading, must be held constant when comparing the fuel cell performance of different membranes and MEAs (Fig. 4 for example). Membrane thickness will change the flux or resistance of both proton and methanol transport. This has been documented by Liu et al. [10] in their work on the DMFC performance of Nafion® membranes at different thicknesses. At low concentrations (2 M), they observed better performance with thinner membranes, but at higher concentrations (4 M), better performance was demonstrated with thicker membranes. Thinner membranes result in higher flux of protons or less resistance to proton transport, therefore higher voltages can be achieved. However, at higher methanol concentration, methanol crossover deters the fuel cell performance, therefore thicker membranes results in a lower methanol flux and higher voltages. In hydrogen PEM fuel cells, where methanol crossover is not a problem, higher performances are observed with thinner membranes [11,12]. In this study, the membrane thicknesses were similar, as shown in Table 1. In addition to membrane thickness, the catalyst loading and Nafion® content

Table 1
Properties of Nafion® 117 and Nafion®/PVA blend membranes

PEM	PVA content (wt%)	Proton conductivity ($\times 10^2$ S cm ⁻¹) ^{a,b}	Methanol permeability ($\times 10^6$ cm ² s ⁻¹) ^{a,c}	Membrane thickness (μ m)
Nafion® 117	0	2.60 \pm 0.15	2.00 \pm 0.56	210
Nafion®/PVA	5	2.07 \pm 0.05	0.65 \pm 0.19	181
Nafion®/PVA	10	0.56 \pm 0.02	0.81 \pm 0.20	201
Nafion®/PVA	20	0.09 \pm 0.01	0.31 \pm 0.09	181

^a Data from Ref. [7].

^b Experiments conducted at room temperature, fully hydrated.

^c Experiments conducted at 25 °C, 2 M methanol feed concentration.

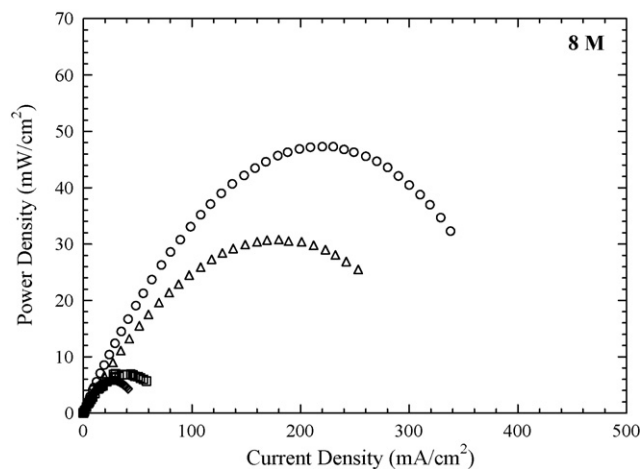


Fig. 5. Power curves of Nafion[®] 117 (Δ) and Nafion[®]/PVA blend membranes at 5 (\circ), 10 (\square), and 20 wt% PVA (\diamond) at an 8 M methanol feed concentration. DMFC experimental conditions—cathode and cell temperature: 80 °C; anode temperature: 23–26 °C; cathode backpressure: 1.76 kg cm⁻² (25 psig); methanol flow rate: 4 mL min⁻¹.

in the catalyst layer can impact electrode kinetics and interfacial resistance for a given MEA. In this study, these parameters were also held constant among different MEAs. Also, DMFC tests were repeated on each membrane at least three times (three different membranes at each composition) to ensure reproducibility of the results shown in this study.

Similar to Fig. 4, Fig. 5 shows the DMFC performance of Nafion[®] 117 and Nafion[®]/PVA blend membranes at 5, 10, 20 wt% PVA, but at a higher methanol feed concentration: 8 M. Unlike Fig. 4, the Nafion[®]/PVA blend membrane at 5 wt% PVA results in a significantly higher overall DMFC performance compared to Nafion[®] 117. The maximum power density is 46 mW cm⁻² compared to 31 mW cm⁻², and the polarization curve extends to higher current densities for the blend membrane. The blend membrane exhibits a better performance compared to Nafion[®] 117 at a higher methanol feed concentration and a similar thickness due to lower methanol permeability, approximately four times lower, as shown in Table 1. However, it is evident that a membrane must possess a minimum proton conductivity to result in satisfactory DMFC performance. The Nafion[®]/PVA blend membranes at 10 and 20 wt% PVA illustrate this point, where the DMFC performance is significantly lower than Nafion[®] 117 even at a higher methanol feed concentration. Fig. 5 shows both the feasibility of using a Nafion[®]/PVA (5 wt% PVA) blend membrane in the DMFC and its potential at higher methanol concentrations (i.e., higher fuel efficiency).

The tradeoff between proton conductivity and selectivity is clearly seen in Fig. 6. It is interesting to note that Nafion[®] 117 and the Nafion[®]/PVA blend at 5 wt% PVA have similar conductivities, but the selectivity of the blend is approximately three-fold higher than Nafion[®] 117. In addition, even though the Nafion[®]/PVA blends containing 10 and 20 wt% exhibit lower methanol permeabilities than Nafion[®] 117, their selectivities were also lower due to low proton conductivities. This resulted in lower DMFC performance. These comparisons help to show

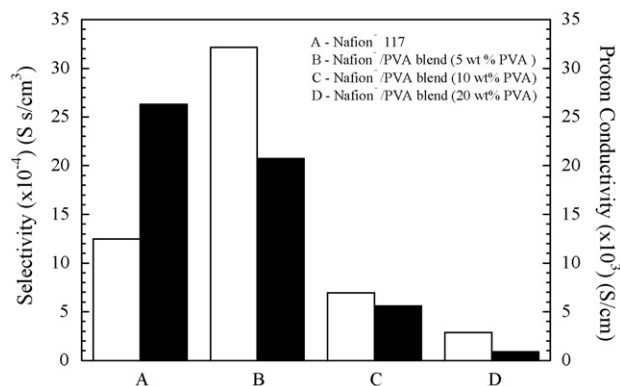


Fig. 6. Selectivities (ratio of proton conductivity to methanol permeability) (open bars) and proton conductivities (solid bars) of Nafion[®] 117 and Nafion[®]/PVA blend membranes at 5, 10, and 20 wt% PVA.

the importance of having both adequate proton conductivity and a lower methanol permeability in order to improve DMFC performance at higher methanol feed concentrations. In this study, a proton conductivity of >0.01 S cm⁻¹ was necessary to achieve a DMFC performance comparable to Nafion[®] 117, while a lower methanol permeability (compared to Nafion[®] 117) can result in a higher DMFC performance.

4. Conclusions

The DMFC performance of Nafion[®]/PVA blend membranes was reported at various compositions, 5, 10, and 20 wt% PVA, and various methanol feed concentrations, 2, 4, 8, and 16 M. The blend membrane at 5 wt% PVA annealed at 230 °C resulted in a fuel cell performance higher than Nafion[®] 117 at 2, 4, and 8 M, where the performance at 8 M was 33% higher. This result coincides with transport properties, measured in a previous study, where the blend has a similar proton conductivity compared to Nafion[®] 117, but a methanol permeability three times lower. Furthermore, the blend membranes at 10 and 20 wt% PVA both have proton conductivities lower (<0.01 S cm⁻¹) than Nafion[®] 117, which resulted in lower DMFC performance at all methanol feed concentrations. Overall, this study demonstrates that polymer blend membranes with Nafion[®] (proton conductive) and PVA (methanol resistant) can result in improved DMFC performance, particularly at high methanol feed concentrations. In addition, the fuel cell results in this study compare well with transport property measurements from a previous study. These results emphasize that membranes with conductivities >0.01 S cm⁻¹ and methanol permeabilities lower than Nafion[®] 117 are required to achieve enhanced DMFC performance at higher methanol concentrations.

Acknowledgments

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