



Short communication

Nafion-impregnated electrospun polyvinylidene fluoride composite membranes for direct methanol fuel cells

S.W. Choi^a, Y.-Z. Fu^a, Y.R. Ahn^b, S.M. Jo^b, A. Manthiram^{a,*}^a Materials Science and Engineering Program, The University of Texas at Austin, Austin, TX 78712, USA^b Opto Electronic Materials Research Center, Korea Institute of Science and Technology, 39-1, Hawolgok-dong, Seongbuk-gu, Seoul 136-791, Republic of Korea

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ABSTRACT

Composite membranes consisting of polyvinylidene fluoride (PVdF) and Nafion have been prepared by impregnating various amounts of Nafion (0.3–0.5 g) into the pores of electrospun PVdF (5 cm × 5 cm) and characterized by scanning electron microscopy, differential scanning calorimetry, X-ray diffraction, and proton conductivity measurements. The characterization data suggest that the unique three-dimensional network structure of the electrospun PVdF membrane with fully interconnected fibers is maintained in the composite membranes, offering adequate mechanical properties. Although the composite membranes exhibit lower proton conductivity than Nafion 115, the composite membrane with 0.4 g Nafion exhibits better performance than Nafion 115 in direct methanol fuel cell (DMFC) due to smaller thickness and suppressed methanol crossover from the anode to the cathode through the membrane. With the composite membranes, the cell performance increases on going from 0.3 to 0.4 g Nafion and then decreases on going to 0.5 g Nafion due to the changes in proton conductivity.

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1. Introduction

Direct methanol fuel cell (DMFC) is an attractive power source for portable devices as it does not require recharging with an electrical outlet. DMFC currently uses Nafion as a polymeric proton conducting membrane as it offers high proton conductivity, good chemical and thermal properties, and sufficient mechanical strength to be employed in DMFC [1,2]. However, DMFC suffers from a high crossover of methanol fuel from the anode to the cathode through the Nafion membrane and the consequent fuel waste and polarization loss at the cathode [3–5].

To overcome the drawbacks of the Nafion membrane, blending of Nafion with polyvinylidene fluoride (PVdF) or their copolymers have been suggested in the literatures [6–8]. Although these membranes exhibit lower methanol crossover than Nafion, they encounter high interfacial resistance due to poor contact with the gas diffusion layer (GDL) in the membrane-electrode assembly (MEA) and relatively low mechanical strength due to the immiscibility between Nafion and PVdF. It is not easy to optimize simultaneously the thermal, chemical, mechanical, and electrochemical properties of such membranes.

Membranes fabricated by electrospinning has been widely studied with respect to several areas such as lithium cells, fil-

ters, biomedical materials, fiber mats in reinforcing components, clothing to protect electromagnetic waves, sensor engineering, radioactive radiation, and electronic devices [9–14]. The interest in the electrospun membranes is due to their unique three-dimensional network structures with fully interconnected pores, high porosity, high solvent uptake, and sufficient mechanical strength [9,10]. We present in this paper for the first time the fabrication and characterization of Nafion-impregnated electrospun PVdF composite membranes and their performance in DMFC. Composite membranes with different Nafion contents are fabricated and the effects of impregnated Nafion content on the thermal properties of the electrospun PVdF membranes as well as the influence of Nafion content on the cell performance and methanol crossover are investigated.

2. Experimental

Microporous PVdF membranes with a thickness of about 100 μm were prepared from a 17 wt.% solution of PVdF (Kynar 761, Elf Atochem) in a mixed solvent (acetone/dimethylacetamide = 5/5, w/w) using an electrospinning method [15,16], followed by vacuum-drying overnight at 80 °C to remove the residual solvent. The experimentally measured thickness values of the membrane are given in Table 1. The electrospun PVdF membrane is hereafter referred to as EPM. The Nafion-impregnated composite membranes were prepared by extending the electrospun PVdF membranes (5 cm × 5 cm) over a glass plate, adding a required

* Corresponding author. Tel.: +1 512 471 1791; fax: +1 512 471 7681.

E-mail address: rmanth@mail.utexas.edu (A. Manthiram).

Table 1
Physical properties of the composite and Nafion 115 membranes

Sample name	Thickness (μm)	Weight of Nafion in composite membrane (g)	Onset temperature ($^{\circ}\text{C}$)	ΔH (J g^{-1})	Crystallinity (X_c) ^a	Proton conductivity (S cm^{-1})
Nafion 115	125	–	–	–	–	3.20×10^{-2}
EPM/Nafion-0.3 g	100	0.3	164.3	28.6	5.71	1.55×10^{-3}
EPM/Nafion-0.4 g	105	0.4	165.5	26.2	5.24	2.25×10^{-3}
EPM/Nafion-0.5 g	110	0.5	165.0	24.0	4.81	2.17×10^{-3}

$$^a X_c = (\Delta H_m^{\text{sample}} / \Delta H_m^{\text{ref}}) \times 100, \Delta H_m^{\text{ref}} = 104.7 \text{ J g}^{-1}.$$

amount (0.3–0.5 g) of Nafion PFSA polymer dispersion in isopropanol (DuPont, DE-520), drying in an air oven at 65°C to evaporate the solvent, and finally drying in a vacuum oven at 100°C for 12 h. After drying, these membranes were stored in de-ionized water. The composite membranes with 0.3, 0.4, and 0.5 g Nafion are, hereafter referred to as, EPM/Nafion-0.3 g, EPM/Nafion-0.4 g, and EPM/Nafion-0.5 g.

The thermal properties of the original and composite membranes were investigated with a PerkinElmer differential scanning calorimeter under flowing N_2 atmosphere with a heating rate of $10^{\circ}\text{C}/\text{min}$ in the range of 50 – 200°C . The cross-sections of the Nafion-impregnated electrospun PVdF membrane were investigated with a JEOL LSM-5610 scanning electron microscope (SEM) after coating the samples with gold. Structural characterizations were carried out with an X-ray diffractometer using $\text{Cu K}\alpha$ radiation in the 2θ range of 10 – 80° at a scanning rate of $1^{\circ} \text{ min}^{-1}$. Proton conductivity values were obtained from the impedance data collected with an HP 4192A LF impedance analyzer in the frequency range of 5 – 13 MHz with an applied voltage of 10 mV after equilibrating the membranes with water vapor at 100% relative humidity (RH).

Electrodes with gas diffusion layer and catalyst layer were prepared as reported elsewhere [17]. The catalyst in the catalyst layer consisted of commercial 40 wt.% Pt–Ru (1:1) in Vulcan carbon (E-TEK) with a metal loading of 0.6 mg cm^{-2} and a Nafion content of 30 wt.%. The catalyst in cathode catalyst layer consisted of commercial 20 wt.% Pt in Vulcan carbon (Alfa Aesar), with a metal loading 1.0 mg cm^{-2} and a Nafion content of 30 wt.%. The content of PTFE in the GDL was 30 wt.%. The electrodes were dried at 100°C for 30 min before fabricating the MEAs with the membranes. The MEAs were fabricated by hot pressing the membrane, cathode, and anode at 140°C with a hydrostatic pressure of 750 psi for 1 min.

The electrochemical performances in DMFC of the MEAs were evaluated with a single-cell fixture having an active area of 5 cm^2 (Electrochem Inc.) and feeding a preheated methanol solution into the anode at a flow rate of 2.5 mL min^{-1} by a peristaltic pump without back pressurization and humidified oxygen into the cathode at a flow rate of 200 mL min^{-1} with a back pressure of 20 psi. The temperature of preheated methanol solution and humidified oxygen were same as that of the cell (65 or 80°C).

Methanol crossover was evaluated by a voltammetric method in which methanol solution was fed at a flow rate of 2.5 mL min^{-1} into the anode side of the MEA while the cathode side was kept in an inert humidified N_2 atmosphere. By applying a positive potential at the cathode side, the flux rate of permeating methanol was determined by measuring the steady-state limiting current density resulting from the complete electro-oxidation at the membrane/Pt catalyst interface at the cathode side.

3. Results and discussion

Fig. 1 shows the cross-sections of the Nafion-impregnated electrospun PVdF composite membranes with various Nafion contents. In these SEM images, PVdF fibers are observed at the inner parts of the membrane, suggesting that the framework of the electro-

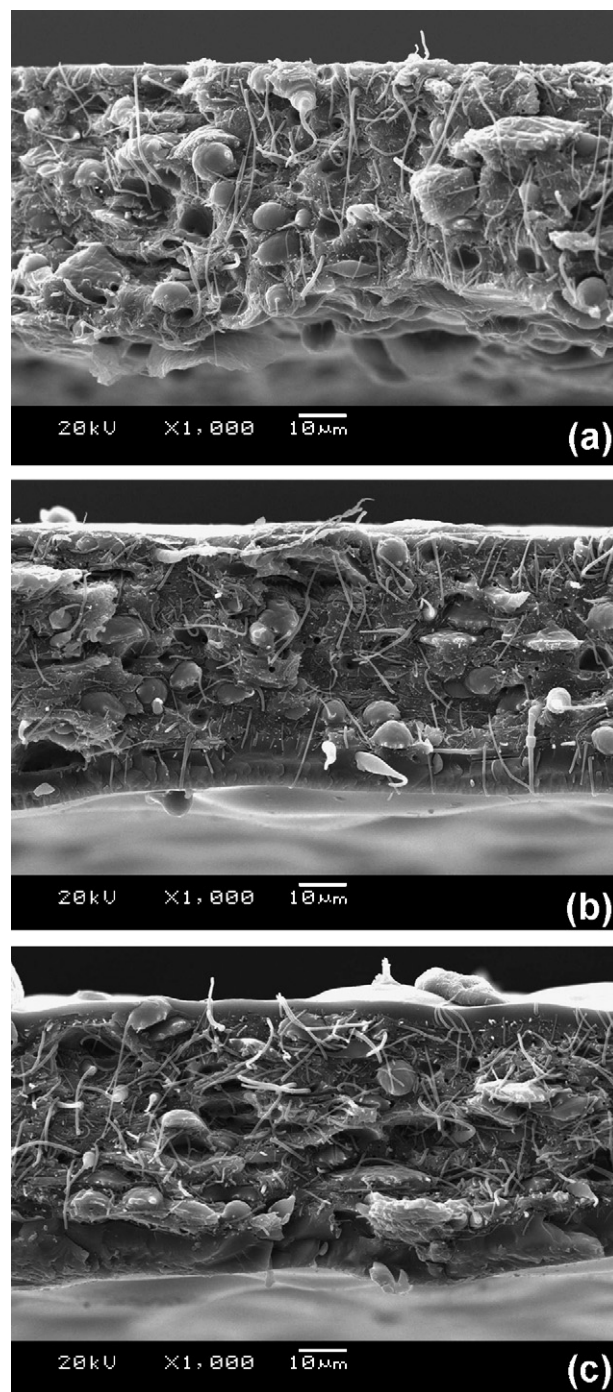


Fig. 1. SEM images of the cross-sections of the Nafion-impregnated electrospun composite PVdF membranes with (a) 0.3 g Nafion (EPM/Nafion-0.3 g), (b) 0.4 g Nafion (EPM/Nafion-0.4 g), and (c) 0.5 g Nafion (EPM/Nafion-0.5 g).

spun PVdF membrane is not affected by Nafion impregnation and the mechanical strength is still maintained. The unfilled pores seen in these composite membranes may result from a rapid evaporation of the highly volatile iso-propanol present in the as-received Nafion solution during the membrane drying step. The thickness and morphology of the composite membranes differ slightly depending on the Nafion content. For example, the composite membrane with 0.3 g of Nafion (EPM/Nafion-0.3 g) consists of a single layer of Nafion-impregnated electrospun PVdF. This membrane has a rough surface that was produced by a rapid evaporation of the solvent molecules during the drying step. In contrast, the composite membranes with 0.4 and 0.5 g of Nafion (EPM/Nafion-0.4 g and EPM/Nafion-0.5 g) show additional Nafion layer on the surface of the Nafion-impregnated electrospun PVdF due to the excess amount of Nafion. The thickness of this additional Nafion layer increases with increasing amount of Nafion in the composite. Interestingly, these two composite membranes with 0.4 and 0.5 g of Nafion have smooth surface morphologies compared to the membrane with 0.3 g of Nafion. It is anticipated that the composite membranes with smooth surface may provide better interfacial contact with the electrodes consisting of gas diffusion and catalyst layers, resulting in better cell performance.

The melting temperatures and the melting enthalpies of the Nafion-impregnated electrospun PVdF membranes were determined from the DSC data shown in Fig. 2. The onset melting temperature, enthalpy values of melting, and the degrees of crystallinity are given in Table 1. In a previous study, the electrospun PVdF membranes that were prepared under similar conditions were found to show an onset temperature of 166 °C and a crystallinity of 43.9%, which are close to the onset temperature of 167 °C and crystallinity of 44.7% found for the as-received PVdF powder [18]. Although the Nafion-impregnated electrospun PVdF membranes show lower crystallinity than the plain electrospun PVdF membrane, they still maintain high onset melting temperature, suggesting that they have sufficient mechanical strength for use as a matrix for proton conduction in the operating temperature of a fuel cell. However, the crystallinity increases with decreasing Nafion content, which could have an influence on the proton conductivity and cell performance.

Fig. 3 compares the XRD patterns of the Nafion-impregnated electrospun PVdF composite membranes with various Nafion contents with those of plain PVdF and Nafion 115 membranes. It is well-known that Nafion 115 membrane exhibits two broad reflections around 2θ values of 18° and 40°. While the reflection at 18°

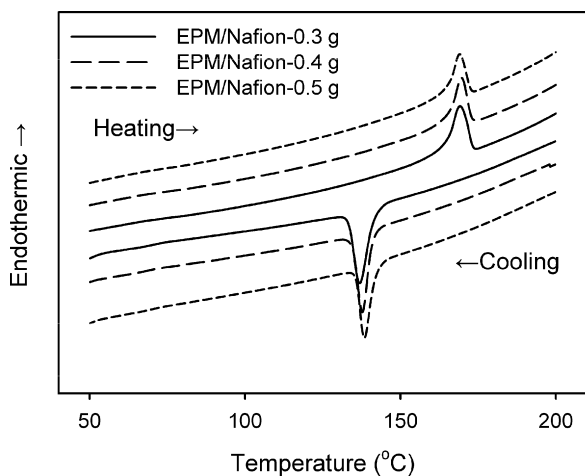


Fig. 2. Thermal behaviors (DSC plots) of Nafion-impregnated electrospun PVdF composite membranes.

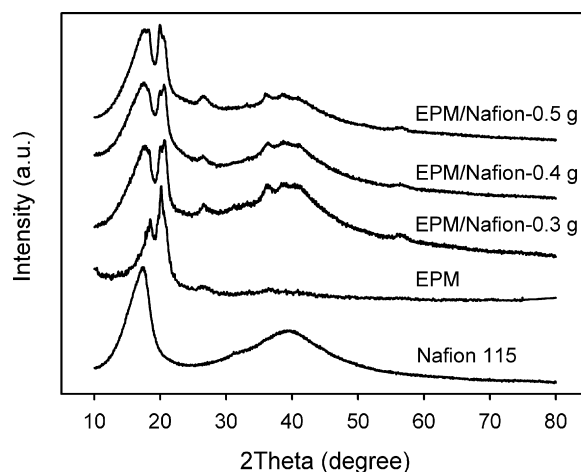


Fig. 3. XRD patterns of the Nafion-impregnated electrospun PVdF composite membranes with various Nafion contents and plain PVdF (EPM) and Nafion 115 membranes.

has been assigned to the crystalline scattering of the polyfluorocarbon chains, that at 40° has been assigned to the scattering from the amorphous ionic clusters of the Nafion membrane [19]. The electrospun PVdF membrane, on the other hand, is known to show two major reflections around 18° and 21° and three minor reflections around 27°, 36°, and 57° [20]. The Nafion-impregnated electrospun PVdF composite membranes show reflections corresponding to both PVdF and Nafion, suggesting that the framework of PVdF fibers is not affected by the impregnation of Nafion. Also, the intensity of the reflections arising from the ionic clusters of Nafion decreases with increasing Nafion content. DSC data indicated that the crystallinity of PVdF decreases with Nafion impregnation (Fig. 2), which is consistent with the increasing amorphous content of PVdF in the XRD data with increasing Nafion content.

Table 1 gives the proton conductivity values at 65 °C of the composite membranes with various Nafion contents. The composite membranes exhibit lower proton conductivity than the value of $3.20 \times 10^{-2} \text{ S cm}^{-1}$ found for Nafion 115 at 65 °C previously [21]. Among the three composite membranes studied, the membrane with 0.4 g Nafion (EPM/Nafion-0.4 g) shows the highest proton conductivity and that with 0.3 g Nafion (EPM/Nafion-0.3 g) shows the lowest conductivity. The lower conductivity of the latter could be due to the insufficient amount of Nafion present in the composite, while the decrease in conductivity on increasing the Nafion content from 0.4 to 0.5 g could be due to the segregation of a larger amount of Nafion into the surface of the latter (EPM/Nafion-0.5 g).

Fig. 4 compares the electrochemical performances of the composite membranes with various amounts of Nafion at 65 °C in 2 M methanol solution with that of Nafion 115 membrane. The composite membranes with 0.4 g Nafion and 0.5 g Nafion show better cell performance than Nafion 115 membrane, which could be partly related to the additional Nafion layers on the surface of the composite membranes as shown in Fig. 1 and the resulting better interfacial contact with the electrodes. The cell performance increases significantly on going from 0.3 to 0.4 g Nafion, and then decreases slightly on going to 0.5 g Nafion. The drastic increase in performance on going from 0.3 to 0.4 g Nafion could be due to the presence of an adequate amount of Nafion in the pores of PVdF and the significant increase in proton conductivity (Table 1). The decrease in performance on going from 0.4 to 0.5 g Nafion could be due to a larger segregation of Nafion into the surface and a slightly increased membrane thickness. The cell performance is known to decrease with increasing membrane thickness due to the increasing ionic resistance [22]. Fig. 5 compares the methanol crossover current density

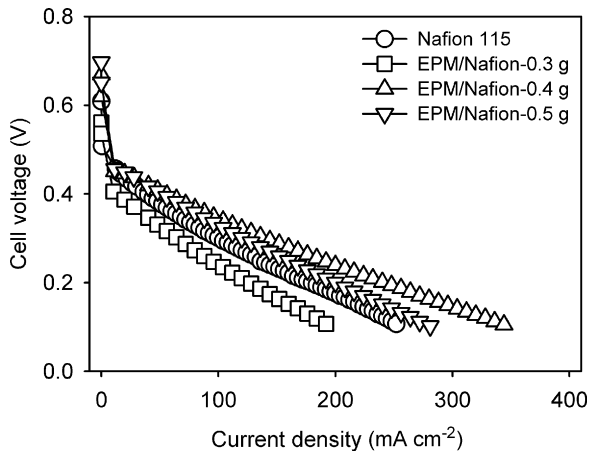


Fig. 4. Comparison of the polarization curves of the Nafion-impregnated electrospun PVdF composite membranes containing various amounts of Nafion with that of Nafion 115 membrane in DMFC at 65 °C in 2 M methanol solution. The data were collected with a methanol flow rate of 2.5 mL min⁻¹ at the anode and an O₂ flow rate of 200 mL min⁻¹ with a pressure of 20 psi at the cathode. The humidifier temperature for O₂ was same as that of the cell temperature. Anode: 0.6 mg PtRu cm⁻²; cathode: 1.0 mg Pt cm⁻².

for the three composite membranes. The three membranes show nearly the same methanol crossover, suggesting that the differences in the cell performance data are primarily due to the differences in the proton conductivity values (Table 1). The methanol crossover current for Nafion 115 membrane is not shown in Fig. 5 as it was too high and exceeded the limit of our equipment (200 mA cm⁻²) at 65 °C and in 2 M methanol solution.

Fig. 6 compares the electrochemical performance of the composite membrane containing 0.4 g Nafion (EPM/Nafion-0.4 g) in single-cell DMFC with that of Nafion 115 membrane at 65 and 80 °C in 1 M methanol solution. At both the temperatures, the composite membrane shows better performance than the Nafion 115 membrane although it has lower proton conductivity than Nafion 115. The better performance is due to the smaller thickness and lower methanol crossover in the composite membrane, as seen in Fig. 7, arising from a three-dimensional network structure of the electrospun PVdF membrane and the associated tortuosity for methanol permeability. The methanol crossover current density for Nafion 115 at 65 °C is higher than that for EPM/Nafion-

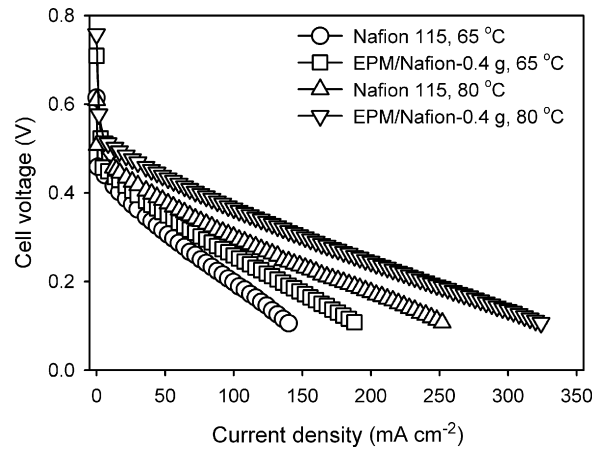


Fig. 6. Comparison of the polarization curves of the Nafion-impregnated electrospun PVdF composite membrane containing 0.4 g Nafion (EPM/Nafion-0.4 g) with that of Nafion 115 membrane in DMFC at 65 and 80 °C and in 1 M methanol solution. The other experimental conditions were same as that in Fig. 4.

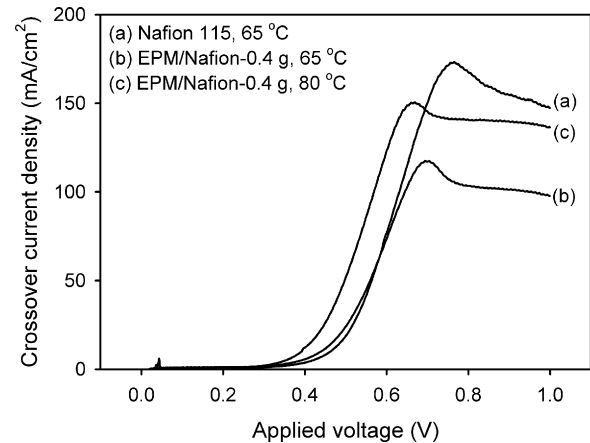


Fig. 7. Comparison of the methanol crossover current density of the Nafion-impregnated electrospun PVdF composite membrane containing 0.4 g Nafion (EPM/Nafion-0.4 g) with that of Nafion 115 membrane. The data were collected with 1 M methanol solution. The methanol crossover current density for Nafion 115 at 80 °C is not shown as the current density exceeded the limit of our equipment.

0.4 g and it is not shown in Fig. 7 at 80 °C as the current density exceeded the limit of our equipment. The data in Figs. 4–7 reveal that the EPM/Nafion-0.4 g is the optimum composition, exhibiting better fuel cell performance than the other composite membranes and Nafion 115 irrespective of the methanol concentration used.

4. Conclusions

Novel composite membranes consisting of electrospun PVdF (5 cm × 5 cm) and various amounts of Nafion have been prepared and evaluated in DMFC. Physical characterization data reveal that the composite membranes still maintain the unique three-dimensional network structure of PVdF. The composite membrane with an optimum Nafion content of 0.4 g exhibits better performance than Nafion 115 membrane in DMFC due to smaller thickness and lower methanol crossover arising from a tortuous framework structure of PVdF despite lower proton conductivity. Nafion contents lower or higher than 0.4 g lead to a decrease in cell performance due to a decrease in proton conductivity although the methanol crossover current density values are similar. The present study demonstrates that composite membranes that can block the methanol crossover while maintaining adequate proton conductivity

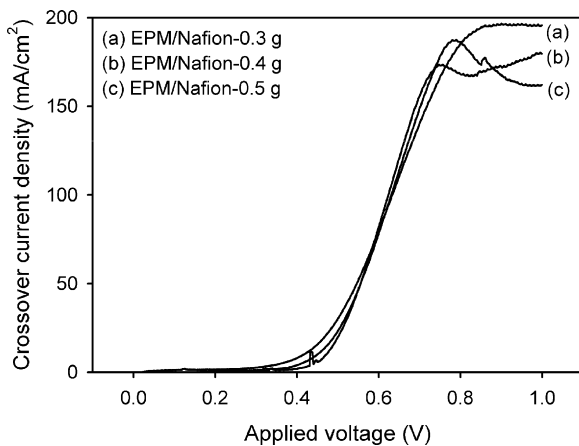


Fig. 5. Comparison of the methanol crossover current densities of the Nafion-impregnated electrospun PVdF composite membrane containing various amounts of Nafion at 65 °C in 2 M methanol solution. The methanol crossover current density for Nafion 115 is not shown as the current density exceeded the limit of our equipment.

ity may offer an attractive strategy to develop practical DMFC with good long term performance.

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