

Short communication

Preparation and characteristics of Nafion membrane coated with a PVdF copolymer/recast Nafion blend for direct methanol fuel cell

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Abstract

In order to enhance the compatibility between the electrode and the membrane and also to reduce the methanol cross-over from the anode to the cathode in direct methanol fuel cells, a Nafion membrane coated with a poly(vinylidene fluoride) copolymer/Nafion blend has been prepared and characterized. The coated Nafion results in a reduction in methanol cross-over and an enhancement in cell performance due to its improved compatibility with the electrodes.

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1. Introduction

Perfluorosulfonate ionomer membranes such as Nafion, Dow XUS and Flemion are used for proton-exchange membranes in fuel cells owing to their good electrochemical stability, satisfactory mechanical strength and high proton conductivity. When such membranes are applied to direct methanol fuel cells (DMFC), methanol cross-over from the anode to the cathode is usually significant. This cross-over not only wastes fuel but also causes performance losses at the cathode due to the consumption of oxygen and catalyst poisoning. Efforts to decrease methanol cross-over have focused on improvement of the polymer electrolyte membrane. Some new membranes have been shown to be successful in reducing the methanol cross-over [1–4], but they either sacrifice the mechanical strength of the native Nafion or increased the cell resistance due to poor compatibility between the membrane and electrode.

Poly(vinylidene fluoride) (PVdF) copolymer is miscible with Nafion-like ionomers [5,6]. In addition, the PVdF copolymer has sufficient mechanical strength and dimensional stability, and lower reactant permeability [7]. In this study, Nafion is coated with a layer that consists of a blend of vinylidene fluoride-hexafluoropropylene copolymer (PVdF copolymer) and recast Nafion. The effect of the coating layer on the electrochemical properties is investigated.

2. Experimental

2.1. Materials

A PVdF copolymer with 85 mol% vinylidene fluoride (Kynar Flex 2751, Mn = 380,000) was supplied from Atofina Chemicals Inc. The Nafion 117 membranes and 20 wt.% Nafion (1000 g eq⁻¹) solutions in a mixture of isopropanol, *n*-propanol and water were purchased from E.I. Dupont de Nemours & Co. The Nafion 117 membrane was pretreated as reported elsewhere [8]. The Nafion solution was used as received. Dimethylformamide (DMF) and methanol were purchased from Merck and

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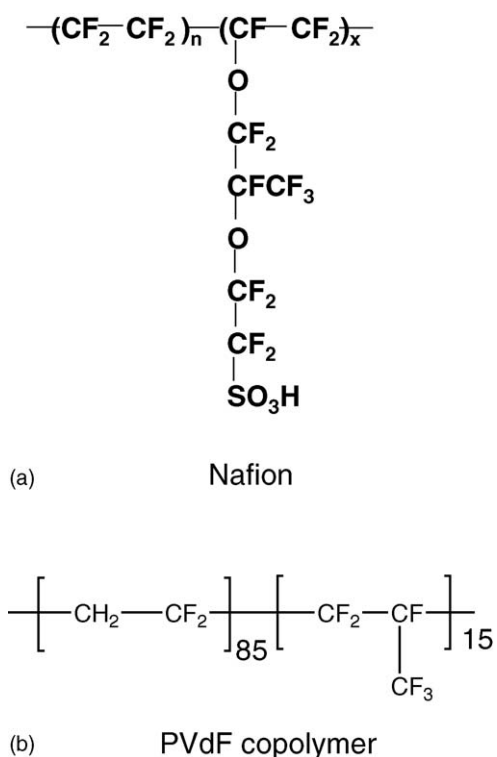


Fig. 1. Chemical structures of: (a) native Nafion 117 and (b) PVdF copolymer.

used without further purification. The chemical structure of the PVdF copolymer and the Nafion membrane are shown in Fig. 1.

2.2. Preparation of blend membrane and coated Nafion

A solution blend of PVdF copolymer with the ionomer was prepared according to the following procedure. First, 0.8 g of PVdF copolymer powder was fully dissolved in DMF, and from 1 g of 5 wt.% Nafion solution was added. The blend of P(VdF-co-HFP) and the ionomer was vigorously until it became homogeneous and transparent. The resulting solution was cast on to a flat glass surface by means of a doctor blade with a gap of 1 mm, then left in an oven at 30 °C for about 1 day and again under vacuum at 65 °C for 36 h to remove the residual solvents. The prepared films were peeled off the plate in a water bath.

The modified Nafion membrane with a coating layer of PVdF copolymer/Nafion blend was prepared by immersion of a Nafion 117 membrane in the blend solution. The thickness of the coated Nafion was increased by 1 μm compared with Nafion 117. For the coating layer and blend membrane, the relative content of PVdF copolymer and the Nafion was 80/20 (w/w).

2.3. Characterization

The ac impedance measurements were performed with a Solartron 1255 frequency response analyzer (FRA) over the frequency range 100 Hz to 10 MHz at room temperature. The proton conductivity was calculated from the bulk resistance of the membranes. The membrane samples were soaked in water for 1 day and then the proton conductivities were measured.

The catalysts for the anode and the cathode were applied to carbon paper (TGPH-090, Toray) by brushing. The catalyst loadings at the anode and the cathode were each 5 mg cm⁻². A 2 M solution of methanol was supplied at the anode with a Masterflex liquid micro-pump at a rate of 1 mL min⁻¹, while the cathode was fed with dried O₂ at a rate of 200 mL min⁻¹ with a flow meter. Cell performance was evaluated by using a DMFC unit cell with a cross-sectional area of 2 cm² and measured with an electronic load (WMPG-1000) that recorded the cell voltage under constant-current conditions.

Methanol cross-over was determined by measuring the limiting current density [9]. A 2 M solution methanol was fed to the anode of the membrane-electrode assembly (MEA), while the cathode was kept in an atmosphere of inert, humidified nitrogen. By applying a dynamic potential from 0.1 to 1 V at 0.05 V min⁻¹ on the cathode, the limiting current was measured.

The MEA was examined with scanning electron microscopy (Phillips SEM 535M). All specimens were sputter-coated with gold and micrographs were taken with an electric field strength of 20–30 kV.

3. Results and discussion

3.1. Adhesion between native Nafion 117 and electrodes

The cell performance is mainly influenced by the interfacial resistance and the electrode structure. The latter is closely related to catalyst utilization. Thus, hot-pressing conditions, which include process temperature, pressure and duration, are very important to cell performance. When the hot-pressing temperature is high and the hot-pressing duration is long, the physical adhesion between the electrodes and the membrane is enhanced and thus the interfacial resistance may decrease. On the other hand, the mass transfer of reactants and products may be hindered in the electrode. Therefore, the hot-pressing temperature and duration must be optimized with respect to the method of fabrication and the composition of the electrode.

The glass transition temperature of native Nafion 117 decreases with increasing water content, namely from 160 °C for a completely dry sample to 99 °C for a fully hydrated sample [10]. The glass transition temperature is 132 °C just before hot-pressing (Fig. 2). Generally, a hot-pressing temperature below 130 °C has been used [9,12,13], i.e., below the glass transition temperature of native Nafion [11]. When the MEA is hot-pressed, the native Nafion may still be a little rigid. Thus, the adhesion between the native Nafion and the electrodes can be somewhat poor.

Scanning electron micrographs for the cross-section of a conventional MEA consisting of: (a) Nafion 117, (b) catalyst layer and (c) carbon paper are given in Fig. 3. The adhesion at the interface between the Nafion 117 and the catalyst layer appears to be rather poor when the MEA is made under conventional hot-pressing conditions. Thus, detachment between the native Nafion and the electrodes can occur and cause an increase in ohmic loss and a decrease in long-term stability. Accordingly, coating layers were introduced on to the surface of the native

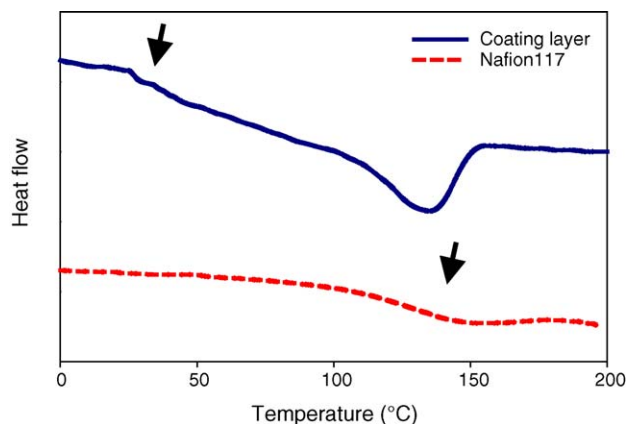


Fig. 2. Differential scanning calorimetric thermograms of coating layer and native Nafion 117.

Nafion 117 for enhancing the adhesion between the electrodes and the membrane and for reducing methanol cross-over.

3.2. Miscibility

Wide angle X-ray diffraction (WAXD) analysis was used to investigate the miscibility of the blend components in the membrane. X-ray diffractions of the recast Nafion, the PVdF copolymer and their blend membrane are given in Fig. 4. The recast Nafion made from the Nafion solution is known to have only a weak WAXD reflection at 18° due to the (100) plane of the crystalline PTFE backbone, and an amorphous halo centred at a 2θ value between 12 and 20° [14]. These features are not expected to contribute significantly to the diffractograms of the blend membrane with pure PVdF copolymer due to the low level of crystallinity of the recast Nafion and its composition in the blend membrane. The diffractogram of the pure PVdF copolymer contains characteristic reflections due to α -form crystallites, specifically the reflections due to the (020), (100) and (120) crystal planes located 20.4 , 18.8 and 18.2° , respectively.

In the blend membrane, there are broad reflections at 18.8 and 18.2° that are associated with the α -form crystallites of

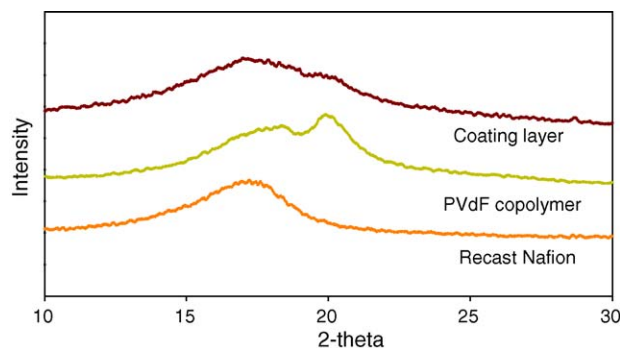


Fig. 4. X-ray diffractions of Nafion, PVdF copolymer and coating layer.

PVdF copolymer. They are similar to the weak reflection at 18° due to the crystalline PTFE backbone in the recast Nafion. By contrast, the characteristic reflection due to the (020) crystal planes located 20.4° has almost completely disappeared. The crystalline morphology of the PVdF copolymer in the blend membrane is influenced by the recast Nafion. This may be explained by a diluent effect on the crystal growth. These data demonstrate that the recast Nafion and the PVdF copolymer are rather miscible. Consequently, the glass transition of the blend membrane is shifted from 132°C (the glass transition of the Nafion) to 27°C (shown in Fig. 2).

Under the hotpress conditions of the MEA, the blend membrane is very flexible compared with native Nafion 117. This is why the blend membrane is introduced as the coating layer to enhance the adhesion between the electrode and the Nafion 117 membrane.

3.3. Methanol cross-over

For a DMFC, a proton-conducting membrane with low methanol permeability is required because methanol cross-over from the anode to the cathode leads to a lower cell voltage and also to a reduction in fuel efficiency. In general, it has been recognized that perfluorinated polymers such as Nafion have undesirably high methanol permeability. While the native Nafion 117 shows a high methanol permeability of $2.32 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ at room temperature, the methanol permeability of the coated membrane is much lower, viz., $9.5 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$.

The limiting current densities of the coated and native Nafion 117 were measured in order to evaluate the rate of methanol cross-over at an open-circuit voltage (OCV). The current density corresponding to oxidation of the transferred methanol at the cathode of the MEA is shown in Fig. 5. Little current is measured at voltages less than about 0.30 V because methanol oxidation requires a higher potential. The coated Nafion exhibits lower limiting current densities at both 30 and 50°C compared with native Nafion 117. The coated Nafion displays up to 23 and 27% reduction in methanol permeation flux at 30 and 50°C , respectively, compared with the native Nafion 117. This is related to an increase in the tortuosity of the conduction pathway in the coating layer. From these results, it is confirmed that the coating layer is an effective in suppressing methanol cross-over.

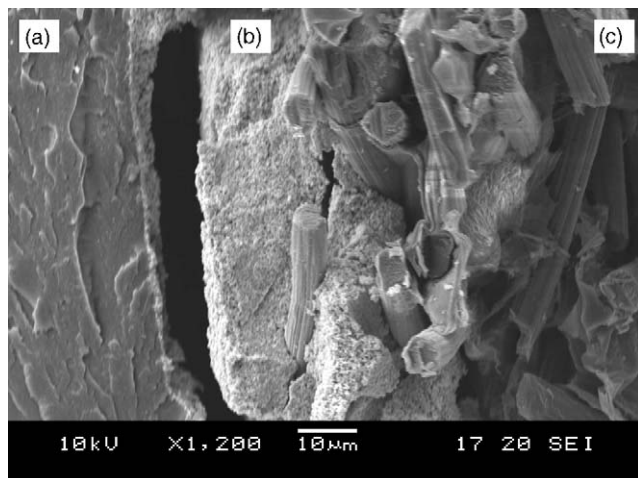


Fig. 3. Scanning electron micrographs of conventional MEA morphology: (a) native Nafion 117, (b) catalyst layer and (c) carbon paper.

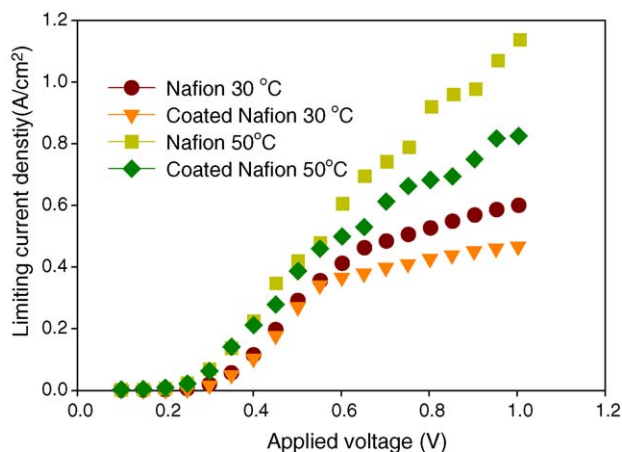


Fig. 5. Limiting current density of native Nafion 117 and coated Nafion at 30 and 50 °C.

3.4. Proton conductivity

The proton conductivities of the native Nafion 117 and the blend membrane based on a PVdF copolymer/the recast Nafion (80/20, w/w) are 1.0×10^{-1} and 5.5×10^{-3} S cm⁻¹ at room temperature, respectively. The lower proton conductivity of the blend membrane is attributed to the low concentration and mobility of the charge carriers in the membrane. In the blend membrane, it is clear that the number of the charge carriers, such as the sulfonic acid groups, is far less than in the native Nafion 117 and the mobility of the protons is also much restricted due to the presence of PVdF copolymer.

The thickness of the coating layer is controlled to about 1 μm so as not to sacrifice the proton conductivity significantly. The proton conductivity of the coated Nafion is 8.3×10^{-2} S cm⁻¹ and is about 80% of that of native Nafion 117.

3.5. Cell performance of coated Nafion

A difference in the cell performance between the native Nafion 117 and the coated Nafion appeared from the third day of hydration. The maximum power densities of the coated Nafion and the native Nafion 117 were 52.5 and 50.8 mW cm⁻², respectively. On the seventh day of hydration, the difference in cell performance at 30 °C became much more significant, as shown in Fig. 6. The maximum power densities of the coated Nafion and the native Nafion 117 were 58.3 and 49.8 mW cm⁻², respec-

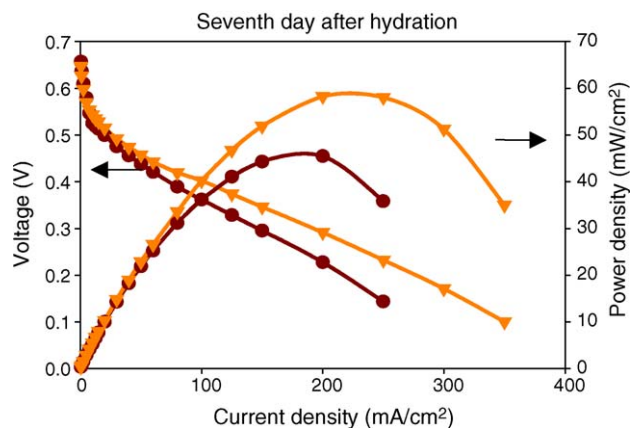


Fig. 6. Polarization curves of: (▼) coated Nafion and (●) native Nafion 117 at 30 °C.

tively. It should be noted that the coated Nafion takes more time to become completely hydrated.

The ohmic resistance is related with the slope of the pseudo-linear middle portion of the current–voltage curves shown in Fig. 6. The larger the resistance, the faster is the drop in the current–voltage curve with increasing current density. The values for the slope of the coated Nafion and the native Nafion 117 are -1.1 and -1.5 , respectively. This shows that the ohmic resistance of the coated Nafion is lower than that of the native Nafion 117. The total ohmic resistance is the combination of the electrode resistance, the membrane resistance and the interfacial resistance between the electrode and the membrane. The electrode resistances of the coated Nafion and the native Nafion 117 are the same. The proton conductivity of the coated Nafion is lower than that of the native Nafion 117. On the other hand, the ohmic loss of the coated Nafion in the polarization curves is smaller than that of the native Nafion 117. This means that the coated Nafion has a lower interfacial resistance.

Scanning electron micrographs of the cross-section of the MEA with and without the coating layer on the seventh day after hydration are presented in Fig. 7. The adhesion of MEA with the coating layer, as shown in Fig. 7(a), is found to be much enhanced compared with that in the absence of the layer, as shown in Fig. 7(b). Thus, the interfacial resistance can be decreased and, thereby, the ohmic resistance of the coated Nafion is lower than that of the native Nafion 117. The enhanced physical contact

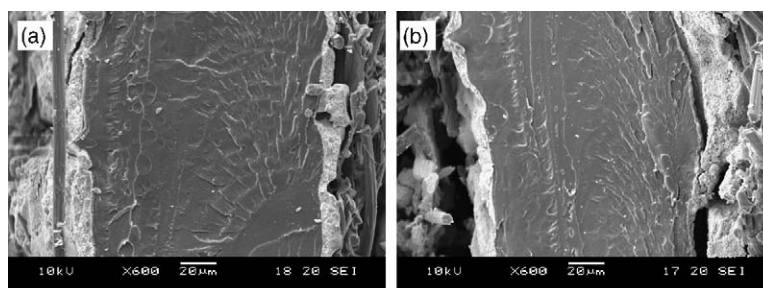


Fig. 7. Scanning electron micrographs of MEA (a) with and (b) without coating layer.

caused by the introduction of a coating layer can lead to an improvement in the long-term stability.

4. Conclusions

A novel modified Nafion membrane is prepared by coating native Nafion 117 with a PVdF copolymer/Nafion blend (80/20, w/w) so as to reduce methanol cross-over and to enhance the adhesion between the electrode and the membrane. The proton conductivity of the coated Nafion is a little lower than that of the native Nafion 117. The coating layer significantly reduces methanol cross-over in a DMFC by comparison with native Nafion. Electrode–membrane adhesion can be enhanced by introduction of the coating layer and this results in an improvement in cell performance.

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