Chemically-modified Nafion[®]/poly(vinylidene fluoride) blend ionomers for proton exchange membrane fuel cells

Min-Kyu Song[a], Young-Taek Kim[a], James M. Fenton[b], H. Russell Kunz[b], Hee-Woo Rhee[a,*]

[a]Department of Chemical Engineering, Hyperstructured Organic Materials Research Center, Sogang University, Seoul 121-742, South Korea
[b]Department of Chemical Engineering, University of Connecticut, Storrs, CT 06269, USA

Abstract

Miscible Nafion[®]/poly(vinylidene fluoride) blend membranes are prepared and characterized PVdF = poly(vinylidene fluoride). The membranes have high miscibility above a 60 wt.% Nafion[®] fraction when both polymers are dissolved in a solvent mixture of N,N'-dimethylacetamide and 2-propanol. Despite the high miscibility, the extremely hydrophobic PVdF component reduces the water uptake of Nafion[®]/PVdF blend, and the proton conductivity is much lower than that of a Nafion[®] 115 membrane even with a high weight fraction of Nafion[®]. To improve water affinity and proton conductivity, PVdF is chemically-modified by means of a dehydrofluorination reaction and H_2SO_4 doping prior to solution blend. The chemically-modified Nafion[®]/PVdF blend membrane shows similar conductance to Nafion[®] 115 without any auxiliary fillers. Nafion[®]/PVdF blend membranes of ~35 μm thickness are hot-pressed between catalyzed carbon paper ELAT[®] electrodes. A 25 cm^2 single cell delivers a maximum power of about 440 mW cm^{-2} at 900 mA cm^{-2} under H_2/O_2, which is comparable to the performance of Nafion[®] 115 under the same operating conditions.
© 2003 Elsevier Science B.V. All rights reserved.

Keywords: Proton exchange membrane fuel cell; Nafion[®]; Polyvinylidene fluoride; Polymer blend; Miscibility

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are of considerable practical interest because they offer high power density and efficiency with near-zero emissions for various applications such as electric vehicles, portable electronics, and residential power generation [1]. Up to now, perfluorosulfonic acid (PFSA) polymer membranes, represented by Dupont's Nafion[®], have been found to be particularly useful for PEMFCs due to their high electrochemical properties as well as excellent chemical resistance [2]. Nafion[®] is usually made with a non-crosslinked hydrophobic poly(tetrafluoroethylene) (PTFE) backbone that has pendant side chains of perfluorinated vinyl ethers which are terminated by hydrophilic cation exchange groups such as carboxylic and sulfonic acid moieties [3].

Nafion[®] resin can be dissolved in a mixture of distilled water and 2-propanol at high temperature (~25 °C) and pressure (250–450 psig) [4]. When the solvent is evaporated

at room temperature, the cast film is very brittle and also soluble in various polar solvents [5]. On the other hand, reinforced composite membranes have recently received much attention [6,7] since Bahar et al. disclosed the preparation of a composite ionomer membrane, Gore-Select[TM], in which microporous expanded PTFE film is repeatedly impregnated with PFSA polymer solution at moderate temperature [8]. A porous PTFE support membrane provides the composite structure with mechanical integrity and dimensional stability. Despite slightly lower proton conductivity, its small thickness of around 25 μm is responsible for a higher conductance than that of a Nafion[®] 117 membrane (~180 μm) [9]. Thus, the Gore-Select[TM] membrane has been reported [10] to show excellent performance in hydrogen fuel cells at temperatures below 90 °C. Nevertheless, the sluggish composite process and the inherently rare ionomer and support medium may increase the overall material cost. In addition, substantial methanol cross-over through the thin film causes a mixed potential and drastically reduces performance in direct methanol fuel cell (DMFC) applications [11].

In these respects, Nafion[®]-based polymer blend membranes have been proposed because miscible polymer blends

* Corresponding author. Tel.: +82-2-705-8483; fax: +82-2-711-0439.
E-mail address: hwrhee@ccs.sogang.ac.kr (H.-W. Rhee).

often produce synergetic effects [12] and can be easily and rapidly prepared by means of a simple casting method, which is a common process used in the plastic industry. Among various counter polymers, poly(vinylidene fluoride) (PVdF) has been shown to be miscible with Nafion®-like ionomers. PVdF has also sufficient mechanical strength and dimensional stability, and its reactant (H_2 or methanol) permeability is much lower than that of Nafion® and is not dependent on film thickness. Thus, a successful combination of the conducting characteristics of Nafion® and the physical stability of PVdF will be achieved if a miscible blend of Nafion® with PVdF can be obtained.

Kyu et al. [13] reported that a blend of Nafion® and PVdF was partially miscible below the crystallization melting temperature of PVdF. Moore et al. [14] studied the effect of the cation-type in Nafion® on the phase separation behaviour in Nafion®/PVdF blend systems, and obtained a highly miscible blend using a tetrabutyl ammonium (TBA) cation-form of Nafion®. On the other hand, it was recently found [15] that a Nafion®/PVdF blend film is not well hydrated despite the high compatibility between the parent polymers, and this results in large decrease in proton conductivity even at a low weight fraction of PVdF [16]. It might be concluded that the hydrophobic PVdF component does not allow water molecules to hydrate the membrane surface [17].

In this study, chemically-modified Nafion®/PVdF blend membranes are prepared in order to increase water uptake and proton conductivity, and their use in a PEMFC system is reported.

2. Experimental

A copolymer of vinylidene fluoride with hexafluoropropylene, PVdF-HEP (Elf-Atochem, Kynar® 2801) was dissolved in N,N'-dimethylacetamide (DMA, Aldrich). To prepare chemically-modified PVdF, Kynar 2801 powders were dehydrofluorinated by 1.5N potassium t-butoxide/dimethylformamide treatment described elsewhere [18], then precipitated polymer was dissolved in DMA. Nafion® gel was directly obtained from commercial 5 wt.% Nafion®/H_2O/2-propanol solution (Solution Technology, Inc., equivalent weight = 1100) by evaporating the alcoholic solvent at ambient temperature, then it was dissolved again DMA. The resultant 5 wt.% Nafion®/DMA solution was ultrasonically mixed with 5 wt.% PVdF/DMA solutions in the presence of additional 2-propanol (IPA) at 100 °C for 6 h. 2 wt.% Nafion®/PVdF/DMA/IPA solutions were coated on to glass plates and dried at 100 °C for 12 h in a convection oven. The chemically-modified Nafion®/PVdF blend membrane was boiled at 80 °C in 3 M H_2SO_4 aqueous solution for 24 h in order to functionalize the unsaturated PVdF component.

Proton conductivity was measured by means of the coaxial probe method with a HP 4194A LCR meter [19]. The polymer membranes were stored in distilled water to adsorb water, and then wiped quickly and insert into an in-house cell that allowed a coaxial probe to be pressed against one side of the membrane. The impedance of ionomer membranes was monitored over the frequency range 50 Hz to 10 MHz. The degree of water absorption, i.e. the ratio of the mass of the hydrated membrane to that of the dry membrane, was measured in accordance with ASTM D570. The thermal properties of blend membranes were evaluated by differential scanning calorimetry (DSC, Perkin-Elmer DSC7) which was calibrated with pure indium as a standard. X-ray diffraction studies were carried out with a Rigaku Rad-C 4037A1 diffractometer in symmetrical reflection geometry using Cu Kα emission. The tensile properties of blend films were measured using an Instron 4201 tester, in accordance with ASTM D882. Test specimens were 6 mm in width and approximately 100 μm in thickness. The grip distance was 50 mm and the cross-head speed was 25 mm min^{-1}.

Commercial, single-sided ELAT® (E-TEK, Inc.) electrodes were used as an anode and a cathode. Catalyst layers of 40 wt.% platinum on Vulcan XC72 carbon black (∼0.4 mg cm^{-2} Pt) were impregnated with commercial Nafion® solution. The weight of the electrode before and after brushing with commercial Nafion® solution was measured, and the Nafion® loading was found to be ∼0.7 and 0.6 mg cm^{-2} for the anode and the cathode, respectively. The final thickness of the gas-diffusion electrodes was around 300 μm, on a support of Toray TGPH090 carbon paper. The membrane and electrode assembly (MEA) was bonded together by hot-pressing under 80 kg cm^{-2} at 140 °C for 5 min, and then mounted into a 25 cm^2 single cell which was connected to a load (Scribner Series 890B Electronic Load).

The cell was compressed under 35 kg cm on each of the eight bolts, which corresponded to an internal pressure of about 1000 kPa. Gaskets made from incompressible PTFE-coated glass fabric (FURON, 275 μm nominal thickness) were placed on both sides of the membrane, and provided a seal on bolting the cell components together. High purity H_2 and O_2, passed through water-filled sparger bottle, were used as a fuel and an oxidant, respectively. Each cell was held at open-circuit for 24 h and at 200 mA cm^{-2} for 12 h for conditioning the MEA before the performance test. Cyclic voltammetry was carried out in a two-electrode system using a potentiostat (EG&G Model 273A) to monitor the redox reaction H_2 on the cathode side under an inert N_2 atmosphere. Polarization curves were recorded below 100 °C when the gas humidifier temperature was maintained at 80 °C for both the fuel and the oxidant gas stream. The gas flux stoichiometry was fixed at 2.0 for the anode and at 3.0 for the cathode by a mass flow controller (M.J.T. MR 500).

3. Results and discussion

3.1. Polymer blend characterization

The compatibility between two candidate polymer materials can be evaluated by various techniques such
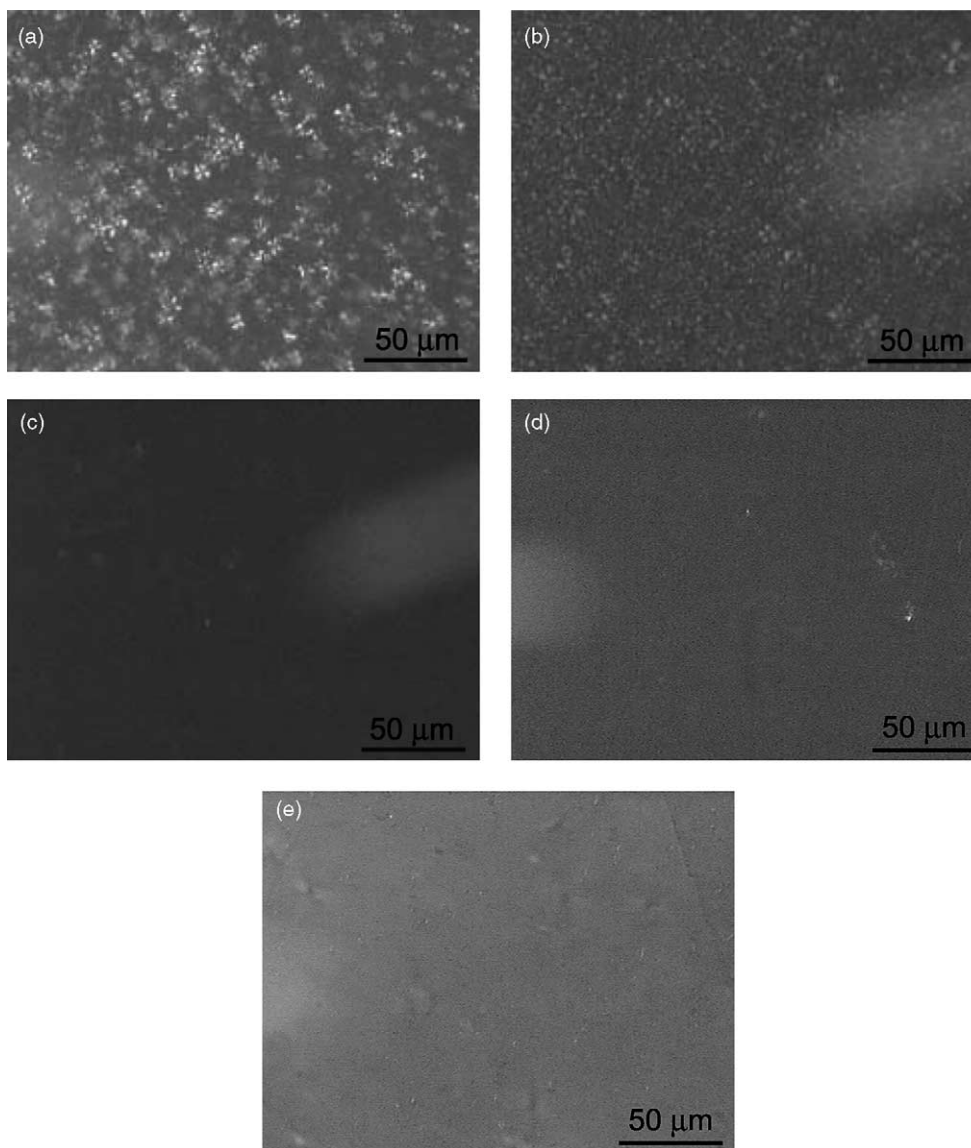
Fig. 1. Optical micrographs of Nafion®/PVdF blend membranes: (a) PVdF, (b) N/P = 4/6, (c) N/P = 6/4, (d) modified N/P = 6/4, (e) Nafion® 115.

as tensile tests, morphology studies, and thermodynamic measurements. In addition, Optical microscopy can be used to detect the possible existence of phase separation in a polymer mixture [20]. Optical micrographs of Nafion®/PVdF (N/P) blend membranes (150 μm nominal thickness) at different blend rations are presented in Fig. 1. In general, PVdF crystallizes in five different polymorphs (α, β, γ, δ, ε) and each crystal structure is different [21]. A pure semi-crystalline PVdF film cast at 100 °C has mixed crystals of the dendrite α- and spherulite γ-form, as shown in Fig. 1(a). The N/P (4/6, w/w) blend also shows coarse and inhomogeous morphology which is indicative of a phase-separated system, see Fig. 1(b). It is noticeable, however, that the distributed crystallites are decreased in size. The phase structure of a N/P (6/4) film is clearly different from pure PVdF and the N/P (4/6) sample, as shown in Fig. 1(c). This sample is featureless, homogeneous

and also optically transparent, which suggest that solution blending of the two polymer components should result in complete mixing at this composition. It is noticed that the chemically-modified Nafion®/PVdF (m-N/P) film also shows similar homogeneity at the same composition, see Fig. 1(d).

The miscibility between Nafion® and PVdF is confirmed by XRD in Fig. 2. Nafion® is known to have a weak peak at $2\theta = 18°$ due to the (1 0 0) plane of the crystalline PTFE backbone, while PVdF displays characteristic peaks at $2\theta = 21$ and $27°$ due to the α-form crystallites [22]. From the diffraction patterns, it is found that the peak intensity at $2\theta = 21°$ gradually decreases with increase of Nafion® content in the blend membrane. The decrease in relative peak intensity at $2\theta = 21°$ for the N/P (6/4) and the chemically-modified N/P (6/4) blends may result from a charge in the crystalline structure of PVdF. DSC thermograms of blend
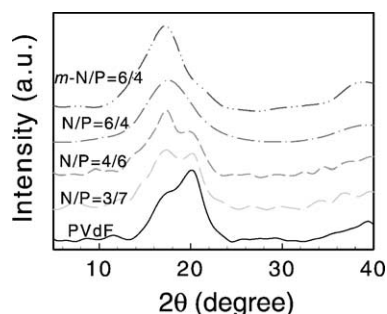
Fig. 2. XRD spectra of Nafion®/PVdF blend membranes at reflection mode.

polymers are also given in Fig. 3. The endothermic peak observed near 150 °C corresponds to the melting of the γ PVdF crystals. The melting temperature at 153 °C is depressed and merged to a lower temperature peak as the fraction of PVdF decreases. The melting temperature depression of a crystalline component means that the formation of a crystal is suppressed by the interaction between two blend components. The XRD and DSC data might reflect a high compatibility of Nafion® with Kynar® and PEGDA at 60 wt.% Nafion®.

Stress–strain curves and the tensile elongation at rupture of Nafion®-based blend films at different blend ratios are presented in Fig. 4. In immiscible polymer blends, the interfacial adhesion is usually not sufficiently strong for the stress to be efficiently transferred from one phase to another during yielding or fracture processes, and thus results in poor mechanical properties [23]. Therefore, measurement of the tensile properties of PEGDA/PVdF blends is another way to estimate the compatibility of PEGDA with PVdF. In particular, tensile elongation at rupture is very sensitive to the strength of the interface and is commonly measured to examine the efficiency of the blend [24]. The maximum break strength and elongation for Nafion® usually exceed 30 MPa and 200%, respectively [25]. In terms of tensile strength, the maximum yield strength for the blends are lower than that of the parent polymer, but the tensile strength at rupture for the chemically-modified N/P (6/4) blend is slightly increased compared with pure PVdF.
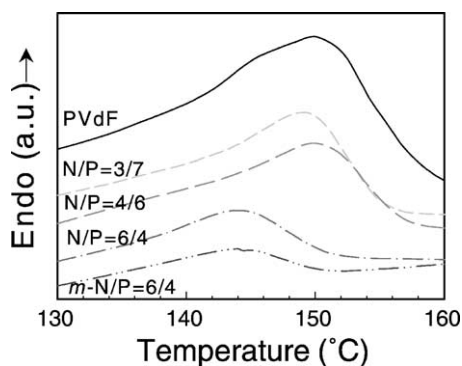
Moreover, N/P (6/4) exhibits elastomeric tensile elongation up to 600%, which indicates good interfacial adhesion between the polymer components. As shown in Fig. 4(b), the elongation at rupture of blend membranes illustrates a positive deviation over the entire blend composition with respect to the rule of mixture (dotted line), even though polymer blends tend to have properties intermediate between those of the separate components. Consequently, this blend can be categorized as highly compatible from an engineering point of view, although thermodynamically it may still be a partially miscible blend, yet with a high degree of homogeneity and phase dispersion.

3.2. Proton conductivity and water retention of chemically-modified membranes

For a cation-exchange polymer to be effective, water is essential to dissociate protons from the sulfonic acid and provide freely mobile protons. It is found, however, that the film surface of N/P blend membranes is less hydrophilic than the Nafion® 115 membrane, even at a highly compatible blend composition, due to the extremely hydrophobic nature of the PVdF component [15]. This is also detrimental to the uniform deposition of the catalyst layer in spray-brushing or hot-pressing of a catalyst layer containing an ionomer, which serves as an ionic bridge between the active sites on the catalyst layer and the membrane surface.

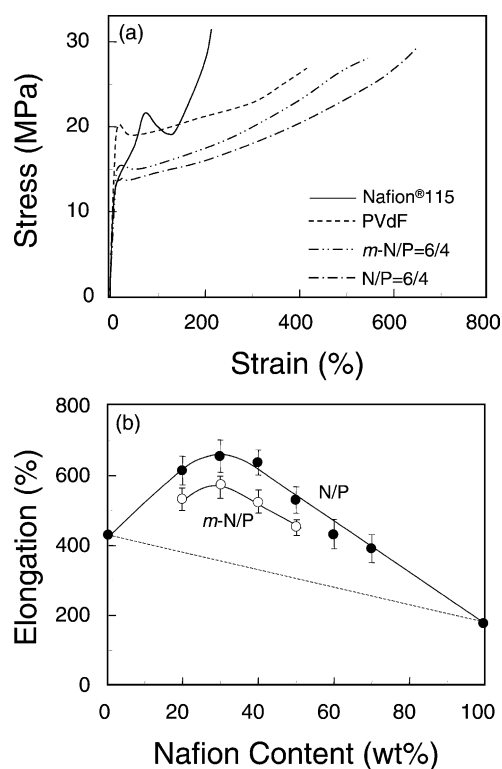In this study, chemical modification of PVdF by potassium t-butoxide is used to improves poor wetting

Fig. 3. DSC thermograms of Nafion®/PVdF blend membranes with different blend ratios.

Fig. 4. Tensile properties of Nafion®/PVdF blend membranes: (a) stress–strain curves; (b) tensile elongation at rapture.

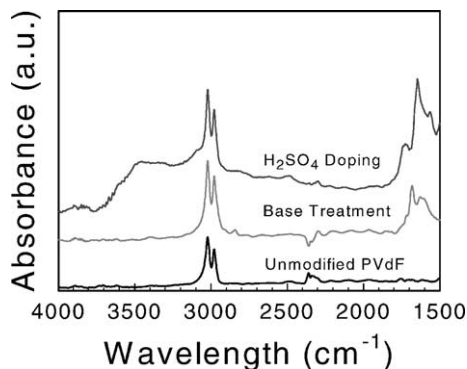Fig. 5. FTIR spectra PVdF during chemical modification step.

Fig. 6. Proton conductivities of Nafion®/PVdF blend membranes at room temperature.

characteristics. This dehydrofluorination reaction introduce distribution of the conjugated double-bond through the PVdF main chain, which results in a colour change from translucent colourless to dark black. The following strong acid treatment destroys the conjugated double-bonds and introduces functionalities that impart hydrophilic characteristics to the resulting polymer and makes it suitable for hydration [17].

The FTIR spectra of a PVdF film with respect to chemical modification steps are shown in Fig. 5. The characteristic peaks for pure PVdF are those near $3000 \, cm^{-1}$ and represent C–H stretching vibration. As the pure PVdF is exposed to potassium t-butoxide, chemical modification occurs as indicated by the rise of a sharp band which extends from 1750 to $1500 \, cm^{-1}$. This band can be associated mainly with the vibrational modes of C=C double bonds formed along the polymer backbone in dehydrofluorinated PVdF [26]. The band around $1615 \, cm^{-1}$ is assigned to the C=C stretching vibrational mode of –(CH=CF)– units, and the broad shoulder at $1715 \, cm^{-1}$ is assigned to the C=C stretching mode of –(CF=CF)– units. Bottino et al. [17] reported that the PVdF film was chemically-modified mainly by the introduction of a large distribution of conjugated double-bonds and polyenes up to 10 C=C, and a smaller amount of oxidized groups. The following treatment of PVdF with H_2SO_4 may destroy the polyene structure, to produce mainly C=O and C=C conjugated bands at $1650 \, cm^{-1}$ and a broad O–H band above $3500 \, cm^{-1}$.

It appears that treatment with a strong base has no effect on the properties of Nafion® in blend membranes because there is no visual colour change for Nafion® itself. As the PVdF component is chemically-modified by potassium t-butoxide solution, N/P (6/4) and chemically-modified N/P (6/4) membrane display a visual change from colourless to pale-brownish transparent, but spectroscopic analysis is not able to classify the formation of the polyene structure in binary blend membranes because of peak overlapping with Nafion®. To verify the change in water affinity after chemical treatment, proton conductivity and water uptake were studied.
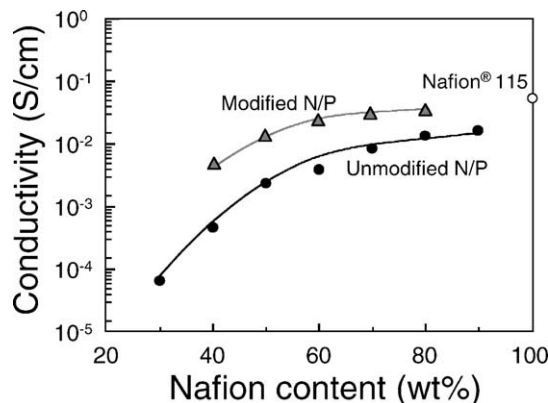
The proton conductivity of blend membranes with different blend ratios at room temperature are presented in Fig. 6. The proton conductivity was estimated by impedance spectra using the coaxial probe method [19]. In this method, when the thickness of the membrane (h) is small compared with the gap size ($b - a$) as well as the skin depth (δ), the current distribution across the membrane can be considered to be uniform and the membrane is characterized by a surface resistivity (R_s) which is defined by $R_s = 1/\sigma h$. The value of R_s is determined from the high-frequency intercept on the real axis in complex impedance spectra. Then, the measured resistance, R_T, is obtained by carrying out the integration [19]:

$$R_T = \int_a^b \frac{R_s}{2\pi r} dr = \frac{R_s}{2\pi} \ln\left(\frac{b}{a}\right) \qquad (1)$$

The conductivity of the membrane is related to the measured resistance by the following expression:

$$\sigma = \frac{1}{2\pi R_T h} \ln\left(\frac{b}{a}\right) \qquad (2)$$

Na$^+$-form Nafion® 115 membrane was boiled in 3 wt.% aqueous H_2O_2 solution for 2 h and then boiled in 1 M H_2SO_4 for 2 h. Finally, the H$^+$-form Nafion® 115 membrane was rinsed with deionized water at $100 \, °C$ for 1 h. Both Nafion® 115 and the blend membranes were equilibrated with water at ambient temperature for 3 days prior to conductivity measurement. The proton conductivity of pure Nafion® 115 reaches about $0.052 \, S \, cm^{-1}$ at room temperature, but that of N/P blend leveled off at around $0.012 \, S \, cm^{-1}$ above a 80 wt.% Nafion® fraction. It is obvious that the non-conducting PVdF component causes a decrease in proton conductivity because this value depends mainly on the water retention, but the decrease is much less given the good compatibility of Nafion® with PVdF at higher Nafion® content. By contrast, the conductivity of chemically-modified N/P (6/4) membranes is approximately $0.032 \, S \, cm^{-1}$ and this is much higher than that of the unmodified N/P (6/4) blend.
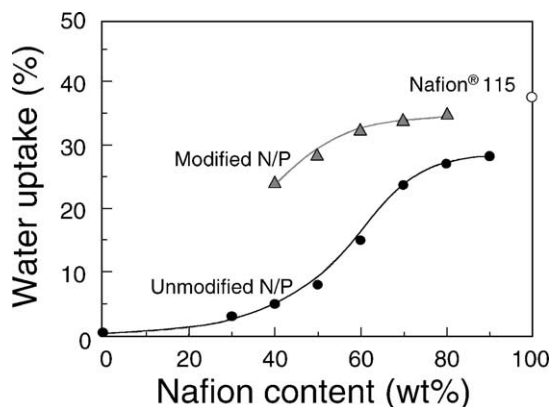
Fig. 7. Water uptake of Nafion®/PVdF blend membranes.

Fig. 8. Cyclic voltammograms of 25 cm² single cell in H_2/N_2 at 25 °C: (a) Nafion® 115; (b) chemically-modified N/P (6/4).

The water uptake of blend membranes is presented as a function of Nafion® fraction in Fig. 7. The dry weight of the samples was obtained after drying for 7 days at ambient temperature in dry room in which the moisture content is below 10 ppm, and then each sample was held in 100% relative humidity chamber at 25 °C for 3 days to obtain the swollen weight. Apparently, absorption from liquid water causes swelling in the polymer chains so that not only water of ionic hydration but also free matrix water is included in the total uptake. The maximum water uptake for Nafion® 115 from liquid water was found to be 0.37 and it is in good agreement with the reported values [27]. There was a non-linear dependence between water uptake and Nafion® fraction in the case of unmodified N/P blend samples. Water uptake was near zero for hydrophobic PVdF itself, as expected. Unmodified N/P blend membranes started to take up water rapidly above 70 wt.% Nafion® fraction, but all samples exhibited negative deviation from the additivity rule. It implies that water molecules did not pass through surface layer because the PVdF backbone strongly prevents the ionomer component from absorbing water molecules. Chemically-modified N/P (6/4) membranes show consider-able increase in water uptake over the entire blend of compositions. It is clear that his enhanced water retention affects proton conductivity jump for modified membranes.

3.3. Twenty-five centimeters square single cell test and performance

The optimum design of electrode structure is one of the most important factors to facilitate electrochemical reaction at the electrode–electrolyte interface in PEMFCs. Recently, Grot and Rajendran [2] reported that a 3-layer electrode structure composed of catalyst, diffusion and support layer improved gas and water management. The active catalyst layer is usually made with Nafion®-impregnated, nano-sized, platinum particles deposited on carbon black (Pt/C) particles. Both intermediate the diffusion layer and the support backing are treated with PTFE, which acts as a hydrophobizing agent as well as a binding agent between the
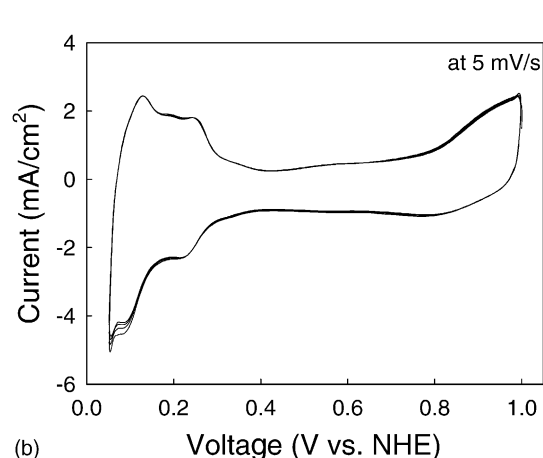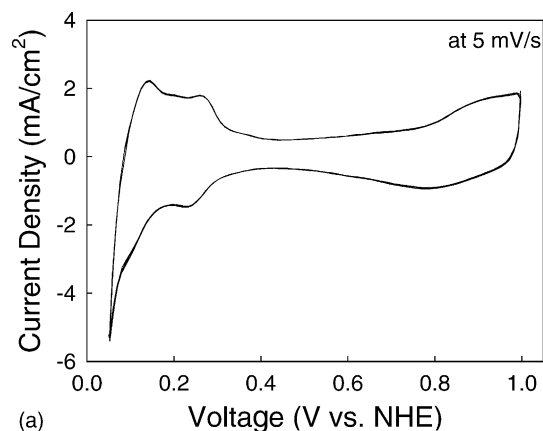
carbon particles. In this study, commercial ELAT® gas diffusion electrodes were used to eliminate the effect of the electrode structure on cell performance.

Typical cyclic voltammograms for 25 cm² single cells at a scan rate of 20 mV s⁻¹ when the anode/cell/cathode (A/C/C) temperature is fixed at 25 °C are shown in Fig. 8. Hydrated N_2 and H_2 gas were fed to the working and the counter electrodes, respectively. The redox peaks observed between 0.1 and 0.4 V correspond to the adsorption and desorption of H_2 on the catalyst sites. Assuming a coulombic charge of 220 mC cm⁻² for a smooth platinum [28], the electrochemical active surface areas were evaluated by subtraction of the capacitive charge from the coulombic charge for the oxidation of the atomic hydrogen adsorbed on the electrode (i.e. the area under the cathodic peak minus the double-layer charge). The ratio between the electrochemically active area and the geometric area is generally indicated as the roughness factor. It is calculated to be ∼27.5 and 28.2 cm² cm⁻² of geometric area for Nafion® 115 and modified N/P (6/4) membrane, respec-tively. This indicates that catalyst utilization is not influenced by the type of membrane used.

By repeating linear sweeps on the same cells at a scan rate of 2 mV s⁻¹, the hydrogen cross-over current is found to be approximately 2.1 and 3.6 mA cm⁻² for Nafion® 115 and
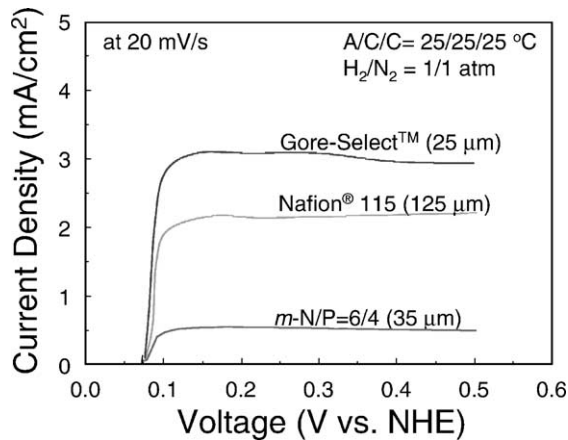
Fig. 9. Hydrogen cross-over current measurement of 25 cm^2 single cell in H$_2$/N$_2$ at 25 °C.

Gore-Select^{TM} membrane, respectively, as shown in Fig. 9. It is necessary to decrease the cross leakage of hydrogen as much as possible because the cross-over raises the over-potential of the cathode side as well as the loss of fuel. Although the rate-determining step of gas permeation through the ionomer membrane is usually the gas-diffusion process in the bulk of the membranes, and is inversely
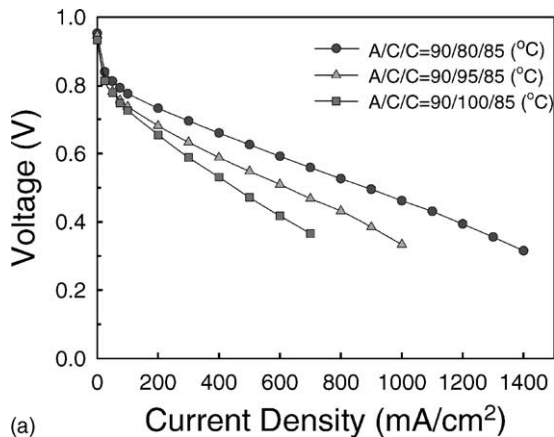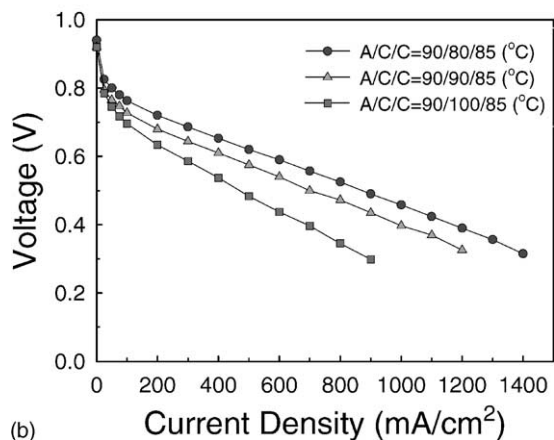
Fig. 10. Polarization curves of 25 cm^2 single cell using different ionomers: (a) Nafion$^{®}$ 115; (b) chemically-modified N/P (6/4).

proportional to the increase in membrane thickness, the gas permeability coefficient has been found to be nearly constant and independent of the thickness [29]. In this study, the maximum cross-over current for the chemically-modified N/P (6/4) membrane is below 0.65 mA cm^{-2}, which is significantly lower than that of commercial Nafion$^{®}$ 115 and Gore-Select^{TM} membrane, even though its thickness is around 40 μm. This can be explained by an increased hydraulic resistance to gas transport caused by the presence of the PVdF component.

The cell performance of the chemically-modified N/P (6/4) membrane is compared to that of Nafion$^{®}$ 115 at different operating temperatures in Fig. 10, where A/C/C denotes the temperature of anode, cell and cathode, respectively. All the voltage–current densities curves display similar polarization behaviour. Activation control leads to large potential drop in the low current density region below 50 mA cm^{-2}. The second region at intermediate current density is mainly affected by the intrinsic ohmic resistance and further potential decay progressively occurs in the diffusion-limited regime at high current density. The shape of the polarization curves is similar in the all ionomers used and the ohmic drop polarization mainly influences the whole fuel cell performance. A peak power density of about 440 mW cm^{-2} for chemically-modified N/P (6/4) blend is obtained in the current range of 0.9–1.0 A cm^{-2} at 80 °C. Although its performance is not significantly different to that of Nafion$^{®}$ 115, there is a slight improvement at higher temperature. This can be attributed to the difference in the overall electrical conductivity of the hot-pressed MEA.

4. Conclusions

A miscible Nafion$^{®}$/PVdF blend is obtained above 60 wt.% Nafion$^{®}$ fraction when a mixture of N,N'-dimethyl acetamide and 2-propanol is used as the solvent. The high miscibility is confirmed by an XRD intensity decrease at $2\theta = 21°$ due to the contribution of PVdF crystal and melting temperature depression around 150 °C in DSC thermograms. In addition, the increase in elongation at rupture for the Nafion$^{®}$/PVdF blend indicates excellent interfacial adhesion between the two polymers. Despite the high compatibility of the Nafion$^{®}$/PVdF blend, the hydrophobic PVdF component significantly reduces water affinity and proton conductivity, which appears to be a major limitation to this blend becoming commercially viable. It is found, however, that the water retention and conductivity of the Nafion$^{®}$-PVdF blend are enhanced by chemical modification of PVdF via a typical alkaline solution treatment and the followed by strong acid doping. Furthermore, a chemically-modified Nafion$^{®}$/PVdF (6/4) membrane shows a much lower hydrogen cross-over current than Nafion$^{®}$ 115, even at a low thickness (~35 μm). It also delivers a maximum power of 440 mW cm^{-2} at 900 mA cm^{-2} without any auxiliary conductive fillers. This performance is comparable to that of Nafion$^{®}$ 115 under the

same operating conditions. Given the synergetic results of the chemically-modified Nafion®/PVdF blend system, it is considered to be a promising low-cost ionomer matrix for PEMFC systems.

References

[1] J.A. Kerres, J. Membrane Sci. 185 (2001) 3.

[2] W.G. Grot, G. Rajendran, US Patent 5,919,583 (1999).

[3] P.D. Beattie, F.P. Orfino, V.I. Basura, K.Z. Zychowska, J. Ding, C. Chuy, J. Schmeisser, S. Holdcroft, J. Electroanal. Chem. 503 (2001) 45.

[4] J.-S. Jiang, D.B. Greengerg, J.R. Fried, J. Membrane Sci. 132 (1997) 273.

[5] R.B. Moore, C.R. Martin, Macromolecules 21 (1988) 1334.

[6] K.M. Nouel, P.S. Fedkiw, Electrochim. Acta 43 (16/17) (1998) 2381.

[7] J.S. Jiang, D.B. Greenberg, J.R. Fired, J. Membrane Sci. 132 (1997) 273.

[8] B. Bahar, A.R. Hobson, J.A. Kolde, U.S. Patent 5,547,551 (1996).

[9] K. Scott, W.M. Taama, P. Argyropulos, J. Membrane Sci. 171 (2000) 119.

[10] W.K. Lee, C.H. Ho, J.W. Van Zee, M. Murthy, J. Power Sources 84 (1) (1999) 45.

[11] K. Scott, W.M. Taama, P. Argyropulos, J. Membrane Sci. 171 (2000) 119.

[12] C. Manea, M. Mulder, J. Membrane Sci. 206 (2002) 443.

[13] T. Kyu, J.C. Yang, Macromolecules 23 (1990) 182.

[14] F.A. Landis, R.B. Moore, Macromolecules 33 (2000) 6031.

[15] M.K. Song, Y.T. Kim, H.W. Rhee, in: Proceedings of Electrochemical Society Meeting, 2–7 September 2001, San Francisco, CA, USA, 2001, p. 425.

[16] J.G. Lin, M. Ouyang, J.M. Fenton, H.R. Kunz, J.T. Koberstein, M.B. Cutlip, J. Appl. Polym. Sci. 70 (1998) 121.

[17] A. Bottino, G. Capannelli, O. Monticelli, P. Piaggio, J. Membrane Sci. 166 (2000) 23.

[18] A.J. Dias, T.J. McCarthy, J. Polym. Sci. 23 (1985) 1057.

[19] C.L. Gardner, A.V. Anantaraman, J. Electroanal. Chem. 395 (1995) 67.

[20] G.C. Kapataidakis, S.P. Kaldis, X.S. Dabou, G.P. Sakellaropoulos, J. Membrane Sci. 110 (1996) 239.

[21] F.J. Lu, S.L. Hsu, Macromolecules 19 (1978) 326.

[22] H. Lee, R.E. Salomon, M.M. Labes, Macromolecules 11 (1978) 171.

[23] A. Linares, J.L. Acosta, Eur. Polym. J. 33 (4) (1997) 467.

[24] N. Moussaif, R. Jérôme, Polymer 40 (1999) 3919.

[25] A.J. Greso, R.B. Moore, K.M. Cable, W.L. Jarrett, K.A. Mauritz, Polymer 38 (6) (1997) 1345.

[26] M.W. Urban, E.M. Salazar-Rojas, Macromolecules 21 (1988) 372.

[27] T. Lehtinen, G. Sundholm, S. Holmberg, F. Sundholm, P. Bjornbom, M. Bursell, Electrochim. Acta 43 (12/13) (1998) 1881.

[28] A.P. Costamagna, C. Yang, A.B. Bocarsly, S. Srinivasan, Electrochim. Acta 47 (2002) 1023.

[29] N. Yoshida, T. Ishisaki, A. Watakabe, M. Yoshitake, Electrochim. Acta 43 (24) (1998) 3749.