Direct methanol fuel cell membranes from Nafion–polybenzimidazole blends

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Abstract

Proton conducting membranes for a direct methanol fuel cell (DMFC) were fabricated from blends of Nafion[®] and polybenzimidazole (PBI) by solution casting. Prior to dissolution in the casting solvent, the sulfonic acid groups of the Nafion component of the blend were partially exchanged with sodium ions. The dependence of membrane proton conductivity and methanol permeability on the extent of proton substitution of Nafion during blending and on the PBI content of the final membrane was studied. It was found that membrane selectivity (the ratio of proton conductivity to methanol permeability) was the highest (four times that of Nafion 117) when fully protonated Nafion was used during blending and when the PBI content was 8%. DMFC performance of Nafion–PBI membranes (approximately 60 μm in thickness) was found to be superior to that of Nafion 117 at 1.0 and 5.0 M methanol feeds.
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Keywords: Direct methanol fuel cell (DMFC); Nafion[®]; Polybenzimidazole (PBI); Proton conducting membrane; Methanol crossover

1. Introduction

A copolymer of tetrafluoroethylene and perfluoro(4-methyl-3,6-dioxa-7-octene-1-sulfonic acid) known under the trade name Nafion[®] is the membrane material of choice for most fuel cell applications. Nafion, however, is costly and does not work particularly well in a direct methanol fuel cell (DMFC) because of its high methanol permeability (crossover). Methanol, that is not oxidized electrochemically at the anode, permeates through the membrane and is oxidized chemically by oxygen (from air) at the cathode, resulting in significant fuel cell performance degradation (a loss in methanol fuel utilization efficiency, poisoning of the cathode by CO intermediate, depolarization of the cathode, excessive water build-up at the cathode, and consumption of O_2 without electricity generation). While the operating conditions of a DMFC can be optimized to minimize, to some extent, methanol crossover (e.g. by the use of dilute methanol feed), development of membrane materials with low methanol permeability is the most obvious solution to the problem. This can be approached in two general ways: (a) synthesis of new materials with improved methanol barrier characteristics or (b) modification of existing materials.

There is extensive literature related to the development of new membrane materials with reduced methanol permeability, including sulfonated or phosphonated polyphosphazenes [1–3], sulfonated poly(arylene ketone) [4–7], sulfonated poly(arylene sulfone) [8–10], sulfonated poly(arylene sulfide sulfone) [11], sulfonated polyimide [12–15], sulfonated styrene block copolymers [16–18], phosphoric acid doped polybenzimidazole [19], radiation grafted polymers [20–23], functional fluoropolymers [24] and various blends [25–28] and composites [29–39]. Upon close inspection of the data in these prior studies, it appears that there is a universal conductivity–methanol crossover correlation, where the proton conductivity decreases as the methanol barrier property of the film improves. Thus, the thickness of a low conductivity, low methanol crossover membrane would have to be reduced in order to minimize membrane resistance losses in a fuel cell, which then negates the improved barrier properties of the membrane.

Alternatively, numerous physical and chemical modifications of Nafion have been reported which claim to reduce membrane methanol permeability. These modifications include: partial sub-

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stitution of the sulfonic acid groups with Cs$^+$ ions [40], Pd coating [41,42], sandwiching a Pd foil between two Nafion 115 films [43], incorporating inorganic nanoparticles into the polymer [44–53], interpolymerization [54,55], blending with vinylidene fluoride–hexafluoropropylene copolymer [56], pore filling [57] and surface treatments [58]. Unfortunately, a reduction of methanol permeability was always accompanied by a significant loss in proton conductivity.

Our group has been investigating blended polymeric membranes and composites for DMFC applications [26,27,59,60]. The systems studied include sulfonated polyphosphazene/polyacrylonitrile, sulfonated polyphosphazene/polyvinylidene-fluoride, sulfonated polyphosphazene/polybenzimidazole and various Nafion blends.

As an alternative to searching for better polyelectrolyte chemistry, one can combine (blend) existing polymers (one of which is a proton conductor like Nafion) in such a way as to make use of either interfacial or geometrical synergistic effects of polymer–polymer interactions. Advantageous morphologies would improve methanol fuel cell performance by restricting, for example, the Nafion component swelling of a blend in such a way that the decrease in methanol crossover is far greater than the concomitant reduction in proton conductivity.

We have already shown [60] that membrane–electrode assemblies fabricated from blended Nafion–FEP membranes generated power density that were similar to or better than that of Nafion 117, with 35–50% less methanol crossover. Also, for these membranes, the Nafion component content in the blend was reduced by a factor of 8, as compared to a commercial Nafion 117 membrane. Therefore, blending of Nafion with FEP leads not only to improvement in fuel cell performance, but also to significant reduction of membrane/MEA costs.

In the present paper, the properties and direct methanol fuel cell performance of Nafion–polybenzimidazole (Nafion–PBI) membrane blends are presented. In contrast to the Nafion–FEP system where the immiscibility of the components was evident, greater compatibility of Nafion and PBI was expected due to the possibility of acid–base interactions between imidazole nitrogens and sulfonic acid protons. PBI should function in such a system as a crosslinker with the resultant reduction of swelling and methanol permeability. It has already been demonstrated that membranes prepared from various acid–base polymer blends offered good mechanical properties and competitive fuel cell performance [61–65]. Hobson and coworkers [66], for example, showed that surface treating Nafion 117 with a PBI solution yielded membranes with reduced methanol crossover, but the maximum power density in a DMFC was very low (21–22 mW cm^{-2} with 2.0 M methanol at 60 °C). Membrane fabrication relied on an acid–base complexation mechanism shown schematically in Fig. 1. Due to the basic character of the imidazole nitrogen, partial or complete transfer of the proton from the sulfonic group occurs with the resultant formation of a hydrogen or ionic bond. Unfortunately, involvement of some fraction of the sulfonic acid groups in PBI crosslinking leads to an unavoidable decrease in the effective ion-exchange capacity and proton conductivity of the blended films which must be
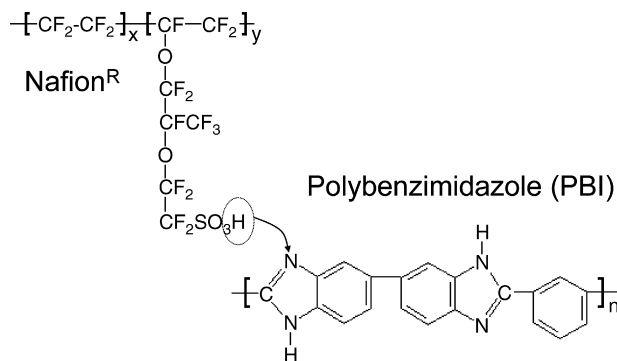

Fig. 1. Acid–base complex formation mechanism between the sulfonic acid group of Nafion and the imidazole nitrogen of PBI.

taken into account when considering the optimum PBI content of the final membrane.

2. Experimental

2.1. Membrane preparation

Dry Nafion powder was obtained by evaporating the solvent from a commercial Nafion solution (Liquion – 1100, a 15 wt.% Nafion solution, purchased from Ion Power Inc., Bear, Delaware, USA). Next, the Nafion powder was equilibrated in an aqueous NaCl/HCl solution with a pre-set Na$^+$/H$^+$ concentration ratio. There was partial exchange of protons with sodium cations on Nafion ion-exchange sites, establishing the protonation degree of the Nafion polymer. The substituted Nafion was dried and mixed with an appropriate amount of PBI (Aldrich) in DMAc solvent. Membranes were solution cast into a glass dish and the solvent was evaporated at 80 °C. Dried films were annealed at 150 °C for 3 h. The resultant membranes (50–100 µm in dry thickness) were removed from the glass dish and conditioned by boiling in 1 M H$_2$SO$_4$ followed by extensive washings with de-ionized water (during the acid boiling step, all Na$^+$ is removed from the membranes). Membranes were stored at room temperature in water for later use.

2.2. Protonation degree

A known weight of dry Nafion polymer that had been previously soaked in a NaCl/HCl solution (0.2–0.4 g of polymer with ion-exchange groups in SO$_3$H and SO$_3$Na forms) was placed in 50 ml of a 2.0 M NaCl solution at 25 °C and shaken occasionally for 48 h. Three 10 ml solution samples were then removed and the amount of H$^+$ released by the polymer was determined by titration with 0.01 M NaOH. The ion-exchange capacity (IEC) of the sample was calculated according to the following equation:

$$IEC\,(mmol\,g^{-1}) = \frac{0.05\nu}{m_{dry}} \qquad (1)$$

where ν (ml) is the endpoint volume of 0.01 M NaOH (average of the three titrations), and m_{dry} (g) is the dry weight of the polymer sample. The protonation degree was then

determined, as

$$\text{protonation degree (\%)} = \frac{\text{IEC}}{\text{IEC of fully protonated Nafion}} \times 100 \tag{2}$$

where the IEC of fully protonated sample is 0.91 mmol g^{-1}.

2.3. Proton conductivity

The proton conductivity of water-equilibrated Nafion and Nafion–PBI membranes was measured in the lateral (in-plane) direction by an ac impedance technique using an open-frame, two-electrode cell [67]. The mounted sample was immersed in deionized water at room temperature and measurements were made at 1 KHz using an Agilent 4338B milliohmmeter.

2.4. Membrane water swelling

Equilibrium water swelling (denoted as W, with units of g sorbed water g^{-1} of dry membrane) was determined at 25 °C according to:

$$W = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}} \tag{3}$$

where m_{wet} and m_{dry} are the weights of the water swollen and dry membrane samples (all in the SO$_3$H form), respectively.

2.5. Methanol permeability

Methanol permeability of membranes was measured using a custom-built two-compartment diffusion cell that was thermostated at 60 °C. The membrane was clamped vertically between two glass compartments, each compartment containing a magnetic stirring bar for solution agitation. The feed compartment was filled with 1.0 M methanol and the receiving chamber contained de-ionized water. The solution in the receiving compartment was circulated continuously through a differential refractometer for real-time determination of the methanol concentration. Methanol permeability (P), with units of cm^2 s^{-1}, was found by first determining the slope of a $\ln[1/(1 - C_R(t)(1 + V_R/V_L))]$ versus t plot (where $C_R(t)$ is the methanol concentration in the receiving compartment at a given time (t) after the start of a permeation experiment, V_L the solution volume in the methanol feed chamber, and V_R is the total volume of the receiving compartment and refractometer recirculation loop) and then substituting the slope into the following formula:

$$P = \frac{\text{slope}\,\delta}{A\left[\frac{1}{V_L} + \frac{1}{V_R}\right]} \tag{4}$$

where A is the membrane area, and δ is the water-equilibrated membrane thickness.

2.6. Scanning electron microscopy (SEM)

Dry membranes were manually fractured after cooling in liquid nitrogen. Specimens were sputter coated with palladium (2 nm thickness) and imaged on a Hitachi S4500 scanning electron microscope at 5 kV.

2.7. Wide angle X-ray scattering

Wide angle X-ray scattering (WAXS) spectra were obtained using a Rigaku D/MAX-2000 diffractometer operated at 45 KV and 40 mA, with a Cu anode. The scan range was 5–25° and the scan rate was 0.25° min^{-1}. Dry membrane samples were placed horizontally on a zero background quartz plate and measurements were taken at 25 °C.

2.8. MEA fabrication

A two layer catalyst system was used for both the anode and cathode. The first anode layer was composed of platinum–ruthenium alloy (1:1, Alfa Aesar) with 7 wt.% Nafion ionomer (5% solution from Aldrich) that was deposited onto an A-6 ELAT/SS/NC/V2 carbon cloth (E-TEK), where the catalyst loading was 3.0 mg cm^{-2}. The second layer, which was painted directly on the first, contained platinum–ruthenium alloy and 30 wt.% Nafion ionomer (5% solution, Aldrich) at a loading of 1.0 mg cm^{-2}. A thin film of Nafion ionomer (1–2 μm thick) was painted over the second catalyst layer. Similarly, the two-layer cathode was made using platinum black catalyst ink and an A-6 ELAT/SS/NC/V2 carbon cloth, where the first layer (3.0 mg cm^{-2}) contained 7 wt.% Nafion and the second layer (1.0 mg cm^{-2}) contained 40 wt.% Nafion. As in the case of the anode, the second Pt-black layer was coated with a thin film of Nafion. Both the anode and cathode were dried at 140 °C for 20 min, soaked in 1.0 M H$_2$SO$_4$ for 1 h, washed thoroughly with distilled water, and finally hot-pressed onto a Nafion–PBI membrane at 140 °C and 500 psi for 3 min, where the Nafion film on each electrode contacted directly the blend membranes.

2.9. Direct methanol fuel cell tests

Steady-state current density/voltage data were collected using a single cell test station (Scribner Series 890B) with mass flow and temperature control. The fuel cell (5.0 cm^2 MEA geometric area) operated at 60 °C, with 1 and 5 M methanol (at a flow rate of 2 ml min^{-1}) and humidified air (70 °C humidification bottle temperature and atmospheric pressure, at a flow rate of 500 sccm). Current–voltage data were collected during the first 5–10 h of fuel cell operation and reflect the initial performance of the membranes in a DMFC. The methanol crossover flux was determined by measuring the carbon dioxide concentration in the cathode air exhaust at open circuit, using a Vaisala GMM12B or GMM220A CO$_2$ detector. The sensor was calibrated with reference CO$_2$/N$_2$ gas mixtures containing 400–5000 ppm CO$_2$.

3. Results and discussion

The blend membrane fabrication procedure involved several steps of which the control of the initial concentration of SO$_3$H versus SO$_3$Na groups in the Nafion powder was the most important. If the casting solution contained the fully protonated
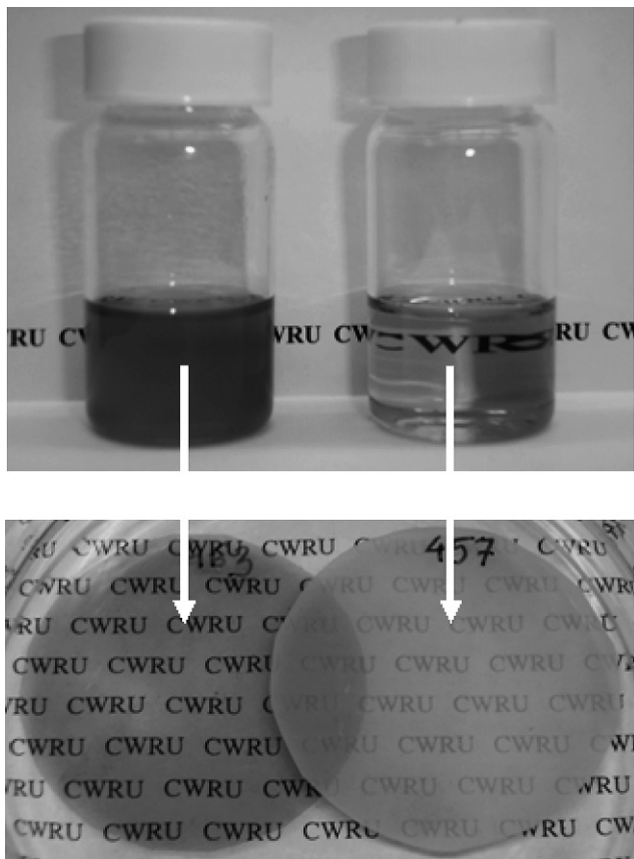
Fig. 2. Turbid suspension of Nafion(H^+)–PBI which gave a transparent recast film, while a transparent solution of Nafion(Na^+)–PBI produced a translucent membrane.

Fig. 3. Ion-exchange isotherms obtained for the dry Nafion powder (full circles) and Nafion 117 (open circles).

form of Nafion, then a turbid suspension was formed immediately upon addition of PBI (i.e. there was partial precipitation of the Nafion–PBI crosslinked complex). After solvent evaporation and annealing, a clear and strong film was obtained from this suspension (see Fig. 2). On the other hand, if the casting solution contained Nafion that was fully exchanged with sodium ions, then the casting solution was clear, with a brownish tint. After solvent evaporation and annealing, a translucent or opaque film was obtained that became quite elastic after swelling with water. In general, we found that membranes with near zero protonation degree were elastic (rubbery) in the water-swollen state for all PBI contents (1–8 wt.%), whereas membranes with a protonation degree >40% were stronger and exhibited increasing stiffness with increasing wt.% PBI. These observations indicated the importance of the initial protonation degree of the Nafion component of the blend on the properties of the final membrane.

3.1. H^+/Na^+ partitioning

In order to prepare Nafion powder with a controlled protonation degree, an experiment was designed to determine the Nafion partitioning equilibrium for external HCl/NaCl solutions of varying composition. The resulting absorption isotherm is shown in Fig. 3. Preferential absorption/substitution was not
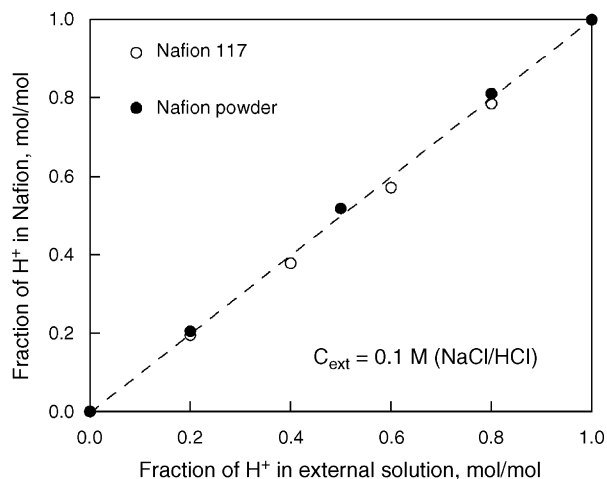
observed and the concentration ratio of Na^+/H^+ in the membrane mirrored that in the solution. As a check on this result, salt/acid uptake experiments were performed with a commercial Nafion 117 membrane and similar results were obtained, as shown in Fig. 3. A similar trend was reported by Okada et al. [68]. It was surprising that the partitioning equilibrium was the same for a commercial Nafion 117 membrane and an un-annealed Nafion powder. It is known [69–71] that there are physico-chemical differences between Nafion 117 and a recast Nafion film (prior to annealing). Based on the above results, it can be concluded that the ion-exchange group morphological details were not important in establishing the Na^+/H^+ partitioning equilibrium.

3.2. Water swelling

The primary purpose of blending Nafion with PBI was to reduce its swelling and thus decrease its methanol permeability. The dependence of Nafion–PBI membrane water content on the combined effects of PBI content and the initial protonation degree is shown in Fig. 4. The swelling decreased from a high of approximately 0.44 (when the membrane was made with Nafion powder in the sodium form only with 1% PBI) to a minimum of 0.15 (Nafion powder in the acid form only with 8% PBI). At a given initial protonation degree of the Nafion powder, there was a decrease in swelling with increasing PBI content. Similarly, there was a decrease in swelling with protonation degree at a given PBI content. At the highest PBI loading (8 wt.%), the sensitivity of membrane swelling to the initial Nafion protonation degree was the most pronounced. Not surprisingly, the dependence of water swelling on PBI content is stronger when the initial protonation degree of Nafion is higher (i.e. when there are more SO_3H groups in Nafion, there is more complexation with PBI). The water swelling of membranes with near zero initial protonation degree and 1–3% PBI were greater than that of commercial Nafion 117 (0.32 swelling). These membranes were also more elastic (rubbery) than those with a higher initial concentration of SO_3H. As will be discuss below, it appears
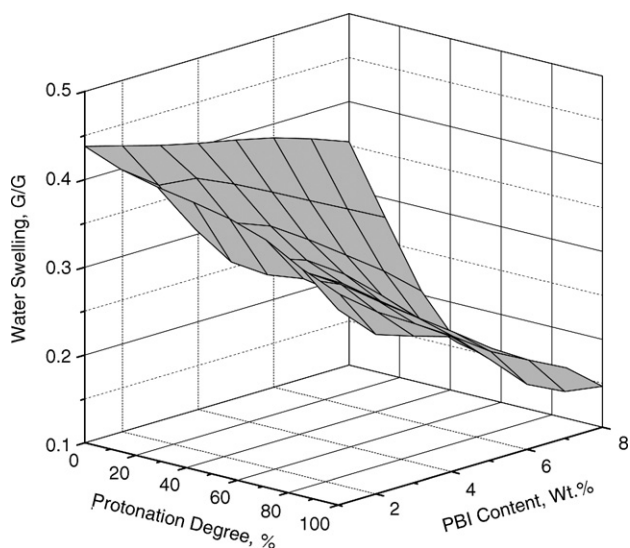
Fig. 4. Dependence of membrane water swelling on the Nafion powder protonation degree and PBI content.

Fig. 5. Membrane proton conductivity as a function of the Nafion powder protonation degree and PBI content.

that there was less Nafion crystallization during membrane annealing when the initial Nafion polymer was in the SO_3Na form. It can be concluded that both the protonation degree and the PBI content have significant influence on the blended membrane water swelling properties and that membranes with a low initial protonation degree swell more than commercial Nafion.

3.3. Proton conductivity

It is known that proton conductivity of sulfonic acid polyelectrolytes is strongly dependent on water content (membrane swelling). As shown in Fig. 4, a significant reduction in water content was observed for membranes containing more than 4% PBI when the protonation degree was >40%. The dependence of proton conductivity on protonation degree and PBI content (Fig. 5) showed a similar trend. The proton conductivity decreased with increasing PBI content and initial protonation degree from a maximum value of 0.11 to a minimum value of 0.015 S cm^{-1} (at 100% initial protonation and 8 wt.% PBI). The proton conductivity of a reference sample of Nafion 117 membrane was measured at 0.10 S cm^{-1} which is slightly less than that obtained with Nafion–PBI blends with near zero protonation degree and 1–2 wt.% PBI (i.e. those membranes that swelled more than Nafion 117 exhibited a conductivity greater than commercial Nafion).

3.4. Methanol permeability

The results presented in Fig. 6 show that crosslinking Nafion with PBI effectively decreased methanol permeability. When the initial protonation degree was >40%, the methanol permeability was significantly less than that in commercial Nafion 117 (3.6×10^{-6} cm^2 s^{-1}). The methanol permeability of a membrane at zero protonation degree and 1 wt.% PBI, was greater than that of commercial Nafion (as was the case for the
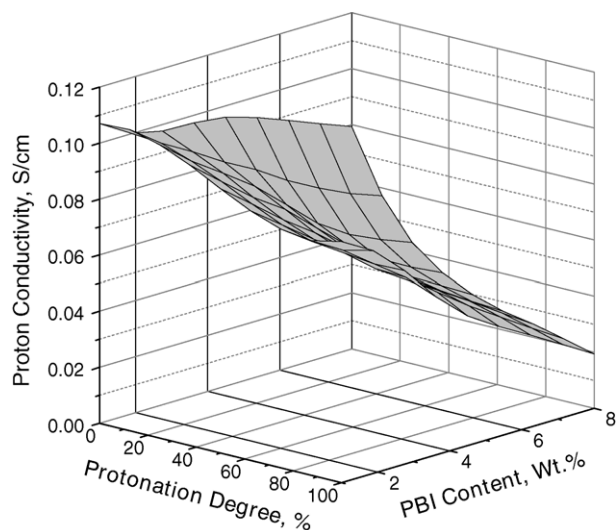
proton conductivity). The relative selectivity of the Nafion–PBI membranes (defined as the ratio of proton conductivity and methanol permeability as compared to a similar ratio for Nafion 117 [72]) ranged from 0.9 for a membrane containing 1 wt.% PBI and 0% initial protonation to 4.0 when the membrane contained 8 wt.% PBI and Nafion was initially in the SO_3H form (100% protonation). The use of the highest selectivity blends in a fuel cell would necessitate the use of an ultra-thin membrane (<20 μm in thickness) to sufficiently lower the MEA sheet (areal) resistance. Thicker membranes (50–100 μm) were employed in the present study (for ease of handling and MEA fabrication), where the optimum selectivity of 1.5–2.0 could be achieved with 3–7 wt.% PBI and an initial protonation degree >40%.
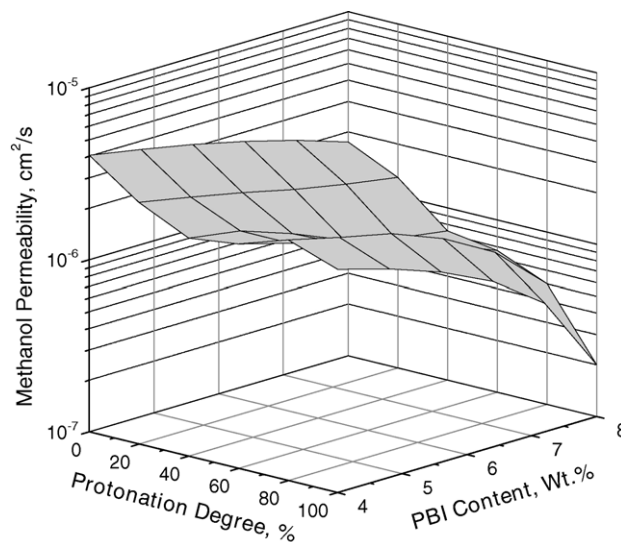

Fig. 6. Dependence of the membrane methanol permeability (at 60 °C) on the Nafion powder protonation degree and PBI content.
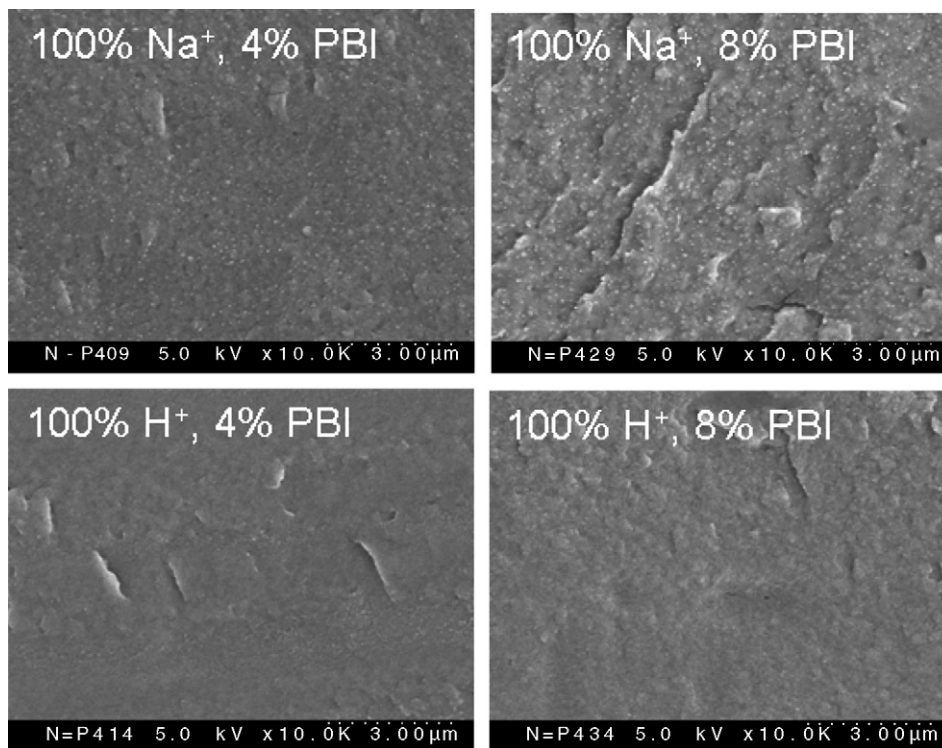
Fig. 7. Scanning electron micrographs of Nafion–PBI membrane samples containing 4 and 8% PBI, prepared from fully sodium exchanged and fully protonated Nafion powder.

3.5. SEM micrographs

As shown in Fig. 2, membranes prepared from Nafion that was fully exchanged with sodium ions were translucent or opaque, while those prepared from fully protonated Nafion were transparent. It was important to determine the morphological origins of these visual differences. Scanning electron microscopy was used to analyze the micro-topography of membrane cross-sections. Representative micrographs are shown in Fig. 7. It is clearly seen in the upper micrographs that sub-micron domains are present, which explains the observed translucency of membranes prepared from fully sodium exchanged Nafion powder. The domain size and domain density increase when the PBI content increases from 4–8 wt.%. A micro-domain-like structure was not observed in blends prepared from fully protonated Nafion powder (lower micrographs in Fig. 7). These membranes were transparent but became brittle (in the dry state) as the PBI content approached 8%. The presence of micro-domains or the lack thereof can be explained in terms of the interactions between the sulfonic acid groups of Nafion and the imidazole units of PBI. When fully sodium exchanged, there are no acidic protons in Nafion and no specific interactions between the sulfonate salt and imidazole groups. When the solvent was evaporated, a phase separation occurred with the resultant precipitation of PBI in the form of small domains. The situation was different when fully protonated Nafion was mixed in solution with PBI. Due to strong acid–base interactions, some precipitation of Nafion–PBI complex began immediately but no phase separation occurred during solvent evaporation. Nodules of Nafion–PBI complex might be

expected in the resultant dry membrane but were not observed in the SEMs; interactions between PBI and Nafion prevented extensive phase separation, hence homogeneous, transparent films formed.

3.6. X-Ray diffraction

Nafion is a semicrystalline polymer and blending with another polymer could influence its degree of crystallinity. Additionally, the annealing conditions (time and temperature) are known to affect the crystallinity properties of recast Nafion films [73–75]. In Fig. 8a and b, two sets of WAXS diffractograms are shown (4 wt.% PBI and different protonation degrees, and 40% protonation degree with different PBI contents). The two thin, vertical lines in each diffractogram mark the position of an amorphous halo and the crystalline peak for Nafion (15.5 and 17.5°, respectively). It can be seen in Fig. 8a that the crystallinity increased when the protonation degree was raised from 0 to 100%. This effect can be explained by the annealing temperature for the blended films (150 °C), which was greater than the T_g of the fully protonated form of Nafion (100 °C) but below that for Nafion in the sodium form (250 °C [76]). Thus, as the initial protonation degree was increased, the structural reorganization of recast Nafion was more efficient, leading to a higher degree of crystallinity. There was a decrease in crystallinity with increasing PBI content for a constant protonation degree (Fig. 8b); at the highest PBI content (8 wt.%), the crystalline peak nearly disappeared and the entire convolute shifted to lower angles. This result indicates that the strongly interacting PBI component of
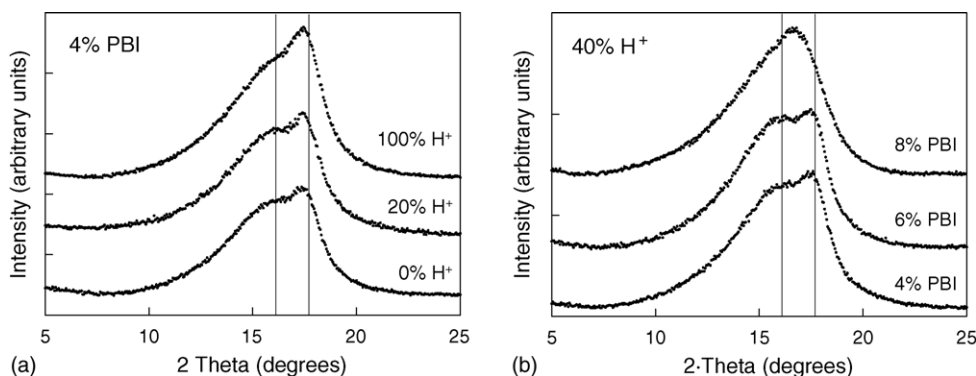
Fig. 8. Wide angle X-ray diffractograms of dry Nafion–PBI membranes: (a) effect of the powder protonation degree, (b) effect of PBI content.

the blended films perturbed the crystallization process of Nafion during annealing, particularly at the highest PBI content.

3.7. DMFC tests

Representative DMFC voltage–current density curves for three Nafion–PBI membranes of different PBI content are shown in Fig. 9, along with reference curves of Nafion 112 and 117 based MEAs. The blended membranes were fabricated from fully protonated Nafion and their thickness was between 60 and 70 μm. The MEA fabricated from a 3 wt.% PBI membrane delivered the highest power density, which was greater than that with either of the two Nafion MEAs. As the PBI content of a blended membrane was increased, the ohmic resistance increased and the DMFC performance decreased. All of the Nafion–PBI membranes exhibited a lower methanol crossover than that of Nafion 117 even though the blended films were two–four times thinner than Nafion 117 (1.25–1.5 times lower crossover, as compared to Nafion 117 and 2.0–2.7 times lower crossover, as compared to Nafion 112). The relatively high open-circuit voltage observed for all the blend membranes (>0.8 V) is an indication of a signifi-

cantly lower methanol crossover as compared to the both Nafion membranes tested.

It should be noted that methanol crossover had a significant impact on the DMFC performance curves. Although the areal resistance (membrane thickness divided by conductivity) of the membrane containing 7 wt.% PBI was nearly four times greater than that of Nafion 112, the V–i curve was only slightly below that of Nafion 112 because of a significant reduction (ca. 37%) in methanol crossover. Similarly, the V–i curve for Nafion 117 lies above that of Nafion 112 membrane, where the increased ohmic loss for the thicker membrane (Nafion 117) is offset by its greater methanol barrier property.

Another set of fuel cell performance curves is shown in Fig. 10, where MEAs were made from Nafion–PBI blends (40% protonation degree with 6 wt.% PBI) of three different thicknesses (55, 75 and 117 μm). The best DMFC result was obtained with the 75 μm thick membrane. Both, the thickest and the thinnest membranes gave lower power densities. Ohmic resistance affects dominated for the thickest film (the areal resistance of the 117 μm membrane was more than 50% greater than for the thinnest blend), whereas the methanol crossover in the 55 μm was too high (more than twice that of the thickest film). Thus, the choice of membrane thickness in a DMFC MEA is criti-
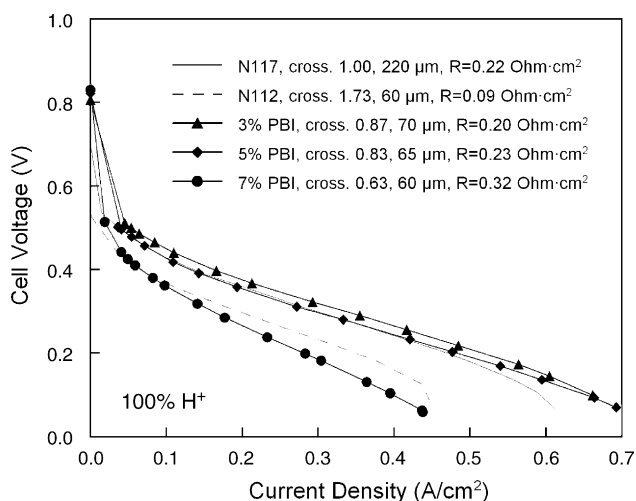

Fig. 9. Effect of PBI content on the DMFC performance of Nafion–PBI membrane samples prepared from fully protonated Nafion powder, with 3, 5 and 7% PBI. Crossover is expressed as a relative fraction of the methanol flux observed for a Nafion 117 membrane at the fuel cell operation conditions. R denotes the areal resistance ($\Omega\,cm^2$).
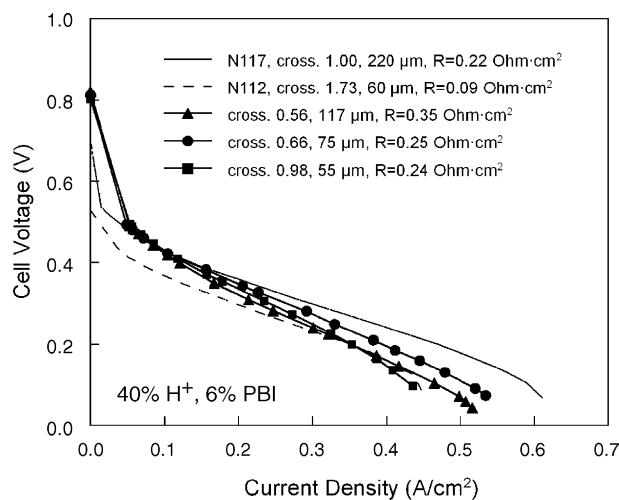

Fig. 10. Membrane thickness effect on the fuel cell performance. Nafion–PBI membranes contained 6% PBI and were prepared from 40% protonated Nafion powder.
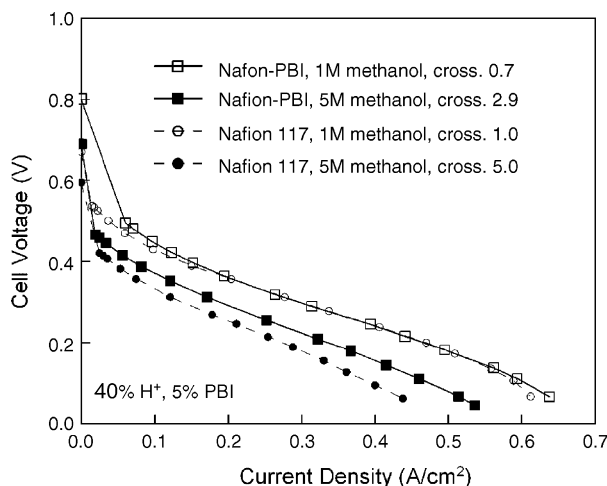
Fig. 11. DMFC performance comparison of Nafion117 and Nafion–PBI membranes at two methanol feed concentrations (1.0 and 5.0 M). The Nafion–PBI membrane contained 5% PBI and was prepared from 40% protonated Nafion powder, with a wet thickness of 80 μm.

cal, where competing effects of power loss due to membrane resistance and power gain due to the reduced crossover must be considered.

Due to the unacceptably high methanol permeability of commercial Nafion membranes most DMFC tests are performed with relatively dilute aqueous methanol solutions (typically 0.5 or 1.0 M). A blended Nafion–PBI membrane (6 wt.% PBI with Nafion 40% in the protonated form) was tested in a DMFC at a methanol feed concentration of 5.0 M. The results of the 5.0 M experiments are shown in Fig. 11, along with fuel cell performance curves for Nafion 117 and data for a 1.0 M methanol feed. The superiority of the blended film is evident, with the Nafion–PBI membrane outperforming Nafion 117 at 5 M methanol, although blended and non-blended Nafions performed equally well (based on power output) at 1.0 M feed methanol. When the methanol feed concentration was increased from 1.0 to 5.0 M, the methanol crossover flux through the Nafion–PBI membrane (already lower than that of Nafion at 1.0 M) increased by a factor of 4, whereas the flux through Nafion 117 at 5.0 M was five times greater than that at 1.0 M.

4. Conclusions

Proton conducting membranes for use in a direct methanol fuel cell were successfully fabricated from blends of Nafion and polybenzimidazole (PBI). The membrane proton conductivity and methanol permeability was dependent on the Nafion protonation degree prior to blending and on the PBI content. Membrane selectivity (defined as the ratio of proton conductivity to methanol permeability) was up to four times greater than that of Nafion 117, which was a favorable predictor of better DMFC performance. The energy density output with a blended membrane containing 4–6 wt.% PBI (with a Nafion protonation degree of 40%) was somewhat better than Nafion 117 at 1.0 M methanol and significantly better at 5.0 M methanol. The blended membranes out-performed Nafion 112 at both 1.0 and 5.0 M feeds.

Methanol crossover in the blended films was 1.2–2.7 times lower than those in Nafion 117/112. The Nafion–PBI membranes were approximately four times thinner than Nafion 117, which means that the MEAs contained four times less expensive fluoropolymer, which is an additional advantage of the blended system.

References

[1] R. Wycisk, P.N. Pintauro, J. Membr. Sci. 119 (1996) 155.
[2] Q. Guo, P.N. Pintauro, H. Tang, S. O'Connor, J. Membr. Sci. 154 (1999) 175.
[3] M.V. Fedkin, X. Zhou, M.A. Hofmann, E. Chalkova, J.A. Weston, H.R. Allcock, S.N. Lvov, Mater. Lett. 52 (2002) 192.
[4] B. Yang, A. Manthiram, Electrochem. Solid-State Lett. 6 (2003) A229.
[5] S. Vetter, B. Ruffmann, I. Buder, S.P. Nunes, J. Membr. Sci. 260 (2005) 181.
[6] X. Li, Ch. Liu, H. Lu, Ch. Zhao, Z. Wang, W. Xing, H. Na, J. Membr. Sci. 255 (2005) 149.
[7] X. Li, Ch. Zhao, H. Lu, Z. Wang, H. Na, Polymer 46 (2005) 5820.
[8] Y.S. Kim, L. Dong, M.A. Hickner, B.S. Pivovar, J.E. McGrath, Polymer 44 (2003) 5729.
[9] W.L. Hickner, M.A. Hickner, Y.S. Kim, J.E. McGrath, Fuel Cells 5 (2) (2005) 201.
[10] L. Li, Y. Wang, J. Membr. Sci. 246 (2005) 167.
[11] K.B. Wiles, F. Wang, J.E. McGrath, J. Polym. Sci. Polym. Chem. 43 (2005) 2964.
[12] Y. Woo, S.Y. Oh, Y.S. Kang, B. Jung, J. Membr. Sci. 220 (2003) 31.
[13] T. Yasuda, K. Miyatake, M. Hirai, M. Nanasawa, M. Watanabe, J. Polym. Sci. Polym. Chem. 43 (2005) 4439.
[14] K. Okamoto, Y. Yin, O. Yamada, Md.N. Islam, T. Honda, T. Mishima, Y. Suto, K. Tanaka, H. Kita, J. Membr. Sci. 258 (2005) 115.
[15] B.R. Einsla, Y.S. Kim, M.A. Hickner, Y.-T. Hong, M.L. Hill, B.S. Pivovar, J.E. McGrath, J. Membr. Sci. 255 (2005) 141.
[16] J. Kim, B. Kim, B. Jung, J. Membr. Sci. 207 (2002) 129.
[17] B. Kim, J. Kim, B. Jung, J. Membr. Sci. 250 (2005) 175.
[18] H. Bashir, J.L. Acosta, A. Linares, J. Membr. Sci. 253 (2005) 33.
[19] J.-T. Wang, R.F. Savinell, J. Wainright, M. Litt, H. Yu, Electrochim. Acta 41 (1996) 193.
[20] K. Scott, W.M. Taama, P. Argyropoulus, J. Membr. Sci. 171 (2000) 119.
[21] T. Hatanaka, N. Hasegawa, A. Kamiya, M. Kawasaumi, Y. Morimoto, K. Kawahara, Fuel 81 (2002) 2173.
[22] V. Saarinen, T. Kallio, M. Paronen, P. Tikkanen, E. Rauhala, K. Kontturi, Electrochim. Acta 50 (2005) 3453.
[23] M. Shen, S. Roy, J.W. Kuhlmann, K. Scott, K. Lovell, J.A. Horsfall, J. Membr. Sci. 251 (2005) 121.
[24] R. Souzy, B. Ameduri, Prog. Polym. Sci. 30 (2005) 644.
[25] C. Manea, M. Mulder, J. Membr. Sci. 206 (2002) 443.
[26] R. Carter, R. Wycisk, H. Yoo, P.N. Pintauro, Electrochem. Solid-State Lett. 5 (2002) A195.
[27] R. Wycisk, J.K. Lee, P.N. Pintauro, J. Electrochem. Soc. 152 (5) (2005) A892.
[28] B. Smitha, S. Sridhar, A.A. Khan, J. Appl. Polym. Sci. 95 (2005) 1154.
[29] B. Ruffmann, H. Silva, B. Schulte, S.P. Nunes, Solid-State Ionics 162–163 (2003) 269.
[30] H.Y. Chang, C.W. Lin, J. Membr. Sci. 218 (2003) 295.
[31] C.W. Lin, R. Thangamuthu, C.J. Yang, J. Membr. Sci. 253 (2005) 23.
[32] D.S. Kim, H.B. Park, J.W. Rhim, Y.M. Lee, Solid-State Ionics 176 (2005) 117.
[33] V.S. Silva, B. Ruffmann, H. Silva, Y.A. Gallego, A. Mendes, L.M. Madeira, S.P. Nunes, J. Power Sources 140 (2005) 34.
[34] V.S. Silva, S. Weisshaar, R. Reissner, B. Ruffmann, S. Vetter, A. Mendes, L.M. Madeira, S. Nunes, J. Power Sources 145 (2005) 485.
[35] C.S. Karthikeyan, S.P. Nunes, L.A.S.A. Prado, M.L. Ponce, H. Silva, B. Ruffmann, K. Schulte, J. Membr. Sci. 254 (2005) 139.
[36] Z. Gaowen, Z. Zhentao, J. Membr. Sci. 261 (2005) 107.

[37] T. Yamaguchi, H. Kuroki, F. Miyata, Electrochem. Commun. 7 (2005) 730.

[38] J. Schauer, L. Brozova, J. Membr. Sci. 250 (2005) 151.

[39] J.-P. Shin, B.-J. Chang, J.-H. Kim, S.-B. Lee, D.H. Suh, J. Membr. Sci. 251 (2005) 247.

[40] V. Tricoly, J. Electrochem. Soc. 145 (1998) 3798.

[41] T. Hejze, B.R. Gollas, R.K. Sauerbrey, M. Schmied, F. Hofer, J.O. Besenhard, J. Power Sources 140 (2005) 21.

[42] H. Tang, M. Pan, S. Jiang, Z. Wan, R. Yuan, Colloid Surf. Physicochem. Eng. Aspect 262 (2005) 65.

[43] C. Pu, W. Huang, K.L. Ley, E.S. Smotkin, J. Electrochem. Soc. 142 (1995) L119.

[44] P.L. Antonucci, A.S. Aroco, P. Creti, R. Ramunni, V. Antonucci, Solid-State Ionics 125 (1999) 431.

[45] P. Dimitrova, K.A. Friedrich, B. Vogt, U. Stimming, J. Electroanal. Chem. 532 (2002) 75.

[46] D.H. Jung, S.Y. Cho, D.H. Peck, D.R. Shin, J.S. Kim, J. Power Sources 118 (2003) 205.

[47] V. Baglio, A.S. Arico, A. Di Blasi, V. Antonucci, P.L. Antonucci, S. Licoccia, E. Traversa, F.S. Fiory, Electrochim. Acta 50 (2005) 1241.

[48] R.F. Silva, S. Passerini, A. Pozio, Electrochim. Acta 50 (2005) 2639.

[49] C.H. Rhee, H.K. Kim, H. Chang, J.S. Lee, Chem. Mater. 17 (2005) 1691.

[50] Y.-S. Park, Y. Yamazaki, Solid-State Ionics 176 (2005) 1079.

[51] K. Lee, J.-H. Nam, J.H. Lee, Y. Lee, S.M. Cho, C.H. Jung, H.G. Choi, Y.-Y. Chang, Y.-U. Kwon, J.-D. Nam, Electrochem. Commun. 7 (2005) 113.

[52] Y.-S. Park, Y. Yamazaki, Polym. Bull. 53 (2005) 181.

[53] J. Sauk, J. Byun, H. Kim, J. Power Sources 143 (2005) 136.

[54] N. Jia, M.C. Lefebvre, J. Halfyard, Z. Qi, P.C. Pickup, Electrochem. Solid-State Lett. 3 (2000) 529.

[55] J. Liu, H. Wang, S. Cheng, K.-Y. Chan, J. Membr. Sci. 246 (2005) 95.

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

[57] J.H. Shim, I.G. Koo, W.M. Lee, Electrochim. Acta 50 (2005) 2385.

[58] M. Walker, K.-M. Baumgartner, J. Feichtinger, M. Kaiser, E. Rauchle, J. Kerres, Surf. Coat. Technol. 116–119 (1999) 996.

[59] R. Wycisk, R. Carter, P.N. Pintauro, C. Byrne, Ion-exchange membranes from blends of sulfonated polyphosphazene and kynar flex PVDF, in: I. Pinnau, B.D. Freeman (Eds.), Advanced Materials for Membrane Separations, ACS Symposium Series 876, ACS, Washington, DC, 2004, p. 335.

[60] R. Wycisk, J. Lin, J. Lee, P.N. Pintauro, J. Chisholm, M. Kellner, Direct methanol fuel cell membranes from blends and composites, in: Proceedings of the ACS Conference Advances in Materials for Proton Exchange Membrane Fuel Cell Systems 2005, Asilomar Conference Grounds, Pacific Grove, California, February 20–23, 2005.

[61] J. Kerres, A. Ullrich, F. Meier, T. Haring, Solid-State Ionics 125 (1999) 243.

[62] M. Walker, K.-M. Baumgartner, M. Kaiser, J. Kerres, A. Ullrich, E. Rauchle, J. Appl. Polym. Sci. 74 (1999) 67.

[63] J.A. Kerres, J. Membr. Sci. 185 (2001) 3.

[64] L. Jorissen, V. Gogel, J. Kerres, J. Garche, J. Power Sources 105 (2002) 267.

[65] J.A. Kerres, Fuel Cells 5 (2) (2005) 230.

[66] L.J. Hobson, Y. Nakano, H. Ozu, S. Hayase, J. Power Sources 104 (2002) 79.

[67] T. Zawodzinski, M. Neeman, L.O. Sillerud, S Gottesfeld, J. Phys. Chem. 95 (1991) 6040.

[68] T. Okada, S. Moller-Holst, O. Gorseth, S. Kjelstrup, J. Electroanal. Chem. 442 (1998) 137.

[69] G. Gebel, Polymer 41 (2000) 5829.

[70] L.A. Zook, J. Leddy, Anal. Chem. 68 (1996) 3793.

[71] K. Broka, P. Ekdunge, J. Appl. Electrochem. 27 (2) (1997) 117.

[72] B.S. Privovar, Y. Wang, E.L. Cussler, J. Membr. Sci. 154 (1999) 155.

[73] Z. Siroma, N. Fujiwara, T. Ioroi, S. Yamazaki, K. Yasuda, Y. Miyazaki, J. Power Sources 126 (2004) 41.

[74] H. Matsuyama, M. Matsui, Y. Kitamura, T. Maki, M. Teramoto, Sep. Purif. Technol. 17 (1999) 235.

[75] K. Lee, A. Ishihara, S. Mitsushima, N. Kamiya, K. Ota, J. Electrochem. Soc. 151 (4) (2004) A639.

[76] K.A. Mauritz, R.B. Moore, Chem. Rev. 104 (2004) 4535.