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Blend Membranes Based on Acid-Base Interactions for Operation at High Methanol Concentrations

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The performances in direct methanol fuel cells (DMFCs) of membrane electrode assemblies (MEAs) fabricated with blend membranes based on sulfonated poly(ether ether ketone) (SPEEK) and poly(sulfone) bearing 2-amino-benzimidazole have been compared with SPEEK and Nafion ionomers in the anode and cathode catalyst layers as well as with that of MEAs fabricated with Nafion 115 membrane and Nafion ionomer in the electrodes. The SPEEK ionomer offers better compatibility with a lower interfacial resistance compared to Nafion ionomer when used with the blend membranes. Also, MEAs fabricated with the blend membrane and SPEEK ionomer in the electrodes exhibit better performance in DMFC compared to that with Nafion membrane and Nafion ionomer due to lower methanol crossover. Moreover, MEAs fabricated with the blend membranes exhibit less performance dependence on methanol concentration (1–10 M) compared to those fabricated with the Nafion membranes, making the former attractive to operate at high methanol-feed concentrations.
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Proton exchange membranes employed in direct methanol fuel cells (DMFCs) require low methanol permeability as well as good proton conductivity. Nafion, which is a perfluorinated sulfonic acid, is currently the choice of membrane for DMFCs due to its high proton conductivity and chemical stability, but it suffers from high methanol crossover from the anode to the cathode during DMFC operation. The methanol crossover through the membrane leads to a loss of voltage at the cathode due to the oxidation of the permeated methanol and poisoning of the cathode catalyst that limits the methanol-feed concentration to <2 M. These difficulties have prompted the development of alternative membranes, including sulfonated poly(ether ether ketone) (SPEEK),[1,2] poly(ethersulfone),[3,4] poly(phosphazene),[5] and poly(ether nitrile).[6]

Our group[7,8] has been pursuing blend membranes based on acid-base interactions between SPEEK (an acidic polymer) and poly(sulfone) bearing benzimidazole side groups (a basic polymer) to suppress methanol crossover. However, the electrochemical performances of these membranes in DMFCs were evaluated with membrane electrode assemblies (MEAs) fabricated with the acid-base blend membrane and Nafion ionomer in the electrodes. We recently showed that the MEAs fabricated with a SPEEK membrane and SPEEK ionomer in the electrodes exhibit better performance in DMFC than that fabricated with a SPEEK membrane and Nafion ionomer in the electrode, which was attributed to a decreased interfacial resistance in the MEA as well as a larger electrochemical active area in the catalyst layer arising from a better compatibility between the electrolyte membrane and electrodes.[9] We present here the electrochemical performance evaluation of MEAs fabricated with acid-base blend membranes (SPEEK + polysulfone bearing 2-amino-benzimidazole) and SPEEK ionomer in the electrodes with an aim to achieve better compatibility between the electrolyte and electrodes and to minimize the polarization losses. Because MEAs with low methanol permeability can enable the operation of DMFCs at higher methanol concentrations (>2 M) and thereby offer higher energy density and rapid response to dynamic loads,[10] we also present here the evaluation of electrochemical performance under various methanol-feed concentrations (1–10 M).

Experimental

Membrane preparation.— Two samples of SPEEK were prepared by sulfonating commercially available poly(ether ether ketone) (PEEK450 PF, Victrex) with concentrated sulfuric acid at room temperature for a specified time,[11] giving a degree of sulfonation of 42 and 49%. The poly(sulfone) bearing 2-amino-benzimidazole (PSf-ABIm) was synthesized by a condensation reaction between a carboxylated poly(sulfone) with a degree of carboxylation of 1.90 and 2-amino-benzimidazole (ABIm) using triphenylphosphite as a dehydrating agent at 100°C for 3 h, as reported by our group before.[8] The SPEEK/PSf-ABIm blend membranes were prepared by blending SPEEK [with an ion exchange capacity (IEC) of either 1.33 or 1.51 meq/g] with different amounts of PSf-ABIm (3 or 5 wt %) using *N*,*N*-dimethylacetamide as a solvent, followed by casting the resultant solution onto a glass plate and drying at 90°C for 24 h.

Equilibrium liquid uptake W_{uptake} was determined by first measuring the weight of the wet membrane after equilibrating the membranes at a desired temperature and methanol concentration for 24 h and then the weight of the dry membrane as

$$W_{uptake} = (W_{wet} - W_{dry})/W_{dry} \times 100 \quad [1]$$

where W_{wet} and W_{dry} are, respectively, the weight of the wet and dry membranes. Proton conductivity of the water-equilibrated membranes was measured in the lateral direction (i.e., in plane) using an open-window-framed two-platinum electrode cell[12] with an HP 4192A LF impedance analyzer.

MEA fabrication and electrochemical characterization.— For fabricating the catalyst layer with the SPEEK ionomer, SPEEK with an IEC of 1.33 meq/g was used for both the anode and cathode electrodes. The SPEEK was first dissolved in *N*,*N*-dimethylformamide (DMF), then a desired amount of the SPEEK/DMF solution (14.5 wt %) was transferred into a water/isopropyl alcohol (IPA) mixture, sonicated for 30–50 min, mixed with the catalyst powder, and sonicated again for 1–2 h. The catalyst layer was prepared by brushing the anode or cathode catalyst ink onto a gas-diffusion layer (A-6 Elat/SS/NC/V2 carbon cloth E-TEK Inc.). In the case of electrodes containing Nafion ionomer, the catalyst powder was dispersed in a water/IPA mixture, followed by mixing with Nafion solution by sonication for 1 h and painting the resultant ink onto the gas-diffusion layer. The MEAs with Nafion membranes were all fabricated with Nafion ionomer in the catalyst layer. The anode catalyst layer consisted of 40 wt % Pt–Ru (1:1) on Vulcan XC-72 carbon black (E-TEK Inc.) with either SPEEK or Nafion ionomer. The cathode catalyst layer consisted of 20 wt % Pt on carbon black (E-TEK Inc.) with either SPEEK or Nafion ionomer. The Pt–Ru and Pt loadings in the anode and cathode were 1.0 mg/cm^2. The MEAs were fabricated by hot pressing the anode

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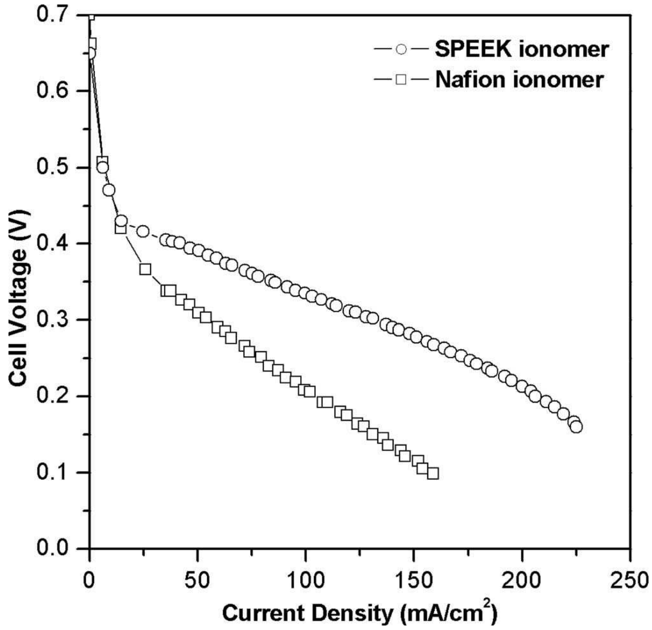

Figure 1. Comparison of the performances in DMFCs of MEAs fabricated with the SPEEK/PSf-ABIm blend membrane and either SPEEK or Nafion ionomer in the electrodes at 1 M methanol concentration.

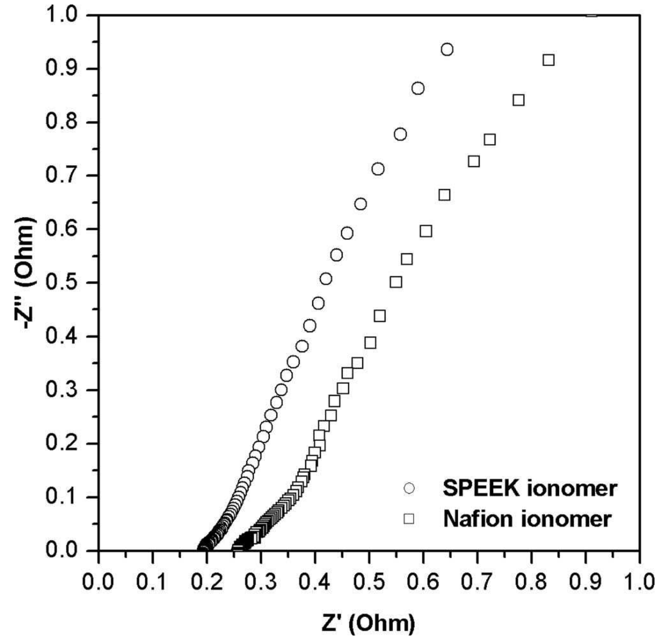

Figure 2. Comparison of the Nyquist plots obtained with MEAs fabricated with the SPEEK/PSf-ABIm blend membrane and either SPEEK or Nafion ionomer in the electrodes.

and cathode electrodes onto either Nafion or SPEEK/PSf-ABIm blend membranes. The hot-pressing conditions were 140°C, 80 psi for 2.5 min and 100°C, 40 psi for 3 min, respectively, with the Nafion and the blend membranes. Fuel cell tests were performed using a single-cell hardware with an active area of 5 cm^2 at 65°C with methanol at a flow rate of 2.5 mL/min and humidified oxygen at a flow rate of 200 mL/min without backpressure.

Methanol crossover was determined by a voltammetric method by feeding methanol solution at a flow rate of 2.5 mL/min into the anode side of the MEA, while the cathode side was supplied with an inert humidified N_2 atmosphere. The flux rate of permeating methanol was determined by measuring the steady-state limiting current density resulting from complete oxidation at the cathode on applying a positive potential.[13]

Impedance analysis was performed with a Volta Lab 80 potentiostat (PGZ 402 Universal potentiostat) at room temperature. The anode and cathode were supplied, respectively, with 1 M methanol (at a flow rate of 2.5 mL/min) and hydrogen (at a flow rate of 10 mL/min). The cathode was used as a dynamic hydrogen electrode for the measurement of anode impedance. The frequency range was 100 mHz to 5 kHz, and the amplitude of the sinusoidal current signal was 5 mV.

Results and Discussion

To investigate the effect of SPEEK vs Nafion ionomer on the performance in DMFCs, SPEEK with an IEC of 1.33 meq/g was used in the SPEEK/PSf-ABIm blend membrane with 3 wt % of PSf-ABIm and as an ionomer in the anode and cathode. The ionomer contents in the catalyst layers were 20 and 30 wt %, respectively, for the SPEEK and Nafion ionomers, which are known to be the optimum contents for the respective ionomers.[9,14] Figure 1 compares the performances in DMFCs at 1 M methanol concentration of the MEAs fabricated with the SPEEK/PSf-ABIm blend membranes and either SPEEK or Nafion ionomer in the catalyst layers. The membranes were held identically, all with a thickness of 50 μm, to exclude the effect of membrane thickness on the performance in DMFC. As seen in Fig. 1, the MEA fabricated with the SPEEK ionomer in the electrodes exhibits superior performance compared to that fabricated with the Nafion ionomer in the electrodes. This is consistent with the results reported by us earlier that the electrodes containing SPEEK ionomer (IEC = 1.33 meq/g, 20 wt %) provided better performances in DMFCs than those containing Nafion ionomer when the MEAs were fabricated with the SPEEK membrane, which was attributed to lower interfacial resistance of the MEA and the increased electrochemical active area of both the anode and cathode electrodes.[9] To investigate the effect of the SPEEK ionomer in the electrodes on the interfacial resistance of the MEAs fabricated with the SPEEK/PSf-ABIm blend membrane, ac impedance measurements were carried out. Figure 2 compares the Nyquist plots obtained with MEAs fabricated with the blend membranes and either SPEEK or Nafion ionomer in the electrodes. The ohmic resistance determined from the intercept of the real z axis in the high-frequency range consists of membrane resistance, interfacial resistance, and electronic resistance of the electrodes and cell hardware. The interfacial resistances were estimated by subtracting the membrane resistances from the ohmic resistances obtained from the Nyquist plots, assuming the electronic resistance of the electrodes and cell hardware is constant and small.[15,16] The calculated interfacial resistances of the MEAs are found to be 0.04 and 0.1 Ω cm^2, respectively, for SPEEK and Nafion ionomer in the electrodes, demonstrating that the interfacial resistance in the MEA is lowered when SPEEK is used as an ionomer in the electrodes due to a better compatibility between the blend membrane and the ionomer in the electrodes.

To examine the effect of the composition in the SPEEK/PSf-ABIm blend membrane on MEA performance in DMFCs, the blend membranes were prepared by blending SPEEK having IECs of 1.33 and 1.51 meq/g with, respectively, 3 and 5 wt % PSf-ABIm, which are denoted hereafter as SPEEK1.33/PSf-ABIm3% and SPEEK1.51/PSf-ABIm5%. The IEC, proton conductivity (σ), and liquid-uptake values of the blend membranes as well as Nafion 117 membrane are given in Table I. The IECs of the SPEEK1.33/PSf-ABIm3% and SPEEK1.51/PSf-ABIm5% membranes, which are dependent on the IEC of the plain SPEEK (acid) and the amount of PSf-ABIm (base) in the blend, are 1.20 and 1.24 meq/g, respectively, as seen in Table I. The lower IEC values of the blend membranes (1.20–1.24 meq/g) compared to the plain SPEEK used as an acid component (1.33–1.51 meq/g) indicates that the sulfonic acid groups in the

Table I. Characterization data of the SPEEK/PSf-ABIm membranes.

Sample[a]	IEC (meq/g)	σ (S/cm)	Liquid uptake (%)[b] Water 25°C	Water 65°C	1 M 25°C	1 M 65°C	5 M 25°C	5 M 65°C	10 M 25°C	10 M 65°C
Sample 1	1.20	0.031	38	51	42	65	53	272	157	597
Sample 2	1.24	0.036	44	63	48	87	58	291	194	611
Nafion 117	0.91	0.090	31	39	36	41	43	50	51	79

[a] Samples 1 and 2 refer, respectively, to SPEEK1.33-3%PSf-ABIm and SPEEK1.51-5%PSf-ABIm membranes.
[b] The molar concentration values refer to methanol concentration.

SPEEK are partially involved in the acid-base ionic interaction. The proton-conductivity values of the blend membranes range from 0.031 to 0.036 S/cm, which are lower than that of the Nafion membrane. In the case of the liquid uptake, the measurements were performed at room temperature and 65°C under methanol concentrations of 0–10 M. As can be seen, the blend membranes uptake more liquid with increasing temperature and methanol concentration compared to that of Nafion membrane, which is attributed to a higher IEC in the former. Nevertheless, the swelling of the blend membranes may be expected to be restricted in the fuel cell environment due to the compressing force in the single-cell hardware. Also, the methanol crossover with MEAs fabricated with the blend membranes may be suppressed, considering the fact that SPEEK that is the main component of the blend membranes has a smaller degree of nanoseparation between the hydrophilic and hydrophobic domains (i.e., narrower hydrophilic channels) compared to that in Nafion on hydration.[17] Moreover, the dry weights of the blend membranes were found to remain unchanged after equilibrating the membranes in methanol solutions (1–10 M), indicating no degradation or dissolution of the blend membranes.

Figure 3 compares the performances in DMFCs at 1 M methanol concentration of the MEAs fabricated with the SPEEK1.33/PSf-ABIm3% membranes (thickness = 60 and 100 μm), SPEEK1.51/PSf-ABIm5% membrane (thickness = 60 μm), and Nafion membranes (Nafion 115 and 117 with thicknesses of 150 and 220 μm, respectively). To compensate for the lower proton conductivities of the blend membranes, the SPEEK/PSf-ABIm membranes were prepared with 1.5–2.5 times lower thickness than the Nafion 115 membrane. SPEEK with an IEC = 1.33 meq/g was used as an ionomer in the electrodes fabricated with the blend membranes, and Nafion was used as an ionomer in the electrodes fabricated with the Nafion membrane. As seen in Fig. 3, the MEAs fabricated with the SPEEK/PSf-ABIm blend membranes regardless of the composition exhibit better performance in DMFCs than those fabricated with Nafion 115 and 117 membranes.

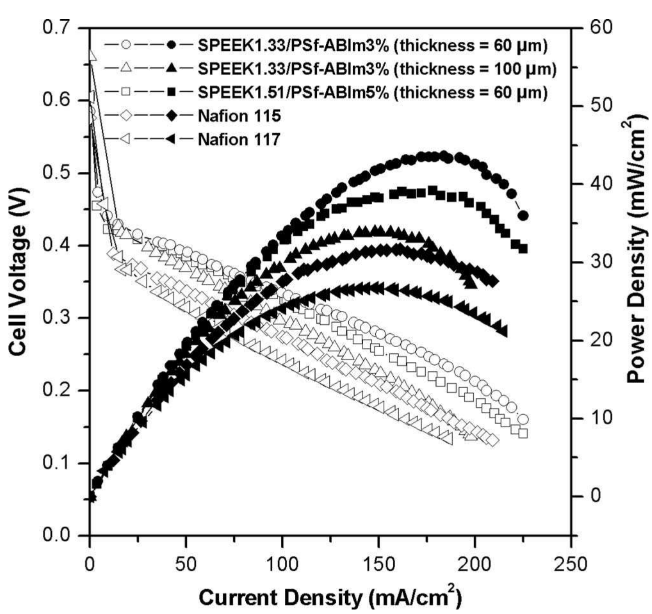

Figure 3. Comparison of the performances in DMFCs of various MEAs with 1 M methanol solution: MEAs fabricated with SPEEK1.33/PSf-ABIm3% membrane (IEC of SPEEK = 1.33 meq/g and 3 wt % of PSf-ABIm) with a thickness of 60 μm, SPEEK1.33/PSf-ABIm3% membrane (IEC of SPEEK = 1.33 meq/g and 3 wt % of PSf-ABIm) with a thickness of 100 μm, SPEEK1.51/PSf-ABIm5% membrane (IEC of SPEEK = 1.51 meq/g and 5 wt % of PSf-ABIm) with a thickness of 60 μm, and Nafion 115 membrane.

The blend membranes in Fig. 3 differ slightly in their performance depending on the blend composition and the IEC of the SPEEK. As seen in the power-density plots in Fig. 3, the highest maximum power density is obtained with the SPEEK 1.33/PSf-ABIm3% membrane with a thickness of 60 μm, and the SPEEK1.33/PSf-ABIm3% membrane with a thickness of 100 μm shows the lowest maximum power density. The latter is due to a higher membrane resistance arising from a larger membrane thickness. With an equivalent thickness of 60 μm, the SPEEK1.51/PSf-ABIm5% membrane shows slightly lower performance in DMFCs than the SPEEK1.33/PSf-ABIm3% membrane. This can be explained by looking at the steady-state methanol-crossover current density in Fig. 4. A higher methanol crossover with the SPEEK1.51/PSf-ABIm5% membrane compared to that with the SPEEK1.33/PSf-ABIm3% membrane leads to a lowering of the cathode potential and a performance loss. Also, the SPEEK1.51/PSf-ABIm5% membrane exhibits higher liquid uptake than the SPEEK1.33/PSf-ABIm3% membrane at 1 M methanol solution at 65°C (see Table I), implying that the higher methanol crossover correlates with higher water uptake. As seen in Fig. 4, the SPEEK1.33/PSf-ABIm3% membrane with a thickness of 100 μm displays the lowest methanol-crossover current density, which is 2.8 times lower than that found with the Nafion 117 membrane. Furthermore, the selectivity of the blend membranes, which is defined as the ratio of proton conductivity to methanol permeability,[18] were calculated using the methanol permeability (P) determined from the methanol-crossover current density with electro-osmotic drag correction[19] and the proton conductivity value measured at room temperature. The selectivities of the SPEEK1.33/PSf-ABIm3% and SPEEK1.51/PSf-ABIm5% blend membranes are found to be, respectively, 1.9 and 1.7 times higher than the Nafion 117 membrane, suggesting that the former offers superior membrane property for DMFC application.

To assess the dependence of DMFC performance on methanol concentration, the polarization measurements were also carried out with 5 and 10 M methanol solutions as shown in Fig. 5 with MEAs fabricated with the SPEEK1.33/PSf-ABIm3% membranes (60 and 100 μm thick) and Nafion membranes (Nafion 115 and 117). While the Nafion membranes exhibit a significant performance loss on increasing the methanol concentration, both the SPEEK1.33/PSf-

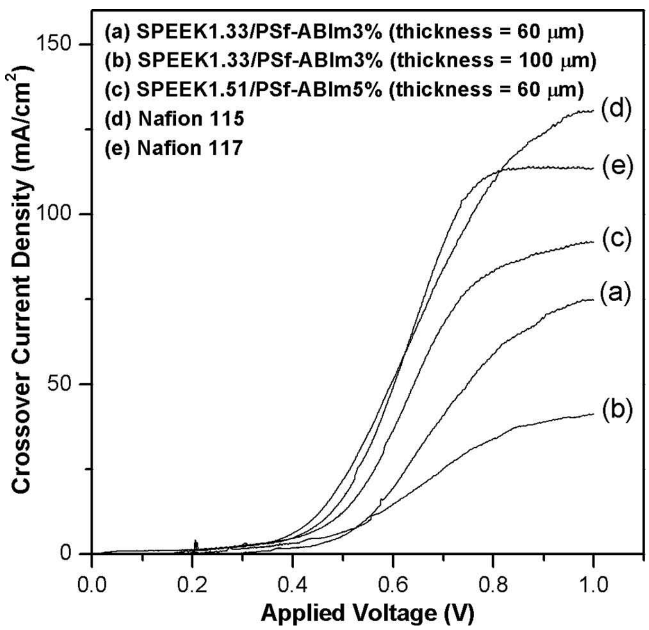

Figure 4. Comparison of the methanol-crossover current densities of various MEAs with 1 M methanol solution: MEAs fabricated with SPEEK1.33/PSf-ABIm3% membrane (IEC of SPEEK = 1.33 meq/g and 3 wt % of PSf-ABIm) with a thickness of 60 μm, SPEEK1.33/PSf-ABIm3% membrane (IEC of SPEEK = 1.33 meq/g and 3 wt % of PSf-ABIm) with a thickness of 100 μm, SPEEK1.51/PSf-ABIm5% membrane (IEC of SPEEK = 1.51 meq/g and 5 wt % of PSf-ABIm) with a thickness of 60 μm, and Nafion 115 membrane.

ABIm3% blend membranes (thickness = 60 and 100 μm) show less performance dependence on methanol concentration. Interestingly, with 10 M methanol solution, the blend membrane with a thickness

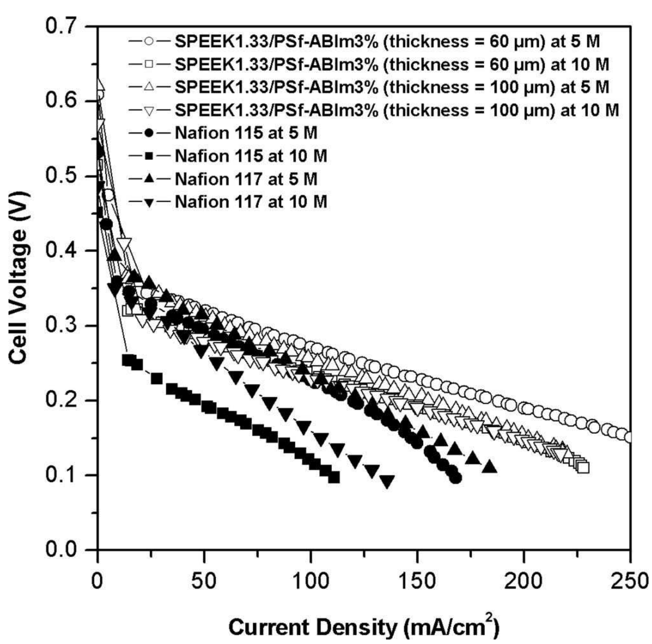

Figure 5. Comparison of the performances in DMFCs of various MEAs with 5 and 10 M methanol solutions: MEAs fabricated with SPEEK1.33/PSf-ABIm3% membrane (IEC of SPEEK = 1.33 meq/g and 3 wt % of PSf-ABIm) with a thickness of 60 μm, SPEEK1.33/PSf-ABIm3% membrane (IEC of SPEEK = 1.33 meq/g^{-1} and 3 wt % of PSf-ABIm) with a thickness of 100 μm, and Nafion 115 membrane.

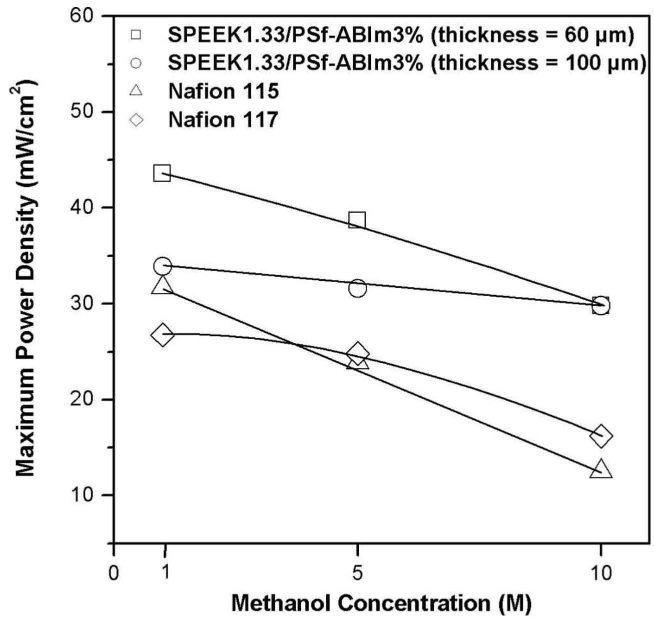

Figure 6. Comparison of the maximum power-density values as a function of methanol concentration for various MEAs: MEAs fabricated with SPEEK1.33/PSf-ABIm3% membrane (IEC of SPEEK = 1.33 meq/g and 3 wt % of PSf-ABIm) with a thickness of 60 μm, SPEEK1.33/PSf-ABIm3% membrane (IEC of SPEEK = 1.33 meq/g^{-1} and 3 wt % of PSf-ABIm) with a thickness of 100 μm, and Nafion 115 membrane.

of 100 μm shows a polarization curve similar to that of the blend membrane with a thickness of 60 μm despite a large membrane resistance due to suppressed methanol crossover with the thicker membrane. Although we could not measure the methanol-crossover current density with the Nafion 115 membrane at methanol concentrations >1 M as it exceeds the current limit of our equipment, the methanol-crossover flux of Nafion membrane has been reported to increase proportionately with methanol concentration.[20] More importantly, the methanol-crossover current density measured at 5 M methanol concentration with the SPEEK1.33/PSf-ABIm3% membrane with a thickness of 100 μm is found to be only 2 times higher than that measured at 1 M methanol concentration, suggesting much less dependence of the fuel cell performance on methanol concentration with the blend membranes compared to that with the Nafion membrane.

To have a better comparison, the maximum power-density values determined from the polarization curves in Fig. 3 and 5 are shown in Fig. 6 as a function of methanol concentration. With 1 M methanol solution, the SPEEK 1.33/PSf-ABIm3% membrane with a thickness of 60 μm exhibits the highest maximum power density, which is 1.4 and 1.6 times higher than those found with, respectively, the Nafion 115 and 117 membranes. As the methanol concentration increases, the difference in the maximum power-density values becomes bigger between the blend membranes and Nafion membranes (Nafion 115 and 117) due to a lower methanol crossover with the blend membrane. The SPEEK1.33/PSf-ABIm3% membrane with a thickness of 100 μm provides excellent performance stability in DMFCs against increasing methanol-feed concentration, resulting in 1.8 times higher maximum power density than that found with the Nafion 117 membrane at 10 M methanol-feed solution.

Conclusions

Blend membranes based on acid-base interactions between SPEEK and PSf-ABIm have been found to exhibit better performance in DMFCs with SPEEK ionomer in the catalyst layer compared to Nafion ionomer due to a better compatibility and lower interfacial resistance. The blend membranes with SPEEK ionomer also exhibit better performance and selectivity in DMFCs than Nafion membranes with Nafion ionomer due to suppressed methanol crossover, despite a lower proton conductivity. Moreover, the former exhibits superior performance stability with increasing methanol-feed solution concentration from 1 to 10 M compared to the latter due to a better methanol-blocking capability. The results were found to be reproducible with multiple experiments. The study demonstrates that the blend membranes offer the potential to operate at higher methanol concentrations compared to Nafion, significantly increasing the energy density and possibly lowering the cathode catalyst loading.

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