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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 polysulfone 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), poly(ethersulfone), poly(phosphazene), and poly(ether nitrile).

Our group has been pursuing blend membranes based on acid-base interactions between SPEEK (an acidic polymer) and polysulfone 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. 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, 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, 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. 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 $W_{\text{uptake}}$ 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

$$W_{\text{uptake}} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100$$

where $W_{\text{wet}}$ and $W_{\text{dry}}$ 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 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/cm². The MEAs were fabricated by hot pressing the anode...
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 cm² 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 N₂ 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.⁷

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, SPEEEK with an IEC of 1.33 meq/g was used in the SPEEEK/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 SPEEEK and Nafion ionomers, which are known to be the optimum contents for the respective ionomers.⁹,¹⁰ Figure 1 compares the performances in DMFCs at 1 M methanol concentration of the MEAs fabricated with the SPEEEK/PSf-ABIm blend membranes and either SPEEEK 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 SPEEEK 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 SPEEEK ionomer (IEC = 1.33 meq/g, 20 wt %) provided higher performances in DMFCs than those containing Nafion ionomer when the MEAs were fabricated with the SPEEEK membrane, which was attributed to lower interfacial resistance of the MEA and the increased electrochemical active area of both the anode and cathode electrodes. To investigate the effect of the SPEEEK ionomer in the electrodes on the interfacial resistance of the MEAs fabricated with the SPEEEK/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 SPEEEK 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 cm², respectively, for SPEEEK and Nafion ionomer in the electrodes, demonstrating that the interfacial resistance in the MEA is lowered when SPEEEK 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 SPEEEK/PSf-ABIm blend membrane on MEA performance in DMFCs, the blend membranes were prepared by blending SPEEEK having IECs of 1.33 and 1.51 meq/g with, respectively, 3 and 5 wt % PSf-ABIm, which are denoted hereafter as SPEEEK1.33/PSf-ABIm3% and SPEEEK1.51/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 SPEEEK1.33/PSf-ABIm3% and SPEEEK1.51/PSf-ABIm5% membranes, which are dependent on the IEC of the plain SPEEEK (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 SPEEEK used as an acid component (1.33–1.51 meq/g) indicates that the sulfonic acid groups in the
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, 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.

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 SPEEK 1.33/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-ABIm3% 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-ABIm3% 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, was calculated using the methanol permeability (P) determined from the methanol-crossover current density with electro-osmotic drag correction 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-

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

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>IEC (meq/g)</th>
<th>Water 25°C</th>
<th>Water 65°C</th>
<th>1 M 25°C</th>
<th>1 M 65°C</th>
<th>5 M 25°C</th>
<th>5 M 65°C</th>
<th>10 M 25°C</th>
<th>10 M 65°C</th>
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<tr>
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<td>51</td>
<td>42</td>
<td>65</td>
<td>53</td>
<td>272</td>
<td>157</td>
<td>597</td>
</tr>
<tr>
<td>Sample 2</td>
<td>1.24</td>
<td>36</td>
<td>41</td>
<td>48</td>
<td>87</td>
<td>58</td>
<td>291</td>
<td>194</td>
<td>611</td>
</tr>
<tr>
<td>Nafion 117</td>
<td>0.91</td>
<td>31</td>
<td>39</td>
<td>50</td>
<td>157</td>
<td>51</td>
<td>79</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*1 The molar concentration values refer to methanol concentration.

*2 The concentration values refer to methanol concentration.

![Figure 3](image-url). 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.
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 of 100 μm shows a polarization curve similar to that of the blend membrane 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 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, SPEEK1.33/PSf-ABIm3% membrane (IEC of SPEEK = 1.33 meq/g and 3 wt % of PSf-ABIm) with a thickness of 60 μm, and Nafion 115 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 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 and 3 wt % of PSf-ABIm) with a thickness of 100 μm, and Nafion 115 membrane.

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.

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 and 3 wt % of PSf-ABIm) with a thickness of 100 μm, SPEEK1.33/PSf-ABIm3% membrane (IEC of SPEEK = 1.33 meq/g and 3 wt % of PSf-ABIm) with a thickness of 60 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 and 3 wt % of PSf-ABIm) with a thickness of 100 μm, and Nafion 115 membrane.

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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