

## Application of Sulfonated Polyimide Membranes to Direct Methanol Fuel Cells

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Sulfonated polyimide (SPI) membrane has been evaluated as an electrolyte membrane for direct methanol fuel cells (DMFCs) in comparison with Nafion<sup>®</sup> 112. The membrane-electrolyte assemblies (MEAs) were made by hot-pressing each membrane, an anode of Pt–Ru dispersed on carbon black (Pt–Ru/CB) and a cathode of Pt/CB with Nafion<sup>®</sup> ionomer. The cell prepared with SPI membrane exhibited a suppressed methanol crossover to a half of Nafion<sup>®</sup> 112, resulting in the improved cell performance.

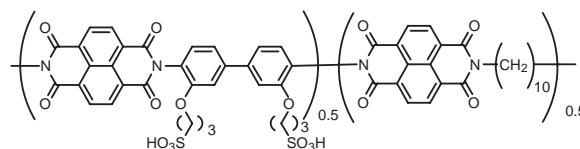
Direct methanol fuel cell (DMFC) is a promising power source for transportations and portable devices. Because DMFC uses aqueous methanol solution directly to generate electrical energy, the system is much simpler than the fuel cells operating with hydrogen prepared by reforming hydrocarbons. However, there are two major obstacles inhibiting the application of DMFC; the poor catalytic activity for the anodic methanol oxidation and a large methanol crossover through the conventional electrolyte membrane from the anode to the cathode side, resulting in a chemical short-circuit reaction.

The methanol crossover causes not only a reduced fuel efficiency but also a reduced voltage efficiency by a mixed potential of oxygen reduction and methanol oxidation at the cathode, resulting in the poor total performance. Considerable technical solutions have been proposed to mitigate this problem. Most of them involve the modification of perfluorosulfonic membranes by addition of Pt nanoparticle catalysts to oxidize crossover methanol with O<sub>2</sub>,<sup>1,2</sup> addition of ceramic oxides,<sup>3,4</sup> addition of proton conductors such as montmorillonite<sup>5</sup> or zirconium phosphate.<sup>6</sup> It seems difficult to reduce the methanol crossover without loss of the proton conductivity of the electrolytes. Such a suppression of methanol crossover was still not enough.

As the other challenges, alternative membranes have been developed such as ethylene-tetrafluoroethylene (ETFE),<sup>7</sup> sulfonated poly(ether ether ketone) (SPEEK),<sup>8</sup> sulfonated polyetherketone (SPEK),<sup>9</sup> phosphoric acid-impregnated polybenzimidazole (PBI),<sup>10</sup> nanoporous proton conducting membrane consisting of high surface area inorganic particles, PVDF, and aqueous acid or mixtures of acids which fill the nanopores.<sup>11,12</sup>

Recently, we have developed sulfonated polyimide (SPI), which exhibits high proton conductivity as well as high thermal and chemical stabilities in aqueous methanol solution.<sup>13</sup> Potential of the cost reduction at the SPI and the simple procedures of polymerization are greatly advantageous in the economic viewpoint, compared with the present Nafion<sup>®</sup> membrane. In this paper, we report the significant suppression of methanol crossover through the novel SPI membrane prepared in our laboratory.

Preparation of SPI membrane (50 μm thickness) was carried out according to the method as described in the literature.<sup>14</sup>



**Figure 1.** The structure of SPI membrane.

Figure 1 shows the molecular structure of SPI.

Catalysts for methanol oxidation and oxygen reduction employed were 54.0 wt % Pt–Ru (1:0.8, by weight ratio)/high-surface area carbon black (HSA-CB) and 45.9 wt % Pt/HSA-CB (Tanaka Kikinzo Kogyo K. K.), respectively. The catalyst paste was prepared by mixing the catalyst powder with Nafion<sup>®</sup> ionomer by a ball mill. The obtained paste was spread on a gas diffusion layer. The gas diffusion layer was consisted of two layers; one was wet-proofed carbon paper backing and the other was a thin PTFE/C layer spread on the surface of the carbon paper backing. Pt loadings at both electrodes were 1.0 mg cm<sup>-2</sup>, and Ru loading at the anode was 0.8 mg cm<sup>-2</sup>. Loading amounts of Nafion<sup>®</sup> ionomer were 2.2 mg cm<sup>-2</sup> for the anode and 1.8 mg cm<sup>-2</sup> for the cathode. The geometrical area of each electrode was 3 cm<sup>2</sup>. A commercial Nafion<sup>®</sup> 112 membrane was also tested in comparison with the SPI membrane. Each MEA was prepared by hot-pressing the SPI or Nafion<sup>®</sup> 112 membrane sandwiched with the above electrodes at 120 °C for 10 sec under the pressure of 0.98 MPa.

Figure 2 shows the IR-free cell voltage and the methanol crossover rate as a function of the current density for the cell prepared with SPI membrane in comparison with that of Nafion<sup>®</sup> 112. The methanol crossover rate through the membrane was measured by detecting CO<sub>2</sub> evolved at the cathode with a gas chromatography and converted to the unit of current density  $j(\text{CH}_3\text{OH})$  equivalent to the methanol oxidation. When the cells were operated with 1 M methanol solution at the anode and dry oxygen at the cathode, the open circuit voltage (OCV) for the cell with SPI membrane was measured at about 0.64 V. This value was higher by ca. 0.04 V than that of Nafion<sup>®</sup> 112 cell. The higher OCV can be brought by the increase in the cathode potential due to the suppressed crossover at SPI membrane. Over the whole current density region, the IR-free cell voltage at the SPI membrane cell was higher than that of Nafion<sup>®</sup> 112 by about 0.02 to 0.04 V.

The value of  $j(\text{CH}_3\text{OH})$  for the SPI membrane at OCV was found to be 0.08 A cm<sup>-2</sup>. It is nearly a half relative to that of Nafion<sup>®</sup> 112 (0.15 A cm<sup>-2</sup>). As the current density was increased, the  $j(\text{CH}_3\text{OH})$  decreased at both cells. This behavior can be ascribed to the lowered methanol concentration at the interface of the anode and the electrolyte membrane, as discussed previously.<sup>1</sup> At 0.2 A cm<sup>-2</sup>, the  $j(\text{CH}_3\text{OH})$  for the SPI membrane was considerably low, 0.035 A cm<sup>-2</sup>. As reported previously,<sup>14</sup> the SPI membrane is stable in aqueous methanol solution even

**Table 1.** Fuel utilization efficiency,  $\varepsilon_F$ , voltage efficiency,  $\varepsilon_V$ , and energy conversion efficiency,  $eff$ , at  $j_F = 100 \text{ mA cm}^{-2}$  in a DMFC with SPI or Nafion<sup>®</sup>112

Electrolyte membrane	$j(\text{CH}_3\text{OH})^a$ ( $\text{mA cm}^{-2}$ )	$E_{\text{cell}}^b$ (V)	$\varepsilon_F^c$	$\varepsilon_V^d$	$eff^e$ (%)
SPI	56.2	0.476	0.640	0.379	24.3
Nafion <sup>®</sup> 112	116.6	0.460	0.462	0.367	16.9

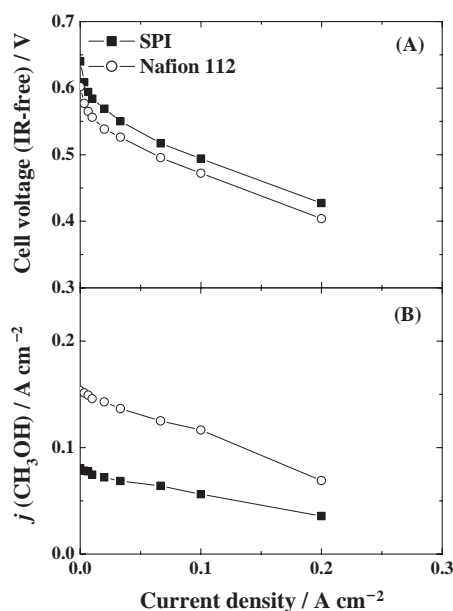
<sup>a</sup> Oxidation current density equivalent to the crossed-over  $\text{CH}_3\text{OH}$ , shown in Figure 2.

<sup>b</sup> Terminal voltage (including IR-loss).

<sup>c</sup> Fuel utilization efficiency,  $\varepsilon_F = j_F / [j_F + j(\text{CH}_3\text{OH})]$ , where  $j_F$  is the faradaic current drawn from the cell.

<sup>d</sup> The voltage efficiency was based on the higher heat value (HHV) of the standard enthalpy  $\Delta H^0 = -726.5 \text{ kJ/mol}$  at  $25^\circ\text{C}$  for reaction of  $\text{CH}_3\text{OH} + 3/2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$ .  $\varepsilon_V = -6FE_{\text{cell}}/\Delta H^0$ .

<sup>e</sup>  $eff = \varepsilon_F \times \varepsilon_V \times 100\%$ .



**Figure 2.** DMFC performances for MEAs prepared with SPI membrane (—■—) or Nafion 112 (—○—). Cell voltage (IR-free) vs current density (A) and methanol crossover rate vs current density (B). Cells were operated at ambient pressure and  $T_{\text{cell}} = 80^\circ\text{C}$  with 1 M methanol ( $1 \text{ mL min}^{-1}$ ) at the anode and  $\text{O}_2$  ( $20 \text{ mL min}^{-1}$ ) at the cathode.

with higher ion exchange capacity than Nafion<sup>®</sup>. In spite of the higher proton concentration, the proton conductivity of the SPI is comparable to that of Nafion<sup>®</sup>, indicating that the hydrophilic diffusion path in the SPI may be narrower. Such a distinct structure is favorable to suppress the methanol crossover.

The lower  $j(\text{CH}_3\text{OH})$  and higher cell voltage in the SPI cell resulted in a higher energy conversion efficiency, which is the product of the voltage efficiency  $\varepsilon_V$  and the fuel utilization efficiency  $\varepsilon_F$ . The  $\varepsilon_F$  in a DMFC can be defined as the ratio of Faradaic consumption rate of  $\text{CH}_3\text{OH}$  ( $j_F$ ) to the total consumption rate [the sum of  $j_F$  and  $j(\text{CH}_3\text{OH})$ ]. These values at  $j_F = 0.1 \text{ A cm}^{-2}$  in both SPI cell and Nafion cell are summarized in Table 1. The energy conversion efficiency ( $eff$ ) for the SPI cell operated at  $0.1 \text{ A cm}^{-2}$  and  $80^\circ\text{C}$  was 24.3%, which is about 1.5 times higher than that for Nafion cell ( $eff = 16.9\%$ ). It was found that such an advantage of high  $eff$  in the SPI cell was more prominent when the DMFC was operated at higher temperature or higher methanol concentration. Detailed data will be shown elsewhere.

A disadvantage of the SPI membrane was a decrease in the proton conductivity at low humidity condition. Indeed, the advantage of high IR-free cell voltage (shown in Figure 2A) was somewhat diminished by the IR loss under the operation with dry  $\text{O}_2$  at the cathode. Further studies on effects of cathode humidifying temperature, cell temperature, and methanol concentration are under progress.

In conclusion, the advantages by using a novel SPI membranes as a proton exchange electrolytes in DMFCs were brought about, i.e. the reduced methanol crossover about 50% relative to that of Nafion<sup>®</sup>112, leading to the enhanced cell voltage.

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