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Investigation of Sulfonated Polyimide Membranes for Direct Methanol Fuel Cells

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Introduction

The suppression of methanol cross-over through a membrane is one of the important targets for DMFC applications. Recently, we found that the sulfonated polyimide (SPI) exhibits high proton conductivity as well as high stabilities in thermally and chemically in methanol [1]. In addition, the low cost of the SPI and the simple procedures of polymerization are great advantage in economic point in comparison with the present perfluoro-sulphonic acid membranes such as Nafion. In this study, we evaluate a novel SPI-5 membrane, developed in our laboratory [2], as an electrolyte for the direct methanol fuel cell compared with the Nafion® membrane. It was found that the mass transport of methanol is suppressed significantly through the membrane, resulting in the improved cell performance. The structure of SPI membrane was shown in Scheme 1.

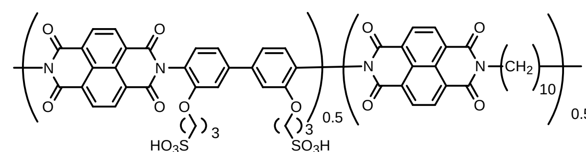
Experimental

In order to compare the membrane properties themselves simply between the SPI-5 and Nafion®, the same catalyst layers incorporated with Nafion® ionomer were formed on the membranes. Catalyst suspension was prepared by ball-milling a suspension of Nafion® ionomer with carbon black supported catalyst for the cathode or anode, and then the obtained paste was coated on a gas diffusion layer. The gas diffusion layer is consisted of two layers; one is wet-proofed carbon paper backing and the other is thin PTFE/C layer coated on the surface of the carbon paper backing. Pt-Ru alloy (Pt/Ru = 40/60 in the atomic ratio) and Pt supported on carbon black were used as anode and cathode catalysts, respectively, where Pt loadings were both 1.0mg Pt/cm^2. To make the MEAs, SPI (50 μm thickness) or Nafion ® 112 membrane was hot-pressed together with the anode and cathode mentioned above under the same condition. Effects of the operating cell temperature, the cathode humidifying temperature (T_{CH}) and the methanol concentration on their polarization characteristics and the methanol cross-over rates were investigated. Methanol cross-over was measured by detecting CO_2 amounts exhausted from the cathode with gas-chromatography [3].

Results and Discussion

Fig. 1 shows the IR free cell voltage and the amount of methanol cross-over as a function of the current density for the cells prepared with SPI membrane or Nafion 112. When the cells were operated with 1M methanol solution at anode and dry oxygen at cathode, IR free cell voltage of the cell consist of SPI membrane was higher about 40mV than that of Nafion 112 over the whole current density region. Equivalent current density to the methanol cross-over via the SPI membrane at OCV was 80mA/cm^2. It was nearly 50% relative to that of Nafion® 112 which was evaluated to be 153mA/cm^2. Especially at 200mA/cm^2, the amount of the methanol cross-over for the SPI membrane was considerably low, i.e., 35mA/cm^2. The cross-over decreases the cell voltage due to the presence of a mixed potential at the cathode. The higher cell voltage for SPI membrane was achieved by the lowered methanol cross-over. Property of the low methanol penetration through the SPI membrane is attributed to the poor affinity of the SPI membrane with water molecules relative to the Nafion membrane. In addition, SPI membranes have no hydrophilic cluster structures which the hydrated ions pass through easily through the membrane such as Nafion membrane. It is considered that these properties can restrain the penetration of the methanol through SPI membrane in some extent. However, these properties also increase the resistance of the membrane. When the cells were operated with 1M methanol solution and dry oxygen, the internal resistance measured by current interruption method was 0.15ohmcm^2 and 0.09ohm/cm^2 for SPI and Nafion 112, respectively. The specific resistance was strongly dependent on the humidifying temperature. Though the resistance of SPI membrane in dry condition was higher than that of Nafion® 112, the resistance became nearly the same as that of Nafion®112 at the 60^{o}C T_{CH}.

Scheme 1



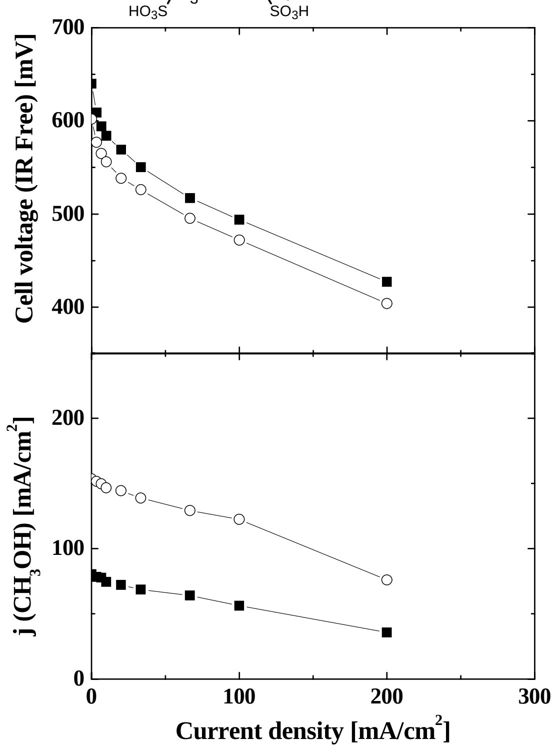


Fig. 1. DMFC performance curves for MEAs prepared with SPI membrane or Nafion 112. Cell voltage (IR free) vs. current density (upper) and methanol crossover vs. current density (bottom) measured. Cell temperature is 80^{o}C. Cathode flow is 20mL/min O_2, and anode flow is 1M methanol (1mL/min). Cells are operated at atmosphere pressure: (-■-) SPI membrane; (-○-) Nafion 112.

References

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