Effect of Proton Exchange Membrane on Performance of Direct Methanol Fuel Cell

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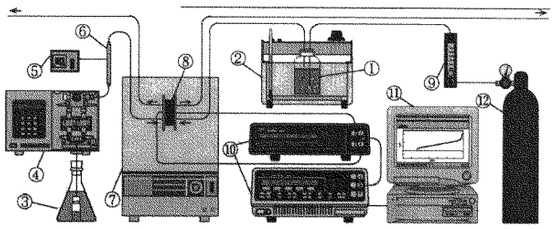
Direct Methanol Fuel Cells (DMFCs) are very attractive power sources for electrical vehicles and portable applications. The permeation control by the method for modifying fixed charge of surface and inside of a Nafion membrane was tried to decrease the methanol crossover flux.[1,2] In this work, cell performances and electrochemical properties for the DMFC system were investigated using as-received Nafion®117 (Du Pont), Aciplex®-S (Asahi Chemical) and modified Nafion membranes.

For charging Nafion membranes with long-chained counter ion, each sample was boiled for 10min and immersed in 0.1 M tetramethylammonium bromide $(CH_3)_4NBr$ (Aldrich) with 0.1M HCl solutions for 1min. The microstructure in as-received Nafion and modified Nafion membranes were evaluated by a small angle X-ray diffraction (SAXRD) measurement using a RIGAKU RU300. Membrane electrode assemblies (MEAs) were prepared by hot press at 398 K with 10 Mpa. The anode and cathode catalyst layer were considered of 2.0 mg/cm^2 of Pt-Ru /C and 2.0 mg/cm^2 of Pt /C (Tanaka Precious Metals) with Nafion, respectively. Figure 1 shows a schematic diagram of the experimental apparatus. Methanol solution of 1.5 M was fed to a vaporizer with 0.20 ml/min and supplied to anode. Oxygen was humidified at 363 K and feed to the cathode with 150 ml/min. Cell performances and electrochemical properties for DMFC system were investigated using the electrochemistry measuring system (Solartron SI 1287, 1260).

Figure 2 shows the cell performance at 363 K and 393 K with as-received Nafion117 (175 μm), Aciplex-S1002 (50 μm), S1004 (100 μm) and S1008 (200 μm). As the maximum, the short circuit current of 392 mA/cm^2 and the open circuit voltage of 658 mV were obtained at 363 K with Nafion117 membrane. The open circuit voltage decreased with reducing the film thickness. Methanol permeated well with a thinner membrane.[2] Thus the increase in methanol permeate flux decreased the open circuit voltage. Cell performances for Aciplex membranes dropped at 393 K as well as Nafion117 membrane. The rate of the short circuit current drop for the thin S1002 membrane was little in comparison with other membrane, because small membrane resistance and small water content prevented the reduction of the proton conductivity.

For the modified Nafion membrane with $(CH_3)_4N^+$, the cell performance decreased in comparison with as-received Nafion117 membrane as shown in Fig. 3. The short circuit current was 156 mA/cm^2 for the modified membrane with $(CH_3)_4N^+$ at 353 K because of low proton conductivity of the membrane with counter ions.[2] However, the open circuit voltage was improved to 635 mV and 732 mV at 343 K and 383 K, respectively. The reduction of the methanol permeate flux raised the open circuit voltage for the modified Nafion membrane in comparison with the as-received Nafion membrane.

1) S. P. Kusumocahyo and M. Sudoh, J. Membr. Sci., 161 77 (1999).
2) K. Okajima, K. Furukawa, T. Hakamata, F. Kaga and M. Sudoh, these proceedings.



1. Humidifer
2. Thermostatic bath
3. CH_3OH solution
4. HPLC pump
5. Temperature controller
6. Vaporizer
7. Drying oven
8. Cell
9. Flow meter
10. Electrochemical interface
11. Personal computer
12. O_2 cylinder

Fig.1 Schematic diagram of the experimental apparatus.

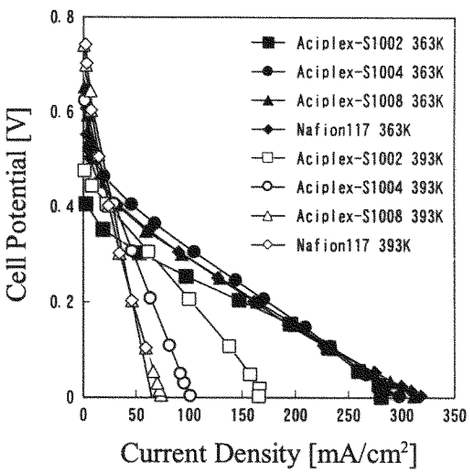


Fig.2 Effect of cluster diameter on solubility coefficient and diffusion coefficient. Nafion membrane.

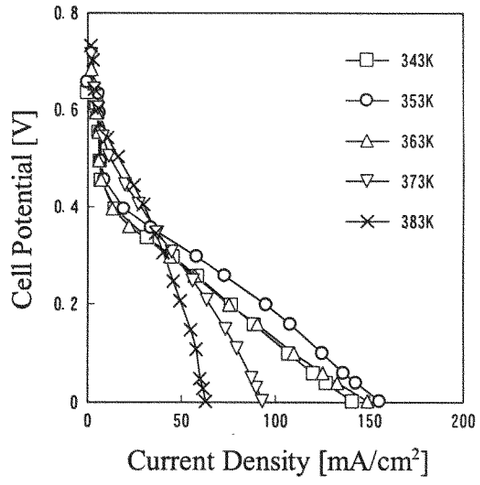


Fig. 3 Temperature dependence on cell performance of DMFC with a modified Nafion membrane.