Effect of Thin Fluoro-ionomer Coating by Plasma Polymerization on Methanol Crossover and Proton Conductivity of Membrane for Direct Methanol Fuel Cell

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Surface modified Nafion membranes were prepared by the method of low temperature plasma polymerization in order to reduce the methanol crossover for Direct Methanol Fuel Cell (DMFC). Two types of barrier layer were laminated on Nafion surface. One is the anion exchange layer and the other is the cation exchange layer. In coating of anion exchanger ionomer, oxygen plasma pre-treatment was very effective for the ionic conductivity improvement compared with argon plasma pre-treatment. The ionic conductivity was improved dramatically and the increase of methanol permeate flux through the membrane was negligible. By coating thin film of a certain fluoro-ionomer, methanol crossover was suppressed rather than Nafion 117 and proton conductivity was almost equal to that of Nafion 117.
Key words: DMFC, PEM, methanol crossover, proton conductivity, plasma polymerization

1. INTRODUCTION

Direct methanol fuel cell (DMFC) is a power source system that anode and cathode are separated with a proton exchange membrane. DMFC has the properties that simply system is possible and can start from the room temperature. So it is expected as the use of power sources for vehicular, portable applications and so on. DMFC shows considerably lower performance than the hydrogen fuel cell because of inefficient methanol oxidation and the methanol crossover through the proton exchange membrane. The methanol crossover wastes fuel and causes performance losses at the cathode due to consumption of oxygen and catalyst poisoning.

Some approaches were reported for improving a polymer electrolyte membrane (PEM). C. Yang et al. investigated a composite Nafion/zirconium phosphate membrane [1]. They reported operating temperature up to ~150 °C by using this membrane and improving DMFC performance. Self-humidifying type membranes [2] and Pore-filling type membranes [3] are also examples as PEM improving approaches.

PEM is required for the characteristics such as chemical and electrical stability, fuel barrier property, proton conductivity, heat-resistance, dimensional stability, mechanical strength and low cost. Generally perfluorosulfonic acid membrane such as Nafion is used for DMFC. Though perfluorosulfonic acid membrane is excellent in the performance of chemical and electrical stability, proton conductivity and mechanical strength, but performance of fuel barrier, heat-resistance and cost are inferior [4-6]. So, various studies have been reported for modification of Nafion [7, 8]. We reported that modified Nafion membranes with long chain counter ion exhibited good performance for pervaporation of acetic acid-water mixture [9]. Then, we applied this method to PEM for DMFC and reported the decrease in methanol crossover [10, 11].

In this paper, another approach to modification of Nafion membrane was examined in order to decrease methanol crossover. Surface modified Nafion membranes were prepared by the method of low temperature plasma polymerization. Two types of barrier layer were laminated on Nafion surface. One is the anion exchange layer and the other is the cation exchange layer. Nafion membrane coated anion exchange layer was expected to have selectivity for the single charge ion [12-13], and the cation exchange layer prepared by plasma polymerization was reported that the dense layer was formed [14]. We evaluated properties of surface modified Nafion membranes such as methanol permeation water content, and proton conductivity.

2. EXPERIMENTAL

2.1 Preparation of surface modified Nafion membranes

The plasma polymerization system is a conventional planar capacitive type consisting of a reaction chamber, a gas feeding system, a pumping system and a RF-power supply (Samco Co., BP-1). Figure 1 shows a schematic diagram of the experimental apparatus for plasma polymerization. After reducing the pressure with a vacuum pump, the frequency of 13.56 MHz is applied between radio-frequency (RF) electrodes and followed by radical generation. Argon plasma or oxygen plasma pre-treatment etching was done in order to activate the surface of base film. Then, the monomer and the base polymer were introduced to the bell jar and were allowed to plasma-polymerize in an atmosphere of argon gas [15-17]. Hexafluoropropylene (HFP, Lancaster

Synthesis) was used as a source gas for the base polymer, and monomer introduced with HFP. As the monomer, 4-vinylpyridine (4VP, Wako Chemical) and trifluoromethanesulfonic acid (TFMSA, Wako Chemical) were used for anion and cation exchange layer, respectively. Nafion 117 membrane (Du Pont) was used as base films. In addition, Hipore 2100 membrane (Asahi-Kasei) was used for characteristic measurements of anion exchange layer made by plasma treatment. The experiments were carried out under the following conditions; pressure was 67 Pa, RF power was 10 - 50 W, and plasma treatment times were 10, 30, and 60 sec. Ar and HFP flow rate were 50 mL/min and 1 mL/min, respectively. In case of preparation of modified membrane with anion exchange layer, the membrane was immersed in 1 vol. % 1-bromopropane / polycarbonate solution for quaternization. The structure of the polymerized layer was evaluated by an absorption of infrared rays.

2.2 Evaluation of membrane

A standard H-Cell arrangement was used to measure methanol crossover flux through the membrane [10]. Compartment A was filled with the mixed solution of 0.25 m^3, which consisted of 0.5 $kmol/m^3$ of H_2SO_4 and 1-5 $kmol/m^3$ of methanol, and compartment B was filled with 0.5 $kmol/m^3$ of H_2SO_4 solution of 0.25 m^3. The effective cross-section of a membrane was 1.766 x 10^{-4} m^2. Magnetic stirrers were used to vigorously stir to ensure uniform mixing. The fixed current (0 - 2.0 kA/m^2) was applied using the electrochemistry system (HOKUTO DENKO, HZ-3000), and sampled B side solution in every fixed time. Methanol concentration was determined by using gas chromatography (Shimadzu, GC-15A). All measurements were done at room temperature. The cell was filled with 0.5 $kmol/m^3$ of H_2SO_4 solution for measuring conductivity [10]. The fixed electric potential AC impedance measurement (frequency: 1 kHz, AC amplitude: 0.1 V) was investigated [18]. Moreover, ion exchange capacity and water content were evaluated [10].
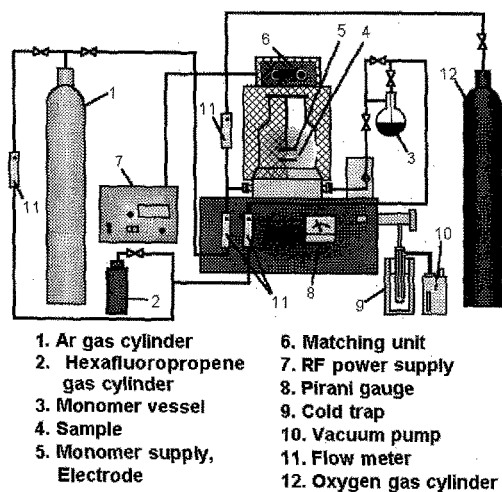
3. RESULTS AND DISCUSSION

3.1 SEM observation and thickness

Figure 2 shows the SEM image of plasma polymerized anion exchange layer on Nafion 117 membrane. A uniform and dense layer was formed, and the thickness of layer was 2.0 μm under polymerization for 60 sec with O_2 plasma pre-treatment.

3.2 Methanol permeability for modified membrane (Anion exchange layer on Nafion)

Figure 3 shows the results of methanol permeate flux for the surface modified Nafion with the anion layer. Although the methanol permeability of O_2 pre-etching membrane was slightly larger than that of Ar pre-etching membrane, the methanol crossover flux for both modified membranes decreased to about one-half in comparison with that for Nafion 117. The methanol crossover was measured under applying current, then that ratio was evaluated. Methanol crossover ratio r ($MeOH/H^+$) is defined as:

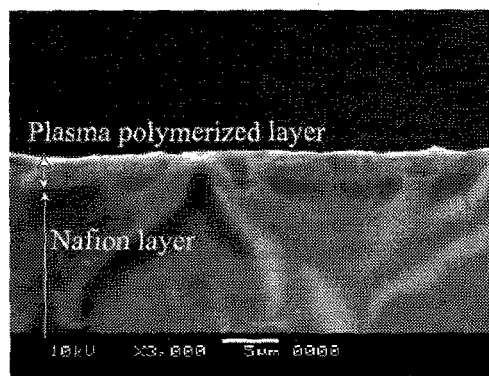$$r = (J_{mf} - J_{m0}) / J_{hf} \qquad (1)$$

Fig. 2. SEM image of plasma polymerized membrane. (60sec, anion exchange layer, pre-etching:O_2)
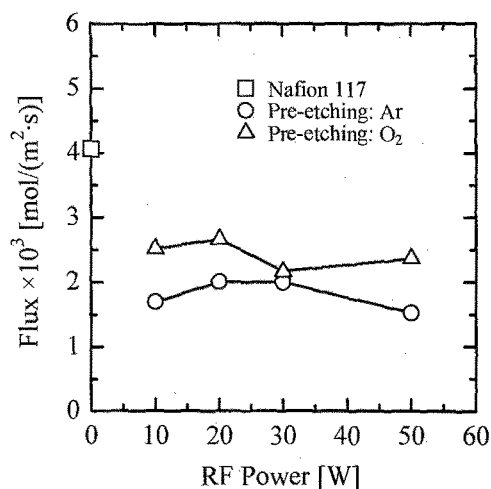

Fig. 3. Relationship between RF power and methanol crossover flux for plasma polymerized membranes. (Anion layer, Methanol concentration: 5 mol/l, Current density: 0 mA/cm^2)

1. Ar gas cylinder
2. Hexafluoropropene gas cylinder
3. Monomer vessel
4. Sample
5. Monomer supply, Electrode
6. Matching unit
7. RF power supply
8. Pirani gauge
9. Cold trap
10. Vacuum pump
11. Flow meter
12. Oxygen gas cylinder

Fig. 1. Schematic diagram of experimental apparatus for plasma polymerization.

where J_{mf} is methanol crossover flux with current, J_{m0} is methanol crossover flux without current, and J_{hf} is proton flux. Although the methanol crossover ratio for Nafion 117 was calculated to be 0.2 [10], those for the Ar pre-etching membrane and the O_2 pre-etching one were reduced to be 0.07 - 0.14 and 0.13 - 0.17, respectively. The proton conductivity drastically decreased to 0.19 S/m with the Ar plasma pre-treatment. This result was approximately 2 % for Nafion 117. In case of the O_2 pre-etching membrane, the proton conductivity was improved to 6.7 S/m. Thus, O_2 plasma pre-treatment was very effective for the proton conductivity improvement compared with Ar plasma pre-treatment. The proton conductivity was improved dramatically and the increase of methanol permeate flux through the membrane was negligible.

3.3 Ion exchange capacity and water content (Anion exchange layer)

The relationship between anion exchange capacity and the water content is shown in Fig. 4. Water content was showed the similar tendency. For the Ar plasma pre-etching polymerized membrane, anion exchange capacity was very low. However, the anion exchange membrane prepared after O_2 pre-treatment was obtained higher anion exchange capacity and methanol crossover flux of the membrane decreased compared to that of Nafion117 membrane (Fig. 3). Therefore, it was supposed that the selectivity for the single charge ion suppressed methanol crossover.

3.4 Proton conductivity and methanol crossover flux on the modified membrane. (Anion exchange layer on Nafion)

Figure 5 shows the relationship between proton conductivity and methanol crossover flux of surface modified Nafion membranes with anion exchange polymerized layer. Target area means that conductivity is more than 5 S/m and methanol permeate flux is less than 25 % that of Nafion 117. In case of Ar plasma pre-treatment, modified membrane showed 50 % of methanol permeate flux and 0.19 S/m of proton
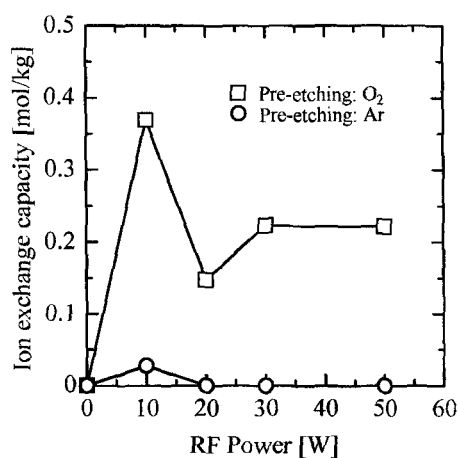
conductivity. On the other hand, the methanol permeate flux was 60 % of Nafion 117 and the proton conductivity increased to 6.7 S/m on O_2 plasma pre-etching membrane. Oxygen plasma pre-treatment was very effective for the ionic conductivity improvement.

3.5 FT-IR observation (Anion exchange layer)

Figure 6 shows the IR spectra obtained after the anion exchange layer polymerization on Nafion 117 using Ar pre-etching and O_2 pre-etching, respectively. In both spectra, several peaks were clearly observed, corresponding to chemical groups involving the Nafion membrane and HFP. The most remarkable difference was observed in the wavenumber region from 950 to 600 cm^{-1}. In particular, the peak corresponding to S-O-C was detected at 890 cm^{-1} on the modified membrane with O_2 plasma pre-treatment. It was suggested that ion pairs were formed on the interface between 4VP and $-SO^{3-}$ group of Nafion in case of Ar plasma pre-etching. Therefore, proton conductivity became low. On the other hand, the surface of Nafion was supposed to be
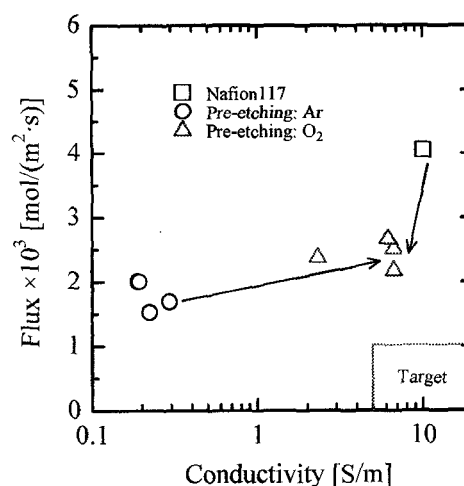

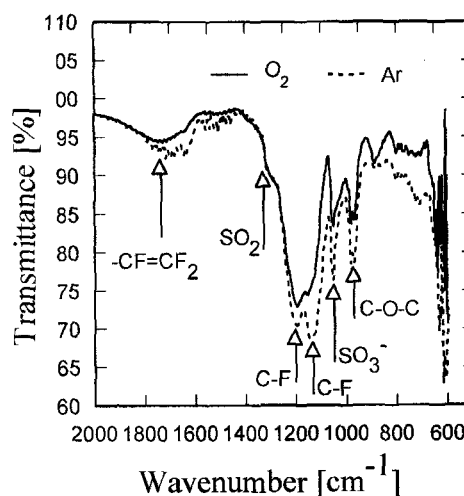Fig. 5. Relationship between conductivity and methanol crossover flux.

Fig. 4. Relationship between RF power and anion exchange capacity for plasma polymerized membranes on Hipore 2100.

Fig. 6. IR spectra of polymerized anion exchange layers on Nafion 117.

activated by O_2 plasma pre-etching [12, 13].

3.6 Layer thickness dependence (Anion exchange layer on Nafion)

Figure 7 shows the dependence of barrier layer thickness on methanol crossover flux. The thickness of polymerization layers were 0.7, 1.0 and 2.0μm for the polymerization time of 10, 30 and 60 sec, respectively. From these results, the dependence of barrier layer thickness to methanol crossover flux was not observed for any applying current. Methanol cross over was sufficiently suppressed by a layer 0.7μm thick.

3.7 Proton conductivity and methanol crossover flux (Cation exchange layer on Nafion)

Surface modified Nafion with cation exchange layer was prepared and evaluated instead of anion exchange polymerized layer. Fig. 8 shows the relationship between conductivity and methanol crossover flux. The proton conductivity was improved to 9.6 S/m, and the methanol permeate flux was 55 % of Nafion 117. Ionic conductivity was almost equal to that of Nafion 117. It

Fig. 7. Dependence of barrier layer thickness on methanol crossover flux.
(anion exchange layer, O_2 pre-treatment)

Fig. 8. Relationship between conductivity and methanol crossover flux.

was supposed that the methanol crossover was suppressed by cross-linking network structure of the dense cation layer.

4. CONCLUSION

Surface modified Nafion membranes were prepared by the method of low temperature plasma polymerization in order to reduce the methanol crossover for DMFC. By coating thin film of a certain fluoro-ionomer using low temperature plasma polymerization, the methanol crossover was suppressed rather than Nafion 117. In coating of anion exchanger ionomer, O_2 plasma pre-treatment was very effective for the ionic conductivity improvement compared with argon plasma pre-treatment. For the membrane polymerized with the cation exchange layer, the methanol crossover flux was decreased to 55 % as compared with that of Nafion 117, and the ionic conductivity was almost equal to that of Nafion 117.

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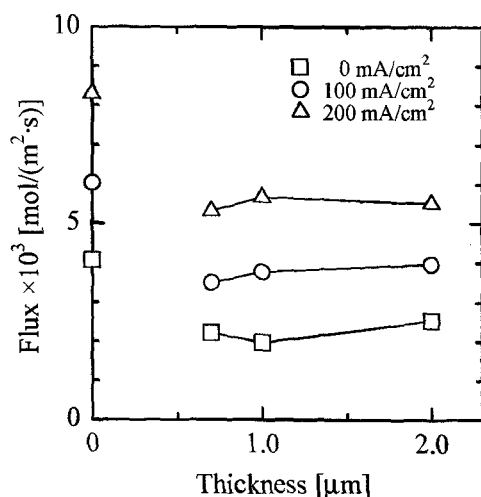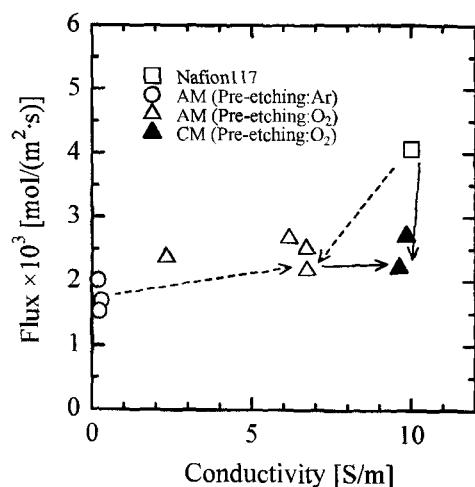[18] M. Sudoh, J. Yamamoto, *Bull. Soc. Sea Water Sci. Jpn.*, **49**, 341-344 (1995). (in Japanese)