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Reduction of Methanol Crossover in a Direct Methanol Fuel Cell by Using the Pt-Coated Electrolyte Membrane

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Abstract : A Pt-layer was deposited on the anode side of a Nafion membrane via a sputtering method in order to reduce methanol crossover in a direct methanol fuel cell (DMFC). The methanol permeationand the proton conductivity through the modified membranes were investigated. The performances of the direct methanol fuel cell were also tested using single cells with a Nafion membrane and the modified membranes. The Pt-layers on the membrane blocked both methanol crossover and proton transport through the membranes. Methanol permeability and proton conductivity decreased with an increase of the platinum layer thickness. At methanol concentration of 2 M, the DMFC employing the modified membrane with a platinum layer of 66 nm-thickness showed similar performance to that of a DMFC with a bare Nafion membrane in spite of the lower proton conductivity of the former. The maximum power density of the cell using the modified membrane with a platinum layer of 66 nm-thickness increased slightly while that of the cell with the bare membrane decreased abruptly when a methanol solution of 6 M was supplied.

Keywords : Direct methanol fuel cell, Modification of the membrane, Pt-sputtered membrane, Methanol crossover.

1. Introduction

Direct methanol fuel cells (DMFCs) offer many advantages such as high energy density, low fuel price, easy fuel handling, a simple system,and low temperature operation. More specifically, DMFCs are promising candidates for portable power sources and power sources of small electric vehicles. However, DMFCs also have several problems, such as low anode performance and high methanol crossover. Methanol crossover through the membrane poses a particularly challenging problem. Because methanol crossover causes depolarization losses at the cathode and low fuel utilization at the anode by the loss of fuel, it leads to decreased performance.1) A considerable amount of research has recently been focused on proton conducting membranes for DMFCs, especially on reduction of the methanol crossover from the anode to cathode.2-8)

In efforts to reduce methanol crossover, new types of membranes have been suggested and commercial membranes have been modified by various methods. Wainright et al.8) suggested polybenzimidazole (PBI) doped with an amphoteric acid, such as phosphoric acid, and sulfuric acid as a polymer electrolyte. They reported that the acid-doped PBI membrane exhibited excellent oxidative and thermal stability and good mechanical flexibility at elevated temperature (200°C). It also showed good proton conductivity at elevated temperature, an almost zero-osmotic drag number, and low methanol gas permeability. Jia et al.9) modified Nafion 117 by impregnating poly (1-methylpyrrole) by in situ polymerization. Although the methanol crossover was decreased in their modified membrane, its proton conductivity was also decreased. Ma et al.10) attempted to reduce methanol crossover by coating a metal layer of Pt/Pd-Ag alloy/Pt on a Nafion polymer membrane via asputtering method. They reported that the performance of a cell with the sputtered Pt/Pd-Ag/Pt layer on Nafion was higher than that of a cell with bare Nafion membrane, and a cell with a Pt/Pd-Ag/Pt layer of 1 m Pd-Ag layer showed the highest performances among 0.1, 0.2, and 1 m-thickness Pd-Ag layers.A sputtering technique for fabrication of an ultra thin catalyst (Pt) layer has also been used in proton exchange membrane fuel cells (PEMFCs), which allows high catalyst utilization.11)

In this study, a Nafion membrane was modified by depositing Pt film on the surface of the anode side using a sputtering method with the goals of decreasing methanol crossover and thus attaining better DMFC performance. The morphology, methanol permeation, and proton conductivity of the modified membranes were investigated and the performance of direct methanol fuel cells with the modified membranes was tested. The effect of the thickness of the platinum layer on the performance of the cell was also investigated.

2. Experimental

2.1. Modification of Nafion membrane

Nafion® 115 (Dupont) with a nominal equivalent weight of 1100 g/equiv. and thickness in the as-received dry state of 127 μm were used as a polymer electrolyte membrane. Prior to mod-

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ification, the Nafion membrane was pretreated by boiling at 80 in each of the following solutions for more than 1 hr sequentially: 1 M H_2O_2 solution, deionized water, 1 M H_2SO_4 solution, and deionized water. After the pretreatment, the membrane was kept in deionized water until use.

The pretreated membranes were dried at 60°C in a vacuum oven for 24 hrs. Thin layers of platinum were deposited on the surface of Nafion 115 membranes under an argon pressure of 5.0×10^{-3} torr at 30 W by sputtering machine (Korea Vacuum Tech, R. F & D. C magnetron sputtering system). Sputtering time was varied from 30 mins to 90 mins. The substrate holder was rotated during deposition to ensure uniformity of the platinum layers throughout the membranes. Platinum was also deposited on a Si plate under the same conditions to measure the thickness of the platinum layer.4)

2.2. Measurement of methanol permeation

Methanol permeation rate was measured using a home-made permeation test cell at room temperature. The permeation through the membrane was determined by measuring the methanol concentration with a gas chromatographer (GC 17A, Shimadzu) equipped with a flame ionization detector (FID). 2-butanol was used as the internal standard for the gas chromatograph. One side (A) of the cell was filled with an aqueous solution of methanol and 2-butanol, and the other side (B) was filled with an aqueous solution of 2-butanol. The concentration of methanol in room B was measured as a function of time. Methanol flux was calculated from the slope of the plot of methanol concentration vs. permeation time.

2.3. Measurement of proton conductivity

Impedance measurements12) were conducted on a cell consisting of a PtRu anode, a Nafion membrane, and a Pt cathode sandwiched between two graphite flow field plates. MEA was conditioned within the testing fixture at 60 with deionized water for 12 hrs. Methanol solution of 2 M was supplied to the anode side of the MEA at a flow rate of 2 ml/min, and the anode was used as a working electrode. H_2 was supplied to the cathode instead of O_2 or air and the cathode was used as both a reference electrode (normal hydrogen electrode, NHE) and a counter electrode.

The conductivity was measured using an AC impedance spectroscope, which was equipped with a frequency-response analyzer (Solartron SI 1260, Impedance/Gain- phase analyzer) and a potentiostat (Solartron SI 1287, Electro-chemical interface). The range of frequency sweep was 5~70 kHz and the AC amplitude was 5 mV.

The ohmic resistance of the membrane was measured at various methanol concentrations and operating temperatures and the proton conductivity was calculated from the following equation.13)

$$\sigma = l/RS \tag{1}$$

where σ: proton conductivity
l: membrane thickness
R: membrane resistance
S: electrode area

2.4. Measurement of the single cell performance

Single cell performance of a DMFC was measured for MEAs consisting of a Nafion membrane, a cathode with Pt black catalyst of 5 mg-Pt/cm^2 and an anode with PtRu black catalyst of 5 mg-Pt/cm^2. Teflonized carbon paper was used for the diffusion layers.

The cell consisted of a MEA sandwiched between two rectangular graphite plates with incorporated flow channels. The anode feed was methanol solution and the cathode feed was pure oxygen gas of ambient pressure. All of the experimental data were collected after the fuel cell was run continuously for 12 hrs, during which time methanol solution was fed to the anode and air was fed to the cathode. We evaluated the performance of the direct methanol fuel cell by plotting the voltage and the power density versus the current density as a function of the operating temperature and the methanol concentration.

3. Results and discussion

The platinum layers were deposited on a Nafion membrane and their thickness was controlled by changing the sputtering time. Platinum was also deposited on a silicon plate under the same conditions to measure the thickness and the amount of deposited platinum. Fig. 1(a) shows SEM images of the cross-section of the Pt-sputtered silicon plate. Platinum was deposited uniformly and the thickness of the platinum layer was increased linearly with increased sputtering time. The thicknesses of the deposited platinum layers

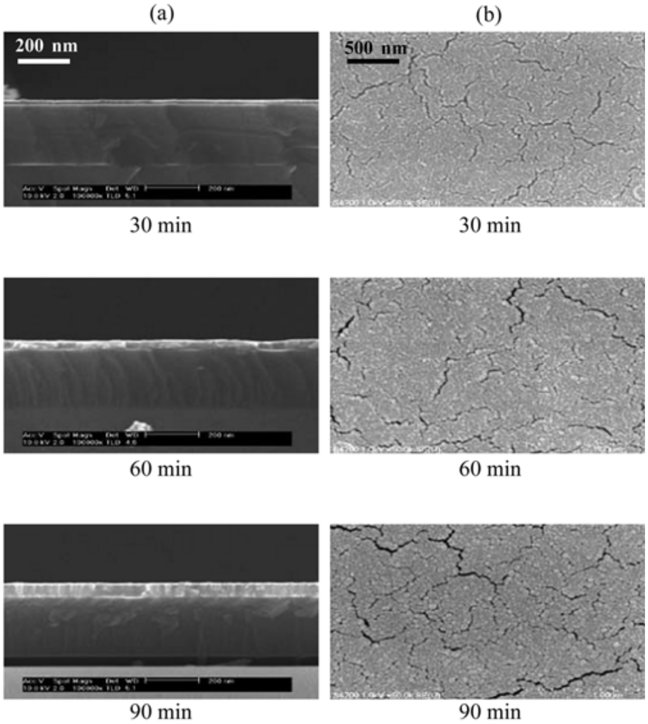

Fig. 1. SEM images of Pt-layers with different sputtering time: (a) cross-section of the Pt-layer deposited on silicon plate, and (b) surface of the Pt-layer on Nafion membrane.

were 20 nm, 42 nm, and 66 nm when the substrate was sputtered for 30 mins, 60 mins and 90 mins, respectively. These platinum layers correspond to 0.04 mg/cm^2, 0.083 mg/cm^2, and 0.13 mg/cm^2, respectively. The membranes with the sputtered Pt-layer are designated as follows according to the thickness of the Pt layer: Pt-20, Pt-42, and Pt-66 (for membranes with a Pt-layer of 20, 42, and 66 nm-thickness, respectively).

Fig. 1(b) shows SEM images of the surface of the Pt-sputtered Nafion membrane. Cracks were found on the surface of the Pt-layer, and they can be more clearly observed with an increase of the Pt-layer thickness. The cracks were caused by the difference in expansion coefficients between the sputtered Pt-layer and the Nafion membrane.[14)] Sputtering was carried out under a high vacuum condition, at which the polymer substrate became completely dry and thereby shrank. After the sputtering process, the Pt-sputtered membrane was stored in the ambient air. The polymer membrane consequently absorbed moisture, causing it to expand, while the sputtered Pt-layer retained almost the same size. As a result, cracking on the Pt-layer occurred.

Fig. 2 shows the methanol flux through the membranes at various methanol concentrations. The methanol flux decreased with an increase of Pt-layer thickness. The methanol flux of the bare Nafion membrane was 2.71×10^{-6} mol/cm^{2}s for the methanol solution of 2 M. The methanol flux through the modified membrane Pt-66 was 1.49×10^{-6} mol/cm^{2}s, which corresponded to a 45% reduction compared to the bare Nafion membrane. Methanol flux increased with increasing methanol concentration, although the rise was not linearly proportional to the methanol concentration. Comparing the methanol flux through the bare Nafion membrane and modified membrane Pt-66, methanol flux was reduced to be 37%, 31%, and 25% for the methanol solutions of 4, 6, and 8 M, respectively.

Fig. 3 shows the effect of the Pt-layer thickness on the proton conductivity. The experiments were carried out with a 2 M methanol solution at 30°C. The value of the bare membrane itself was 0.069 S/cm, which is somewhat lower than that reported in the literature (0.08 S/cm).[15,16)] The discrepancy may be caused by differences in the method of measurement. In previous works, Pt-electrodes were placed on the same surface of the membrane and surface conductivity was measured. However, in the present experiments, the electrodes were placed on the opposite side of the membrane and the proton conductivity was measured across the thickness of the membrane. The ohmic resistance of graphite plates and the contact resistance were also affected, because the proton conductivity of the membrane was measured with a working DMFC. As shown in Fig. 3, the proton conductivity was decreased with an increase of the Pt-layer thickness. The proton conductivity of membrane Pt-66 was 0.0572 S/cm, which corresponded to a 17% reduction relative to the bare Nafion membrane. The Pt-layer on the surface of the electrolyte membrane acted as a barrier to proton conduction.

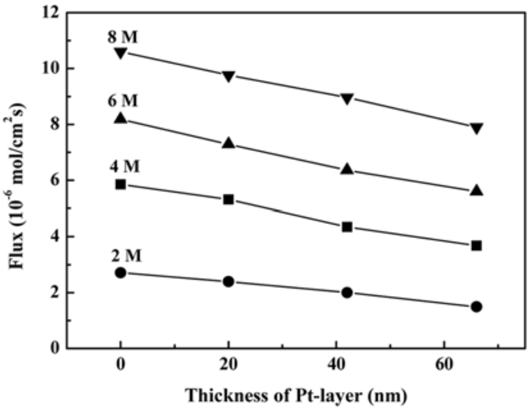

Fig. 2. Plot of methanol flux through the modified membrane versus the thickness of Pt-layer as a function of methanol concentration.

Fig. 4 shows the effect of the operating temperature on the proton conductivity. The test temperature was changed from 30°C to 60°C. Bare Nafion membrane and the modified membrane exhibited a marked increase in proton conductivity with increasing test temperature. This is because temperature plays a major role in the kinetics of proton transfer in the polymer membrane by affecting the mobility of the polymer chains.

From the above results, it is found that both the methanol crossover and the proton conductivity decreased by sputtering the Pt-layer on the proton conducting membrane. There-

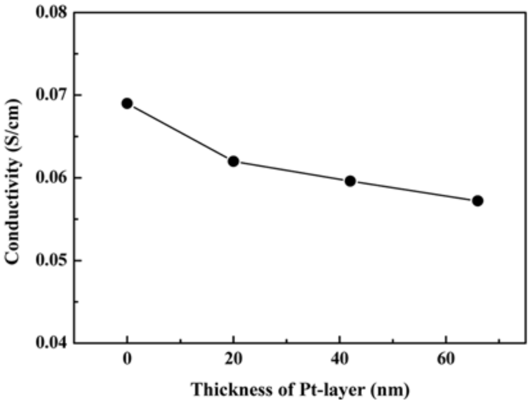

Fig. 3. Effect of the Pt-layer thickness on the proton conductivity in the modified membrane (30°C).

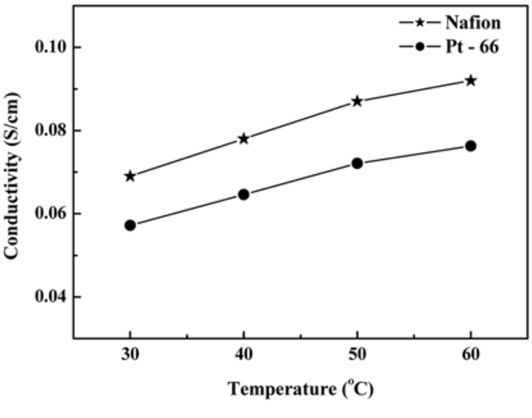

Fig. 4. Effect of the operating temperature on the ionic conductivity.

fore, the effect of the Pt-layer on the cell performance could not be determined, because the decrease of methanol crossover and the decrease of proton conductivity have conflicting effects on the cell performance.

Fig. 5 shows the effect of the Pt-layer on the single cell performance. The performances were obtained with 2 M-methanol solution at 30°C. The power density of the cell with membrane Pt-20 was substantially lower than that of the cell with a bare Nafion membrane, because a Pt-layer of 20 nm-thickness on the bare membrane was insufficient in terms of resisting methanol crossover and because proton conductivity was low relative to the bare Nafion membrane. Comparing the cells with a bare Nafion membrane and with membrane Pt-66, it is found that the Pt-layer enhanced the performance at a low current density range (<125 mA/cm^2). Although the proton conductivity was considerably lower, the decreased methanol crossover compensated the decrease of the proton conductivity. The performance of the cells with Pt-sputtered membranes increased with increasing thickness of the Pt-layer. This appears to be attributable to the effect of reduced methanol crossover being dominant over the effect of lowered proton conduction at these operation conditions.

Open circuit voltage (OCV) and overall power density increased with an increase of operating temperature for all the modified membranes. Fig. 6 shows the effect of the Pt-layer on the single cell performance according to the operating temperature. The maximum power densities of the cells with a bare Nafion membrane and with membrane Pt-66 were 74.4 mW/cm^2 and 72 mW/cm^2, respectively, at 30°C. The difference in the maximum power density between the two membranes was only 3% at 30°C and 7% at 60°C. The higher performance at high temperature is attributed to the combined effect of a reduction of ohmic resistance and activation polarization.

DMFC performances of the membranes were compared for various methanol concentrations at 30°C (Fig. 7). The peak power density of the cell with the bare Nation membrane occurred at 150 mA/cm^2 when 1 M-methanol was supplied and the effect of concentration polarization was found from 150 mA/cm^2 in the I-V curve. However, concentration polarization was not found when a methanol concentration exceeding 2 M was used for the anode fuel. The maximum power density of the cell was the highest when the methanol concentration was 2 M, and thereafter decreased with increasing methanol concentration.

Fig. 7 shows the effect of the sputtered Pt-layer on the single cell performance as a function of methanol concentration. When 1 M-methanol was supplied, the maximum power density of the cell with the bare Nafion membrane was higher than that of the cell with membrane Pt-66. When 2 M-meth-

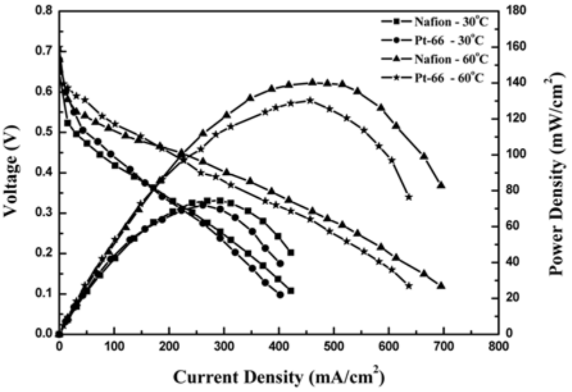

Fig. 6. Effect of the Pt-layer on the cell performance according to the operating temperature (2 M-methanol, O$_2$).

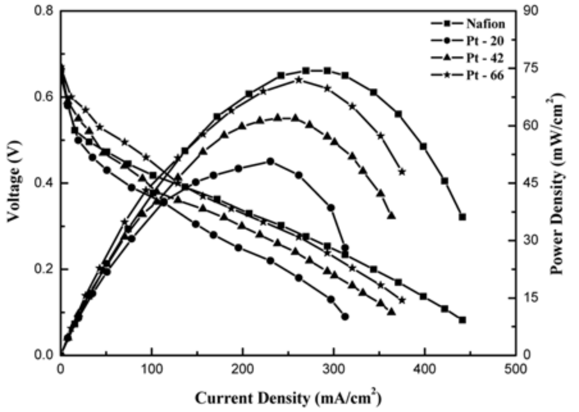

Fig. 5. Effect of the Pt-layer thickness on the cell performance (2 M-methanol, O$_2$, 30°C).

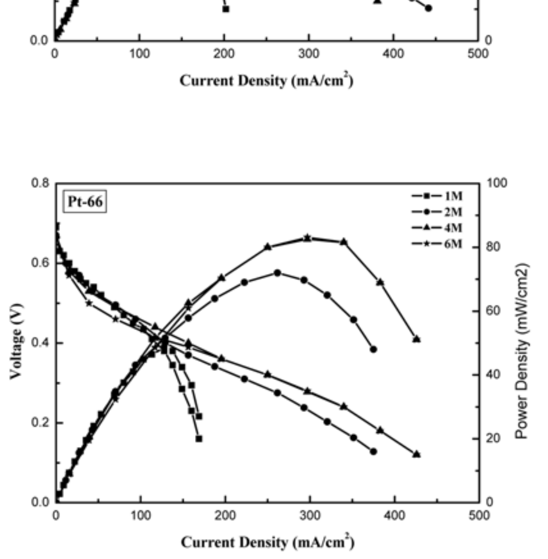

Fig. 7. Effect of the Pt-layer on the cell performance according to the methanol concentration (O$_2$, 30°C).

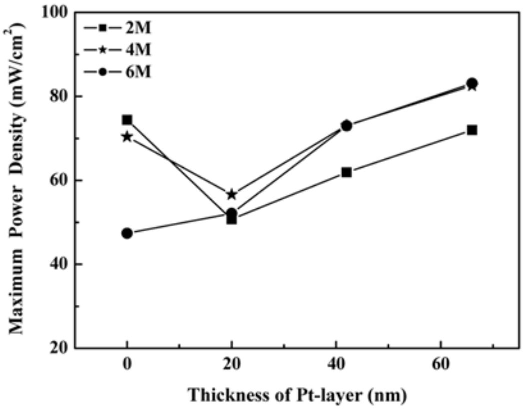

Fig. 8. Plot of maximum power density versus Pt-layer thickness on Nafion membrane as a function of methanol concentration.

anol solution was supplied, the DMFC with membrane Pt-66 showed slightly lower performance compared to the cell with the bare Nafion membrane. When 6 M-methanol solution was supplied, the maximum power density of the cell with membrane Pt-66 was 1.8 times higher than that of the cell with the bare Nafion membrane. The power density of the cell with membrane Pt-66 was 83.1 mW/cm^2 for the 6 M-methanol solution, which corresponded to a 16% increase relative to the 2 M-methanol solution. The bare Nafion membrane showed a value of 47.4 mW/cm^2 for the 6 M-methanol solution, which corresponded to a 36% decrease relative to the 2 M-methanol solution.

Fig. 8 shows the maximum power densities of the cells with bare Nafion membranes and Pt-sputtered membranes at various methanol concentrations. When methanol solution having a concentration lower than 4 M was supplied, the cell performance decreased and then increased with increasing Pt-layer thickness. However, when methanol solution having high concentration (6 M) was supplied, the cell performance increased with increasing Pt-layer thickness, because the bare Nafion membrane was severely influenced by methanol crossover at high methanol concentration.

4. Conclusion

In this study, a Nafion membrane was modified by depositing a Pt thin film via the sputtering method on the surface of the membrane on the anode side to reduce methanol crossover. The Pt layers were deposited uniformly and the thickness increased from 20 to 66 nm with increased sputtering time. The proton conductivity decreased with increased sputtering time and increased with an increase of the operating temperature, regardless of the methanol fuel concentration. The amount of methanol transferred through the membrane decreased with an increase of the Pt-layer thickness. The maximum power density of the cell with membrane Pt-66 was maintained and even slightly increased with an increase of the methanol concentration, while the maximum power density of the cell with a bare Nafion membrane abruptly decreased. Pt-sputtered membranes can be used in DMFCs utilizing high-concentration methanol, affording numerous advantages such as reduced system volume and increased fuel charging time.

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