Performance Evaluation of Platinum Dispersed Self-humidifying Polymer Electrolyte Membrane Prepared by Using RF Magnetron Sputter

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ABSTRACT

The performance evaluation on Pt loading in the self-humidifying polymer electrolyte membrane for Polymer Electrolyte Membrane Fuel Cell(PEMFC) was investigated by using single cell test and measurement of membrane resistance. The self-humidifying membrane comprised two membranes made of perfluorosulfonylfluroride copolymer resin and fine Pt particles lying between them, coated by sputtering. From the results of performance characteristics of self-humidifying membrane cell with different Pt loading, a single cell using self-humidifying membrane with 0.15 mg/cm² Pt loading showed better performance than that with the others over entire current density. Also, a single cell with 0.15 mg/cm² Pt loading had a lower resistance value than the other cells under externally nonhumidifying condition. It is indicated that the water produced in the membrane cell with 0.15 mg/cm² Pt loading showed a higher provision to maintain ionic conductivity of the membrane than the other cells. The optimum amount of Pt particles embedded in the membrane for self-humidifying PEMFC was determined to be about 0.15 mg/cm².

Key words : PEMFC, Self-humidifying membrane, Sputtering, Single cell performance

1. Introduction

Polymer Electrolyte Membrane Fuel Cells(PEMFCs) have attracted enormous interest as a primary power source for vehicular and stationary applications because of its high power density, low weight, and simplicity of operation.[1] In PEMFC, Polymer Electrolyte Membrane (PEM) requires water to maintain its proton conductivity during operation as a power source. So far, in order to retain an optimum hydration level of the fuel cell, water has been supplied for the membrane indirectly by humidifying systems, and then water content of membrane changes dynamically with the operating conditions. However, the humidification unit increases volume and weight of fuel cell system, thereby decreasing its overall power density. The simplest PEMFC system would be one where no auxiliary humidification system is required. Great advantages in terms of further fuel cell simplification can be achieved if the humidification process can be eliminated or minimized.

Watanabe et al.[2,3] have proposed a special membrane, which was recast from solubilised polymer electrolyte membrane incorporated with nanometer-size particles of Pt and metal oxides, such as silicon oxide or titanium oxide. This membrane was modified by dispersion of Pt particles (~0.09 mg/cm²) inside the membrane via cation exchange followed

by reduction. The Pt particles embedded in the membrane act as a recombination site for permeated hydrogen and oxygen, thereby producing the water molecule. Yang et al.[4] developed a new self-humidifying membrane, which was adopted the perfluorosulfonylfluoride copolymer resin with melt-fabricable property and sputtering technique, to investigate the optimum conditions for its manufacture and the exact mechanism for self-humidification. This method referred fabrication of the form of sandwich, which was comprised of two membranes made of perfluorosulfonylfluoride copolymer resin and fine Pt particles lying between them. The Pt particles were coated onto the one side of the membrane by a sputtering method.

Although some researchers have reported fuel cell performances and mechanical properties of the self-humidifying membranes,[2-4] there were few investigations on the variation of fuel cell performance characteristics of the self-humidifying membranes related to the change in Pt loading embedded in the membrane. The aim of this work has two objectives. One is to provide a new method to prepare a self-humidifying electrolyte membrane and the optimum condition for its fabrication. The other is to find the optimum Pt loading for self-humidification occurring in the membrane fabricated by the present method. For these purposes, the self-humidifying membranes containing various amounts of Pt particles were prepared in the form of sandwich, which was composed of two membranes made of perfluorosulfonylfluroride copolymer resin and fine Pt particles lying between them. The Pt particles were coated onto the one side of membrane by a sputtering method. The optimum

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condition for fabrication of a self-humidifying membrane was investigated based upon the results from the differential temperature (DTA)-weight (TGA) analyses, visual inspections. The cross-sectional morphology of the self-humidifying membrane has been investigated using by Scanning Electron Microscopy (SEM). The effect of Pt loading embedded in the self-humidifying membrane on the cell performance was examined, and therefore, the variation of membrane resistance along with the Pt loading was investigated. From the results of experiments, the optimum Pt loading embedded in the self-humidifying membrane was determined.

2. Experimental

Perfluorosulfonylfluoride resin (NAFION® R-1100 resin, DuPont Fluoroproducts, USA) was used as a precursor for fabrication of self-humidifying PEM. The precursor resin was analyzed using DTA-TGA (Thermal Sciences, PL-STA 150), in order to determine the fabrication conditions of the membrane. The DTA-TGA measurement was carried out in the temperature range 25–700°C in air at a scan rate of 10 x°C/min.[5] Fig. 1 illustrates the preparation procedure of the self-humidifying membrane and the manufacture of the MEA. Perfluorosulfonylfluoride resin was pre-formed as a sheet shape by hot pressing in the temperature range 200–250 C. The pre-formed membrane was used as a substrate and fine Pt particles were coated on one side of the membrane surface using a radio frequency(rf) magnetron sputter. Then, a self-humidifying membrane was obtained by joining another uncoated pre-formed membrane with the

coated side of the Pt sputtered membrane. The delivered power of an rf source was 50 W, and the dwelling time for the Pt sputtering was changed in the time range 5–30 min. The self-humidifying membrane with F^+ form was converted into Na^+ form to give a suitable property in the fabrication of MEA. In order to obtain a self-humidifying membrane using the Na^+ form, the membrane was boiled in a solution of 20% NaOH/Methanol (2 : 1 in ratio of volume) for 7 h at 90°C, followed by rinsing repeatedly with de-ionized water.

20 wt% Pt/C (Johnson-Matthey Inc.) was used as an electrocatalyst. In order to raise the stability of electrocatalyst, the protonated form of Nafion within the slurry was converted into the thermoplastic form by the addition of 1M Tetrabutyl Ammonium Hydroxide(TBAOH) in methanol containing hydrophobic anion of TBA^+. The paintability of the slurry was improved by the addition of glycerol, in the approximate ratio of 1 : 1 (in ratio of weight) with the Nafion solution. The catalyst slurry was applied to one side of transfer film by using decal method. Then, the coated layer was dried for 6 h in the vacuum oven at 140°C. The slurry coated on the transfer film was hot pressed on each side of dried Na^+ form self-humidifying membrane for 2 min at 195°C with a pressure of 77 bar. The content of electrocatalyst loading was controlled to be 0.2 mg Pt per cm^2, and the MEA was converted into H^+ form by immersing it in 0.5 M H_2SO_4 for 7 h at 90°C, followed by washing repeatedly in de-ionized water.

The procedures of the assembly and the measurement of cell performance were described in detail in our previous papers.[4,6,7] Performance of single cells for the self-humidifying membranes with various Pt loading was evaluated under the atmosphere of hydrogen and oxygen reactant gases with an active area of 50 cm^2 at 50°C. During the single cell measurement, milliohmmeter (Agilent 4338B, Japan) was used to examine the variation of resistance along with the amount of Pt particles embedded in the membrane

3. Results and Discussion

In order to determine the pre-forming temperature for the membrane, DTA-TGA analyses were made on the precursor resin. Fig. 2 shows the results of DTA-TGA analyses for the precursor resin. Weight loss accompanied by exothermic reaction starts at around 380°C and finishes at around 500°C, indicating the occurrence of decomposition of the precursor resin. Based upon the result, membrane sheet was pre-formed by hot pressing precursor resin at various temperatures below 380°C. At temperatures above 230°C, the pre-formed sheet involves pores inside the sheet. Presence of pores in the sheet acts as a barrier to proton conduction and decreases fuel cell performance by enhancing the crossover of the hydrogen and oxygen both through the membrane. From the successive hot pressing followed by examination, the optimum temperature for the fabrication
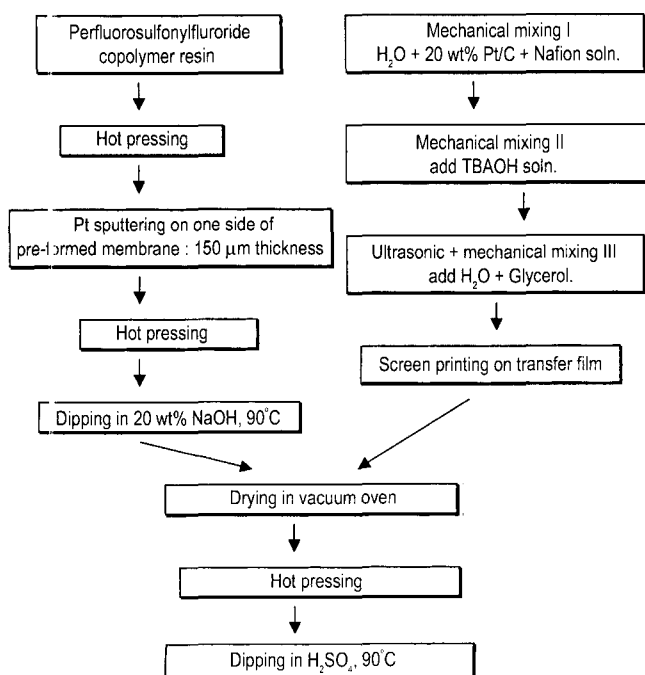

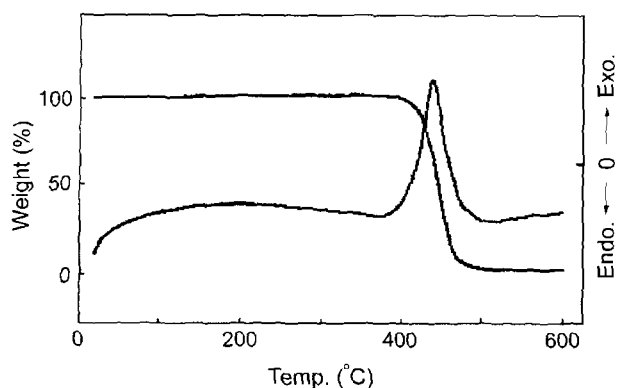Fig. 1. Flow chart for preparation of self-humidifying membrane and MEA.

Fig. 2. Weight (TG) and differential temperature (DTA) versus temperature curves for perfluorosulfonylfluoride precursor resin measured in air at a scan rate of 10°C/min.
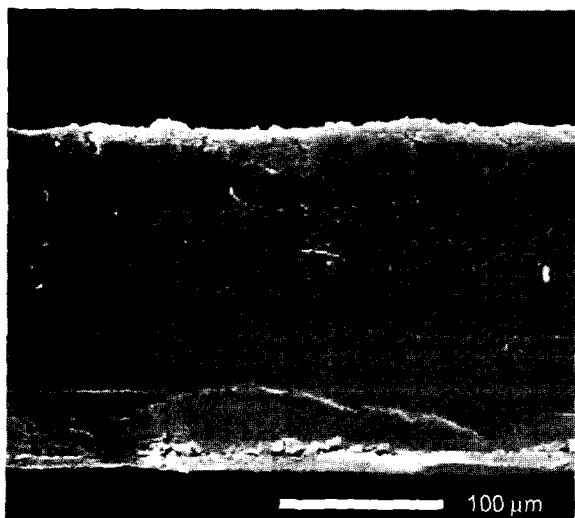

Fig. 3. Scanning electron micrograph for cross section of MEA made with self-humidifying membrane and Pt/C electrocatalyst.

of pore-free membrane sheet was determined to be 230°C.

The cross-sectional SEM picture of the MEA with a self-humidifying membrane and Pt/C electrocatalyst is presented in Fig. 3. The electrocatalyst layers were observed both side top and bottom and the membrane was in the center. Fig. 3 shows that the membrane was well adhered to the porous electrocatalyst layer without any delamination. The thickness of the electrocatalyst layer and membrane of the MEA was approximately 30 and 150 µm, respectively.

The amount of Pt particles embedded in the self-humidifying membrane was determined to be 0.05, 0.10, 0.15 and 0.20 mg/cm² by using inductively coupled plasma mass spectrometry (ICP-MS, PQ3, VG Elemental Ltd. UK). Fig. 4 shows the performance of the single cells using self-humidifying membranes with various Pt loading measured without external humidification under the reactant gases of hydrogen and oxygen of ambient pressure at 50°C. At low current density, there was a little difference in the cell performance for the various Pt loading. At high current densities, how-
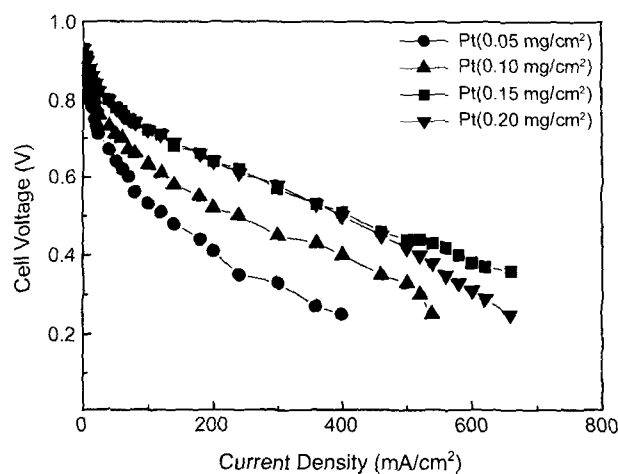

Fig. 4. Performance of single cells using self-humidifying membranes with various Pt loading measured at 50°C and ambient pressure without any external humidification: (●) 0.05 mg/cm² Pt loading; (▲) 0.10 mg/cm² Pt loading; (■) 0.15 mg/cm² Pt loading; (▼) 0.20 mg/cm² Pt loading.

ever, it was shown that as the amount of Pt particles embedded in the membrane increased, the cell performance increased. In the low current density region where activation polarization predominates, the intrinsic property of the catalysts in the electrode is an important factor, whereas in the ohmic polarization region at high current density, the ionic conductivity of polymer electrolyte is more essential.[8] The ionic conductivity of polymer electrolyte depends on water content in the membrane.[9,10] In particular, a self-humidifying membrane cell with 0.15 mg/cm² Pt loading showed higher output performance than that with the other Pt loading. Again, the rate of proton transfer through the self-humidifying membrane with 0.15 mg/cm² Pt loading was greater than that through the others. This clearly shows that water content of the self-humidifying membrane with 0.15 mg/cm² Pt loading was higher than that with the other Pt loading. Consequently, Pt particles embedded in the membrane played an important role in maintenance the humidity in the PEM. Pt particles were conceived to provide sites for the catalytic recombination of hydrogen and oxygen reactant gases permeated from anode and cathode, thereby producing water inside membrane. On the other hand, at high current densities, self-humidifying membrane cell with 0.20 mg/cm² Pt loading shows lower output performance than that with 0.15 mg/cm² Pt loading. This result may be due to increasing the amount of Pt particles embedded in the membrane. As the amount of Pt particles embedded in the membrane increase, the resistance of the membrane will be increased, and consequently the ionic conductivity of polymer electrolyte membrane will be decreased.

In order to analyze how Pt particles embedded in the membrane were behaved, resistance measurements have been made for self-humidifying membrane with various Pt loading. The changes of the resistance in the self-humidify-
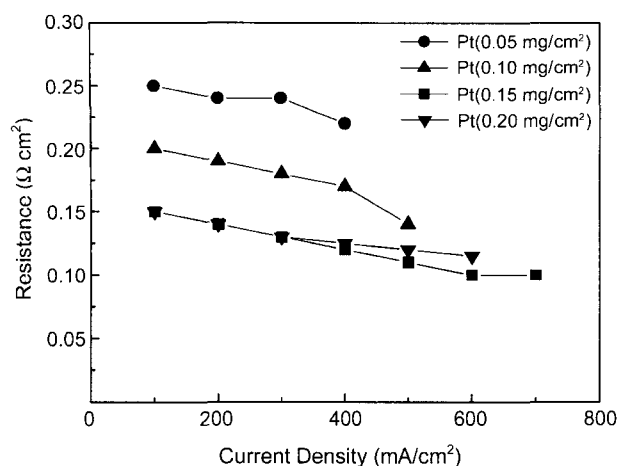
Fig. 5. Changes of resistance of self-humidifying single cells with various Pt loading as a function of current density. The operation conditions of cells and the used symbols are the same as those of captions of Fig. 4.

Fig. 6. Cell voltage decay curves for self-humidifying single cells with various Pt loading measured under application of constant load of 200 mA/cm² at 50 °C and ambient pressure: (●) 0.05 mg/cm² Pt loading; (▲) 0.10 mg/cm² Pt loading; (■) 0.15 mg/cm² Pt loading; (▼) 0.20 mg/cm² Pt loading.

ing nembrane cell without any external humidification are illustrated in Fig. 5 as a function of current density. The resistance of self-humidifying membrane cell with 0.15 mg/cm² Pt loading was still large, ca. 0.14 cm² at the current density less than 400 mA/cm², and decreased slightly at a higher current density. The self-humidifying membrane cells with 0.05 and 0.10 mg/cm² Pt loading showed a high resistance than that with 0.15 mg/cm² over the entire current density range. This indicates that the rate of proton conduction through the self-humidifying membrane cell with 0.15 mg/cm² Pt loading exceeds that the others. Considering the result in terms of water content in the membrane again, the water content in the self-humidifying membrane cell with 0.15 mg/cm² Pt loading seemed to be higher as compared to that in case of self-humidifying membrane cell with the other Pt loading. Adding to Pt particles in the membrane, the performance of fuel cell under externally nonhumidifying conditions increased, resulting from the self-humidification with water produced by the recombination of crossover hydrogen and oxygen reactant gases on the Pt particles in the PEM.[11] This result suggests that the water produced by recombination permeated hydrogen and oxygen reactant gases on the Pt particles embedded in the membrane is the major motive force for the water content in the nembrane rather than electroosmotic drag under externally nonhumidifying conditions. However, the self-humidifying membrane cell with 0.20 mg/cm² Pt loading showed a higher resistance value than that with 0.15 mg/cm² at high current density. The reason it has large value at high current density is that because the amount of Pt particles embedded in the membrane was more increase than 0.15 mg/m² Pt loading. Therefore, as the Pt content embedded in the membrane increased, the resistance of the membrane increased because the ionic conductivity of the membrane decreased. Hence, the adequate control of the amount of Pt particles embedded in the membrane for self-humidification
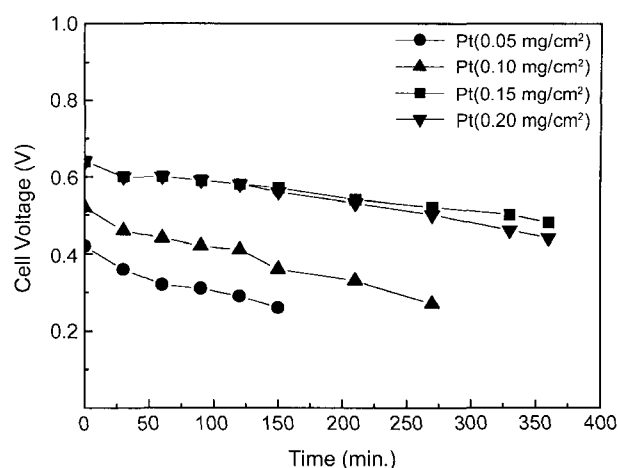
is very important.

The stability test of the single cells using self-humidifying membrane with different Pt loading was performed under application of 200 mA/cm² at 50°C and ambient pressure. Fig. 6 shows the cell voltage decay curve for the single cells using self-humidifying membrane with various Pt loading under externally nonhumidifying condition. From the result in Fig. 6, it appears that the performances of the self-humidifying membrane cells with 0.15 and 0.20 mg/cm² Pt loading were very similar over the entire range. However, the self-humidifying membrane cell performances with 0.05 and 0.10 mg/cm² Pt loading decay slowly with increasing time. It is considered that the self-humidifying membrane cells with Pt loading lower than 0.15 mg/cm² could not provide adequate water for the catalytic recombination of the crossover hydrogen and oxygen reactant gases at the operating condition of constant current density. Again, this is because of decreasing a catalytic site for production the water, which was made by recombination hydrogen and oxygen reactant gases on the Pt particles embedded in the membrane. Therefore, the ability of proton transfer of the self-humidifying membrane with little Pt loading showed lower than highly dispersed Pt containing membrane. The water produced by self-humidification process relies strongly on the amount of Pt particles embedded in the membrane. Accordingly, the amount of Pt particles embedded in the self-humidifying membrane must be precisely controlled. If the Pt loading in the membrane is too low, a recombination site for permeated hydrogen and oxygen to produce water molecule will be decreased. Consequently, water produced by Pt particles embedded in the membrane was not sufficient to maintain the ionic conductivity of the membrane. But, the amount of Pt particles embedded in the membrane is too much, the internal resistance of the mem-

brane will be increased, and the ionic conductivity of the membrane will be decreased. Based upon the results of experiments, a self-humidifying membrane cell with 0.15 mg/cm² Pt loading showed higher output performance and lower cell resistance than the others. Hence, the optimum amount of Pt particles embedded in the self-humidifying membrane was about 0.15 mg/cm².

4. Conclusions

In this work, the performance evaluation on Pt particle embedded in the self-humidifying membrane for Polymer Electrolyte Membrane Fuel Cell(PEMFC) was presented, using perfluorosulfonylfluroride copolymer resin and sputtering technique. The optimum amount of Pt particles embedded in the membrane for self-humidifying PEM was determined to be about 0.15 mg/cm², based upon the results of single cells performance characteristics and resistance measurements. From the comparison of single cells performance with different Pt loading, a self-humidifying membrane cell with 0.15 mg/cm² Pt loading showed higher performance than that of the others particularly at high current density region. In addition, from the dependence of resistance of the membrane on different Pt loading, the cell with 0.15 mg/cm² Pt loading had a lower resistance value than the other cells under externally nonhumidifying condition. It is indicated that the water produced in the membrane cell with 0.15 mg/cm² Pt loading showed a higher provide to maintain ionic conductivity of the membrane than the other cells. Again, the low resistance value of the cell with 0.15 mg/cm² Pt loading was related to increase the water generated by the catalytic recombination of the crossover hydrogen and oxygen reactant gases at the operating condition. However, as the amount of Pt particles embedded in the membrane increased, the resistance of the membrane increased due to the diminution of ionic conductivity of the membrane.

Acknowledgement

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