The effect of platinum loading in the self-humidifying polymer electrolyte membrane on water uptake

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Abstract

The effect of Pt loading in the self-humidifying polymer electrolyte membrane (PEM) for polymer electrolyte membrane fuel cell (PEMFC) on the water uptake was investigated. The self-humidifying membrane was composed of two membranes made of perfluorosulfonylfluoride copolymer resin and fine Pt particles lying between them coated by a sputtering method. The membrane electrode assembly (MEA) was made using the decal method. The optimum amount of Pt particles embedded in the membrane for the self-humidification PEMFC was determined to be about 0.15 mg/cm^2, based upon the measurements of single cell performance characteristics and resistance.
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1. Introduction

The polymer electrolyte membrane fuel cell (PEMFC) has 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]. The polymer electrolyte membrane (PEM) requires water to maintain its proton conductivity during operation. In order to retain the optimum hydration level of the fuel cell, water has to be supplied to the membrane by a humidifying system, and the water content in the membrane changes dynamically with the operating conditions. In general, the humidification unit increases the volume and weight of the fuel cell system, thereby decreasing its overall power density. Thus, a PEMFC system without an auxiliary humidification unit has great advantages.

Watanabe et al. [2,3] have investigated a self-humidifying membrane by recasting the solubilized Nafion® ionomer and incorporating in it nanometer-size Pt and metal oxide particles. The Pt and oxide particles were incorporated into the membrane by the reduction of solutions containing metal ions. The Pt particles embedded in the membrane act as water generation sites by recombination of permeated hydrogen and oxygen. Yang et al. [4] developed a new self-humidifying membrane using a melt-fabricable perfluorosulfonylfluoride copolymer resin and a sputtering technique. Although some researchers have reported the fuel cell performance and mechanical properties of the self-humidifying membranes, 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 is to investigate the influence of the Pt loading on the water uptake in the self-humidifying membrane. For this purpose, the self-humidifying membranes containing various amounts of Pt particles were prepared using a melt-fabricable perfluorosulfonylfluoride copolymer resin and a sputtering technique. The self-humidifying membrane cell performance and resistance were measured. From the results of the experiments, the optimum Pt loading embedded in the self-humidifying membrane was determined and the role of Pt particles was discussed in terms of water uptake and ionic conductivity.

2. Experimental

2.1. Preparation of self-humidifying membrane and membrane electrode assembly (MEA)

The self-humidifying membrane for the PEMFC was prepared by using melt-fabricable perfluorosulfonylfluoride resin (Nafion® R-1100 resin, DuPont Fluoroproducts, USA). Fig. 1 illustrates the preparation procedure of the self-humidifying membrane and the manufacture of the

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┌─────────────────────────────┐          ┌─────────────────────────────┐
│  Perfluorosulfonylfluroride │          │    Mechanical mixing I      │
│      copolymer resin        │          │ H₂O + 20wt% Pt/C + Nafion soln. │
└─────────────────────────────┘          └─────────────────────────────┘
              │                                        │
              ▼                                        ▼
     ┌─────────────────┐                    ┌─────────────────────────────┐
     │   Hot pressing  │                    │     Mechanical mixing II    │
     └─────────────────┘                    │       add TBAOH soln.       │
              │                             └─────────────────────────────┘
              ▼                                        │
┌─────────────────────────────────┐                   ▼
│  Pt sputtering on one side of   │        ┌─────────────────────────────┐
│ pre-formed membrane : 150μm thickness │  │ Ultrasonic + mechanical mixing III │
└─────────────────────────────────┘        │     add H₂O + Glycerol.     │
              │                             └─────────────────────────────┘
              ▼                                        │
     ┌─────────────────┐                              ▼
     │   Hot pressing  │                    ┌─────────────────────────────┐
     └─────────────────┘                    │ Screen printing on transfer film │
              │                             └─────────────────────────────┘
              ▼
┌─────────────────────────────┐
│ Dipping in 20wt% NaOH, 90°C │
└─────────────────────────────┘
              \                        /
               ▼                      ▼
          ┌─────────────────────────────┐
          │    Drying in vacuum oven    │
          └─────────────────────────────┘
                        │
                        ▼
          ┌─────────────────────────────┐
          │        Hot pressing         │
          └─────────────────────────────┘
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          ┌─────────────────────────────┐
          │   Dipping in H₂SO₄ 90°C     │
          └─────────────────────────────┘
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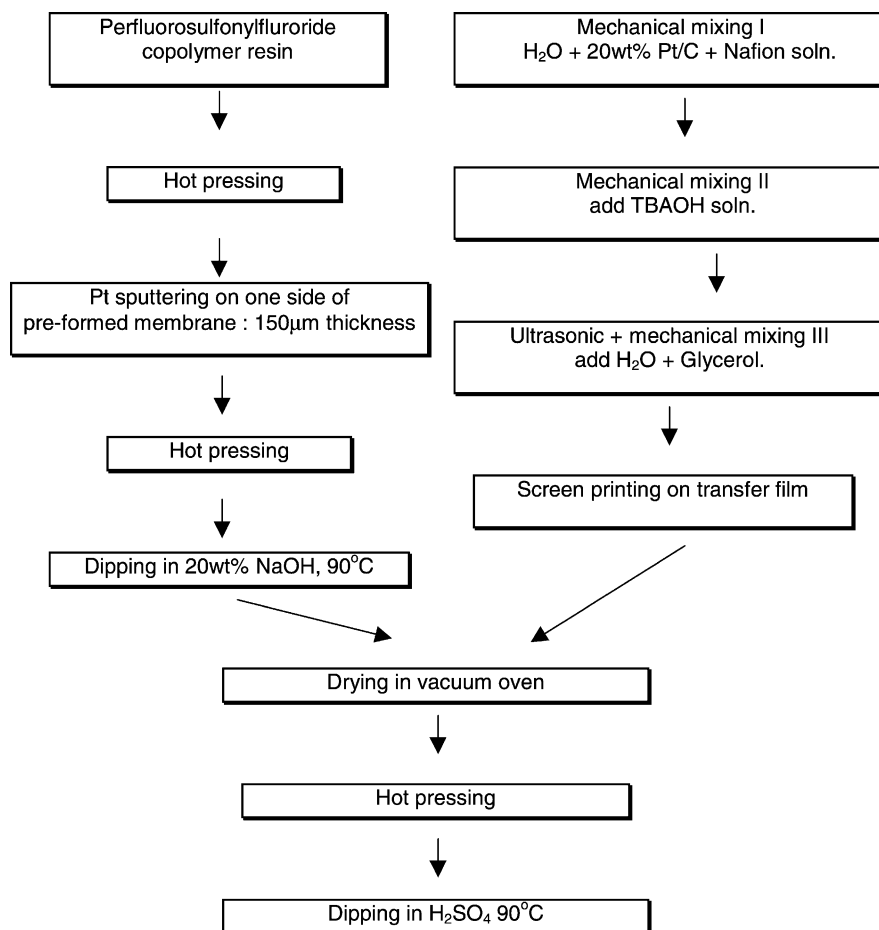
Fig. 1. Flow chart for preparation of self-humidifying membrane and MEA.

membrane electrode assembly (MEA). Perfluorosulfonyl-fluoride copolymer resin was pre-formed as a sheet shape by hot pressing at the temperature of 230 °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 varied within the time range 5–30 min. 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/cm^2 by using inductively coupled plasma mass spectrometry (ICP, PQ3, VG Elemental Ltd., UK). The self-humidifying membrane in the F form was converted into the Na$^+$ form to give a suitable property in the fabrication of the 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.

A 20 wt.% Pt/C (Johnson-Matthey Inc.) was used as an electrocatalyst. In order to raise the stability of the electrocatalyst, the protonated form of Nafion$^®$ within the slurry was converted into the thermoplastic form by the addition of 1 M tetrabutyl ammonium hydroxide (TBAOH) in methanol containing the hydrophobic anion 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 the transfer film by a decal method. Then, the coated layer was dried for 6 h in a vacuum oven at 140 °C. The Pt/C coated on the transfer film was hot pressed on both sides of a dried self-humidifying membrane of the Na$^+$ form for 2 min at 195 °C under pressure of 77 bar. The electrocatalyst loading was controlled to be 0.2 mg Pt/cm^2. The MEA was converted into the H$^+$ form by immersing it in 0.5 M H$_2$SO$_4$ for 7 h at 90 °C, followed by washing repeatedly in the de-ionized water.

2.2. Measurement of single cell performance

The procedures of the assembly and the measurement of cell performance were described in detail in our previous papers [5–7]. The performance of a single cell for self-humidifying membranes with various Pt loading was evaluated under an atmosphere of hydrogen and oxygen reactant gases with an active area of 50 cm^2 at 50 °C.

During the single cell measurement, a milliohmmeter (Agilent 4338B, Japan) was used to examine the variation of resistance with the amount of Pt particles embedded in the membrane.

3. Results and discussion

3.1. Membrane electrode assembly

A cross-sectional SEM picture of the MEA with a self-humidifying membrane and a Pt/C electrocatalyst is presented in Fig. 2. The electrocatalyst layers were observed both sides at the top and the bottom and the membrane was in the center. Fig. 2 shows that the membrane was well adhered to the porous electrocatalyst layer without any delamination. The thicknesses of the electrocatalyst layer and the membrane of the MEA were approximately 30 and 150 μm, respectively.

3.2. Single cell performance

Fig. 3 shows the performance of the single cell using self-humidifying membranes with various Pt loadings measured without external humidification under reactant gases of hydrogen and oxygen at ambient pressure and 50 °C. There was a little difference in the cell performance for the various Pt loadings in low current density region; however, the cell performance increased with increase in the amount of Pt particles embedded in the membrane in the high current density region. In particular, a self-humidifying membrane cell with 0.15 mg/cm^2 Pt loading showed higher performance than that with the other Pt loadings.
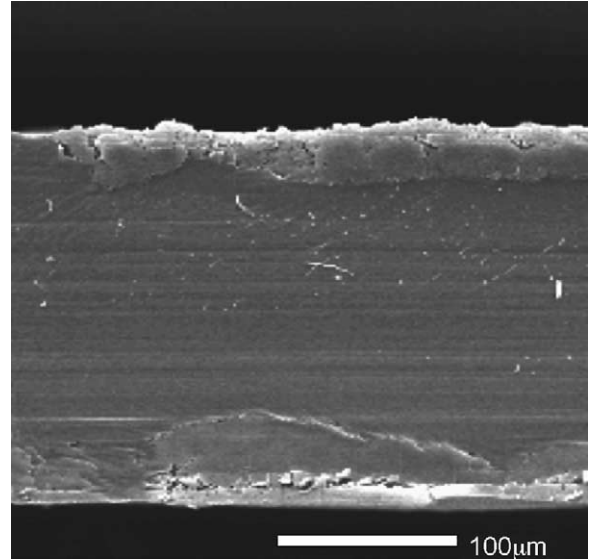
Fig. 2. Scanning electron micrograph for a cross-section of MEA made with self-humidifying membrane and Pt/C electrocatalyst.

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 the polymer electrolyte is more important [8]. The ionic conductivity of the polymer electrolyte depends on the water content of the membrane. The good performance using a self-humidifying membrane cell with 0.15 mg/cm^2 Pt loading suggests that the water content of the self-humidifying membrane with 0.15 mg/cm^2 Pt loading is higher than that with other Pt loadings. Consequently, the Pt particles embedded in the membrane played an
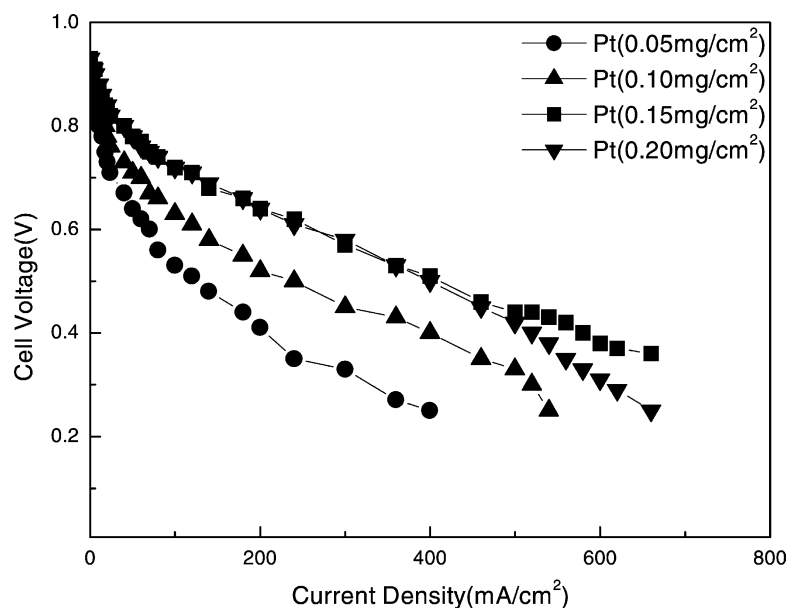

Fig. 3. Performance of single cells using self-humidifying membranes with various Pt loadings measured at 50 °C and ambient pressure without any external humidification: (●) 0.05 mg/cm^2 Pt loading; (▲) 0.10 mg/cm^2 Pt loading; (■) 0.15 mg/cm^2 Pt loading; (▼) 0.20 mg/cm^2 Pt loading.
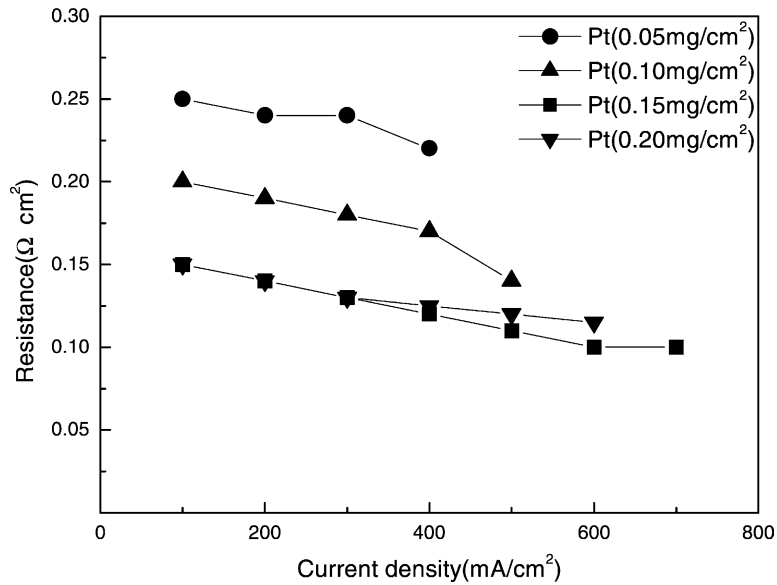
Fig. 4. Changes of resistance of self-humidifying single cells with various Pt loadings as a function of the current density. The operation conditions of cells and the symbols used are the same as those in the captions for Fig. 3.

important role in enhancing the proton conductivity in the PEM. The Pt particles were conceived to provide sites for the catalytic recombination of hydrogen and oxygen reactant gases permeated from the anode and the cathode, thereby producing water inside the membrane. By contrast, at high current density, the self-humidifying membrane cell with 0.20 mg/cm^2 Pt loading shows lower performance than that with 0.15 mg/cm^2 Pt loading. In general, as the amount of Pt particles embedded in the membrane increases, the resistance of the composite membrane is increased due to hindrance of proton conduction through the membrane.

The change of the cell resistance using the self-humidifying membrane cell without any external humidification is illustrated in Fig. 4 as a function of the amount of Pt loading. The cell resistance with 0.15 mg/cm^2 Pt loading was still large, ca. 0.14 Ω cm^2 at the current density less than 400 mA/cm^2, and decreased slightly at a higher current density. The self-humidifying membrane cells with 0.05 and 0.10 mg/cm^2 Pt loading showed a higher resistance than that with 0.15 mg/cm^2 over the entire current density range. This indicates that the water content in the membrane cell with 0.15 mg/cm^2 Pt loading was higher than that of the
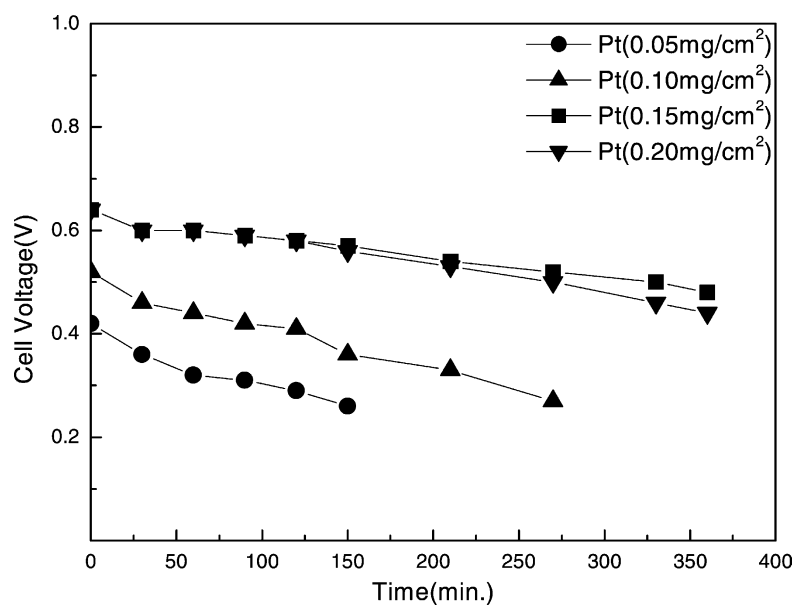

Fig. 5. Cell voltage decay curves for self-humidifying single cells with various Pt loadings measured under the application of a constant load of 200 mA/cm^2 at 50 °C and ambient pressure: (●) 0.05 mg/cm^2 Pt loading; (▲) 0.10 mg/cm^2 Pt loading; (■) 0.15 mg/cm^2 Pt loading; (▼) 0.20 mg/cm^2 Pt loading.

other cells and that the rate of proton conduction through the membrane with 0.15 mg/cm^2 Pt loading is faster than through the others.

Based upon the results, as the concentration of Pt particles embedded in the membrane was increased, the amount of water in the self-humidifying membrane was probably increased. However, the self-humidifying membrane cell with 0.20 mg/cm^2 Pt loading showed a higher resistance value than that with 0.15 mg/cm^2 at high current density. The reason is that the resistance of the membrane was increased with increasing Pt particles. In general, the proton conductivity in the membrane was decreased with increase in the Pt particle doping. Therefore, as the Pt content embedded in the membrane increased, the resistance of the membrane increased.

Fig. 5 shows the cell voltage decay curve for the single cell using a self-humidifying membrane with various Pt loadings under a constant load of 200 mA/cm^2 at 50 °C and ambient pressure. The cells with 0.15 and 0.20 mg/cm^2 Pt loading were very similar over the entire range. However, the cell performances with 0.05 and 0.10 mg/cm^2 Pt loadings decay slowly with increasing time. It is considered that the self-humidifying membrane cells with Pt loading lower than 0.15 mg/cm^2 could not provide water sufficiently by the catalytic recombination of the crossover hydrogen and oxygen. This means that the number of catalytic sites for the production of water is not enough to maintain the ionic conductivity of the membrane and that the water produced by the self-humidification process relies strongly on the amount of Pt particles. However, when the amount of Pt particles embedded in the membrane is more than 0.15 mg/cm^2, the cell performance is lowered due to the negative effect of an increase of membrane resistance. Based upon the results of these experiments, the self-humidifying membrane cell with 0.15 mg/cm^2 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 determined to be about 0.15 mg/cm^2.

4. Conclusions

In this work, the effect of Pt particles embedded in the self-humidifying membrane for the polymer electrolyte membrane fuel cell (PEMFC) on the water uptake was presented, using a perfluorosulfonylfluroride copolymer resin and a sputtering technique. From the comparison of single cell performance with different Pt loadings, the self-humidifying membrane cell with 0.15 mg/cm^2 Pt loading showed the best performances, particularly in the high current density region. Furthermore, from the dependence of cell resistance on the amount of Pt loading, the cell with 0.15 mg/cm^2 Pt loading had a lower resistance value than the other cells under the externally nonhumidifying condition. It is indicated that the Pt particles embedded in the self-humidifying membrane act as a water generation site by catalytic recombination of crossover hydrogen and oxygen, and this enhances the proton conduction. However, the addition of Pt particles over 0.15 mg/cm^2 in the membrane hinders the proton conduction and lowers the cell performance. Hence, the optimum amount of Pt particles embedded in the membrane for a self-humidifying PEMFC was determined to be about 0.15 mg/cm^2, based upon the results of single cell performance characteristics and resistance measurements.

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