

A novel preparation method for a self-humidifying polymer electrolyte membrane

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Abstract

A novel method for the preparation of a self-humidifying membrane used for polymer electrolyte membrane fuel cell (PEMFC) and optimum condition for the fabrication are presented. Generation of water molecules on the Pt particles embedded in the membrane by the recombination of permeated hydrogen and oxygen is attributed to the appearance of higher performance of a single cell adopting the self-humidifying membrane. The mechanism for water production is strongly substantiated by the experimental result from IR spectrum with absorption peaks corresponding to the characteristic OH stretching bond, observed only in the case of the self-humidifying membrane kept in hydrogen and oxygen mixture gases. The new preparation method involves fabrication of a sandwich structure, which is comprised of two membranes made of perfluorosulfonylfluoride copolymer resin and fine Pt particles lying between them, coated by sputtering. The optimum pre-forming temperature for the pore-free membrane sheet is determined to be 230 °C, based upon the results of successive experiments. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Attempts have been made to remove the externally humidifying unit from the polymer electrolyte membrane fuel cell (PEMFC) system by endowing the electrolyte membrane with self-humidifying ability [1,2]. Watanabe et al. [1,2] suggested a method to fabricate the self-humidifying polymer electrolyte membrane (PEM).

The method involved dispersion of Pt based electroless plating and of oxide particles, such as SiO₂ or TiO₂ throughout the membrane. They proposed the higher performance of a single cell adopting the self-humidifying PEM to Pt dispersed throughout the membrane that acts as a recombination site for permeated hydrogen and oxygen to produce water molecules. However, electroless plating had several disadvantages, such as a considerable amount of remaining impurity, non-uniform distribution of Pt particles throughout the membrane and finally formation of an electron conducting path by the network of dispersed Pt particles.

Dhar [3] suggested the use of a very thin membrane, which allows the water molecules produced on the cathode surface to diffuse into the membrane, thereby humidifying the membrane. However, a thin membrane is detrimental to

the cell performance by increasing crossover of reactant gases. Furthermore, the durability of a cell is shortened by insufficient structural robustness.

The aim of this work has two objectives. One is to provide a new method to prepare a self-humidifying electrolyte membrane and to determine the optimum condition for its fabrication. The other is to find the exact mechanism for self-humidification occurring in the membrane fabricated by the present method as well as to provide experimental evidence for the self-humidifying mechanism.

For these purposes, PEM was fabricated in the form of sandwich, which was composed 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. The optimum condition for fabrication of a self-humidifying membrane was investigated based upon the results from the differential temperature (DTA)–weight (TGA) analyses, visual inspections and performance characteristics of single cells using self-humidifying PEM. From the results of the current–voltage relationship for single cells, the self-humidifying mechanism has been discussed in terms of a recombination of hydrogen and oxygen on embedded Pt particles in the membrane. Experimental evidence for the validity of the self-humidifying mechanism has been presented from IR absorbance measurements.

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2. Experimental

2.1. Material

Perfluorosulfonylfluoride resin (Nafion[®] R-1100 resin, DuPont Fluoroproducts, USA) was used as a precursor for fabrication of a self-humidifying PEM. The precursor resin was analyzed using DTA–TGA (Thermal Sciences, PL–STA 1500), in order to determine the fabrication conditions of the membrane [4]. The DTA–TGA measurement was carried out in the temperature range 25–700 °C in air at a scan rate of 10 °C/min. The morphology of the precursor resin beads was examined by a scanning electron microscope (SEM, Philips, XL30SFEG).

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

Perfluorosulfonylfluoride precursor resin was taken in a stainless steel frame (100 mm × 100 mm, $t = 0.140$ mm), and pre-formed as a sheet 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 by a sputtering technique for 10 min at an rf power of 50 W. Then, a self-humidifying membrane was obtained by joining another uncoated pre-formed membrane with the coated side of the Pt sputtered membrane. The self-humidifying membrane of 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 of Na⁺ form, the membrane was boiled in the 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.

The catalyst slurry was prepared by mixing 20 wt.% Pt/C (Johnson-Matthey Inc.), 5 wt.% Nafion[®] solution, glycerol, and 1 M tetrabutyl ammonium hydroxide (TBAOH) solution. Fabrication of the MEA was performed by a decal method. First, the catalyst slurry was printed onto the transfer film. The content of electrocatalyst loading was controlled to be 0.2 mg Pt per cm². Then, the coated layer was dried for 2 h in the vacuum oven at 140 °C. Finally, the Pt/C coated on the transfer film was hot pressed on both sides of dried self-humidifying membrane of Na⁺ form for 2 min at 195 °C with a pressure of 77 bar. According to previous works [5,6], the MEA was converted into H⁺ form by immersing in 0.5 M H₂SO₄ for several hours at 90 °C, followed by washing repeatedly in de-ionized water.

2.3. Measurements of single cell performance and Infrared spectroscopy

Procedures of the assembly and the measurement of cell performance were described in detail in our previous papers [4–6]. Performance of single cells for the self-humidifying and as received membranes was evaluated under the atmosphere of hydrogen and oxygen with an active area of 50 cm²

(7 cm × 7.1 cm) at 50 °C. In order to examine whether Pt embedded in the membrane indeed recombines hydrogen and oxygen to form water inside the membrane, IR absorbance measurements have been made for the self-humidifying and as received membranes using FT-IR spectrometer (Bruker IFS66/FRA 106, Bruker, Germany).

3. Results and discussion

3.1. Perfluorosulfonylfluoride precursor resin

A typical scanning electron micrograph of a perfluorosulfonylfluoride precursor resin bead is presented in Fig. 1. The resin bead has transparent elliptical form. The mean particle size of the resin bead ranges approximately from 1.5 to 3.6 mm.

In order to determine the pre-forming temperature for the membrane, DTA–TGA analyses were made on the precursor resin. Fig. 2 illustrates the results of DTA–TGA analyses for the precursor resin. Weight loss accompanied by exothermic

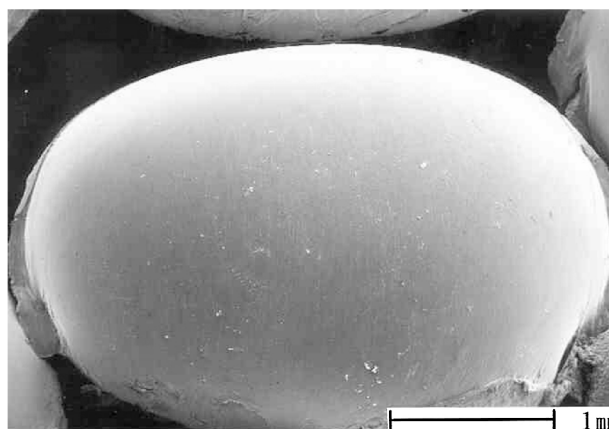


Fig. 1. Scanning electron micrograph of perfluorosulfonyl fluoride precursor resin.

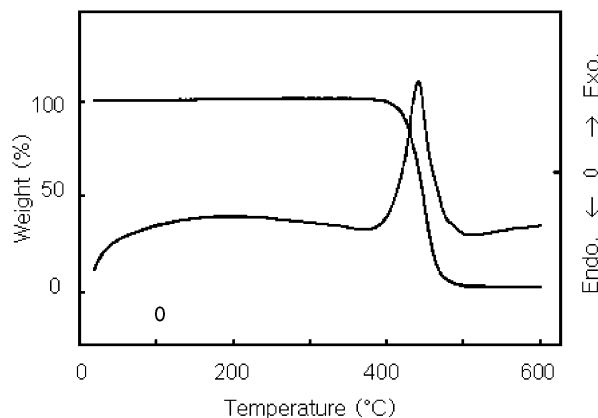


Fig. 2. TG and DTA vs. temperature curves for perfluorosulfonyl fluoride precursor resin measured in air at a scan rate of 10 °C/min.

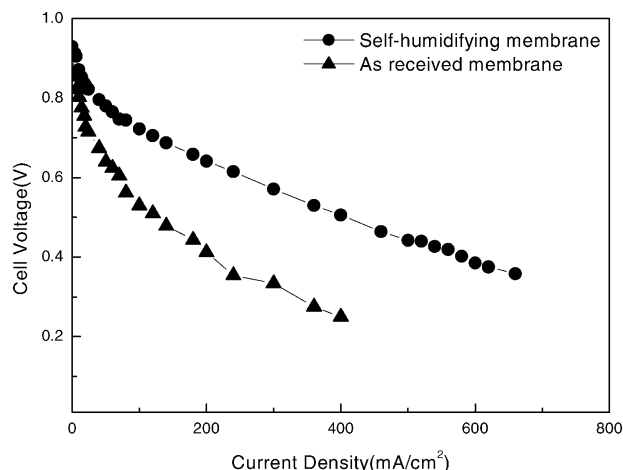


Fig. 3. Performance of single cells using self-humidifying (●) and as received membranes (▲) measured at 50 °C under externally nonhumidifying conditions.

reaction starts at around 380 °C and finishes at around 500 °C, indicating the occurrence of decomposition of the precursor resin [7]. Based upon the result, the membrane sheet was pre-formed by hot pressing a 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 cross over of the hydrogen and oxygen both through the membrane. From successive hot pressing followed by examination, the optimum temperature for the fabrication of pore-free membrane sheet was determined to be 230 °C.

3.2. MEA and single cell performance

The amount of Pt particles embedded in the self-humidifying membrane was determined to be about 0.27 mg/cm² by using inductively coupled plasma mass spectrometry (ICP, PQ3, VG Elemental Ltd., UK). The thickness of the self-humidifying membrane was approximately 200 μm. Fig. 3 shows the performance of the single cells using self-humidifying and as received membranes measured without external humidification under the reactant gases of hydrogen and oxygen of ambient pressure at 50 °C. In the case of an externally nonhumidifying condition, the self-humidifying membrane cell shows considerably higher performance in comparison with that of the as received membrane cell over the entire voltage range. This result first indicates that the rate of proton transfer through the self-humidifying membrane is greater than that through the as received one. Again, considering that the rate of proton conduction is a function of water content in the membrane, the result suggests that water content in the self-humidifying membrane is higher than that of the as received one. The increased water content of the self-humidifying membrane seems to originate from the embedded Pt particles inside the membrane.

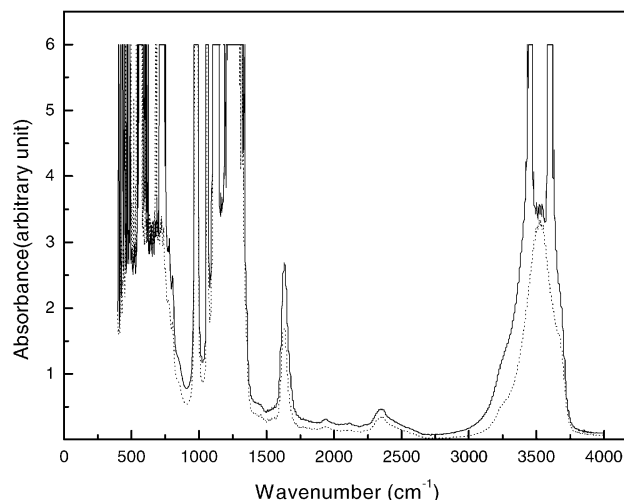


Fig. 4. Infrared absorbance spectra of membranes at different conditions. All the membranes were initially dried in vacuum oven for 14 days at 90 °C. Dotted (· · ·) and straight (—) lines indicate as dried membrane and membrane kept in completely dried H₂ and O₂ mixture gas of ambient pressure for 7 days at room temperature, respectively.

From the studies of Pt and oxides dispersed in the self-humidifying membrane, Watanabe et al. [1,2] suggested that Pt particles embedded in the membrane act as a recombination center for permeated hydrogen and oxygen, thereby producing water inside the membrane. However, the validity of the suggested mechanism for water generation on the Pt particles embedded inside the membrane has not been experimentally proved yet. In order to examine whether water is indeed produced by the recombination of permeated hydrogen and oxygen on the Pt particles embedded in the membrane, IR absorbance measurements have been made for the self-humidifying and as received membranes.

Infrared absorbance spectra of the membranes treated at different conditions are illustrated in Fig. 4. For measurements, all the membranes were initially completely dried in the vacuum oven for 14 days at 90 °C. Among the dried membranes, several samples were kept in the completely dried hydrogen and oxygen gas mixture at ambient pressure for 7 days at room temperature. It should be noted that the absorbance peaks of the characteristic OH stretching band appearing at 3450 and 3600 cm⁻¹ are observed only in the self-humidifying membrane kept in the hydrogen and oxygen mixture gas. A typical OH stretching peak of H₂O appears at 3450 cm⁻¹. The peak at 3600 cm⁻¹ is assigned to water, which is partially bonded to fluorocarbon and has one proton available for hydrogen bonding. Therefore, the IR absorbance result clearly substantiates the validity of the mechanism for water production that Pt particles embedded in the self-humidifying membrane act as a recombination center for permeated hydrogen and oxygen.

Other peaks excepting the two peaks at 3450 and 3600 cm⁻¹ for the both types of membranes show almost the same position and feature. The peak at 3520 cm⁻¹ is assigned to water, which forms hydrogen bonds and the strength is significantly weaker

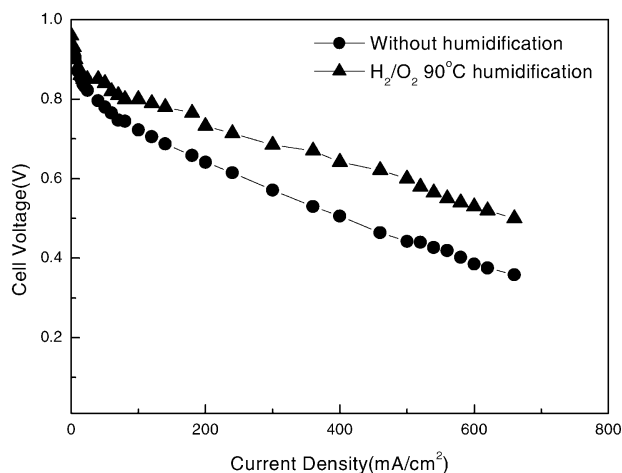


Fig. 5. Performance of single cells using self-humidifying (●) and as received membranes (▲). The former and latter were externally nonhumidified and humidified, respectively.

than that of the hydrogen bonds in pure water, indicating that less extensive hydrogen bonding exists in a small cluster form of water. The shape of the curve around the peak at 3520 cm^{-1} is consistent with the result given by other researchers [8–10]. A characteristic bonding peak for H_3O^+ ions appears at around 1600 cm^{-1} [8]. At peaks below 1400 cm^{-1} , S=O and S–OH stretching peaks of the $-\text{SO}_3\text{H}$ group and $-\text{SO}_3^-$ stretching peaks are observed [8,9].

Performance of single cells using self-humidifying and as received membranes is presented in Fig. 5. The former and latter were externally nonhumidified and humidified, respectively. As received membrane cell shows better performance than that of the self-humidifying membrane cell over the entire voltage range. This result indicates that the rate of proton conduction through the externally humidified as received membrane exceeds that through the self-humidifying membrane. Considering the result in terms of water content in the membrane again, the water content in the self-humidifying membrane seems to be lower as compared to that in the case of external humidification.

The reason why the water content in the self-humidifying membrane is lower than that in the externally humidifying as received one could be explained as follows. The self-humidification occurs presumably by at least three steps. The first step is permeation of hydrogen and oxygen through the membrane, the second is internal adsorption of reactant gases on Pt particles embedded and the final step is the recombination of internally adsorbed hydrogen and oxygen on the Pt particles. Among the three successive steps, the rates of the last two steps are considered to be faster than that of the first step. In fact, the last two steps are the same process occurring swiftly on the cathode surface of PEMFC, while crossover by permeation of hydrogen and oxygen is in general accepted as very slow, compared to the last two steps. After all, slow rate of crossover of hydrogen and oxygen seems to limit the water production rate in the self-humidifying membrane.

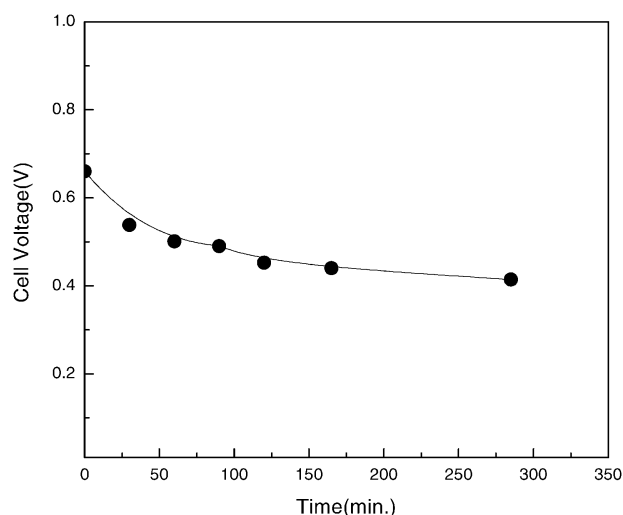


Fig. 6. Cell voltage decay curve for self-humidifying single cell, measured at $50\text{ }^\circ\text{C}$ under application of constant load of 200 mA/cm^2 .

The stability of the single cell using self-humidifying membrane was examined for 300 min under application of a constant load of 200 mA/cm^2 at $50\text{ }^\circ\text{C}$. Fig. 6 shows the cell voltage decay curve for the single cell using the self-humidifying membrane. The cell voltage initially decays slowly with increasing time and finally reaches a steady state value of about 0.45 V at 200 mA/cm^2 , representing the stable nature of the self-humidifying membrane.

4. Conclusions

In this work, a novel preparation method of a self-humidifying membrane for the PEMFC was presented, using perfluorosulfonylfluoride copolymer resin and a sputtering technique, in addition to the optimum fabrication condition for it. The new preparation method involved fabrication of a sandwich structure, which is comprised of two membranes made of perfluorosulfonylfluoride copolymer resin and fine Pt particles lying between them coated by the sputtering. The optimum pre-forming temperature for the pore-free membrane sheet was determined to be $230\text{ }^\circ\text{C}$, based upon the results of the DTA–TGA analyses, visual inspections and performance characteristics of single cells.

From the comparison of performance for the single cells using self-humidifying and as received membranes, higher performance of self-humidifying cell was attributed to the fact that the presence of Pt particles in the membrane increases the proton conductivity of the membrane, due to the generation of water molecules on the Pt particles by the recombination of permeated hydrogen and oxygen. The result from the IR absorbance measurements substantiated the validity of the argument. The IR absorbance peaks appearing at 3450 and 3600 cm^{-1} corresponding to the characteristic OH stretching bond were observed only in the case of self-humidifying membrane kept in the completely dried hydrogen and oxygen mixture gases.

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