

Development of novel self-humidifying composite membranes for fuel cells

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Abstract

A novel preparation method for self-humidifying membranes of proton exchange membrane fuel cells (PEMFCs) was developed. Using solution-cast method, PTFE porous substrates in these composite membranes can increase their strength and distribute self-humidifying layers adjacent to the anode side. Compared with the cells fabricated with ordinary membranes, the performance of the cells with these self-humidifying proton exchange membranes (PEMs) are dramatically improved in both cell voltage and the current density under dry conditions, and the cell using the Pt/C-PEM shows the best and most stable performance. EIS technique revealed that these self-humidifying composite membranes could minimize membrane conductivity loss under dry conditions.

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1. Introduction

Significant research has been focused on the development of proton exchange membrane fuel cells (PEMFCs). Using a solid electrolyte, such as a solid polymer referred to as a proton exchange membrane (PEM), fuel cells have no electrolyte leakage. But the performance of fuel cells can be greatly influenced by the thickness and humidification state of the solid PEMs. Good performance can be obtained if thin and fully-humidified membranes are used, because water molecules can promote proton transport and thin membranes can reduce ionic resistance. Since thin membranes have low mechanical strength, composite membranes (such as Nafion/PTFE membrane) can be used.

In our previous work, we developed Nafion/PTFE composite membranes [1–3]. The composite membranes have many advantages: high mechanical strength, good dimensional stability upon hydration and dehydration, ease of handling and superior cell performance with very thin membranes. But one problem of this thin composite membrane is that it has a larger gas permeation rate than commercial membranes [1]. Hence, a very thin Nafion/PTFE composite membrane reduces the cell open circuit voltage (OCV) to a

mixed potential, resulting from both hydrogen oxidation and oxygen reduction at the cathode catalyst surface. This phenomenon not only reduces the cell performance and OCV but also generates some unsafe problems. The reaction heat generated by the crossover gases can cause local hot spots, localized membrane drying and higher membrane resistance.

In order to solve this problem, we devised a novel multi-layer composite membrane [4], by adding Pt or Pt/C particles to the membrane casting solution. The novel thin composite membrane has the advantages of the Nafion/PTFE membrane, and it can effectively suppress gas crossover and can also be used as a self-humidifying membrane. The novel self-humidifying composite membrane solves the problems of the Nafion/PTFE membrane, and converts its disadvantages to advantages by using a self-humidifying layer (Pt particles) in the membrane to combine the permeated oxygen and hydrogen to form water to humidify the membrane. Thus, by simply changing the composition of the cast membrane solutions and following the fabrication procedure of Nafion/PTFE membrane, a self-humidifying function can be obtained.

Compared with this method, other fabrication methods of making self-humidifying membranes have many disadvantages. Watanabe and co-workers [5–7] proposed a method of fabricating self-humidifying composite membranes with highly dispersed nanometer-size Pt and/or metal oxides. However, electroless plating had several disadvantages, including a considerable amount of residual

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impurity, non-uniform distribution of Pt particles throughout the membrane and formation of an electron-conducting path via the network of dispersed Pt particles [8]. Also, this process is very time-consuming, showing its disadvantages to big fuel cell systems. Recently, Yang et al. [8] and Kwak et al. [9] developed a new self-humidifying membrane using a melt-fabricable perfluorosulfonylfluoride copolymer resin (F-type Nafion) and a sputtering technique. PEM was fabricated in the form of sandwich, which was composed of two F-type Nafion resins and a sputtered Pt layer in the middle, followed by a hot-press and hydrolysis process. This method is also time-consuming, furthermore, the resulting membrane is very thick (about 200 μm) and gas permeability and water generated in the membrane are very limited. A disadvantage of the two methods is that the Pt loading in the membranes cannot be directly controlled.

The objective of the present study is to develop a new, simple and controllable fabrication method for a self-humidifying membrane, to solve the problems with Nafion/PTFE membrane and to increase the cell performance under dry gas condition. Based on the Nafion/PTFE composite membrane, the novel self-humidifying membranes utilize the porous PTFE membrane to distribute Pt particles in the middle of the composite membrane. The Pt loading and thickness of the membrane can be easily controlled. The fabrication method, membrane characterization and cell performances of the novel self-humidifying composite membrane will be discussed in detail.

2. Experimental

2.1. Membrane preparation

Nafion solution was obtained by dissolving perfluorosulfonated ionomer polymers (such as Nafion 117 membranes) in mixed solvent of water and alcohols under high temperature and high pressure.

Composite membranes were prepared by the following procedure: the Nafion solution made above and home-made Pt black or 20 wt.% Pt/Vulcan XC-72 powder were mixed ultrasonically to form a catalyst ink. Porous PTFE films (manufactured in Shanghai) with pore diameter about 0.1–0.3 μm were used as a support to make different composite membranes. The porous PTFE support films were first cleaned by soaking them in ethanol for half an hour at room temperature, and they were then extended over a flat glass plate. After that, the Nafion solution or viscous ink with Pt black or Pt/C particles made above was poured on to the PTFE films. The glass plate was dried in a hot plate at 50–60 $^{\circ}\text{C}$, and finally dried on a vacuum oven at 140–150 $^{\circ}\text{C}$ for 10 h. In the process, gravity dragged Nafion solution into the pores of the PTFE films while Pt/C or Pt black particles were retained on their surface. After the evaporation of solvent, Nafion resin completely plugged the micropores, thus making the composite membranes air-tight. In the experi-

ment, a stainless steel holder was used to prevent membrane distortion and hold cast solutions on the surface of the PTFE substrate.

Using this method, it is possible to design a novel self-humidifying composite membrane structure. The Pt/C catalyst layer can be arranged in the composite membrane adjacent to the anode side. The thickness and Pt loading of the composite membranes can be easily controlled by the amount of Nafion solution and Pt black or Pt/C catalyst particles used in cast solution in the experiment. The amount of Pt loading in the composite membranes was controlled at 0.06 mg/cm^2 . The thickness of the composite membranes was about 35 μm . Different structures with Pt black or Pt/C particle added to the composite membranes were tested in this paper. For simplification, the Nafion/PTFE membrane is denoted as PTFE-PEM; similarly, the composite membrane with Pt black and Pt/C particles are denoted as Pt-PEM and Pt/C-PEM, respectively.

2.2. Membrane electrode assembly preparation and single cell test

The 20 wt.% Pt/Vulcan XC-72 (Pt/C) catalysts, carbon paper, PTFE suspension and Nafion solution (Du Pont) were used for electrode preparation. The Pt loading of the anode and cathode is 0.3 mg/cm^2 and the dry loading of Nafion is 0.6–1.2 mg/cm^2 . Two electrodes with effective area 5 cm^2 were hot-pressed to one piece of membrane to form a MEA.

The MEA was mounted in a single cell with stainless steel end plates and stainless steel mesh flow field as current collectors. First, the cells were operated with humidified reactant gases, under these conditions: humidifier temperature $T_{\text{H}_2}/T_{\text{O}_2} = 80/80$ $^{\circ}\text{C}$; cell temperature 80 $^{\circ}\text{C}$; gas pressure $P_{\text{H}_2}/P_{\text{O}_2} = 0.20/0.20$ MPa. After stable performance was obtained, the cells were then operated with dry gases. Before operation with dry gases, the cells were dried overnight with dry N_2 .

2.3. Electron microscope analysis of PTFE film, Pt black and Pt/C

Analysis by transmission electron microscopy (TEM) was conducted on the Pt black and Pt/C catalyst powders. The powders were dispersed in ethanol, using an ultrasonic bath, and then mounted on standard copper TEM grids. The surface of the PTFE porous film was observed by a scanning electron microscope (SEM). A JEM-1200EX microscope was used for TEM and SEM analysis.

2.4. EDX analysis

The composite membranes were cut in liquid nitrogen (77 K) to expose their cross-sections. Then, the cross-sections were tested by Oxford Instruments X-ray Microanalysis 1350 to obtain the elemental distribution across the composite membrane.

2.5. Electrochemical impedance spectroscopy (EIS)

The electrochemical responses of MEAs prepared with different self-humidifying composite membranes were characterized with the electrochemical impedance spectroscopy (EIS) technique. The amplitude of the AC signal was 5 mV rms and the frequency was typically varied from 1 mHz to 100 kHz. A frequency response detector (EG&G Model 1025) and potentiostat/galvanostat (EG&G Model 373A) were used. The anode at which hydrogen oxidation takes place was used as the reference and also as the counter electrode, the cathode was used as the working electrode.

3. Results and discussion

3.1. Electron microscope results of PTFE film, Pt black and Pt/C

Fig. 1 presents electron microscope graphs of the surface of the PTFE porous films (SEM), the carbon-supported-platinum (Pt/C) catalyst particles and the Pt black (TEM). It is found that the PTFE film had a rough surface with the mean pore diameter of about 0.1–0.3 μm . The carbon particles are balls with a diameter of about 30 nm, many small black Pt particles are visible on the surfaces of the carbon particles. The diameters of the Pt/C catalyst particles are

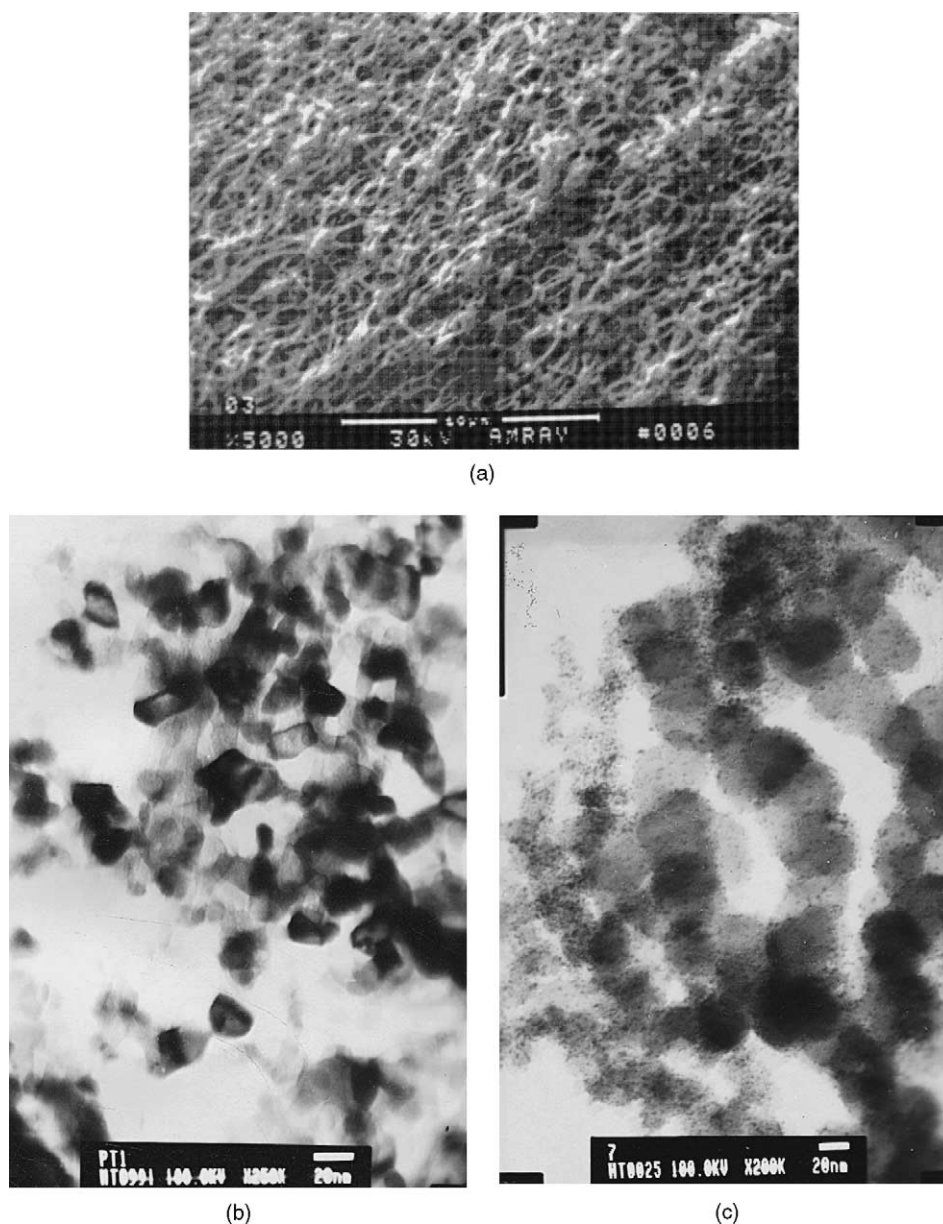


Fig. 1. Electron microscope photograph of: (a) PTFE microporous film (SEM); (b) Pt black (TEM); (c) Pt/C catalyst particles (TEM).

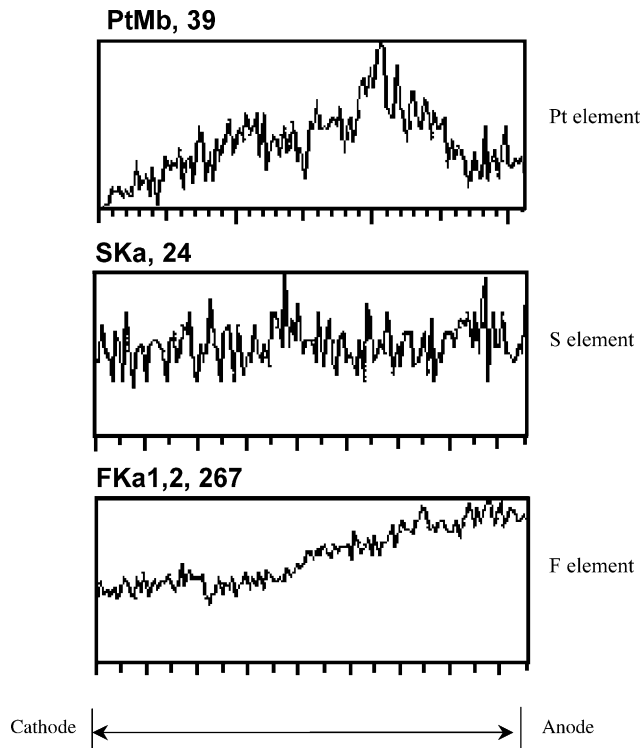


Fig. 2. EDX result of Pt-PEM.

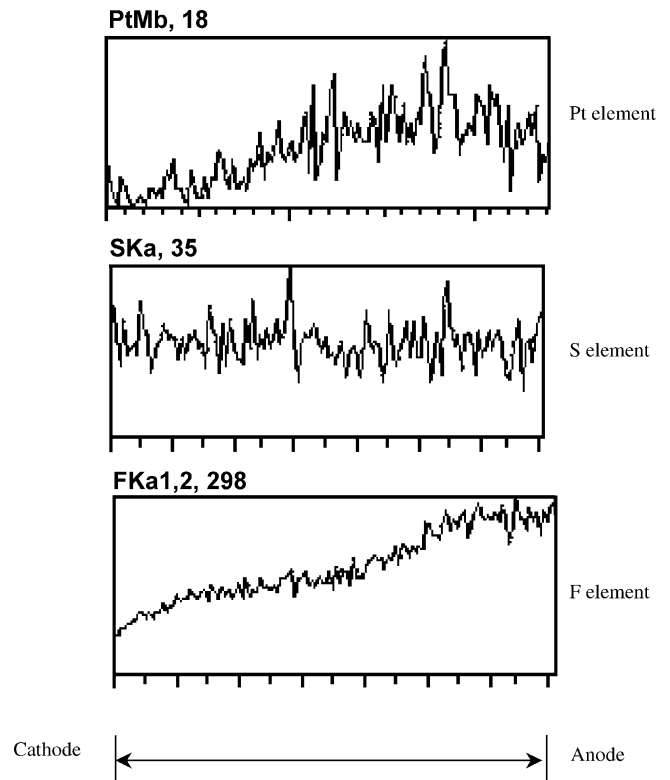


Fig. 3. EDX result of Pt/C-PEM.

uniform, ranging from 2 to 3 nm. The diameters of the Pt black particles are between 15 and 20 nm.

3.2. EDX study of Pt/C-PEM and Pt-PEM

In the experiment, the thickness of porous PTFE films used is approximately 5 μm and the obtained composite membranes are controlled at about 35 μm thick. Figs. 2 and 3 show the EDX results of the cross-section of Pt-PEM and Pt/C-PEM. It can be seen that in the two composite membranes, sulphur (S) is dispersed homogeneously along the cross-section of the membranes, which means that Nafion solution can penetrate into the pores of the PTFE film, making the sulfonic acid groups uniformly dispersed in the membranes; fluorine (F) is not distributed homogeneously in the membrane due to the asymmetric position of the PTFE films in the composite membranes; the most interesting feature is that in the EDX spectra Pt is distributed in the composite membrane adjacent to the anode side.

From Fig. 1, the mean pore diameters of the porous PTFE are much larger than those of the Pt black and Pt/C particles. In our experiment, when Nafion solution with the Pt black or Pt/C particles was poured on the surface of the porous PTFE film, small parts of the particles in the solution can penetrate into the pores of the PTFE film. But from the EDX results, we believe that larger parts of the particles can deposit on the surface of PTFE films to form the self-humidifying layer, because it is supposed that bigger agglomerates or

clusters of Pt black or Pt/C particles with Nafion may be too large to penetrate into the porous PTFE film. Another reason may be due to the high surface tension that prevents the Pt/Nafion agglomerates from penetrating into the pores. Because Nafion has the same backbone as PTFE, some parts of Nafion resin in the catalyst ink can penetrate the porous PTFE films, reaching the glass plate substrate to form a thin Nafion layer at the bottom, cutting the electron transfer between the self-humidifying layer and the catalyst layer; other Nafion resin in the solution forms another Nafion layer on top of the self-humidifying layer, also cutting the electron transfer between the self-humidifying layer and the catalyst layer. The schematic diagram of the composite self-humidifying membrane is shown in Fig. 4.

In the experiment, without the PTFE films, the Pt particles will deposit at the bottom of the membrane. If this membrane is used to fabricate a MEA, Pt particles in the

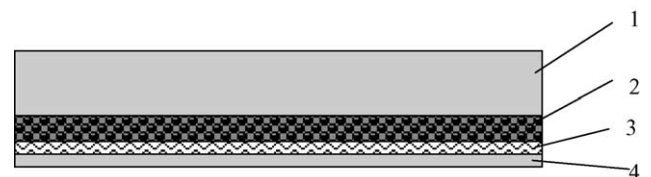


Fig. 4. Schematic diagram of the composite self-humidifying membrane: (1) Nafion layer; (2) Pt self-humidifying layer; (3) porous PTFE membrane; (4) Nafion layer.

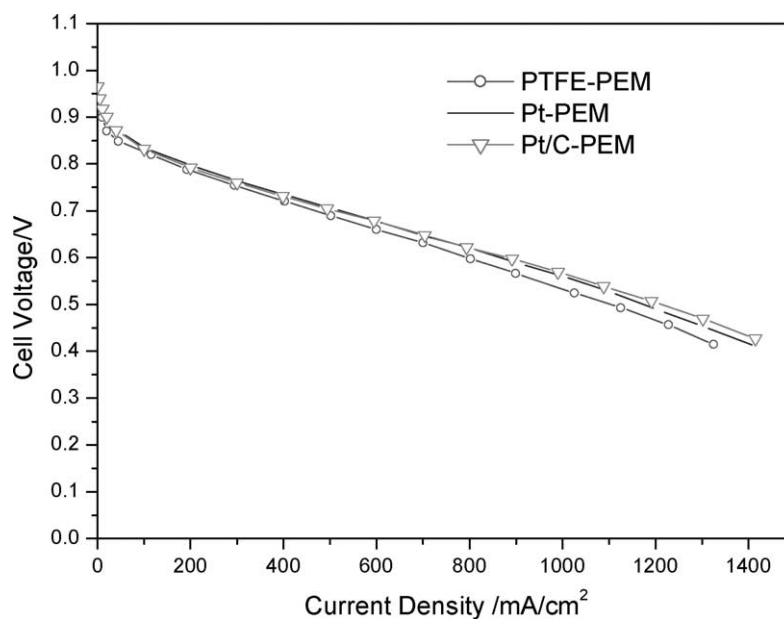


Fig. 5. Potential–current polarization curves of H_2/O_2 fuel cells using three different PEMs operated at 80°C under externally humidified condition ($T_{H_2}/T_{O_2} = 80/80^\circ\text{C}$).

membrane can connect with those in the electrode, so the Pt particles in the membrane are an extension of the electrode, without the self-humidification function. While for the new Pt-PEM or Pt/C-PEM, the PTFE film not only served to reinforce the composite membrane but also functioned as a good method to retain Pt particles in the composite membrane adjacent to the anode side. In dry conditions, such a Pt distribution can chemically catalyze the reaction of the crossover gases to generate water, humidifying the proton exchange membranes.

3.3. Performance of PEMFCs operating under humidified and dry conditions

The I – V curves for cells based on PTFE-PEM, Pt-PEM and Pt/C-PEM operated under humidified and dry conditions are shown in Figs. 5 and 6. Under humidified condition, the cells using the three different kinds of composite membranes show almost the same performance. The performance of the cells using Pt/C-PEM and Pt-PEM slightly exceeds that of the cell using PTFE-PEM, because the Pt self-humidifying

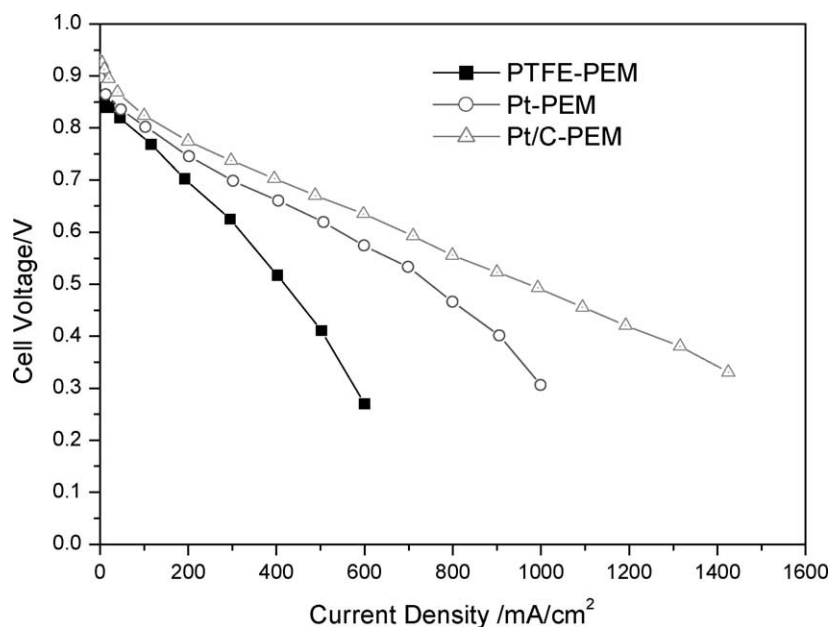


Fig. 6. Potential–current polarization curves of H_2/O_2 fuel cells using three different PEMs operated at 80°C without any external humidification.

layer in the self-humidifying composite membranes can effectively suppress the crossover of reactant gases in fuel cells, and thus lower the cathode overpotential and consequently improve the cell performance. Under dry conditions, the cell using PTFE-PEM shows a poor I - V curve, resulting in poor output performance, e.g. 0.208 W/cm^2 at 0.4 A/cm^2 and 0.52 V . Compared with the cell based on PTFE-PEM, performance of the cells using Pt-PEM and Pt/C-PEM dramatically improved in cell voltages and current densities. The cell using the Pt/C-PEM shows the best performance, e.g. 0.280 W/cm^2 at 0.4 A/cm^2 and 0.70 V .

The cells using Pt-PEM and Pt/C-PEM have higher OCVs than the cell using the PTFE-PEM under both humidified and dry conditions, because the Pt black and Pt/C layers in the composite membranes provide sites for the catalytic recombination of H_2 and O_2 diffusing from the respective anode and cathode, and thus block the crossover of reactant gasses [5–7]. The OCVs of the three different composite membranes are shown in Table 1. The cell using Pt/C-PEM has higher OCVs than the fuel cells based on the other two composite membranes, which were 0.995 and 0.932 V under humidified and dry conditions, respectively. Since the OCV is a good measurement of H_2 or O_2 crossover through the PEMs to the cathode or anode, respectively [7], compared with PTFE-PEM and Pt-PEM, Pt/C-PEM has the strongest ability to suppress the gas crossover and retain water, thus the good and stable performance of the cell using Pt/C-PEM under dry condition may be attributed to its relatively small resistance when humidified with water produced by the recombination of crossover gases and back-diffusion from cathode to anode.

In the operation of a PEMFC using unhumidified gases, at low current densities, the cell may begin to dry out because there is insufficient water produced from the fuel cell reaction to reverse the drying; at high current densities, as the electro-osmotic flux of water from anode to cathode is inadequately compensated by the back-diffusive flux, the locus of drying is in the vicinity of the anode. So, we believe that new self-humidifying composite membrane can retain the water near the anode electrode side under dry conditions, resulting good performance.

Yang et al. [8] indicated that the self-humidification occurs in several steps, including: gas permeation through the membrane, reactant gas adsorption on Pt particles and recombination of hydrogen and oxygen, where gas permeation through the membrane is the rate-limiting step. That means

gas permeation rate through the membrane determines the water production rate. In our experiment, a very thin (about $35 \mu\text{m}$ thick) composite self-humidifying membrane was used, which not only promoted the water produced at the cathode side to diffuse to the anode side, but also generated more water by self-humidification because of a high gases permeation rate. On the other hand, because of its hygroscopic property, the carbon powder in the Pt/C is expected to adsorb the water produced in the self-humidifying layer near the anode region and to release the water once the PEM needs it. Moreover, the Pt/C particles near the anode could enhance the back-diffusion of water produced by Faradic reaction at the cathode through the thin composite membrane by this hygroscopic property, resulting in very efficient humidification on the PEM on the anode side dried by electro-osmotic drag.

3.4. Electrochemical impedance spectroscopy (EIS) of fuel cells under different conditions

Even though a very thin self-humidifying composite membrane was used in the experiment, the cell performance in dry conditions were still inferior to that in humidified conditions. The EIS technique was used to reveal what causes the performance difference between the two states. EIS can reveal that lack of sufficient humidification of the reactant gases brings about cell performance losses because of three different factors, which are well resolved in the impedance spectrum: an increase in the membrane resistance, an increase in the resistance of the ionomeric component within the catalyst layer, and an increase of the interfacial impedance for the oxygen reduction reaction (ORR) [10].

Figs. 7 and 8 show AC impedance spectra of the cells based on PTFE-PEM and Pt/C-PEM operated under humidified and dry conditions. It can be seen that most of the AC impedance spectra exhibit two distinct arcs: one high frequency arc and one low frequency arc. The high frequency arc is almost unchanged at all cell voltages. It is supposed that the high frequency arc might be attributed to the internal distributed ohmic resistance and the contact capacitance in the granular electrode structure [11,12]. In our experiment, the high frequency arc is more distinct than that reported in the literature, and it may be due to the thick catalyst layer of the electrode prepared by conventional method in the experiment. Especially at low current densities and dry condition, there was insufficient water in the granular electrode structure, the agglomerates contract, so the grain boundary resistance increases, resulting in a thinner and longer path for the migration of ions, increasing the distributed resistance and capacitances. Then, we may conclude that if the fuel cell is fully humidified, the high frequency arc may not be so distinct as observed in the AC impedance spectra. The intercept of the high frequency arc with the real axis represents the total ohmic resistance of the cell (R_Ω), which can be expressed as a sum of the contributions from uncompensated contact resistance and ohmic resistance

Table 1
Open circuit voltages of fuel cells using three different composite membranes under humidified and dry conditions

| Membranes | Open circuit voltage (V) | |
|-----------|-----------------------------|----------------------|
| | Under humidified conditions | Under dry conditions |
| PTFE-PEM | 0.940 | 0.840 |
| Pt-PEM | 0.948 | 0.897 |
| Pt/C-PEM | 0.995 | 0.932 |

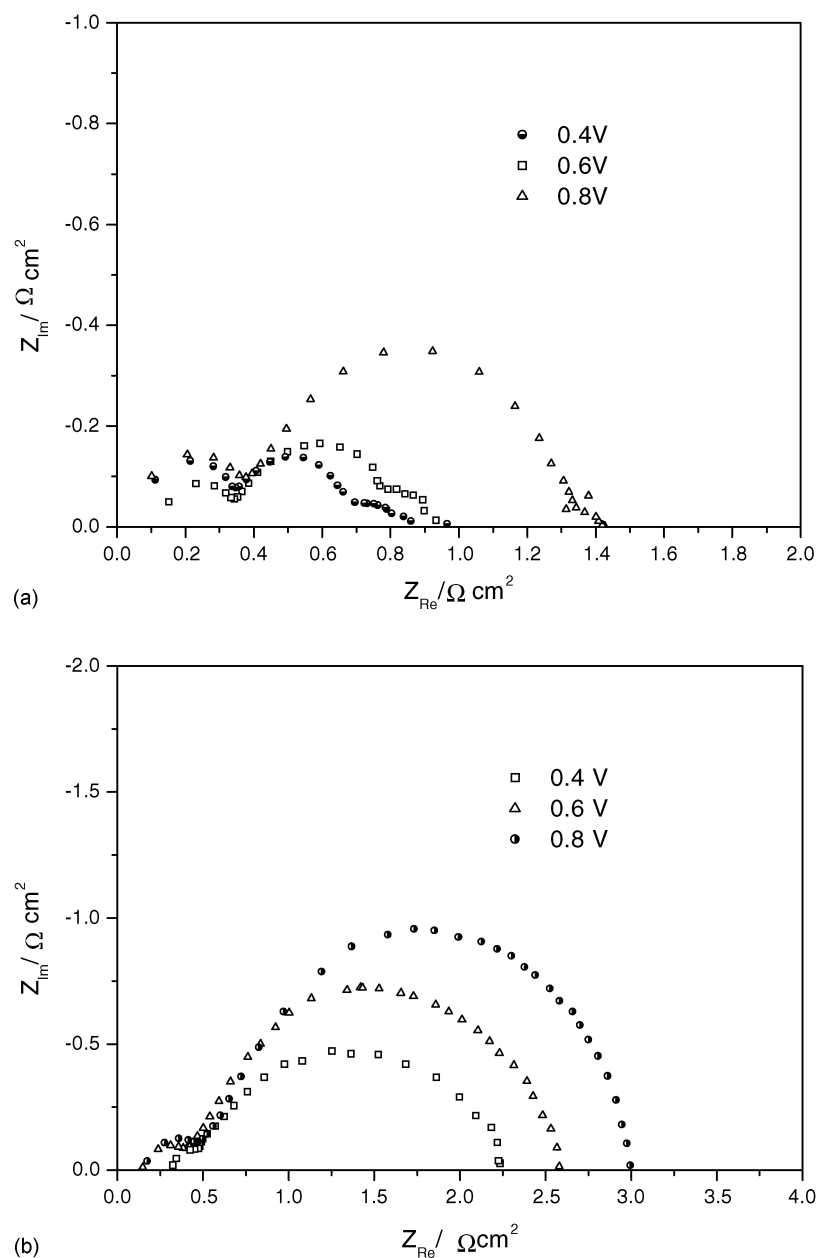


Fig. 7. AC impedance spectra at several potentials for cell using PTFE-PEM under humidified (a) and dry (b) conditions.

of the cell components such as membrane, catalyst layer, backing, end plate, and that between each of them [13]. The diameter of the low frequency arc, representing the charge transfer resistance (R_p) across the catalyst/electrolyte interface, which is inversely proportional to the rate of ORR, decreases with decreasing cell voltage (i.e. the overpotential increases). This phenomenon was observed in all the electrode and membrane employed in our experiments.

From humidified to dry conditions, in the AC impedance spectra of the cell using Pt/C-PEM, R_{Ω} shows a little difference. While for the PTFE-PEM-based cell, R_{Ω} decreases by about $0.1 \Omega \text{ cm}^2$. Assuming contact resistance and other component ohmic resistance are constant during the change from humidified to dry conditions, the R_{Ω} changes are sup-

posed to be the membrane resistance change. Then, we may conclude that the new self-humidifying composite membrane has the ability to maintain membrane conductivity in dry conditions. While for Pt/C-PEM, the cell performance decay from humidified to dry conditions may be due to the increase of R_p from dry to humidified conditions.

When cells previously operated using humidified gases are now operated using dry gases, the polymer electrolyte membrane and the polymer electrolyte contained in the catalyst layer undergo contraction to decrease the area of the electrolyte covering the platinum catalyst, that is, the reaction area decreases. The movement of protons tends to take place with difficulty, resulting in the increase of the interfacial charge transfer resistance of the cell. Under dry

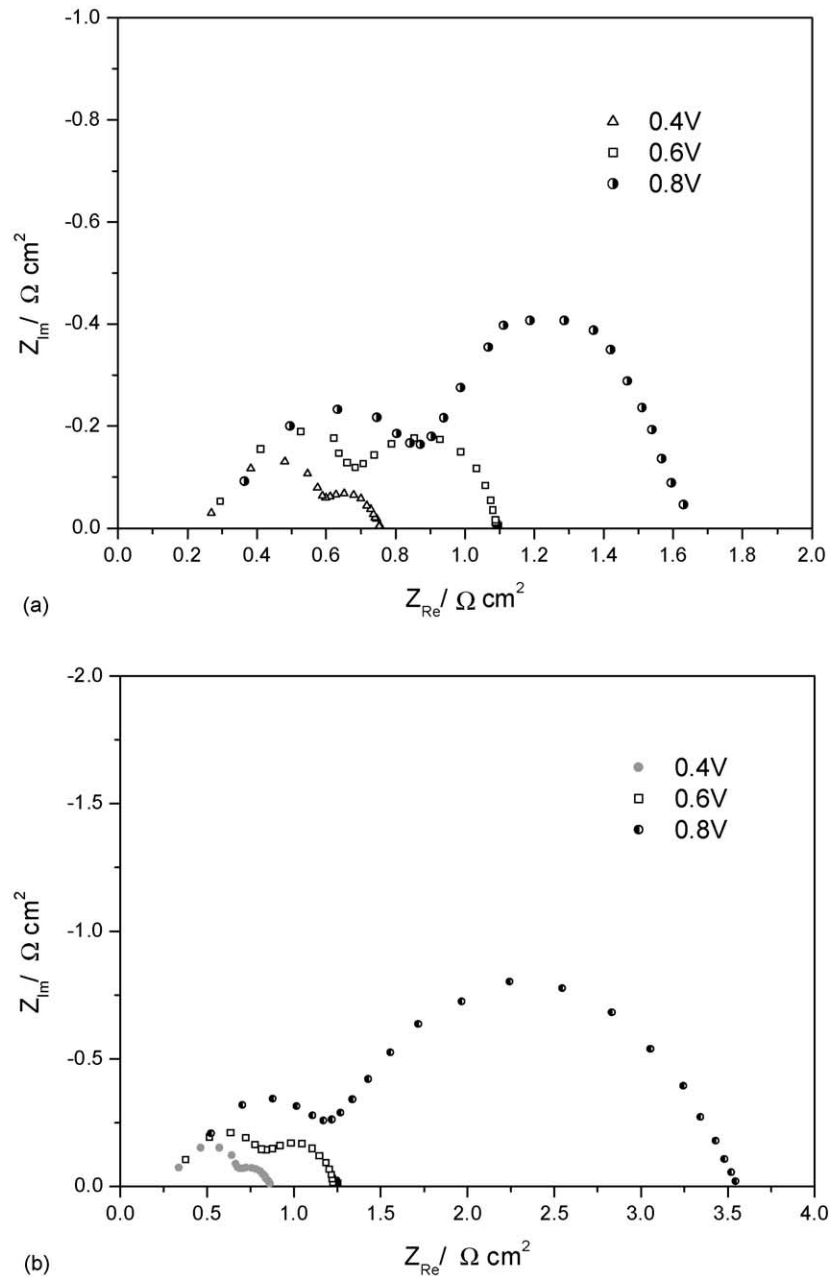


Fig. 8. AC impedance spectra at several potentials for cell using Pt/C-PEM containing 0.06 mg Pt/cm² under humidified (a) and dry (b) conditions.

conditions, even the Pt/C-PEM can maintain the membrane conductivity comparable to that under humidified condition, the interfacial charge transfer resistance is still large, resulting in poor cell performance. From what has been discussed above, we conclude that an increase of the interfacial charge transfer impedance for ORR is the most important factor that causes poor fuel cell performances under dry conditions.

For the cell using PTFE-PEM under humidified conditions, the spectra develop one lower-frequency semi-circle, which is supposed to be associated with water-related gas transport limitations or flooding [12,14]. For a PTFE-PEM cell, all permeated H₂ reacts chemically with O₂ in the cathode catalyst layer, and the resulting water flux leaving

the cathode makes O₂ diffusion to the inner layer extremely difficult [7]. By contrast, for Pt/C-PEM cell, all crossover H₂ recombines inside the PEM, and most of the generated water is exhausted toward the anode side, resulting in no restriction of O₂ diffusion to the inner catalyst layer, therefore there is no flooding phenomenon in the EIS spectra of the cell using Pt/C-PEM under humidified conditions.

4. Conclusions

Novel structure self-humidifying composite membranes for a PEMFCs were prepared by introducing a Pt

self-humidifying layer into the Nafion/PTFE membranes. The composite self-humidifying composite membrane has a multi-layer structure. EDX spectra results showed that the Pt humidifying layer concentrated near the catalyst layer of the anode. The cells using Pt-PEM and Pt/C-PEM had superior performance and higher OCVs than the cell using the PTFE-PEM under both humidified and dry conditions. Under dry conditions, the cell using the Pt/C-PEM showed the best and most stable performance. EIS techniques clarified that the Pt/C-PEM membrane can minimize membrane conductivity loss and thus improve the cell performance and that performance losses operated with dry gases were caused by an increase of the interfacial (electrolyte/catalyst) charge transfer resistance for ORR.

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