

# A study on the characteristics of the diffusion layer thickness and porosity of the PEMFC

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## Abstract

In the preparation of electrodes for the proton exchange membrane (PEMFC), the effect of the fabrication method and the thickness of the gas diffusion layer and the impregnation method of Nafion solution on the cell performance was investigated, and unit cell tests were performed. The gas diffusion layer was prepared by rolling, spraying, and screen printing methods, and Nafion solution was impregnated using spraying and brushing methods.

The diffusion layer in a PEMFC consists of a thin layer of carbon black mixed with polytetrafluoroethylene (PTFE) that is coated onto a sheet of macro-porous carbon backing cloth. The effects of different fabrication methods and thicknesses of gas diffusion layer are discussed in the light of porosimetry and  $I$ – $V$  polarization curves and variables related to the electrode analyzed by numerical simulation.

The spraying method proved to be more profitable for cell performance than the brushing method for the impregnation of Nafion solution because it reduced the charge transfer resistance and extended the three-phase region. The goals of this work are to find the optimum thickness of the gas diffusion layer and to undertake an analysis of the system.

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*Keywords:* PEMFC; Gas diffusion layer; Thickness of electrode; Nafion impregnation

## 1. Introduction

Proton exchange membrane (PEMFC) fuel cells are considered promising alternative power plants for transportation because of their high efficiency, high power density, low emissions, low operation temperature, and low noise [1–4]. However, like many emerging technologies, PEMFC must overcome certain engineering and economics obstacles if they are ever to become commercially viable. Hence, in order to ensure, without spatial concession, high power from a commercial-scale system, it is predicted that cell operation at a higher current condition per unit electrode area will be necessary.

From the perspective of electrode performance, the reduction of catalyst loading and improvement of catalyst utilization and performance are important issues. In addition to issues related to the electrocatalyst, the structure and property of the carbon support will impact catalyst utilization and overall cell performance. This layer is porous to allow for distribution of the gas to unexposed areas of the flow channel and this distribution allows for complete

utilization of the electrode. Therefore, the main task of electrode design is to ensure that all reactants have ready access to a sufficiently large catalytically-active interface between the electrolyte and the current-carrying electrode.

Although the gas diffusion layer in a PEMFC plays a critical role in the understanding of performance, the gas diffusion layer remains poorly understood because of a lack of attention and research devoted to its characterization and interactive effects with the other two main repeating units, the catalyst-coated membrane and the bipolar plate [5].

It should be recognized that the electrode is a field where multi-component and multi-phase flows are taking place. Electrochemical behavior of electrode in PEMFCs is influenced by several factors, including inner structure and composition. In other words, for a given catalyst loading, the performance of electrode is dependent on both its structure such as the porosity and the specific surface area and electrode composition [12]. The characteristics of these two factors affecting the electrode are determined by the preparation method of the electrodes. With regard to the preparation of electrodes for PEMFCs, a number of works have been established that offer general necessary conditions. The gas diffusion layer in a PEMFC consists of a thin layer of carbon black mixed with polytetrafluoroethylene (PTFE) that is coated onto a sheet of macro-porous carbon backing

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cloth. This diffusion layer provides a physical micro-porous support for the catalyst layer while allowing gas transport to and from the catalyst layer. Although the diffusion layer is a seemingly minor component in a fuel cell, it has been shown that altering the composition of the diffusion layer can lead to substantial improvements in the performance of the cell [6–10]. The improvements reported relate to the thickness of the layer and the porosity of the layer which functions as the electrical contact resistance and excludes water at the membrane [8,11].

In PEMFC, a noble metal has been used for high performance. Platinum has proven to be the best catalyst for both the hydrogen-oxidation and oxygen-reduction reactions. To lower the platinum loading and to improve further the performance of the electrode, it is necessary to prepare an electrode with high platinum utilization. The electrodes with the platinum layer at the front surface have been developed because the structure of the electrode determines the electrochemically-active surface areas in fuel cell [12,13]. The use of a solid polymer as an electrolyte causes the problem of non-active catalysts in the electrode. Therefore, an ionic conductor like Nafion solution is impregnated on the electrode surface to extend the catalytic reaction area by forming passages of ionic transfer [12,14–17].

Generally, electrode reactions in porous electrodes, especially gas diffusion electrodes, involve complicated factors and it is difficult to evaluate the influence of one parameter separately with other properties being constant. For example a change in the ionomer content affects gas permeability, catalytic activity and ionic resistance simultaneously [17–19]. It is, therefore, important to analyze the relations between a single parameter and a single property in designing the microstructure of the electrodes. Since PEMFC has many parameters that influence cell performance, mathematical models are a very useful tool for understanding the PEM fuel cell in regard to mass transport and electrochemical phenomena and for optimizing various operating parameters to improve performance and efficiency.

In this work, PEMFC electrodes were prepared by applying different porous gas diffusion layers onto each face of a carbon cloth support, finding the optimum porosity and thickness of the gas diffusion layer and analyzing the variables related to the electrode by simulation. Also, we made high performance electrodes using various Pt/C coating methods with Nafion solution, and the effect of coating method and amount of Nafion solution impregnated in the electrode on the performance was analyzed by impedance spectroscopy.

## 2. Experimental

### 2.1. Preparation of membrane–electrode assembly

The electrode was composed of a gas diffusion layer and a catalyst layer. The gas diffusion layer was prepared on

wet-proofed carbon cloth with PTFE. The mixture of carbon powder (Vulcan XC-72, Cabot Co.), 30 wt.% of PTFE and isopropyl alcohol (IPA) was mechanically mixed in a supersonic mixer and deposited by rolling, spraying, and screen printing methods. The carbon and PTFE loading were maintained at a fixed ratio of 10:3. The viscous mixture was screen-printed on to the wet-proofed carbon cloth and then dried for 1 day.

Two different methods were applied to fabricate the catalyst layer on the gas diffusion layer. One was to coat Pt/C surface by brushing 5 wt.% Nafion solution on the catalyst surface after spraying the ink of Pt/C and IPA on the gas-diffusion layer. The other was to coat the Pt/C surface by spraying the ink of the Pt/C, Nafion solution, and IPA on the gas diffusion layer. All the ink was prepared using commercial Pt/C (20 wt.%, Electrochem Inc.) and the Pt loading was fixed at 0.4 mg/cm<sup>2</sup> in both methods.

A polymer electrolyte membrane, Nafion 115 (127 μm, DuPont Co.) was treated with boiling H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub> to remove organic and metallic impurities for 1 h, respectively, and then washed in distilled water for 1 h [9–11]. The membrane and electrode assemblies (MEAs) were made by hot-pressing the pretreated electrode (5 cm<sup>2</sup>) and the membrane under the conditions of 120 °C, 130 atm for 3 min.

### 2.2. Cell operation and electrochemical analyses

The reactants were pure hydrogen and oxygen and the operating temperature of the cell was 70 °C. The potential–current density characteristic curves of cell were measured using a dc Electronic Load (6060B, Hewlett Packard Co.).

Impedance spectroscopy at the interface of the membrane and the electrode was obtained using a Lock-in Amplifier (M5210, EG&G Co.). The range of measurement frequency was from 100 MHz to 5 kHz and the amplitude was 5 mV. The cell was kept at the constant potential of 0.7 V.

### 2.3. Numerical simulation

In this paragraph, a description of the mathematical model developed for the solid polymer electrolyte fuel cell is presented. The following are the governing equations.

$$\text{Continuity : } \frac{\partial(\varepsilon\rho)}{\partial t} + \nabla(\rho u) = 0$$

Momentum conservation :

$$\frac{\partial}{\partial t}(\rho\vec{v}) + \nabla \cdot (\rho\vec{v}\vec{v}) = -\nabla p + \nabla \cdot (\vec{\tau}) + \rho\vec{g} + \vec{F}$$

$$\text{Darcy's law : } \nabla p = -\frac{\mu}{\alpha} \vec{v}$$

Energy conservation :

$$\begin{aligned} & \frac{\partial}{\partial t}(\rho E) + \frac{\partial}{\partial x_i}(u_i(\rho E + p)) \\ &= \frac{\partial}{\partial x_i} \left( k_{\text{eff}} \frac{\partial T}{\partial x_i} - \sum_j h_j J_j + u_j (\tau_{ij})_{\text{eff}} \right) + S_h \end{aligned}$$

Species conservation :

$$\begin{aligned} & \frac{\partial}{\partial t}(\varepsilon \rho C^k) + \nabla \cdot (\gamma \rho u C^k) \\ &= \nabla \cdot (\rho_l D_{l,\text{eff}}^k \nabla C_l^k + \rho_g D_{g,\text{eff}}^k \nabla C_g^k) \\ & \quad - \nabla \cdot [(C_l^k - C_g^k) j_l] + m^k \end{aligned}$$

Fluent (version 6.0) is used to solve the coupled governing equations. The data relevant to vary the thickness of the gas diffusion layer were obtained by using this tool.

### 3. Results and discussion

#### 3.1. Effects of gas diffusion layer parameters

Fig. 1 shows SEM images to compare the surface condition of the gas diffusion layers with fabricating method. Fig. 1(a) is rolled-surface. It is so flat and dense that the distance between carbon particles is very short. Fig. 1(b) and (c) are sprayed-surface and screen-printed surface, respectively. The pore size is large enough for the continuous supply of reactants and it is thought to be more profitable to coat the catalyst layer because it has rough surface.

The pore-size distribution in the diffusion layer analyzed by porosimeter is shown in Fig. 2. The total porosities of the rolling, spraying and screen printing methods are 51, 57, 61%, respectively. Actually, the distribution of pore sizes is a more important parameter than the total porosity since the different modes of gas and water transport are regulated by the specific volumes of small and large pores. To identify these structural changes in different pore-size ranges, the pores in the diffusion layer are divided, according to size, into five classes and attention is focused on three size range, namely: macropores (pore diameter from 5 to 20  $\mu\text{m}$ ) and micropores (pore diameter from 0.03 to 0.06  $\mu\text{m}$ ), which are two pore ranges that show conspicuous variation in the specific pore volume, and mesopores (the intermediate range between 0.06 and 5  $\mu\text{m}$ ). The pores larger than about 100  $\mu\text{m}$  stem from fissures on the surface of the diffusion layer [8].

According to other research [6,8], water transport is assumed to occur simultaneously in two ways; micro- and macro-transport. The role of micropores is in transferring the condensed water from the condensation sites towards the flowing macro-droplets of water. Macropores contribute to reducing the mass transport limitation due to water flooding since they can provide gas diffusion paths toward the catalytic region until the micropores and the smaller pores are completely closed by water droplets. However, the porosity in the electrodes excludes water, the diffusion layer which

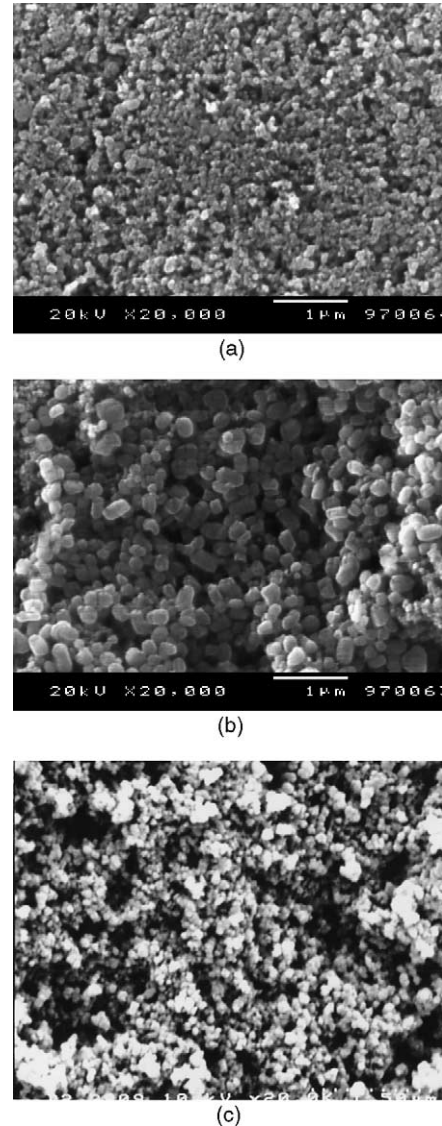
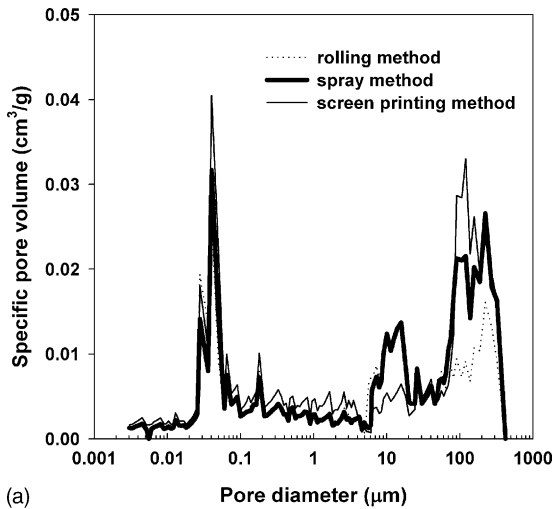


Fig. 1. SEM surface images of the gas diffusion layer (a) rolling; (b) spraying; (c) screen printing.

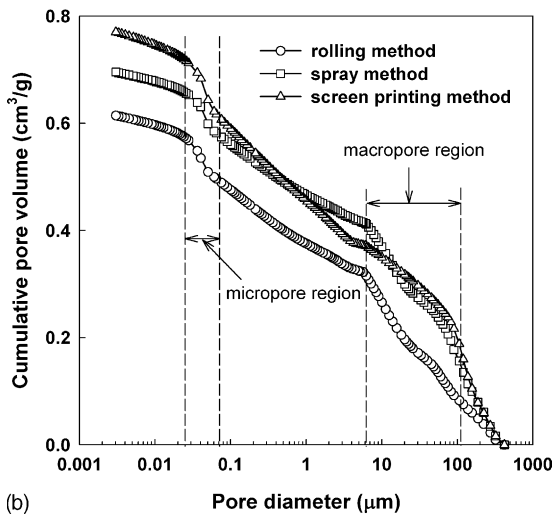
consists of macropores only, is the source of electrical contact resistance [8]. In the case of gas transport to the catalyst sites [21], the main contribution to gas transport will be due to Knudsen diffusion in the micropores and a molecular diffusion mechanism in the macropores. A detailed characterization of the pore size is, therefore, an important prerequisite for designing the electrode.

In Fig. 2, the screen printing and rolling methods have two distinctive regions where pore volume increases sharply ranging from 5 to 20  $\mu\text{m}$ , i.e. macropores and from 0.03 to 0.06  $\mu\text{m}$ , i.e. micropores.

With the same catalyst layer, the effect of the gas diffusion layer on cell performance was examined through performance tests of a  $\text{H}_2/\text{O}_2$  single-cell and is illustrated in Fig. 3. In the rolling method, the distinctive drop in cell voltage suggests that the presence of water saturation in the



(a)



(b)

Fig. 2. (a) Specific and (b) cumulative pore volume distribution of the gas diffusion layer according to the fabrication method.

diffusion layer not only imposes more resistance to gas diffusion toward the catalyst layer, it also influences catalyst flooding (partial coverage of catalyst particles with liquid water) where as, in the spraying and screen printing methods, lower diffusion losses were observed since better distribution of pores makes the liquid and gas phase separate effectively.

A comparison of the polarization curves of the electrodes with different thickness and the same catalyst layer in the electrode is illustrated in Fig. 4. Since the catalyst layers were the same, the performance differences must have originated from the gas diffusion layer. The diffusion layer was fabricated by the screen printing method and the thickness of the electrode was varied as 90, 114, 123, 136, 196 µm by controlling the carbon loading at; 2.83, 3.73, 4.12, 5.55, 6.79 mg/cm<sup>2</sup>, respectively. As seen in Fig. 4, the best performance was obtained at the intermediate loading of diffusion layers. The effect of electrode thickness on the fuel cell performance has been investigated in previous work

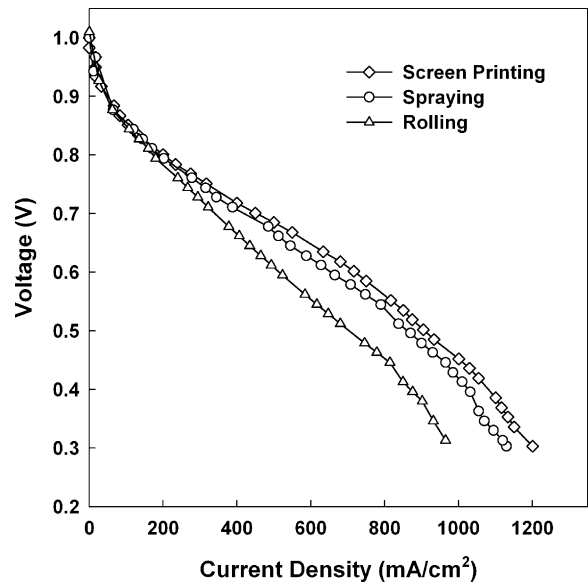


Fig. 3. Influence of different gas diffusion layer fabrication methods on cell performance of H<sub>2</sub>/O<sub>2</sub> single cells.

[11,20]. The thickness of the diffusion layer has competing tendencies where, by the improvement in one property, another property will worsen. A thin layer improves the gas supply and facilitates the removal product of water, but it has high electronic resistance and does not give a non-permeable support for coating with the catalyst layer during electrode fabrication. Therefore, permeation of the catalyst layer into the diffusion layer makes poor ionic contact with the Nafion membrane. On the other hand, a thick layer hampers the accessibility of gas due to the lengthened path in the layer and has poor gas diffusivity. Hence, an intermediate thickness enhances the electrode performance best.

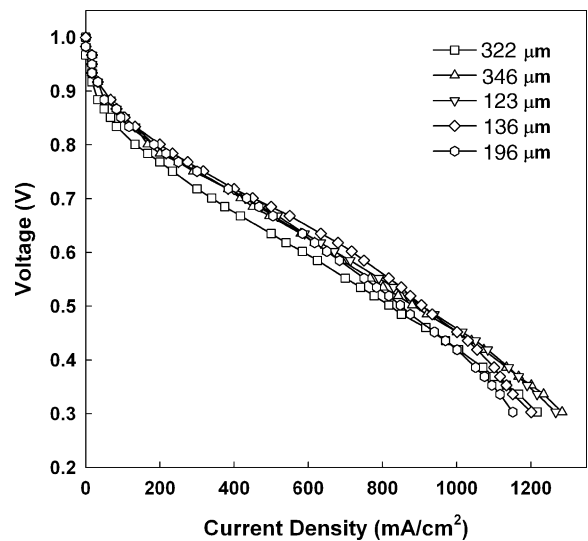


Fig. 4. Comparison of polarization curves of electrodes with different thickness in the electrode.

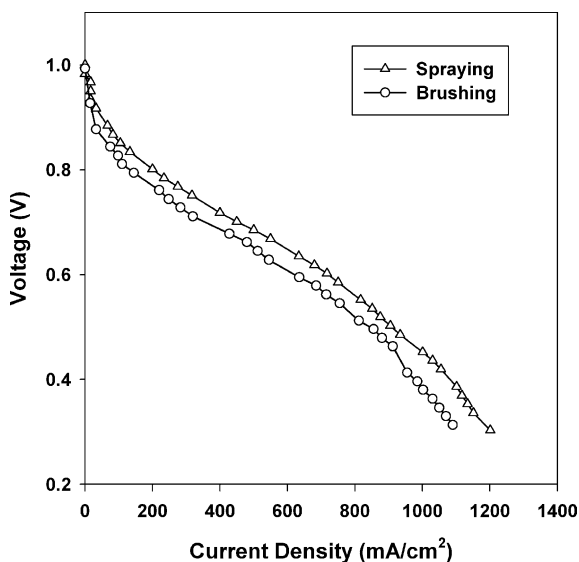


Fig. 5. Effects of impregnation methods of Nafion solution on the cell performance.

### 3.2. Effects of impregnation of Nafion solution

Fig. 5 shows the effects on the cell performance of the impregnation method of Nafion solution at the catalyst layer. The gas diffusion layer was fabricated by the screen printing method. The electrode coating Pt/C the surface by spraying the ink of the Pt/C, Nafion solution and IPA on the gas-diffusion layer showed a better performance than that coating Pt/C by brushing Nafion solution on the catalyst surface after spraying the ink of Pt/C and IPA on the gas-diffusion layer. The current density of the sprayed-electrode reached  $450 \text{ mA/cm}^2$  at  $0.7 \text{ V}$  and this value was higher than that of brushed-electrode ( $340 \text{ mA/cm}^2$ ). In the case of the brushed-electrode, the impregnation of Nafion solution was so irregular and unequal that the ionomer could penetrate into the gas diffusion layer. This can be a critical barrier for gas transport. Fig. 6 depicts the schematic models of electrodes fabricated with the spraying and brushing method. Fig. 6(a) is spraying and the ionomer is uniformly distributed, while Fig. 6(b) is brushed and the ionomer penetrates deeply into

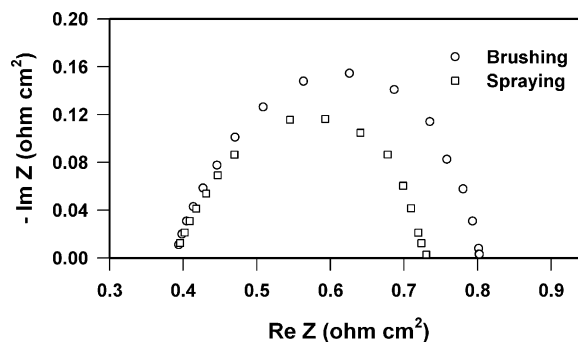


Fig. 7. Nyquist plots with impregnation method of Nafion solution at  $0.7 \text{ V}$  (ImZ, imaginary impedance; ImRe, real impedance).

the gas diffusion layer and is not equally distributed. The essential point of the electrode is to equip the structure to contact gas, electrolyte and catalyst site simultaneously. In this regard, it is thought that Fig. 6(a) is desirable for PEMFC.

The same result was obtained from the impedance data. The Nyquist plots of sprayed- and brushed-electrodes are compared in Fig. 7. The applied potential was  $0.7 \text{ V}$  and the internal resistance was almost same, but the charge transfer resistance was smaller in the sprayed-electrode than in the brushed one. This proves that the uniformly distributed ionomer of the sprayed-electrode reduced the charge transfer resistance effectively.

Fig. 8 displays the effect on the cell performance of the amount of Nafion solution impregnated in the catalyst layer. The addition of ionomer like Nafion solution improved the performance of the cell because it expanded the three-phase region within the electrode. So this method has been used from the early stages of electrode development. However, an excessive addition of ionomer causes a problem, disturbing the diffusion of reactants. In our experiments, the optimal amount of Nafion solution was  $12 \text{ mg/cm}^2$ . Above that, the cell performance decreased. In the case of  $8 \text{ mg/cm}^2$ , the amount of ionomer was so small that it could not play its role well and the cell performance also was lower. The Nyquist plots of each electrode are compared in Fig. 9. The values of charge transfer resistance obtained from these plots were in good agreement with the cell performance data. The

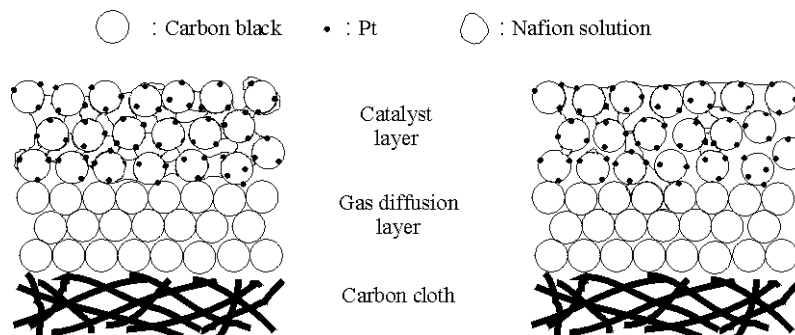


Fig. 6. Schematic model of electrodes fabricated with spraying and brushing methods.

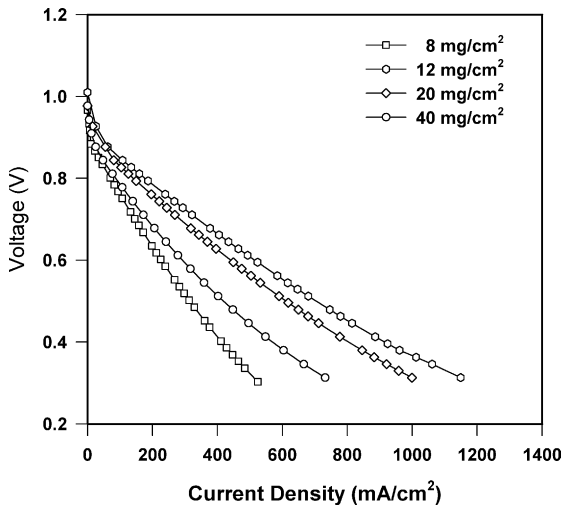


Fig. 8. Effect of the amount of Nafion solution on the cell performance at 70°C, 1 atm (gas diffusion layer: screen printing; Nafion solution: spraying).

charge transfer resistance of the electrode with 12 mg/cm<sup>2</sup> was 0.3347 Ω cm<sup>2</sup>.

3.3. Numerical simulation

The operating conditions used in this model are as follows:

- Inlet velocity: 2.14 m/s;
- Inlet temperature: 353 K;
- Cell temperature: 348 K;
- Electrode porosity: 0.57.

Fig. 10 is the concentration distributions according to the thickness of the diffusion layer. These show that the concentration drops between the inlet and outlet channels. And the effect of diffusion layer thickness with the decrease of the oxygen concentration is shown as the diffusion layer thickness is increased.

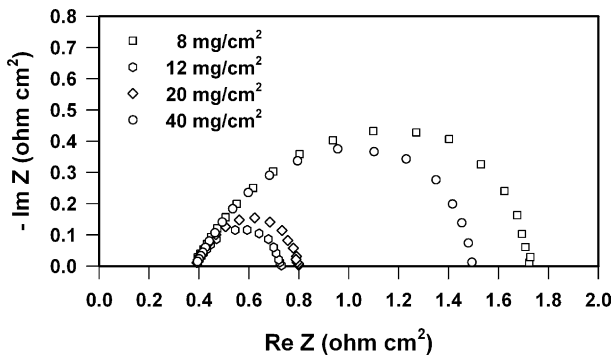
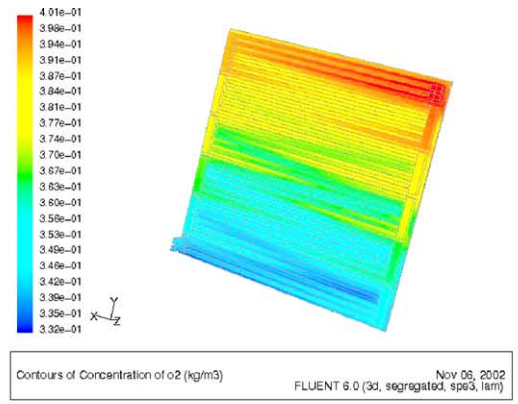
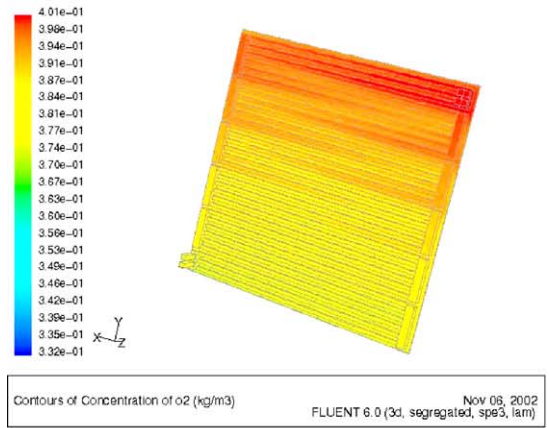


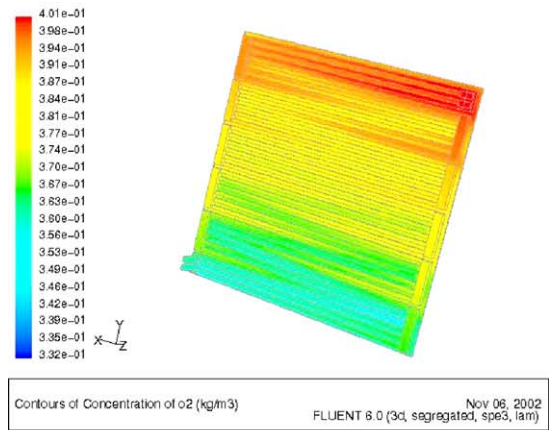
Fig. 9. Nyquist plots with the amount of Nafion impregnation at 0.7 V, 1 atm (gas diffusion layer: screen printing; Nafion solution: spraying) (ImZ, imaginary impedance; ImRe, real impedance).



(a)



(b)



(c)

Fig. 10. Contour of oxygen concentration distribution in the (a) 300; (b) 400; (c) 450 μm thickness.

4. Conclusion

In this study, the correlation of characteristics of the gas diffusion layer and the Nafion impregnation method on the cell performance was investigated. For an improvement of performance in PEMFC, an ionic conductor like Nafion solution has been impregnated on the electrode surface. In this study, the characteristics of electrodes fabricated

by spraying and brushing methods were compared and analyzed. In the gas diffusion layer, the sprayed- and screen-printed layer showed better performance because it had more porous structure and better gas permeability compared with the rolled-layer. In the catalyst layer, the electrode coating Pt/C surface by spraying ionomer mixture directly on the gas-diffusion layer proved to have better performance than that coating Pt/C by brushing the ionomer on the catalyst surface after spraying the catalyst mixture on the gas-diffusion layer. Consequently, the direct coating method of Pt/C with the ionomer is estimated to enable a reduction in the non-active catalyst sites. Simulation of fluid in the channel and the gas diffusion layer was investigated for the effects of electrode variables: gas diffusion layer thickness, porosity, and distribution of pore size. The results show that the application of simulation enables the design of the flow channel and the structure of the electrode effectively.

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