Korean J. Chem. Eng., **22**(5), 661-665 (2005)

Effect of Temperature, Oxidant and Catalyst Loading on the Performance of Direct Formic Acid Fuel Cell

Jeong Soo Kim, Jae Keun Yu, Hyo Song Lee, Jin Yong Kim, Young Chun Kim*, Jong Hee Han*, In Hwan Oh* and Young Woo Rhee†

Department of Chemical Engineering, Chungnam National University, 220, Gung-dong, Yuseong-gu, Daejeon 305-764, Korea
*Fuel Cell Research Center, Korea Institute of Science and Technology, 39-1, Hawolgok-dong, Sungbuk-gu, Seoul 136-791, Korea

(*Received 13 December 2004 • accepted 14 March 2005*)

Abstract−We investigated the effect of temperature, oxidant and catalyst loading on the performance of direct formic acid fuel cell (DFAFC). When oxidant was changed from air to oxygen, the power density was increased to 17.3 mW/cm^2 at 25 °C. The power density of DFAFC operated with oxygen showed a maximum value of 40.04 mW/cm^2 with the temperature rise from room temperature to 70 °C. The highest power density of DFAFC using air was observed for Pt-Ru black catalyst with loading of 8 mgPt/cm^2 at room temperature. At 70 °C; however, the performance of catalyst with the loading of 4 mgPt/cm^2 was higher than that of 8 mgPt/cm^2. The DFAFC, operated with oxygen and catalyst of 4 mgPt/cm^2 loading, showed the best performance at all temperature range. The enhancement of cell performance with an increase of catalyst loading is believed to come from an increase of catalyst active sites. However, operated at higher temperature or with oxygen, the cell with higher catalyst loading showed lower performance than expected. It is speculated that the thick catalyst layer inhibits the proton transport.

Key words: Fuel Cell, Formic Acid (HCOOH), Anode Catalyst, DFAFC, Temperature

INTRODUCTION

A direct methanol fuel cell (DMFC) can operate well at relatively low temperature, and has high efficiency, simple design and no leakage of electrolyte. So, DMFC has been extensively studied as a promising power and energy supplier for portable power devices. However, DMFC using methanol as a fuel has several problems, such as fuel crossover and CO poisoning of cathode catalyst [Cruickshank and Scott, 1992; Heinzel and Barragan, 1999; Lee et al., 1998; Nakagawa and Xiu, 2003; Park et al., 2004; Son, 2004; Yang et al., 2002; Yoon et al., 2003]. As a solution for these problems, formic acid was proposed as a substitute fuel for miniature fuel cells [Rice et al., 2002]. In the previous work, we confirmed that formic acid can be used as a fuel of fuel cell [Kim et al., 2004].

Formic acid exists as a liquid phase like methanol at room temperature. It is easily found in nature, and it is not harmful to humans, so it is approved by the US Food and Drug Administration (FDA) for use as a food additive. Also, the theoretical open circuit potential (OCP) for formic acid is 1.45 V, which is higher than that of hydrogen with 1.23 V and methanol with 1.18 V. Because formic acid is a strong electrolyte, it is expected to facilitate both electron and proton transfers. In addition to these advantages, formic acid partially dissociates in solution, forming a formate anion. The formate anion diffuses very slowly through Nafion® membrane. On the contrary, methanol dissociates cation diffusing rapidly through Nafion® membrane. Slow diffusion of formic acid is expected to result in low fuel crossover and enable use at high concentrations. In the work reported by Rhee and co-workers, permeation of formic acid through Nafion membrane is sharply slower than that of methanol [Rhee et al., 2003]. Also, Rice and co-workers obtained current density of 134 mA/cm^2 and power density of 48.8 mW/cm^2 using catalyst developed in-house [Rice et al., 2002]. This previous work supports that formic acid has potential as fuel of a fuel cell. Though research on the DFAFC started in USA at the end of 2001, sufficient work has not been carried out yet in comparison with DMFC.

In this study, we investigated the effects of temperature, oxidant and catalyst loading on the performance of DFAFC. Temperature was changed from 25 °C to 70 °C and the oxidants were air and oxygen. The anode catalyst loaded on the membrane was 4 mgCatalyst/cm^2, 4 mgPt/cm^2 and 8 mgPt/cm^2, respectively. The purpose of this study is to understand the significance of various parameters in DFAFC system.

EXPERIMENTAL

In this study, Nafion® 117 (Dupont) was used as a polymer electrolyte membrane. To remove impurities, Nafion® membrane was preconditioned prior to fabrication of membrane electrode assembly (MEA). First, it was boiled in 5% hydrogen peroxide at 80 °C. Then, it was boiled in 0.5 M H_2SO_4 at 80 °C to let protons change to form of hydrogen ion. Finally, the treated membranes were stored in millipore water prior to use [Rhee et al., 2003].

The electrode support plays a role that sustains electrode and helps diffusion of fuel and oxidant. Therefore, it should have high porosity, and high electron conductivity to accumulate current generated at electrode [Cho and Lim, 2004; Jung, 2004; Lee and Won, 2003]. In this study, carbon cloth (Torey Co.) was used as an electrode support. The electrode support of cathode side was particularly treated teflon to manage water.

The catalyst inks were prepared by dispersing the catalyst nanopar-

---

[†] To whom correspondence should be addressed.
E-mail: ywrhee@cnu.ac.kr

ticles into appropriate amount of millipore water and 5 wt% Nafion® solution (EW 1100, Aldrich). To disperse particles, the solution was stirred by ultrasonic waves. Then, both the anode and cathode catalyst inks were directly painted by using a 'direct painting' technique onto either side of a Nafion® 117 membrane [Rice et al., 2002, 2003; Ha et al., 2002, 2004; Zhu et al., 2004]. A carbon cloth diffusion layer was placed on top of both the anode and cathode catalyst layers. The active cell area was 2.25 cm^2 (1.5 cm×1.5 cm).

In this study, commercial catalysts were used. All of cathode catalysts were Pt black (HISPEC™ 1000, Johnson-Matthey), and the amount of Pt loaded on membrane was 7 mg/cm^2. The anode catalyst was Pt-Ru black (HISPEC™ 6000, Johnson-Matthey), and different amounts of catalyst for each experiment were used.

96% A.C.S. grade formic acid (Aldrich) was used as a fuel and was diluted to 9 M. The oxidant was air or oxygen. Initially, the MEA was conditioned within the testing fixture at 70 °C with air and then with formic acid at room temperature for several hours. The anode/cathode flow fields were machined into conductive graphite blocks. Formic acid was supplied to the anode side of MEA at a flow rate of 1 ml/min. humidified oxidant was supplied to the cathode at a flow rate of 200 ml/min.

The single-cell test fixture was designed for use with formic acid. In this study, we evaluated fuel cell performance in terms of potential and power density vs. current density according to the temperature, oxidant and catalyst loading. A schematic diagram of the experimental system is shown in Fig. 1.

RESULTS AND DISCUSSION

Fig. 2 shows the effect of oxidation gas, air or oxygen, on the performance of DFAFC. The fuel cell was operated at room temperature with anode catalyst loading of 4 $mgPt/cm^2$. The OCP of fuel cell operated with air was 0.552 V. The maximum current density and power density were 130 mA/cm^2 and 27.72 mW/cm^2, respectively. On the other hand, the fuel cell operated with oxygen showed OCP of 0.625 V, and the maximum current density and power density were 240 mA/cm^2 and 48.51 mW/cm^2, respectively. Namely, the change of oxidant enhanced the performance of the DFAFC system by 48%. Nakagawa et al. reported the effect of oxidant gas at direct methanol fuel cell (DMFC) system. According to the report, the power density with air feeding was almost twice as high as that with air feeding. They explained that the increase of fuel cell performance may be related to the mass transfer of oxygen at the cathode because the mass transfer, like gas diffusion and surface diffusion, responds at a relatively high frequency. The reason for the increase of DFAFC performance may be explained by the same consideration since the DFAFC system is similar to DMFC system [Nakagawa and Xiu, 2003]. An increase of oxygen concentration will make the mass transfer of oxygen easier and faster. And the faster mass transfer of oxygen will enhance the reaction rate. As a result, the DFAFC with oxygen feeding will show better performance than that with air feeding. Reactions at anode and cathode sides of DFAFC may be represented as follows:

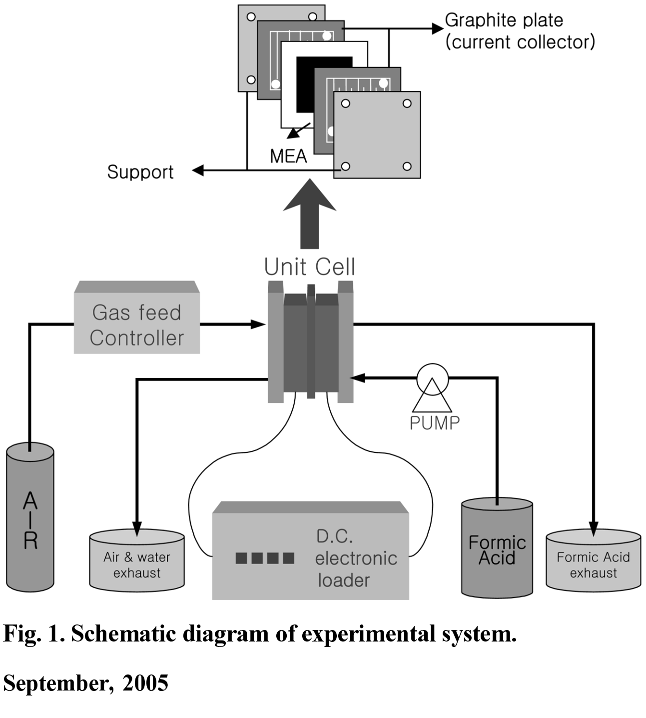

Fig. 1. Schematic diagram of experimental system.

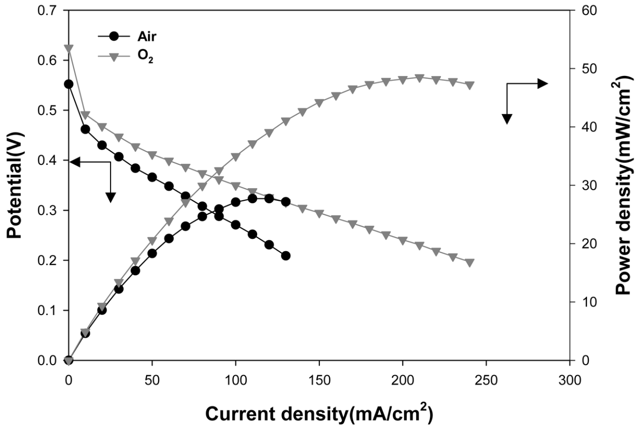

Fig. 2. Effect of oxidation gas on the performance of fuel cell (9 M HCOOH, 25 °C, Pt-Ru black 4 $mgPt/cm^2$).

$$\text{anode: } HCOOH \rightarrow 2H^+ + CO_2 + 2e^- \tag{1}$$

$$\text{cathode: } 2H^+ + \frac{1}{2}O_2 + 2e^- \rightarrow H_2O(l) \tag{2}$$

$$\text{overall: } HCOOH + \frac{1}{2}O_2 \rightarrow H_2O(l) + CO_2 \tag{3}$$

Also, we might assume the total reaction rate be generally expressed by Eq. (4) as follows:

$$v = k[HCOOH]_{ads}[O_2]_{ads}^{1/2} \tag{4}$$

Here, k is the reaction rate constant, and $[HCOOH]_{ads}$ and $[O_2]_{ads}$ are mean concentrations of formic acid and oxygen adsorbed on the active sites of catalyst, respectively. The concentration of oxygen adsorbed on the active sites of catalyst will increase with changing of oxidant from air to oxygen, causing faster reaction rate. As a result, the oxidant change from air to oxygen will enhance the fuel cell performance.

Fig. 3 shows the fuel cell performance with an increase of temperature. Anode catalyst was loaded with 4 $mgPt/cm^2$, and oxygen was used as an oxidant. Operating temperature of fuel cell was changed

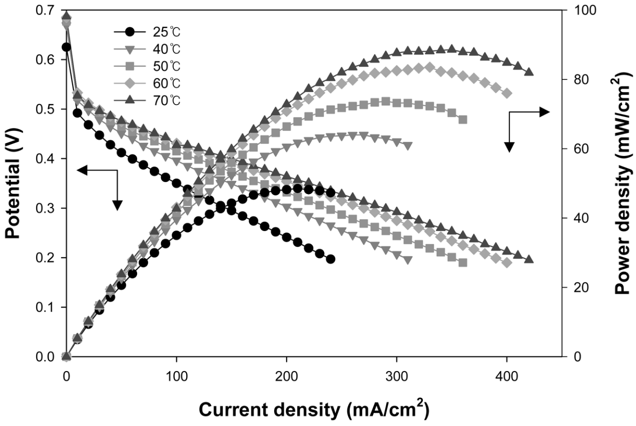

Fig. 3. Effect of temperature on the performance of fuel cell (9 M HCOOH, O_2, Pt-Ru black 4 mgPt/cm^2).

Table 1. Comparison of OCP, maximum current density, maximum power density at different temperatures (9 M HCOOH, O_2, Pt-Ru black 4 mgPt/cm^2)

Temperature (°C)	OCP (V)	Max. current density (mA/cm^2)	Max. power density (mW/cm^2)
25	0.625	240	48.51
40	0.669	310	63.99
50	0.677	360	73.66
60	0.685	400	83.49
70	0.687	420	88.55

from 25 °C to 70 °C. The fuel cell performance increased with the increase of operating temperature. The fuel cell showed a maximum current density of 420 mA/cm^2 and power density of 88.6 mW/cm^2 at 70 °C. The increase of the fuel cell performance can be explained by the Arrhenius relation shown in Eq. (5).

$$k=A\ \exp(-E_a/RT) \tag{5}$$

Here the reaction rate constant k is an important factor for the reaction rate. According to Eq. (5), the reaction rate constant k increases with increasing temperature. As a result, the reaction rate of the fuel cell increases, and fuel cell performance increases as well. However, the degree of increase of cell performance decreases with the increase of temperature as shown in Table 1. OCP, maximum current density and maximum power density of fuel cell were summarized for the fuel cell with catalyst loading of 4 mgPt/cm^2 at different temperatures. The fuel cell showed a maximum power density difference of 15.5 mW/cm^2 between 25 °C and 40 °C. On the other hand, the difference in power density was only 5.1 mW/cm^2 between 60 °C and 70 °C. The reason for this may be that Nafion® membrane demonstrates relatively better proton conductivity at 55-70 °C lessening the temperature effect. In this temperature range, the conductivity is highest in the case of minimum water content, too. This may be related to the movement of the main loop of polymer in Nafion® membrane. The movement of the main loop is most active in this temperature range so that the proton can be much more easily transported [Reike and Vanderborgh, 1987].

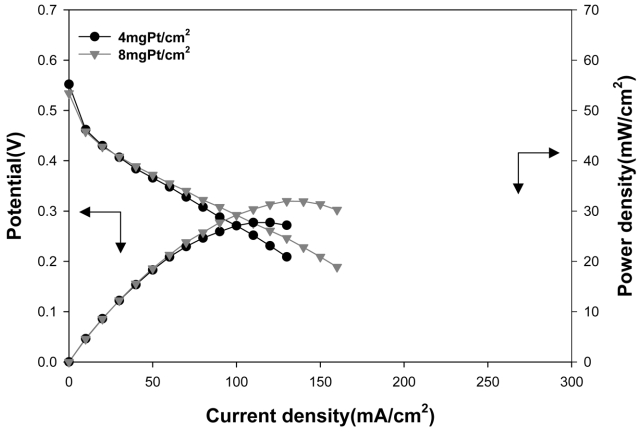

Fig. 4. Effect of catalyst loading on the performance of fuel cell at 25 °C (9 M HCOOH, Air, Pt-Ru black).

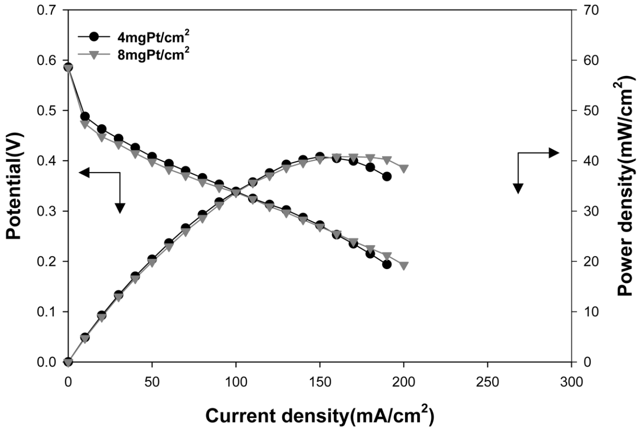

Fig. 5. Effect of catalyst loading on the performance of fuel cell at 40 °C (9 M HCOOH, Air, Pt-Ru black).

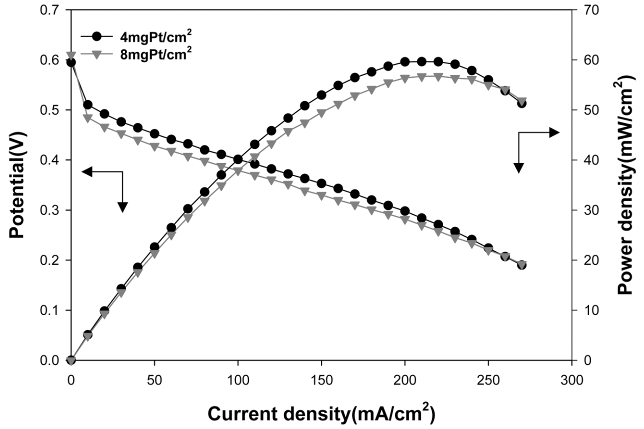

Fig. 6. Effect of catalyst loading on the performance of fuel cell at 70 °C (9 M HCOOH, Air, Pt-Ru black).

The result on the change of catalyst loadings was quite interesting. The performance curves of fuel cell were compared by changing catalyst loadings, oxidant and temperature. Fig. 4, 5, and 6 show the effect of anode catalyst loading on the performance of fuel cell with air feeding at different temperatures. Catalyst loadings were 4 mgPt/cm^2 and 8 mgPt/cm^2, respectively. The fuel cell with catalyst loading of 8 mgPt/cm^2 demonstrated very good performance at 25 °C as shown in the previous research of our laboratory [Kim et al., 2004]. One might expect the better performance with higher catalyst loading. However, a fuel cell with the increase of temperature demonstrated better performance with less catalyst loading of 4 mgPt/cm^2 as shown in Figures. In low temperature, a fuel cell with larger amount of catalyst will show better cell performance since a larger amount of catalyst plays a more significant role in accelerating the reaction rates. On the other hand, since the reaction rates will be rapidly increased according to Eq. (5), the proton will be produced more rapidly. At the same time, the transfer of proton through the membrane may be inhibited by a thick catalyst layer, diminishing the effect of increasing temperature. This is considered in terms of a trade-off between kinetic and mass transfer limitation, indicating the importance of using the proper amount of catalyst. This effect of catalyst loadings was confirmed in fuel cell by using oxygen as an oxidant, too.

Figs. 7 and 8 show the effect of catalyst loading with oxygen as an oxidant on the fuel cell performance. Anode catalyst loadings were 4 mgCatalyst/cm^2, 4 mgPt/cm^2, and 8 mgPt/cm^2, respectively. The fuel cell with anode catalyst loadings of 4 mgPt/cm^2 showed the best performance in all temperature ranges. This result is different from cell performance with air as an oxidant as shown in Fig. 4, 6. This result implies that the proton produced rapidly by increasing oxygen concentration cannot transport effectively through Nafion® membrane due to the thick catalyst layer. At low temperature, the fuel cell with catalyst loadings of 8 mgPt/cm^2 showed better performance than that with catalyst loadings of 4 mgCatalyst/cm^2. It is speculated that catalyst loading of 4 mgCatalyst/cm^2 was not sufficient for oxidation of formic acid. As the temperature increased, however, the fuel cell performance with catalyst loadings of 4 mgCatalyst/cm^2 showed better than that with catalyst loadings of 8 mgPt/cm^2. This may be explained by the same reasoning. Namely, the thick catalyst layer inhibits the transfer of protons, causing poor performance of the fuel cell. The DMFC system has an optimum catalyst loading according to the research of Nakagawa et al. [Nakagawa and Xiu, 2003]. Likewise, it is obvious from our results that the selection of optimum catalyst loading will be very important in DFAFC system, too.

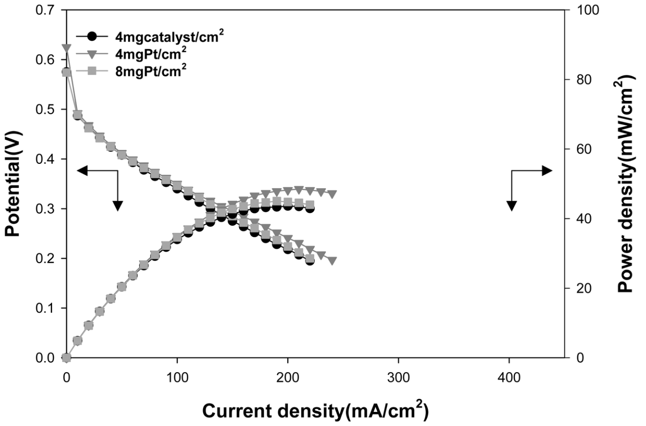

Fig. 7. Effect of catalyst loading on the performance of fuel cell at 25 °C (9 M HCOOH, O^2, Pt-Ru black).

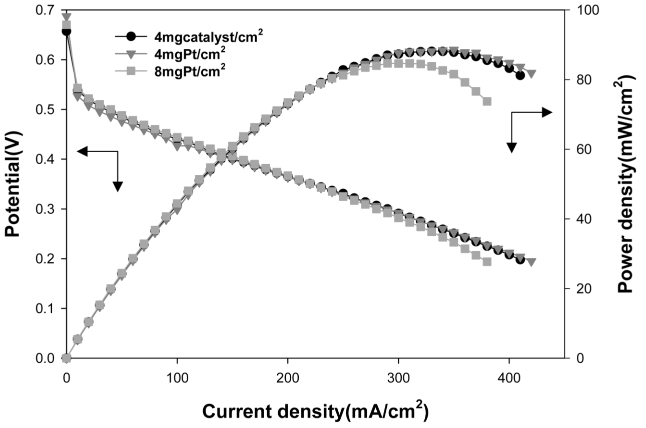

Fig. 8. Effect of catalyst loading on the performance of fuel cell at 70 °C (9 M HCOOH, O_2, Pt-Ru black).

CONCLUSIONS

The concentration of oxygen had a significant effect on the direct formic acid fuel cell performance. The fuel cell with oxygen feeding showed the maximum power density of 48.51 mW/cm^2 at 25 °C. This result corresponds to 17.31 mW/cm^2 improvement when compared to a fuel cell operated with air at the same condition. Also, the operating temperature of the fuel cell had a great effect on the DFAFC performance. The DFAFC with oxygen feeding generated the maximum power density of 88.55 mW/cm^2 at 70 °C, which corresponds to about 82.5% enhancement compared to that obtained at 25 °C.

Higher catalyst loading of anode resulted in better cell performance at low temperature. However, higher catalyst loading caused the inhibition of proton transfer at high temperature with oxygen, lessening the temperature increasing effect. Therefore, it is important to select optimum catalyst loading in designing the DFAFC system.

ACKNOWLEDGMENT

This work was supported by Korea Energy Management Corporation (2003-N-FC03-04-P-03-0-000).

REFERENCES

Cho, E. A. and Lim, T. H., "R&D on Polymer Electrolyte Membrane Fuel Cells," *Prospectives of Industrial Chemistry*, **7**, 22 (2004).

Cruickshank, J. and Scott, K., "The Degree and Effect of Methanol Crossover in the Direct Methanol Fuel Cell," *J. Power Sources*, **70**, 40 (1992).

Ha, S., Adams, B. and Masel, R. I., "A Miniature Air Breathing Direct Formic Acid Fuel Cell," *J. Power Sources*, **128**, 119 (2004).

Ha, S., Rice, C. A., Masel, R. I. and Wieckowski, A., "Methanol Conditioning for Improved Performance of Formic Acid Fuel Cells," *J. Power Sources*, **112**, 655 (2002).

Heinzel, A. and Barragan, V. M., "A Review of the State-of-the-art of the Methanol Crossover in Direct Methanol Fuel Cells," *J. Power Sources*, **84**, 70 (1999).

Jung, D. H., "R&D Status of Direct Methanol Fuel Cell," *Prospectives* *of Industrial Chemistry*, **7**, 14 (2004).

Kim, J. S., Yu, J. K., Jung, E. M., Lee, H. S., Kim, J. Y., Han, J. H., Oh, I. H. and Rhee, Y. W., "The Performance of Direct Formic Acid Fuel Cell with Various Catalyst," *Korean Chem. Eng. Res.*, **42**, 630 (2004).

Lee, J. H. and Won, J. O., "Polymer Electrolyte Membranes for Fuel Cells," *Polymer Science and Technology*, **14**, 418 (2003).

Lee, S. J., Mukerjee, S., McBreen, J., Rho, Y. W., Kho, Y. T. and Lee, T. H., "Effect of Nafion Impregnation on Performances of PEMFC Electrodes," *J. Electrochim. Acta*, **43**(24), 3693 (1998).

Nakagawa, N. and Xiu, Y., "Performance of a Direct Methanol Fuel Cell Operated at Atmospheric Pressure," *J. Power Sources*, **118**, 248 (2003).

Park, G. G., Sohn, Y. J., Yang, T. H., Yoon, Y. G., Lee, W. Y. and Kim, C. S., "Effect of PTFE Contents in the Gas Diffusion Media on the Performance of PEMFC," *J. Power Sources*, **131**, 182 (2004).

Reike, P. C. and Vanderborgh, N. E., "Temperature Dependence of Water Content and Proton Conductivity in Polyperfluorosulfonic Acid Membranes," *J. Membrane Science*, **32**, 313 (1987).

Rhee, Y. W., Ha, S. Y. and Masel, R. I., "Crossover of Formic Acid through Nafion® Membranes," *J. Power Sources*, **117**, 35 (2003).

Rice, C., Masel, R. I., Waszczuk, P., Wieckowski, A. and Barnard, T., "Direct Formic Acid Fuel Cells," *J. Power Sources*, **111**, 83 (2002).

Rice, C., Masel, R. I. and Wieckowski, A., "Catalysts for Direct Formic Acid Fuel Cells," *J. Power Sources*, **115**, 229 (2003).

Son, J. E., "Hydrogen & Fuel Cell Technology," *Korean Chem. Eng. Res.*, **42**, 1 (2004).

Yang, T. H., Park, G. G., Pugazhendhi, P., Lee, W. Y. and Kim, C. S., "Performance Improvement of Electrode for Polymer Electrolyte Membrane Fuel Cell," *Korean J. Chem. Eng.*, **19**, 417 (2002).

Yoon, W. L., Park, J. W., Rhee, Y. W., Han, M. W., Jeong, J. H., Park, J. S., Jung, H., Lee, H. T. and Kim, C. S., "Operating Characteristics of Integrated NG Reformer System for 5 kW Class PEM Fuel Cell," *HWAHAK KONGHAK*, **41**, 389 (2003).

Zhu, Y., Ha, S. Y. and Masel, R. I., "High Power Density Direct Formic Acid Fuel Cell," *J. Power Sources*, **130**, 8 (2004).