Preparation of Pt-Pd catalysts for direct formic acid fuel cell and their characteristics

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Abstract–Pt-Pd catalysts were prepared by using the spontaneous deposition method and their characteristics were analyzed in a direct formic acid fuel cell (DFAFC). Effects of calcination temperature and atmosphere on the cell performance were investigated. The calcination temperatures were 300, 400 and 500 °C and the calcination atmospheres were air and nitrogen. The fuel cell with the catalyst calcined at 400 °C showed the best cell performance of 58.8 mW/cm^2. The effect of calcination atmosphere on the overall performance of fuel cell was negligible. The fuel cell with catalyst calcined at air atmosphere showed high open circuit potential (OCP) of 0.812 V. Also the effects of anode and cathode catalyst loadings on the DFAFC performance using Pt-Pd (1 : 1) catalyst were investigated to optimize the catalyst loading. The catalyst loading had a significant effect on the fuel cell performance. Especially, the fuel cell with anode catalyst loading of 4 mg/cm^2 and cathode catalyst loading of 5 mg/cm^2 showed the best power density of 64.7 mW/cm^2 at current density of 200 mA/cm^2.

Key words: Pt-Pd Catalyst, Formic Acid, DFAFC

INTRODUCTION

Direct formic acid fuel cells (DFAFCs) are expected as power sources of portable devices such as laptop computers, cellular phones, personal digital assistants (PDA) etc. Formic acid exists as a liquid phase like methanol at room temperature, is not harmful to humans, and is approved by the US Food and Drug Administration (FDA) for use as a food additive. Formic acid also has a higher theoretical electro-motive force (EMF), 1.45 V in a fuel cell, as calculated from the Gibbs free energy, than either hydrogen (1.23 V) or methanol (1.18 V) of direct methanol fuel cells (DMFCs) [1,2].

Since formic acid is a strong electrolyte, it is expected to facilitate both electronic and proton transport within the anode compartment of the fuel cell. 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 [3,4]. In the work reported by Rhee et al., permeation of formic acid through Nafion® membrane is much slower than that of methanol [5].

It is desirable to develop more active catalysts to improve cell efficiency and power density while reducing overall precious metal loadings. Recently, it has been widely studied on the catalyst with new metal for improvement of cell performance. The Pt-Ru catalyst is used as the best catalyst for electro-oxidation of methanol in

direct methanol fuel cells [6]. In a direct formic acid fuel cell, the Pt-Ru catalyst was reported to improve dehydrogenation reaction more than pure Pt, but it reduces the cell performance due to slow dehydrogenation reaction at low potential. The mechanism of formic acid oxidation on platinum is well established as the so-called dual pathways of dehydrogenation and dehydration represented by reactions (1) and (2) [2,7]:

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

$$HCOOH \rightarrow CO_{ads} + H_2O \rightarrow CO_2 + 2H^+ + 2e^- \tag{2}$$

The preferred reaction for the complete oxidation of formic acid is a dehydrogenation reaction (reaction (1)), where CO$_2$ is directly produced through the formation of active intermediates. But, the main reaction for formic acid oxidation on pure Pt is a dehydration reaction (reaction (2)), leading to an accumulation of CO$_{ads}$. So, platinum surfaces have been modified by electro-deposition, not involving the formation of alloy, with various elements such as Pd, Pb, As, Au and Bi. These attempts to avoid poisoning show an increase in apparent reaction rate for formic acid oxidation [8,9]. According to Rice et al., the addition of palladium enhanced the reaction (1), which was not inhibited by CO$_{ads}$, through the anode polarization and CO stripping experiment [10]. Our previous works showed that Pt-Pd catalyst had excellent performance in DFAFC. Choi et al. also confirmed excellent performance in DFAFC using Pt-Au catalyst [7].

In this study, the effects of calcination atmosphere, calcination temperature, and anode and cathode catalyst loadings on the DFAFC performance were investigated in terms of cell power density. Calcination atmospheres were air and nitrogen, and calcination temperature ranged from 300 °C to 500 °C.

EXPERIMENTAL

1. Preparation of Pt-Pd Catalysts

Generally, spontaneous deposition, forced deposition, and electrolytic deposition method have been reported for the preparation of Pt-Pd catalyst [11-13]. In this study, the Pt-Pd (1 : 1) catalyst was prepared by using the spontaneous deposition method. This method was originally to deposit the metal particles using cyclic voltammetry. But, Attard and Bannister reported a modified method to deposit the metal particles without use of cyclic voltammetry [13]. In this study, the Pt-Pd catalysts were prepared without use of cyclic voltammetry. First, a catalyst ink of Pt black nanoparticles was made of Pt black and millipore water without use of ionomer. Then, this catalyst ink was mixed with palladium nitrate solution by using a stirrer. This mixture was precipitated for 24 hours, and dried at 70 °C. Next, dried mixture catalyst was sieved to nanoparticle size. Finally, it was calcined at desired temperature under air or nitrogen atmosphere for 2 hours.

2. Single Cell Testing

The catalyst inks of anode and cathode were prepared by dispersing the catalyst nanoparticles into the appropriate amount of millipore water and 5 wt% Nafion® solution. To disperse the particles, the solution was stirred by ultrasonic waves. Then, catalyst ink of anode was dispersed by dispersing agents (isopropylalcohol+1-propanol). Membrane electrolyte assemblies (MEAs) were made by using a 'direct painting' method. Both the anode and cathode catalyst inks were directly painted onto either side of the Nafion® 117 membrane. The active cell area was 2.25 cm² (1.5 cm×1.5 cm).

In this study, all of cathode catalysts were Pt black (HISPEC™ 1000, Johnson-Matthey) and anode catalysts were Pt-Pd (1 : 1) prepared in house. The catalyst loading was changed depending on experimental conditions. A carbon cloth was used as a gas diffusion layer and it was placed on top of both the anode and cathode catalyst layers. Carbon cloth of cathode side was particularly treated teflon to manage water. The mixed solution of 9 M HCOOH and 1 M HBF₄ was used as a fuel to control the oscillatory behavior of potential during experiment. The oxidant was air in all experiments.

The single cell test fixture was designed for use with formic acid. A schematic diagram of the experimental system is shown in Fig. 1. 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 and 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. All experiments
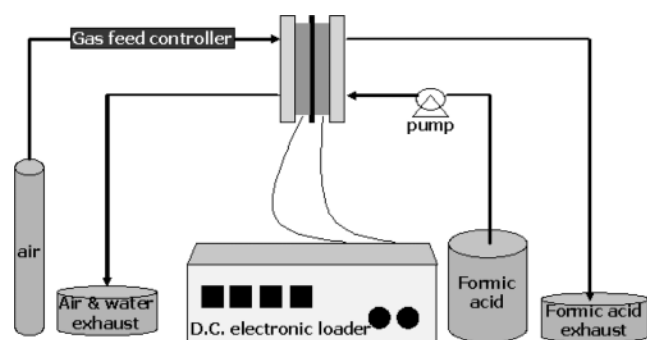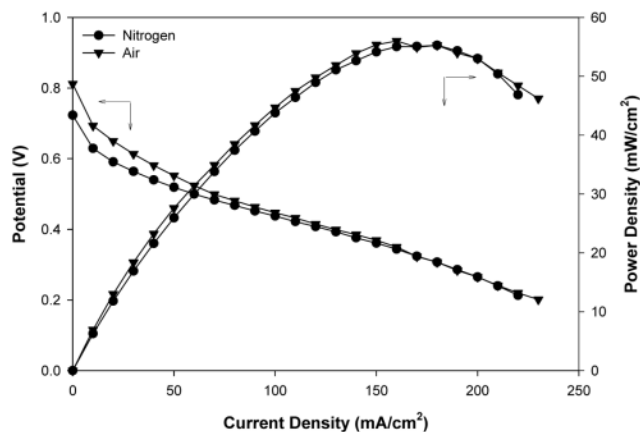

Fig. 2. Effect of calcination atmosphere on the performance of fuel cell (calcination temperature: 500 °C, operating temperature: 25 °C).

were performed at room temperature and repeated over 3-times to demonstrate the reproducibility.

RESULTS AND DISCUSSION

Fig. 2 shows the effect of calcination atmosphere on the fuel cell performance. The catalysts were calcined under either nitrogen or air atmosphere. Calcination temperature was 500 °C. Anode catalyst was Pt-Pd with 4 mg/cm² catalyst loading and cathode catalyst was Pt black with 7 mg/cm² catalyst loading. The fuel cell with the catalyst calcined under air atmosphere showed open circuit potential (OCP) of 0.812 V. This OCP value is higher than that of nitrogen atmosphere. But the fuel cell performance was rapidly decreased as the current increased. So, overall performance showed a little difference between the two cases. It is believed that PdO is present in the form of crystals at the surface of the Pt-Pd particles [14], since palladium reacts with oxygen at high temperature. Also, it is speculated that catalytic activity is inhibited by absorption of by-products.

Fig. 3 shows the effect of calcination temperature on the fuel cell
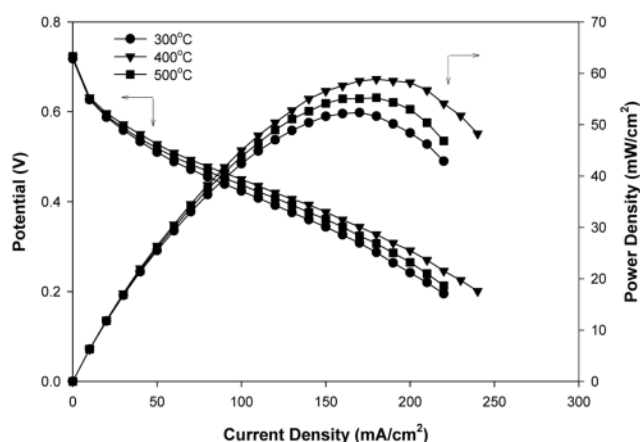

Fig. 3. Effect of calcination temperature on the performance of fuel cell (calcination atmosphere: Nitrogen, anode catalyst: Pt-Pd 4 mg/cm², cathode catalyst: Pt black 7 mg/cm², operating temperature: 25 °C).
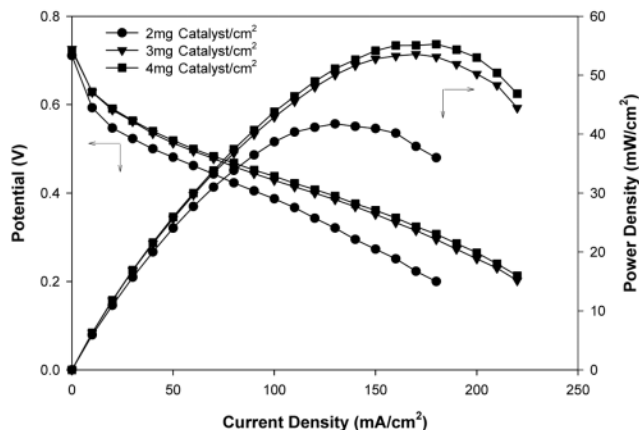

Fig. 1. Schematic diagram of experimental apparatus.

Fig. 4. Effect of anode catalyst loading on the performance of fuel cell (operating temperature: 25 °C, cathode catalyst: 7 mg/cm².).

performance. The calcination temperature of the catalyst ranged from 300 °C to 500 °C, and the calcination atmosphere was nitrogen atmosphere. The fuel cell showed the best performance with a maximum power density of 58.8 mW/cm² at 400 °C, and the poorest performance was shown at 300 °C. This result implies that morphology and composition of catalyst are changed according to calcination temperature. Kim et al. reported the composition changes between Pt-Ru/C catalyst calcined at 300 °C (a_{fcc}=0.392 nm) and Pt-Ru/C catalyst calcined at 400 °C (a_{fcc}=0.388 nm), and showed the performance difference through a single cell test [15]. The change of active surface area, as the calcination temperature changes, had an effect on the fuel cell performance. The low cell performance at 300 °C indirectly showed that the impurities were not completely removed and, therefore, inhibited the catalytic activity.

Figs. 4 and 5 show the effect of catalyst loadings on the fuel cell performance. Nine experiments with different catalyst loadings of anode and cathode were performed. Table 1 shows the maximum power densities on the nine sets of catalyst loadings. The maximum power density demonstrated the tendency of performance increase as the catalyst loading increased. But, a large amount of catalyst shows a slight decline in performance.
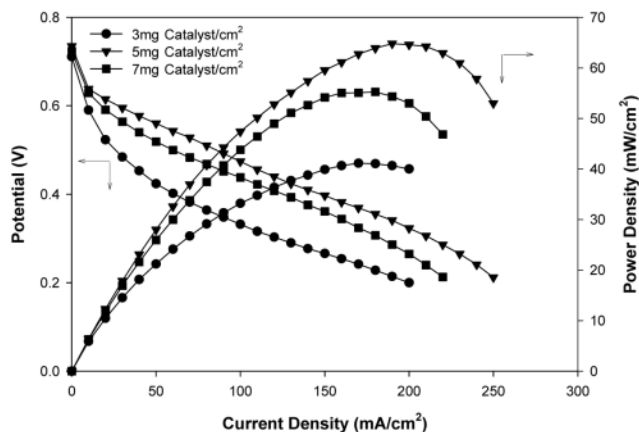

Fig. 5. Effect of cathode catalyst loading on the performance of fuel cell (operating temperature: 25 °C, anode catalyst: 4 mg/cm².).

Table 1. Comparison of maximum power density with different catalyst loading (mW/cm²)

		Anode (Pt-Pd (1 : 1))		
		2 mg/cm²	3 mg/cm²	4 mg/cm²
Cathode	3 mg/cm²	34.1	38.4	41.1
(Pt black)	5 mg/cm²	42.4	62.6	64.7
	7 mg/cm²	41.7	53.6	55.3

Fig. 4 shows the effect of anode catalyst loading on the fuel cell performance. The catalyst loadings of anode were varied as 2, 3 and 4 mg/cm² for the same cathode catalyst loading of 7 mg/cm². The fuel cell performance increased with increase of anode catalyst loading. The difference in maximum power density between anode catalyst loadings of 3 and 4 mg/cm² was not significant. The fuel cell with anode catalyst loading of 2 mg/cm² showed very low performance compared with the other catalyst loadings. This result is indicative of the existence and significance of optimum anode catalyst loading, which might be explained in terms of a trade-off between kinetic and mass transfer limitations [3,16]. The thick catalyst layer inhibits the transfer of protons, causing poor performance of the fuel cell.

Fig. 5 shows the effect of cathode catalyst loading on the fuel cell performance. The cathode catalyst loadings were varied as 3, 5 and 7 mg/cm² with the fixed anode catalyst loading of 4 mg/cm². The fuel cell with cathode catalyst loading of 5 mg/cm² showed the maximum power density of 64.7 mW/cm² at the current density of 200 mA/cm². It is very interesting to note that this value is much higher than 26.8 mW/cm² obtained in similar DFAFC experiment with Pt-Ru catalyst [17]. The fuel cell with cathode catalyst loading of 3 mg/cm² showed the lowest performance among the three catalyst loadings. These results showed a similar tendency as those of DMFC [18]. Like the catalyst loading of anode, that of cathode had a significant effect on MFAFC performance. Especially, the fuel cell performance with cathode catalyst loading of 5 mg/cm² was better than that of 7 mg/cm². It is obvious from our results that the selection of optimum catalyst loading will be very important in DFAFC.

CONCLUSION

Calcination conditions and catalyst loadings of anode and cathode had significant effects on the DFAFC performance. The fuel cell with catalyst calcined under air atmosphere showed a higher OCP of 0.812 V compared with that with catalyst calcined under nitrogen atmosphere. The fuel cell with calcined catalyst at 400 °C under nitrogen atmosphere showed the best performance of 58.8 mW/cm² when Pt-Pd of 4 mg/cm² was used as anode catalyst and Pt black of 7 mg/cm² as cathode catalyst.

The fuel cell with anode catalyst loading of 4 mg/cm² and cathode catalyst loading of 5 mg/cm² showed the highest power density of 64.7 mW/cm² at room temperature. This value is much higher than 26.8 mW/cm² reported in DFAFC using Pt-Ru catalyst at similar condition. It is concluded that Pt-Pd catalyst is an excellent material for formic acid oxidation and for determining optimum catalyst calcination condition and catalyst loading is significant in designing the DFAFC system.

REFERENCES

1. S. Ha, C. A. Rice, R. I. Masel and A. Wieckowski, *J. Power Sources*, **112**, 655 (2002).
2. C. Rice, R. I. Masel, P. Waszczuk, A. Wieckowski and T. Barnard, *J. Power Sources*, **111**, 83 (2002).
3. J. S. Kim, J. K. Yu, H. S. Lee, J. Y. Kim, Y. C. Kim, J. H. Han, I. H. Oh and Y. W. Rhee, *Korean J. Chem. Eng.*, **22**, 661 (2005).
4. J. H. Sauk, J. Y. Byun, Y. C. Kang and H. Y. Kim, *Korean J. Chem. Eng.*, **22**, 605 (2005).
5. Y. W. Rhee, S. Y. Ha and R. I. Masel, *J. Power Sources*, **117**, 35 (2003).
6. S. K. Lee, D. J. Kim, J. Y. Lee, S. T. Chung and H. Y. Ha, *Korean J. Chem. Eng.*, **22**, 406 (2005).
7. J. H. Choi, K. J. Jeong, Y. J. Dong, J. H. Han, T. H. Lim, J. S. Lee and Y. E. Sung, *J. Power Sources*, in press (2006).
8. T. H. Yang, G. G. Park, P. Pugazhendhi, W. Y. Lee and C. S. Kim, *Korean J. Chem. Eng.*, **19**, 417 (2002).
9. X. Cheng, C. Peng, M. You, L. Liu, Y. Zhang and Q. Fan, *Electrochimica Acta*, **51**, 4620 (2006).
10. C. Rice, R. I. Masel and A. Wieckowski, *J. Power Sources*, **115**, 229 (2003).
11. P. Waszczuk, T. M. Barnard, C. Rice, R. I. Masel and A. Wieckowski, *Electrochemistry Communications*, **4**, 599 (2002).
12. M. J. Llorca, E. Herrero, J. M. Feliu and A. Aldaz, *J. Electroanal. Chem.*, **373**, 217 (1994).
13. G. A. Attard and A. Bannister, *J. Electroanal. Chem.*, **300**, 467 (1991).
14. A. Morlang, U. Neuhausen, K. V. Klementiev, F. W. Schutze, G. Miehe, H. Fuess and E. S. Lox, *Applied Catalysis B: Environmental*, **60**, 191 (2005).
15. T. Y. Kim, M. Takahashi, M. Nagai and K. Kobayashi, *Electrochimica Acta*, **50**, 817 (2004).
16. N. Nakagawa and Y. K. Xiu, *J. Power Sources*, **118**, 248 (2003).
17. J. S. Kim, J. K. Yu, E. M. Jung, H. S. Lee, J. Y. Kim, Y. C. Kim, J. H. Han, I. H. Oh and Y. W. Rhee, *Korean Chem. Eng. Res.*, **42**, 630 (2004).
18. B. C. Bae, B. K. Kho, T. H. Lim, I. H. Oh, S. A. Hong and H. Y. Ha, *J. Power Sources*, **158**, 1256 (2006).