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Formic acid oxidation by carbon-supported palladium catalysts in direct formic acid fuel cell

Jae Ho Choi*, Soon Young Noh*, Sam Duck Han*, Soo Kyung Yoon, Chang-Soo Lee*, Taek-Sung Hwang*, and Young Woo Rhee*,†**

*Department of Chemical Engineering, Chungnam National University, Daejeon 305-764, Korea
**Ajou University, Suwon 443-749, Korea

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Abstract−The oxidation of formic acid by the palladium catalysts supported on carbon with high surface area was investigated. Pd/C catalysts were prepared by using the impregnation method. 30 wt% and 50 wt% Pd/C catalysts had a high BET surface area of 123.7 m^2/g and 89.9 m^2/g, respectively. The fuel cell performance was investigated by changing various parameters such as anode catalyst types, oxidation gases and operating temperature. Pd/C anode catalysts had a significant effect on the direct formic acid fuel cell (DFAFC) performance. DFAFC with Pd/C anode catalyst showed high open circuit potential (OCP) of about 0.84 V and high power density at room temperature. The fuel cell with 50 wt% Pd/C anode catalyst using air as an oxidant showed the maximum power density of 99 mW/cm^2. On the other hand, a fuel cell with 50 wt% Pd/C anode catalyst using oxygen as an oxidant showed a maximum power density of 163 mW/cm^2 and the maximum current density of 590 mA/cm^2 at 60 °C.

Key words: Pd/C, Formic Acid, DFAFC, Anode Catalyst

INTRODUCTION

Direct methanol fuel cells (DMFCs), which have been widely studied during the past 20 years, are considered as possible power sources for portable electronic devices and electric vehicles. These fuel cells offer a variety of benefits such as high specific energy and the ready availability and portability of methanol. On the other hand, the problem of methanol crossover from the anode to the cathode through the membrane leads to low system efficiency. Methanol crossover prevents utilization of high concentration of methanol; the limit is generally less than 2 M.

Recently, the advantages of a direct formic acid fuel cell (DFAFC) have been progressively recognized compared with DMFC [1]. 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 [2]. In addition to these advantages, formic acid partially dissociates in solution, forming a formate anion. The formate anion diffuses very slowly through a Nafion® membrane. However, methanol dissociates cation diffusing rapidly through a Nafion® membrane. Slow diffusion of formic acid is expected to result in a low fuel crossover that enables it to be used at a high concentration as a fuel [3,4]. Rhee et al. [5] reported that the permeation of formic acid through a Nafion® membrane is much slower than that of methanol. It has two orders of magnitude smaller crossover flux through a Nafion® membrane than methanol, and then as high as 20 M concentrated formic acid can be used in the operation of DFAFC. Thus, the power density of DFAFC can be higher than that of DMFC, although the energy density of methanol is higher than that of formic acid.

Carbon-supported platinum catalysts for the electro-oxidation of formic acid are poisoned severely by the adsorbed CO intermediate of the reaction [6-8]. It has been demonstrated that Pt-Ru and Pt-Pd alloys can diminish this CO poisoning effect to some extent, but still it is significantly limited by the catalytic activity for formic acid oxidation [9,10]. It is desirable to develop more active catalysts to improve cell efficiency and power density by reducing overall precious metal loadings. Recently, it has been widely studied on the catalyst with a new metal for improvement of cell performance. Marsel et al. [11] and Liu et al. [12] have disclosed that unsupported palladium catalysts can overcome CO poisoning effect and thereby yield high performances in the DFAFC.

It is well known that catalytic activity is strongly dependent on the shape, size and distribution of the metal particles. Conventional preparation techniques are based on wet impregnation and chemical reduction of the metal precursors which often do not provide an adequate control of the particle shape and size [13]. Accordingly, there are continuing efforts to develop alternative synthesis methods based on microemulsion [14], nanochemistry [15,16], or microwave irradiation [17-20]. In principle, all of these methods are more conductive to generating colloids and clusters of particles at the nanoscale, and with greater uniformity.

This study attempts to investigate the characteristics of carbon-supported palladium catalysts in DFAFC. The effects of anode catalyst types, different oxidation gases and system operating temperatures on the DFAFC performance were investigated in terms of cell power density.

EXPERIMENTAL

1. Preparation of Pd/C Catalysts

The 30 wt% and 50 wt% carbon-supported palladium catalysts were prepared by the applied impregnation method. The preparation procedure consisted of the following steps: (1) Carbon-black (Vul-

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

can XC-72) was preconditioned to remove the impurities at 5 M HCl for 12 hours; (2) the appropriate amount of dried carbon black and $PdCl_2$ (Aldrich, A.C.S. Reagent) was dispersed into an appropriate amount of Millipore water; (3) carbon black solution and $PdCl_2$ solution were mixed and stirred for 24 hours; (4) this mixed solution was impregnated by using 0.5 M $NaBH_4$; (5) finally, this solution was filtered, rinsed in Millipore water and dried at 80 °C for 24 hours. The prepared catalysts were characterized by using low temperature (77 K) nitrogen adsorption isotherms. Adsorption measurements were performed on a Micromeritics ASAP2010 volumetric adsorption apparatus; high purity nitrogen (99.9999%) was used. Prior to measurement, the catalysts were degassed at 432 K for 3 hours in the degas pot of the adsorption analyzer. The BET equation was used to obtain the specific surface areas.

2. Single Cell Test

The catalyst inks of anode and cathode were prepared by dispersing the catalyst nanoparticles into an appropriate amount of Millipore water and 5 wt% Nafion® solution. To disperse particles, the solution was treated by ultrasonic waves. Then, catalyst ink of anode was dispersed by dispersing agent (isopropyl alcohol, 1-propanol). Membrane electrolyte assembly (MEA) was made by using the 'direct painting' method. Both anode and cathode catalyst inks were directly painted onto either side of Nafion® 117 membrane. The active cell area was 2.25 cm^2 (1.5 cm×1.5 cm).

In this study, all of cathode catalysts were Pt black (HISPEC™ 1000, Johnson-Matthey). Pd black, 30 wt% Pd/C and 50 wt% Pd/C prepared in house were used as an anode catalyst at each experiment. At all experiments, the Pd/C anode catalyst loading was 4 mg/cm^2 and the cathode catalyst loading was 5 mg/cm^2. A carbon cloth was used as an oxidation gas and fuel diffusion layer and it was placed on top of the each side of catalyst layers. In order to manage water produced during the cell operation, carbon cloth coated with teflon was used for the cathode side.

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

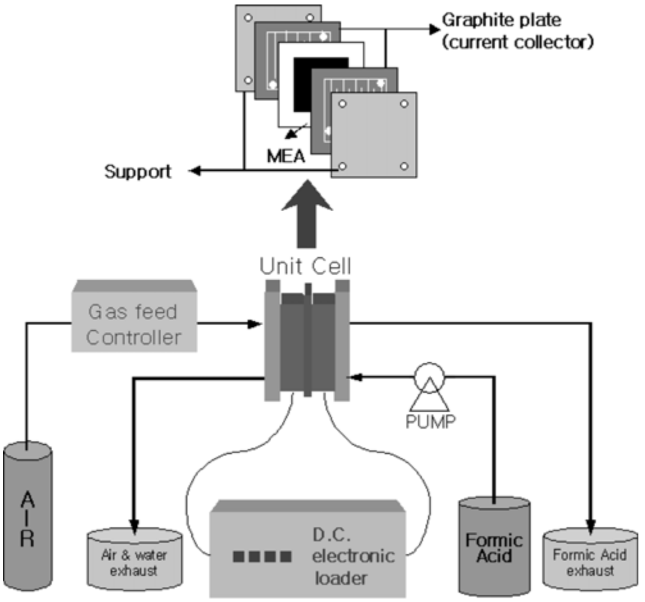

Fig. 1. Schematic diagram of DFAFC unit cell testing system.

Table 1. BET surface area of palladium catalysts supported on carbon

Catalyst	BET surface area (m^2/g)
30 wt% Pd/C	123.7
50 wt% Pd/C	89.9

Initially, the MEA was conditioned within the test fixture at 70 °C with humidified 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. All of experiments were repeated over 3 times to demonstrate the reproducibility.

RESULTS & DISCUSSION

Table 1 shows the active surface area of the catalysts using BET analysis. As expected, 30 wt% Pd/C catalyst has a high surface area of 123.7 m^2/g and 50 wt% Pd/C catalyst has a surface area of 89.9 m^2/g. The prepared Pd/C catalysts have higher surface areas than commercial Pd black of which surface area is 20-50 m^2/g. In general, the carbon-supported Pd catalysts perform quite well. Their performance tends to be lower than the high surface area Pd black on a total catalyst weight basis. However, the carbon-supported catalysts tend to do as well or better than the unsupported Pd black when compared on a per Pd weight basis or active surface area basis. The more efficient use of Pd in the carbon-supported catalysts means that Pd loadings, and thus, overall catalyst expense, can be reduced. However, there is a limited amount of total catalyst (Pd+carbon) that can be loaded onto a fuel cell membrane, typically 6-8 mg/cm^2 of membrane surface area for these carbon-supported catalysts. Therefore, the total amount of Pd on the membrane can often be much less than that of an unsupported catalyst, offsetting the improved efficiency of use of Pd. In addition, for a given amount of Pd, the catalyst layer will be thicker for a carbon-supported catalyst, potentially causing mass transfer problems at higher current

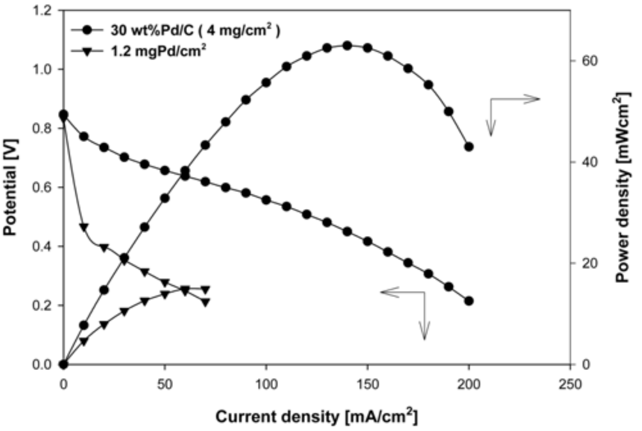

Fig. 2. The performance of carbon supported Pd and unsupported Pd black catalyst with 1.2 mg Pd/cm^2 (3 M HCOOH, air, 25 °C).

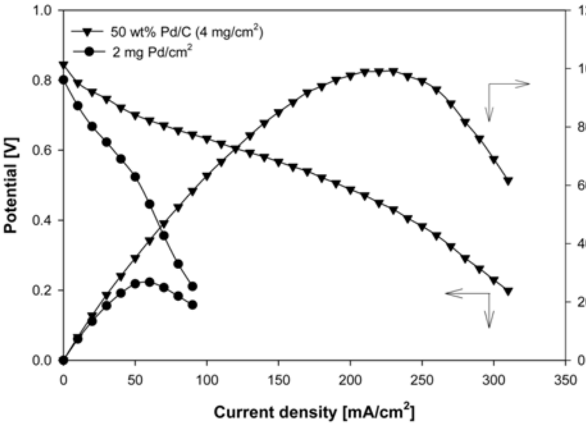

Fig. 3. The performance of carbon supported Pd and unsupported Pd black catalyst with 2 mg Pd/cm^2 (3 M HCOOH, air, 25 °C).

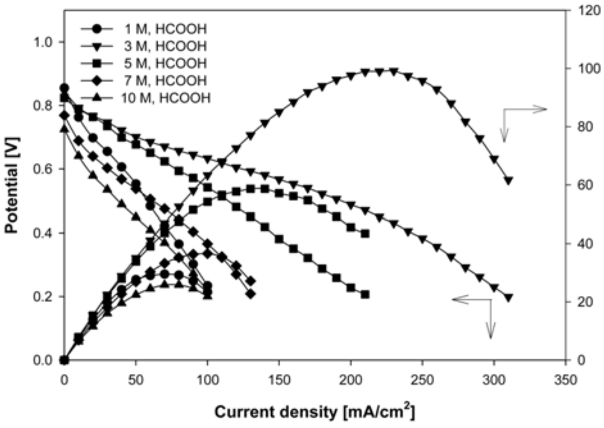

Fig. 4. Effect of the different formic acid concentration on the performance.

densities [21].

Figs. 2 and 3 illustrate a performance comparison of carbon-supported palladium based on the same amount of palladium loading with 1.2 or 2 mgPd/cm^2. By both measures, carbon-supported palladium catalysts show higher performance than unsupported palladium catalysts. The maximum power densities of 30 and 50 wt% Pd/C were 63, 99 mW/cm^2, respectively. On the other hand, 1.2 and 2 mgPd/cm^2 catalysts show the maximum power densities of 15 and 27 mW/cm^2. We can know that the cell performance is significantly increased due to added carbon black. Especially, 50 wt% Pd/C catalyst shows higher performance than other catalysts such as Pt-Ru and Pt-Pd with anode catalyst loading of 4 mg/cm^2 in DFAFC [3,22]. It is considered that, as shown in Table 1, carbon-supported palladium catalysts have higher surface area than commercial palladium catalysts. So, it will provide a sufficient reaction site for formic acid oxidation.

In Table 2, the maximum power densities and maximum current densities of a fuel cell are summarized for the DFAFC with palladium loading of 1.2 and 2 mgPd/cm^2 at room temperature. The maximum current density means current measured at the point that electric circuit stops working.

The OCP has no difference between unsupported palladium catalysts and carbon-supported catalysts. However, we can see that the performance of carbon-supported catalysts was quite different from unsupported palladium catalysts. Even though 30 wt% Pd/C catalyst shows higher surface area than 50 wt% Pd/C catalyst, as shown in Table 1, 50 wt% Pd/C catalyst shows the highest maximum power density of 99 mW/cm^2 and maximum current density of 310 mA/cm^2. As shown in Table 2, the maximum power densities were normalized by the geometrical surface area of MEA. However, when the cell performance on a per weight basis of palladium was compared, 30 wt% Pd/C catalyst generated a maximum power density of 52.5 mW/mg. This value is higher than 50 wt% Pd/C catalyst, which provides the maximum power density of 49.5 mW/mg. Even if carbon black provides high surface area to catalyst layer, it indicates that the cell performance is mainly affected by content of palladium. Consequently, 30 wt% Pd/C with low Pd content of 1.2 mgPd/cm^2 might not provide a sufficient reaction site for formic acid oxidation.

Table 2. Comparison of maximum power density and maximum current density with different anode catalysts

Cathode catalyst: 5 mgPt/cm^2			
Anode catalyst	O.C.P. (V)	Maximum power density (mW/cm^2)	Maximum current density (mA/cm^2)
1.2 mgPd/cm^2	0.834	15	70
2 mgPd/cm^2	0.838	27	100
30 wt% Pd/C (4 mg/cm^2)	0.847	63	200
50 wt% Pd/C (4 mg/cm^2)	0.845	99	310

Fig. 4 shows the effect of formic acid feed concentration in DFAFC. The cell performance curves were acquired over a broad range of formic acid feed concentrations of 1-10 M. Five different formic acid concentrations of 1, 3, 5, 7 and 10 M were examined. At 25 °C, the OCPs of the cell were 0.855, 0.845, 0.824, 0.769 and 0.725 V, respectively. 3 M formic acid generated the largest maximum power density of 99 mW/cm^2. However, 1 M formic acid cannot sustain cell operation at high current densities due to appearances of mass transport limitation. Also, the maximum power densities were significantly decreased when the formic acid concentration was increased from 3 M to 10 M. Zhu et al. [23] reported that as the concentration of formic acid increased, the crossover through a Nafion® membrane and cell resistance increased. Moreover, this phenomenon occurs at lower temperature, rather than at higher temperature. Raising temperature will reduce the hydroscopic ability of formic acid because the interaction between molecules decreases. When over 3 M formic acid is fed, there is a significant performance loss due to the reasons mentioned above.

Fig. 5 shows the performance of Pd/C catalyst in DFAFC by using air as an oxidant at 60 °C. The cell performance increased as the content of palladium increased. Also, higher temperature results in higher performance, which is mainly due to the increase of reaction rate constant. 50 wt% Pd/C shows the maximum power density of 130 mW/cm^2. This value is much higher than that of Pt-Pd

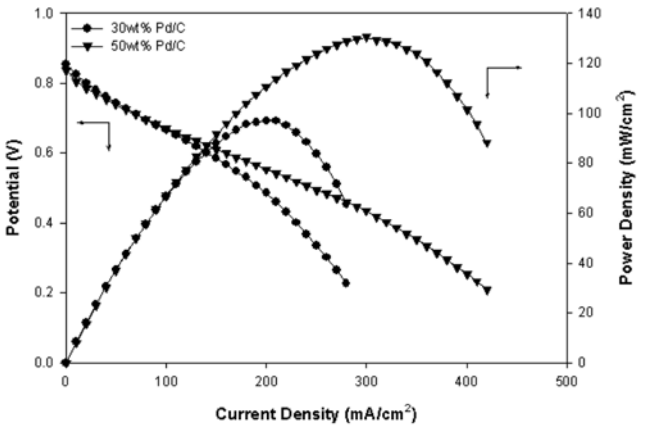

Fig. 5. Effect of Pd/C anode catalysts on the performance of DFAFC at 60 °C.

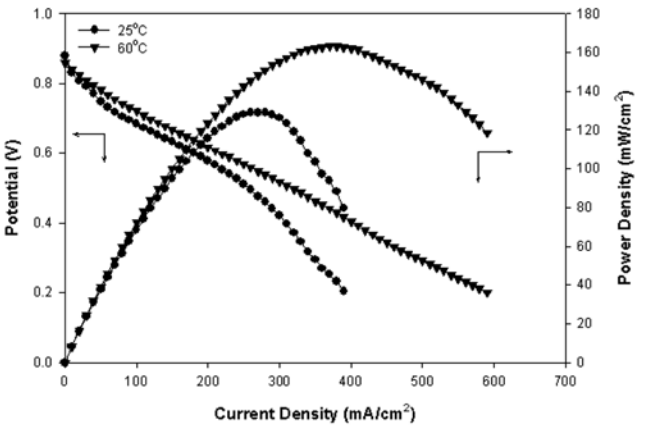

Fig. 6. Effect of operating temperature on the performance of DFAFC with 50 wt% Pd/C anode catalyst and oxygen as an oxidant.

catalyst (with maximum power density of 73 mW/cm^2) performed at the same experimental conditions [22]. It is believed that Pt-Pd still limits significantly the catalytic activity for formic acid oxidation by CO poisoning effect.

Fig. 6 shows the effect of 50 wt% Pd/C on the performance in DFAFC with oxygen as an oxidant. The maximum power density is 129 mW/cm^2 and the maximum current density is 390 mA/cm^2 at 25 °C. On the other hand, the maximum power density is 163 mW/cm^2 and the maximum current density is 590 mA/cm^2 at 60 °C. Liu et al. [12] reported an excellent performance of Pd nanoparticles supported on activated carbon prepared by a simple microwave-assisted polyol procedure. According to Liu et al. [12], the cell using 30 wt% Pd/C showed a maximum power density of 120 mW/cm^2 at 25 °C. On the other hand, at 50 °C, the maximum power density was 166 mW/cm^2. At a low temperature, our result shows higher performance than theirs. However, the cell performance is lower at a high temperature. This value may result from the difference of the metal content between the two researches. Catalytic activity is strongly dependent on the shape, size and distribution of the metal particles. Namely, the different tendencies of these results are demonstrated by the preparation techniques [24]. In order to use higher loadings of Pd dispersed on carbon, promoters or different preparation methods may be beneficial to reduce Pd nanoparticle size and agglomeration. The increasing temperature enhances the performance of the DFAFC system about 26%. This increasing gap is lower than that of Pt-Ru with 72% and Pt-Pd with 44% in DFAFC [22]. It is speculated that operating temperature has less effect on the performance due to the high activity of carbon supported palladium catalyst.

CONCLUSION

The impregnation method was used to prepare carbon-supported Pd catalysts for formic acid oxidation in DFAFC. Pd/C catalysts had a high BET surface area. Especially, 30 wt% Pd/C catalyst showed a surface area of 123.7 m^2/g. At the single cell test, as the content of palladium was increased, the cell performance was increased. Also, Pd/C catalyst had high power density at room temperature. The fuel cell with 50 wt% Pd/C using air as an oxidant showed the maximum power density of 99 mW/cm^2 at the room temperature, when 3 M formic acid was supplied. This value is much higher than 63 mW/cm^2 tested in DFAFC by using 30 wt% Pd/C catalyst at the same condition.

The cell operating temperature had little effect on the performance due to the high activity of carbon supported Pd catalyst. The increase of the temperature from 25 °C to 60 °C enhanced the performance of the DFAFC system about 26%. The fuel cell with 50 wt% Pd/C catalyst using oxygen as an oxidant at 60 °C showed the highest maximum power density of 163 mW/cm^2 at current density of 380 mA/cm^2. It is concluded that palladium is an excellent candidate for dehydrogenation reaction of formic acid oxidation and Pd/C is a promising anode catalyst for the DFAFC system.

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