Performance characterization of Pd/C nanocatalyst for direct formic acid fuel cells

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Abstract

Previous work has demonstrated that unsupported Pd (Pd black) based direct formic acid fuel cells (DFAFCs) show unusually high power density at the ambient temperature. In this paper finely dispersed Pd particles have been deposited on carbon supports (Vulcan XC-72®). In particular, both 20 and 40 wt.% Pd on carbon supports (Pd/C) nanocatalysts have been synthesized and their performances, as an anode catalyst for DFAFC, with different formic acid feed concentrations at a moderate temperature have been evaluated. The 20 and 40 wt.% Pd/C based DFAFCs, with dry air and zero backpressure, can generate a maximum power density of 145 and 172 mW cm^{-2} at 30 °C, respectively. Their open cell potentials are 0.90 V. In comparison to the unsupported Pd, we found that the 20 wt.% Pd/C in the DFAFC shows a lower total current, but a higher current per gram of precious metal than the Pd black catalyst. The supported catalysts also show less deactivation at the high formic acid concentrations.
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1. Introduction

Direct formic acid fuel cells (DFAFCs) have been demonstrated to have great potential for micro-power generations. Formic acid is a liquid at room temperature, which makes it to be more convenient and less dangerous when handled, stored, and transported than gaseous hydrogen [1–4]. It has two orders of magnitude smaller crossover flux through a Nafion® membrane than methanol, which allows to use its highly concentrated fuel solutions in the DFAFCs [1,2,4]. The formic acid also has a higher theoretical electro-motive force (EMF) in a fuel cell, as calculated from the Gibbs free energy, than either hydrogen or direct methanol fuel cells (DMFCs) [1].

Although DFAFCs offer an exciting potential for use in future micro-electronic devices, more research is needed in developing a better formic acid electrooxidation catalysts. In previous work, it was demonstrated that Pt based catalysts for electrooxidation of formic acid were poisoned severely by an adsorbed CO intermediate [5,6]. Pt/Ru and Pt/Pd alloys were able to diminish this CO poisoning effect to some extent, but CO poisoning still significantly limited their catalytic activities for formic acid oxidation [5,7,8]. Recently, noble Pd catalysts were found which produced the unusually high performances in the DFAFCs by overcoming this CO poisoning effect [5,9]. In one of these recent works, unsupported Pd (Pd black) based DFAFCs produced a maximum power density of 271 mW cm^{-2} at 30 °C. In that work, however, the Pd loading was very high (8 mg Pd cm^{-2}) [9].

In polymer electrolyte membrane (PEM) fuel cells, Pt efficiency was enhanced and its loading was reduced when Pt was deposited onto a finely divided carbon support [10]. The surface of the carbon can be coated with highly disperse noble metal particles like Pt, Pd, and Ru. This allows for much lower noble metal loadings in the catalyst layer while gaining the benefit of the high surface area of the carbon support. Additionally, carbon supported catalysts are nice to use because carbon is a cheap, conductive support allowing for efficient current collection from the catalyst layer, yet carbon is also quite inert, remaining resistant to the most chemicals includ-

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ing formic acid. The standard carbon catalyst support used in the literature as well in commercial applications is Vulcan XC-72® [5].

The carbon supported Pd catalyst has never been tested for the DFAFC. The carbon supported Pd catalyst in the DFAFC would reduce Pd loading by increasing Pd efficiency. Furthermore, it was found that the catalytic activity of the Pd for oxidizing formic acid increases as its particle size decreases [5]. Hence, the decorating the Pd nanoparticles on the carbon supports would increase the catalytic activity of the Pd and its overall performances in the DFAFCs. In this paper, both 20 and 40 wt.% of the Pd on Vulcan XC-72® are synthesized and their performances are characterized in the DFAFCs at a near room temperature.

2. Experimental

Membrane electrode assemblies (MEAs) with a 5 cm^2 active cell area were fabricated using a 'direct paint' technique to apply the catalyst layer. The 'catalyst inks' were prepared by dispersing the catalyst nanoparticles into appropriate amounts of Millipore® water and a 5% recast Nafion® solution (1100 EW, from Solution Technology Inc.). Anode and cathode 'catalyst inks' were directly painted onto either side of a Nafion® 112 membrane. For all MEAs in this study, the cathode consisted of unsupported platinum black nanoparticles (27 m^2 g^{-1}, Johnson Matthey) at a standard loading of 8 mg cm^{-2}. The anode consisted of either carbon supported or unsupported Pd catalysts. A carbon cloth diffusion layer (E-TeK) was placed on top of both the cathode and anode catalyst layers. Both sides of the cathode carbon cloth were Teflon® coated for water management. A single cell test fixture consisted of machined graphite flow fields with direct liquid feeds and gold plated copper plates to avoid corrosion (Fuel Cell Technologies Inc.).

Three different anode catalysts were investigated in this study: (i) 20 wt.% Pd on Vulcan XC-72® (20 wt.% Pd/C), (ii) 40 wt.% Pd on Vulcan XC-72® (40 wt.% Pd/C), and (iii) high surface area Pd black from Sigma–Aldrich (Pd black). The anode catalyst loading of the Pd/C catalysts were 6 mg cm^{-2} including the mass of the carbon supports. The loading of the Pd black catalyst was 2.4 mg cm^{-2}. The carbon supported catalysts were prepared by a metal chloride reduction process. First, the Vulcan XC-72 carbon was conditioned according to Biella et al. [11], by stirring in 10 M HCl in Millipore water for 12 h and then rinsing with Millipore water until the pH reached 7. Next, a certain volume of a 8 g l^{-1} PdCl$_2$ solution in 5 M HCl and Millipore water was added to a beaker depending on the desired wt.% of Pd:

(1) for the 20 wt.% Pd and Pd Au on carbon, 5 ml of solution was added;
(2) for the 40 wt.% Pd on carbon, 14 ml of solution was added.

One milliliter of a 5 g l^{-1} polyvinyl alcohol (PVA) in Millipore water solution was also added to the beaker. One Hundred milligrams of carbon was then added along with enough water to make 1 l total. The solution was then stirred vigorously while 50 ml of freshly prepared 0.05 M NaBH$_4$ in Millipore water was added drop-wise. When this was done, the pH of the solution was raised to ~11 by addition of 5 M NaOH. The solution was then stirred vigorously for 1 h, after which the catalyst was allowed to settle for an additional 30 min. The carbon supported catalyst was then filtered, rinsed in Millipore water and dried at 80 °C for 8 h.

The MEAs were initially conditioned within the test fixture at 60 °C under H$_2$/air fuel cell operating mode for 2 h, while holding the cell potential at 0.6 V. Cell potential was controlled by a fuel cell testing station (Fuel Cell Technologies Inc.). H$_2$ flow rate was set to 200 sccm; the gas stream was humidified at 70 °C prior to entering the cell, and a backpressure of 20 psi was applied. Air flow rate to the cathode was 390 sccm; the gas stream was humidified to 70 °C, and a backpressure of 20 psi was applied.

Both upward and downward voltage scans were applied for each cell polarization measurement. The plots in the two scan directions were averaged and presented in this paper as a single curve. For the cell polarization measurements, the different formic acid concentrations (GFS Chemicals, from 88% ACS grade) were fed to the anode at a flow rate of 1 ml min^{-1}. On the cathode, dry air was supplied at a flow rate of 390 sccm without any backpressure. Constant voltage tests were performed at 0.39 V for the DFAFCs with 3 M formic acid at a flow rate of 1 ml min^{-1}. The dry air was supplied to the cathode at a flow rate of 390 sccm without any backpressure.

The anode polarization curves were acquired by replacing the cathode dry air gas stream with H$_2$. The anode potential was stepped from 100 to 800 mV in 50 mV increments at 5 s intervals using a Hewlett-Packard, model 6033 A, power box. The Pt/H$_2$ combination on the cathode side of the test fuel cell acted as a dynamic hydrogen reference electrode (DHE), as well as a high surface area counter electrode. The H$_2$ flow was maintained at a rate of 100 sccm, under a backpressure of 10 psi, and humidified at 45 °C prior to entering the cell. Different concentrations of formic acid were supplied to the anode side of the test fuel cell, at a flow rate of 1 ml min^{-1}, with the anode catalyst acting as the working electrode for the electrochemical cell.

3. Results

Fig. 1(A) illustrates the current voltage characteristics of the DFAFCs with 20 wt.% Pd/C, 40 wt.% Pd/C, and unsupported Pd black catalysts at 30 °C. Note that the currents are normalized by the geometrical surface area of the MEA (5 cm^2) in Fig. 1(A). According to Fig. 1(A), the DFAFC with the 20 wt.% Pd/C catalyst produces the current density of 55
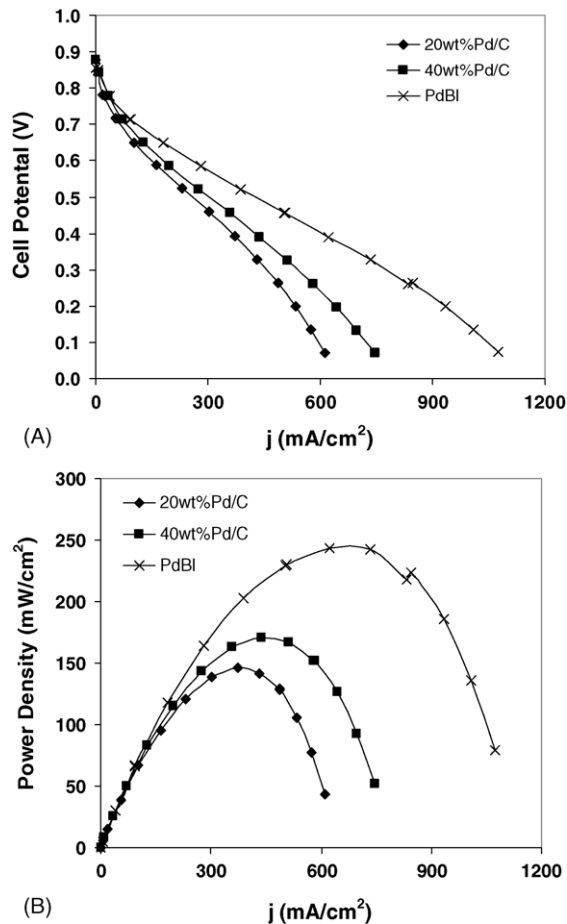
(A)

(B)

Fig. 1. (A) fuel cell polarization plots and (B) power density curves with 3 M formic acid at 30 °C. The current densities were normalized by the geometrical surface area of the MEA (5 cm²). The flow rate of formic acid was 1 ml min⁻¹. Dry air was supplied to the cathode at a flow rate of 390 sccm without backpressure. The fuel cell temperature was set at 30 °C. Both supported and unsupported Pd anode catalysts were used on each measurement as it is indicated by the captions in the figure. PtBl catalyst was used for the cathode electrode.

and 372 mA cm⁻² at 0.71 and 0.39 V, respectively. As the Pd content is increased from 20 to 40 wt.%, the current density is also increased from 55 to 70 and 372 to 438 mA cm⁻² at 0.71 and 0.39 V, respectively. In Fig. 1(A), the DFAFC with the Pd black catalyst out performs the DFAFCs with the 20 and 40 wt.% Pd/C catalysts. For example, Fig. 1(A) shows that the DFAFC with the Pd black catalyst provides 50 mV advantages over the DFAFC with the 40 wt.% Pd/C catalyst at 180 mA cm⁻².

In Fig. 1(B), the results from Fig. 1(A) are shown as power density versus current density. As in Fig. 1(A), the powers were normalized by the geometrical surface area of the MEA (5 cm²) in Fig. 1(B). The maximum power density attained on each of the three anode catalysts for the DFAFC is: 146, 171, and 243 mW cm⁻² at 0.39 V for the 20 wt.% Pd/C, 40 wt.% Pd/C, and Pd black catalysts, respectively.

Fig. 2 shows the same voltage current characteristic plots of Fig. 1(A), except the currents are now normalized by the
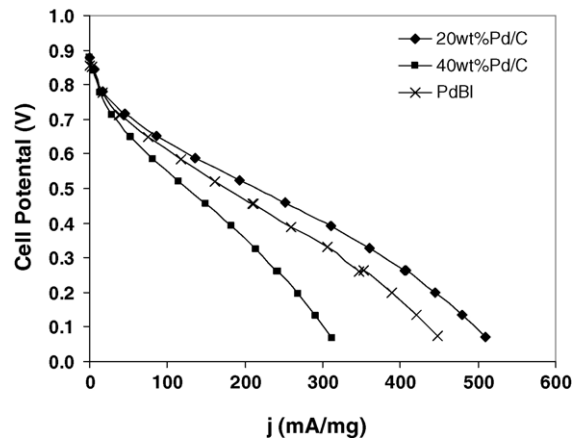

Fig. 2. Fuel cell polarization plots with 3 M formic acid at 30 °C. The currents were normalized by the total weight of the Pd metals that are presented at the anode. The flow rate of formic acid was 1 ml min⁻¹. Dry air was supplied to the cathode at a flow rate of 390 sccm without backpressure. The fuel cell temperature was set at 30 °C. Both supported and unsupported Pd anode catalysts were used on each measurement as it is indicated by the captions in the figure. PtBl catalyst was used for the cathode electrode.

total weight of the Pd. Interestingly Fig. 2 illustrates that the DFAFC with the 20 wt.% Pd/C catalyst out performs the DFAFC with the Pd black catalyst per weight base of the Pd. For example, Fig. 2 shows that the DFAFC with the 20 wt.% Pd/C catalyst provides 50 mV advantages over the DFAFC with the Pd black catalyst at 210 mA mg⁻¹. In Fig. 2, the DFAFC with the 40 wt.% Pd/C catalyst shows the lowest performance on a per weight base of the Pd.

Fig. 3 shows the effect of varying the formic acid feed concentration from 3 to 20 M on power density of the DFAFC with the three different types of the Pd catalysts at 30 °C. The power density is attained from cell polarization curves at 0.39 V and normalized by the geometrical surface area of the MEA (5 cm²). Over the entire cell potential range that we studied, the DFAFC with the Pd black catalyst shows
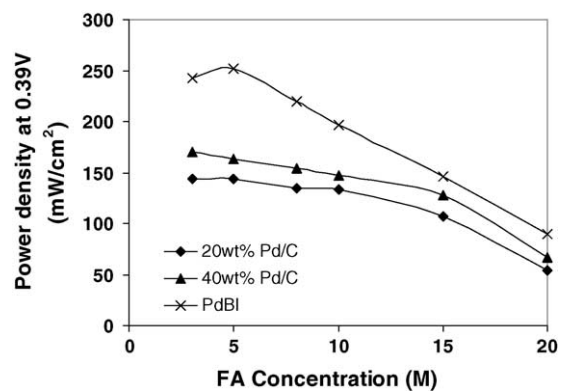

Fig. 3. Plot of power density vs. formic acid feed concentration at 0.39 V cell potential. The cell temperature was set at 30 °C. The formic acid flow rate to the anode was 1 ml min⁻¹. The dry air was supplied to the cathode at a flow rate of 390 sccm without backpressure. Both supported and unsupported Pd anode catalysts were used on each measurement as it is indicated by the captions in the figure. PtBl catalyst was used for the cathode electrode.

the largest current densities that are followed by the 40 and 20 wt.% Pd/C catalysts. According to Fig. 3, the optimum formic acid concentration is between 3 and 5 M for the all three types of the Pd catalysts. At the 5 M formic acid concentration, Fig. 3 shows that the power densities of the DFAFCs are 251, 163, and 143 mW cm^{-2} for the Pd black, 40 wt.% Pd/C, and 20 wt.% Pd/C catalysts, respectively. In Fig. 3, the power density of the DFAFC with the Pd black catalyst at 0.39 V is decreased almost linearly, as the feed concentration of formic acid is increased from 5 to 20 M. According to Fig. 3, the DFAFC with the Pd black catalyst at 15 M gives the power density of 146 mW cm^{-2}, which is about 42% performance reduction from its power density at 5 M formic acid.

In Fig. 3, the DFAFCs with the 20 and 40 wt.% Pd/C catalysts also show the performance degradation as the formic acid feed concentration is increased from 3 to 20 M. However, this formic acid concentration effect on the performances of the 20 and 40 wt.% Pd/C catalysts is much smaller than the Pd black catalyst in the DFAFCs. According to Fig. 3, the DFAFCs with the 20 and 40 wt.% Pd/C catalysts at 15 M give the power densities of 107 and 128 mW cm^{-2}, respectively, which are only 23% performance reduction from their power densities at 5 M formic acid.

Fig. 4(A) and (B) plots the anode polarization curves of the DFAFCs with the Pd black and 40 wt.% Pd/C catalysts, respectively, for different formic acid feed concentrations ranging from 3 to 20 M at 30 °C. The anode polarization plot differs from the cell polarization plot, in that the anode potential is directly reference against a DHE. This removes the effects of the cathode, thereby facilitating the quantitative analysis of the isolated anode performance. In Fig. 4(A) and (B), the current densities are attained by normalizing the total oxidation currents by the geometrical surface area of the MEA (5 cm^2). At the anode potentials higher than 0.45 V versus DHE, both DFAFCs with the Pd black and 40 wt.% Pd/C catalysts show a mass transport limitation at 3 M formic acid in the supply of formic acid to the anode. According to Fig. 4(A) and (B), the mass transport limitation of formic acid to the anode is not as evident if formic acid concentration is above 5 M. In general, Fig. 4(A) shows that the activity of the Pd black catalyst in the DFAFC is decreased severely as the feed concentration of formic acid is increased from 5 to 20 M. According to Fig. 4(A), the oxidation reaction of 15 M formic acid on the Pd black catalyst produces only 393 mA cm^{-2} at 0.4 V versus DHE, which is approximately 40% performance reduction from that of 3 M formic acid.

Unlike the Pd black catalyst, Fig. 4(B) shows that the activity of the 40 wt.% Pd/C catalyst in the DFAFC is less influenced by increased feed concentration of formic acid. According to Fig. 4(B), as the feed concentration of formic acid is increased from 5 to 10 M, the 40 wt.% Pd/C catalyst in the DFAFC at the cell potential below 0.45 V versus DHE shows no significant performance loss. As the feed concentration of formic acid is further increased from 10 to 15 M, the activity of the 40 wt.% Pd/C catalyst in the DFAFC begins to show a small decrease, but not as much as the Pd black catalyst.
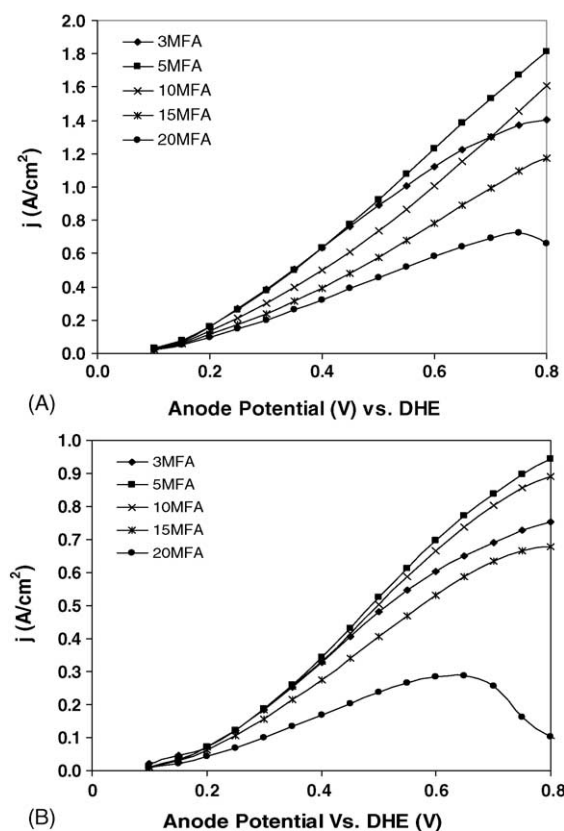

Fig. 4. Anode polarization curves of the DFAFCs with (A) the Pd black and (B) 40 wt.% Pd/C catalysts at 30 °C with different formic acid concentrations. The formic acid flow rate to the anode was 1 ml min^{-1}. The PtBl based cathode was set-up as a dynamic hydrogen reference electrode/counter electrode: humidified (45 °C) H$_2$ was supplied at a flow rate of 100 sccm.
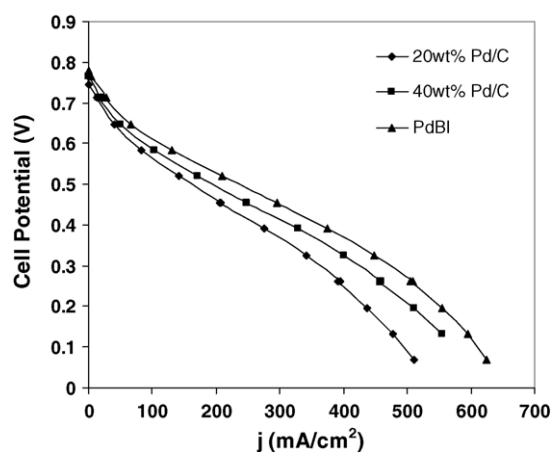

Fig. 5. Fuel cell polarization plots with 15 M formic acid at 30 °C. The current densities were normalized by the geometrical surface area of the MEA (5 cm^2). The flow rate of formic acid was 1 ml min^{-1}. Dry air was supplied to the cathode at a flow rate of 390 sccm without backpressure. The fuel cell temperature was set at 30 °C. Both supported and unsupported Pd anode catalysts were used on each measurement as it is indicated by the captions in the figure. PtBl catalyst was used for the cathode electrode.
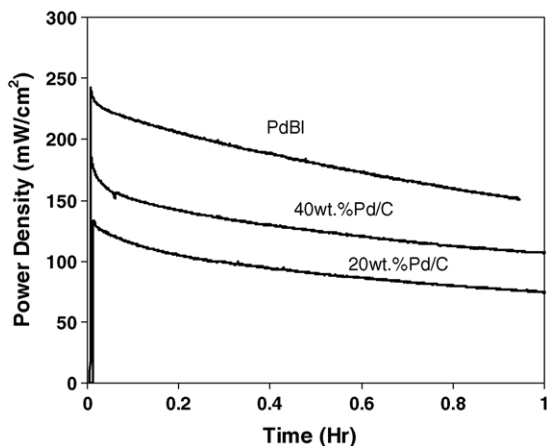
Fig. 6. Constant voltage tests at a cell potential of 0.39 V on the DFAFCs with the 20 wt.% Pd/C, 40 wt.% Pd/C, and Pd black anode catalysts. The feed concentration of formic acid was 5 M at 1 ml min^{-1}. The cell temperature was set at 30 °C.

Fig. 5 compares the current voltage characteristics of the DFAFCs with the 20 wt.% Pd/C, 40 wt.% Pd/C, and Pd black catalysts at 15 M formic acid and 30 °C. In Fig. 5, the currents are normalized by the geometrical surface area of the MEA (5 cm^2). Fig. 5 shows that the performances of the DFAFCs with the carbon supported Pd catalysts are comparable to the DFAFC with the unsupported Pd black catalyst at 15 M formic acid. For an example, in Fig. 5, the DFAFC with the 40 wt.% Pd/C catalyst and 15 M formic acid produces the current density of 330 mA cm^{-2} at 0.39 V, nearly on par with the DFAFC with the Pd black catalyst at the similar conditions.

Fig. 6 provides constant voltage tests of the DFAFCs with the 20 wt.% Pd/C, 40 wt.% Pd/C, and Pd black catalysts at 0.39 V and 30 °C. Initially the DFAFCs generate approximately 243, 185, and 133 mW cm^{-2} with the Pd black, 40 wt.% Pd/C, and 20 wt.% Pd/C catalysts, respectively. However, all three catalysts are deactivated with time

at about the same rate. The power densities of the DFAFCs after holding the cell potential at 0.39 V for 0.95 h are 151, 108, and 78 mW cm^{-2} for the Pd black, 40 wt.% Pd/C, and 20 wt.% Pd/C catalysts, respectively. In longer runs we found that there continues to be a slow decay in the activity of all three catalysts in the DFAFCs.

We found that, if a high anodic potential (higher than 1.0 V versus DHE) is applied to both supported and unsupported Pd catalysts in the DFAFCs, their catalytic activities can be easily and quickly reactivated. For example, Fig. 7(B) shows the regeneration plot of the DFAFC with the 20 wt.% Pd/C catalyst. Typically, we apply the anodic potential of 1.0 V versus DHE on the Pd based anode catalysts of the DFAFCs for less than 5 s. Fig. 7(A) shows that the DFAFC with the 20 wt.% Pd/C catalyst is deactivated as the cell operation time is increased. Fig. 7(B) shows the performance of the same DFAFC after the 20 wt.% Pd/C anode catalyst is reactivated. With the reactivated 20 wt.% Pd/C anode catalyst, the DFAFC initially produces the current density of 129 mW cm^{-2}, which is about 97% of its original power density before the 20 wt.% Pd/C catalyst is deactivated (133 mW cm^{-2}). In comparison between Fig. 7(A) and (B), the reactivated DFAFC with the 20 wt.% Pd/C catalyst performs just as good as the original DFAFC before its deactivation.

4. Discussion

The results in Figs. 1 and 2 show that the DFAFC with the Pd black catalyst out performs the DFAFC with the 40 wt.% Pd/C catalyst, even though both DFAFCs have the same Pd loading at 2.4 mg Pd cm^{-2}. This indicates that the Pd black is more active for oxidizing formic acid than the 40 wt.% Pd/C catalyst on a per Pd weight basis. Fig. 2 shows that the DFAFC with the 20 wt.% Pd/C catalyst out performs other two if their currents are normalized by the total weight of the Pd metal. According to Fig. 2, the 20 wt.% Pd/C catalyst shows
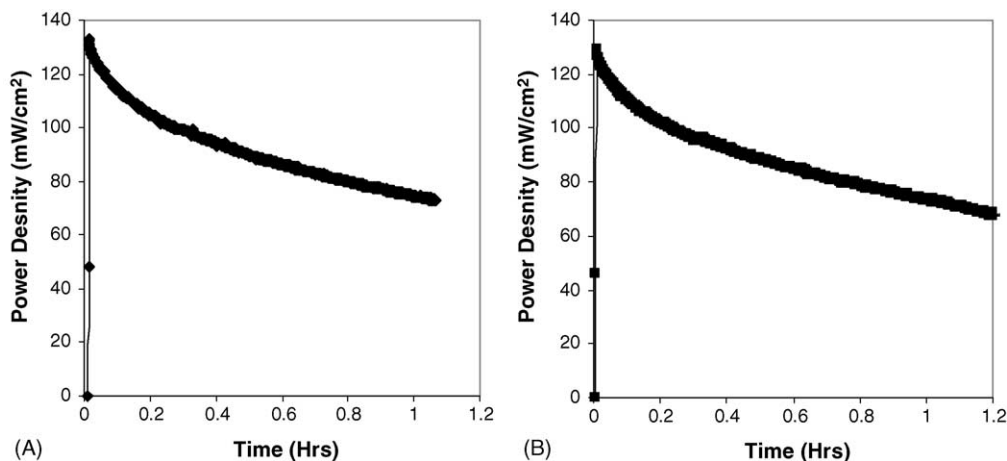

Fig. 7. Constant voltage tests at a cell potential of 0.39 V on the DFAFC with the 20 wt.% Pd/C anode catalyst in 5 M formic acid at 1ml min^{-1}. The cell temperature was set at 30 °C: (A) constant voltage test from Fig. 6 and (B) constant voltage test after reactivating the 20 wt.% Pd/C catalyst by applying 1.0 V vs. DHE anodic potential for less than 5 s.

a better Pd efficiency than the Pd black and 40 wt.% Pd/C catalysts in the DFAFCs. Despite this higher Pd efficiency of the 20 wt.% Pd/C catalyst, interestingly Fig. 1 shows that it produces the least performance in the DFAFC due to its low Pd loading. Because of the carbon presence, a maximum loading of the carbon supported catalysts (total weight of the carbon supports and Pd metals) is 6 mg cm^{-2} on the MEA. Based on this, maximum Pd loadings of the DFAFCs with the 20 and 40 wt.% Pd/C catalysts are 1.2 and 2.4 mg Pd cm^{-2}, respectively. In this paper, these maximum Pd loadings of the carbon supported catalysts are used, while the loading of the Pd black was fixed at 2.4 mg Pd cm^{-2}. In Fig. 1, the DFAFCs with the Pd black and 40 wt.% Pd/C catalysts generate the higher current densities than the DFAFC with the 20 wt.% Pd/C catalyst, simply because they have more of the Pd metal.

In Fig. 3, the power density of the DFAFC with the Pd black catalyst decreases rapidly as the feed concentration of formic acid is increased from 5 to 20 M. In previous work, it was believed that the concentration of formic acid dimmers in the fuel solution would be increased as formic acid concentration is increased. Since the dimmers are kinetically less active than the monomers, it suggested that the activity of the Pd black for oxidizing formic acid would be decreased as formic acid concentration is increased [9]. This view is consistent with Fig. 4(A). According to Fig. 4(A), at potential of less than 0.45 V versus DHE, the activity of the Pd black in the DFAFC is decreased as the feed concentration of formic acid is increased from 5 to 20 M. Unlike the Pd black catalyst in Fig. 4(A), Fig. 4(B) shows that the increased formic acid concentration has less influence on the activities of the carbon supported Pd catalysts in oxidizing formic acid (only 40 wt.% Pd/C catalyst sample is shown in Fig. 4(B)). Consequently, the power densities of the DFAFCs with the 20 and 40 wt.% Pd/C catalysts do not decrease as much as that of the DFAFC with the Pd black catalyst, as the feed concentration of formic acid is increased from 3 to 15 M in Fig. 3.

It is important to use the highest possible fuel concentration for practical fuel cell applications, because the higher fuel concentration has a higher energy density. Additionally, the water management becomes much easier in fuel cells, if the highly concentrated fuel is used. Because the high formic acid concentration has a less influence on the activity of the carbon supported Pd catalyst, the supported Pd catalysts would give an advantage over the Pd black catalyst for operating the DFAFCs. Fig. 5 supports this view. Fig. 5 shows that, at 15 M formic acid, the performance of the DFAFC with the 20 wt.% Pd/C catalyst is comparable to that of the DFAFC with the Pd black catalyst, even though former has 50% less Pd metal than the latter.

Fig. 6 shows the constant voltage tests of the DFAFCs with the 20 wt.% Pd/C, 40 wt.% Pd/C, and Pd black catalysts using 5 M formic acid at 30 °C. The DFAFCs with these three types of the Pd catalysts are all deactivated continuously after running them for 1 h. Interestingly we can regenerate the most of their original performances, if we apply a high anodic potential to the anode of the DFAFCs for a short time interval. As an example, Fig. 7(B) shows the performance of the DFAFC with the 20 wt.% Pd/C catalyst, after the activity of its Pd has been regenerated. Comparing Fig. 7(A) and (B), the DFAFC with the regenerated 20 wt.% Pd/C catalyst performs as good as its original DFAFC. Practically, in order to maintain high activities of the Pd based catalysts, one can apply a short electrical pulse to the DFAFCs for every other hour using a capacitor.

5. Conclusions

The DFAFC with the 20 wt.% Pd/C catalyst shows a higher Pd efficiency than the DFAFC with the Pd black catalyst at the moderate temperature. However, the DFAFC with the 20 wt.% Pd/C catalyst produces much less total current (or current density based on the geometrical surface area of the MEA) than the DFAFC with the Pd black catalyst at 3 M formic acid, because of its low Pd loading. The DFAFCs with the 20 and 40 wt.% Pd/C catalysts are deactivated much less than the DFAFC with the Pd black catalyst as the feed concentration of formic acid is increased from 5 to 15 M. Consequently, the DFAFCs with the 20 and 40 wt.% Pd/C catalysts generate comparable total currents to the DFAFC with the Pd black catalyst at 15 M formic acid. At 1.2 mg cm^{-2} of Pd loading, 30 °C, and 15 M formic acid, the DFAFC with the 20 wt.% Pd/C catalyst produces a power density of 107 mW cm^{-2} at 0.39 V. This significant power density output of the DFAFC, with highly concentrated formic acid and very low Pd loading at the moderate temperature, makes it very attractive power source for the small portable electronic devices. The performances of the DFAFCs with both supported and unsupported Pd catalysts are deactivated with the operation time, but applying a high anodic potential to its anode can regenerate the most of their activities.

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