The behavior of palladium catalysts in direct formic acid fuel cells

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Abstract

Previous work has considered the behavior of platinum based catalysts in direct methanol and Direct Formic Acid Fuel Cells (DFAFCs). In this paper, we explore the behavior of palladium-based anode catalyst for DFAFCs. The palladium catalysts produce significant performance enhancements. DFAFCs operated with dry air and zero back-pressure can generate power densities of 255∼230 mW cm^{-2} at relatively high voltages of 0.40∼0.50 V in a concentration range of formic acid from 3.0 to 15.0 M at a room temperature of 20 °C, which are not quite different from a hydrogen–air polymer exchange membrane (PEM) fuel cell with power density of 320 mW cm^{-2} obtained under the comparable conditions, and much higher than a direct methanol fuel cell (DMFC) with power density of 50 mW cm^{-2}. The stability of the membrane electrode assembly (MEA) with palladium catalyst has also been evaluated. There is some decay in performance over several hours. However, the performance loss of DFAFCs can be fully recovered by applying a positive potential at the fuel cell anode after short-term life test. These results demonstrate that DFAFCs with palladium anode catalyst have exceptional properties for portable power applications.
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1. Introduction

Direct Formic Acid Fuel Cells (DFAFCs) are potential alternative power sources for portable devices such as cellular phones, personal digital assistants (PDAs), laptop computers, etc. because a substantial performance can be achieved at ambient temperature and a low permeation of formic acid through polymer exchange membrane (PEM), which allows utilizing relatively high concentration of formic acid [1,2]. In our most recent paper [2], the performance of DFAFCs with platinum–ruthenium black anode catalyst was reported, in which relatively high power densities of 110 and 84 mW cm^{-2} have been obtained at 30 and 18 °C, respectively, with dry air and zero back-pressure. The performance is considerably higher than direct methanol fuel cells (DMFCs) operated under the same conditions. Methanol not only has a sluggish oxidation process at most of the catalysts, in-

cluding Pt–Ru black catalyst, but also has a higher crossover [3–6] from anode through electrolyte membrane to cathode, which limits utilization of high concentration of methanol to achieve good fuel cell performance.

Platinum–ruthenium black is the best anode catalyst for methanol oxidation in DMFCs. However, it is not the state of the art anode catalyst for formic acid oxidation in DFAFCs. It is desirable to explore proprietary anode catalysts for DFAFC operation to further enhance its performance.

In this paper, we report an exceptional DFAFC performance with a proprietary palladium black anode catalyst [7].

2. Experimental

A single-cell test fixture was designed for use with formic acid (FA) and built by Fuel Cell Technologies Inc. [2]. The anode/cathode flow fields were machined into graphite blocks. The formic acid/air was fed into the cells' graphite blocks

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through Teflon swagelock fittings, directly mounted onto the anode/cathode graphite blocks respectively.

The MEAs were fabricated using a 'direct paint' technique to apply the catalyst layer, with an active area of 5 cm^2. The 'catalyst inks' were prepared by dispersing the catalyst nano-particles into appropriate amounts of deionized water and a 5% Nafion^{TM} solution (1100 EW, from Solution Technology Inc.). Then both the anode and cathode 'catalyst inks' were directly painted onto either side of a Nafion^{TM} 115 membrane. For all MEAs prepared in this study, the cathode consisted of unsupported platinum black nano-particles (Johnson Matthey, HiSpec 1000) at a high loading that is generally not less than 5 mg cm^{-2}. The anode consisted of unsupported palladium black catalyst nano-particles or unsupported platinum–ruthenium black nano-particles (Johnson Matthey, HiSpec 6000) at a loading that is generally not less than 8 mg cm^{-2}. A carbon-cloth diffusion layer (E-Tek) was placed on top of both the cathode- and anode-catalyst layers. Both sides of the cathode-side carbon-cloth were Teflon^{TM}-coated for water management.

MEAs were directly conditioned under formic acid–air operation. Once no further change in cell performance and resistance was observed with time, the conditioning was ended. In this paper, both upward- and downward- voltage scans were used for each polarization measurement. The plots in the two scan directions were averaged and presented here as a single curve. For the cell polarization measurements, the anode fuel used was different concentrations formic acid (GFS Chemicals, 88% ACS grade). For the cathode, air was supplied at a flow rate of 300 ml min^{-1} without any back-pressure and humidification. Methanol solution (Fisher Scientific, ACS grade) was fed through the anode under methanol–air operation. At a flow rate of 200 mL min^{-1}, hydrogen gas was flowed to the anode without any back-pressure for hydrogen–air operation.

The anode activity was independently evaluated by measuring anode polarization plots. In these experiments, formic acid solutions were flowed through the anode at a rate of 1.0 mL min^{-1}, with the fuel cell cathode serving as a combined reference/counter electrode (a dynamic hydrogen electrode, DHE). The rate of hydrogen gas flow through the cathode was 100 mL min^{-1}. The anode potential scan rate was 2.0 mV s^{-1}.

To evaluate intermediate species during formic acid oxidation in an electrochemical cell, the palladium black was coated on the surface of solid gold electrode as a working electrode. A cyclic voltammetric scan was applied to the working electrode. The working potential was controlled with a PARC M 263A potentiostat and the potential reported here was versus normal hydrogen electrode.

3. Results and discussion

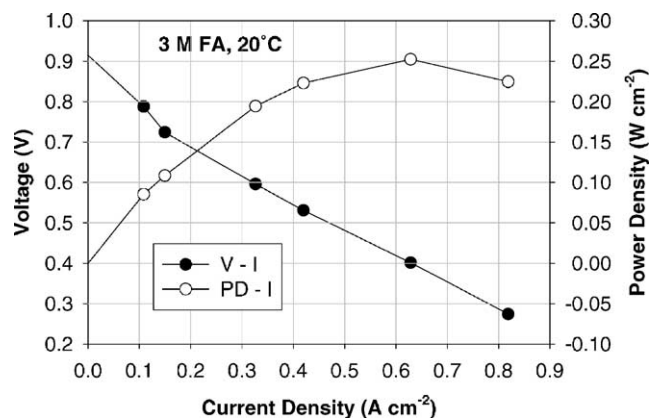According to the results in our previous publication [2], 3.0 M formic acid, may be used for the performance evalua-

Fig. 1. The polarization plot and power density plot of formic acid (FA)/air fuel cells at 20 °C. The concentration of formic acid used was 3.0 M. The flow rate of formic acid to the anode was 1 mL min^{-1}. Air was supplied to the cathode at a flow rate of 300 mL min^{-1} without any back-pressure or humidification.

tion of DFAFCs at different temperatures, since it minimizes effects of mass transport limitation and formic acid crossover. The polarization plot and power density plot of the DFAFC with 3.0 M formic acid at 20 °C are shown in Fig. 1. The DFAFC with palladium anode catalyst generates an exceptional performance using dry air at a room temperature of ca. 20 °C. The open circuit voltage observed is ca. 0.90 V. At 0.10 A cm^{-2}, the cell voltage is above 0.80 V, which indicates that the palladium anode catalyst has a high activity for formic acid oxidation at a relatively low-anode potential and hence the DFAFC can be operated at a significantly higher voltage. Furthermore, a maximum power density of ca. 253 mW cm^{-2} is observed at 0.40 V (see Fig. 1 and Table 1). It has been expected that a liquid fuel-fed fuel cell could generate a maximum power density of ca. 100 mW cm^{-2} to meet portable power needs at an ambient temperature. The liquid formic acid-fed fuel cell generates the maximum power density 2.5 times higher than 100 mW cm^{-2}.

Fig. 2 compares the performance of DFAFCs to that of a PEM fuel cell and a DMFC. The performance of the DFAFC varies strongly with the catalyst type. With a platinum–ruthenium black anode catalyst, the current density of DFAFC at 0.40 V is ca. 0.14 A cm^{-2}, which is approximately double that of DMFC. However, when a palladium black anode catalyst is used, the anode activity is substantially enhanced. A current density of ca. 0.63 A cm^{-2} is

Table 1
Comparison of maximum power densities

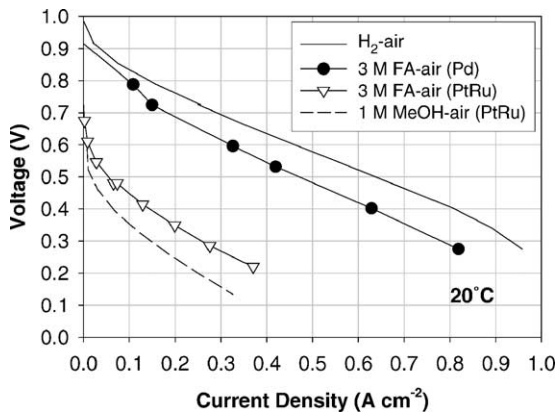| Fuel cells at 20 °C	Maximum power density (mW cm^{-2})
H$_2$–air (Pd)	320
3.0 M FA–air (Pd)	253
3.0 M FA–air (PtRu)	84
1.0 M MeOH–air (PtRu)	50

Fig. 2. The polarization plots of fuel cells under hydrogen/air operation, formic acid (3.0 M)/air (Pd or PtRu anode) and methanol (1.0 M)/air (PtRu anode), at 20 °C. The flow rate of hydrogen to the anode was 200 mL min^{-1}. The flow rate of formic acid (3.0 M) and methanol (1.0 M) to the anode were 1 mL min^{-1}. Air was supplied to the cathode at a flow rate of 300 mL min^{-1} without any back-pressure and humidification.

Table 2
Power densities of DFAFCs at different temperatures

Temperature (°C)	Power density at 0.40 V (mW cm^{-2})
20	253
30	300
40	350
50	375

observed at 0.40 V. The DFAFC with palladium black anode catalyst outperformed the DFAFC with platinum–ruthenium black anode catalyze more than 200% if the maximum power densities are considered, and outperformed the DMFC with a platinum–ruthenium black electrode more than 400%. However, palladium black is not a good anode catalyst for methanol oxidation.

It is very impressive that the DFAFC performance with a palladium anode catalyst is relatively close to that of hydrogen–air fuel cell, as shown in Fig. 2. Clearly, the exceptional power densities of the fuel cell fed by a liquid fuel should have somewhat approached to its limit since it is hard to imagine that DFAFC can outperform hydrogen–air PEM fuel cell.

Fig. 3 represents polarization plots of the DFAFCs with 3.0 M formic acid at different cell temperatures. At 50 °C,
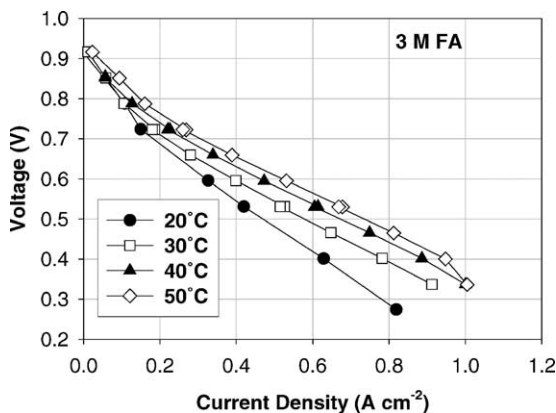
current densities of 0.10, 0.50, and 0.90 A cm^{-2} are generated at 0.84, 0.61, and 0.43 V, respectively. High current densities, up to 1.0 A cm^{-2}, may be generated at ca. 0.30∼0.40 V at the temperatures from 30 to 50 °C. On the other hand, substantial performance in kinetic region (e.g. 0.1 A cm^{-2}) can be achieved, i.e. the cell voltages are beyond 0.8 V. It is well known that the fuel crossover increases with temperature that lowers cell performance in the kinetic region [2–6]. The high voltage output at 0.1 A cm^{-2} also reflects a smaller crossover effect and the unique characteristic of low crossover of formic acid, which has been reported in our previous publication [2]. Above 50 °C, there is no further performance benefit because the performance not only depends on temperature-related kinetic of formic acid oxidation, but also on effects of partial pressure of oxygen, and formic acid crossover. The maximum power densities of 350 and 375 mW cm^{-2} are achieved at 40 and 50 °C, respectively. Even around ambient temperatures around 20 and 30 °C, the maximum power densities of 253 and 300 mW cm^{-2}, can still meet, the general power need of portable electronic devices (see Table 2).

Anode polarization plots of 3.0 M formic acid, as shown in Fig. 4, indicate that the oxidation of formic acid at palladium anode is almost independent on cell temperatures tested. At a low potential (e.g. 0.2 V), the anode polarization current density is as high as ca. 0.4 A cm^{-2}. Significant current densities around 0.1 A cm^{-2} can still be observed at 0.1 V. These results imply that the formic acid oxidation at the palladium anode may have a very low activation energy. Therefore, the rate constant for formic acid oxidation

Fig. 3. Formic acid/air fuel cell polarization plots at 20, 30, 40, and 50 °C. The flow rate of formic acid (3.0 M) to the anode was 1 mL min^{-1}. Air was supplied to the cathode at a flow rate of 300 mL min^{-1} without any back-pressure and humidification.
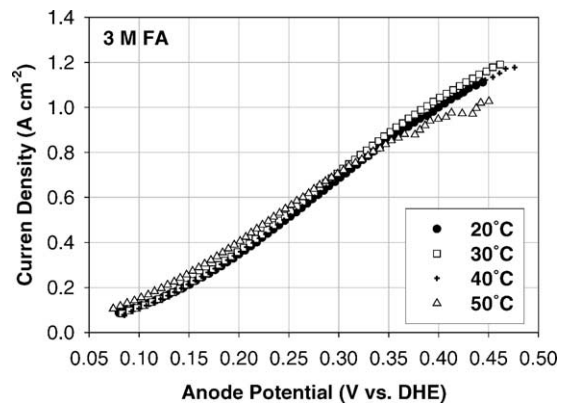

Fig. 4. Anode polarization plots of fuel cells with formic acid (3.0 M), at 20, 30, 40, and 50 °C. The flow rate of formic acid to the anode was 1 mL min^{-1}. Hydrogen was supplied to the cathode at a flow rate of 100 mL min^{-1}.

is approximately temperature independent. This is also evidence that formic acid oxidation at a palladium anode does not obey bi-functional mechanism [8]. The bi-functional mechanism refers to a sluggish oxidation of an intermediate species CO that will be facilitated by oxygen-containing species generated at the catalyst/electrode surface. This reaction rate constant would be clearly temperature is dependent. A decomposition route of formic acid, therefore, could not be related to CO intermediate. Palladium nano-particles may facilitate the decomposition of formic acid, which has a low-activation energy. Therefore, increasing the temperature does not enhance its decomposition significantly. Reasonably, the fuel cell polarization benefit (in Fig. 3) with increasing temperature may mainly come from the cathode reaction, i.e. temperature-dependent oxygen reduction.

In order to confirm that formic acid oxidation is via the direct decomposition route, rather than the CO intermediate route, a conventional three-electrode electrochemical cell was used for cyclic voltammetric measurement at a palladium black-working electrode. At first, the potential was cyclically swept from 0.6 to 0.1 V in 10.0 M formic acid solution at a low scan rate of $2\,mV\,s^{-1}$. After the potential sweep, the working electrode was rinsed with nitrogen purged Milli-Q water to remove any un-reacted formic acid. Then the removal of chemisorbed species from the catalyst surface was carried out in an electrochemical cell with $0.5\,M\,H_2SO_4$ by applying a single voltammetric scan between 0.05 and 1.2 V at $20\,mV\,s^{-1}$. As demonstrated by the plot (solid line) in Fig. 5, a very big anodic oxidation peak was observed with the peak potential at ca. 0.30 V. There is no CO oxidation peak observed at potentials around 0.60~1.0 V, in which adsorbed CO layer should be oxidized on various precious or transition metal electrodes, such as platinum and palladium [9,10]. The peak around 0.30 V definitely results from the adsorbed species on/in a palladium electrode because the pal-

ladium electrode surface is cleaned up beyond 0.40 V, which may be confirmed by comparing the cyclic voltammogram with the one of a clean palladium black electrode (dash line). Currently, there is no further evidence about what kind of species or compound(s) the adsorbed species is/are. However, formate anion may be a most likely candidate since it can be oxidized at such a low potential. At least CO intermediate may be excluded. In addition, hydrogen may also be adsorbed on the electrode surface or even penetrate in to the bulk phase of the palladium black [11]. This may be one of the reasons that result in the very big oxidation peak around 0.30 V.

For portable power applications, a highly concentrated fuel feed is desirable. In addition to 3.0 M formic acid, 10.0, 15.0, and 20.0 M formic acid were fed through the anode, respectively. There was no difference between 3.0 and 10.0 M formic acid, as shown in Fig. 6. Even though 15.0 M formic acid was fed, the polarization behavior was not quite different from that with 3.0 and 10.0 M. The maximum power densities are 253, 255, and 230 mW cm^{-2} for 3.0, 10.0, and 15.0 M formic acid, respectively (Table 3). When 20.0 M formic acid is fed, there is a significant performance loss

Fig. 6. The polarization and power density plots of fuel cells with formic acid (3.0, 10.0, 15.0, and 20.0 M) at 20 °C. The flow rates of formic acid to the anode were 1 mL min^{-1} for 3.0 M and 0.5 mL min^{-1} for 10.0, 15.0, and 20.0 M. Air was supplied to the cathode at a flow rate of 300 mL min^{-1} without any back-pressure and humidification.
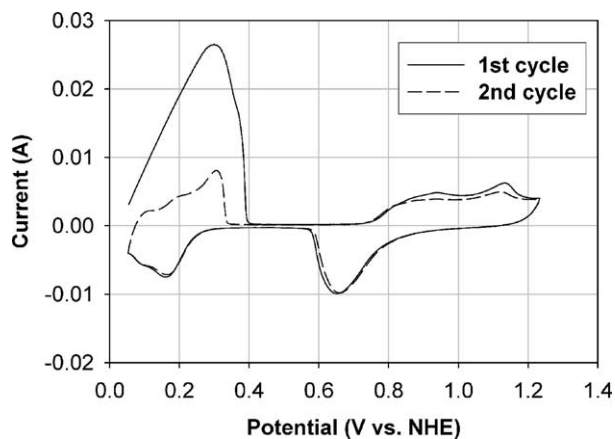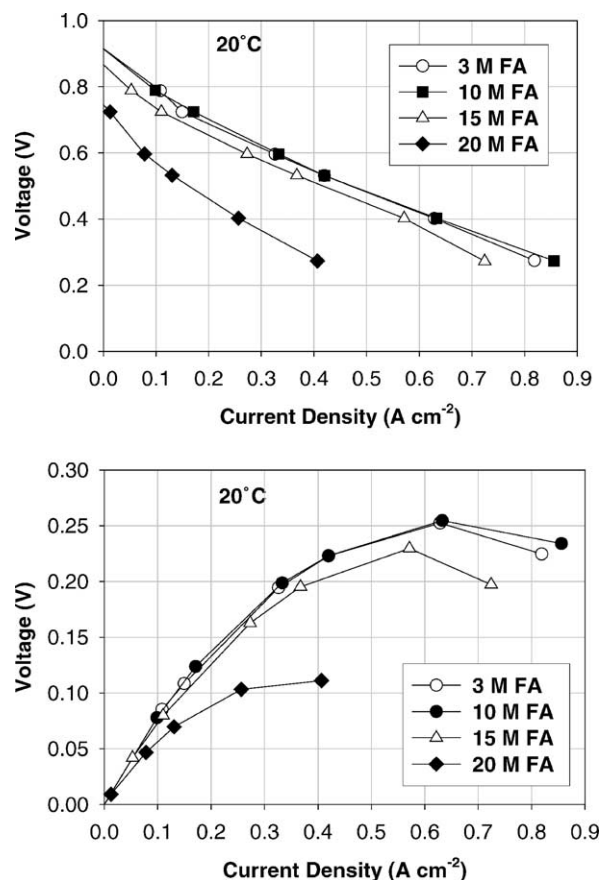

Fig. 5. Cyclic voltammograms of a palladium black electrode with and without adsorbant layer in conventional three-electrode electrochemical cell, the electrolyte solution was $0.50\,M\,H_2SO_4$. The palladium black electrode with adsorbant layer was obtained by rinsing the palladium black electrode after completed cyclic sweep between 0.60 and 0.10 V in 10.0 M formic acid solution at a low scan rate of $2\,mV\,s^{-1}$.

Table 3
Power densities under different concentrations of formic acid

Concentration of formic acid (M)	Power density at 0.40 V (mW cm^{-2})
3.0	253
10.0	255
15.0	230
20.0	103

and an accompanying increase in high-frequency resistance of the membrane from a normal 0.23 to 0.4 Ω cm^2. The hydroscopic property of formic acid may be a possible reason causing increase in the resistance [2]. Other reasons also need to be explored, such as lower activity of the palladium catalyst for highly concentrated formic acid. This can be separately verified by anode polarization measurement, as shown in Fig. 7. The identical anode polarization behavior for oxidation of formic acid in 3.0 and 10.0 M can be observed at 20 °C. However, the current density for 15.0 M formic acid oxidation was lower than that of 3.0 and 10.0 M. This behavior makes the fuel cell polarization with 15.0 M formic acid inferior to that with 3.0 and 10.0 M formic acid. An even lower current density of 20.0 M formic acid oxidation at palladium anode was observed in Fig. 7. The possible reason for the anodic reaction behavior of 15.0 and 20.0 M formic acid, in particular, may be that formic acid exists in another form in highly concentrated conditions, e.g. dimers. More research on highly concentrated formic acid will be very helpful to fully understand the mechanism of formic acid oxidation. However, a power density of 103 mW cm^{-2} may still be achieved at 0.40 V even using 20.0 M (ca. 80 wt.%) formic acid.

Although the utilization of high concentration of formic acid would facilitate fuel cell design and raise energy density of fuel cell devices for portable applications, it is also the possible that the performance loss of fuel cells is caused by higher membrane resistance and a lower oxidation reaction rate, such as in the case of 20.0 M formic acid.

Fig. 8. Time dependence of current density (short-term life test) at a fuel cell voltage of 0.53 V at 20 °C. The flow rate of formic acid to the anode was 0.3 mL min^{-1} for 10.0 M and 15.0 M. Air was supplied to the cathode at a flow rate of 300 mL min^{-1} without any back-pressure and humidification.

Fig. 9. The polarization plots of fuel cells with formic acid (10.0 and 15.0 M) at 20 °C. The flow rate of formic acid to the anode was 0.5 mL min^{-1} for 10.0 and 15.0 M. Air was supplied to the cathode at a flow rate of 300 mL min^{-1} without any back-pressure and humidification. The fuel cell polarization plots were measured before and after short-term life test (LT). After short-term life test, the anodes were activated by doing anode polarization (AP) at an anode potential of 1.2 V prior to fuel cell polarization measurement.
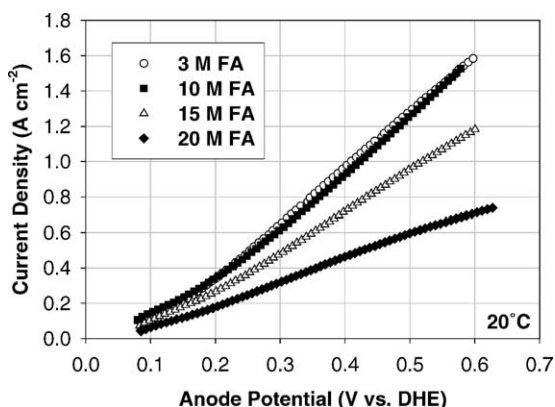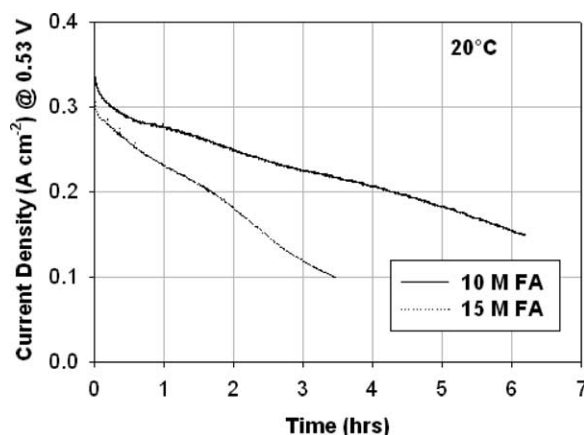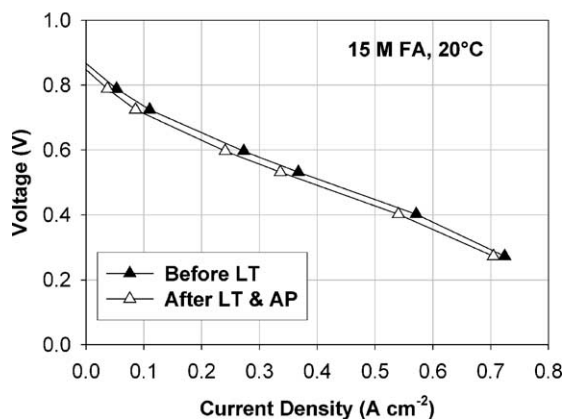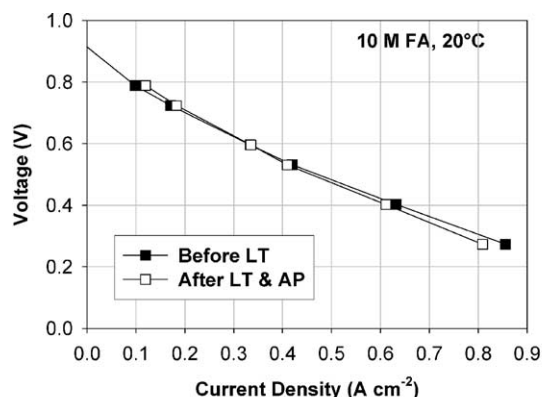

Fig. 7. Anode polarization plots of fuel cells with formic acid (3.0, 10.0, 15.0, and 20.0 M) at 20 °C. The flow rate of formic acid to the anode was 1 mL min^{-1}. Hydrogen was supplied to the cathode at a flow rate of 100 mL min^{-1}.

Time-dependent changes in current densities (short-term life test) of the fuel cells with 10.0 M and 15.0 M formic acid were observed at a constant voltage of 0.53 V, as shown in Fig. 8. There is no alteration of high-frequency resistance during the testing period. But the current significantly drops in six-hour operation of the fuel cell with 10.0 M formic acid. However, the current drop with 15.0 M formic acid in three-hour operation is even more than that with 10.0 M formic acid. Interestingly, the fuel cell performance can be completely recovered by just doing anode polarization at a certain potential, e.g. 1.2 V for a few seconds after the short-term life tests, as shown in Fig. 9. The results indicate that there may be adsorbants/poisoning species accumulated on/in the catalyst layer during the tests and these species can be completely removed during the anode polarizations. In addition, the recovery method of fuel cell performance may be practically effective in the applications.

4. Conclusions

Palladium nano-particles acting as extraordinary anode catalysts, for direct formic acid fuel cells (DFAFCs) have been illustrated. Fuel cells with a wide range of formic acid concentrations from 3.0 to 15.0 M may generate the maximum power densities of from 255 to 230 mW cm^{-2} using the palladium anode catalyst at 20 °C, which is not only much higher than that using the well-accepted platinum–ruthenium black catalyst under the same conditions but also is approaching to the performance of hydrogen–air PEM fuel cell under comparable conditions. In comparison with DMFCs and DFAFCs using platinum–ruthenium anode catalysts, the DFAFCs using the palladium anode catalyst produce substantially higher power at relatively high voltages, e.g. interestingly, from 0.4 to 0.9 V. Increasing temperature does not significantly enhance activity of the palladium catalyst for formic acid oxidation, but still provides a performance gain for oxygen reduction at the cathode. A power density of 375 mW cm^{-2} can be achieved at 50 °C. The DFAFCs operated with highly concentrated formic acid still accumulate poisoning adsorbant on the palladium catalyst layer during, a life test; however, it can be completely to removed by applying a certain potential to the anode. Thus, the fuel cell performance may be completely recovered. Even using 20.0 M formic acid, a maximum power density of 110 mW cm^{-2} can be achieved at 20 °C although dehydration of membrane may occur in this case.

Acknowledgements

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