



## Performance degradation of direct formic acid fuel cell incorporating a Pd anode catalyst

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### ABSTRACT

Electrochemical and physical analysis is employed to verify the performance degradation mechanism in direct formic acid fuel cells (DFAFCs). The power density of a single cell measured at  $200 \text{ mA cm}^{-2}$  decreases by 40% after 11 h of operation. The performance of the single cell is partly recovered however, by a reactivation process. Various analytical methods such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), and electrochemical impedance spectroscopy (EIS) are used to investigate the mechanism of performance degradation. The analytical results show that the electrolyte membranes in the DFAFC are stable for 11 h of operation after the reactivation process. The major factors causing performance degradation in the DFAFC are an increment in the anode charge-transfer resistance and a growth in the particle size of the Pd anode catalyst. The anode charge-transfer resistance, confirmed by EIS, increases with operation time and is due to poisoning of the catalyst surface. Although it is not clear what chemical species poisons the catalyst surface, the catalyst surface is cleaned by the reactivation process. Performance losses caused by surface poisoning are completely recovered by the reactivation process. Increase in catalyst size induces a reduction in active surface area, and the performance loss caused by the growth in catalyst size cannot be recovered by the reactivation process.

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### 1. Introduction

Direct liquid fuel cells (DLFCs) are considered a promising candidate to replace batteries in portable electronics such as cell-phones, portable multimedia players, and laptop computers. Among the different types of DLFCs, direct methanol fuel cells (DMFCs) have received the most attention over many years [1–3]. Nevertheless, direct methanol fuel cells are still under development due to drawbacks that include slow kinetics, methanol cross-over, and toxicity. Each of these drawbacks must be overcome to commercialize DMFCs. For these reasons, some researchers have tried to find alternative fuels for DLFCs, namely, formic acid [4–7], ethanol [8–10], and propanol [11,12]. Among them, formic acid has attracted particular interest due to its many advantages as an alternative fuel. Formic acid is a liquid at room temperature and is safe when in dilute form [13,14]. The cross-over flux of formic acid through Nafion® is lower than that of methanol [15], and this enables the use of thinner membranes and the utilization of concentrated formic acid solution as a fuel. Also, low cross-over flux decreases the loss in cell performance caused by the mixed electrode potential.

Electro-oxidation of formic acid on a catalyst is faster than that of methanol because formic acid has a very simple molecular structure and its theoretical electromotive force (emf) is higher than that of methanol. These intrinsic characteristics of formic acid permit operation of direct formic acid fuel cells (DFAFCs) at a power density about 3–6 times greater than that of DMFCs at room temperature [5].

Since the components of DFAFCs are the same as those of DMFCs, except for the anode catalyst, many researchers have focused on the development of anode catalysts for DFAFCs. In general, DFAFCs use anode catalysts based on precious metals such as Pt and Pd. Many workers have investigated Pt black [7] and Pt-bimetallic catalysts (e.g., PtRu [16,17], PtAu [18–20], PtPb [21–23], and PtBi [24,25]). Ha et al. [5,26] have demonstrated that a Pd-based anode is highly active for the electro-oxidation of formic acid and that single cells with a Pd catalyst give a maximum power density of  $240 \text{ mW cm}^{-2}$  at a current density of  $600 \text{ mA cm}^{-2}$ . Since then, Pd black and Pd-bimetallic catalysts such as PdIr [27], PdV [28], PdSn [29] and PdCo [30] have been studied intensively. In most cases, however, the Pd-based catalysts deactivated rapidly with operation time. Although the rapid deactivation of the Pd-based catalysts in DFAFCs caused serious performance deterioration, the performance could be recovered to previous levels by applying an anodic potential (1.0 vs. a dynamic hydrogen electrode) to the anode [5,31,32]. These observations suggest that deactivation of the Pd-based catalysts in

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DFAFCs might be caused by poisoning of their surfaces, but the exact deactivation mechanism has still to be elucidated. In this study, an attempt is made to identify the deactivation mechanism by operation of a single cell and application of various electrochemical and physical analyses.

## 2. Experimental

### 2.1. MEA preparation and single-cell operation

Membrane-electrode assemblies (MEA) were fabricated in-house by means of direct paint technique as described in elsewhere [5–7]. The active area of the electrode was  $9\text{ cm}^2$ . The catalyst inks were prepared by dispersing catalyst powders in appropriate amounts of Millipore water and 5 wt.% recast Nafion® solution (1100EW, Sigma–Aldrich). The catalyst inks for the anode and cathode were painted directly on both sides of a Nafion® 115 membrane. Pt black (HiSPEC™ 1000 from Johnson Matthey) was used as the cathode catalyst layer at a loading of  $7\text{ mg cm}^{-2}$ . Pd black (High Surface Area from Sigma–Aldrich) was used as the anode catalyst at a loading of  $8\text{ mg cm}^{-2}$ . The final anodic and cathodic catalyst layers contained 10 and 15 wt.% Nafion®, respectively.

The cell polarization of the prepared MEA was measured by a galvanostatic method using an electric loader (EZPD, ESL-300Z) at  $30^\circ\text{C}$ . An aqueous solution of 5 M formic acid was fed into the anode at a constant flow rate of  $5\text{ ml min}^{-1}$ , while dry air was supplied to the cathode at a flow rate of 800 sccm. Continuous operation of the single cell was carried out at a constant current density of  $200\text{ mA cm}^{-2}$ . To recover deactivated MEAs, a reactivation process was conducted. In the reactivation process,  $\text{H}_2$  was introduced at the cathode side, while 5 M formic acid was supplied to the anode side. The  $\text{H}_2/\text{Pt}$  in the cathode side acts as dynamic hydrogen electrode (DHE). In this study, a potential of 1.1 V vs. DHE was applied to the anode of the deactivated DFAFC for 3 s. The details of this procedure have been presented in elsewhere [5,31].

### 2.2. Electrochemical and physical analysis

Electrochemical impedance spectroscopy and cyclic voltammetry were carried out to characterize the electrochemical properties of the prepared MEAs. A coupled frequency response analyzer (Solartron 1260) and potentiostat (Solartron 1286) controlled by a computer were used for electrochemical analysis. For the analysis, 5 M formic acid and deionized water were fed to the anode at a flow rate of  $5\text{ ml min}^{-1}$ . To use the cathode as a counter electrode as well as a DHE, hydrogen gas was supplied to the cathode at a flow rate of 400 sccm.

Impedance spectra were measured between 1 kHz and 1 Hz with 10 steps per decade at  $30^\circ\text{C}$ . The amplitude of the sinusoidal potential signal was fixed at 10 mV. To avoid inductance along the electrical cable, the length of the cables was minimized and the cables were not in tangled. Cyclic voltammetry (CV) was performed at a scan rate of  $20\text{ mV s}^{-1}$  by sweeping potential between 0 and 1.2 V (vs. DHE) at  $30^\circ\text{C}$ . Before the measurements, deionized water was fed to the anode (the working electrode) for at least 20 min in order to remove any remaining formic acid from the catalyst surface.

Various physical techniques were used to observe the morphology of the Pd catalysts. At various points during operation, MEAs were examined by SEM (FEI XL-30 FEG) and TEM (Philips STEM CM-30).

## 3. Results and discussion

### 3.1. Performance degradation and reactivation

The cell polarization and power density plots measured while using 5 M formic acid solution and dry air at  $30^\circ\text{C}$  are presented in Fig. 1. Initially, the cell displayed high performance and the maximum power density was  $187\text{ mW cm}^{-2}$  at  $556\text{ mA cm}^{-2}$ . The cell performance drastically decreases (as reported in the literature [31–33]), and the maximum power density measured after 11 h of operation is  $76\text{ mW cm}^{-2}$  at  $200\text{ mA cm}^{-2}$ , which represents only 40% of the initial value. As shown in Fig. 1, the cell performance could be recovered by a simple reactivation process that applies an anode potential of 1.1 V (vs. DHE) for 3 s. After reactivation process, the cell performance is recovered immediately and the maximum power density returns to a value of  $136\text{ mW cm}^{-2}$  at  $333\text{ mA cm}^{-2}$ . When surface poisoning of the anode catalyst is the only major reason for performance degradation, the performance of the cell should be recovered to its initial value after a reactivation process that cleans the surface of the anode catalyst. In this case, however, the cell performance did not fully recover to its initial value; the maximum power density after the reactivation process is about 73% of its initial value. This implies that the degradation in cell performance involves one or more mechanisms other than surface poisoning of the anode catalyst. To identify the mechanism of performance degradation in a DFAFC with the Pd-based anode, a variety of characterization methods were employed; the results are presented below.

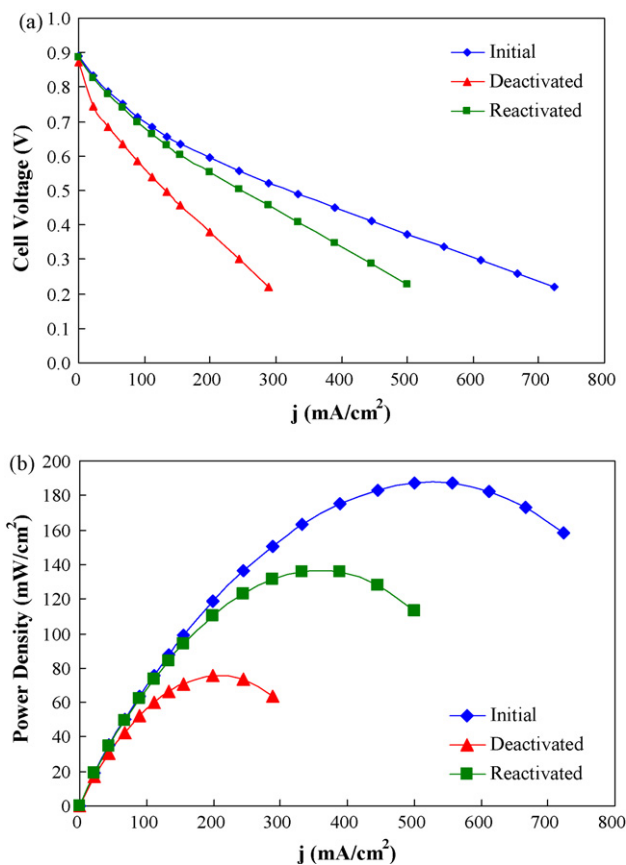


Fig. 1. Single cell (a) polarization and (b) power density plots at initial, deactivated and reactivated steps. 5 M formic acid and dry air without back pressure fed to anode and cathode at flow rates of  $5\text{ ml min}^{-1}$  and 800 sccm, respectively, at  $30^\circ\text{C}$ .

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