Effect of Particle Size on Performance of Palladium Catalyzed Formic Acid Fuel Cells

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Palladium (Pd) nano-particles have been demonstrated to act as a well-performed anode catalyst for direct formic acid fuel cells (DFAFCs) in our most recent researches. Exceptional DFAFC performances with Pd black anode catalyst have been achieved at room temperatures in both active and passive fuel cell fixtures, which make DFAFCs feasible to be applied as alternative power sources of portable devices.

The key to better performance in any type of fuel cell is the properties of its electrode materials. Nano-scale particles generally exhibit properties different from their bulk materials. The size of catalyst particles is one of the most important factors that determine the performance of fuel cells. It may determine electrode structures, effective utilization of catalysts and active site density and distribution in the electrode structures. The objective of this paper is to show that particle size has a dramatic influence on the behavior of Pd catalyzed formic acid fuel cells.

Experimental

The MEAs were fabricated using a 'direct paint' technique to apply the catalyst layer onto a NafionTM 115 membrane, with an active area of 5 cm². The cathode consisted of Pt black (Johnson Matthey, HiSpec 1000). The anode consisted of Pd black (a patent pending [1] Renew Power catalysts with 23, 40 and 60 m²/g, respectively).

The cell polarization was measured at 20°C. The anode fuel used was different concentration solution of formic acid (GFS Chemicals, 88% ACS grade). On the cathode, air was supplied at a flow rate of 300 ml min⁻¹ without any back-pressure and humidification. The anode activity was independently evaluated by measuring anode polarization plots.

Results and Discussions

Fig. 1A is polarization plots of DFAFCs (3 M) at 20°C, using Pd anode catalysts with different surface areas. For Pd (23 m²/g), a current density of 0.18 A/cm² is observed at 0.40 V, which generates a substantial power density of 72 mW/cm². However, when the Pd (40 m²/g) is used the current density observed at 0.40 V is dramatically enhanced to ca. 0.63 A/cm², which corresponds to a maximum power density of 253 mW/cm². Exceptional performances above 100 mW/cm² can be achieved at relatively high voltages of 0.40 ~ 0.75 V. Another Pd catalyst with a surface area as high as ca. 60 m²/g does not provide any further benefit in the DFAFC

fed by 3 M formic acid, compared to the one with 40 m^2/g . Anode polarization measurement indicates that there is no difference of Pd activity for formic acid oxidation (3 M) in the cases of the catalysts with surface area of 40 and 60 m^2/g . But the activity of Pd with surface area of 23 m^2/g is much lower than that of the other two catalysts.

A representative result of DFAFCs with highly concentrated formic acid is shown in Fig. 1B, obtained by using 15 M formic acid. The maximum power density of the cell with Pd ($60 \text{ m}^2/\text{g}$) is 230 mW/cm², which indicates that the power does not vary much ($230 \sim 255 \text{ mW/cm}^2$) in a wide range of concentration of formic acid ($3 \sim 15 \text{ M}$). However, performance loss of the cell (Pd, $40 \text{ m}^2/\text{g}$) becomes very significant when 15 M formic acid is fed through anode. The loss is even larger in the case of Pd with surface area of $23 \text{ m}^2/\text{g}$.

Using highly concentrated formic acid (10, 15 and 20 M, respectively), the finer the size of Pd powder the better the performance of DFAFCs. The nano-particles with higher surface area (smaller particle size) can be uniformly distributed in the catalyst layers and provide more active sites to overcome poisoning effect during anodic oxidation reaction of formic acid. Thus, exceptional performances may be achieved even using highly concentrated formic acid.



Figure 1 Polarization plots of D*FA*FCs with Pd anode (23, 40 and 60 m^2/g , respectively) at 20°C. (A) 3 M; (B) 15 M formic acid (FA). The FA flow rate 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.

1. R.I. Masel, Y. Zhu and R. Larsen, US patent submitted, 2004.