

The preparation of high activity DMFC Pt/C electrocatalysts using a pre-precipitation method

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Abstract

It is suggested that a Pt/C cathodic catalyst for the direct methanol fuel cell (DMFC) can be prepared with a pre-precipitation method, in which, H_2PtCl_6 is precipitated onto the carbon black as $(\text{NH}_4)_2\text{PtCl}_6$ before H_2PtCl_6 is reduced to Pt. The electrocatalytic activity of this Pt/C-A catalyst for oxygen reduction is excellent because the Pt/C catalyst prepared with this pre-precipitation method possesses a small average particle size, low relative crystallinity and a large electrochemically active surface area. In addition, the pre-precipitation method is simple and economical and it can be used to prepare a Pt/C catalyst on a large scale.

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Keywords: Direct methanol fuel cell; Pt/C catalyst; Preparation method; Oxygen reduction

1. Introduction

There has been an increasing interest in the development of proton exchange membrane fuel cells (PEMFC) and the direct methanol fuel cell (DMFC) in the recent years [1,2]. Thus, they are developing very quickly. However, they have similar problems, e.g. the O_2 reduction proceeds at a very slow kinetic rate in both the PEMFC and DMFC. The exchange current density of the oxygen reduction reaction at the Pt catalyst electrode is as low as 10^{-10} A cm^{-2} , whereas for the H_2 oxidation reaction, it is very high, at $\sim 10^{-4}$ A cm^{-2} [3,4]. Therefore, obtaining a cathodic catalyst with a high electrocatalytic activity for oxygen reduction is important for the development of both PEMFCs and DMFCs [5–10].

In general, two ways have been developed to increase the electrocatalytic activity of the Pt catalyst for oxygen reduction. First, Pt-based complex catalysts, such as Pt–Co, Pt–Fe, Pt–Cr, etc. [11,12] were developed. Second, the Pt catalysts with an optimum structure were prepared by a suitable preparation method

because structural factors, such as the average size and the relative crystallinity of the metal particles, the electrochemically active area and the alloying extent of the complex catalysts, etc. can significantly affect the final electrocatalytic activity of the catalysts [13]. Moreover, the preparation method has an important influence on the structure of the catalysts. Therefore, the preparation methods for the Pt-based catalysts for DMFC were studied by many investigators [14–18].

Among the many preparation methods, the conventional impregnation method [19,20] is often used because of its simplicity. However, the catalysts prepared with this method show a large average size of the metal particles, a broad particle size distribution and a high relative crystallinity so that the electrocatalytic activity of these catalysts for the oxygen reduction reaction is low. Most of other preparation methods, such as the colloidal method [21,22], etc. are too complicated.

In this paper, an improved impregnation method called a “pre-precipitation method” is presented. The Pt/C catalyst prepared with this method possesses a large specific surface area and a suitable average size of the Pt particles. Thus, the electrocatalytic activity of these Pt/C catalysts for the oxygen reduction reaction is higher than that prepared by the conventional impregnation method.

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2. Experimental

2.1. Preparation of the catalysts

The procedure for the pre-precipitation method in preparing the Pt/C catalyst with a 20 wt.% Pt is as follows: 400 mg Vulcan XC-72 carbon black (Cabot Co.) was impregnated with 13 mL 0.386 M H_2PtCl_6 solution for 2 h in order to ensure most of H_2PtCl_6 is adsorbed onto the carbon black. Then, 100 mL 10 M NH_4Cl solution is added into the suspension with stirring. H_2PtCl_6 adsorbed on the carbon black is precipitated due to the formation of $(\text{NH}_4)_2\text{PtCl}_6$. The suspension is continuously stirred for 1 h at 80 °C and pH 9.2 for the complete precipitation. With the dropwise addition of 600 mL 0.2 M NaBH_4 at 80 °C for 3 h, $(\text{NH}_4)_2\text{PtCl}_6$ is reduced to Pt particles adsorbed onto the carbon black. Subsequently, the suspension is filtered and washed with the hot triply distilled water until no Cl^- is detected. Finally, the catalyst is dried in an air oven at 110 °C for 4 h. The catalyst prepared with the pre-precipitation method is noted as the Pt/C-A catalyst.

For comparison, a Pt/C catalyst with 20 wt.% Pt is called the Pt/C-B catalyst and was prepared with the conventional impregnation method. The preparation procedure was similar to the pre-precipitation method except that the NH_4Cl solution was not added into the suspension of carbon black and H_2PtCl_6 .

2.2. Catalyst characterization

The measurements of the transmission electron microspectra (TEM) were carried out with a JEOL 2010 microscope operating at 200 kV with nominal resolution. The sample was prepared by dispersing the catalyst/ethanol suspension onto a 3-mm diameter copper grid covered with carbon film and then evaporating the solvent in air.

The X-ray diffraction (XRD) measurements of the catalysts were performed with a D/may- γ diffractometer (Philips Co.) using a $\text{Cu K}\alpha$ ($\lambda = 1.5405 \text{ \AA}$) radiation source operating at 40 kV and 200 mA.

The X-ray photoelectron spectra (XPS) were measured using a Kratos XSAM-800 spectrometer with an $\text{Mg K}\alpha$ radiator.

2.3. Electrochemical measurements

The electrochemical measurements were carried out with a Princeton Applied Research Model 273A potentiostat/Galvanostat and a conventional three-electrode electrochemical cell at 25 °C. In the electrochemical cell, a Pt plate was used as the auxiliary electrode and a saturated calomel electrode (SCE) electrode was used as the reference electrode. The working electrode was prepared as follows: a glassy carbon disk electrode was polished with 0.3 and 0.05 μm Al_2O_3 sequentially and washed. A certain amount of the Pt/C catalyst and the 5 wt.% Nafion solution (Du Pont) was mixed and sonicated for 30 min. The slurry was laid on the surface of the glassy carbon electrode. After drying, a working electrode was obtained [23]. The loading of Pt on the glassy carbon electrode was 1 mg cm^{-2} .

The cyclic voltammetric measurements were carried out in a 0.5 M H_2SO_4 solution. The solution was bubbled with pure oxygen for 15 min before the experiments. The scan rate was 50 mV s^{-1} .

2.4. Measurements of single cell performance

In the single cell, the Pt–Ru/C catalyst with 40 wt.% Pt + 20 wt.% Ru/C and the Pt/C catalyst with 20 wt.% Pt were used as the anodic and cathodic catalysts, respectively. Nafion 117 membrane (Du Pont Co.) was used as the proton exchange membrane.

The preparation of the membrane electrode assembly is the same as that in reference [24]. The slurry of the anodic or cathodic catalyst was prepared by dispersing the required amount of the catalyst into a mixture of an appropriate amount of isopropanol, de-ionized water and a 10 wt.% Teflon solution. The slurry was then sonicated for 30 min. The slurries of the anodic and cathodic catalysts were spread onto untreated and water-proofed carbon papers (Toray paper, E-TEK, TGPH-090), respectively. Then, they were dried in an air oven at 80 °C for 20 min, followed by a thermal treatment at 340 °C for 30 min to remove the dispersion agent in the Teflon solution. Before hot pressing, a 5 wt.% Nafion solution was sprayed onto the catalyst side of the electrode. The MEA was prepared by pressing the anodic and cathodic electrodes onto two sides of a Nafion 117 membrane with a pressure of 75 kg cm^{-2} for 90 s. The Pt contents were 2.5 and 2.0 mg cm^{-2} in the anodic and cathodic electrodes, respectively. The apparent surface area of the electrode was 5 cm^2 . Finally, the single cell was installed.

The performance of the single cell was measured with a Fuel Cell Test System (Arbin Co.). A 2.0 M CH_3OH solution with a flow rate of 20 mL min^{-1} and oxygen with a flow rate of 0.5 L min^{-1} at 0.05 MPa were used. The single cell was operated at room temperature.

3. Results and discussion

3.1. Catalyst characterization

Fig. 1 is the TEM image of the Pt/C-A catalyst. It can be observed from Fig. 1 that the Pt particles in the Pt/C-A catalyst are highly dispersed. Fig. 2 shows the histogram of the particle sizes obtained from Fig. 1. It can be observed from Fig. 2 that the average size of the Pt particles in the Pt/C-A catalyst is 3.0 nm. The smallest size of the Pt particles is 1.5 nm, whereas the largest is about 4.5 nm, indicating that the size distribution of the Pt particles is narrow.

Fig. 3 presents the TEM image of the Pt/C-B catalyst. Comparing with the TEM image of the Pt/C-A catalyst (Fig. 1), the Pt particles in the Pt/C-B catalyst shows a poor distribution and some Pt particles are severely aggregated. The average size of the Pt particles in the Pt/C-B catalyst is 6.0 nm and the size distribution of the Pt particles is wide (Fig. 4).

Assuming that the Pt particles are spherical, the specific surface area of the Pt particles in the Pt/C catalysts can be calculated

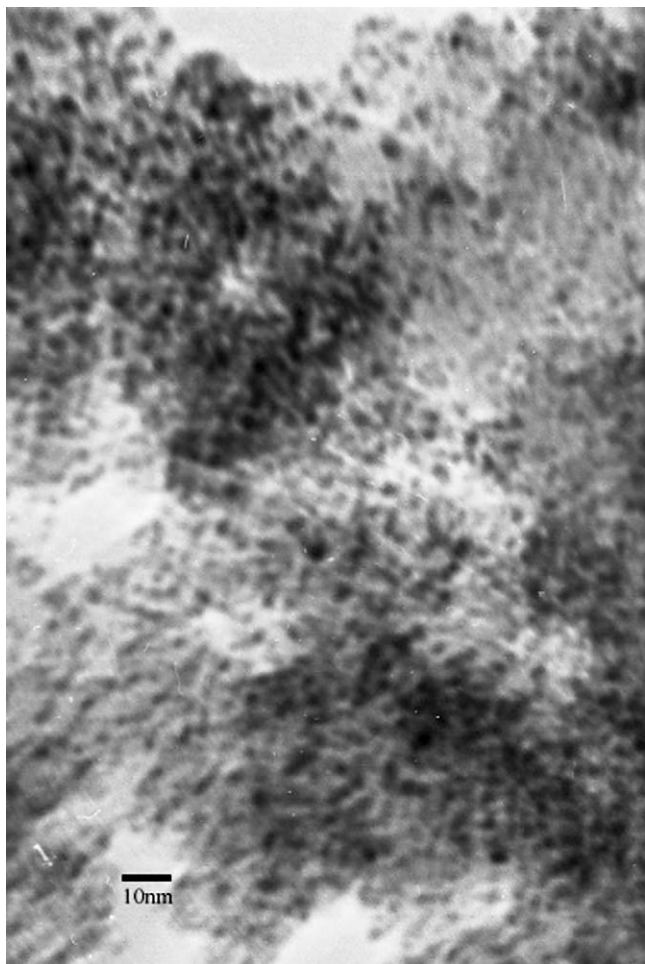


Fig. 1. The TEM image of the Pt/C-A catalyst.

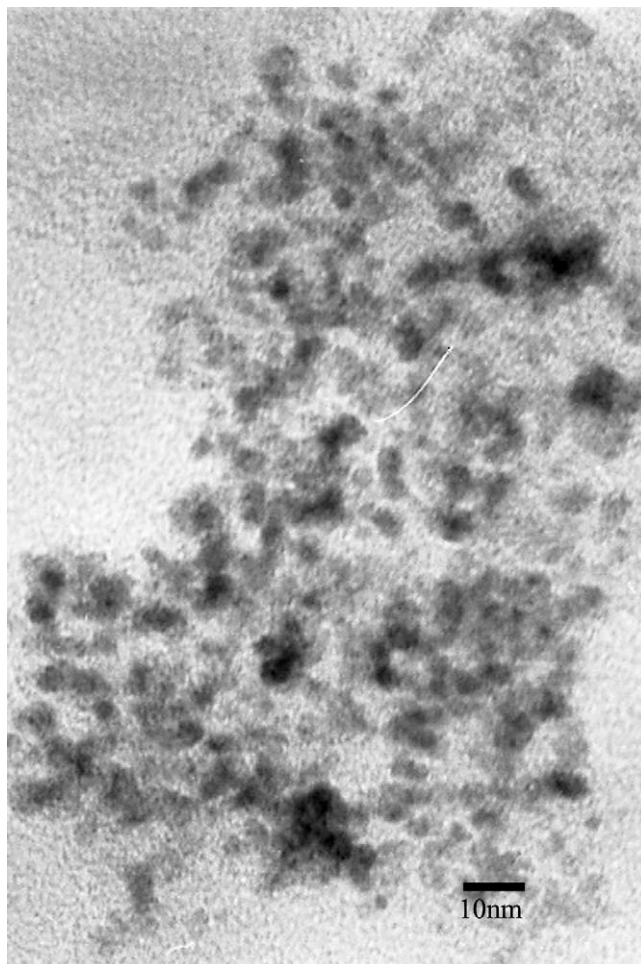


Fig. 3. The TEM image of Pt/C-B catalyst.

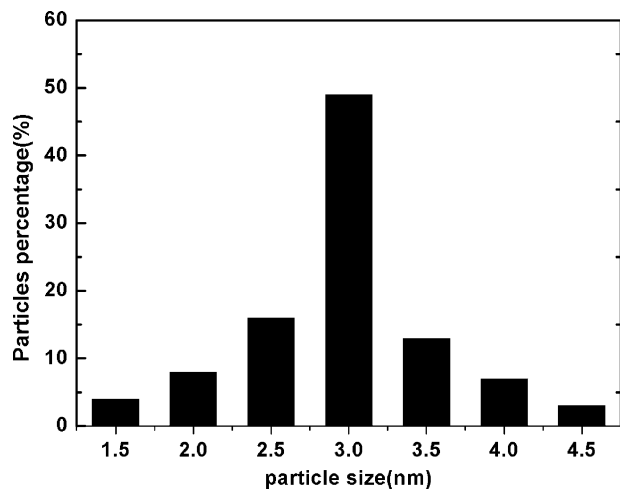


Fig. 2. Histograms of the distribution of Pt particle size from Fig. 1 for the Pt/C-A catalyst.

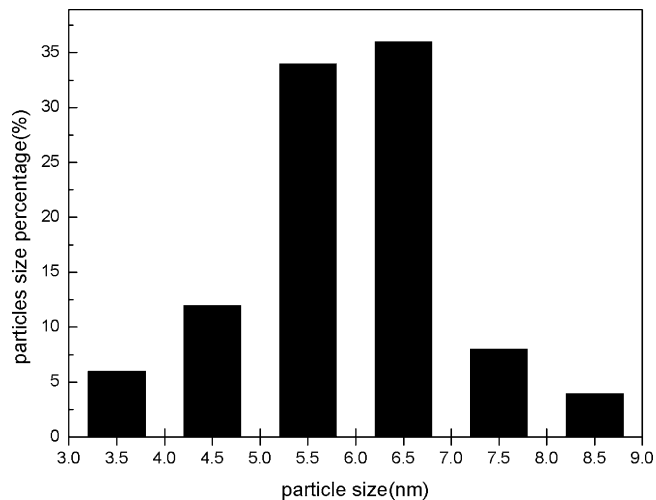


Fig. 4. Histograms of the distribution of the Pt particle size from Fig. 3 for the Pt/C-B catalyst.

from the following equations [25]:

$$S = \frac{6000}{\rho d}$$

where d is the average size of the Pt particles (nm), S the specific surface area of the Pt particles ($\text{m}^2 \text{g}^{-1}$) and ρ is the Pt density (21.4 g cm^{-3}). The specific surface areas of the Pt/C-A and Pt/C-B catalysts are 93.4 and $46.7 \text{ m}^2 \text{g}^{-1}$, respectively.

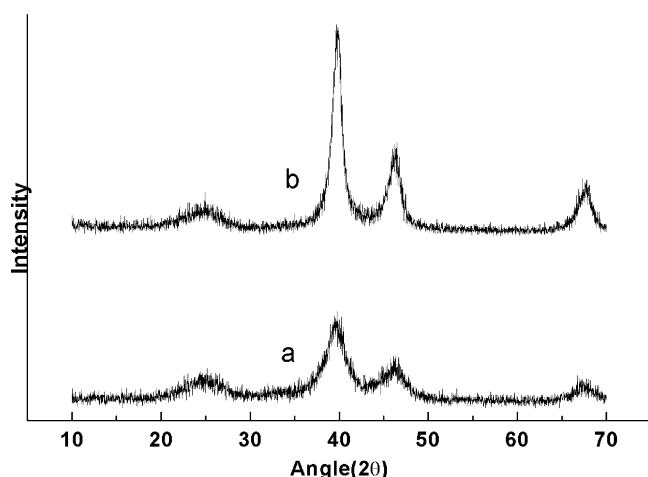


Fig. 5. The XRD patterns of (a) the Pt/C-A and (b) Pt/C-B catalysts.

Fig. 5 shows the XRD patterns of the Pt/C-A and Pt/C-B catalysts. In both XRD patterns, the diffraction peak at 24.5° observed is due to (002) crystal face of carbon. The 2θ values of other diffraction peaks are as the same as to that of (111), (200), (220) crystal faces of the face centered cubic crystalline of Pt (JCPDS card 04-0802), illustrating that the Pt particles in both Pt/C-A and Pt/C-B catalysts possess the face centered cubic structure. However, it can be found that the diffraction peaks of the Pt/C-B catalyst (Fig. 5, curve b) are broader than that of the Pt/C-A catalyst (Fig. 5, curve a), indicating that both the average size and the relative crystallinity of the Pt particles of the Pt/C-A catalyst are less than that of the Pt particles of the Pt/C-B catalyst.

Using Antolini's method [26], the relative crystallinity of the Pt particles can be evaluated from the ratio of the intensities of the diffraction peaks of Pt(111) and C(002) crystal faces. The relative crystallinities of the Pt/C-A and Pt/C-B catalysts are 2.62 and 7.12, respectively. The (220) diffraction peak was used to calculate the metal particle sizes according to the Scherrer formula [27]. The average sizes of the Pt particles of the Pt/C-A and Pt/C-B catalysts are 3.3 and 6.2 nm, respectively.

The above results can be explained as follows: when the H_2PtCl_6 solution is mixed with carbon black, some H_2PtCl_6 is adsorbed onto the carbon black. The H_2PtCl_6 in the solution is easily reduced. Thus, most of H_2PtCl_6 was reduced in the solution because after H_2PtCl_6 in the solution is reduced, the H_2PtCl_6 adsorbed onto the carbon black would be desorbed. Therefore, after most of the H_2PtCl_6 in the solution is reduced, most of the Pt particles obtained are suspended in the solution. Thus, they are easily aggregated before they are dispersed onto the surface of the carbon black. Thus, large Pt particles are obtained. This is the main reason why the large Pt particles are obtained with the conventional impregnation method. Whereas in pre-precipitation method, H_2PtCl_6 and NH_4Cl can form a precipitation of $(\text{NH}_4)_2\text{PtCl}_6$, which is adsorbed onto the carbon surface, resulting in the Pt particles being anchored to the carbon black and thus not easily aggregated.

Table 1 lists the XPS data of the Pt/C-A and Pt/C-B catalysts. The Pt(4f) signal is recognized and ascribed to Pt and PtO. The

Table 1
Data from curve-fitted XPS spectra

Catalysts	Species	Binding energy of 4f _{7/2} (eV)	Relative intensity (%)
Pt/C(A)	1	70.805	80.57
	2	72.816	19.43
Pt/C (B)	1	70.546	69.63
	2	72.813	30.37

binding energies for Pt are 70.805 eV for the Pt/C-A catalyst and 70.546 eV for the Pt/C-B catalyst. The corresponding values for PtO are 72.816 eV for the Pt/C-A catalyst and 72.813 eV for the Pt/C-B catalyst. The relative intensities of the peak for Pt are found to be 80.57% for the Pt/C-A catalyst and 69.63% for the Pt/C-B catalyst, indicating that the Pt content in the Pt/C-A catalyst is higher than that in the Pt/C-B catalyst.

The cyclic voltammograms of the Pt/C-A and Pt/C-B catalysts in 0.5 M H_2SO_4 solution are given in Fig. 6. It can be seen from Fig. 6 that the hydrogen adsorption and desorption peaks are located at about -0.1 V and the Pt redox peaks are at about 0.5 and 0.9 V. It was found that the area of the hydrogen adsorption and desorption peaks for the Pt/C-A catalyst (Fig. 6, curve a) are much larger than that for the Pt/C-B catalyst (Fig. 6, curve b), indicating that the electrochemically active surface area of the Pt/C-A catalyst is much larger than that of the Pt/C-B catalyst. According to the adsorption charge of the hydrogen monolayer being $210 \mu\text{C cm}^{-2}$ on the surface of a smooth Pt electrode [28], the electrochemically active surface area of Pt are $90 \text{ m}^2 \text{ g}^{-1}$ for the Pt/C-A catalyst and $45 \text{ m}^2 \text{ g}^{-1}$ for the Pt/C-B catalyst. This result is close to that calculated from the TEM results.

3.2. Electrochemical performances

Fig. 7 displays the linear sweep voltammograms of oxygen at the Pt/C-A and Pt/C-B catalyst electrodes in a 0.5 M H_2SO_4 solution. It is observed in Fig. 7 that the reduction potential of oxygen at both catalyst electrodes is located at about 0.6 V. However, the limiting current density for the oxygen reduction at the Pt/C-A catalyst electrode is 1.5 times larger than that for

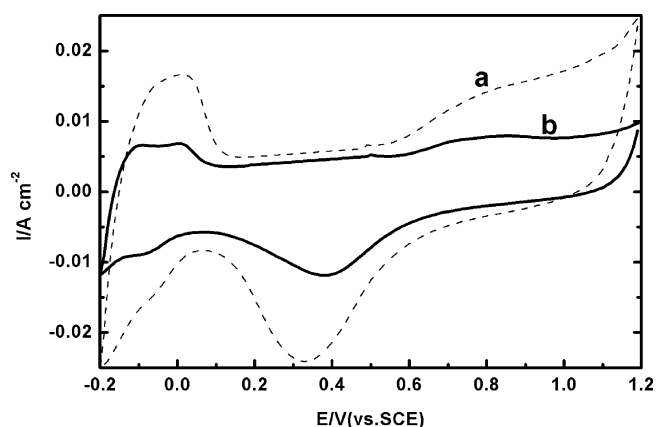


Fig. 6. Cyclic voltammograms of (a) the Pt/C-A and (b) Pt/C-B catalyst electrodes in 0.5 M H_2SO_4 solution.

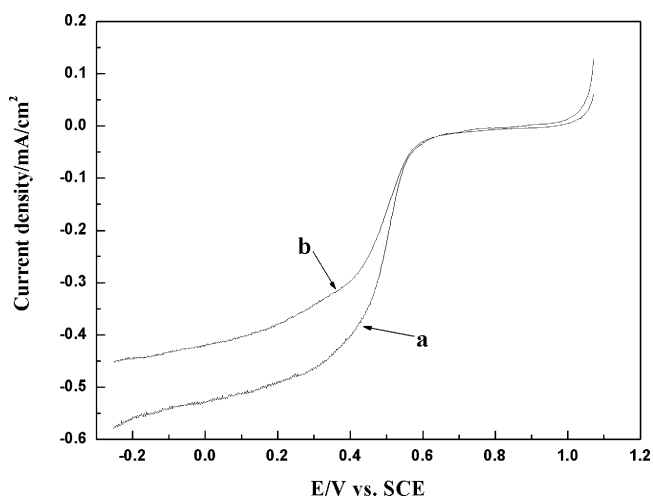


Fig. 7. Linear sweep voltammograms of O_2 at (a) the Pt/C-A and (b) Pt/C-B catalyst electrodes in 0.5 M H_2SO_4 solution.

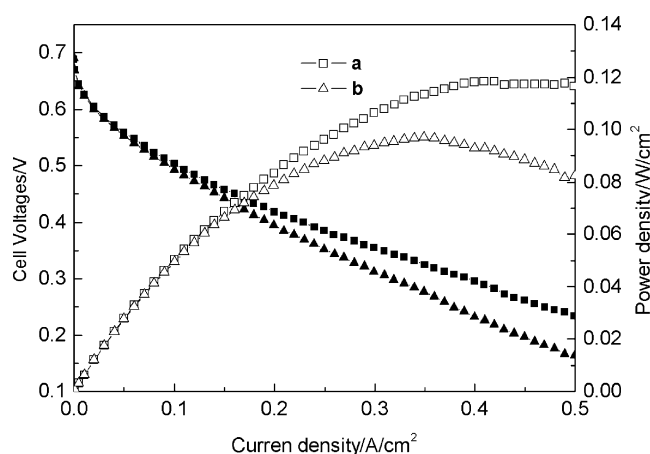


Fig. 8. The relationship between the current density and the voltage of a single DMFC with (a) the Pt/C-A and (b) Pt/C-B cathodic catalyst electrodes.

the Pt/C-B catalyst electrode, demonstrating that the electrocatalytic activity of Pt/C-A catalyst for the oxygen reduction is much higher than that of the Pt/C-B catalyst. The high electrocatalytic activity of the Pt/C-A catalyst for oxygen reduction can be attributed to the high electrochemically active area of the Pt/C-A catalyst due to the small average size and low relative crystallinity of the Pt particles in the Pt/C-A catalyst.

Fig. 8 shows the relationship curves between the current density and the voltage of the single DMFC with the Pt/C-A or Pt/C-B cathode catalyst. It was observed that when the current density is 100 mA cm^{-2} , the voltage of the cell with the Pt/C-A catalyst is 0.43 V (Fig. 8, curve a), which is higher than 0.35 V for the Pt/C-B catalyst (Fig. 8, curve B). The results further demonstrate that the electrocatalytic activity of the Pt/C-A catalyst is better than that of the Pt/C-B catalyst.

4. Conclusions

It is suggested that the Pt/C cathode catalyst for a DMFC is prepared by the pre-precipitation method, in which, H_2PtCl_6

is precipitated onto the carbon black as $(\text{NH}_4)_2\text{PtCl}_6$ before H_2PtCl_6 is reduced to Pt. The results of XRD, TEM, XPS and the cyclic voltammetry indicate that the average size, the relative crystallinity and the electrochemically active area of the Pt particles in the Pt/C catalyst prepared with the pre-precipitation method are 3.0 nm, 2.62 and $90 \text{ m}^2 \text{ g}^{-1}$, respectively. While the corresponding values for the Pt/C catalyst prepared by the conventional impregnation method are 6.0 nm, 7.12 and $45 \text{ m}^2 \text{ g}^{-1}$, respectively. Therefore, the results of the linear sweep voltammetry indicate that the limiting current density for the oxygen reduction at the Pt/C-A catalyst electrode is 1.5 times larger than that of the Pt/C-B catalyst electrode. The results from the relationship between the current density and the voltage of the single DMFC with the Pt/C-A or Pt/C-B cathode catalyst indicated that when the current density is 100 mA cm^{-2} , the voltage of the cell with the Pt/C-A catalyst is 0.43 V, while it is only 0.35 V for the Pt/C-B catalyst. The above results illustrate that the electrocatalytic activity of the Pt/C-A catalyst for the oxygen reduction is better than that of the Pt/C catalyst because the Pt/C-A catalyst possesses a small average particle size, low relative crystallinity and a large electrochemically active surface area. In addition, the pre-precipitation method is simple and economical. It can be used to prepare a Pt/C catalyst on a large scale. Therefore, the pre-precipitation method for the preparation of carbon supported Pt electrocatalysts is an excellent preparation method.

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