

Short communication

High activity Pt/C catalyst for methanol and adsorbed CO electro-oxidation

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Abstract

A high active Pt/C(b) catalyst was prepared by chemical reduction. The experimental results showed that the Pt/C(b) catalyst formed by reduction of hexachloroplatinic acid with formic acid has excellent catalytic properties for methanol and adsorbed CO(CO_{ad}) electro-oxidation. The electrocatalytic activity of the catalyst was characterized as having a specific surface activity of 33.38 mA cm⁻² at 0.6 V (versus Ag-AgCl). The Pt in the catalyst was well dispersed on carbon with an electrochemically-active specific surface area (ESA) of 84.16 m² g⁻¹ and a BET specific surface area of 192.34 m² g⁻¹ and an average particle size of about 2.6 nm. The catalyst showed a very good stability for 12 h. © 2006 Elsevier B.V. All rights reserved.

Keywords: Methanol; CO; Catalytic activity; Platinum nanoparticles

1. Introduction

In recent years the direct methanol fuel cell (DMFC) has received increasing attention because of the ready availability and portability of methanol and its high specific energy [1–3]. DMFC is considered as a possible power source for portable electronic devices and cars. But one major problem in the development of a DMFC is the low activity of the catalysts for methanol oxidation [4,5]. The element Pt is the most active catalyst for methanol electro-oxidation, but it is well known that a carbon supported Pt catalyst is poisoned by the adsorbed CO-like intermediates [6–8], which limits the catalytic activity for methanol electro-oxidation. It is generally accepted that the catalytic activity is strongly dependent on the shape, size and distribution of the Pt particles [9,10]. Many methods, such as microemulsions [11], microwave irradiation [12,13], solid reaction method, organic colloid method, inorganic colloid method, chemical reduction [14], impregnation method [15] have been used to prepare Pt based catalysts. All of these preparation techniques are aimed at generating Pt particles on the nanoscale and with uniformity. Among these methods, chemical

reduction is the simplest. In this work, simple chemical reduction was used to prepare Pt/C catalysts and the physicochemical properties, the stability and electrochemical activities of the nanostructure catalysts for methanol and adsorbed CO were investigated.

2. Experimental

2.1. Preparation of catalysts and electrodes

The Pt/C(a) was prepared according to Ref. [16].

The preparation of Pt/C(b) was: first a mixture of the required quantity of the carbon support (Vulcan XC-72R activated carbon black) and glycol was agitated ultrasonically and the hexachloroplatinic acid solution was added into the mixture at a temperature of 85° C then, the formic acid solution was added drop by drop to reduce H₂PtCl₆ at 85° C for 1 h. Next, the slurry obtained was filtered and washed with triply distilled water until no Cl⁻ was detected. Finally the slurry was filtered and dried in the vacuum condition at 25° C. The Pt/C catalyst prepared contained 20 wt.% Pt.

A certain amount of the Pt/C catalyst was dispersed in ethanol, Nafion and PTFE and agitated ultrasonically for 5 min. After the slurry was spread on a carbon paper and dried at the room temperature in the air, the Pt/C electrode was obtained. The

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Pt loading for all electrodes for experiment is 1 mg cm^{-2} . The geometrical surface area of all electrodes prepared was 0.5 cm^2 .

Commercial Pt/C(E-TEK) was used for comparison.

2.2. Electrochemical measurements

The experiments were performed in a dual electrochemical cell apparatus operating in an anaerobic environment. Electrochemical measurements were carried out by using a CHI650A electrochemical analyzer. The scan rate was 10 mV s^{-1} . Pt/C electrodes were used as the working electrode. An Ag–AgCl electrode and Pt gauze were used as the reference and the counter electrode, respectively. All chemicals were of analytical grade. All the solutions were prepared with triply distilled water. The nitrogen purity is 99.99%.

The electrochemical measurements were performed in the solution of $0.5 \text{ mol L}^{-1} \text{ CH}_3\text{OH} + 0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ at 25°C and 60°C . N_2 was used for careful purging before each experiment in order to avoid any O_2 contamination of the electrolyte. In order to measure the electrochemical behavior of the CO_{ad} , high-purity CO was bubbled into the solution for 10 min to allow complete adsorption of CO on Pt/C electrodes. After the adsorption period, the dissolved CO was removed from the solution by bubbling highly purified N_2 for at least 10 min.

2.3. Physical characterization of the catalysts

The morphology of the catalyst surface was obtained by using a scanning electron microscope (SEM) (Hitachi S-4800HSD made in Japan) and the working voltage was 20 kV. The sample was also examined by TEM on a Tecnais-G2 Twins. For TEM examination, the sample was first ultrasonicated in ethanol for 20 min and then deposited onto 3 mm Cu grids covered with a continuous carbon film. XRD patterns of the catalysts were measured with an X-ray diffractometer (Japanese D/max-IIIb) using a Cu $\text{K}\alpha$ source operated at 40 keV, tube current is 30 mA. The BET specific surface test was obtained by Malvern Company NOVA2000e and the adsorption gas was nitrogen.

3. Results and discussion

3.1. methanol and CO_{ad} electro-oxidation at Pt/C electrodes

Fig. 1 shows the cyclic voltammograms in the solution of $0.5 \text{ mol L}^{-1} \text{ CH}_3\text{OH} + 0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ at 25°C . It was observed that methanol electro-oxidation on Pt/C(a) started at about 0.4 V, and the positive scan oxidation peak current was 71.7 mA cm^{-2} . On Pt/C(b), the onset potential of methanol oxidation was about 0.3 V, which was a more negative value by 100 mV compared to Pt/C(a). The positive scan peak current on Pt/C(b) was 147.3 mA cm^{-2} . It is noticeable in Fig. 1 that the Pt/C(b) shows the highest peak current density for methanol electro-oxidation among the catalysts investigated here. It is also found that the peak potential of methanol oxidation is almost the same on Pt/C(a) and Pt/C(b) and there was a slight positive shift

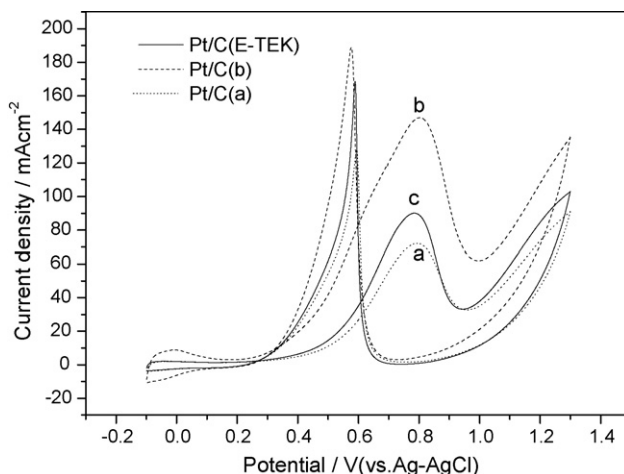


Fig. 1. Cyclic voltammograms of CH_3OH at Pt/C catalysts in the solution of $0.5 \text{ mol L}^{-1} \text{ CH}_3\text{OH} + 0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$, scan rate: 10 mV s^{-1} , 25°C .

compared to Pt/C(E-TEK). From the point of view of current density and the onset potential, Pt/C(b) was more active for methanol electro-oxidation than Pt/C(a) and Pt/C(E-TEK).

Fig. 2 shows the cyclic voltammograms in the solution of $0.5 \text{ mol L}^{-1} \text{ CH}_3\text{OH} + 0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ at 60°C . At this higher temperature the oxidation peak current of methanol on the three electrodes is much higher compared with that at 25°C (Fig. 1), but the oxidation peak potentials are more positive. It was also found that methanol electro-oxidation on Pt/C(a) and Pt/C(b) started at more positive values than on Pt/C(E-TEK) at 60°C .

Fig. 3 shows the linear sweep curves of CO_{ad} at Pt/C(a) and Pt/C(b) electrodes in the $0.5 \text{ M H}_2\text{SO}_4$ solution at 25°C . It is obvious that the peak current density of CO_{ad} oxidation at Pt/C(b) electrode is much greater than that on Pt/C(a) and the onset potential of CO_{ad} oxidation at Pt/C(b) occurs at about 0.5 V—a slightly negative shift compared to that at Pt/C(a). The peak potential of CO_{ad} oxidation at Pt/C(b) is 0.63 V, about 40 mV—more positive than that at Pt/C(a). The onset

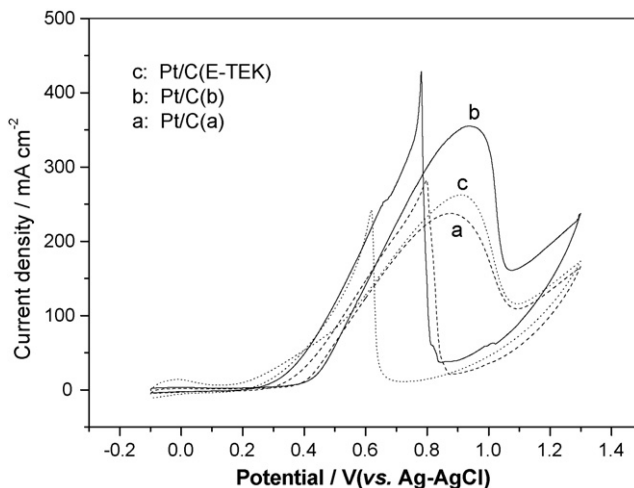


Fig. 2. Cyclic voltammograms of CH_3OH at different Pt/C catalysts in the solution of $0.5 \text{ mol L}^{-1} \text{ CH}_3\text{OH} + 0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$, scan rate: 10 mV s^{-1} , 60°C .

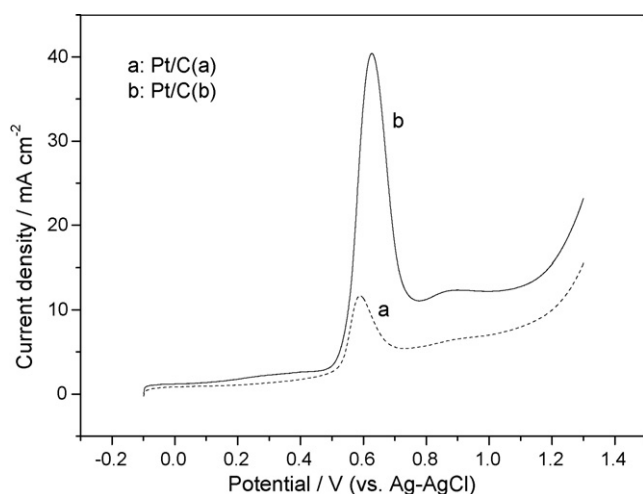


Fig. 3. Linear sweep voltammograms of different Pt/C electrodes in the solution of $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$, scan rate: 10 mV s^{-1} , 25°C .

potential and peak potential of CO_{ad} oxidation has no obvious change when the temperature increased to 60°C (Fig. 4), but the peak current density increased about 10 mA cm^{-2} at Pt/C(b) electrode, while it decreased about 2 mA cm^{-2} on the Pt/C(a) electrode compared to the results at 25°C (Fig. 3). The results show that the Pt/C(b) is more active for CO_{ad} electro-oxidation than Pt/C(a) and it can also be concluded that the CO_{ad} oxidation is not as sensitive to temperature as methanol.

3.2. Chronoamperometry

Fig. 5 shows the chronoamperometry curves for Pt/C(a), Pt/C(b) and commercial Pt/C(E-TEK) catalysts and the methanol oxidation reaction which were biased at 0.6 V (versus Ag-AgCl) in the solution of $1.0 \text{ mol L}^{-1} \text{ CH}_3\text{OH} + 0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ at 25°C for 12 h. An initial rapid decrease in the current density with time was found for both catalysts, this could be due to the formation of CO_{ad} and other intermediate species during methanol oxidation. After that, the current decreased slowly and

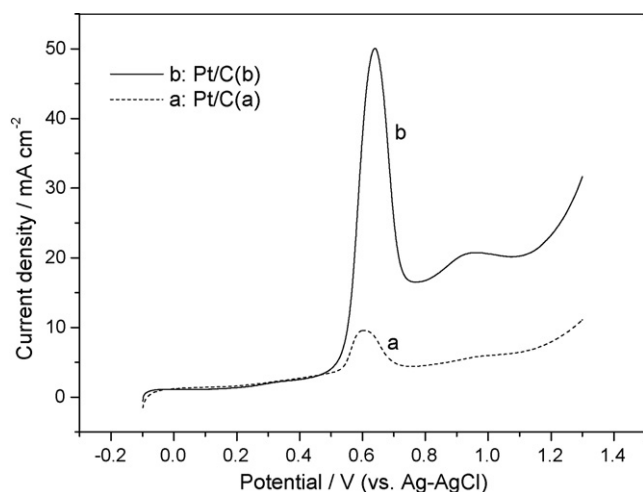


Fig. 4. Linear sweep voltammograms of different Pt/C electrodes in the solution of $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$, scan rate: 10 mV s^{-1} , 60°C .

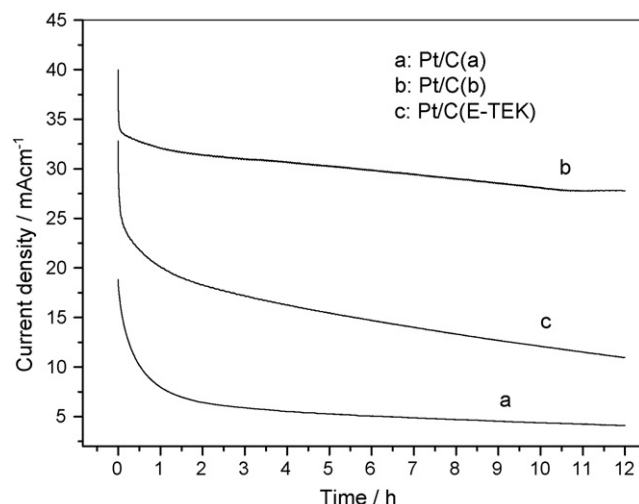


Fig. 5. Chronoamperometric curves for the catalysts in the solution of $1.0 \text{ mol L}^{-1} \text{ CH}_3\text{OH} + 0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$, 25°C , 0.6 V vs. Ag-AgCl.

achieved a pseudo-steady state, the decay can be attributed to the adsorbed anion SO_4^{2-} on the surface of the catalyst, which can restrict the methanol oxidation reaction [17]. The current density stabilized within 2 min for Pt/C(b) catalyst and about 80 min for Pt/C(a) after application of the set potential. The current density for the Pt/C(b) catalyst was over 23 mA cm^{-2} higher than that for the Pt/C(a). The long-term poisoning rate (δ) can be calculated by measuring the linear decay of the current for a period of more than 500 s from Fig. 5 by using the following equation [18]:

$$\delta = \frac{100}{I_0} \times \left(\frac{dI}{dt} \right)_{t > 500 \text{ s}} \quad (\% \text{ s}^{-1}) \quad (1)$$

where $(dI/dt)_{t > 500 \text{ s}}$ is the slope of the linear portion of the current decay and I_0 is the current at the start of polarization back extrapolated from the linear current decay. Fig. 6 shows the chronoamperometry curves for the catalysts during different periods of time of methanol electro-oxidation. The dotted lines are linearly fitted. The calculated δ values and specific surface area activity from Fig. 6 are given in Table 1.

Table 1

Specific surface area activity and poisoning rate of the catalysts towards the methanol oxidation reaction measured in $1.0 \text{ mol L}^{-1} \text{ CH}_3\text{OH} + 0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$, 25°C , 0.6 V vs. Ag-AgCl

	δ (s^{-1})			
	10–30 min	30–120 min	120–630 min	630–720 min
Pt/C(a)	0.21	0.0062	0.00096	0.00094
Pt/C(b)	0.0016	0.00075	0.00037	0.0000019
Pt/C(E-TEK)	0.0067	0.0029	0.0011	0.0014
	Specific activity (mA cm^{-2})			
	10 min	30 min	120 min	630 min
Pt/C(a)	13.73	10.88	6.42	4.312
Pt/C(b)	33.38	32.72	31.44	27.88
Pt/C(E-TEK)	23.88	21.86	18.30	11.808

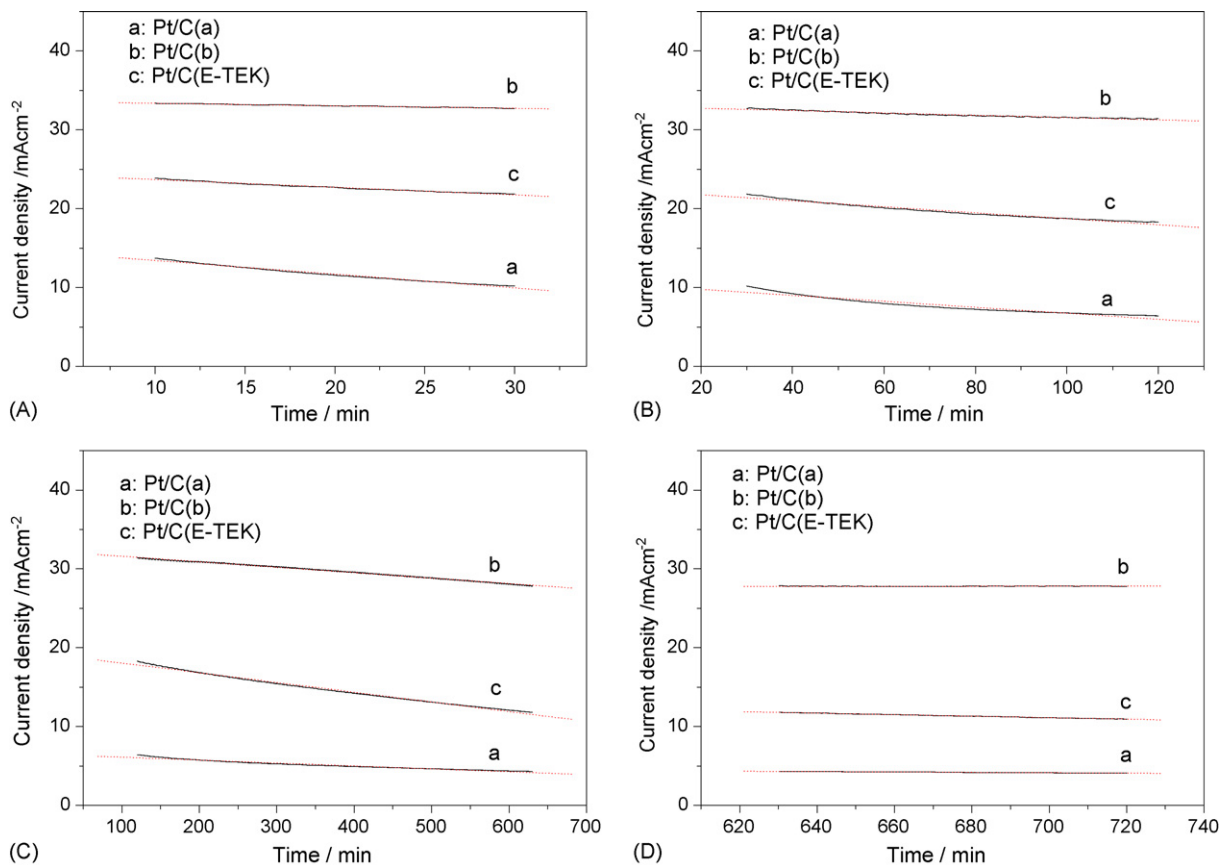


Fig. 6. Chronoamperometric curves for the Pt/C catalysts during different periods of time in the solution of $1.0 \text{ mol L}^{-1} \text{ CH}_3\text{OH} + 0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$, 25°C , 0.6 V vs. Ag-AgCl. Dotted lines are linear fitted.

Table 1 shows the poisoning rate of the Pt/C catalysts which followed the order: Pt/C(a) > Pt/C(E-TEK) > Pt/C(b) during 10–30 min. During 30–120 min, the poisoning rate of the catalysts was changed slowly especially for Pt/C(a), but the order was the same. The poisoning rate was greatly reduced for all the catalysts and the order changed to Pt/C(E-TEK) > Pt/C(a) > Pt/C(b) during the period from 120 min to 630 min. After 630 min, the poisoning rate decreased slightly for Pt/C(a) and increased slightly for Pt/C(E-TEK). The poisoning rate is almost zero for Pt/C(b) compared with the other two catalysts during 630–720 min. Table 1 also shows that the Pt/C(b) had the highest specific activity of the three catalysts at any period of time. As a whole, the Pt/C(b) has the lowest poisoning rate and the highest specific activity among the catalysts investigated here and it also indicated its higher tolerance to intermediate species formed during the methanol oxidation reaction.

3.3. XRD measurement and surface analysis

Fig. 7 shows XRD patterns of the Pt/C(a) and Pt/C(b) catalysts. The XRD measurements show characteristic diffraction peaks that are indexed to the Pt(1 1 1), Pt(2 0 0), Pt(2 2 0) and Pt(3 1 1) planes of the Pt face-centered cubic crystal structure, respectively. The diffraction peak at $2\theta = 25^\circ$ pertains to carbon black (0 0 2) planes of the crystal structure. The average particle size of the Pt/C(a) and Pt/C(b) catalysts can be calculated from

the XRD pattern by means of the Scherrer equation [18].

$$d = \frac{0.9\lambda}{B_{2\theta} \cos \theta_{\max}} \quad (2)$$

In Eq. (2), d is the average particle size of platinum, λ the wavelength of X-ray used ($\lambda = 1.54056 \text{ \AA}$); $B_{2\theta}$ the full-width

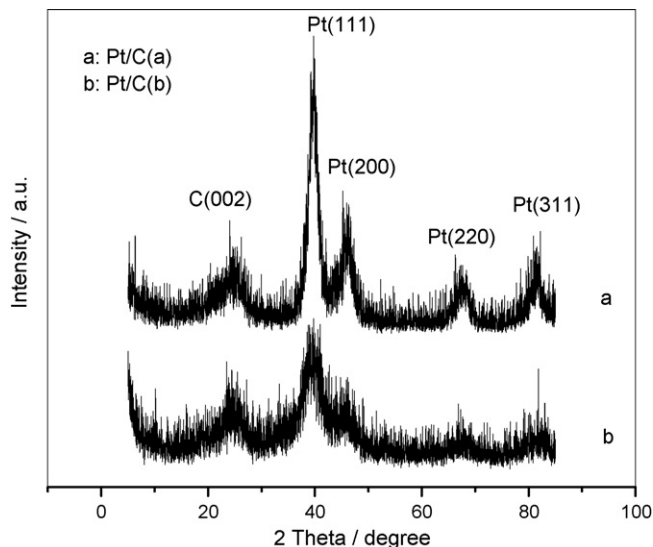


Fig. 7. XRD patterns of the catalysts.

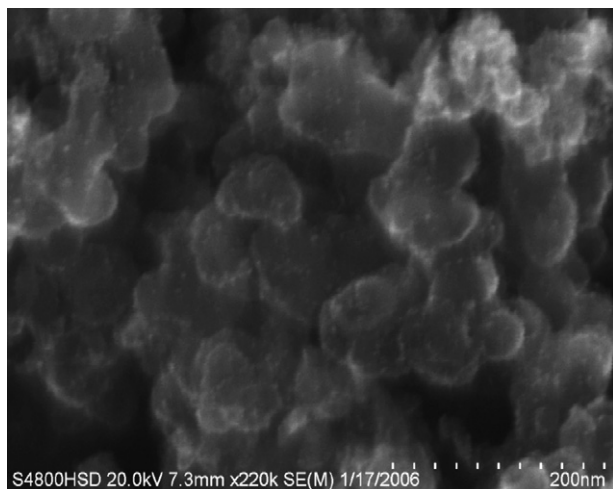


Fig. 8. SEM image of the Pt/C(b) catalyst.

at half-maximum of respective diffraction peak and θ_{\max} is the angle at position of peak maximum. The Pt(2 2 0) diffraction peak is used here to calculate the Pt particle size for its little carbon interference in the XRD pattern. The average particle size obtained from the XRD patterns is 3.9 nm for Pt/C(a) and 2.6 for Pt/C(b). The result shows that the particles of platinum are highly dispersed on Pt/C(b). This can also be seen in the SEM image of Pt/C(b) catalyst (Fig. 8). The large particles, which were about 50 nm and the bright dots on the carbon surface, are platinum particles. This shows a remarkably uniform and high dispersion of platinum particles. Fig. 9 is the TEM image of Pt/C(b). It can be seen that the particle size of Pt is about 3 nm, which agrees with the calculated results from XRD.

We measured the BET specific surface area and electrochemical specific surface area (ESA) for Pt/C(a) and Pt/C(b) catalysts. The surface area of ESA was calculated by using the following

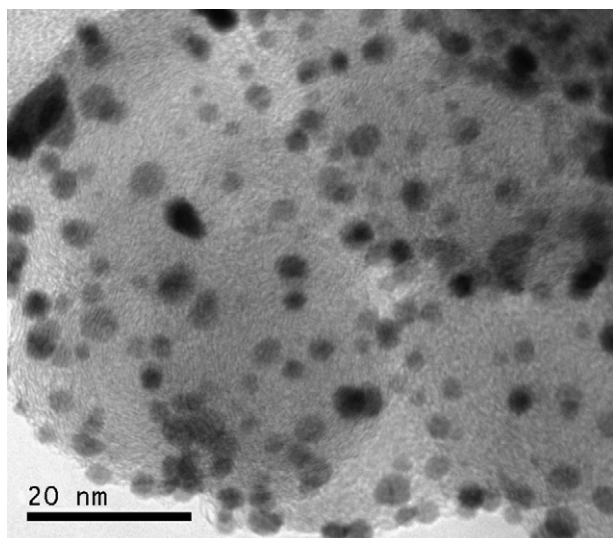


Fig. 9. TEM image of the Pt/C(b) catalyst.

Table 2

The electrochemical specific surface area (ESA) and BET specific surface area of different Pt/C catalysts

Samples	ESA ($\text{m}^2 \text{g}^{-1}$)	BET ($\text{m}^2 \text{g}^{-1}$)
Pt/C(a)	32.93	184.37
Pt/C(b)	84.16	192.34

equation.

$$S = \frac{0.1 \times Q/k}{WL} (\text{m}^2 \text{g}^{-1}) \quad (2)$$

where W is the weight of the catalyst (g), L the weight percent of platinum (wt.%) and Q is the coulometry of hydrogen desorption (mc), $k = 210 \mu\text{C cm}^{-2}$.

The specific BET surface area and ESA surface area of these two catalysts are summarized in Table 2. The data in Table 2 show that the Pt/C(b) catalyst has the largest BET and ESA surface area, which are $192.34 \text{ m}^2 \text{g}^{-1}$ and $84.16 \text{ m}^2 \text{g}^{-1}$, respectively. The large ESA value of Pt/C(b) indicated that the Pt at Pt/C(b) catalyst was well dispersed which may contribute to the high specific activity.

4. Conclusion

20 wt.% Pt/C(b) nanocatalysts were prepared by a simple method of chemical reduction of hexachloroplatinic acid in glycol solution using formic acid as the reducing agent. The catalyst exhibited a high activity for methanol and adsorbed CO electro-oxidation. The SEM analysis indicated that well dispersed Pt particles were obtained on the carbon support and a high electrochemical specific surface area of $84.16 \text{ m}^2 \text{g}^{-1}$ was confirmed by the SEM results. The XRD analysis showed a small Pt particle size of 2.6 nm of the Pt/C(b), which is agreement with the results from the TEM. The chronoamperometric tests conducted on all three catalysts demonstrated that Pt/C(b) had the lowest poisoning rate and the highest activity during methanol electro-oxidation which indicated a greater tolerance for intermediate species formed during the methanol oxidation.

Acknowledgements

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