

# Microwave synthesis and characterization of acetate-stabilized Pt nanoparticles supported on carbon for methanol electro-oxidation

Jie Zhao<sup>a</sup>, Peng Wang<sup>a</sup>, Weixiang Chen<sup>a,\*</sup>, Run Liu<sup>a</sup>, Xiang Li<sup>a</sup>, Qiulin Nie<sup>b</sup>

<sup>a</sup> Department of Chemistry, Zhejiang University, Hangzhou 310027, PR China

<sup>b</sup> Hangzhou Institute of Electronic Engineering, Hangzhou 310018, PR China

Received 21 November 2005; received in revised form 31 December 2005; accepted 6 January 2006

Available online 20 February 2006

## Abstract

Acetate-stabilized Pt nanoparticles supported on carbon were prepared by a microwave heating polyol method, in which a small amount of sodium acetate solution was added as a stabilizing agent in the synthesis solution. The Pt/C catalysts were characterized by energy-dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM) and X-ray diffraction (XRD). It was found that the Pt nanoparticles were small and uniform in size, and highly dispersed on XC-72 carbon supports. The mean size of the Pt particles was 5.1, 4.3, 3.5 and 2.8 nm, respectively, correspondingly for adding 0, 0.1, 0.3 and 0.5 mL of 1.0 M sodium acetate solution in 50 mL of the synthesis solution. The effects of the amount of acetate solution added on the Pt particle size and size distribution were investigated. The electrochemical measurements demonstrated that the Pt/C catalysts prepared in this way exhibited a much higher electrocatalytic activity for methanol electro-oxidation than a comparative Pt/C catalyst prepared without adding acetate.

© 2006 Elsevier B.V. All rights reserved.

**Keywords:** Pt nanoparticles; Carbon supports; Electrocatalysts; Sodium acetate; Methanol electro-oxidation

## 1. Introduction

Direct methanol fuel cells (DMFCs) have been the subject of great interest in recent years due to their potential application in electric vehicles and as portable power sources [1–4]. Although several electrocatalysts have been employed for the oxidation of methanol [5–7], Pt and Pt-based alloys are the preferred anode catalysts due to their high electrocatalytic activity. It is well known that the catalytic activity strongly depends on the size and size distribution of the metal particles, and their dispersion on supports [8]. It was reported that Pt particles with about 3.0–4.0 nm exhibited a higher mass electrocatalytic activity for oxygen reduction [9,10], and Pt–Ru particles with ~3.0 nm displayed the highest mass catalytic activity for methanol electro-oxidation [11]. Therefore, metal particles with high electrocatalytic activity should have a suitable size and narrow size distribution. But the conventional preparation techniques based on wet impregnation and the chemical reduction

of metal precursors do not provide satisfactory control of particle shape and size [8]. Synthesis of highly dispersed supported Pt particles with size-control and uniform size still remains a challenge for high performance catalysts. Hence, there are continuing efforts to develop alternative synthesis methods based on microemulsions [12], supercritical fluid [13], sonochemistry [14,15], and microwave irradiation [16–18]; all of which are in principle more conducive to generating colloids and clusters on the nanoscale and with greater uniformity.

Reduction of metal salts in a liquid polyol solution has been proven to be an effective method for preparing colloidal metal particles in the micrometer, submicrometer and nanometer size range [19,20]. In this polyol process, the liquid polyol acts as a solvent for the metal salts, reducing and growth medium for the metal particles. Conductive heating was often used in the conventional polyol process. However, microwave heating may be a better synthesis option in view of its uniformity, speed, energy efficiency and implementation simplicity. The microwave in combination with the polyol process has been used to synthesize fine metal colloids, such as Pt, Ru, Ag and Pd [16–18]. In their microwave polyol process [16–18], the polymers, especially polyvinyl pyrrolidone (PVP), were employed as protective

\* Corresponding author. Tel.: +86 571 87952477; fax: +86 571 87951895.  
E-mail address: [weixiangchen@css.zju.edu.cn](mailto:weixiangchen@css.zju.edu.cn) (W. Chen).

agents to avoid metal particle agglomeration. But the polymer stabilizers must be removed at relatively high temperature in the area of electrocatalysts [21]. Because the heat treatment would cause agglomeration of metal particles and alter the properties of the catalysts, the microwave polyol process using polymers as stabilizers was limited in the synthesis of these electrocatalysts.

Electrostatic stabilization is an alternative way to obtain colloidal metal particle dispersions in solution. The citrate anion has been used as a stabilizer to prepare noble metal nanoparticles such as gold [22], palladium [23], silver [24] and platinum [25,26]. Bock et al. have also reported that the glycolate anion acted as a stabilizer for the size-controlled Pt–Ru colloids via the synthesis solution pH [27]. Recently, sodium acetate was also found as a good stabilizer for preparing Pt and Ru nanoparticles in the liquid polyol process [28,29]. These carboxylic anions used as stabilizers were possibly preferred to polymer stabilizer for the synthesis of electrocatalysts because the anions were easily removed by washing with deionized water at room temperature.

In the present work, acetate-stabilized Pt nanoparticles with uniform size supported on XC-72 carbon were prepared by a microwave assisted polyol process. The size-controlled Pt/C electrocatalysts were obtained by adjusting the amount of sodium acetate added to the synthesis solution. The effects of the amount of acetate solution added on Pt particle size of Pt/C catalysts were investigated. It was found that acetate could be used as a good stabilizer for preparing fine and uniform Pt nanoparticles. The Pt/C electrocatalysts prepared in this way displayed a high electrocatalytic activity for methanol electro-oxidation.

## 2. Experimental

### 2.1. Reagents

Vulcan XC-72 carbon with a specific surface area (BET) of  $240 \text{ m}^2 \text{ g}^{-1}$  and an average particle size of 40 nm were purchased from Cabot Co. and Nafion (perfluorinated ion exchange resin, 5 wt.% solution) was obtained from Aldrich. A platinum precursor ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ), ethylene glycol (EG), sulfuric acid and sodium acetate (NaAc) were purchased from Shanghai Chemical Products Ltd. Deionized water was used to prepare the solutions and high-purity nitrogen gas was also used in the experiments.

### 2.2. Preparation of Pt/C electrocatalysts

In a typical procedure, 2.0 mL of 0.05 M aqueous  $\text{H}_2\text{PtCl}_6$  solution and 50 mL of EG were put into a 100 mL beaker. 0.0, 0.1, 0.3 or 0.5 mL of 1.0 M sodium acetate were added to the EG solution, respectively. Then the mixture was uniformly mixed with 80 mg of Vulcan XC-72 carbon using ultrasound. The beaker was placed in the center of a microwave oven (National NN-MX200WF, 2450 MHz, 800 W) and heated for 60 s at 800 W. The resulting suspension was filtered and the residue was washed with acetone and deionized water. The solid products were dried at  $100^\circ\text{C}$  for 12 h in a vacuum oven. The normal mass fraction of Pt in Pt/C electrocatalysts is about 20%.

### 2.3. Characterizations of Pt/C electrocatalysts

Energy dispersion X-ray spectra analysis (EDX, JEOL JSM-5600LV scanning electron microscope) was used to determine the metal mass fraction of the Pt/C catalysts. XRD patterns were obtained on a D8 Advance Bruker X-ray diffractometer equipped with Cu  $\text{K}\alpha$  as the radiation source ( $\lambda = 0.154056 \text{ nm}$ ) and operating at 40 kV and 40 mA. TEM images were recorded on a JEM-200CX transmission electron microscopy with an acceleration voltage of 160 kV. Sample preparation for TEM examination involved the ultrasonic dispersion of the sample in ethanol and placing a drop of the suspension on a copper grid covered with perforated carbon film. The mean particle size and size distribution were obtained from a few randomly chosen areas in the TEM images containing about 150–200 particles.

### 2.4. Electrochemical measurements

Electrocatalytic activities of Pt/C electrocatalysts for methanol electro-oxidation were measured by cyclic voltammetry and chronoamperometry using a CHI 660B potentiostat/galvanostat and a three-electrode test cell at  $30^\circ\text{C}$ . The electrolyte solution was 2.0 M  $\text{CH}_3\text{OH}$  in 1.0 M  $\text{H}_2\text{SO}_4$ . A Pt foil and a saturated calomel electrode (SCE) were used as the counter and reference electrode, respectively. All potentials in this work are reported with respect to the SCE. The working electrode was a thin layer of Nafion-impregnated catalyst cast onto a vitreous carbon disk with 4.0 mm diameter held in a Teflon cylinder. The working electrode was obtained in the following way: a slurry was first prepared by sonicating a mixture of 500 mg of deionized water, 10 mg of Pt/C electrocatalyst and 200 mg of Nafion solution; then 2.0  $\mu\text{L}$  of the slurry was pipetted and spread on the vitreous carbon disk; the electrode was finally dried at  $80^\circ\text{C}$  for 10 min. The active specific surface area of the Pt particles was calculated according to a hydrogen electroadsorption curve. The potential was cycled between +0.25 and  $-0.25 \text{ V}$  at  $50 \text{ mV s}^{-1}$  in a 1.0 M  $\text{H}_2\text{SO}_4$  electrolyte to obtain the voltammograms of hydrogen adsorption. All electrolyte solutions were deaerated by high purity nitrogen for 30 min prior to any electrochemical measurement.

## 3. Results and discussion

### 3.1. EDX and XRD characterizations of Pt/C catalysts

Fig. 1 shows a typical EDX spectrum of the Pt/C catalysts. The EDX analysis shows that the Pt mass percentage in Pt/C electrocatalysts prepared in this work was 19.2–20.6%, which coincides with the ratio of Pt to carbon support in the starting mixture. XRD patterns of the Pt/C electrocatalysts are shown in Fig. 2. The rather wide diffraction peaks at  $2\theta = 25.0^\circ$  are attributed to the graphite structure (002) of XC-72 carbon. The other diffraction peaks at  $2\theta = 39.8^\circ$  (1 1 1),  $46.4^\circ$  (2 0 0) and  $67.8^\circ$  (2 2 0) can be indexed to face-centered cubic platinum. The diffraction peak at  $2\theta = 39.8^\circ$  for Pt(1 1 1) corresponds to the interplanar spacing of  $d_{111} = 0.227 \text{ nm}$ . The results are consistent with the standard powder diffraction file of Pt (JCPDS

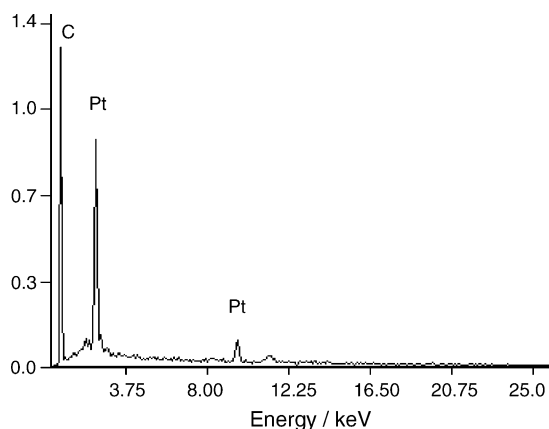


Fig. 1. A typical EDX spectrum of the Pt/C catalyst.

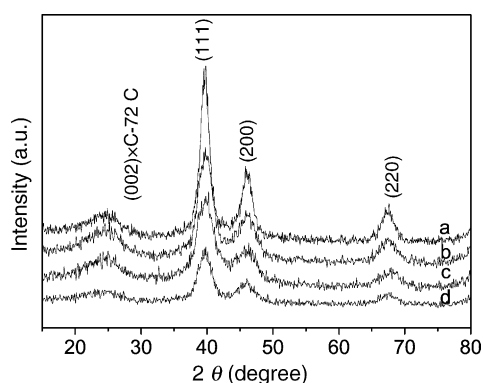


Fig. 2. XRD patterns of Pt/XC-72 catalysts prepared by microwave polyol process adding (a) 0.0 mL, (b) 0.1 mL (c) 0.3 mL and (d) 0.5 mL of 1.0 M sodium acetate solution to the synthesis solution.

No. 04-0802). Fig. 2 also shows that the full width at half max (FWHM) of XRD peaks of Pt particles which increases with the increase of the amount of sodium acetate added, indicating that the Pt particles become smaller. The mean size of the Pt particles was calculated by the Scherrer equation [30]. The results are listed in Table 1. The mean size of the Pt particles decreases from  $4.8 \pm 0.2$  to  $2.6 \pm 0.2$  nm when the amount of sodium acetate solution added to the synthesis solution increases from 0.0 to 0.5 mL.

### 3.2. TEM characterizations of Pt/C catalysts

Fig. 3 shows TEM images and histograms of the Pt particle size distribution of the Pt/C catalysts prepared by the microwave

Table 1  
Mean size of Pt particles of the Pt/C catalysts prepared by adding different amounts of acetate solution to the synthesis solution

Pt/C catalyst	Mean particle size (nm)	
	XRD	TEM
Pt/C catalyst (NaAc = 0.0 mL)	$4.8 \pm 0.2$	$5.1 \pm 0.2$
Pt/C catalyst (NaAc = 0.1 mL)	$3.9 \pm 0.2$	$4.3 \pm 0.2$
Pt/C catalyst (NaAc = 0.3 mL)	$3.2 \pm 0.2$	$3.5 \pm 0.2$
Pt/C catalyst (NaAc = 0.5 mL)	$2.6 \pm 0.2$	$2.8 \pm 0.2$

polyol process with adding sodium acetate to the synthesis solution. Fig. 3(a) shows that the Pt nanoparticles prepared without adding sodium acetate exhibit a large average size of 5.1 nm and a broad size distribution ranging from  $\sim 1.0$  to  $\sim 9.0$  nm. Moreover, the Pt particles are not well dispersed on the carbon support due to their apparent agglomeration. Fig. 3(b)–(d) shows that Pt nanoparticles become smaller and more uniform when a small amount of sodium acetate solution is added to the synthesis solution. The average sizes of Pt particles are 4.3, 3.5 and 2.8 nm, respectively, corresponding to 0.1, 0.3 and 0.5 mL of 1.0 M sodium acetate solution in 50 mL of synthesis solution, which agrees with the results from the XRD (Table 1). In addition, as shown in Fig. 3, Pt nanoparticles are hardly agglomerated and highly dispersed on the carbon surface in the case of adding the proper amount of sodium acetate solution to the EG solution. Therefore, it is evident that acetate can be used as a good stabilizer for preparing small and uniform Pt nanoparticles highly dispersed on carbon support by the microwave assisted polyol process.

### 3.3. Effects of adding acetate on Pt particle size of Pt/C catalysts

The general mechanism for the synthesis of metal nanoparticles by the microwave polyol process is as follows: ethylene glycol has a high dielectric constant and a high reduction capability. When the ethylene glycol solution was exposed to microwave radiation, it was rapidly heated. The temperature of the ethylene glycol solution was measured and was about 170–180 °C at the end of microwave heating. At high temperature, the ethylene glycol would be decomposed to generate reducing species for reduction of the metallic salt precursor to metal particles. The preparation of monodisperse metal particles generally requires control of the nucleation and growth steps. The fast and uniform microwave heating accelerated reduction and nucleation steps, thus greatly facilitated the formation of monodisperse metal particles with fine and uniform size. But in a liquid-phase process, metal particles have a strong tendency to coalesce during their formation. Polymer protective agents, commonly PVP, have been used to avoid the agglomeration of metal particles. The polymer must be removed at high temperature for Pt/C electrocatalysts, but the heat treatment would cause the agglomeration of metal particles. Therefore, electrostatic stabilization is preferred to polymer stabilizers in the case of electrocatalysts. Anions, namely citrate ions, have been used with aqueous colloidal solutions of Ag, Pd, Au, and Pt [22–26]. Acetate anions are found to permit the formation of non-agglomerated Ru particles in polyols [31]. Recently, it was reported that fine and uniform Pt and Ru nanoparticles could be prepared in liquid polyols by adding acetate [28,29]. This means that acetate can be used as a stabilizing agent for preparing non-agglomerated Pt and Ru nanoparticles with small and uniform size. The stabilizing function is due to the acetate anions which with metal particles can form chelate-type complexes via their carboxyl groups. Since acetate was added in the polyol solution as a stabilizer for preparing Pt/C electrocatalysts in this work, its amount added in the synthesis solution would be a key factor that influences the size

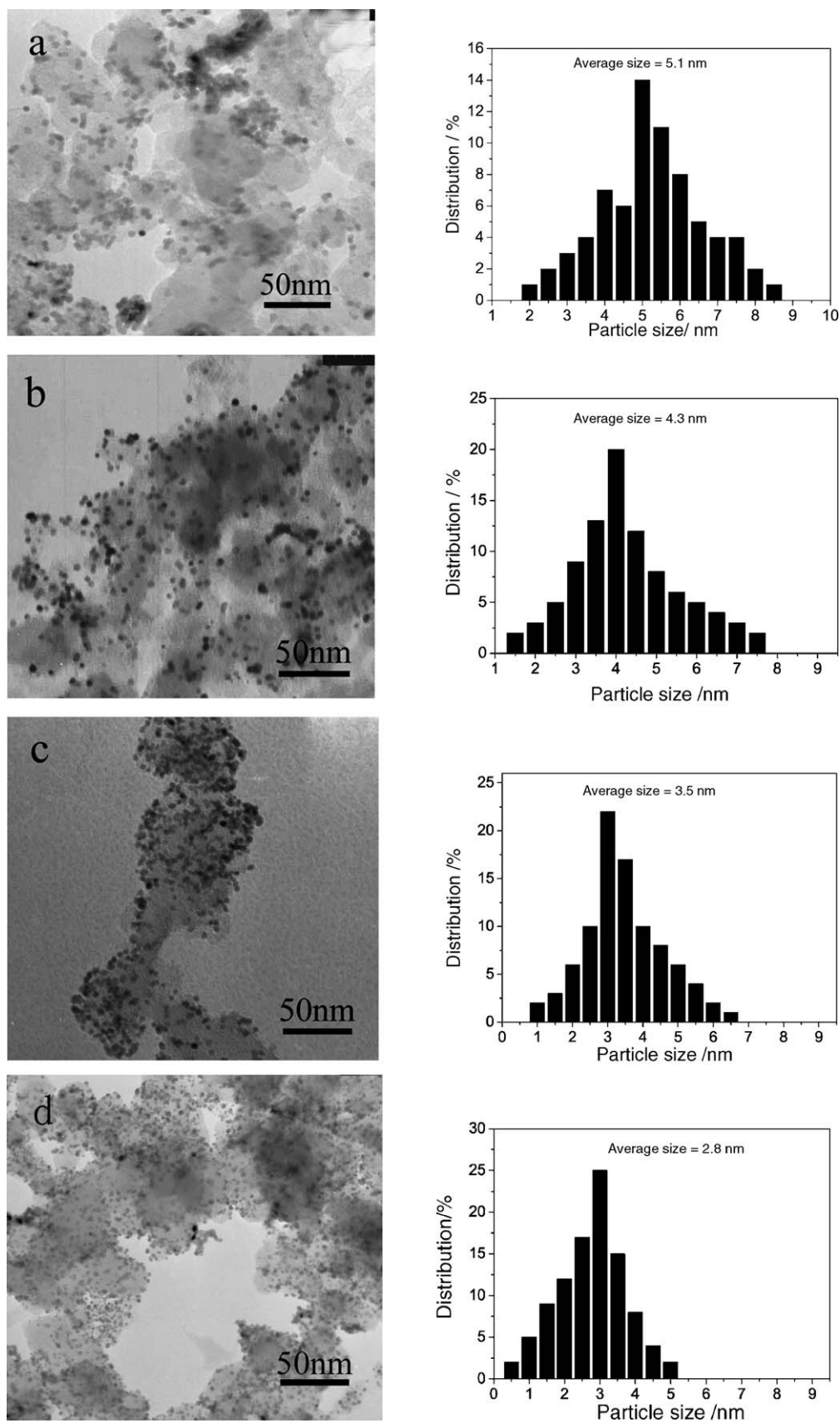


Fig. 3. TEM images and histograms of Pt particles size distributions for Pt/C electrocatalysts prepared by microwave polyol process adding (a) 0.0 mL, (b) 0.1 mL, (c) 0.3 mL and (d) 0.5 mL 1.0 M of sodium acetate solution to the synthesis solution.

and uniformity of Pt particles. As shown in Fig. 3, Pt particles become smaller and more uniform with increase of amount of acetate solution added in the synthesis solution. When 0.5 mL of 1.0 M acetate solution was added into 50 mL of EG solution, Pt nanoparticles have a sharp and narrow size distribution with average size of 2.8 nm. The size of majority of Pt particles ranged from 2.0 and 5.0 nm, with only few particles larger than 5.0 nm or lower than 2.0 nm. Therefore, Pt particle size can be selected by varying the amount of sodium acetate added in the synthesis solution. However, it was observed that the recovered solution was brown when 0.7 mL of 1.0 M sodium acetate solution was added into 50 mL of the EG solution in our experiments. This means that some of Pt nanoparticles were not adsorbed on the XC-72 carbon surface. This is due to the relatively stable complex formation between acetate anions and metal particles at a high acetate/Pt ratio which prevents Pt particles adsorbing onto the carbon surface. According to our study, the amount of acetate solution added in 50 mL of the EG solution shouldn't exceed 0.5 mL of 1.0 M acetate solution.

#### 3.4. Active specific surface area of Pt/C catalysts

In general, the real surface area of Pt particles is one of the important parameters to determine the catalytic properties of electrocatalysts for methanol electro-oxidation since this reaction is surface-sensitive. The active specific surface area of Pt particles for Pt/C catalysts could be estimated from the integrated charge in the hydrogen adsorption region of the cyclic voltammogram, as shown in the hatched area of Fig. 4. The areas in  $\text{m}^2 \text{g}^{-1}$  were calculated from the following formula assuming a correspondence value of  $0.21 \text{ mC cm}^{-2}$  (calculated from the surface density of  $1.3 \times 10^{15} \text{ atom cm}^{-2}$ ), a value generally admitted for polycrystalline Pt electrodes [12] and the Pt loading

$$A_{\text{EL}} (\text{m}^2 \text{g}^{-1} \text{Pt}) = Q_{\text{H}} / (0.21 \times 10^{-3} \text{ C g}^{-1} \text{Pt})$$

where  $A_{\text{EL}}$  is the active specific surface area of Pt particles obtained electrochemically,  $Q_{\text{H}}$  the amount of charge exchanged during the electroadsorption of hydrogen atoms on Pt and C is the Coulomb.

Fig. 4 shows a typical hydrogen electroadsorption voltammetric profiles on Pt/C catalyst in 1.0 M  $\text{H}_2\text{SO}_4$  aqueous solution. The hatched area represents the amount of charge of the electroadsorption of hydrogen of Pt particles. The calculation results of the specific surface of Pt particles are listed in Table 2. It

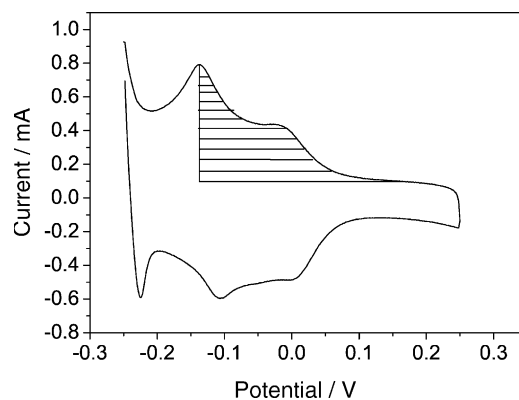


Fig. 4. A typical hydrogen electroadsorption voltammetric profile for a Pt/C electrocatalyst in 1.0 M  $\text{H}_2\text{SO}_4$  at a scan rate of  $50 \text{ mV s}^{-1}$  and room temperature. The Pt/C catalyst was synthesized by the microwave polyol route by adding 0.5 mL of 1.0 M NaAc solution to the synthesis solution. The hatched area represents the amount of charge of the electroadsorption of hydrogen on Pt.

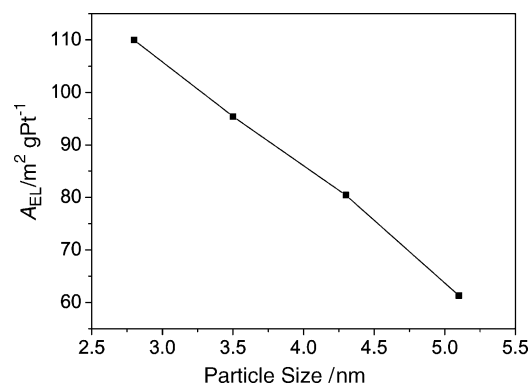


Fig. 5. The relationship between the particle size and the electrochemically active specific surface of Pt/C electrocatalysts.

can be seen that the Pt/C catalysts prepared in polyol with adding acetate solution have much higher Pt surface area than that prepared in polyol without adding acetate. Moreover, the active surface area of Pt particles increases with the increase of the amount of sodium acetate added in polyol solution. This is not surprising in view of smaller and more uniform Pt nanoparticles obtained by adding sodium acetate into the synthesis solution. Fig. 5 shows the relationship between the particle size and the active specific surface. It is clearly showed that the active specific surface increase with the decrease of Pt particle size.

Table 2

Active specific surface areas of Pt particles for Pt/C catalysts as determined by hydrogen electroadsorption

Pt/C catalysts	$d$ (nm)	$m(\text{Pt})$ ( $\mu\text{g}$ )	$Q_{\text{H}}$ (mC)	$S_{\text{EL}}$ ( $\text{cm}^2$ )	$A_{\text{EL}}$ ( $\text{m}^2 \text{g}^{-1} \text{Pt}$ )
Pt/C catalysts (NaAc = 0.0 mL)	$5.1 \pm 0.2$	5.71	0.735	3.5	61.3
Pt/C catalysts (NaAc = 0.1 mL)	$4.3 \pm 0.2$	5.71	0.964	4.59	80.4
Pt/C catalysts (NaAc = 0.3 mL)	$3.5 \pm 0.2$	5.71	1.144	5.45	95.4
Pt/C catalysts (NaAc = 0.5 mL)	$2.8 \pm 0.2$	5.71	1.319	6.28	110.0

$Q_{\text{H}}$ : the amount of charge exchanged during the electroadsorption of hydrogen atoms on Pt particles;  $S_{\text{EL}}$ : the specific surface area of Pt particles obtained electrochemically;  $A_{\text{EL}}$ : the specific surface area of Pt particles obtained electrochemically.

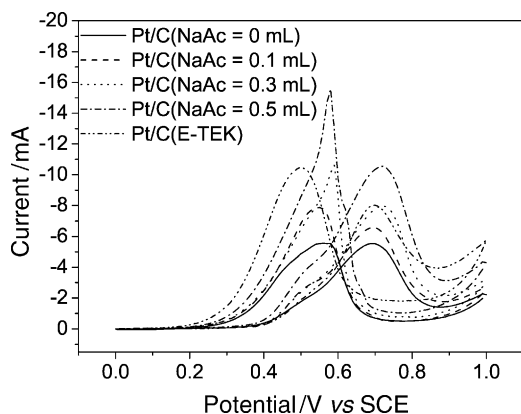


Fig. 6. Cyclic voltammograms of methanol electro-oxidation on Pt/C catalysts in 2.0 M CH<sub>3</sub>OH/1.0 M H<sub>2</sub>SO<sub>4</sub> electrolyte at a scan rate of 20 mV s<sup>-1</sup> at 30 °C. The catalysts were prepared by the microwave polyol process adding (a) 0.0 mL, (b) 0.1 mL, (c) 0.3 mL and (d) 0.5 mL 1.0 M sodium acetate solution to the synthesis solution.

### 3.5. Methanol electro-oxidization over Pt/C catalysts

Fig. 6 shows the cyclic voltammograms of methanol electro-oxidization over Pt/C electrocatalysts prepared in this work and a commercial E-TEK Pt/C catalyst in 2 M CH<sub>3</sub>OH/1 M H<sub>2</sub>SO<sub>4</sub> electrolyte at the room temperature. It can be seen from Fig. 6 that the electro-oxidation of methanol began at about 0.35–0.40 V versus SCE. The current peaks at about 0.70–0.72 V versus SCE in the forward scan are attributed to methanol electro-oxidation. As shown in Fig. 6, the Pt/C electrocatalyst prepared without adding acetate in the synthesis solution displays the lowest current peak for methanol electro-oxidation among these Pt/C electrocatalysts. The low electrocatalytic activity is due to large Pt particle size and a broad size distribution. When a small amount of sodium acetate solution was added in the synthesis solution, Pt/C catalysts displayed higher current peaks for methanol electro-oxidation. The current peaks increase with increase in the amount of sodium acetate solution added to the synthesis solution. In addition, as shown in Fig. 6, when 0.3 mL of the sodium acetate solution was added to the polyol solution, the Pt/C catalyst exhibited almost the same current peak as the E-TEK Pt/C catalyst. When 0.5 mL of the sodium acetate was added, the Pt/C catalyst exhibited a higher current peak than the E-TEK Pt/C catalyst, which demonstrated that the former displayed better electrocatalytic activity for methanol electro-oxidation than the E-TEK Pt/C catalyst. The improvement in electrocatalytic activity was due to the Pt particles of Pt/C catalyst prepared by adding proper sodium acetate in the polyol solution which were small, uniform and highly dispersed. Fig. 7 shows the current peak of methanol electro-oxidation as a function of the active specific surface area of the Pt/C catalysts. It is clearly shown that the current peak increases with the increase of the active specific surface area of the Pt/C catalysts.

The difference is significant enough that the current at 0.4 V versus SCE can be used as an indicator of the catalytic activity of the catalysts under moderate polarization conditions. Pt/C electrocatalysts were therefore biased at 0.4 V versus SCE and

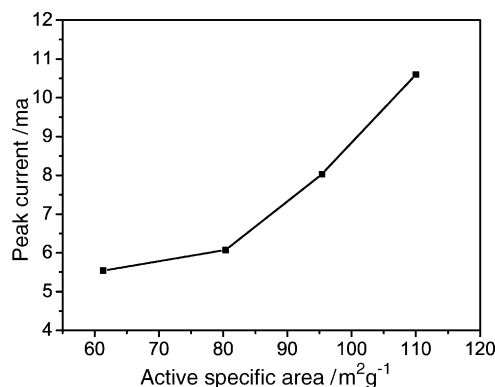


Fig. 7. The peak current of methanol electro-oxidation as a function of the active specific surface area of the Pt/C electrocatalysts.

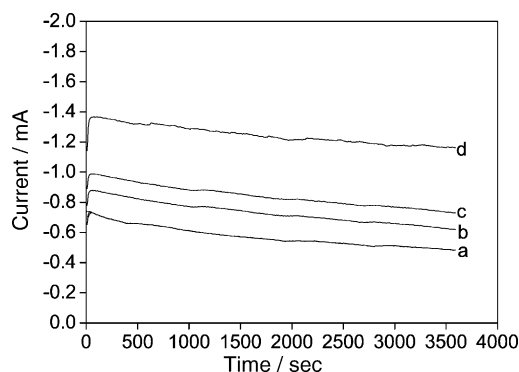


Fig. 8. Polarization current vs. time plots for the methanol electro-oxidation in 2 M CH<sub>3</sub>OH/1 M H<sub>2</sub>SO<sub>4</sub> electrolyte at 0.4 V (vs. SCE) at 30 °C. The catalysts were prepared by microwave polyol process adding (a) 0.0 mL, (b) 0.1 mL, (c) 0.3 mL and (d) 0.5 mL 1.0 M sodium acetate solution to the synthesis solution.

the changes of the polarization currents of methanol electro-oxidation with time were recorded as shown in Fig. 8. Fig. 8 shows that the Pt/C catalysts prepared by adding proper amount of sodium acetate to the polyol solution exhibited not only higher initial current but also a higher current at the same time than the Pt/C catalyst prepared without adding sodium acetate. This indicates that the catalyst prepared by adding acetate displays a better performance than that prepared without adding acetate. In addition, the currents of methanol electro-oxidation over the Pt/C catalysts decreased moderately with time as shown in Fig. 8. The current decay is due to that the intermediate products of methanol oxidization such as CO and other ions in the electrolyte which are easily adsorbed onto the Pt nanoparticles, and inhibit methanol electro-oxidation. It should be noticed that the Pt/C catalysts prepared by adding 0.1, 0.3 and 0.5 mL of the acetate solution still remained 70%, 74% and 85% of the initial current after 1.0 h, respectively, while the Pt/C catalyst prepared without adding acetate remained at only 65% of the initial current after 1.0 h. This indicates that the former shows a more stable electrocatalytic activity than the latter.

## 4. Conclusion

A Pt/C electrocatalyst with small, uniform and highly dispersed Pt nanoparticles was synthesized by a facile microwave-

assisted polyol method by adding the proper amount of sodium acetate to the synthesis solution as a stabilizer. It was found that a small amount of sodium acetate solution could be used as a good stabilizer for preparing Pt/C catalysts in polyol solution. The mean size of the Pt particles was 5.1, 4.3, 3.5 and 2.8 nm, respectively, when the amount of the sodium acetate added in the synthesis solution was 0.0, 0.1, 0.3 and 0.5 mL. A better electrocatalytic performance for methanol oxidation by the Pt/C catalyst prepared by adding proper acetate to the polyol solution was demonstrated by cyclic voltammetry and chronoamperometry. The improvement in electrocatalytic performance was because the Pt/C catalyst prepared by the microwave polyol process had small, uniform and highly dispersed Pt nanoparticles when the proper amount of acetate solution was added to the synthesis solution. The method in this paper is simple, effective, and could be used as an alternative process for preparing high performance electrocatalysts.

### Acknowledgments

This work was financially supported by the Research Fund for the Doctoral Program of Higher Education (No. 20050335086), Scientific Research Foundation for Returned Overseas Chinese Scholars of State Education Ministry (No. 2004-527) and Zhejiang Provincial Natural Science Foundation (Nos. Y404265 and 200053).

### References

- [1] X. Ren, M.S. Wilson, S. Gottesfeld, *J. Electrochem. Soc.* 143 (1996) L12.
- [2] L. Liu, C. Pu, R. Viswanathan, Q. Fan, R. Liu, E.S. Smotkin, *Electrochem. Acta* 43 (1998) 3657.
- [3] M.P. Hogarth, G.A. Hards, *Platinum Met. Rev.* 40 (1996) 150.
- [4] B.D. McNicol, D.A.J. Rand, K.R. Williams, *J. Power Sources* 83 (1999) 15.
- [5] K.L. Ley, R. Liu, C. Pu, Q. Fan, N. Leyarowska, C. Segre, E.S. Smotkin, *J. Electrochem. Soc.* 144 (1997) 1543.
- [6] A.S. Arico, Z. Poltarzewski, H. Kim, A. Morana, N. Giordano, V. Antonucci, *J. Power Sources* 55 (1995) 159.
- [7] B. Gurau, R. Viswanathan, R. Liu, T.J. Lafrenz, K.L. Ley, E.S. Smotkin, A. Sapienza, B.C. Chan, T.E. Mallouk, S. Sarangapani, *J. Phys. Chem. B* 102 (1998) 9997.
- [8] I.S. Armadi, Z.L. Wang, T.C. Green, A. Henglein, M.A. El-sayed, *Science* 272 (1996) 1924.
- [9] K. Kinoshita, *J. Electrochem. Soc.* 137 (1990) 845.
- [10] M. Peuchert, T. Yoneda, R. Betta, *J. Electrochem. Soc.* 133 (1986) 944.
- [11] Y. Takasu, H. Itaya, T. Iwazaki, R. Miyoshi, T. Ohnuma, W. Sugimoto, Y. Murakami, *Chem. Commun.* 341 (2001).
- [12] Z.L. Liu, J.Y. Lee, M. Han, W.X. Chen, L.M. Gan, *J. Mater. Chem.* 12 (2002) 2453.
- [13] Y.H. Lin, X.L. Cui, C.H. Yen, C.M. Wai, *Langmuir* 21 (2005) 11474.
- [14] K. Okitsu, A. Yue, S. Tanabe, H. Matsumoto, *Chem. Mater.* 12 (2000) 3006.
- [15] T. Fujimoto, S. Terauchi, H. Umehara, I. Kojima, W. Henderson, *Chem. Mater.* 13 (2001) 1057.
- [16] W.Y. Yu, W.X. Tu, H.F. Liu, *Langmuir* 15 (1999) 6.
- [17] W.X. Tu, H.F. Liu, *Chem. Mater.* 12 (2000) 564.
- [18] S. Komarneni, D.S. Li, B. Newalkar, H. Katsuki, A.S. Bhalla, *Langmuir* 18 (2002) 5959.
- [19] L.K. Kurihara, G.M. Chow, P.E. Schoen, *Nanostruct. Mater.* 5 (1995) 607.
- [20] F. Bonet, V. Delmas, S. Grugeon, R.H. Urbina, P.Y. Silvert, K. Tekaiia-Elhsissen, *Nanostruct. Mater.* 11 (1999) 1277.
- [21] L. Dubeau, C. Coutanceau, E. Garnier, J.M. Leger, C.J. Lamy, *Appl. Electrochem.* 33 (2003) 419.
- [22] Y. Lin, G.B. Pan, G.J. Su, X. Hong, L.J. Wan, C.L. Bai, *Langmuir* 19 (2003) 10000.
- [23] J. Turkevich, G. Kim, *Science* 169 (1970) 873.
- [24] Z.S. Pillai, P.V. Kamat, *J. Phys. Chem. B* 108 (2004) 945.
- [25] A. Henglein, M. Giersig, *J. Phys. Chem. B* 104 (2000) 6767.
- [26] J.W. Guo, T.S. Zhao, J. Prabhuram, C.W. Wong, *Electrochim. Acta* 50 (2005) 1973.
- [27] C. Bock, C. Paquet, M. Couillard, G.A. Botton, B.R. Macdougall, *J. Am. Chem. Soc.* 126 (2004) 8037.
- [28] J. Yang, T.C. Deivaraj, H.P. Too, J.Y. Lee, *Langmuir* 20 (2004) 4241.
- [29] G. Viau, R. Brayner, L. Poul, N. Chakroune, E. Lacaze, F. Fievet-Vincent, F. Fievet, *Chem. Mater.* 15 (2003) 486.
- [30] B.E. Warren, *X-ray Diffraction*, Addison-Wesley, Reading, MA, 1996.
- [31] N. Chakroune, G. Viau, S. Ammar, L. Poul, D. Veautier, M.M. Chehimi, C. Mangeney, F. Villain, F. Fievet, *Langmuir* 21 (2005) 6788.