



Performance of Pt/C catalysts prepared by microwave-assisted polyol process for methanol electrooxidation

Yuan-Yuan Chu, Zhen-Bo Wang*, Da-Ming Gu, Ge-Ping Yin

School of Chemical Engineering and Technology, Harbin Institute of Technology, No. 92 West-Da Zhi Street, Harbin 150001, China

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ABSTRACT

Pt nanoparticles catalysts supported on the Vulcan XC-72 carbon black with different mean sizes have been synthesized by microwave-assisted polyol process and characterized by energy dispersive analysis of X-ray (EDAX), X-ray diffraction (XRD), and transmission electron microscopy (TEM). The results of physical examinations show that Pt nanoparticles have a narrow size distribution and are highly dispersed on the surface of carbon support, and Pt loading in Pt/C catalyst is the similar with the theoretical value. The results of cyclic voltammetry and chronoamperometry demonstrate that the Pt/C catalyst prepared by microwave-assisted polyol process at the pH value of about 12 exhibits the highest catalytic activity for methanol electrooxidation. The activity of Pt/C catalyst is also related to the microwave heating time, and the optimal heating time is 40 s in this work.

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1. Introduction

Direct methanol fuel cell (DMFC) uses directly methanol without prior complicated reforming. DMFC has been receiving increasing attention due to its advantages of easy transportation and storage of the fuel, reduced system weight, size, and complexity, and high energy efficiency [1–4]. However, one of the major problems is the poisoning of anode catalyst by carbon monoxide from methanol electrooxidation, which results in the slow kinetics of anode methanol oxidation reaction (MOR). As is well known, the catalysts with a small particle size and good dispersion on their supports displayed excellent catalytic behavior. So the preparation of such nanoparticles with uniform size metal particles on the carbon support remains to be a challenging work. It is of great importance to find a simple, fast, and efficient approach to prepare high performance catalyst for fuel cell applications.

As a rapid and uniform heating method, microwave-assisted polyol process has been widely used in preparing metal particles [5–10]. In this method, ethylene glycol (EG) is commonly used as a solvent and reducing agent for the metal salt compounds, and a protecting agent for the metal nanoparticles. Chen et al. [11] prepared Pt/XC-72 carbon with particle size 3.5–4.0 nm by microwave polyol process with heating time of 50 s, which has good electrocatalytic properties for methanol electrooxidation. Zhao et al. [12] used graphite nanofibers (GNFs) as a support that can prevent

agglomeration of Pt particles to prepare Pt/GNFs catalyst with the microwave-assisted heating polyol process, which also showed high electrochemically active for methanol electrooxidation. Chen et al. [13] prepared carbon nanotubes (CNTs) supported Pt catalyst with uniform particle size and well dispersed on the surface of CNTs with the similar technique.

Li et al. [14] investigated the effect of pH value of reaction solution from 3.6 to 9.2 on particle size and electrocatalytic activity of Pt/CNTs catalysts for methanol electrooxidation, and indicated that the Pt/CNTs catalyst prepared at the reaction solution pH value of 7.4 exhibited the best performance for methanol electrooxidation than other samples. In addition, Zhao et al. [15] also reported the influence of pH value of reaction solution from 3.4 to 9.5 on the particle size and uniformity of Pt catalysts prepared by microwave-assisted polyol process and pointed that Pt nanoparticles with average size of 2.7 nm prepared at the pH value of 9.5 showed the highest activity for methanol electrooxidation. It has been proved that the alkalinity of the EG solution is a key factor improving the formation of small and uniform colloidal particles and stabilization of unprotected metal colloids. Wang et al. [16] had modified the polyol process by introducing ethylene glycol solution of alkaline pH value (>12) without the addition of a stabilizing agent and obtained stable Pt, Rh, and Ru colloids with small particle size. In addition, Yang and coworkers [17] thought that hydroxide ions were needed for the generation of acetate ions which are responsible for stabilizing the metal nanoparticles in ethylene glycol. From reports above, the activity evaluation on the performance of Pt/C catalyst prepared at higher pH values by microwave-assisted polyol process is still an open question. So we explore the influences of pH

* Corresponding author. Tel.: +86 451 86417853; fax: +86 451 86413707.
E-mail address: wangzhenbo1008@yahoo.com.cn (Z.-B. Wang).

values of reaction solution from 9 to 12.8 on the particle size and electrocatalytic activity of Pt/C catalysts for methanol electrooxidation in this paper. Few reports focus on the effect of the different microwave heating times on the performance of Pt/C catalyst. Most researchers prepared catalysts by consecutive microwave heating time of 50 s [18] or 60 s [14,15]. Shen and Tian [19] prepared highly dispersed Pt/C (Pt loading 60%) catalyst by intermittent microwave heating (IMH) that is alternative heating with on 10 s–off 40 s for five times. In present work, the influences of the microwave heating time on the particle size and uniformity of Pt nanoparticles and their electrocatalytic activity for methanol electrooxidation were investigated.

2. Experimental

2.1. Pt/C catalysts prepared by microwave-assisted process

Pt/C catalysts with the Pt loading of 20 wt.% were prepared by microwave-assisted polyol process in ethylene glycol (EG) solution with H_2PtCl_6 as a precursor salt. Briefly, 50 mg Vulcan XC-72 carbon black was dispersed into 30 mL ethylene glycol and isopropyl alcohol (v/v = 4:1) in 100 mL beaker under ultrasonic treatment for 1 h to form uniform carbon ink, then 1.7 mL of $0.037813 \text{ mol L}^{-1}$ H_2PtCl_6 -EG solution with the subsequent mixing process for 3 h. The pH value of the ink was adjusted by adding 1 mol L^{-1} NaOH-EG solution drop by drop. The different pH values from 9 to 12.8 was measured by the PHS-32 meter, the beaker was placed the center of a microwave oven (2450 MHz, 800 W) and argon gas was feed into the ink for 15 min to remove oxygen for intermittent microwave heating (IMH) in a 10 s on–20 s off alternative program for four times or consecutive heating (CH) time for 30 s, 40 s, and 50 s to fix platinum nanoparticles on carbon support. The solution was allowed to cool down to room temperature with continuous stirring, and then 0.1 mol L^{-1} HNO_3 was added into the cooled mixture to adjust the solution pH value to 4. The mixture was kept stirring for 12 h and then the product was washed repeatedly with ultra-pure water ($18.2 \text{ M}\Omega \text{ cm}$) until no Cl^- ions were detected. The homemade Pt/C catalyst was dried for 3 h at 80°C and then stored in a vacuum vessel. All chemicals used were of analytical grade.

2.2. Electrode preparation and electrochemical measurement

2.2.1. Preparation of working electrode

The ultrasonically re-dispersed catalyst suspension ($5 \mu\text{L}$) was spread by pipette onto the glassy carbon disk substrate. The subsequent evaporation of solvent leads to the formation of the deposited catalyst layer ($28 \mu\text{g}_{\text{metal}} \text{ cm}^{-2}$), onto which $5 \mu\text{L}$ of a dilute aqueous Nafion[®] solution (5 wt.% solution in a mixture of lower aliphatic alcohols and DuPont water) was applied. The resulting Nafion[®] film with a thickness less than $0.2 \mu\text{m}$ had the sufficient strength to keep carbon particles permanently on the glassy carbon electrode without producing significant film diffusion resistances [20]. The glassy carbon working electrode with 3 mm of diameter and 0.0706 cm^2 of electrode area was polished with $0.05 \mu\text{m}$ alumina to a mirror finish before being used as the substrate for carbon-supported catalyst.

2.2.2. Electrochemical measurements

Electrochemical measurements were carried out in a conventional sealed three-electrode electrochemical cell at 25°C , with the glassy carbon disk electrode made in the above mentioned procedure as the working electrode and a piece of Pt foil (1 cm^2) as the counter electrode. The reference electrode was a reversible hydrogen electrode (RHE) with its solution connected to the working electrode by a Luggin capillary whose tip was placed appropriately close to the working electrode. All chemicals used were of analytical grade, and solutions were prepared with ultra-pure water

(MilliQ, Millipore, $18.2 \text{ M}\Omega \text{ cm}$). The solution of 0.5 mol L^{-1} H_2SO_4 containing 0.5 mol L^{-1} CH_3OH was kept on constantly stirring and purging with ultra-pure argon gas. The cyclic voltammograms (CV) were recorded within a potential range from 0.05 V to 1.2 V. The chronoamperometric curves were plotted with CHI650A electrochemical analysis instrument controlled by an IBM PC. In order to get rid of the possible contaminations caused by Nafion[®] film, the working electrode was treated by continuously cycling at 0.05 V s^{-1} until a stable response was obtained before the measurement curves were recorded. Fresh electrolyte solution was used for each time electrochemical measurement in order to ensure repeated results. All potentials are reported versus RHE.

2.3. Characterization of physical properties

2.3.1. X-ray diffraction (XRD)

XRD analysis of catalyst was carried out with the D/max-rB diffractometer (made in Japan) using a Cu K α X-ray source operating at 45 kV and 100 mA, scanning at a rate of 4° min^{-1} with an angular resolution of 0.05° of the 2θ scan to get the XRD pattern.

2.3.2. Transmission electron micrograph (TEM)

TEM for the catalyst samples were taken by a Japan JEOLJEM-2010EX transmission electron microscope with a spatial resolution of 1 nm. Before taking the electron micrographs, the catalyst samples were finely ground and ultrasonically dispersed in isopropyl alcohol, and a drop of the resultant dispersion was deposited and dried on a standard copper grid coated with a polymer film. The applied voltage was 100 kV.

2.3.3. Energy dispersive analysis of X-ray (EDAX)

For a rapid EDAX analysis of chemical composition, the Hitachi-S-4700 analyzer was coupled to a scanning electron microscope (SEM, Hitachi Ltd., S-4700), with the incident electron beam energies ranging from 3 to 30 keV, which impinges the sample surface from the normal angle. The measurement time was 100 s, and the EDAX spectra were obtained by using the ZAF correction, which takes account of the matrix influence.

3. Results and discussion

3.1. Physical measurements of Pt/C catalysts

EDAX patterns of the Pt/C catalysts are shown in Fig. 1. The mass fractions of Pt in Pt/C catalysts prepared by microwave-assisted ethylene glycol process ranged from 17.3 wt.% to 18.2 wt.% at the reaction solution pH value of 12 (Fig. 1A) and 11 (Fig. 1B), respectively, which are close to the theoretical values of 20 wt.%.

XRD patterns of Pt/C catalysts prepared at different pH values are presented in Fig. 2. The first peak at 2θ about 26.2° is attributed to Vulcan XC-72 carbon support. The major peaks located at 2θ of 39.7° , 46.2° , 67.4° , and 81.2° are ascribed to Pt(1 1 1), Pt(2 0 0), Pt(2 2 0), and Pt(3 1 1) characteristic diffraction peaks, respectively, which forms a face-centered cubic (f.c.c.) structure. Pt(2 2 0) diffraction peak is relatively broad, indicating that the particle size of Pt/C catalysts is relatively small. The Pt(2 2 0) peak is selected to calculate the average particle size of Pt/C nanoparticles according to Debye–Scherrer formula [21] because it is isolated from the diffraction peaks of carbon support. The average sizes of Pt nanoparticles are about 2.9, 2.6, 2.2, 2.1, and 2.3 nm, respectively, at the pH values of 9, 10, 11, 12, and 12.8, as presented in Table 1. The results above indicate that the higher pH value of reaction solution can improve the size uniformity and dispersion of Pt nanoparticles on the surface of Vulcan XC-72 carbon support.

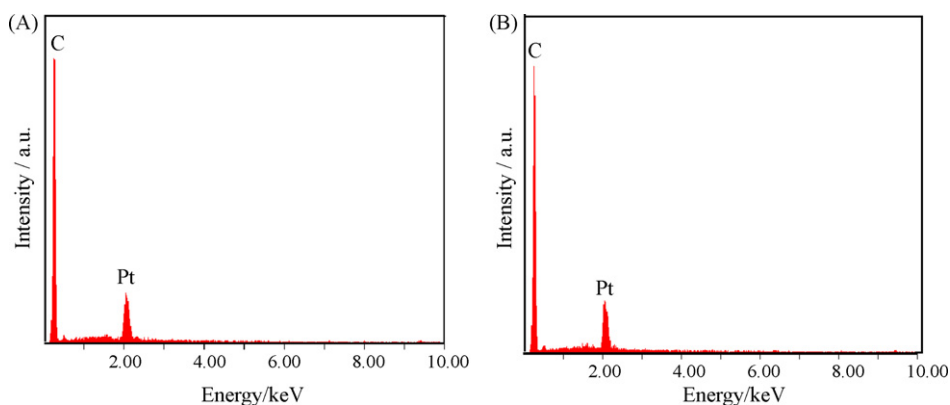


Fig. 1. EDAX patterns of the Pt/C catalysts prepared at the solution pH values of 12 (A) and 11 (B).

Table 1

Comparison of particle size, ESA, CSA, and Pt utilization of various Pt/C catalysts.

Pt/C catalyst	pH value	Particle size from XRD (nm)	EAS from CV ($\text{m}^2 \text{g}^{-1} \text{Pt}$)	CSA from XRD ($\text{m}^2 \text{g}^{-1} \text{Pt}$)	η_{Pt} (=ESA/CSA) utilization (%)
1	9	2.9 ± 0.1	53.8	96.7	55.6
2	10	2.6 ± 0.1	61.7	107.8	57.2
3	11	2.2 ± 0.1	72.3	127.4	56.7
4	12	2.1 ± 0.1	83.7	133.5	62.7
5	12.8	2.3 ± 0.1	67.3	121.9	55.2

Fig. 3 presents the TEM image of Pt/C catalyst at the reaction solution pH value of 12. It can be seen from TEM image that the size of Pt/C nanoparticles is small, and their dispersion on carbon support is very even without agglomeration. It is well known that the even distribution and a smaller particle size of Pt nanoparticles on the carbon support are key factors for enhancing its electrocatalytic activity and efficiency [22,23].

3.2. Effect of pH value on the performance of Pt/C catalyst

Fig. 4 shows the CV curves for homemade Pt/C catalysts in a solution of $0.5 \text{ mol L}^{-1} \text{H}_2\text{SO}_4$ at a scan rate of 50 mV s^{-1} at 25°C . In Fig. 4, the integrated charge in the hydrogen absorption region of cyclic voltammograms was used to calculate the electrochemically active surface (EAS), which reflects the intrinsic electrocatalytic activity of a catalyst, from the recognized formula assuming a correlation value of 0.21 mC cm^{-2} (calculated from a surface density of $1.3 \times 10^{15} \text{ at. cm}^{-2}$), a value generally admitted for poly-crystalline Pt electrode [24].

$$\text{EAS} = \frac{Q_{\text{H}}}{0.21 \times 10^{-3} \text{C} \times (g_{\text{catalyst}})} \quad (1)$$

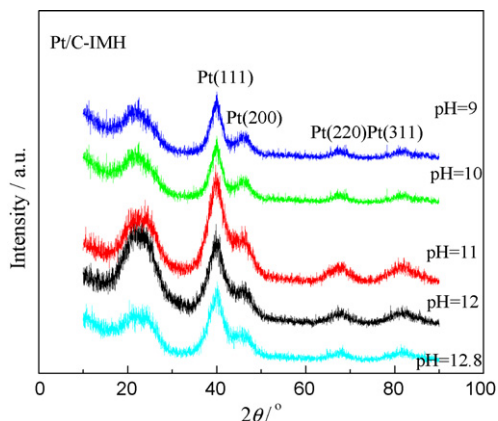


Fig. 2. XRD patterns of the Pt/C catalysts prepared at different solution pH values.

where Q_{H} is the amount of charge-exchanged during the electroadsorption of hydrogen atoms on Pt surface (insert picture in Fig. 4) and C is C. The EAS calculations of homemade catalysts are listed in Table 1. It can be seen that the EAS of Pt/C catalysts increase with the increase of the reaction solution pH values from 9 to 12, and reaches the maximum and the catalyst's utilization (EAS/chemical surface area (CSA)) at the pH value of 12 is also the highest, and then the EAS of Pt/C catalyst decrease under the higher pH value of 12.8. This is not surprising in view of the decrease of the average particle size of Pt nanoparticles with the increasing of the pH value and the smallest mean particle size under the pH value of 12.

Fig. 5 shows the CV curves of methanol electrooxidation on the homemade Pt/C catalysts in an Ar-saturated solution of $0.5 \text{ mol L}^{-1} \text{H}_2\text{SO}_4$ containing $0.5 \text{ mol L}^{-1} \text{CH}_3\text{OH}$ at a scan rate of 20 mV s^{-1} at 25°C . It can be observed from Fig. 5 that the onset potential

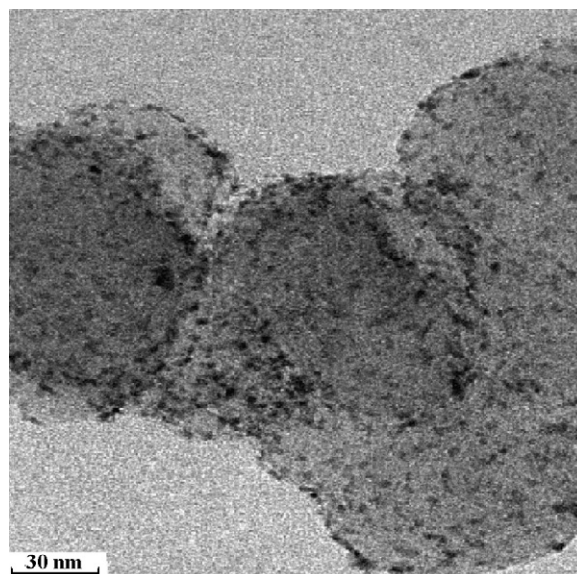


Fig. 3. TEM micrograph of the Pt/C catalyst prepared at the solution pH value of 12.

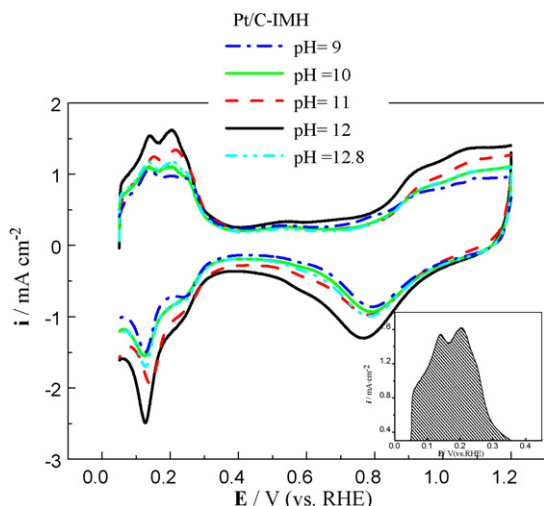


Fig. 4. Cyclic voltammograms of Pt/C catalysts prepared at different solution pH values in an Ar-saturated solution of $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ at 25°C . Scanning rate: 0.05 V s^{-1} .

and peak potential for methanol electrooxidation on Pt/C catalysts prepared at different pH values are almost the same, about 0.60 V and 0.87 V (vs. RHE), respectively. But, their peak currents are obviously different. It can be seen that the current measured on the Pt/C catalyst prepared at the reaction solution pH value of 12 reaches 11.6 mA cm^{-2} , which exhibits the highest current density at all corresponding samples. The results above indicate that the Pt/C catalyst prepared at the pH value of 12 shows better catalytic performance for methanol electrooxidation than other samples. It is because that it has small and uniform particle size and narrow size dispersion on Vulcan XC-72 carbon support.

Fig. 6 shows the chronoamperometric curves at a constant potential jumping from 0.05 V to 0.6 V in an Ar-saturated solution of $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ containing $0.5 \text{ mol L}^{-1} \text{ CH}_3\text{OH}$ at 25°C . The final current density at 1000 s are 0.12 , 0.15 , 0.34 , 0.44 , and 0.16 mA cm^{-2} at the pH value of 9, 10, 11, 12, and 12.8, respectively. It is clear that the Pt/C catalyst at the pH value of solution of 12 has the maximal current density in accordance with the results of CV curves of methanol electrooxidation, which clearly demonstrates again that the more uniform particle size distribution, the better catalytic activity for methanol electrooxidation. Moreover, the final pH values of reaction solutions are about 0.3 , 0.7 , 7.8 , 11.6 , and 12.4 when the initial pH values of reaction solutions are 9, 10,

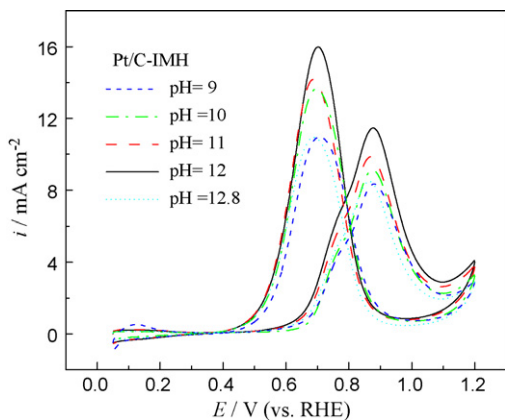


Fig. 5. Cyclic voltammograms of methanol electrooxidation in an Ar-saturated solution of $0.5 \text{ mol L}^{-1} \text{ CH}_3\text{OH}$ and $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ at 25°C on the Pt/C catalysts prepared at different solution pH values at 25°C . Scanning rate: 0.02 V s^{-1} .

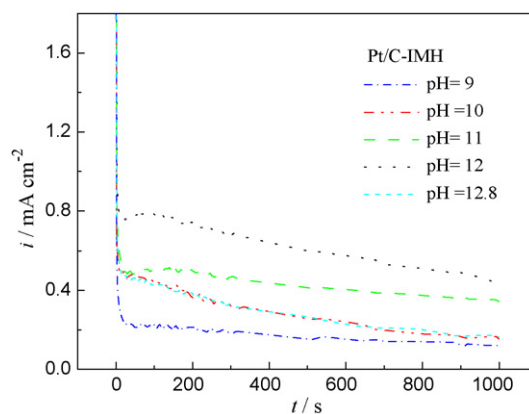


Fig. 6. Chronoamperometric curves of methanol electrooxidation in an Ar-saturated solution of $0.5 \text{ mol L}^{-1} \text{ CH}_3\text{OH}$ and $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ on the Pt/C catalysts prepared at different solution pH values at 25°C . Potential jumps from 0.05 V to 0.6 V .

11, 12, and 12.8, respectively. The final pH value of reaction solution correlates with the catalytic performance of Pt/C catalyst for methanol electrooxidation. It may be concluded that the Pt/C catalysts with the higher final solution pH value results in smaller and more uniform particle size. Because the glycolate anion forms in alkaline ($\text{pH} > 6$) media and acts as a good stabilizer for the Pt colloids, while in lower final pH value ($\text{pH} < 2$), glycolate is nearly non-existing and replaced by glycolic acid which is a poor stabilizer [25], leading to the catalyst particle size agglomeration. But in much higher final pH value of reaction solution, the ionic strength of the glycolate anion may be too strong to prevent the deposition of Pt colloids on the carbon support. In addition, the electrostatic interaction [26] between non-occupied electrons of glycolate anion and negative charges of carbon surface repulses each other, which also may result in agglomeration or the non-uniform distribution on the carbon support. Those may cause the decline of Pt utilization, which in turn decreases catalytic activity of Pt/C catalyst for methanol electrooxidation.

3.3. Effect of microwave heating time on the performance of Pt/C catalyst

In this section, it aims to investigate the exact influence microwave heating time on the resulting particle characteristic, which was rarely reported. CVs of methanol electrooxidation on homemade Pt/C catalysts prepared for consecutive heating times of 30 s , 40 s , and 50 s , respectively, are presented in Fig. 7. The EAS of Pt/C catalysts prepared for different heating times are calculated from CVs in a solution of $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ as shown curves inserted in Fig. 7. It can be seen that the peak current densities on homemade Pt/C catalysts increase firstly and then decrease with the microwave heating time. The catalytic activity of Pt/C catalyst prepared for heating time of 40 s is the highest. The temperature of reaction solution reaches about 110°C , 130°C , and 150°C for consecutive heating times of 30 s , 40 s , and 50 s , respectively. Although the EAS calculations of Pt/C catalysts for different heating times are almost the same (insert picture in Fig. 7), their catalytic behavior for methanol electrooxidation is evidently different. It is because that the Pt/C catalyst prepared at the solution temperature of about 130°C (heating time of 40 s) has a suitable and uniform particle size for methanol electrooxidation, that is 2.1 nm from XRD pattern (Fig. 8) with well dispersed on carbon support. When the particle size of Pt catalyst is too large or too small, it is not benefit for methanol adsorption and oxidation [27], as the heating times of samples were 30 s and 50 s with Pt nanoparticle sizes of 2.5 nm and 1.7 nm , respectively. In addition, the too

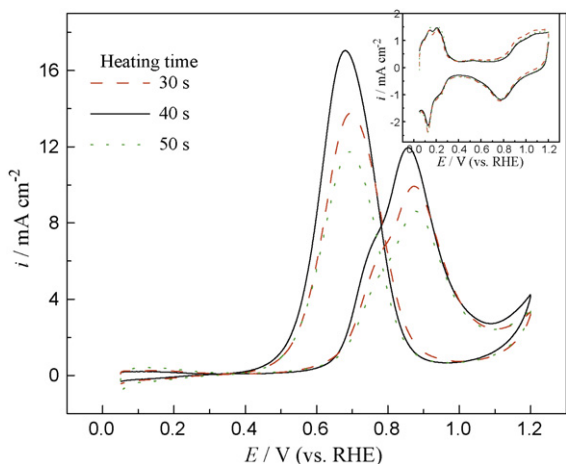


Fig. 7. Cyclic voltammograms of methanol electrooxidation in an Ar-saturated solution of $0.5 \text{ mol L}^{-1} \text{ CH}_3\text{OH}$ and $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ at 25°C on the Pt/C catalysts prepared for different microwave heating times at 25°C . Scanning rate: 0.02 V s^{-1} (insert picture: cyclic voltammograms in an Ar-saturated solution of $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ on the Pt/C catalysts. Scanning rate: 0.05 V s^{-1}).

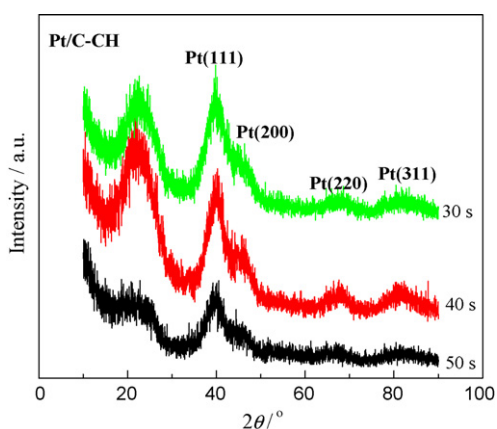


Fig. 8. XRD patterns of the Pt/C catalysts prepared for different microwave heating times.

small catalyst particles may be buried in the micropores of carbon black support [28], which declines the utilization of Pt and results in the decrease of Pt/C catalyst performance. The investigation showed the PtRu/C catalyst with particle size of 2 nm presented the highest activity for methanol electrooxidation [29]. This size is

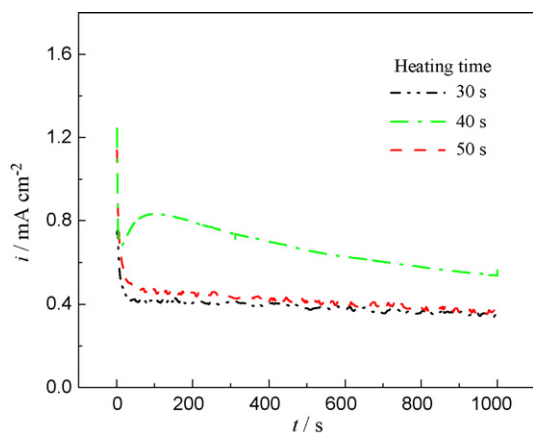


Fig. 9. Chronoamperometric curves of methanol electrooxidation in an Ar-saturated solution of $0.5 \text{ mol L}^{-1} \text{ CH}_3\text{OH}$ and $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ on the Pt/C catalysts prepared for different microwave heating times at 25°C . Potential jumps from 0.05 V to 0.6 V.

similar to that of homemade Pt/C catalyst prepared for the heating time 40 s, which is in favor of methanol electrooxidation. So, the activity of Pt/C catalyst prepared for the heating time of 40 s with the particle size of 2.1 nm for methanol electrooxidation is the highest.

Fig. 9 shows the chronoamperometric curves at a constant potential jumping from 0.05 V to 0.6 V in an Ar-saturated solution of $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ containing $0.5 \text{ mol L}^{-1} \text{ CH}_3\text{OH}$ at 25°C . The final current density at 1000 s for the microwave heating time of 40 s reaches the maximal current density, which enhances to about 150% of that for microwave heating times of 30 s and 50 s, which is similar to the results of cyclic voltammetry. The significant improvement further demonstrates that the Pt/C catalyst prepared for the microwave heating time of 40 s has the maximal stability for methanol electrooxidation.

4. Conclusions

Pt nanoparticles supported on the Vulcan XC-72 carbon black with different particle size of Pt were prepared by microwave-assisted polyol process. The fast and uniform microwave irradiation heating provided a more homogeneous environment for the quick nucleation and the growth of Pt nanoparticles. The pH value of reaction solution and the microwave heating time were demonstrated to be the important factors influencing the particle size of Pt/C catalyst and their activity for methanol electrooxidation. When the pH value of reaction solution is 12 and the microwave heating time is 40 s, the Pt/C catalyst exhibits the best performance for methanol electrooxidation.

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