Short communication

Pulse-microwave assisted polyol synthesis of highly dispersed high loading Pt/C electrocatalyst for oxygen reduction reaction

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Abstract

In the present investigation, a high loading Pt/C up to 50% (weight ratio) was prepared by a pulse-microwave assisted polyol synthesis method, in which the metal reduction can be accomplished in 2 min. X-ray diffraction (XRD) and transmission electron microscopy (TEM) results showed that the Pt particles were highly dispersed on the support and had a narrow particle distribution with a mean particle size of about 2.7 nm. Based on the electrochemical properties characterized by cyclic voltammetry and rotating disk electrode techniques, it was found that the as-prepared 50% Pt/C exhibited a comparable activity for oxygen reduction reaction with respect to the commercial one.
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Keywords: Oxygen reduction reaction; Pt/C; Pulse-microwave assisted polyol synthesis method

1. Introduction

Platinum catalyst is still the main electrocatalyst widely employed in proton exchange membrane fuel cells (PEMFCs) due to its high activity and superior stability. Until now, it is still desirable to rapidly synthesize the highly dispersed supported platinum with uniform particle size. Impregnation and colloid methods are conventionally adopted for the preparation Pt-based catalysts [1–4]. However, the former cannot avoid the larger particle size and broader size distribution, while the latter is always quit complex. The modified polyol method has been successfully used in the synthesis of high active Pt/C with a high loading (40%) [5]. On the other hand, in this process the metal reduction takes at least 3–6 h. Therefore, it is necessary to develop an effective way for time-saving preparation of the highly dispersed and high loading Pt/C catalyst. Microwave irradiation has exhibited a remarkable effect on nanoparticles preparation [6–11]. Chen et al. has already prepared Pt and PtRu supported on carbon or carbon nanotubes with ∼3 nm and uniform dispersion by microwave heated polyol synthesis method [12–14].

However, in their cases, only lower metal loading catalyst was prepared and characterized. Considering that high loading Pt/C catalyst is desirable for fuel cell in order to make the system compact, in the present investigation, highly dispersed high loading Pt/C up to 50% was obtained by a pulse-microwave assisted polyol method (PMP), in which the metal reduction was accomplished in 2 min in the presence of ethylene glycol (EG). The pulse-microwave procedure was adopted in order to avoid the agglomeration of the metal particles at high temperatures. This is due to the fact that continuous microwave can easily cause a quite rapid heating rate for carbon materials. In this process, EG acts not only as dispersant and reducing agent, but also as the microwave additive due to the fact that the dielectric constant (41.4 at 25 °C) and dielectric loss for ethylene glycol are high, and consequently rapid heating takes place under the microwave radiation. The support, carbon (Vulcan XC-72R, Cabot Corp.) is also a microwave-sensitive material, which is believed to play an important role in the acceleration of the metal reduction.

2. Experimental

2.1. Catalyst preparation

The 50% Pt/C electrocatalysts were easily and fast prepared by a novel pulse-microwave assisted polyol method. The pri-

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mary steps of this synthesis process are given as follows. In a beaker, chloroplatinic acid, the starting precursors was well mixed with ethylene glycol in an ultrasonic bath, and then XC-72R carbon black (Cabot Corp., $S_{BET} = 236.8 \, m^2 \, g^{-1}$) were added into the mixture. After adjusted pH value of system more than 10 by the drop-wise addition of $1.0 \, mol \, L^{-1}$ NaOH/EG, the well-dispersed slurry was obtained with stirring and ultrasonication for 30 min. Thereafter, the slurry was microwave-heated in the form of pulse every 5 s for several times. In order to promote the adsorption of the suspended Pt nanoparticles onto the support, hydrochloric acid was adopted as the sedimentation promoter. The resulting black solid sample was filtered, washed and dried at 80 °C for 10 h in a vacuum oven. Pt/C (Johnson Matthey Corp.) was also employed as a reference cathode electrocatalyst for oxygen electroreduction. The commercial and as-prepared Pt/C catalysts are denotes Pt/C-JM and Pt/C-PMP, respectively.

2.2. Catalyst characterization

The XRD measurements were carried out on a D/Max-IIIA (Rigaku Co., Japan) using Cu Kα radiation ($\lambda = 0.15406$ nm), and operating at 40 kV and 40 mA. The 2θ angular regions between 10° and 90° were explored at a scan rate of 5° min^{-1} and the 64–72° angle range was scanned at 1° min^{-1} in order to obtain Pt particle size precisely according to the Scherrer formula [15]. TEM investigations were carried out in a JEOL JEM-2010(HR) operating at 200 kV to get information of the mean particle size and size distribution of Pt particles of the catalysts. The histogram of the prepared Pt-based catalyst was made by measuring more than 300 particles.

All electrochemical measurements were conducted on a PARSTAT 2273 instrument in a thermostat-controlled standard three-electrode cell at room temperature adopting a saturated calomel electrode (SCE) and a platinum foil as the reference electrode and the counter electrode, respectively. A glass carbon (GC) disk electrode, polished to a mirror-finish with a 0.05 μm alumina suspension before each experiment, was used as substrate for the electrocatalyst thin film in the electrochemical measurements. The thin film catalyst layer as the working electrode was prepared as follows: a mixture containing 5.0 mg electrocatalyst, 0.9 mL ethanol and 0.1 mL Nafion solution (5 wt.%) was dispersed in a ultrasonic bar for 15 min to obtain a well-dispersed ink. The catalyst ink was then quantitatively transferred onto the surface of the GC electrode by using a micropipette, and dried under infrared lamp to obtain a catalyst thin film. The Pt loading was 0.203 mg cm^{-2} for 40% Pt/C and 0.255 mg cm^{-2} for 50% Pt/C respectively. An aqueous solution containing 0.5 mol L^{-1} H$_2$SO$_4$ was used as electrolyte, which was deareated with high-pure nitrogen gas. Rotating disk electrode (RDE) was carried out in an oxygen-saturated 0.5 mol L^{-1} H$_2$SO$_4$ solution with a potential range from 0.9 to 0 V (*vs.* SCE) at a rotating speed of 2500 rpm and the scan rate was 5 mV s^{-1}.

3. Results and discussion

Fig. 1 shows the X-ray diffraction (XRD) results of the as-prepared Pt/C with different metal loadings. As clearly displayed
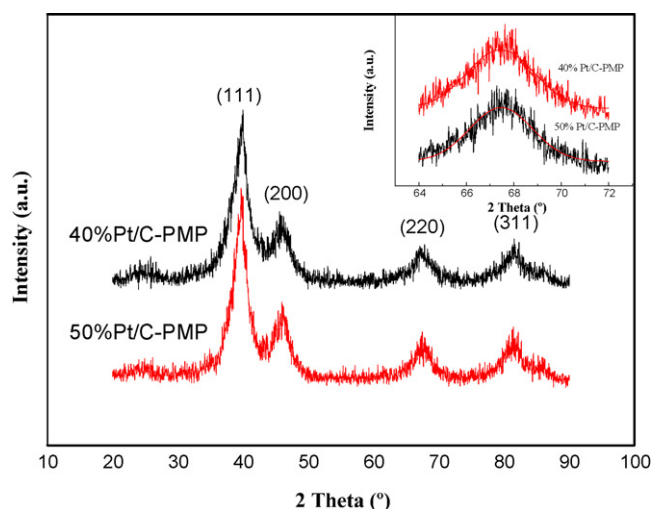

Fig. 1. XRD spectra of the as-prepared 40% and 50% Pt/C catalysts. The inset is the corresponding detailed Pt (2 2 0) peaks scanned at 1° min^{-1}.

in Fig. 1, both Pt/C catalysts exhibited the typical characteristics of a crystalline Pt face centered cubic (fcc) structure. The fitted (2 2 0) plane was used to calculate the metal particle size according to the Scherrer formula [15]. The particle size (*d*) of 40 wt.% Pt/C-PMP and 50 wt.% Pt/C-PMP are 3.1 and 2.9 nm, respectively, which are smaller than that of 50 wt.% Pt/C-JM (3.5 nm, as-received raw data from Johnson Matthey Corp.).

In Fig. 2(a), the TEM image of the 50 wt.% Pt/C-PMP sample is presented. As shown, the spherical platinum particles on carbon are uniform and well distributed. Based on the measurements of 300 particles in random regions, the average particle size was estimated to be 2.7 nm, which is close to the XRD results. The corresponding histogram (Fig. 2(b)) reveals that the particle size distribution is rather narrow and exhibits the features of a Gaussian distribution.

Fig. 3 plots the cyclicvoltammetry (CV) curves of all the investigated Pt/C catalysts in the deaerated 0.5 mol L^{-1} H$_2$SO$_4$ by adopting the thin porous coating microelectrode technique [16] with 0.77 mg cm^{-2} catalyst loading. From the integrated charge in the hydrogen adsorptions peak areas in the CV curves and the Pt poly-crystallite hydrogen adsorptions constant 210 μC cm^{-2} Pt, the electrochemical surface areas (S_{ESA}), the chemical surface area (S_{CSA}) and the Pt utilization efficiency for these catalysts can be calculated using Eqs. (1)–(3), respectively as below [17–18]:

$$S_{ESA} \left[\frac{m^2 \, Pt}{mg \, Pt} \right]$$

$$= \frac{charge \, [\mu C \, cm^{-2}]}{210 \, [\mu C \, cm^{-2} \, Pt] \times Pt \, loading \, [mg \, cm^{-2}]} \times 10^4 \quad (1)$$

$$S_{CSA} = \frac{6 \times 10^4}{\rho d} \quad (2)$$

$$Pt \, utilization \, efficiency \, (\%) = \frac{S_{ESA}}{S_{CSA}} \times 100 \quad (3)$$
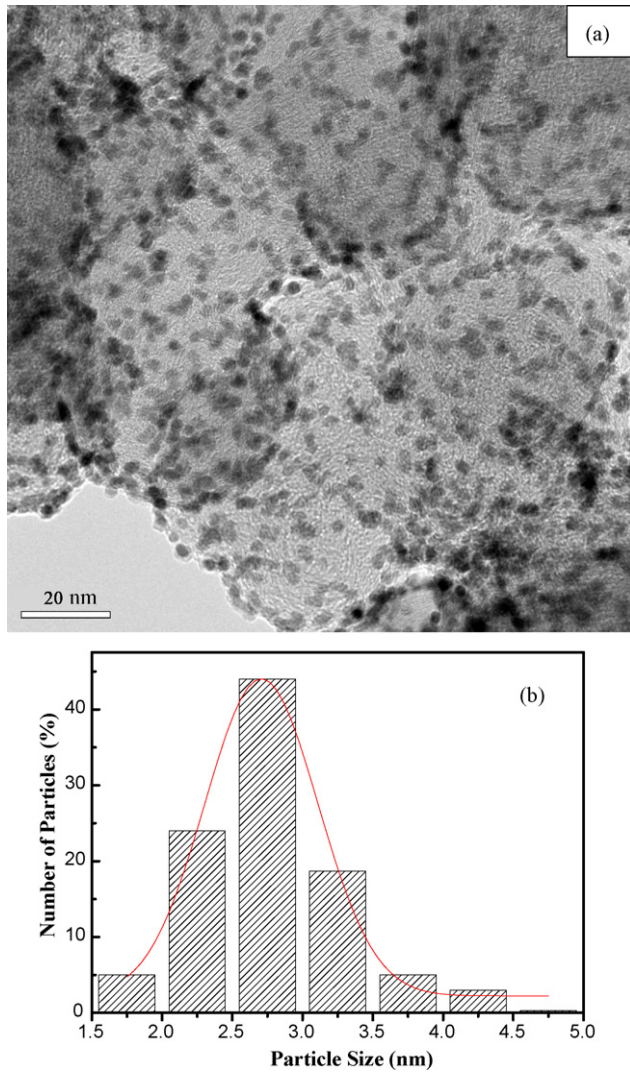
Fig. 2. TEM analysis of 50 wt.% Pt/C-PMP with 12,000 magnification: (a) TEM image and (b) the corresponding particle size distribution.
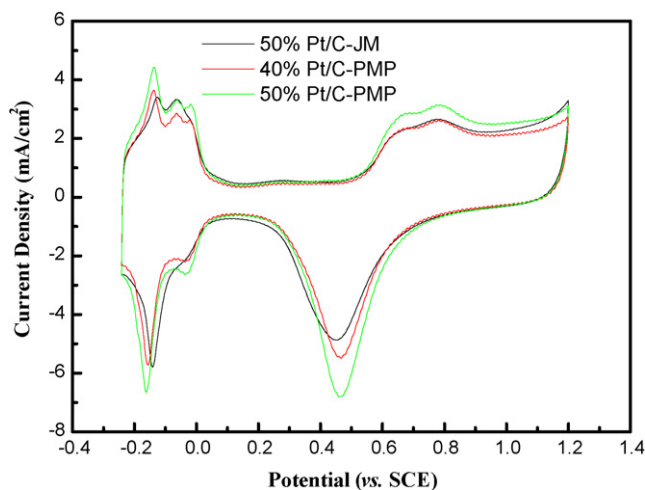
Table 1
Summary of the physico-chemical and electrochemical characterizations for the commercial and as-prepared Pt/C electrocatalysts

Catalyst	d (nm)	S_{CSA} ($m^2\,g^{-1}$)	S_{ESA} ($m^2\,g^{-1}$)	Pt utilization (%)
50% Pt/C-JM	3.5	80.1	40.5	50.6
40% Pt/C-PMP	3.1	90.4	48.9	54.1
50% Pt/C-PM	2.9	96.7	48.8	50.5

In Eq. (2), d is the mean Pt particle size in Å (from XRD result) and ρ is the density of Pt metal ($21.4\,g\,cm^{-3}$).

Based on the experimental results and the above equations, the corresponding S_{ESA}, S_{CSA} and Pt utilization efficiency for the commercial and as-prepared Pt/C catalysts are obtained and summarized in Table 1. It can be clearly seen from Table 1 that 50 wt.% Pt/C-PMP has an electrochemical area of $48.8\,m^2\,g^{-1}$, similar to that of 40 wt.% Pt/C-PMP and about 20% higher than that of 50 wt.% Pt/C-JM. In the case of the same Pt loading, Pt unitilization efficiency is almost the same. This suggests that even for high loading Pt/C electrocatalysts, the PMP can still provide desirable electrocatalsyts characterized by satisfactory dispersion and high activity with respect to the commercial one.

The polarization curves for the oxygen reduction reaction of all the investigated Pt/C catalysts, in O$_2$-saturated $0.5\,mol\,L^{-1}$ H$_2$SO$_4$ employing rotating disk electrode (RDE), are given in Fig. 4. It can be found that the respective half-wave potential $E_{1/2}$ (the corresponding potential at half of the limiting current density) of 40 wt.% Pt/C-PMP, 50 wt.% Pt/C-PMP and 50 wt.% Pt/C-JM are 0.79, 0.79 and 0.68 V (vs. SCE). It is known that the mass activity for Pt/C catalysts was the corresponding net kinetic current (i_{kin}) of ORR at a given potential divided by the mass of Pt. The i_{kin} was obtained by using formula (4):

$$I_{kin} = \frac{i_{lim} i_{obs}}{i_{lim} - i_{obs}} \qquad (4)$$

where i_{lim} is the limiting current and i_{obs} is the observed current value. Based on the experimental results as shown in Fig. 4 and
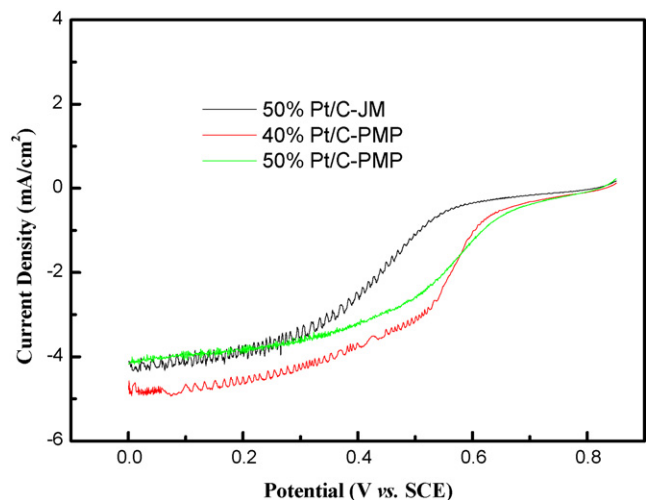

Fig. 3. Cyclic voltammetry curves of the commercial and as-prepared Pt/C catalysts in $0.5\,mol\,L^{-1}$ H$_2$SO$_4$ at room temperature. Scan rate: $20\,mV\,s^{-1}$.

Fig. 4. Polarization curves of the commercial and as-prepared Pt/C catalysts in O$_2$-saturated $0.5\,mol\,L^{-1}$ H$_2$SO$_4$ at 2500 rpm recorded at $5\,mV\,s^{-1}$.

formula (4), it can be found that 40 wt.% Pt/C-PMP has the highest mass activity of 42.8 mA mg^{-1}, which is higher than that of 50 wt.% Pt/C-PMP and 50 wt.% Pt/C-JM. This indicates that the as-prepared Pt/C catalysts possess higher activity than Pt/C-JM, which could be attributed to the bigger electrochemical surface area as shown in Table 1. A reasonable explanation is the high dispersion and uniform distribution of platinum particles on the carbon support exist in the former two cases. It is worth noticing that $E_{1/2}$ in the present case is a bit less than the reported results [19], which could be attributed to the different adopted electrolyte. In their case, RDE was tested in 0.5 mol L^{-1} HClO$_4$, which is a week anion-adsorption acid [20].

4. Conclusion

In conclusion, the present pulse-microwave assisted polyol method is a simple, practical and effective for the very rapid synthesis of high dispersed high loading Pt-based electrocatalyst. Especially, the quite short metal reduction process (2 min) is attractive and interesting from the economic point of view. Moreover, the as-prepared Pt/C catalysts exhibited a comparable electrocatalytic activity for oxygen reduction reaction to the commercial one.

Acknowledgement

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