

Preparation of high active Pt/C cathode electrocatalyst for direct methanol fuel cell by citrate-stabilized method

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Received 19 January 2010; accepted 3 March 2010

Abstract: Platinum nanoparticles supported on carbons (Pt/C, 60%, mass fraction) electrocatalysts for direct methanol fuel cell (DMFC) were prepared by citrate-stabilized method with different reductants and carbon supports. The catalysts were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and cyclic voltammetry (CV). It is found that the size of Pt nanoparticles on carbon is controllable by citrate addition and reductant optimization, and the form of carbon support has a great influence on electrocatalytic activity of catalysts. The citrate-stabilized Pt nanoparticles supported on BP2000 carbon, which was reduced by formaldehyde, exhibit the best performance with about 2 nm in diameter and 66.46 m²/g (Pt) in electrocatalytic active surface (EAS) area. Test on single DMFC with 60% (mass fraction) Pt/BP2000 as cathode electrocatalyst showed maximum power density at 78.8 mW/cm².

Key words: direct methanol fuel cell; catalyst; Pt/C; citrate; reductant; carbon support

1 Introduction

There is a growing demand for the environmentally friendly energy conversion system and the direct methanol fuel cell (DMFC) system is one of the most promising candidates. In DMFC, noble metal Pt catalyst plays an irreplaceable role with its superiority of electrocatalytic performance. Since high costs may inhibit widespread use, it is essential to reduce cost, and improve activity and utilization[1]. It is well known that the electrocatalytic activity of the metal is strongly dependent on the particle shape, size and size distribution. However, synthesis of highly dispersive supported Pt with uniform nanoparticle size still remains to be a challenge, especially for high metal loading. Therefore, good preparation methods and proper supports are needed urgently.

There are many methods to prepare Pt/C catalyst, such as impregnate[2], sol-gel[3], ion exchange[4], polyol methods[5]. For any method of preparation, the fundamental to obtain good product performance is to control the nucleation and growth of particles during reduction. As we all know, the nanoparticles are

thermodynamically unstable and their apparent stability comes from an acquired kinetic hindrance to agglomeration. It was also reported that citrate, the water-soluble surfactant with small molecular, is a good stabilizing agent for the preparation of Pt nanoparticles in aqueous solution[6–7]. This function is rendered by the three-carboxyl anions of the citrate, which can be adsorbed on the surface of metal particles and exert either hydrophobic or coulombic effects on the metal particles, thereby stabilizing them[8]. In the first instance, citrate was used as reductant and stabilizer to prepare Pt nanoparticles by TURKEVICH et al[9] in 1986. Recently LIN et al[10] examined the Pt state in the solution and experimentally demonstrated that PtCl₆²⁻ could not be reduced by citrate below 90 °C and citrate was considered as the most likely oxygen donor. Well-dispersed 20% Pt/C (mass fraction, the same bellow) catalysts (3.8 nm) prepared with sodium borohydride as the reductant and citric acid as the stabilizing agent were reported by GUO et al[11], who proposed a citrate complexation stabilizing mechanism. However, further investigation for 60% Pt/C catalysts (2–3 nm) with higher activity still challenged the synthesis condition. The types of reductant and carbon

support have great effects on the reduction of PtCl_6^{2-} and dispersion of Pt nanoparticles on support[12], which could definitely influence the activity of Pt/C catalysts. Unfortunately, little studies have been reported in this area.

In the present study, citrate-stabilized method is employed to prepare 60% Pt/C electrocatalyst. The stabilizing effect of citrate is discussed with different citrate/Pt molar ratios. Selective reductant and carbon support are separately controlled for developing a homogeneously dispersed Pt/C catalyst.

2 Experimental

2.1 Preparation of electrocatalysts

Vulcan XC-72 carbon ($S_{\text{BET}}=236 \text{ m}^2/\text{g}$), Vulcan XC-72R carbon ($S_{\text{BET}}=236 \text{ m}^2/\text{g}$), and BP2000 carbon ($S_{\text{BET}}=1362 \text{ m}^2/\text{g}$) from Cabot corporation were used as support, which were pretreated at 600°C for 2 h in nitrogen atmosphere and then dispersed in deionized water by ultrasonic, respectively. A calculated amount of sodium citrate was dissolved in chloroplatinic acid solution (60 mg Pt), followed by adding $\text{NH}_3\cdot\text{H}_2\text{O}$ to adjust the pH to 8–8.5. The mixture was then added with a well-stirred suspension of 40 mg carbon support. After stabilizing for 16 h at 50°C , excess of NaBH_4 solution served as a reducing agent was added dropwise to the suspension. Stirring was continued for 2 h. Finally, the suspension was filtered, and the residue was washed with copious water and dried at 60°C for 6 h in vacuum. The obtained sample was hereafter referred to as Pt/C-B.

For formaldehyde as reducing agent (denoted as Pt/C-F), excess of formalin instead of NaBH_4 solution was added after stabilizing, and the temperature was regulated to 85°C . The samples prepared with different carbon support were signed as Pt/XC-72, Pt/XC-72R and Pt/BP2000, respectively. The same loading of 60% (mass fraction) was adopted for all samples.

2.2 Characterization of electrocatalysts

The XRD patterns were recorded on a Bruker D8-Discover micro X-ray diffractometer with a $\text{Cu K}\alpha$ radiation source ($\lambda=1.5406 \text{ \AA}$) at 40 kV and 40 mA. TEM on a JOEL JEM-2000EX operating at 200 kV was used to examine the particle size and dispersion on carbon. The TEM sample was prepared by ultrasonically suspending the catalyst in ethanol and then depositing a small drop of the suspension onto a $d3 \text{ mm}$ copper grid covered with continuous amorphous carbon film.

2.3 Electrochemical measurements

Cyclic voltammetry (CV) was employed to obtain the electrochemical active area of different catalysts. The CV measurements were carried out by a standard

three-electrode electrochemical cell at room temperature with a saturated calomel electrode (SCE) as the reference electrode, Pt foil as the counter electrode, and a glassy carbon (GC) electrode with synthesized catalyst as the working electrode. The three electrode cell system was purged with nitrogen gas for 30 min before electrochemical analysis. All of the electrochemical measurements were made in nitrogen atmosphere. The electrolytes used were 1 mol/L H_2SO_4 , and the potential window was -0.2 to 1 V (vs SCE) with scanning rate of 50 mV/s . The electrochemical active surface (EAS) of catalyst was calculated by the coulombic charge for hydrogen desorption on Pt sites[13].

The above prepared Pt/BP2000 catalyst was tested as cathode catalysts in single direct methanol fuel cells. Nafion 115 membrane from DuPont Corporation was used as the membrane material. A mixture of catalyst and 5% (mass fraction) Nafion solution was firstly ultrasonic treated and then uniformly sprayed onto the membrane with a cross-section area of 5 cm^2 and dried, followed by hot pressing at 150°C and 5 MPa for 2 min with the gas diffusion layers (Toray-90 carbon paper). The anode catalyst was 60% (mass fraction) PtRu/C catalyst (Johnson Matthey) with a PtRu loading of 3 mg/cm^2 . The cathode catalyst has a Pt loading of 2.8 mg/cm^2 . The performance test of DMFC was conducted in a single cell at 60°C . The anode fuel was 1 mol/L methanol aqueous solution at a flow rate of 3 mL/min . The cathode was fed with air of 0.2 MPa pressure.

3 Results and discussion

3.1 Stabilizing effect of citrate

The stabilizing effect on Pt nanoparticles prepared by using sodium citrate was investigated. The powder XRD patterns of catalysts prepared by using NaBH_4 with different molar ratios of citrate and Pt at 1:1, 2:1, 4:1 and 8:1 are presented in Fig.1. In addition, the XRD pattern of catalyst prepared without sodium citrate is also shown. The diffraction peaks at $2\theta\approx 39^\circ, 46^\circ, 67^\circ$, and 81° in all XRD patterns are due to the (111), (200), (220) and (311) plane of metal Pt face-centered cubic (fcc) crystal structure, respectively. Compared to the pattern of Pt/C catalysts prepared without citrate, there is no shift in 2θ for citrate-stabilized Pt/C. This indicates that there is no crystal structure change in Pt/C catalyst by the addition of sodium citrate during synthesis. However, it is important to note the broadening diffraction peak in the patterns of citrate-stabilized Pt/C, which represents the lessening of the Pt particle size according to the Scherrer formula[14]. The average particle diameter may be estimated from the parameters calculated by Scherrer formula. The Pt particle diameters with different proportion of citrate and Pt are shown in Fig.2. It can be

seen that the average particle diameters of citrate-stabilized Pt/C (3.5 nm) are much smaller than that of Pt/C catalysts prepared without citrate (6.5 nm), and varying the molar ratio of citrate/Pt from 1:1 to 8:1 has no apparent effect on the size of the particles. These may be because the presence of citrate results in some Pt—O bonding initially, a smaller Pt—Pt coordination number and a slower particle growth process[15]. HENGLEIN et al[16] reported a similar retarding effect of citrate when PtCl_4^{2-} was reduced by H_2 . The coordination of citrate to newly formed Pt particle may slow down the particle growth, and this causes the stabilizing effect of citrate.

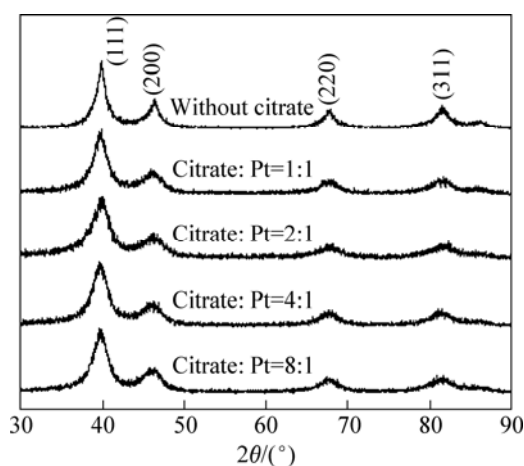


Fig.1 Powder XRD patterns of Pt/C catalysts prepared with different proportions of citrate and Pt

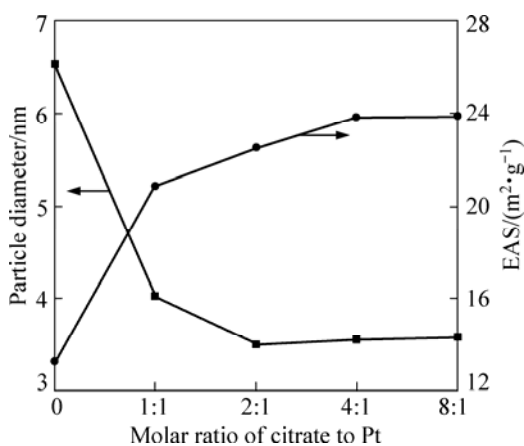


Fig.2 Pt particle diameter and electrochemistry active surface (EAS) vs proportion of citrate and Pt

Therefore, the addition of citrate definitely contributes to small particle size, which corresponds to large specific surface area and high electrocatalytic activity. Figure 3 shows cyclic voltammety curves of Pt/C prepared with or without citrate. Compared to Pt/C prepared without citrate, the sample with molar ratio of citrate and Pt at 2:1 has a higher current density, which indicates the higher electrocatalytic activity. The coulombic charge for hydrogen desorption was used to

calculate the electrochemistry active surface (EAS) of the platinum in electrode[17]:

$$\text{EAS} = Q_{\text{H}} / (210 \cdot m) \quad (1)$$

where m represents the platinum loading in the electrode; Q_{H} is the charge for hydrogen desorption which is corresponding to the integral area above the hatched part in Fig.3; 210 represents the charge required to oxidize a monolayer of H_2 on bright Pt. The contribution of “double layer” charge (hatched part in Fig.3) is exclusive for every sample.

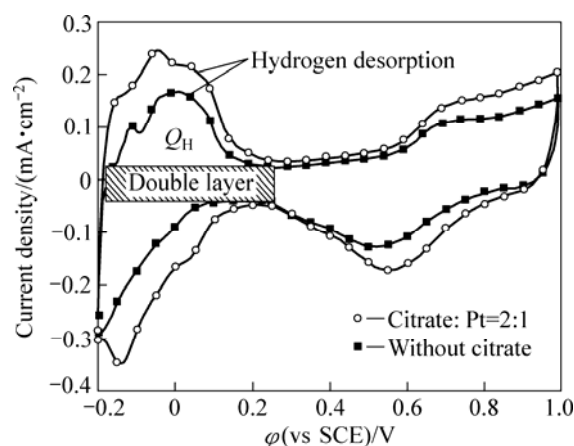
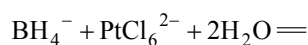


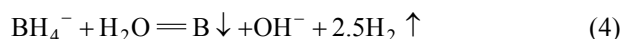
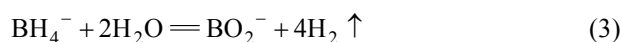
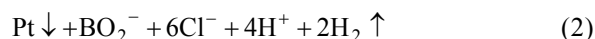
Fig.3 Cyclic voltammety curves of Pt/C prepared with or without citrate

The EAS of Pt/C catalyst calculated from CV versus the amount of citrate are sketched in Fig.2 too. There is great improvement in EAS of Pt/C catalyst by the addition of citrate during synthesis, which is due to the smaller particle size of Pt. When the molar ratio of citrate to Pt is no less than 2:1, the particle diameter and EAS are both becoming steady-going. Further increasing the amount of citrate has little impact on particle size and EAS. Hence, citrate was employed with the molar ratio of citrate to Pt at 2:1 in the following research.

3.2 Influence of different reductants

Figure 4 compares the powder XRD patterns of the Pt/C catalysts reduced by sodium borohydride and formaldehyde solution. The pattern of sample Pt/C-F shows diffraction peak broadening phenomenon. Pt particle diameters, calculated from the XRD patterns using Scherrer formula, are 3.7 nm and 2.0 nm, respectively. The sodium borohydride and formaldehyde are relatively strong reducing agent. With sodium borohydride as reductant, the following three independent reactions may take place in the system during reduction of metal chlorides[18]:





This means the non-metallic boron may deposit with Pt together on the surface of support. The secondary reactions (3) and (4) will influence the nucleation rate of Pt particles and dispersion on support surface.

Comparatively, formaldehyde is more stable. The reduction reaction of chloroplatinic by formaldehyde is shown in Eq.(5). The reduction enables to prepare small and uniform Pt nanoparticle in the present situation. This result is evident from the TEM images shown in Figs.5(a) and (c). In the case of NaBH_4 as reductant, the Pt particles accumulate like clumps on many parts of the carbon support with average diameter of 3.54 nm, and the size distribution, which is statistic from random sample of 100 nanoparticles in TEM images, is rather wide (see Fig.5(b)). But for Pt/C-F catalyst shown in Fig.5(c), the particles are smaller (average diameter of 2.2 nm), and more uniform in size and dispersion(see Fig.5(d)).

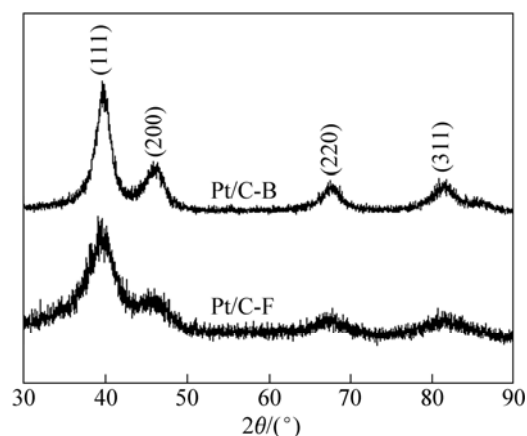
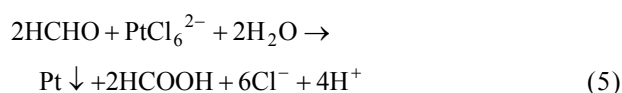


Fig.4 Powder XRD patterns of Pt/C catalysts reduced by sodium borohydride (Pt/C-B) and formaldehyde (Pt/C-F) solution, respectively

3.3 Influence of different carbon supports

The main function of carbon support is to disperse the active metal Pt in catalyst for fuel cell[19]. The influence of the type of carbon as a supporting material was examined by using catalysts containing about 60% Pt on Vulcan XC-72, Vulcan XC-72R or BP2000 carbon. These samples were all prepared with molar ratio of

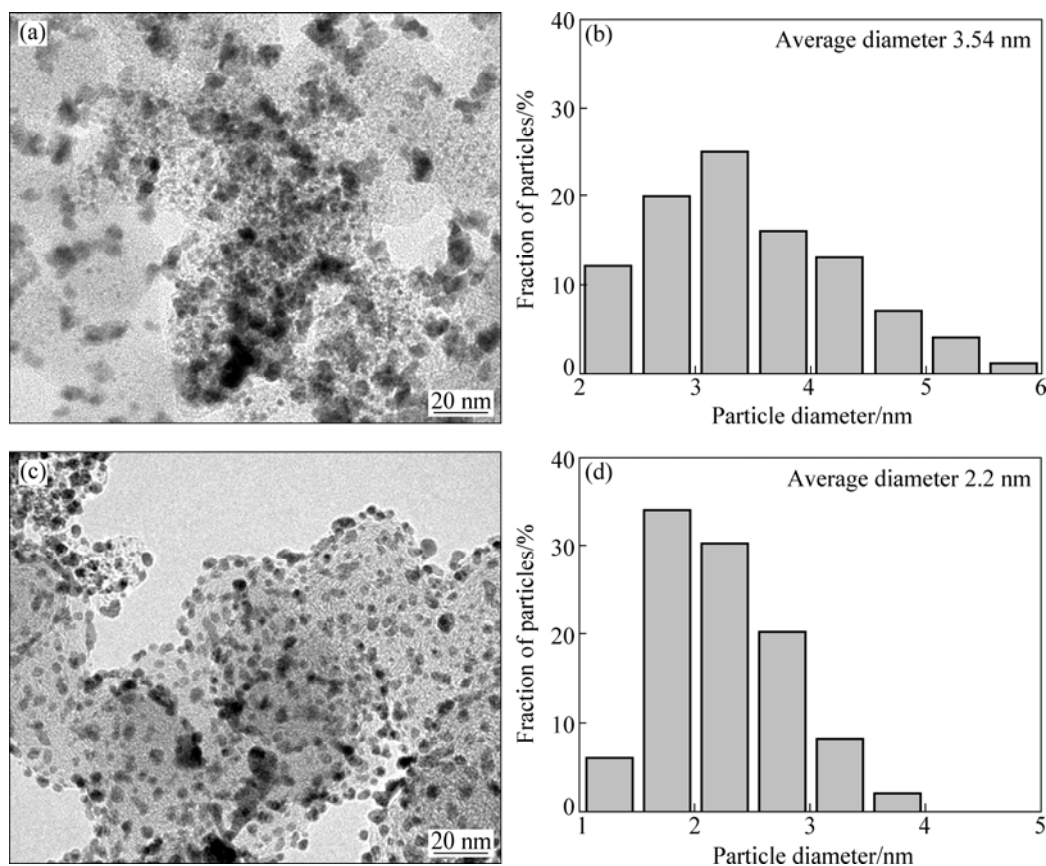


Fig.5 TEM micrographs and particle size distribution of Pt/C catalyst prepared with different reductants: (a) and (b) Sample Pt/C-B; (c) and (d) Sample Pt/C-F

citrate to Pt of 2:1 and reduced by formalin. The BP2000 was chosen because of its high mesoporosity and high surface area that could make it suitable for electrocatalyst supports, whereas Vulcan XC-72 and Vulcan XC-72R were chosen because they are commonly used as electrocatalyst support. The particle diameters obtained from XRD and EAS measured from CV for Pt/XC-72, Pt/XC-72R and Pt/BP2000 are presented in Table 1. In the corresponding XRD patterns (Fig.6), catalysts show almost identical patterns, which reveals that the platinum crystallites are similar in structure and size on the three different carbon supports. Nevertheless, the particles aggregated on the high-surface-area BP2000 show higher activity, and their EAS is $66.46 \text{ m}^2/\text{g}$. Compared to XC-72R, BP2000 with higher surface area has more mesopore and absorptive site, which can disperse the Pt particles better, and improve the utilization of catalyst.

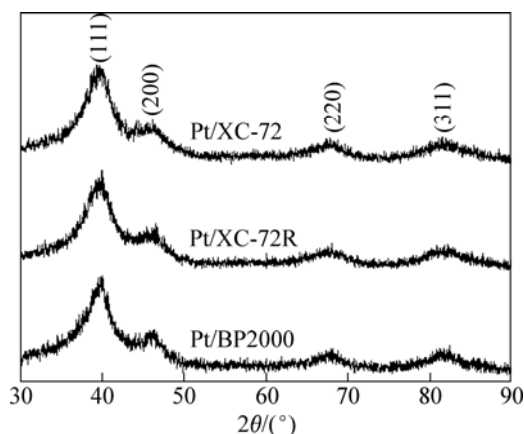


Fig.6 Powder XRD patterns of Pt/C catalysts prepared with different carbon supports

Table 1 Comparison of catalysts prepared with different carbon supports

Catalyst	Support	Particle diameter/nm	EAS/($\text{m}^2 \cdot \text{g}^{-1}$)
Pt/XC-72	XC-72	2	46.5
Pt/XC-72R	XC-72R	2.04	44.61
Pt/BP2000	BP2000	2.75	66.46

3.4 DMFC performance

The electrocatalytical activities of 60% Pt/ BP2000 electrocatalyst were tested as cathode electrocatalyst in a DMFC at 60°C . Figure 7 shows the single cell performance. The open-circuit voltage is 0.78 V. The voltage drops with the increase of current density, which comes from two aspects: one is the electrochemical activation polarization of the electrode reaction (corresponding part at low current density in Fig.7); another is the linear ohmic polarization of the cell internal resistance (corresponding part at high current

density in Fig.7). At 0.5 V, the single cell yields a current density of $72 \text{ mA}/\text{cm}^2$. Power density was also obtained from cell potential and current density data as shown in Fig.7. The maximum power density of DMFC with 60% Pt/C electrocatalyst is $78.8 \text{ mW}/\text{cm}^2$ when the current density is $262 \text{ mA}/\text{cm}^2$. This kind of fine cell performance can not be presented without the high activity cathode Pt/C catalyst with both small size and uniform size distribution.

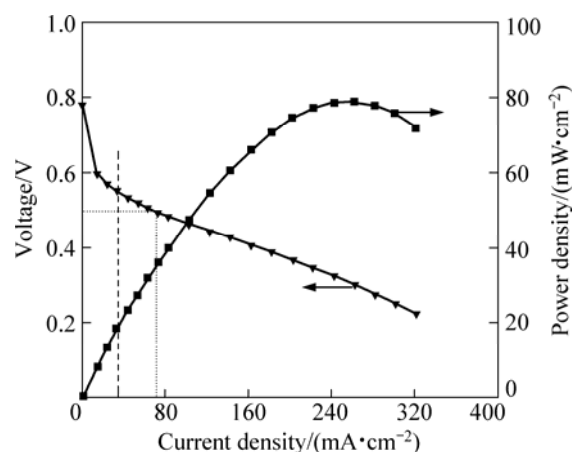


Fig.7 Performance of single DMFC with 60% Pt/BP2000 as cathode electrocatalysts

4 Conclusions

1) The addition of citrate to chloroplatinic acid solution definitely contributes to small size of Pt particles, which corresponds to large specific surface area and high electrocatalytic activity. When the molar ratio of citrate to Pt is more than 2:1, the particle diameter and EAS are both becoming steady-going. Further increasing the amount of citrate has little impact on particle size and EAS.

2) Compared to NaBH_4 , formaldehyde is a more stable reductant in this system. The Pt particles reduced by formaldehyde are smaller (2.2 nm), and more uniform in size and dispersion than that by NaBH_4 .

3) Compared to XC-72R, BP2000 with higher surface area have more mesopore and absorptive site, which can disperse the Pt particles better, and improve the utilization of catalyst.

4) The CV analysis demonstrates that the EAS area of the 60% Pt/BP2000 reaches $66.46 \text{ m}^2/\text{g}$ (Pt). The DMFC testing also shows good cell performance. This method for preparation of supported nanoparticles with simple process and controllable conditions is suitable for industrial production.

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柠檬酸盐稳定法制备直接甲醇燃料电池高活性 Pt/C 催化剂

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摘要: 采用不同还原剂和碳载体, 通过柠檬酸盐稳定法制备直接甲醇燃料电池用担载量为 60% 的 Pt/C 催化剂, 通过 X 射线衍射(XRD), 透射电子显微镜(TEM)和循环伏安(CV)等手段对催化剂进行表征。结果表明: 柠檬酸盐加入和还原剂优化可以很好地控制铂纳米颗粒的粒径, 而碳载体的选择对催化剂的电催化活性有很大影响。在采用柠檬酸钠做稳定剂、甲醛做还原剂、BP2000 碳粉做载体的条件下, 制备的 60% Pt/BP2000 催化剂性能最佳, 平均粒径约 2 nm, 电化学活性面积为 66.46 m²/g。使用该材料作为阴极催化剂的直接甲醇燃料电池单电池最大功率密度可达到 78.8 mW/cm²。

关键词: 直接甲醇燃料电池; 催化剂; Pt/C; 柠檬酸; 还原剂; 碳载体

(Edited by LAI Hai-hui)