



Pt nanoparticles supported on monodisperse carbon spheres for methanol oxidation in alkaline media



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ABSTRACT

The Stöber method is extended to prepare carbon spheres (CS) by polymerizing resorcinol and formaldehyde. The obtained monodisperse CS are used as the supports of Pt nanoparticles for methanol oxidation in alkaline media. Compared with Pt supported on commercial Vulcan XC-72R carbon (Pt/C) electrocatalysts, Pt supported on carbon spheres (Pt/CS) electrocatalysts, which give peak current density 2.6 times higher and 100 mV more negative shift toward methanol oxidation, shows better electrocatalytic activity. This is attributed to the higher electrochemical active surface area of Pt/CS with $56 \text{ m}^2 \text{ g}^{-1}$, as compared with that of Pt/C with $28 \text{ m}^2 \text{ g}^{-1}$.

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1. Introduction

Alkaline direct methanol fuel cells (alkaline DMFCs) have received more and more attention due to their potential advantages such as more facile methanol oxidation reaction, lower methanol crossover from anode to cathode, and easier water management [1,2].

For catalysts preparation, it is important to choose a suitable catalyst support for methanol oxidation, owing to the fact that it can improve the catalytic activity and reduce the use of noble metal catalysts. Carbon nanomaterials, considered as one of the most ideal catalyst supports for fuel cells, have been widely used. For example, carbon nanotubes [3,4], carbon nanofibers [5,6], carbon aerogels [7,8], and carbon spheres [9–20] have been widely adopted as electrocatalyst supports for alcohol electrooxidation and oxygen reduction reaction. Among them, carbon spheres have advantages of high specific surface area, excellent electronic conductivity, good chemical durability, and suitable porosity for mass transport, and they have been proved as promising catalyst supports for DMFCs [9–20]. Different methods to prepare carbon spheres have been reported. Among them, the Stöber method has been extended to prepare carbon spheres with desired diameter and narrow particle size distribution by polymerization of resorcinol and formaldehyde in a mixture of ethanol and aqueous ammonia [17]. This synthesis method with resorcinol/formaldehyde (R/F) as carbon source is a very facile and versatile procedure for making polymer beads and is considered to be of low cost and suitable for supports of fuel cells.

In this work, the Stöber method is extended to synthesize monodisperse carbon spheres by polymerizing resorcinol and formaldehyde. The prepared carbon spheres are used to support Pt nanoparticles for methanol oxidation in alkaline media. Compared with Pt supported on commercial Vulcan XC-72R carbon (Pt/C) electrocatalysts, the Pt/CS electrocatalysts exhibit higher electrocatalytic activity for methanol oxidation in alkaline media.

2. Experimental

Preparation of the CS: According to the extension of the Stöber method reported recently by Liu et al., monodisperse carbon spheres were synthesized by using R/F as precursors [17]. The whole synthesis was carried out in a 100 ml round-bottom flask equipped with a magnetic stirrer. Typically, 0.1 ml 25 wt% aqueous ammonia solution was added to the solution containing 8 ml absolute ethanol and 20 ml deionized water. After stirring for 1 h, 0.2 g resorcinol was added and stirred to complete dissolution. Then, 0.28 ml 37 wt% formaldehyde was added dropwise to the solution. The mixtures were stirred for 24 h at 30 °C. After that, the mixtures were transferred to a Teflon container and placed in a sealed metal autoclave vessel, which was then placed in an oven for 24 h at 100 °C under a static condition. The obtained mixtures were recovered by centrifugation and dried at 100 °C for 48 h in air. The solid products were carbonized in a horizontal vacuum tubular furnace under nitrogen atmosphere. The samples were heated up to 350 °C with a heating rate of $1 \text{ }^\circ\text{C min}^{-1}$ and maintained for 2 h, and subsequently heated to 600 °C with a heating rate of $1 \text{ }^\circ\text{C min}^{-1}$ and

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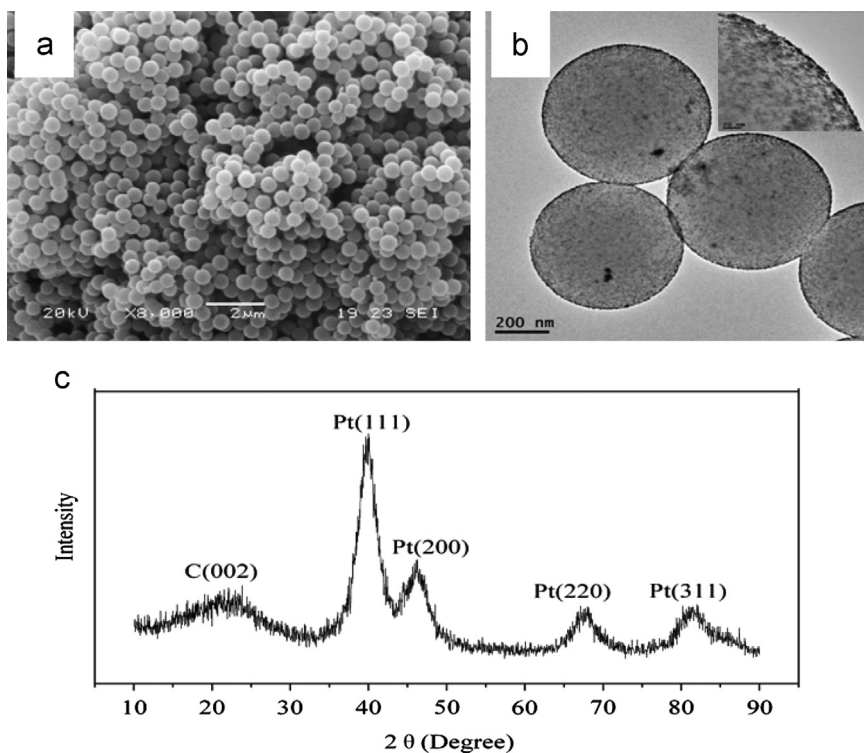


Fig. 1. (a) SEM images of CS, (b) TEM images of Pt/CS and (c) XRD patterns of the Pt/CS.

kept for 4 h. At last, the samples were cooled down to room temperature.

Preparation of Pt/CS electrocatalysts: Pt supported on carbon spheres (Pt/CS) was prepared by the ethylene glycol (EG) method [7]. Carbon spheres or Vulcan XC-72R carbon powders (80 mg) were mixed with 150 ml EG under ultrasonic treatment for 30 min to form uniform ink. The solution of H_2PtCl_6 in EG containing 20 mg Pt was slowly added into the CS or XC-72R slurry. The mixture was stirred for 2 h until it got impregnated. The pH of the mixture was then adjusted to 10 by dropping 0.5 M NaOH in EG. The solution was heated to 130 °C for 3 h in an oil bath. The mixture was filtered and washed with deionized water for 4–5 times after cooling, then air-dried at 50 °C for 12 h, and the Pt/CS or Pt/C electrocatalysts were finally obtained.

Characterization of the materials: The materials' structures were determined by X-ray diffraction (XRD) with a $\text{Cu K}\alpha$ radiation source on Rigaku D/max-2500. The morphologies of the electrocatalysts were characterized by scanning electron microscopy (SEM, JSM 5600LV, Japan) and transmission electron microscopy (TEM, JEM-2100UHR, Japan) operating at 200 kV.

Electrochemical measurement: To prepare working electrodes, 6.0 mg Pt/CS or Pt/C electrocatalysts were dispersed in 4.0 ml isopropanol, 1.4 ml deionized water, and 0.6 ml Nafion solution (5 wt%, DuPont) suspension under ultrasonic treatment for 30 min to well mixed ink. The catalyst ink (35 μl) was deposited on the clear glassy carbon electrode (3 mm in diameter), and dried at room temperature. The total Pt loadings were controlled at 0.1 mg cm^{-2} . The cyclic voltammograms and chronoamperometry were carried out with a CHI660D electrochemical workstation (CH Instrument, Shanghai Chenhua Instrument Corporation, China). A standard three-electrode cell was used at room temperature (20 °C). A modified glassy carbon electrode was served as a working electrode. A platinum wire and Ag/AgCl were used as a counter electrode and a reference electrode, respectively. The potential range was from -1.0 to 0.4 V and the scan rate was 50 mV s^{-1} .

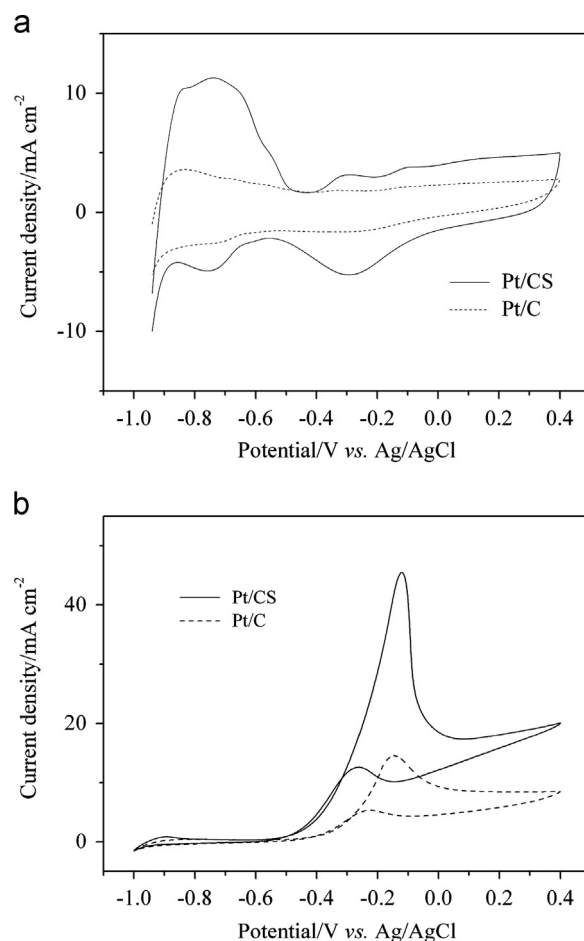


Fig. 2. (a) Cyclic voltammograms of Pt/CS and Pt/C in 1.0 M NaOH at 50 mV s^{-1} and (b) cyclic voltammograms of Pt/CS and Pt/C in 1.0 M NaOH+1.0 M CH_3OH at 50 mV s^{-1} .

3. Results and discussion

Fig. 1a presents the SEM image of the CS. It can be seen that the obtained CS are basically uniform in size and morphology, and have smooth surfaces with an average diameter of 500 nm. Fig. 1b shows the TEM image of Pt/CS, which indicates that the spherical morphology is basically retained after the incorporation of Pt nanoparticles. Both the dark dots and the increase in surface roughness can be clearly seen on the surface of the CS, which proves the presence of Pt nanoparticles on the surface. Fig. 1c shows the XRD pattern of Pt/CS electrocatalysts. The diffraction peak at 2θ of 22.6° is observed, which corresponds to C(002) facet of graphitic carbon and indicates that the carbon spheres are partially graphitized from the amorphous nature. The crystal structure of Pt in the Pt/CS is face-centered cubic (fcc), which is confirmed by the diffraction peaks at 39.6° , 46.3° , 67.4° , and 81.6° , respectively corresponding to (111), (200), (220), and (311) facets of the face-centered cubic structure of Pt crystal. According to the Debye–Scherrer equation [15], the Pt (220) peak is used to calculate the average Pt particles. The average Pt particle size of Pt/CS is about 4.0 nm.

The electrocatalytic properties of Pt/CS and Pt/C electrocatalysts are characterized electrochemically in 1.0 M NaOH solution at scan rate of 50 mV s^{-1} , as shown in Fig. 2a. The electrochemical active surface area (EASA) can be estimated by measuring the charge with hydrogen adsorption curves (Q_H) according to the equation which has been reported [7,15]. The EASA for Pt/CS ($56 \text{ m}^2 \text{ g}^{-1}$) is higher than that of Pt/C ($28 \text{ m}^2 \text{ g}^{-1}$), probably because of the higher Brunauer–Emmett–Teller (BET) surface area of the CS ($504 \text{ m}^2 \text{ g}^{-1}$, obtained from reference [17]), as compared with that of commercial Vulcan XC-72R ($254 \text{ m}^2 \text{ g}^{-1}$).

Fig. 2b presents the electrocatalytic activity for methanol oxidation in 1.0 M NaOH+1.0 M CH_3OH solution at scan rate of 50 mV s^{-1} . For Pt/CS electrocatalysts, the anodic peak, which appears around -0.12 V in the forward scan, corresponds to the methanol oxidation, while the other anodic peak in the reverse scan around -0.27 V is due to the oxidation of incompletely oxidized species generated during the forward scan. The peak current density value of Pt/CS electrocatalysts is 45 mA cm^{-2} , which is about 2.6 times higher than that of Pt/C electrocatalysts (17 mA cm^{-2}). In addition, the onset potential on Pt/CS is 100 mV, more negative than that on Pt/C electrocatalysts for methanol oxidation.

The result of chronoamperometric measurements performed at -0.5 V in 1.0 M NaOH+1.0 M CH_3OH is shown in Fig. 3. Methanol oxidation on Pt/CS electrocatalysts can sustain higher current density than that on Pt/C electrocatalysts at the same Pt loading, indicating that the Pt/CS has higher electrocatalytic activity, which results from a higher electrochemically active surface area of Pt/CS.

4. Conclusions

An extension of the Stöber method is applied to prepare the monodisperse carbon spheres by polymerizing resorcinol and formaldehyde. The high surface area and the unique structure

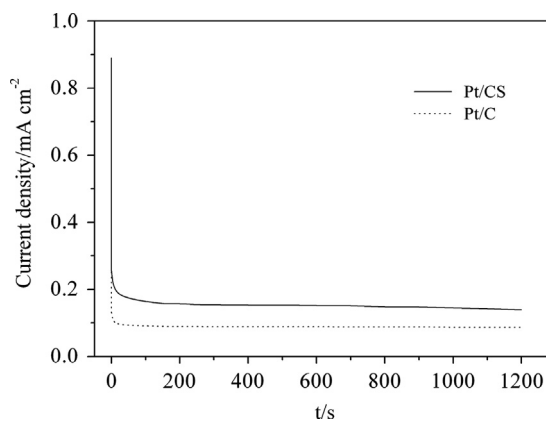


Fig. 3. Chronoamperometric results of Pt/CS and Pt/C at -0.5 V in 1.0 M NaOH +1.0 M CH_3OH .

make carbon spheres suitable supports for Pt electrocatalysts. Compared with Pt/C electrocatalysts, Pt/CS electrocatalysts show better electrocatalytic activity toward methanol oxidation, which is attributed to the high electrochemically active surface area of CS. The results suggest that CS have promising application potential as electrocatalysts supports in alkaline direct methanol fuel cells.

Acknowledgments

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