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Highly graphitic carbon black-supported platinum nanoparticle catalyst and its enhanced electrocatalytic activity for the oxygen reduction reaction in acidic medium

Haijing Liu[1], Jin Li[1], Xinhua Xu, Feng Wang*, Jingjun Liu, Zhilin Li, Jing Ji

State Key Laboratory of Chemical Resource Engineering, Beijing Key Laboratory of Electrochemical Process and Technology for Materials, Beijing University of Chemical Technology, Beijing 100029, PR China

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ABSTRACT

Highly graphitic carbon black (GCB) was synthesized by heat-treating commercial carbon black (CB, Vulcan XC-72) at 2800 °C. The resulting GCB with a high degree of graphitization was analyzed by X-ray diffraction patterns (XRD), Raman spectroscopy and high-resolution transmission electron microscopy (HR-TEM) and was then used as the support material for synthesizing a platinum–GCB (Pt/GCB) hybrid catalyst. This catalyst was obtained through a simple chemical reduction using ethylene glycol as the reducing agent, which is amenable to large-scale production. The results show that the Pt nanoparticles are highly dispersed on the GCB with an average diameter of 3.6 nm and a narrow particle size distribution. The electrochemical results obtained using cyclic voltammetry (CV), linear sweep voltammetry (LSV) utilizing a rotating disk electrode (RDE) and electrochemical impedance spectroscopy (EIS) show that the Pt/GCB electrocatalyst exhibits higher conductivity, stability, and electrocatalytic activity for the oxygen reduction reaction. The ORR proceeds through a four-electron process and when compared with Pt nanoparticles supported on Vulcan XC-72 (Pt/Vulcan XC-72) prepared under the same conditions, the Pt/GCB exhibits a significant enhancement for the ORR reaction.

1. Introduction

The oxygen reduction reaction (ORR) is one of the most important electrochemical reactions as it is widely applied in fuel cells, air-batteries, corrosion, and biological processes [1–4]. Nonetheless, the ORR process involves complex multi-electron steps with sluggish kinetics, resulting in high overpotentials, even with carbon supported platinum (Pt/C), which is currently considered the best electrocatalyst for the ORR [5]. Thus, much effort has been devoted to improving the kinetics of the ORR on Pt/C electrocatalysts, including alloying Pt with early transition metals such as Fe, Co, or Ni [6–8] and developing alternative carbon support materials [9].

Theoretically, the specific activity of a catalyst is strongly dependent on the catalyst size, the size distribution, and the support material. Carbon black, such as Vulcan XC-72, one of the most utilized support materials, has been widely utilized for the production of commercial Pt/C electrocatalysts for the ORR, due to its reasonable balance of electron conductivity, surface area, and cost [10]. However, Vulcan XC-72 is intrinsically unstable at high potentials under an oxidizing environment, and this negatively influences the stability and activity of the supported electrocatalysts [11]. After extended operation in acidic medium in which the ORR occurs, Vulcan XC-72 is slowly corroded to surface oxides and eventually to CO_2 at the cathode of a fuel cell. This is due to the corrosive acidic environment, accelerated corrosion due to the presence of Pt, and the corrosion inherent to the ORR [12–14]. As the carbon becomes corroded, the supported Pt nanoparticles fall from the support material and aggregate into larger particles; thus, the electrochemical active surface area (ECSA), along with the catalytic activity, is highly reduced. To improve the activity and stability of the Pt/C, various graphitized carbon support materials, such as carbon nanotubes (CNTs) [15,16], carbon nanofibers [17,18], and carbon nanocoils [19] have been explored as alternatives to the Vulcan XC-72 support. Although these carbon materials appear promising as highly efficient electrocatalytic systems for the ORR, some obstacles remain (e.g., complex and costly synthetic methods) and require further investigation.

Herein, commercial Vulcan XC-72 was heat treated under high temperatures to obtain graphitized carbon black (GCB). Then, the appropriate reducing agent for Pt on GCB was determined. The number of electrons involved in the ORR on Pt/GCB was determined and compared to that of Pt/Vulcan XC-72. The GCB was

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* Corresponding author. Tel.: +86 10 64451996; fax: +86 10 64451996.
E-mail address: wangf@mail.buct.edu.cn (F. Wang).

[1] These authors contribute equally to this work.

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then used as a support material to synthesize the Pt electrocatalyst (Pt/GCB) through a simple chemical reduction using ethylene glycol as a reducing agent, which is amenable to large-scale production [20]. The synthesized Pt/GCB exhibited higher conductivity and electrocatalytic activity for the ORR through a four-electron process. When compared to the Pt nanoparticles supported on Vulcan XC-72 (Pt/Vulcan XC-72) prepared under the same conditions, the Pt/GCB shows a significant catalytic enhancement for the ORR.

2. Experimental methods

2.1. Catalyst synthesis and characterization

The graphitized carbon black (GCB) was synthesized by heat-treating Vulcan XC-72 (Cabot Corp. Japan) at 2800 °C for 4 h under an argon atmosphere. The GCB and Vulcan XC-72 were used as support materials to prepare the electrocatalysts, respectively labeled Pt/GCB and Pt/Vulcan XC-72. Prior to Pt deposition, the carbon black powder was first refluxed in a 65 wt.% HNO_3 solution. The treated carbon black powder was then filtered and washed with deionized water and dried at 80 °C in a vacuum oven for 12 h. In a typical catalyst preparation using the ethylene glycol reduction method, the treated carbon black powder (100 mg) was first dispersed in ethylene glycol (50 mL) by sonication for 30 min in a 100 mL three-necked flask. Then, 15.4 mL of 0.01 mol L^{-1} chloroplatinic acid in ethylene glycol was added, and the pH value of the mixed solution was adjusted to 9–10 by the addition of a 1 mol L^{-1} NaOH solution. Subsequently, the reaction mixture was refluxed for 3 h at 130 °C with constant stirring. The flask was then allowed to cool, and the obtained catalyst was filtered, washed with deionized water and dried at 80 °C in a vacuum oven for 24 h.

The surface morphology, degree of carbon support material graphitization and the size and dispersion of the Pt nanoparticles on the carbon support material were studied by HR-TEM (JEM-3010, JEOL). Raman spectroscopy was performed using a Horiba Jobin Yvon LabRam HR800 confocal microscope Raman spectrometer with an excitation wavelength of 632.8 nm to characterize the degree of graphitization of the carbon support materials. The X-ray diffraction (XRD) of GCB, Vulcan XC-72, Pt/GCB and Pt/Vulcan XC-72 was performed using a Rigaku RINT/PC X-ray diffractometer using Cu Ka radiation (λ = 1.54056 Å).

2.2. Electrochemical measurements

Electrochemical measurements, including cyclic voltammetry (CV), a rotating disk electrode (RDE) technique and electrochemical impedance spectra (EIS) were conducted with an EG&G Model 2273 potentiostat/galvanostat utilizing a conventional three-electrode test cell. The counter electrode used was a platinum plate, and the reference electrode was a saturated calomel electrode (SCE). The catalyst was dispersed on a glassy carbon (GC) electrode (area: 0.071 cm^2) and was used as the working electrode. The working electrode was prepared as follows: before loading the catalyst on a glassy carbon disk, the disk was first polished with alumina paste (average size 0.05 μm), then washed with deionized water and dried under air. Five milligrams of the electrocatalyst was dispersed by sonication for 30 min in a mixture of 1 mL of ethanol and 50 μL of Nafion solution (5 wt.%) (DuPont, USA). After sonication, 32 μL of the solution was transferred onto the glassy carbon disk and dried at 60 °C for 30 min. The electrocatalyst loading was approximately 0.5 mg cm^{-2} based on the geometric area of the glassy carbon disk. All electrochemical experiments were conducted at 25 °C.

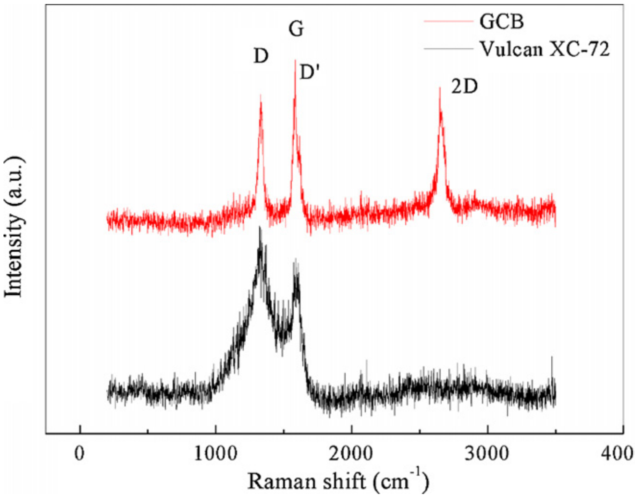

Fig. 1. Raman spectra of the GCB and Vulcan XC-72.

3. Results and discussion

3.1. Structure and morphology of Vulcan XC-72 and GCB

Raman spectroscopy is a standard non-destructive tool for the characterization of various carbon materials [21]. As shown in Fig. 1, the GCB exhibited a D band at ~1330 cm^{-1}, a G band at ~1580 cm^{-1} with a shoulder at ~1615 cm^{-1} (D′ band), and a 2D band at ~2650 cm^{-1}, whereas Pt/Vulcan XC-72 showed two bands centered at ~1299 cm^{-1} (D band) and ~1585 cm^{-2} (G band). We observed that the Raman shift of the G band for GCB was slightly lower than that of the Vulcan XC-72, which is caused by a higher degree of graphitization. The Raman spectra shown in Fig. 1 were analyzed using a set of Gaussian functions to describe the bands, and the results of the peak-fitting analysis are given in Table 1.

Systematic changes were observed when comparing the Raman spectra of the GCB and Vulcan XC-72. GCB shows a decrease in the width of the D, G, and 2D bands and the I_D/I_G ratio and an increase in the I_{2D}/I_G ratio, which is indicative of higher graphitic ordering, as well as increased hardness and decreased electrical resistivity [22–24]. The in-plane crystallization, which describes the average extension of the ordered graphite, can be calculated from the formula reported by Tuinstra et al. [25]:

$$L_a = (4.35\,\text{nm}) \times (I_G/I_D) \quad (1)$$

L_a is calculated to be 1.18 nm for Vulcan XC-72, while this parameter is 5.24 nm for GCB, which also suggests a higher degree of graphitization in the GCB.

The XRD spectra for the GCB and Vulcan XC-72 are shown in Fig. 2. For GCB, the diffraction peaks at ca. 26°, 43°, and 54° are attributed to the (0 0 2), (1 0 0) and (0 0 4) planes of the hexagonal graphite structure (JCPDS No.41-1487), respectively. The (0 0 2) and (1 0 0) peaks of GCB are relatively sharper than those of the Vulcan XC-72, suggesting a higher degree of graphitization, which agrees with the conclusions obtained from the Raman spectra. The *d*-spacing calculated from the (0 0 2) peak, according to the Bragg formula, is 0.343 nm for GCB, which is closer to ideal graphite (d_{002} = 0.335 nm, JCPDS No. 41-1487) than that of the Vulcan XC-72 (0.386 nm). This result suggests that the GCB exhibits a much higher degree of graphitization than Vulcan XC-72.

Fig. 3 shows a typical HR-TEM image of Vulcan XC-72 and the GCB. As shown in Fig. 3(a), the Vulcan XC-72 spheres are comprised of discontinuous graphite sheets with an inter-planar spacing of 0.39 nm, which is assigned to the (0 0 2) plane, indicating the low degree of graphitization. As shown in the HR-TEM image of the GCB