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A carbon riveted Pt/Graphene catalyst with high stability for direct methanol fuel cell

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ABSTRACT

Pt/Graphene catalyst was prepared by microwave-assisted polyol process, and carbonization was riveted onto the catalyst surface to enhance the catalyst stability. The physical properties of the obtained catalysts were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The electrochemical activities and stabilities of the catalyst toward methanol electrooxidation were evaluated by cyclic voltammetry and chronoamperometry. The XRD and TEM results show that the Pt nanoparticles, which are dispersed onto the graphene nanosheets evenly with the diameter of 3–5 nm, form the face-centered cubic (fcc) crystal structure and can be separated by the carbonization. The cyclic voltammetry and chronoamperometry results indicate that the carbon riveted Pt/Graphene has much greater stability than Pt/Graphene with similar activity.

1. Introduction

Direct methanol fuel cell (DMFC) is an attractive and a leading candidate power source for portable and micro-power devices due to its simple structure, high energy density, low pollutant emissions, and instantaneous recharging time [1–4]. However, there are still some drawbacks limiting the commercialization of DMFCs such as slow kinetics of methanol oxidation reaction (MOR) and methanol crossover, etc. Furthermore, another critical problem of DMFC is the low stability of the catalyst due to the agglomeration of Pt nanoparticles, which diminishes the electrochemical activity area of noble metal particles during the electrochemical reaction. Therefore, it is quite necessary to improve the stability of the catalyst.

Previously, a lot of work has been carried out to use carbon based nano-structures, such as carbon nanotubes (CNTs) [5,6], graphite nanofibers (GNFs) [7], to replace Vulcan XC-72 as catalyst support in order to enhance the activity and stability to some extent. Recently, much attention has been paid to graphene due to its stable physical and chemical properties and large surface area. Wang et al. [8] and Bong et al. [9] synthesized PtRu/graphene catalysts with different load, which showed high activity and stability. It was also reported that Pt/RGO [10], Pt–TiO_2–rGO [11] and other graphene based catalysts [12,13] also revealed excellent performances due to the not only similar stable physical and chemical properties, but also large surface area of graphene. Thus graphene has been considered as one of the most promising support for catalyst of DMFC.

To enhance the stability of catalyst ulteriorly, a method of in situ carbonization of carbohydrate has been reported [15,16], which can prevent the agglomerating of Pt nanoparticles. In this study, we prepared Pt nanoparticles on graphene nanosheets by microwave-assisted polyol method and then riveted carbonization which was obtained by in situ carbonization of glucose onto the surface of Pt/Graphene catalyst. The physical properties of the obtained catalysts were characterized by X-ray diffraction and transmission electron microscopy. The electrochemical activities and stabilities of the catalyst toward methanol electrooxidation were evaluated by cyclic voltammetry and chronoamperometry.

2. Experimental

2.1. Materials preparation

The carbon riveted Pt/Graphene was prepared in the following steps, as shown schematically in Fig. 1. Firstly, Pt/Graphene catalyst was prepared by a microwave-assisted polyol method. 50 mg graphene oxide was dispersed into 30 ml ethylene glycol (EG) and isopropyl alcohol (v/v = 4:1) in 100 ml beaker under stirring for 1 h and ultrasonic treatment for 3 h to form uniform ink. Then H_2PtCl_6–EG solution was added and stirred for 2 h. The pH value was adjusted to about 12 using NaOH–EG solution, the mixture was placed in a house-hold microwave oven (800 W) and heated for 80 s. The as-received products were washed with ultrapure

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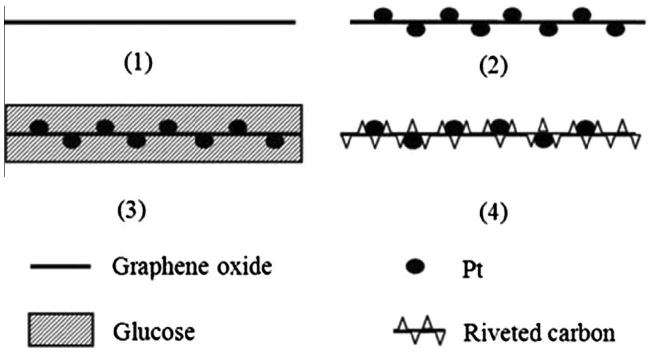

Fig. 1. Schematic diagram of the carbon riveting process. (1) graphene oxide; (2) deposition of Pt nanoparticles onto graphene nanosheets; (3) coating Pt/Graphene with glucose; (4) in situ carbonization of glucose.

water and filtrated, followed by drying under 80 °C for 12 h in vacuum. After that, the prepared Pt/Graphene of 5 mg and glucose ($C_6H_{12}O_6 \cdot H_2O$) of 1.2 mg were dispersed into 5 ml ultrapure water in a 50 ml beaker under ultrasonic treatment for 1 h. The mixture was first dried at 80 °C until the water completely evaporated and then heated in nitrogen atmosphere at 400 °C for 2 h in a tube furnace. The product was cooled to room temperature in nitrogen and then stored in vacuum.

2.2. Preparation of the working electrode

The catalyst slurry was prepared by ultrasonically dispersing 4 mg catalyst in the solution of 0.2 ml ethanol, 0.8 ml ultrapure water and 20 μl Nafion (5 wt.% solution in a mixture of lower aliphatic alcohols and DuPont water) for 30 min. A glassy carbon electrode (GCE) with the diameter of 4 mm was polished with alumina suspensions and served as the underlying substrate of the working electrode. A quantity of 5 μl of the dispersion was extracted out on the top of the GC followed by drying under room temperature for 4 h.

2.3. Structural and electrochemical measurements

X-ray diffraction (XRD) and transmission electron microscopy (TEM) were adopted to characterize the morphological and structural properties of the prepared catalyst.

The electrochemical surface area (ESA) of the catalysts was compared in a nitrogen-saturated 0.5 M H_2SO_4 solution. The electrocatalytic activity for the methanol oxidation reaction was measured in a nitrogen-saturated solution of 0.5 M H_2SO_4 + 0.5 M CH_3OH. The Pt metal loading was 3.9 μg and 3.6 μg respectively and all tests were conducted at room temperature. The glassy carbon disk electrode was made by the above mentioned procedure as the working electrode and a piece of Pt foil with the area of 1 cm^2 was used as the counter electrode. The Hg/Hg_2SO_4 reference electrode (−0.68 V relative to the reversible hydrogen electrode, RHE) was placed near the working electrode. The 0.5 M H_2SO_4 solution was purged with ultrapure nitrogen gas for about 15 min. In this work, the activity and stability of the catalysts were studied by cyclic voltammograms (CV) which was recorded with CHI650D electrochemical analysis instrument with the potential range from −0.75 V to 0.5 V and the scan rate of 50 mV s^{-1}. Before recording the measurement curves, the working electrode was treated by continuous cycling at the scan rate of 50 mV s^{-1} for 50 cycles and a stable response was obtained in order to get rid of the possible effects caused by Nafion. To compare the long-term performance of the two catalysts for methanol oxidation, chronoamperometry tests were used in a solution of 0.5 M H_2SO_4 and 0.5 M CH_3OH for 1500 s with the potential of 1.02 V. In order to ensure reproducible results, fresh electrolyte solution was used for each electrochemical measurement. In this paper, all the reported potentials were versus the Hg/Hg_2SO_4 electrode.

3. Results and discussion

Fig. 2 shows the XRD pattern of Pt/Graphene and carbon-riveted Pt/Graphene. The diffraction peaks of Pt [(111), (200), (220), (311) and (222)] are distinctly observed in the spectrum, indicating that Pt forms the face-centered cubic (fcc) crystal structure. For the carbon riveted Pt/Graphene, the diffraction peak of amorphous carbon also appears at about $2\theta = 25°$, implying that glucose has been carbonized and riveted on the surface of Pt/Graphene.

Fig. 3 shows the TEM images of Pt/Graphene and carbon-riveted Pt/Graphene. It can be seen that the Pt nanoparticles with the diameter of about 5 nm are successively dispersed onto the surface of graphene nanosheets. Compared the two structures in Fig. 3(a) and Fig. 3(b), the analysis result confirms that the crystallite sizes of carbon riveted Pt/Graphene increase obviously. This indicates that Pt nanoparticles are coated by the carbon structure after in situ carbonization of glucose, which can effectively enhance the stability of the carbon-riveted Pt/Graphene by anchoring the crystallites and inhibiting migration and agglomeration (coalescence) of the Pt nanoparticles [14].

Fig. 4 demonstrates the CV curves of Pt/Graphene and carbon-riveted Pt/Graphene in 0.5 M H_2SO_4 solution before and after 100 cycles. The ESA of Pt can be calculated with columbic charges accumulated during hydrogen adsorption and desorption:

$$ESA = \frac{Q_H}{0.21 \times M_{pt}} \tag{1}$$

Where Q_H (mC) is the charge due to the hydrogen adsorption/desorption in the hydrogen region of the CVs, 0.21 mC cm^{-2} is the electrical charge associated with monolayer adsorption of hydrogen on Pt, and M_{Pt} (g) is the loading of Pt metal on the working electrode. The calculated ESAs of Pt/Graphene before and after cycling are 27.84 $m^2\ g^{-1}{}_{Pt}$ and 15.14 $m^2\ g^{-1}{}_{Pt}$, respectively. The ESA only remains 54% after 100 cycles, indicating a poor stability of the Pt/Graphene catalyst. At the same time, the ESAs of Pt/Graphene-C before and after cycling are 16.87 $m^2\ g^{-1}{}_{Pt}$ and 13.03 $m^2\ g^{-1}{}_{Pt}$, respectively. And the ESA still remains 77% after 100 cycles, imply-

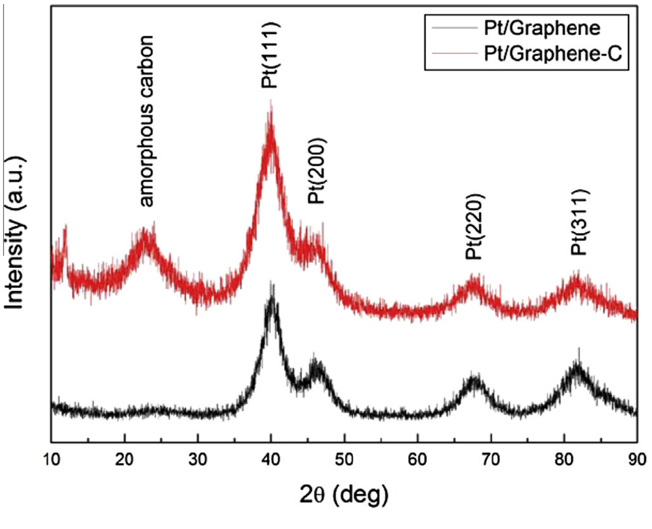

Fig. 2. X-ray diffraction patterns of Pt/Graphene and carbon-riveted Pt/Graphene.