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One step synthesis of Pt/CeO_2–graphene catalyst by microwave-assisted ethylene glycol process for direct methanol fuel cell

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ABSTRACT

Pt/CeO_2–graphene catalyst was rapidly prepared by an efficient one step microwave-assisted process using ethylene glycol (EG) as a green reducing agent. Platinum particles are better dispersed on CeO_2–graphene composite support with smaller sizes. In electrochemical test, Pt/CeO_2–graphene exhibited higher and more durable electrocatalytic activities for methanol oxidation than a comparative Pt/graphene catalyst. The enhanced performance might ascribe to the general promotion of CO_{ads} electrooxidation reaction kinetics by the addition of CeO_2.

1. Introduction

Direct methanol fuel cell (DMFC) has been of great research interest due to its simple structure, high energy density and low pollutant emission, and is considered the most potential energy carrier to meet the continuously increasing demand for portable electronic devices [1–3]. However, catalyst in DMFC still faces many challenges like poor activity and low stability owing to CO poisoning. In recent years, researchers found that metal oxides-based composites (e.g., Pt/CeO_2, Pt/Fe_3O_4, Pt/TiO_2, and Pt/SnO_2) could form synergic effect to deal with the problem [4–7]. Among those widely used metal oxides, the rare earth cerium oxide attracted considerable interest because of its fluorite structure whose cation can switch between the +3 and +4 oxidation states and can act as the role of an oxygen buffer [8]. Some researchers have incorporated CeO_2 into commonly used supporting materials, such as carbon black [9], carbon nanotubes [10], and the results show that the addition of CeO_2 could improve catalytic performance.

Graphene, a two dimensional monolayer carbon material, is quickly becoming the most potential supporting material owing to its unique properties [11,12]. However, only a few reports have considered combining Pt, CeO_2 and graphene to synthesize high qualified catalysts with enhanced electrocatalytic activity and stability. Even the reported ones, such as Yu et al. [13], who prepared Pt–CeO_2/GN electrocatalyst by a hydrothermal process and then a chemical reduction process, their fabrication method of composite catalysts usually involves two or more steps which is very complicated. Therefore, it is very essential to corporate the mentioned three components and use a facile and time-saving coupling method to simplify synthesis process.

Herein, we firstly prepared Pt nanoparticles on the CeO_2–graphene composites by a fast and efficient one step microwave-assisted ethylene glycol method. In the method, ethylene glycol is regarded as a reducing agent for the metal salt compounds and a protecting agent for the metal nanoparticles. 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

Synthesis process: Firstly, 2.85 mg CeO_2 and 20 mg graphene oxide were dispersed into 40 ml ethylene glycol (EG) and 10 ml isopropyl alcohol in a breaker under stirring for 1 h and ultrasonic treatment for 3 h to form uniform ink. Then 0.73 ml H_2PtCl_6–EG solution was added and stirred for 2 h. The pH value of the ink was adjusted by NaOH–EG solution drop by drop until its value

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reached 12. Then argon gas was fed into the ink to expel oxygen. The next step was to place the beaker in the center of a microwave oven (Galanz, 2450 MHz, 800 W) for consecutive heating time for 80 s. The solution was cooled down to room temperature and then dilute HNO_3 solution was added into the mixture to adjust pH value to 4. The mixture was kept stirring for 12 h and then the product was washed repeatedly with ultrapure water until no Cl^- was detected. The homemade Pt/CeO_2–graphene catalyst was dried for 3 h at 80 °C in a vacuum oven and then stored in a vacuum vessel. The theoretical loading of Pt metal is 20 wt% in the sample.

For the purpose of comparison, the Pt/graphene catalyst was prepared without the addition of CeO_2 using the similar procedure mentioned above.

Preparation of the working electrode: The catalyst slurry was prepared by ultrasonically dispersing 4 mg catalyst in the solution of 0.2 ml ethanol and 0.8 ml ultrapure 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.

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 activity and stability of the catalysts were studied by cyclic voltammetry (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 to get a stable response. To compare the long-term performance of the two catalysts for methanol oxidation, chronoamperometry (CA) tests were used in a solution of 0.5 M H_2SO_4 and 0.5 M CH_3OH for 3600 s with the potential of 1.02 V. All the reported potentials were versus the Hg/Hg_2SO_4 electrode.

3. Results and discussion

Fig. 1 compares XRD patterns of Pt/CeO_2–graphene and Pt/graphene. Both samples show peaks characteristic of Pt, that is, (1 1 1) at $2\theta=39.8$, (2 2 0) at $2\theta=68.3$, and (3 1 1) at $2\theta=80.8$. In the XRD pattern for Pt/CeO_2–graphene, five diffraction peaks [(1 1 1), (2 0 0), (2 2 0), (3 1 1), and (4 2 0)] of CeO_2 were observed, corresponding to $2\theta=28.6$, 33.1, 47.5, 56.5, and 79, respectively. The spectrums indicate Pt forms the face-centered cubic (fcc) crystal structure and CeO_2 is with the cubic fluorite structure, and both coexist in the catalysts.

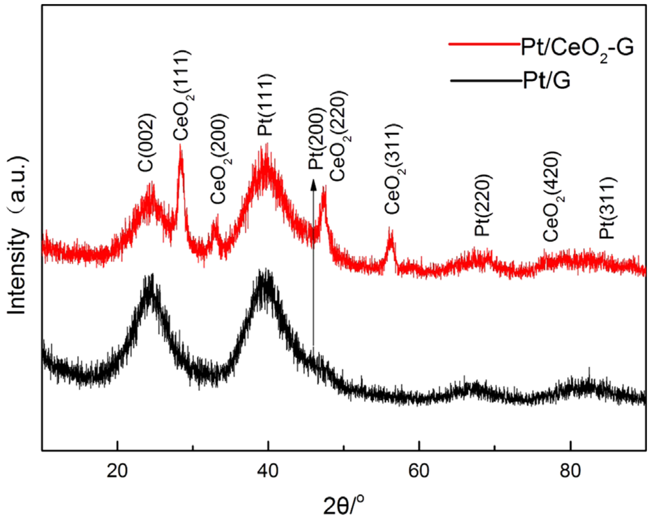

Fig. 1. XRD patterns of Pt/CeO_2–graphene and Pt/graphene.

Fig. 2 shows the TEM images of Pt/graphene and Pt/CeO_2–graphene. Compared with Fig. 2(b), the sizes of platinum particles, shown in Fig. 2(a), become smaller and are better dispersed on graphene support owing to ceria incorporation. To clearly see the morphological structure of Pt and CeO_2, HRTEM test of Pt/CeO_2–graphene was conducted, it can be seen that the reduced Pt particles have been successfully adhered to ceria particles deposited on graphene sheets. The larger sphere with about 4 nm is CeO_2 particle, contacting with Pt particles as presented with smaller sizes of about 2 nm.

Fig. 3(a) demonstrates the cyclic voltammogram (CV) curves of Pt/CeO_2–graphene and Pt/graphene in 0.5 M H_2SO_4 solution. The electrochemical surface area (ESA) is an important parameter describing the catalytic properties for electrooxidation and could be estimated from the integrated charge in the hydrogen adsorption region of the cyclic voltammogram. The calculated ESAs of Pt/CeO_2–graphene and Pt/graphene are 33.25 $m^2\,g^{-1}$ Pt and 24.46 $m^2\,g^{-1}$ Pt, respectively. The higher ESA of Pt/CeO_2–graphene should be due to smaller Pt nanoparticle sizes and better dispersion with the addition of CeO_2.

Fig. 3(b) shows the CV curves of methanol oxidation on the Pt/CeO_2–graphene and Pt/graphene. It can be seen that both of the catalysts have two peaks of methanol oxidation reaction. One is located at 0.23 V in the positive direction and other is at -0.02 V in the negative scan direction. It also reveals the peak current density of Pt/CeO_2–graphene is much higher than that of Pt/graphene, which can be ascribed to the reason that CO_{ads} electrooxides more easily due to the effect of CeO_2 co-catalyst as oxygen storage material. The OH_{ads} species on CeO_2 can transform CO-like poisoning species to CO_2, releasing the active sites on Pt surface for further methanol electrooxidation.

Fig. 3(c) shows CO adsorption–oxidation curves on the Pt/CeO_2–graphene and Pt/graphene. Compared to the Pt/graphene catalyst, the onset and the peak potentials for CO_{ads} oxidation on Pt/CeO_2–graphene catalyst were shifted negatively, which was an indication that the addition of CeO_2 contributed to weakening the CO adsorptive bond on the Pt active sites. The ESA from CO stripping voltammetry can directly reflect the CO-oxidizing ability of the catalysts, assuming that the formation of a monolayer of linearly adsorbed CO and the coulombic charge required for oxidation of CO_{ads} to be 484 μC cm^{-2} [14]. The calculated ESA for the two catalysts were 16.3 $m^2\,g^{-1}$ and 11.4 $m^2\,g^{-1}$ by using the CO_{ads} oxidation charge after subtracting the background current, which implies that CeO_2 can help improve catalytic activity for CO_{ads} electrooxidation.

Fig. 3(d) shows typical current density–time responses for methanol oxidation measured at a fixed potential of 1.02 V. The Pt/CeO_2–graphene catalyst shows higher current density during almost the whole test, and the currents of the two catalysts at 3600 s were 1.14 and 0.38 mA cm^{-2}.

4. Conclusions

In summary, Pt/CeO_2–graphene and Pt/graphene catalysts were successfully synthesized by microwave-assisted glycol process. XRD patterns show that the Pt forms the face-centered cubic (fcc) crystal structure and CeO_2 is with the cubic fluorite structure. TEM images reveal Pt nanoparticles are better dispersed with smaller sizes by the addition of CeO_2. Electrocatalytic activity and stability of the mixture support with CeO_2 are evidently enhanced in comparison with that of single graphene. The reason for the