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Investigation of Co_3O_4 nanorods supported Pd anode catalyst for methanol oxidation in alkaline solution

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Abstract

A Co_3O_4 nanorod supported Pd electro-catalyst for the methanol electro-oxidation (MEO) has been fabricated by the combination of hydrothermal synthesis and microwave-assisted polyol reduction processes. The crystallographic property and microstructure have been characterized using XRD, SEM and TEM. The results demonstrate that Pd nanoparticles (PdNPs) with a narrow particle size distribution (3−5 nm) are uniformly deposited onto the surface of Co_3O_4 nanorods. Electrochemical measurements show that this catalyst having a larger electrochemically active surface area and a more negative onset-potential exhibits enhanced catalytic activity of 504 mA/mg Pd for MEO comparing with the Pd/C catalyst (448 mA/mg Pd). The dependency of log$I$ against log$v$ reveals that MEO on Pd-Co_3O_4 electrode is under a diffusion control. Electrochemical impedance spectroscopy (EIS) measurement agrees well with the CV results. The minimum charge transfer resistance of MEO on Pd-Co_3O_4 is observed at −0.05 V, which coincides with the potential of MEO peak.

Key words

Pd nanoparticles; Co_3O_4 nanorods; methanol electrooxidation; catalytic activity; charge transfer resistance

1. Introduction

Direct methanol fuel cells (DMFCs) show great potential as a future power source for portable applications due to some unquestionable advantages over analogous devices [1]. The methanol electro-oxidation (MEO) in anodic electrode is considered as clean energy converters with very low emission and high energy efficiency [2]. In recent years, great research focused on the enhancement of electro-catalytic ability and reliability of electrode catalysts in DMFCs [3]. Several factors proposed can influence the catalytic stability of electrode catalysts. One well known reason for the gradually decay electro-catalytic performance of catalysts is associated with the generation of strong adsorbed CO-like intermediates [3]. The electrochemistry corrosion of the inert carbon supports of cathodic catalysts at a high potential, resulting in the decrease of the electrochemical active surface area (EASA) and agglomeration of noble metal nano-particles has been considered as another crucial reason [4].

Electrochemical corrosion leads to the physical structural degradation of carbon materials and dissolution of noble metal nanoparticles, which eventually results in the EASA decrease of the cathodic catalysts [5]. Moreover, it has been demonstrated that noble metals can accelerate the carbon supports corrosion [6,7]. These results lead to a gradually inactivation of the cathodic catalyst and thus reduce the long-term stability of DMFC. Therefore, more non-carbon materials, such as metal oxides (TiO_2, SnO_2 and Co_3O_4), have been used as the cathodic catalyst supports to overcome those issues.

Meanwhile, more non-carbon materials can also act as the anodic catalyst supports. Recently, only a few studies have been reported to develop metal oxides as the alternate anodic catalyst supports [8−10]. Zhang et al. [10] fabricated a catalyst based on electrospun PdO-Co_3O_4 nanofiber composite for the MEO in alkaline solution. This catalyst exhibited a high catalytic activity of 722.4 mA/mg Pd toward the MEO. TiO_2 spheres supported Pt catalyst for the oxidation of alcohol has been reported by Hua et al. [11] The results indicated that Pt/TiO_2 spheres exhibited an enhanced catalytic activity and stability in comparison with Pt/C catalyst.

Co_3O_4 shows great application in lithium ion cell electrode material, oxidizing agent and automotive catalyst [9]. In addition, mesoporous Co_3O_4 supported Au catalysts show higher catalytic performance in the electro-oxidation of CO

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due to the oxygen defects in Co_3O_4 and strong interaction between Au nanoparticles and Co_3O_4 [9]. Therefore, it motivates us to fabricate a catalyst for the MEO in which Co_3O_4 nanorods are used as the support and its surfaces are uniformly decorated by Pd nano-particles (PdNPs). In this work, we reported for the first time the electrochemical performance of Co_3O_4 nanorods supported Pd electro-catalyst towards the MEO. The catalytic activity and stability for the MEO on Pd-Co_3O_4 and Pd/C electrodes were studied, and the kinetics of MEO on the catalyst were analyzed.

2. Experimental

2.1. Synthesis of Co_3O_4 nanorods and supported Pd catalyst

2 mmol $Co(NO_3)_2{\cdot}6H_2O$, 4 mmol NH_4F and 10 mmol $CO(NH_2)_2$ were mixed with 50 mL deionized water. After ultrasonic treatment for 30 min, the mixture was put into a stainless steel autoclave and sealed at 105 °C for 5 h, and then cooled down to the room temperature. The mixture solutions were filtered and washed with deionized water. Finally, the sample was dried in an oven at 350 °C for 2 h.

Co_3O_4 nanorods with 30 wt% Pd loading were fabricated by a microwave-assisted polyol reduction process with 0.0565 mol/L $PdCl_2$-EG as a precursor solution. Firstly, as-prepared Co_3O_4 nanorod was impregnated into the solution containing $PdCl_2$ and KBr. 1 mol/L NaOH-EG solution was used to adjust the pH value of the mixture to 9 and then followed by ultrasonic treatment for 30 min to form a uniform suspension. Secondly, the beaker was put into the microwave oven and heated at 800 W for 50 s. The slurry was continuously stirred at room temperature overnight, and then 0.1 mol/L HCl was added into the mixture to adjust pH value of the solution to 4. Finally, after stirring for 3 h, the as-prepared Pd- Co_3O_4 catalyst was filtrated and dried for 12 h at 80 °C. As a comparison, Pd/C was also fabricated by the same method.

2.2. Physical characterization of catalysts

The microstructure morphologies of the Pd-Co_3O_4 catalysts were investigated using an S-530 scanning electron microscope (SEM, HITACHI) equipped with an Oxford energy dispersive X-ray spectroscopy and a JEM 2100 transmission electron microscope (TEM, JEOL). Rint D/max2000 wide angle goniometer (Rigaku Co. Ltd.) system using Cu K_α source was employed to analysis XRD spectra of the catalysts at the 2θ extension from 20° to 90° with a step of 6 °/min.

2.3. Electrochemical measurements

Cyclic voltammetry (CV) measurements were performed on a CHI660D electrochemical workstation (Shanghai Chenhua, China) at 25 °C. Pt sheet served as counter electrode, and a Hg/HgO electrode (MMO) was used as the reference electrode. The fabrication process of the working electrode is as follows: 5 μL catalyst ink, prepared by mixing 2.0 mg Pd-Co_3O_4 powders with 1 mL 5 wt% Nafion ethanol solution (DuPont Corp., U.S.A.), was dropped on a polished glassy carbon working electrode (= 5 mm) using a microsyringe and dried at room temperature.

3. Results and discussions

3.1. Characterization of Pd/C and Pd-Co_3O_4 catalysts

In XRD spectra of Figure 1(a), the recognizable diffraction peaks can be observed at ca. $2\theta = 39°$, 45°, 67° and 80°, which are assigned to the planes of Pd (111), (211), (220), and (311), respectively. A face-centered cubic (fcc) structure of Pd can be indexed according to these diffraction peaks. Those located at $2\theta = 19°$, 32°, 37°, 44.7°, 56°, 59°, 65° are attributed to the Co_3O_4 (111), (220), (311), (400), (422), (440), (511) planes, respectively. It can be seen from Figure 1(b) that spinel structure Co_3O_4 has been successfully prepared by the hydrothermal synthesis. All diffraction peaks are very sharp with strong intensity, indicating that the prepared Co_3O_4 nanorods have a large size in length and diameter. Those results reveal that both fcc structure Pd and spinel structure Co_3O_4 are observed in Figure 1(c). The average PdNPs crystallite sizes in Pd/C and Pd-Co_3O_4 were calculated using the Scherrer's equation based upon the Pd (111) plane diffraction peak, which are 3.73 and 3.5 nm, respectively.

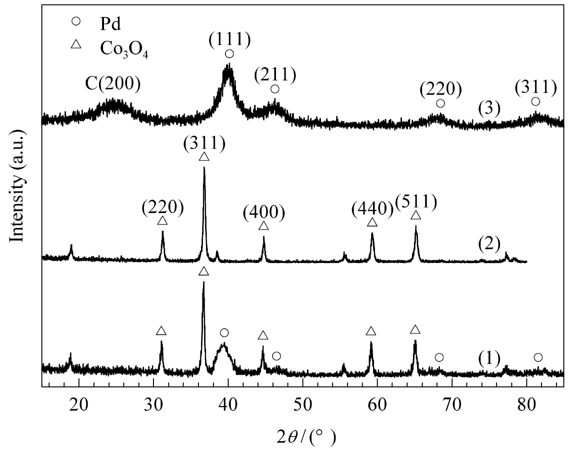

Figure 1. XRD patterns of (a) Pd/C, (b) Co_3O_4 and (c) Pd-Co_3O_4

As seen from Figure 2(b), the Pd deposited onto Co_3O_4 catalyst has been successfully prepared. The first step results in Co_3O_4 nanorods with an average diameter and length of 100 nm and 500 nm (Figure 2a). Then the Co_3O_4 nanorods acted as the support for polyol reduction Pd. After microwave polyol reduction process, Co_3O_4 nanorods were uniformly decorated by PdNPs due to the positive effect of KBr stabilizer. In fact, Br^- can be adsorbed on the surface of Pd particles, and control the growth of Pd to get the uniform PdNPs [3]. Figure 2(e) shows the image of Pd/C prepared