In situ electrodeposition of graphene/nano-palladium on carbon cloth for electrooxidation of methanol in alkaline media

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HIGHLIGHTS

- In-situ electrodeposition of graphene–Pd nanocomposite was achieved on a cheap carbon cloth.
- Well-dispersed Pd was obtained by this facile method.
- This nanocatalyst exhibits high electrocatalytic activity and stability for methanol oxidation.
- Excellent tolerance toward electrode poisoning was observed in alkaline media.

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ABSTRACT

Electrocatalytic oxidation of methanol in alkaline medium is studied using graphene nano-palladium/carbon cloth (G-Pd/CC). X-ray diffraction, scanning electron microscopy (SEM) and atomic absorption spectrometry are used to characterize G-Pd/CC electrode. Electrochemical characterizations are performed using cyclic voltammetry (CV), chronoamperometry and electrochemical impedance spectroscopy (EIS). The results show that the application of CC as a substrate for G-pd reveals excellent characteristics such as high catalytic activity, stability, tolerance toward poisoning effects for electrooxidation of methanol in alkaline medium. All results show that this electrode is a good candidate for application in direct methanol fuel cells.

1. Introduction

Direct liquid fuel cells, such as direct alcohol fuel cells (DAFCs) have attracted much attention as one of the most viable candidates to replace batteries as a source of portable power [1,2]. Methanol and ethanol are popular alternative fuels for DAFCs. Methanol has higher theoretical energy density than other alcohols and is miscible with water [2].

Among the electrocatalysts for alcohols oxidation, Pt and Pt-based alloys have been extensively investigated [3]. However, some challenges such as the cost of Pt or Pt-based electrocatalysts, slow reaction kinetics and electrode poisoning by CO like intermediates which are formed in the alcohol oxidation reaction still remain as problems in using Pt-based catalysts. To overcome such problems, Pt-free electrocatalysts were developed. Among these materials, Pd-based catalysts are less expensive and have a comparable or even better electrocatalytic activities than Pt-based catalysts for alcohol oxidation [4,5].

Although Pd itself has been proven to be a suitable catalyst for electrooxidation of alcohols in alkaline media, more efforts are needed for further improvement of electrocatalytic performance of Pd-based catalysts. Supporting on materials with large surface areas such as carbon black, activated carbon, carbon nanofibers and carbon nanotube [4–6] is one approach. Graphene, as a new carbon nanomaterial with two-dimensional lattice made of sp^2 hybridized carbon atoms, has recently attracted great attention due to its unique electrical, optical, and mechanical properties [7,8]. These unique properties yield potential for applications in energy conversion and storage systems such as fuel cells, batteries, supercapacitors, sensors and solar cells. Many methods have been proposed for graphene production [7,9]. Among these methods,

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electrochemical reduction of graphene oxide (GO) has been attractive because it is simple, fast, and green [7]. Chen et al. showed that GO in solution can be electrochemically reduced to yield graphene on a glassy carbon electrode (GCE) surface [10]. Also, Jiang et al. reported one-step co-electrodeposition of graphene/Pd composite film on the GCE for formic acid electrooxidation [11]. This method is a one-step, simple and fast strategy for co-deposition of graphene and Pd [11] or graphene and Au [7]. In this method, nanoparticles are sandwiched between graphene sheets and a multilayer composite is formed [7]. Recently, a layer by layer Pt graphene is fabricated on the carbon fiber for electrooxidation of methanol [12]. The layer by layer structure exhibits greatly enhanced catalytic activity toward methanol electrooxidation. However, the fabrication method is complicated and has several steps [12].

In the present study, the use of carbon cloth, which has been widely used in fuel cells as current collector due to its good conductivity, high stability and commercial availability, is described as a substrate for fabrication of a graphene-nanoPd/carbon cloth (G-Pd/CC) [11]. Here, graphene and nano-Pd were deposited in situ on CC. The electrocatalytic behavior of the G-Pd/CC is investigated toward methanol electrooxidation in alkaline media. The results show that the G-Pd/CC provides high electrocatalytic activity and good tolerance toward poisoning species for methanol oxidation reaction in an alkaline media. The electrochemical behaviors of this electrode are investigated using cyclic voltammetry (CV), chronoamperometry and electrochemical impedance spectroscopy (EIS).

2. Experimental

2.1. Reagents and apparatus

The graphene oxide (GO) was synthesized by the modified Hummers' method [13]. All chemicals were analytical grade. All electrochemical measurements were carried out using a potentiostat/galvanostat (PGSTAT302) equipped with FRA board for EIS measurements. A three electrode cell containing G-Pd/CC(CC was purchased from E-TEK, 3.6 cm^2) as working electrode, platinum disk as the counter electrode and SCE electrode as the reference electrode was used. CC was used as a substrate for deposition of G-nanoPd. One side of CC was covered with Teflon paper and the electric contact was established via a copper wire. G-Pd composite, was electrodeposited in situ on the CC using a similar method described elsewhere [11]. Briefly, the repetitive cyclic voltammetry (CV, 10 cycles) scanning were carried out from −1.5 V to 0.6 V at 25 mV s^{-1} in a phosphate buffer solution (PBS 0.067M, pH 9.18) containing 0.6 mg mL^{-1} GO and 1 mM palladium chloride (with magnetic stirring and N$_2$ bubbling). For comparison, Pd/CC electrode was prepared by electrodeposition under the same conditions without the addition of GO. GO was deposited in the same way without the addition of palladium salt in the electrolyte. The electrolyte used for electrochemical characterization of the prepared electrode was 1 M KOH and cyclic voltammograms were recorded at a scan rate of 50 mV s^{-1}. The electrolyte solution was deaerated with pure nitrogen for about 10 min prior to each experiment. EIS measurements were carried out from 100 KHz to 10 mHz with a 10 mV Ac amplitude. EIS results were analyzed by using ZMan 2.0 software (ZAHNER-Elektrik GmbH & Co. KG). Scanning electron micrographs (SEM) of the electrode surfaces were obtained by using scanning electron microscopy (Hitachi S-41 field emission SEM (FESEM), model XL30) at an accelerating voltage of 25 kV. Also, the size of the Pd nanoparticles on the graphene nano sheets was evaluated by transmission electron microscopy (TEM, Zeiss, EM10C, 80 KV). Pd loading on the modified electrode was determined by atomic absorption spectrometry (Varian Model SpectrAA 220 (Mulgrave, Vic., Australia).

3. Results and discussion

3.1. Characteristics of G-Pd/CC composite

Fig. 1A shows SEM image of bare CC. The SEM image of reduced GO is shown in Fig. 1B. A typical wrinkled sheet structure of graphene is observed that provides a substrate with large rough surface for nanoparticles modification. A similar morphology has been reported previously [10]. The average size of the Pd nanoparticles on the graphene nano sheets were evaluated from TEM images (Fig. 2D, E, F) and found to be about 8 nm. Also, as shown in Fig 2, Pd nanoparticles can be observed under the graphene sheets. This is because the deposition of Pd nanoparticles was started before deposition of graphene during cathodic scans and yielding a layer of Pd nanoparticles [7]. Then in the high enough cathodic potential (>−1.0 V), GO reduction was occurred and covered the Pd nanoparticles [7,10]. This event repeated several time during cyclic voltammetric scans and led to the formation of multi layered Pd and graphene [7]. Also, as shown in Fig. 2, the nanoparticles of Pd are dispersed homogenously and are not aggregated compared to the case when only Pd is electrodeposited on the CC (Fig. 1C). This may be attributed to the strong anchoring effect between Pd nanoparticles and the graphene surface, which prevents aggregation of the NPs [7,12]. As previously confirmed, the remaining oxygen-containing groups on the reduced GO could provide binding sites for anchoring precursor metal ions or metal nanoparticles [12,14]. Also, aggregation of graphene sheet was prevented when Pd nanoparticles lied between graphene layers and consequently enhanced surface area of G-Pd composite [7]. The EDX spectrum of G-Pd/CC electrode shown in Fig. 1D consists of a sharp peak at 0.28 keV associated with C Kα due to the carbon atoms of G and CC, and a predominant peak at 2.84 keV from Pd Lα$_1$ due to the Pd element [15].

The amount of Pd loading on graphene nanosheets was determined using atomic absorption spectrometry after dissolution of Pd nanoparticles in aqua regia. The Pd loading values for G-Pd/CC and Pd/CC were 0.35 mg and 0.19 mg, respectively. The larger capacity for Pd loading in the G-Pd structure may be attributed to larger surface area of graphene and formation of multi layered structure in this case.

3.2. Voltammetric studies

Fig. 3 shows voltammetric data illustrating the growth of Pd and G-Pd on the CC. As clearly observed, for electrodeposition of G-Pd, the reductive peak current (lower than −1.0 V) increased larger than those in the Pd reduction which indicates that co-deposition of graphene and Pd has been occurred [11].

Fig. 4 shows the cyclic voltammograms (CVs) of 1 M KOH solution (blank solution) at Pd/CC and G-Pd/CC electrodes. As shown in this figure, two regions can be observed. In the first region, between −1.0 and −0.6 V, two well-defined anodic peaks (−0.9 and −0.65 V) and one cathodic peak (−0.9 V) corresponding to the hydrogen adsorption and desorption are observed, respectively [16]. In the second region, between −0.6 and 0.4, a plateau region-type feature (approximately between −0.40 V and 0.40 V) in the positive scan is attributed to the oxidation of Pd and a strong reduction peak (between −0.4 and −0.6 V) in cathodic scan is the characteristic peak for the reduction of PdO$_x$ [17,18]. It should be pointed out that the hydrogen adsorption, desorption for Pd/CC electrodes only form one pair of peaks. Moreover, the current of the G-Pd/CC electrode is much larger than that at the Pd/CC electrode,