



One-pot synthesis of Palladium Silver nanoparticles decorated reduced graphene oxide and their application for ethanol oxidation in alkaline media



Karim Kakaei*, Maryam Dorraji

Department of Physical Chemistry, Faculty of Science, University of Maragheh, P.O. Box. 55181-83111, Maragheh, Iran

ARTICLE INFO

Article history:

Received 7 June 2014

Received in revised form 17 July 2014

Accepted 24 July 2014

Available online 19 August 2014

Keywords:

electrochemical exfoliation
graphene oxide
palladium silver nanoparticles
ethanol oxidation

ABSTRACT

We report a Pd-Ag (1:1)/graphene (PdAg/G) catalyst through a one-step strategy, for the ethanol oxidation in alkaline media. Graphene is synthesized from graphite electrodes using ionic liquid-assisted electrochemical exfoliation. Graphene-supported Pd-Ag electrocatalyst is then reduced by ethylene glycol as a stabilizing agent to prepare highly dispersed PdAg nanoparticles on carbon graphene oxide to be used as ethanol oxidation in direct ethanol fuel cell (DEFC) catalysts. X-ray diffractometer and scanning electron microscopy techniques are used to investigate the crystallite size and the surface morphologies respectively. The electrochemical characteristics of the Pd-Ag(1:1)/G, Pd/G and Ag/G catalysts are investigated by cyclic voltammetry (CV) in nitrogen saturated sulfuric acid aqueous solutions and in mixed sulfuric acid and ethanol aqueous solutions. Detailed electrochemical studies (involving chronoamperometry, cyclic voltammetry and linear sweep voltammetry) prove that the electro-catalytic oxidation of ethanol at the Pd-Ag(1:1)/G is more stable, occurring at lower potential, giving lower Tafel slopes compared to Pd/G and Ag/G catalysts, which can reveal the particular properties of the exfoliated graphene supports and PdAg alloy.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Development of novel catalysts with highly electro-catalytic activity for ethanol oxidation has been receiving much attention due to activity of anodic materials is one of the main factors influencing the practical application of direct ethanol fuel cells (DEFCs) [1]. The main advantages of alkaline medium comes from the fact that the electrode reaction kinetics in this medium is higher than in the acid medium, enabling the use of non-platinum catalysts [2]. Moreover, the alkaline media provides a less corrosive environment for the electrodes. Although alkaline media has advantages, it still has a major drawback in the fact that fuel cells exchange membranes are more difficult to achieve (since these have to conduct OH⁻ groups instead of protons). This makes current fuel cell technology based on alkaline fuel cells more difficult to realize.

The use of ethanol as fuel has several advantages in comparison to methanol and H₂: it is a cheap liquid fuel, possesses high volume energy capacity, non-toxic and with a high thermodynamic

efficiency. But, DEFCs have a lower theoretical potential (1.15 V vs. 1.23 V for H₂-fuel cells at the standard condition) [3].

However, the electrochemical oxidation of ethanol is complex because of 12 electrons should be released to split the C-C bond [4]. During the oxidation of ethanol, adsorbed carbon monoxide is formed while acetaldehyde, acetic acid and carbon dioxide are the main products. The production of acetic acid and acetaldehyde can reduce the fuel cell efficiency [5,6]. It was found that the dissociative adsorption of ethanol proceeds rather quickly and the rate-determining step is the removal of the adsorbed ethoxy by the adsorbed hydroxyl [7,8].

Platinum electrodes show efficient catalytic activity for ethanol oxidation in acidic and alkaline media. But the widely application of Pt catalysts as anodes in DEFCs is limited by the high cost of the platinum; whereupon non-platinum catalysts have been used as anode catalysts for DEFCs [9,10]. Palladium is a relatively low price noble metal and 50 times more available in the earth than Pt [11]. The Pd electrode exhibits no electrocatalytic activity for ethanol oxidation in acidic solutions while it shows high electroactivity for ethanol oxidation in alkaline solutions [12–16]. There are two main ways to improve catalytic activity of catalysts nowadays. The first case is choosing a suitable substrate material. For this purpose, the Pd electrocatalyst has recently

* Corresponding author. Tel.: +98 421 2276068; fax: +98 421 2276066.

E-mail addresses: kakaiei@maragheh.ac.ir, k.kakaiei56@yahoo.com (K. Kakaiei).

been produced in highly dispersed form on various supports, such as carbon Vulcan [17], carbonized TiO₂ nanotube [18], multi-walled carbon nanotubes (MWCNT) [19] and carbon microspheres [20]. It was found that reduced graphene oxide (RGO) has very intriguing physical properties that suggest it can have a wide variety of applications [21–27]. Graphene has received significant attention in recent years due to their unique electronic, physical, mechanical, thermal and chemical properties, such as excellent conductivity, high surface area, ease of functionalization and potentially low manufacturing cost [25,26]. In the second strategy, considering the synergistic effect, the Pd catalyst surface is modified by the addition of a second metal [28–30]. One of the most promising catalysts involves Pd–Ag bimetal for alcohol oxidation in alkaline medium [7,14,31–34]. Nguyen et al. [14] found that Pd–Ag/C exhibited an excellent activity, enhanced CO tolerance and better stability than Pt/C and Pd/C. The activated CNTs-supported Pd–Ag(1:1) catalyst was synthesized by Li and coworkers [33], and demonstrated larger electroactive surface and better catalytic activity for methanol oxidation in alkaline media. Li et al. [31] prepared bimetallic PdAg catalysts with Pd/Ag atomic ratios varying from 4/1 to 1/2 by an impregnation–reduction method. They showed that, the catalytic activities for the Pd_xAg_y/C catalysts toward the EOR are improved by alloying Pd with Ag. Liu et al. synthesized the graphene oxide by hummer method and then co-reduced Pd–Ag on graphene and indicates that the PdAg/RGO nanocomposites are of interest as promising candidates for application in ethanol fuel cell. However, this approach is not applicable for large-scale production of graphene.

Based on above, the combination of RGO, Ag and Pd provides good opportunities for making novel and high performance catalysts. In our previous work, we prepared RGO supported Pt by electrochemical reduction method [25]. The results suggest that the Pt/RGO show an enhanced electro-catalytic activity for the oxidation of methanol in acidic media in comparison to the Pt/C(E-TEK) catalyst. So that, we used urea choline chloride as an ionic liquid in order to synthesize GO nanosheets by electrochemical method using graphite rod and it is applied as the basis of Pd and Ag nanoparticles. We have also obtained binary and ternary composite of Pd, RGO, and Ag via impregnation method and studied them as electro-catalysts on glassy carbon electrode (GCE) for the ethanol oxidation in alkaline medium. Results obtained were very encouraging and will be discussed in this article.

2. Experimental

2.1. Graphene and GO generation

The preparation of the GO and graphene was described previously [25] but we shall briefly repeat the main features here. The graphite rod was inserted as anode into the ionic liquid (IL)/water solution, placed parallel to the other graphite rod as counter-electrode with a separation of 1 cm. The ionic liquid Urea choline chloride was mixed with water at 1:1 ratio. Static potentials of 5 V were used to the two electrodes using a DC power supply. The exfoliation products were washed with water and surfactant until the pH was neutral and the products were separated by filter and ultra-centrifugation at 10,000 rpm at 25 °C. Three stages in the electrochemical exfoliation are occurred. In stage I, there is an induction period before visible signs of exfoliation can be detected. The color of the electrolyte changed from colorless to yellowish and then dark brown. In stage II, a visible corrosion and expansion of the graphite in anode side can be seen. In stage III, the expanded flakes peel off from the anodes and form the black slurry with the electrolyte.

2.2. Preparation of Ag/G, Pd/G and PdAg/G

For the synthesis of graphene-supported Pd–Ag (PdAg(1:1)/graphene) catalysts, 50 mg of graphene oxide was dispersed in 20 ml of ethylene glycol solution as reducing agent [35,36] and sonicated for 1 h. Subsequently, 1 ml of palladium chloride solution (5 mg/mL) and 1 ml of silver nitrate (AgNO₃) solution (5 mg/ml) were added to the graphene oxide solution and sonicated for 2 h. The pH of the solution was adjusted to 10 using sodium hydroxide (NaOH) solution (0.5 mol/L), and then the solution was stirred under flowing argon at 130 °C for 8 h. The solid material produced was then centrifuged, washed 3 times with deionized water and finally dried in a vacuum oven at 45 °C for 24 h. For the synthesis of the graphene-supported Pd (Pd/G) and graphene-supported Ag (Ag/G) catalysts, the only difference was the omission of AgNO₃ solution in the solution of graphene oxide or PdCl₂. For comparative purposes, deposition of Pd nanoparticles on vulkan carbon was also achieved by the similar procedure.

2.3. electrochemical measurements

All the electrochemical experiments were performed with a conventional three-electrode electrochemical cell using a μAUTOLAB Type III Potentiostat–Galvanostat with computerized control by GPES (General Purpose Electrochemical Software) software at room temperature. A Pt rod of 3.1 cm² apparent area was used as the auxiliary electrode and a double junction Ag/AgCl/KCl (saturated) electrode was employed as the reference electrode. All potentials given in this work are referred to the saturated hydrogen electrode (SHE) in the working electrolyte electrode. A glassy carbon disk held in a Teflon cylinder with a geometrical surface area of 0.031415 cm² was used as working electrode.

To prepare the working electrode, 5.0 mg as-prepared catalysts were dispersed in 2 ml solution containing of 1.91 μ of isopropyl alcohol and 90 μ of Nafion solution (5 wt%, DuPont) under ultrasonic stirring for 30 min. A 4 μ aliquot of the slurry was dropped onto the polished GCE by using a micropipette and dried at oven at 60 °C. The total Pd loading on the electrode was kept at 5 μg. Before measurements, the electrolyte (1 M KOH or 1 M KOH + 0.5 M C₂H₅OH solution) was bubbled with N₂ for 35 min to remove dissolved oxygen.

2.4. Physical Measurements of Electrocatalysts

2.4.1. ICP

Inductively coupled plasma (ICP) study of the dissolved electrocatalysts were conducted to estimate bulk Pd and Ag contents. For these measurements ones dissolved 5 mg of each sample in a mixture of hydrochloric acid and nitric acid (3:1). The solutions were refluxed at 120 °C and finally the percentages of Pd and Ag were determined by ICP according to the standard solution of Pd and Ag. For the calibration curve, the various solution with proper concentration of Ag (5, 10, 20, 30, 50 and 100 ppm) and Pd (5, 10, 20, 30, 50 and 100 ppm) were prepared. The error of this experiment is around 2–5%.

2.4.2. XRD

XRD analysis was carried out for the electrocatalysts by using an XPERT MPD Philips diffractometer with a Cu X-ray source operating at 40 kV and 30 mA. The XRD patterns were obtained at a scanning rate of 1° min⁻¹ with a step size in the 2θ scan of 0.02° in the range 2–100°. The average particle size was calculated from the (2 2 0) diffraction plane using the Scherrer equation [37]. The lattice

Download English Version:

<https://daneshyari.com/en/article/185155>

Download Persian Version:

<https://daneshyari.com/article/185155>

[Daneshyari.com](https://daneshyari.com)