



Palladium nanoparticles/nanostructured carbon black composite on carbon–ceramic electrode as an electrocatalyst for formic acid fuel cells



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ARTICLE INFO

Article history:

Received 16 December 2014
Revised 21 April 2015
Accepted 17 May 2015
Available online 10 June 2015

Keywords:

Pd nanoparticles
Carbon black
Carbon–ceramic
Formic acid
Electrooxidation

ABSTRACT

Palladium nanoparticles/nanostructured carbon black composite (PdNPs/NCB), supported on the carbon–ceramic electrode (CCE), has been prepared by a chemical reduction method using sodium borohydride as a reducing agent. The synthesized composite was characterized by scanning electron microscopy, high resolution transmission electron microscopy, energy-dispersive X-ray spectroscopy, X-ray diffraction and electrochemical methods to delineate its surface morphology, nanostructure properties, composition, crystal phases and electrochemical properties. The obtained modified electrode, PdNPs/NCB/CCE, was used as an efficient electrocatalyst for the oxidation of formic acid. Electrochemical techniques including cyclic voltammetry and chronoamperometry were applied for electrocatalytic investigations and it was found that the PdNPs/NCB/CCE was catalytically more active than the Pd nanoparticles supported on the CCE without NCB (PdNPs/CCE). The effect of some experimental factors was studied and optimum conditions were suggested. The obtained results show that the PdNPs/NCB/CCE has satisfactory stability and reproducibility for electrooxidation of formic acid when stored in ambient conditions and improved electrocatalytic activity in continued cycling which make it more attractive for formic acid fuel cell applications.

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1. Introduction

Direct formic acid fuel cells (DFAFCs) are attractive and clean power sources due to the non-toxicity and non-flammability properties of formic acid and its easy storage and transportation, so that the DFAFCs can be used as a suitable power source for portable electronic and micro electromechanical systems [1–4]. Although the energy density of a DFAFC is lower than that of a direct methanol fuel cell, its power density is significantly higher than one; consequently, for many systems, especially smaller power systems, the advantages of DFAFCs can outweigh those of its primary direct liquid fuel cell contender, the direct methanol fuel cell [2,5,6].

Pt-based electrocatalysts are widely used in direct liquid fuel cells. However, these electrocatalysts easily undergo carbon monoxide (CO) poisoning in DFAFCs; it was found that the electrooxidation of formic acid on the Pt-based electrocatalysts is through the indirect pathway: electrooxidation of formic acid via the formation of adsorbed CO. Also, the high cost and limited resources of this precious metal prevent the commercialization of the DFAFCs [7,8]. Therefore, a large number of researches have been focused on the exploration of less expensive and more abundant non-Pt electrocatalysts with enhanced

performance. Pd-based electrocatalysts have received significant attention in the recent years due to their high performances in formic acid electrooxidation and are now considered as good candidates for electrocatalysis in DFAFCs [9,10]. On the other hand, among the Pd-based electrocatalysts, Pd nanoparticles (PdNPs) have higher electrocatalytic activity and lower cost in comparison with Pt nanoparticles and these facts make them as an attractive alternative for Pt in DFAFCs. In addition, PdNPs catalyze the formic acid electrooxidation via direct oxidation pathway and exhibit great resistance to CO-like poisoning intermediates [9]. In direct pathway, formic acid oxidized directly to carbon dioxide without formation of CO poisoning intermediate [11–13].

In order to further improve the electrocatalytic activity of the PdNPs and also to minimize the overall cost of DFAFCs, PdNPs are deposited on/in different conductive supports [14–17]. Previous investigations have shown that the electrocatalytic activity and durability of PdNPs depend not only on their features but also on the type of support and its properties [18]. So, the performance of a catalyst support in fuel cell environments is of great importance in development of novel electrocatalysts [16–18]. Corrosion resistance, electrical conductivity, porosity and synergistic effects with electrocatalyst nanoparticles are also important factors in choosing a good catalyst support. If the electrocatalyst nanoparticles cannot preserve their structure and composition over the lifetime of the fuel cell, any change in their morphology, structure and composition will result in

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a loss of electrochemical activity [19]. Carbon materials are one of the most widely used electrocatalyst supports in different forms such as carbon nanotubes, carbon nanofibers, carbon aerogels, nanoplates of graphene, and *etc.* [20,21]. These supports increase the availability of electrocatalysts surface area and mass transfer of reactants [22–24]. A survey in the literature shows that the carbon black (CB) was used as catalyst support in some reports [25–32] due to its low cost, higher surface-area-to-volume ratio, higher tensile strength, higher resistance to abrasion and high availability. However, despite such potential capability of CB, there is only one report on the immobilization of boron-doped Pd nanoparticles supported on CB [26] and its application as an electrocatalyst for formic acid electrooxidation.

In the present study, we prepared Pd nanoparticles/nanostructured carbon black composite (PdNPs/NCB), loaded on the carbon–ceramic electrode; including interesting properties such as high porosity, conductivity, relative chemical inertness, good mechanical properties, physical rigidity and stability in various solvents and stability [33–36], via a simple and efficient method. The obtained modified electrode, PdNPs/NCB/CCE, was used as an efficient electrocatalyst for oxidation of formic acid. It was found that the PdNPs/NCB/CCE was catalytically more active than the Pd nanoparticles supported on CCE without NCB (PdNPs/CCE) and had satisfactory stability and reproducibility when stored in ambient conditions or continues cycling which make it more attractive for formic acid fuel cell applications. Of course, it should be noted that, for practical application of the PdNPs/NCB/CCE electrocatalyst as an anodic material in DFAFCs, further studies are necessary. Therefore, additional works should be done in the future to gain more detailed insight into the applications of electrode systems in DFAFCs.

2. Material and methods

2.1. Chemicals

Methyl trimethoxy silane (MTMOS) and palladium chloride were purchased from Sigma-Aldrich. Sodium borohydride, graphite powder, methanol, hydrochloric acid, nitric acid, sulfuric acid and formic acid were purchased from Merck and nanostructured carbon black was purchased from US Research Nanomaterials. All solutions were freshly prepared with double distilled water.

2.2. Preparation of the electrocatalyst

Carbon–ceramic electrode (CCE) as an electrode substrate for supporting the synthesized composite was fabricated by the sol-gel process according to the following procedure: 0.9 ml MTMOS was mixed with 0.6 ml methanol and 0.6 ml of 0.1 M HCl. The mixture was stirred to form a clear and homogeneous solution. 0.3 g of graphite powder was added to the solution and stirred for another 5 min. Then the homogeneous mixture was packed into a Teflon tube (with 3 mm inner diameter and 10 mm length) and dried it for at least 24 h at room temperature. To set up an electronic contact, a copper wire was inserted through the end of prepared electrode.

The preparation of the composite can be described as follows: NCB was functionalized, NCB is chemically inert so for deposition of electrocatalyst nanoparticles it is necessary to functionalize the surface of NCB via the oxidation of NCB with HNO_3 and H_2SO_4 or H_2O_2 to introduce the hydroxyl (–OH), carboxyl (–COOH) and carbonyl (–CO) groups on its surface [37], under reflux condition in a boiling solution of mixed acids (H_2SO_4 : HNO_3 , 1:3, v/v ratio) for 8 h, and the obtained functionalized NCB filtrated and washed with double distilled water and dried at 60 °C under vacuum condition for 10 h. Then, 40 mg of functionalized NCB was dispersed in 100 ml ethanol/water (1:1, v/v ratio) and sonicated for 1 h to form a uniform suspension. PdCl_2 solution (10 mg of PdCl_2 in 5 ml water) was added to the suspension. The suspension was stirred for 2 h. Then a fresh solution of

sodium borohydride (100 ml, 1 mg/ml) was added drop wise into the suspension during 2 h under vigorous stirring to reduce Pd precursor. After adding the sodium borohydride, the mixture was stirred for another 2 h. Finally, the suspension was filtered and obtained black solid, as-prepared PdNPs/NCB composite with a Pd loading of 13 wt%, was washed with double distilled water for several times and dried overnight in oven at 70 °C.

For preparation of the electrocatalyst (PdNPs/NCB/CCE), CCE was polished with an emery paper grade 1500. To load the synthesized composite on CCE, it is necessary to prepare composite ink. For preparation of the composite ink, 5 mg of composite sample was added into 1 ml ethanol. The mixture was ultrasonically dispersed for 1 h to obtain homogeneous ink. Next, 50 μl of the obtained ink was uniformly loaded onto freshly polished CCE and was dried under ambient condition. The loading density of the PdNPs/NCB composite on the CCE surface was about 3.57 mg/cm^2 .

2.3. Instrumentation

The electrochemical experiments were carried out using a SAMA (SAMA Co. Iran) instrument (potentiostat/galvanostat) equipped with a USB electrochemical interface. A conventional three electrodes cell was used at room temperature: A disc of PdNPs/NCB/CCE (with a geometrical surface area of 0.070 cm^2) was used as working electrode, an Ag/AgCl electrode and a platinum wire were used as the reference and auxiliary electrodes, respectively. A LEO1430 vp (Carl Zeiss, Germany) scanning electron microscope (SEM) equipped with energy-dispersive X-ray spectroscopy (EDXS) was used to surfaces and morphology, nanostructure properties and chemical composition characterization of the PdNPs/NCB composite. X-ray diffraction (XRD) pattern was recorded with a Bruker AXS model D₈ Advance (Karlsruhe, Germany) instrument with $\text{Cu-K}\alpha$ radiation source (1.54 Å) at 40 kV and 35 mA at room temperature. The 2θ angular regions between 5° and 90° were explored at a scan rate of 5°/min. High resolution transmission electron microscopy (HRTEM) investigation was made on a Carl Zeiss 906 E (Gottingen, Germany) microscope with a 10 kV accelerating voltage and grid size 200 meshes.

3. Result and discussion

3.1. Physical characterization of the composite

Fig. 1(a) shows the surface morphology of the bare CCE immediately after polishing with an emery paper, grade 1500. As seen in this image the surfaces of the bare CCE is dense, scaly and consist of platelets, defined by the layer structure of graphite, which are relatively uniform in size. The platelets are characterized by an interconnected network of carbon powder particles held together by the silica gel [38]. Rough and porous surface of CCE made it as a suitable substrate for the immobilization of composite or dispersion of metal nanoparticles. Fig. 1(b) displays a typical SEM image of NCB, demonstrating that NCB consists of aggregates of the *ca.* 25–60 nm main CB particles leading to a regular and uniform surface. Fig. 1(c) shows the SEM image of PdNPs/NCB composite. The white visible spots are believed to be PdNPs lying on the NCB surface. To obtain the acceptable scientific information about the PdNPs on the NCB surface, SEM-energy dispersive X-ray-analysis (SEM/EDX), HRTEM and XRD experiments were carried out. Fig. 1(d) shows the corresponding EDX spectrum of PdNPs/NCB composite. The peaks corresponding to Pd, C and O elements, confirm the existence of PdNPs in the prepared composite. It should be noted that, O atoms derived from functional groups such as hydroxyl, carboxyl and carbonyl which are formed on outer walls of the NCB during functionalization process. XRD pattern of the prepared composite is shown in Fig. 1(e). The 2θ angular regions from 5° to 90° were explored at a scan rate of 5°/min in order to obtain the particle size using Debye–Scherrer's formula [39]. In the XRD pattern,

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