Electrochimica Acta 203 (2016) 41–50

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Highly efficient electrocatalytic oxidation of glycerol by Pt-Pd/Cu trimetallic nanostructure electrocatalyst supported on nanoporous stainless steel electrode using galvanic replacement

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ARTICLE INFO

Article history:
Received 15 March 2016
Accepted 6 April 2016
Available online 7 April 2016

Keywords:
Alkaline fuel cells
Pt-Pd/Cu trimetallic electrocatalyst
Nanoporous stainless steel
Galvanic replacement
Glycerol electrooxidation

ABSTRACT

In this work, glycerol electrooxidation in alkaline solution, as an interesting fuel in fuel cells, was studied at a modified Cu filled nanoporous stainless steel (NPSS) electrode decorated by Pt and Pd (Pt-Pd/Cu/NPSS). Firstly, nanopores were fabricated on the surface of a stainless steel support (NPSS) by anodizing and then Cu was filled into the pores by electrodeposition (Cu/NPSS) using multiple step potential. The Cu/NPSS electrode was decorated with Pt and Pd using galvanic replacement method by immersion into a precursor solution containing Pt and Pd. The surface morphology and composition characterization of the prepared electrode indicate the formation of the Pt and Pd nanoparticles with an average diameter of about 45 nm. The electrochemical studies of the Pt-Pd/Cu/NPSS electrocatalyst revealed that the electrooxidation of glycerol in 1.0 M KOH solution in compare to Pd/Cu/NPSS and Pt/Cu/NPSS, gives higher current density (J) by a factor of 4.2 which occurs at a lower onset potential ($E_{onset} = -0.54$ V). It was found that the electrochemical active surface area (EASA) of the electrode in comparison with the Pd/Cu/NPSS and Pt/Cu/NPSS electrodes is more than 1.3 times and it was more resisting to the poisoning components. The proposed electrocatalyst demonstrates vastly superior electrocatalytic properties, indicating a great potential in direct alkaline alcohol fuel cells application.

1. Introduction

In recent years, reducing of fossil fuel resources and increasing worldwide energy demand impel scientists to focus on other energy resources. Fuel cells, due to their clean exhaust and high-energy efficiency are environmentally friendly and regarded as promising future power sources [1–3]. Direct alkaline alcohol fuel cells (DAAFCs) provide higher energy density and have found more advanced applications [4,5]. Among alcohols used in DAAFCs, polycarbon alcohols produce higher energy density. In this case, glycerol that is produce in a large scale as one of the byproducts of the biodiesel production is an inexpensive one [6]. Furthermore, its oxidation products are not toxic, so it is classified as a green fuel.

The high cost of fuel cells electrocatalysts (especially Pt-based electrocatalysts) is one of the obstacles against becoming economical [7,8]. Although recent studies try to replace Pt with non-precious or less precious metals, it is still more practical for real sample fuel cell applications [3]. A solution to reduce the cost, mitigate poisoning effect and improve the power output of DAAFCs, is to alloy Pt with non-precious or less precious metals such as Pd, Au, Ru, Ni, Rh, Cu, Mo and Bi [4,9]. It is found that adding of these elements disrupts the continuity of the Pt lattice and provides sites for OH adsorption to remove CO from the noble metal through its oxidation [10,11]. Among these metals, Pd has remarkable electrocatalytic activity in alkaline media [12]. To improve the catalytic performance of noble metals, modifying nanostructures and dispersing nanoparticles of noble metals with small size on the surface of the substrate could greatly be effective [5,7]. In this case, a simple and effective method is the galvanic replacement of a less-noble metal with a nobler one, which makes nanostructures with lower amount of required noble metals and higher efficiency [12]. Moreover, electrocatalyst support has a crucial role on the performance and prime cost of the catalyst/substrate. Stainless steel (SS) is an inexpensive, corrosion resistant, electrically conductive and mechanically stable substrate [13]. The surface of SS, before the formation of nanostructures, is not adhesive enough for other deposited metals. In order to improve the surface characterizations of SS and increase its surface

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http://dx.doi.org/10.1016/j.electacta.2016.04.024

area, anodizing has been used as an inexpensive and effective technique to form uniform and size controllable nanoporous structure [14].

The catalytic performance of the Pd/Cu/NPSS electrocatalyst for glycerol electrooxidation was previously reported. The results show that the galvanic replacement of Pd with the electrodeposited Cu onto the NPSS provides a bimetallic electrocatalyst. Utilize of this method provides a nanoscale layer of Pd nanoparticles with less amount of Pd. The aim of this paper is to improve the catalytic performance of the electrode by adding small amount of Pt to Pd/Cu/NPSS. For this purpose, Pt and Pd replaced Cu and then, the performance of the new catalyst was investigated. It was found that the new electrocatalyst (Pt-Pd/Cu/NPSS), exhibits higher electrocatalytic activity and stability for glycerol oxidation in alkaline media in comparison with Pd/Cu/NPSS.

2. Experimental

2.1. Materials and reagents

$CuSO_4.3H_2O$ (Merck), $H_2PtCl_6.6H_2O$ (99.9%, Merck), $PdCl_2$ (99.9%, Merck), perchloric acid (70%, Merck), ethylene glycol (99.0%, Merck), boric acid (99.5%, Merck), potassium hydroxide ($\geq$85%, Merck), hydrochloric acid (37%, Merck) and glycerol (Hopkins and Williams Ltd) were used. Double distilled water was used in all experiments.

2.2. Instrumental

A homemade DC power supply (Sepahan Tak) was used to perform anodizing. An Autolab PGSTAT 30 (Echo Chemie, The Netherlands) with a conventional three-electrode electrochemical cell was used for Cu electrodeposition and all the electrochemical measurements. A saturated calomel electrode (SCE) was applied as the reference electrode (RE) while Pt rod was used as the counter electrode (CE). A field emission scanning electron microscope (FESEM, Hitachi S4160) operated at an accelerating voltage of 25.0 kV was used to examine the morphology of the prepared electrodes. To determine the catalyst chemical composition, an energy dispersive X-ray spectrometer (EDS) attached to the SEM (Seron technology AIS2300C) was used. The structures of the Pt-Pd/Cu/NPSS electrocatalyst was examined by X-ray diffraction (XRD, Philips X'PERT MPD; Germany) equipped with Cu Kα radiation operating at 40 kV and 35 mA in the 2θ range from 20° to 90° employing a scan rate of $0.05^{\circ}\ s^{-1}$. The amount of the Pt and Pd loading through galvanic replacement reaction were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES, Perkin Elmer Optima 7300DV; USA).

2.3. Modified NPSS Electrodes preparation

A 308 stainless steel rod with a diameter of 2.4 mm was used as the electrocatalyst support. It was embedded into Teflon, to obtain an electrode with a constant geometric area of $0.045\ cm^2$. According to our previous work [13], SS was polished, anodized and electrodeposited with Cu. Pulsed electrodeposition technique, with an optimum three pules steps contains cathodic-anodic-delay time, was continuously applied 9 times in deoxygenated copper solution under N_2 atmosphere.

For spontaneous deposition of Pt and Pd, the Cu/NPSS electrode was immediately immersed into a 0.1 M HCl solution containing 4.0 mM $H_2PtCl_6.6H_2O$ and $PdCl_2$ by atomic ratio of 1:2 (Pt:Pd) for 25 min (the optimal concentration and time). The prepared electrode was named Pt-Pd/Cu/NPSS.

For comparison, Pt/Cu/NPSS and Pd/Cu/NPSS electrodes were prepared under the same conditions. In addition, a pure Pt rod with a diameter of 2.0 mm (embedded into Teflon to obtain an electrode with a constant geometric area of $0.031\ cm^2$) was used for comparison.

2.4. Electrochemical measurements

The electrocatalytic activity of the electrode was evaluated in 1.0 M KOH solution with or without 5.0 wt% glycerol in N_2-saturated solution at room temperature. The reported potentials in this work are versus the SCE reference electrode. The cyclic voltammetry (CV) traces were recorded in the potential range from -1.0 to 0.3 V at a scan rate of $50\ mV.s^{-1}$. Electrochemical impedance spectroscopy (EIS) was used to study the electron transfer kinetics of glycerol on Pt-Pd/Cu/NPSS, Pd/Cu/NPSS and Pt/Cu/NPSS. Stability tests were carried out using chronoamperometry and chronopotentiometry techniques.

3. Results and discussion

3.1. Microscopic and spectroscopic characterizations

Fig. 1a indicates the self-organized nanopores that formed on the surface of SS at the voltages of 35 V. In top view FESEM image of the Cu/NPSS electrode (Fig. 1b), filling of nearly all the pores and out of them in the pore direction is observed.

Fig. 1c-e depict FESEM images of the Pt-Pd/Cu/NPSS, Pd/Cu/NPSS and Pt/Cu/NPSS electrode surfaces and determine the size of nanoparticles that are formed during galvanic replacement. FESEM image of the Pt-Pd/Cu/NPSS electrode (Fig. 1c) indicates that a compact layer of nanoscale particles with a diameter of about 45 nm covers the surface of the electrode. On the surface of Pd/Cu/NPSS, a fragmentary layer of nanoparticles with the average diameter of about 51 nm is formed (Fig. 1d). This discontinuity reduces the efficiency of the catalyst per geometric area of the electrode. In Fig. 1e Pt nanoparticles on the surface of Pt/Cu/NPSS are aggregated, which affects the performance of the electrode for electrochemical reaction in comparison with the Pt-Pd/Cu/NPSS and Pd/Cu/NPSS electrodes.

In order to determine the chemical composition of the catalyst, an EDS analysis was performed from different parts of the electrode surface and the spectrum related to one of these points is shown in Fig. 2a. Existence of Cu peaks in EDS spectrum revealed that Cu atoms were not completely participated in galvanic replacement with Pt and Pd.

The average values of atomic ratio from different parts of the Pt-Pd/Cu/NPSS electrode surface for Pt, Pd, Cu and the main components of SS such as Fe and Cr are 12.96%, 15.93%, 4.22%, 52.98% and 13.91%, respectively.

In order to explain the crystalline structure of the catalyst, XRD pattern of Pt-Pd/Cu/NPSS (Fig. 2b) compared with the peak position of Pt, Pd and stainless steel references (Fig. 2c). The XRD peaks of SS (indicated by foursquare patterns) are located in 2θ of 43.59°, 50.77° and 74.58°. In the case of Pt and Pd, it is noticeable that the values of all fcc crystalline planes are between the values of Pt and Pd references and separated peak of these metals was not detectable (single fcc structure). In addition, the high and sharp peaks indicated their well crystallinity. The peaks at 2θ of 40.19°, 46.81°, 68.43°, 82.39° and 86.85° correspond to the Pt-Pd (111), (200), (220), (311) and (222) crystal planes, respectively.

3.2. Electrochemical characterization of the Pt-Pd/Cu/NPSS electrode

Fig. 3a shows cyclic voltammograms of the Pt-Pd/Cu/NPSS, Pt/Cu/NPSS and Pd/Cu/NPSS electrodes between -1.0 to 0.3 V at a scan rate of $50\ mV.s^{-1}$ under nitrogen atmosphere in 1.0 M KOH. Anodic and cathodic peaks at potentials lower than -0.6 V are related to