Journal of Power Sources 257 (2014) 156–162

Contents lists available at ScienceDirect

Journal of Power Sources

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

Au- and Pd-modified porous Co film supported on Ni foam substrate as the high performance catalysts for H_2O_2 electroreduction

Fan Yang, Kui Cheng, Ke Ye, Xue Xiao, Fen Guo, Guiling Wang, Dianxue Cao*

Key Laboratory of Superlight Material and Surface Technology of Ministry of Education, College of Material Science and Chemical Engineering, Harbin Engineering University, Harbin 150001, China

HIGHLIGHTS

- Electrodeposition of Co film for spontaneous deposition of Au or Pd is reported.
- The 3D porous electrode exhibits good catalytic performance for H_2O_2 reduction.
- The 3D porous electrode is consisted of numerous interconnected nanoparticles.

ARTICLE INFO

Article history:
Received 18 August 2013
Received in revised form
20 January 2014
Accepted 21 January 2014
Available online 31 January 2014

Keywords:
Gold
Palladium
Cobalt film
Spontaneous deposition
Surface-modification
Hydrogen peroxide electroreduction

ABSTRACT

Non-noble metal film electrode (Co/Ni foam) modified with noble metals (Au and Pd) has been reported. Highly porous Co film is firstly prepared electrochemically on the commercial Ni foam substrate and in turn serves as a hard template and a redox inducer for modification by spontaneous deposition of Au or Pd. The electrodes (Au-modified Co/Ni foam and Pd-modified Co/Ni foam) are characterized by scanning electron microscopy equipped with energy dispersive X-ray spectrometer, and X-ray diffractometer. The catalytic performance of the 3D porous electrodes is evaluated by voltammetry and chronoamperometry. Results reveal that Au- and Pd-modified Co/Ni foam exhibit excellent catalytic performance and good stability for H_2O_2 electroreduction compared with Au and Pd particles supported on Ni foam, benefitting from the unique 3D structure which can ensure high utilization of catalyst and quick releases of gas bubbles produced by H_2O_2 decomposition from the electrode.

1. Introduction

Fuel cells are a promising power-generation technology for the direct conversion of chemical energy into electricity. They play a crucial role in solving the problems of energy crisis and environmental pollution. In recent years, H_2O_2-based fuel cells, such as direct methanol–hydrogen peroxide fuel cell [1–3], direct borohydride–hydrogen peroxide fuel cell [4–6], hydrazine–hydrogen peroxide fuel cell [7–9] and direct peroxide–peroxide fuel cell [10–15], have been widely investigated. Note that H_2O_2 is often used as oxidant instead of O_2 in these types of liquid-based fuel cells, indicating that improving H_2O_2 electroreduction performance could further improve the cell performance. Generally, given remarkable physicochemical properties of noble metals in the Pt group, they are considered as the best catalysts for electrochemical reaction [16–19]. However, recent studies [20] have reported that Pt-based catalysts alone account for 38–56% of the cost of polymer electrolyte membrane fuel cells, and the cathode consumes around 90% of Pt catalysts because of its sluggish oxygen reduction reaction (ORR) kinetics. Being a more economic and plentiful metal than Pt, Au has been investigated for its electrocatalytic activity [21–24], furthermore, it has also been demonstrated to have no significant catalysis to H_2O_2 decomposition unlike Pt and other noble metals, ensuring the high utilization efficiency of H_2O_2 [25]. Pd has also attracted considerable attention because it has very similar properties to Pt (e.g., same group of the periodic table, same *fcc* crystal structure, and similar atomic size) while being less expensive and more abundant than Pt [26,27]. Indeed, Au and Pd have been studied intensively as the most promising Pt-free catalysts.

In order to further reduce the cost of catalysts and improve the cell performance, many researchers have focused on the preparation of nanostructures with various special morphology and size. Currently, nanoporous foam materials represent a very promising type of structured materials having a number of interesting, even

---

* Corresponding author. Tel./fax: +86 451 82589036.
E-mail address: caodianxue@hrbeu.edu.cn (D. Cao).

0378-7753/$ – see front matter © 2014 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jpowsour.2014.01.100

unique properties and through this method, many non-noble/noble metal and -based foams can be successfully prepared [28–30]. Kiani and co-workers [30] have present indirect fabrication of Ag and Pd foams based on electrochemical deposition of scarified Cu foam at a Cu sheet, and spontaneous galvanic replacement. The groups of Yu and Huang [31] have prepared porous Pd and PdNi using hydrogen bubble dynamic template and they have also proved that the catalysts exhibit excellent catalytic activity and stability towards methanol oxidation. Fabricated foam electrodes show electrocatalytic properties with several benefits. First, the procedure is very simple and fast and can perform at room temperature using commercially available reagents in water as a green solvent with no need to any additive. Second, based on this method, we could design catalysts and metal foams for practical application since it is possible to save the usage of precious metals like Au, Pd and Ag, only by surface modification of other cheap metals. In fact, the catalyst on the surface is the actual catalytic active species, implying that the inner catalyst has little catalysis. Interestingly, the coated amount of noble metals on the surface of metal foam could be also easily controlled. Their great potential for rapid electrochemical reactions arising from the high surface area and superior mass transport, makes Au- and Pd-modified Co/Ni foam electrodes the potential candidates for the application in fuel cells.

In the present paper, we described the preparation of Au and Pd-modified porous Co film electrodes via a two-step procedure: at first, the electrodeposition of porous Co film on Ni foam substrate at high current density, then the spontaneous deposition of Au and Pd by immersion of the Co deposits in the solutions containing Au and Pd ions (Eqs. (1) and (2)).

$$\mathrm{Co(0) + Pd^{2+} \rightarrow Co^{2+} + Pd(0)} \tag{1}$$

$$\mathrm{3Co(0) + 2Au^{3+} \rightarrow 3Co^{2+} + 2Au(0)} \tag{2}$$

We report a study aiming to significantly improve the utilization of precious Au and Pd catalysts and their catalytic performance. We chose Ni foam as the substrate due to its high electrical conductivity and a desirable open 3D structure. A 3D porous Co particle layer was electrodeposited on Ni foam which greatly increases the surface area of Ni foam substrate. The obtained 3D Au and Pd-modified Co/Ni foam electrode exhibit high catalytic performance and good stability for electroreduction of H_2O_2.

2. Experimental

2.1. Preparation and characterization of Au and Pd-modified Co/Ni foam electrodes

The Au and Pd-modified Co/Ni foam electrodes were prepared in two steps. Step one consisted of electrodeposition of porous Co film by applying a constant current of -2.0 A cm^{-2} for 100 s to electrochemical cell, containing 0.1 mol L^{-1} $CoSO_4$ + 1.0 mol L^{-1} $(NH_4)_2SO_4$ + 0.7 mol L^{-1} NH_4OH aqueous solution. The growth of Co film was accompanied by gas evolution at all times until the electrochemical deposition was terminated. The spontaneous deposition of Au was performed by immersion of the porous Co layers in the solution containing 1.0 mmol L^{-1} $HAuCl_4$ + 0.1 mol L^{-1} NaCl for 30 s. The same procedure was followed for Pd-modified Co/Ni foam electrode in 1.0 mmol L^{-1} Na_2PdCl_4 + 0.1 mol L^{-1} NaCl for 10 s. Prior to use, the Ni foam (10 mm × 10 mm × 1.1 mm, 110 PPI, 320 g m^{-2}; Changsha Lyrun Material Co., Ltd. China) was degreased with acetone, etched with 6.0 mol L^{-1} HCl for 5 min, and then rinsed with deionized water extensively. For comparative study, Ni foam supported Au particles (Au/Ni foam) and Pd particles (Pd/Ni foam) were also prepared by the same method as that for Au- and Pd-modified Co/Ni foam without porous Co film deposits. The depositions were carried out in a three-electrode electrochemical cell controlled by computerized potentiostat (Autolab PGSTAT302, Eco Chemie). The Ni foam served as the working electrode, which was placed between two pieces of platinum foil in parallel as the counter electrodes. A saturated calomel electrode (SCE) was used as the reference electrode.

The electrode morphology was characterized by a scanning electron microscope (SEM, JEOL JSM-6480) equipped with an energy dispersive X-ray spectrometer (EDX). The structure was analyzed using an X-ray diffractometer (Rigaku TTR III) with Cu K radiation (λ = 0.1514178 nm). The Au and Pd loading were measured using an inductive coupled plasma emission spectrometer (ICP, Xseries II, Thermo Scientific). Au and Pd in the 1.0 cm^2 electrodes was first dissolved in aqua regia solution and then diluted to 1 L solution for the ICP measurement.

2.2. Electrochemical measurements

The catalytic performance of the Au and Pd-modified Co/Ni foam electrodes for H_2O_2 electroreduction was measured by linear scan voltammetry and chronoamperometry with the same configuration as that for electrodeposition with the exception that the two Pt foil counter electrodes were placed behind D-porosity glass frits. The electrolyte for H_2O_2 electroreduction was H_2O_2-containing KOH solution. The reported current densities were calculated using the geometrical area of the electrode. All solutions were made with analytical grade chemical reagents and ultra-pure water (Milli-Q 18 MΩ cm). All measurements were performed at ambient temperature (20 ± 2 °C) under N_2 atmosphere.

3. Results and discussion

3.1. Characterization of porous Co film and Au-modified Co/Ni foam electrode

Fig. 1 shows the low and high-magnification SEM images of porous Co film supported on commercial Ni foam substrate, fabricated by electrodeposition in an electrolyte of 0.1 mol L^{-1} $CoSO_4$ + 1.0 mol L^{-1} $(NH_4)_2SO_4$ + 0.7 mol L^{-1} NH_4OH at a constant cathodic current of -2 A cm^{-2} for 100 s. It can be observed from Fig. 1A that the as-prepared Co film was uniformly covered on the surface of Ni foam skeleton and exhibited a 3D porous structure with highly porous nanoramified walls, with diameters of some micrometres (Fig. 1B), left by hydrogen bubbles that evolve at large cathodic current density (-2 A cm^{-2}). Much narrower pores were also visible. More importantly, the walls of the Co film consisted of numerous interconnected nanoparticles and showed continuous nanopores. Additionally, the surface of the 3D porous Co film exhibited a wrinkle appearance, consisting of an assembly of flake-like structures with rippled morphology due to its ultrathin feature. Evidently, the numerous nanoflakes with a lateral size of several hundred nanometers were intercrossed with each other, creating loose porous nanostructures with abundant open space and electroactive surface sites (Fig. 1C and D), providing a superior framework for Au or Pd modification.

In order to prepare the Au-modified Co/Ni foam electrode, the as-fabricated Co film electrode was then rapidly transferred to a solution containing 1.0 mmol L^{-1} $HAuCl_4$ + 0.1 mol L^{-1} NaCl for 30 s. As seen from Fig. 2A, the initial morphology of porous Co deposits was still well-preserved after the spontaneous deposition of Au. Fig. 2B and C shows that Au is uniformly distributed on the surface of Co nanoparticles and the surface of the as-formed Co film becomes rougher. The Au surfaces can be fully utilized because all the Au particles are accessible to H_2O_2 and electrolytes. Besides,