Journal of Power Sources 294 (2015) 136–140

Contents lists available at ScienceDirect

Journal of Power Sources

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

Short communication

Three-dimensional nanoporous gold–cobalt oxide electrode for high-performance electroreduction of hydrogen peroxide in alkaline medium

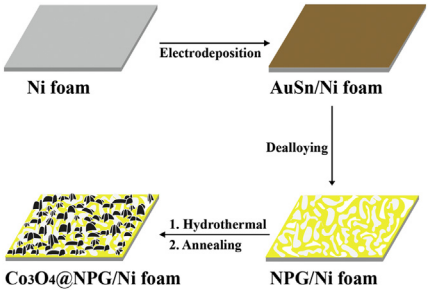
Zhihao Li [a], Yanghua He [a], Xi Ke [a, **], Lin Gan [c], Jie Zhao [d], Guofeng Cui [a, b, *], Gang Wu [e, ***]

[a] Electronic Packaging Electrochemistry Laboratory, School of Chemistry and Chemical Engineering, Sun Yat-sen University, Guangzhou 510275, China
[b] SYSU-CMU Shunde International Joint Research Institute, Shunde 528300, China
[c] Key Laboratory for Polymeric Composite and Functional Materials of Ministry of Education of China, Sun Yat-sen University, Guangzhou, 510275, China
[d] School of Mechanical and Automotive Engineering, South China University of Technology, Guangzhou 510640, China
[e] Department of Chemical and Biological Engineering, University at Buffalo, The State University of New York, Buffalo, NY 14260, United States

HIGHLIGHTS

- NPG film/Ni foam serves as the 3D hierarchical porous conductive scaffold.
- Co_3O_4 nanosheet arrays were hydrothermally grown on the 3D NPG/Ni foam composite.
- Co_3O_4@NPG/Ni foam exhibits superior activity and stability toward peroxide reduction.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 22 April 2015
Received in revised form
8 June 2015
Accepted 11 June 2015
Available online xxx

Keywords:
Cobalt oxide
Nanoporous gold
Nickel foam
Hydrogen peroxide electroreduction
Hierarchical porous materials

ABSTRACT

Using a simple hydrothermal method combined with a post-annealing treatment, cobalt oxide (Co_3O_4) nanosheet arrays are grown on three-dimensional (3D) nanoporous gold (NPG) film supported on Ni foam substrates, in which NPG is fabricated by chemically dealloying electrodeposited Au–Sn alloy films. The morphology and structure of the Co_3O_4@NPG/Ni foam hybrids are characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The electrochemical activity of the Co_3O_4@NPG/Ni foam electrode toward hydrogen peroxide electroreduction in alkaline medium is studied by cyclic voltammetry (CV), linear sweep voltammetry (LSV), and chronoamperometry (CA). The results demonstrate that the Co_3O_4@NPG/Ni foam electrode possesses exceptionally high catalytic activity and excellent stability for the peroxide electroreduction, resulting mainly from the unique electrode architecture. The combined 3D hierarchical porous structures of NPG/Ni foam with the open and porous structures of Co_3O_4 nanosheet arrays facilitate the mass transport and charge transfer. Therefore, the metal oxides supported on 3D hierarchical porous NPG/Ni foam framework may hold great promise to be effective electrodes for electrocatalytic reduction of peroxide and other electrochemical reactions.

* Corresponding author. Electronic Packaging Electrochemistry Laboratory, School of Chemistry and Chemical Engineering, Sun Yat-sen University, Guangzhou 510275, China.
** Corresponding author.
*** Corresponding author.
E-mail addresses: xikeciac@gmail.com (X. Ke), cuigf@mail.sysu.edu.cn (G. Cui), gangwu@buffalo.edu (G. Wu).

http://dx.doi.org/10.1016/j.jpowsour.2015.06.069
0378-7753/

1. Introduction

Fuel cells, which convert the chemical energy directly into electric energy, are emerging as leading alternative energy conversion devices for portable power supply [1,2]. Oxygen from ambient air is generally required as an oxidant in fuel cell devices [3], while an additional oxygen tank in the system is needed in oxygen-free environments such as underwater and outer space, which significantly decreases the energy density of fuel cells. In this context, there has been considerable interest in developing liquid-based fuel cells that use hydrogen peroxide as an alternative oxidant [4]. Examples of these types of fuel cells include metal/hydrogen peroxide fuel cell [5], direct borohydride/hydrogen peroxide fuel cell [6] and hydrazine/hydrogen peroxide fuel cell [7]. Compared with oxygen, peroxide as an oxidant offers some important advantages: higher power density, higher theoretical voltage and faster reduction kinetics [8,9]. In order to further improve the performance of these peroxide-based fuel cells, it is essential to design cathode electrocatalysts with high catalytic activities for electrochemical reduction of peroxide. Conventionally, noble metal nanoparticle electrocatalysts, such as Pt [10], Pd [11] and their alloys [12], exhibit remarkably high catalytic activity and superior stability toward peroxide electroreduction. However, the limited supply and thus relatively high cost of these noble metals severely limit their practical applications. Therefore, it is imperative to search for much cheaper alternative cathode catalysts for the peroxide electroreduction to replace the noble metal catalysts. Recently, nanostructured transition metal oxides catalysts, for example, Mn_3O_4 [13], Co_3O_4 [14] and CuO [15], have been exploited as potential candidates. Among them, Co_3O_4 has attracted particular attention for peroxide electroreduction owing to its excellent electrocatalytic activity and stability, as well as its earth abundance and environmental benignity. However, the intrinsically poor electrical conductivity of Co_3O_4 severely limits its practical application. To overcome this shortage, Co_3O_4 nanostructures are usually supported on various conductive substrates such as Ti foil [16] and Ni foam [17]. These conductive substrates can not only support and disperse the oxides but, more importantly, could also facilitate the electron transfer between the oxides and the conducting supports, thus improving the electrocatalytic performances.

Recently, nanoporous gold (NPG), with large surface area, excellent electric conductivity, superior chemical stability and good biocompatibility, has gained significant interest because of its unique nanostructure together with excellent optical and catalytic properties [18–20]. It has been regarded as a very promising candidate material for application in various areas such as catalysis [21], energy storage [22], metal-enhanced fluorescence [23] and sensors/biosensors [24,25]. NPG films are typically prepared by chemically dealloying commercial Au–Ag alloy leaves in a concentrated HNO_3 solution. However, these free-standing thin films are brittle and difficult to handle, and thus require an extremely careful transfer method to place them onto other substrates. More recently, we have developed a facile two-step strategy for fabricating NPG films through electrodeposition followed by chemically dealloying Au–Sn alloy films, enabling the preparation of high-quality NPG films directly supported on various substrates such as copper foil, stainless steel sheet and Ni foam [26]. Among them, NPG films supported on Ni foam substrate (NPG/Ni foam) with a hierarchical porous architecture is regarded as a promising electrode material for catalytic applications, as it can facilitate fast electron and ion transport through 3D interconnected pathways. Its application for electrocatalytic reduction of peroxide in neutral [26,27] and acidic medium [28,29] have been reported. However, its application in alkaline medium has not been previously demonstrated.

In this work, we report Co_3O_4 nanosheet arrays supported on three-dimensional (3D) hierarchical porous NPG-covered Ni foam, referred to as Co_3O_4@NPG/Ni foam, as a binder-free electrode for high-performance electrochemical reduction of peroxide in alkaline medium. The 3D hierarchical porous NPG/Ni foam hybrid was employed as the conductive scaffold to load the Co_3O_4 nanostructures and improve the electrical conductivity of the overall electrode material. Such a unique electrode architecture provides not only a large electrochemical active surface area but also a fast pathway for electron transport and mass transfer. Electrochemical studies showed that the Co_3O_4@NPG/Ni foam electrode exhibited high electrocatalytic activity and excellent stability/durability toward the peroxide electroreduction, which makes it a promising candidate for a cathode electrocatalyst for peroxide-based fuel cells.

2. Experimental section

2.1. Materials synthesis

Ni foam (approximately 1 cm × 7 cm) was pretreated with 5 M HCl solution for 30 min in order to remove the oxide layer on the surface, and then rinsed thoroughly with deionized water. The Au–Sn alloy electrodeposition was carried out in a two-electrode system with the clean Ni foam as working electrode and a Pt plate as counter electrode. The Au–Sn alloy film was galvanostatically electrodeposited on Ni foam in an Au–Sn alloy plating solution (Huizhou Leadao Electronic Material Co., Ltd.) with a current density of 5 A dm^{-2} for 10 min at 45 °C. After electrodeposition, the Ni foam was rinsed with deionized water and dried in air. Then, the sample was immersed into a 5 M NaOH and 1 M H_2O_2 solution for 3 days at ambient conditions to selectively etch Sn away from Au–Sn alloy film, leading to the formation of an NPG film on Ni foam. After etching, the Ni foam was carefully rinsed with deionized water and dried in air. Then, the NPG/Ni foam was wrapped with a Teflon tape with exposure area of ~1 cm^2, and immersed into a Teflon-lined stainless steel autoclave containing a 30 mL mixture of 0.3 mM $Co(NO_3)_2$, 0.6 mM NH_4F and 1.5 mM urea. The autoclave was then sealed and heated in an electric oven at 180 °C for 35 min. After cooled down to room temperature, the samples were carefully rinsed with deionized water and then dried in the oven at 60 °C for 1 h. Finally, the samples were annealed at 300 °C for 2 h for synthesis of crystalline Co_3O_4. As a control experiment, the Ni foam without NPG film was employed to prepare a Co_3O_4/Ni foam hybrid by following the same procedure.

2.2. Characterization and electrochemical measurements

The microstructure of the samples was investigated using field-emission scanning electron microscopy (SEM, JEOL, JSM-6700F, 15 keV). X-ray diffraction (XRD) measurements were performed on a Rigaku D/max-2200/PC diffractometer using Cu Kα radiation. Electrochemical measurements were carried out on a Gamry Reference 600 electrochemical workstation in a three-electrode setup with 3 M KOH as the electrolyte. The Co_3O_4@NPG/Ni foam electrode, a Pt plate electrode and an Ag/AgCl electrode acted as the working electrode, counter electrode and reference electrode, respectively. The electrochemical impedance spectroscopy (EIS) measurements were conducted in a frequency range from 100 kHz to 0.1 Hz with a perturbation amplitude of 5 mV. All electrochemical measurements were performed at ambient temperature (25 ± 2 °C).

3. Results and discussion

The crystalline phase of the as-prepared Co_3O_4@NPG/Ni foam