



Electrodeposited PdNi₂ alloy with novelly enhanced catalytic activity for electrooxidation of formic acid

Chunyu Du^{a,*}, Meng Chen^{b,*}, Wengang Wang^b, Geping Yin^a, Pengfei Shi^a

^a School of Chemical Engineering and Technology, Harbin Institute of Technology, Harbin 150001, China

^b College of Materials Science and Chemical Engineering, Harbin Engineering University, Harbin 150001, China

ARTICLE INFO

Article history:

Received 20 January 2010

Received in revised form 7 March 2010

Accepted 31 March 2010

Available online 11 April 2010

Keywords:

Direct formic acid fuel cell

Anode catalyst

Palladium–nickel alloy

Electrodeposition

ABSTRACT

Bimetallic palladium–nickel (PdNi₂) alloy catalyst has been prepared for the electrooxidation of formic acid through a simple electrodeposition approach. Scanning Electron Microscopy and X-ray Diffraction revealed that the particle morphology and the crystalline lattice of PdNi₂ alloy were highly different from those of Pd. Although the PdNi₂ catalyst had less noble Pd content, the cyclic voltammetry and chronoamperometry results clearly demonstrated that its catalytic activity was significantly higher than that of Pd. The novel enhancement of catalytic activity was mainly ascribed to the weak absorption strength of intermediates on Pd through the interaction between Pd and additive Ni, which facilitated the formic acid oxidation through direct pathway.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Recently, alternative sources of energy have been of intensive concern due to environmental problems and a decline in the availability of fossil fuels. The direct formic acid fuel cell (DFAFC), as one of the potential power sources for portable electronic devices or transportation vehicles, has increasingly attracted a great deal of attention [1,2]. Compared with other direct liquid fuel cells (e.g. direct methanol fuel cell), the DFAFC has some extraordinary advantages including high electromotive force, low toxicity, limited fuel crossover, high practical power densities, etc. [3,4].

Highly active catalysts for formic acid oxidation are crucial to the development of DFAFC. Initially, Pt was employed to be the catalyst for formic acid oxidation [5–7]. The rate of formic acid oxidation on Pt, however, was insufficient for practical applications, because this oxidation was mainly through the CO pathway and thus Pt was easy to be poisoned by CO intermediate [8,9]. Recently, Pd has been explored to catalyze the reaction of formic acid oxidation [10–13]. Although Pd was demonstrated to provide better performance than Pt, it was still not satisfactory, and more importantly Pd was also subject to significant deactivation by poisoning intermediates [14,15]. Alloying has been proved to be an effective method to improve the activity of Pd catalysts. Liu et al. [16] found that the addition of Sn to Pd could increase lattice parameters of Pd crystal and the Pd₂Sn catalyst had better activity than Pd. PdCo was synthesized by Wang et al. [17] through a reduction reaction in aqueous solution, and exhibited high

activity than Pd. Yu and Pickup [18] proved that PdPb catalyst could provide superior initial performance relative to Pd and was more resistant to deactivation.

In this paper, we propose PdNi alloy as the catalyst of formic acid oxidation for the DFAFC. A PdNi₂ alloy catalyst was prepared through a facile method of electrochemical deposition on a graphite carbon electrode (GCE). The physical features and electrochemical activity of the alloy were investigated for the electrooxidation of formic acid. It was shown that the activity of the PdNi₂ alloy catalyst was significantly superior to Pd, which, as far as we know, was reported for the first time.

2. Experimental

The PdNi alloy catalyst described herein was prepared through a facile method of constant-current electrodeposition on a GCE with a Pt foil as counter electrode at room temperature. Before use, the GCE was polished with emery paper and Al₂O₃ slurry, and ultrasonically cleaned in toluene for a few minutes, then dried in the air. The electrodeposition was conducted for 3 min at a current density of 1.2 mA cm⁻² with aqueous solution of 4 mM Pd(NH₃)₂Cl₂ + 50 mM NiSO₄ + 0.1 M NH₄Cl as the electroplating bath. For comparison, Pt, Pd and Ni catalysts were also electrodeposited by the same procedure with the bath composed of 4 mM H₂PtCl₆ + 0.1 M NH₄Cl, 4 mM Pd(NH₃)₂Cl₂ + 0.1 M NH₄Cl and 50 mM NiSO₄ + 0.1 M NH₄Cl, respectively.

Scanning Electron Microscopy (SEM) was carried out with a JEOL SEM system operated at 20 kV to characterize the morphology of the catalysts, and the particle size was recorded by taking the size average of about 200 particles. The composition of the catalysts was

* Corresponding authors. Du is to be contacted at Tel.: +86 451 86403216; fax: +86 451 86413720. Chen, Tel.: +86 451 82569890; fax: +86 451 84346500.

E-mail addresses: cydu@hit.edu.cn (C. Du), chenmeng@hrbeu.edu.cn (M. Chen).

determined using the energy dispersive X-ray spectroscopy (EDX). X-ray Diffraction (XRD) measurements of the catalysts were performed on a Rigaku Model D/max-rB diffraction system using a $\text{CuK}\alpha$ radiation source. Because the electrodeposited PdNi alloy and graphite substrate have overlapped diffraction peaks that lead to unambiguous peak identification, XRD was measured on Pd and PdNi alloy particles deposited on carbon paper instead of GCE.

Electrochemical measurements were conducted using a CHI604D Potentiostat (CH Instruments Inc.) in a conventional three-electrode electrochemical cell. A GCE, on which Pt, Pd, Ni or PdNi alloy catalyst was deposited, was used as the working electrode, and a Pt foil and an $\text{Hg}/\text{Hg}_2\text{SO}_4$ electrode (0.656 V vs. NHE) were used as the counter and reference electrodes, respectively. In this communication, all potentials were quoted with respect to NHE. The hydrogen adsorption–desorption experiment was carried out in a 0.5 M H_2SO_4 solution at a scan rate of 50 mV s^{-1} . The activity of the catalysts towards the oxidation of formic acid was evaluated by cyclic voltammetry (CV) and chronoamperometry (CA) in a solution of 0.5 M $\text{H}_2\text{SO}_4 + 0.5 \text{ M HCOOH}$. For the CO stripping experiment, CO was bubbled into a 0.5 M H_2SO_4 solution for 20 min when the electrode potential was fixed at 0.01 V. Then, N_2 was bubbled into the solution for 30 min to remove CO in the solution. Prior to all the electrochemical measurements, the electrolytes were deoxygenated by bubbling with high purity N_2 for 40 min. All the electrochemical measurements were conducted at room temperature.

3. Results and discussion

Fig. 1a and b presents SEM images of the electrodeposited Pd and PdNi alloy particles. The Pd particles were complex polyhedrons, which should result from the preferential growth of some crystal facets during the electrodepositing process. With Ni alloying, the shape of PdNi particles was changed to uniform spheres with somewhat rough surfaces. This morphology change was apparently

due to the presence of Ni, which played an important role in the nucleation and growth of PdNi alloys [19]. From the SEM observation, the average particle size of the PdNi alloy was 114 nm, which was slightly smaller than that of Pd (127 nm). The relatively small particle size of the PdNi alloy catalyst, in addition to its rough surface, was in favor of increasing the activity for formic acid oxidation. The composition of the PdNi alloy was determined to be PdNi_2 by EDX analysis.

Fig. 1c gives XRD patterns of the electrodeposited Pd and PdNi alloy. The pattern of Pd showed clearly the characteristic peaks of Pd (111), (200) and (220) crystal faces at the 2θ values of 40.07° , 46.53° and 68.19° , respectively, which illustrated that the Pd particles possessed the face-centered cubic crystalline structure. In addition to the peaks of Pd, a characteristic peak of the carbon substrate was also present at 54.34° . In the pattern of the PdNi alloy, when Ni was alloyed with Pd, the characteristic peaks of Pd were interestingly disappeared and new diffraction peaks indexed respectively to the Ni (111), (200) and (220) faces were observed. These phenomena suggested that Pd had entered into the Ni lattice forming the PdNi alloy with Ni structure.

Fig. 2a shows CV curves of the electrodeposited Pd, Ni and PdNi₂ alloy catalysts in 0.5 M H_2SO_4 solution. The well-separated peaks below 0.3 V on Pd and PdNi₂ alloy catalysts were attributed to the hydrogen adsorption/desorption on the surface of Pd atom, because the absorption of hydrogen on Ni was negligible as observed in the CV curve of Ni. The hydrogen absorption/desorption peaks emerged at about 0.0 V and 0.2 V were respectively associated with the weak and strong interactions between hydrogen and Pd. Apparently, the PdNi₂ alloy displayed larger peaks of strong interaction and smaller peaks of weak interaction than Pd, indicating that the strength of hydrogen adsorption on PdNi₂ was enhanced by the presence of Ni. The anodic peaks above 0.75 V and the cathodic peaks at ca. 0.7 V were related to the oxidation of metals and the reduction of the formed oxides, respectively. There seemed a slight negative shift of the onset

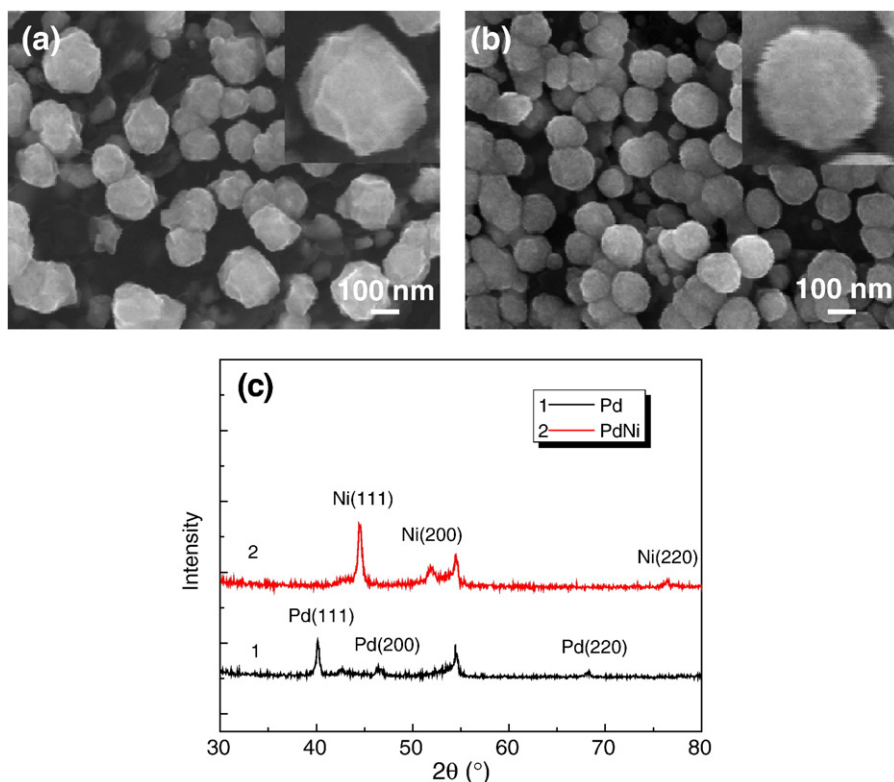


Fig. 1. (a) SEM image of the Pd. Inset: magnified Pd particle. (b) SEM image of the PdNi alloy. Inset: magnified PdNi particle. (c) XRD patterns of the electrodeposited Pd and PdNi alloy on carbon paper.

Download English Version:

<https://daneshyari.com/en/article/180175>

Download Persian Version:

<https://daneshyari.com/article/180175>

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