



Full Length Article

Electrocatalytic performance for methanol oxidation on nanoporous Pd/NiO composites prepared by one-step dealloying



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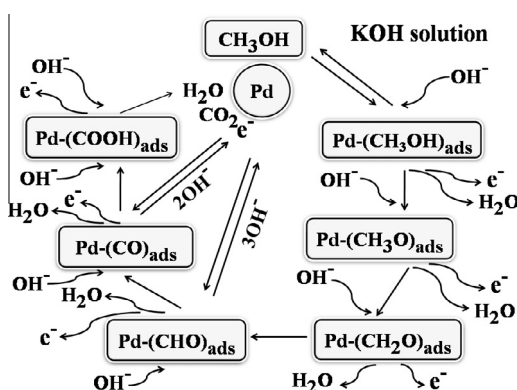
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HIGHLIGHTS

- Nanoporous Pd/NiO composites were prepared by one-step dealloying strategy.
- The composites exhibited a three-dimensional nanoporous structure.
- The performance of the as-prepared sample was 4 times that of nanoporous Pd.

GRAPHICAL ABSTRACT

Schematic illustration of the methanol oxidation mechanism on the np-Pd/NiO composites in alkaline media.



ARTICLE INFO

Article history:

Received 13 October 2015
 Received in revised form 12 April 2016
 Accepted 20 April 2016
 Available online 4 May 2016

Keywords:

Nanoporous Pd/NiO composites
 Al-Pd-Ni alloy
 Dealloying
 Electrocatalytic performance
 Methanol oxidation

ABSTRACT

Nanoporous Pd/NiO composites were prepared for methanol oxidation in alkaline media by one-step dealloying from the melt-spun Al-Pd-Ni precursor alloys. The structure, morphology, composition and electrocatalytic activities of the composites were characterized. The results demonstrated that the composites exhibited a uniform bicontinuous and interpenetrating three-dimensional nanoporous structure. Pore channels with a length of less than 10 nm ran throughout the whole ribbons. The nanoporous Pd/NiO composites possessed better electrocatalytic performance compared to nanoporous Pd, and the composite dealloyed from $\text{Al}_{84.7}\text{Pd}_{15}\text{Ni}_{0.3}$ showed the highest catalytic activity, which was about 4 times as high as that of nanoporous Pd. The improvement of the electrocatalytic properties was attributed to the increased electrochemical active specific surface areas and the synergistic effect between Pd and NiO.

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1. Introduction

The anode electrocatalyst is crucial for the performance of direct methanol fuel cells (DMFCs) [1]. At present, lots of investigations have been focused upon Pt and Pt-based materials which are believed to be the best catalysts for low temperature fuel cells

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[2–5]. However, the commercialization of Pt and Pt-based catalysts in fuel cells is severely restricted by their high cost, sluggish kinetics, poor stability, low utilization and weak methanol-tolerant capacity [6,7]. Pd is 50 times more abundant in nature and less expensive than Pt, and exhibits superior catalytic properties due to its better resistance to CO poisoning, which makes it a potential electrocatalyst for replacing Pt in DMFCs [8–10].

Particularly, it is well accepted that the performance of catalysts is mainly governed by the electrochemical activity and kinetic feature of active materials. In a nutshell, it is crucial to enhance the kinetics of ion and electron transport in electrodes and at the electrode/electrolyte interface to improve the electrocatalytic activity [11]. Nanoporous (np) structure with a typical three-dimensional bicontinuous interpenetrating enables the full exposure of active materials to the electrolyte and provides a short transportation path for electron and ion, as well as high structural stability with no agglomeration, thus leading to faster reaction kinetics and higher electrocatalytic reactivity [11–15]. According to other research [16], np-Pd has been successfully prepared by dealloying and exhibits catalytic performance. With the aim of further avoiding the formation of poisoning species on electrode surfaces and improving the electrochemical activity, Pd-based catalysts have been employed [17]. The preparation of oxide promoted Pd electrocatalysts has been focused on for alcohol oxidation, which has been proven to be an effective way to combine the merits of individual components [18,19]. In our previous work, TiO₂ has been successfully formed in np-Pd by a simple one-step dealloying in a NaOH solution, and adding a small amount of TiO₂ in np-Pd can significantly promote the electrocatalytic activity towards methanol/ethanol oxidation compared to np-Pd [20].

In order to minimize the amount of noble metal and improve the catalytic activity for methanol oxidation reaction, one strategy is to combine noble metal with other cheaper metals to form noble metal-based alloys, such as Pt–Ru–Cu and Pd–Ni [4,7]. Another strategy is to synthesize noble metal-based composites, such as Pt–CeO₂/C and Pt–MgO/C [21,22]. NiO used in this work is a very successful material which shows excellent electrochemical performance in various fields, such as catalysis [23], battery cathodes [24] and fuel cell electrodes [25], with high thermal stability and good resistance to corrosion [26]. Hence, the np-Pd/NiO composite was prepared by a simple one-step dealloying Al–Pd–Ni in order to cutting cost and improve the catalyst activity, which is very different from other research. In other studies, noble metals are usually loaded on the oxide supports. However, simple deposition of noble metal nanoparticles on oxide supports leads to poor dispersion and bad stability, resulting in a lower utilization for noble metal and the reduction of catalytic efficiency. Moreover, oxide supports as a semiconductor will also lead to the performance decline due to the reduction of the electrocatalyst conductivity. In the np-Pd/NiO composite, np-Pd as the support and NiO as the promoter make the composite possess good stability, deposition and conductivity, which well solves the above mentioned problems. The electrocatalytic behaviors of the composite for methanol oxidation in alkaline media were measured. Moreover, the dealloying mechanism and the effect of NiO on the electrocatalytic performance have been discussed.

2. Experimental

2.1. Preparation of nanoporous composites

The preparation procedure of the precursor alloys is described according to our previous work [20]. Al_{85-x}Pd₁₅Ni_x ($x = 0, 0.1, 0.3, 0.5, 0.7, 1.0$, at.%) alloys with nominal composition were prepared by an arc melting in high purity Ar atmosphere. The mixture of

pure Al (99.90%), pure Pd (99.99%), and pure Ni (99.90%) in a water-cooled copper crucible was melted by arc using a nonconsumable tungsten electrode. Several times of remelting were performed with the ingot turned upside down. The 3 g broken ingot inserted into a quartz tube was heated by high frequency induction, and the melt-spun ribbons were achieved after the metal solution was blown onto the surface of a pure Cu roller melt spinning at a speed of 33 ms⁻¹. The thickness of the obtained ribbons was approximately 30 μm and the width about 3 mm.

The melt-spun Al–Pd–Ni precursor ribbons were dealloyed in a 20 wt% NaOH solution at room temperature until no obvious bubbles emerged. The Ref. [16] and our work indicate that the reaction rate increases with the content of NaOH increasing in the alkali solution, and much more of NaOH could result in the coarsening of the ligaments/pores. Therefore, 20 wt% NaOH was adopted for dealloying Al–Pd-based alloys. Subsequently, the dealloying was continuously carried out in the same solution at 60 ± 5 °C for 48 h. The dealloyed samples were washed with distilled water and dried at 50 °C in a drying oven box.

2.2. Microstructural characterization

The phase constitutions of the as-quenched ribbons and the dealloyed samples were analyzed with a Bruker D8 advanced X-ray Diffractometer (XRD). The microstructures were characterized by a JEM-2100 High-Resolution Transmission Electron Microscope (HRTEM, JEOL Ltd) and a JSM-7000F Scanning Electron Microscope (SEM, JEOL Ltd) equipped by an Energy Disperse Spectroscopy (EDS). An Axis Ultra Kratos X-ray Photoelectron Spectrometer (XPS) was employed to measure the valence states of Pd and Ni using Al Kα X-ray source (1486.68 eV).

2.3. Electrochemical measurements

Electrochemical experiments were carried out using a Versa-STAT MC workstation at room temperature. A standard three-electrode cell, consisting of np-Pd/NiO composites as the working electrode (diameter: 3 mm), pure Pt net as the counter electrode (1 cm²), and Ag/AgCl (sat. KCl) electrode as the reference electrode was used. The preparation process of the working electrode was described below: 2 mg fine ground dealloyed samples, 0.5 mg acetylene black, 200 μL isopropanol, and 200 μL Nafion solution (0.5 wt %) were ultrasonically mixed. Then, 2 μL of the homogeneously mixed catalyst ink was placed on a freshly polished glassy carbon (GC) electrode with a diameter of 3 mm, and the dealloyed sample loading was kept at 10 μg. Voltammetric behavior was characterized in a 0.5 M KOH solution. The electrocatalytic performance for methanol oxidation was evaluated in a 0.5 M KOH + 0.5 M methanol solution. The testing solution was purged by nitrogen for 30 min before the electrochemical measurement.

3. Results and discussion

3.1. Microstructural characterization of the np-Pd/NiO composites

Fig. 1 shows the XRD patterns of the melt-spun Al_{85-x}Pd₁₅Ni_x ($x = 0.1, 0.3, 0.5, 0.7, 1$, at.%) ribbons before and after dealloying. The as-quenched Al–Pd–Ni ribbons were composed of α-Al (Pd, Ni) and intermetallic compound Al₃Pd (PDF No. 44-1021), as shown in Fig. 1(a). With the increase of the Ni content (≥ 0.5 at. %), the compound NiAl₁₀O₁₆ appeared in the ribbons. The principal peaks of all the dealloyed Al–Pd–Ni ribbons were located at 40.1°, 46.7° and 68.1°, corresponding to the planes (111), (200) and (220) of metallic Pd, respectively (Fig. 1(b)). The results confirmed that all the dealloyed samples were composed of only face

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