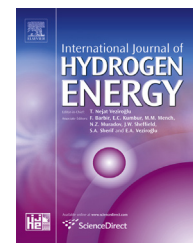


Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

ScienceDirect

journal homepage: [www.elsevier.com/locate/ije](http://www.elsevier.com/locate/ije)

# In situ synthesis of nickel–boron amorphous alloy nanoparticles electrode on nanoporous copper film/brass plate for ethanol electro-oxidation

Shujin Zhang<sup>a</sup>, Yixiong Zheng<sup>a,\*</sup>, Linshan Yuan<sup>a</sup>, Xiulin Wang<sup>a</sup>,  
Lihua Zhao<sup>b</sup>

<sup>a</sup> College of Material Science and Engineering, Huaqiao University, Xiamen 361021, PR China

<sup>b</sup> College of Materials, Xiamen University, Xiamen 361005, PR China

## ARTICLE INFO

### Article history:

Received 21 June 2013

Received in revised form

9 December 2013

Accepted 17 December 2013

Available online 23 January 2014

### Keywords:

Dealloying

Brass

Nanoporous copper film

Nickel–boron amorphous alloy

Ethanol oxidation

Microinjection method

## ABSTRACT

Ni–B amorphous alloy nanoparticles electrode (Ni–B/NPCF) has been synthesized in situ by microinjection method on nanoporous Cu film (NPCF) fabricated on brass plate by dealloying method. The structure, morphology and electrochemical performance of the electrode are obtained by X-ray diffraction, scanning electron microscopy, cyclic voltammetry (CV), double potential step chronoamperometry (DPSCA) and linear sweep voltammetry (LSV). The results show the Ni–B alloy is amorphous with atom clusters structure consisting of nanoparticles with the size of 50–100 nm. The values of proton diffusion coefficient and redox species of the Ni–B/NPCF electrode are more than an order of magnitude as big as the reported values. Ethanol oxidation in KOH solution at the Ni–B/NPCF electrode suggests the onset oxidation potential has a negative shift of 49 mV and the oxidation peak current increases by 43.36 times, and the reaction activation free energy decreases by 254.37 kJ mol<sup>-1</sup>, in comparison with the bulk Ni electrode. In addition, the reaction rate constant for ethanol oxidation at the Ni–B/NPCF electrode is improved by about two orders of magnitude compared with the reported value. Finally, the CV test indicates the Ni–B/NPCF electrode has a relatively stable redox behavior after 1000 potential cycles.

Copyright © 2013, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

## 1. Introduction

As fossil fuels are depleted over time and have caused a series of environmental problems, there is an urgent need for high-efficient, clean, safe and inexpensive new energy sources. In recent years, direct alcohol fuel cells (DAFCs) have attracted much attention due to their low pollution, high efficiency, high energy density, low operating temperature and

expediency operation [1,2]. Direct methanol fuel cell (DMFC) as a promising portable mobile power is slowly appearing in public, but methanol is noxious and harmful to the environment [3]. Ethanol considered as a potential alternative fuel has the advantages of innocuity, greater availability and higher theoretical mass energy compared to methanol [2–4], as a result, the researches on direct ethanol fuel cell (DEFC) have been arousing more and more interests. The fast and complete ethanol oxidation reaction is hard to actualize because of

\* Corresponding author. Tel.: +86 595 22692512.

E-mail addresses: [552199419@qq.com](mailto:552199419@qq.com) (S. Zhang), [yixiongzheng@126.com](mailto:yixiongzheng@126.com) (Y. Zheng).

the difficulty of cleaving C–C bond [5]. Therefore, the preparation of high active catalysts for ethanol oxidation is of a great significance. These common efficient catalysts for electro-oxidation of ethanol are noble metals such as Pt [1,4,6], Pd [6,7] and their alloys [2,8–11], but the high price and finite reserves limit their commercial applications.

The cheap Ni and its compounds as catalytic materials have a good electrochemical activity and stability, which show a potential application prospect to substitute for noble metals. Earlier studies have showed that the anodic oxidation of Ni-based catalysts in alkaline media could form NiOOH species that can oxidize small alcohol molecules [12,13]. Nanostructured metal catalysts with high specific surface area often exhibit better performance compared to the bulk [14]. Therefore, different morphologies and structures of Ni-based catalysts for ethanol oxidation have been prepared by various carriers and methods. For example, Berchmans et al. fabricated NiO electrode on glassy carbon (GC) [15]; Liao and co-worker prepared Ni/C electrode by electroless technique [16]; Hassan et al. used commercial carbon as a carrier for electroless Ni–B coatings electrode [17]; Kong et al. fabricated the nickel nanowire electrode using porous Al<sub>2</sub>O<sub>3</sub> membrane as a template [18]. Weng et al. developed Ni thin film on Al<sub>2</sub>O<sub>3</sub> substrate by sputtering [19]; Tian et al. have successfully obtained highly ordered Ni–Cu alloy nanowire arrays by differential pulse current electro-deposition into the pores of a porous anodic Al<sub>2</sub>O<sub>3</sub> membrane [20]; Jin et al. fabricated Ni nanoparticles electrode supported on functional multi-walled carbon nanotubes (MWCNT) surfaces by direct electrodeposition [21]; Liu et al. exhibited that MWCNT supported Ni catalysts were chemically synthesized via a hydrazine reduction [22]; Zheng et al. prepared nano Ni–B amorphous alloy powder microelectrode and electroless Ni–B amorphous alloy microdisk electrode using porous Pt as a carrier [23]; Muench et al. developed unsupported Ni and Ni–B tubes by template method [14]; Wang et al. investigated the non-noble catalysts Ni–Co/graphene and Ni/graphene electrode [24].

Although these mentioned Ni-based catalysts have a good electrocatalytic activity for ethanol oxidation, the low special surface area of carriers such as GC weakly combined with nanoparticles may reduce the activity of these catalysts under long-time operating conditions. Additionally, Al<sub>2</sub>O<sub>3</sub> substrate is easily dissolved in alkaline and acid medium, and there is a tendency for nanoparticles to agglomerate over time. In recent years, Nanoporous metals (NPMs) have received considerable interest due to their advantages of high specific surface area, high conductivity and excellent corrosion resistance [25–27], and they are regarded as an excellent catalyst scaffold material.

Ni-based amorphous alloys have the characteristic of short-range order of atom clusters and long-range disorder structure, and they exhibit excellent catalytic activity for hydrogenation and hydrogen evolution [28,29]. But so far few papers have been reported about their application in fuel cells. In recent years, a lot of researches have been done on Ni–B amorphous alloy in our previous work [23,30–32]. In the present study, NPCF is fabricated on brass plate by dealloying method [33]. Ni–B/NPCF electrode was synthesized in situ by microinjection method on NPCF and investigated its catalytic activity towards ethanol oxidation.

## 2. Experimental section

### 2.1. Preparation of the catalyst

The brass electrodes welded on Cu wires were prepared with the brass plates (4 mm × 5 mm). Prior to dealloying, these brass electrodes were polished to a mirrorlike smoothness by different sizes of metallographic abrasive paper, and cleaned in deionized water, acetone and deionized water for 10 min with ultrasonic, respectively. NPCF was fabricated by selective dissolution of Zn from the brass electrodes in 0.5 M H<sub>2</sub>SO<sub>4</sub> at 303 K for 5 h. After dealloying, the brass electrodes were rinsed by deionized water and immersed in deionized water for 1 h to remove residues of H<sub>2</sub>SO<sub>4</sub> solution. Finally, they were dried with blower at room temperature, and those welded sides were covered by insulation glue.

The Ni–B/NPCF electrode was synthesized in situ by microinjection method. The reducing agent was 0.1 M NaOH (Sinopharm) solution containing 0.488 M KBH<sub>4</sub> (Sinopharm), and the source of nickel was 0.098 M NiCl<sub>2</sub>·6H<sub>2</sub>O (Sinopharm) solution [34]. 5 μL NiCl<sub>2</sub>·6H<sub>2</sub>O and 5 μL KBH<sub>4</sub> solution were injected into the NPCF in turn by microinjector at room temperature, and the reaction was almost finished until no bubbles. Then the residual black liquid mixture should be removed. Repeating the same process, four Ni–B/NPCF electrodes with 5, 15, 25, 35 reaction times were prepared as summarized in Table 1, respectively. The Ni–B/NPCF electrodes should be rinsed with deionized water every 5 times in order to remove the loose structure and dried with blower at room temperature. Meanwhile, these generated large bubbles should be torn. After synthesized in situ, the Ni–B/NPCF electrodes should be rinsed by deionized water and immersed in deionized water for 1 h to remove residues of plating bath. Finally, they were dried with blower at room temperature. All reagents used for the experiment were of analytical grade and the solutions were prepared using deionized water.

The bulk Ni electrode was prepared with the Ni foil (4 mm × 5 mm) welded on copper wire, and the following treatment was same as the brass plate before dealloying.

### 2.2. Physical characterization

X-ray diffraction (XRD) patterns of the brass, NPCF and Ni–B/NPCF electrode were recorded using a Rigaku SmartLab 3 kW X-ray diffractometer with Cu K<sub>a</sub> radiation at 40 kV and 30 mA. Meanwhile, the XRD analysis was operated at a scan rate of 4° min<sup>−1</sup>. Morphological features of the NPCF and Ni–B/NPCF electrode were examined by scanning electron microscope (SEM, LEO-1530, Germany).

**Table 1** – Preparation of different Ni–B electrodes.

Electrode sample	Carrier	Reaction times
Ni–B-5/NPCF	NPCF	5
Ni–B-15/NPCF	NPCF	15
Ni–B-25/NPCF	NPCF	25
Ni–B-35/NPCF	NPCF	35
Ni–B-25/SBP	Smooth brass plate (SBP)	25

Download English Version:

<https://daneshyari.com/en/article/1270615>

Download Persian Version:

<https://daneshyari.com/article/1270615>

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