



Short communication

Nanoporous Cu film/Cu plate with superior catalytic performance toward electro-oxidation of hydrazine

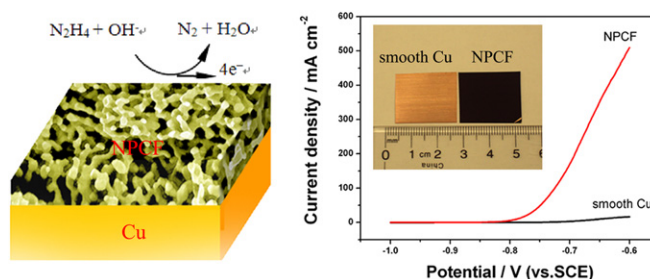
Falong Jia*, Jinhua Zhao, Xinxing Yu

College of Chemistry, Central China Normal University, Wuhan 430079, PR China

HIGHLIGHTS

- ▶ Nanoporous Cu formed by LSV dealloying of surface Cu–Zn alloy in short time.
- ▶ Lower onset oxidation potential of hydrazine on nanoporous Cu than smooth Cu.
- ▶ Superior activity of nanoporous Cu toward oxidation of hydrazine.
- ▶ Higher stability of nanoporous Cu than Cu nanoparticles.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 7 July 2012

Received in revised form

26 August 2012

Accepted 27 August 2012

Available online 5 September 2012

Keywords:

Copper

Fuel cell materials

Catalysis

Hydrazine

ABSTRACT

Nanoporous Cu film (NPCF) is fabricated on Cu plate by a novel electrochemical dealloying process in dilute HCl solution. The as-synthesized low-cost NPCF/Cu is used as anode in electro-oxidation of hydrazine for the first time and exhibits superior catalytic activity. The current density from hydrazine oxidation on NPCF is much higher than that on smooth copper. In addition, the NPCF electrode shows unexpected higher stability than Cu nanoparticles in similar size. It is believed that this low-cost NPCF electrode possesses potential application in the hydrazine fuel cell or other catalytic fields.

© 2012 Elsevier B.V. All rights reserved.

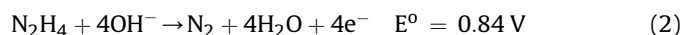
1. Introduction

Hydrazine has been considered as a candidate of fuels for fuel cells due to its high energy density. Compared with other conventional fuel cells, the direct hydrazine–air fuel cell (DHFC) has the following advantages [1]: (1) higher theoretical electromotive force of hydrazine cell (1.61 V) than conventional methanol–air fuel cells (1.21 V), (2) higher energy density of hydrazine fuel cell (5400 Wh L⁻¹) than that of methanol fuel cell

(4820 Wh L⁻¹), (3) near ambient working temperature. The total reaction of hydrazine fuel cell can be written as [2]:



In alkaline solution, the electro-oxidation of N₂H₄ could be realized by the following reaction:



However, there are still some problems to be solved before its marketization. One of the key challenges is the development of low-cost catalysts for the hydrazine oxidation with superior catalytic activity as well as stability. By now, electro-oxidation of

* Corresponding author. Tel./fax: +86 27 67867953.

E-mail address: fjia@mail.ccnu.edu.cn (F. Jia).

hydrazine had been investigated on various metals such as gold [3] and palladium [4]. Although noble metals exhibited satisfied catalytic performance and stability, their expensive cost still hindered the application of DHFC. Therefore, development of noble-metal free catalysts is highly desirable and important.

In the field of catalysis, metal nanoparticles normally exhibited superior performance than bulk materials due to their large surface-to-volume ratio and small-size effect, indicating a potential solution for the development of optimum catalysts for DHFC. Although copper nanoparticles were successfully used as catalysts in some organic reactions [5], its application in DHFC was seldom reported. Considering the practical use, Cu nanoparticles should be loaded on conductive substrates through adsorption method. There was a potential risk for these nanomaterials falling off during the long-term working, which would lead to the decrease of activation area. To avoid this problem, nanoporous copper as a whole integration could be a feasible solution. Among the ways to prepare nanoporous copper, dealloying process provided effective routes, which was involved with the selective dissolution of less noble elements from alloys (e.g. Cu–Mn, Cu–Al) [6,7]. Although dealloying of Zn from CuZn alloy is a well known phenomena in the field of corrosion [8], it was seldom reported that bulk Cu–Zn alloy was used to fabricate porous copper. The reason could be that the potential difference between Cu/Cu²⁺ and Zn/Zn²⁺ was not high enough to protect active nano-scaled Cu from corrosion during the etching of Zn. With dealloying process carried on from surface into deep area, the initially formed Cu tended to be corroded due to long exposure to etching solution.

The choice of solutions and dealloying parameters were also important in the fabrication processes. In our previous work, a thin film of nanoporous Cu was formed directly on the Cu plate by chemical dealloying of surface Cu–Zn alloy in alkaline solution [9]. However, it was found that over-corrosion of Cu always existed in the nanoporous film and part of NPCF tended to peel off from the plate. In this work, we chose electrochemical dealloying method to fabricate NPCF on Cu substrate and dealloying process could be finished in short time (<1 h). With precise control of potential applied on the sample, the corrosion speed could be well controlled and uniform nanoporous structure was obtained. The NPCF was found to be a good catalyst in the electro-oxidation of hydrazine (N₂H₄) and showed superior stability. It is believed that this NPCF/Cu electrode has a potential application in fuel cell device with hydrazine as energy source.

2. Experimental section

2.1. Preparation of NPCF electrodes

Copper plates (Sinopharm Chemical, 99.99%) were cleaned in acetone and then dipped into solution of 50 g L⁻¹ (NH₄)₂S₂O₈ and

5 g L⁻¹ H₂SO₄ for 30 s to remove oxide film. Then Zn was electro-deposited onto copper (0.5 cm² exposed area) at 20 mA cm⁻² for 5 min from a commercial Zn plating solution (Fengfan Plating Corp.) [9]. Then, Cu–Zn sample was rinsed, dried and heated at 150 °C for 1 h under protection of N₂ gas. Finally, electrochemical dealloying of Cu–Zn sample was conducted through linear sweep voltammetry (LSV) by using a CHI660D electrochemical workstation. The applied potential was scanning from –1.0 V to –0.2 V at speed of 0.5 mV s⁻¹. Platinum plate, saturated calomel electrode (SCE) and Cu–Zn sample were used as reference electrode, counter electrode and working electrode, respectively.

2.2. Characterization and measurements

The microstructure and composition of the samples was characterized by field emission scanning electron microscopy (FESEM; JEOL-6700F) and energy dispersive X-ray Spectrometer (EDS; Oxford INCA.). X-ray diffraction (XRD) patterns of dealloyed Cu–Zn sample were recorded on a Rigaku diffractometer using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). The electrochemical oxidation of N₂H₄ was carried out in solution with 3 M NaOH and 1 M N₂H₄. The NPCF electrode, graphite plate and SCE were used as working electrode, counter electrode, and reference electrode, respectively. Smooth Cu working electrode was polished by aluminum oxide powder (~20 nm) before measurement. As for the test of Cu nanoparticles, 8 mg powder of Cu nanoparticles (~50 nm, Beijing Dk Nano technology Corp.) was dispersed in 1 ml AS-4 ionomer (Tokuyama Corp., Japan) suspension (5 wt.% in *n*-propanol) under ultrasonic condition and 5 μ l of mixture was dropped onto glass-carbon electrode as working electrode.

3. Results and discussion

Fig. 1 shows the cross-sectional SEM images and components analysis of Cu–Zn samples. The thickness of deposited pure Zn layer was about 2.6 μ m. After thermal treatment, some Zn remained as elementary substance on the top while a certain amount of Zn diffused into the Cu substrate. The atomic ratio of Cu increased gradually until the depth of film reached the pure Cu substrate. These results demonstrated that thermal treatment was an efficient way to form surface Cu–Zn alloy on Cu substrate.

Electrochemical dealloying of Cu–Zn sample was conducted in dilute HCl solution through linear sweep voltammetry (LSV) and results were listed in Fig. 2a. As for the Cu–Zn sample without thermal treatment, there was one anodic peak at potential ranging from –1.0 V to –0.77 V, which corresponded to the stripping of pure Zn. Since Cu substrate started to be oxidized at potential higher than –0.2 V, the ending potential of LSV was set as –0.2 V. After

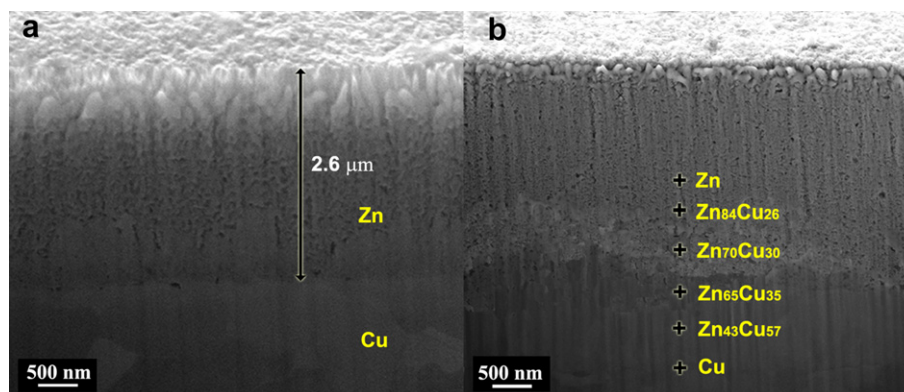


Fig. 1. Cross-sectional SEM images of Cu–Zn samples before (a) and after (b) thermal treatment.

Download English Version:

<https://daneshyari.com/en/article/7741759>

Download Persian Version:

<https://daneshyari.com/article/7741759>

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