

Regular Article

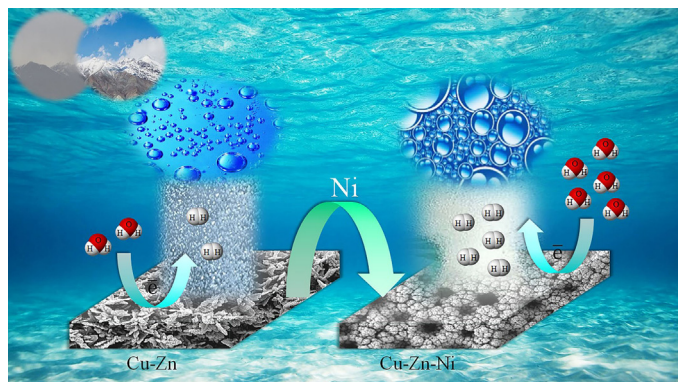
One step electrochemical route to the fabrication of highly ordered array of cylindrical nano porous structure and its electrocatalytic performance toward efficient hydrogen evolution



H. Ashassi-Sorkhabi*, S. Abolghasemi-Fakhri, B. Rezaei Moghadam, H. Javan

Electrochemistry Research Laboratory, Department of Physical Chemistry, Faculty of Chemistry, University of Tabriz, Tabriz, Iran

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 26 October 2017

Revised 4 January 2018

Accepted 8 January 2018

Available online 8 January 2018

Keywords:

Porous structure

Reaction kinetics

Hydrogen evolution

Electrocatalyst

Tafel plot

ABSTRACT

An efficient and non-precious metal catalyst is a key factor for hydrogen evolution reaction (HER). Here we report that the fabrication of highly ordered porous arrays of Cu-Zn-Ni alloy has been carried out in a one-step electrochemical route at a constant apparent current density of $-3 \text{ A}\cdot\text{cm}^{-2}$. The optimum film composition and reactivity of the electrodes for catalytic hydrogen evolution reaction were analyzed by using different current densities, deposition time and bath concentration. For this purpose, onset potentials in linear sweep voltammograms (LSV) were compared. The structure and morphology of nanoporous Cu-Zn-Ni and Cu-Zn alloy were characterized by SEM and energy dispersive X-ray (EDS) analysis.

The experimental results on the behavior of electrocatalytic activity of prepared alloys showed that the addition of nickel to the alloys improves of the electrocatalytic performance of the electrodes toward HER. In addition, enhancement of electrochemical activity toward hydrogen evolution can be attributed to the large electrochemical active surface area and porous structure of Cu-Zn-Ni alloy. In order to improvement of reaction kinetics, Tafel plots were derived from LSV voltammograms, and the exchange current densities for HER on synthesized electrodes (Cu-Zn and Cu-Zn-Ni alloys) were calculated about 3.2×10^{-5} and $2.1 \times 10^{-3} \text{ mA}\cdot\text{cm}^{-2}$, respectively.

© 2018 Elsevier Inc. All rights reserved.

* Corresponding author.

E-mail address: habib.ashassi@gmail.com (H. Ashassi-Sorkhabi).

1. Introduction

Today, due to rapidly growing in global demand for new energy sources and environmental protection, development of technologies such as electrochemical energy conversion has attracted increasing attention. Hydrogen (H_2) is considered as a cost-effective and renewable alternative clean energy carrier [1,2].

In aqueous solutions under high current density condition, H^+ reduces to molecular hydrogen that as the metal deposition, bubble growth also occurs simultaneously. Hydrogen bubbles during the deposition process act as a dynamic template. Bubble generation mechanism at around the electrode surface has an important effect on metal deposition process. Hydrogen bubbles generation process at surface electrode consist of three steps of nucleation, growth and separation from electrode surface. Electrochemical generation of hydrogen gas caused to releases of hydrogen molecules into the solution bulk or it's following into the interface of liquid and gas which results in the growth of bubbles. Also, the increase of current density at around the electrode surface easily saturated with H_2 molecules that led to the heterogeneous nucleation. The growth of bubbles continues until they are in contact with the electrode surface. During the growth and the stop time of the bubble at the surface, the contact angle is reduced and, ultimately, the bubbles are removed from the electrode surface [3–5]. In this regard, porous films with unique structural features are being used as ion exchangers, separators, membranes, sensors, energy stores and catalysts [6]. Their promising structures with nano and micro size holes through their many active sites have attracted much attention specially toward hydrogen production [7–11]. Generally, most volume of these structures is being formed by vacancies which caused to further sites of defect by enlarging real active surface area, permeability, stability and improving inherent catalytic activity of electrode materials [12–14]. Recently, significant interest has been directed toward the synthesis of composites that consist of metal nanoparticles [15]. Moreover many porous alloys as an electrode materials from different metals such as Ni, Co, Mo, Zn, W and some metal oxides such as SnO_2 , Cu_2O , Fe_3O_4 [15–18] have already been used in various energy systems like: fuel cells [19,20], solar cells [21,22], batteries [23,24], supercapacitors [25] and hydrogen generation [26–28]. Thus, choosing the type of support materials, atomic ratio of elements with high efficiency and the way of their synthesis count as important challenges.

Typical nickel-based catalysts due to their special properties are the most common and have been widely used in various applications specially in a flexible and sustainable manner for hydrogen evolution reaction (HER) [29–31]. Zhang and his co-workers [32] prepared porous Ni-Cu alloy films composed of nanosheets on copper plate under constant potential and studied the films' capability for the HER in alkaline media.

However, recently some other cheap and more available metals in comparison with nickel, such as copper, are studied for HER catalysis [33–36]. Several approaches have been developed to prepare nano composites of metallic nanoparticles. One of the three routes have been adopted in-situ, ex-situ and electrochemical method [18]. Wang and his coworkers [37] have successfully synthesized 3D CoNiCu nano-network structures with controllable compositions by a facile electrochemical method and studied their activity towards HER. The effect of increasing the second or third metal on thee electrochemical performance and surface morphology of prepared alloys were studied by several researchers and they confirmed that the alloying of copper with some other transition metals such as Zn [38] and Ni-Zn [39], enhances the hydrogen evolution kinetics and caused to release the bubbles at lower over-voltage in comparison with pure Cu.

Among the various manufacturing processes which is reported in literatures [40–42], hydrogen co-evolution during electrochem-

ical deposition offer facile and one step route to form porous structures with varying degrees of metallic interconnectivity and pore size [43–46].

Also alloys that made by this method, have an acceptable resistance, valuable physical and chemical futures, higher deposition rates, easy to control alloy composition, industrial applicability and some other specific advantages [47]. Electrodeposition and electrocatalytic activity of Cu and its alloys have been studied by different researchers [33,38,45,46]. Sattayasamitsathit and his coworkers [48], prepared porous electrodes. They selected copper and its alloys because of some mentioned advantages and this was the first time that a copper nanoporous film was being fabricated on a solid copper surface by simple electrodeposition-chemical etching technique.

In this study our goal is achievement of better electrocatalytic properties of copper by alloying. Therefore, co-electrodeposition of metals was performed by using dynamic hydrogen bubble template and galvanostat method from citrate bath. We investigated the effect of some factors such as apparent current density, time and concentration on porous Cu-Zn alloy, and then the effect of adding nickel to optimum Cu-Zn bath was studied. Finally surface morphology and electrocatalytic properties of electrodes have been evaluated by different electrochemical techniques for HER in alkaline media.

2. Experimental

2.1. Preparation of copper electrodes

The copper sheets as working electrodes were mounted in a polyester resin so that a 1 cm^2 surface area was remain uncovered. The electrodes were polished with SiC papers up to 1000 grade, degreased and rinsed using distilled water, then were dried. A copper wire attached to working electrode was used for electrical circuit propose.

2.2. Materials and electrochemical procedure

The cell used for deposition of alloys was a three-electrode system consists of copper samples as working electrode, Pt plate and Hg/Hg_2Cl_2 as a counter and reference electrodes, respectively. The working and counter electrodes in deposition baths (see Tables 1, 2) were spaced 20 mm apart from each other. The electrochemical experiments were performed with an AUTOLAB PGSTAT30 potentiostat-galvanostat device and sodium hydroxide was used as supporting electrolyte with a concentration of 1 M and were obtained from Merck (Germany). In order to provide high apparent current density for electrodeposition of materials, Autolab potentiostat was equipped with a suitable booster. The polarization tests were conducted at the potential of -0.35 to -1.25 V (SHE) with scan rate of 1 mV s^{-1} . All of the mentioned potentials through the text, has been reported versus standard hydrogen electrode (SHE). The electrochemical impedance spectroscopy (EIS) measurements were performed using an Autolab equipped with a frequency response analyzer, FRA. The perturbation voltage was 5.0 mV (rms) sinusoidal voltage with frequencies

Table 1
Deposition baths for synthesis of Cu-Zn electrode.

Bath number	$CuSO_4(M)$	$ZnSO_4(M)$
1	0.1	0.175
2	0.125	0.125
3	0.175	0.08
4	0.25	0.05

Download English Version:

<https://daneshyari.com/en/article/6992291>

Download Persian Version:

<https://daneshyari.com/article/6992291>

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