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Metallurgically prepared NiCu alloys as cathode materials for hydrogen evolution reaction

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HIGHLIGHTS

- Ni–Cu alloys with various Cu contents were prepared by powder metallurgy method.
- Ni–Cu alloy exhibits chemical composition related synergistic effect for HER activity.
- Ni–10Cu alloy electrode presents a most efficient activity for HER.
- Two time constants are observed in Nyquist curve and both of them related to the kinetics of HER.

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ABSTRACT

Ni–Cu bimetallic alloys with Cu content of 5, 10, 20, 30 and 50 wt% are prepared by powder metallurgy method, which consisted of powder mixing, pressing and sintering processes. The X-ray diffraction (XRD) measurement confirms that all the five Ni–Cu alloys possess the f.c.c. structure. The hydrogen evolution reaction (HER) activity of the prepared Ni–Cu alloy electrodes was studied in 6 M KOH solution by cathodic current-potential curves and electrochemical impedance spectroscopy (EIS) techniques. It was found that the electrocatalytic activity for the HER depended on the composition of Ni–Cu alloys, where Ni–10Cu alloy exhibited considerably higher HER activity than Ni plate and other Ni–Cu alloys, indicative of its chemical composition related intrinsic activity.

1. Introduction

Hydrogen is the cleanest energy source and a promising alternative energy carrier for the future. Among the various approaches designed to produce hydrogen, alkaline water electrolysis is one of the most mature and effective methods for production of hydrogen in high purity and large quantities [1–3]. However, the main problems with electrolytic hydrogen are the low electrode catalytic efficiency, high cost and energy consumption. Nickel is the most used conventional cathode for alkaline water electrolysis due to its high electroactivity towards the hydrogen evolution reaction (HER) in a strong alkaline solution and relatively low cost. Further improvement of its electroactivity by increasing the real surface area or increasing intrinsic catalytic activity has been a long standing challenge. Recently, Ni-transition metal alloys have been investigated to exhibit high HER activity and durability as cathode electrocatalysts in alkaline water electrolysis due to an electrocatalytic synergetic effect in comparison to their individual activities [4–8]. The addition of the alloying transition metal is expected to alter the electrode reaction mechanism leading to a change in the activation energy of the HER [9].

Among the Ni-based alloy electrodes, Ni–Cu alloys have shown potential for use as the cathode in the alkaline HER due to the improved electrocatalytic activity [10], high corrosion resistance [11] and good stability [12]. So far, many literature dealing with NiCu alloys as HER catalysts have been reported. Solmaz et al. [10] reported that the electrodeposited Ni–Cu alloy exhibited several times higher current densities for HER than Ni and claimed that the enhanced catalytic activity of NiCu alloy was related to its large roughness factor and a synergistic interaction between Ni and Cu atoms. Based on this, they developed porous NiCuZn ternary alloy catalyst by alkaline leaching for long-term electrolysis in alkaline solution [13]. Yin et al. [14] obtained a hierarchical porous $Ni(OH)_2$/

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NiCu electrode by brush plating, electrochemical dealloying and hydrolysis, which exhibited high hydrogen evolution reaction activity. Gatta et al. [15] also reported the electrodeposited Ni–Cu alloy films were an efficient HER catalyst in a KOH solution. Zhao et al. [16] demonstrated that NiCu/Al_2O_3/NCN composite displayed a high electrochemical stability in alkaline solution and relatively high activity for HER due to its relatively high real surface area and high intrinsic electrocatalytic effect of NiCu alloy particles. Chen et al. [17] fabricated a 3D NiCu composite electrode with hierarchical structure by an electrochemical method and found the HER activity was improved by the increased surface area.

The majority of presently studied Ni–Cu alloy electrodes are prepared by electrochemical deposition [10,12,15–20]. Though this method is simple, fast and cost-effective, it is not easy to accurately control stoichiometric composition of the resultant alloy, which is strongly influenced by the electrolyte concentration, deposition current or potential and deposition time [19,21]. Alternatively, powder metallurgy technique is a classical method to prepare alloys via a powder mixing, pressing and sintering process, which is ease of operation and precisely controlling the alloy components as well as suitable for large scale production. Rosalbino et al. fabricated ternary Ni–Fe–M (M = Cr, Mn, Cu) sintered alloys in view of their possible applications as electrocatalytic materials for HER [22].

To the best of our knowledge, there is a lack of study on the HER activity of metallurgically prepared Ni–Cu alloy electrodes. In this work, five kinds of Ni–Cu alloys with Cu content of 5, 10, 20, 30 and 50 wt% are prepared by powder metallurgy method. The surface microstructure of the developed Ni–Cu alloys was then analyzed using metallographic microscope and X-ray diffraction (XRD) techniques. The cathodic current-potential curves and electrochemical impedance spectroscopy (EIS) experiments were conducted in 6 M NaOH solution to investigate their electrocatalytic activities to HER.

2. Experimental

2.1. Preparation of Ni–Cu alloy electrode

Commercially pure carbonyl Ni (3–5 μm) and Cu (70 μm) powders were used as raw materials and mixed in the ratio of Ni–5 wt% Cu, Ni–10 wt% Cu, Ni–20 wt% Cu, Ni–30 wt% Cu and Ni–50 wt % Cu. The Ni and Cu powders were ball-mixed for 3 h using a mixer, and pressed to compacts with a dimension of 50 mm × 10 mm × 2 mm under a pressure of 300 MPa. The specimens were then sintered in a vacuum furnace under 1×10^{-3} Pa at a heating rate of 2 °C min^{-1} up to 800 °C and maintained at 800 °C for 4 h followed by furnace cooling to room temperature. The as-prepared Ni–Cu alloys are denoted as Ni–5Cu, Ni–10Cu, Ni–20Cu, Ni–30Cu and Ni–50Cu, respectively. Pure nickel plate is used as control group.

2.2. Characterization of Ni–Cu alloy

The microstructure of Ni–Cu alloys is studied with metallographical test (LEICA M4000 M digital microscope) after an etching treatment of the alloy surface in 10 wt% HNO_3 solution for 20 s. The phase composition of Ni–Cu alloys was analyzed by X-ray diffractometry (XRD: D/MAX-255) with the Cu-Kα radiation (40 kV). The tube voltage and the tube electric current of XRD were 40 kW and 250 mA, respectively. The Ni–Cu alloy plates were ground with SiC emery papers up to 2000 grit, and successively polished with 1 μm diamond paste, then ultrasonically cleaned in pure ethanol and dried under an air pressure stream. Finally, the as-cleaned Ni–Cu plate is sealed with Epoxy adhesive, leaving one side exposed with a geometric surface area of 1 cm^2, and used as the working electrode. Pt foil and Hg/HgO (6 M NaOH) electrode were used as the counter and reference electrode, respectively. The electrochemical measurements were carried out using the CHI660D electrochemical workstation (Chenhua Instrument Company) at room temperature unless otherwise specified. The working electrode was polarized at −1.5 V for 600 s prior to each experiment. Cathodic polarization curves and cyclic voltammogram curves were recorded in 6 M NaOH solution at a scan rate of 1 and 10 mV s^{-1}, respectively. All the cathodic currents are normalized to the geometric area of Ni–Cu alloys. The EIS measurements were conducted at selected overpotentials in the frequency range of 10 kHz to 0.01 Hz, and with the perturbation amplitude of 5 mV. The measured data were fitted by means of the Zview software. A pure nickel plate with an exposed geometric surface area of 1 cm^2 is used as a control group.

3. Results and discussion

3.1. Characterization of Ni–Cu alloy

Fig. 1 shows the metallographic examination for the as-prepared Ni–Cu alloys with different Cu content. As could be seen from Fig. 1, there exist white and grey phases in the metallographic structure, wherein the white phase is corresponding to Ni atoms and the grey phase is attributed to Cu atoms.

X-ray diffraction (XRD) was used for the structural characterization of the Ni–Cu alloys. The resulting diffraction patterns are shown in Fig. 2. As could be seen from Fig. 2, all the five Ni–Cu alloys exhibit the presence of (111), (200) and (220) reflections indicating the f.c.c. structure of the Ni–Cu alloy (JCPDS file card no.: 07-1406). A close observation indicates a shift in the diffraction angle towards lower angles with increasing copper content in the Ni–Cu alloys in comparison to the diffraction peaks of pure Ni plate as seen in Fig. 2a. It is well known that nickel and copper atoms can form infinite solid solution. Accordingly, Ni–Cu alloys are regarded as a solid solution with an f.c.c. Ni-rich structure with Cu atoms substitutionally dissolved in Ni. Taking into account the larger atomic radius of Cu (0.1278 nm) than that of Ni (0.1245 nm), it is considered that the dissolution of Cu atoms in Ni matrix and partially replacement with Ni atoms may result in the expansion of the Ni lattice, and thus lead to the downward shifts in diffraction angle. A similar result is reported for Ni–Cu alloy films by pulsed electrodeposition [23].

3.2. Electrocatalytic evolution of hydrogen on Ni–Cu alloy electrode

Linear polarization measurements were performed in 6 M NaOH solution to investigate the electrocatalytic activity of Ni–Cu alloy electrodes for hydrogen evolution. The cathodic current–potential curves of Ni plate and five Ni–Cu alloys were presented in Fig. 3 and were corrected for the IR-drop. The electrochemical parameters are summarized in Table 1. Obviously, as shown in Fig. 3, the measured cathodic currents of the Ni–Cu alloy electrodes for HER significantly increased than that of the Ni electrode. Additionally, the cathodic currents are directly proportional to the hydrogen evolution rate and the cathodic current densities (*I*-200 and *I*-300) of Ni–Cu alloy electrodes at overpotentials of η-200 and η-300 mV are compared. All Ni–Cu alloys are very active for the HER, showing a superior overall catalytic activity over pure Ni. It can be seen that the HER current of Ni–10Cu alloy is the highest and that of Ni plate is the lowest at the same overpotential. For example, the current density values on Ni–10Cu and Ni–5Cu at −300 mV overpotential (η_{-300}) are approximately 110 and 65 mA cm^{-2}, respectively, which are 106 and 61 mA cm^{-2} larger than that on pure Ni plate