A facile electrochemical fabrication of hierarchically structured nickel–copper composite electrodes on nickel foam for hydrogen evolution reaction

Zuwei Yin, Fuyi Chen[*]

State Key Laboratory of Solidification Processing, Northwestern Polytechnical University, Xian 710072, China

HIGHLIGHTS

- We prepare 3D NiCu precursor by galvanic replacement reaction between Ni foam and copper ion.
- $CuCl_2$ is the best dipping solution because the formation and hydrolysis of $CuCl_n^{1-n}$.
- An activation process was done to remove the oxide.
- CV treatment was done to fabricate a hierarchical architectural structure.
- The hierarchical architectural NiCu electrode has the best HER activity of all the electrodes.

ARTICLE INFO

ABSTRACT

A NiCu composite electrode with hierarchical structure has been successfully fabricated by an electrochemical method, which consisted of galvanic replacement reaction (GRR), activation process and cyclic voltammetry (CV) treatment. The three-dimensional (3D) Ni–Cu precursors were prepared firstly by dipping Ni foam into three kinds of different copper ion solutions and identified that $CuCl_2$ is a favorite electrolyte. This may be attributed to the adsorption of chloride ion on copper surface to form the $CuCl_n^{1-n}$ complex and the hydrolysis of $CuCl_n^{1-n}$. After an activation process to reduce the hydrolytic product Cu_2O into Cu, a CV treatment was performed to form a hierarchical structure to improve the surface area and to heighten the hydrogen evolution reaction (HER) activity. The optimal number of CV cycles is 3.

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1. Introduction

Growing concerns about global warming and energy security have necessitated the realization of renewable sources as a viable alternative to fossil-fuel-based technologies. Because hydrogen is the cleanest energy source and an ideal energy carrier, several researchers have focused on its production methods. Among the various approaches designed to produce hydrogen, alkaline water electrolysis HSN proven to be a promising method [1–3]. Its advantages over other hydrogen production methods include the use of water as a feedstock as its availability is relatively unlimited and can be procured from almost any part of the planet. Moreover, high-purity hydrogen in large quantities can be obtained in this manner

[4]. However, the primary problems in the production of electrolytic hydrogen are the high costs involved and high energy consumption. To make this technique more efficient and economical, it is imperative to select inexpensive electrode materials that exhibit good hydrogen evolution reaction (HER) activity.

The ideal properties of an electrode used for water electrolysis are (i) large surface area, (ii) good electrical conductivity, (iii) good stability, (iv) low over-potential, (v) low cost and (vi) ease of fabrication [5]. Due to its high HER activity, good corrosion resistance, abundant availability and relatively low cost, nickel and its alloys are some of the most studied non-precious electrode materials for alkaline water electrolysis [6–8].

Galvanic replacement reaction (GRR) is a type of single-step reaction that utilizes the differences between the standard electrode potentials of various elements, resulting in the deposition of nobler elements and the dissolution of lesser noble components [9]. Usually, it only requires a beaker and consumes almost zero

energy. The electroless nature of GRR affords them the unique and significant advantage of simplicity. Recently, it was employed to fabricate several electrocatalysts for various reactions. However, noble metals have been primarily investigated, such as Pt, Pd, Au, and Ag [10–13]. Only a few studies involving catalysts prepared for the HER have been undertaken. In our study, we prepared the NiCu precursor for hydrogen evolution by means of GRR between Ni foam and Cu^{2+}.

Cyclic voltammetry (CV) treatment has been used to roughen the porous electrodes and produce hydroxide for the electrochemical capacitors [14]. In our previous paper [15], we performed deposition–dealloying cycling before selective electrochemical dissolution to fabricate a hierarchical porous structure. In the present study, we conducted a deposition–dealloying cycling treatment after GRR to obtain hierarchically structured NiCu (HSN) electrodes with better HER activity.

Among the Ni-based electrodes under investigation, NiCu has shown potential for using as a cathode during alkaline HER. Initially, Solmaz et al. [16] reported that electrodeposited NiCu alloy could prove to be an efficient HER catalyst in a KOH solution. The stability and corrosion behavior with long-term electrolysis was also investigated [17]. Wang et al. [18] obtained a porous 3D NiCuCo nano-network structure by means of a facile electrodeposition method; the electrodeposition parameter was also discussed. Giz et al. [19] obtained a NiCuFe alloy in an acetate bath by electrochemical co-deposition, which exhibited good stability in a chlor-alkaline solution. They adopted the conventional electrodeposition technique to fabricate NiCu-based alloys. This process consumed a large amount of time; therefore, we replaced it with a rapid brush plating method as compared to that in our earlier study. Both these methods need relatively complex equipment and consume large amounts of energy.

In this study, we fabricated a 3D NiCu precursor by dipping Ni foam in a copper ion solution, which requires simpler equipment and consumes lower energy than conventional electrodeposition techniques and brush plating methods. The effect of the anion was also discussed; $CuCl_2$ solution was selected as the dipping solution. Then, an activation process was employed and a HSN electrode was prepared using the CV treatment. The electrocatalytic performance of the developed electrodes in terms of HER was evaluated using a 1 M KOH solution based on their cathodic polarization curves and electrochemical impedance spectroscopy (EIS) data. The results confirmed that a combination of GRR and CV treatment can yield high HER activity of NiCu composite electrodes.

2. Experimental

2.1. Electrode fabrication

2.1.1. Fabrication of NiCu precursors

The NiCu precursors were obtained by immersing Ni foam in a copper ion solution. Before performing GRR, the Ni foam was degreased with acetone and dipped in 0.1 M H_2SO_4 solution for 15 min to remove the oxide on the surface. All the instances of the Ni foam had an exposure surface area of 1 cm^2 to the solution. The other surface was covered with resin.

The copper ion concentration was maintained at 0.5 M, and $CuCl_2$, $CuSO_4$ and $Cu(NO_3)_2$ solutions were selected. Different instances of Ni foam were dipped in these three solutions. For each dipping solution, the immersing time was set as 0.5 h, 1 h, 1.5 h, 2 h, 3 h and 4 h. The HER activity for all the electrodes was measured, and the dipping solution with the optimum dipping time was selected.

2.1.2. Activation process

The results confirmed that the $CuCl_2$ solution was the most suitable for fabricating NiCu precursors by using GRR. Further, electrode dipping in 0.5 M $CuCl_2$ for 1 h exhibited the highest HER activity. Therefore, we selected this electrode to fabricate HSN electrodes. Here, we need to remove the hydrolytic product Cu_2O from the Ni foam dipped in $CuCl_2$ solution.

A conventional three-electrode cell system was formulated, and the selected NiCu precursor was used as the working electrode. The saturated calomel electrode (SCE) was used as the reference electrode and gauze platinum electrode, the auxiliary electrode. Constant-potential electrolysis was performed at −1.6 V for 20 min in order to reduce Cu_2O to Cu. The current–time curves were recorded.

2.1.3. CV treatment

After the activation process, CV treatment was performed. A typical three-electrode cell system was formulated and the prepared NiCu was used as the working electrode. The solution comprised a mixture of 0.02 M $CuSO_4$, 0.3 M $NiSO_4$ and 0.2 M $Na_3C_6H_5O_7$ at a pH of 4. The pH was adjusted by means of H_2SO_4 solution. CV treatment was performed between −1.0 V and 0.4 V versus SCE at a scan rate of 10 mV s^{-1} for 1, 2, 3, 4 and 5 cycles. By means of deposition–dealloying cycling, we can get HSN electrodes because of the 3D NiCu precursors. The obtained electrodes were labeled as HSN-1, HSN-2, HSN-3, HSN-4 and HSN-5.

2.2. Physical characterization

The morphologies and chemical compositions of the samples were examined using a scanning electron microscope (SEM; Tescan Vega 3) and an auxiliary X-ray energy dispersive spectroscope (EDS), respectively. The measurements were conducted at an acceleration potential of 20 keV. X-ray diffraction (XRD) was performed using an X'Pert PRO X-ray diffractometer (PANalytical) to investigate the crystal structures. The diffractograms were measured at room temperature between 10° and 90° (2θ) under a goniometer speed of 2°/min.

2.3. Electrochemical measurements

The electrochemical measurements were carried out using the CHI660C electrochemical workstation (Chenhua Instrument Company). A typical three-electrode setup was used. The fabricated electrodes served as the working electrode; SCE, the reference electrode; and Au electrode, the auxiliary electrode. All the tests were performed in 1 M KOH solution at room temperature. Before tests, the KOH solution was purified by nitrogen for 30 min. The Purpose is to remove oxygen and carbon dioxide. Then we made a constant-potential electrolysis at −1.6 V to remove the inpurities brought by electrode itself. All the working electrodes had an exposure surface area of 1 cm^2 to the solution. The other surface was covered with resin. The cathodic polarization curves were obtained, and the EIS experiments were conducted. The scan rate for polarization measurements was maintained at 1 mV s^{-1}. The EIS measurements were performed at an input signal amplitude of 5 mV, and the measurement frequency range was set from 100 kHz to 10 mHz. The measured data were fitted by means of the Zview software.

3. Results and discussion

3.1. Preparation of 3D NiCu precursors

3.1.1. Selection of dipping solution

Here, 3D NiCu precursors were fabricated by means of GRR between Ni foam and Cu^{2+}, and the dipping solution with the