



Two-step Preparation of Porous Nickel-sulfur Electrode for Hydrogen Evolution in Alkaline Water Electrolysis



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ABSTRACT

This work reports the preparation of 3D porous nickel-sulfur electrode for hydrogen evolution reaction (HER). The construction of the 3D porous structure is achieved by hydrogen bubbles dynamic templates, prepared from Cu electrodeposition at high current density. Subsequently, a nickel-sulfur film is electrodeposited on the 3D porous copper structure. The nickel-sulfur film with high crystal Ni₃S₂ content is achieved only through controlling deposition current. And the relationship between crystal structure and deposition current has been revealed. The porous crystal Ni₃S₂ electrode is significantly active for HER with a lower onset overpotential and an additional negative potential leading to a rapid increase in the cathodic current. And the developed electrode shows a lower charge transfer resistance for HER, which takes both advantages of high intrinsic activity and large real surface area. Besides, the electrode shows a higher electrochemical stability during the long-term electrolysis test.

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1. Introduction

The energy issue is the most important topic of the 21st century. As one of methods to replace fossil fuels such as petroleum and natural gas in the future, hydrogen is a promising alternative energy: only water is produced in the combustion of hydrogen. However, current hydrogen production processes mainly rely on steam reforming and coal gasification, in which a large amount of carbon dioxide is inevitably formed as a byproduct. An alternative process to produce hydrogen is water electrolysis. Compared with other methods for hydrogen production, the water electrolysis technology is a sustainable method which can utilize renewable energy sources such as solar and wind power [1]. Meanwhile, the water splitting reaction does not involve the emission of carbon dioxide.

The practical widespread application of water electrolysis is limited by its high energy consumption. The energy consumption can be reduced by using more active electrode for hydrogen evolution reaction (HER). Platinum (Pt) and its alloys have a higher electrocatalytic activity for HER. However, issues related to their high price and scarcity severely limit wider commercialization, which have motivated many research efforts to find alternative Pt-free electrode systems.

Many active and stable HER catalysts have been developed, such as MoS₂ [2], WS₂ [3], CoSe₂ [4], etc, which have been proved very promising for reducing energy consumption. In this way, polymer binders, such as Nafion and PTFE, are usually used to immobilize catalysts on the electrode surface for practical applications [5]. The whole process is time-consuming and polymer binders may block active sites [6]. Fortunately, there is a good way to solve them: synthesizing electrocatalytic film directly onto the electrode surface without binder. In this way, some surface modification techniques can be utilized. One major approach to enhance the HER activity is alloying, which can improve intrinsic electrocatalytic activity. Many alloys have been intensively studied, including Ni-Cu [7], Ni-Se [8], Ni-P [9], Fe-P [10], Ni-Mo [11], Ni-Sn [12], Ni-S [13–15], etc. Among these, Ni-S binary alloy electrodes, especially Ni₃S₂ phase with strong adsorption of hydrogen in the Ni matrix, exhibit excellent intrinsic activity [13]. The other strategy is to increase electrochemically active site, which is frequently achieved by template synthesis method (e.g. zeolite template [16], anodic aluminum oxide [17] and organic particle template [18]). Importantly, the hydrogen bubble templated electrodeposition is an artful method to increase surface area [19], based on which porous Ni has shown an outstanding electrochemical activity for HER [20]. Besides, there are also other methods that could be used to increase real surface area, such as alkaline leaching method [21] and nano-structure self-assembled [22]. However, electrode

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materials taking both advantages of high intrinsic activity and large real surface area remain insufficiently explored.

In this study, 3D porous copper structure with large real surface area is prepared by electrodeposition using hydrogen bubbles as the dynamic templates. Copper is a kind of current collector materials with high electrical conductivity. And Copper is a low-cost metal material. Subsequently, a Ni-S film with high Ni₃S₂ content is electrodeposited on the 3D copper template through controlling deposition current. The electrocatalytic activity of the developed electrode for HER is evaluated in 30 wt.% KOH solution using polarization curves and electrochemical impedance spectroscopy (EIS). The electrochemical stability is evaluated through the long-term electrolysis test.

2. Experimental

Before electrodeposition experiments, copper plates as the substrates were ground using an increasingly finer grit grinding steps by emery paper #600, #800, #1000 successively, then ultrasonically cleaned in acetone to remove the grease. After that, the degreased copper plates were put into 4M HCl for 5 min to get rid of copper oxides and fully washed with distilled water. The formation of electroactive coatings on such prepared copper substrate was done by electrodeposition, following the scheme shown in Fig. 1. First of all, it was constructed a 3D porous copper structure by means of electrodeposition at high current density using a DC regulated power supply. A mixed solution of 1.5 M H₂SO₄, 50 g/L CuSO₄·5H₂O, 0.2 mL/L HCl and 71 g/L Na₂SO₄ was used as the electrolyte to prepare 3D porous copper structure. The pre-treated copper plates were served as the cathode and anode in the electroplating process. The 3D porous copper structure was electrodeposited at a 3.0 A/cm² cathodic current density at 303 K for 20 s in an environment without O₂. In the process, the hydrogen bubbles function as a dynamic template during Cu deposition. Afterwards, the cathode copper plate was acted as a template for the Ni-S electrodeposition. The Ni-S electrolyte contained 300 g/L NiSO₄·6H₂O, 45 g/L NiCl₂·6H₂O, 38 g/L H₃BO₃, 100 g/L Na₂S₂O₃·5H₂O and 0.1 g/L SDS. The porous Ni-S electrode was electrodeposited at 318 K for 30 min, and the cathodic current density was controlled to be 6, 8, 10 and 12 mA/cm² respectively. In this process, the pH remained 4.0 using the mixed solution of HCl and H₂SO₄ (volume ratio of 3:1). In the following discussions, the obtained porous NiS electrodes were designated as Porous NiS-6, Porous NiS-8, Porous NiS-10 and Porous NiS-12, corresponding to different current density, respectively. For comparison, a Ni film was electrodeposited on the 3D porous copper structure in a Watt nickel solution (300 g/L NiSO₄·6H₂O, 45 g/L NiCl₂·6H₂O, 38 g/L H₃BO₃) to prepare porous Ni electrode.

The morphology and crystalline structure of electrodes were characterized by SEM and XRD. The alloy composition was detected by EDX. Electrochemical measurements were performed in a typical three-electrode cell with a platinum counter electrode and a Hg/HgO reference electrode by an electrochemical

workstation (Princeton Applied Research 273, USA). The electrolyte was 30 wt.% KOH solution. Before electrochemical testing, the surface areas outside test areas were sealed by epoxy resin. The apparent surface area used for testing was 1 cm × 1 cm. For EIS, sine wave voltages (5 mV) at frequencies ranging from 100 kHz to 10 MHz were superimposed on a given electrode potential (−1.2 V vs. Hg/HgO). The EIS data were analysed by the Zsimpwin software. The polarization curves were obtained at the scanning rate of 1 mV/s. Time-dependent potential curve of the electrodes was recorded in 30 wt.% KOH solution at a constant current density of 100 mA/cm² for 10 h. An emulational electrolyzer was manufactured to further estimate the electrochemical stability. In the electrolyzer, as-prepared electrode was employed as the cathode, Nickel Foam (surface density: 480 g/m²) as the anode, asbestos cloth (thickness: 2 mm) as the diaphragm. Meanwhile a magnetic drive pump was used to keep 1 M KOH electrolyte circulate in the electrolyzer. The electrolysis current density was 100 mA/cm². The operation of electrolysis was suspended for 2 hours every 8 hours to simulate intermittent industrial operation and the bath voltage variation with time was recorded.

3. Results and Discussion

3.1. Morphological and structural characterization of the fabricated electrodes

SEM image of the 3D porous copper template is illustrated in Fig. 2. The pore size in the copper structure is about 20–40 μm and the wall thickness is about 10 μm. In the deposition process, the hydrogen bubbles arising from the electrochemical reduction of H⁺ function as dynamic templates. Cu is electrodeposited and grows within the interstitial spaces between the hydrogen bubbles on the substrate. Ni-S binary alloy films are electrodeposited on the

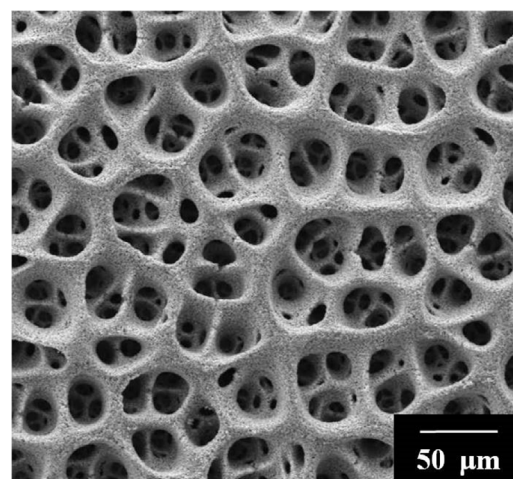


Fig. 2. SEM image of copper template.

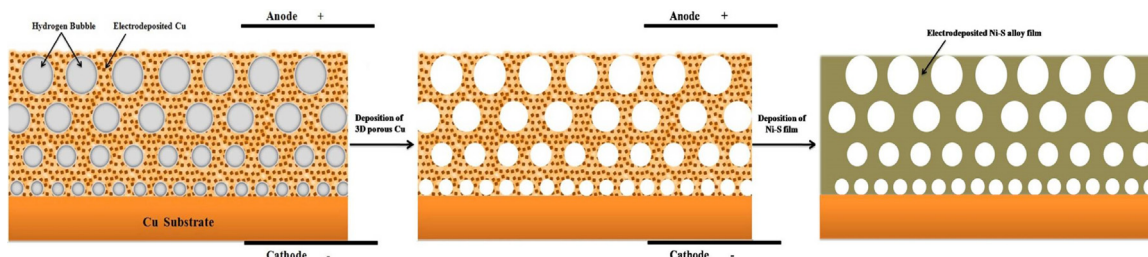


Fig. 1. Schematic illustration for the fabrication of 3D porous nickel-sulfur electrode.

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