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Electrodeposition of nickel–copper alloys to use as a cathode for hydrogen evolution in an alkaline media

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ABSTRACT

The electrocatalytic activity of nickel–copper (Ni–Cu) alloy coated electrodes for the hydrogen evolution reaction (HER) in an alkaline media was studied. The Ni–Cu alloys were electrodeposited on a Cu substrate by direct current (DC) and pulse current (PC) electrodeposition in a fixed plating bath. A wide alloy composition range (6–81 mol% Ni) was achieved by controlling the applied current density between 5 and 300 mA cm⁻². It was found that the electrocatalytic activity for the HER depended on the composition of the Ni–Cu alloys, where electrodes having low Ni content gave high electrocatalytic activities. DC electrodeposition resulted in better electrocatalytic performances than PC. Pulse plating parameters other than the magnitude of the applied current density did not substantially influence the electrocatalytic performance of the Ni–Cu alloy electrodes. Ni content was found to have a stronger effect on the electrocatalytic activity for the HER than the deposit morphology.

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1. Introduction

Due to the energy and environmental crisis, hydrogen (H₂) is currently considered to be one of the promising alternative energies for the future. It has the highest chemical energy per mass and can be produced from a diverse variety of feedstocks. Once produced, it is a clean fuel that does not emit greenhouse or other environmentally damaging gases in the energy production process and is ideal for fuel cells. Although various methods can be used to produce H₂, most processes involve the emission of carbon dioxide (CO₂) since they

normally use fossil fuels or hydrocarbon-based feedstocks. One of the alternative approaches for H₂ production that does not emit CO₂ during the H₂ production process is water electrolysis in an alkaline medium. This process produces H₂ using electrical energy to split hydrogen atoms from water through the electrochemical process. The advantages over other H₂ production processes include the use of water as the feedstock, since it has relatively unlimited resources and can be found in almost every part in the planet. When using renewable energy sources for electricity production, it is potentially an entirely clean production process. Moreover, it yields H₂ with the highest level of purity that is suitable for a

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use in fuel cells. However, the production of H_2 by the water electrolysis is expensive due to its high cost and energy consumption.

The cost and energy consumption for water electrolysis could be reduced by using inexpensive electrode materials that have a high electrocatalytic activity for the electrode reactions. Cathodes for alkaline water electrolysis are mainly made from Ni due to its high electroactivity towards the H_2 evolution reaction (HER), desirable mechanical and chemical stabilities in a strong alkaline solution and relatively low cost. However, further improvement of its electroactivity would lower the energy consumption level. One approach to enhance the electroactivity of Ni electrodes towards the HER is to form Ni-transition metal alloys, such as with Co, V, W, Fe, Mo, Zn and Cu [1–14] where the Ni-based alloy electrodes are fabricated by electrodeposition. The addition of the transition metal(s) is expected to alter the electrode reaction mechanism leading to a change in the activation energy of the HER [15]. The choice of the alloying metal(s) and the electrodeposition conditions influence the physical and chemical properties of the resultant Ni-based alloy electrodes, which in turn affect their electroactivity for the HER. Among the Ni-based alloy electrodes studied, Ni–Cu alloy has shown potential for use as the cathode in the alkaline HER due to the improved electrocatalytic activity [10], high corrosion resistance [16] and good stability [17]. Although several studies have reported the preparation of Ni–Cu alloys by electrodeposition [18–22], no extensive studies on the effect of the physical and chemical properties of the deposited Ni–Cu alloys, which are controlled by the electrodeposition conditions, on their electroactivity for the HER have been reported.

In this study, Ni–Cu alloy electrodes for use in the HER in an alkaline medium were formed using direct current (DC) and pulse current (PC) electrodeposition under different electrodeposition modes and parameters to manipulate the surface morphology and composition of the Ni–Cu alloys. The influence of the Ni–Cu alloy physical and chemical properties on their electroactivity for the HER was then evaluated. For most parts, the Cu substrate was mechanically polished to a mirror surface to avoid the geometric effect in the electrodeposition and the HER processes. Later, when stated, a non-mirror surface substrate was used to evaluate the importance of the surface structure on the physical and chemical properties and the electroactivity of the Ni–Cu alloy electrodes. The structural and morphological characteristics and compositions of the Ni–Cu deposited coatings were studied by X-ray diffractometry (XRD), scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDX), respectively. The electroactivity of the prepared electrodes for the HER was investigated by Tafel analysis and galvanostatic measurements. The electrodeposition conditions and Ni and Cu contents in the alloy electrodeposits that yielded the best electroactivity for the HER were revealed.

2. Experimental

The electrodeposition was performed in a cylindrical electrochemical cell containing 100 cm³ plating solution.

Galvanostatic electrodeposition (DC or PC) was performed using an Autolab PGSTAT 30 Potentiostat (Eco Chemie) with a three-electrode system. The working electrode was a 0.357 cm diameter (0.1 cm² area) copper disc polished with silicon carbide (SiC)-type abrasive paper (320, 800 and 2000 grades sequentially), and then either with 0.05 μm Al₂O₃ powder (Buehler) to a mirror finish or (where stated) not, so as to investigate the effect of the morphology of the deposited Ni–Cu alloy on the electroactivity. Platinum (Pt) gauze and a Ag/AgCl (saturated KCl) electrode were used as the counter electrode and the reference electrode, respectively.

A sulfate-plating bath containing 0.02 M NiSO₄·7H₂O, 0.002 M CuSO₄ and 0.2 M Na₂C₆H₅O₇, adjusted to pH 5 by sulfuric acid, was used for all Ni–Cu alloy electrodeposition. The Ni²⁺ concentration in the plating solution was selected to be relatively higher than Cu²⁺ concentration to make up for the thermodynamically less favorable Ni²⁺ reduction so that Ni would be electrodeposited along with Cu. The unplated Cu electrode, Cu deposit obtained from the plating bath containing 0.1 M CuSO₄·5H₂O and 0.5 M H₂SO₄ (pure Cu) and the Ni deposit obtained from the plating bath containing 0.107 M NiSO₄·7H₂O, 0.049 M NiCl₂·6H₂O and 0.02 M H₃BO₃ (pure Ni) were used for comparison.

DC electrodeposition was performed at current densities of 5, 10, 50, 100, 150 and 300 mA cm⁻² on the Cu discs to achieve a charge density of 150 C cm⁻². However, the charge density was reduced to 15 C cm⁻² for the PC electrodeposition to reduce the deposition time. The duration of each electrodeposition was set to ensure the desired charge density. For PC electrodeposition, when the effect of the peak current density was studied, the average current density and pulse frequency were fixed at 10 mA cm⁻² and 100 Hz, respectively. The magnitude of the pulse current density was varied from between 12.5 and 300 mA cm⁻² by adjusting the pulse duty cycle (ratio of the on-time and the summation of the on- and off-

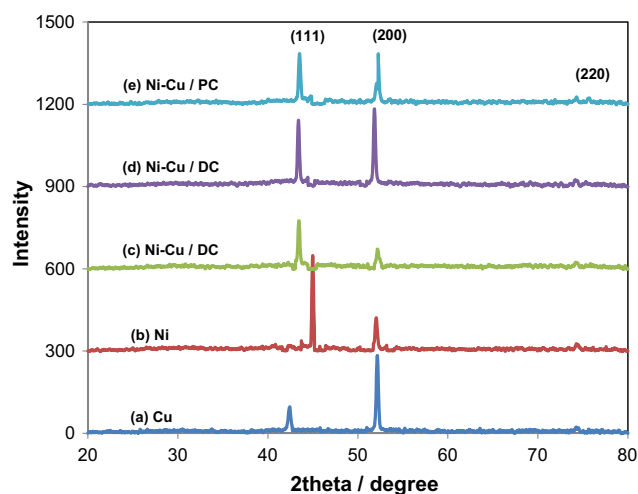


Fig. 1 – XRD patterns of the (a) Cu and (b) Ni deposited electrodes prepared by DC electrodeposition, and (c–e) Ni–Cu deposited electrodes prepared by (c,d) DC electrodeposition at a current density of (c) 10 and (d) 300 mA cm⁻², and (e) PC electrodeposition at a peak current density of 12.5 mA cm⁻².

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