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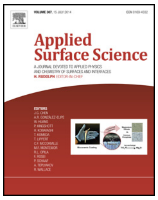

Fabrication and evaluation of nickel cobalt alloy electrocatalysts for alkaline water splitting

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ABSTRACT

As a catalyst for the hydrogen evolution reaction (HER) in alkaline water splitting, NiCo alloys of various compositions were prepared through electrodeposition onto Cu substrates. The composition of each alloy catalyst was varied by controlling the molar ratio of Co^{2+} ions in the electrolyte. With an increase in the Co content, the morphologies of the NiCo alloys were progressively changed from a round to polygonal shape. The NiCo alloys all exhibited a Ni rich surface, as confirmed by the bulk-to-surface compositional ratio and degree of alloying. The catalytic activities of the NiCo alloys toward the HER of water splitting were electrochemically tested in a KOH electrolyte, and the specific activities were characterized by considering the electrochemical surface areas of Ni and Co. The effect of alloying was demonstrated to be a significant enhancement of HER activity, resulting from a change in the electronic structures of Ni and Co.

1. Introduction

The production of hydrogen via water splitting is one of the most promising options for establishing a hydrogen economy in the near future [1,2]. Unlike carbon-based hydrogen production methods (e.g., hydrocarbon steam reforming, coal gasification, and biomass pyrolysis), water splitting is inherently more environmentally friendly, and can produce zero carbon dioxide emissions when associated with renewable energy sources such as solar and wind [3,4]. This has proven to be a major motivation for research into water splitting, even though it still has a relatively lower efficiency and higher production cost when compared to more conventional methods [5]. Among the various water splitting methods available, alkaline water splitting has emerged as a strong candidate for commercialization as it enables the large-scale and cost-effective production of hydrogen. Furthermore, the requisite conditions of high pH also allows for the use of non-noble metals as catalysts [6]. However, the slow kinetics of the HER with non-noble catalysts, particularly under conditions in which there is a lack of proton sources, remains a major hurdle to the realization of this process [6].

For decades, tremendous effort has been directed toward the development of well-defined catalysts for the HER [7–26]. From the reported studies, Ni is revealed to be one of the most promising catalyst for the alkaline HER among the non-noble metals [7,8]. A study on the correlation between HER activities on monometallic surfaces and the calculated hydrogen binding energy (BE_H) [9] supports the feasibility of Ni. In addition, various methods have been investigated to modify the intrinsic activity of Ni, such as forming Ni alloys [10–20], developing Ni complexes [21–25], and controlling the crystal orientation [26]. Nørskov and his colleagues presented a theoretical evaluation of the HER activity of binary surface alloys that took into consideration their BE_H, as-derived by density functional theory (DFT) [27]. From this, the strongest candidates for alloying with Ni were identified as Cu, Co, and Fe. [27]. In a previous study, we reported the high activity and durability of electrodeposited NiCu alloy catalysts for the HER in alkaline water splitting [11]. This found that the specific activity of the HER, as normalized by the real surface area of the Ni, is highly enhanced by the addition of Cu at concentrations close to 50%. Although the specific activity of the Ni was significantly improved, the NiCu alloy catalysts still presented a serious drawback in that pure Cu was revealed to be an almost inactive material with regards to the HER; and

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Table 1
Nomenclature of Ni, NiCo, and Co electrodeposited at −1.6 V_{SCE} for 15 s, as well as their respective electrolyte configuration.

Types of electrodes (bulk composition)	Electrolyte configuration
Ni100	0.50 M Ni + 0.50 M H_3BO_3
$Ni_{94}Co_6$	0.50 M Ni + 0.01 M Co + 0.50 M H_3BO_3
$Ni_{85}Co_{15}$	0.50 M Ni + 0.02 M Co + 0.50 M H_3BO_3
$Ni_{72}Co_{28}$	0.50 M Ni + 0.05 M Co + 0.50 M H_3BO_3
$Ni_{49}Co_{51}$	0.50 M Ni + 0.10 M Co + 0.50 M H_3BO_3
$Ni_{17}Co_{83}$	0.50 M Ni + 0.30 M Co + 0.50 M H_3BO_3
Ni_8Co_{92}	0.50 M Ni + 0.50 M Co + 0.50 M H_3BO_3
Co_{100}	0.50 M Co + 0.50 M H_3BO_3

consequently, the exposed Cu surface could not contribute to its activity. This provided the motivation to focus on other transition metals to form alloys with Ni; hence the use of Co in this study.

Among the non-noble metals, Co is known to be one of the more highly active materials for the HER [7,28,29]. As a result, a number of research groups have previously investigated the catalytic activity of NiCo alloys for the HER of alkaline media through the compositional control of alloys [13–15]. For example, Dell'Era et al. prepared NiCo alloys with Co concentrations ranging between 1.5 and 100% by using an alloy electrodeposition method [13]. From electrochemical measurements, it was revealed that NiCo alloys with a Co content of 64% demonstrate the highest exchange current density, with a value of 5×10^{-5} A cm^{-2}. Vasan et al. studied the alternating current impedance of the HER in a region of severe overpotentials, using NiCo alloys with Co concentrations between 20 and 80% [14]. They found that a NiCo alloy with a molar ratio of 1.0 exhibits the lowest overpotential of 266 mV at 100 mA during the HER. Although these studies reported the significance of NiCo alloy composition on HER activity, systematic approaches that combine the alloying effects and their catalytic activities are still rare. This is particularly true when it comes to the characterization of NiCo alloy properties, and correlating these with any observable enhancement of HER activity.

The results presented in this study demonstrate the preparation and characterization of NiCo alloy catalysts of various compositions, through the alloy electrodeposition method. Various analyses, incorporating microscopic and spectroscopic methods, were used to investigate the properties of the NiCo alloys, such as morphology, bulk and surface concentration, crystal structure, electrochemically active surface area (ECSA), and electronic structure. The electrochemical measurement of the catalytic activities of NiCo alloy catalysts was conducted by cyclic voltammetry (CV) in a highly concentrated alkaline electrolyte. These results were then further correlated to the material properties of the alloys. This therefore provides important information pertaining to the effect of alloying on the catalytic activities for the HER.

2. Experimental

In order to control the composition of NiCo alloys during deposition, 0.50 M of $NiSO_4 \cdot 6H_2O$ (DAE JUNG, 5611-4400) and 0.01–0.50 M of $CoSO_4 \cdot 7H_2O$ (DAE JUNG, 2872-4405) were used as metal precursors, with a supporting electrolyte of 0.50 M of H_3BO_3 (DAE JUNG, 2036-4405) [30]. Each precursor with the supporting electrolyte was also used individually for the deposition of pure Ni and pure Co. Prior to deposition, all electrolytes were first purged with N_2 gas for 30 min in order to remove any dissolved oxygen. The nomenclatures of the electrodeposited Ni, NiCo alloys, and Co are presented in Table 1 according to their bulk composition, along with their respective electrolyte configurations.

A conventional three-electrode cell system was used for all depositions and electrochemical measurements. For the deposition processes, a Cu foil (Sigma Aldrich, 349178) was used as the working electrode. Since Cu is inactive to H_2 production via alkaline water splitting, its effect on the evaluation of the catalytic activities of the alloys deposited on it could be reasonably eliminated, as confirmed and presented in Section 3. Prior to deposition, the Cu foil was immersed for 2 min in an etching solution consisting of KOH (0.034 M) and citric acid (0.020 M) in order to remove any residual native Cu oxides. The area of the working electrode exposed to the electrolyte was 1.33 cm^2, other parts being sealed by a custom-made Teflon holder. A Pt wire and a saturated calomel electrode (SCE, Digi-Ivy, A150) were used as the counter and reference electrodes, respectively; and all deposition processes were controlled using a potentiostat (Autolab PGSTAT302, Metrohm).

Characterization of the electrodeposited Ni, NiCo alloys, and Co were performed using various microscopic and spectroscopic methods. The morphologies of the deposits were observed by field emission scanning electron microscope (FESEM, Hitachi, s-4800); whereas the bulk and surface molar concentrations were measured by energy dispersive spectroscopy (EDS, JEOL, JSM-6701F) and X-ray photoelectron spectroscopy (XPS, KRATOS, PHI 5800). Finally, the crystal structure of all deposits was analyzed by X-ray diffraction (XRD, Bruker-AXS, New D8-Advance).

All the electrochemical measurements can be described as follows: For all depositions, chronoamperometry (CA) was conducted at −1.6 V_{SCE} for 15 s. The surface characterization to evaluate the formation of Ni and Co hydroxides was carried out electrochemically in a 0.5 M NaOH solution at room temperature, using CV at a scan rate of 10 mV s^{-1}. In order to calculate the real surface area, the charges required for the formation of Ni and Co hydroxides were divided by the monolayer charge per real surface area, assuming the monolayer charges of Ni (514 $\mu C\,cm_{Ni}^{-2}$) and Co (600 $\mu C\,cm_{Co}^{-2}$) [31,32]. To test the catalytic activity of the deposits toward the HER, CVs were recorded in a 6.0 M KOH solution at room temperature across a potential range of between −1.00 V_{SCE} and −1.60 V_{SCE} for 20 cycles, at a scan rate of 50 mV s^{-1}.

3. Results and discussion

Fig. 1 shows FESEM images of Ni, NiCo alloys, and Co electrodeposited at a potential of −1.6 V_{SCE} for 15 s. As can be seen, the morphologies of these deposits are significantly affected by the composition of the electrolyte. For the Ni (denoted as Ni_{100}) electrodeposited in an electrolyte containing 0.50 M Ni^{2+} precursor (Fig. 1a), circular grains about 250 nm in size were observed that sparsely covered the exposed area. On the other hand, with the addition of a small amount of Co^{2+} precursor (0.01 M), the uncovered area disappears with an accompanying slight decrease in grain size (Fig. 1b). This indicates that Ni deposition is accelerated with a high nucleation rate by the presence of Co^{2+} precursor in the electrolyte. With an increase in this Co^{2+} precursor from 0.02 M (Fig. 1c) to 0.50 M (Fig. 1g), the grain size is gradually increased and accompanied by a morphological change from a round to polygonal shape. This change is particularly notable with an increase in concentration from 0.05 to 0.30 M (Fig. 1d–f). In the case of the latter electrolyte concentration of 0.50 M Co^{2+} (denoted as Co_{100}), it can be seen that the most of Cu surface is covered by electrodeposited Co grains with a size of c.a. 390 nm (Fig. 1h).

The bulk and surface molar concentrations of the electrodeposited NiCo alloys were analyzed by EDS and XPS, respectively. The values obtained were then plotted according to the Co^{2+}/Ni^{2+} ratio in the electrolyte, as shown in Fig. 2. As this ratio increases from 0.02 to 1.00, the bulk molar concentration of Co in the NiCo deposits gradually increases from 6 to 92%. It should be noted that these bulk molar concentrations are always higher than the Co^{2+} ratio in the respective electrolytes, even though the standard