Chemistry and Materials

The Center for Science Innovation

Research Article

Chem. Mater. 2 (3) 2023, 72-76

Synthesis of CoNi by Electrodeposition Technique and its Application as an Electrocatalyst for Water Splitting

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Received
22 August 2023

Received in revised form
16 September 2023

Accepted
23 October 2023

Published online
31 October 2023

DOI
https://doi.org/10.56425/cma.v2i3.64

Abstract

Water splitting is regarded as a highly efficacious methodology for obtaining hydrogen, intending to be employed for the purpose of renewable fuel production. However, the performance of this technique is constrained by the sluggish kinetics of the hydrogen evolution reaction in alkaline environments and the oxygen evolution reaction, which leads to significant energy inefficiency and excessive potential requirements. To enhance the reaction kinetics and efficiency of water splitting, there exists a pertinent requirement for an electrocatalyst that exhibits commendable efficiency. The primary objective of this study is to construct a cobalt-nickel (CoNi) electrocatalyst that facilitates water splitting. The present study employs the technique of electrodeposition for its experimental procedures. The findings of the study indicated that the CoNi sample, as observed through scanning electron microscopy with energy dispersive X-ray spectroscopy (EDX) analysis, exhibited a flattened, circular form and agglomeration. The EDX analysis yielded elemental composition results indicating a cobalt content of 20.51% and nickel content of 79.49% The X-ray diffractometer analysis reveals that the CoNi metal alloy has manifested a crystalline structure with a cubic configuration. The electrochemical impedance spectroscopy found that the charge transfer resistance of CoNi with the electrolyte solution was 1.48 kΩ. The data collected from the chronoamperometry test indicates the presence of a consistent and unchanging electrical current. Additionally, the cyclic voltammetry test presented E_{pa} and E_{pc} values of 0.4469 V and 0.3037 V, respectively, leading to a calculated ΔE of 0.1432 V. The research findings establish that the CoNi alloy, synthesized via the electrodeposition technique, exhibited a performance-effective electrocatalyst that closely approached the desired outcome.

Keywords: CoNi, electrocatalyst, electrodeposition, water splitting.

1. Introduction

Hydrogen is a promising energy source that holds substantial potential to contribute significantly towards ensuring sustainability in the coming years [1]. Electrochemical water splitting has been identified as a viable approach in harnessing hydrogen as a desirable strategy. This approach represents an efficacious methodology for the conversion of electrical energy into chemical energy, specifically in the context of hydrogen. Electrochemical water splitting is a process that arises from the combination of two half-reactions known as the oxygen evolution reaction (OER) and the hydrogen evolution reaction (HER). However, the water splitting (WS) process is impeded by the sluggish rate at which the paired proton transfer process occurs. Additionally, sluggish kinetics of the HER in alkaline environments and the OER at the anode can result in substantial energy usage and elevated excess potential [2].

The present issues necessitate the employment of an efficient electrocatalyst to enhance both the reaction kinetics and the efficiency of water splitting. An alternative approach involves the utilization of an electrocatalyst,

specifically platinum (Pt). The platinum electrocatalyst is the most efficient HER and a good electrocatalyst for OER, but there are shortcomings, namely scarcity and high cost that can hinder its application on a large scale [3]. Therefore, other materials are needed to replace platinum and develop WS electrocatalysts that are efficient, have low cost, and are abundant [4]. Transition metals, especially cobalt, nickel, and iron, have been widely studied in the field of materials for WS electrocatalysts because they have good chemical structure, chemical properties, and catalytic activity [5]. Nickel is a good catalyst for alkaline HER among non-precious metals, low cost, and abundant on earth [6]. To improve the performance of nickel catalysts can be combined with other metals, namely cobalt. Cobalt nickel (CoNi) alloys possess numerous notable advantages, rendering them extensively employed in electromagnetic devices and high-temperature electrochemical devices. In particular, CoNi exhibits the capability to facilitate electrochemical reactions essential for the breakdown of water. CoNi has the physical property of corrosion and will have a longer life and good performance during the electrolysis process. In addition, the potential of CoNi electrodes can affect the electrochemical reactions that occur during the electrolysis process [7].

Several studies have been conducted to synthesize CoNi as a WS electrocatalyst including research conducted by Zhang *et al.* using a modified dielectric discharge plasma method to produce CoNi-MOFs, the results showed a current density of 10 mA/cm^2 [8]. Huang *et al*. reported the use of the urea hydrolysis method to produce $CoNi_2S_4$@CoS_2/NF 3D, and the results showed that the $CoNi_2S_4$@CoS_2/NF 3D catalyst was efficient for water splitting [9]. Research conducted by Tan *et al.* on using the electrodeposition method to produce a bimetallic nickel cobalt (NiCo) nanosphere for HER and OER, the result showed a current density of 10 mA/cm^2 [10].

In this study, CoNi bimetal was synthesized using the electrodeposition method. The electrodeposition method has many advantages including providing a simple, fast, energy-efficient, low-cost route, that can be carried out at ambient conditions. Also, morphology and the properties of the materials can be controlled by manipulating various parameters, such as voltage, electric current, reaction time, and chemical concentration [3,11,12]. The CoNi electrocatalyst was then tested for water splitting with 1.0 M KOH using cyclic voltammetry (CV).

2. Materials and Method

2.1 Synthesize of CoNi thin film

The materials used in this study were $NiSO_4.6H_2O$ (Sigma Aldrich), $CoSO_4.7H_2O$ (Sigma Aldrich), H_3BO_3 (Merck), KOH (Merck), and NaOH (Merck). The electrolyte solution for CoNi sample synthesis was prepared using a solution containing 0.5 M $NiSO_4.6H_2O$, 0.010 M $CoSO_4.7H_2O$, and 0.5 M H_3BO_3. The deposition was carried out with the electrodeposition method for 15 minutes on a copper substrate with a voltage of -1.5 V at room temperature. Before electrodeposition, the substrate was polished mechanically with sandpaper and washed with deionized water and ethanol. The electrodeposition method was performed in a three-electrode cell with platinum (Pt) as a counter electrode, Ag/AgCl as reference electrodes, and copper rods as working electrodes. The obtained deposit was rinsed with distilled water and dried.

2.2 Characterization

The morphology and composition of CoNi sample were analyzed using scanning electron microscopy coupled to energy-dispersive X-ray spectroscopy (SEM-EDX, FEI brand type: Inspect-S50). An X-ray diffractometer (XRD, PANalytical AERIS) was used to examine structures and phases.

2.3 Electrochemical test

Electrochemical impedance spectroscopy (EIS) analysis was carried out to examine the impedance of CoNi using 0.5 M KCl solution in the frequency range of 100 kHz - 0.1 Hz. The catalytic activity of CoNi was investigated in 1 M KOH solution using CV technique at a scan rate of 100 mV/s and a voltage range of -0.75 V to 0.75 V. While the chronoamperometry (CA) measurement was conducted to determine the stability of sample in 1 M NaOH solution.

3. Results and Discussion

SEM enables high-resolution observation of a sample surface, allowing a better understanding of the structure, shape, and surface texture of a sample. Figure 1 shows the SEM results at 5000x magnification of the CoNi alloy synthesized using the electrodeposition method. It can be seen that the CoNi sample exhibits agglomerated particles forming a flattened surface. Particle aggregation results in strong bonding and high interaction between the particles caused by higher nickel concentration. When the concentration of nickel is higher, the samples become less dispersed with larger molecules [13]. When the size of nickel exceeds a certain threshold, they start to aggregate,

leading to an increase in the size distribution of the nickel particles [14].

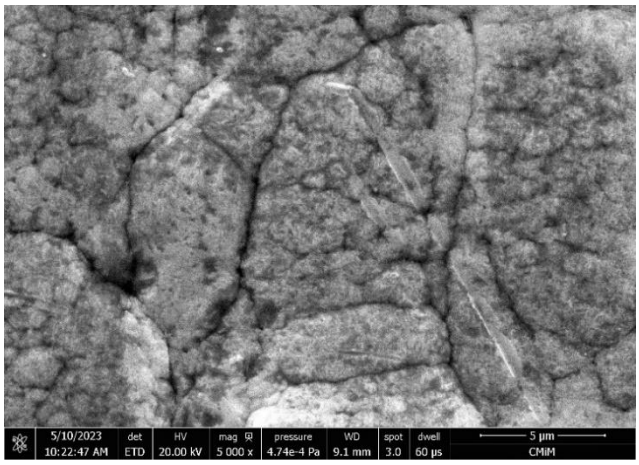

Figure 1. SEM micrographs of CoNi thin film.

Figure 2 shows the EDX spectrum of CoNi where the presence of Co and Ni elements in the sample is revealed. The ratio of Co to Ni resulting from the deposition process on the copper is shown in Table 1. The analysis results proved that the CoNi thin film was formed on the substrate.

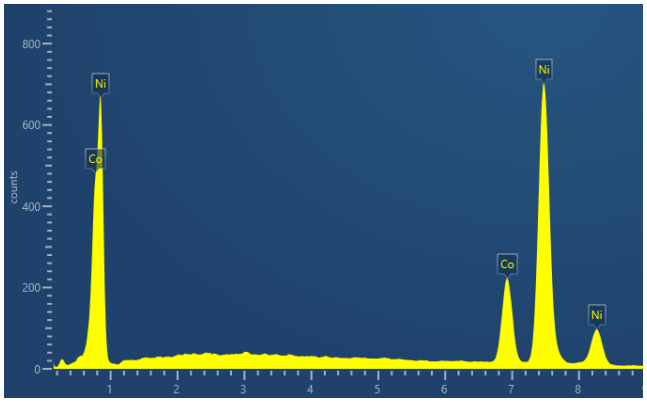

Figure 2. EDX spectrum of the CoNi thin film.

Table 1. Co/Ni ratio formed on copper wire.

Element	Measurement	
	Weight%	Atomic%
Co	20.57	20.51
Ni	79.43	79.49

The result of the XRD characterization is shown in Fig. 3. The Miller index is (111), (200), (220), and (311) can be observed to exhibit four main peaks located at position 2θ with corresponding angles of 44.35°, 51.72°, 76.38°, and 92.83° [15]. This observation suggests the formation of a CoNi metal alloy possessing a cubic crystal structure. The presence of a strong and sharp diffraction peak shows that the sample is crystalline [16].

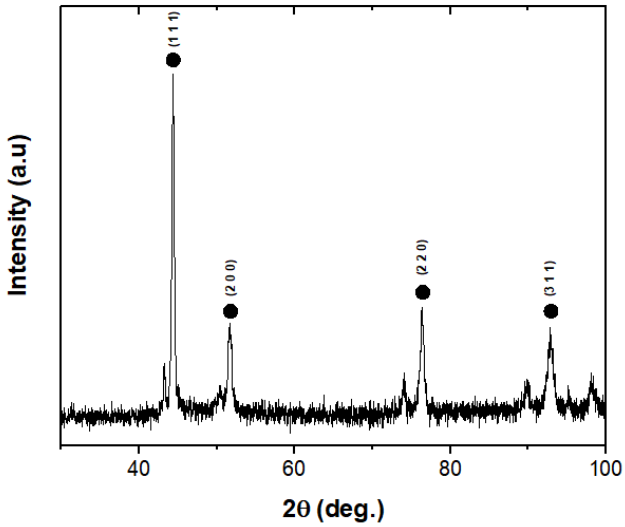

Figure 3. XRD pattern of CoNi thin film.

The main purpose of EIS analysis is to study material properties, intrinsic material properties, or specific processes that can affect the conductance, resistance, or capacitance of a system in electrochemistry. In Figure 4, the EIS measurement results are presented as a Nyquist plot exhibiting a low charge transfer resistance (R_{ct}) value which indicates good electron transfer kinetics [17]. The experimental data acquired in this investigation reveal an R_{ct} value of 1.48 kΩ and a solution resistance value of 7.55 Ω with a curve model is R-C parallel. These measured values suggest the existence of electron charge transfer, which may consequently impinge upon the electron transfer kinetics rate [18].

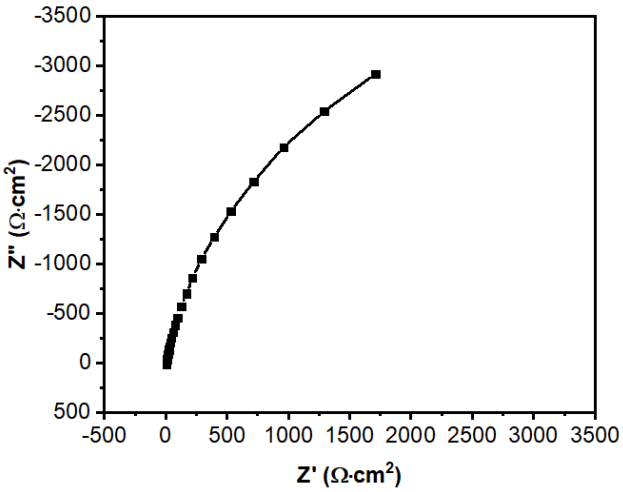

Figure 4. Nyquist plot of CoNi thin film.

The stability of the CoNi electrodes was investigated with chronoamperometry at a constant potential step (-

1.634 V). As shown in Figure 5, the peak on the graph represented the steady potential at the electrode over a period and the change in current observed over that period of time. The current density of CoNi decreased immediately after starting OER. Furthermore, the current density on CoNi stabilizes at -450 mA after 7200 s. The presence of peaks in the CA curve signifies the occurrence of a redox reaction at the electrode surface, resulting in either oxidation or reduction of a species, which subsequently leads to a change in the current [19].

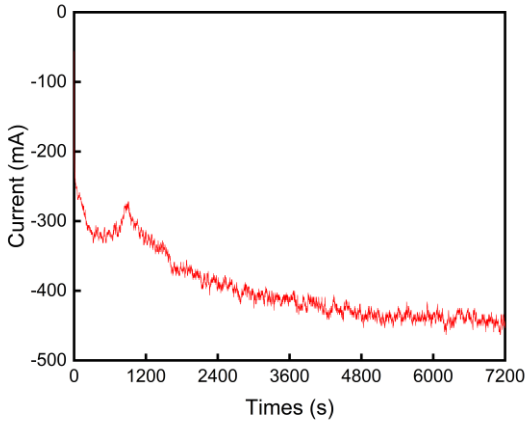

Figure 5. Chronoamperometry test (relationship of current versus time) for 7200 seconds of CoNi thin film.

Figure 6 shows the results of the CV test. The CV test was conducted with a three-electrode system at room temperature, which aims to investigate the catalytic activity of CoNi as an electrocatalyst for water splitting. The reaction that occurs is as follows [20] :

anode: $2H_2O_{(l)} \rightarrow O_{2\,(g)} + 4H^+_{(aq)} + 4e^-$ (1)

cathode: $4H^+_{(aq)} + 4e^- \rightarrow 2H_{2(g)}$ (2)

Water is oxidized at the anode to give off electrons. In Figure 6, the anodic peak appears which indicates an increase in current when the electrode potential increases as the oxidation reaction occurs.

Based on the voltammogram, the value of the comparison between anodic peak current (I_{pa}) and cathodic peak current (I_{pc}), I_{pa}/I_{pc} is 1, which means that the reaction that occurs is a reversible reaction [21]. The reversible reaction has the same anodic and cathodic peak currents, which results in a peak current ratio of 1.00. This shows that the redox reaction is completely reversible and that the same number of electrons are involved. Meanwhile, the E_{pa} (potential peak anodic) and E_{pc} (potential peak cathodic) values were 0.4469 V and 0.3037 V, resulting in an ΔE (peak-to-peak separation) of 0.1432 V. A smaller peak-to-peak separation indicates a reversible reaction, related to the number of electrons transferred in a redox reaction, the rate of electron transfer, and the diffusion coefficient of the species involved [22]. The small ΔE separation value and I_{pa}/I_{pc} equal indicate that CoNi has the potential to be an effective electrocatalyst for water splitting.

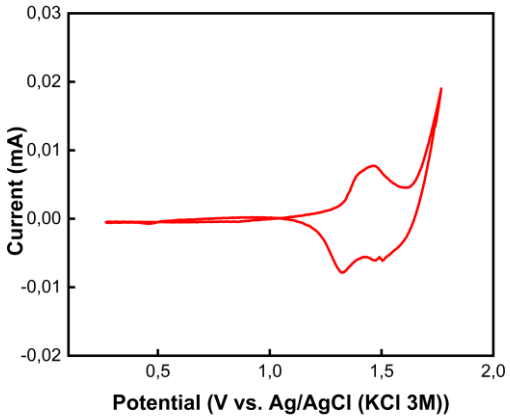

Figure 6. Cyclic voltammetry (relationship of current versus potential) of CoNi thin film.

4. Conclusion

Cobalt nickel electrocatalysts were successfully prepared through the electrodeposition method using three electrode systems. CoNi is able to facilitate the electrochemical reaction involved in water splitting. The catalytic activity for OER shows that the redox reaction is completely reversible and that the same number of electrons are involved, the E_{pa} and E_{pc} values were 0.4469 V and 0.3037 V, resulting in a ΔE of 0.1432 V because water is oxidized at the anode to give off the electron, the anodic peak appears which indicates an increase in current when the electrode potential increases as the oxidation reaction occur. The small peak-to-peak separation value and I_{pa}/I_{pc} equal indicate that CoNi has the potential to be an effective electrocatalyst for water splitting.

Acknowledgment

The author would like to acknowledge Badan Riset dan Inovasi Nasional (BRIN) dan Lembaga Pengelola Dana Pendidikan (LPDP) for funding this work through grant 1/RIIM II/LPPM/IV/2023.

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