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Electrodeposition of CoNi Bimetallic Catalyst for Ethanol Electrooxidation Application

Abdul Asywalul Fazri[1,*], Alvida Nor Puspita[1], Selvia Ningsih[1], Annisa Auliya[1,2]

[1]Department of Chemistry, Faculty of Mathematics and Natural Science, Universitas Negeri Jakarta, Jl. Rawamangun Muka, Jakarta 13220, Indonesia

[2]The Center for Science Innovation, Jakarta Timur 13120, Indonesia

*Corresponding author: abdulasywalulfazri05@gmail.com

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Abstract

Platinum is potentially employed as a catalyst in direct ethanol fuel cells (DEFCs). However, its scarcity and susceptibility to carbon monoxide poisoning give rise to novel challenges necessitating resolution. Transition metals such as nickel and cobalt are regarded as highly auspicious catalysts for DEFCs due to their perceived potential to reduce the expenditure associated with the synthesis procedure. In the present investigation, the synthesis of a cobalt-nickel (CoNi) catalyst with bimetallic properties was effectively accomplished through the electrodeposition technique utilizing the stimulator mode. Subsequently, an evaluation was conducted to assess the catalyst's proficiency in ethanol electrooxidation. The CoNi samples underwent comprehensive characterization through the utilization of various analytical techniques, namely X-ray diffraction (XRD), scanning electron microscopy (SEM), elemental dispersive X-ray analysis, and electrochemical impedance spectroscopy (EIS). The XRD analysis confirmed the formation of CoNi, while the SEM characterization demonstrated that the CoNi samples exhibited a homogeneous morphological feature. The impedance measured by the EIS technique displayed a resistance to charge transfer value of 21.21 kΩ, while the solution resistance value amounted to 66.67 kΩ. The catalytic efficiency of the specimens in ethanol electrooxidation was evaluated using the cyclic voltammetry technique, resulting in a peak current density of 3.14 mA/cm^2 proving the potential of bimetallic CoNi to be a low-cost catalyst for ethanol electrooxidation process.

Keywords: catalyst, CoNi, electrodeposition, ethanol electrooxidation.

1. Introduction

The demand for renewable energy sources has been steadily increasing in response to fossil fuels' scarcity and adverse environmental impact. Direct Ethanol Fuel Cells (DEFCs) have garnered significant attention from researchers worldwide as a promising new and renewable energy source. Ethanol, the fuel used in DEFCs, is easily mass-produced, flexible, and environmentally friendly [1]. The conversion process of ethanol into electrical energy requires suitable catalysts. Platinum-based catalysts are the most used in DEFCs due to their high catalytic activity in ethanol electrooxidation reactions [2]. However, platinum has several drawbacks, one of which is its limited abundance, making the development of platinum-based catalysts costly. Additionally, platinum catalysts are prone to carbon monoxide (CO) poisoning, which reduces their catalytic activity and stability in ethanol electrooxidation reactions [3]. Therefore, research on alternative transition metal materials with abundant reserves, low cost, and high activity potential is highly needed [4].

From the earth-abundance perspective, nickel is one of the most abundant transition metals. Nickel is known to exhibit good catalytic activity towards small organic molecules in alkaline media [5]. However, its catalytic activity for ethanol electrooxidation reactions is still insufficient. This is attributed to its electronic properties, which are not well-suited for ethanol and can produce side products that inhibit the ethanol electrooxidation reaction

[6]. To enhance its catalytic activity, nickel needs to be combined with other transition metals to form bimetallic catalysts. Cobalt is one such alloy that can improve the catalytic activity of nickel in ethanol electrooxidation reactions [7]. Although cobalt itself does not exhibit high electrocatalytic activity, it can be used as a co-catalyst to suppress CO poisoning, thereby reducing the inhibition of the catalytic activity caused by side reactions during ethanol electrooxidation [8].

Despite successful synthesis, the catalytic activity produced by cobalt nickel (CoNi) catalysts is still rarely reported [9]. Therefore, this paper will synthesize CoNi catalysts using the electrodeposition method with the stimulator mode to increase its catalytic activity toward ethanol electrooxidation reaction. The electrodeposition method offers various advantages, including low cost, time efficiency, reproducibility, no requirement for sample preparation, and better control over CoNi particle growth [10, 11]. The bimetallic CoNi catalyst will be deposited on a copper wire and then tested for its catalytic performance in ethanol electrooxidation using the cyclic voltammetry (CV) method.

2. Materials and Method

2.1. Chemicals and materials

Chemicals used for sample preparation and electrochemical measurements were cobalt sulfate heptahydrate ($CoSO_4.7H_2O$) (Merck), nickel sulfate hexahydrate ($NiSO_4.6H_2O$) (Merck), copper wire, boric acid (H_3BO_3) (Merck), ethanol (C_2H_5OH), potassium hydroxide (KOH) (Merck), and deionized water (aquadest). All chemicals were used as received without further purification.

2.2 Preparation of CoNi bimetallic electrocatalyst

A precursor solution was prepared by dissolving 0.05 M $CoSO_4.7H_2O$, 0.15 M $NiSO_4.6H_2O$, and 0.2 M boric acid in deionized water. The sample preparation was performed using the potentiostatic technique. The applied potentials were controlled using the stimulator mode with a lower voltage of -1.75 V and an upper voltage of -1.00 V. The deposition was carried out for 15 minutes on a copper wire substrate with a diameter of 2 mm at room temperature. During the electrodeposition process, a Pt wire electrode was used as the counter electrode, Ag/AgCl (KCl 3 M) as the reference electrode, and the copper wire as the working electrode. The deposited samples were then rinsed with deionized water and dried at room temperature.

2.3 Characterization

The deposited samples were subjected to various analytical techniques for characterization. X-ray diffraction (XRD) was employed to identify the crystal phases present in the samples. Scanning electron microscopy (SEM) was employed to analyze the surface morphology of the samples. Energy-dispersive X-ray spectroscopy (EDX) was used to determine the composition of the samples deposited on the copper wire. Additionally, electrochemical impedance spectroscopy was employed with a 0.1 M KOH electrolyte, spanning a frequency range from 100 kHz to 0.1 Hz, to determine the impedance of the CoNi samples. The catalytic efficiency of the specimens for the electrooxidation of ethanol was assessed using CV in an aqueous solution of 0.1 M ethanol +0.1 M KOH with a voltage range spanning from -0.75 V to 0.75 V, and a scan rate of 100 mV/s, utilizing a reaction vessel with a volume of 25 mL.

3. Results and Discussion

Figure 1 shows the results of CoNi electrodeposition on a copper substrate. The formation of a silver color on the copper substrate after CoNi electrodeposition using boric acid indicates the presence of a cobalt-nickel layer formed on the copper substrate. The cobalt-nickel coating from chloride-based impregnation appears in dark grey and exhibits a dull surface due to the attached hydrogen bubbles that develop during electrodeposition [14].

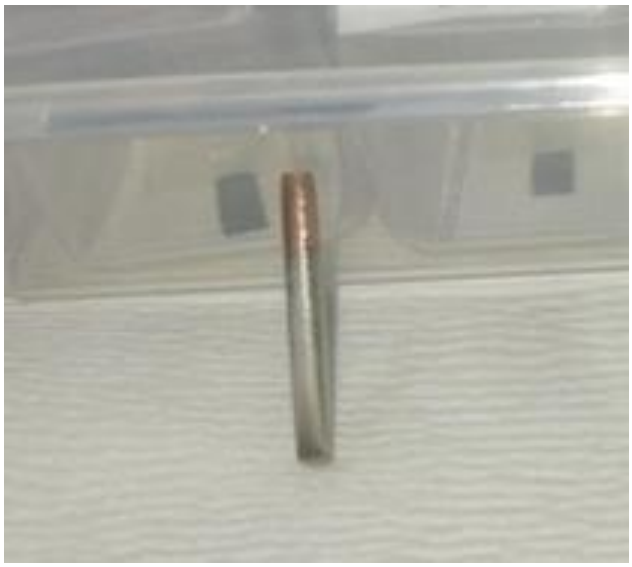

Figure 1. CoNi synthesis results using a copper wire substrate with the addition of boric acid.

Figure 2 shows the XRD pattern with diffraction peaks at 2θ with 44.27°, 51.58°, and 75.94°, corresponding to Miller indices (111), (200), and (202), respectively. These diffraction patterns confirm the formation of the CoNi bimetallic catalyst sample with the peak at 44.27° was linked to the face-centered cubic structure [12,13], which agrees with crystallography open database files number 96-210-0638 and 96-901-0969.

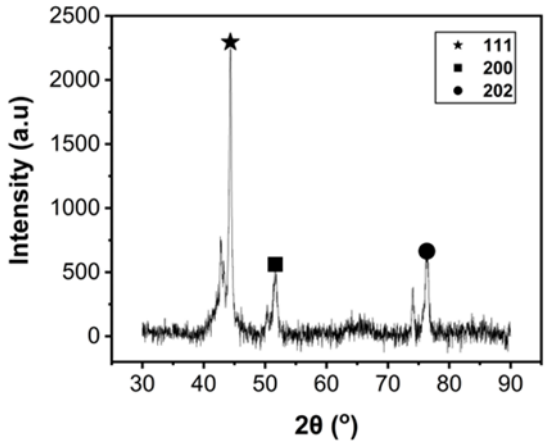

Figure 2. XRD pattern of CoNi bimetallic catalyst.

The morphology of the CoNi thin film synthesized through the electrodeposition method is shown in Figure 3. The CoNi sample with a 1:3 ratio exhibits a very smooth grainy surface with well-dispersed cracks. The morphology structure in this study differs from previous reports, such as spherical with small grains [15]. This difference is attributed to the decrease in cobalt content, leading to a smoother surface morphology [14].

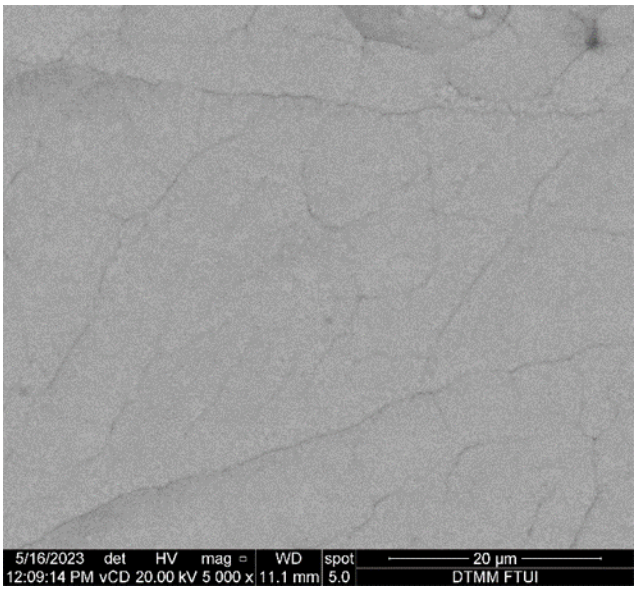

Figure 3. FESEM surface morphology of CoNi.

EDX spectrum of the CoNi thin film is shown in Fig. 4. The EDX spectrum confirms the presence of Co and Ni elements, indicating the successful electrodeposition of CoNi on the copper wire substrate. The atomic fractions of Co and Ni are 29.09% and 70.91%, respectively. The EDX measurement results show that the sample ratio is close to the initial precursor ratio of 1:3.

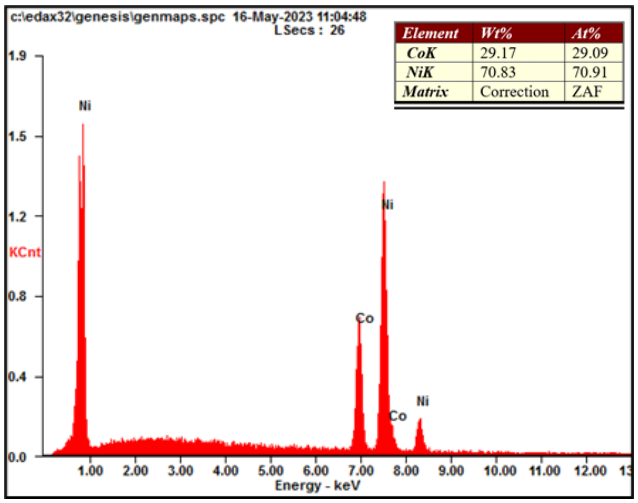

Figure 4. EDX spectrum of CoNi.

The electrochemical impedance spectroscopy measurements were conducted in a 0.1 M KOH electrolyte with a frequency range from 100 kHz to 0.1 Hz to identify charge transfer. The results are presented in a Nyquist plot (Fig. 5), which depicts the charge transfer resistance (R_{ct}) and solution resistance (R_s) values forming a semi-circle. The half-circle diameter on the Nyquist plot indicates the electron transfer resistance and the electrode interface properties [16]. The semi-circle at high frequencies represents the characteristic of the R_{ct} [17, 18]. Based on the plot, R_s and R_{ct} values are 21.2 kΩ and 66.6 kΩ, respectively.

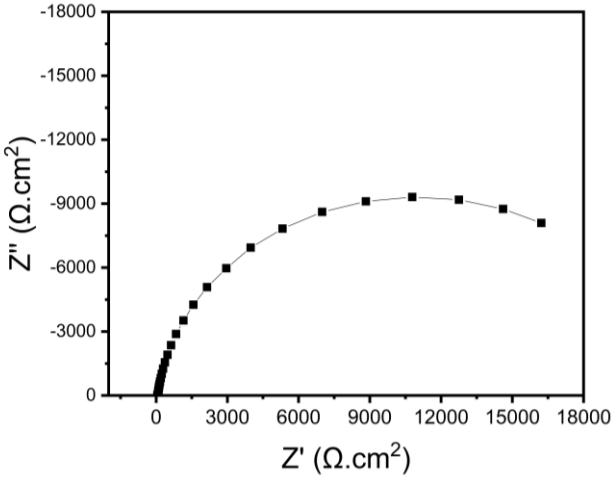

Figure 5. Nyquist plot for CoNi alloy.

The result shows that CoNi exhibits relatively low impedance, which allows efficient charge separation as a photoanode. The R_{ct} result indicates high recombination of charge carriers and decreased charge transfer, leading to reduced catalytic activity [19].

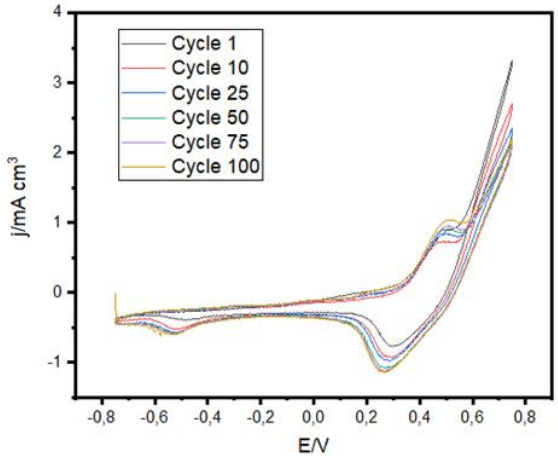

Figure 6. Cyclic voltammogram of CoNi electrocatalyst for ethanol electrooxidation.

The CV analysis indicates the catalytic performance of CoNi for the electrooxidation of ethanol, which exhibits a declining trend as the number of measurement cycles increases. The anodic peak current within the voltage range of 0.4 V exhibits a linear variation, which can be readily observed.

The anodic peaks in the cyclic voltammogram indicate the catalytic activity of the CoNi catalyst. The CoNi catalyst exhibited the highest recorded current density of 3.14 mA/cm^2 in the initial cycle. This finding demonstrates a notable advancement when compared to earlier investigations, wherein a current density of a mere 0.8 mA/cm^2 was achieved [9]. The observed phenomenon entails a continuous decrease in current throughout successive CV cycles. This finding suggests the presence of carbon monoxide poisoning on the catalyst surface or structural impairments caused by the aggregation or distortion of the CoNi catalyst [20]. Upon the completion of the cycles, a current density of 2.09 mA/cm^2 was attained. The CoNi catalyst has demonstrated considerable resistance to ethanol electrooxidation, as evidenced by its ability to sustain 66% of the initial current density even after undergoing 100 cycles which is better than the other commonly used catalyst for ethanol electrooxidation [2].

4. Conclusion

The bimetallic CoNi catalyst was successfully synthesized using the electrodeposition method with a cobalt-to-nickel molar ratio of 1:3. The diffraction pattern confirms the presence of CoNi with a face-centered cubic structure as a dominating phase in the sample. The resulting catalyst exhibited a smooth morphology with minor cracks, indicating some aggregation during the electrodeposition process. The catalytic activity achieved was relatively high, reaching 3.14 mA/cm^2 at a voltage of 0.7 V during ethanol electrooxidation. Therefore, the CoNi transition metal alloy proves to be a promising alternative catalyst for ethanol electrooxidation reactions with a lower cost.

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