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Electrodeposition of Co_xNi_y Thin Film and Its Catalytic Activity for Ethanol Electrooxidation

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Abstract

Platinum is often used as a catalyst in ethanol electrooxidation. Still, it has many disadvantages being expensive and its active site can be poisoned by CO. Transition metal of Co and Ni can become a catalyst in alcohol electrooxidation at a lower cost to synthesize. In this work, bimetallic CoNi were successfully prepared by electrodeposition method with different Co/Ni ratios to enhance ethanol electro-oxidation. Samples of CoNi are characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray (EDX), and electrochemical impedance spectroscopy (EIS). XRD diffractogram confirmed the formation of CoNi. Morphology of CoNi in SEM characterization showed that CoNi with ratio 5:1 has the more dispersed particle and the greatest surface area. EDX characterization indicated that the relative weight of different Co/Ni ratios, the composition wt.% Co is 81.15% and wt.% Ni is 18.85% in CoNi 5:1, wt.% Co is 60.96% and wt.% Ni is 30.94% in CoNi 2:5, while wt.% Co is 50.19%, and wt.% Ni is 49.81% in CoNi 5:5. EIS characterization showed that CoNi with ratio of 5:1 has faster electron kinetics. Electrooxidation of ethanol used cyclic voltammetry (CV) method. The best results from the ethanol electrooxidation reaction were obtained for CoNi with a ratio of 5:1 because of the greatest surface area that showed in scanning electron microscopy and fast electron transfer kinetics compared to others ratio of $CoxNi_y$.

Keywords: catalysts, Pt, CoNi, electrodeposition, ethanol electrooxidation

1. Introduction

The problems caused by petroleum as a primary energy used worldwide are increasing. In addition, petroleum is non-renewable energy and would result in a scarcity of energy sources in the future. Renewable energy is the well-known solution to solve this problem. The most studied renewable energy sources in the world are hydrogen, methanol, and ethanol. [1]. Energy resources from ethanol or direct ethanol fuel cells (DEFCs) have many advantages compared to hydrogen and methanol, such as lower cost, more energy produced, low toxicity, and environmental safer [2,3]. The process of obtaining energy from ethanol requires an appropriate electrocatalyst. Platinum and its alloy with other metals are currently used as a catalyst in DEFCs because of its performance in breaking the C-C bond in ethanol [4,5]. Unfortunately, platinum as a catalyst has many disadvantages, such as higher synthesis costs, low reserves, and the active site can be poisoned by CO [6,7]. The combination of other transition and inert metals to enhance the catalytic activity is widely studied [8,9], but does not solve the problem in terms of its cost. Therefore, synthesizing catalysts with other transition metals can be studied further by considering the cost efficiency.

Nickel is one of the transition metals abundant on earth, lower cost, and considered to be a suitable promising catalyst for small organic molecules in alkaline media [10]. Still, it is not good enough to become a catalyst for electrooxidizing alcohol [11]. To enhance the performance of nickel for a better catalyst, bimetallic of another transition metal is combined with nickel [12]. Another metal that combines with nickel is cobalt [13]. Cobalt is one of the metal transitions that can be used as catalyst. The previous study stated that CoNi with rich nickel could became a better catalyst for electrooxidizing alcohol [14].

In this work, bimetallic CoNi was deposited in the copper wire to make a less expensive and good performance to electrooxidize ethanol. Bimetallic CoNi will be synthesized using the electrodeposition method with various Co/Ni ratios. The electrodeposition method has many advantages, such as lower cost and can manipulate the size and shape of CoNi with various parameters [15]. The CoNi catalyst was then tested for electrooxidizing of ethanol with NaOH solution using cyclic voltammetry (CV) method.

2. Materials and Method

Thin film of CoNi was prepared using $CoSO_4.7H_2O$ and $NiSO_4.6H_2O$ with various Co/Ni ratio. The solution of $CoSO_4.7H_2O$ and $NiSO_4.6H_2O$ were mixed and diluted with aquadest. The solution pH was adjusted using boric acid to 4.0. The comparison of the concentration can be observed in Table 1.

Table 1. The ratio of Co and Ni concentration.

Sample	Concentration of Co (M)	Concentration of Ni (M)
CoNi 5:1	0.125	0.025
CoNi 5:2	0.125	0.050
CoNi 5:5	0.125	0.125

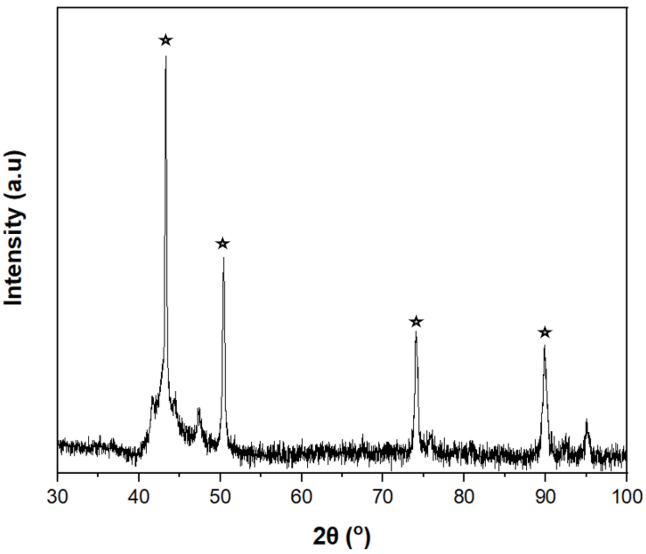

Figure 1. XRD pattern of CoNi nanoparticle.

The synthesis was carried out at -1.5 V and the deposition time was 15 minutes on a copper wire substrate with a diameter of 4 mm at room temperature. In the electrodeposition process, Pt wire is used for the counter electrode, Ag/AgCl (3 M) is used for the reference electrode, and copper wire is used for the working electrode. The deposition results that deposited are washed using distilled water and dried.

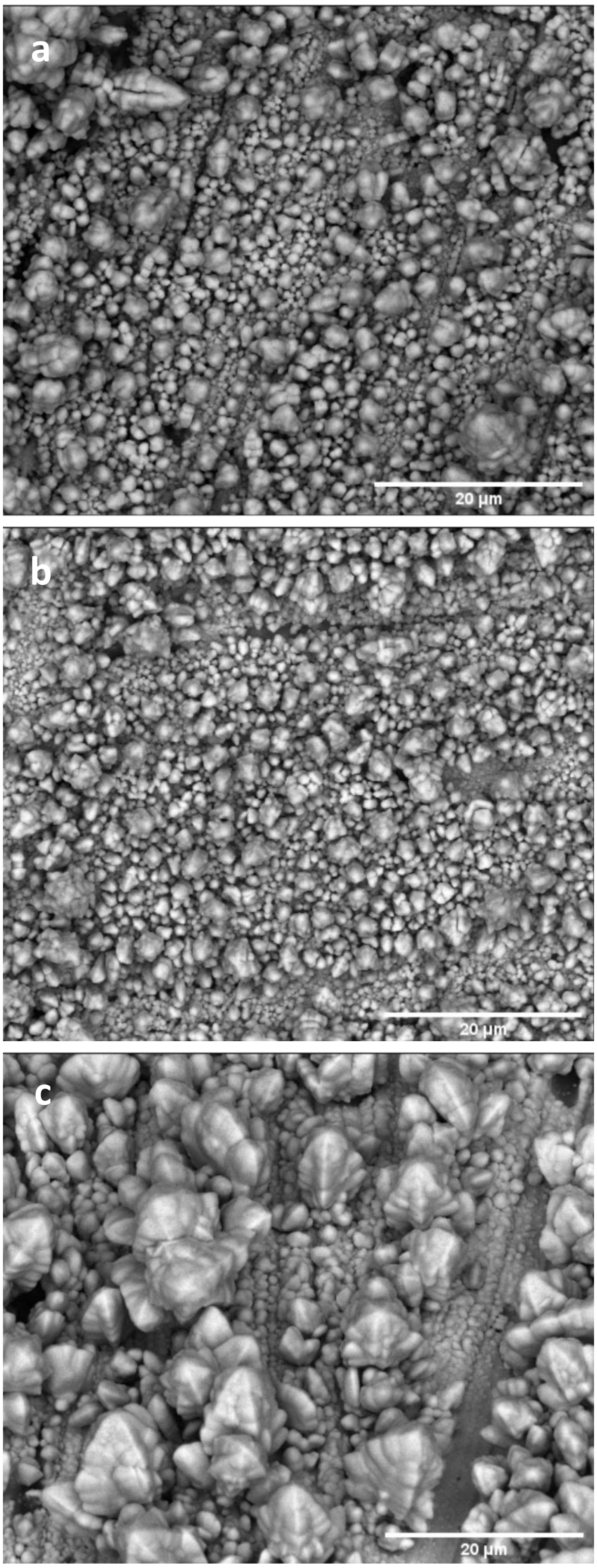

Figure 2. Morphology of CoNi with different Co/Ni ratios: (a) 5:1, (b) 5:2, and (c) 5:5.

The sample was then characterized by X-ray diffraction (XRD) to identify the CoNi phases, scanning electron microscopy (SEM) to determine the morphology of the sample, energy dispersive X-ray (EDX) to determine the composition of the CoNi that was deposited in copper wire, and electrochemical impedance spectroscopy (EIS) to determine the impedance of the CoNi system using 0.1 M KOH solution with a frequency range of 100 kHz – 0.1 Hz. Ethanol electrooxidation was carried out by the CV method using 1.0 M ethanol pro-analyst and 25 mL of 0.1 M NaOH with a scan rate of 100 mV/s and a voltage range of -0.75 V – 0.75 V.

3. Results and Discussion

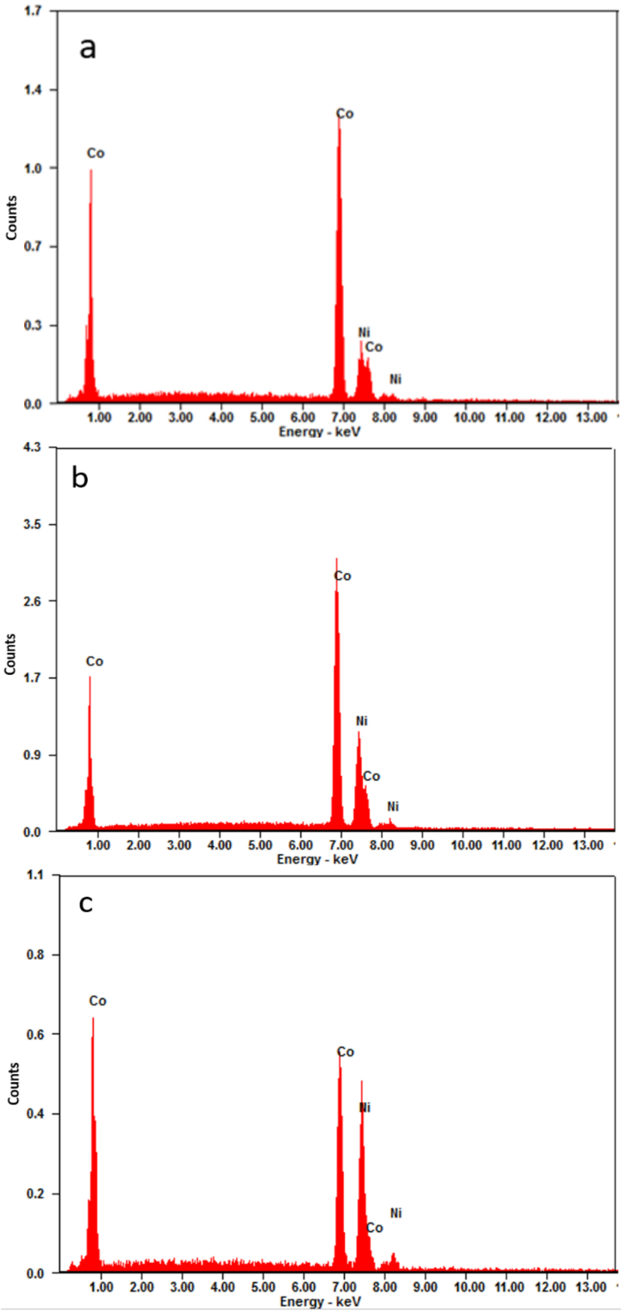

Figure 3. EDX spectrum of CoNi with different Co/Ni ratios (a) CoNi 5:1, (b) CoNi 5:2, and (c) CoNi 5:5.

XRD characterization result is shown as a diffraction pattern in Fig. 1. The diffraction pattern has four highest peaks at 2θ 43.41°, 50.50°, 74.19°, and 90.17° corresponding to miller index of (111), (200), (220), and (311) with face-centered cubic (fcc) phases and Pm-3m space group which confirmed that bimetallic of CoNi has been formed [16,17]. No other spectra had been identified in the diffraction pattern show the phase purity of CoNi with ratios 5:1.

Table 2. Ratio of CoNi with different Co/Ni ratios in EDX.

Sample	Co	Ni
CoNi 5:1	81.15%	18.85%
CoNi 5:2	69.06%	30.94%
CoNi 5:5	50.19%	49.81%

The morphologies of CoNi synthesized at various Co/Ni ratios are shown in Fig. 2. CoNi sample synthesized at various Co/Ni ratios has a spherical and irregular in shape. As the concentration of nickel increased, the sample is less dispersed with larger molecule. The particles are aggragated caused by the higher concentration of nickel, resulting in stronger unsaturated bonds and higher interaction between particle [18]. It shown to the morphologies of CoNi with a ratio of 5:1 has more dispersed particle to the others Co/Ni ratio. The smaller particle of CoNi can oxidize more ethanol molecule due to its greater surface area [19]. The EDX characterization of CoNi with various Co/Ni ratios has been shown in Fig. 3. The ratio of Co/Ni that formed in copper wire is shown in Table 2.

The CoNi samples were then tested by EIS to determine the impedance of the system. The results of the EIS test are represented as a Nyquist plot with a semicircle shape indicating that resistance to electron transfer and a linear line shape means indicating a diffusion process [20]. Nyquist plot of CoNi and copper wire have been shown in Fig. 4. The smallest charge transfer resistance (R_{ct}) is found in the CoNi sample with various Co/Ni ratios 5:1 and the highest R_{ct} is found in copper wire. It indicated that CoNi with various Co/Ni ratios have better electron kinetics than copper wire and data show the more dispersed particle of CoNi with ratio of CoNi 5:1 provides faster electron kinetics than other Co/Ni ratios due to greatest surface area.

Table 3. Ethanol electrooxidation of CoNi electrocatalyst with different Co/Ni ratios.

CoNi Sample	Potential (V)	Current (mA/cm^2)
5:1	0.30	0.80
5:2	0.34	0.48
5:5	0.38	0.46

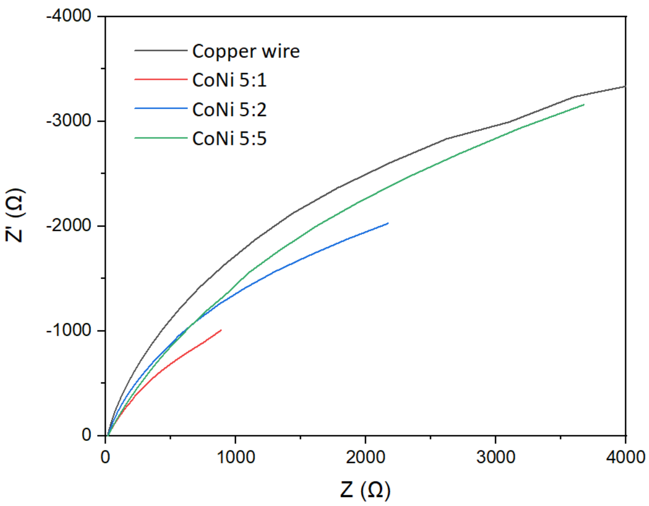

Figure 4. Nyquist plot for CoNi electrocatalyst with different Co/Ni ratios.

CoNi samples with various Co/Ni ratios were evaluated to catalytic activity towards ethanol electrooxidation reaction. Ethanol electrooxidation was carried out in an alkaline medium because the result in previous study stated that the process will be faster and have good performance for electrooxidizing ethanol [21,22]. The result of ethanol electrooxidation shown in Fig. 5. and its representation is shown in Table 3.

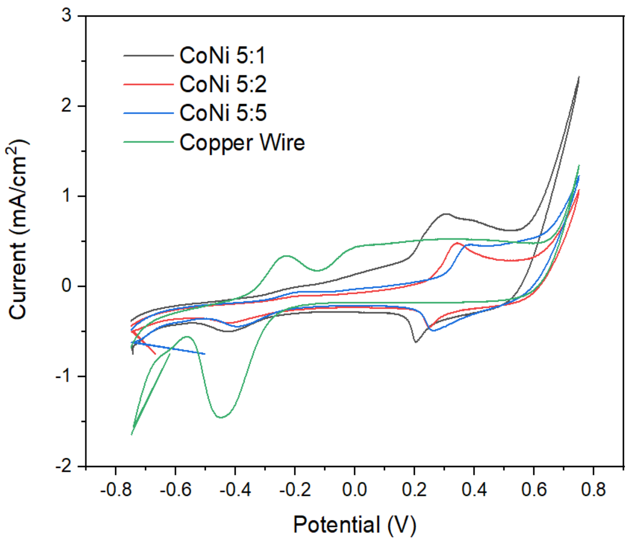

Figure 5. Cyclic voltammogram of CoNi electrocatalyst with different Co/Ni ratios using ethanol 1.0 M and NaOH 0.1 M.

The result of ethanol electrooxidation using CV method confirmed that the CoNi sample with a ratio of 5:1 had the best catalytic activity. The highest peak obtained at the CoNi 5:1 is found at the voltage of 0.30 V with an oxidation peak is 0.80 mA. Previous study explained that increasing nickel in the CoNi sample would decrease its catalytic activity properties against alcohol oxidation because Ni active site can be inhibited by CO [11,23]. Therefore, the CoNi sample with a ratio of 5:1 has better catalytic activity than other Co/Ni ratios and copper wire for ethanol electrooxidation.

4. Conclusion

Bimetallic CoNi with various Co/Ni ratios were successfully prepared by the electrodeposition method. CoNi with a Co/Ni ratio of 5:1 have monodispersed particles compared to other Co/Ni ratios. Electron transfer kinetics with a Co/Ni ratio of 5:1 is the fastest compared to other Co/Ni ratios. The catalytic activity for the electrooxidation of ethanol was better in CoNi 5:1, which was 1.21 mA at a voltage of 0.30 V because have the monodispersed particle, greater surface area, and highest kinetic transfer electron amongst other Co/Ni ratios.

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