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EFFECT OF CRYSTALLINITY TO OVERPOTENTIAL ON Ni_3Fe ALLOY AS ELECTROCATALYST IN HYDROGEN EVOLUTION REACTION

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ABSTRACT

EFFECT OF CRYSTALLINITY TO OVERPOTENTIAL ON Ni_3Fe ALLOY AS ELECTROCATALYST IN HYDROGEN EVOLUTION REACTION. Ni-Fe alloys can be used as electrocatalyst for the hydrogen evolution reaction (HER) in an alkaline solution. HER consumed highly energy and overpotential driven. The overpotential value corresponding to the electron transfer in reaction can be affected either by metal combination or alloy as a cathode. Ni_3Fe alloy had been successfully synthesized by the electrodeposition method using direct-current (DC) on a 304 L type stainless steel substrate. The modified Watts bath deposition was used $NiCl_2.6H_2O$ and $FeCl_3.6H_2O$ as precursors of the alloy. The optimum conditions of the reaction were obtained at pH of the solution is 2.20±0.02 with 25 mA/cm^2 current density at 55 °C for 160 minutes. Ni_3Fe alloy was characterized by Powder X-ray Diffraction (PXRD), Energy-Dispersive X-ray Spectroscopy (EDX), and Scanning Electron Microscopy (SEM). The electrocatalytic property of Ni_3Fe alloy was electrochemically measured in 1 M KOH solution by polarization method using a Tafel plot with a scanning rate of 1 mV/s. As a result, the mass ratio of Ni^{2+}/Fe^{3+} in bath deposition influenced the electrocatalytic property of Ni_3Fe alloy. Ni_3Fe alloy with a higher crystallinity lowered the overpotential value of HER up to 67% compared to Ni metal.

Keywords: Ni_3Fe alloy, Electrocatalyst, HER, Overpotential, Electrodeposition.

ABSTRAK

EFEK KRISTALINITAS TERHADAP OVERPOTENSIAL PADA PADUAN Ni_3Fe SEBAGAI ELEKTROKATALIS UNTUK REAKSI EVOLUSI HIDROGEN. Paduan Ni-Fe dapat digunakan sebagai elektrokatalis untuk reaksi evolusi hidrogen (HER) dalam larutan basa. HER membutuhkan energi tinggi yang digerakkan oleh nilai overpotensial. Nilai overpotensial berkaitan dengan proses transfer elektron pada reaksi yang dapat dipengaruhi pada penggunaan campuran ataupun paduan logam sebagai katoda. Paduan Ni_3Fe telah berhasil disintesis melalui metode elektrodeposisi dengan arus searah (DC) pada substrat *stainless steel* tipe 304 L. Tipe *Watts bath* termodifikasi dipilih dengan $NiCl_2.6H_2O$ dan $FeCl_3.6H_2O$ sebagai prekursor untuk paduan Ni_3Fe. Kondisi optimum reaksi diperoleh pada pH larutan 2,20±0,02 dengan rapat arus 25 mA/cm^2 pada temperatur 55 °C selama 160 menit. Paduan Ni_3Fe dikarakterisasi dengan difraksi sinar-X serbuk (PXRD), spektroskopi dispersi energi sinar-X (EDX), dan mikroskopi pemindaian elektron (SEM). Sifat elektrokatalitik paduan Ni_3Fe diukur secara elektrokimia dalam larutan KOH 1 M melalui metode polarisasi menggunakan plot *Tafel* dengan laju pemindaian 1 mV/s. Hasil menunjukkan bahwa perbandingan massa Ni^{2+}/Fe^{3+} dalam *bath* deposisi mempengaruhi sifat elektrokatalitik dari paduan Ni_3Fe. Paduan Ni_3Fe dengan kristalinitas lebih lebih tinggi dapat menurunkan nilai overpotensial HER mencapai 67% jika dibandingkan dengan logam Ni.

Kata kunci: Paduan Ni_3Fe, Elektrokatalis, HER, Overpotensial, Elektrodeposisi.

INTRODUCTION

Hydrogen gas has been widely used in many industries, as in the food industry, ammonia productions, refining petroleum and metals[1], also as an energy carrier in hydrogen fuel cells [2,3]. Due to its high demand, an efficient, low cost, and sustainable production method of the hydrogen gas was important. Water electrolysis was a common method to produce highly pure and largely quantities hydrogen gas [4]. Nevertheless, the large energy consumption about 1.8-2.0 V at 300-1000 A/m^2 current density became the main drawback of water electrolysis [5]. This large energy consumption was caused by the high overpotential value of hydrogen evolution reaction (HER) [5]. Overpotential value was accumulated from the activation energy of the rate of reaction, and the resistance caused by the formation of bubbles on the surface of the electrode [5].

An electrocatalyst is a material that provides lower activation energy in another reaction mechanism for a specific type of electrochemical reaction at high current density. The good electrocatalyst will have synergetic interaction between two different metals and enlarge the actual surface area to increase the electron transfer kinetics [5,6]. The electrocatalyst activity can be measured from the overpotential of the catalyst toward the reaction [6]. Recently, several researches were developed to obtain an efficient, low-cost, and corrosion-resistant electrocatalyst. Ezaki, et al. (1993) reported that the overpotential value of HER for 3*d* block transition metals in the 4th period became smaller as the increasing in atomic number and reached the minimum value in Ni metal [8]. The change in overpotential value of alloys is influenced by the difference in electronic properties of metals that enhance the number of active site on the surface leading to the increase of the corrosion resistance [9]. Furthermore, Ni- [7-9,13], Mo- [6,14,15], Fe- [14], and Co-based [15] alloys are considered as the prospective electrocatalysts to replace currently used Pt and Ru metals [16]. However, passivation and corrosion phenomena during the water electrolysis process are very likely to occur in non-noble metals [9].

Nickel is known as an electrocatalyst material that has good corrosion-resistant in alkaline solution [1]. Su, et al (2019) had successfully synthesized Ni-Fe alloy at a very low pH solution by rapid electrodeposition method. Iron(III) ion is used as precursor compared to iron(II) ion which is easily oxidized in bath solution [17]. Bath composition of precursors and additives affects the properties of alloy. Yet, properties of Ni-Fe alloy electrodeposited from nickel(II) and iron(III) ion as electrocatalyst for HER in an alkaline solution are not widely reported. In this work, Ni_3Fe alloy is synthesized by electrodeposition method, the effect of crystallinity to overpotential and electrocatalytic properties are further investigated.

EXPERIMENTAL METHOD

Materials and Instruments

All chemicals were commercially available and used without any further purification. Nickel(II) chloride hexahydrate (≥98%, Merck), iron(III) chloride hexahydrate (≥99%, Merck), boric acid (Merck), sodium citrate tribasic dehydrate (>99.5%, Fluka 71405), potassium hydroxide (≤ 100%, Merck), saccharin, sulfuric acid (98%, Merck), and acetone (Merck). Stainless steel (SS) 304 L was used as substrate.

Laboratory DC Power Supply GWINSTEK GPS-30300 was connected with software BTS Test Control 5.3.0013 as an electrical source for the electrodeposition reaction. Rigaku MiniFlex 600 with D/teX Ultra 1D silicon detector using Cu-K_α (λ= 1.540593 Å) as an X-ray source was used to determine crystalline phase of alloy with scanning rate 10°/min (2θ = 30-90°). JEOL-JSM 6510LA for analysing elemental composition and morphology on the alloy surfaces with accelerating voltage 15 kV. All electrochemical measurements were carried out using Voltalab PGZ 301 instrument with the Volta Master 4 software. Hofmann voltameter was used to measure the hydrogen gas volume from HER.

METHOD AND PROCEDURE

Ni-Fe alloy was electrodeposited onto SS plate with a thickness and diameter of approximately 1 mm and 1 cm, respectively. Before electrodeposition, the substrate was mechanically polished with emery paper (1000 to 5000 grit) then sonicated in acetone for 15 minutes, washed with distilled water, and dried. The electrodeposition was performed galvanostatically with the two-electrode system using direct-current (DC). SS as the working electrode and Pt wire as the auxiliary electrode. Ni-Fe alloys were synthesized by modifying the previous report [18]. The amount of Ni^{2+} was constant (23.5 g/L) with Ni^{2+}/Fe^{3+} mass ratio of (A) 11.2, (B) 8.4, and (C) 6.5. The pH was set to 2.2±0.02 and the electrodeposition was performed at 25 mA/cm^2 current density and stirred for 160 minutes at 55±2 °C.

A three-electrode system cell was used in the electrochemical measurement. A platinum sheet with 1 cm^2 surface area and saturated calomel electrode (SCE) were employed as auxiliary and reference electrodes, respectively. The electrocatalytic and corrosion resistance properties of Ni_3Fe alloys were acquainted by Tafel plot with a scan rate of 1 mV/s. Electrochemical measurements were conducted in 1 M KOH solution at room temperature and under atmospheric pressure without hydrogen gas purging.

RESULT AND DISCUSSION

In this modified Watts bath, boric acid, saccharin, and sodium citrate tribasic dehydrate were employed as buffer, surfactant, and complexing agents, respectively. These additives were aimed to control the formation of Fe(OH)$_3$ which caused oxygen formation [17] and anomaly co-deposition of Ni-Fe alloys [18]. The use of iron(III) ion in bath deposition is expected to be more stable compared to iron(II) ion [19]. Moreover, the Fe(OH)$_3$ formation can be controlled by pH of solution which indirectly affects the properties of alloy. At pH < 2 of solution, iron(III) ion is hardly deposited due to the reaction competition with HER. Meanwhile, at pH > 3, Ni-Fe alloys have been deposited along with cracking [1]. Reducing the cracking of Ni-Fe alloys were achieved at pH of solution is 2.20±0.02 in the modified Watts bath conducted for 160 minutes.

The PXRD patterns of Ni-Fe alloys were shown in Figure 1 (a). These patterns fit in well with reference which corresponding to the characteristic peaks of Ni$_3$Fe [20]. The broadening peaks observed from the patterns of Ni$_3$Fe alloys indicate that the crystallite size is relatively small. Incorporation of Fe atoms with slightly larger metalic radii than Ni (Ni: 0.125 nm, Fe: 0.126 nm [30]) also contributes to these broadening peaks. The crystallite size of Ni$_3$Fe were calculated with Scherrer's formula [21].

The lower the mass ratio and the larger the amount of Fe result smaller crystallite size of alloys (Table 1). In anomaly co-deposition when the surface pH of substrate is high enough to form ferrous hydroxide which is adsorbed preferentially and consequenly block the deposition of nickel. Also higher pH reduced activation and difussion polarization. According to the three-dimensional nucleation rate theory, it is lowering the overpotential of alloy deposition. As result the number of nucleation sites increased [18].

Substitution mechanism may occur during the alloying deposition. Since Fe atoms substitute Ni atoms as host metal, the spacing lattice (d_{hkl}) expands. Figure 1(a) shows the peaks shifting of 2θ to smaller value. The crystal structure of Ni$_3$Fe alloys was determined from Miller indices in corresponding to face-centered cubic (FCC) with Fe atom at the corner of the cubic, namely, superlattice cubic [22].

The amount of iron in deposition proportionally affects the internal stress of alloy. Internal stress is generated from the adjustment between the top and the underneath layers through shrinking and expanding during the deposition process [18]. Thus, to reduce the internal stress, saccharin was employed as a surfactant which has a structure that can form a bond with hydrophobic and hydrophilic compounds. SEM images of Ni$_3$Fe alloys are showed in Figure 1(b),(c). The smooth surface morphology without cracking and peeling demonstrates a strong adhesion of alloy on the SS substrate.

Elemental composition analysis of Ni$_3$Fe (C) alloy was revealed by Energy-Dispersive X-Ray Spectroscopy (EDX). Figure 1(d) indicates that the alloy contains iron, nickel, carbon, and a little bit of oxygen. It is found there are about 61% and 19% atom of Ni and Fe, respectively. Hence, the atomic ratio of Ni$_3$Fe is 3:1 (with approximation) and fit in well to Ni$_3$Fe phase.

Figure (2) shows the polarization curves of Ni$_3$Fe alloy as cathode conducted in 1 M KOH solution at room temperature and atmospheric pressure. The

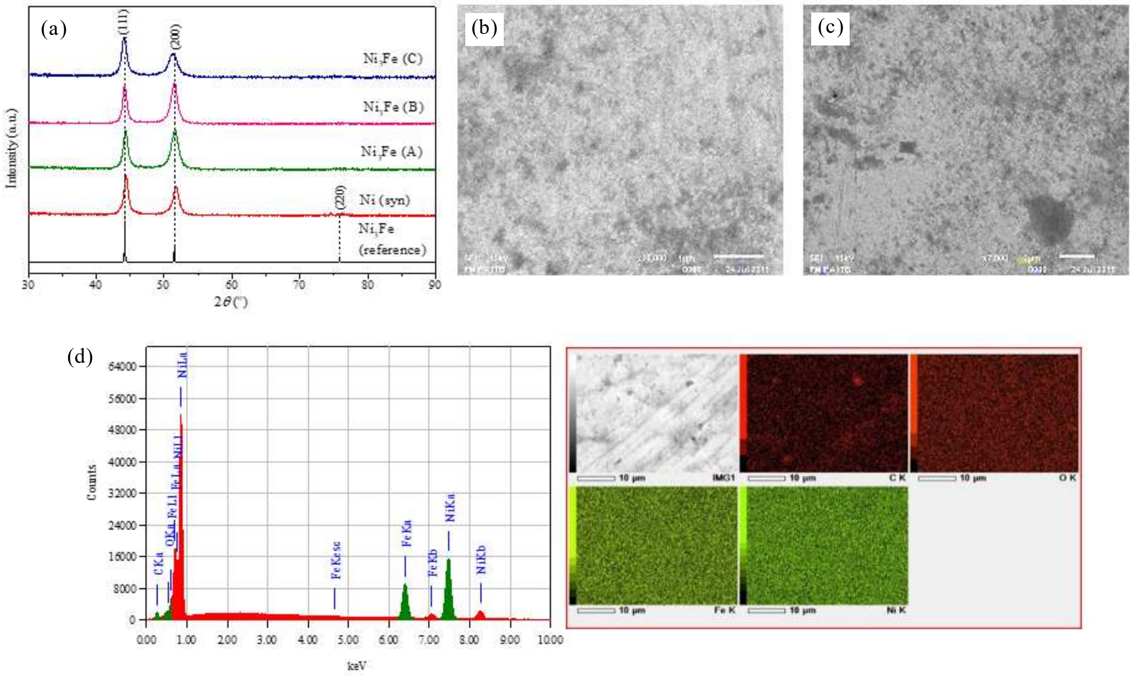


Figure 1. (a) PXRD patterns of Ni$_3$Fe alloys with Ni^{2+}/Fe^{3+} mass ratio of (A) 11.2, (B) 8.4, and (C) 6.5; SEM images of Ni$_3$Fe (C) with magnification (b) 3000x, and (c) 7000x; (d) EDX analysis of Ni$_3$Fe (C).

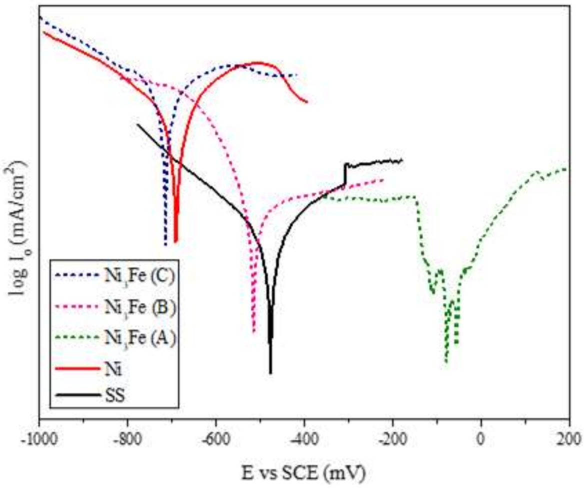


Figure 1. Polarization curve of SS, Ni, and Ni_3Fe alloy.

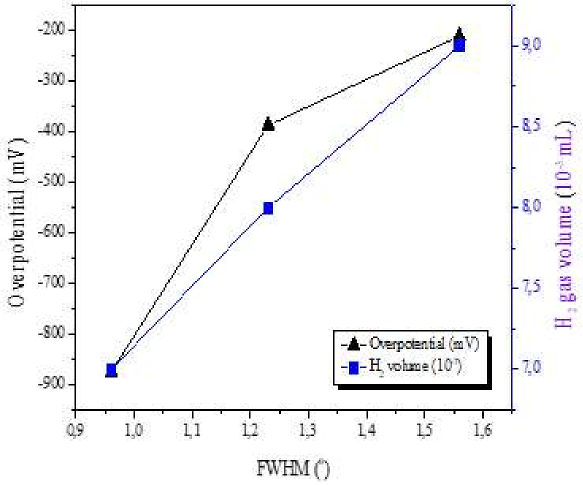


Figure 3. Correlation graphic between FWHM with overpotential and H_2 gas volume.

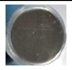
overpotential value of HER is proportional to crystallite size of Ni_3Fe alloy compared with Ni (Table 1). The decreasing crystallite size lead increasing in active edges of grain boundary more exposed for HER. It consequence supressing the overpotential value of HER [6,31]. The catalytic activity of electrodes increase with decreasing crystallite size.

The substitution of Fe atoms in Ni crystal structure promotes the electrocatalytic properties of HER in alkaline solution. These results are similar to other cathodes previously reported in alkaline solution using Ni-Fe-Co-graphene (169 mV) [23], Ni-Fe-S (222 mV)[7], and Fe-Co alloys (145 mV) [24]. The HER process will be initiated by discharging of the hydrated proton that exists in the electrolyte. During the process, an electron from the metal electrode surface must be transferred to the proton. Therefore, the region with the excess of the electron is expected more active than the region on the electrode surface with a deficient one. It could be concluded that the HER reaction is favourable at electronegative sites than electropositive sites. The addition of metal with the character more positive, like Fe to Ni, is effective in lowering the hydrogen overpotential of Ni alloy. The increase of Fe concentration caused the excess charges at the near the base metal (Ni) to increase as well, hence the overpotential of the Ni-Fe alloy will decrease [8].

Table 1 showed the important kinetics parameters of cathode are exchange current density (I_o) and Tafel slope (b). Among all the type of synthesized Ni_3Fe alloy that have the lowest overpotential value of HER is Ni_3Fe (C). In this work, the exchange current densities of Ni and Ni_3Fe (C) are calculated to be 5.70 x 10^{-5} A/cm² and 10.07 x 10^{-5} A/cm², respectively, delivering better electrocatalytics efficiency of Ni_3Fe (C) alloy. The Tafel slope Ni_3Fe (C) is -123.5 mV/s is lower than Ni, that is -340.0 mV/s, imlplying its favourable HER catalytics kinetics. The bigger exchange current density, the higher the electrocatalytic efficiency probably caused by the synergistic effect of Ni and Fe on the alloy due to their ability to facilitate hydrogen desorption [6].

Corrosion behaviour of Ni_3Fe alloys that influenced by iron content in deposits was studied. Corrosion potential (E_{corr}) is indicating the activity of

Table 1. Crystallite size, electrode kinetics parameter of cathode, and overpotential value measurements at 10 mA/cm².

Cathode	Mass ratio (Ni^{2+}/Fe^{3+})	Crystallite size (nm)	b_c (mV/s)	I_o (10^{-5} A/cm²)	E_{corr} (mV)	η (mV)	Alloys
SS	-	-	-220.1	0.09	-477.0	880.2±12	
Ni	-	11.7±0.6	-340.0	5.70	-691.3	576.4±264	
A	11.2	10.7±2.0	-326.6	0.04	-304.6	874.7±6	
B	8.4	10.6±0.4	-349.4	0.04	-515.8	389.9±80	
C	6.5	7.4±2.4	-123.5	10.07	-890.0	210.7±51	

deposits in a corrosive environment. It was found that the corrosion potential E_{corr} (Table 1) shifts toward more negative values as the iron percentage in the deposit increased.

The crystallographic orientation of the metal will determine also the character of the electron surface and as result the catalytic activity is influenced. In HER, rate reaction increases following the number of atomic density of the surface, meanwhile the catalytic activity follows the increase of the electron work function [29]. Ni-Fe alloy have FCC crystal structure which has atoms coincide at the surface of the structure. This increases the atomic density then eases the electron transfer. The ease in the process of electron transfer in a crystal system has a linear correlation with decreases in overpotential values. Therefore, with the increasing FWHM in plane (200) it can facilitate the transfer of electrons in the HER reaction process so it supress the overpotential value. Ni_3Fe (C) alloy has the lowest overpotential value with the largest FWHM in the field (200). As the result of the reaction is hydrogen volume gas that measure by Hoffman voltameter in 0.1 M KOH solution as summarized in Table 2.

Table 2. Miller indexes of alloy, FWHM, H_2 gas volume, and its overpotential value.

Cathode	Miller indices plane	FWHM (°)	H_2 volume (mL)	η_{10} (mV)
A	(111) (200)	0.607 0.961	0.007	-874.7±6
B	(111) (200)	0.677 1.231	0.008	-389.9±80
C	(111) (200) (220)	0.875 1.560 10.800	0.009	-210.7±51
Ni	(111) (200) (220)	0.685 0.986 1.140	0.007	-576.4±264

CONCLUSION

In this work, Ni_3Fe has been successfully synthesized galvanostatically from nickel and iron (III) chloride hexahydrate precursors. The intrinsic properties and morphology of alloy's surface depended on the composition and condition of the electrodeposition bath. The intrinsic properties affected the electrocatalytic properties of alloy which was measured electrochemically by using polarization method. It was found that decreasing the mass ratio of Ni^{2+}/Fe^{3+} caused the reduction of the crystallite size of alloys. An alloy that has a strong diffraction peak at (200) plane showed good catalytic behaviour. The overpotential value of HER of the alloy is smaller than Ni, i.e. -210.7 and -576.4 mV, respectively.

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