

# The Growth of FeCoNi nanoparticles Electrodeposited from CTAB-assisted Sulfate Electrolyte

S Budi\*, A Afrizal, E Handoko and R Fahdiran

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

\*setiabudi@unj.ac.id

**Abstract.** This paper presents our preliminary investigation on the deposit growth characteristic of FeCoNi nanoparticles prepared using potentiostatic electrodeposition. The FeCoNi electrodeposition was conducted in sulfate electrolyte containing cetyl trimethylammonium bromide (CTAB). Prior to the deposit preparation, cyclic voltammetry analysis was carried out to determine co-deposition potential of iron, cobalt and nickel ions. Mechanism of the deposit growth was studied based on the recorded potentiostatic current transient. The  $(i/i_m)$  versus  $(t/t_m)$  plot indicated that nucleation and particles growth of FeCoNi was found to follow the instantaneous type closely, but with a very fast particle growth phase before entering diffusion stage. This growth characteristic produced fine nanoparticles of FeCoNi with homogeneous size distribution.

## 1. Introduction

Electrodeposition is well-known as one of the bottom-up material preparation techniques that can fabricate nanoparticles of metals and alloys on a substrate by using a reasonable technology. In this techniques, the growth of deposits might be controlled in a relatively simple manner through various reaction conditions such as agitation [1], pH, temperature [2], deposition time and electrolyte composition used as a source of metal ions [3,4]. In addition, properties of the deposits formed can also be enhanced by adjusting the employed electrodeposition potential or current. These advantages have been the main reasons deciding electrodeposition as metal or metal alloy preparation techniques such as Co-Ni-Cu nanoalloys [4,5], Ni-Cu-Mo coating [6], Co-Cu nanostructures [7], It nanoparticles [8], SmS thin films [9], and FeCoNi alloys [10–12]. The latter has attracted many attention due to its potential application for magnetic devices. One the promising application of the FeCoNi alloy is as a microwave absorbing film since the alloy possesses high permeability in microwave area [13]. Permeability is a key factor in the microporous absorption capacity of a material especially in the wide frequency range [14]. Fe-Co-Ni alloy also exhibits as high as to 2.0-2.1 Tesla of magnetic saturation [15] with low coercivity values [10] which are required for anti-radar applications.

Many reports of the electrodeposition of FeCoNi alloys has been focused to reveal their microstructures and magnetic properties [10,11,16–18]. However, the information on the deposit growth characteristics of the FeCoNi alloys prepared using electrodeposition is still very limited. Whereas, different nucleation and particles growth will resulted in different deposits microstructure [19] that should strongly affect their physical and chemical properties. This paper reports the results of our preliminary work to investigate the characteristics of nucleation and particles growth of FeCoNi



nanoparticles electrodeposition. The electrodeposition of FeCoNi nanoparticles was performed with a fixed voltage in a sulfate electrolyte containing cetyl trimethylammonium bromide (CTAB) additive at room temperature. Characteristics of nucleation and growth of FeCoNi particles were then studied from the current transient recorded during the deposition process.

## 2. Materials and method

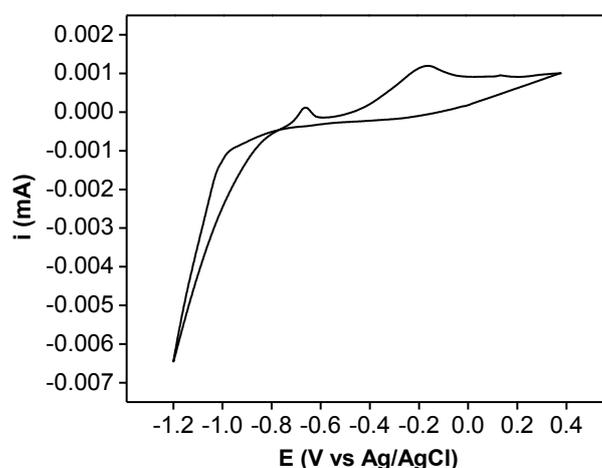
### 2.1. Materials

The materials used in this work are analytical grade chemicals supplied by Merck. The hydrated metal salts i.e. iron(II) sulfate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ), cobalt(II) sulfate heptahydrate ( $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ ) and nickel(II) sulfate ( $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ ) were used as the source of metal ions deposited on the substrate. Boric acid ( $\text{H}_3\text{BO}_3$ ) acid was used as buffer in the electrolyte. cetyl trimethylammonium bromide ( $\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{Br})(\text{CH}_3)_3$ ) was used as an additive.

### 2.2. Method

The FeCoNi nanoparticles were grown on an indium tin oxide coated polyethylene terephthalate (ITO-PET) substrate by potentiostatic techniques from a sulfate electrolyte using Edaq EA 163 potentiostat controlled by echart software. The electrodeposition was carried out in a three-electrode cell with a platinum wire and an Ag/AgCl as counter electrode and reference electrode, respectively. In purpose to determine co-deposition potential of the Fe, Co and Ni, cyclic voltammetry studies were firstly conducted with the same electrochemical system. The occurrence of a reaction can be seen through the changes in the flow of current in the system which observed in the form of peaks either on anodic or cathodic scans of the cyclic voltammogram. The electrodeposition process was then performed with a potential of -1.10 V vs. Ag/AgCl at room temperature. The obtained deposit was washed with double distilled water and dried with high purity nitrogen gas ( $\text{N}_2$ ) of 99.99%. During the electrodeposition, potentiostatic current transient was recorded using Edaq e-corder 401. The micro-analysis of the FeCoNi deposits was carried out using a dispersive energy X-ray analyzer (EDX) to ensure the presence of all three deposited metals and their composition. An atomic absorption spectrometer (AAS) was also employed to determine the alloy composition. To observe the changes on the particles size, morphological analysis was performed using field emission scanning electron microscope (FESEM) on the FeCoNi electrodeposited at different deposition times with refer to the recorded potentiostatic current transient.

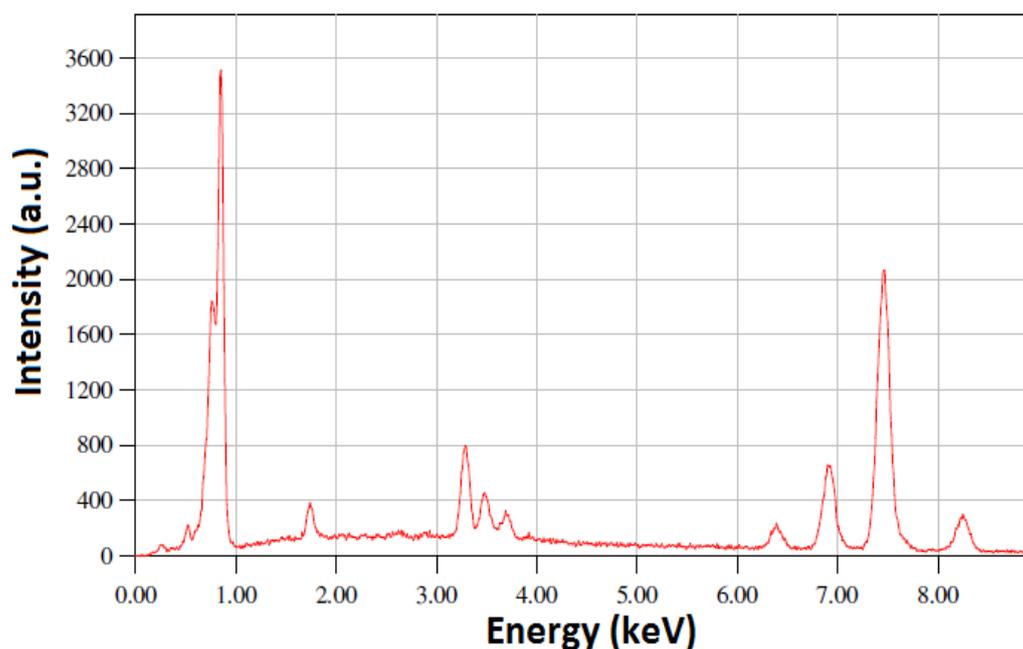
## 3. Results and discussion



**Figure 1.** Cyclic voltammogram of sulfate electrolyte containing 0.01 M  $\text{FeSO}_4$ , 0.02 M  $\text{CoSO}_4$ , 0.17 M  $\text{NiSO}_4$ , 0.400 M  $\text{H}_3\text{BO}_3$  and 0.002 M CTAB.

In metal alloys electrodeposition, the ions of different metals are deposited simultaneously so that the ongoing process is known as co-deposition. Since the metal ions of different elements have different reduction potential as well, to be able to reduce them at the same time it is necessary to determine an appropriate co-deposition potential. In addition, metal electrodeposition potential generally differs from its standard reduction value due to the overpotential occurrence. Therefore, prior to the electrodeposition of FeCoNi, an electrochemical study was conducted to determine the initiation of the metal co-deposition potential using cyclic voltammetry technique.

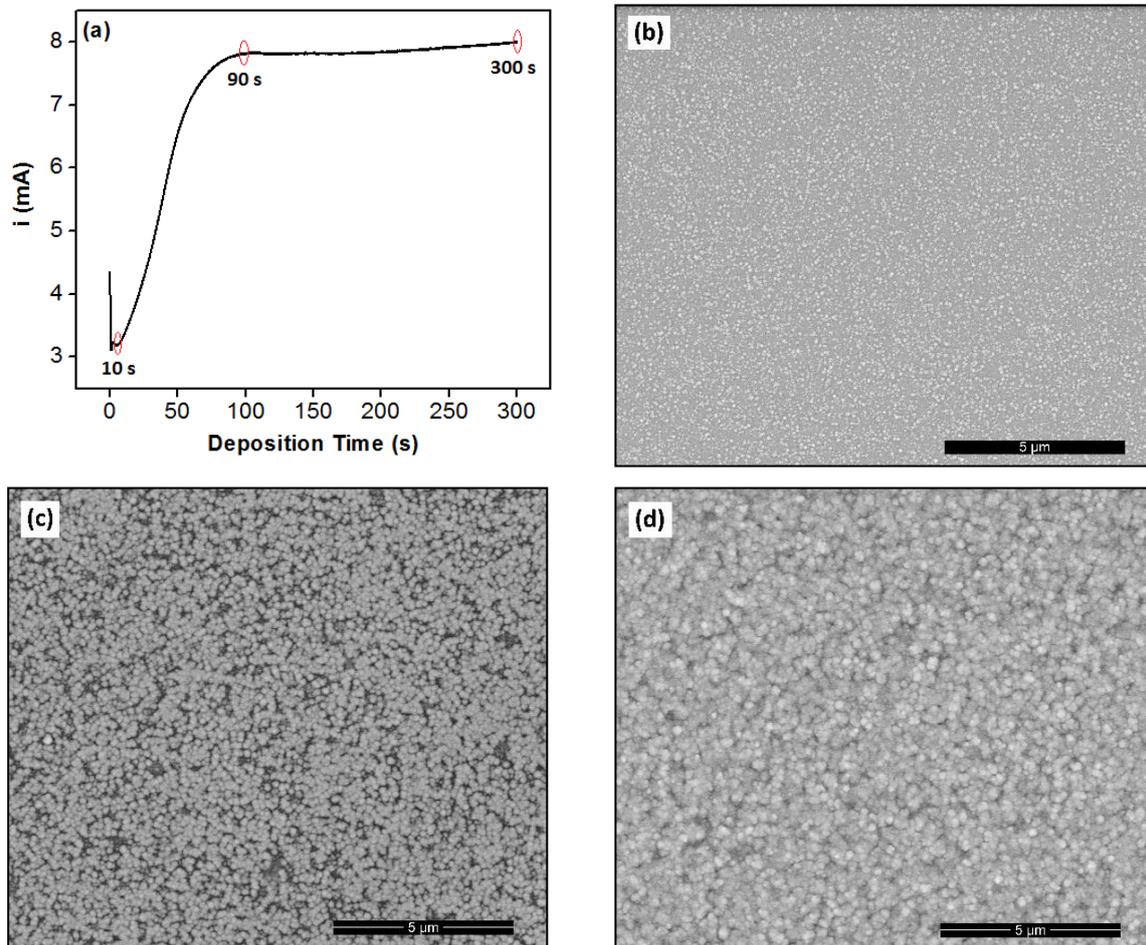
Figure 1 shows a cyclic voltammogram of the sulfate electrolyte indicating the metal ion co-deposition potential characterized by an increase of the cathodic current. The current rise showed that the reduction reaction has taken place at the electrolyte-electrode interface by involving the current in the system [4]. This indicates that the initiation of FeCoNi co-deposition from the electrolyte system has been occurred at potential of -0.98 V vs. Ag/AgCl. The reduction potential from this measurements is much more negative than the standard reduction potential of  $\text{Fe}^{2+}$  (-0.44 V),  $\text{Co}^{2+}$  (-0.28 V), and  $\text{Ni}^{2+}$  (-0.25 V). This gap should be attributed to the presence of other species which may inhibit electron transfer in the interface of the electrodes causing the overpotential of the metal deposition process [4,20]. According to Lowenheim [21], overpotential occurs in the process of metal deposition to overcome kinetic barrier so that chemical reactions in the system can take place. The anodic peaks were also observed in the obtained cyclic voltammogram at scanning toward more positive potential derived from the oxidation process of the previously deposited metals [4,22]. For deposit preparation using potentiostatic technique, metal or alloy electrodeposition may be carried out at a potential equal to or more negative than the initiation one. To produce deposit with a high deposition rate, in this study, the electrodeposition of FeCoNi nanoparticles was carried out at potential of -1.10 V vs. Ag/AgCl.



**Figure 2.** EDX spectrum of the FeCoNi nanoparticles.

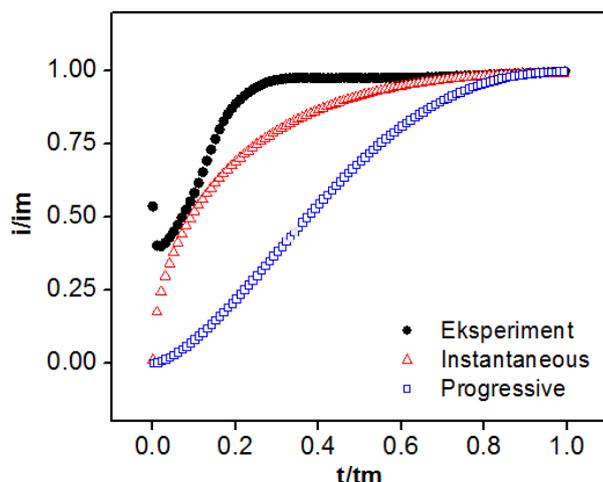
Furthermore, the electrodeposition was performed on an ITO-PET substrate. The formation of FeCoNi deposit was confirmed by the EDX spectrum shown in Figure 2. Based on the AAS measurements, the deposit was composed by 25.3 wt.% of Fe, 28.8 wt.% of Co and 45.9 wt.% of Ni. In addition to these three metals, it was also observed other elements derived from the substrate of ITO coated PET. Figure 3 shows the recorded current transient during the electrodeposition of the FeCoNi alloy. From the potentiostatic transient, the current flow at the first 10-second deposition time indicated nucleation process has been taken place. This phase was then followed by a significant increase of the current until

duration of the deposition time of 90 seconds which should be associated to the particles growth stage. At 90 seconds, the deposition current flow reached  $\sim 8$  mA and then relatively steady until the duration of deposition time 300 s indicated the diffusion phase taking place produced a dense deposit of the FeCoNi.



**Figure 3.** Potentiostatic current transient (a) and FESEM micrograph of FeCoNi nanoalloy electrodeposited at deposition time of 10 s (b), 90 s (c) and 300 s (d).

To confirm this discussion, micrographs of the FeCoNi deposits prepared with three different deposition times was examined by FESEM and shown in Figure 3b-d. The micrographs exhibit different morphological deposits in terms of size and particle density. A 10-second deposition time micrograph shows the very fine particles assumed as nucleus grown thoroughly over the surface of the substrate (figure 3b). At deposition time of 90 seconds, the nucleus were found to grow up until reach bigger particles with the size range of 100 – 150 nm (figure 3c). At deposition time of 300 s, there was no significant changes found on the electrodeposited particles size (figure 3d). However, a dense deposit with a uniform particles size was obtained. These morphological characteristics of the FeCoNi deposits agree with the typical current transient discussed previously (figure 3a).



**Figure 4.** Comparison between experimental potentiostatic current transient for FeCoNi deposition from sulfate electrolyte containing CTAB and theoretical dimensionless models for instantaneous and progressive nucleation.

To further confirm the mechanism growth of the FeCoNi nanoparticles, the experimental transient current was compared with the theoretical currents based on the equations proposed by Scharifker and Hills [23]. Based on the plot of  $i/i_m$  versus  $t/t_m$  shown in Figure 4, the FeCoNi nanoparticle co-deposition process does not exhibit exactly the same characteristics as both theoretical models neither instantaneous nor progressive. Nevertheless, the deposit characteristics composed of fine particles grown on relatively uniform deposits indicate that the nucleation process and FeCoNi growth in the system tested closer to the instantaneous nucleation type with rapid particle growth periods resulting in deposits with size distributions very homogeneous particles.

#### 4. Conclusion

Electrodeposition of FeCoNi nanoparticles from sulfate electrolyte containing CTAB was investigated. The cyclic voltammetry studies show that the initiation of co-deposition of Fe, Co, and Ni ions from the electrolyte system occurred at cathodic potential of -0.98 V vs Ag/AgCl. The electrodeposition occurred with very fast particle growth phase resulted in fine nanoparticles of FeCoNi. Typical current transient also indicated that FeCoNi electrodeposition tend to follow instantaneous nucleation type with lead to homogeneous particles size distribution.

#### Acknowledgement

This work was funded by Universitas Negeri Jakarta and Kemenristek DIKTI trough PSNI research fund with contract number of

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