

# HIGH NICKEL DEPOSITION AT LOW VOLTAGE ELECTROPLATING PROCESS BY A COMBINATION OF ANIONS

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**ABSTRACT:** This research has been performed to understand the impact of the combination of nickel anions of sulfate ( $\text{SO}_4^{2-}$ ), and chloride ( $\text{Cl}^-$ ) in the solution towards nickel deposition. The evaluation was performed for the voltage, weight, and efficiency. The electroplating of nickel was performed by chemical cleaning of the specimen surface, nickel deposition in the nickel solution under specific current density, and post-cleaning to remove the residual solution. The nickel solution was consist of sulfate, and chloride anions compared with nickel sulfate solution only. The result showed that the presence of chloride anions in a sulfate solution lowered the voltage, increased the weight of nickel deposition, and increased efficiency compared with the impact on sulfate solution only. The voltage of a solution consisting of chloride and sulfate decreased by more than 30%, compared with sulfate solution only. The weight of nickel deposited on the specimen surface increased clearly. As the number of chloride anions increased, the nickel deposition increased linearly. Interestingly, the highest nickel weight was achieved at a low chloride anion concentration. The heaviest nickel deposited is 0.7 g was achieved under 0.07 A/cm<sup>2</sup> and 15 g/l chloride anions. The nickel deposition efficiency in the combination of sulfate and chloride anions is always higher than 80% compared with nickel sulfate solution only.

**KEYWORDS:** *Anions Combination; Chloride Effect; Impact; Nickel Deposition*

## 1.0 INTRODUCTION

The deposition of nickel on metals by electroplating improves the appearance of the metal surface. In general, it is used as a decoration that gives a bright color and/or meets technical needs, such as increasing the material's resistance to corrosion or other requirements. Another benefit of nickel electroplating is it improves the physical quality of materials, such as increasing wear resistance, protecting the surface of materials from corrosion, and having the right hardness. The glossy nickel deposition on the specimen surface causes dust, oil, and water challenging to stick on the specimen surface so that the specimen has good aesthetics. Another advantage is the surface will not easily corrode. So, it improves not only the appearance but also extends the performance and the durability of materials [1-6].

There are many methods to deposit nickel, which are electroless plating, electroplating, chemical reduction, pulsed current plating, chemical vapor deposition, thermal spraying, and weld surfacing [6-12]. Among those methods, electroplating is an interesting method due to its low cost, ease of control, and versatility [12]. The schematic of the nickel electroplating is shown in Figure 1. Two electrodes are immersed in the solution. The specimen role is a cathode and is charged with the negative source of DC power, another one is an anode with a positive source of DC power. The process on the specimen is a reduction, while on the anode, it is oxidation [13]. The reactions on the electrodes can be explained through the following equations:



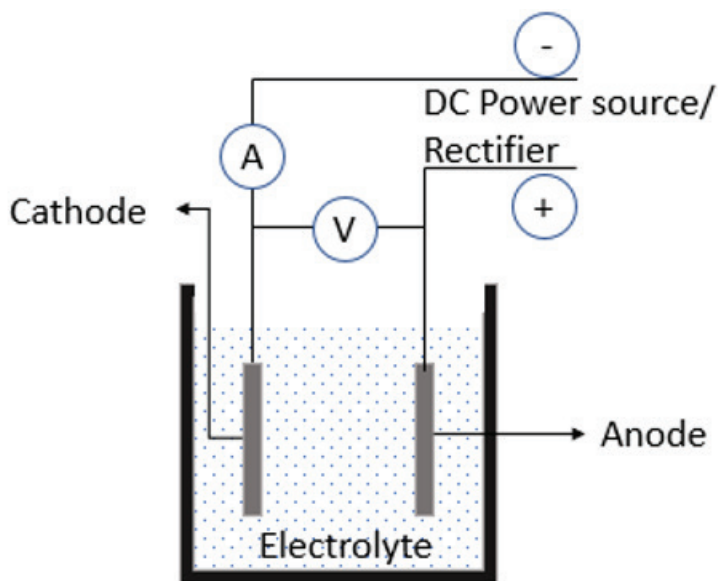


Figure 1: Schematic of the electroplating cell

Usually, the solution for nickel electroplating is Watts baths. The bath consists of nickel sulfate ( $\text{NiSO}_4$ ), nickel chloride ( $\text{NiCl}_2$ ), and boric acid ( $\text{H}_3\text{BO}_4$ ). Nickel sulfate is a primary source of nickel ions since it is readily soluble, commercially available, and relatively cheap. The second one is nickel chloride which increases the diffusion coefficient of nickel ions and assists anode corrosion. The minor quantity of nickel chloride is usually enough to diminish anode passivity, specifically at high current densities. The last one is boric acid which is used to maintain the pH of the bath solution at a specific value by playing a role as a buffering agent [8]. The presence of nickel chloride and boric acid in the bath improves the physical properties of nickel electrodeposition [23].

Many researchers are concerned about nickel electroplating. The nickel deposit properties are closely related to the electroplating parameters, such as aeration, composition, bath compound, temperature, stirring, current density, and the distance of anode to cathode [9, 15-16]. The properties of nickel electroplating can easily be adjusted through operating conditions such as temperature, voltage, current density, pH, time, and additives [9, 14, 18]. Some researchers are concerned about the effect of the electroplating bath and its concentration on nickel properties deposited. The color of nickel has been reported to be affected by electrolytic concentration, and temperature [14]. The electroplating bath consisting of Ni-Mo-B was reported to increase surface hardness [17]. Anions were also reported

to affect the orientation and the structure of nickel deposited on a specimen [14]. The use of Se<sup>2-</sup> anion of nickel has been reported by Anand et al. [18] in the solar/photoelectrochemical cell application.

Although the nickel solution generally contains sulfate and chloride anions, the report on those anions towards nickel deposition is still scarce. Thus, this study intends to characterize the nickel deposition of those combinations. The analysis was carried out to identify a potential difference, weight gain, and weight efficiency of a combination of sulfate and chloride in a solution. The results of this study may reveal the potential combinations of sulfate and chloride anions.

## **2.0 MATERIALS AND METHODS**

### **2.1 Materials**

This electroplating process used low carbon steel as a specimen with a surface area of 27 cm<sup>2</sup>. The chemicals used were NaOH, HCl, NiSO<sub>4</sub>, NiCl<sub>2</sub>, and H<sub>3</sub>BO<sub>4</sub> (industrial grade), and they were used as received (without additional purification). The solute was immersed in demineralized water. The total volume of the solution was a liter. The anode and cathode were connected to a DC supply by a copper wire.

### **2.2 Methods**

The nickel electroplating process was performed through three main steps: pre-process, electroplating, and post-electroplating. The pre-process step consisted of cleaning the specimen (low carbon steel) through consecutive surface grinding, washing by soap, immersing in a 10% NaOH solution for 10 minutes, and immersing in a 10% HCl solution for 5 minutes. All chemical cleaning processes are carried out at room temperature. The nickel electroplating process was performed in a specific composition solution that is heated to a temperature of 50°C by varying the current and duration of the process. The batch composition and the operating condition were shown in Table 1. The distance between the cathode and the anode is 8 cm, and the ratio of the cathode to the anode is equal to 1. The low carbon steel specimen was charged by the negative current. Post-electroplating cleaning was performed in hot water for 30 minutes. After completing each process, the next step is rinsing with water.

Table 1: The parameters of nickel solution

Nickel Electroplating Parameters	
NiSO <sub>4</sub> .6H <sub>2</sub> O	150 g/l
NiCl <sub>2</sub> .6H <sub>2</sub> O	0–90 g/l
H <sub>3</sub> BO <sub>4</sub>	40 g/l
Current Density	0.01–0.07 A/cm <sup>2</sup>
Time	20 min
Temperature	50°C
Anode to Cathode	1:1
Conductor	Copper

Table 2 shows the nomenclature of nickel chloride in the solution. The letter C stands for chloride, while the number after the letter is the concentration of nickel chloride. For example, C00 means the nickel chloride concentration is 0 g/l.

Table 2: The nomenclature of nickel chloride

The concentration of NiCl <sub>2</sub> .6H <sub>2</sub> O in the solution (g/l)	Nomenclature
0	C00
15	C15
30	C30
60	C60
90	C90

### 2.3 Analysis

The effect of chemical cleaning on the weight loss of the specimen was investigated. The weighing of the specimen was performed before and after chemical cleaning by two types of abrasive solutions are 10% NaOH and 10% HCl solution. The amount of nickel deposition was determined by weighing the specimen before and after the electroplating process. The effectiveness of electroplating can be expressed through process efficiency. It is well-defined as the ratio between the nickel's weight obtained from the real process and the weight obtained from Faraday's equation [19] such as

$$W = \frac{Mit}{nF} \times 100\% \quad (3)$$

where W is the weight of a nickel, M is the molecular weight of the electroplated substance, i is the current (ampere), t is the electroplating time (seconds), n is the number of electrons transferred for ion reduction, and F is the Faraday number (96,500 Coulomb).

### 3.0 RESULTS AND DISCUSSION

#### 3.1 The Effect of the Chemical Cleaning on Specimen Surface

The objective of the cleaning process is to remove contaminants on the specimen surface, such as dust, oil, and rust. The cleaning was performed by chemical solutions. During chemical cleaning, a small amount of specimen was lost. The weight loss of low carbon steel due to this process is a maximum of 0.0017 g. The weight loss during chemical cleaning was relatively very small in contrast to the nickel deposition far below minimum nickel deposition that is 0.1 g as shown in Figure 3.

The color of the specimen surface before chemical cleaning was dark, and it turn bright. The dark color was caused by the oxide layer. After chemical cleaning, the specimen surface turned bright. That means the chemical cleaning removed the oxide layer, and etched low carbon steel surface very thin. The chemical cleaning cleans the specimen surface area, effectively.

#### 3.2 Effects of Nickel Chloride on Voltage

Two kinds of nickel, which it presents as nickel sulfate and nickel chloride, are readily soluble in the water. The solubility of nickel sulfate and nickel chloride was shown in Table 3.

Table 3: The solubility of nickel [20]

Component	The solubility per liter
NiCl <sub>2</sub> .6H <sub>2</sub> O	2540 (20°C)
NiSO <sub>4</sub> .6H <sub>2</sub> O	625 (0°C)

The number of NiCl<sub>2</sub>.6H<sub>2</sub>O of this experiment is quite low (maximum 90 g/l) compared with its solubility as shown in Table 3. In addition, it is also well-known, as mentioned in the solubility rule that the chlorides, bromides, and iodides of all metals except lead, silver, and mercury(I) are soluble in water. Nickel is also classified as one of the transition metals. The salts that are soluble in water dissociate into their ions and are electrolytes. Nickel Chloride (NiCl<sub>2</sub>) is a salt that is soluble in water so that it dissociates into Ni<sup>2+</sup> cations and Cl<sup>-</sup> anions represented by the following equation:



Both the  $\text{Ni}^{2+}$  and  $\text{Cl}^-$  anions dissolve completely in water. Nickel(II) is a d8 ion and produces stable planar square complexes besides octahedral or tetrahedral. It contains the green hexaquaonickel(II) ion  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ [21]. Hexaquaonickel(II) ion is a mono-nuclear metal aquo complex. It is a coordination compound containing metal ions with only water as a ligand. These complexes are the predominant species in aqueous solutions of many metal salts. The water molecules role as Lewis bases, donating a pair of electrons to the metal ion and creating a dative covalent bond with it.

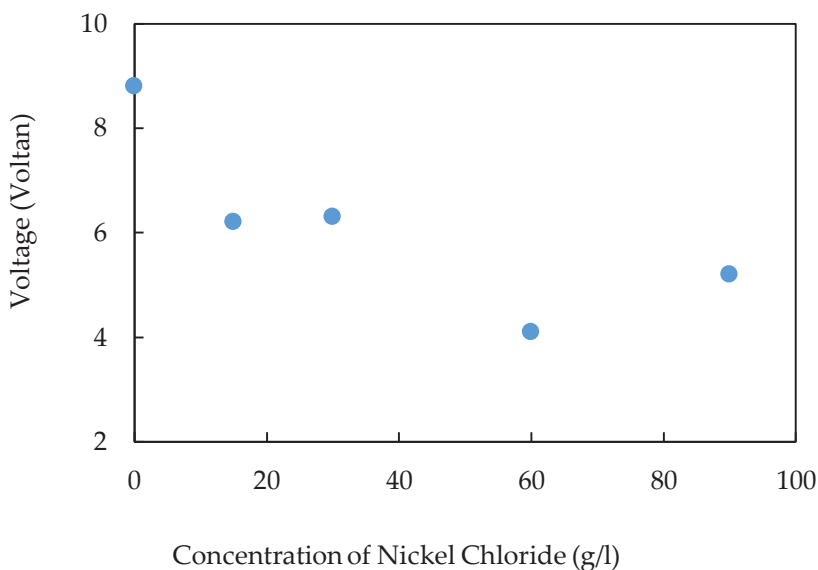


Figure 2: Effect of nickel chloride concentration on voltage output at a current of  $0.07 \text{ A/cm}^2$

The effect of the presence of nickel chloride on the Watts bath toward voltage can be seen in Figure 2. That is clear that the presence of nickel chloride has a lower voltage (4 to 6 V), in contrast to the absence of nickel chloride required a higher voltage (around 9 V). That means the addition of nickel chloride 60 g/l decreases the potential difference between positive and negative poles. As the nickel chloride concentration increases, the voltage tends to decrease. These conditions indicate that nickel chloride decreases the electrolyte resistance, and reducing polarization. This is in line with the previous report as in [8] that the chloride ion is to improve anode dissolution by reducing polarization, it improves the cathode efficiency, and improves the electrical conductivity of the solution.

### 3.3 Effect of Anion on Nickel Weight

The effect of the current density on nickel deposition is presented in Figure 3. Below the current density of  $0.05 \text{ A/cm}^2$ , the amount of nickel deposition is relatively the same. At a higher current density than  $0.05 \text{ A/cm}^2$ , the amount of nickel deposition without chloride ion was the lowest, and it tends to be constant. Interestingly, the nickel deposition reached the highest amount at the addition of  $15 \text{ g/l}$  of  $\text{NiCl}_2$ . It also showed that the amount of nickel deposition is always higher than others in all current densities. This condition has led to speculation that a small amount of chloride ions ( $15 \text{ g/l}$ ) is needed to improve nickel deposition. A higher concentration of chloride ion is not necessary. So that it is necessary to verify the interaction.

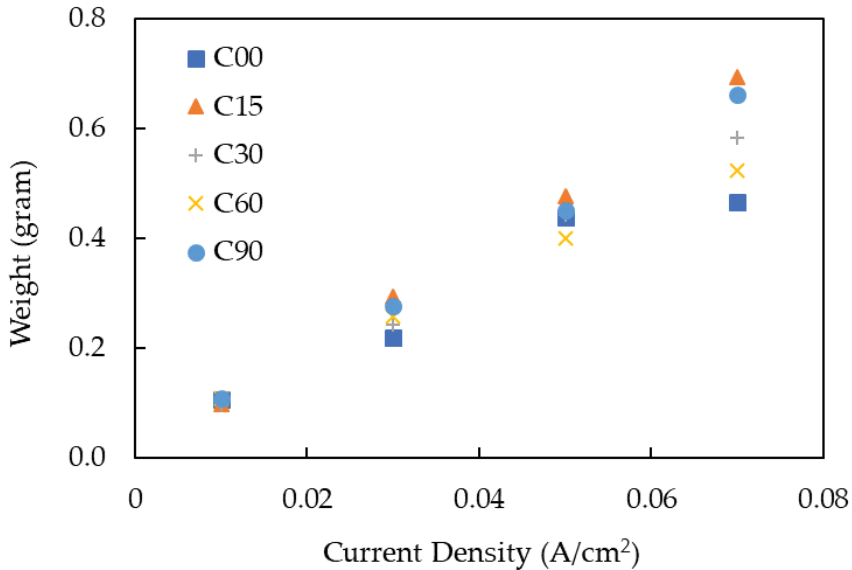


Figure 3: The effect of current density on the amount of nickel deposition

Birlik and Azem [2] reported that the nickel deposited on low carbon steel has a diffraction pattern around  $44^\circ$ ,  $51^\circ$ , and  $76^\circ$  identified as  $\text{Ni}(111)$ ,  $\text{Ni}(200)$ , and  $\text{Ni}(220)$ , respectively. As the nickel chloride concentration increases stepwise, the nickel phase of  $\text{Ni}(200)$  steadily increases; however,  $\text{Ni}(220)$  steadily decreases. It leads to the presumption that the present nickel chloride provokes the  $\text{Ni}(200)$  growth and prevents  $\text{Ni}(220)$  growth. Considering that the amount of nickel deposition increases and the peaks of  $\text{Ni}(200)$  increase in the combination of chloride and sulfate ions, it seems that  $\text{Ni}(200)$  is quickly deposited rather than the nickel phase  $\text{Ni}(220)$ .



### 3.4 Electroplating Efficiency

The nickel deposition efficiency was evaluated by the comparison of the real and theoretical calculations. Figure 4 shows the effectiveness of nickel deposition with and without NiCl<sub>2</sub> in the solution. The nickel deposition efficiency of the nickel sulfate is the lowest. The highest efficiency of nickel deposition is achieved by adding 15 g/l of nickel chloride into the sulfate solution.

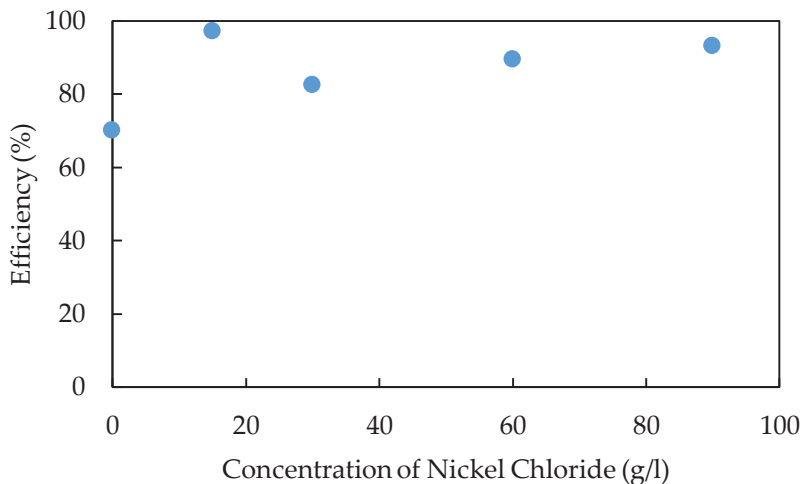


Figure 4: Nickel electroplating efficiency at the current density of 0.03 A/cm<sup>2</sup> and electroplating time, 20 minutes

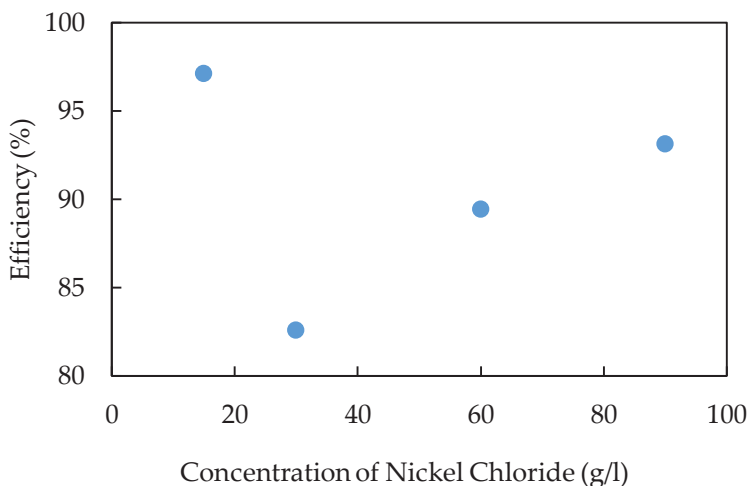


Figure 5: Micrograph of nickel deposition efficiency at the current density Of 0.03 A/cm<sup>2</sup> and electroplating time, 20 minutes

Figure 5 shows the micrograph of nickel deposition efficiency as a function of nickel concentration at a current density of  $0.03 \text{ A/cm}^2$ , and an electroplating time of 20 minutes. It shows the efficiency of nickel deposition at a current density of  $15 \text{ A/cm}^2$  is 97%. Agboola et al. [13] reported cathode efficiency normally is 93% - 97% for most nickel processes. The efficiency is almost 100% as reported by Wesley [22]. This is reasonable cause that Agboola et al. [13] used a high nickel concentration compared with this work.

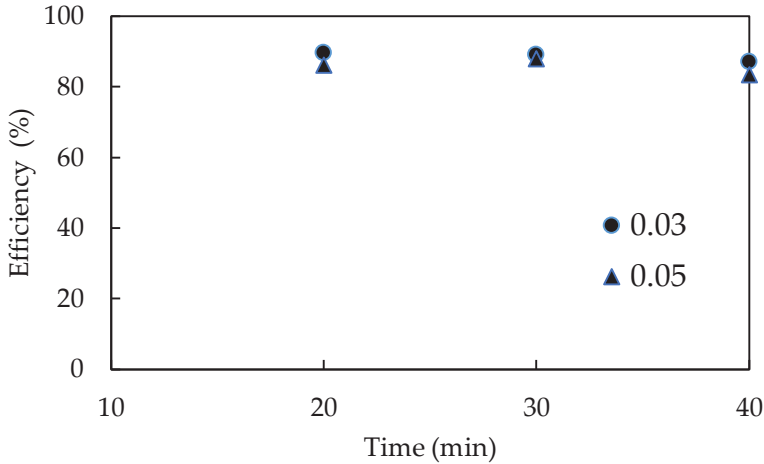


Figure 6: The nickel deposition efficiency of the electroplating bath in the presence of 15 g/l of nickel chloride while the dot of 0.03 denotes the current densities of  $0.03 \text{ A/cm}^2$  and the triangle, 0.05 denotes the current densities of  $0.05 \text{ A/cm}^2$

Other experiments were performed to confirm the high efficiency achieved by 15 g/l of nickel chloride. Figure 6 shows the effect of current density at a specific time for 15 g/l nickel chloride. The results show that at the current density of  $0.03 \text{ A/cm}^2$  and  $0.05 \text{ A/cm}^2$  the nickel deposition efficiency is always higher than 80%. Other results are shown in Figure 7. The efficiency is above 80%, except at  $0.07 \text{ A/cm}^2$ , which shows a little decrease in efficiency (80%).

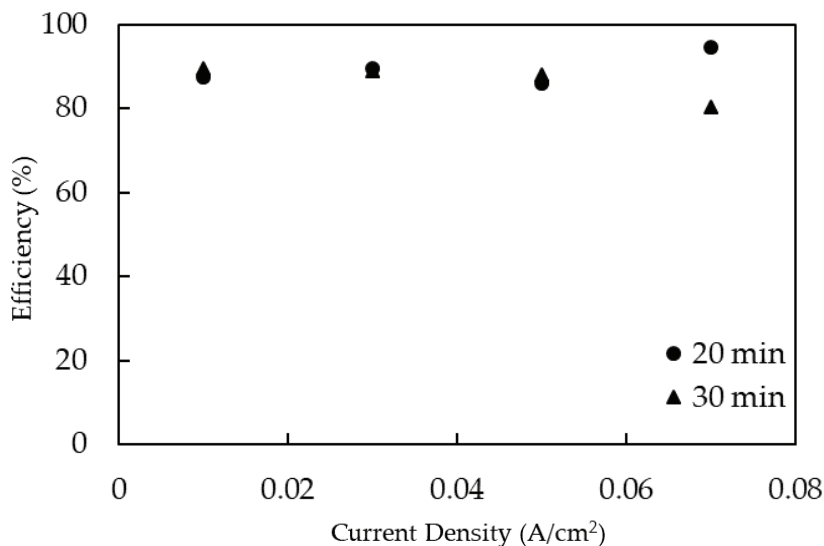


Figure 7: The nickel deposition efficiency of the electroplating bath in the presence of 15 g/l of nickel chloride for 20 and 30 minutes

#### 4.0 CONCLUSION

The nickel deposition through electroplating was performed after cleaning the specimen surface. The weight loss of the specimen due to chemical cleaning is relatively small compared with that of nickel deposited onto the specimen. So that the weight loss due to chemical cleaning could be neglected. Nickel was successfully deposited on the specimen using an elementary solution containing nickel sulfate and boric acid only. It was also successfully deposited in that solution with some nickel chloride. The potential difference of solution consist of nickel chloride lowered 20%, and the efficiency was always higher than 80% compared with an elementary solution. Interestingly, the highest amount of nickel deposition was achieved when 15 g/l nickel chloride was present in the solution. The speculation that arises regarding the use of nickel chloride in the nickel deposition is the Ni(200) is quickly deposited compared with Ni(220). The phenomena of higher nickel deposition and efficiency at the combination of nickel sulfate and nickel chloride may use for other applications such as nickel recovery from nickel sulfate industrial waste. The required energy could be minimized, and the recovery rate of nickel from industrial waste could be increased.

## ACKNOWLEDGMENTS

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