Study of corrosion behavior on the addition of sodium citrate in nickel electroplating on SPCC steel using EIS

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Abstract. The addition of sodium citrate to nickel electroplating process as additive is useful for refining the grain size of nickel deposit. The refining of grain size in nickel deposit as coating layer can improve surface performance, one of which corrosion resistance. This paper aims to investigate the effect of sodium citrate addition as grain refiner to promote corrosion resistance on SPCC steel. This experiment used Watt’s Bath solution of NiSO4 300 g/L, NiCl4 45 g/L, H3BO3 60 g/L, wetting agent 0.2 cc/L. Sodium citrate was added in composition of 45g/L and 60g/L. Nickel were deposited by direct current using current density on 6 A/dm2 at the acidity level of 5 for 30 minutes by keeping the operating temperature stable at 50°C. The grain size of nickel deposit was observed through Optical Microscope and Atomic Force Microscope (AFM). The corrosion behavior of SPCC was observed by linear polarization and Electrochemical Impedance Spectroscopy (EIS) methods using 3% NaCl solution. Based on the research, the addition of sodium citrate as grain refiner will increasing corrosion resistance on SPCC steel from 0.35 to 0.05 mm/year.

1. Introduction
SPCC steel has poor corrosion resistance, it could be easily oxidized in atmospheric condition. In industry, this type of steel is widely used because of its very good mechanical properties [1]. Preventive treatment is needed to prevent the failure because of its poor corrosion resistance. One of the easiest method is using electroplating process to make a layer that can prevent the surface of steel interacted directly with the atmosphere [2]. Metal whose reduction potential lower than the substrate could be use in electroplating process [3]. Nickel is either metal whose has potential reduction lower than ferrous. Nickel electroplating itself is a process to deposited nickel onto surface of substrate material with chemical reaction under direct current electricity [4],[5].

Nanocrystalline material is an important material that used by industry these days because of its good chemical properties. This type of material could be use as subject material in electroplating method. In present days, there are many researches focus on improving the performance of this material, but there is a plenty of researches that have been focused on its corrosion behavior when this material use as coating [6]. To improve the corrosion resistance of nickel nanocrystalline, refining grain size is one of the method that can used. Its corrosion resistance will increase corresponded to finer grain size of electroplated nickel [7]. This increasing of the behavior is because the density of grain boundary increased so that the passive layer could be form shortly [8].

Refining of the grain has been demonstrated with saccharine as brightener [9]. The utilization of saccharine as brightener could make intergranular embrittlement [10]. Because of that, these days has been used another compound to replacing saccharine. One of them is sodium citrate, it has been demonstrated in patent WO 1994012695 [11]. Although sodium citrate has been demonstrated in a
patent and has lower price than saccharine, there has not been much research which study sodium citrate as grain refinement and its mechanism [12]. This present work is aimed to study the corrosion resistance on SPCC steel with electroplated nickel with addition of sodium citrate. Corrosion resistance of this layer will be measured using linear polarization method and Electrochemical Impedance Spectroscopy (EIS). Atomic Force Microscope topography was used to measure the roughness.

2. Experimental

In this experiment was used Steel Plate Cold Rolled Coiled (SPCC) with a thickness about 1.6mm as cathode and carbon as anode during electroplating process. The chemical composition of SPCC was determined by Optical Emission Spectroscopy (OES) in Table 1.

| Material | Chemical Composition (%) |
|----------|--------------------------|
| SPCC     | C 0.0448, Mn 0.181, P 0.0107, S 0.0076 |

Mechanical and chemical preparation were performed on SPCC strips (10mm x 35mm x 1.6mm). Surface preparation for the steel was done by manually polishing with amery papers in 60, 120, and 180 grade. It was done to remove oxide layer in the surface which form because of the oxidation process with the atmosphere. After that, SPCC strips degreased using 10wt% NaOH at temperature of 70°C for 11 minutes and pickling using 30 wt % HCl at room temperature for 10 minutes. The last preparation step is etching using H_2SO_4 10wt% for 4 minutes.

Electroplated Ni were prepared by direct current (DC) electroplating from an electrolyte containing nickel sulphate (about 300 g/L), nickel chloride (about 30 g/L) and boric acid (about 30 g/L) at temperature of 50°C and pH 5 for 20 minutes. The current density was used at 6 A/dm^2 which is obtained based on hull cell test. This paper will investigated the corrosion behavior of SPCC steel in three condition that are a) plating Ni, b) plating Ni + 45g/L of sodium citrate and c) plating Ni + 60g/L of sodium citrate.

For the electrochemical testing, the sample was first mounted with epoxy where 1 cm^2 of its surface was exposed to electrolyte and the backside one was providing electrical connection. The electrochemical measurements were carried out in a three-electrode cell. SPCC coated with Ni was used as the working electrode, a platinum wire was used as the counter electrode, and Silver-Silver Chloride (SSC) was used as the reference electrode. The electrochemical measurement was analyze using AUTOLAB potentiostat/galvanostat system. Before all the measurements, the sample was immersed into electrolyte for 120 second to stabilize the open circuit potential (OCP). The aqueous solution containing 3wt.% NaCl was used as electrolyte in electrochemical cell and pH of electrolyte was measured at 6. The analysis of linear polarization result was analyzed using software NOVA 1.11.2.

The linear polarization method was used to determine the value of corrosion potential (E_{corr}) and corrosion current density (i_{corr}). And the potentiodynamic anodic polarization curves were also acquired based on this method. The linear polarization resistance was determined by performing linear sweep voltammetry (LSV) at a scanning rate of 10 mV/s. Scan direction was determined by start potential at -0.2 V and stop potential at 1.0 V. The measurement of EIS was conducted at the open circuit potential. The applied potential was 10 mV and the frequency ranged from 0.01 Hz to 100 kHz. Physical characterization of the samples consisted of roughness of the grain result from electroplating process. Atomic force microscope topography was used to measure the roughness of each electroplated nickel layer.
3. Results and discussion

3.1. Effect of sodium citrate on grain size

Figure 1. AFM topographic measurement for a) Ni plating, b) Ni plating + sodium citrate 45 g/L, c) Ni plating + 60 g/L; and particle distribution graphic for d) Ni plating, e) Ni plating + sodium citrate 45 g/L, f) Ni plating + 60 g/L.

Figure 1 a), b), and c) shows the result of AFM topographic measurement for all samples. Based on Figure 1, there is differences of the surface roughness which clearly show that all of samples have different range of grain size. Sample with the finest grain is sample electroplated nickel with the addition of 60 g/L sodium citrate.

Figure 1 d), e), and f) shows particle distribution graphic of all samples. Based on those graphics, grain size of electroplated nickel without additive is micrometer sized with the biggest size is about 3μm. Electroplated nickel with additive has finer grain size, it is nanometer sized with the biggest size...
of the addition of 45 g/L sodium citrate is about 900nm and the biggest size of the addition of 60 g/L sodium citrate is about 660nm. It can be concluded the addition of sodium citrate affected the grain size of electroplated nickel. The finest grain size is when the addition up to 60 g/L.

3.2. Effect of sodium citrate addition on corrosion resistance

3.2.1 Linear polarization measurement

Figure 2 shows polarization curve of the result of polarization measurement using linear polarization method. It shows that electroplated nickel with the addition of sodium citrate has more negative potential and the addition of 60 g/L sodium citrate has the most negative corrosion potential of all. More negative potential in the polarization measurement with 3wt.% NaCl shows that the material has better corrosion resistance [7].

![Polarization Curve](image)

**Figure 2.** Polarization curve of electroplated nickel on SPCC steel with the addition and without the addition of sodium citrate as additive in 3wt% NaCl solution.

The result of polarization measurement can be seen in Table 2. Corrosion potential (E_{corr}) of electroplated nickel on SPCC steel become more negative from -538.3 to -571.7 mV vs SSC along with the decreasing of current density from 30.4 to 4.34 μA cm\(^{-2}\). The corrosion rate also decreased from 0.35 to 0.05 mm/year. The indication of decreasing potensial corrosion, current density, and corrosion resistance is the presence of sodium citrate as additive [7], [13], [16]. The addition of sodium citrate in electroplating process will refine grain structure of nickel layer on surface of the substrate. Refining of the grain size developed by transition of grain orientation that will inhibit the grain growth. This transition occur because of the changing of the surface energy [9]. Besides that, the addition sodium citrate to produce finer grain size affected to decreasing value of tafel slope (\(\beta_a\) and \(\beta_c\)). The lower value of tafel slope with decreasing grain size indicates has lower corrosion. This relates to the Stearn Geary equation:

\[
i_{corr} = \frac{\beta_a \beta_c}{2.303 \times R_P (\beta_a + \beta_c)}
\] (1)
where $i_{corr}$ is the current density of corrosion and $R_p$ is the polarization resistance. Based on the equation, the decrease of $\beta_a$ and $\beta_c$ will decrease the corrosion rate.

In the NaCl solution, the corrosion potential ($E_{corr}$) of the nickel layer will decrease as the corrosion resistance observed in Figure 2. The potential decrease is indicated because of the influence of the presence of the catalyst on the hydrogen reduction process in the form of a defect in the crystal lattice on the steel surface. It has been observed that in the presence of trapped hydrogen at dislocations, grain boundaries, and vacancies or pores are able to alter the kinetics of hydrogen evolution [19].

| Sample                        | $\beta_a$ (mV/dec) | $\beta_c$ (mV/dec) | $E_{corr}$ (mV) | $i_{corr}$ (μA.cm$^{-2}$) | Corrosion Rate (mm/year) |
|-------------------------------|-------------------|-------------------|----------------|----------------------------|--------------------------|
| Ni Plating                    | 141.7             | 132.5             | -538.3         | 30.4                       | 0.35                     |
| Ni Plating + Sodium Citrate 45 g/L | 93.3              | 30.8              | -553.4         | 12.7                       | 0.15                     |
| Ni Plating + Sodium Citrate 60 g/L | 59                | 51.2              | -571.7         | 4.34                       | 0.05                     |

In the polarization curve of all the samples, there is passive condition when the line being steady state towards the current density. This passive condition occur because of the appearance of passive layer on electroplated nickel on surface of the substrate. This passive layer could be form easier when the electroplated nickel has nano grain size particle because it has bigger grain boundary density. This is also an indication of increasing corrosion resistance of nickel electroplated layer [8].

3.2.2 **Electrochemical impedance spectroscopy (EIS) measurement**

The Nyquist impedance plots for Ni plating with no additive and addition additive in 3wt.%NaCl solution at room temperature are shown in Figure 2. The Nyquist plots of Ni plating in NaCl solution exhibit one capacitive loop in the entire frequency range. For measuring the corrosion behavior of the Ni deposits in NaCl solution, an equivalent circuit model consists of solution resistance ($R_s$), charge transfer resistance ($R_{ct}$) and constant phase element (CPE) has been proposed to simulate the metal/solution interface. The equivalent-circuit model for the corrosion behavior of Ni plating in the NaCl solution is shown in Figure 4.

![Figure 3. Electrochemical Impedance Spectra of SPCC Steel with electrodeposited nickel in the addition and without the addition of sodium citrate as additive](image_url)
Table 3. Equivalent circuit parameters determined by modelling impedance spectra of Ni plating in 3 wt.% NaCl solution

| Sample                                      | Rs (Ω.cm²) | Rct (Ω.cm²) | Constant Phase Element (μF.cm²) |
|---------------------------------------------|------------|-------------|---------------------------------|
| a. Ni Plating                               | 6.05       | 22.27       | 12.97                           |
| b. Ni Plating + Sodium Citrate 45 g/L       | 5.32       | 78.7        | 53.22                           |
| c. Ni Plating + Sodium Citrate 60 g/L       | 6.48       | 89.85       | 24.03                           |

Figure 4. The equivalent-circuit model for the corrosion behavior of Ni plating in the 3 wt.% NaCl solution.

The equivalent circuit model is based on the following equations:

\[ Z(\omega) = \frac{1}{R_{ct}} + \frac{1}{j\omega C_{ph}} \]  

\[ Z_{ph}(\omega) = 1/R_{ct} + 1/Y_0(j\omega) \]

where \( \omega \), \( R_s \), \( Z_s/e(\omega) \), \( R_{ct} \), \( Y_0 \) are the angular frequency, solution resistance, impedance of solution/electrode interface, charge-transfer resistance and double layer capacitance, respectively.

Charge transfer resistance (\( R_{ct} \)) is the resistance offered by the metal atoms to get in contact with the electrolyte ionization time. The largest \( R_{ct} \) values have the highest corrosion resistance. Based on this research, the highest \( R_{ct} \) was owned by nickel plating with addition sodium citrate as much as 60g/L. The constant phase element (CPE) is used as a substitute for double-layer capacitor to fit the impedance data of the interface between an electrode and the surrounding electrolyte [19].

The simplified equivalent circuits shown in the insets of Figure 4 are used to model the electrode/electrolyte interface and the simulated results are shown in Table 3. The Nyquist plots (Figure 3) of the Ni plating in NaCl solution exhibit an increasing semicircle with decreasing grain size (addition sodium citrate 60g/L) and the corresponding \( R_{ct} \) values also increase. \( R_{ct} \) value of addition sodium citrate 60g/L is 4 times larger than that of Ni plating without addition additive. So, the refining grain size within addition sodium citrate as much as 60 g/L should exhibit better corrosion resistance in NaCl solution.

The increased corrosion resistance in nickel electroplating results is indicating due to the presence of passive layers. Nickel is one of the metals that easily form a passive layer. The electroplating process within the addition of sodium citrate will refining the grain size of the plating results where the grain has a high grain boundary density. On the formation of a passive layer in the presence of high grain boundary density will increase the number of active sites to form rapidly passive and protective passive film [20]. The layer of nickel plating has a lower grain size will have a high fraction of the passive layer due to the high density of nucleation site of the passive layer, so that the rate of corrosion that occurs in this layer will be lower [19].
4. Conclusions

[1]. The addition of sodium citrate as an additive will refine the grain size of nickel electroplating. The soluble sodium citrate additive in the electrolyte solution will be adsorbed and becomes a barrier from the diffusion path on the active surface of the grain growth. Impaired grain growth and increase in the frequency of the grain nuclei continuously will produce grains with finer size.

[2]. The corrosion resistance of the nickel plating layer with the addition of sodium citrate additive has increased. This can be seen from the value of corrosion rate that decreased.

[3]. The finer grain size produced by nickel electroplating with addition sodium citrate will have higher grain boundary fractions. This will lead to high nucleation density for the site of the passive layer, so that the passive layer is formed will be more stable. This stable passive layer will make the movement of electrons obstructed and the electrons are difficult to move to the surface to perform electrochemical reactions. The inhibited electrochemical reaction will decrease the corrosion rate and in other words increasing the corrosion resistance of the material.

[4]. Addition of 60 g/L sodium citrate has better impact to refinement grain size than 45 g/L. It also provide higher corrosion resistance on the performance of nickel electroplated.

5. References

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