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The Effects of Aniline Concentration and Deposition Time on Polyaniline Conductance as Substrate in Fe/Ni Electrodeposition

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Abstract

The research aims to determine the influence of aniline concentration and deposition time on the characteristics of polyaniline prepared using potentiostatic and galvanostatic electrodeposition methods. FTIR characterization data shows the typical peak of polyaniline in the form of the presence of a quinoid function group at a wavenumber of 1596.16 cm^{-1}. The typical diffraction pattern of polyaniline using XRD was detected at peaks of 2θ 21.1007° and 23.5995°. Polyaniline formed using SEM has a surface morphology that grows in a stacked and irregular manner and has a high conductance value so that it can be used as a substrate in Fe/Ni electrodeposition. The results of the Fe/Ni electrodeposition process when viewed using SEM cause the polyaniline surface morphology to be covered by a Fe/Ni alloy by having an elemental composition from the EDS test data, are iron (Fe) 68.15% and nickel (Ni) 24.83%. Fe/Ni levels from AAS data attached to $PANI_{(pot)}$-Fe/Ni are 1.1912 ppm and 0.8288 ppm; in $PANI_{(gal)}$-Fe/Ni are 1.2219 ppm and 0.8392 ppm.

Keywords: Electrodeposition, Fe/Ni, galvanostatic, polyaniline, potentiostatic

1. Introduction

Polymer material engineering technology has discovered organic compounds that can be made into a conductive polymer. Conductive polymers can conduct electricity due to delocalized bonding electrons so that they have a high conductivity, which reaches 7.5 x 10-5 S /cm [1]. Conductive polymers are widely applied in electronics, supercapacitors, sensors, and metal coatings [2]. The most widely studied conductive polymer is polyaniline (PANI), this is due to some of the advantages of polyaniline, namely electrical conductivity that can be controlled through doping, good environmental stability, soluble in organic solvents, light, flexible, and can be synthesized with simple synthesis technology so that polyaniline is widely applied in the fields of electronics, electricity, thermoelectric, electromagnetic, electrochemistry, membranes, and sensors [3]. Polyaniline is one of the semiconductor materials with an electrical conductivity of 1 x 10^{-3} S/cm because it has a reactive N-H group in its polymer chain [4].

Polyaniline morphology is influenced by preparation conditions, solvents, surfactants, oxidants, monomer types, concentrations of filtering substances, template types, and synthesis methods [5]. The synthesis method that can be used to produce polyaniline is electrodeposition polymerization of aniline solution dissolved in H_2SO_4 solution [6]. Previously, polyaniline has been synthesized using a two-electrode system where there is a weakness in this system, namely polyaniline deposits do not stick firmly to the substrate surface [7]. Therefore, in this study will be done polyaniline synthesis

using electrodeposition technique of three electrode system with potentiostatic and galvanostatic systems. Variations in concentration and deposition time are applied to obtain the optimum conductance value of polyaniline so that the optimum polyaniline sample can be determined to be used as a substrate in the Fe/Ni alloy electrodeposition.

2. Materials and Methods

The sample preparation was conducted by the electrodeposition method using a three-electrode system with platinum as a counter electrode, Ag/AgCl as a reference electrode, and stainless steel (SS) 304 as a working electrode). firstly, stainless steel substrate 304 is done by cutting the SS measuring 30 mm x 10 mm x 0.2 mm.

Polyaniline synthesis was performed by potentiostatic method at a potential of 900 mV for 5 minutes. It is done using aniline solution 0.5 M dissolved in solution H_2SO_4 0.5 M. Fe/Ni alloy electrodeposition in polyaniline is performed by potentiostatic method at -1.2 V potential for 120 minutes. This process is carried out using an electrolyte solution containing $FeSO_4$ 0,05 M, $NiSO_4$ 0.15 M, and boric acid 0.4 M. Then the solution is taken as much as 30 ml and inserted into the electrodeposition cell.

Characterization was conducted using spectrophotometer Fourier Transform Infrared (FTIR), X-ray Diffractometer (XRD), Scanning Electron Microscope (SEM), Energy Dispersive Spectroscope (EDS), and LCR-meter (impedance, capacitance, resistance spectroscopy).

3. Results and Discussion

In **Figure 1.** Demonstrate the Fe/Ni alloy electrodeposition scheme on a stainless steel (SS) 304 substrate resulting in polyaniline covered in Fe/Ni alloy (PANI-Fe/Ni). The results of the sample formed are shown in **Figure 2.** The polyaniline forms a dark green thin layer of emeraldine salt phase on the SS substrate. Then the polyaniline surface coated by the Fe/Ni alloy undergoes a discoloration in certain parts that turn yellowish silver due to the Fe/Ni alloy layer.

Polymerization of aniline into polyaniline begins with the oxidation process of aniline, this stage is known as the introduction period. The oxidation process of aniline occurs without the need for the addition of oxidant agents, but oxidation can occur because it is triggered by electrons derived from electric currents flowing in the potentiostat circuit. Furthermore, anilines join each other undergoing the process of elongating polymer chains to form polyaniline, this stage is known as chain propagation step.

Based on the results of FTIR measurements in **Figure 4.** It shows the peaks of the amen, quinoid, and benzenoid groups. Based on the discussion of FTIR results, it can be confirmed that polyaniline has been successfully formed by the technique of potentiostatic electrodeposition at a potential difference of 900 mV and a time of 5 minutes. The function of measuring the conductance value of polyaniline to see the effect of variations in the concentration of aniline solution and which deposition time can produce polyaniline with the highest conductance value so that it will be selected as a substrate for Fe/Ni alloy electrodeposition.

Table 1. FTIR Polyaniline Spectrum Data

Wavenumber (cm^{-1})	Peak identification
3632.12	Stretching O-H from H_2O
3460.00	Stretching N-H
3008.00	Aromatic C-H stretching
2310.00	Measured air during measurement
1596.16	Quinoid
1479.47	Benzenoid
1313.58	Stretching C-N
1243.18	Stretching C-N
1150.29	Bending C-H
809.17	Bending C-H outside the field

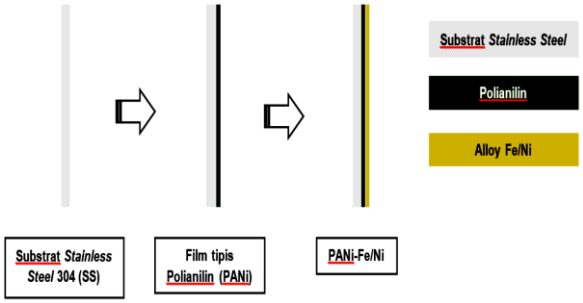

Figure 1. Fe/Ni Alloy Electrodeposition Scheme

a) b)

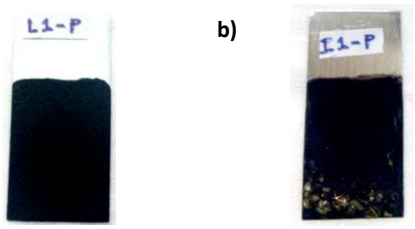

Figure 2. Synthesis of a) PANI; b) PANI-Fe/Ni

Measuring the conductance value of a material is essential for determining the conductivity of a material. Conductance values are directly proportional to the conductivity value which can be seen from the formula of the relationship between the conductance value and the conductivity value of a material as follows:

$$\sigma = G \times L/A$$

Information:

σ = conductivity (S/cm or $\Omega^{-1}.cm^{-1}$)
L = thickness of the material tested (cm)
G = conductance (S)
A = cross-sectional area of material (p.l) (cm^2)

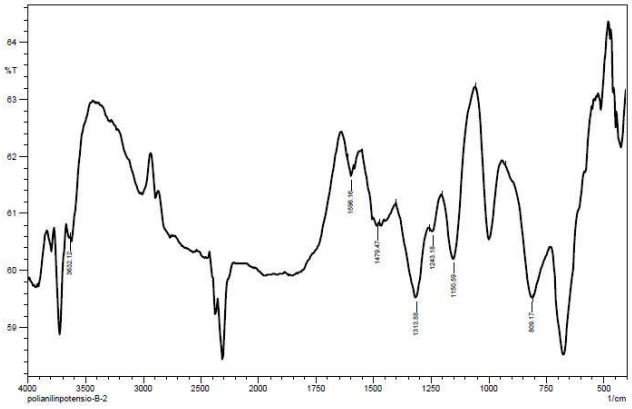

Figure 4. 5-minute polyaniline FTIR spectrum

Polyaniline that has been formed with variations in the concentration of aniline solution is measured conductance value using LCR-Meter as the data listed in **Table 2.** The concentration of aniline solution that shows the highest conductance value in both the potentiostatic and galvanostatic electrodeposition methods is at the concentration of aniline solution 0.5 M. Therefore, in the next step there is a variation in the deposition time of aniline solution 0.5 M with the method of electrodeposition of potentiostatic and galvanostatic.

Polyanilines that have been formed with variations in deposition time are measured conductance values using LCR-Meter as the data listed in **Table 3.** The deposition time that shows the highest conductance value with the potentiostatic electrodeposition method is 5 minutes, while with the galvanostatic electrodestment method is 10 minutes. Based on these results it can be concluded that the concentration variable used is an aniline solution 0.5 M and the variable deposition time used is 5 minutes in the potentiostatic method and 10 minutes in the galvanostatic method. These parameters are selected for the synthesis of polyaniline which will be used as a substrate for Fe/Ni alloy electrodes.

Table 2. Polyaniline conductance values variation in concentration and deposition time

f (kHz)	Polyaniline (potentiostatic) 5 minutes		
1	Aniline 0.5 M 0.87616 S	Aniline 0.25 M 0.48117 S	Aniline 0.1 M 0.23836 S
	Polyaniline (galvanostatic) 10 minutes		
	Aniline 0.5 M 311.27×10^{-4} S	Aniline 0.25 M 192.02×10^{-4} S	Aniline 0.1 M 10.701×10^{-4} S

Table 3. Polyaniline conductance values of deposition time variation

F (kHz)	Polyaniline (potensiostatik)		
1	Aniline 5 minutes 46.66×10^{-4} S	Aniline 10 minutes 2.8269 S	Aniline 15 minutes 6.1508 S
	Polianilin (galvanostatik)		
	Aniline 10 minutes 17.78×10^{-4} S	Aniline 20 minutes 17.16×10^{-4} S	Aniline 30 minutes 12.68×10^{-4} S

Based on the SEM micrograph in **Figure 4a.** Polyaniline has a porous rod-shaped morphology that intersects with a diameter of about 5 µm. Small polyaniline pores provide a wider surface area making it possible to react more quickly with other compounds. Polyaniline as a material has a small particle size and a large surface area so that it can facilitate electron transfer and be used as a substrate.

Then after being coated by the Fe/Ni alloy, the rod-shaped morphology of polyaniline is no longer visible as shown in **Figure 4b.** This indicates that polyaniline has been successfully coated by Fe/Ni alloys. The morphological shape of the surface of the Fe/Ni alloy synthesis has a shape that corresponds to the morphology of the surface of the Fe/Ni alloy in reference. Based on the description above it can be concluded that the synthetic polyaniline can be used as a substrate in the electrode position of the Fe/Ni alloy.

The composition of PANI-Fe/Ni is derived from the EDS measurements in Figure 5. That the PANI-Fe/Ni sample consists of carbon (C) 6.95%, chrome (Cr) 0.07%, iron (Fe) 68.15%, and nickel (Ni) 24.83%. The presence of the element carbon (C) may come from polyaniline because the polyaniline structure of emeraldine salt is mostly composed of carbon as presented in **Figure 6.** In addition, the presence of carbon and chrome is also possible derived from stainless steel substrate 304. Stainless steel 304 has a maximum carbon (C) of 0.08% [11]. Based on these results, the elements detected mostly are iron (Fe) and nickel (Ni), so indicating the electrodeposition of Fe/Ni alloys on the surface of polyaniline substrates has been successfully carried out.

Based on the polyaniline XRD diffraction as shown in **Figure 7.** There are two sharp peaks at 2θ = 21.488° and 25.295°. The two detected peaks are almost in accordance with the reference that there are two peaks at 2θ = 21.1007° and 23.5995° [10]. Thus it can be concluded that polyaniline has been successfully formed because in the diffraction pattern there are two typical peaks of polyaniline.

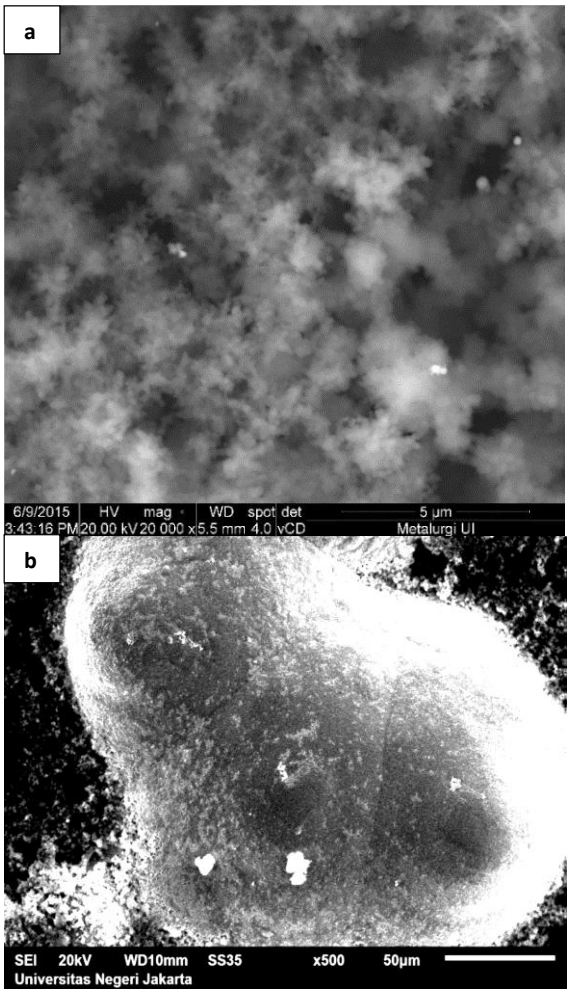

Figure 4. SEM micrograph a) PANI b) PANI-Fe/Ni

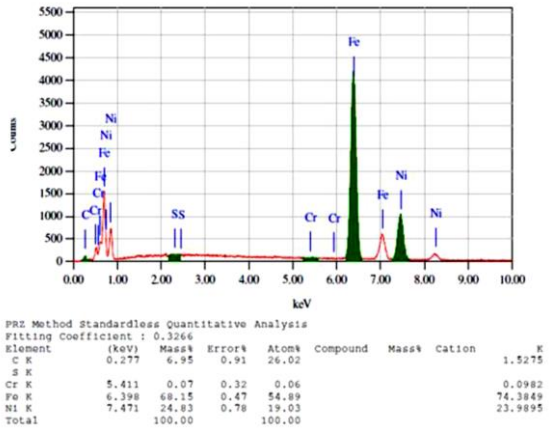

Figure 5. PANI-Fe/Ni Composition EDS Graph

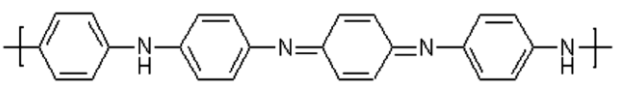

Figure 6. Structure of PANI Emeraldine [12]

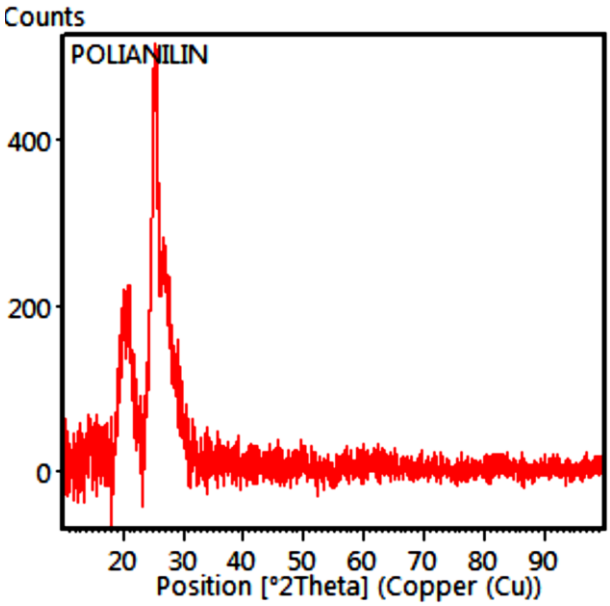

Figure 7. Polyaniline X-ray Diffraction Pattern

Then in **Figure 8.** shows the pattern of X-ray diffraction of the Fe/Ni alloy layer in polyaniline (PANI-Fe/Ni) using the potentiostatic method with a potential difference of -1.2 V for 120 minutes.

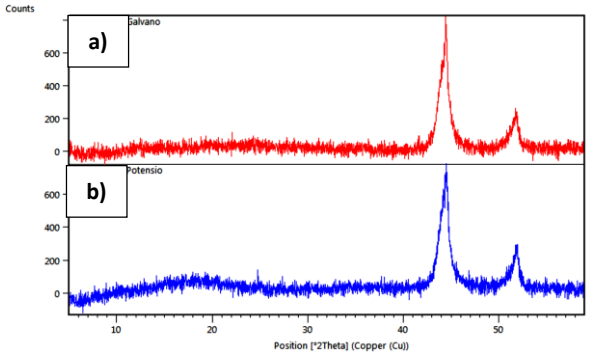

Figure 8. X-ray Diffraction Pattern $PANI_{(galvanostatik)}$-Fe/Ni b) $PANI_{-(potentiostatic)}$-Fe/Ni

X-ray diffraction pattern in **Figure 8a.** indicates a single widened peak that is at 2θ = 44.4473°; d[Å] = 2.03663; hkl = 111 has an FCC-shaped crystal phase of ɣ-(Fe,Ni) and 2θ = 51.8313°; d[Å] = 1.76251; hkl = 200 has a α-(Fe,Ni) crystal phase in the form of BCC can be well defined by the crystalline region formed due to the formation of Fe/Ni alloys in synthesis. The detected powder composition consists of Awaruite ($Fe_{1.00}Ni_{3.00}$) 34%, Tetrataenite ($Fe_{2.03}Ni_{1.97}$) 45%, Tetrataenite ($Fe_{1.00}Ni_{1.00}$) 21%. This corresponds to the reference that Awaruite (Fe_1Ni_3) crystal phase BCC shaped with d[Å] = 1,202 and 1,102, Tetrataenite (Fe_2Ni) FCC-shaped crystal phase with d[Å] = 1,887, Tetrataenite ($FeNi_2$) FCC-shaped crystal phase with d[Å] = 1,285, Tetrataenite (FeNi) FCC-shaped crystal phase

with d[Å] = 1,630 and 1,588, Tetrataenite (FeNi) BCC-shaped crystal phase with d[Å] = 1,768 [8].

Then for the X-ray diffraction pattern in **Figure 8b.** This indicates that a single dilated peak located at 2θ = 20.06301° can be well defined by the presence of a crystalline region dispersed in an amorphous medium (polyaniline amorphous properties). The ring plane of benzinoid and quinoid groups in the polyaniline chain serves for the determination of crystal structure [8]. The peak detected in the XRD pattern of polyaniline synthesis is one of the main peaks in the reference polyaniline diffraction pattern at 2θ = 21.1007° and 23.5995° [10]. The above X-ray diffraction pattern also shows two sharp peaks that are at 2θ = 44.4950°; d[Å] = 2.03455; hkl = 111 has a crystal phase ɣ-(Fe,Ni) in fcc shape and 2θ = 51.8901°; d[Å] = 1.76065; hkl = 200 has a crystal phase α-(Fe,Ni) in the form of BCC can be well defined the presence of crystalline regions formed due to the formation of Fe/Ni alloys in synthesis. The powder composition contained in detect consists of Awaruite ($Fe_{1.00}Ni_{3.00}$) 8.9%, Tetrataenite ($Fe_{2.03}Ni_{1.97}$) 10.9%, Tetrataenite ($Fe_{1.00}Ni_{1.00}$) 5%, and also detected several percent impurities. This corresponds to the reference that Awaruite (Fe_1Ni_3) crystal phase BCC shaped with d[Å] = 1,202 and 1,102, Tetrataenite (Fe_2Ni) FCC-shaped crystal phase with d[Å] = 1,887, Tetrataenite ($FeNi_2$) FCC-shaped crystal phase with d[Å] = 1,285, Tetrataenite (FeNi) FCC-shaped crystal phase with d[Å] = 1,630 and 1,588, Tetrataenite (FeNi) BCC-shaped crystal phase with d[Å] = 1,768 [9].

Thus it can be concluded that the Fe/Ni alloy layer in polyaniline layered Fe/Ni alloy (PANI-Fe/Ni) with a potentiostatic method with a potential difference of -1.2 V for 120 minutes has been successfully formed because in the pattern of X-ray diffraction there are two distinctive peaks of the Fe/Ni alloy.

This test aims to strengthen the detection of the presence of Fe and Ni levels in the sample so that the truth can be confirmed that PANI-Fe/Ni samples that have been successfully formed contain Fe/Ni alloys. **Tables 4 and 5.** Below shows data on the absorption of atomic absorption spectrophotometry from PANI-Fe/Ni formed by a potentiostatic method at a potential difference of -1.2 V for 120 minutes.

Table 4. Table of AAS Absorbance Values of Fe Elements in PANI-Fe/Ni

Concentration of Fe Solution	Absorbance
Standard 0.5 ppm	0.1046
Standard 1 ppm	0.1402
Standard 2 ppm	0.3710
$PANI_{(potensiostatik)}$-Fe/Ni	0.1999
$PANI_{(galvanostatik)}$-Fe/Ni	0.2155

Table 5. Table of AAS Absorbance Values of Ni Elements in PANI-Fe/Ni

Concentration of Ni Solution	Absorbance
Standard 0.5 ppm	0.1360
Standard 1 ppm	0.2513
Standard 2 ppm	0.4646
$PANI_{(potensiostatik)}$-Fe/Ni	0.2396
$PANI_{(galvanostatik)}$-Fe/Ni	0.2125

Data from measurements using AAS showed the value of Fe and Nilevels in the sample of PANI-Fe/Ni synthesis results, namely the concentration of Fe levels in $PANI_{(pot)}$-Fe/Ni is 1.1912 ppm, the concentration of Fe levels in $PANI_{(gal)}$- Fe/Ni is 1.2219 ppm, the concentration of Ni levels in $PANI_{(pot)}$-Fe/Ni is 0.8288 ppm, and the concentration of Ni levels in $PANI_{(gal)}$-Fe/Ni is 0.8392 ppm. Based on the discussion of AAS results data above it can be concluded that PANI-Fe/Ni has been successfully formed. Polyaniline was successfully utilized as a substrate in Fe/Ni alloy electrodes.

4. Conclusion

Polyaniline was successfully synthesized using electrodeposition methods. The FTIR characterization shows a distinctive peak of a quinoid function group at a wavenumber of 1596.16 cm^{-1}. The typical diffraction pattern of polyaniline using XRD was detected at peaks of 2θ 21.10° and 23.59°. The polyaniline shows a surface morphological characteristics indicating their grows in a stacked and irregular manner and has a high conductance. The results of the Fe/Ni Electrodeposition process when viewed using SEM cause the polyaniline surface morphology to be covered by a Fe/Ni alloy by having an elemental composition from the EDS test data, namely iron (Fe) 68.15% and nickel (Ni) 24.83%. Fe/Ni levels from AAS data attached to $PANI_{(pot)}$-Fe/Ni are 1.19 ppm and 0.82 ppm; in $PANI_{(gal)}$-Fe/Ni are 1.22 ppm and 0.83 ppm.

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