Electrodepolymerisation of polyaniline film for use as an electrode in FeNi alloy electrodeposition

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Abstract. Polyaniline can be used as an electrode because it is a conductive polymer whose conductivity can be adjusted through a doping-dedoping process. This study aimed to synthesise polyaniline film for use as a substrate for Fe-Ni alloy electrodeposition. A polyaniline layer was synthesised using the galvanostatic technique with a current of 1 mA in three-electrode cells. The results of Fourier transform infrared analysis showed that the deposit formed was the emeraldine salt phase of polyaniline. The formation of a polyaniline deposit was confirmed by differential scanning calorimeter and X-ray diffractometer. The scanning electron microscope micrograph showed that the layer growing on the substrate was porous polyaniline, which had uniform morphological characteristics. This polyaniline was used as a substrate in the electrodeposition of FeNi alloys and produced a uniform silvery layer even though it grew above the porous substrate.

1. Introduction
Electrodeposition is widely used for material synthesis in the form of thin layers. Polymers, metals and alloys can be deposited using electrodeposition techniques. The properties of materials obtained using these techniques are determined by the reaction conditions and types of precursors used [1–3]. Also important in the mechanism of deposition is the substrate used as a host material, in this case, the working electrode, where the deposit grows [4–6]. Therefore, substrate selection is one of the essential factors in producing deposits with the characteristics needed. At present, materials often used as substrates include platinum [5], gold [6], copper [7], and indium tin oxide (ITO) [8,9]. Substrates made from metal, besides having a heavyweight, are expensive. This has become a challenge in synthesising materials using electrodeposition techniques from the process and technology side, also known as the low-cost method. Polymers are lightweight and low cost. Decades ago, polymers like polyaniline were developed as conductive materials giving them the potential to be used as electrodes. The electrical conductivity of polyaniline can be adjusted through a doping-dedoping process [10]. Apart from being conductive, polyaniline also has high thermal stability [11], so it can support applications in the fields of sensors, membranes, electronics, electricity and electromagnetism. It can be synthesised through electrodeposition or oxidative polymerisation [12-14]. The synthesis of polyaniline through oxidative polymerisation requires many reagents and is inefficient for industrial use because it produces much
waste. In contrast, the electrodeposition method, which is known as the electropolymerisation method in polymer preparation, is a fast and efficient technique that can produce adherent polyaniline [15].

In this study, a layer of polyaniline conductive polymer was synthesised using an electrodeposition technique. The layer was then used as a substrate in the electrodeposition of FeNi. Alloys of FeNi are magnetic materials that can be used in high-temperature thermomagnetic power generation [16]. Elemental and morphological analysis confirmed that a FeNi layer could be deposited evenly over a polyaniline layer. The results of this study indicated that a conductive polymer-based substrate synthesised using electrodeposition is a lightweight and inexpensive alternative for use in magnetic alloy electrodeposition.

2. Materials and Methods
The materials used in this study were hydrogen peroxide (35%), sulfuric acid (98%), aniline (99%) nickel sulphate heptahydrate, iron sulphate hexahydrate, and boric acid purchased from PT. Merck Indonesia. The solution was prepared using double-distilled water. For electrodeposition, three-electrode cells with Ag/AgCl were used as reference electrodes, and platinum wire was used as the counter electrode. Polyaniline was prepared using galvanostatic techniques with a current range of 1 mA controlled using eDAQ Modular Potentiostat EA163 models. A 304 stainless steel (SS 304) plate with a thickness of 0.2 mm and a size of 30 mm x 10 mm was used as a substrate for the electrodeposition of polyaniline. Before being used, the SS 304 plate was soaked in piranha solution for 24 h, then rinsed with double-distilled water and dried. Polyaniline electrodeposition was carried out for 5 min in 0.5 M aniline solution in 0.5 M sulfuric acid. The polyaniline layer formed was then rinsed and dried at room temperature. Electrodeposition of FeNi was carried out using a potentiostatic technique at a voltage of -1.2 above the polyaniline layer for 60 min from a solution containing 0.02 M nickel sulphate, 0.18 M iron sulphate and 0.4 M boric acid. The samples obtained were analysed using a Fourier transform infrared (FTIR) spectrometer (Shimadzu IR Prestige 21) to determine the presence of functional groups of polyaniline. Thermal properties of the material were tested using a differential scanning calorimeter (DSC; NETZSCH 200 F3 Maia). X-ray diffraction analysis was carried out using an X-ray diffractometer (XRD; PANalytical Empyrean). The morphology of the deposit was characterised using a JEOL JSM-651OLA scanning electron microscope (SEM). Elemental analysis was done using an energy dispersive X-ray (EDX) spectrometer.

3. Results and Discussion
Polyaniline deposited on the SS 304 substrate has been shown in Figure 1a. The dark green colour of the synthesised polyaniline indicated the formation of polyaniline in the form of emeraldine salt, which has conductive properties. As shown in Figure 2, SEM micrographs indicated polyaniline deposits composed of agglomerated fine particles, producing a highly porous layer. This deposit structure indicated that at the initiation stage, small droplets of polyaniline were formed on the surface of the substrate, which then formed a loose open structure [15,17].
In the FTIR spectrum shown in Figure 3, absorption peaks that showed the formation of a polyaniline deposit were clearly observed. The absorption peak at wave number 815.92 cm$^{-1}$ showed the bending of the C-H group outside the field of the para-position of the 1.4-substituted benzene aromatic ring (B-NH-B). The absorption peak at wave number 1152.52 cm$^{-1}$ showed the bending of the C-H group in the plane of quinoid nitrogen (N=Q=N) as well as aromatic ring deformation. This peak is characteristic of polyaniline and occurs due to electric charge delocalisation, which is caused by deprotonation [6]. The absorption peak at wave number 1249.93 cm$^{-1}$ showed the stretching of the aromatic C-N group of benzenoid units. The absorption peak at wave number 1314.54 cm$^{-1}$ showed the stretching of the C-N group from the quinoid unit (Q-B-Q). The absorption peak at wave number 1492.93 cm$^{-1}$ showed the stretching of C=C groups on the benzenoid unit. The absorption peak at wave number 1592.31 cm$^{-1}$ showed the stretching of a C=C group in the quinoid unit. The intensity of the peaks showed the oxidation state of the polyaniline, which was deposited in the form of emeraldine salt [7]. The absorption peak at wave number 2330.14 cm$^{-1}$ indicated the presence of air at the time of measurement. The absorption peak at wave number 3010.94 cm$^{-1}$ showed the stretching of the aromatic C-H group. The absorption peak at wave number 3490.91 cm$^{-1}$ showed the secondary stretching of the N-H group [8]. The absorption peak at wave number 3718.92 cm$^{-1}$ showed the stretching of the O-H group, which indicated the presence of water in the sample. This was because the sample was still wet at the time of measurement.
Figure 3. FTIR spectrum of deposited polyaniline

Figure 4. DSC of electrodeposited polyaniline

Polyaniline DSC thermograms (Figure 4) showed two endothermic peaks and one exothermic peak. Endothermic peaks were found at 110.6°C and 303.1°C. Endothermic peaks were observed at 110.6°C, which showed the transition of polyaniline glass. This was in accordance with literature showing that the glass transition temperature is within the range 90–120°C. The endothermic peak at 303.1°C showed the loss of dopant acid and the melting point of polyaniline. Based on previous studies, endothermic peaks showing a loss of dopant acid and the melting point of polyaniline are within the range 250–350°C. This peak corresponded to the synthesis of polyaniline, which uses sulfuric acid as a dopant. If a polyaniline chain doped by acid is arranged in a more crystalline structure, more energy will be needed to remove acid from it [9]. The exothermic peak at 213.8°C showed the crosslinking reaction of the polymer produced by the coupling of two neighbouring N=Q=N groups to two NH-B-NH groups through the N chain, which was adjacent to the quinoid ring [10]. The presence of this crosslinking reaction was supported by FTIR spectrophotometry, which detected the presence of quinoid and benzenoid groups as described above. Based on DSC and FTIR analyses, polyaniline was successfully synthesised.
Figure 5. SEM micrograph (a) and EDX spectrum (b) of the FeNi alloy electrodeposited on the polyaniline film

The SEM micrograph shown in Figure 5a shows the structure of the FeNi alloy, which was successfully deposited on the surface of the polyaniline layer. In these micrographs, parts that were not entirely covered by the FeNi layer were observed. The inequality of the layers may have been due to the high porosity of the polyaniline deposit and its non-uniform surface characteristics. The results of EDX testing confirmed the presence of Fe and Ni in deposits (Figure 5b). Semi-quantitative analysis carried out in the deposit area produced an average composition of iron and nickel at 60.59% and 39.41%, respectively. The formation of FeNi alloy deposits on the surface of the polyaniline layer showed that the polyaniline synthesised using the electropolymerisation technique can be used as a conductive substrate for metal alloy electrodeposition. This conclusion was supported by the XRD diffraction pattern (Figure 6), which showed peaks from cubic structure of FeNi alloy at 2θ 43.97°, 51.2° and 75.0° correspond to diffraction planes of (111), (002) and (022) respectively.

Figure 6. XRD pattern of FeNi alloy electrodeposited on the polyaniline film

4. Conclusion
Polyaniline was synthesised in the form of a thin layer using a galvanostatic electrodeposition technique. The synthesised polyaniline was in the emeraldine salt phase, which is a conductive and porous deposit
with uniform morphological characteristics throughout. Using this layer as an electrode showed that polyaniline synthesised using the techniques in this study can be used as a substrate for the electrodeposition of FeNi alloys. This study has provided a lightweight and low-cost alternative substrate for use in metal alloy electrodeposition.

5. References
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