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Preparation and Characterization of Nano Size NiOOH by Direct Electrochemical Oxidation of Nickel Plate

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Nickel oxyhydroxide (NiOOH) had been produced by direct electrochemical oxidation of nickel (Ni) plate in 0.1 M potassium hydroxide (KOH) solution. Ni plate was used as a working electrode, while four different metals, copper (Cu), gold (Au) and nickel (Ni) plates and platinum (Pt) wire were used as a counter electrodes. A black precipitation which was proportional with the working electrode decay was produced after a few hours of oxidation process. The product formed was then dried and characterized using X-ray Photoelectron Spectroscopy (XPS), X-ray Diffractometer (XRD), Thermal Gravimetric Analysis (TGA) and Energy Dispersive X-ray (EDX). Field Emission Scanning Electron Microscopy (FESEM) was used to measure the particle size of the product. The characterization results confirmed that the compound synthesized was a nano size NiOOH.

Keywords: NiOOH, auxiliary electrode, particle size, characterization

1. INTRODUCTION

NiOOH has been widely used in rechargeable battery where charge and discharge reaction for active ingredient in the rechargeable battery occurred according to the following reaction [1]:

$$\mathrm{NiOOH + H_2O + e} \underset{\textit{charge}}{\overset{\textit{discharge}}{\rightleftarrows}} \mathrm{Ni(OH)_2 + OH^-}$$

Recently, a method to obtain a high purity NiOOH was successfully produced by oxidation of spherical $Ni(OH)_2$ in alkaline medium involving one step electrolysis [2, 3]. A mixtures of $Ni(OH)_2$

and graphite together with polytetrafluoroethylene (PTFE) has been used as a working electrode while platinum was used as a counter electrode in various concentration of KOH solution as supporting electrolyte. Further study was then carried out and NiOOH was successfully produced, where various concentration of $KMnO_4$ as catalyst was mixed together with $Ni(OH)_2$ in NaOH solution, foam nickel was used as anode and cathode [4]. A method used to generate β-NiOOH was carried out by mixing together $Ni(NO_3)_2$ and KOH with Br_2 which β and γ crystal were formed. The redox reaction for the conversion of β Ni(II) to Ni(III) are shown below [5, 6]:

$$Ni^{II}(OH)_2 \leftrightarrow Ni^{III}O(OH) + H^+ + e^-$$

A simple and a different method compare to the earlier studies was then carried out where, NiOOH was produced by electrooxidation process of Ni metal plate by the following reaction:

$$Ni \rightarrow Ni(OH)_2 \rightarrow NiOOH$$

Ni metal was oxidized to NiOOH directly without catalyst utilization. Therefore this paper will reported a cleaner and pollution free technique in NiOOH preparation due to no oxidants and catalyst consumed in the process. Ni metal was used as a working electrode while various metals such as Pt, Au, Cu and Ni itself were used as a counter electrode. KOH solution had been used as supporting electrolyte throughout.

2. EXPERIMENTS

2.1 Reagent

Standard KOH solution was prepared by directly dissolved KOH salt (R & M Chemicals) in deionized distilled water.

2.2 Electrode preparation

Ni plate (99.99%, Aldrich Chemical Company) with the thickness of 0.15 mm was cut into 2 cm x 10 cm plate and used as a working electrode (anode). As a counter electrodes, Au with a thickness of 0.5 mm was cut into 1 cm x 1 cm square, Cu and another Ni plates with the thickness between 0.15 – 0.5 mm were cut into 2 cm x 1 cm pieces and Pt wire were used throughout. The counter electrode (cathode) was prepared with a slight modification of a method as published before [6]. The metal was then attached to a silver wire and sealed in a glass rod. Silver conductive paint was then used to glue the wire onto the metals surface of the metals plate. Subsequently, epoxy glue was applied to cover the silver wire connecting surface.

2.3 Electrochemical oxidation process

CPX 200 DUAL 35V 10A PSU power supply completed with connecting wire was used as a power supply. All experiments were carried out at room temperature. The electrosynthesis was performed using a two electrodes system, Ni plate has been used as working electrode (anode), while various metal plate (Au, Cu and Ni and Pt) were used as a counter electrode (cathode) and 0.1 M KOH as a reaction medium. The setup was contained in a single undivided electrochemical glass cell with capacity of 50 mL. High purity nitrogen gas was used to deaerate the sample and reactor environment for at least 10 minutes prior to each run to maintain a nitrogen blanket during the oxidation process. The electrosynthesis was then performed using those two electrodes system for 6 hours. The black precipitate obtained was then rinsed with deionized water to remove all traces of KOH and dried at a room temperature for further characterization.

2.4 Characterization of NiOOH produced

The dried product was characterized using X-ray Photoelectron Spectroscopy, XPS (Kratos Analytical Digital 500, Glassman High Voltage Inc.), X-ray Diffractometer, XRD (model Philips X-ray Diffractometer with Ni filter CuKα 40 kV radiation), Thermal Gravimetric Analysis, TGA (Mettler Toledo model STGA/SDTA851), Energy Dispersive X-ray, EDX and Field Emission Scanning Electron Microscopy, FESEM. FESEM and EDX were performed on the Zeiss microscope model Supra 55VP to examine the morphology and elements composition of the electrode surface. Au metal was used for sputtering process. Conductivity study was carried out using impedance analysis method by mean of Electrochemical Impedance Spectroscopy (EIS) AC current model SI 1255 complete with High Frequency Resonance Analyzer (HFRA) and electrochemical interface, Solartron Schlumberger SI 1286 model.

3. RESULTS AND DISCUSSION

3.1 Preparation of NiOOH

Results obtained shows that aeration process with nitrogen was needed to ensure that the reacted solution and whole cell or the reactor was under inert condition as it was necessary because there will be unwanted (greenish participate) oxidation product obtained without the deaeration process. This indicates that the availability of dissolved oxygen in the solution will inhibit the reaction process for the production of NiOOH. From the observation, OH^- was required for the oxidation process to occur. A greenish product {probably $Ni(OH)_2$} was also being produced if divided cell was used to separate between anode and cathode. Assuming that the electrons are needed to flow the current between the salt bridge make it is not enough for the oxidation process for the working electrode. Table 1 summarised the optimum operating condition for the optimum NiOOH produced at a minimum time period.

Table 1. Optimum operating conditions

Working electrode	Nickel plate
Auxiliary electrode	Platinum
Supporting electrolyte	Potassium hydroxide
Voltage	30 Volts

As already discuss elsewhere, the preparation of the NiOOH by one step electrolysis process involving the losing of an electron from the anode surface of $Ni(OH)_2$ [7]. The same process may also occurred during the oxidation process of Ni metal plate. During the electrooxidation process, it was observed that the reaction occurs very vigorously, however as the gas emitted from both anode and cathode were tested, they were neither hydrogen nor oxygen, the most possible bubble produced at both anode and cathode are water vapor, as the electrode become hotter due to high voltage applied. The total reaction at cathode may be written as follows as they were sign of oxidized product (black color compound) on the electrode surface at the beginning of oxidation process.

$$Ni + 3OH^- \rightarrow NiOOH + H_2O$$

After a few hours of electrolysis, the black compound started to precipitate at the bottom of electrochemical cell with the decay of the anode surface. During electrolysis, the formation of the black product was much faster when Au and Pt were used compared to Cu and Ni as a counter electrodes or cathode. The reaction also more vigorously occurred when the earlier metals were used as a counter electrode.

3.2. Characterization of the electrooxidation product

The prepared NiOOH green nano-material were characterized using XPS, XRD, EDX and TGA while FESEM was used to determined the morphology and individual particle size.

Table 2. Binding energy (eV) of Ni $2p_{3/2}$ from experimental result and references

Compound	This Experiment	References	
		[8]	[9]
NiOOH	858.043	858.2 ± 0.2	856.1 - 861.7

XPS (X-Ray Photoelectron Spectroscopy): Characterization worked carried out using XPS conformed that the compound formed in the electrooxidation process of nickel plate in alkaline medium (KOH) was NiOOH. XPS narrow scan spectrum for $Ni2p_{3/2}$ and O1s was as shown in Figure 1 and Figure 2. NiOOH is determined by using binding energy recorded from the XPS spectrum. The binding energy for Ni2$p_{3/2}$ obtained from this experimental data was also compared with standard data from various references and the results were summarized in Table 2.

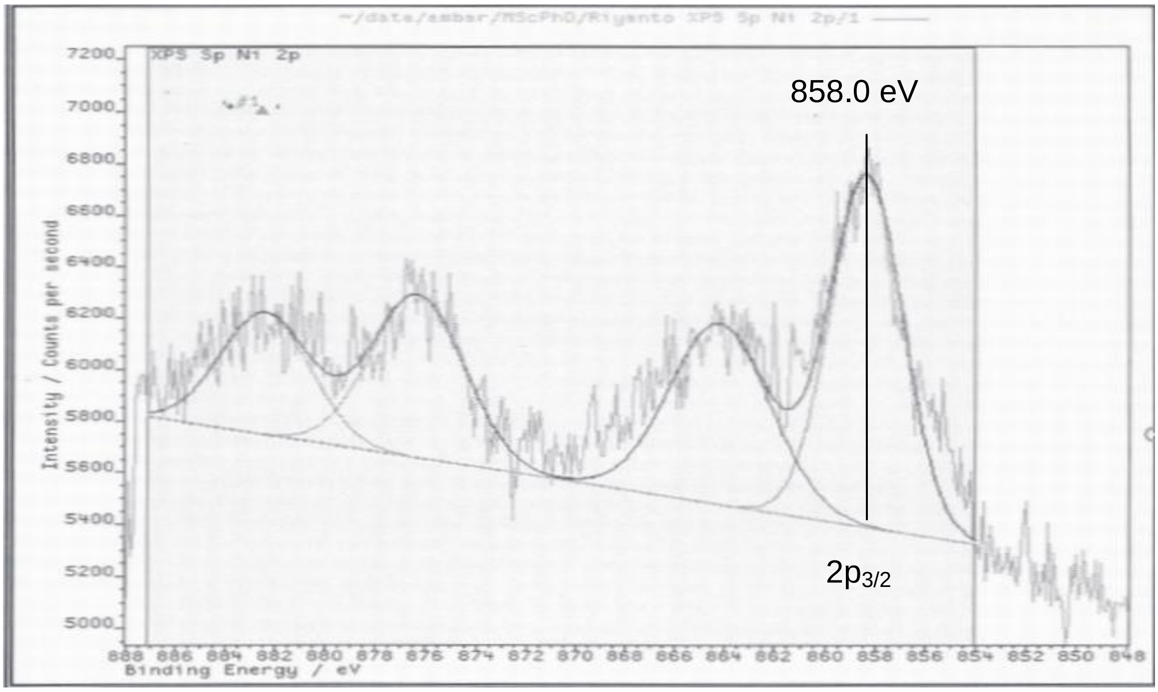


Figure 1. Ni2$p_{3/2}$ XPS spectrum for NiOOH

Figure 1 showed that Ni 2$p_{3/2}$ binding energy was 858.043 eV. Based on binding energy data in Table 2, compounds which possess binding energy of 858.043 eV was NiOOH [8, 9]. The results was supported by Schulze and Gulzow which states that binding energy of 852.3 eV in Ni 2$p_{3/2}$ is related to nickel metal, binding energy of 853.3 eV is related to NiO, while binding energy for NiOOH is 858.1 eV [10]. Figure 2 shows the O1s XPS spectrum for NiOOH. Binding energy for O1s was 533.680 eV. Binding energy of 533.680 eV for O1s was related to NiOOH [11].

Table 3. 2θ angle data from XRD spectrum

This experiment	Barnard et al. [12]
14.225^{o}	12.6^{o}
25.829^{o}	25.4^{o}
43.326^{o}	43.0^{o}
64.993^{o}	$65\text{-}68.0^{o}$

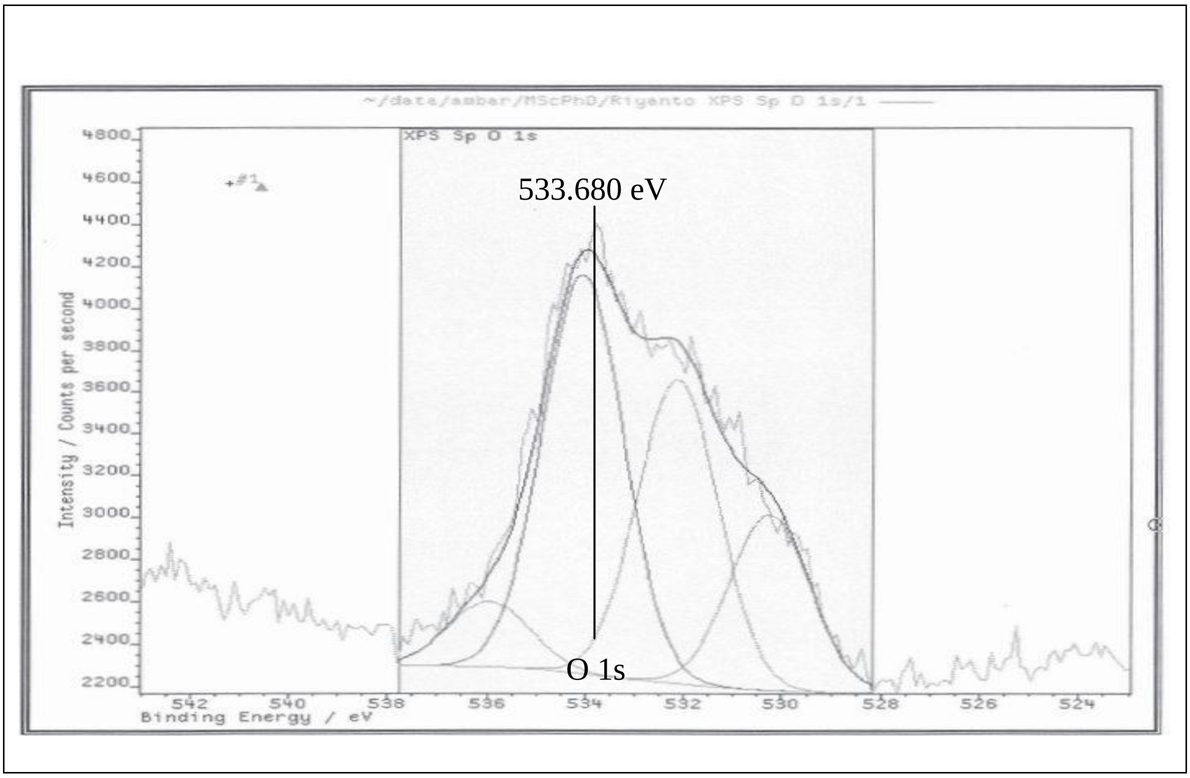


Figure 2. Ni O1s XPS spectrum for NiOOH

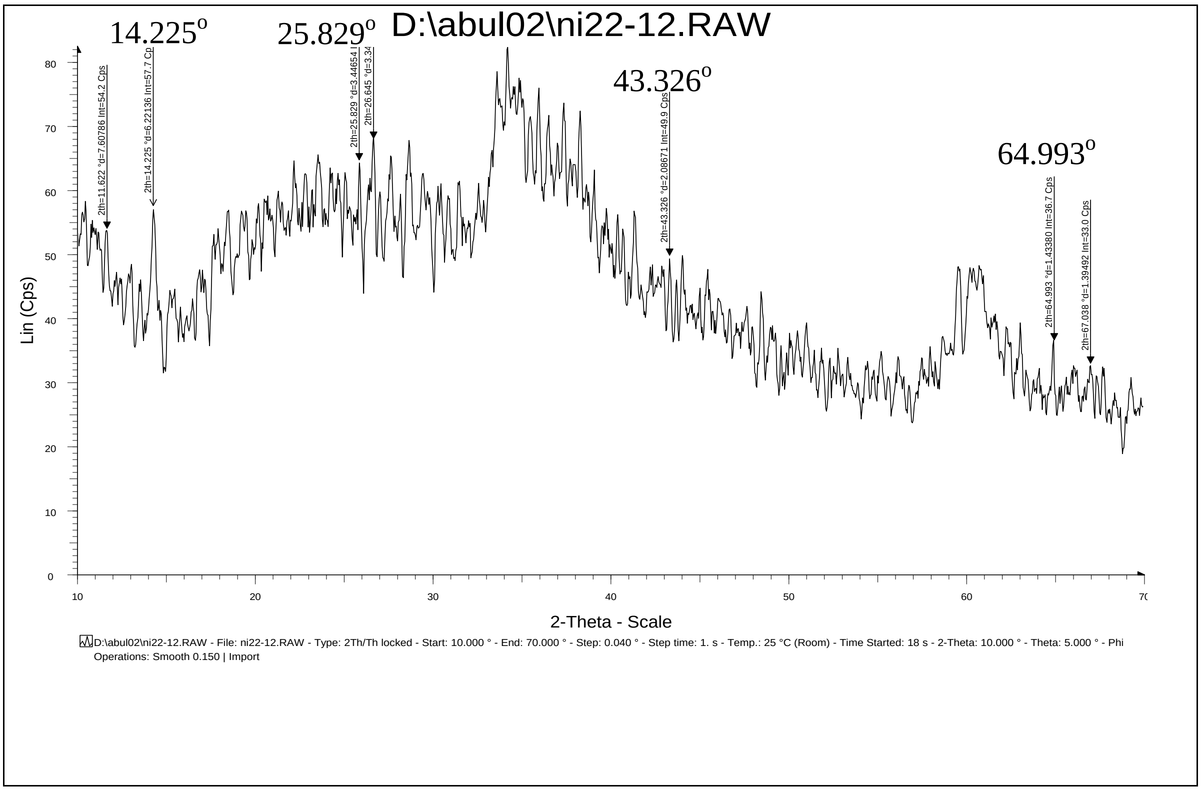


Figure 3. NiOOH XRD spectrum for NiOOH produced

XRD (X-Ray Diffractometer): XPS result was supported by data obtained in XRD analysis. XRD spectrum for NiOOH synthesized was shown in Figure 3. XRD analysis is based on 2θ angle. Comparison between XRD data for 2θ angle between experimental results with data reported by other researcher is as summarized in Table 3 [12]. Table 3 contain 2θ angle specific for NiOOH. Although there is some differences, however it was significant. A 2θ angle for NiOOH was 12.6^o, 25.4^o, 43^o and 65-68^o with CuKα ray [12]. Low peak intensity obtain from XRD spectrum shows that the NiOOH obtained from the electrosynthesis have an amorphous structure.

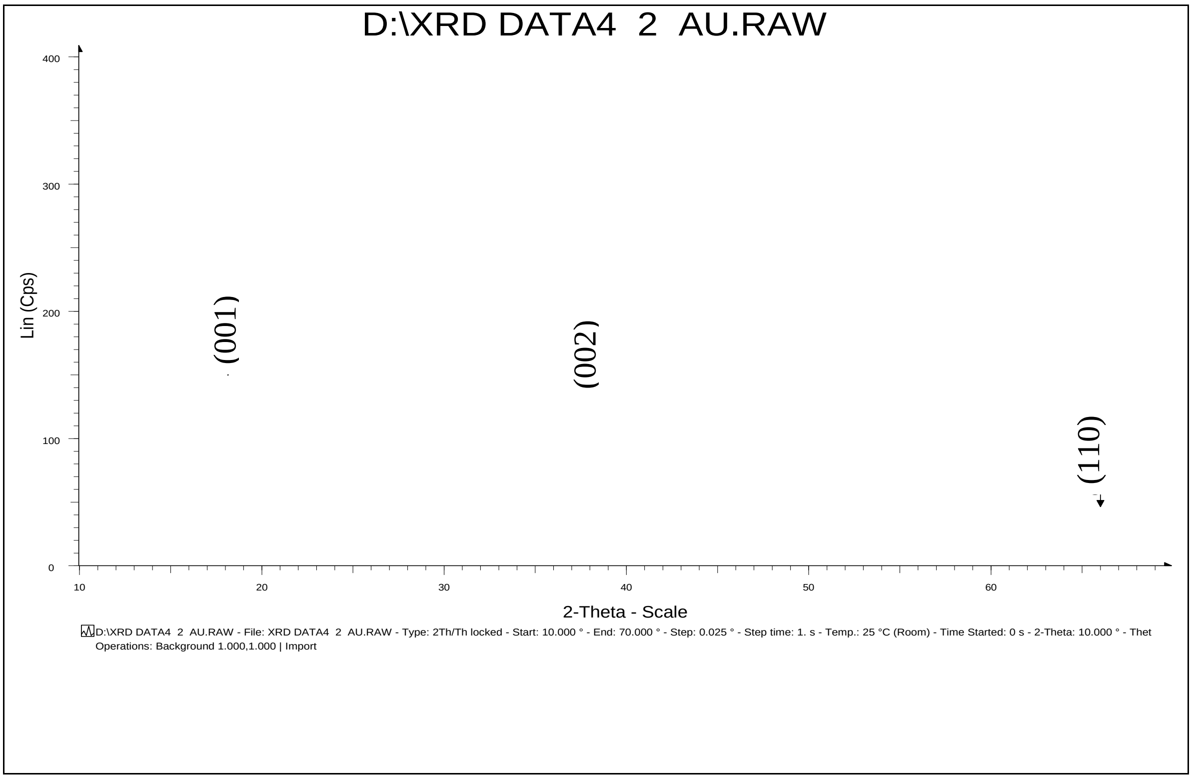


Figure 4. XRD pattern of the NiOOH sample prepared by oxidation of Ni plate

Figure 4 illustrates the XRD pattern of the NiOOH sample prepared by oxidation of Ni plate . By referring to the Joint Committee of Powder Diffraction Standard (JCPDS 6-0141), this diffraction peak corresponds to (001), (002) and (110) crystal face of NiOOH, indicating that the product is β-NiOOH.

TGA: Characterization of NiOOH using thermal gravimetric analysis (TGA) was as demonstrated in Figure 5. Water loss in material surface occurs at 0 to 120 ^{o}C (a). On the other hand, water loss between β-NiOOH layer occurred at 120 to 280 ^{o}C (b). While β-NiOOH decomposition temperature originated from 280 to 400 ^{o}C (c) based on β-NiOOH decomposition equation below, NiO residue present at 400 to 600 ^{o}C (d).

$$2\beta\text{-NiOOH} \rightarrow 2\text{NiO} + \tfrac{1}{2}\text{O}_2 + \text{H}_2\text{O}.$$

EDX (Energy Dispersion X-Ray): EDX was used to analyze elements composition on the surface of electrosynthesis product. EDX spectrum and data of NiOOH produced using Ni and Cu as an auxiliary electrode shows that elements obtained on surface were C, O, Ni and Au, with the addition of K element when Au and Pt used as auxiliary electrodes (Figure 6). The presence of C was probably effected from impurity and K from electrolyte (KOH) used while Au was used as coating material. O and Ni elements representative NiOOH and as a result, EDX able to support others characterization techniques (XPS, XRD and TGA).

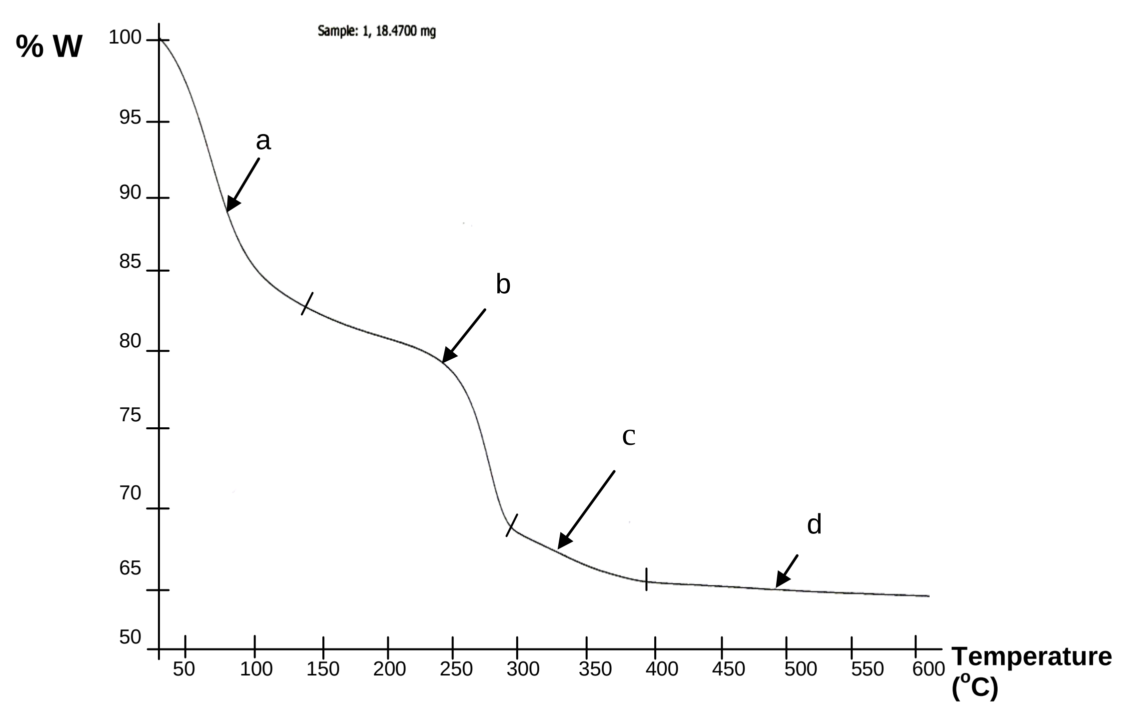


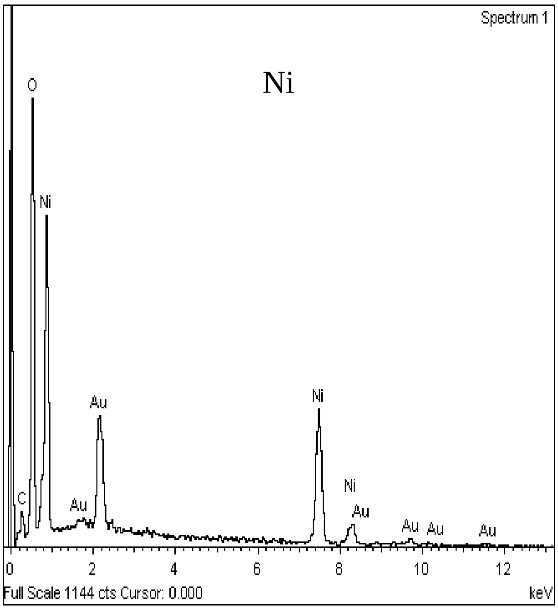
Figure 5. TGA of NiOOH produced

FESEM (Field Emission Scanning Electron Microscope): FESEM was used to measure the particle size of NiOOH produced. FESEM micrographs of NiOOH that produced by elctrooxidation process were shown in Figure 7. Different particle size was obtained when different counter electrodes were used. The average of NiOOH particle size obtained was 26.8, 22.26, 27.34 and 23.04 nm when Ni, Pt, Au and Cu were used as a counter electrodes respectively. Based on the result obtained, indicated that the different in the average of particle size was not significant and particles of NiOOH formed was agglomerated probably due to hydrated samples. The result may explains that the used of different auxiliary electrodes does not affected the particle size of NiOOH produced.

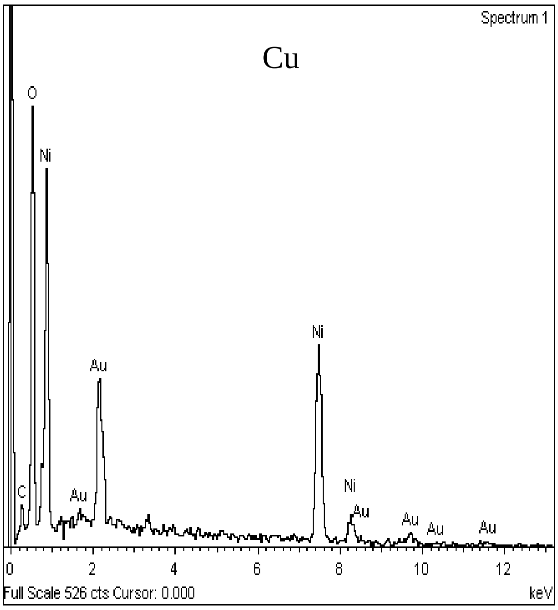
Conductivity study: For conductivity study, NiOOH was mixed with little amount of PVC with a ratio of 95:5 (w/w) used to make an electrode using an electrode preparation technique as previously reported [6, 13]. The conductivity of NiOOH-PVC electrode (diameter = 13 mm, thickness = 0.2 mm, containing 95% NiOOH and 5% of PVC, weigh portion) was determined using an impedance analysis method using Electrochemical Impedance Spectroscopy (EIS) AC current model SI 1255 complete with High Frequency Resonance Analyzer (HFRA) and electrochemical interface, Solartron Schlumberger SI 1286 brand. Based on the impedance plot obtained (Figure 8), resistant value obtained was incorporated into conductivity equation as shown below:

$$\sigma = l/AR \; ;$$

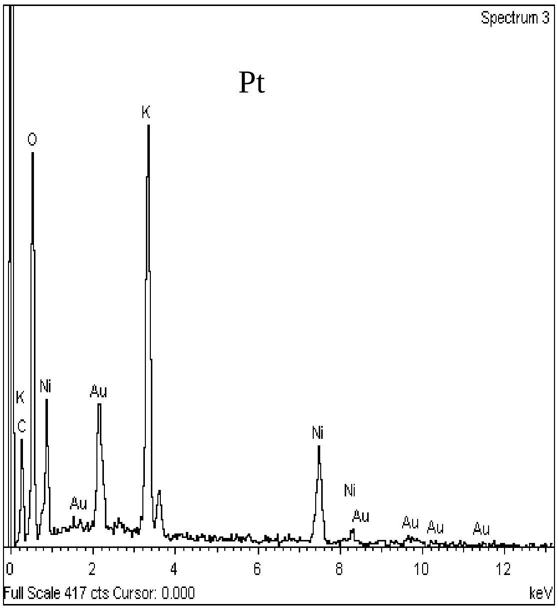
where σ, *l, A and R* are conductivity, length/diameter, area and resistance respectively.



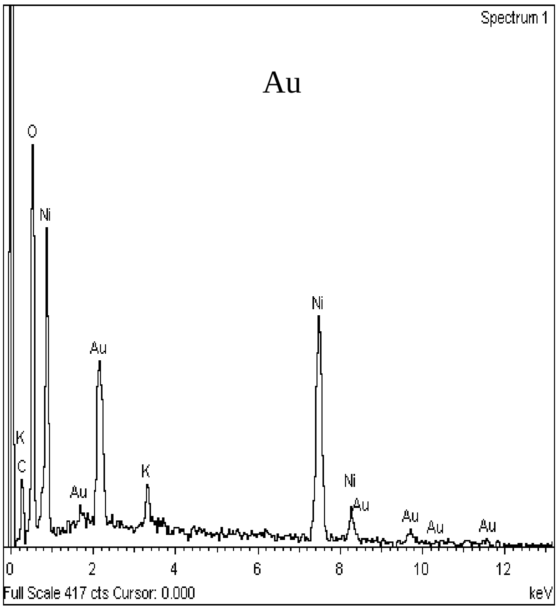
Element	Weight %	Atomic %
C	4.05	10.84
O	29.48	59.21
Ni	49.74	27.22
Au	16.74	2.73



Element	Weight %	Atomic %
C	3.90	11.60
O	22.55	50.38
Ni	57.70	35.14
Au	15.86	2.88



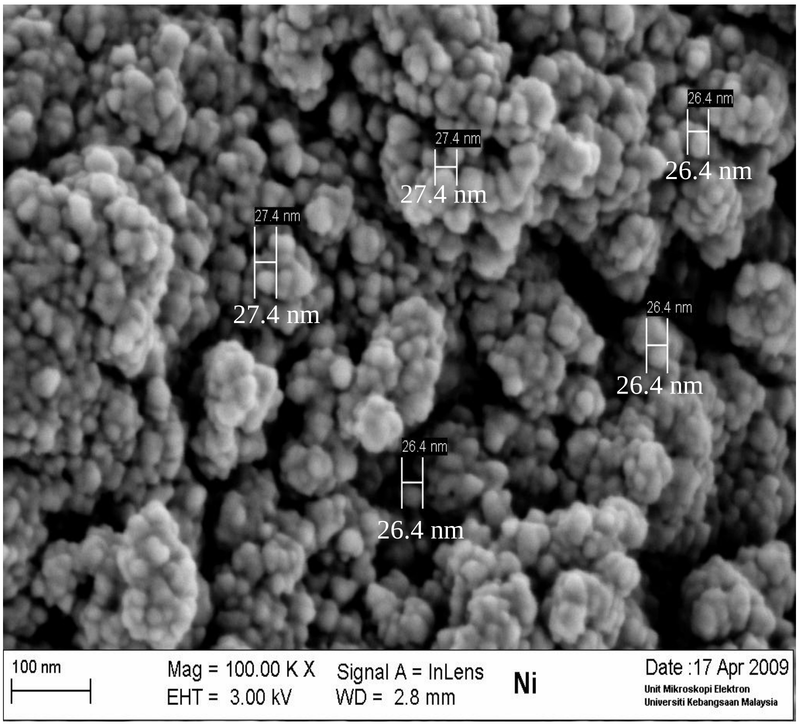
Element	Weight %	Atomic %
C	6.45	14.88
O	32.41	56.09
K	19.82	14.03
Ni	27.74	13.09
Au	13.58	1.91

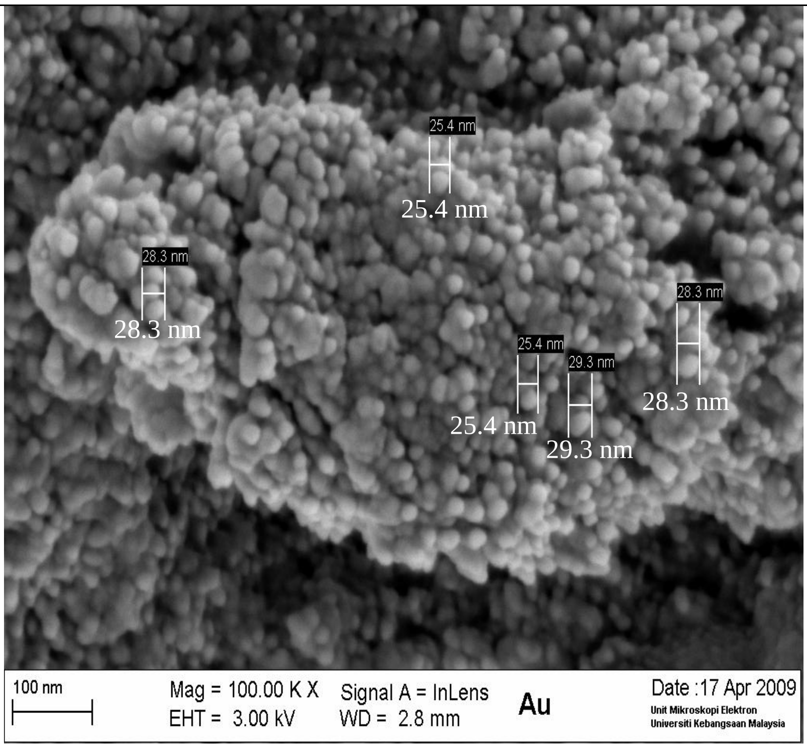


Element	Weight %	Atomic %
C	8.33	23.13
O	20.17	42.07
K	1.53	1.31
Ni	54.25	30.83
Au	15.72	2.66

Figure 6. EDX spectrums and data of NiOOH produced using Ni, Au, Pt and Cu as auxiliary or counter electrodes

Frequency range used in this method is 10 mHz – 100 mHz with 10 mV vibration amplitude. After calculated, conductivity for NiOOH-PVC is 6.1×10^{-1} Sm^{-1}, which could be consider as a good conductor.


26.4 nm
27.4 nm
27.4 nm
26.4 nm
26.4 nm
100 nm
Mag = 100.00 K X
EHT = 3.00 kV
Signal A = InLens
WD = 2.8 mm
Ni
Date :17 Apr 2009
Unit Mikroskopi Elektron
Universiti Kebangsaan Malaysia


25.4 nm
28.3 nm
28.3 nm
25.4 nm
29.3 nm
100 nm
Mag = 100.00 K X
EHT = 3.00 kV
Signal A = InLens
WD = 2.8 mm
Au
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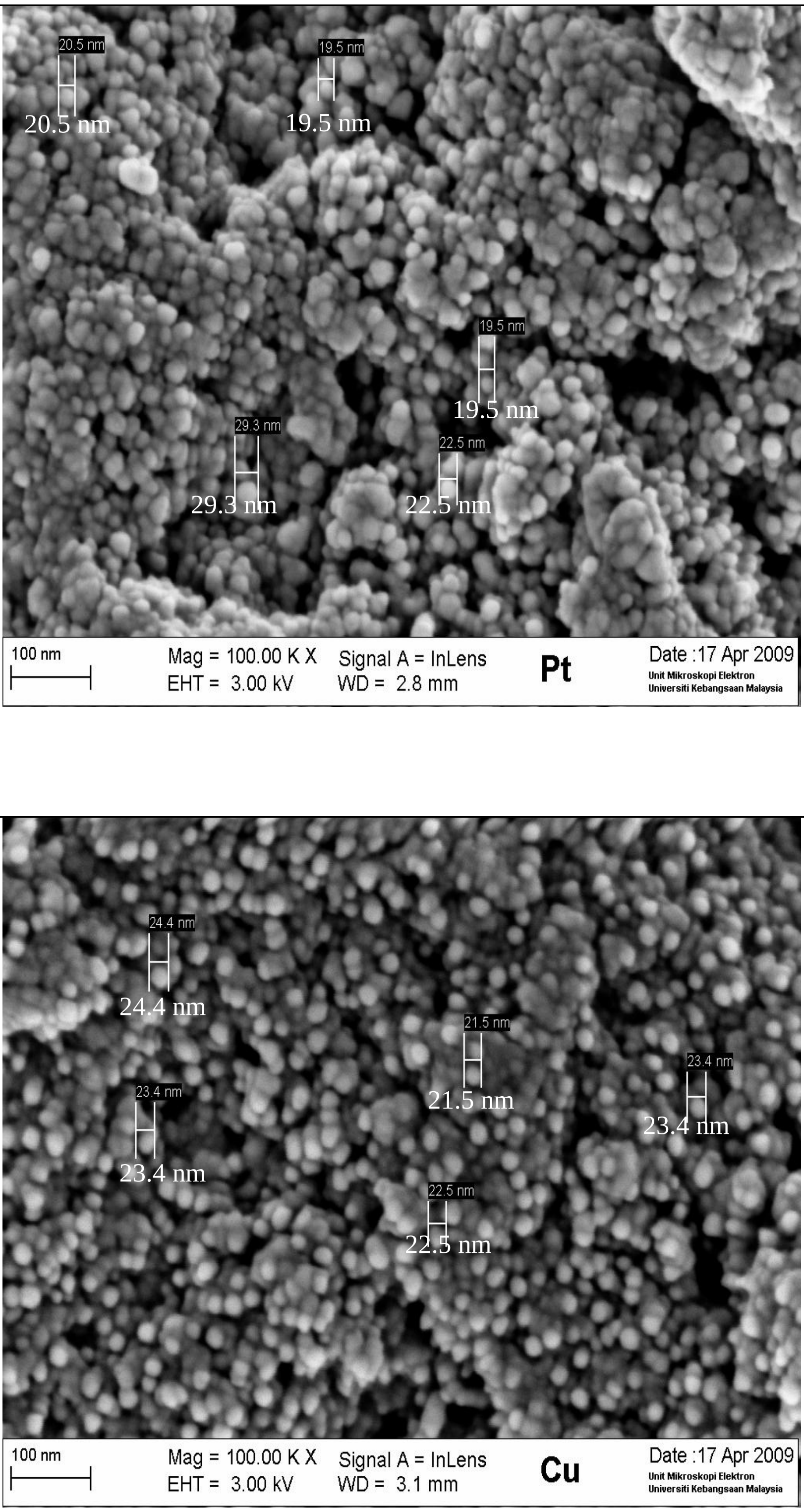

Figure 7. FESEM micrograph of NiOOH produced using Ni, Au, Pt and Cu as an auxiliary or counter electrodes respectively

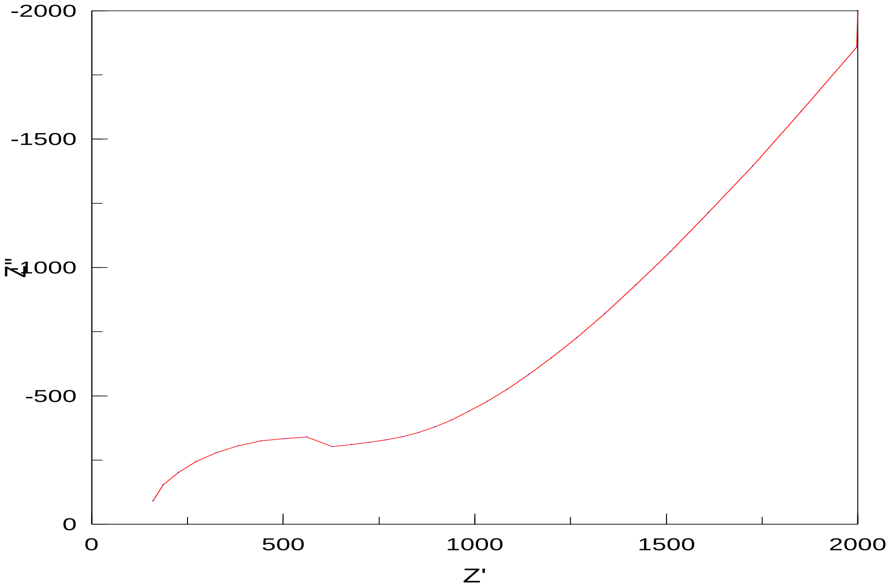

Figure 8. Impedance plot for NiOOH-PVC

4. CONCLUSION

Characterization results using XPS, XRD and TGA have proved that a black precipitate product produced from the electrooxidation of Ni plate in alkaline media was high purity NiOOH. Study of surface morphology by FESEM shows that the results obtained was a nano size NiOOH.

ACKNOWLEDGMENTS

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