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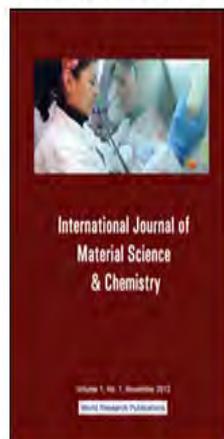Prof. Marco Nemesio
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# Electrosynthesis and Characterization of Nickel Hydroxide (Ni(OH)2)

**Authors:** *Mohamed Rozali Othman and Riyanto*

**Keywords :** *Electrosynthesis; nickel hydroxide; XPS, XRD, Cyclic Voltammetry.*

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## ABSTRACT

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# Electrosynthesis and Characterization of Nickel Hydroxide (Ni(OH)$_2$)

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Electrosynthesis of Ni(OH)$_2$ by electrochemical method followed by characterization process using X-Ray Photoelectron Spectroscopy (XPS), X-Ray Diffraction (XRD) and Cyclic Voltammetry (CV) has been carried out. Preparation of Ni(OH)$_2$ has been carried out by electrolysis in 0.1 M KOH using Ni sheet as working electrode, Pt sheet as counter electrode and SCE as reference electrode. Electrolysis at potential constant 0.3 V and electrolysis time 6 h yielded a green Ni(OH)$_2$ compound formed on the surface on Ni sheet electrode. The cyclic voltammetry test indicates that the cycling process of Ni(OH)$_2$ is a quasi-reversible process and pure compound. Based on analysis using XPS and XRD techniques, compound formed was proved to be pure Ni(OH)$_2$.

**Key words**: Electrosynthesis; nickel hydroxide; XPS, XRD, Cyclic Voltammetry

## INTRODUCTION

A nickel hydroxide electrode was useful in an alkaline secondary battery. Nickel hydroxide which has been used as a positive electrode active material of alkaline storage batteries inherently has a very low electric conductivity, but it is converted to a trivalent nickel oxyhydroxide having a somewhat higher conductivity by charging. The electrical conductivity of nickel hydroxide, which is the active material of the paste type positive electrode, varies with a variation on oxidation number of nickel. The oxidation of nickel hydroxide in charging process of a battery thus proceeds smoothly, but the reduction in discharging process does not proceed smoothly, due to the lowered electrical conductivity in the terminal stage of discharging process (Gille et al., 2002).

Nickel hydroxide is used as a premium product in certain catalyst formulation, in batteries and in pigment applications. Due to recent developments in the electronics industry, the demand for portable electronics such as wireless phones, camcorder and portable computers has greatly increased. In accordance with this trend, the demand for batteries has likewise increased. As electronic devices are getting smaller and lighter with increasingly demanding performance requirements, a battery with high energy density and high capacity is needed. In response, great advances in the performance of Ni-Cd and lead acid batteries have been realized. However, as a result of cadmium and lead being known pollutants, environmental concerns have increased

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regulation on the use of these materials. Therefore, there is a significant need for the development of a pollution free rechargeable battery. An increase in the regulation of vehicle emission has also increased the need for development of a pollution free vehicle (Yeo and Johnson, 2001).

Nickel hydroxide is commonly used as an active material for nickel positive electrodes in Ni-based rechargeable batteries, electrochromic devices and as promising catalyst for oxygen evolution reaction (OER). Some properties of nickel hydroxide electrodes (such as high power density, very good cyclability and high specific energy) have made them very viable for an extended range of applications. It is reported that there are four phases produced over the lifetime of a nickel hydroxide electrode, namely, α-Ni(OH)$_2$, γ-NiOOH, β-NiOOH and β-Ni(OH)$_2$ (Shen and Xu, 2006; Kibria and Taradfar, 2002) and the electrochemical reactions of nickel hydroxide can be shown simply by:

$$\alpha\text{Ni(OH)}_2 \rightleftharpoons \gamma\text{NiOOH} + H^+ + e^-$$

$$(1)$$

$$\beta\text{Ni(OH)}_2 \rightleftharpoons \beta\text{NiOOH} + H^+ + e^-$$
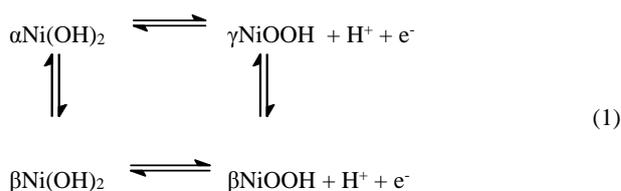
Rechargeable batteries which meet these needs include Ni-MH (metal hydride) batteries, Ni-Fe batteries and Ni-Zn batteries. These batteries replace the cadmium negative electrode in a

conventional Ni-Cd battery with metal hydride, Fe and Zn respectively. Since these batteries are pollution free and have higher theoretical capacities than Ni-Cd batteries, they are the current focus of research and development. A nickel hydroxide electrode which is used in the conventional Ni-Cd battery is also used as the positive electrode in these rechargeable batteries. The development of high capacity nickel hydroxide electrodes is a key to the feature commercialization of these rechargeable batteries (Bagotsky, 2006).

The properties of nickel hydroxide used as an active material in a nickel hydroxide electrode differ depending on the production method. Generally, nickel hydroxide is produce using the neutralization method in which nickel salt and hydroxide salt are mixed and then a small amount of water is added. The precipitate particles are so coarse and their size distribution is so wide (raging from 1 to hundreds of microns) that it is often only usable after being pulverized. The precipitates irregular shape and low density render it inappropriate for use in a battery. Nickel hydroxide also was produced by precipitation from aqueous nickel salt solutions and caustic soda in presence of ammonia in a continuously operated stirring reactor (Gille et al., 2002).

In order to produce high density spherical nickel hydroxide, it should be grown gradually. Nickel ions first from complex ions with ammonia and then neutralize or raise the temperature of the solution, thus reducing and controlling the reaction rate so that nickel hydroxide is gradually precipitated by decomposition of the nickel ammonium complex. Nickel hydroxide precipitated in this manner has a high density, but it is difficult to control the reaction rate and particle size, the fluctuation of the composition and the deviation of the solutions pH during the reaction render its stable and continuous production difficult. Nickel hydroxide is manufactured by precipitating nickel sulphate solution by sodium hydroxide (Subbaiah et al. 2003).

Preparation of $Ni(OH)_2$ through precipitation technique need costly materials, complicated dissociation technique and expense of high process. This process has many weaknesses, in consequence a production process of nickel hydroxide with electrochemical technique or more knowledgeable by the name of electrosynthesis technique was proposed. In this paper, we demonstrate that a new technique for the production of nickel hydroxide $(Ni(OH)_2)$ by electrochemical method. Characterization of $Ni(OH)_2$ produced was carried out using XPS, XRD and cyclic voltammetry (CV).

# EXPERIMENTAL MATERIALS
### Solution
All solutions were prepared by dissolving their analytical grade reagent (Merck) in deionised distilled water. KOH was used as the supporting electrolyte. Nitrogen was used to deaerate the solutions and to keep an inert atmosphere over the reaction solution during the oxidation process.

# METHODS
### Preparation of a nickel sheet electrode

Ni metal foil (99.98% purity, Aldrich Chemical Company) was used to prepare Ni electrode. A 0.5 mm thick Ni foil was cut into approximately 1 cm x 1 cm piece and connected to silver wire with silver conducting paint prior covered with epoxy gum.
### Characterization using XPS and XRD
The XPS was obtained from a Kratos Analytical, Digital 500, Ion pump system controller, Glassman High Voltage Inc. Minibeam Gun Control and Mg Kα (1253.6 eV) X-ray. While diffraction patterns was obtained using a X-ray diffraction (XRD) from a Phillips X-ray Diffractometer employing Ni filtered CuKα radiation (40 kV) at scan rate of $1/2^o$ min$^{-1}$.
### Electrochemical behavior of nickel hydroxide
Universal Pulsa Dynamic EIS, Voltammetry, Voltalab potentiostat (Model PGZ 402) was used for electrochemical behavior measurements; data acquisition was accomplished using the Voltamaster 4 software. Cyclic Voltammetry experiments was performed in a three electrodes system using Ni sheet as a working electrode (anode), SCE as reference electrode and platinum wire as the counter electrode. All potentials given are with respect to the SCE reference electrode.
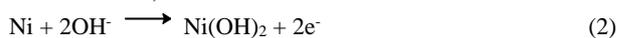### Experimental procedure
The electrolysis process was carried out in 0.1 M KOH supporting electrode at room temperature. Experiments were performed in a three electrodes system using Ni sheet as a working electrode (anode), SCE as reference electrode and platinum wire as the counter electrode. All potentials given are with respect to the SCE. The electrolysis of Ni sheets in KOH was performed using potentiostatic (chronocoulometry) method in 25 mL capacity glass electrochemical cell.

# RESULT AND DISCUSSION

### The mechanism of electrochemical oxidation
The preparation of $Ni(OH)_2$ with the electrochemical oxidation technique was based on the oxidation reaction at anode. Anode used in this research is made of nickel. Nickel represents the easy metal oxidized in KOH (Tarasevich et al., 2005; Kim and Park, 1999; Cox and Pletcher, 1990). Electrolysis at potential constant will cause the oxidation process occurred in anode. Nickel in anode will be oxidized to form the $Ni^{2+}$ and react OH from KOH to form the $Ni(OH)_2$. $Ni(OH)_2$ compound formed on the surface of nickel electrode was observed by the formation of green sponge on the working electrode surface. Fig. 1 shows the schematic diagram of spongy material formed on the electrode surface. The mechanism of electrochemical oxidation process using nickel anode material proposed by many researcher were as follows (Yeo and Johnson, 2001; Cox and Pletcher, 1991; Casella, et al., 1999; Casella and Gatta, 1999; Medway et al., 2006; Grden and Klimek, 2005; Seghiouer et al., 1998; De Souza et al., 1998; Zoltwski, 1993; Hahn et al., 1986 dan 1987):

$$Ni + 2OH^- \longrightarrow Ni(OH)_2 + 2e^- \qquad (2)$$

$$OH^- + Ni(OH)_2 \rightleftharpoons NiOOH + H_2O + e^- \qquad (3)$$

The reaction can be written in other form like:

$$Ni \xrightarrow[\text{surface}]{H_2O/KOH} Ni(OH)_2 \underset{\text{surface}}{\overset{-e}{\rightleftharpoons}} NiO(OH) + H^+ \qquad (4)$$
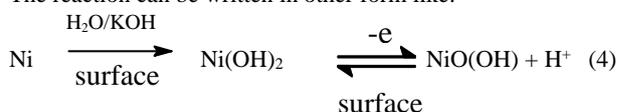
There are two important factor in making the $Ni(OH)_2$ by electrochemical technique, the electrolysis potential and the concentration of KOH. Other, electrolysis time also has an effect because $Ni(OH)_2$ can react furthermore to form NiOOH. Appropriate potential is require to be determined to obtain the oxidation potential area of nickel in KOH. The oxidation area of Ni (I) to Ni (II) occurred at negative potential, while Ni(II) formed at positive potential [11]. Oxidation of the Ni(II) to Ni(III) at potential of about 350 mV.
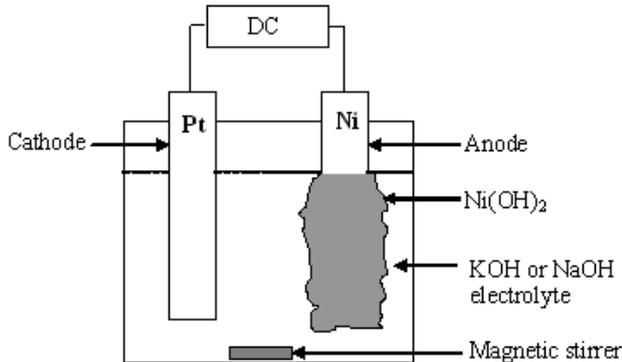


**Figure1: Schematic diagram of electrolysis cell for the synthesis of $Ni(OH)_2$**

Fig. 1 shows a spongy compound formed only at the electrode surface because its backside is closed by epoxy gum used for the insulation of silver conductivity point. Silver conductivity point used to attach the nickel electrode by silver wire. This electrode design will cause only a part of electrode surface come into contact with the solution, which is inappropriate for the industrial scale process.
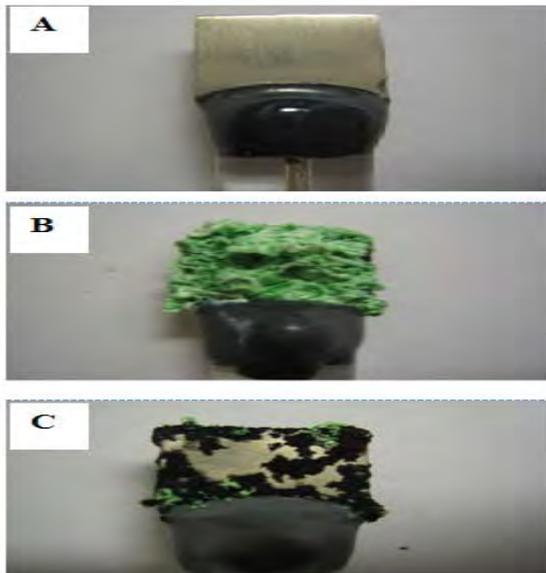


**Figure 2: Ni sheet electrode (A) and sponge formed on the Ni sheet electrode for electrolysis in 0.1 KOH M at potential (B) 0.3 and (C) 1.05 V/SCE for 6 h**

Fig. 2B and 2C shows a spongy product from the electrolysis of Ni in 0.1 M KOH at a potential 0.3 V/SCE and 1.05 V/SCE for

6 h. Electrolysis in 0.1 M KOH at 0.3 V/SCE will yield the green color sponge (Fig. 2B), while a black color sponge was produced from the electrolysis in 0.1 M KOH at 1.05 V/SCE (Fig. 2C). Different colors sponge because difference potential was applied. Green colors at Fig. 2B was estimated as $Ni(OH)_2$. The oxidation of green $Ni(OH)_2$ into black NiOOH ($Ni_2O_3.H_2O$) according to reaction (3).

**Characterizations of $Ni(OH)_2$**
**Characterizations using cyclic voltammetry**
Fig. 3A and 3B show the cyclic voltammograms of $Ni(OH)_2$ in 0.1 M KOH using Pt electrodes for cathode. One of the ways to clarify the oxidation area can be done by changing the scan rate.
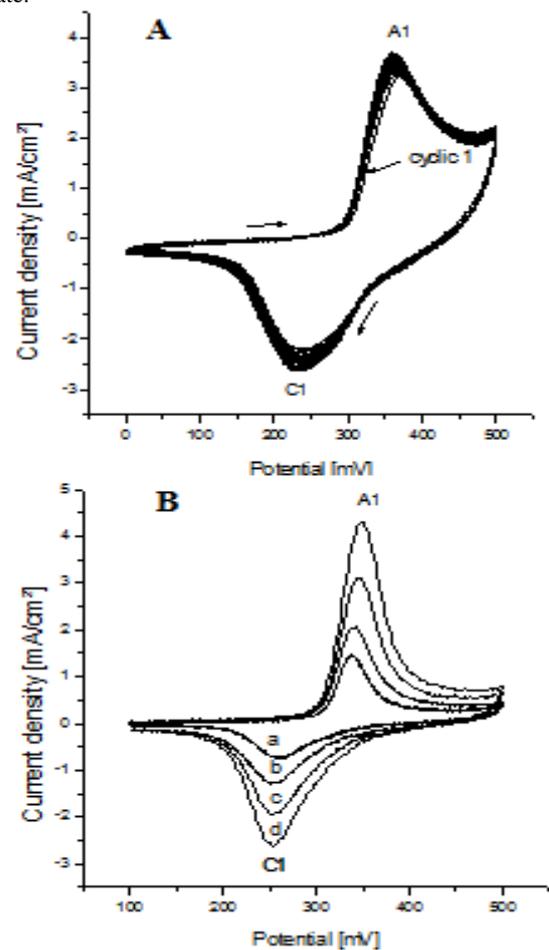


**Figure 3: Cyclic voltammogram of $Ni(OH)_2$ (anode) in 0.1 M KOH using Pt wire electrode cathode: A) 10 cyclic and B) scan rate a: 10 b: 20 c: 30 and d: 40 mV/sec.**

With increasing scan rates, the anodic peak slightly shifted to the more positive potential direction and the cathodic peak moved towards a little to the negative potential (Fig. 3B). The peak current densities increased remarkably with increasing scan rates, but the ratio of the anodic to cathodic peak current ($I_a/I_c$) lies above unity. It indicates that the Ni(II) to Ni(III) oxide transformation process is quasi reversible (Kim and Park, 1999).

Anodic peak (peak A1) in Fig. 3A and 3B represent the oxidation of Ni(II) to Ni(III) through the changing of Ni(OH)$_2$ to NiOOH (Casella, et al., 1999; Casella and Gatta, 1999; Medway et al., 2006; Grden and Klimek, 2005; Seghiouer et al., 1998; De Souza et al., 1998; Zoltwski, 1993; Hahn et al., 1986 dan 1987). Oxidation of Ni (0) to Ni (II) occurred at more negative potential or hydroxide region (not shown in this cyclic voltammogram). The mechanism involved in the anodic peak (A1 in Fig. 3A and 3B) representing Ni (III) region or oxyhydroxide region (Medway et al., 2006; Hahn et al., 1986 dan 1987):

$$Ni + 2OH^- \longrightarrow \alpha\text{-}Ni(OH)_2 + 2e^- \qquad \text{at } -0.8 \text{ up}$$
$$\text{to } -1.5 \text{ V/SCE} \qquad (5)$$

$$\alpha\text{-}Ni(OH)_2 \longrightarrow \beta\text{-}Ni(OH)_2$$
$$\text{at } -0.8 \text{ V up to } 0 \text{ V/ SCE} \qquad (6)$$

$$\beta\text{-}Ni(OH)_2 + OH^- \longrightarrow NiOOH + H_2O + e^-$$
$$\text{at } 0.1 \text{ V/ SCE} \qquad (7)$$
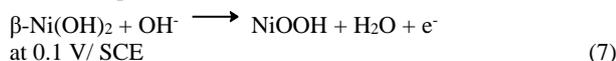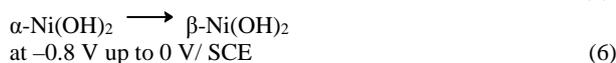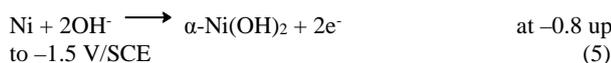
1986 dan 1987). Using ellipsometry, measurements were taken in different regions of the first anodic/cathodic cycle of Ni in 1.0 M KOH solution, during a 3.5 sec potential arrest at the following potential: (i) the region corresponding to a bare Ni surface (-0.9 V); (ii) the region corresponding to the oxidation of Ni to Ni(OH)$_2$ (-0.4 V); (iii) the region corresponding to the oxidation of Ni(OH)$_2$ to NiOOH (+0.05V); (iv) the region corresponding to the reduction of NiOOH to Ni(OH)$_2$ (+0.2 V) and (v) the region corresponding to the reduction of all types of oxides to metallic Ni (-0.9 V) (Bagotsky, 2006).

**Characterizations using XPS and XRD**

In order to determine the sponge substances, analysis of sponge formed on the surface of Ni sheet electrode from the electrolysis in 0.1 M KOH at potential 0.3 V/SCE was analyzed using XPS and the spectrum obtained were shown at Fig. 4. Fig. 4A shows that the binding energy of Ni 2$_{p3/2}$ is 856.036 eV. The binding energy for Ni(OH)$_2$ obtained in the literature are 856.2 ± 0.2; 856.1; 856.1 ± 0.1 and 855.1, 855.6, respectively (Table 1) (Hahn et al., 1986 dan 1987; Luo et al., 1996; Juskenas et al., 2005; Oliveira and Rego, 2006; Moulder, et al. 1992). From these data, confirms that the spongy material is Ni(OH)$_2$.

Analysis of Ni(OH)$_2$ structure using XPS is very difficult as the binding energy recorded are almost the same as to NiOOH. The binding energy for NiOOH as reported by many authors was 858.2 ± 0.2 eV and 856.1-861.7, respectively (Table 1) (Casella, et al., 1999; Casella and Gatta, 1999; Oliveira and Rego (2006). From their data, indicates that the sponge analysed with the binding energy equal to 858.043 eV is belong Ni 2$_{p3/2}$ NiOOH. The signal at 852.3 eV binding energy is related to the Ni 2$_{p3/2}$ photoelectrons of metallic nickel, where for NiO this signal is shifted to 853.3 eV (Schulze and Gulzow, 2004). Suggested, the signals of Ni 2$_{p3/2}$ photoelectron with higher binding energy are related to electrochemically formed nickel hydroxide, Ni(OH)$_2$ and nickel oxyhydroxide, NiOOH. The nickel oxide layer clearly has considerable hydroxide and this may be in the form of nickel α- or β-oxyhydroxide (Luo et al., 1996). The final oxide/hydroxide composition may be affected by alloying. There are small differences in XPS core data for such compounds, but the Ni$_{2p}$ region is too complex to

conclusively identify. The data of the binding energy for selected nickel compounds according to some authors are as summarized in Table 1. Result of analysis of Ni(OH)$_2$ and NiOOH supported by data of spectrum O$_{1s}$ from Fig. 4B.
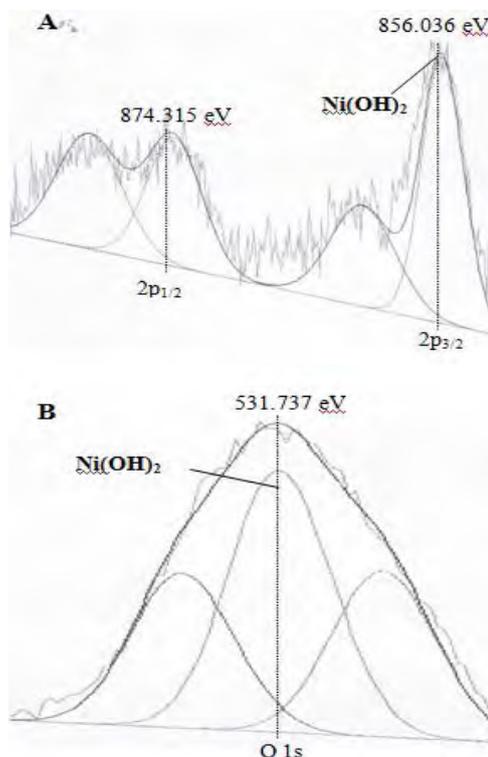


**Figure 4: XPS spectrum A) Ni 2p; B) O1s at green color sponge material**

**Table 1: XPS binding energy (eV) data for Ni 2$_{p3/2}$**

| Name of compounds | Binding energy from literature (eV) | | | | | This study |
|---|---|---|---|---|---|---|
| | [13] | [24] | [25] | [26] | [27] | |
| Ni metal | 852.7 ± 0.1 | 852.0 | 852.4 ± 0.1 | 852.6-853.8 | 852.7 | |
| NiO | 854.0 ± 0.2 | 854.2 | 854.0 ± 0.1 | 853.6-857.2 | 853.5-854.3 | |
| Ni$_2$O$_3$ | - | - | - | 855.8-856.0 | 857.3 | |
| Ni(OH)$_2$ | 856.2 ± 0.2 | 856.1 | 856.1 ± 0.1 | 855.1 | 855.6 | 856.036 |
| NiOOH | 858.2 ± 0.2 | - | - | 856.1-861.7 | - | |

**Table 2: Data of 2θ angles characteristic from XRD**

| 2θ angles characteristic from XRD | | |
|---|---|---|
| Barnard [29] | | This study (Fig. 5) |
| Ni(OH)$_2$ | NiOOH | Ni(OH)$_2$ |
| 19.1° | 26.6° | 18.6° |
| 31.1° | 25.4° | 33.2° |
| 38.5° | 43° | 38.9° |
| 59.1° | 65-68° | 59.1° |

**Figure 5: XRD spectrum from green color sponge**

Fig. 5 shows the diffraction pattern obtained from the Ni sheet electrode surface after the electrolysis 0.1 M KOH (green color sponge). Table 2 shows $2\theta$ angles characteristic for the compound of $Ni(OH)_2$ and $NiOOH$. According to the result analysis by XRD, prove that green color sponge produced from the electrolysis of Ni sheet in 0.1 M KOH is $Ni(OH)_2$. By comparing $2\theta$ angles characteristic between research result by $2\theta$ angles characteristic from result of literature data shows compound which green colors is $Ni(OH)_2$ (Barnard and Crickmore, 1980).

**Conclusion**

The $Ni(OH)_2$ powder has been prepared by electrolysis using Ni sheet electrode and Pt wire electrode (cathode) in 0.1 M KOH. The electrolysis conditions are the room temperature, anodic potential 0.3 V and electrolysis duration of 360 h. Based on XPS and XRD analysis, electrolysis using Ni sheet electrode in 0.1 M KOH will be yielded $Ni(OH)_2$ with green colors on electrode surface. The cyclic voltammetry test indicates that the cycling process of $Ni(OH)_2$ is a sub-reversible process and pure compound. Our future study will be focused on increasing the optimization conditions electrolysis and study application is this material for electrode.

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