

# Synthesis and Characterization of Nano Fibrillar Nickel Hydroxide with a New Phase

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**Abstract**— Nano structured nickel hydroxide has been synthesized by sol gel method at two different pH conditions (9 and 11). The synthesized products were characterized by Fourier Transform Infrared Spectroscopy (FT IR), X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Thermogravimetry / Differential Thermal Analysis (TG/DTA) and Cyclic Voltammetry (CV). Fibrillar Ni(OH)<sub>2</sub> was formed at pH 9.0. It is understood from XRD pattern; a new phase of nickel hydroxide formed. The crystallite size and surface area were calculated and found to be in the range of 18.79 to 19.15 nm and 75.50 to 76.95 m<sup>2</sup>/g, respectively. The morphology of nickel hydroxide also changes with different pH conditions. The results indicate that the observed phase is new, which is entirely different from *alpha* and *beta* phases

**Keywords**— nickel hydroxide; sol-gel; thermogravimetry; nano fibre

## I. INTRODUCTION

Nickel hydroxide has of great importance especially due to its significant electro chemical behavior and great potential applications in rechargeable Ni based batteries, are used widely in various fields [1,2]. Ni(OH)<sub>2</sub> has a hexagonal layered structure with two polymorphs,  $\alpha$  and  $\beta$ -Ni(OH)<sub>2</sub>. There are several methods to synthesis  $\beta$  phase nickel hydroxide [3-5] with a stoichiometric formula Ni(OH)<sub>2</sub>.  $\beta$ -Ni(OH)<sub>2</sub> exhibit a hexagonal plate like morphology and O-H group of the adjacent layer are not hydrogen bonded. The phases obtained by sonochemical treatment of freshly prepared nickel nitrate and urea in presence of argon at pH 6.8, using microwave assistant hydrothermal method [6] are the phases with  $\alpha$  form [7]. Phases obtained by precipitation using ammonia, strong alkalies and by electro synthesis [8] have been differently formulated as 3Ni(OH)<sub>2</sub>.2H<sub>2</sub>O and Ni(OH)<sub>2</sub>.H<sub>2</sub>O and are designed as  $\alpha$  [9, 10]. Due to large interlayer spacing and water of hydration, there is extensive hydrogen bonding between the hydroxyl group and intercalated water molecule. Consequently, they loss their orientation due to the water layer and it is expected that the morphology of  $\alpha$  phase turbo static and leads to considerable disorder in their atomic level leading in broad band in X-ray diffraction pattern. Portemer et al [11] reported that the  $\alpha$  phase are not simple hydrated hydroxide but are not non-stoichiometric. Rajamathi et al [12] reported the  $\alpha$  phase with a stoichiometry as Ni(OH)<sub>2-x</sub>A<sub>n-x/n</sub>.mH<sub>2</sub>O (A<sub>n-</sub> = anion) where x can vary from 0.05 - 0.4 and m = 0.6 - 1 depending upon their experimental conditions.

Faure et al [13] reported for badly crystallized  $\beta$  phase ( $\beta bc$ ). The  $\beta$  phase containing adsorbed anions and displayed very broad pattern in XRD suggesting disorder in their lattices. It is interestingly noted that the polymorphism in Ni(OH)<sub>2</sub> is not only limited to  $\alpha$  and  $\beta$  phases. Kammath and Subbanna [14] have synthesized a mixture of both  $\alpha$  and  $\beta$  phase nickel hydroxide. They also reported a new phase nickel hydroxide which is intermediate between  $\alpha$  and  $\beta$  [12]. Bernald et al [15] also reported the existence of new phase nickel hydroxide and substantiated with spectral analysis. However, the structural evidences of the new phase nickel hydroxide are not yet been resolved. In line with the above we succeeded in synthesizing a new phase of nickel hydroxide in presence surfactant, SDS. Here we report, structural, spectral and thermal evidences for the existence of the new phase which is neither  $\alpha$  nor  $\beta$ .

## II. MATERIALS AND METHODS

### A. Preparation

Nickel hydroxide was synthesized by mixing of 0.1 M of nickel nitrate hexahydrate and surfactant (SDS) in 0.1 M NaOH solution. 0.1 M NaOH solution was added drop wise to the above mixture with constant stirring for 4 h at two different pH conditions were maintained at 9.0 and 11.0. The total volume was maintained at 50 mL. The obtained green colored nickel hydroxide was filtered and washed four times with doubly distilled water and dried under hot air oven at 100°C for 24 h. The products of two different experimental pH conditions, 9.0 and 11.0 are labeled as A and B, respectively. All the chemicals used were of analytical grade, supplied by E-Merck.

### B. Characterization

The obtained nickel hydroxide, A and B were characterized by powder X-ray diffraction, XRD (Shimadzu 6000 X-ray diffractometer, CuK $\alpha$ ,  $\lambda = 1.5418$ ), Fourier Transform Infrared Spectroscopy, FT IR (Shimadzu FTIR 8400 spectrophotometer in the range of 400 to 4000 cm<sup>-1</sup>, KBr pellet), Scanning Electron Microscopy, SEM (JEOL – JSM 6306 scanning electron microscope) and Thermogravimetric / Differential Thermal Analysis, TG/DTA (NETZSCH STA 409 C/CD) were recorded at a heating rate of 10°C/min from 25 to 1200°C, under nitrogen atmosphere.

### C. Electrochemical studies

Cyclic voltammetric measurements were carried out using a Bio-Analytical System (BAS) model CV-50W electrochemical analyzer. The three-electrode cell comprised of a reference Ag/AgCl, auxiliary platinum and working glassy carbon (GC, 0.07 cm<sup>2</sup>) electrode. The GC was polished with alumina powder before each measurement. Tetrabutylammonium perchlorate (TBAP 0.1M) was used as supporting electrolyte. All the experimental solution was purged with nitrogen for 30 min. prior to each set of experiments. Scanning the voltammogram for the bare solution containing the electrolyte checked the purity of the supporting electrolyte and solvent used.

### III. RESULTS AND DISCUSSION

The powder XRD pattern of nickel hydroxide synthesized at pH 9.0 (A) and 11.0 (B) are shown in Fig. 1a and 1b, respectively. The d value of predominant reflections of A and B are given in Table 1. Apart from regular  $\alpha$  and  $\beta$  phases some new reflections are also observed in Fig.1. For comparison the structural features of various standards nickel hydroxide phases with prominent reflections are listed in Table 2.

For comparison, the XRD data of as-synthesized products with literature, standard  $\alpha$  and  $\beta$  phases are given in Table 1. The following conclusions can be drawn from Table 1. (i) a strong intense peak with d values reflections 3.044 - 3.038 Å, does not match with either the  $\alpha$  or  $\beta$  phases (ii) the second intense peak observed at 4.341 - 4.337 Å also does not match with any of the reflection of  $\alpha$  or  $\beta$  phase of nickel hydroxide (iii) the remaining reflections of the patterns is identical to that of  $\alpha$  and  $\beta$  phases, suggesting mixture of  $\alpha$  and  $\beta$  phases. Rajamathi et al [12] also observed a new phase of nickel hydroxide synthesized using nickel salts are nitrate, chloride and sulphates. They reported a new phase of nickel hydroxide with d-reflections 5.61 - 5.37 Å, which falls in between the value of reflections of  $\alpha$  and  $\beta$  phase of nickel hydroxide, 7.6 Å ( $\alpha$  phase) and 4.6 Å ( $\beta$  phase). We report here a two separate and intense d reflections of 3.044 - 3.038 Å and 4.341 - 4.337 Å for A and B, respectively. The average crystallite sizes of the products A and B were calculated using Debye Scherrer equation and found to be 19.15 and 18.79 nm, respectively. The surface area of the products A and B were calculated to be 75.5 and 76.95 m<sup>2</sup>/g, respectively.

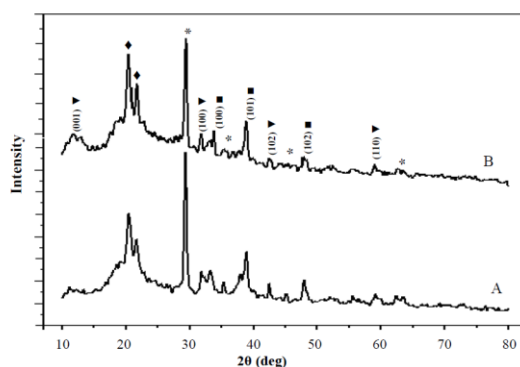


Figure 1 shows the XRD pattern of a) product A and b) product B (▶ -  $\alpha$  phase; ■ -  $\beta$  phase; ◆ - SDS; \* - new phase)

Table 1. Comparison of  $d_{obs}/\text{Å}$  of product A and B with standard  $\alpha$  and  $\beta$  nickel hydroxides

| As-synthesized products |                    |            |                    | Literatures [3, 8, 13] |                    |            |                    |
|-------------------------|--------------------|------------|--------------------|------------------------|--------------------|------------|--------------------|
| A                       |                    | B          |                    | $\alpha$               |                    | B          |                    |
| 2 $\theta$              | $d_{obs}/\text{Å}$ | 2 $\theta$ | $d_{obs}/\text{Å}$ | 2 $\theta$             | $d_{obs}/\text{Å}$ | 2 $\theta$ | $d_{obs}/\text{Å}$ |
| 29.31                   | 3.0443             | 29.36      | 3.0389             | 13.6                   | 7.560              | 18         | 4.620              |
| 20.44                   | 4.3414             | 20.46      | 4.3372             | 21.5                   | 3.780              | 33         | 2.706              |
| 38.85                   | 2.3159             | 21.68      | 4.0952             | 36.2                   | 2.667              | 39         | 2.332              |
| 20.78                   | 4.2712             | 38.90      | 2.3133             | 60.1                   | 1.546              | 52         | 1.755              |
| 21.60                   | 4.1099             | 33.89      | 2.6429             |                        |                    | 60         | 1.563              |
| 47.82                   | 1.9005             | 31.83      | 2.8091             |                        |                    |            |                    |
| 31.79                   | 2.8121             | 47.80      | 1.9011             |                        |                    |            |                    |
| 33.14                   | 2.7006             | 48.20      | 1.8862             |                        |                    |            |                    |
|                         |                    | 58.97      | 1.5650             |                        |                    |            |                    |
|                         |                    | 11.78      | 7.564              |                        |                    |            |                    |

The FT IR spectra of the nickel hydroxide product A and B are shown in Fig. 2A and 2B, respectively. The nickel hydroxide A, shows a broad band at 3600 cm<sup>-1</sup> and sharp peak at 1630 cm<sup>-1</sup> are assigned to hydrogen bonded O-H vibration and bending vibration of water molecules, respectively. In nickel hydroxide B, the sharp and broad peaks are observed at 3640 and 3480 cm<sup>-1</sup> are due to the O-H stretching vibrations with non hydrogen bonded and hydrogen bonded, respectively. The intercalated anions such as NO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup> and SO<sub>4</sub><sup>2-</sup> were observed for product A and B. Some additional peaks are also observed that may be due to surfactant. Standard  $\alpha$  phase show a broad O-H stretching vibration at 3500 cm<sup>-1</sup> is due to the hydrogen bonding and intercalated water molecules are observed at 640 and 470 cm<sup>-1</sup>. Standard  $\beta$  phase are characterized by a sharp non hydrogen bonded O-H stretching vibration at 3650 cm<sup>-1</sup> and vibrations at 540 and 470 cm<sup>-1</sup> in the low frequency region. FT IR absorption confirms the presence of both  $\alpha$  and  $\beta$  phases of nickel hydroxide. It is seen from XRD pattern, the highest reflection peak at 3.04 - 3.05 Å could be due to new phase nickel hydroxide or the phases are related to basic nickel salts like Ni(OH)(NO<sub>3</sub>), Ni<sub>3</sub>(OH)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub>, Ni<sub>2</sub>(OH)<sub>3</sub>(NO<sub>3</sub>). The SEM image of the products A and B are shown in the Fig. 3A and 3B, respectively. Bundles of fibrous morphology were observed in product A with the thickness of 3.04 Å with irregular matrix.

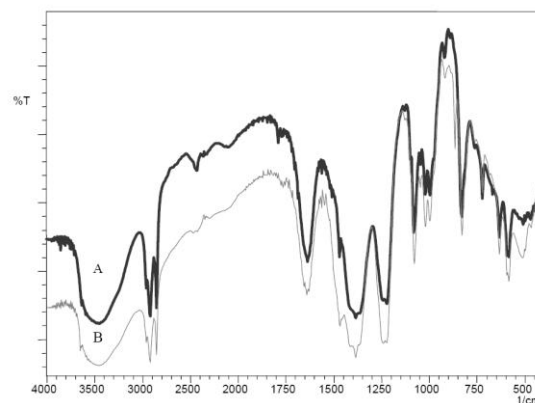


Figure 2 shows the FT IR Spectrum of a) product A and b) product B

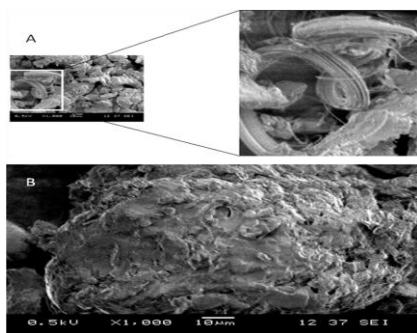


Figure 3 shows the SEM images of a) product A and b) product B

There are four stage decomposition pattern was observed in the products A and B. The first stage at 110 (A) and 105.4°C are due to desorption of water molecules in the compound. The second and third stage weight losses are observed at 225.2 (A) - 236.3°C (B) and 293.4 (A) - 303.1°C (B), respectively. The second and third stage weight losses 45 (A) and 39% (B) are due to removal of surfactant, evolution of intercalated water molecules and anions from the new phase nickel hydroxides A and B to form unstable  $\text{NiO}_x$ . The presence of intercalated anions such as  $\text{NO}_3^-$ ,  $\text{CO}_3^{2-}$  and  $\text{SO}_4^{2-}$  are also supported by FT-IR. The weight losses of 5.3 (A) and 7.45% (B) in the fourth stage should be caused due to the decomposition of an unstable  $\text{NiO}_x$  that changed into stable NiO at 460 - 830°C. In DTA thermogram, broad and sharp endothermic peak at 125 (A) and 105 - 120°C (B), respectively, are due to desorption of surface moisture and water molecules in the compounds. The endothermic peak at 238.3 (A) and 246.8°C (B) are due to the second stage of decomposition. The sharp endothermic dip is observed at 307.2 (A) and 323.5°C (B) are due to the third stage decomposition and the broadband at 515 (A) and 550°C (B) indicate the large energy require for the decomposition of unstable  $\text{NiO}_x$  to stable NiO. The DTA results are complementary to the TG results. Standard  $\beta$  phase suffers a net weight loss of 18.2% and the  $\alpha$  phase suffers a net loss of 34%, in the present case the net loss was found to be 56 and 49% for product A and B, confirms the observed phase is new.

In order to understand the electrochemical activity of the as-synthesized products with new phase, CV studies were attempted using glassy carbon working electrode in acetonitrile solution. A respective voltammogram has been shown in Fig. 4 and the potential data are given in Table 2. Only one anodic oxidation peak for product A appeared at -1035 mV was recorded prior to oxygen evaluation.

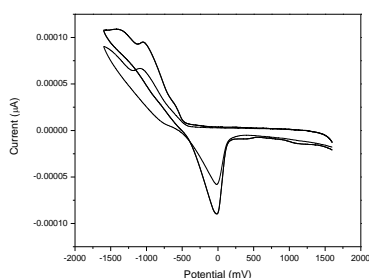


Figure 6 shows Cyclic Voltammogram of a) Product A and b) Product B

Table 2. CV data of the new phase nickel hydroxide

| Products | Potential (mV) |     |            |
|----------|----------------|-----|------------|
|          | Ea             | Ec  | $\Delta E$ |
| A        | -1035          | -20 | -1015      |
| B        | -1088          | -22 | -1066      |

Similarly, only one oxyhydroxy reduction peak at about -20 mV was observed on the reverse sweep. Similar voltammogram were also observed for product B, the anodic peak corresponding to nickel hydroxide oxidation shift to a more negative potentials and the cathodic peak potential corresponding to nickel oxyhydroxide reduction shift to lower potential compared to A. Product A exhibits higher  $\Delta E$  value shows the higher reversibility for the redox reactions. On the basis of electrocatalytic activity obtained from CV, battery properties of new phase nickel hydroxides are now under investigation.

#### IV. CONCLUSION

The presence of the most intense reflections at 3.04 – 3.03Å in XRD pattern shows the as-synthesized nickel hydroxides are in new phase. It is expected that the nickel hydroxide exist has basic nickel salts with intercalated water molecules and the anions as evident from FT IR analysis. The observed  $d$  value reflections are quite different from the basic salts of nickel suggesting the possibilities of new phase. Further, the lines could not be indexed to a single phase. In thermogravimetry,  $\beta$  phase suffers a net weight loss of 18.2% and the  $\alpha$  phase suffers a net loss of 34%, in the present case the net loss was found to be 56 and 49% for product A and B, respectively. TG/DTA results correlate with the DTA results. TG and DTA results confirm the formation of new phase nickel hydroxide. Electrochemical studies (CV) shows, Product A exhibits higher  $\Delta E$  value shows the higher reversibility for the redox reactions compared to product B.

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