

# Preparation, characterization and electrolytic behavior of $\beta$ -nickel hydroxide

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Received 10 January 2002; received in revised form 22 February 2002; accepted 12 March 2002

## Abstract

Nickel hydroxide is prepared by neutralizing  $\text{NiSO}_4$  solution with 4.8 M NaOH, followed by washing the precipitate and treating the slurry hydrothermally at different temperatures. The parameters varied are: initial nickel concentration; effect of presence of sodium ions during hydrothermal treatment; aging time after hydrothermal treatment. The samples so prepared are chemically analyzed and the physical and electrolytic properties such as tap density, percentage weight loss and discharge capacity are determined. On increasing the temperature from 60 to 160 °C, the discharge capacity increases from 52 to 112 mAh g<sup>-1</sup>. At 200 °C, the discharge capacity decreases to 94 mAh g<sup>-1</sup>. Allowing the hydroxide precipitate to age after hydrothermal treatment also causes a decrease in discharge capacity. The presence of excess sodium ions during hydrothermal treatment yields nickel hydroxide with a very low discharge capacity. The maximum discharge capacity of 160 mAh g<sup>-1</sup> is obtained for nickel hydroxide prepared under the following conditions: nickel concentration 43 g l<sup>-1</sup>, neutralizing agent sodium hydroxide, time of hydrothermal treatment 2 h, temperature during hydrothermal treatment 160 °C. XRD patterns and FTIR spectra confirm the precipitate to be  $\beta$ -nickel hydroxide. The sample contains 62.89 wt.% Ni with a tap density of 0.96 g cm<sup>-3</sup>. TG–DTA measurements show a weight loss of 19% with an endothermic peak at 325 °C which corresponds to the decomposition of nickel hydroxide to nickel oxide. The present method of preparing nickel hydroxide through hydrothermal treatment reduces the aging time to 2 h and gives a product with good filtration characteristics. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Nickel hydroxide; XRD; TG–DTA; Hydrothermal; Electrolytic properties

## 1. Introduction

Extensive work on nickel hydroxide electrodes is being conducted because of the use of such electrodes in Ni–Cd, Ni–Zn, Ni–Fe and Ni–MH (metal hydride) storage batteries [1–5]. Due to this commercial importance, several methods of preparation have been developed [6–10]. Bihan [6], for example, prepared turbostratic nickel hydroxide by adding ammonia to a nickel nitrate solution at room temperature. The nickel hydroxides reported in the literature differ from each other in terms of their crystal structure [7,8], degree of hydration [9] and short-range structure as revealed by infrared spectroscopy [10]. In general, the precipitated nickel hydroxide is allowed to age for several days to obtain the desired product. Recently, a number of studies have been reported [11–18] on the utilization of hydrothermal precipitation/treatment techniques to prepare ceramic oxides, hydroxides and ferrites with novel features. In the present work, an effort has been made to precipitate nickel

hydroxide at room temperature, subject it to hydrothermal treatment, and study the structural and electrolytic properties of the resulting product.

## 2. Materials and methods

Nickel hydroxide samples were prepared by neutralizing nickel sulfate solution which contained 43 to 100 g l<sup>-1</sup> nickel with 4.8 M sodium hydroxide solution to attain a final pH of 12.0 at room temperature. The green hydroxides so obtained were washed thoroughly with distilled water (except in one case where the effect of sodium ions was studied) and the aqueous suspensions were treated hydrothermally at different temperatures for 2 h. Hydrothermal treatment was performed in a titanium Parr autoclave (model 4561, 300 cm<sup>3</sup> capacity) which had provision for temperature control, agitation, gas inlet/outlet, sampling, and cooling. In one of the experiments, the precipitated nickel hydroxide slurry was subjected to hydrothermal treatment without removing sodium ions. The products were filtered and dried at 70 °C for 36 h.

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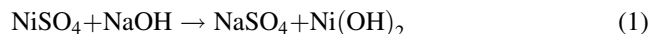
The X-ray diffraction patterns of samples were obtained by using a Phillips powder diffractometer (model PW 1170) in the  $2\theta$  range  $10\text{--}70^\circ\text{C}$  at a scanning rate of  $2^\circ\text{min}^{-1}$  using a Ni filtered Cu target. The FTIR spectra of samples were recorded with a Perkin-Elmer P-500 spectrophotometer using the KBr pellet method. Thermal analysis was carried out with a METTLER TOLEDO STAR<sup>e</sup> system. The nickel content in the precipitated hydroxide was estimated by dissolving 0.1 g of each sample in sulfuric acid and analyzing, after required dilutions, by means of a Perkin-Elmer atomic absorption spectrophotometer (model 372). Measurements of weight loss at  $800^\circ\text{C}$  were carried out by heating the samples in a muffle furnace for 2 h. The tap density was obtained by placing a known weight of each sample in a  $10\text{ cm}^3$  graduated cylinder and tapping it till a constant volume was obtained.

Nickel hydroxide electrodes were prepared for charge–discharge measurements. The 1 g of each nickel hydroxide sample was placed in a mortar. This was then mixed with 0.5 g of graphite powder and 0.06 g of nickel powder in order to increase the electronic conductivity. Thereby, 2 wt.% polyvinyl alcohol was used as the binder. The mixture was then pressed (at  $1\text{ t cm}^{-2}$ ) into a pellet of 20 mm diameter on nickel-coated stainless steel which act as a current-collector. The positive electrode was then placed in a cell between two cadmium electrodes, the capacity of the latter two electrodes was much greater than the positive electrode in order to avoid any limitation due to the negative electrodes. The electrolyte 1 M KOH solution, charge–discharge properties were measured by means of an instrumental set up which consisted of a Aplab7118 regulated dc power supply, an ammeter, and a voltmeter. Electrochemical cycling was performed galvanostatically at a current density of  $32\text{ mA cm}^{-2}$  for 17 h during charging. Discharging was continued to 0.85 V at a current density of  $6.4\text{ mA cm}^{-2}$ . The rest period between charging and discharging was 10 min. Before the start of cycling, a strong overcharge was applied to the electrode for 20 h.

### 3. Results and discussion

#### 3.1. Effect of temperature during hydrothermal treatment

The formation of nickel hydroxide by neutralizing nickel salt with sodium hydroxide takes place through a simple chemical reaction:



Washing of precipitated  $\text{Ni}(\text{OH})_2$  results in removal of sodium sulfate and excess free alkali from the system prior to hydrothermal treatment. The effect of temperature during hydrothermal treatment on tap density, nickel content and weight loss at  $800^\circ\text{C}$  for precipitated nickel hydroxide is given in Figs. 1–3, respectively. On increasing the temperature of hydrothermal treatment from 60 to  $160^\circ\text{C}$ , the tap

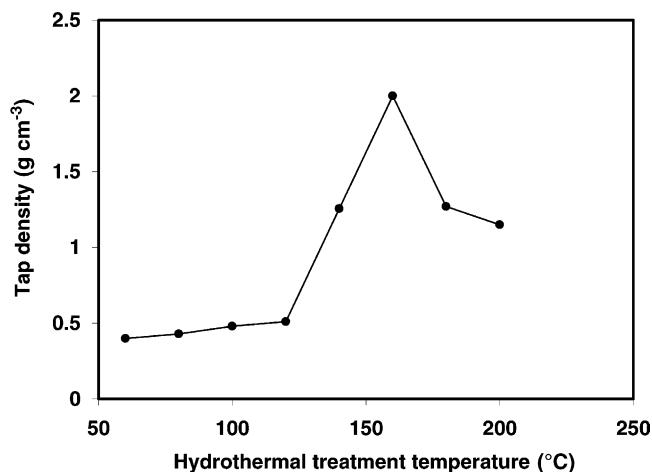


Fig. 1. Effect of hydrothermal treatment temperature on tap density of nickel hydroxide samples. Conditions: initial Ni concentration  $100\text{ g l}^{-1}$ , NaOH 4.8 M, pH of precipitation 12.0, pH prior to hydrothermal treatment 7.5, hydrothermal treatment time 2 h.

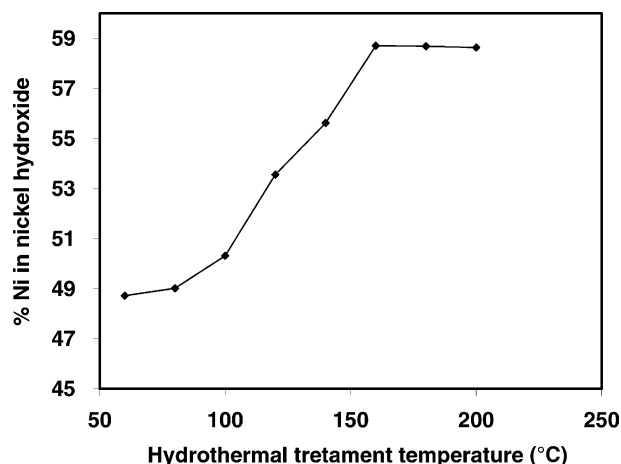


Fig. 2. Effect of hydrothermal treatment temperature on wt.% Ni in nickel hydroxide samples. Conditions same as for Fig. 1.

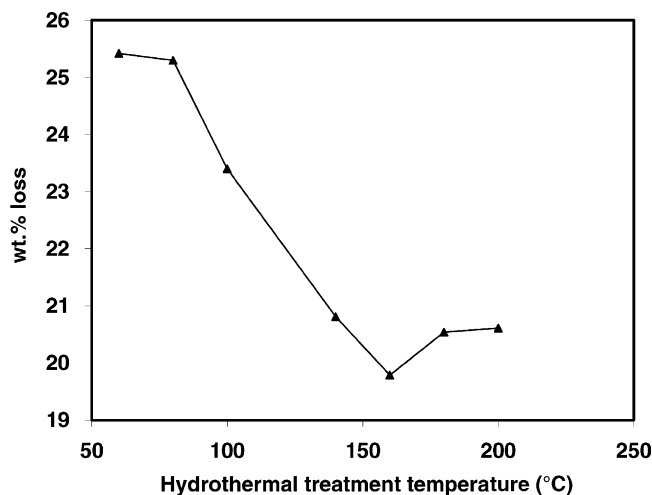
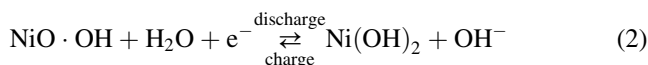


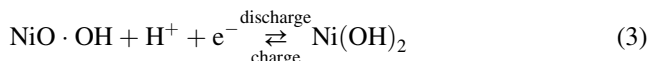
Fig. 3. Effect of hydrothermal temperature on wt.% loss at  $800^\circ\text{C}$  in nickel hydroxide samples. Conditions same as for Fig. 1.

density increases from 0.4 to 2.0 g cm<sup>-3</sup>, the wt.% Ni increases from 48.7 to 58.7, and the weight loss at 800 °C decreases from 25.4 to 19.7%. The theoretical weight loss for conversion of nickel hydroxide to NiO should be ~19%. The weight loss of the sample obtained at 160 °C is close to the theoretical value. On increasing the temperature further from 160 to 200 °C, the tap density decreases to 1.15 g cm<sup>-3</sup>. Increase in the treatment temperature from 160 to 200 °C does not, however, significantly affect the wt.% Ni in the precipitate and wt.% loss at 800 °C (Figs. 2 and 3).

The charge and discharge reactions are as follows.



The active component of the battery is NiO·OH. The reaction mechanism involves diffusion of hydrogen ions through the solid-state lattices of Ni(OH)<sub>2</sub> and NiO·OH to give a continuous change in the composition of active material. The actual course of the reaction may be represented as



The effect of temperature on the discharge capacity of nickel hydroxide treated at temperature in the range 60–200 °C is shown in Fig. 4. The capacity passes through a maximum at around 160 °C. The increase in discharge capacity with increase in treatment temperature could be due to loss of water of hydration and the formation of dehydrated nickel hydroxide of composition Ni(OH)<sub>2</sub>, whereas decrease in the discharge capacity may be due to the formation of some NiO during heating at temperature >160 °C.

### 3.2. Effect of initial nickel concentration

The properties of nickel hydroxide samples obtained at two initial nickel sulfate concentrations, namely, 43 and 100 g l<sup>-1</sup> while maintaining the remainder of the conditions the same are given in Table 1. Discharge capacities of 112 and 160 mAh g<sup>-1</sup> are achieved by using initial nickel concentrations of 100 and 43 g l<sup>-1</sup>, respectively. The amount of Ni in the sample prepared by using 43 g l<sup>-1</sup> initial nickel was 62.87% which is close to the theoretical value of 63.3 wt.%. Watanabe et al. [19] have reported that the Ni content in four typical samples of β-Ni(OH)<sub>2</sub> varies between

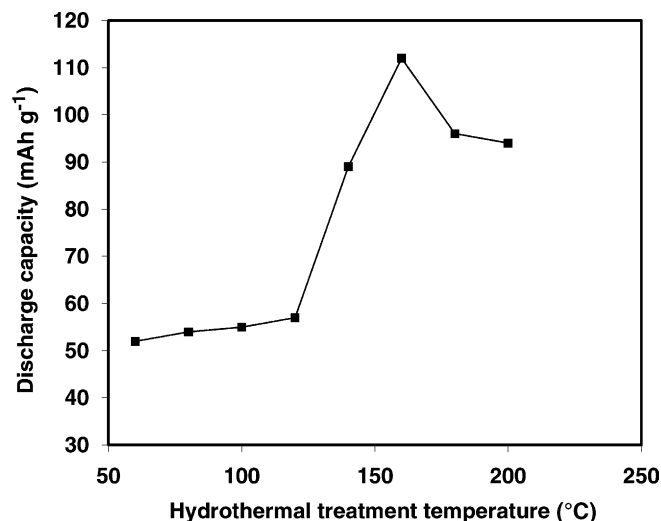


Fig. 4. Effect of hydrothermal temperature on discharge capacity of nickel hydroxide samples. Conditions same as for Fig. 1.

Table 1  
Effect of initial nickel concentration on properties of nickel hydroxide

Concentration of Ni (g l <sup>-1</sup> )	Tap density (g cm <sup>-3</sup> )	Discharge capacity (mAh g <sup>-1</sup> )	Ni (wt.%)	Loss at 800 °C (wt.%)
100	2.0	112	58.71	19.8
43	0.96	160	62.87	19.0

Conditions: NaOH 4.8 M, precipitation pH 12.0, pH prior to hydrothermal treatment 7.6, temperature 160 °C, time 2 h.

61.5 and 61.9 wt.%. The discharge capacity of 160 mAh g<sup>-1</sup> obtained in this work is comparable with the literature value of 120–180 mAh g<sup>-1</sup> for electrochemically prepared Ni(OH)<sub>2</sub> [20].

### 3.3. Effect of presence of alkali during hydrothermal treatment

The results obtained for nickel hydroxide samples with or without removal of alkali prior to hydrothermal treatment are compared in Table 2. The discharge capacity of the sample after removal of sodium ions prior to hydrothermal treatment was 160 mAh g<sup>-1</sup> as opposed to 56 mAh g<sup>-1</sup> obtained for the sample without removal of alkali. This

Table 2  
Effect of presence of alkali during hydrothermal treatment at 160 °C for 2 h on properties of nickel hydroxide using initial Ni concentration 43 g l<sup>-1</sup>

Preparation description	Tap density (g cm <sup>-3</sup> )	Discharge capacity (mAh g <sup>-1</sup> )	Ni (wt.%)	Loss at 800 °C (wt.%)
RT <sup>a</sup> after removal of NaSO <sub>4</sub> , precipitation pH 12.0, pH prior to hydrothermal treatment 7.5 (sample S <sub>1</sub> )	0.96	160	62.87	19.0
HT without removal of NaSO <sub>4</sub> , precipitation and hydrothermal treatment pH 12.0 (sample S <sub>2</sub> )	1.1	56	53.14	23.56

<sup>a</sup> HT: hydrothermal treatment.

Table 3  
Effect of ambient temperature aging time on hydrothermally treated nickel hydroxide sample

Period of ambient temperature aging (h)	Tap density ( $\text{g cm}^{-3}$ )	Discharge capacity ( $\text{mAh g}^{-1}$ )	Ni (wt.%)	Loss at 800 °C (wt.%)
0	0.96	160	62.8	19.0
12	1.34	137	62.7	19.63
24	1.49	135	62.6	19.7
36	1.66	135	62.6	19.7
48	2.04	135	62.6	19.7

Conditions: initial Ni concentration  $43 \text{ g l}^{-1}$ , hydrothermal treatment temperature  $160 \text{ }^\circ\text{C}$ , time 2 h.

decrease in discharge capacity may be due to incorporation of sodium ions in  $\text{Ni}(\text{OH})_2$ . Low amount of Ni in the sample obtained without removal of sodium ions indicates the presence of water of hydration/impurities in the sample.

#### 3.4. Effect of aging time after hydrothermal treatment

In another series of experiment, the effect of aging time at room temperature was studied after hydrothermal treatment of nickel hydroxide. The results are given in Table 3. The discharge capacity of the hydrothermally treated sample without any aging is  $160 \text{ mAh g}^{-1}$  and decreases to  $137 \text{ mAh g}^{-1}$  on keeping the sample at room temperature for 12 h (Fig. 5). Further increase in aging time does not have any significant effect on the discharge capacity, but an increase tap density is observed. In the previous section, however, it was noted that increase of hydrothermal temperature up to  $160 \text{ }^\circ\text{C}$  resulted in an increase in both tap density and discharge capacity. These results indicate that tap density is not directly related to the electrolytic property of nickel hydroxide and is merely a physical property. Nevertheless, it is considered to be an important parameter because it determines the compactness of the product.

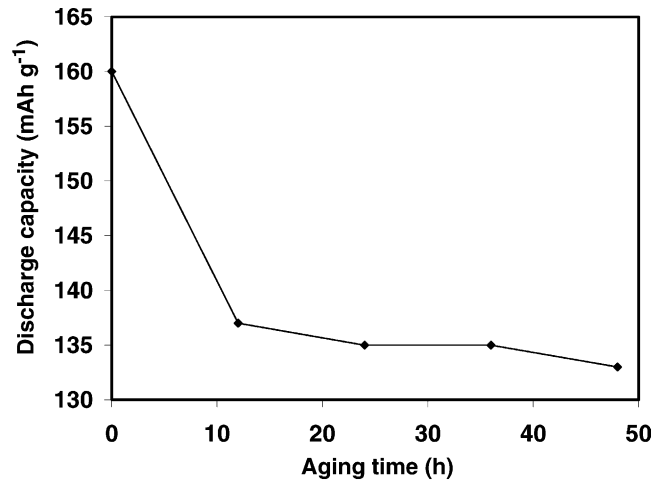


Fig. 5. Effect of ambient temperature aging on discharge capacity of hydrothermally treated nickel hydroxide samples. Conditions of precipitation: Ni  $43 \text{ g l}^{-1}$ , NaOH 4.8 M, pH of precipitation 12.0, pH after removing Na 7.5, hydrothermal treatment temperature  $160 \text{ }^\circ\text{C}$ , time 2 h.

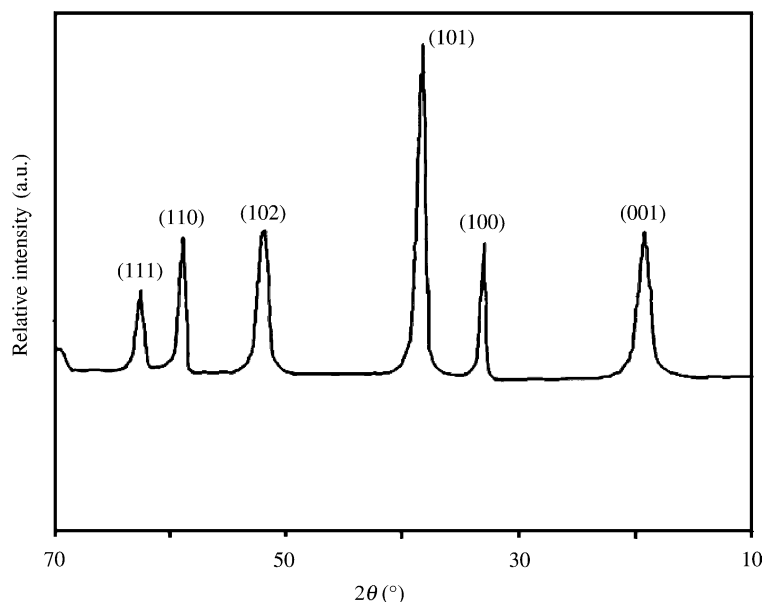


Fig. 6. XRD pattern of typical nickel hydroxide (sample  $S_1$ , Table 2) obtained by hydrothermal treatment at  $160 \text{ }^\circ\text{C}$ .

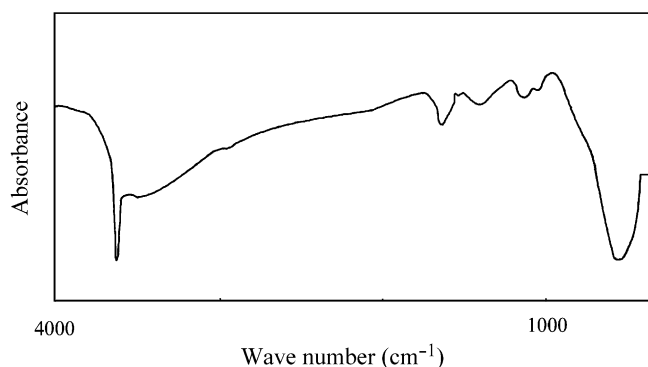


Fig. 7. FTIR spectra of typical nickel hydroxide (sample S<sub>1</sub>, Table 2) obtained by hydrothermal treatment at 160 °C.

### 3.5. Characterization of Ni(OH)<sub>2</sub> sample

The nickel hydroxide sample which gave a maximum discharge capacity of 160 mAh g<sup>-1</sup> was characterized by XRD, FTIR and TG–DTA. The XRD pattern (Fig. 6) show that all the major peaks match with the reported values of β-nickel hydroxide [21].

The IR spectrum of the sample is presented in Fig. 7. There is a sharp peak in the region 3700–3300 cm<sup>-1</sup> and this confirms that the product is β-nickel hydroxide [22]. This sharp peak in the OH stretching region is shown by β-Ni(OH)<sub>2</sub> because of the absence of hydrogen bonding between hydroxyl groups [23]. The peaks in the 800–1800 cm<sup>-1</sup> range could be due to the presence of anions which are probably not completely eliminated during the washing stage [2,24]. The band centered around 460 cm<sup>-1</sup> is the Ni–O stretching mode [3].

The TG–DTA of the sample (Fig. 8) shows a 19% weight loss which matches with the theoretical value for dehydroxylation of nickel hydroxide to nickel oxide. The DTA curve displays only one endothermic peak around 325 °C which is due to the decomposition of the nickel hydroxide phase.

### 3.6. Advantage of hydrothermal precipitation route

In the present work, a maximum discharge capacity of 160 mAh g<sup>-1</sup> is obtained for nickel hydroxide and is comparable with the literature value of 120–189 mAh g<sup>-1</sup> for electrochemically prepared nickel hydroxide [20]. The precipitate can be obtained after 2 h of hydrothermal treatment unlike electroless nickel hydroxide preparation of which takes a longer time [3]. Moreover, the sample obtained in the present work is easy to filter. By contrast, Baraldi et al. [2] reported that filtration creates difficulties during preparation of nickel hydroxide under alkali-deficient conditions. Hence, the β-nickel hydroxide prepared here is superior to other products in three different aspects, namely, good discharge behavior, easy filtration, and preparation within a few hours.

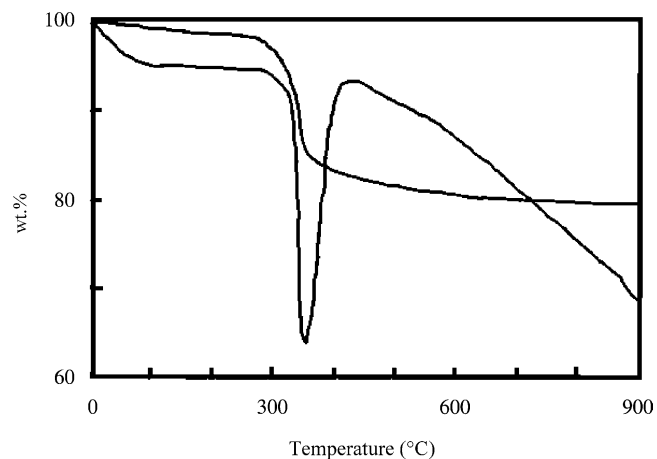


Fig. 8. TG–DTA of typical nickel hydroxide (sample S<sub>1</sub>, Table 2) obtained by hydrothermal treatment at 160 °C.

## 4. Conclusions

Nickel hydroxide has been prepared by neutralizing NiSO<sub>4</sub> solution with sodium hydroxide solution followed by thorough washing of the precipitate with distilled water and treating the aqueous suspension hydrothermally at different temperatures which range from 60 to 200 °C for 2 h. The various other parameters studied are, effect of initial nickel concentration, presence of alkali during hydrothermal treatment, and aging time after hydrothermal treatment. A maximum discharge capacity of 160 mAh g<sup>-1</sup> is obtained for a sample obtained under the following conditions: initial nickel concentration 43 g l<sup>-1</sup>, NaOH 4.8 M, sodium removal prior to hydrothermal treatment temperature 160 °C, time 2 h (Fig. 5). XRD and FTIR analysis of the precipitate confirm it to be β-nickel hydroxide. The weight loss of the sample was 19% and the DTA curve shows a single endothermic peak which corresponds to conversion of nickel hydroxide to nickel oxide.

## Acknowledgements

The authors are grateful to the Director, Regional Research Laboratory, Bhubaneswar, for permission to publish this work. The authors also thank Sh. K. Sanjay and Sh. Devbrata Mishra for assistance with this study.

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