

Temperature-induced control over phase selection among hydroxides of nickel

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Abstract. While at low (4°C) temperatures, addition of ammonia to aqueous metal nitrate solutions induces the precipitation of α -nickel hydroxide and at high (25–65°C) temperatures, β -Ni(OH)₂ is formed. The crystallinity of the product improves at higher temperatures of precipitation and the product obtained at 65°C is devoid of various disorders such as stacking faults, turbostraticity and interstratification. This provides a simple and efficient alternative to the hydrothermal synthesis of crystalline β -Ni(OH)₂. The temperature induced control over phase selection provides direct experimental evidence for the metastability of α -nickel hydroxide. Crystalline β -Ni(OH)₂ is, however, a poor electrode material for alkaline secondary cells and exhibits a capacity of only 75 ± 10 mAh/g, against the theoretically expected 289 mAh/g.

Keywords. Nickel hydroxide; crystallinity; disorder; ammonia precipitation.

1. Introduction

Nickel hydroxide is a positive electrode material of all nickel based alkaline secondary cells (Falk and Salkind 1969). It is generally prepared by precipitation from an aqueous nickel salt solution by the addition of a strong alkali such as NaOH (Hui *et al* 1995). The resultant hydroxide is usually in a highly disordered state. The disorder manifests itself in the non-uniform broadening of reflections observed in the powder X-ray diffraction (PXRD) patterns of the material (Barnard *et al* 1981; Delmas and Tessier 1997; Rajamathi *et al* 2000). It has been generally suggested that the incidence of various kinds of disorder bestows upon nickel hydroxide superior electrochemical properties (Bernard *et al* 1996; Tessier *et al* 1999; Jayashree *et al* 2000). Nickel hydroxide exhibits a variety of disorders such as point defects (Bernard *et al* 1996; Cornilsen *et al* 1990), stacking faults (Tessier *et al* 1999), turbostraticity and interstratification (Rajamathi *et al* 2000; Ramesh *et al* 2003a). We have been, for some time, interested in developing synthetic strategies that enable us to engineer specific predetermined disorders into nickel hydroxide and correlate them with the reversible discharge capacity (Bernard *et al* 1996; Ramesh *et al* 2003b, 2005). As a first step in this direction, it is imperative to develop a suitable methodology that yields ‘perfectly’ ordered crystalline nickel hydroxide.

Crystalline brucite-like β -Ni(OH)₂ is generally prepared by prolonged (24 h) hydrothermal treatment (120–180°C)

of the poorly crystalline, freshly precipitated nickel hydroxide gel (Fievet and Figlarz 1975; Delmas and Tessier 1997). Other techniques of precipitation such as electrochemical nitrate reduction (McHenry 1967) and homogeneous precipitation by urea hydrolysis (Dixit *et al* 1996) have been reported to yield α -nickel hydroxide, which is a hydrated version of the β -form.

Other precipitation reagents can also be used for the synthesis of nickel hydroxide. Genin *et al* (1991) used a weak base such as ammonia to affect the precipitation of nickel hydroxide and obtained α -nickel hydroxide. As a part of our continuing interest in the synthesis of α -nickel hydroxide (Dixit *et al* 1996; Jayashree and Kamath 1999), we reinvestigated the ammonia precipitation of nickel hydroxide. In this paper, we report the synthesis of highly crystalline β -Ni(OH)₂ by ammonia precipitation at temperatures above 25°C, but α -nickel hydroxide at lower (4°C) temperatures. However, the electrochemical performance of pasted electrodes comprising of crystalline β -nickel hydroxide is inferior to that of poorly crystalline β -nickel hydroxide. The poorly crystalline nickel hydroxide was obtained by cycling of α -phase of nickel hydroxide in alkali.

2. Experimental

Ammonia (2 M, 100 mL) was added at the rate of 5 mL min⁻¹ to a nickel nitrate (1 M, 50 mL) solution placed in a thermostat. Separate precipitation reactions were carried out at different temperatures (4°C, 25°C and 65°C). We label these samples as NH4, NH25 and NH65, respectively. In all cases the blue nickel amine complex was

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formed in addition to a green precipitate of nickel hydroxide. The precipitation, was, therefore, not quantitative. In all the cases, the precipitates were aged in mother liquor for 18 h at the respective precipitation temperatures, filtered, washed copiously and dried at ambient temperature over P_2O_5 . Nickel hydroxide was also prepared by the addition of nickel nitrate solution (1 M, 50 mL) to NaOH (2 M, 100 mL) and green slurry obtained was hydrothermally treated in mother liquor at 170°C for 18 h. The sample was designated as HT170.

All nickel hydroxide samples were characterized by wet chemical analysis as described elsewhere (Jayashree and Kamath 1999) to obtain their approximate formula. The nickel content was estimated by the DMG method. The OH^- content was estimated by dissolving a known weight of the sample in excess acid and back titrating the excess against a standard NaOH solution using a pH meter. In case of NH65, the $[OH^-]/[Ni^{2+}]$ ratio was found to be 2. In instances of non-stoichiometry, the excess positive charge was made good by the inclusion of nitrate ions. The unaccounted weight was attributed to water to arrive at an approximate formula. TGA (lab. built system, heating rate, $5^\circ C \text{ min}^{-1}$) and drying studies were carried out to determine the moisture content of the samples (Ramesh *et al* 2003b). The results of TGA studies were found to be consistent with the results of wet chemical analysis. PXRD patterns were obtained using a JEOL Model JDX8P powder X-ray diffractometer (Cu/CoK α source, $\lambda = 1.5418/1.79 \text{ \AA}$) and infrared spectra were obtained using a Nicolet Model Impact 400D FTIR spectrometer. Rietveld refinement was carried out on NH65 nickel hydroxide sample using the FullProf program (Rodriguez-Carvajal 2000). Cell parameters and atomic position coordinates were obtained from the literature (Greaves and Thomas 1986).

2.1 Electrochemical studies: Preparation of pasted electrodes

Electrodes were prepared by mixing the nickel hydroxide sample with graphite powder and an aqueous suspension of PTFE in the ratio of 0.6 : 0.3 : 0.1. The mixtures were thoroughly ground to obtain a paste like consistency. This paste was pressed at 120 kg cm^{-2} on either sides of a nickel foam ($2.9 \times 2.3 \text{ cm}$) support at ambient temperature. The electrodes were dried at $65^\circ C$ and soaked in 6 M KOH for 24 h before being galvanostatically (current, 5.5 mA; 21 h) charged to 120% of the theoretical capacity computed for a $1e^-$ exchange (289 mAh/g). Nickel plates were used as counters and all potentials were measured using a Hg/HgO/ OH^- (6 M KOH) reference. These electrodes were then discharged at a current of 40 mA to a cut off voltage of 0 V at ambient temperature ($28\text{--}30^\circ C$). This discharge current was chosen to yield a C/2 rate for the expected theoretical capacity of the electrode. The actual discharge rate varied from 1.2–0.5 C depending on the charge storage capacities of different electrodes.

3. Results and discussion

Genin *et al* (1991) not only reported the synthesis of α -nickel hydroxide by ammonia precipitation, but they also succeeded in intercalating a variety of anions, including long chain carboxylates between the hydroxide slabs. However, our attempts to reproduce the results of Genin *et al* (1991) always resulted in the formation of β -Ni(OH) $_2$. This was a cause of considerable concern to us, until we realized that temperature can seriously affect the outcome of precipitation reactions. Genin *et al* (1991) had ignored the effect of temperature. Using a thermostated water bath, at $4^\circ C$, ammonia-induced precipitation yielded α -nickel hydroxide (sample NH4), an observation that matched with those of Genin *et al* (1991). But what was very striking was the precipitation of highly crystalline β -Ni(OH) $_2$ (NH25) at $25^\circ C$ and above. In figure 1 we compare the PXRD patterns of NH4 with that of NH25. The NH4 has a low angle reflection at 7.6 \AA characteristic of

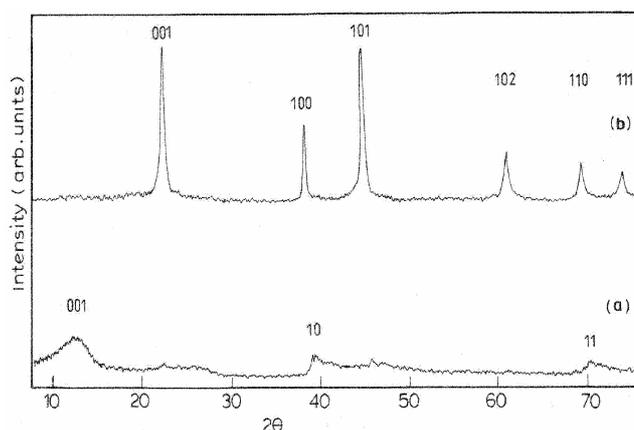


Figure 1. Powder X-ray diffraction patterns of the NH4 sample (a) compared with that of the NH25 sample (b).

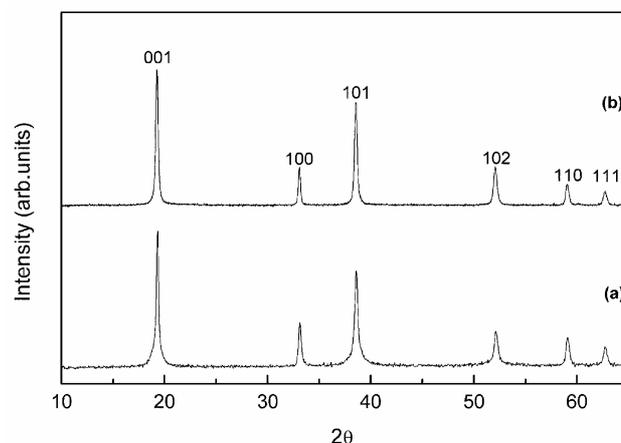


Figure 2. Powder X-ray diffraction patterns of a hydrothermally crystallized nickel hydroxide sample at $170^\circ C$ (a) compared with that of the NH65 sample (b).

Table 1. Parameters obtained from structure refinement by the Rietveld method. (a) Space group: $P-3m1$.

Sample	z-position of the O atom	Profile parameters				Conventional Rietveld factors for points with Bragg contribution			
		U	V	W	η	R_{wp}	R_B	χ^2	DW-stat
NH65	0.2167	0.5990	-0.3355	0.1071	0.7843	9.80	3.02	2.09	1.9813

(b) Cell dimensions and thermal parameters

Sample	B_{ov} (\AA^2)	a (\AA)	c (\AA)
NH65	2.4313	3.130(2)	4.615(4)

Table 2. Results of wet chemical analysis of nickel hydroxide samples.

Sample	Weight percentage				Total weight loss [†] (%)	Approximate formula
	Ni^{2+}	OH^-	NO_3^-	H_2O		
NH4	52.00	28.54	6.04	13.41	32.03 (33.75)	$\text{Ni}(\text{OH})_{1.89}(\text{NO}_3)_{0.11} \cdot 0.84\text{H}_2\text{O}$
NH25	58.24	32.32	3.69	5.746	24.18 (26.16)	$\text{Ni}(\text{OH})_{1.94}(\text{NO}_3)_{0.06} \cdot 0.32\text{H}_2\text{O}$
NH65	61.81	35.68	–	2.52	20.46 (21.45)	$\text{Ni}(\text{OH})_{2.0} \cdot 0.133\text{H}_2\text{O}$
HT170	61.76	35.40	–	2.46	21.6 (21.4)	$\text{Ni}(\text{OH})_{2.0} \cdot 0.13\text{H}_2\text{O}$

[†]Values in parentheses are calculated on the basis of the approximate formula

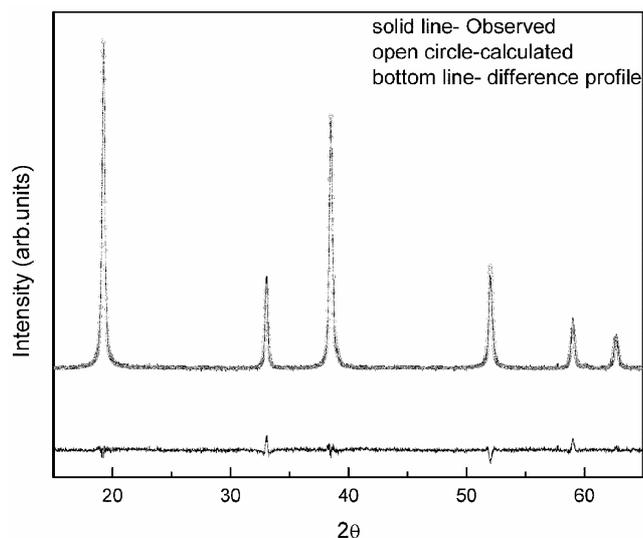


Figure 3. Result of the Rietveld refinement of the PXRD pattern of NH65 nickel hydroxide: observed (solid line), refined (open circle). The lower trace is the error function.

the interlayer distance of α -nickel hydroxide. NH25 shows all the reflections characteristic of β - $\text{Ni}(\text{OH})_2$ (JCPDS PDF No. 14-117). In figure 2 we compare the PXRD pattern of NH65 with that obtained for the hydrothermally synthesized sample (170°C, 18 h). In contrast to poorly crystalline samples obtained by strong alkali precipitation (Jayashree *et al* 2000), NH65 exhibits sharp peaks comparable with that of the hydrothermally synthesized sample.

In figure 3 is shown the result of structure refinement of NH65 sample using the Rietveld method. The refined atomic position coordinates and goodness of fit values are

given in table 1. The atomic coordinates and Ni–O bond length are in close agreement with the values reported by Greaves and Thomas (1986). The goodness of fit values are in the acceptable range considered by Young (1993). From Rietveld refinement of NH65, there is a reasonable evidence to suggest that the NH65 nickel hydroxide sample is highly crystalline and devoid of stacking faults, turbostraticity and interstratification which are ubiquitous in other preparations of nickel hydroxide. Ammonia precipitation can, therefore, be used as an energy efficient alternative to prolonged hydrothermal treatment.

Wet chemical analysis read together with thermogravimetric data and drying studies (see table 2) indicate that the NH65 sample is a stoichiometric hydroxide having the formula, $\text{Ni}(\text{OH})_2$ and contains only 1–2% by weight moisture. NH4 is hydroxide deficient and intercalates anions and water molecules (observed moisture content, 6.4%), as expected of α -nickel hydroxide.

Transmission electron micrographs of the NH4 and NH65 samples are shown in figure 4. It is clear that while NH4 exhibits turbostratic disorder similar to the samples reported by Genin *et al* (1991), NH65 exhibits platelet morphology.

Pasted electrodes comprising of the NH65 sample were electrochemically cycled for the determination of their reversible charge storage capacity. The stabilized capacity was found to be only $75 \pm 10 \text{ mAh g}^{-1}$ of active material ($0.26 e/\text{Ni}$ atom). In contrast, the NH4 samples yield 175 mAh g^{-1} ($0.6 e/\text{Ni}$ atom) (figure 5). This low capacity of NH65 is in keeping with earlier observations made on crystalline materials by other workers (Acharya *et al* 1993; Tessier *et al* 1999; Jayashree *et al* 2000). NH4 (α -phase)

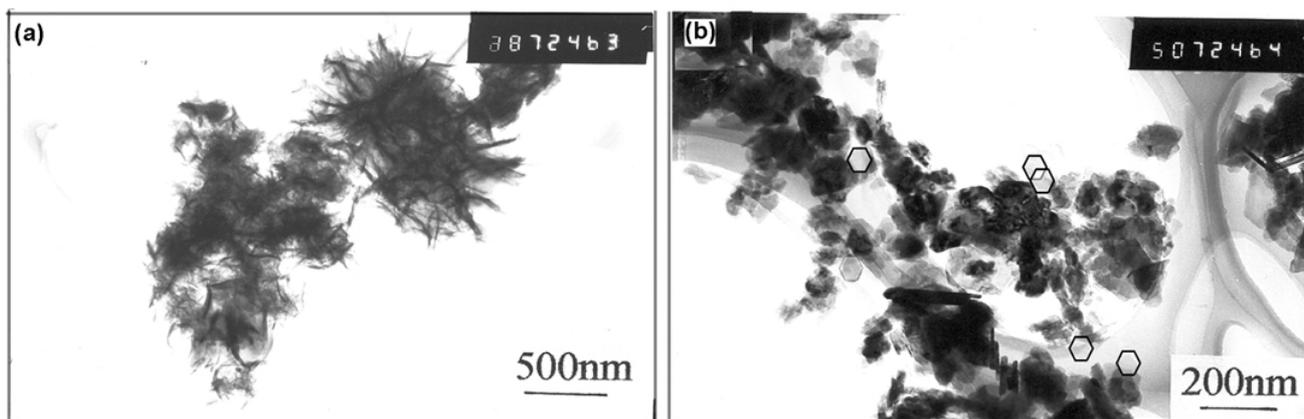


Figure 4. HRTEM image of the crystallites of NH4 (a) and NH65 (b) samples.

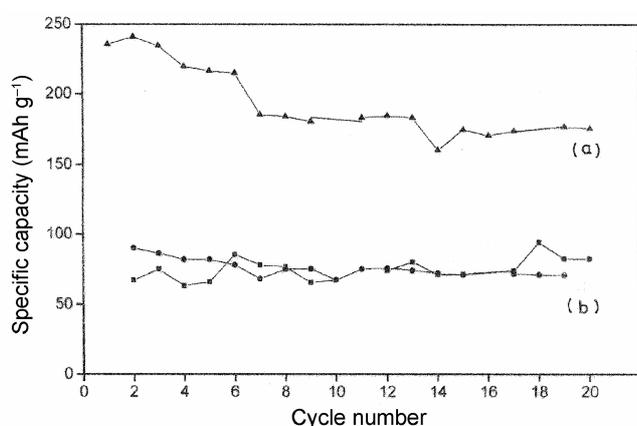


Figure 5. Cycle life data of the pasted electrodes comprising of the NH4 (a) and NH65 (b) samples.

being a metastable phase transforms into poorly crystalline β -nickel hydroxide on cycling in 6 M KOH at ambient temperature (28–30°C). This is directly evident from the marginal decrease in the electrochemical performance of NH4 sample (see figure 5(a)). It is generally suggested that structural disorder/poor crystallinity enhances the charge storage capacity of nickel hydroxide.

4. Conclusions

The precipitation of α -nickel hydroxide at low (<4°C) temperature and of β -Ni(OH)₂ at high (>25°C) temperature provides direct experimental evidence for the metastability of the α -modification.

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