Short Communication

On the relationship between α-nickel hydroxide and the basic salts of nickel

Michael Rajamathi, P. Vishnu Kamath *

Department of Chemistry, Central College, Bangalore University, Bangalore 560001, India

Abstract

α-Nickel hydroxide is isostructural with the hydroxide-rich basic salts of nickel. The anions in the basic salts are strongly grafted to the nickel hydroxide sheets, but in α-nickel hydroxide, the anions are loosely intercalated between the hydrated nickel hydroxide sheets, $[Ni(OH)_{2-x}(H_2O)_x]^{x+}$. The loose intercalation causes the sheets to become disordered and leads to a turbostratic structure. In contrast, the nickel hydroxy-anion sheets in the basic salts are stacked together in a highly ordered fashion. The basic salts of nickel transform into the α-hydroxide upon ageing in a tartarate buffer, into β-hydroxide at pH 4, and into β_{bc} (bc: badly crystallized) phase in 1 M KOH. © 1998 Elsevier Science S.A.

1. Introduction

Nickel hydroxide is widely used as a positive electrode material in nickel-based, alkaline, secondary cells [1]. It crystallizes in a layered hexagonal structure and exists in two polymorphic forms known as α- and β-forms [2]. The α-form of nickel hydroxide has superior electrochemical properties compared with the β-form. It is unstable, however, in alkaline medium and rapidly transforms into a β-like phase, known as β_{bc} (bc: badly crystallized) [3]. Considerable effort has been devoted to understanding the structure and composition of the α-hydroxide and to enhancing its stability in alkaline medium [4–6]. Recent work [7–9] has shown that α-nickel hydroxide is a hydroxyl-deficient phase that contains intercalated anions and water molecules. The composition of α-nickel hydroxide can be represented by the general formula $[Ni(OH)_{2-x}A^{n-}_{x/n} \cdot yH_2O]$ where $x = 0.2$–0.4; A = chloride, nitrate, sulfate or carbonate, and $y = 0.6$–1.

A survey of the literature reveals the existence of a number of basic salts of nickel such as $Ni(OH)(NO_3)$ [10], $Ni_3(OH)_4(NO_3)_2$ [11], and $Ni_2(OH)_3(NO_3)$ [12] and the corresponding carbonate, sulfate and chloride analogues. The compositions of all these basic salts can also be written in terms of a general formula $[Ni(OH)_{2-x}A^{n-}_{x/n} \cdot yH_2O]$ where $x = 1$, 0.67 and 0.5, respectively, and $y = 0$–2.

In view of the close compositional similarity between the α-hydroxide and the basic salts of nickel, it is considered useful to investigate the structural and compositional relationship between these two classes of compounds, especially in view of the fact that the electrochemical performance of the α-hydroxide derives directly from its structure, composition and state of hydration. In this paper, the basic salt $Ni_3(OH)_4(NO_3)_2$ (nickel hydroxy nitrate, NHN) is chosen for detailed investigations.

2. Experimental

2.1. Synthesis

NHN was prepared according to the method reported by Gallezot and Prettre [11] by mixing 18 g of nickel nitrate and 2 g of urea in 2.4 ml of water and heating the slurry to 150–170 °C for 2 h. The resultant cake was ground, washed with water and acetone, filtered and dried to constant weight at 65 °C.

Model α-nickel hydroxide was synthesized as described elsewhere [9]. A nickel nitrate solution (strength 0.25 M) was cathodically reduced using a platinum flag electrode

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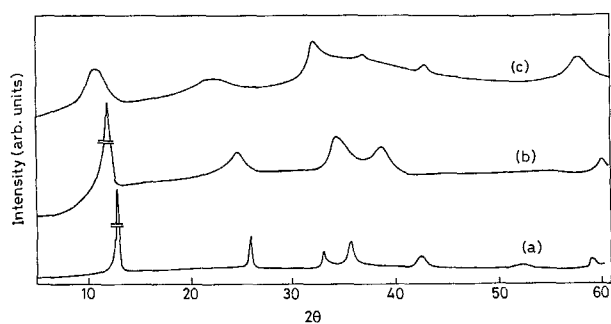* Corresponding author. Tel.: +91-221 16 79; e-mail: Vijaya@cge.iisc.ernet.in

Fig. 1. Powder XRD patterns of (a) as-prepared, and (b) tatarate aged NHN compared with that of (c) α-nickel hydroxide.

(surface area 2 cm^2) under galvanostatic conditions (current density 20 mA cm^{-2}) in a divided cell for 2 h. A platinum flag dipped in a KNO$_3$ solution of matching ionic strength was taken as the anode. The nickel hydroxide formed at the cathode was filtered, washed with water, and dried to a constant weight at 65 °C.

Ageing experiments were carried out by suspending 0.5 g batches of the NHN in 25 ml of the medium with intermittent stirring for 48 h. Ageing was carried out in dilute nitric acid (pH: 4), sodium tartarate buffer (pH: 8) and 1 M KOH (pH: 14). The samples after ageing were filtered, washed and dried to constant weight at 65 °C.

Table 1
Powder XRD data of the as-prepared and aged samples of NHN compared with those of α-nickel hydroxide

hkl[a]	d (Å) Nickel hydroxy nitrate		α-Nickel hydroxide
	(as-prepared)	(aged)	
003	6.90	7.31	7.56
006	3.45	3.66	3.78
100	2.71		
101	2.52	2.64	2.67
102	2.14		
105		2.33	2.34
107		2.03	2.03
110	1.57		1.55
a (Å)	3.13	3.07	3.09
c (Å)	20.70	21.90	22.68

[a]The patterns were indexed according to these hkl values on a hexagonal cell.

2.2. Wet chemical analysis

All the samples were analysed by wet techniques as described elsewhere [13]. The nickel content was estimated gravimetrically. The total base content was estimated by dissolving an accurately weighed amount of the sample in excess acid and then titrating the excess acid against a standard base using a pH meter. The hydroxide content in all the samples studied in this paper was less than what was expected for a stoichiometric metal hydroxide. This deficiency of negative charge was made up by assuming the presence of anions (nitrate in the present instance). The unaccounted weight was attributed to water of hydration in order to obtain an approximate formula for all the phases.

2.3. Physical characterization

The as-prepared and aged samples were characterized by powder X-ray diffractometry (XRD) (Jeol JDX8P powder X-ray diffractometer, Cu Kα radiation) and infrared spectroscopy (Nicolet Impact 400D Fourier-transform infrared (FT-IR) spectrometer, KBr pellets, 4 cm^{-1} resolution).

3. Results

The powder XRD patterns of the as-prepared and the tartarate buffer aged samples of NHN are shown in Fig. 1 and compared with that of the α-nickel hydroxide. The prominent d spacings are listed in Table 1. The XRD pattern of NHN displays sharp lines that are characteristic of an ordered phase and match well with the literature data (PDF No. 22-752). The first line appears at 6.9 Å followed by another at 3.45 Å. Wet chemical analysis (Table 2) yields a [OH$^-$]/[Ni^{2+}] ratio 1.4 as against the expected 1.33, thus showing a minor departure from the ideal composition. The approximate composition is Ni(OH)$_{1.4}$(NO$_3$)$_{0.6}$.

The model α-nickel hydroxide also has a low angle reflection 7.56 Å followed by another at 3.8 Å. The peaks are broad, as expected of disordered phases. In addition, the pattern shows a pronounced asymmetry toward the higer 2θ side in the 2.7–2.3 Å region due to the ($hk0$)

Table 2
Results of wet chemical analysis of the as-prepared and tartarate aged samples of NHN and α-nickel hydroxide

Sample	Composition (wt.%)		Mole ratio	Molecular formula[a]
	Ni^{2+}	OH$^-$	[OH$^-$]/[Ni^{2+}]	
NHN as prepared	51.9	21.0	1.40	Ni(OH)$_{1.4}$(NO$_3$)$_{0.6}$
NHN aged in tartarate	49.8	27.0	1.87	Ni(OH)$_{1.87}$(NO$_3$)$_{0.13}$ · 1.5H$_2$O
α-nickel hydroxide	51.2	26.9	1.80	Ni(OH)$_{1.8}$(NO$_3$)$_{0.2}$ · 0.65H$_2$O

[a] Approximate formulae have been calculated from [OH$^-$]/[Ni^{2+}] mole ratios assuming that the only anion present is nitrate.

reflections, a feature characteristic of turbostratic structures.

The NHN sample aged in the tartarate buffer exhibits all the characteristics of the α-phase. The interlayer spacing increases from 6.9 to 7.3 Å with an additional peak at 3.7 Å. The sharp lines of NHN in the 2.7–2.3 Å region transform into a broad band characteristic of the α-phase. It is clear that tartarate ageing has transformed the NHN into a α-type hydroxide. The $[OH^-]/[Ni^{2+}]$ ratio rises to 1.87 and yields the formula $[Ni(OH)_{1.87}(NO_3)_{0.13} \cdot 1.5H_2O]$, which is very close to the composition of α-nickel hydroxide given in the literature, i.e., $[Ni(OH)_{1.8}(NO_3)_{0.2} \cdot 0.65H_2O]$ [9]. It is interesting that all the three phases can be indexed on hexagonal cells (Table 1). This shows them to be isotypic.

The IR spectra of the as-prepared and the tartarate aged samples of NHN are given in Fig. 2, together with the spectrum of α-nickel hydroxide. All the three samples display a broad band in the high wavenumber (3700–3000 cm^{-1}) region due to hydrogen-bonded OH groups. There is an absorption at 2190 cm^{-1} due to the isocyanate ion (NCO^-) which is one of the products of urea hydrolysis [14] and, therefore, can be expected to be included in the interlayer region during synthesis. In the low wavenumber (800–400 cm^{-1}) region, there are bands due to the $\delta(Ni-O-H)$ (660 cm^{-1}) and $\nu(Ni-O)$ (480 cm^{-1}) vibrations. Bands due to the nitrate groups are observed in the 1600–1000 cm^{-1} region. The as-prepared NHN shows four strong absorptions. Three of these (ν_1: 1305, ν_3: 990 and ν_4: 1520 cm^{-1}, respectively) have been assigned to the strongly bound nitrate group, while the fourth (1380 cm^{-1}) arises from the interaction of the sample with the KBr in the pellet [15]. For α-nickel hydroxide, ν_4 shifts to 1450 cm^{-1} and the other absorptions are present at 1305 cm^{-1} and 1000 cm^{-1} (ν_2). This pattern is characteristic of the nitrate ion loosely bound in $C_{2\nu}$ symmetry between the nickel hydroxide sheets. The prominent difference between the two phases is the splitting, $\Delta\nu$, between ν_4 and ν_1 which changes from 215 cm^{-1} in NHN to 145 cm^{-1} in
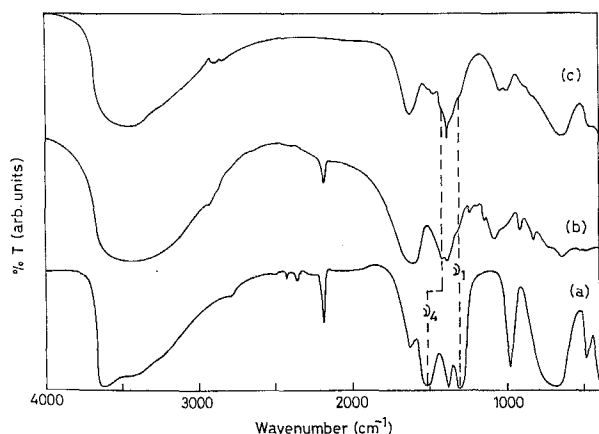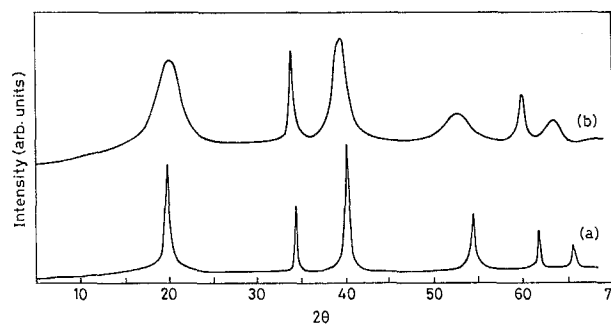

Fig. 3. Powder XRD patterns of NHN aged in (a) an acidic (pH: 4) buffer and (b) in 1 M KOH.

α-nickle hydroxide. The tartarate aged sample of NHN has an IR spectrum very similar to that of α-nickel hydroxide.

Upon ageing in other media, the NHN transforms to β-type nickel hydroxide. A crystalline β-Ni(OH)$_2$ is obtained from an acidic buffer (pH: 4) while a badly crystallized (bc) β_{bc}-phase is obtained from 1 M KOH (see Fig. 3).

4. Discussion

Both α-nickel hydroxide and NHN have a hexagonal structure. The powder XRD patterns of the two phases are very similar, except for a small difference in the interlayer spacing. Compositionally, both are obtained by creating hydroxyl deficiencies in the parent brucite-type nickel hydroxide (β-Ni(OH)$_2$) phase. Therefore, the two are isostructural compounds. The main difference between the two arises in the bonding of the nitrate ions. The large splitting, $\Delta\nu$, between the ν_4 and the ν_1 vibrational modes of the nitrate ion in the IR spectrum of NHN reveals that the nitrate is bound strongly and directly to the metal ion. This kind of strong coordination is termed as 'grafting' [16]. The smaller $\Delta\nu$ in α-nickel hydroxide is indicative of a loose bonding between the sheets and rules out any strong coordination with the metal (see Fig. 4). The fact that NHN can be transformed to α-nickel hydroxide by soft chemical ageing in a tartarate buffer shows the close relationship between the structures of these two phases. The transformation of the grafted nitrate into a loosely intercalated species leads to an increase in the interlayer spacing in α-nickel hydroxide compared with

Fig. 2. IR spectra of (a) as-prepared and (b) tartarate aged NHN compared with that of (c) α-nickel hydroxide.
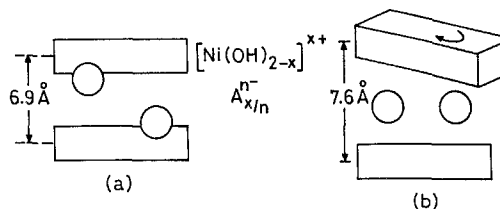

Fig. 4. A schematic representation of (a) grafted NHN sheets compared with (b) intercalated turbostratic α-nickel hydroxide sheets.

NHN, and introduces disorder in the form of turbostraticity as the layers lose the strong orienting effect due to the grafted ions. The increased disorder in α-nickel hydroxide is evident from the broad peaks observed in its XRD pattern. At the same time, some of the nitrate is exchanged for hydroxyl ions and causes an increase in the hydroxyl to metal ratio.

Ageing of NHN in acid medium proceeds via dissolution and reprecipitation leading to the formation of crystalline β-Ni(OH)$_2$. On the other hand, in 1 M KOH, the strong dehydrative and corrosive nature of the medium removes all but the adsorbed nitrate species from NHN and leads to the formation of a β_{bc}-type nickel hydroxide.

Acknowledgements

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