# On the existence of a nickel hydroxide phase which is neither α nor β

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A novel phase of nickel hydroxide with an average interlayer spacing 5.4–5.6 Å has been synthesized which is neither α nor β type but is an interstratification of both. It ages to the β form in strong alkali. These observations have implications on the dissolution–reprecipitation mechanism suggested for the α→β transformation of nickel hydroxide.

Owing to the wide application of nickel hydroxide as a positive electrode material in nickel-based alkaline secondary cells,[1] there is considerable interest in its solid-state chemistry,[2,3] especially because the structural and compositional characteristics of nickel hydroxide affect its behaviour during reversible cycling. Nickel hydroxide exhibits a rich polymorphism and a number of phases have been identified.

The phases obtained by the hydrothermal treatment of freshly precipitated gels,[4] dioxygen oxidation of nickel powder in the presence of ammonia,[5] or by boiling a solution of nickel hexammine complex[6] are stoichiometric phases of the formula $Ni(OH)_2$ and are designated β. β-$Ni(OH)_2$ is isostructural with brucite [$Mg(OH)_2$] and consists of an ordered stacking of well oriented $Ni(OH)_2$ slabs. This anhydrous phase exhibits a hexagonal platelet morphology and the OH groups of the adjacent layers are not hydrogen bonded.

Phases obtained by precipitation using ammonia[7] or strong alkalis at pH 10[8] and by electrosynthesis[9] are hydrated and contain 0.66–1 mol of water. They have been variously formulated as $3Ni(OH)_2{\cdot}2H_2O$[10] and $Ni(OH)_2{\cdot}H_2O$[11] and are designated α. These hydrated phases have a larger interlayer spacing (7.56 Å) and include water molecules in their interlamellar spaces. Consequently, there is extensive hydrogen bonding between the hydroxy groups and the intercalated water molecules. The hydroxide slabs lose their orientation due to the presence of interleaving water layers and the morphology of the α phases is turbostratic. The considerable disorder results in broad bands in the X-ray diffraction pattern.

Employing an ordered oxide precursor, $NaNiO_2$, Braconnier *et al.*[12] succeeded in preparing a highly ordered α phase with sharp lines in the X-ray diffraction pattern by a *chimie douce* route. This phase has been formulated as $Ni(OH)_2{\cdot}0.75H_2O$ and is termed α*.

The structural, compositional and morphological features of these phases have been reviewed by Oliva *et al.*[2] Recent work[13] has conclusively shown that the α phases are not simple hydrated hydroxides but are non-stoichiometric. They are hydroxy deficient and include a variety of anions in the interlayer region along with water molecules. The α phases have now been reformulated as $Ni(OH)_{2-x}A^{n-}{}_{x/n}{\cdot}mH_2O$ ($A^{n-}$ = anion) where $x$ can vary from 0.05 to 0.4 and $m = 0.6$–1 depending upon the method of preparation and work-up.

Compositional tinkering by doping nickel hydroxide with 20 mol% of Al[14] or $Co^{III}$[15] has resulted in the formation of layered double hydroxide (LDH) phases which are isostructural with α-nickel hydroxide, and contain anions and water molecules intercalated between the layers. These are known as stabilised α phases.

Among the β type also, modified phases such as $β_{bc}$ (bc = badly crystallised) have been identified.[8] The $β_{bc}$ phases are stoichiometric but contain adsorbed anions and display very broad peaks in their XRD patterns indicative of considerable disorder.

There have been suggestions that the polymorphism in nickel hydroxide is not limited only to the α and β phases. Kamath and Subbanna[16] observed the existence of a nickel hydroxide phase with a short-range structure having features of both α and β phases. Spectroscopic studies of Bernard *et al.*[17] also point towards the possible existence of a new phase of nickel hydroxide. However clear structural evidence has not been provided by any of these authors. In the course of our efforts to prepare α-nickel hydroxide by the method of Delmas[8] we succeeded in synthesizing a new phase. Here we present structural, spectroscopic and chemical evidence for the existence of such a phase which is neither α nor β but contains some structural ingredients of both.

## Experimental

### Synthesis

Nickel hydroxide samples were prepared by the addition of a standard NaOH solution (0.4 mol $dm^{-3}$) to a solution of a nickel salt (nitrate, chloride or sulfate; 0.2 mol $dm^{-3}$ ) until the pH of the solution was 10. At this point, nickel was quantitatively precipitated. The precipitate was immediately filtered in a fast filter paper (Whatman No.2) and washed three or four times with distilled water. Then the precipitate was transferred into a beaker and further washed by decantation until the washings turned neutral. It was then filtered once again and dried to constant mass at 65 °C. This is a slight departure from the washing and drying procedure of Delmas *et al.*[8] which leads to an α phase.

Additionally, α, β and $β_{bc}$ phases were prepared as model compounds by well known literature methods.

### Wet chemical analysis

All nickel hydroxide samples were analysed by wet chemical techniques. The nickel content was estimated gravimetrically; the hydroxy content was estimated by dissolving an accurately weighed amount of the sample in excess acid and backtitrating the excess acid with NaOH pH metrically; the anion content was assumed to obtain charge neutrality; and the unaccounted mass was attributed to the water content. This yielded an approximate formula for the phases which was verified by thermal analysis. Consistent results could be obtained for all phases except those obtained from nickel nitrate solution due to possible carbonate contamination.

### Physical characterization

The nickel hydroxide samples were characterized by powder X-ray diffractometry (JEOL JDX8P powder X-ray diffractometer, $\lambda = 1.541$ Å), IR spectroscopy (Nicolet Impact 400D FTIR spectrometer, 4 cm$^{-1}$ resolution, KBr pellets) and electron microscopy (JEOL JEM 200CX electron microscope). Thermogravimetry data were recorded on a home-made system at a heating rate of 2.5 °C min$^{-1}$ from 25 to 700 °C.

## Results

The structural features of the various model nickel hydroxide phases are shown in Fig. 1 and prominent reflections are listed in Table 1. While the highest *d*-value reflection appears at 4.6 Å in the β phase, the α phase has a low-angle reflection at 7.6 Å followed by another at 3.8 Å. In addition, in the 2.7–2.3 Å region, the α phase shows a broad band with an asymmetry on the higher $2\theta$ side characteristic of turbostratic phases while the β phase shows a two-peak pattern which is indicative of a more ordered structure.

Fig. 2 shows the powder X-ray diffraction patterns of the nickel hydroxide samples synthesized here and prominent reflections are listed in Table 2. These patterns have the following characteristics. (*i*) The first peak appears at 5.4–5.6 Å, which does not match with the first line of either the α or the β phase. (*ii*) The second peak is observed at 4.1–4.4 Å, which also does not match with any reflection of the α or the β phase. (*iii*) The *d* values corresponding to the first and the second lines are not multiples of each other as would be expected for a cell with a superstructure. (*iv*) The remaining pattern on the high-angle side is identical to that of a β phase. (*v*) The observed *d*-spacings are essentially independent of the salt from which the nickel hydroxide is obtained.

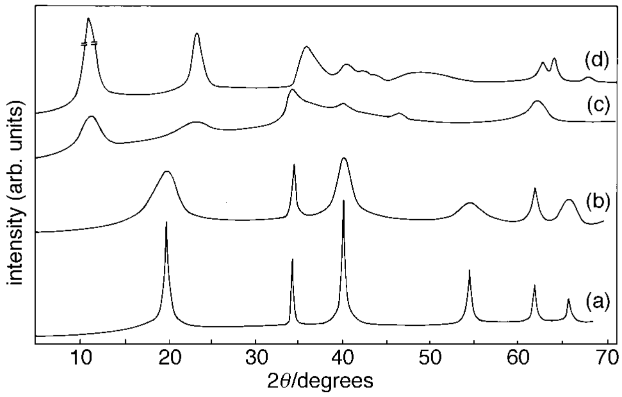

**Fig. 1** Powder X-ray diffraction patterns of β (a) and $\beta_{bc}$ (b) nickel hydroxides compared with those of α (c) and stabilized α (d) nickel hydroxides

**Table 1** Comparison of powder X-ray diffraction data of the various nickel hydroxide phases

| | $d_{obs}$/Å | | | $d_{obs}$/Å | |
|---|---|---|---|---|---|
| *hkl* | α-nickel hydroxide | stabilised α-nickel hydroxide | *hkl* | β-nickel hydroxide | $\beta_{bc}$-nickel hydroxide |
| 003 | 7.56 | 7.89 | 001 | 4.62 | 4.60 |
| 006 | 3.78 | 3.89 | 100 | 2.706 | 2.698 |
| 101 | 2.667 | 2.542 | 101 | 2.332 | 2.338 |
| 105 | 2.338 | 2.321 | 102 | 1.755 | 1.755 |
| 107 | 2.032 | 2.222 | 110 | 1.563 | 1.561 |
| 110 | 1.546 | 1.501 | | | |

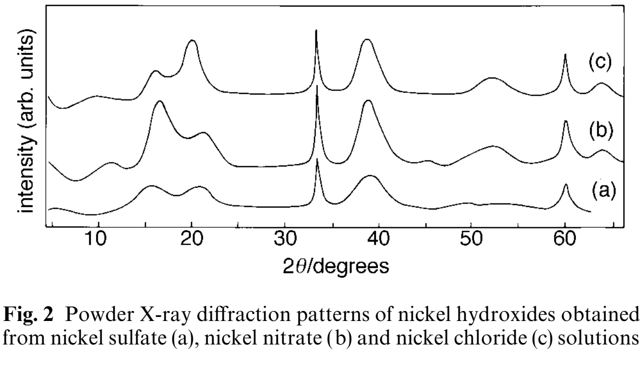

**Fig. 2** Powder X-ray diffraction patterns of nickel hydroxides obtained from nickel sulfate (a), nickel nitrate (b) and nickel chloride (c) solutions

**Table 2** Powder X-ray diffraction data of the new nickel hydroxide phases (present work)

| $d_{obs}$[a]/Å new nickel hydroxide phase obtained from | | |
|---|---|---|
| nickel sulfate | nickel nitrate | nickel chloride |
| 5.61 | 5.37 | 5.40 |
| 4.23 | 4.13 | 4.41 |
| 2.698 | 2.691 | 2.691 |
| 2.321 | 2.326 | 2.326 |
| — | 1.755[b] | 1.755[b] |
| 1.556 | 1.558 | 1.558 |

[a] Lines below 3 Å are identical to that of the β phase. [b] Broad.

The results of wet chemical analysis of these samples are given in Table 3. The new phases synthesized by us are hydroxy deficient and incorporate anions in the interlayer region. They can also be formulated in the manner of α-nickel hydroxide as $Ni(OH)_{2-x}(A^{n-})_{x/n} \cdot yH_2O$ ($x = 1.80$–$1.85$; $y = 0.5$–$1$).

Fig. 3 shows IR spectra of the new nickel hydroxide samples. Model β phases are characterized by a sharp non-hydrogen bonded OH stretch at 3650 cm$^{-1}$ and characteristic absorptions at 540 and 470 cm$^{-1}$ in the low-frequency region. Model α phases show a broad OH stretching band owing to extensive hydrogen bonding with the intercalated water molecules and characteristic absorptions at 640 and 470 cm$^{-1}$.[2] In addition, the α phase exhibits strong absorptions due to the intercalated anions in the 1600–1000 cm$^{-1}$ region.[13] The nickel hydroxide samples prepared by us show characteristics of both the α and the β type hydroxides by (*i*) the presence of a sharp OH peak together with a broad band centered around 3300 cm$^{-1}$, (*ii*) strong anion related vibrations in the 1600–1000 cm$^{-1}$ region and (*iii*) presence of absorptions at 640, 570 and 470 cm$^{-1}$ in the low-frequency region.

Fig. 4 shows thermogravimetric data of the new nickel hydroxide phases obtained from nitrate, chloride and sulfate solutions. While the model β phase suffers a net loss of 18.1% (expected 19.4%) and the α phase suffers a net loss of 34% (25% in the case of the sulfate containing α phase), in the present instance the net loss is between 23 and 25% for chloride and sulfate containing nickel hydroxides and 32.6% for the nitrate containing sample. The observed mass losses are intermediate between the losses observed for α and β phases. However the two-step thermogram is similar to the behaviour of the β rather than the α phase.[18]

Fig. 5 shows the results of electron microscopic investigations. The electron diffraction pattern shows a *d*-spacing of 5.4 Å. The low magnification bright field image shows a fine fibrillar morphology. A representative high-resolution image shows the emergence of some dark lines with thickness 5.4 Å within an amorphous matrix. However these bands are not packed in an orderly manner.

## Discussion

The absence of the most intense reflections of both the α (7.6 Å) and the β (4.6 Å) phases clearly shows that the samples prepared by us are not a mixture of these two polymorphs.

Compositionally the phases reported here are related to the basic nickel salts.[19] Basic nickel salts such as $Ni(OH)(NO_3)$, $Ni_3(OH)_4(NO_3)_2$ and $Ni_2(OH)_3(NO_3)$ and their chloride and

**Table 3** Results of wet chemical analysis of the new nickel hydroxide phases (present work)

| precursor | composition (mass%) $Ni^{2+}$ | $OH^-$ | $A^{n-}$ | $H_2O$ | mass% loss[a] (TG) | molecular formula |
|---|---|---|---|---|---|---|
| $NiSO_4$ | 55.0 | 29.0 | 8.1 | 7.5 | 23.5<br>(22.9) | $Ni(OH)_{1.82}(SO_4)_{0.09}\cdot0.44H_2O$ |
| $Ni(NO_3)_2$ | 48.9 | 26.0 | 8.3 | 16.7 | 32.6<br>(37.6) | $Ni(OH)_{1.84}(NO_3)_{0.16}\cdot1.1H_2O$[b] |
| $NiCl_2$ | 54.9 | 28.6 | 6.8 | 9.8 | 25.5<br>(24.9) | $Ni(OH)_{1.80}Cl_{0.20}\cdot0.58H_2O$ |

[a]Values in parentheses correspond to those expected from the proposed formulae. [b]The formula is inaccurate due to possible carbonate contamination.

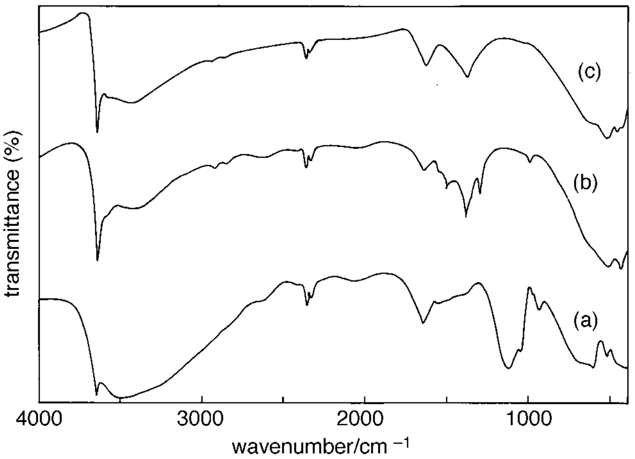

**Fig. 3** IR spectra of nickel hydroxides obtained from nickel sulfate (a), nickel nitrate (b) and nickel chloride (c) solutions

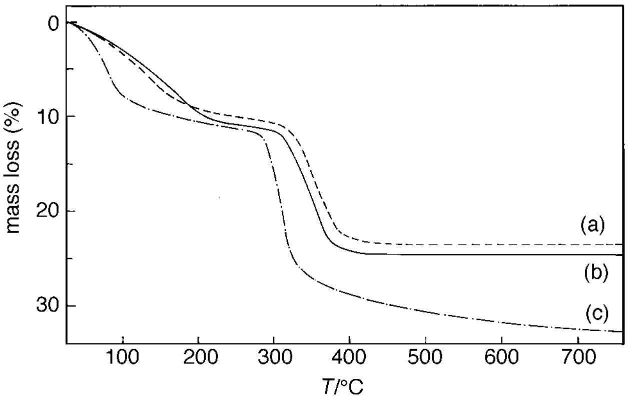

**Fig. 4** Thermogravimetry data for nickel hydroxides obtained from nickel sulfate (a), nickel chloride (b) and nickel nitrate (c) solutions

sulfate analogues can also be formulated as $Ni(OH)_{2-x}(A^{n-})_{x/n}$, ([OH]/[Ni] = 1.0–1.5) throwing open the possibility that the new phase is that of a basic salt. However, none of these basic salts have a *d*-spacing of 5.4–5.6 Å. Also the diffraction patterns of the basic salts are quite different from the ones reported here. All these observations indicate that the observed phase is new. However, the lines could not be indexed to a single phase, with either a hexagonal or a monoclinic cell.

The IR spectra reflect the short-range structure of a solid. The presence of IR absorptions corresponding to both the α and the β phases clearly indicates the presence of both α and β type coordination for the nickel ion, despite the absence of any long-range order of the α or the β type. These observations can be reconciled in one of the two following ways: (*i*) the line at 5.4 Å could be due to a new phase which is intermediate between the α and β phases or (*ii*) the line at 5.4 Å could arise

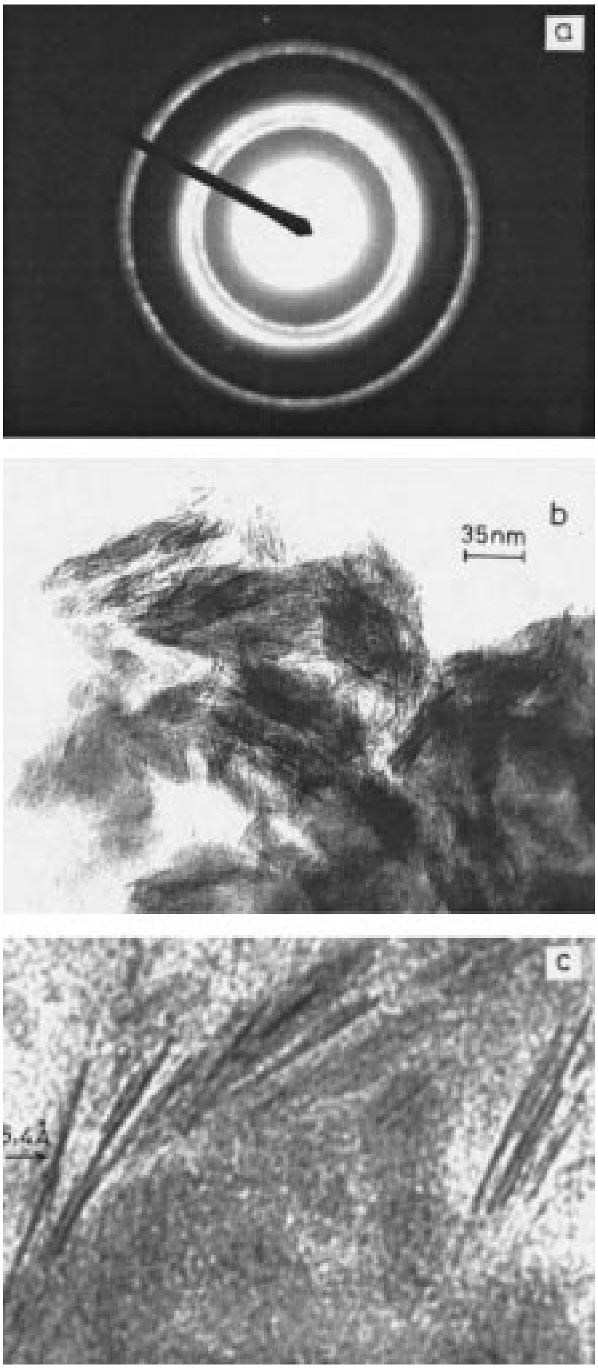

**Fig. 5** Electron diffraction pattern of nickel hydroxide obtained from nickel nitrate (a); a low magnification image (b) and a high magnification image (c) of a representative particle

due to interstratification of the α and β motifs which are intimately and randomly mixed in every particle of the sample (see graphical abstract.)

The possibility of a new phase can be eliminated by the fact that the XRD patterns cannot be indexed as a single phase and the high-resolution electron micrograph does not show a uniform packing of slabs of 5.4 Å thickness.

The broad peak at 5.4–5.6 Å lies between the reflections due to the (003) plane of the α phase and the (001) plane of the β phase and the 4.1–4.4 Å peak lies between the reflections due to the (001) plane of the β phase and the (006) plane of the α phase. This feature is characteristic of interstratified phases.[20] The observed average interlayer spacing of 5.4–5.6 Å would correspond to a 30% abundance of the α motif.

The α phase of nickel hydroxide is known to be unstable in strong alkali and ages rapidly to the β form. Based on detailed investigations, it has been proposed that the α→β transformation proceeds by the dissolution–reprecipitation mechanism.[4] The observation of the interstratified phase with a structure and composition intermediate between that of the α and β phases gives credence to the nucleation-cum-growth mechanism for the α→β transformation. This is strengthened by our observation of the formation of the β phase from the new phase upon aging in alkali.

In conclusion, we report the synthesis and characterisation of a new nickel hydroxide which is neither of the α nor of the β variety.

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