Characterization of a turbostratic α-nickel hydroxide quantitatively obtained from an NiSO$_4$ solution

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Abstract

Turbostratic α-nickel hydroxide has been obtained with an almost quantitative yield from NiSO$_4$ solution. The chemical analyses and the infrared study show that a lot of SO$_4^{2-}$ anions are adsorbed and intercalated between Ni(OH)$_2$ slabs. The large value of the intersheet distance and the infrared study show that the greater part of the intercalated SO$_4^{2-}$ anions are free in the Van der Waals space. During thermal treatment, the H$_2$O loss is associated with a linking of SO$_4^{2-}$ anions with Ni^{2+} cations, as shown by the splitting of the $\nu_3(SO)_4^{2-}$ band in the infrared spectrum.
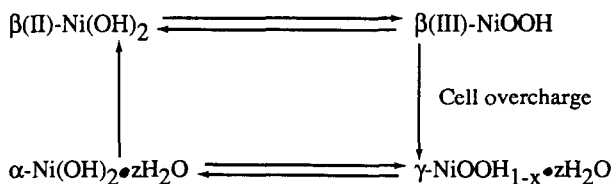
Introduction

The electrochemical cycling of the positive electrode of Ni/Cd or Ni/H$_2$ batteries takes place between β(II)-Ni(OH)$_2$ and β(III)-NiOOH phases. These two materials exhibit a layer structure made of NiO$_2$ sheets, between which protons are intercalated. Such a description allows a comparison with the processes involved in lithium intercalation compounds. Both phases crystallize in the hexagonal system, the c parameter, corresponding to the intersheet distance, is equal to 4.6 Å for the reduced β(II) phase and to 4.7 Å for the oxidized phase (β(III)).

After a strong overload of the cell or a long period of floating, a γ-type phase with an expanded c parameter of 7 Å may be formed; then, after the cell discharge, the β(II) phase is recovered. The repetition of such a process results in considerable damage to the nickel oxide electrode (NOE) as a result of mechanical constraints. The various reactions involved in the NOE are summarized by the well known Bode diagram [1].

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Electrochemical cycling

$$\beta(II)\text{-Ni(OH)}_2 \rightleftharpoons \beta(III)\text{-NiOOH}$$

Cell overcharge

$$\alpha\text{-Ni(OH)}_2 \bullet z\text{H}_2\text{O} \rightleftharpoons \gamma\text{-NiOOH}_{1-x} \bullet z\text{H}_2\text{O}$$

A layer of water molecules is inserted between the Ni(OH)$_2$ slabs of the α-phase. In the case of the γ-oxyhydroxide the inserted species are H$_2$O molecules and alkali ions.

The $\alpha \leftrightarrow \gamma$ cycling which appears on this diagram exhibits, from a theoretical point of view, several advantages compared with the $\beta(II) \leftrightarrow \beta(III)$ cycling:

— a large number of electrons exchanged per nickel atom, as the oxidation level of nickel in the γ-phase is close to 3.5;
— a decrease in the mechanical constraints resulting from the suppression of the $\beta(II) \rightarrow \gamma$ reaction;
— a higher diffusion coefficient for the proton due to the presence of the layer of water molecules between NiO$_2$ slabs.

Unfortunately, the α-type phase obtained either chemically (precipitation by NH$_4$OH from an Ni(NO$_3$)$_2$ solution) or electrochemically (electrochemical deposition from an Ni(NO$_3$)$_2$ solution) is unstable in KOH medium and leads to a $\beta(II)$-type phase by a dissolution, germination, and growth mechanism, as shown by Le Bihan *et al.* [2].

It has been shown in our laboratory that hydrated, cobalt-substituted nickel hydroxides (designated by α^*) obtained by *chimie douce* techniques are stable at room temperature in KOH electrolyte [3]. These phases were easily characterizable from a structural point of view, but the large size of the particles could reduce their electrochemical activity. In order to overcome this problem, we have tried to obtain similar materials from precipitation techniques. Thus, the first step consisted in developing a method of α-phase precipitation combining high yield and particles of minimum size. In this paper we shall describe the first results involving the characterization of an α-nickel hydroxide, obtained by an almost quantitative precipitation from a nickel sulfate solution. The effects of the addition of cobalt to this material will be reported in a forthcoming paper.

Obtaining an α-phase with a high precipitation yield

α-Phases are prepared either by chemical precipitation or by electro-chemical deposition. The chemical precipitation is presently effected by adding an NH$_4$OH solution to an Ni(NO$_3$)$_2$ solution. In this case, the precipitation yield is close to 10 per cent. Furthermore, the presence of NO$_3^-$ anions remaining in the NOE leads to corrosion problems, NiSO$_4$ was therefore

chosen as the starting salt. As NH$_4$OH gives a precipitation pH close to 10, it was considered that the formation of the α-hydroxide was related to the pH value rather than to the presence of NH$_4$$^+$ cations. Moreover, as NH$_4$OH is harmful, NaOH was chosen as precipitating agent.

When an NiSO$_4$ solution is added dropwise to an NaOH solution, the pH value remains close to 13. By contrast, if the NaOH solution is added dropwise to the NiSO$_4$ solution, pH control can be carried out. Further, in order to obtain particles of minimum size, other parameters were optimized.

Preliminary results showed that the particle size is minimized if the temperature ranges from 0 to 25 °C, and also if the precipitation duration is small (a few minutes). These parameters were then fixed, and a precipitation under pH control was performed.

Effect of pH on the nature of the precipitated nickel hydroxide

The pH variation versus the NaOH/NiSO$_4$ molar percentage was followed, and is reported on Fig. 1. It shows that a 100% precipitation rate corresponds to a pH value close to 13. Under these conditions, a β(II)-type phase is recovered. A pH value of 10 is obtained after adding about 80% of the theoretical amount of NaOH. It should be noted that the NaOH/2NiSO$_4$ ratio differs from the precipitation yield: a 90% yield is obtained with an 80% NaOH/2NiSO$_4$ ratio. This result suggests, as will be confirmed below, that SO$_4$$^{2-}$ anions are involved in the precipitation. In this latter case, an α-type phase is recovered, as shown by the X-ray diffraction study. Unfortunately, α-phases are unstable in alkaline medium, and a badly crystallized β(II)-type phase (designated by β$_{bc}$) is obtained if the slurry is washed with water and dried for 15 h at 70 °C.

In order to delay the α→β$_{bc}$ transformation, the washing and drying conditions were optimized. As a first step, the slurry is washed five times with water, then with acetone, and filtered. The resulting cake is dried by mechanical extrusion of the liquid, then in a drying oven at 30 °C. Under these conditions, an α-type phase is recovered.
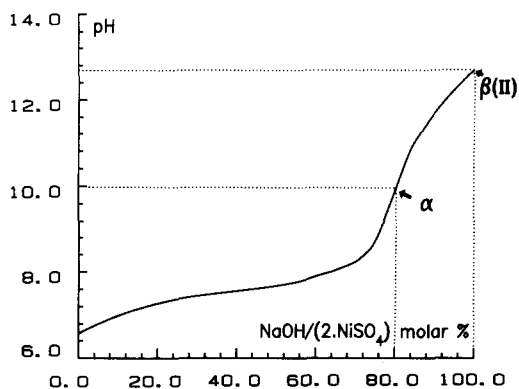

Fig. 1. Evolution of the pH value vs. the NaOH/2NiSO$_4$ molar percentage.

Materials characterization

X-ray diffraction study

X-ray diffraction patterns of the powdered compounds were recorded using Cu Kα radiation. The patterns of both α and β_{bc} phases are reported in Fig. 2. Although these layered materials are very poorly crystallized, the main planar distances, which allow their characterization, can be deduced from the X-ray diffraction patterns. The first diffraction line (001) which appears for small diffraction angles gives the intersheet distance and shows, unambiguously, the presence ($c_\alpha = 9$ Å) or absence ($c_{\beta, bc} = 4.6$ Å) of a layer of water molecules between the Ni(OH)$_2$ slabs. The other interesting diffraction line is the (110) line which, in the hexagonal symmetry, gives the a_{hex} parameter directly ($a_{hex} = 2d_{110}$). This value is close to 3.1 Å for both α or β_{bc} phases.

The X-ray diffraction pattern of this α phase appears similar to that of the α phase obtained by Figlarz et al. from Ni(NO$_3$)$_2$ and NH$_4$OH solutions, and also emphasizes its turbostratic character [2, 4]: the Ni(OH)$_2$ slabs are parallel, equidistant, but completely misoriented with regard to one another. The large dissymetric band of the X-ray diffraction spectrum between 30 and 45° in 2θ is characteristic of this turbostratic nature and results from the overlap of the (101) diffraction lines of the β(II)-nickel hydroxide spectrum. The beginning of this large band at $2\theta = 35.5°$ corresponds to the (100) line of the β(II)-Ni(OH)$_2$ spectrum, and the a_{hex} parameter can be estimated from this particular point: $a_{hex} = 3.1$ Å.

The X-ray diffraction lines of the α phase are so large (Fig. 2(a)) that the particle size cannot be deduced from Scherrer's formula [5]. In the case of the previously described α-hydroxide, the following values have been reported [2]: $H = 30$ Å and $D = 80$ Å along the c_{hex} and a_{hex} axes, respectively. In this paper, the hydroxide particles are assumed to have a cylindrical shape (H = thickness, D = diameter).
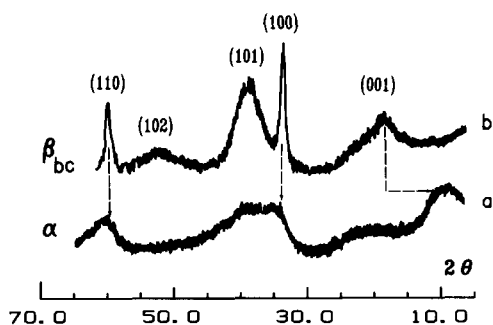

Fig. 2. X-ray diffraction spectra of α- and β_{bc}-nickel hydroxides obtained by precipitation from NiSO$_4$ and NaOH solutions.

Chemical stability of the α phases in alkaline or water medium

α Phases evolve rapidly in concentrated alkaline medium (5 N KOH) leading, after a few minutes, to a β_{bc}-type phase. Then the size of the particles increases with time and a crystallized β(II)-type phase ($H = 40$ Å, $D = 120$ Å) is recovered after 24 h.

The reaction speed is considerably reduced in water at room temperature: a mixture of α and β_{bc} phases is recovered after 4 days.

Chemical cycling of α-type phases

In order to simulate the electrochemical charge–discharge of the NOE, chemical cycling reactions have been performed. NaClO has been used as oxidizing agent [6], while the reduction reaction was effected with H_2O_2 [7]. According to previous work, the oxidation with NaClO leads to a β(III)-type phase, while oxidation with an NaClO + KOH mixture gives the γ-oxyhydroxide as K^+ ions are necessary to stabilize this structure [8].

X-ray diffraction spectra of the various oxidized and reduced phases are reported in Fig. 3.

Oxidation in a diluted NaClO solution (1 M) leads to a poorly crystallized β(III)-NiOOH phase. The spectrum of this oxyhydroxide is shown in Fig. 3(b). The starting α-phase pattern is given for comparison (Fig. 3(c)). When this oxyhydroxide is reduced with an H_2O_2 solution (11 vol.), a β_{bc}-type phase is obtained, as shown by the X-ray diffraction spectrum reported in Fig. 3(a). The oxidation and reduction reactions are particularly well emphasized by the variation of the a_{hex} parameter. This value, deduced from
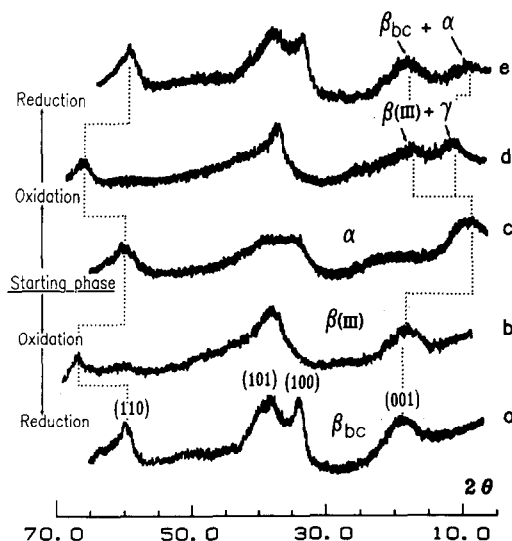

Fig. 3. X-ray diffraction spectra of the chemically cycled (oxidation reduction) α-nickel hydroxide. The β(III)- and γ-oxyhydroxides are obtained by action of NaClO and NaClO + KOH solutions, respectively.

the (110) line, is close to 3.1 Å in the reduced phases and becomes equal to 2.8 Å in the oxidized phases.

Oxidation with (1/5 4 M NaClO + 4/5 5 N KOH) solution should lead to a γ-type phase. In fact, a mixture of γ- and β(III)-oxyhydroxides is recovered, as shown by the X-ray diffraction pattern in Fig. 3(d). To explain this behavior, it is assumed that the β(III) phase arises from the reduction of the γ-oxyhydroxide by the action of water during washing. Indeed, the γ-phase has so small particles that its reactivity is such that in some experiments washing this material with acetone has led to spontaneous ignition. As a result, reduction of this oxidized mixture leads to the formation of β_{bc} and α phases as shown by Fig. 3(e). The presence of the β_{bc}-type phase was confirmed by infrared study performed on the reduced material.

Chemical analysis

Chemical analysis shows that the nickel content in α phases ranges from 44 to 48%, while it is theoretically equal to 63.3% in stoichiometric $Ni(OH)_2$. This result suggests the presence of many adsorbed or intercalated species. Indeed, great amounts of SO_4^{2-} anions were found in α and β_{bc} phases. In α phases, the SO_4^{2-}/Ni^{2+} molar ratio always ranges from 0.20 to 0.25, while in β_{bc}-type phases, the SO_4^{2-} content increases considerably as the particle size of the nickel hydroxide decreases (Table 1). In the case of sample 3, the (001) line is so large that Scherrer's formula cannot be used.

Chemical analysis also shows the presence of a large amount of water molecules in α phases with an average H_2O/Ni molar ratio close to 1.15.

Thermal decomposition of α-type phases

The TGA curve of the α-turbostratic nickel hydroxide is given on Fig. 4. It shows a continuous weight loss between room temperature and 100 °C, which is in accordance with the removal of the adsorbed and a part of the intercalated water molecules. At 160 °C, 0.3 water molecules are still inserted between the $Ni(OH)_2$ slabs. Beyond this temperature, all the intercalated water molecules are removed, and dehydroxylation occurs. This study

TABLE 1

SO_4^{2-}/Ni^{2+} molar ratio vs. the particle sizes of β(II) phases

Sample number	Precipitation duration Precipitation temperature	D (Å)	H (Å)	SO_4^{2-}/Ni^{2+} molar ratio
1	few minutes 80 °C	170	50	0.10
2	1 hour 25 °C	150	30	0.12
3	few minutes 25 °C	100	–	0.17
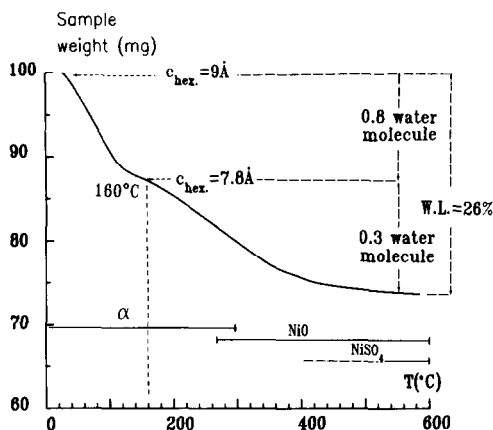
Fig. 4. TGA curve of α-nickel hydroxide (1 °C min^{-1} under nitrogen flow).

gives an H_2O/Ni molar ratio close to 1.1, which is in accordance with that found by chemical analysis (1.15).

The X-ray diffraction versus temperature study shows that the intersheet distance of the α-type phase decreases from 9 Å at 25 °C to 7.8 Å at 160 °C without other modification of the X-ray diffraction pattern. The X-ray diffraction study effected at higher temperature shows that sheet destruction begins at 270 °C, as indicated by the appearance of the NiO diffraction lines and the disappearance of the (001) line characteristic of the α phase. This decomposition is total at 300 °C, leading to a mixture of NiO and $NiSO_4$. This thermal evolution of α phase obtained from $NiSO_4$ and NaOH solutions is similar to that of α phase prepared from $Ni(NO_3)_2$ [9].

Infrared characterization

The experiments were carried out on a Perkin Elmer 983 spectrometer. The samples were mixed with nujol and then pressed between two CsI windows.

The infrared spectra of β(II), β_{bc} and α phases are shown on Fig. 5. For β_{bc}-hydroxide, two materials have been considered: the first (Fig. 5(b)) was obtained directly by precipitation, and the other results from the evolution of the α phase in KOH medium (Fig. 5(d)).

In order to have a reference compound, a relatively well crystallized β(II)-$Ni(OH)_2$ ($H = 75$ Å and $D = 200$ Å) was also studied. Its spectrum (Fig. 5(a)) presents:
— a narrow band at 3650 cm^{-1}, corresponding to the stretching vibration ν(OH),
— a strong band at 520 cm^{-1}, due to the hydroxyl groups' lattice vibration, δ(OH),
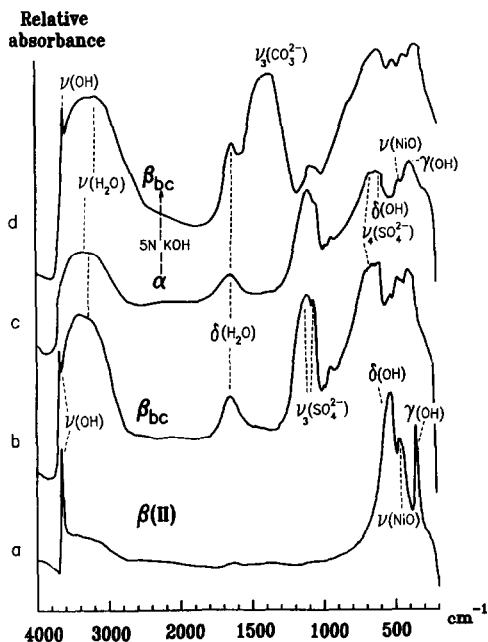— a narrow band at 345 cm^{-1}, due to the out-of-plane vibration, γ(OH),

Fig. 5. Infrared spectra of $\beta(II)$-, β_{bc}- and α-nickel hydroxides in the 200–4000 cm^{-1} range.

— a weak band at 460 cm^{-1} which characterizes the Ni–O lattice vibration ν(Ni–O).

These results are in good agreement with those previously reported by Kober from deuteriated material [10].

The spectra of β_{bc} (Fig. 5(b)) and α (Fig. 5(c)) phases show the presence of large bands at 3350 cm^{-1} and 1650 cm^{-1}, respectively, due to the stretching and bending modes of water molecules.

The interpretation of the central part of the spectrum ranging from 800 to 1500 cm^{-1} will be developed below. In the case of β_{bc}-nickel hydroxide, the narrow ν(OH) band at 3650 cm^{-1} remains and shows the presence of free hydroxyl groups characteristic of $\beta(II)$ phases. By contrast, for α phases, the disappearance of the narrow ν(OH) band shows that all OH groups are linked by hydrogen bonds to water molecules. Moreover, this behavior is emphasized by the shift of the δ(OH), γ(OH) and ν(NiO) bands to higher frequencies. Such behavior has been reported previously for α phases prepared from Ni(NO$_3$)$_2$ solution [12].

Infrared spectroscopy does not allow one to distinguish intercalated from adsorbed water molecules. In the case of the α phases, both types must be present. By contrast, for the β_{bc} phase, water molecules are only adsorbed, since the small interslab distance excludes the intercalation of such molecules.

Anionic species characterization

The large band around 1100 cm^{-1} on the infrared spectra of α and β_{bc} phases obtained by precipitation is characteristic of SO$_4^{2-}$ anions.

The free sulfate ion exhibits the high symmetry point group T_d, and only the ν_3 and ν_4 bands at 1104 and 613 cm^{-1}, respectively, are infrared active [13]. If the anion is linked to a metal, the symmetry is lowered and a splitting of the degenerate mode occurs simultaneously with the appearance of new bands in the infrared spectrum. The symmetry lowering caused by the bonding is different for the unidentate and the bidendate complexes. When the anion is unidentate, the symmetry becomes C_{3v} and each of the ν_3 and ν_4 bands splits into two, appearing at 1040 and 1120 cm^{-1}, and 645 and 604 cm^{-1}, respectively, for a material such as [Co(NH$_3$)$_5$SO$_4$]Br [12]. When the sulfate anion is bidendate, the symmetry becomes C_{2v} and each ν_3 and ν_4 band splits into three [13]. The vibration frequencies related to SO$_4^{2-}$ anions observed for α and β_{bc} phases are reported in Table 2 with reference compounds for comparison.

The enlarged shape of the ν_3 vibration of α and β_{bc} phases is reported in Fig. 6 between 800 and 1300 cm^{-1}. The splitting observed for the β_{bc} phase shows that the SO$_4^{2-}$ anions are unambiguously unidentate. In this case, the value of the c parameter (4.6 Å) does not allow the presence of sulfate anions intercalated between the slabs. These anions are therefore only adsorbed; they are directly linked to Ni^{2+} cations in substitution of OH groups. For the α phase, the splitting is not so apparent and a single vibration seems to be superposed on the split one. This behavior suggests the presence of free SO$_4^{2-}$ anions. As shown by the very large intersheet distance of the α phase (9 Å), these anions can be intercalated between the Ni(OH)$_2$ slabs. From these data, one can assume that free SO$_4^{2-}$ anions are intercalated, while the linked ones must be mainly adsorbed, as for the β_{bc}-hydroxide.

TABLE 2

SO$_4^{2-}$ anion vibration in α and β_{bc} phases, and in reference compounds for various anion symmetries

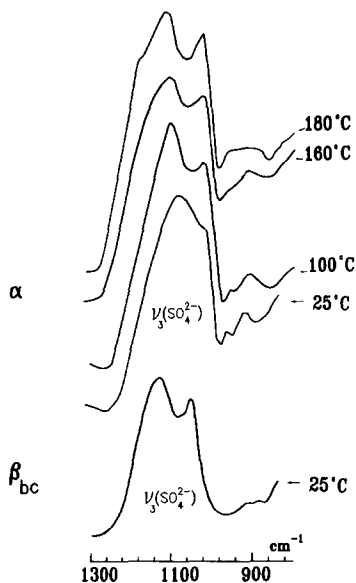| Material	Symmetry	ν_1 (cm^{-1})	ν_2	ν_3	ν_4
α		960	–	1030 1110	650 610
β_{bc}		970	440–460	1050 1125	660 600
Free SO$_4^{2-}$ anion	T_d	–	–	1104	613
[Co(NH$_3$)$_5$SO$_4$]Br	C_{3v}	970	438	1032–1044 1117–1143	645 604
[(NH$_3$)$_4$Co⟨NH$_2$/SO$_4$⟩Co(NH$_3$)$_4$][NO]$_3$	C_{2v}	995	462	1050–1060 1170 1105	641 610 571

Fig. 6. Splitting of the $\nu(SO_4^{2-})$ infrared band of β_{bc} phase and α-nickel hydroxide thermally treated ($25 \to 180$ °C).

All these results, given by the infrared spectra, show that the cohesion of the misoriented sheets is not only due to water molecules linked by hydrogen bonds to hydroxyls of the $Ni(OH)_2$ slabs, but is also due to intercalated sulfate anions. However, the presence of SO_4^{2-} anions sets a charge equilibrium problem. In order to achieve electrical neutrality, two hypotheses can be developed: OH^- vacancies in the $Ni(OH)_2$ slabs or H_3O^+ intercalation in the Van der Waals space.

— The simultaneous presence of an OH^- vacancy and a free SO_4^{2-} anion in the same area (in order to respect the second Pauling rule) would lead to a linking of the SO_4^{2-} anion to the nickel ion. Moreover, the SO_4^{2-} anions are free in the Van der Waals space (i.r. spectroscopy) and the presence of OH^- ion vacancies would lead to a large amount of penta-coordinated Ni^{2+} cations. Such an environment is not particularly stable for Ni^{2+} cations. The hypothesis of OH^- vacancies has been excluded from both arguments.

— The hypothesis of H_3O^+ cation intercalation in the Van der Waals gap does not seem likely as the material is obtained in basic medium (pH = 10). An intermediate situation has therefore been considered: substitution of H_2O molecules for OH^- ions or, in other words, protonation of the hydroxyl groups. In this case, the excess of charge due to SO_4^{2-} anions is directly compensated for by Ni^{2+} cations. Such a charge compensation mechanism that preserves the octahedral environment of nickel is fully compatible with the experimental conditions of precipitation (pH = 10). Moreover, the partial substitution of H_2O molecules for OH^- groups agrees with the 80% NaOH/ $2NiSO_4$ ratio used for the precipitation.

As previously mentioned, when the α phase is set aside for a short time in concentrated KOH, a β_{bc}-type phase is formed. The infrared study performed on this material (Fig. 5(d)) shows that the greater part of the sulfate anions are removed from the hydroxide and replaced by CO_3^{2-} anions.

Influence of temperature on SO_4^{2-} bonding

As previously discussed, a large part of the water molecules is removed from the intersheet space between 25 and 160 °C. Moreover, the intersheet distance decreases from 9 to 7.8 Å. These materials have been characterized by infrared spectroscopy.

The study shows that the free intercalated sulfate anions could be linked to the sheet at around 100 °C. The infrared spectra of the α phases at increasing temperatures (100, 160 and 180 °C) are reported on Fig. 6 between 800 and 1300 cm^{-1}. These spectra show that above 100 °C, SO_4^{2-} groups become more and more linked. It should be noted that at 180 °C, a shoulder appears in the vicinity of 1180 cm^{-1} (Fig. 6). This could indicate a new decrease in the symmetry (which becomes C_{2v}) and therefore a bidentate linking. The fact that SO_4^{2-} anions are linked to the sheet above 100 °C is emphasized by the following experiment: when the material heated at 130 °C is wetted again, the intersheet distance remains close to 8 Å. This shows that the strong bond formed between the SO_4^{2-} anion and the Ni^{2+} cation is not broken in these conditions.

It has been shown previously that at 160 °C, a large part of the water molecules (adsorbed and intercalated) was removed from the α phase. One can assume that the H_2O molecules which are in substitution with OH$^-$ groups are also released. Therefore, one oxygen of the SO_4^{2-} ion occupies this available site and thus an Ni^{2+}–SO_4^{2-} bond is formed.

Such a linking of SO_4^{2-} anions at increasing temperatures has already been observed by El Malki *et al.* [14] on the chromium copper hydroxides: $[Cu_2Cr(OH)_6](SO_4)_{1/2} \cdot n H_2O$, which belong to the layer double hydroxides (LDHs) family [15]. When this material, which crystallizes in the rhombohedral system, is heated, the interlayer distance exhibits a strong decrease from 8.12 Å at 25 °C to 7.13 Å at 120 °C. The infrared study also shows that SO_4^{2-} anions are linked at moderate temperature (80–120 °C).

Conclusions

The precipitation of nickel hydroxide from an $NiSO_4$ solution controlled by pH conditions leads to an α-type phase. The precipitation yield is almost quantitative; this result should be compared with the poor yield (10%) obtained for the classical preparation from $Ni(NO_3)_2$ and NH_4OH solutions. It may be assumed that the formation of nickel aminocomplexes must drastically reduce the amount of precipitated nickel hydroxide.

The α-type phase exhibits the classical turbostratic character; nevertheless the high precipitation speed considerably reduces the particle size. As pre-

viously described, this α-nickel hydroxide is unstable in KOH medium, leading to a β_{bc} phase, then to the classical $\beta(II)$-hydroxide.

The chemical analysis and the infrared study have shown the presence of many SO_4^{2-} anions which are either adsorbed or intercalated between the $Ni(OH)_2$ slabs of the α-hydroxide. The infrared characterization has shown that the intercalated SO_4^{2-} anions are principally free at room temperature. This result is corroborated by the very large value (9 Å) of the intersheet distance. By contrast, the adsorbed SO_4^{2-} anions of the β_{bc} phase are linked to the nickel ions. In order to compensate for the excess of negative charge due to SO_4^{2-} anions, the hypothesis of partial substitution of water molecules for hydroxyl ions has been advanced. In KOH medium, these H_2O molecules are replaced by OH^- anions, so that SO_4^{2-} anions are removed in order to preserve the charge neutrality. This reaction could explain the higher instability of these α phases versus the previously described phase.

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