

Preparation and characterization of cobalt-substituted α -nickel hydroxide stable in KOH medium

Part II. α -Hydroxide with a turbostratic structure

C. Faure and C. Delmas*

Laboratoire de Chimie du Solide du CNRS and Ecole Nationale Supérieure de Chimie et Physique de Bordeaux, Université Bordeaux I, 351 cours de la Libération, 33405 Talence Cédex (France)

P. Willmann

Centre National d'Etudes Spatiales, 18 avenue E. Belin, 31055 Toulouse Cédex (France)

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Abstract

α -Turbostratic cobalted nickel hydroxides have been obtained by precipitation, with an NaOH solution, from nickel and cobalt salts. Several preparation methods have been developed in order to obtain a material containing Ni^{2+} and Co^{3+} ions. Depending on the experimental procedure, carbonate and sulfate anions are inserted between the (Ni, Co)(OH)₂ slabs, in order to compensate for the excess of positive charge due to the presence of trivalent cobalt ions in the hydroxide. These materials have been characterized by chemical analysis, X-ray diffraction, TGA, and u.v.–visible spectroscopy. The resulting $\alpha_{\text{Co}^{3+}}$ phase is stable in KOH medium if the cobalt amount is at least equal to 20%. By contrast, the $\alpha_{\text{Co}^{2+}}$ hydroxide is spontaneously transformed to a $\beta(\text{II})$ hydroxide, whatever the cobalt amount.

Introduction

The effect of cobalt on nickel electrodes has been studied for many years, but most of the investigations deal with its influence on $\beta(\text{II})$ -type phases [1, 2]. Recently, in our laboratory, it was shown that the substitution of at least 20% of cobalt for nickel allows the formation of an α^* -hydrated phase, stable in KOH medium at room temperature [3, 4]. This material, obtained by *chimie douce* reactions from the $\text{NaNi}_{1-x}\text{Co}_x\text{O}_2$ precursor, exhibits very large particles ($D = 10^4$ Å and $H = 10^3$ Å [5]). As the electrochemical activity is generally strongly related to the particle size, precipitation techniques were used in an attempt to obtain similar compounds, but with small particles.

Several reaction procedures have been explored to obtain a nickel hydroxide substituted with trivalent cobalt ion. The first method (Part I of

*Author to whom correspondence should be addressed.

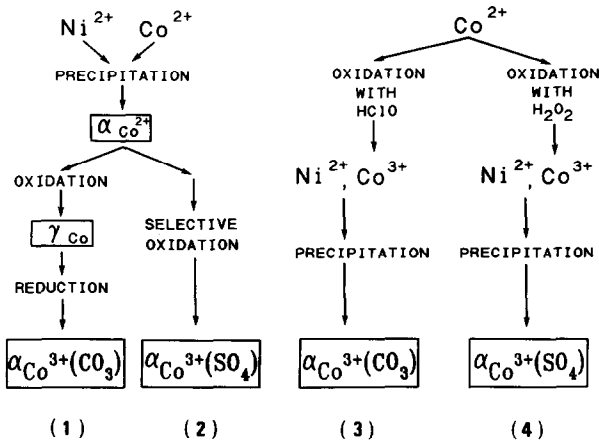


Fig. 1. Schematic representation of the processes involved in the formation of an $\alpha_{\text{Co}^{3+}}$ phase.

this article) [5] consisted of following Bode's diagram [6]: preparation of a cobalt-substituted $\beta(\text{II})$ -type phase (designated by $\beta_{\text{Co}^{3+}}$), oxidation to γ_{Co} , then reduction to $\alpha_{\text{Co}^{3+}}$, as in the case of the *chimie douce* reactions [4].

The other preparative methods which were investigated in our lab. are summarized in Fig. 1 and consist of:

precipitation of an α phase substituted with divalent cobalt ions (designated as $\alpha_{\text{Co}^{2+}}$), followed by oxidation of the cobalt ions in order to form a stabilized $\alpha_{\text{Co}^{3+}}$ phase;

direct precipitation of the trivalent cobalt substituted α phase (designated as $\alpha_{\text{Co}^{3+}}$). However, this process requires the solution of a lot of chemical problems resulting from the instability of trivalent cobalt ions in the starting solution.

This paper will describe the chemical properties of these materials. In order to simplify the ensuing discussion, the various $\alpha_{\text{Co}^{3+}}$ phases have been designated according to the nature of the anionic species inserted between the $\text{M}(\text{OH})_2$ ($\text{M} = \text{Ni}, \text{Co}$) slabs:

$\alpha_{\text{Co}^{3+}(\text{CO}_3)}$ for materials obtained by processes (1) and (3);

$\alpha_{\text{Co}^{3+}(\text{SO}_4)}$ for materials obtained by processes (2) and (4).

Materials preparation

Preparation of an $\alpha_{\text{Co}^{3+}}$ phase from an $\alpha_{\text{Co}^{2+}}$ phase (processes (1) and (2))

It is known that after initial oxidation, cobalt ions remain in the trivalent state within a nickel hydroxide lattice [7]. The aim, then, is to prepare an $\alpha_{\text{Co}^{2+}}$ phase and to oxidize the material in order to form trivalent cobalt ions and thus stabilize the α phase.

The precipitation conditions of an α -type phase, reported in a previous paper, were transposed to the cobalted phases [8]. Cobalt and nickel sulfate

solutions are mixed in a suitable ratio. Then a 2 N NaOH solution is added to the mixture until the pH reaches a value close to 10. As the $\alpha_{\text{Co}^{2+}}$ -type phase is stable in water medium, the slurry is first washed with water, then with acetone, and filtered. The resulting cake is dried at 70 °C. The blue powder obtained under these conditions is an α -type phase in which all substituting cobalt ions stay in the divalent state.

As will be shown, $\alpha_{\text{Co}^{2+}}$ phases are unstable in KOH medium, whatever the cobalt content. In order to stabilize the α -type phase, or, in other words, to avoid any transformation to a $\beta(\text{II})$ -type phase, an oxidation of the cobalt ions within the material has to be carried out. Two oxidation procedures were undertaken.

(i) The first, schematized by process (1) in Fig. 1, really simulates the electrochemical cycling of the $\alpha_{\text{Co}^{2+}}$ -type phase. The hydroxide is easily oxidized to a γ_{Co} phase, with a solution of 1/5 NaClO (4 M) and 4/5 KOH (5 N) as oxidizing agent, in one day at room temperature. The oxyhydroxide is then reduced with a diluted H_2O_2 solution (11 vol.) [9]. During this last step, nickel ions are reduced to the divalent state, while the cobalt ions remain trivalent.

(ii) The second consists of selective oxidation of cobalt ions in $\alpha_{\text{Co}^{2+}}$ -hydroxide (process (2) in Fig. 1). For that purpose, an H_2O_2 solution is used as oxidizing agent [10] and cobalt ions are then oxidized to the trivalent state while nickel ions stay divalent. The oxidation reaction from $\alpha_{\text{Co}^{2+}}$ -type phase to $\alpha_{\text{Co}^{3+}}$ -type phase is emphasized by the blue to green-brown color change.

During the $\text{Co}^{2+} \rightarrow \text{Co}^{3+}$ oxidation step, anions are inserted between the hydroxide slabs to compensate for the positive charge excess due to Co^{3+} cations. When process (1) is used, carbonate anions contribute to the electrical neutrality, while sulfate anions are the anionic species inserted between the $\text{M}(\text{OH})_2$ slabs when process (2) is used. These various points will be developed below.

Preparation of an $\alpha_{\text{Co}^{3+}}$ phase by direct precipitation (processes (3) and (4))

These precipitation techniques are schematized by processes (3) and (4) in Fig. 1.

The direct precipitation of an $\alpha_{\text{Co}^{3+}}$ phase requires two steps:

- the first consists of oxidizing cobalt ions within the solution,
- the second consists of precipitation of the material.

Oxidation of cobalt ions

The oxidation of cobalt ions in solution can be realized either by HClO or H_2O_2 solutions.

The oxidation with an HClO solution (process (3) in Fig. 1) is the most difficult, since HClO and Co^{3+} are very unstable. HClO tends to decompose spontaneously during the experiments, while Co^{3+} ions exist in solution only in the presence of an excess of the oxidizing agent. Moreover, the cobalt

solution must always be strongly acidic ($\text{pH} \leq 1.5$) in order to avoid any precipitation of a cobalt oxide. The oxidizing HClO solution consists of NaClO and HNO_3 solutions. The cobalt nitrate solution (0.3 M) is first acidified with an HNO_3 solution (1 N) to $\text{pH} \leq 1.5$. The oxidizing NaClO solution (4 M) is then slowly added dropwise, along with an HNO_3 solution, in a manner such that the pH remains below 1.5. The precipitation must follow the oxidation immediately because the spontaneous decomposition of HClO ($2\text{HClO} \rightarrow \text{H}_2\text{O} + \text{Cl}_2 + \frac{1}{2}\text{O}_2$) leads to a pH increase and then to a parasitic cobalt oxide precipitation.

The oxidation of cobalt ions with an H_2O_2 solution is easier to achieve (process (4) in Fig. 1). The cobalt sulfate solution (0.3 M) is mixed with a pure H_2O_2 solution (110 vol.). As the oxidation power of H_2O_2 increases with pH [10], the cobalt ion oxidation occurs when the 2 N NaOH solution is added (see next paragraph). Cobalt ions are then simultaneously oxidized and precipitated to form the $\alpha_{\text{Co}^{3+}}$ -nickel hydroxide.

Precipitation of the $\alpha_{\text{Co}^{3+}}$ phase

The precipitation procedure is the same for processes (3) and (4) (Fig. 1).

The nickel sulfate solution (1.5 M) is mixed with the trivalent cobalt solution; the mixture is then vigorously agitated (250–300 rpm) while the 2 N NaOH solution is rapidly added dropwise until a pH value close to 10 is reached. The slurry is agitated for 15 h, washed with water and acetone, and filtered. Under these conditions, an $\alpha_{\text{Co}^{3+}}$ -type phase is recovered.

To obtain an $\alpha_{\text{Co}^{3+}}$ phase, three points must be given special attention:

(i) the precipitation speed must be very high, particularly when the oxidation of cobalt ions is undertaken with an HClO solution (process (3), Fig. 1); otherwise a $\beta(\text{II})$ -type phase is formed. In fact, as we have shown previously, the HClO solution tends to decompose rapidly, leading to a spontaneous reduction of the cobalt ion from the trivalent to the divalent state. Additionally, if the pH increases slowly (slow precipitation speed), Co_3O_4 formation may occur before the hydroxide precipitation.

(ii) the pH value must be close to 10 at the end of the precipitation in order that a material with particles as small as possible is obtained. The effect of pH is different on $\alpha\text{-Ni}(\text{OH})_2$ phases and on $\alpha_{\text{Co}^{3+}}$ phases. To prepare an α phase from NiSO_4 and NaOH solutions, the pH value must not exceed 10 at the end of the precipitation because a higher value leads to the formation of a $\beta(\text{II})$ -type phase [8]. In the case of $\alpha_{\text{Co}^{3+}}$ phases, the hydroxide is stabilized by the presence of trivalent cobalt ions, so the material does not evolve to a $\beta(\text{II})$ -type phase when the pH reaches a value close to 13. The only effect is an increase in particle size with pH. The shape of the $\text{NaOH}/2\text{NiSO}_4$ molar ratio versus pH curve is the same as that previously reported for $\alpha\text{-Ni}(\text{OH})_2$ precipitation [8].

(iii) stirring is important to ensure homogenization of the slurry and to facilitate the absorption of anionic species in the precipitate. As shown

previously, the insertion of anions within the stabilized hydroxide is necessary in order to compensate for the charge excess due to trivalent cobalt ions [3, 4]. When process (3) (Fig. 1) is used, the $\text{NaClO} + \text{HNO}_3$ medium increases the sulfate salt precipitation (Na_2SO_4), carbonate anions from the atmosphere are then inserted in the material. When process (4) (Fig. 1) is used, the solubility of Na_2SO_4 is considerably increased in presence of H_2O_2 solution [11]. Sulfate anions then become the main anionic species in solution, and are consequently inserted between the $\text{M}(\text{OH})_2$ slabs.

Whatever the preparation procedure for an $\alpha_{\text{Co}^{3+}}$ phase (oxidation of an $\alpha_{\text{Co}^{2+}}$ phase or direct precipitation), the material is stable in concentrated KOH medium as will be shown subsequently in this paper.

At this point in the discussion, it is important to stress that the $\alpha_{\text{Co}^{2+}}$ -hydroxide can be obtained spontaneously, whereas a great deal of chemistry is required to obtain the $\alpha_{\text{Co}^{3+}}$ -type. By contrast, for $\beta(\text{II})$ -type phase, the $\beta_{\text{Co}^{3+}}$ type is spontaneously obtained, even from divalent cobalt solutions. Moreover, we did not manage to stabilize the $\beta_{\text{Co}^{2+}}$ phase.

Chemical properties

In this section, all results involving X-ray diffraction study, chemical analyses, and UV-Vis study, will be reported; general discussion about each property will take place later.

Results

Most experimental data will be reported for materials with 20% of cobalt ions substituting for nickel ions. Thus, when the cobalt content is not clearly indicated, the study refers to 20% cobalt materials. In fact, experiments have been carried out in the 20–55% cobalt range and the results are very similar.

X-ray diffraction study

The X-ray diffraction patterns were recorded using $\text{Cu K}\alpha$ radiation. Those given in Fig. 2 concern materials obtained using procedures (1) and (2) from $\alpha_{\text{Co}^{2+}}$ phase (Fig. 2(b)). The selective oxidation (process (2)) of $\alpha_{\text{Co}^{2+}}$ phase gives an $\alpha_{\text{Co}^{3+}}(\text{SO}_4)$ material (Fig. 2(a)), while the chemical cycling (process (1)) gives, successively, γ_{Co} (Fig. 2(c)) and $\alpha_{\text{Co}^{3+}}(\text{CO}_3)$ phases (Fig. 2(d)).

The X-ray diffraction spectra of $\alpha_{\text{Co}^{3+}}$ phases obtained by direct precipitation employing processes (3) and (4) are reported in Fig. 3(a) and (b), respectively.

Chemical analyses

The weight percentage of all elements (except for oxygen) present in $\alpha_{\text{Co}^{2+}}$, $\alpha_{\text{Co}^{3+}}$ and γ_{Co} phases are reported in Table 1. Two compositions are given for the stabilized $\alpha_{\text{Co}^{3+}}$ material corresponding to each family: $\alpha_{\text{Co}^{3+}}(\text{CO}_3)$ and $\alpha_{\text{Co}^{3+}}(\text{SO}_4)$.

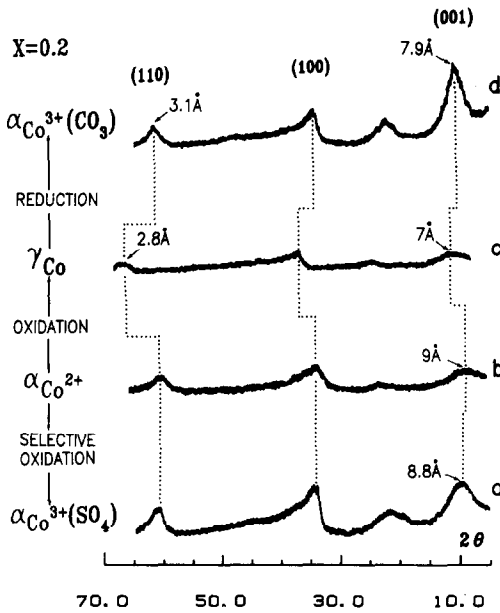


Fig. 2. X-ray diffraction spectra of $\alpha_{\text{Co}^{3+}}(\text{SO}_4)$, γ_{Co} , and $\alpha_{\text{Co}^{3+}}(\text{CO}_3)$ phases compared with that of the starting $\alpha_{\text{Co}^{2+}}$ hydroxide (processes (1) and (2), Fig. 1) ($x=0.2$).

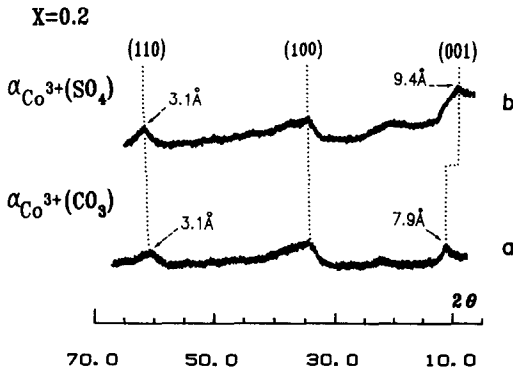


Fig. 3. X-ray diffraction spectra of $\alpha_{\text{Co}^{3+}}(\text{CO}_3)$ and $\alpha_{\text{Co}^{3+}}(\text{SO}_4)$ phases obtained, respectively, by processes (3) and (4) (Fig. 1) ($x=0.2$).

In all the α_{Co} phases, the presence of a small amount of sodium ion (<2.5 wt.%), is due to the formation of sodium salts during the precipitation (NaNO_3 , Na_2SO_4 , NaCl). These adsorbed salts were not completely removed by washing of the precipitated hydroxide. The hydrogen atoms are from the hydroxyl ions of the sheets, and from intercalated and adsorbed water molecules in all the reduced or oxidized phases. Chemical analysis also shows the presence of carbonate and sulfate anions in all materials. It also indicates a large amount of alkali ion in the γ_{Co} phase.

TABLE 1

Weight percentage of all elements (except oxygen) present in $\alpha_{\text{Co}^{2+}}$, $\alpha_{\text{Co}^{3+}}$, and γ_{Co} phases

Weight percent.	$\alpha_{\text{Co}^{2+}}$	$\alpha_{\text{Co}^{3+}}(\text{CO}_3)$	$\alpha_{\text{Co}^{3+}}(\text{SO}_4)$	γ_{Co}
Ni	33.45	32.52	33.10	34.07
Co	9.64	9.00	9.23	9.55
C	0.50	1.67	0.25	0.84
S	5.92	1.50	4.70	<0.1
H	2.70	3.34	3.38	3.01
Na	2.16	2.5	0.79	0.52
K	0	0	0	5.94

TABLE 2

Oxidation level of the transition ions in the reduced $\alpha_{\text{Co}^{3+}}(\text{CO}_3)$ phases versus the cobalt content

Cobalt content: x	0.10	0.20	0.30	0.40	0.50
Oxidation level	2.07	2.22	2.28	2.35	2.52

Oxidation level of the transition ions in the reduced or oxidized phases

The average oxidation level of the metallic ions was determined volumetrically ($\text{I}_2 + \text{Na}_2\text{S}_2\text{O}_3$ method). For all materials with 20% cobalt ions substituting for nickel ions, the oxidation level is equal to 2.20 ± 0.05 . In the case of the $\alpha_{\text{Co}^{3+}}(\text{CO}_3)$ phases, the variation of oxidation level versus cobalt content has been determined. The results are summarized in Table 2. For the reduced $\alpha_{\text{Co}^{2+}}$ phases, the oxidation level of the transition ions remains close to 2 whatever the cobalt content. For the oxidized γ_{Co} phases, the average oxidation level is equal to 3.2 and this value is also independent of the cobalt content.

The u.v.-visible diffuse reflectance spectra of $\alpha_{\text{Co}^{2+}}$ and $\alpha_{\text{Co}^{3+}}(\text{CO}_3)$ phases were recorded on a Cary 2415 Varian spectrophotometer. They are reported in Fig. 4.

Discussion

Table 2 shows that the oxidation level of the transition ions in the reduced $\alpha_{\text{Co}^{3+}}$ phases is close to $2+x$. Such behavior suggests the presence of $(1-x)\text{Ni}^{2+}$ and $x\text{Co}^{3+}$ ions within the sheets. Optical study confirms this hypothesis. The optical spectrum of the $\alpha_{\text{Co}^{3+}}$ phase is identical with that found for the $\alpha'_{\text{Co}^{3+}}$ phase (see Fig. 3, ref. 5).

On the spectra of the $\alpha_{\text{Co}^{2+}}$ phase, the ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$ and ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}(\text{P})$ transitions of Ni^{2+} ions are observed. Two new absorption bands noticed on Fig. 4 correspond to the ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{P})$ and ${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}(\text{F})$

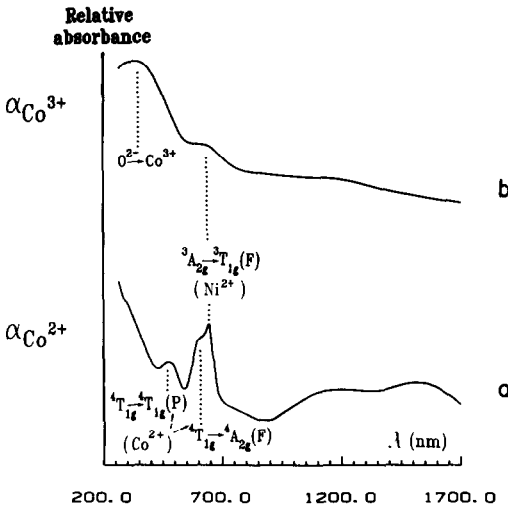


Fig. 4. u.v.-visible absorption spectra of $\alpha_{\text{Co}^{2+}}$ and $\alpha_{\text{Co}^{3+}}$ (CO_3) hydroxides ($x=0.2$).

bands reported by Feitknecht for $\beta\text{-Co}(\text{OH})_2$ [12]. They confirm the presence of Co^{2+} ions in this hydroxide. Simultaneously, they show the absence of Co^{2+} ions in the $\alpha_{\text{Co}^{3+}}$ phase. It should also be noted that the charge transfer band appears in the $\alpha_{\text{Co}^{2+}}$ phase at a higher energy than in the $\alpha_{\text{Co}^{3+}}$ phase, as was expected.

The value of the oxidation level of the transition ions in γ_{Co} phases is lower than that commonly found for oxyhydroxides prepared by *chimie douce* reactions. This difference (3.2 instead of 3.5) is due to the small particle size of the $\alpha_{\text{Co}^{3+}}$ phases which promote an important material reactivity: γ_{Co} phases are spontaneously partially reduced during washing.

All the reduced $\alpha_{\text{Co}^{2+}}$ and $\alpha_{\text{Co}^{3+}}$ phases exhibit the classical turbostratic character generally found in α -type nickel hydroxides. This means that the $\text{M}(\text{OH})_2$ slabs are parallel, equidistant, but totally misoriented with regard to one another [13]. In contrast to the γ_{Co} phases obtained either by *chimie douce* reactions from the precursor $\text{NaNi}_{1-x}\text{Co}_x\text{O}_2$ [2], or by chemical oxidation of a $\beta_{\text{Co}^{3+}}$ phase [6], which have a $P3$ type packing [14], the γ_{Co} phase (Fig. 2(c)) formed from an $\alpha_{\text{Co}^{2+}}$ phase exhibits a turbostratic character. Although, the X-ray diffraction patterns of all these layered oxyhydroxides and hydroxides are quite flat, interesting structural parameters can be derived from a comparison with well crystallized $\beta(\text{II})$, α' , and α^* -nickel hydroxides [5, 15, 2]. All these materials crystallize with hexagonal symmetry; the c parameter is related to the intersheet distance, while the a parameter gives the Ni-Ni distance within the $\text{Ni}(\text{OH})_2$ sheets directly. The first broad line which appears for small diffraction angles (around 10° in 2θ) corresponds to the (001) line, and gives the intersheet distance, while the second band (between 20 and 25° in 2θ) corresponds to the (002) line. The other interesting diffraction line lies in the $60\text{--}70^\circ$ range in Fig. 2. This interplanar distance

corresponds to the (110) plane for $\beta(\text{II})\text{Ni}(\text{OH})_2$, α^* , or α' phases. It enables one to find the parameter in the hexagonal symmetry which is equal to the in plane M–M distance. The large asymmetric diffraction band (between 30 and 40° in 2θ) is characteristic of a turbostratic material and corresponds to the (10*l*) lines.

The 'hexagonal' cell parameters, or strictly speaking the intralayer M–M distance, and the intersheet distance of all materials involved in this study are reported in Figs. 2 and 3. The spectra of the reduced and oxidized phases differ by the value of the ' α_{hex} '-parameter. This value, close to 3.1 Å in the reduced phases, becomes equal to 2.8 Å in the oxidized phases as a result of the ionic radius difference between Ni^{2+} and Ni^{3+} ions. We note an important difference between the intersheet distance of $\alpha_{\text{Co}^{2+}}$ or $\alpha_{\text{Co}^{3+}(\text{SO}_4)}$ and $\alpha_{\text{Co}^{3+}(\text{CO}_3)}$ phases that results from the nature of the intercalated species. Whatever the cobalt content, the intersheet distance ranges from 8.8 to 9.4 Å for the $\alpha_{\text{Co}^{3+}(\text{SO}_4)}$ phases (Fig. 2(a) and 3(b)), while it is lower than 8 Å for the $\alpha_{\text{Co}^{3+}(\text{CO}_3)}$ phases (Fig. 2(d) and 3(a)). Such an intersheet distance variation suggests a difference between the overall composition and the local structure of the intersheet space in $\alpha_{\text{Co}^{3+}}$ phases. As will be discussed later, carbonate or sulfate anions are inserted between adjacent sheets in order to provide the electrical neutrality of the material.

In $\alpha_{\text{Co}^{3+}(\text{CO}_3)}$ phase, which exhibits an intersheet distance lower than 8 Å, large amounts of CO_3^{2-} anions are present within the material. The direct correlation between the amounts of sulfate and sodium ions shows that these anions come from Na_2SO_4 , which is only a washing residue. In the $\alpha_{\text{Co}^{3+}(\text{CO}_3)}$ phase, the intersheet distance does not allow the presence of the free, inserted sulfate anions between the $\text{M}(\text{OH})_2$ slabs, and therefore the charge excess due to trivalent cobalt ions is mainly compensated for by the insertion of carbonate anions. In $\alpha_{\text{Co}^{3+}(\text{SO}_4)}$ and $\alpha_{\text{Co}^{2+}}$ phases that exhibit a higher value of their intersheet distance ($c_{\text{hex}} \geq 8.8$ Å), large amounts of sulfate anions are found, while the carbonate amount is minimized by comparison with that previously reported for the $\alpha_{\text{Co}^{3+}(\text{CO}_3)}$ phase (Table 1). As the amount of Na^+ ions is very small in comparison with that of the sulfate ions, these anions are not only supplied by Na_2SO_4 , and we can assume that in these materials with large intersheet distances, sulfate anions are inserted between the slabs, while carbonate anions are mainly adsorbed.

In the case of $\alpha_{\text{Co}^{2+}}$ phases, the presence of sulfate anions in large excess between the $\text{M}(\text{OH})_2$ slabs, required by the very large intersheet distance, sets a problem about the charge compensation. As for the previously reported $\alpha\text{-Ni}(\text{OH})_2$ obtained from NiSO_4 and NaOH solutions, the presence of H_2O molecules in substitution with OH groups has been assumed in order to ensure the electrical neutrality [8].

All these hypotheses about the distribution of anionic species developed from chemical analyses, and from the value of the material intersheet distances, are confirmed by the infrared study reported in a forthcoming paper [16].

For the γ_{Co} phases, alkali ions and water molecules are inserted between MOOH_x slabs. The carbonate anions ($\text{CO}_3^{2-}/(\text{Ni} + \text{Co})$) molar ratio is equal

to 0.09) are assumed to be adsorbed on the particles, as in γ phases the intercalation of anionic species has never been reported. This hypothesis is corroborated by the following observation. These materials exhibit very small particles in comparison with the γ phases obtained by *chimie douce* reaction from $\text{NaNi}_{1-x}\text{Co}_x\text{O}_2$. In the latter materials, the $\text{CO}_2^{2-}/(\text{Ni} + \text{Co})$ molar ratio is very small (equal to 0.01).

Thermal evolution of $\alpha_{\text{Co}^{3+}}$ phases compared with that of $\alpha_{\text{Co}^{2+}}$ phases

The TGA experiments were performed on $\alpha_{\text{Co}^{2+}}$ and $\alpha_{\text{Co}^{3+}}$ phases, using the same experimental conditions ($1\text{ }^\circ\text{C min}^{-1}$ under nitrogen flow). Whatever the preparation route, the shape of the TGA curves is independent of the cobalt content.

The TGA curve of the $\alpha_{\text{Co}^{3+}}(\text{CO}_3)$ and $\alpha_{\text{Co}^{2+}}$ phases (with 20% of cobalt substituted for nickel) are reported on Fig. 5(a) and (b), respectively. For both materials, a first loss of water is observed between 40 and 140 $^\circ\text{C}$, which corresponds to the removal of adsorbed- and part of the intercalated water molecules. In the case of the $\alpha_{\text{Co}^{3+}}(\text{CO}_3)$ material, at 180 $^\circ\text{C}$ almost

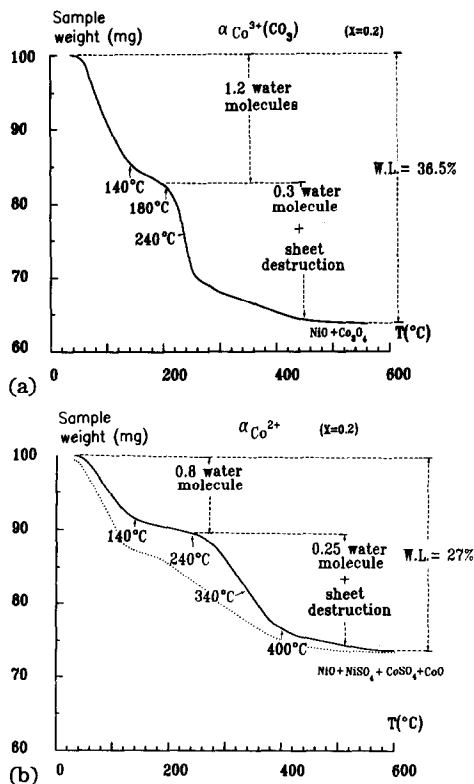


Fig. 5. (a) TGA curve of the $\alpha_{\text{Co}^{3+}}(\text{CO}_3)$ hydroxide ($x=0.2$); (b) TGA curve of the $\alpha_{\text{Co}^{2+}}$ -hydroxide ($x=0.2$) (—), and of the α -phase ($\cdots\cdots$) [8] ($1\text{ }^\circ\text{C min}^{-1}$, under nitrogen flow).

1.2 water molecules per formula unit have been removed. Beyond this temperature, the remaining water molecules and the carbonate anions are eliminated. Simultaneously, the destruction of the $M(OH)_2$ sheets occurs, and a mixture of NiO and Co_3O_4 is recovered. For the $\alpha_{Co^{2+}}$ material a plateau is observed between 140 and 240 °C, it shows that the material is stable within this temperature range. The second loss occurs beyond this latter temperature (it corresponds to the removal of the remaining water molecules and the sulfate anions), and sheet destruction occurs, leading to the formation of NiO, $NiSO_4$, CoO and Co_3O_4 .

The second weight loss permits calculation in both cases of the amount of water remaining in these materials above 180 and 240 °C: 0.3 and 0.25 for $\alpha_{Co^{3+}}(CO_3)$ and $\alpha_{Co^{2+}}$ phases, respectively.

X-ray diffraction studies performed on both materials versus temperature are in accordance with TGA results. The α -type structure is conserved up to 180 and 240 °C for $\alpha_{Co^{3+}}(CO_3)$ and $\alpha_{Co^{2+}}$ phases, respectively.

TGA curves lead to results similar to those of chemical analyses, and the molar ratios are close to 1.1 and 1.5 for $\alpha_{Co^{2+}}$ and $\alpha_{Co^{3+}}$ phases, respectively. In both cases, a partially dehydrated α_{Co} phase can be stabilized, as shown by the TGA and X-ray diffraction study versus temperature. The intersheet distance of these partially dehydrated phases is close to 7.2 Å. This material is more thermally stable in the case of the $\alpha_{Co^{2+}}$ phase than in that of the $\alpha_{Co^{3+}}$ phase. However, both TGA curves should be compared with that of α -Ni(OH)₂ phases prepared from $NiSO_4$ and NaOH solutions [8]. This previously reported curve [8], has been added to Fig. 5(b) (dotted line) for comparison. In this latter case, the water loss was almost continuous, and the plateau present in the 140–180 °C range for the $\alpha_{Co^{3+}}$ curve and in the 140–240 °C range for the $\alpha_{Co^{2+}}$ curve, is not observed. The only difference between α -Ni(OH)₂ and the $\alpha_{Co^{2+}}$ chemical formulae results from a partial substitution of Co^{2+} ions for Ni^{2+} ions in the latter material. The difference in stability between the two phases would then result from a higher bond strength for partially cobaltated phases. This point is also emphasized by the difference in behavior of these two materials in pure water: α -nickel hydroxide slowly transforms to a β_{bc} -type phase, and after four days in water medium a mixture of α - and β_{bc} phase is recovered, while the $\alpha_{Co^{2+}}$ -type phase remains stable after two weeks in water.

Evolution of the cobaltated α -phases in KOH medium

The general purpose of this work was to find α -type phases stable in the electrochemical generator. It is necessary that all materials must be stable in KOH medium. Therefore, all the reduced phases were systematically tested in KOH solution for times varying between one week and three months: 100 mg of the reduced phase was mixed with 10 ml of a 5 N KOH solution at room temperature, and X-ray diffraction patterns were recorded periodically.

For cobalt contents ranging from 20 to 55%, $\alpha_{\text{Co}^{3+}}(\text{CO}_3)$ phases are stable in concentrated KOH medium at room temperature. As will be developed subsequently, the only phenomenon observed is a small increase in the particle size, and a gradual loss of the turbostratic character.

Evolution of $\alpha_{\text{Co}^{3+}}(\text{SO}_4)$ phases compared with those of $\alpha_{\text{Co}^{2+}}$ -phases ($x_{\text{Co}} \geq 0.2$)

The X-ray diffraction spectra of $\alpha_{\text{Co}^{2+}}$ phases and $\alpha_{\text{Co}^{3+}}(\text{SO}_4)$ phases containing 20% of cobalt ions (Fig. 6(a) and (c)) are identical, but the behavior of these materials in concentrated KOH medium differs.

The $\alpha_{\text{Co}^{2+}}$ -type phase is unstable in KOH medium and spontaneously transforms to a $\beta(\text{II})$ -type phase as shown in Fig. 6(b). This behavior is identical with that reported for the non-cobalted phase, $\alpha\text{-Ni}(\text{OH})_2$. When this $\beta(\text{II})$ -hydroxide is formed, a spontaneous oxidation of cobalt ions occurs, and the $\beta_{\text{Co}^{3+}}$ phase obtained is similar to that of the $\beta_{\text{Co}^{3+}}$ material previously reported. It should be noted that cobalt ions are more stable in the trivalent state in $\beta(\text{II})$ phases, while they stay preferentially in the divalent state in α -type phases.

In contrast to the $\alpha_{\text{Co}^{2+}}$ phase, the $\alpha_{\text{Co}^{3+}}(\text{SO}_4)$ phase is stable in KOH medium, and after a one week stability test an α phase is recovered (Fig. 6(c), (d)). However, we have noticed a decrease in the intersheet distance of the material which was placed in a 5 N KOH medium ($c'_{\text{hex}} = 7.9 \text{ \AA}$ instead of 9.4 \AA). This result, corroborated by the chemical analysis, shows that a $\text{CO}_3^{2-}/\text{SO}_4^{2-}$ exchange occurs in the material, and its formula then appears

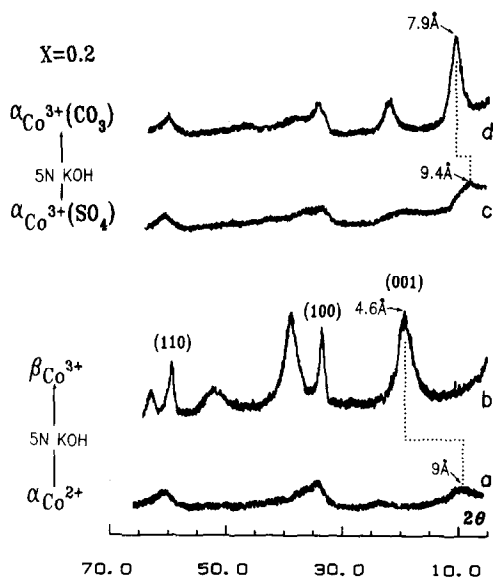
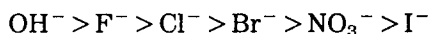
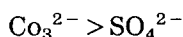


Fig. 6. X-ray diffraction spectra showing the evolution of $\alpha_{\text{Co}^{2+}}$ and $\alpha_{\text{Co}^{3+}}(\text{SO}_4)$ phases in KOH medium ($x = 0.2$).

similar to that of an $\alpha_{\text{Co}^{3+}}(\text{CO}_3)$ phase. Such an exchange agrees with the results published by Mendiboure and Schöllhorn, who studied the anionic exchange properties of the reevesite mineral [17]. Reichle also showed that layer double hydroxides (LDHs) have a selectivity toward intercalated anionic species [18]:



This exchange reaction was also characterized by the infrared study of both starting and final materials. These results, which will be published in a forthcoming paper [16], emphasize the occurrence of this exchange reaction.

Influence of the cobalt concentration on the stability of $\alpha_{\text{Co}^{3+}}$ phases

As $\alpha_{\text{Co}^{3+}}(\text{SO}_4)$ phase is spontaneously converted to an $\alpha_{\text{Co}^{3+}}(\text{CO}_3)$ phase in KOH medium, the results of the stability tests given in this section are identical whatever the preparative method used. In the previous section we have shown that $\alpha_{\text{Co}^{3+}}$ phase, containing 20% of cobalt ions, is stable in KOH medium at room temperature, and experiments performed on higher cobalt content phases (from 20 to 55%) confirm these results.

By contrast, $\alpha_{\text{Co}^{3+}}(\text{CO}_3)$ phase (Fig. 7(a)) with a 10% cobalt content, is unstable in alkaline medium, and the X-ray diffraction spectrum of the recovered material is characteristic of a $\beta_{\text{Co}^{3+}}$ -type phase (Fig. 7(b)). The results are identical for the $\alpha_{\text{Co}^{3+}}$ materials containing 5 or 15% of trivalent cobalt ions [19].

Influence of the stability test duration

A stability test in 5 N KOH ranging from one week to three months was performed on an $\alpha_{\text{Co}^{3+}}(\text{CO}_3)$ phase containing 30% of cobalt ions, and

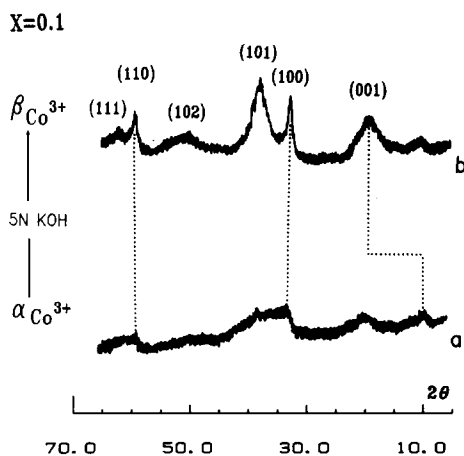


Fig. 7. X-ray diffraction spectra showing the instability of $\alpha_{\text{Co}^{3+}}(\text{CO}_3)$ hydroxide in KOH medium ($x=0.1$).

the X-ray diffraction spectra of the resulting materials are reported in Fig. 8. These patterns show that the material is totally stabilized since the α -type structure remains even after a three months stability test. However, we note a small increase in the particle size of the material with experimental duration in 5 N KOH. While the size of the particles of the starting $\alpha_{\text{Co}^{3+}}(\text{CO}_3)$ phase cannot be determined from Scherrer's formula [20], after a three months test, the particle size has slowly increased: $D = 80 \text{ \AA}$ and $H = 50 \text{ \AA}$. We also note a reorganization of the structure along the \vec{c} -axis showed by the loss of the turbostratic character. As such a phenomenon cannot occur in the solid state, a dissolution-germination growing mechanism has to happen, and the material recovered is an $\alpha'_{\text{Co}^{3+}}$ -type phase which can be indexed in the hexagonal system with a $P3$ packing [14]. Such a material should be compared with $\alpha'_{\text{Co}^{3+}}$ and $\alpha^*_{\text{Co}^{3+}}$ phases, obtained, respectively, from $\beta_{\text{Co}^{3+}}$ phase and by *chimie douce* reactions from the $\text{NaNi}_{1-x}\text{Co}_x\text{O}_2$ precursor [3, 4].

As a result of all the stability tests performed on $\alpha_{\text{Co}^{3+}}(\text{SO}_4)$, $\alpha_{\text{Co}^{3+}}(\text{CO}_3)$, and $\alpha_{\text{Co}^{2+}}$ phases, we may assume that:

- (i) $\alpha_{\text{Co}^{2+}}$ phases are unstable in KOH medium, whatever the cobalt concentration;
- (ii) a cobalt content at least equal to 20% is necessary to avoid transformation of the $\alpha_{\text{Co}^{3+}}$ phase into the $\beta_{\text{Co}^{3+}}$ -phase;
- (iii) if the starting $\alpha_{\text{Co}^{3+}}$ phase contains sulfate anions, these anions are exchanged by carbonate ions during the stability test;
- (iv) during long range stability tests, the particle size of the $\alpha_{\text{Co}^{3+}}$ phase slowly increases. Simultaneously a loss of the turbostratic character is observed.

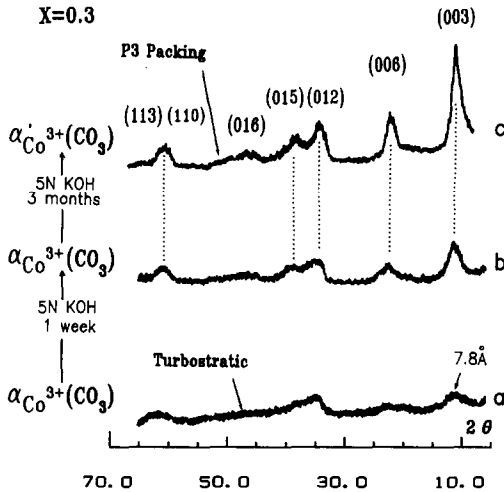


Fig. 8. X-ray diffraction spectra showing the evolution of $\alpha_{\text{Co}^{3+}}(\text{CO}_3)$ hydroxide ($x=0.3$) in 5 N KOH medium after one week and after three months.

All these results encourage the idea that the stabilization of α -phases is not the result of the presence of cobalt ions alone, but rather by the presence of trivalent cations.

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