

## Structure and properties of precipitated nickel–iron hydroxides

L. Demourgues-Guerlou 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 Cedex (France)*

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### Abstract

Iron-substituted nickel hydroxides have been prepared by precipitation for  $y$  iron substitution rates ranging from 0.10 to 0.50. Chemical and physical studies have shown, as in the case of the homologous ‘chimie douce materials’, the presence of  $(1-y)\text{Ni}^{2+}$  and  $y\text{Fe}^{3+}$  ions within the slab; the compensation of the excess of positive charge mainly results from the intercalation of  $\text{CO}_3^{2-}$  ions in the interslab space. The IR study and the chemical analysis provide evidence for the presence of  $\text{SO}_4^{2-}$  ions in  $T_d$  symmetry (originating from the precipitation medium) that are mainly adsorbed on the grain surface. These materials are stable in concentrated KOH solution but their ageing in such a medium induces a modification of the crystallinity as well as a spontaneous exchange of  $\text{CO}_3^{2-}$  ions for  $\text{SO}_4^{2-}$  ions.

### Introduction

The stabilization of the cycling between  $\gamma$ -nickel oxyhydroxide and the  $\alpha$ -hydroxide at the positive electrode of Ni/Cd, Ni–MH or Ni/H<sub>2</sub> batteries is of great interest since it is likely to improve the capacity as well as the lifetime of the electrode [1]. Previous studies in our laboratory have shown that the substitution of at least 20% of cobalt for nickel leads to well-crystallized  $\alpha^*$ -phases or turbostratic  $\alpha$ -phases, depending on whether they are prepared by ‘chimie douce’ or precipitation ways, respectively [2, 3]. These materials are closely related to the hydrotalcites [4]. The cobalt ions stay in the trivalent state in both reduced ( $\alpha$ ) and oxidized ( $\gamma$ ) phases while the nickel ions are divalent in the reduced phase and both trivalent and tetravalent in the oxidized form [5, 6]. As a consequence, the cobalt ions do not directly take part in the  $\alpha/\gamma$  cycling.

We have undertaken the study of the homologous iron-substituted nickel hydroxides. Mendiboure *et al.* [7] have previously studied hydrotalcite-type compounds  $\text{Ni}_{1-y}\text{Fe}_y(\text{OH})_2(\text{CO}_3)_{y/2}(\text{H}_2\text{O})_z$  prepared by precipitation, especially with regard to the anionic-exchange reactions, around the  $y=0.25$  composition which corresponds to the formula of the mineral reevesite [7, 8]. In a first step, in order to obtain compounds with a better crystallization state and therefore easily characterizable by X-ray diffraction, we have used ‘chimie douce’ preparation techniques. In a previous paper [9] we have reported the characterization of the iron-substituted  $\alpha^*$ -phases prepared, by this method,

\*Author to whom correspondence should be addressed.

from the  $\text{NaNi}_{1-y}\text{Fe}_y\text{O}_2$  sodium nickelate precursors for  $0.10 \leq y \leq 0.50$ . In these materials, the slab contains divalent nickel and trivalent iron ions;  $\text{CO}_3^{2-}$  ions are intercalated in the interslab space in order to compensate the excess of positive charge due to  $\text{Fe}^{3+}$  ions within the slab. This behaviour, already observed for the cobalt substituted hydroxides [2], can be considered as a generalization of the reevesite case [8] for a variable iron range. Besides, while the cobalt ions are trivalent in the  $\gamma$ -oxidized phases, iron substitution induces the presence of  $\text{Fe(IV)}$  ions [10, 11].

This paper deals with the physical and chemical characterization of the iron-substituted hydroxides prepared by a classical precipitation route. The main interest of these materials, which differ from those obtained from 'chimie douce' by their poorer crystallization state, lies in their reduced crystallite size which is likely to improve the electrochemical activity. The electrochemical properties of these materials are reported elsewhere [12].

### Material preparation

$\alpha$ -Phases have been prepared by chemical precipitation with 2 M NaOH from a solution of iron and nickel sulfate salts mixed in the appropriate ratio. Two different precipitation procedures have been tested:

(i) The first preparation method is almost similar to that performed by Faure *et al.* [3] for obtaining cobalt-substituted  $\alpha$ -phases containing  $\text{Co}^{3+}$  ions, except that the trivalent iron ions are directly available in the iron sulfate solution. The latter is mixed with the divalent nickel sulfate solution and the mixture is stirred while the 2 M NaOH solution is rapidly added until a pH value close to 10 is reached.

(ii) The second precipitation method is that reported by Mendiboure *et al.* [7]. The nickel and iron sulfate solution is slowly dropped into the 2 M NaOH solution under stirring (so that the precipitation is carried out at  $\text{pH}=13$ ).

In both cases, the slurry obtained is stirred for 15 h, then washed with water and acetone, filtered and finally dried at 50 °C.

Whatever the precipitation procedure, an  $\alpha$ -type phase is always recovered. The fact that the pH has no effect on the ideal formula of the phase obtained has already been observed in the case of the trivalent cobalt-substituted phases [3]. The  $\alpha$ -phase is indeed stabilized by the presence of trivalent substituting ions (presently iron), contrarily to the unsubstituted  $\alpha$ -phase (obtained from  $\text{NiSO}_4$  and NaOH solutions) which evolves to a  $\beta(\text{II})$ -type phase if the pH exceeds 10 [13].

Nevertheless, the precipitation pH has an influence on the crystallization state of the material: for the first method (i), an increase of the final pH value induces an increase in the crystallite size and, in the same way, the second procedure (ii) leads to larger crystallites than the first one. Additionally, the effect of precipitation speed has to be noticed: in both methods, the faster the precipitation, the worse the crystallization state.

Iron-substituted hydroxides have been prepared by precipitation for various compositions ranging from  $y=0.10$  to 0.50.  $\alpha$ -Type materials are obtained, except for the  $y=0.10$  composition which leads to an interstratified phase, as previously observed for the same composition prepared by 'chimie douce' techniques [9].

### Characterization of the precipitated iron-substituted hydroxides

As in the homologous materials prepared by 'chimie douce' route ( $\alpha^*$ -phase), the study of the precipitated iron-substituted hydroxides, which is detailed hereafter, shows

the presence of divalent nickel and trivalent iron ions within the slab as well as the insertion of carbonate ions in the interslab space in order to compensate the excess of positive charge due to  $\text{Fe}^{3+}$  ions [13]. The materials obtained by precipitation and by 'chimie douce' techniques are essentially different in their texture: the crystallinity and, particularly, the particle size.

#### X-ray diffraction study

The X-ray diffraction (XRD) patterns of the  $\alpha$ -type phases with  $\gamma=0.3$  composition prepared by the (i) ( $\alpha_{\text{I}}$ -phase) and (ii) ( $\alpha_{\text{II}}$ -phase) precipitation methods are given in Fig. 1(a) and (b) in comparison with the XRD pattern of the  $\alpha^*$ -phase obtained by 'chimie douce' (Fig. 1(d)). Since both  $\alpha_{\text{I}}$  and  $\alpha_{\text{II}}$ -phases lead after ageing in 5 M KOH medium (electrolytic medium) to identical materials, only the XRD pattern of the  $\alpha_{\text{K}}$  phase resulting from the ageing of the  $\alpha_{\text{II}}$ -phase in KOH has been reported in Fig. 1(c).

In spite of the presence of broader lines for the precipitated  $\alpha_{\text{I}}$  and  $\alpha_{\text{II}}$ -phases, the XRD patterns of these materials exhibit strong analogies with that of the  $\alpha^*$ -phase and can, as in this case, be indexed in the rhombohedral system with a  $P3$ -type packing of oxygen layers. The indexing with a hexagonal unit cell is reported in Fig. 1. The reticular distances of the (003) and (110) lines allow to evaluate the hexagonal parameters of the precipitated materials:  $c_{\text{hex.}} = d_{(003)}$  and  $a_{\text{hex.}} = 2 d_{(110)}$ . The values thus obtained are:  $a_{\text{hex.}} = 3.1 \pm 0.1 \text{ \AA}$  and  $c_{\text{hex.}} = 23.1 \pm 0.3 \text{ \AA}$ . As a result of the broadness of the various diffraction lines, no significant variation of the parameters with the iron amount has been detected.

Faure *et al.* [3] have reported that, in the case of the homologous cobalt system, the precipitation with a 2 M NaOH solution from nickel and cobalt salts gives rise to an  $\alpha$ -hydroxide poorly crystallized with a turbostratic structure, characterized by slabs misoriented with regard to one another [3]. This behaviour is emphasized on the XRD pattern by the presence of a very large band in the  $30\text{--}50^\circ$  angular range resulting from the overlap of the (10 $l$ ) lines [3]. Nevertheless, according to Faure *et al.* [3] a chemical cycling process from a cobalt substituted  $\beta(\text{II})$ -nickel hydroxide, i.e., an oxidation in ( $\text{NaClO} + \text{KOH}$ ) solution of this material to a  $\gamma$ -type phase followed by a reduction in  $\text{H}_2\text{O}_2$  medium, leads to a material called  $\alpha'$  which no more exhibits

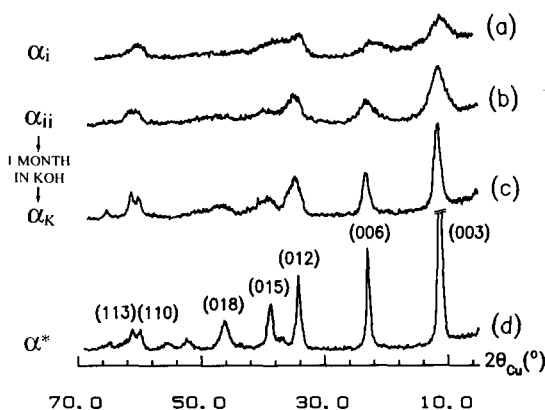


Fig. 1. X-ray diffraction patterns of (a) the  $\alpha_{\text{I}}$ , (b)  $\alpha_{\text{II}}$  iron-substituted precipitated phases with  $\gamma=0.3$ , and (c) the  $\alpha_{\text{K}}$ -material resulting from ageing in 5 M KOH of  $\alpha_{\text{II}}$ ; (d) the X-ray pattern of the homologous  $\alpha^*$ -phase prepared by 'chimie douce' is given for comparison.

the turbostratic character and which crystallizes in the rhombohedral system with the  $P3$ -structural type [14]. The iron-substituted  $\alpha$ -hydroxides we obtained by direct precipitation are quite similar to the cobalt substituted  $\alpha'$ -type materials and therefore do not exhibit any turbostratic character.

The diffraction lines corresponding to the precipitated  $\alpha_i$ - or  $\alpha_{ii}$ -phases are much broader than those observed for the 'chimie douce'  $\alpha^*$ -phase as a result of the poorer crystallinity state of the materials obtained by precipitation. The particle size of the various materials presented in Fig. 1 has been evaluated from the line broadening by using Scherrer's formula [15]. The results obtained by assuming the particles to be cylinder-shaped with  $H$  thickness and  $D$  diameter from a calculation involving the (003) and (110) lines are summarized in Table 1.

The effect of the precipitation procedure on the crystallite size is clearly illustrated in Table 1. The crystallites of  $\alpha_{ii}$ -phase, prepared by precipitation at  $\text{pH}=13$ , are larger than those of  $\alpha_i$ -phase, prepared at  $\text{pH}=10$ .

The crystallite sizes calculated from Scherrer's formula for the iron-precipitated materials are very close to those obtained in the homologous cobalt-substituted phases [3, 5]. In the latter materials, these sizes calculated from the X-ray line broadening are in agreement with the particle size observed by transmission electron microscopy (TEM). On the other hand, for the iron-substituted  $\alpha^*$ -phase prepared by 'chimie douce', the crystallite size determined from Scherrer's formula (Table 1) is considerably smaller than the particle size evaluated on the basis of the scanning electron microscopy pictures reported by Braconnier [16]. In this case, the  $D$  diameter and the  $H$  height of the hexagonal platelets lie indeed in the  $10^4$  and  $10^3$  Å, respectively. In order to explain such a discrepancy, it should be kept in mind that Scherrer's formula allows only to determine the extent of the diffraction coherent domains while the particles observed by TEM may be constituted of several different crystallized domains. We have recently observed this behaviour by high resolution TEM for iron-substituted  $\alpha^*$ -phases.

#### *Chemical stability of the $\alpha$ -phases in alkaline medium*

The  $\alpha$ -phases ( $y \geq 0.2$ ) are indefinitely stable in a 5 M KOH medium. Comparison of the XRD pattern of the starting  $\alpha_{ii}$ -phase to that of the  $\alpha_K$ -phase obtained after a stay in KOH medium (Fig. 1) evidences a line narrowing. This behaviour may be attributed to an increase in crystallite size, emphasized in Table 1, and/or to a decrease in the number of structural defects and strains in the material.

As far as the  $\alpha^*$ -phases are concerned, they are also stable in the KOH solution and no modification of XRD pattern is observed.

TABLE 1

Crystallite size calculated from the X-ray diffraction patterns of the various iron substituted  $\alpha$ -type nickel hydroxides

Material	$\alpha_i$ (a)	$\alpha_{ii}$ (b)	$\alpha_K$ (c)	$\alpha^*$ (d)
$H$ (Å) (along the $c_{\text{hex}}$ axis)	30	50	70	190
$D$ (Å) (along the $a_{\text{hex}}$ axis)	70	70	90	110

### Cationic oxidation state

The results reported throughout this paragraph concern the precipitated  $\alpha_{ii}$ -type phases; nevertheless, the  $\alpha_i$ -ones exhibit a behaviour quite similar to that of the  $\alpha_{ii}$ -ones.

As previously published [9], the average oxidation state of the metal cations in the slab for the iron-substituted hydroxides prepared by 'chimie douce' is close to  $2+y$ . Quite similar results are obtained in the case of the materials obtained by precipitation (Table 2).

The above-mentioned results suggest, as expected, the presence of  $(1-y)\text{Ni}^{2+}$  and  $y\text{Fe}^{3+}$  ions within the slab. The trivalent oxidation state of iron is unambiguously shown by a  $^{57}\text{Fe}$  Mössbauer spectroscopy study of the  $\alpha(y=0.20)$ -phase [11].

Moreover, this result is in good agreement with the study of the magnetic properties. Magnetic susceptibility measurements have been carried out with a DSM8 susceptometer (MANICS) over the 4–300 K temperature range (average magnetic field of 18 kG). The sample was placed in a polytetrafluoroethylene (PTFE) crucible. For  $y \leq 0.40$ , the materials exhibit a Curie–Weiss-type behaviour as emphasized in Fig. 2 by the thermal variations of reciprocal magnetic molar susceptibilities for the  $y=0.2$  and  $0.4$  compositions. Table 3 shows a relatively good agreement between the experimental values of Curie constants and the theoretical ones calculated according to the hypothesis of  $(1-y)\text{Ni}^{2+}$  and  $y\text{Fe}^{3+}$  ions within the slab (spin only model). Nevertheless, there is a small discrepancy between the two values for  $y=0.40$ . This effect is not understood at this time.

The values of the paramagnetic Curie temperatures are very small, smaller than those measured for the materials prepared by 'chimie douce', that are better ordered

TABLE 2

Average oxidation state of the nickel and iron ions vs. iron concentration in the precipitated iron-substituted hydroxides

	Iron concentration $y$				
	0.10	0.20	0.30	0.40	0.50
Oxidation state $\pm 0.05$	2.13	2.22	2.31	2.41	2.45

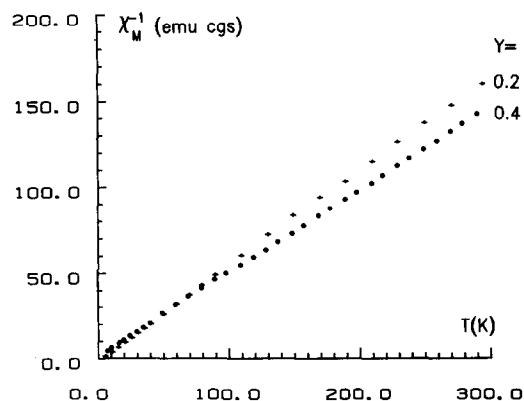


Fig. 2. Thermal variations of reciprocal molar magnetic susceptibilities of the  $\alpha$ -phases with  $y=0.2$  and  $0.4$ .

TABLE 3

Experimental and theoretical values (calculated provided that  $(1-y)\text{Ni}^{2+}$  and  $y\text{Fe}^{3+}$  are present within the slab) of the Curie constants and paramagnetic Curie temperatures obtained for the iron-substituted  $\alpha$ -phases ( $0 \leq y \leq 0.40$ )

$y$	$C_{\text{exp.}}$	$C_{\text{theor.}}$	$\theta p$ (K)
0	1.18	1.00	10
0.10	1.45	1.34	4
0.20	1.82	1.67	2
0.30	2.13	2.01	-5
0.40	2.07	2.35	-5

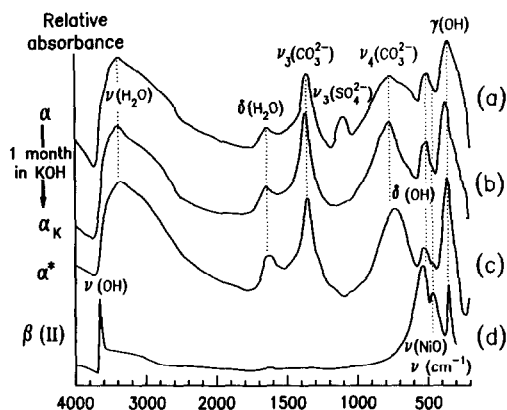


Fig. 3. Comparison of the infrared spectra of (a) a 30% iron-substituted  $\alpha$ -phase prepared by precipitation technique (ii), (b) the  $\alpha_K$  phase resulting from ageing in 5 M KOH solution, (c) the homologous  $\alpha^*$ -phase prepared by 'chimie douce' route, and (d) the  $\beta(\text{II})\text{-Ni}(\text{OH})_2$  phase.

[9]. Nevertheless, the general tendency shows, as in the case of the 'chimie douce' materials, the appearance, with increasing  $y$ , of antiferromagnetic interactions within the slab thanks to the strong  $t_{2-t_2}$  (Ni-Fe and Fe-Fe) direct overlap.

#### Infrared spectroscopy

All the spectra have been recorded on a Perkin-Elmer 983 spectrometer in the  $200\text{--}4000\text{ cm}^{-1}$  range. The powders were dispersed in Nujol and placed between two CsI plates.

Figure 3 allows comparison of the infrared spectra of a precipitated  $\alpha$ -phase ( $y=0.30$ ) (precipitation procedure (ii)), of the  $\alpha_K$ -material resulting from ageing of the latter phase in a KOH medium as well as of the homologous phase prepared by the 'chimie douce' route ( $\alpha^*$ ). The well-known spectrum of the unsubstituted  $\beta(\text{II})$ -phase is also displayed for comparison [17]. The infrared study of the  $\alpha^*$ -phases in comparison with the  $\beta(\text{II})$ -phase has already been reported elsewhere [9].

Let us recall that the spectrum of the  $\beta(\text{II})$ -phase is constituted of:

(i) a narrow band at  $3650\text{ cm}^{-1}$  due to the  $\nu(\text{OH})$  stretching vibration, which indicates the OH groups in a free configuration;

(ii) bands at  $520$  and  $350\text{ cm}^{-1}$ , respectively, corresponding to the  $\delta(\text{OH})$  planar deformation and to the  $\gamma(\text{OH})$  out-of-plane deformation, respectively, and

(iii) a band with weak intensity around  $460\text{ cm}^{-1}$  resulting from the Ni–O lattice vibration [18].

The spectra of the  $\alpha$ ,  $\alpha_K$  and  $\alpha^*$  iron-substituted phases exhibit strong similarities:

(i) the appearance of the large bands around  $330$  and  $1650\text{ cm}^{-1}$ , due to the  $\nu(\text{H}_2\text{O})$  stretching vibration and the  $\delta(\text{H}_2\text{O})$  bending vibration of water molecules, results from the presence of a large amount of water molecules either adsorbed on the particle surface or intercalated in the interslab space;

(ii) the disappearance of the narrow band at  $3650\text{ cm}^{-1}$  suggests that the OH groups are no more free but hydrogen bonded with the water molecules present in the interslab space;

(iii) the bands at  $1360$  and  $780\text{ cm}^{-1}$  for the precipitated  $\alpha$ -phase ( $1360$  and  $740\text{ cm}^{-1}$ , respectively, for the  $\alpha^*$ -phase) correspond to the  $\nu_3$  and  $\nu_4$  vibration modes of  $\text{CO}_3^{2-}$  ions in  $D_{3h}$  symmetry. The displacement of the  $\nu_3$  vibration frequency in comparison with the values observed in the  $\text{CaCO}_3$  reference compound ( $1429$ – $1492\text{ cm}^{-1}$ ) shows that the intercalated  $\text{CO}_3^{2-}$  anions are not really 'free' but symmetrically hydrogen bonded with the water molecules. This effect is corroborated by the existence of a shoulder around  $3000\text{ cm}^{-1}$ , particularly perceptible for the precipitated phases. This has been shown by some authors [19, 20] to result from the stretching vibration of OH groups bonded to carbonate ions. The interslab structure of the  $\alpha$ -phases has been schematically represented in Fig. 4. It is quite similar to that already observed in the related hydrotalcite materials [8] and in the homologous  $\alpha^*$ -phases obtained by 'chimie douce'.

As previously discussed, the interslab distance close to  $7.8\text{ \AA}$  indicates that the orientation of the carbonate ions is parallel to the  $\text{NiO}_2$  slabs.

The main difference between the infrared spectra of the precipitated  $\alpha$ -phase and the  $\alpha^*$ -phase prepared by 'chimie douce' consists of the presence of an additional band at  $1100\text{ cm}^{-1}$  and a shoulder at  $620\text{ cm}^{-1}$  in the case of the precipitated phase. These frequencies correspond to the  $\nu_3$  and  $\nu_4$  vibration modes of free  $\text{SO}_4^{2-}$  ions ( $T_d$  symmetry) [18], which originate from the metal salt solution used for the precipitation.

The intersheet distance close to  $7.8\text{ \AA}$  is too small to allow the existence of a large amount of  $\text{SO}_4^{2-}$  ions in the intersheet space. Indeed, in the homologous cobalt-substituted  $\alpha$ -phases, the insertion of  $\text{SO}_4^{2-}$  ions imposed an intersheet distance close to  $9\text{ \AA}$  [21]. Consequently, the sulfate ions may be mainly adsorbed on the iron-substituted materials presently studied. However, we can assume that during the precipitation reaction an intermediate phase with  $\text{SO}_4^{2-}$  ions in the interslab space is formed; an exchange of  $\text{SO}_4^{2-}$  for  $\text{CO}_3^{2-}$  ions occurs afterwards in agreement with the selectivity of the intercalated anions proposed by Mendiboure *et al.* [7]. The preference order is:  $\text{CO}_3^{2-} \gg \text{SO}_4^{2-} > \text{Cl}^- > \text{ClO}_4^- > \text{NO}_3^- > \text{CH}_3\text{COO}^-$ . Nevertheless, some  $\text{SO}_4^{2-}$  ions may remain trapped in the interslab space and consequently induce

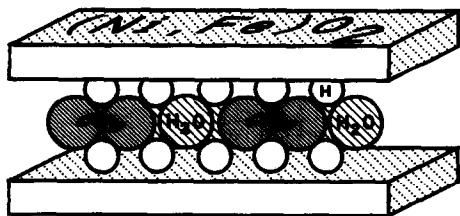


Fig. 4. Schematic representation of the interslab space in the  $\alpha$ -phase.

a slab puckering, which results in a line broadening on the XRD pattern, as observed in Fig. 1(a) and (b).

The fact that the  $\text{SO}_4^{2-}$  anions stay in  $T_d$  symmetry (no splitting of  $\nu_3(\text{SO}_4^{2-})$  band) suggests that they are not directly involved in chemical bonds with a metal ion (in substitution of an OH group). This is in accordance with their lability during ageing of the material in a KOH medium, as shown in Fig. 3(b) by the disappearance of the  $\nu_3(\text{SO}_4^{2-})$  and  $\nu_4(\text{SO}_4^{2-})$  bands. The simultaneous increase in intensity of the  $\nu_3(\text{CO}_3^{2-})$  band may be attributed to an exchange of the  $\text{SO}_4^{2-}$  ions for  $\text{CO}_3^{2-}$  ones. This is corroborated by chemical analysis of the material: as an example in the case of the  $y=0.3$  composition, the  $\text{SO}_4^{2-}/(\text{Ni}+\text{Fe})$  molar ratio decreases from 0.07 in the freshly-precipitated material down to 0.01 in the material obtained after ageing in KOH medium; conversely the  $\text{CO}_3^{2-}/(\text{Ni}+\text{Fe})$  molar ratio increases from 0.14 up to 0.20. One can also assume that a part of the  $\text{SO}_4^{2-}$  ions, which were inserted between the  $(\text{Ni}, \text{Fe})(\text{OH})_2$  slabs, is also exchanged leading to a more homogeneous material. This evolution may account for the X-ray line narrowing observed in Fig. 1(c) for the  $\alpha_K$ -material.

## Conclusions

Iron-substituted nickel hydroxides can be directly obtained by precipitation. These materials exhibit strong similarities with those previously obtained by 'chimie douce' from  $\text{NaNi}_{1-y}\text{Fe}_y\text{O}_2$  substituted sodium nickelates. Nevertheless, the two materials are essentially different in their texture.

The precipitated materials, as they exhibit smaller particles, are expected to present a better electrochemical activity. The electrochemical properties of the iron-substituted hydroxides as a positive electrode in Ni/Cd batteries will be reported in a forthcoming paper.

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