

## Electrochemical behavior of $\alpha$ -cobalated nickel hydroxide electrodes

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### Abstract

Cobalt substituted  $\alpha$ -nickel hydroxides obtained by precipitation techniques have been used as positive electrodes of Ni–Cd batteries. As these materials are indefinitely stable in KOH solution, the electrochemical cycling between  $\alpha$  and  $\gamma$  phases allows up to 1.3  $e^-$  per (Ni + Co) atom to be reversibly exchanged at the C/5 rate. Nevertheless, during long-range cycling, a slow evolution from the  $\gamma/\alpha$  couple to the  $\beta(\text{III})/\beta(\text{II})$  couple occurs. It has been assigned to a partial reduction of  $\text{Co}^{3+}$  ions to  $\text{Co}^{2+}$  ions at the end of the discharge process. The evolution of the number of exchanged electrons ( $NEE$ ) versus the cobalt amount is discussed.

### Introduction

The addition of cobalt to  $\text{Ni}(\text{OH})_2$  which is the positive electrode material of nickel–cadmium cells was first reported by Edison at the beginning of this century [1] and interest in the additive has continued ever since. However, whereas most previous studies have been confined to compositions up to 0.15 in molar cobalt ratio [2, 3], this work examines those ranging from 0.10 to 0.55. Recently, we have shown that the substitution of at least 20% of cobalt for nickel allows the formation of an  $\alpha^*$ -hydrated phase stable in KOH medium at room temperature [4, 5]. These materials were prepared by 'chimie douce' techniques from the  $\text{NaNi}_{1-x}\text{Co}_x\text{O}_2$  phases used as precursor. More recently, Armstrong and Charles confirmed that a large cobalt addition to the nickel electrode ( $x=0.45$ ) allows the stabilization of the  $\gamma/\alpha$  cycling [6]. The  $\alpha$ -cobalated material was, in that case, prepared by cathodic deposition from nitrate solutions. We have also shown that stabilized  $\alpha$ -phases can be obtained from precipitation techniques [7–9]. Depending on the preparation, the hydrated cobalt substituted nickel hydroxide can exhibit a well-ordered  $\alpha'$  or a turbostratic  $\alpha$  structure. In such materials, the charge excess due

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to trivalent cation is compensated by the insertion of carbonate or sulphate anions between the hydroxide slabs

This paper deals with the electrochemical study of  $\alpha_{\text{Co}^{3+}}(\text{CO}_3)$  phases obtained by direct precipitation

## Experimental

### *Electrodes preparation*

The cobalt substituted nickel hydroxides have been tested as positive electrode material in alkaline batteries (pocket type) using large capacity cadmium electrodes (in order to be positive electrode limited) and 5 N KOH as free electrolyte. The mixture of the nickel hydroxide and graphite (30% by weight) is pasted onto a nickel foam supplied by SORAPEC. The electrode is then pressed at  $10^3$  bars in order to assure a good electronic contact between the foam and the active powder. Its thickness becomes then close to 0.8 mm. The electrode is finally protected by a separator film in order to reduce the loss of active material during electrochemical cycling.

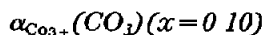
### *Electrochemical tests*

The charge and discharge reactions are realized at the C/5 rate, which means that the current density is chosen in order that the nominal capacity (corresponding to one electron per (Ni+Co) atom) will be reached in 5 h. The electrochemical experiments were monitored by an HP 1000 A600 computer using a software previously described for the cycling of lithium batteries [10]. They were performed in the following conditions: the first three charges are 20, 15 and 7.5 h, respectively, each of them being followed by a discharge down to 0.9 V. The process of the third cycle is then repeated for the following ones. As during the first two cycles the positive electrode is strongly overcharged, the capacity recovered during these discharges has not been taken into account during the discussion of the results.

## Result and discussion

### *Evolution of the number of exchanged electrons per (Ni+Co) atom versus cycle number*

$\alpha_{\text{Co}^{3+}}(\text{CO}_3)$  phases were electrochemically tested for cobalt compositions ranging from 0.10 to 0.55. The variation of the number of exchanged electrons (*NEE*) versus the cycle number for the various cobalt contents is reported on Fig. 1. The *NEE* decreases for each cobalt composition when the cycle number increases. A decrease of the *NEE* is also observed when the cobalt rate increases in the  $0.20 \leq x \leq 0.55$  range. This point will be discussed in the following section.



As the  $\alpha_{\text{Co}^{3+}}$  phase is unstable in KOH medium for  $x=0.10$ , this material

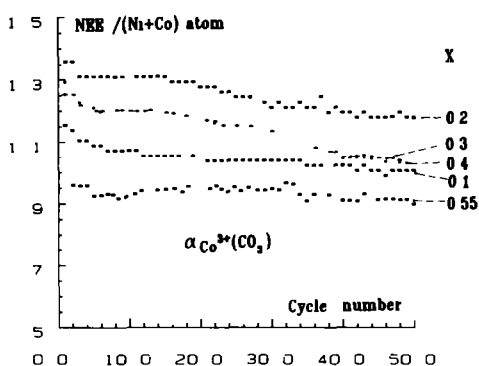
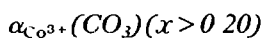


Fig 1 Variation of the number of exchanged electrons ( $NEE$ ) vs the cycle number for various cobalt amounts

will be considered separately. It will in fact rapidly transform into a  $\beta(II)$  type phase and after a few cycles (less than 10), the electrochemical cycling principally occurs between  $\beta(II)$  and  $\beta(III)$  type phases. However, we notice that the  $NEE$  remains higher than 1 during the first 40 cycles and such a result should be compared to the classical  $\beta(II)$ - $Ni(OH)_2/\beta(III)$ - $NiOOH$  cycling in which only  $0.9 e^-$  per Ni atom is experimentally exchanged. Thus, a small cobalt content seems to improve the electrochemical capacity of the nickel electrode. Previous workers have also observed an increase in electrode capacity when cobalt is added to the nickel hydroxide but have not clearly shown its nature. The improvement in performance has been explained as being due to (i) increased charging efficiency [3], (ii) better electronic conductivity in the reduced state [3], (iii) formation of an  $\alpha$  phase during the charge reaction [11]. For Armstrong *et al*, who studied the impedance behavior of nickel hydroxide and nickel/cobalt hydroxide electrodes in alkaline solution, the addition of cobalt improves the electrode kinetics by lowering the charge transfer resistance of the reaction process [12, 13].



From Fig 1, for all cobalt compositions with  $x > 0.20$ , a decrease of the  $NEE$  after the first 15 cycles is seen. This behavior is mainly observed when the cobalt/(nickel + cobalt) ratio is equal to 0.20, 0.30 and 0.40. A long-term electrochemical test was therefore performed on the  $\alpha_{Co^{3+}}(CO_3)$  phase ( $x = 0.20$ ) and the  $NEE/(Ni + Co)$  atom versus the cycle number is given in Fig 2. If the  $NEE$  is equal to 1.3 during the first 15 cycles, it gradually decreases and becomes lower than 1 after 100 cycles. Such a capacity decrease suggests a slow transformation from the  $\gamma/\alpha$  couple to  $\beta(III)/\beta(II)$  during the electrochemical cycling. In order to check this hypothesis, a study of the shape of the discharge curve of the electrode made from the  $\alpha_{Co^{3+}}(CO_3)$  phase ( $x = 0.20$ ) has been performed, the discharge curves obtained after 3, 10, 20, 30, 40 and 130 cycles are reported on Fig 3(a). It is seen that the shape of the discharge curve illustrates the

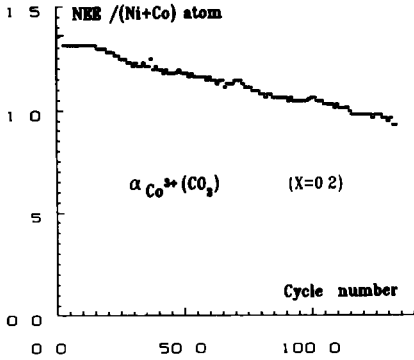


Fig 2 Variation of the number of exchanged electrons (*NEE*) during long-term cycling of the  $\alpha_{Co^{3+}}(CO_3)$  ( $x=0.2$ ) phase

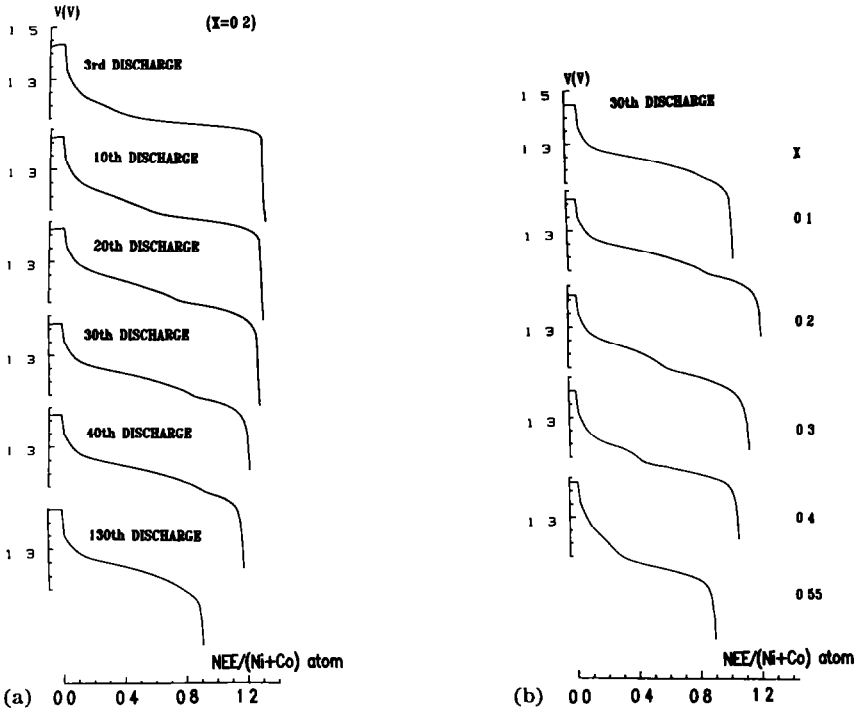


Fig 3 Modifications of the shape of the discharge curve (a) for increasing cycle number ( $x=0.2$ ), (b) for increasing cobalt amount (30th cycle)

presence of two phenomena. Several groups of workers have shown that the discharge potential obtained from a  $\beta(III)$  phase is higher than that obtained from a  $\gamma$  phase [14–16]. The first part of the curve is therefore

attributed to the  $\beta(\text{III})/\beta(\text{II})$  system while the second one (at lower potential) is assigned to the  $\gamma/\alpha$  one. From these discharge curves, we can assume that the proportion of the  $\beta(\text{II})$  material in the discharged electrode increases with cycle number at the expense of the  $\alpha_{\text{Co}^{3+}}$  phase. The X-ray diffraction spectra of the discharged and charged electrode material after 50 cycles are reported in Fig 4(a) in comparison with that of the starting phase. They confirm that the reduced and oxidized materials are formed by a mixture of  $\alpha$  and  $\beta(\text{II})$  hydroxides and by  $\gamma$  and  $\beta(\text{III})$  oxyhydroxides, respectively, with a high percentage of the  $\beta(\text{II})$  or  $\beta(\text{III})$  phases. After 130 cycles, the discharge curve shape (Fig 3(a)) and the X-ray diffraction spectrum show that the electrode material has been totally turned into the  $\beta(\text{II})$  phase after the discharge. Thus although the  $\alpha_{\text{Co}^{3+}}$  phases are chemically stable in concentrated KOH medium (when the cobalt ratio is higher than 0.20) even after a long-term stability test [7, 8], they gradually transform into a  $\beta(\text{II})$  type phase during the electrochemical test so that the  $\gamma/\alpha$  cycling is slowly replaced by the  $\beta(\text{III})/\beta(\text{II})$  one.

However, as shown by the 30th discharge curve, reported in Fig 3(b), for various cobalt amounts, it is seen that the  $\alpha \rightarrow \beta(\text{II})$  reaction is slowed down when the cobalt rate increases. For the highest cobalt amount ( $x = 0.55$ ), the  $\beta(\text{II})$  phase formation is minimized and the  $\gamma/\alpha$  cycling is almost stabilized. The X-ray diffraction spectra of the discharged and charged electrode material (after 50 cycles) are reported in Fig 4(b) in comparison with the spectrum of the starting  $\alpha_{\text{Co}^{3+}}(\text{CO}_3)$  phase ( $x = 0.55$ ) the reduced or oxidized materials are principally composed of  $\alpha$  or  $\gamma$  phases.

#### *Simulation of the curve shape modification induced by the $\gamma/\alpha \rightarrow \beta(\text{III})/\beta(\text{II})$ transition*

In order to illustrate the relation between the shape of the discharge curve and the relative amount of  $\beta(\text{III})/\beta(\text{II})$  and  $\gamma/\alpha$  couples, a simulation program was realized. This program determines the potential variation of an electrode (during the discharge) when two electrochemical systems are

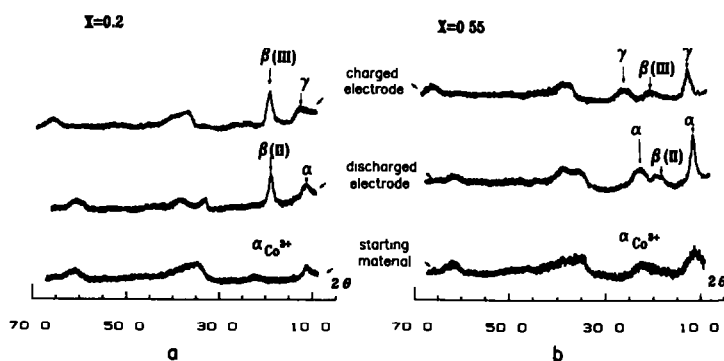


Fig 4 Comparison of the X-ray diffraction spectra of charged and discharged electrode materials (after 50 cycles) to that of the starting phase (a)  $x = 0.2$ , (b)  $x = 0.55$

simultaneously present. It requires that the discharge curves of each system are known. From these data, the decreasing potentials are scanned. For each potential value, the program adds the number of electrons already exchanged in each system according to the ratio of  $\gamma/\alpha$  and  $\beta(\text{III})/\beta(\text{II})$  couples. The discharge curves corresponding to the  $\gamma_{\text{Co}} \rightarrow \alpha_{\text{Co}^{3+}}$  ( $x=0.20$ ) and  $\beta_{\text{Co}^{3+}}(\text{III}) \rightarrow \beta_{\text{Co}^{3+}}(\text{II})$  reactions, respectively, are reported in Fig 5(a). As was previously discussed, the half discharge potential of the second reaction exhibits a higher value (1.238 V) than that of the first one (1.175 V). The theoretical shape of voltage curves obtained for increasing the ratio of the  $\beta(\text{III})/\beta(\text{II})$  couple to  $\gamma/\alpha$  is reported in Fig 5, b and c. The evolution of the discharge curve is quite similar to that reported in Fig 3 from experimental data. These results show unambiguously that the  $\gamma/\alpha$  cycling is slowly replaced by the  $\beta(\text{III})/\beta(\text{II})$  one. Moreover, as previously mentioned, this comparison confirms that the evolution from the  $\gamma/\alpha$  cycling to the  $\beta(\text{III})/\beta(\text{II})$  one is slowed down when the cobalt amount increases.

#### Comparison with previous results

The electrochemical stabilization of the  $\gamma/\alpha$  cycling for high cobalt rates has also been studied by Armstrong and Charles on electrodeposited materials [6]. They showed, in accordance with our results, that for lower additive levels, the  $\gamma/\alpha$  reaction gradually converts to the more commonly observed

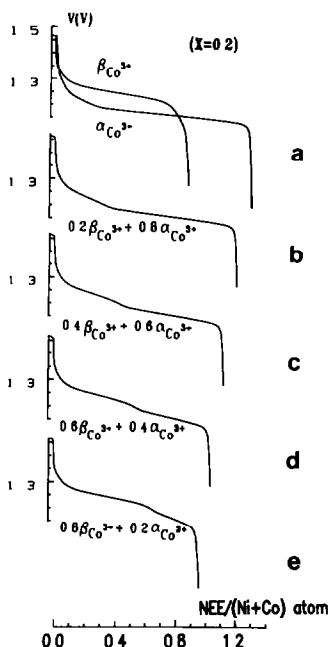


Fig 5 Shape of discharge curves for various ratios of  $\gamma/\alpha$  and  $\beta(\text{III})/\beta(\text{II})$  couples (a) experimental curves obtained from  $\beta_{\text{Co}^{3+}}$  and  $\alpha_{\text{Co}^{3+}}$  phases, (b-e) simulated curves

$\beta(\text{III})/\beta(\text{II})$  one [6] A comparison should also be made with the electrochemical cycling of  $\alpha_{\text{Co}^{3+}}^*$  phases obtained by 'chumie douce' reactions from the  $\text{NaNi}_{1-x}\text{Co}_x\text{O}_2$  precursor phase The  $\gamma/\alpha^*$  cycling is then completely stabilized for  $x=0.20$  [17] Such an electrochemical behavior difference between  $\alpha_{\text{Co}^{3+}}$  and  $\alpha_{\text{Co}^{3+}}^*$  phases is not exactly understood but seems to be directly linked to the difference in texture and more particularly to the particle size

#### Evolution of the NEE versus the cobalt rate

During the first 15 cycles, we can consider that the electrochemical cycling of cells using  $\alpha_{\text{Co}^{3+}}(\text{CO}_3)$  phases as starting material principally occurs between  $\alpha$  and  $\gamma$  phases The NEE is then almost constant whatever the cobalt amount (higher or equal to 0.20) It is then possible to study the evolution of the NEE and the discharge potential, versus the cobalt rate

From Fig 1 it can be seen that the NEE decreases when the cobalt rate increases During the first 15 cycles, the NEE is equal to 1.3, 1.2 and 1.17 when the cobalt amount  $x$  is equal to 0.20, 0.30 and 0.40, respectively For the  $\alpha_{\text{Co}^{3+}}(\text{CO}_3)$  phases ( $x=0.55$ ), the NEE remains lower than 1

This behavior is directly related to the oxidation level of cobalt and nickel ions in the oxidized and reduced phases During the electrochemical cycling, the average oxidation level of the transition ions is equal to  $2+x$  in the reduced  $\alpha_{\text{Co}^{3+}}$  hydroxide, while it is close to 3.5 in the  $\gamma$  phases at the end of the charge process [18] Thus between the charge and discharge reactions,  $[3.5-(2+x)]e^-$  per (Ni+Co) atom are theoretically expected to be exchanged as schematically illustrated on Fig 6 This scheme also explains that for a cobalt ratio lower than 0.20, as the  $\gamma/\alpha$  cycling is not stabilized, only  $1-x$  electron is expected to be exchanged during  $\beta(\text{III})/\beta(\text{II})$  cycling Experimentally, these values can be slightly modified, as we have already

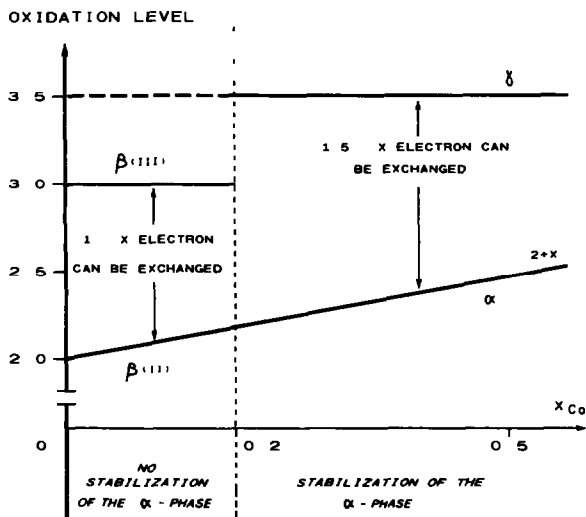


Fig 6 Variation of the theoretical NEE vs the cobalt amount

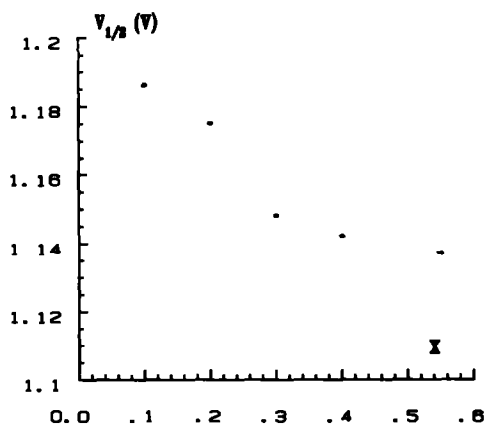


Fig 7 Variation of the half discharge potential of the  $\gamma_{Co} \rightarrow \alpha_{Co}$  reaction (first cycle) vs the cobalt amount

mentioned, because the oxidation level in  $\beta(III)$  or  $\gamma$  phases is not so strictly defined. Moreover, as a result of the low electronic conductivity of the reduced phases, it is always difficult or even impossible to come back to the completely reduced material.

These results obtained during the electrochemical cycling of these  $\alpha_{Co^{3+}}(CO_3)$  phases are almost identical to the theoretical ones during the first 15 cycles. The optimal capacity is reached as early as the initial cycles because the very small size of the particles confers on the whole material a very good electrochemical activity.

#### *Evolution of the half discharge potential versus the cobalt rate*

During the first cycles, it is also possible to relate the evolution of the potential at the half discharge time ( $V_{1/2}$ ) to the cobalt amount, because the electrochemical cycling really occurs between  $\alpha_{Co^{3+}}$  and  $\gamma_{Co}$  phases. The half discharge potentials ( $V_{1/2}$ ) obtained for various cobalt amounts ( $0.10 \leq x \leq 0.55$ ), after the first electrochemical cycle, are reported in Fig 7 which shows that the  $V_{1/2}$  value decreases when the cobalt rate increases. This result was well known for the  $\beta(III)/\beta(II)$  system. Nevertheless, the physical reason for this phenomenon is not well understood [11, 12, 19–23].

#### **Hypotheses about the instability of the $\alpha_{Co^{3+}}(CO_3)$ phase**

In order to try to understand why the  $\alpha_{Co^{3+}}$  phases are unstable during electrochemical cycling, the following hypotheses were made.

The first one is to consider that as  $H^+$  ions are released from the material during the charge process, a local decrease of the pH value can occur in



some parts of the electrode (intergranular space) which are not well soaked with the electrolyte. It was previously shown on  $\gamma$  phases (either cobalted or not) prepared by 'chimie douce' reactions from  $\text{NaNi}_{1-x}\text{Co}_x\text{O}_2$  phases [4, 24], that these oxyhydroxides evolve to  $\beta(\text{III})$  phases in acidic medium for a pH close to 2.5. If such a phenomenon occurs during electrochemical cycling, the reduced material formed during the discharge reaction would be a  $\beta(\text{II})$  type phase. In order to avoid such an acidic concentration in some local part of the electrode during the charge reactions, the electrolyte solution was concentrated and electrochemical tests were then performed on the  $\alpha_{\text{Co}^{3+}}(\text{CO}_3)$  ( $x=0.20$ ) phase in a 10 N KOH solution. No improvement or stabilization of the capacity was observed after the first 15 cycles and the reduced material recovered after 50 cycles was again principally formed of a  $\beta(\text{II})$  type phase as after the cycling in 5 N KOH.

Another hypothesis was to consider that since the discharge reaction occurs down to 0.9 V, the trivalent cobalt ions may be partially reduced to the divalent state leading to the formation of an unstable  $\alpha_{\text{Co}^{2+}}$  material [8]. An electrochemical cycling was therefore performed from the  $\alpha_{\text{Co}^{3+}}(\text{CO}_3)$  phase ( $x=0.20$ ), the discharge reaction being limited to 1.15 V. As only a partial electrode discharge occurs in these conditions, the charge time has been reduced in order to keep the charge time/discharge time ratio close to 1.2. After 40 cycles in such conditions, an overall discharge down to 0.9 V has been realized. The shape of this discharge curve is characteristic of a  $\gamma/\alpha$  reaction with a half discharge potential equal to 1.12 V. Moreover the charged and discharged electrode materials recovered are essentially made of  $\gamma$  and  $\alpha$  phases. Such an interesting result suggests that  $\alpha_{\text{Co}^{3+}}$  phases have to be tested with a discharge reaction limited to an end of discharge potential higher than about 1 V. In this case the  $\gamma/\alpha$  cycling can be stabilized for a 0.20 cobalt ratio because cobalt ions will not be reduced to the divalent state. Experiments are currently being performed in this way.

## Conclusions

The substitution of at least 20% of cobalt for nickel in the positive electrode material of Ni/Cd batteries allows the partial stabilization of the  $\gamma/\alpha$  cycling. The number of exchanged electrons per (Ni + Co) is theoretically equal to  $1.5-x$  ( $x$  cobalt substitution rate) and this value is almost reached during the first electrochemical cycles. Nevertheless, during long-term electrochemical tests down to 0.9 V the  $\gamma/\alpha$  system is slowly replaced by the  $\beta(\text{III})/\beta(\text{II})$  one, especially for the lowest cobalt amounts. This transformation could be due to the partial reduction of trivalent cobalt ions to the divalent state at the end of the discharge reaction. Systematic experiments are in progress in order to determine precisely the exact value of the end of discharge potential which preserves the  $\gamma/\alpha$  cycling. It should be kept in mind that for numerous applications a 1 V limit voltage value is classically used.

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