



# Structural study of $\text{NiO}_2$ and $\text{CoO}_2$ as end members of the lithiated compounds by in situ high resolution X-ray powder diffraction

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## Abstract

In-situ X-ray diffraction has been carried out on  $\text{Li}_x\text{NiO}_2$  and  $\text{Li}_x\text{CoO}_2$  batteries, using the high resolution powder diffractometer BM16 at ESRF (Grenoble, France). Diffraction was performed in transmission geometry through 1-mm thick Bellcore-type plastic batteries. The batteries were controlled in potentiostatic mode. During these experiments, end-members  $\text{NiO}_2$  and  $\text{CoO}_2$  have been isolated, and high resolution patterns have been recorded in order to solve their structures from powder data.  $\text{NiO}_2$  structure is of  $\text{CdI}_2$  type, with a monoclinic distortion.  $\text{CoO}_2$  seems to be of  $\text{CdCl}_2$  type also with a monoclinic distortion. © 1999 Elsevier Science S.A. All rights reserved.

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## 1. Introduction

In-situ X-ray diffraction has been carried out on  $\text{Li}_x\text{NiO}_2/\text{C}$  and  $\text{Li}_x\text{CoO}_2/\text{C}$  plastic Li-ion batteries (Bellcore technology). These oxides have been widely studied as materials for rechargeable lithium batteries. In-situ X-ray diffraction has been shown to be extremely useful in characterizing structural modifications of insertion compounds over a wide range of intercalation compositions [1]. This technique allows a real-time characterization of the insertion compounds without the drawbacks of the ex-situ method, which includes a need for a large number of samples, the risk of atmospheric contamination and the adverse effect of self-discharge. The Li intercalation process has been followed by means of a MacPile system [2] operating in potentiostatic mode. The aim of

this part of this study was to determine accurately the structure of the final phases  $\text{Li}_0\text{NiO}_2$  and  $\text{Li}_0\text{CoO}_2$ .

## 2. Experiment

Plastic batteries have been mounted in transmission geometry on BM16 at ESRF. This beam line is designed to perform powder diffraction studies with a very high angular and energy resolution. This of course, facilitates the indexing of powder diffraction patterns, the refinement and solution of crystal structures from powder data. It is also possible to follow the evolution of the diffraction patterns with time on a scale of a few minutes. The diffraction data have been collected with a nine-crystals analyzer and the angular range from 0 to  $80^\circ 2\theta$  at  $\lambda = 0.65 \text{ \AA}$  for  $\text{NiO}_2$  and  $\lambda = 0.40 \text{ \AA}$  for  $\text{CoO}_2$  was scanned in about 10 min. Data from each analyzer were scaled and added, and the data from each scan could be added. When  $x$  was equal to 0 (e.g.,  $\text{NiO}_2$ ,  $\text{CoO}_2$ ), all the similar patterns were added in order to improve the statistics.

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### 3. Results

#### 3.1. NiO<sub>2</sub>

First of all, the contribution of aluminum and copper collector grids were identified and subtracted. Then, each diffraction line of NiO<sub>2</sub> was fitted with a pseudo-Voigt function. The unit cell was determined using DICVOL [3]. Only one solution in monoclinic symmetry has been found. The indexation of the lines clearly shows that only three space groups are consistent with the observed extinctions: *C2/m*, *Cm* or *C2*. The final refinement led us to the centric group *C2/m* as the only solution. Cell parameters were refined in pattern matching mode using FullProf [4], and led to the following parameters:  $a = 4.8754(3) \text{ \AA}$ ,  $b = 2.8141(2) \text{ \AA}$ ,  $c = 5.5820(3) \text{ \AA}$ ,  $\beta = 125.836(4)^\circ$ .  $Z = 2$  has been determined from the estimated density of NiO<sub>2</sub>. At the same time, integrated intensities were extracted, and direct methods have been performed using SIRPOW92 [5]. The structural model proposed consist of the *C2/m* (no. 12) space group, with a Ni at position (0, 0, 0) (2a) and an oxygen at ( $x$ , 0,  $z$ ) (4i) with  $x = 0.493(4)$  and  $z = 0.231(2)$ . At the end of the refinement, there remained a problem in the description of the profile. There are two origins to this problem. The first one resides in asymmetric lines at low angles, due to the axial divergence of the beam. This has been corrected using a modified pseudo-Voigt function in FullProf. The second problem was due to a few lines of NiO<sub>2</sub> that are larger than the other ones. This can be explained by an anisotropy of the powder leading to two line families. Two identical phases with different Cagliotti polynomials have been defined to solve this problem. This led to a better profile description ( $R_{WP}$

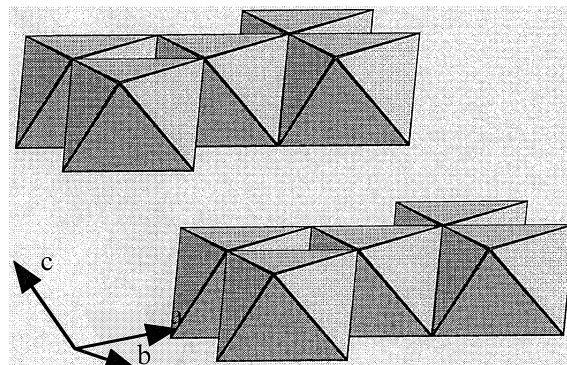


Fig. 2. NiO<sub>2</sub> structure representation.

= 13.8%) and to a structure reliability factor  $R_B = 7.7\%$ . Finally, site occupancies have been refined and a perfect stoichiometry for NiO<sub>2</sub> was achieved. The final Rietveld plot is shown in Fig. 1. NiO<sub>2</sub> structure is shown in Fig. 2.

#### 3.2. CoO<sub>2</sub>

The same study was carried out for CoO<sub>2</sub> but a complete study as for NiO<sub>2</sub> could not be achieved. The diffraction lines are complex and seem to contain many reflections preventing their decomposition. An average hexagonal cell was obtained assuming that each observed diffraction peak consisted of only one reflection. Then a distortion to the corresponding orthohexagonal cell has been used. The refinement of this cell in pattern matching mode (*Cmmm* space group) shows a correct description of the observed diagram. This cell has a volume twice that of one described in Ref. [6]. In this reference, the authors pro-

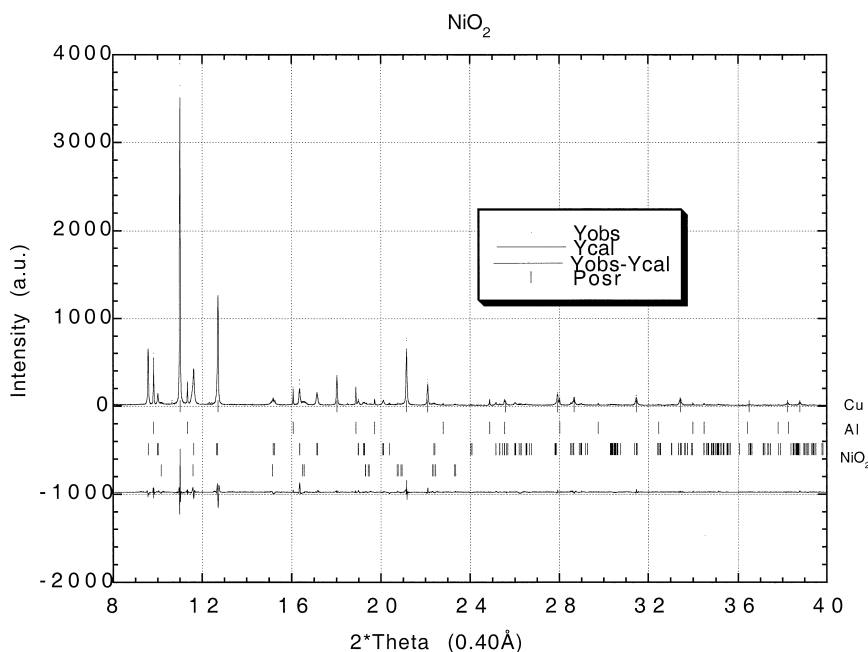


Fig. 1. Rietveld plot for NiO<sub>2</sub>.

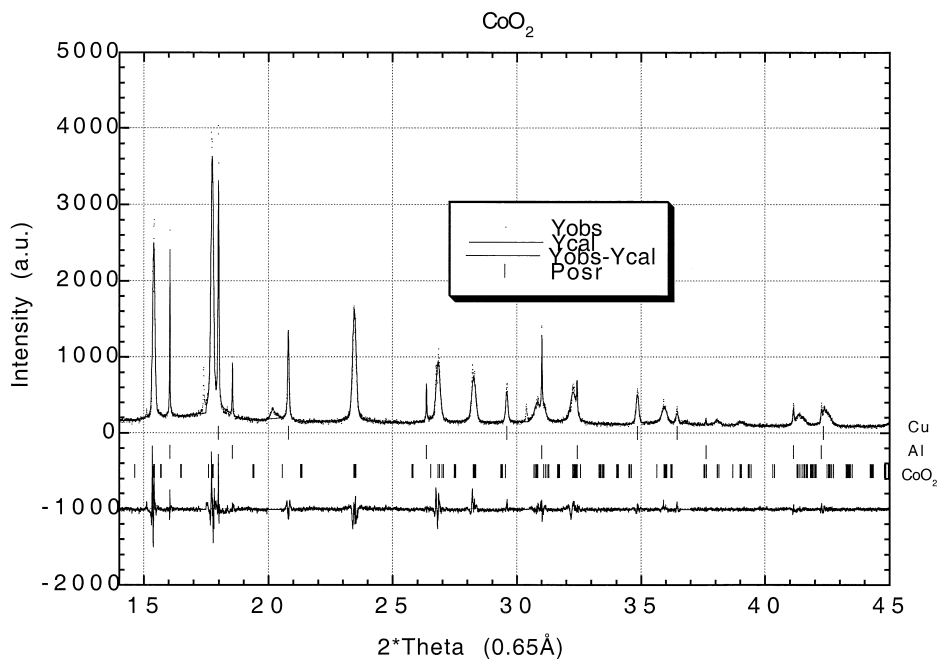


Fig. 3. Pattern matching plot for  $\text{CoO}_2$ .

posed a  $\text{CdCl}_2$ -type structure for  $\text{CoO}_2$ . This structure is a layered structure, and is not compatible with the  $mmm$  symmetry; for this reason, a monoclinic distortion was used here. The pattern matching of the  $\text{CoO}_2$  phase in monoclinic symmetry with space group  $Cm$  led to  $R_{\text{WP}} = 10.8\%$ , and is shown on Fig. 3. The cell parameters are  $a = 4.8413(3) \text{ \AA}$ ,  $b = 2.8031(1) \text{ \AA}$ ,  $c = 12.7474(3) \text{ \AA}$ ,  $\beta = 90.10(1)^\circ$ . Referring to the  $\text{CdCl}_2$  structure,  $Z = 6$  has been determined. The position of the cobalt and oxygen atoms was determined respectively from the cadmium and chloride atoms. The positions of the cobalt atoms were successfully refined in the  $Cm$  space group (no. 8) and are reported in Table 1. The centrosymmetric space group  $C2/m$  has been unsuccessfully tried. Oxygen atoms were more problematic because the refinement did not converge.  $C2/m$  and  $C2$  space groups were attempted unsuccessfully, which could be due either to the high overlapping of the diffraction lines making the extraction of integrated intensities very difficult or to a local disorder of oxygen atoms so that the observed structure is an average structure.

Table 1  
Cobalt atoms positions

	$x$	$y$	$z$
Co1	0	0	0
Co2	0.001(2)	0	0.325(5)
Co3	0.003(2)	0	0.675(5)

As the positions of the oxygen atoms are still unknown, it was impossible to calculate O–O distances and to verify the theoretical calculation predicting that O–O bindings may occur in this type of layered compound [7].

#### 4. Conclusion

Refinement of the  $\text{NiO}_2$  structure has been successfully performed.  $\text{NiO}_2$  is stoichiometric and adopts a distorted  $\text{CdI}_2$  structure. The refinement of  $\text{CoO}_2$  structure is more problematic. Cobalt atom positions have been determined but further work remains to determine oxygen atoms positions. Overall, this study stresses the advantage of BM16 high resolution, without which the cell parameters of  $\text{CoO}_2$  could not have been determined.

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