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# Magnetic clusters in $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ nanomaterials used as cathodes in lithium-ion batteries

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## Abstract

We have prepared LiNi<sub>1-y</sub>Co<sub>y</sub>O<sub>2</sub> ( $0 \le y \le 1$ ) compounds as polycrystalline nanomaterials ( $d \approx 400$  nm) using a low-temperature sol-gel method. XRD studies indicate that these materials are single phase for  $0.2 \le y \le 1$  with an ordered distribution of Li and Ni/Co in the layered structure. Nevertheless, as this technique provides only averaged structural information, it is still possible that locally there are some defects, among them disorder, that could affect the electrochemical behaviour of these materials. In fact, through FTIR spectroscopy we observe for the Li-O band a slight deviation from a linear behaviour for high nickel content ( $y \leq 0.2$ ), that is attributed to the presence of Ni cations in the predominantly lithium layers (octahedral interstices). In addition, by means of magnetic measurements,  $\chi_m(T)$  and M(H), we detect in all the samples a ferrimagnetic signal, that gets smaller and smaller as the Co content increases, but that indeed reveals the presence of some Ni<sup>2+</sup> ions occupying Li<sup>+</sup> places, that would lead to the formation of small ferromagnetic islands. From those magnetic measurements we have estimated the size of those nanometric magnetic inhomogenities that decreases upon Co doping from  $R_{(y=0)} = 3.5$  nm to  $R_{(y=0.4)} = 0.5$  nm. This result confirms that the addition of Co<sup>3+</sup> inhibits the presence of interlayer Ni<sup>2+</sup> and therefore favours a better lamellar structure, only obtained for y > 0.4.

## 1. Introduction

Lithiated metal oxides, having the layered  $\alpha$ -NaFeO<sub>2</sub> structure, have been extensively studied as cathodes in rechargeable lithium batteries. Only LiCoO<sub>2</sub> [1] is currently used in commercial devices, but its use as a cathode material finds limitations due to its high cost and its structural instability. Another attractive candidate is LiNiO<sub>2</sub> but it is quite difficult to prepare it in a very reproducible way as a result of a tendency to non-stoichiometry due to the presence of some extra Ni<sup>2+</sup> ions occupying Li sites and some lithium deficiency [2], so that the real chemical formula should be expressed as  $Li_{1-x}Ni_{1+x}O_2$ . An appealing alternative that alleviates the disadvantages of both LiCoO<sub>2</sub> and LiNiO<sub>2</sub> is the solid solution  $LiNi_{1-y}Co_yO_2$  [3].

The good electrochemical performance of these compounds relies on a well layered structure, in which Li and (Co, Ni) cations do not mix but occupy alternating fcc (111) planes [3, 4]. Characterization techniques such as IR, Raman

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and ESR spectroscopies, as well as magnetic measurements, have been proposed to be specially powerful tools to study this cation ordering and therefore to estimate the potentiality of these materials for electrochemical purposes [5, 6].

From the synthetic point of view, these materials can be prepared by traditional (and most often used) high-temperature ceramic methods or by means of more recently introduced low-temperature wet chemistry routes. And interestingly enough, it has been shown that the synthetic conditions have a great impact on the electrochemical characteristics of the electrode materials and that a small particle size favours the rate of capability on charging/discharging the electrochemical cells [7].

In this work we concentrate on small-particle-size ( $d \approx 400 \text{ nm}$ ) materials prepared by a soft-chemistry route. These samples are stoichiometric, according to ICP analysis. The charge–discharge voltage profiles of these Li/LiNi<sub>1-y</sub>Co<sub>y</sub>O<sub>2</sub> cells show good reversibility during the first cycle and high capacities (in the range of 130–140 mA h g<sup>-1</sup>, close to the theoretical value 164 mA h g<sup>-1</sup>, when discharged to a cut-off voltage of 2.5 eV).

We investigate their cationic ordering and possible chemical heterogeneities mainly by means of magnetic measurements, and we compare these results with the information obtained in the same samples by IR spectroscopy.

## 2. Experimental details

Single-phase  $LiNi_{1-v}Co_vO_2$  compounds were obtained by a wet-chemical method. The sol-gel process for preparation of  $LiNi_{1-\nu}Co_{\nu}O_{2}$  oxides was similar to that described elsewhere [8]. Analytical pure metal acetates and carboxylic acid, namely succinic C<sub>4</sub>H<sub>6</sub>O<sub>4</sub>, were mixed and dissolved in distilled water to form a sol. Optimal synthetic conditions and the effect of molar ratio (M/A) of total metal ions (M =Li + Co + Ni) to carboxylic acid (A) on the physicochemical properties of LiNi<sub>1-v</sub>Co<sub>v</sub>O<sub>2</sub> powders were investigated. Wellstructured compounds were obtained for the metal/acid ratio M/A = 1:1. The sol was evaporated to dryness at 80 °C to form the gel. During this process, the mass precursor darkened progressively as a result of oxidation of divalent cations  $(Ni^{2+}, Co^{2+})$  to trivalent cations  $(Ni^{3+}, Co^{3+})$ . The so-obtained ashes were heated at 400 °C for 2 h, yielding brownish-black materials of submicrometre size. The powder mass was slightly ground and then fired at 800 °C for 2 h in air followed by a calcination in oxygen for 2 h to improve the crystallinity of  $LiNi_{1-\nu}Co_{\nu}O_{2}$  final products.

Composition of the final products was determined using a VG Plasma Quad II-S option induced-coupled-plasma mass spectrometer (ICP-MS). X-ray powder diffraction (XRPD) patterns were obtained with a Siemens D-5000 diffractometer and Cu K $\alpha$  = 1.5418 A radiation. The morphology and size of the particles were studied in a scanning electron microscope (SEM), JEOL 6400. FTIR spectra were recorded at room temperature using an IFS113v Bruker interferometer equipped with a 3.5  $\mu$ m-thick beamsplitter, a Globar source and a DTGS/PE far-infrared detector. Magnetic properties were studied in a Quantum Design MPMS SQUID magnetometer. Zero-field-cooled (ZFC) and field-cooled (FC) magnetic susceptibility data were obtained in a field of 50 Oe in the



a<sub>hex</sub>

Figure 1. Schematic representation of the layered structure of perfectly lamellar  $LiNi_{1-y}Co_yO_2$  compounds.

temperature range 4.2 K  $\leq T \leq 300$  K. Hysteresis loops in ZFC conditions were obtained at 5, 50, 100 and 300 K varying the field up to  $\pm 50$  kOe.

#### 3. Results and discussion

#### 3.1. Sample characterization

The elemental analysis (ICP-MS) data indicate that these  $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$  samples have a composition near the nominal stoichiometry. Nevertheless the accuracy on the quantification of the amount of lithium is limited by the difficulty of detecting such light atoms.

XRPD was used to identify the crystalline phase of the so-obtained crystalline phases. For  $0.2 \le y \le 1$  Bragg peaks are indexed in the hexagonal crystallographic system ( $R\overline{3}m$  space group) showing materials with the expected  $\alpha$ -NaFeO<sub>2</sub>-type structure [9, 10]. This is a modified NaCl structure in which closely packed triangular lattices of each kind of atom are stacked in layer order (Ni<sub>1-y</sub>Co<sub>y</sub>), O, Li, O and (Ni<sub>1-y</sub>Co<sub>y</sub>) with ABC stacking. In this structure, lithium ions occupy the octahedral sites between (Ni<sub>1-y</sub>Co<sub>y</sub>O<sub>2</sub>)<sub>n</sub> infinite slabs formed by edge-sharing (Ni<sub>1-y</sub>Co<sub>y</sub>O<sub>2</sub>)O<sub>2</sub> octahedra as shown by the schematic representation in figure 1.

The hexagonal lattice parameters, *a* and *c*, were calculated by Rietveld refinement. The compositional dependence of the crystallographic parameters of  $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$  powders synthesized by this sol–gel method are in good agreement with values reported in the literature [11, 12] and they are characteristic features of the  $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$  solid solution. Another important feature is that these materials show a high *c/a* ratio (*c/a* > 4.95) and a clear splitting of the (006)–(102) and (108)–(110) Bragg lines, as well as an intensity ratio  $I_{(003)}/I_{(004)} > 1$  that has been



Figure 2. Typical SEM micrograph of  $LiNi_{1-y}Co_yO_2$  powders prepared by the succinic acid method.



Figure 3. FTIR absorption spectra of the obtained  $LiNi_{1-y}Co_yO_2$  samples.

acknowledged to be an indication of an ordered distribution of lithium and Ni/Co in the layered structure.

As an example of the morphology study we show in figure 2 a typical SEM micrograph from the JEOL 6400. The individual grains are well formed and quite small, with the majority of particles well below the micrometre size and a mean particle diameter of 400 nm.

FTIR measurements were made to investigate the local environment of cations in the cubic closed-packed oxygen array of the LiNi<sub>1-y</sub>Co<sub>y</sub>O<sub>2</sub> lattice. Infrared modes correspond to vibrations involving primarily atomic motion of oxygen anions against their cationic neighbours [13]. Consequently, these modes are very sensitive to the cationic local environment in the host matrix. Figure 3 shows the FTIR absorption spectra of LiNi<sub>1-y</sub>Co<sub>y</sub>O<sub>2</sub>. The high-wavenumber region, at about 400–600 cm<sup>-1</sup>, corresponds to the broad rock-salt band, which has broken into several distinct components. The bands



**Figure 4.** (a) ZFC and FC molar magnetic susceptibility of the LiNiO<sub>2</sub> sample measured under a field H = 50 Oe ( $5 \le T$  (K)  $\le 300$ ). (b) ZFC magnetization versus applied field at T = 5, 50, 100, 200 and 300 K.

located around 600 cm<sup>-1</sup> are attributed to the asymmetric stretching modes of the MO<sub>6</sub> group, whereas bands at about 400–500 cm<sup>-1</sup> are assigned to the bending modes of the O–M–O bonds. The far-infrared region, in which an isolated strong band is centred at about 240–260 cm<sup>-1</sup>, is attributed to the vibration of elongated LiO<sub>6</sub> octahedral groups. Thus, FTIR measurements confirm XRPD data showing the formation of pure LiNi<sub>1-y</sub>Co<sub>y</sub>O<sub>2</sub> phase for  $0.2 \le y \le 1$ .

Because FTIR spectroscopy is capable of probing directly the surrounding environment of the cation, we have studied the effect of the Co substitution on the frequency of the stretching modes in  $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$  oxides [14]. It is worth pointing out that the variation of the frequency modes against Co content corresponds to features of a solid solution. We observe for the Li–O band a slight deviation from a linear behaviour for high nickel content ( $y \leq 0.2$ ), that is attributed to the presence of Ni cations in the predominantly lithium layers (octahedral interstices), which disturbs the IR resonant frequency of the vibration of the  $O^{2-}$  anions against their Li<sup>+</sup> ion near neighbours. These results show that FTIR of LiCo<sub>1-y</sub>Ni<sub>y</sub>O<sub>2</sub> materials allows the accurate detection of shortscale heterogeneity, complementing the XRD results, which only provide information about the long-range structure.

#### 3.2. Magnetic properties

The first general observation is that the samples with high Ni content ( $y \le 0.2$ ) show ferrimagnetic behaviour with a  $T_c$  that



**Figure 5.** (a) ZFC and FC molar magnetic susceptibility of the  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  sample measured under a field  $H = 50 \text{ Oe} (5 \le T \text{ (K)} \le 300)$ . (b) ZFC magnetization versus applied field at T = 5, 50, 100 and 300 K.

quickly decreases as y increases ( $T_c$  (y = 0) ~ 215 K,  $T_c$  (y = 0.2) ~ 65 K), as seen in the  $\chi_m(T)$  and M(H) curves (figures 4 and 5).

Taking into account that perfectly stoichiometric LiNiO<sub>2</sub> is considered to be a frustrated AF compound [15], this ferrimagnetic response would be indicative of the existence of Ni<sup>2+</sup> ions occupying Li<sup>+</sup> places [15, 16]. Those interslab ions would lead to a ferromagnetic ordering of the Ni ions in two adjacent (Ni<sub>1-y</sub>Co<sub>y</sub>O<sub>2</sub>)<sub>n</sub> slabs and to the formation of small ferromagnetic islands in their surroundings with the concomitant apparent ferrimagnetic behaviour.

In the samples with intermediate substitutions (0.2 <  $y \leq 0.4$ ), the magnetic behaviour is different (figures 6 and 7). Partial substitution of Ni<sup>3+</sup> by Co<sup>3+</sup> suppresses the ferrimagnetic response, reflecting that the addition of Co<sup>3+</sup> inhibits the presence of interlayer Ni<sup>2+</sup> and therefore favours a better lamellar structure. Moreover, the positive Curie–Weiss constant that we calculate for 100 K < T < 300 K ( $\theta \approx$  +30 K) shows that the Ni–O–Ni nearest-neighbour interaction is still present at intermediate substitution levels.

Apart from these general trends, magnetic measurements can also provide an approximation to the size of those magnetic islands. In this context, a blocking temperature that decreases as the Co content increases—is observed in all the ZFC–FC  $\chi_m(T)$  curves. In the high-field region, at this temperature, it is possible to obtain the magnetic anisotropy,



**Figure 6.** (a) ZFC and FC molar magnetic susceptibility of the LiNi<sub>0.7</sub>Co<sub>0.3</sub>O<sub>2</sub> sample measured under a field H = 50 Oe ( $5 \le T$  (K)  $\le 300$ ). (b) ZFC magnetization versus applied field at T = 5, 100 and 300 K.

K, from the magnetization measurements versus the magnetic field.

To do so, we have to take into account that the magnetization approach to saturation can be fitted to the expression [17]

$$M(H) = M_S \left( 1 - \frac{a}{H} - \frac{b}{H^2} \right) + cH$$

where  $M_S$  is the saturation magnetization, and *a*, *b* and *c* are suitable constants. Two examples of these fits for the samples with y = 0.2 and 0.4 can be seen in figures 8(a) and (b).

Furthermore, the b constant is related to the magnetic anisotropy, K, by the expression [18]

$$b = \beta \frac{K^2}{M_S^2}$$

where  $\beta$  is a constant that depends on the type of material.

Assuming a typical value for the  $\beta$  constant (i.e.  $\beta = 0.0762$  [19]), we can deduce the magnetic anisotropy constant from first magnetization curves from

$$K = \left(\frac{bM_S^2}{0.0762}\right)^{1/2}.$$

Following this procedure, we find that the magnetic anisotropy value, that is  $6.5\times10^6~erg~cm^{-3}$  for the LiNiO\_2



**Figure 7.** (a) ZFC and FC molar magnetic susceptibility of the LiNi<sub>0.6</sub>Co<sub>0.4</sub>O<sub>2</sub> sample measured under a field H = 50 Oe ( $5 \le T$  (K)  $\le 300$ ). (b) ZFC magnetization versus applied field at T = 5, 100 and 300 K.

**Table 1.** Blocking temperature  $(T_B)$ , magnetic anisotropy (K) and calculated radii of the nanometric magnetic islands present in  $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$  nanoparticles.

y (Co content)	$T_B$ (K)	$K (\text{erg cm}^{-3})$	<i>R</i> (nm)
0	200	$6.5 \times 10^{6}$	≈3.5
0.20	50	$4.2 \times 10^{7}$	$\approx 1.2$
0.25	5	$7.7 \times 10^{7}$	$\approx 0.5$
0.30	5	$6.3 \times 10^{7}$	$\approx 0.5$
0.40	5	$5.7 \times 10^{7}$	$\approx 0.5$

sample at 200 K, increases upon cobalt doping, as summarized in table 1.

Interestingly enough, these values are related to the volume of the magnetic clusters that lead to the blocking temperature in the ZFC–FC  $\chi_m(T)$  curves. In this context, we can assume [17]

$$KV = 25k_BT_B$$

where V is the volume of the magnetic clusters,  $k_B$  is the Boltzmann constant and  $T_B$  is the blocking temperature of each particular sample.

Now, supposing that those magnetic clusters are spherical, we have calculated their mean radii, that are indicated in table 1. Specially interesting is the tendency those results show: the size of these magnetic clusters decreases upon Co doping and they are really small for y > 0.25.



Figure 8. Magnetization approach to saturation and fitting to the expression indicated in the text for to: (a)  $LiNi_{0.8}Co_{0.2}O_2$  and (b)  $LiNi_{0.6}Co_{0.4}O_2$ .

## 4. Conclusions

Despite the fact that XRD gives indication of an ordered distribution of Li and Ni/Co in the layered structure of  $LiNi_{1-y}Co_yO_2$  nanomaterials with y > 0.2 and ICP indicates a composition near the nominal stoichiometry, FTIR measurements show short-scale heterogeneities, attributed to the Ni<sup>2+</sup> cations in the predominantly lithium layers. In addition, magnetic measurements reveal the presence of small ferromagnetic islands in these materials arising from the fact that some Ni2+ ions are occupying Li+ places, that lead to a ferromagnetic ordering of the Ni ions in two adjacent  $(\text{LiNi}_{1-\nu}\text{Co}_{\nu}\text{O}_{2})_{n}$  slabs. From those magnetic measurements we have estimated the size of those nanometric magnetic islands that clearly decreases upon Co doping. This result confirms that the addition of  $\text{Co}^{3+}$  inhibits the presence of interlayer Ni<sup>2+</sup> and therefore favours a better lamellar structure, but that the process is progressive and depends on the Co content, so that 'ideal' lamellar structures are only obtained for y > 0.4.

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