Lithium-nickel cobalt oxides with spinel structure prepared at low temperature. XRD, XPS, and EIS measurements

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ABSTRACT

Li, Co and Ni mixed oxides of composition $\text{LiNi}_x\text{Co}_{2-x}\text{O}_4$ ($x = 0.25, 0.5, 0.75$ and 1) were prepared at 280°C by the Pechini sol-gel method. The Rietveld refinement of the X-ray diffraction data indicated that all the obtained compounds crystallize in the $\text{Fd}3\text{m}$ space group characteristic of cubic spinel-related oxides. XPS studies on these oxides reveal the presence of Ni^{2+} , Ni^{3+} , Co^{3+} and Co^{4+} ions at the surface. The diffusion coefficients of the Li^+ ion in the oxide lattice, determined by EIS measurements, are larger ($10^{-13} \text{ cm}^2 \text{ s}^{-1} \leq D \leq 10^{-10} \text{ cm}^2 \text{ s}^{-1}$) than that shown by the non-substituted cobalt-lithium oxide, LiCo_2O_4 ($D = 10^{-16} \text{ cm}^2 \text{ s}^{-1}$) and present similar values to those of layered oxides of related composition.

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1. Introduction

The demands for advanced energy storage devices, motivated by a variety of different needs, have increased significantly in recent years. Rechargeable lithium-ion battery (LiB) has become the best device for electric and hybrid electric vehicles [1]. Layered lithium oxides LiMO_2 ($\text{M} = \text{Co}, \text{Ni}, \text{Mn}$) and their doping metal variants are well-established commercial LiB cathode materials. Particularly, LiCoO_2 commercialized from 1991, has been the more successful oxide. However, the cobalt is expensive and unfriendly with the environment. Therefore, $\text{LiCo}_{1-x}\text{Ni}_x\text{O}_2$ cathode material, where Co is replaced by Ni, has been intensively studied [2–4]. The structure of this oxide system (S.G. $\text{R}3\text{m}$) is formed by bidimensional layers of CoO_2 units [5]. On the other hand, it is well known that lithium cobaltite, LiCo_2O_4 , prepared at $300\text{--}400^\circ\text{C}$, crystallizes in the spinel structure (S.G. $\text{Fd}3\text{m}$) containing vacant octahedral sites susceptible to the reversible insertion of Li-ions [6–8]. We have reported in a previous work good Li-ion insertion-extraction properties on lithium cobaltite LiCo_2O_4 synthesized at 400°C [9].

In this work, we have attempted the synthesis at low temperature (280°C) by a sol-gel method [10] of the nickel-substituted lithium cobaltite $\text{LiNi}_x\text{Co}_{2-x}\text{O}_4$, having a spinel-related structure. The 3D lattice parameters were refined by the Rietveld method [11,12], and the surface composition was studied by XPS. Electrochemical impedance

spectroscopy (EIS) technique [13] was used to evaluate the Li^+ ion diffusion coefficient in the oxides.

2. Experimental

Oxides of the $\text{LiNi}_x\text{Co}_{2-x}\text{O}_4$ series ($x = 0.25, 0.5, 0.75$ and 1) were synthesized using the Pechini method [10]. This is a sol-gel procedure

Fig. 1. Observed and calculated XRD profiles of $\text{LiNi}_{0.5}\text{Co}_{1.25}\text{O}_4$. S.G. $\text{Fd}3\text{m}$. $R_{\text{wp}} = 12.7\%$, $R_{\text{exp}} = 11.4\%$, $\chi^2 = 3.35\%$.

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Table 1

Cation distributions of the $\text{LiNi}_x\text{Co}_{2-x}\text{O}_4$ oxides. Experimental and calculated cell parameter. The brackets indicate the octahedral sites.

x	Cationic distribution	a_{exp}/nm	$a_{\text{calc.}}/\text{nm}$
0.25	$\text{Li}^+[\text{Ni}^{3+}_{0.25}\text{Co}^{3+}_{0.75}\text{Co}^{4+}]$	0.803	0.801
0.5	$\text{Li}^+[\text{Ni}^{3+}_{0.5}\text{Co}^{4+}_{1.5}]$	0.807	0.804
0.75	$\text{Li}^+[\text{Ni}^{3+}_{0.75}\text{Co}^{3+}_{0.25}\text{Co}^{4+}]$	0.809	0.806
1	$\text{Li}^+[\text{Ni}^{3+}\text{Co}^{4+}]$	0.811	0.808

that involves the dissolution of the nitrates (or carbonates) of the respective metals in a 1:4 v/v mixture of 1 mol dm^{-3} of citric acid and etilenglicol. Upon heating, esterification takes place (120 °C) and, after drying in vacuum at 180 °C, polymerization occurs. Increasing gradually the temperature at 1.5 °C min^{-1} from 180 °C to 280 °C in oxygen atmosphere, a polycrystalline and ultra fine powder is obtained after 48 h. The nominal composition was corroborated by chemical analysis.

The XRD data were recorded with a Siemens 5000 diffractometer using $\text{CoK}\alpha$ radiation (0.178897 nm) and a scanning rate of 4° min^{-1} . The XPS spectra were recorded under a vacuum better than 1×10^{-8} mbar, using Al $\text{K}\alpha$ radiation (1486.6 eV) and a constant pass energy of 50 eV. All binding energies ($\text{BE} \pm 0.2$ eV) were referred to the C 1 s signal (284.6 eV).

The studies of EIS were performed in a Swagelok™ type cell [14] using an oxide pellet (1 mm thickness) containing acetylene black and Teflon in a 90:5:5 mass ratio. As anode and reference electrode a metallic Li-wire was used. The electrolyte was a 1 M LiBF_4 solution in EC:DMC 1:1 (w/w). All components of the electrochemical cell were assembled under Ar-atmosphere. The impedance measurements were obtained using a 301 Voltalab PGZ Radiometer. An alternating perturbation of

200 mV and a frequency (ω) between 100 KHz and 1 MHz were employed.

3. Results and discussion

The XRD data refined by Rietveld method corroborate that all oxides crystallize in a cubic spinel structure (S.G. Fd3m). As an example, the observed and calculated diffraction patterns for $\text{LiNi}_{0.5}\text{Co}_{1.5}\text{O}_4$, are shown in Fig. 1.

In order to obtain the probable cationic distribution for each composition, crystallographic distribution were proposed, starting from the XRD measurements, assuming that ions Li^+ , Ni^{2+} , Ni^{3+} , Co^{3+} , Co^{4+} can be present according to their energetic preference to occupy tetrahedral (4) and octahedral (6) sites [15]. We have used the relationship of Poix [16] that allows estimating the a cell parameter of oxides on the basis of the ion-oxygen length as a function of oxygen coordination: $a = 2.0995A + (5.8182B^2 - 1.4107A^2)^{1/2}$ where $A = \sum x_i(\text{M}_i\text{O})_4$ and $2B = \sum y_i(\text{M}_i\text{O})_6$, x_i and y_i are the stoichiometric coefficients and M_iO the cation-oxygen distances. The following values were used [17]: $\text{Ni}^{2+}\text{O}_4 = 0.209$; $\text{Li}^+\text{O}_6 = 0.204$; $\text{Co}^{3+}\text{O}_6 = 0.189$; $\text{Co}^{4+}\text{O}_6 = 0.178$; $\text{Ni}^{3+}\text{O}_6 = 0.196$ nm.

The calculated value of a is compared with the experimental one to evaluate the validity of the cationic distribution. Table 1 shows the proposed distributions. The large concentration of Co^{4+} ions for $x=0.5$ can be accepted considering the low molar Curie constant ($0.2 \text{ cm}^3 \text{K mol}^{-1}$) obtained from the magnetic measurements (Faraday method) at 300 K [18].

The XPS results suggest that Ni^{2+} , Ni^{3+} , Co^{3+} and Co^{4+} are present in the surface of the oxides. In the case of Co (Fig. 2A), the spectra were fitted considering two-spin orbit doublets (Do) and three satellite (S) peaks. We have adopted the criterion of fixing equal widths for the

Fig. 2. Co 2p (A) and Ni 2p (B) XP spectra recorded from $\text{LiNi}_x\text{Co}_{2-x}\text{O}_4$ samples: a) $x=0.25$, b) $x=0.5$, c) $x=0.75$, d) $x=1$.

Table 2

Results obtained from the fit of A) Co 2p XP spectra, B) Ni 2p XP spectra.

A							
	Do 1		Do 2		Sat. 1	Sat. 2	Sat. 3
	Co 2p _{3/2}	Co 2p _{1/2}	Co 2p _{3/2}	Co 2p _{1/2}			
BE (eV)	778.8 ± 0.2	793.9 ± 0.2	780.5 ± 0.2	796.0 ± 0.2	783.1 ± 0.2	788.5 ± 0.2	803.4 ± 0.2
FWHM (eV)	2.0 ± 0.1	2.2 ± 0.1	2.0 ± 0.2	2.5 ± 0.3	4.1 ± 0.4	3.3 ± 0.3	5.0 ± 0.2
Assignment	Co ³⁺		Co ⁴⁺		Co ⁴⁺	Co ³⁺	Co ³⁺ + Co ⁴⁺
B							
	Do 1		Do 2		Sat. 1	Sat. 2	Sat. 3
	Ni 2p _{3/2}	Ni 2p _{1/2}	Ni 2p _{3/2}	Ni 2p _{1/2}			
BE (eV)	852.4 ± 0.2	870.1 ± 0.2	854.5 ± 0.2	871.6 ± 0.2	859.5 ± 0.2	863.3 ± 0.7	877.3 ± 0.1
FWHM (eV)	1.9 ± 0.2	1.9 ± 0.2	3.1 ± 0.2	3.4 ± 0.2	4.9 ± 0.4	5.0 ± 0.4	6.5 ± 0.1
Assignment	Ni ²⁺		Ni ³⁺				

two main Co 2p_{3/2} lines of the two spin-orbit doublets. The BE's and the line widths obtained are given in Table 2. The most intense doublet (Do1) and the shake up satellite appearing at 788.5 eV (S2) can be assigned unequivocally to Co³⁺ [19]. In a recent XPS paper, Dupin et al. [20] have reported a binding energy for Co⁴⁺ similar to that shown in the present study. Therefore the doublet (Do2) is associated to Co⁴⁺. The Ni 2p_{3/2} spectra recorded from these compounds also show a complex structure (Fig. 2B) with two different spin-orbit doublets and three satellite peaks. In this case, it was not possible to fix the line width of the two main Ni 2p_{3/2} lines to be equal, since this constraint clearly resulted in a very poor fit. A better fit was obtained when the doublet appearing at lower binding energy (Do1) was fitted with a narrower line width than that of the doublet appearing at higher binding energy (Do2). The results are given in Fig. 2B and Table 2. The small intensity doublet is associated to a Ni²⁺ component while the most intense doublet is ascribed to a Ni³⁺ component.

The surface composition does not fit completely the bulk cation distribution determined by XRD. This is not totally surprising since, in fine grained materials like these, the solubility of the different cations can depend on grain size leading to different composition at the surfaces or the interfaces at the grain boundaries between the different crystallites [21].

A way to estimate how easy it is to move the lithium ions inside the oxide network is to measure the diffusion coefficient, D. This parameter was determined using the EIS technique. Fig. 3 shows the Nyquist diagrams for the series of the studied oxides. As it is well-known, the

part corresponding to the charge transfer is located in the semicircles of the diagrams while the diffusional part is located in the linear zone of the diagram corresponding to the low frequency region. In this zone the Warburg impedance, Z_W, which is proportional to $\omega^{-1/2}$, can be determined. From the slope, σ , of the straight lines of the Warburg graphs (Z_W versus $\omega^{-1/2}$, not shown), it was possible to obtain D_{Li+} for each composition by means of the expression: $\sigma = RT/(nF)^2 [\sqrt{2/D^2 C^0}]$, where $RT/(nF) = 25.693 \cdot 10^{-3} (\text{A})$, $F = 96485 [\text{C/mol}]$, $C^0 = 1 \text{ mol/dm}^{-3}$ (electrolyte concentration). In the case of the x = 0.5 composition, the charge transfer region is remarkably more important than the diffusional zone. It can be observed that this composition contains the largest Co⁴⁺ cation concentration in octahedral sites. According to this, a greater electrical repulsion on the Li⁺ ions would diminish their diffusion coefficient. The D_{Li+} values obtained for the several x-compositions, are: 2.3×10^{-10} (x = 0.25); 2.1×10^{-13} (x = 0.5); 1.4×10^{-13} (x = 0.75) and 2.2×10^{-13} (x = 1) (cm²/s).

4. Conclusions

This work shows that is possible to prepare LiNi_xCo_{2-x}O₄ (x = 0.25, 0.5, 0.75 and 1) at 280 °C crystallizing in a spinel S.G. Fd3m structure. XRD and XPS studies indicate the presence of Li⁺, Ni³⁺, Co³⁺, Co⁴⁺ ions. These ions particularly Co⁴⁺ ions should be responsible for the wide charge region observed on EIS measurements. Li⁺ diffusion coefficients as a function of nickel composition are in the order of $10^{-13} \text{ cm}^2 \text{ s}^{-1}$ that can be also attributed to Co⁴⁺ concentration. D-values are similar in magnitude to those presented in the literature of layered oxides of related composition, Li_xNi_{0.8}Co_{0.2}O₂ [22] and Li_xNi_{0.8}Co_{0.2}O₂ [23].

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Fig. 3. Nyquist diagrams of LiNi_xCo_{2-x}O₄ oxides. ♦: x = 0.25, ○: x = 0.5, ▲: x = 0.75, □: x = 1.

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