

Quantitative structural analysis of the transition from LT-Li_xCoO₂ to HT-Li_xCoO₂ using the rietveld method: correlation between structure and electrochemical performance

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Abstract

A quantitative phase analysis was made of Li_xCoO₂ powders obtained by two distinct chemical methodologies at different temperatures (from 400 to 700 °C). A phase analysis was made using Rietveld refinements based on X-ray diffraction data, considering the Li_xCoO₂ powders as a multiphase system that simultaneously contained two main phases with distinct, layered and spinel-type structures. The results showed the coexistence of both structures in Li_xCoO₂ obtained at low temperature (400 and 500 °C), although only the layered structure was detected at higher temperatures (600 and 700 °C), regardless of the chemical powder process employed. The electrochemical performance, evaluated mainly by the cycling reversibility of Li_xCoO₂ in the form of cathode insertion electrodes, revealed that there is a close correlation between structural features and the electrochemical response, with one of the redox processes (3.3 v/3.9 v) associated only with the presence of the spinel-type structure.

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1. Introduction

Lithium transition metal oxides can be used as insertion materials mainly in lithium battery (rocking chair battery) technology, where they are applied as positive electrodes due to their favorable potential allied to their high specific density and their capacity for reversible lithium intercalation/deintercalation processes. Among these oxide materials, compounds with layered structures such as LiCoO₂, LiNiO₂, and LiNi_{1-x}Co_xO₂ have shown the best electrochemical performance in applications involving lithium battery devices [1–7].

Lithium cobalt oxide (Li_xCoO₂), which was first described as promising cathode materials by Mizushima et al. [8], is currently the lithium insertion compound most widely employed for rocking chair batteries due to the simplicity of its preparation and its high capacity performance [9]. This material has an ordered rocksalt structure (layered structure) with a trigonometric symmetry $R\bar{3}m$ when synthesized at high temperature [10]. However, to the best of our knowledge, the crystal structure of Li_xCoO₂ obtained at low temperature (LT-Li_xCoO₂) has so far not been entirely elucidated. Moreover, LT-Li_xCoO₂-containing electrodes discharge at potentials ~0.5 V more negative than HT-Li_xCoO₂, thus revealing weaker electrochemical oxidizing properties.

The difficulty involved in distinguishing phases present in LT-Li_xCoO₂ is mainly due to the very similar structure of the spinel and layered structures (Fig. 1), whose diffraction patterns are highly coincident, precluding a straightforward structural analysis. It is, therefore, almost impossible to observe the contribution of layered and spinel-type

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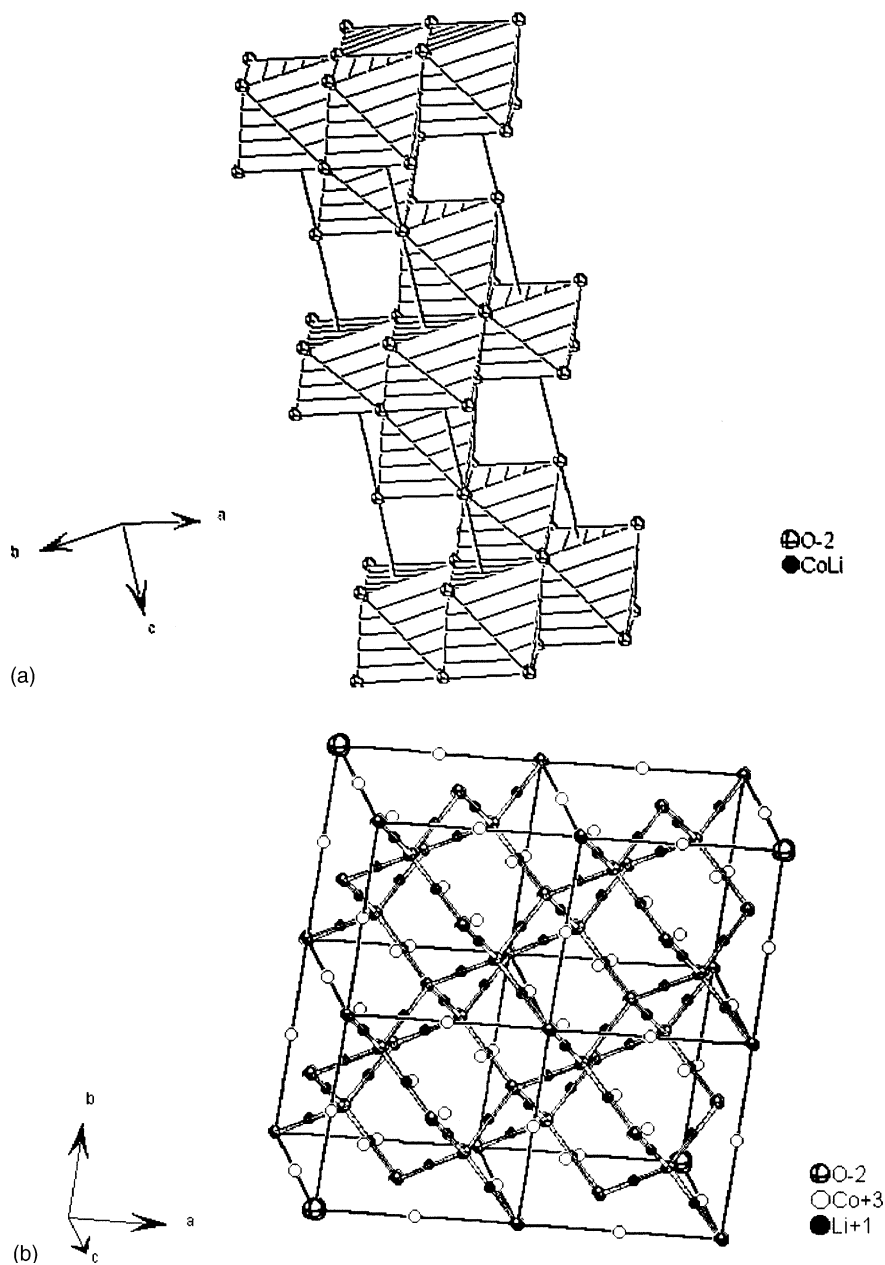


Fig. 1. (a) Layered and (b) spinel Li_xCoO_2 structures.

structures in a qualitative analysis of X-ray patterns. For this reason, Rietveld refinements (RR) have been considered a good mathematical tool and procedure for a more precise quantitative structural analysis using X-ray or neutron diffraction patterns, even for multiphase compounds involving phases with similar structures, which can be reasonably evaluated.

Several attempts have been made to solve the structural problem of the $\text{LT-Li}_x\text{CoO}_2$ compound by means of non-quantitative analysis. In one of these attempts, Gummow et al. [11] observed the presence of a structural ‘anomaly’ when the Rietveld analysis was applied in X-ray and neutron patterns of $\text{LT-Li}_x\text{CoO}_2$. The authors suggested that $\text{LT-Li}_x\text{CoO}_2$ compounds have a spinel-like character

for an $\text{LT-Li}_x\text{CoO}_2$ compound obtained by solid-state reaction at 400°C . Despite evidence of the presence of a spinel-type phase, the structural refinement index (R_{BRAGG}) showed values higher than 8, indicating a problem in the structural model proposed. One possible reason suggested for this ‘anomaly’ is the existence of two or more phases with similar diffraction patterns in addition to those considered in the analysis.

Spectroscopic techniques, such as SPES, 6Li MAS NMR, Ni^{3+} EPR [12], XANES and EXAFS [13] techniques, have also been used to elucidate the possible two or more structures involved in the $\text{LT-Li}_x\text{CoO}_2$ ceramic system. However, there is still no consensus for the exact structures and electrochemical processes in lithium insertion cathodes based

on Li_xCoO_2 synthesized at low temperatures. Spectroscopic analyses indicate only the presence of a Li_xCoO_2 spinel-type structure or an intermediate structure, but the crystal structure of the Li_xCoO_2 oxide obtained at low temperature is not yet clear.

The main goal of the present work is to quantify the possible structures existing in the Li_xCoO_2 system obtained at low temperature (LT- Li_xCoO_2) using quantitative analysis of phase. To achieve this goal, the structural evolution of LT- Li_xCoO_2 into HT- Li_xCoO_2 was quantitatively studied by means of Rietveld refinements using X-ray diffraction data and a multiphase approach. This means that the presence of phases with distinct crystal structures was considered in the refinements. The degree of lithium site substitution for cobalt was considered simultaneously, during the refinement when the spinel-type structure was detected. The effect of two distinct powder synthesis processes in each amount of phase was also quantitatively evaluated, and an estimation made of the crystalline features of both powders synthesized by Pechini and combustion methods at different temperatures. Finally, the structural features and amount of phase were correlated to the electrochemical cycling performance and mainly to the voltammetric patterns under different conditions of electrode composites based on LT- and HT- Li_xCoO_2 powders. Charge-discharge curves were also evaluated.

2. Experimental

In this work, Li_xCoO_2 powders were prepared by two different methodologies: Combustion synthesis and the Pechini-type process. The resulting powders from these two syntheses were heat treated at 400, 500, 600, and 700 °C for 12 h. The X-ray patterns of Li_xCoO_2 powders from all the temperatures and from the two distinct synthesis processes were refined by the Rietveld approach to garner information on the crystal structure.

The Li_xCoO_2 powders prepared by combustion synthesis were produced using hexahydrated nitrate cobalt (Synth) and lithium nitrate (Riedel) as oxidant and cation reactant sources. Urea was used as the fuel (reductive reactant) in a 1:1:10 mol (lithium nitrate:cobalt nitrate:urea) ratio. The mixture of the metal nitrates and fuel was partially homogenized with ultra-pure water (Mille-Q, 18 M Ω) in a glassy silica crucible (250 ml, TSL). The mixture was heated in an ambient atmosphere at an external temperature of 300 °C. The powders were produced through a strong combustion reaction, with the mean combustion temperature reaching 1200 °C, which was measured by a laser pyrometer. The resulting as-synthesized powders were post heat-treated at 400, 500, 600, and 700 °C for 12 h at a 5 °C min⁻¹ heating rate and a 4 °C min⁻¹ cooling rate. This heat treatment was applied to allow the phases and structures to rise close to thermodynamic equilibrium at each of these temperatures. These powders were qualitatively characterized by X-ray

diffraction (XRD, SIEMENS D5000) with Cu K α radiation in the 2 θ range from 5° to 75° in 0.03° steps and 1 s step times. New X-ray diffraction data were then collected for the structural analysis in the 2 θ range from 20° to 100°, in 0.03° steps and 10 s step times.

The Li_xCoO_2 powders were also synthesized by Pechini-type process, which is based on the sol-gel method (a derivative sol-gel process), in which homogeneous fine oxide particles are synthesized by a chelation reaction between the metal source and a hydroxycarboxylic acid (citric acid) followed by a polyesterification reaction between the excess hydroxycarboxylic acid and a polyhydroxyalcohol (ethylene glycol) under ambient atmosphere conditions [14].

For the preparation of the Li_xCoO_2 powders by the Pechini methodology, the same metal source (metal nitrates) as that used in the combustion synthesis was used. Anhydrous citric acid (Synth) and ethylene glycol (Merck) were used as hydroxycarboxylic acid and polyhydroxylic alcohol, respectively. Metal salts were added in ethylene glycol preheated to 60 °C. The citric acid was slowly added after complete solubilization, resulting in a clear solution that was immediately heated to 110 °C for 1 h to promote the polyesterification reaction and, consequently, the formation of the powder precursor resin. This resin was subjected to the same thermal treatment as that used to heat-treat the powder by combustion synthesis, including the same heating and cooling rates.

Structural and quantitative phase analyses were made of the heat-treated powders obtained by combustion synthesis and the Pechini-type process, using the RR method on X-ray diffraction data obtained under the above mentioned conditions. For the Rietveld refinements, the rocksalt layered Li_xCoO_2 with a $R\bar{3}m$ space group and Li_xCoO_2 ($x = 0.5$) and Co_3O_4 spinel, both with a $Fd\bar{3}m$ space group, were considered. The crystallographic parameters used for each phase are given in Table 1. The refinements were carried out using the DBWS 9807a program [15].

Electrodes (composites) based on Li_xCoO_2 powders were used to obtain electrochemical responses. The electrodes were prepared with poly(vinylidene fluoride; PVDF) (Aldrich) as binder, carbon black (Union Carbide, 0.03 Ω in.⁻³) and Li_xCoO_2 powders in a 5:10:85 (w/w) ratio. The mixture was sonicated for 12 h and applied on both faces of platinum plates (0.5 cm \times 1.0 cm). The final electrodes were dried at 120 °C for 24 h under reduced pressure.

The electrochemical measurements were carried out using a three-electrode configuration. The composites based on Li_xCoO_2 were used as working electrode and metallic lithium as counter and reference electrode. The electrolyte was composed of a mixture of the ethylene carbonate (EC, Carlo Erba, 98%, double-distilled previously) and dimethylcarbonate (DMC, Aldrich, 99.5%) reactants in a 1:1 (v/v) ratio. The support electrolyte used in the experiments was 1 M anhydrous lithium perchlorate (Aldrich, 95%). Both preparation of the solutions and electrochemical measurements were evaluated in a home-made glove box with argon atmosphere with humidity less than 5 ppm at room temperature.

Table 1
Crystallographic parameters of different structures applied on the Rietveld refinements

$\text{Li}_x\text{Co}_2\text{O}_4$ spinel		Li_xCoO_2 rocksalt layered		Co_3O_4	
Atom	X, Y, Z	Atom	X, Y, Z	Atom	X, Y, Z
Li (8a)	1/8, 1/8, 1/8	Li (3a)	0, 0, 0	Co (16c)	1/8, 1/8, 1/8
Co (16d)	1/2, 1/2, 1/2	Li (3b)	0, 0, 1/2	Co(16d)	1/2, 1/2, 1/2
Co (16c)	0, 0, 0	Co (3a)	0, 0, 0	O (32e)	1/4, 1/4, 1/4
O (32e)	1/4, 1/4, 1/4	Co (3b)	0, 0, 1/2		
		O (6c)	0, 0, 1/4		

The electrochemical response of the electrode composites was evaluated by cyclic voltammetry technique using a potentiostat–galvanostat (PARC, EG&G, model 283). The correlation between the conditions of synthesis, structure and cycling electrochemical performance were analyzed by means of voltammetric cycles obtained in the potential range of 2.5–4.2 V versus Li/Li^+ at different scan rates (0.1 up to 5 mV s^{-1}). Li_xCoO_2 powders synthesized by combustion were the main powders used to establish and illustrate the correlation between synthesization temperature conditions, Li_xCoO_2 structure and cycling electrochemical response. This choice is clarified in the sections below.

The first discharge curves for Li_xCoO_2 synthesized by combustion and Pechini methods were obtained applying a discharge rate of C/6. The discharge curves were obtained before a charging up to 4.2 V versus Li/Li^+ . The electrochemical cell configuration and the solution were same mentioned previously.

3. Results and discussion

3.1. Structural characterization of Li_xCoO_2 powder oxides

Fig. 2, which presents the XRD pattern of as-synthesized powder obtained by combustion synthesis, clearly shows the presence of several phases including Li_xCoO_2 , Co_3O_4 and CoO phases. As can be observed, there was no time for the as-synthesized powder to reach structural and thermodynamic phase equilibrium.

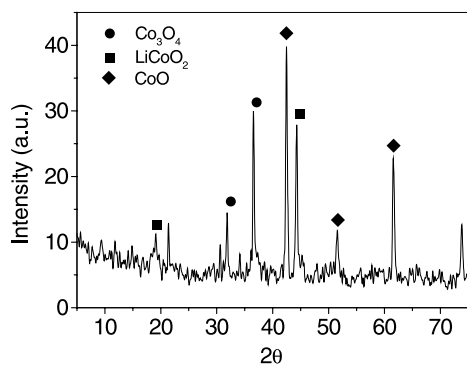


Fig. 2. XRD patterns for the material as-synthesized by combustion synthesis, using the qualitative X-ray routine.

Fig. 3a presents XRD patterns after the combustion synthesized powders were heat-treated at 400, 500, 600, and 700°C for 12 h, as described in the experimental section. Fig. 3b shows XRD patterns for powders obtained by the Pechini-type process subjected to the same heat treatment. These XRD patterns indicate that Li_xCoO_2 is formed as a single phase through any form of synthesis applied to prepare the powder at 400°C .

A comparison of Figs. 3a and b reveals that the only apparent effect of increased heat treatment temperature is an increase in the degree of crystallinity. However, such a visual analysis of XRD patterns is insufficient to differentiate between diffraction planes of spinel cubic and rocksalt layered rhombohedral structures. Therefore, the RR was used to observe the Li_xCoO_2 ($R\bar{3}m$ and $Fd\bar{3}m$) phases and the Co_3O_4 spinel phase ($Fd\bar{3}m$).

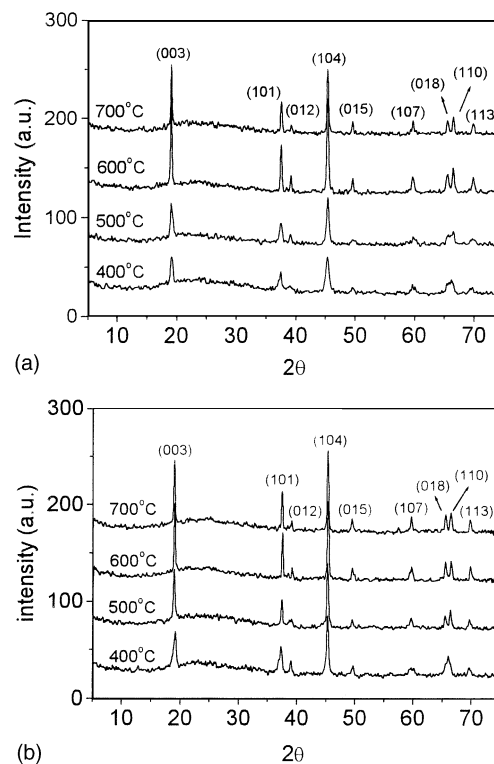


Fig. 3. XRD patterns for Li_xCoO_2 compound obtained after different heat treatments. (a) Compound obtained by combustion synthesis, and (b) compound obtained by the Pechini method. The qualitative X-ray routine was used.

Fig. 4 presents the diffractograms observed, calculated and the difference between them (Rietveld plot) for Li_xCoO_2 prepared by combustion synthesis and treated at 400 and 700 °C. An excellent agreement was found between the experimental and calculated X-ray patterns, as is also evidenced by the R_w and S index values shown in Tables 2 and 3. Two phases ($R\bar{3}m$ and $Fd\bar{3}m$) were observed in the Li_xCoO_2 samples treated at 400 and 500 °C. However, upon raising the heat treatment temperature (600 and 700 °C), the Li_xCoO_2 spinel-type phase was no longer observed, demonstrating that the transition temperature of the spinel-type Li_xCoO_2 to the layered obtained structure lies between 500 and 600 °C. The same behavior was found in compounds by the Pechini route.

Most of the quantitative results obtained by RR are summarized in Tables 2 and 3, which present unit cell parameters, weight percentage of each Li_xCoO_2 phase, the degree of substitution of lithium and cobalt ions in the rocksalt layered phase, and agreement factors defined by Young and Wiles [16]. In all the refinements, the R_{BRAGG} index presented satisfactory low values, indicating a good refined crystal structure model representative of the real case. In all the analyzed samples, Co_3O_4 was the minority phase, with an amount of less than 2 wt.%, which is considered to exert a negligible influence on the electrochemical response.

In both preparation routes, the amount of spinel phase decreased as the heat treatment temperature rose, disappearing at temperatures above 600 °C. On the other hand, the amount of rocksalt layered phase and its crystallite size increased as the heat treatment temperature increased, reaching a maximum at temperatures of 600 and 700 °C (~100 wt.%). Furthermore, in the material prepared by the Pechini method, the amount of layered phase at low temperatures was greater

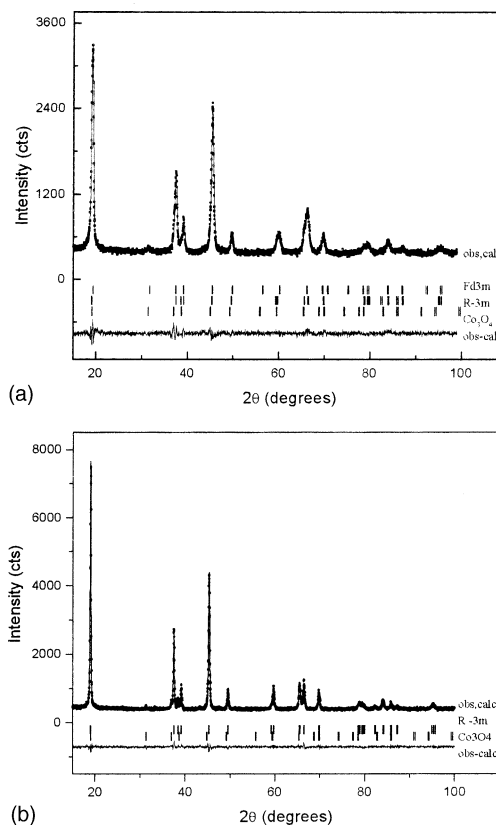


Fig. 4. Experimental and calculated X-ray patterns from refinements made by the Rietveld method. Li_xCoO_2 obtained at (a) 400 °C and (b) 700 °C. The quantitative X-ray routine was used.

Table 2
Results of Rietveld refinements in Li_xCoO_2 obtained by combustion synthesis at different temperatures

T (°C)	Li_xCoO_2 spinel ($Fd\bar{3}m$)			LiCoO_2 layered ($R\bar{3}m$)				Agreement factors
	Lattice parameter (Å)	wt.%*	R_{BRAGG} (%)	Lattice parameters/Å	Site substitution (%)	wt.%*	R_{BRAGG} (%)	
400	$a = 8.0045$ (8)	42	1.99	$a = 2.8201$ (3) $c = 14.0529$ (2)	Li (3a) = 94.0 Co (3a) = 6.0 Li (3b) = 2.0 Co (3b) = 98.0	56	2.46	$R_w = 4.90$ $S = 1.06$
500	$a = 7.9962$ (7)	22	2.92	$a = 2.8155$ (1) $c = 14.0538$ (8)	Li (3a) = 97.0 Co (3a) = 3.0 Li (3b) = 3.0 Co (3b) = 97.0	77	2.69	$R_w = 4.76$ $S = 1.08$
600	–	–	–	$a = 2.81443$ (7) $c = 14.0613$ (8)	Li (3a) = 99.2 Co (3a) = 0.8 Li (3b) = 0.1 Co (3b) = 99.9	99	2.82	$R_w = 5.04$ $S = 1.08$
700	–	–	–	$a = 2.81417$ (7) $c = 14.0612$ (8)	Li (3a) = 99.2 Co (3a) = 1.0 Li (3b) = 1.5 Co (3b) = 98.5	99	2.56	$R_w = 5.02$ $S = 1.11$

* The difference to 100% in the wt.% is the percentage of Co_3O_4 in the material.

Table 3
Results of Rietveld refinements in Li_xCoO_2 obtained by the Pechini method at different temperatures

T ($^{\circ}\text{C}$)	Li_xCoO_2 spinel ($Fd\bar{3}m$)			LiCoO_2 layered ($R\bar{3}m$)				Agreement factors
	Lattice parameter (\AA)	wt.%*	R_{BRAGG} (%)	Lattice Parameters (\AA)	Site Substitution (%)	wt.%*	R_{BRAGG} (%)	
400	$a = 7.9887$ (6)	14	2.77%	$a = 2.81469$ (9) $c = 14.0469$ (1)	Li (3a) = 98.7 Co (3a) = 1.3 Li (3b) = 2.2 Co (3b) = 97.8	84	2.34	$R_w = 4.92\%$ $S = 1.07$
500	$a = 7.9969$ (9)	13	2.83%	$a = 2.8158$ (1) $c = 14.0570$ (8)	Li (3a) = 98.8 Co (3a) = 1.2 Li (3b) = 1.7 Co (3b) = 98.3	86	3.05	$R_w = 5.07\%$ $S = 1.09$
600	–	–	–	$a = 2.81501$ (7) $c = 14.0562$ (8)	Li (3a) = 98.2 Co (3a) = 1.8 Li (3b) = 4.1 Co (3b) = 95.1	99	2.67	$R_w = 5.25\%$ $S = 1.11$
700	–	–	–	$a = 2.81502$ (7) $c = 14.0568$ (8)	Li (3a) = 97.9 Co (3a) = 2.1 Li (3b) = 2.6 Co (3b) = 97.4	99	3.73	$R_w = 5.10\%$ $S = 1.13$

* The difference to 100% of wt.% is the percentage of Co_3O_4 in the materials.

than the amount obtained in the material prepared by combustion synthesis. The unit cell parameters of the layered phase at 600 and 700 $^{\circ}\text{C}$ showed no significant variation in compounds obtained by the Pechini route, but significant variations were found in materials prepared by combustion. As was expected, the microstrain was greater in the material prepared by combustion, since the particles suffer severe mechanical shock during preparation. Nevertheless, in both preparation routes, the powders' crystallite size increased as the treatment temperature rose, although it was slightly smaller in the material prepared by combustion synthesis.

The results presented here demonstrate how the preparation methodology influences the powders' features. It also indicates how important the preparation is for the electrochemical response, since it determines the amount of layered structure in the powder or compound, which is desirable for higher electrochemical performance in battery devices. In the case discussed here, the Pechini-type synthesis of $\text{LT-Li}_x\text{CoO}_2$ powder proved superior to combustion synthesis in the formation of larger amounts of layered structure. Hence, the way the powder is synthesized may determine the kinetics of phase formation and interfere in the amount of phase formed at each temperature. This powder characterization procedure also demonstrates the ability of each powder synthesis methodology to prepare mixed phases at lower temperatures, indicating that the formation of Li_xCoO_2 layered phase can coexist with other similar structured phases. This is a more plausible picture than the one based solely on the presence of a distinct phase with an intermediate structure between the layered and spinel-type, as suggested in the literature [11,17,18].

The spinel-type structure can still be observed in Li_xCoO_2 powder obtained at 500 $^{\circ}\text{C}$, but is no longer present above

this temperature. This tendency, which was observed in these two different powder preparation methods, suggests that the structural transformation from a spinel-type to a layered Li_xCoO_2 structure occurs at higher temperatures located in the range of 500–600 $^{\circ}\text{C}$.

The differences observed in the percentage (degree of substitution) of lithium 3a sites by cobalt atoms, i.e. 6 and 1.3% between the Li_xCoO_2 layered structure obtained at 400 $^{\circ}\text{C}$ by combustion synthesis and the Pechini process, respectively, indicates that the layered structure at 400 $^{\circ}\text{C}$ depends on the powder synthesis method. These results also reveal that the layered structure obtained at 400 $^{\circ}\text{C}$ is slightly disordered in Li_xCoO_2 compounds obtained by the combustion synthesis, since the degree of substitution can be used to make inferences about structural stability and disorder. Therefore, the values of degree of substitution shown in Tables 2 and 3 indicate that the structural disorder decreased with the rise in thermal temperature applied during synthesis of the compounds. In other words, these values demonstrate that the structural stability and order increased with the thermal treatment, which is thermodynamically logical.

3.2. Electrochemical performance of Li_xCoO_2 -based electrodes

As shown in Tables 2 and 3, the difference in the amount of $\text{LT-Li}_x\text{CoO}_2$ oxide phase obtained by combustion is more pronounced than the powder obtained by the Pechini-type process. Thus, the $\text{LT-Li}_x\text{CoO}_2$ oxide obtained by combustion synthesis is the best choice to demonstrate and illustrate here the role that the amount of phase plays in the electrochemical response of Li_xCoO_2 -based electrodes, even though the electrochemical features of electrodes based on

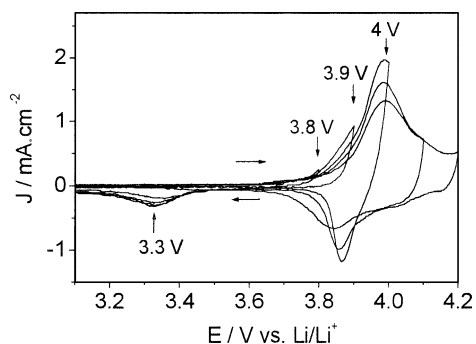


Fig. 5. Cyclic voltammograms for electrodes based on Li_xCoO_2 obtained by combustion synthesis at 400°C at different final potentials.

Li_xCoO_2 powders produced by the Pechini-type process are similar to those produced by combustion synthesis.

The cyclic voltammetry technique was used to evaluate the general electrochemical features and cycling performance of electrode composites based on Li_xCoO_2 obtained by combustion synthesis. Fig. 5 presents the cyclic voltammograms of these electrodes obtained at 400°C with different final positive potentials (up to 4.2 V versus Li/Li^+), clearly illustrating the correspondent redox processes [19–21].

Fig. 5 shows no redox processes up to 3.8 V during anodic scanning. However, at a potential above 3.8 V , such as 3.9 V , an anodic current appeared, while a 3.3 V cathodic peak was also observed during the cathodic scan. There was a correlation between the 3.9 V anodic and 3.3 V cathodic

processes, forming a redox process pair. The anodic current increased again at 4.0 V , and an additional cathodic peak was observed at 3.85 V . Therefore, there were at least two pairs of redox processes in this system. Based on the voltammogram features, it can also be concluded that the anodic processes overlapped (since the two processes occurred at very similar potentials). Nonetheless, these processes were detected separately. An additional, less perceptible pair of redox processes was also identified between 4.1 and 4.0 V .

Fig. 6 (a–d) shows the first cyclic voltammograms for composites based on Li_xCoO_2 obtained at different temperatures. As shown in Figs. 5 and 6, three main redox processes were involved in the electrode composites based on Li_xCoO_2 obtained at 400 and 500°C . These processes were observed at ($3.9\text{ v}/3.3\text{ v}$), ($4.0\text{ v}/3.85\text{ v}$) and ($4.1\text{ v}/4.0\text{ v}$), at a scan rate of 1 mV s^{-1} . The redox process at ($3.9\text{ v}/3.3\text{ v}$) was no longer observed at higher temperatures, i.e. 600 and 700°C .

Although the redox processes involved in cyclic voltammetric curves of Li_xCoO_2 compounds have been intensively investigated, there is no consensus about its nature in literature [19–21]. The process at 4 V (anodic peak) has been attributed mainly to cobalt oxidation and deintercalation of the lithium ion up to $x = 0.5$ from octahedral sites of rocksalt layered structure [14], which is believed to contribute most significantly to energy storage capacity. However, this process has also been attributed to an increase in the covalent interaction between cobalt and oxygen atoms, which results in a redox process in oxygen atoms with deintercalation of lithium ions [22].

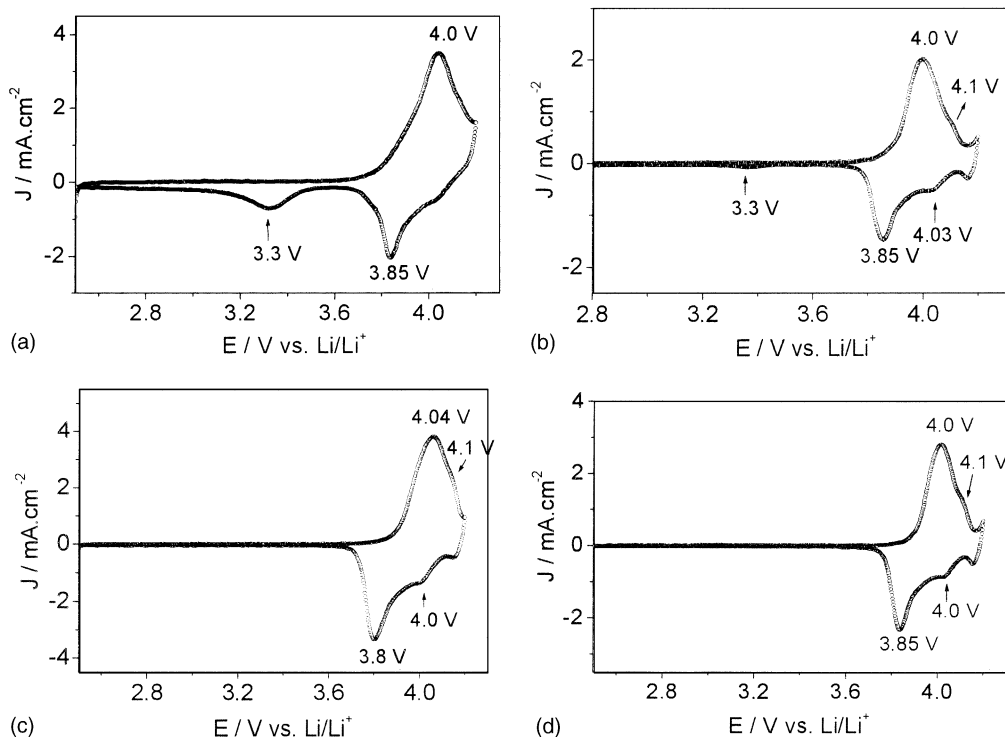


Fig. 6. Cyclic voltammograms for composite electrodes based on Li_xCoO_2 obtained by combustion synthesis at different temperatures: (a) 400°C , (b) 500°C , (c) 600°C , and (d) 700°C .

The (3.9 v/3.3 v) processes (Figs. 5, 6a and b) have not only been associated with the presence of an intermediate phase with structural features between the Li_xCoO_2 layered and spinel-type structure but also to the coexistence of distinct spinel-type structures, e.g. both totally lithiated Li_xCoO_2 and/or $\text{Li}_{0.5}\text{CoO}_2$ spinel-type structures. The latter picture, based on the presence of only a spinel-type structure, implies two distinct insertion/removal kinetic steps, one on the octahedral and the other on the tetrahedral sites [17] of such spinel-type structures [18]. It is important to point out here that the sites available for ions depend on the structure, and that a given structure may contain different types of sites. As an example, two types of sites are the most favorable for Li^+ insertion in spinel-type structures: the tetrahedral and octahedral sites.

The 4.1 V anodic process has been attributed to an ordered/disordered phase transition produced by the transformation of a tetragonal phase into a monoclinic phase, at potentials above 4.0 V in the layered structure. According to this phase transition, the specific experimental capacity is one half of the theoretical one (273 mAh g^{-1}) [14].

Based on an analysis of Fig. 6, one can conclude that the intensity of the redox processes at 3.9 and 4.0 V is closely associated with the amount of spinel-type phase calculated from a Rietveld analysis of X-ray patterns. As expected, the current associated with the redox process at 3.9/3.3 (v/v) decreased when the temperature rose from 400 to 500 °C. In addition, this redox process at 3.9/3.3 (v/v) disappeared completely at 600 and 700 °C. This finding is evidence that the redox process at 3.9/3.3 (v/v) was an electrochemical contribution of spinel-type phase from the LT- Li_xCoO_2 compounds. Indeed, when the spinel-type phase changed completely to a layered structure (a transition occurring in a temperature range of 500 to 600 °C, as mentioned earlier herein), the process at 3.9/3.3 (v/v) also disappeared. These results are in agreement with the picture that assumes the coexistence of two different electroactive materials resulting from the presence of these two (or more) distinct phases, as was found in this study. This finding, however, contradicts the other picture of intercalation/deintercalation processes that attribute the redox process to a two-step lithium deintercalation, the first to tetrahedral sites and the second to octahedral sites in the same structure [17], as mentioned previously. Although the coexistence of two different structures was confirmed in this study using the RR method, it should be emphasized that the lithiated Li_xCoO_2 ($x > 0.5$) and $\text{Li}_{0.5}\text{CoO}_2$ spinel-type structures were unidentifiable by the Rietveld analysis presented here. Therefore, we were unable to define the nature of the spinel-type phase appearing simultaneously with the layered phase.

In addition, as shown in Fig. 6, it was also observed that the redox process associated with the Li_xCoO_2 spinel-type phase was less electrochemically reversible than the redox process associated with layered Li_xCoO_2 ($\Delta E \sim 600 \text{ mV}$ for the spinel-type compared to $\Delta E \sim 150 \text{ mV}$ for the process associated to the layered phase). The reason for this

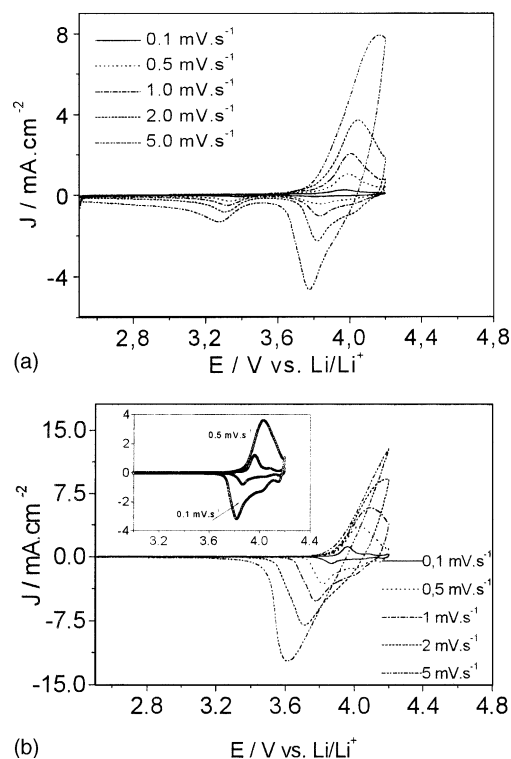


Fig. 7. Cyclic voltammogram versus scan rate for composite electrodes based on Li_xCoO_2 obtained by combustion synthesis at (a) 400 °C and (b) 700 °C.

difference is that the kinetics of the tetrahedral sites of the spinel-type structure, one of the main intercalation site in this type of structure [11], is slower for lithium removal/insertion than for octahedral sites, which are the main intercalation sites of layered structures. The slower kinetics of lithium removal/insertion results from differences between the volumes of the tetrahedral and octahedral sites.

Fig. 7 shows the dependence of the cyclic voltammograms on the scan rate for composites based on Li_xCoO_2 obtained at 400 °C (Fig. 7a) and 700 °C (Fig. 7b). An analysis of this figure reveals the strong dependence of the redox processes of both spinel-type and layered structure on the scan rate. This dependence is clearly illustrated in Fig. 8 by the scatter plot of cathodic peak currents at 3.3 and 3.85 V versus the square root of the scan rate for the materials obtained at 400 °C (Fig. 8a) and 700 °C (Fig. 8b).

A linear correlation was observed in the LT- Li_xCoO_2 -based electrodes with LT- Li_xCoO_2 powder obtained at 400 °C between the cathodic peak current (i_{pc}) and the square root of the scan rate ($v^{1/2}$), for the redox process related to the spinel-type structure, represented by the potential of the 3.3 V, indicating that this process was limited by mass transport. Pearson's linear correlation factor (R), in this case, was $R = 0.998$. However, the behavior of the redox process in relation to the layered structure was an almost, though not completely, linear process ($R = 0.986$). This behavior suggests that the lower stability of the layered structure obtained at a low temperature was related to

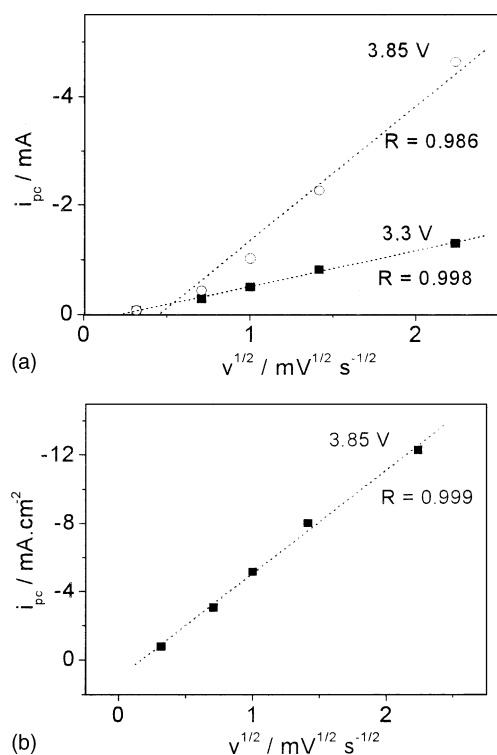


Fig. 8. Cathodic peak currents versus the square root of the scan rate for composite electrodes based on Li_xCoO_2 obtained by combustion synthesis at (a) 400 °C and (b) 700 °C.

the almost linear correlation, insofar it indicated another possible process occurring simultaneously with the mass transport. This new process may have been a homogeneous reaction inside the host (structural modification during the mass transport of Li^+ into insertion sites), and will be the subject of a future paper.

The thermodynamic stability of the layered structure can be discussed in terms of its lower crystallinity (or higher disorder), due mainly to a greater density of structural defects that must exist in the layered phase obtained at low temperature. It is interesting to note that the correlation between the almost linear process and structural stability is reinforced by the fact that the same behavior was found in the spinel-type structure at 500 °C. Higher structural stability in the spinel-type phase is expected for powders obtained at lower temperatures. Therefore, it can be concluded that this behavior, even in the spinel-type process at 500 °C, which occurred on a smaller magnitude than in the layered process, is associated with structural phase stability.

Indeed, in the case of the Li_xCoO_2 -based electrode whose Li_xCoO_2 oxide component was obtained at 700 °C, the correlation between i_{pc} and $v^{1/2}$ in the redox process, which was attributed to the layered structure, was linear, showing a value of $R = 0.999$. Therefore, contrary to the LT- Li_xCoO_2 -based electrode, the higher linear correlation obtained between i_{pc} and $v^{1/2}$ in the HT- Li_xCoO_2 -based electrode also indicates that the electrode based on oxide prepared at a higher temperature possessed a higher layered

Table 4

Crystallite size, rms microstrain $\langle \epsilon \rangle$ and c/a ratio calculated by Rietveld refinement for the layered Li_xCoO_2 phase present in the materials prepared by the Pechini and combustion routes

Pechini-type process			Combustion synthesis		
Crystallite size (Å)	Microstrain (%)	c/a ratio	Crystallite size (Å)	Microstrain (%)	c/a ratio
492	.3	4.9905	248	.3	4.9831
566	.1	4.9922	663	.5	4.9916
1163	.1	4.9934	847	.3	4.9963
1001	.1	4.9935	945	.2	4.9965

structural stability, particularly owing to its higher crystallinity (which resulted in a more ordered structure). Higher structural order is achieved by processing powder at temperatures above 600 °C, at which layered structures reach a higher degree of thermodynamic stability, as previously suggested.

Table 4 gives the crystallite size and c/a ratio obtained from a Rietveld refinement of the layered phase. The crystallite size and c/a ratio tend to stabilize at temperatures above 600 °C, which explains the improved cycling performance of powders prepared at higher temperatures. It is also worth mentioning that the crystallite size is larger in powders obtained by the Pechini-type process than by combustion synthesis. From a thermodynamic standpoint, powders produced from the Pechini-type process have probably a more stable layered structure than those processed by combustion synthesis.

The above statement is reinforced by Fig. 9, which illustrates the voltammetric feature of composites based on Li_xCoO_2 obtained at 400 and 700 °C by combustion synthesis after five cycles (5 voltammetric cycles). A strongly reduced current in the redox process of the layered structure was observed in Li_xCoO_2 electrodes obtained at 400 °C (Fig. 9a), although this decrease in the current was less marked in the redox process of the spinel-type structure.

These results confirm that the spinel-type structure is more structurally stable at 400 °C than the Li_xCoO_2 layered structure. They also indicate that structural stability has a determinative effect on the electrochemical cycling performance. The cyclic voltammograms taken from composites based on Li_xCoO_2 obtained at 700 °C (Fig. 9b) showed a low current loss as a function of the voltammetric cycling numbers. This low current loss also reinforces the assumption that a lower cycling performance between the spinel-type and layered structures has to do with the overall differences in the structural stability of such phases.

Figs. 10a and b present the discharge curves for $\text{Li}_{1-x}\text{CoO}_2$ synthesized by combustion and Pechini methods, respectively. For the Li_xCoO_2 synthesized at lower temperatures it is observed two plateaus, which are related to reduction of Co ions with Li^+ deintercalation processes in the spinel and layered structures (plateaus 1 and 2, respectively). Concerning Li_xCoO_2 synthesized by combustion

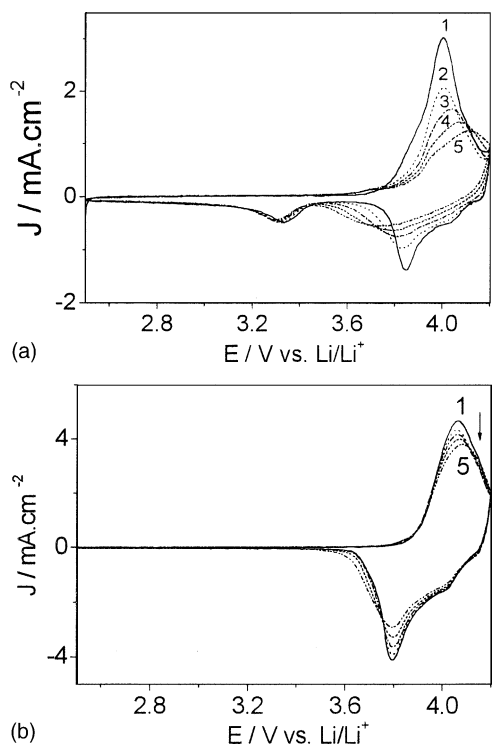


Fig. 9. Cyclic voltammograms versus the cycling number for composite electrodes based on Li_xCoO_2 obtained by combustion synthesis at (a) 400°C and (b) 700°C .

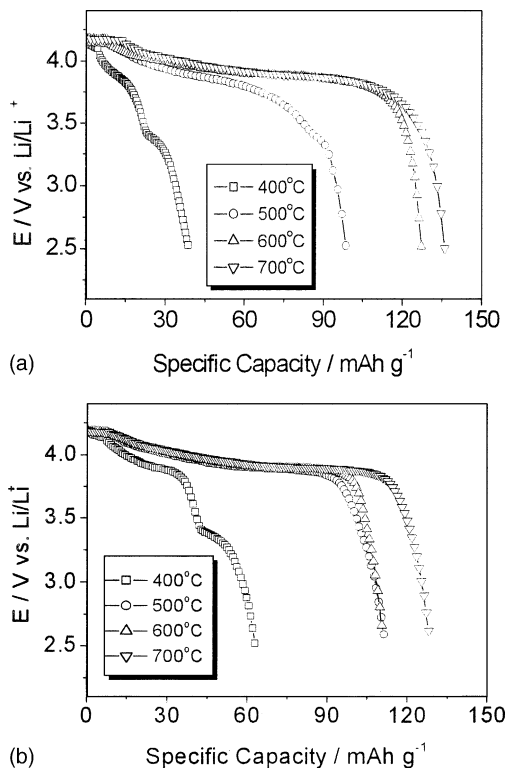


Fig. 10. First discharge curves for composites based on Li_xCoO_2 prepared by (a) combustion synthesis and (b) Pechini method at different temperatures.

method at 400°C , the first specific capacity is close to 40 mAh g^{-1} , a value that can be associated to the majority presence of spinel structure, in which the deintercalation process is disfavored due to the lower volume of the unit cell.

The increasing of heat treatment temperature provides an increasing of specific discharge, which is in agreement to our quantitative Rietveld and a phase transition from LT- to HT- Li_xCoO_2 . Similar to Li_xCoO_2 synthesized by combustion method at 400°C , the material obtained by Pechini method (Fig. 10b) presents two plateaus, but with higher specific capacity (65 mAh g^{-1}) comparing to that obtained by combustion method. This feature is related to the presence of a lower amount of spinel-type phase compared to that material obtained by the combustion method as shown by RR. For material prepared by Pechini synthesis and heat treated at 500°C , the specific capacity is similar to that treated at 600°C .

In general, although the RR shows the presence of spinel-type structure for the material obtained at 500°C , which can also be inferred by the slope of the discharge curve, the increase of specific capacity compared to the combustion synthesis material might be associated with the fraction of layered structure formed. Such increase of specific capacity is likely a result of higher stability (performance) related to the better phase crystallization provided by the Pechini method.

It is noteworthy the materials synthesized at higher temperatures (600 and 700°C) present specific capacities close to expected ($\sim 136\text{ mAh g}^{-1}$), indicating the stable features of HT- Li_xCoO_2 for synthesis used herein.

Variations in structural stability depend on several factors. After the insertion of large amounts of guest ions at room temperature, for instance, stable insertion host compounds often become metastable, i.e. if they are heated, their structure changes or decomposes into other compounds or phases. Consequently, the higher current loss along several charge/discharge cycles (cycling) found in a layered structure produced at lower temperatures may be associated with its lower stability. The structure's stability then increases during lithium insertion/removal, and for this reason it loses its cycling capability. This behavior is reflected in a lower specific capacity and energy storage efficiency, which limits the application of battery devices containing Li_xCoO_2 electrodes obtained at low temperatures. It is not possible, at this time, to make inferences about the mechanism by which an unstable structure changes to a more stable one during Li^+ insertion/removal processes. Our preliminary analysis on the impedance spectra of such Li_xCoO_2 -containing electrodes have revealed that cycling instability is associated with the different modes of charging the host, which is based on the dynamics of the ions in the structure. This picture is beginning to unfold, providing information that unstable structures permanently retain Li^+ guest ions in some specific sites, thereby reducing the number of sites for insertion/removal

processes and altering the electrode's electrochemical potential. The investigation of this aspect will be the subject of a future study.

4. Conclusions

According to our X-ray analysis based on the Rietveld method, the transition from spinel-type structure to layered structure occurs in a 500 to 600 °C temperature range. The Pechini-type synthesis of LT-Li_xCoO₂ powder is superior to combustion synthesis for the formation of larger amounts of layered structure and, hence, for improved electrochemical performance.

Our electrochemical analyses revealed the presence of at least two different redox processes, which were attributed to spinel-type and layered phase contributions. From our electrochemical analysis of cycling stability, we also concluded that the layered structure obtained at 400 °C possesses low structural stability owing to disorder and/or low crystallinity.

The analysis of cycling performance in LT- and HT-LiCoO₂ (with different amounts of spinel-type and layered phases) indicated that structural stability is a determining factor of cycling performance and energy capacity, for it prevents structural changes during insertion/removal processes (of an unstable structure into the same, though more stable, structure). Thus, increasing the heat-treatment temperature favors the formation of a more stable layered structure, which in turn improves electrochemical cycling stability.

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