Chemical obtaining of LiMO\textsubscript{2} and LiM\textsubscript{2}O\textsubscript{4} (M=Co, Mn) oxides, for cathodic applications in Li-ion batteries

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Abstract. This paper describes the synthesis and characterization of two spinel and olivine-type multicomponent oxides based on LiMO\textsubscript{2} and LiM\textsubscript{2}O\textsubscript{4} systems (M=Co and Mn), which represent the current state of the art in the development of cathodes for Li-ion batteries. A simple combustion synthesis process was employed to obtain the nanometric oxides in powder form (crystal sizes around 5-8 nm), with a number of improved surface characteristics. The characterization by X-Ray Diffraction (XRD), Scanning and Transmission Electron Microscopy (SEM, TEM) and X-Ray Fluorescence (XRF), allowed to evaluate the morphology and the stoichiometric compositions of solids, obtaining a concordant pure crystalline phase of LiCoO\textsubscript{2} and LiMn\textsubscript{2}O\textsubscript{4} oxides identified in a rhombohedral and cubic phase with punctual group R-3m (1 6 6) and Fm-3m (2 2 5) respectively. The electrical characterization of materials developed by impedance spectroscopy solid state, allowed to determine a p-type semiconducting behaviour with conductivity values of 6.2×10\textsuperscript{-3} and 2.7×10\textsuperscript{-7} S for LiCoO\textsubscript{2} and LiMn\textsubscript{2}O\textsubscript{4} systems, consistent with the state of the art for such materials.

1. Introduction

The lithium ion batteries are defined as storage systems for the electrochemical energy conversion through the exchange of lithium ions (Li\textsuperscript{+}) between an anode (graphite) and a cathode of oxide nature (usually olivines) [1]. Since its first commercialization in 1991 [2], the Li-ion batteries play an outstanding position in the market with a production of billions of units per year, for powering portable electronic devices and currently used as generation systems in hybrid (HEV), electric (EV) and plug-in electric (PHEV) vehicles [3]. From point of view of functional applications, these devices operate by the interaction of an anode an electrolyte and a cathode, being the latter a critical component that can be influenced by aspects like crystalline phase, purity and particle size, which determines the efficiency of the battery. Among the most advantaged materials for these applications are the olivines (LiCoO\textsubscript{2}-LiFePO\textsubscript{4}) and spinels (LiMn\textsubscript{2}O\textsubscript{4}), whose electrochemical properties are strongly depending on aspects as homogeneity and microstructure, which is related with the used synthesis method [4].

This situation has promoted the research in the synthesis of ceramic systems to improve the conduction phenomena, preferably to development of mixed electronic ionic conductors (MIEC’s), which represents the opportunity to improve the quality of the Li-ion batteries [5]. Among the most used synthesis methods in the preparation of cathodic materials are the so-called solid-state reaction, co-precipitation, sol-gel, hydrothermal and Pechini technique, among others [6], which has led to the obtaining of highly effective materials for a wide form of applications. However, the need to improve the performance of these electrochemical ceramics in the cyclic process of electric load, require the
preservation of the morphologic and surface properties in materials, which cannot always be achieved by implementing of traditional synthesis methods [7]. It is for this reason that the present work tries to find from the perspective of the materials chemistry, a route based on combustion process that allow to obtain ceramic oxides based on an olivine (LiCoO$_2$) and spinel (LiMn$_2$O$_4$) configuration; which permit to improve the current performance of the lithium-ion batteries cathodes.

2. Experimental

For the synthesis of lithium oxides, corresponding nitrates of LiNO$_3$, Co(NO$_3$)$_2$·6H$_2$O and Mn(NO$_3$)$_2$·9H$_2$O were adjusted to a 1.0mol·L$^{-1}$ concentration. The amount of each precursor in each system was adjusted according to the corresponding hydrolysis constants with the subsequent addition of a solution of citric acid 1.0mol·L$^{-1}$ in a molar ratio 0.5:1, with respect to the total cation content as has been established elsewhere [8]. Each system remained at reflux for 2 hours, after which the resulting sol was heated at 120°C to evaporate the solvent and obtain the corresponding solid precursor, which were calcined at 850°C for 15 hours to guarantee the consolidation of crystalline phases. The calcined solids were characterized by X-Ray Diffraction (XRD), on a PANalytical X’pert PRO MPD equipment provided with an ultra-fast X’Celerator detector in Bragg-Brentano configuration, using the Cu K$_\alpha$ radiation ($\lambda$=1.54Å). The diffractograms were taken between 10 and 90° 2θ and the results were analysed using the X’pert High Score software [9].

The morphological evaluation of solid was performed by Scanning Electron Microscopy (SEM), in a Leica-Zeiss LEO 440 electron gun equipment with an accelerating voltage of 30kV. The analysis by Transmission Electron Microscopy (TEM) was done on a JEOL 2100 equipment provided with a thermionic LaB$_6$ gun with an accelerating voltage of 200kV. The composition of the solids was evaluated by X-ray fluorescence (XRF) on a Bruker S8 Tiger system, while the electrical and conductivity properties of the materials were evaluate using the solid state impedance spectroscopy technique (IS), in a GAMRY potentiostat-galvanostat instrument between 1 and 10MHz [10].

3. Results and discussion

The structural characterization of the oxides by XRD using the High Score X’Pert software and the ICDD database, led to a classification according to the reference materials LiCoO$_2$: ICSD code: 00-016-0427 with rhombohedral geometry and space group R-3m (166) and LiMn$_2$O$_4$: ICSD code: 00-018-0736, with cubic geometry and space group Fm-3m (225), according to preliminary works [11-12]. The crystallite size was obtained by means of the Debye-Scherrer equation, resulting in the presence of nanometric crystallites in the range of 5-8nm, using the most intense diffraction signals in each case. The Figure 1 shows the diffraction patterns obtained by Rietveld refinement, confirming the effectiveness of the synthesis process in the obtaining of the crystalline structures.

![Figure 1. Indexed XRD patterns of LiCoO$_2$ and LiMn$_2$O$_4$ oxides with its corresponding Rietveld refinement patterns.](image-url)
The detailed analysis of the diffraction patterns, led to the characterization of the corresponding cell parameters in both systems, which are shown in Table 1, confirming the formation of high crystallized oxides along (0 0 3) and (1 1 1) facets for the LiMn$_2$O$_4$ and LiCoO$_2$ ceramics respectively.

**Table 1. Crystalline characteristics of obtained solids.**

| Material   | Cell parameters (Å) | Crystalline system       |
|------------|---------------------|--------------------------|
| LiCoO$_2$  | a=2.8166            | Rhombohedral R-3m (166)   |
|            | b=2.8166            |                          |
|            | c=14.045            |                          |
|            | $\alpha=\beta=90^\circ$ |                        |
| LiMn$_2$O$_4$ | a=8.2400          | Cubic Fm-3m (225)        |
|            | b=8.2400            |                          |
|            | c=8.2400            |                          |
|            | $\alpha=\beta=\gamma=90^\circ$ |                    |

The subsequent refinement of experimental diffraction data using the ELMIX software yielded to find the corresponding unit cells of LiCoO$_2$ and LiMn$_2$O$_4$ systems, where could be identified the form in which the cell size in both compositions change dramatically, mainly in the case of LiMn$_2$O$_4$ system [13]. According to Cabrera *et al.*, in the spinel structure with Fm-3m space group the oxygens occupy the 32e positions and the manganese occupies the half of the octahedral positions 16d, leaving the lithium in the tetrahedral 8a position, which gives in the material a superior possibility to diffusion as shown in Figure 2 [14].

![Figure 2. Calculus unit cell for LiCoO$_2$ and LiMn$_2$O$_4$ systems, obtained by the ELMIX software.](image)

The scanning and transmission electron microscopy analysis, was possible to identify that the solids are composed of homogeneous aggregates with regular morphology with crystallite sizes around 5-8nm with interplanar distances about 0.45nm for the main diffraction signal, in coherence with
previous XRD results and works done by Okubo et. al., in similar perovskite compositions [15]. These results demonstrate that synthesis methodology favours the obtaining of pure crystalline phases, attributed to the low temperature consolidation during spontaneous combustion, as shown in Figure 3.

Figure 3. Scanning (a-f) and transmission (g-h) electron microscopy images of LiCoO$_2$ and LiMn$_2$O$_4$ solids obtained by the combustion technique.

The characterization by XRF and Energy-Dispersive X-Ray Scanning (EDS), allowed evaluating the quantitative composition of samples and assessing the consistency of the proposed and obtained compositions as shown in Table 2.

| Material     | Proposed composition (%) | Obtained composition (%) |
|--------------|--------------------------|--------------------------|
|              | Li$_2$O | Co$_3$O$_4$ | MnO$_2$ | Total | Li$_2$O | Co$_3$O$_4$ | MnO$_2$ | Total |
| LiCoO$_2$    | 15.25  | 84.75    | 0.0     | 100    | 15.20  | 84.79    | 0.0     | 99.99 |
| LiMn$_2$O$_4$| 6.26    | 0.0      | 93.74   | 100    | 6.24   | 0.0      | 93.75   | 99.99 |
In Figure 4, the signals corresponding with the characteristic $K_{\alpha}$ emission lines are observed, demonstrating in a quantitative form the relative concentrations of each synthesized material, testing the appropriate composition in each case.

![Figure 4. Patterns of energy-dispersive of X-ray (EDX) obtained for LiCoO$_2$ LiMn$_2$O$_4$ systems.](image1)

The analysis by solid-state impedance spectroscopy (IS), allowed to define the behaviour of materials with respect to potential (V), in order to set the values of electrical resistivity and conductivity. The Nyquist plots, shown in Figure 5 display two semicircles one with a smaller diameter related with the LiCoO$_2$ oxide and other with a wide real resistivity related with LiMn$_2$O$_4$ system, indicating how the charge transfer is more effective in the olivine case, due to the arrangement of atoms in its structure [16-17]. The data expressed in terms of an equivalent circuit, show a capacitive behaviour (C) of the solids, whose resistance is associated with a polarization phenomenon ($R_{\text{sol}}$). While the effect of electron transfer (R) is clear for cobalt composition, the problems related with diffusion phenomenon (W), is evident in manganese composition, in which the main carrier could be attributed to ions movement across the wide crystalline structure according to Bard et al. [18].

![Figure 5. Nyquist plots for LiCoO$_2$ and LiMn$_2$O$_4$ systems.](image2)

The detailed analysis of impedance, confirm a p-type semiconductor behaviour, where the coefficient of chemical diffusion apparently evaluates the resistance values to the transfer of charge in the low frequency region, where the material changes from an electronic conductor to show a phenomenon of resistance to charge transfer, shown in Figure 5. These results, allow evaluating the effect of carriers charge in obtained solids by the effect mobility of oxygen vacancies, which may be formed on the surface of oxides by effect of the applied potential [19-20]. The values derived from the resistivity, allow identify conductivities around 6.2×10$^{-3}$S and 2.7×10$^{-7}$S for the LiCoO$_2$ and LiMn$_2$O$_4$ oxides, in accordance with current state of art for cathodic materials used in design of Li-ion batteries [21].
4. Conclusions
The synthesis method based on combustion process permit to obtain high pure crystalline materials in short reaction times at low temperatures with an excellent stoichiometric control. The XRD results, allow establishing the formation of crystalline phases in the nanometric range between 5 and 8 nm. The microstructural analysis performed by SEM-TEM analysis corroborate in both cases the obtaining of homogeneous solids with regular morphology, in which is clear that further thermal treatment consolidates the materials and permit to eliminate carbonaceous remnant of previous combustion stage with excellent results. The microcomposition results obtained by means X-ray fluorescence and EDX analysis show a strong consistency between proposed and obtained compositions. Finally, the solid-state impedance analysis, demonstrates that LiCoO$_2$ system has a p-type semiconducting behaviour in contrast with LiMn$_2$O$_4$ system, in which a mixed behaviour of conductivity was discovered, mainly associated with ions as carrier charge, which is in accordance with the study of these systems for the design of advanced cathodes for lithium-ion batteries.

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