SYNTHESIS AND CHARACTERIZATION OF Li_yNiCoO_X THIN FILMS PREPARED VIA SOL-GEL METHOD

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LiCoO₂ is the most widely used cathode material for commercial rechargeable lithium batteries due to its advantages, which include easy preparation, high voltage, good reversibility and high theoretical specific capacity. However, this lithiated oxide often suffers from structural instability and safety problems, especially when the lithium content is lower than 0.5 or the charge voltage exceeds 4.3V. In order to tackle the problems associated with cost and system stability, we investigated in this work the effects of substitution of cobalt for nickel using the sol gel method.

DTA profile of the gel precursors are given in Figure 1. One endothermic peak defined at around 212 °C is related to solvent evaporation (ethylene glycol) in both cases. The curve for the LiCoO₂ precursor shows just one exothermic peak at 480 °C due to crystallization process. On the other hand, three exothermic peaks are observed to $\text{Li}_{y}\text{NiCoO}_{x}$ at 357, 388 and 476 °C. The peak at 476 °C was attributed to cobalt phase and the two others are probably related to crystallization of niquel phases. The material crystalline structure will be investigated by X-ray diffraction analysis.

Figure 2 compares the electrochemical response of two materials. It is evident the increase of capacitive current to Li_yNiCoO_x film. The shape of this curve suggests their amorphous character. However, in both voltammograms, the anodic peak potential is the same indicating that in the mixing oxide predominats the cobalt phase.

Impedance analysis in the $LiCoO_2$ film and Li_yNiCoO_x films in $LiClO_4$ 1 mol L^{-1} PC/EC, was employed to obtain more information about lithium intercalation/de-intercalation process. The impedance spectra are illustrated in Figure 3. The impedance spectra consist just in an inclined line associated with a capacitive behavior. Due to the several reports about, the $LiCoO_2$ in the literature, the variation of impedance response as a function of the potential or lithium de-intercalation process was analyzed only to mixing oxide film. With the increase of applied potential, the impedance of the system becomes smaller until a minimum at approximately 3.75 V remains constant from this potential. This response indicates the increase of Li_yNiCoO_x conductivity with the lithium de-intercalation process.

These preliminary data about the mixing oxide film are encouraging and the detailed electrochemical studies on these systems are under progress.

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Fig. 1 – Differential thermal analysis of the gel precursors at a heating rate of 5 $^{\circ}$ C.min⁻¹.



Fig. 2 – Steady state cyclic voltammogram in $PC/EC/1.0 \text{ mol.L}^{-1} \text{ LiClO}_4$; at 5mV.s^{-1} .



Fig. 3 – Nyquist diagram from Li_yNiCoO_x . Perturbation amplitude 0.01 V and frequency range from 10^{-2} to 10^5 Hz.