Synthesis and characterization of $LiNiO_2$ targets for thin film deposition by pulsed laser ablation

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(Recibido: 26 de septiembre de 2005; Aceptado: 31 de octubre de 2005)

In order to deposit $LiNiO_2$ thin films by pulsed laser deposition (PLD), a $LiNiO_2$ target was prepared by a solid-state reaction from NiO and Li_2O. The effect of the Li_2O wt. % excess on the final product was studied. X-Ray Diffraction and Micro-Raman Spectroscopy were used to analyze the structure of the obtained targets. A stoichiometric target prepared by the solid-state reaction was used for thin film deposition. The influence of laser fluence and annealing temperature on the structural properties of the deposited thin films was analyzed by Micro-Raman spectroscopy.

Keywords: Thin Films; Pulsed Laser Deposition; Micro Raman Spectroscopy; Lithium Microbatteries

1. Introduction

It is well known that $LiMO_2$ (M = Co, Ni) materials exhibit excellent electrochemical features as cathodes in lithium batteries owing to their layered structure. Particularly, $LiNiO_2$ offers some significant advantages when compared to $LiCoO_2$. For instance, $LiNiO_2$ is cheaper and exhibit a higher specific capacity [1]. However, $LiNiO_2$ with the correct stoichiometry is very difficult to obtain [2].

In the last years the fabrication of thin films as cathode materials has been of interest owing to their application in the development of microbatteries. In order to obtain cathode materials in thin film form some Physical Vapor Deposition (PVD) techniques have been employed. Deposition of $LiCoO_2$ thin films has been reported using RF sputtering [3], and pulsed laser deposition [4]. A common problem found with these deposition techniques is that the deposited thin films are lithium deficient, due to the high volatility of lithium. In order to overcome these difficulties, laser ablation of lithium enriched $LiCoO_2$ targets has been used.

Laser ablation has attracted great attention in the last few years as a versatile technique to deposit a wide variety of materials in thin film form. In this method the material is evaporated from a solid target and transferred to the substrate in the form of plasma consisting of various species including neutrals, ions and clusters [5]. This technique has some advantages over other deposition techniques; particularly important are the possibility of growing films under inert atmospheres and the stoichiometry conservation. These features make this technique a good candidate to grow oxides like $LiMO_2$ (M = Co, Ni).

In this work, it is reported the preparation of $LiNiO_2$ targets with the correct stoichiometry as well as the use of these targets for thin film deposition by the laser ablation technique. The targets were prepared by a solid-state reaction varying the precursor's proportions and the thermal treatment. In the case of the thin film deposition the effects of the laser fluence and the post-deposition treatments were studied.

2. Experimental

2.1 Synthesis of the $LiNiO_2$ targets

Lithium oxide (Li_2O, 97 % purity) and nickel oxide (NiO, 99.99 % purity) were used as precursors to synthesize the lithium nickel oxide ($LiNiO_2$) via a solid state reaction, according to

$$\tfrac{1}{2}\, Li_2O + NiO \longrightarrow LiNiO_2$$

Several samples were prepared starting from three mixtures of Li_2O and NiO, adding in each case, 20, 30 and 50 wt. % in excess of Li_2O. This was done in order to compensate the loss of lithium. The obtained mixture powder was pressed at 3 Tons/cm^2 to make disks, 3 mm thick and 15 mm in diameter, which were thermally treated in air as it is described in table 1.

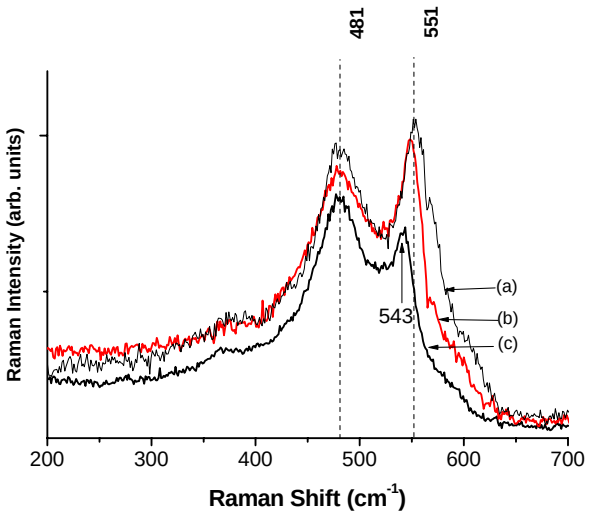

Figure 1. Micro-Raman spectra of the targets. (a) 20 wt % of Li_2O, (b) 30 wt % of Li_2O, (c) 50 wt % of Li_2O, annealed at 500°C/24h.

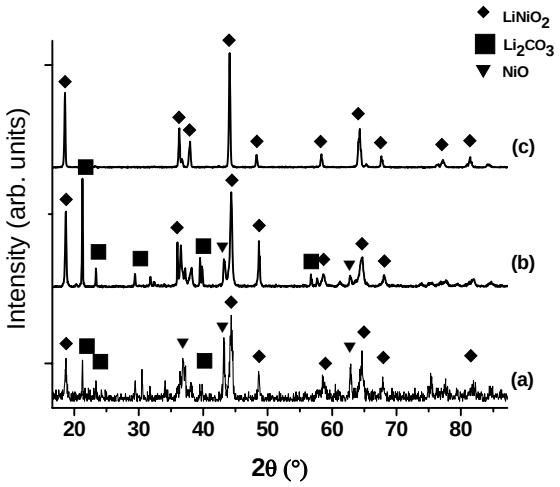

Figure 2. XRD patterns of LiNiO targets. (a) 20 wt % of Li_2O, (b) 30 wt % of Li_2O, (c) 50 wt % of Li_2O, annealed at 500°C/24h.

2.2 Thin film deposition

The $Li_{1-x}Ni_{1+x}O_2$ thin films were deposited by the laser ablation technique using an experimental configuration reported elsewhere [6]. The pellet prepared with 50 wt. % of Li_2O in excess was used as the target. As the energy source a Nd-YAG laser (1064 nm) with a pulse duration of 28 ns and a repetition rate of 10 Hz was used to ablate the target. Pieces of silicon wafers (100) conveniently cleaned with ethylic alcohol were used as substrates. The target and substrate were placed inside the deposition chamber and the distance between them was fixed at approximately 3 cm. The silicon substrate was heated with a homemade oven at 160 ^oC. The substrate temperature was measured with a thermocouple attached to the substrate surface. Deposition was carried out under an argon atmosphere at a pressure of $1x10^{-2}$ Torr in an attempt to avoid lithium lost confining the plasma plume. The laser fluence was varied from 3.8 to 15 J/cm^2. The deposition time was 25 min for all deposits. Additionally, the effect of a post-deposition annealing treatment at 300ºC for 2 hours in air was studied.

2.3 Materials characterization

The $LiNiO_2$ targets and deposited thin films as well, were characterized by Micro-Raman Spectroscopy (MRS) using a LabRam HR 800 system, equipped with a He-Ne laser emitting at 633 nm; X-Ray Diffraction (XRD) measurements were carried out in a Siemens D 5000 difractometer.

3. Results and discussion

3.1 Target characterization

The Raman spectroscopy has been widely used to characterize lithiated oxides owing to its sensitivity to the local environment of lithium ions in lithium compounds [7].

The Raman spectra of $LiNiO_2$ are composed by two peaks with the symmetry A_{1g} and E_g. The A_{1g} peak appears at 545 cm^{-1} and the E_g peak is located at 465 cm^{-1}. It is worth mentioning that the intensity ratio of these peaks depends on the laser wavelength used for the Raman measurements [8]. Figure 1 shows the micro-Raman spectra corresponding to the samples labeled as T20, T30 and T50, prepared in the conditions established in table 1. In general terms, two peaks compose the spectra. For the sample T20 these peaks are located at 481 and 551 cm^{-1} whereas for the sample T50 it is observed a shift to 543 cm^{-1} for the A_{1g} peak and a decrease of its intensity. This behavior of the Raman spectrum for the sample with 50-wt % of LiO_2, can be interpreted in terms of an improvement in the crystalline degree as the intensity of this Raman peak has been reported to be very sensitive to the long range order [8]. Therefore these Raman results seem to indicate that the higher the lithium excess, the more crystalline oxide is obtained.

Figure 2 shows the diffraction patterns corresponding to the samples T20, T30 and T50 (table 1). The X-Ray Diffraction results show that for the sample corresponding to the 20 wt % of Li_2O, figure 2a, some peaks corresponding to $LiNiO_2$ are present but with low intensity; additionally, peaks associated with NiO are observed indicative that the reaction between the two precursor

Table 1.

Target	**Excess of Li_2O** (wt. %)	**Annealing temperature/time**
T20	20	500°C/24h
T30	30	500°C/24h
T50	50	500°C/24h

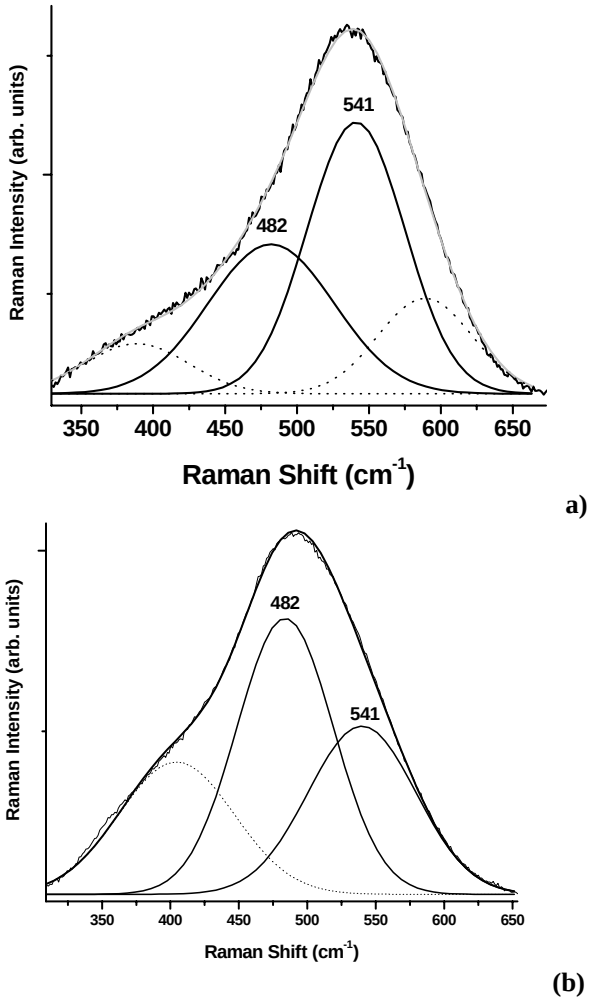

Figure 3. Micro-Raman spectra of a thin film deposited at 7.6 J/cm^2, (a) as deposited and (b) after a thermal treatment at 300 ^{o}C .

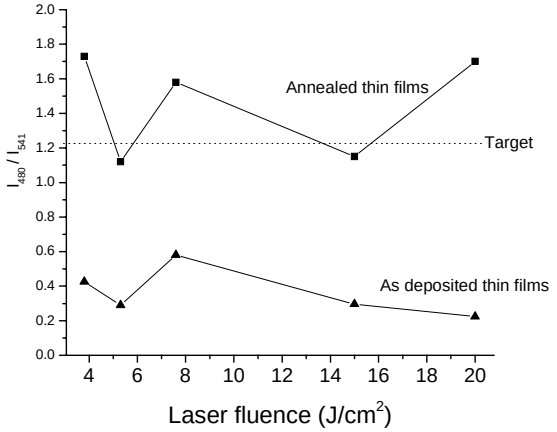

Figure 4. The intensity ratio, I(480)/I(541), for two sets of thin films as a function of the laser fluence.

oxides has not finished yet, probably due to a lack of lithium oxide.

The diffractogram displayed in figure 2b, corresponding to the sample T30, is constituted by peaks indexed to reflection planes of $LiNiO_2$, NiO and Li_2CO_3. The presence of NiO indicates that in this case the solid-state reaction at 500 ^{o}C takes place, but the NiO does not react totally. In this case it is clearly observed an increase in the intensity of the peaks associated to $LiNiO_2$ suggesting, on one side that the crystalline quality of the sample was improved, and on the other that a greater quantity of LiO_2 reacted with the NiO. The presence of peaks attributed to Li_2CO_3 is due to the fact that LiO_2 easily absorbs CO_2 from the atmospheric air. In Figure 2c it can be seen only the presence of peaks corresponding to $LiNiO_2$, indicating that with a 50-wt % excess of LiO_2 the solid-state reaction gives as a result $LiNiO_2$ without undesirable phases.

3.2 Thin films characterization

Figure 3a shows the Raman spectrum corresponding to the as deposited thin film using a laser fluence of 7.6 J/cm^2. It is worth mentioning that the Raman spectra of the films deposited varying the fluence were very similar to the spectrum displayed in figure 3a no matter the laser fluence used. As it is observed the spectrum consists of an asymmetric broad band with a maximum at 538 cm^{-1}. All the films were subjected to a post-deposition annealing treatment at 300ºC for 2 hours. In figure 3b it is displayed the spectrum of the film deposited at a laser fluence of 7.6 J/cm^2 after the thermal treatment, this spectrum is very similar to that spectrum shown in figure 3a corresponding to the thin film deposited using the T50 $LiNiO_2$ target. When compared with the spectra of figure 1, the broad band suggest the convolution of the two peaks, A_{1g} and E_g. In order to perform a deeper analysis, the Raman spectra were fitted using 4 Gaussians in each case, in order to obtain the frequency and the relative intensities of the two peaks of interest. Figure 3 shows the peaks at 482 and 541 cm^{-1} corresponding to the A_{1g} and E_g modes. It can be seen that the relative intensity of the fitted bands totally changes for the annealed thin film (spectrum 3b) as compared to the as deposited one.

Figure 4 shows the intensity ratio, I(480)/I(541), for two sets of thin films as a function of the laser fluence. As a reference it is indicated the intensity ratio for the target (1.2). For the as deposited films the intensity ratio remains almost constant at around 0.4, whereas for the annealed samples the intensity ratio shifts to higher values close to 1.3 that roughly corresponds to the target. These results indicate that the annealing treatment improves the crystalline quality.

4. Conclusions

It was found that the solid-state reaction between Li_2O and NiO is a convenient way to produce $LiNiO_2$. Depending on the LiO_2 wt %, it was possible to obtain

$LiNiO_2$ with the correct stoichiometry and without the presence of the $LiCO_3$ impurity phase.

It was shown that $LiNiO_2$ thin films could be easily grown by pulsed laser deposition. The obtained results suggest that a post-deposition thermal treatment is suitable to obtain thin films of a material with an equivalent microstructure to that of the ablated target.

Acknowledgements

J. López-Iturbe thanks to CONACyY México for the partial support received for the realization of this work.

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