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## Electronic structure of $\text{Li}_x\text{NiO}_y$ thin films

A. Urbano<sup>a,\*</sup>, S.C. deCastro<sup>a</sup>, R. Landers<sup>a</sup>, J. Morais<sup>a</sup>, A.D. Siervo<sup>a</sup>,  
A. Gorenstein<sup>a</sup>, M.H. Tabacniks<sup>b</sup>, M.C.A. Fantini<sup>b</sup>

<sup>a</sup>Instituto de Física (Gleb Wataghin), Universidade Estadual de Campinas, DFA/IFGW/UNICAMP,  
CP 6165, CEP 13084-970 Campinas, SP, Brazil

<sup>b</sup>Instituto de Física, Universidade de São Paulo, São Paulo, Brazil

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### Abstract

In this work, thin films of  $\text{Li}_x\text{NiO}_y$  were deposited by rf reactive magnetron sputtering, from a  $\text{LiNiO}_2$  target. The composition of the films was analyzed by Rutherford backscattering spectroscopy. The electronic structure was analyzed by photoelectron spectroscopy, using either X-ray ( $\text{Al K}\alpha$ ) or synchrotron light (120 eV). X-ray diffraction showed a clear presence of  $\text{Li}_2\text{CO}_3$  in the target material, after some deposition runs. The presence of superficial lithium carbonate was also evidenced, for all films. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Lithium nickel oxides; Microbatteries; Photoelectron spectroscopy; Thin films

### 1. Introduction

$\text{LiNiO}_2$  in powder form is one of the most studied materials for applications in lithium ion batteries [1,2]. However, the storage of this material in air can cause degradation, mainly by reaction with atmospheric  $\text{CO}_2$ , and formation of  $\text{Li}_2\text{CO}_3$  [3].

In thin film form, only a few studies have been reported [4–6]. In this work,  $\text{Li}_x\text{NiO}_y$  films were deposited by rf reactive magnetron sputtering. The samples were characterized by surface and bulk techniques, and the presence of superficial  $\text{Li}_2\text{CO}_3$  was evidenced. The surface carbonate seems not to drastically affect the electrochemical performance of the film, but it acts de-intercalating lithium from the host material, which affect the charge capacity in secondary devices.

### 2. Experimental

The films were deposited by rf sputtering on tin dioxide/7059 corning glass substrates and on ultra dense amorphous carbon wafers. The target material was produced by heat treatment of  $\text{LiOH}\cdot\text{H}_2\text{O}$  and  $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$  mixture. The

final powder was cold pressed, in the dimensions of the target. The films were deposited in an oxygen plus argon atmosphere, under a  $7 \times 10^{-3}$  mbar total pressure. The oxygen flow ( $\phi_{\text{O}}$ ) was varied between 0 (pure Ar atmosphere) and 9.0 sccm, at room temperature. The power levels were either 100 or 150 W.

Rutherford backscattering spectroscopy (RBS) analysis was done using a 2.4 MeV  $\text{He}^+$  beam, with scattering angles of 100 and 170° ( $\alpha, \alpha'$ ). Photoelectron spectroscopy was used to investigate the core-level and valence band spectra of the different films. Some films were submitted to a constant current electrochemical deintercalation process in  $\text{LiClO}_4/\text{PC}$ , and cleaned by immersion in isopropyl alcohol before analysis. A pressed  $\text{Li}_2\text{CO}_3$  sample, and a thermally oxidized nickel were also analyzed. The equipment was a VSW: HA100 using radiation  $\text{Al K}\alpha$ . The binding energies were referenced to the C 1s line of surface carbon taken as 284.6 eV. The pressure in the chamber was kept around  $2 \times 10^{-9}$  Torr. The valence band was also studied by photoelectron spectroscopy, at the TGM beamline (National Laboratory of Synchrotron Light, LNLS, Campinas, Brazil) using the surface science work station. The excitation energy was 120 eV.

The X-ray diffraction (XRD) measurements were performed on fresh synthesized  $\text{LiNiO}_2$  powder or on the powder scratched from the target surface, after a few depositions. The diffractograms were obtained using Ni filtered  $\text{Cu K}\alpha$  radiation.

\* Corresponding author. Tel.: +55-19-7885411;

fax: +55-19-7885376.

E-mail address: aurbano@ifi.unicamp.br (A. Urbano).

### 3. Results and discussion

Fig. 1 presents the C 1s, O 1s and Ni 2p XPS spectra for films deposited under different conditions. The sample number indicates the deposition run, beginning with a fresh target (e.g. sample 1 was deposited at the first run; sample 8, at the eighth run). Spectra for deintercalated samples are also shown. Two main peaks are present at all the C 1s spectra (Fig. 1a). The peak located at  $\sim 290$  eV is attributed to C in carbonate [7] (present at 289.9 eV at the  $\text{Li}_2\text{CO}_3$  reference sample). The peak centered at 284.6 eV is assigned to hydrocarbon present in the residual gas of the analysis chamber.

The O 1s spectra (Fig. 1b) also present two peaks. For all samples, with the exception of the sample 8, the peak at higher energies is centered at  $\sim 531.4/531.7$  eV, and is the characteristic of carbonate binding energies; the  $\text{Li}_2\text{CO}_3$  control sample presents the single O 1s peak at 531.5 eV. This binding energy is dislocated to higher energies (532.6 eV) for sample 8; this shift is an indication of the presence of OH groups at the sample surface. The second O

1s peak is located at  $\sim 529.3/530.1$  eV, at an energy characteristic of NiO [8,9].

The Ni  $2p_{3/2}$  spectra (Fig. 1c) presents the well known double peaked lines, centered at  $\sim 855.4$  and  $\sim 861.2$  eV (satellite). These energies are characteristic of Ni valence state in  $\text{Ni}_2\text{O}_3$  (855.8 and 861.4 eV) or  $\text{Ni}(\text{OH})_2$  (856.6 and 862.4 eV) and higher than the energies observed for NiO (854.5, 856.3) [10]. Interestingly, the deintercalated sample did not present any energy shift for core levels, in comparison with the as-grown sample (Fig. 1).

Fig. 2 presents the valence band spectra, at two different excitation energies. The Li 1s peak is centered at  $\sim 55$  eV. This energy is characteristic of the presence of  $\text{Li}_2\text{CO}_3$  [7], in accordance with the observations for the core level spectra. Also, the O 2s (energy range 18–32 eV) and the C 2p + O 2p lines (energy range 3.2–15 eV) presents a series of peaks that can be attributed to the carbonate. For the as-grown sample 8, the Ni 3d signal at  $\sim 1.0$  eV (XPS and UPS data) is also present (see the spectrum for the nickel oxide sample, Fig. 2), but disappears for the deintercalated sample (UPS data).

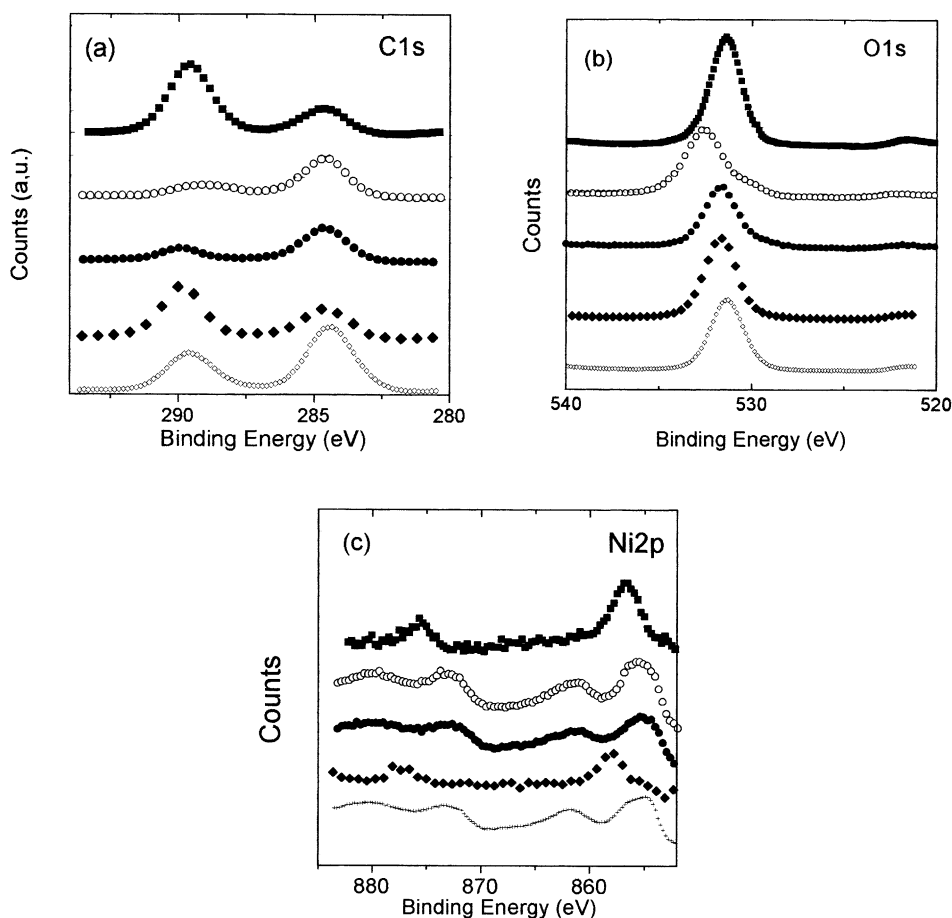


Fig. 1. Core level photoelectron spectra. Excitation energies: Al K $\alpha$  (1486.6 eV): (a) C 1s spectra; (b) O 1s spectra and (c) Ni 2p spectra (■) sample 2, film deposited at  $P = 100$  W,  $\text{O}_2$  flow = 9 sccm, as-grown; (○) sample 8, film deposited at  $P = 150$  W,  $\text{O}_2$  flow = 9 sccm, as-grown; (●) sample 8, film deposited at  $P = 150$  W,  $\text{O}_2$  flow = 9 sccm, de-intercalated; (◆) sample 1, film deposited at  $P = 100$  W, without  $\text{O}_2$  flow; (◇)  $\text{Li}_2\text{CO}_3$  powder; (+) nickel oxide.

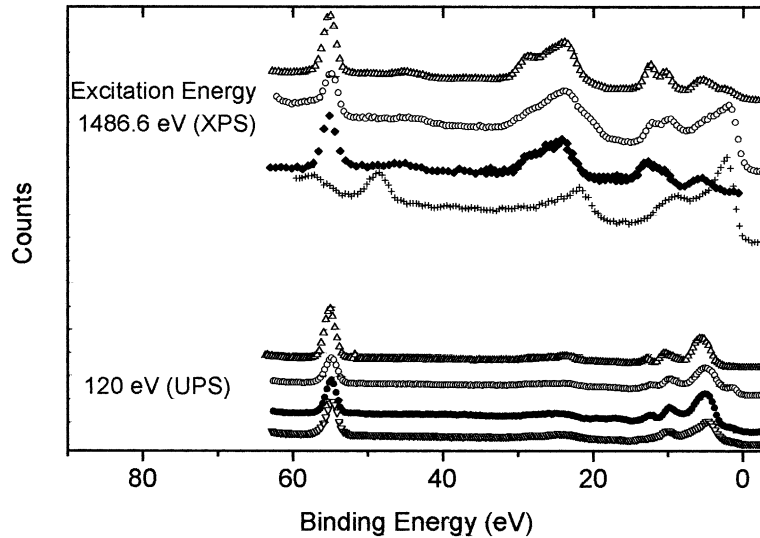


Fig. 2. Valence band photoelectron spectra at two different excitation energies: Al K $\alpha$  (1486.6 eV, upper spectra) and synchrotron radiation (120 eV, lower spectra). Samples: ( $\Delta$ ) sample 9, film deposited at  $P = 150$  W, without O<sub>2</sub> flow during deposition; ( $\circ$ ) sample 8, film deposited at  $P = 150$  W, O<sub>2</sub> flow = 9 sccm, as-grown; ( $\bullet$ ) sample 8, film deposited at  $P = 150$  W, O<sub>2</sub> flow = 9 sccm, de-intercalated; ( $\blacklozenge$ ) Li<sub>2</sub>CO<sub>3</sub> powder; (+) nickel oxide; ( $\nabla$ ) LiNiO<sub>2</sub> powder.

Table 1  
Atomic ratios ( $\pm 20\%$ ) calculated from XPS data

Sample	Power of rf (W)	O 1s/C 1s	O 1s/CCO <sub>3</sub>	O 1s/Ni 2p	O 2s/O 1s	Li 1s/O 1s
1	100	1.5	2.5	>100	0.7	1.6
2	100	1.6	2.2	>100	0.7	1.6
8	150	0.7	3.2	10	1.6	0.70
Deintercalated 8	150	0.6	2.6	22	1.5	0.80
9	150	1.6	2.3	31	1.4	1.05
Li <sub>2</sub> CO <sub>3</sub>	–	0.94	2.5	–	0.80	1.2
Ni <sub>oxid</sub>	–	0.75	–	3.2	1.1	–

Table 1 presents the atomic ratios, calculated from the XPS data. The huge O 1s/Ni 2p values can be explained only if the sample surface is dominated by carbonate compounds. On the other hand, Fig. 3 presents a characteristic RBS spectra. The carbon pre-peak, located at 0.60 MeV, is well separated from the main substrate signal. Also, the oxygen signal presents a non-statistical bump, located at 0.86 MeV. These two features are a clear indication of the presence of a carbon–oxygen compound located at the sample surface. The O/Ni ratio, calculated from this data, is 2.3 (sample 2); the values obtained from XPS data (Table 1) are much higher, which is compatible with the fact that XPS is a surface technique in contrast to the bulk character of the RBS technique.

Fig. 4 presents the XRD data from the LiNiO<sub>2</sub> powder, which was used to construct the target for film deposition. The experiments were performed both from a fresh synthesized powder (Fig. 4a) and from the powder scratched from the target surface, after a few depositions (Fig. 4b). A clear

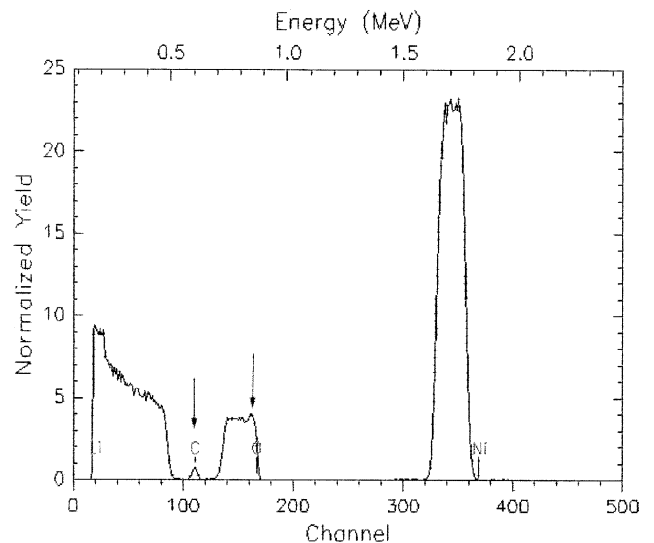


Fig. 3. RBS spectrum, sample 2.

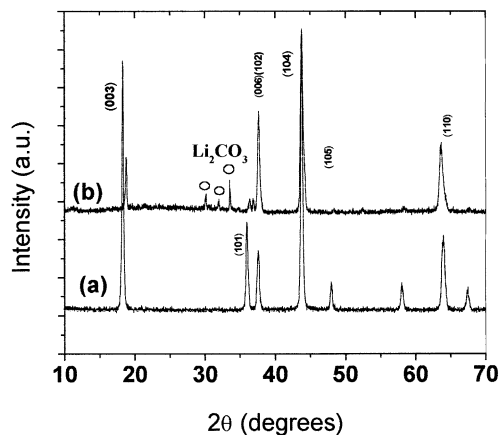


Fig. 4. XRD from (a) a fresh LiNiO<sub>2</sub> powder and (b) powder scratched from the surface of the target, after a few depositions. The Li<sub>2</sub>CO<sub>3</sub> diffraction peaks are indicated by the open circles around  $2\theta = 30^\circ$ .

presence of Li<sub>2</sub>CO<sub>3</sub> is seen in the diffractogram relative to the bombarded target.

The main conclusion, from these data, is that LiNiO<sub>2</sub> is a very sensitive material to C–O atmosphere. The sputtering process, even from a carbonate-contaminated target, can destroy the carbonate groups, and the main compound present in the films are carbonate-free. After deposition,

the films react with air, and a thin Li<sub>2</sub>CO<sub>3</sub> layer is formed, but only at the sample surface. The electrochemical process, or the cleaning process, is unable to destroy, or can reconstruct, this superficial carbonate layer..3

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