

Spectroscopic investigations on laser ablated $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ thin films

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Thin films of $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ were prepared by pulsed laser deposition technique. Two important deposition parameters such as substrate temperature and oxygen partial pressure during the thin film deposition were controlled. The structural properties of the films have been investigated as a function of deposition conditions, which play important role in the physical and chemical characteristics of the material. The films deposited at 700 °C in an oxygen partial pressure of 100 mTorr exhibited R3m layered structure. FTIR and Raman measurements confirm the XRD data showing the formation of pure phase $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$. The growth of $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ films were studied in relation to the deposition parameters for their effective utilization as cathode materials in solid state microbattery application.

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1. Introduction

Lithiated transition metal oxides such as LiMO_2 (Where M = Co, Ni, Mn etc.) have received considerable attention in recent years as high voltage positive electrode materials for use in secondary lithium batteries. Among these, the high cycling stability and high cell potential against lithium makes LiCoO_2 an attractive cathode material in the fabrication of all solid state rechargeable microbatteries [1, 2].

LiCoO_2 is considered to have high specific density, high voltage, long cycle life and good reversibility for lithium intercalation – deintercalation process. It is easy to prepare but its high cost and toxicity remain problems to be solved. Intensive investigations have been carried out on doped $\text{LiCo}_{1-x}\text{M}_x\text{O}_2$ oxides (M = Mn, Cr, Al, Ti, B, Mg, etc.), which show interesting structural and electrochemical properties [3, 4]. Other isostructural lithium mixed oxides have been considered for substitution in LiCoO_2 host material to reduce the material cost. Among various lithium based mixed oxides, LiNiO_2 is one of the most significant material. This compound has the advantages of presenting a higher specific capacity for lithium cycling, less toxic and low cost; nevertheless, it is difficult to prepare in the layered structure due to the tendency of lithium and nickel to disorder, leading to a deterioration of their electrochemical performance. However, the layered structure can be stabilized in mixed Co/Ni compounds $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$, for nickel contents up to $x \leq 0.8$, resulting in improvements in the crystallinity, good particle-size distribution, cycle life and rate of the electrodes [5, 6]. Doping with non-transition metals such as nickel has gained increasing interest for the following reasons: (1) the low cost and low toxicity, (2) the fact that nickel substitution for transition metal oxides leads to higher lithium intercalation voltages, (3) the nickel doping

stabilizes the layered structure and extends the cyclability and enhances the capability of the electrochemical cells and inhibits the formation of Ni^{2+} impurities and stabilizes the two dimensional character of the structure [7]. Therefore, $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ has attracted much attention as a candidate for cathode material.

The growth of LiCoO_2 thin films with preferred orientation is known to be crucial. Several thin film deposition techniques such as RF sputtering [1, 8-11], pulsed laser deposition [8, 12-16], electrostatic spray deposition [17] and chemical vapour deposition [18, 19] were employed for the growth of LiCoO_2 thin films. PLD has been widely recognized as a very promising, versatile and efficient method for the deposition of metal oxide thin films [20]. In particular, it has been successfully employed for the deposition of simple and complex metal oxide materials with desired composition, structure, physical and chemical properties. When PLD is carried out in the atmosphere of a chemically reactive gas (a process known as Reactive Pulsed Laser Deposition (RPLD)), the flux of the laser ablated material interacts with the gas molecules all along the transit from the target to the collector surface. The resulting deposited layer was found to have a chemical composition substantially the same as the base or starting material. Poly-crystalline layered R $\bar{3}$ m phase thin films of LiCoO_2 were grown by PLD by Julien et al. [21]. This LiCoO_2 cathode active films were found to deliver a specific capacity of 195 mC/ μm^2 in the voltage range 2.0 - 4.2 V. Xia et al. [22] prepared LiCoO_2 thin films by pulsed laser deposition on Pt/Ti/SiO₂/Si (Pt) and Au/MgO/Si (Au) substrates, respectively. However the investigations on the structural studies of LiCoO_2 films that are essentially depend upon the deposition parameters give a scope for effective utilization of these thin films in the fabrication of microbatteries. Hence in the present study the influence of deposition parameters on the structural properties of pulsed laser deposited $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ thin films were reported.

2. Experimental

$\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ thin films were grown by pulsed laser deposition technique on silicon substrates maintained at temperatures in the range 500 – 700 °C. PLD target was prepared by sintering a mixture of high purity LiCoO_2 and NiO powders (Cerac products) with excess of lithium i.e. $\text{Li}/\text{Co} + \text{Ni} = 1.2$ by adding Li_2O to compensate the loss of lithium during the deposition. The mixture was crushed, pressed and sintered at 800 °C to get quite robust targets and used for the growth of films. The typical substrates i.e. Si wafers were cleaned using HF solution. The target was rotated at 10 rotations per minute with an electric motor to avoid depletion of material at any given spot. The laser used in these experiments is the 248 nm line of a KrF excimer laser (Luminics PM 882) with 10 ns pulse with a repetition rate of 10 Hz. The rectangular spot size of the laser pulse was 1x3 mm and the energy 300 mJ. The power density at the target surface was 10 Jcm^{-2} . The target substrate distance was 4 cm. The deposition temperature was maintained with thermocouple and temperature controller. During the deposition pure oxygen was introduced into the deposition chamber and desired pressure was maintained with a flow controller.

The structure of the films was characterized by X-ray diffraction (XRD) using a diffractometer (Philips model PW 1830) with nickel filtered $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The diffraction pattern were taken at room temperature in the range $10^\circ < 2\theta < 60^\circ$ using step scans. The step size and the scan rate were set at 0.1 and 0.2 degree per minute, respectively. The Raman spectra of $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ films were recorded between 200 and 1000 cm^{-1} at room temperature in a quasi-backscattering configuration at a spectral resolution of 2 cm^{-1} . The Raman-laser apparatus (Jobin-Yvon U1000) was equipped of holographic grating double-monochromator, an intermediate spatial filter and a computer-controlled photon-counting system. The emission from a laser (Spectra-Physics, 2020 argon-ion) with a wavelength of 514.5 nm was used. The frequency stability and the accuracy of the apparatus were checked recording the Raman spectrum of silicon. To avoid sample photo-decomposition or denaturation, RS spectra were recorded using a low power density of 100 W/cm^2 . FTIR absorption spectra were recorded at room temperature using a Bruker IFS 113v interferometer.

3. Results and discussion

Pulsed laser deposited $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ films are pin-hole free as revealed from optical microscopy and well adherent to the substrate surface. The thicknesses of $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ films are 250 nm. The influence of oxygen

partial pressure ($p\text{O}_2$) and deposition temperature (T_s) on the microstructural properties were systematically studied. The chemical compositional studies made on $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ films revealed that a minimum of 100 mTorr oxygen partial pressure is required to grow nearly stoichiometric films.

3.1 Structure

Fig.1 shows the X-ray diffraction patterns of $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ films grown on silicon wafers maintained at temperatures in the range 500 - 700 °C in oxygen partial pressure $p\text{O}_2 = 100$ mTorr. A single-phase $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ with an $\alpha\text{-NaFeO}_2$ - type layered structure was obviously grown at 500 and 700 °C, in $p\text{O}_2 = 100$ mTorr. XRD peaks were indexed in the hexagonal system assuring the R3m symmetry. It is assumed that Li-ions are in octahedral sites between $(\text{Ni}_x\text{Co}_{1-x}\text{O}_2)_n$ infinite slabs formed by edge sharing $(\text{Ni}_x\text{Co}_{1-x})\text{O}_2$. Hexagonal cell parameters of the oxide lattices are in good agreement with reported values in the literature [23]. Both the XRD's are dominated by a strong Bragg peak located at $2\theta = 19^\circ$. Hexagonal cell parameters of the oxide lattices, which are calculated by least squares refinement, are given in Table1.

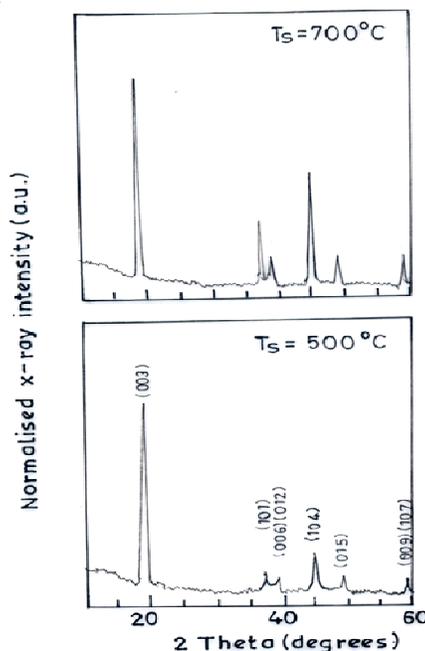


Fig.1 XRD patterns of $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ thin films deposited at different substrate temperatures in $p\text{O}_2 = 100$ m Torr.

Table 1

Sample	Lattice parameters		c/a	$I_{(003)}/I_{(104)}$
	a (\AA)	c (\AA)		
$T_s = 500$ °C	2.841	14.113	4.967	1.42
$T_s = 700$ °C	2.827	14.101	4.987	1.76

As the Nickel content increases in $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$, both the metal-metal intra sheet distance and the metal-metal interlayer distance decrease in an almost linear. The lattice vibrations are attributed to the difference in the size between the trivalent nickel and cobalt ions, and the increase of the $(\text{Ni}_x\text{Co}_{1-x}\text{O}_2)_n$ sheet covalency [23]. Constructing the crystallographic $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ layers by substituting the sites of the Ni^{3+} ions for the Co^{3+} ions and calculating correspondingly the c/a value, one reveals that the hexagonal-close-packed lattice is still maintained, in other words, no cation mixing between Ni^{3+} and Li^+ ions present in octahedral sites if the c/a value is higher than the critical value 4.90. The ratios of intensities of XRD lines $I_{(003)}/I_{(104)}$ are considered to be indicators of the ordering of lithium and other transition metal cations (Ni and/or Co) [24, 25]. In Fig.1, the cation ordering peaks at (003) and (101) could be observed for the samples deposited at 500 and 700 °C. Thus $\text{LiNi}_{0.2}\text{Co}_{0.8}\text{O}_2$ films exhibit XRD patterns with well defined orientations with well defined c/a ratio indicating that an ordered distribution of lithium and transition metal ions exists in the structure. The XRD results confirm the formation of pure phase.

3.2 FTIR and Raman studies

The Raman scattering and Fourier transform infrared spectra of thin films of $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ are shown in Fig. 2 and Fig. 3 respectively. The layered $\text{LiNi}_{0.2}\text{Co}_{0.8}\text{O}_2$ material exhibits only two Raman-active modes at 480 and 586 cm^{-1} . The ideal $\alpha\text{-NaFeO}_2$ -type structure belongs to the $R3m$ symmetry. The transition metal cations (i.e., cobalt and nickel) and the lithium ions are located at Wyckoff sites 3(b) and 3(a) respectively, in a cubic close packed oxygen array. The Li^+ and $\text{Co}^{\text{III}}/\text{Ni}^{\text{III}}$ ions are ordered along the (111) direction of the rock-salt cubic lattice leading to a two-dimensional structure.

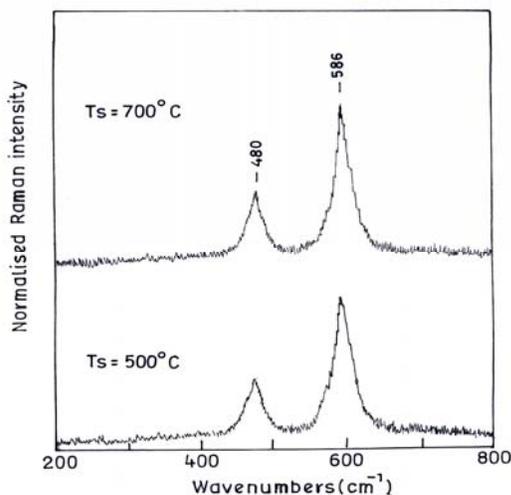


Fig. 2. Raman scattering spectra of $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ thin films deposited at different substrate temperatures in $p\text{O}_2 = 100 \text{ m Torr}$.

The factor group analysis of the D_{3d}^5 spectroscopic symmetry yields six optical modes [26, 27]. Two modes are Raman active (A_{1g} & E_g) and four are infrared active ($2A_{2u}$ & $2E_u$). It should be noted that (1) the Raman-active modes include only the oxygen vibrations in the direction parallel (A_{1g}) or perpendicular (E_g) to the c -axis, (2) due to the presence of a centre of symmetry, there is a mutual exclusion in the IR and Raman spectra, (3) because FTIR spectroscopy is capable of probing directly the surrounding environment of the cation. It has been demonstrated that the IR resonant frequencies of alkali metal cations in their octahedral interstices in inorganic oxides are located in the frequency range 200–300 cm^{-1} .

The work on transition metal substitution in LiMO_2 compounds has also showed that vibrational mode component of the LiO_6 octahedra appears invariably around 250 cm^{-1} [28]. Thus, the IR resonant frequency of LiO_6 groups appears at 269 and 234 cm^{-1} in the LiCoO_2 and LiNiO_2 layered structures ($R3m$ space group), respectively. As far as the low-wave-number peak is concerned, the isotopic lithium replacement in LiMO_2 has proved that this IR band between 200 and 300 cm^{-1} is associated with a vibration of a relatively isolated LiO_6 octahedron [29].

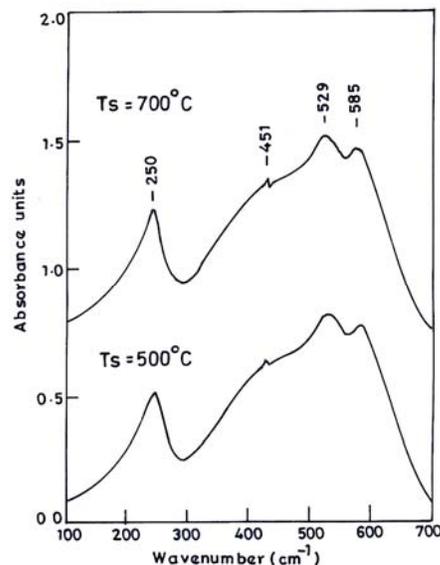


Fig.3 FTIR spectra of $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ thin films deposited at different substrate temperatures in $p\text{O}_2 = 100 \text{ m Torr}$.

The band situated at 250 cm^{-1} is assigned with confidence to an asymmetric stretching vibration of the Li^+ ion with O^{2-} near neighbours. However, a small mixing of Li-O stretching and O-M-O bending motion is present in the low wave number peak. The high frequency bands of the FTIR absorption spectra of $\text{LiNi}_{0.2}\text{Co}_{0.8}\text{O}_2$ located at 585 cm^{-1} is attributed to the asymmetric stretching mode

of MO_6 group, whereas the low-frequency bands at 529 and 451 cm^{-1} are assigned to the bending modes of O-M-O chemical bonds. The Raman peak located at 586 cm^{-1} is assigned with confidence to the symmetric stretching vibration of MO_6 octahedra, while the peak located at 480 cm^{-1} is attributed to the Raman active bending mode of O-M-O chemical bonds. As the deposition temperature increases in $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ compounds, we observed the sharpness of the peaks in both FTIR and Raman spectra. Thus FTIR and Raman measurements confirm the XRD data showing the formation of pure phase $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$.

4. Conclusions

$\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ thin films were grown using the pulsed laser deposition technique, in which the control of the deposition parameters promotes the film stoichiometry. The structural properties of the films have been investigated as a function of deposition conditions, which play important role in the physical and chemical characteristics of the material. $\text{LiNi}_{0.2}\text{Co}_{0.8}\text{O}_2$ films exhibited XRD patterns with well defined orientations with well defined c/a ratio indicating that an ordered distribution of lithium and transition metal ions exists in the structure. FTIR and Raman measurements confirm the XRD data showing the formation of pure phase $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$. These results suggest that the open and porous structured $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ PLD films find potential applications as binder free electrode in the fabrication of all solid state microbatteries.

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