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Microstructural and electrochemical properties of $LiNi_xCo_{1-x}O_2$ thin films prepared by pulsed laser deposition

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Thin films of $LiNi_xCo_{1-x}O_2$ 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 films deposited at 700 ^oC in an oxygen partial pressure of 100 mTorr exhibited R3m layered structure. The SEM data demonstrated that the films exhibited a smooth surface roughness with spherical droplets. The grain size increased with the increase of substrate temperature. The electrochemical measurements were carried out on $Li//LiNi_xCo_{1-x}O_2$ cells with a lithium metal foil as anode and $LiNi_xCo_{1-x}O_2$ film as cathode of 1.5 cm^2 active. Cyclic voltammetry (CV) measurements have been carried out at sweep rate α = 1 mVs^{-1}. Specific capacity as high as 210 $mC/cm^2\mu m$ was measured for the film grown at 500 ^oC.

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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]. Its theoretical specific capacity and energy densities are 274mAh/g and 1070 Wh/kg respectively. Experimentally it has been observed that the material delivers only capacity around 140 mAh/g due to structural considerations.

$LiCoO_2$ 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 $LiCo_{1-x}M_xO_2$ 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 $LiNi_xCo_{1-x}O_2$, 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, $LiNi_xCo_{1-x}O_2$ has attracted much attention as a candidate for cathode material.

The layered $LiCoO_2$ consists of a close packed network of oxygen ions with Li and Co ions on alternative (111) planes of the cubic rock - salt sublattice. The edges of CoO_6 octahedral were shared to form CoO_2 sheets and lithium ions can move in two-dimensional directions between CoO_2 sheets. Thus the layered $LiCoO_2$ has an anisotropic structure and there by electrochemical lithium insertion / extraction behaviour must depend strongly on the orientation of the microcrystallites. 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 R3m 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 cm^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/SiO_2/Si (Pt) and Au/MgO/Si (Au) substrates, respectively. However the investigations on the microstructural 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 microstructural and electrochemical properties of pulsed laser deposited $LiNi_xCo_{1-x}O_2$ thin films were reported.

2. Experimental

$LiNi_xCo_{1-x}O_2$ 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. Li/Co + 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 CuK$_\alpha$ radiation (λ= 1.5406 A^0). The diffraction pattern were taken at room temperature in the range $10^0 < 2\theta < 60^0$ using step scans. The step size and the scan rate were set at 0.1 and 0.2 degree per minute, respectively. The surface topography was investigated by scanning electron microscopy (SEM) using Philips XL 30. Electrochemical measurements were carried out on Li//$LiNi_xCo_{1-x}O_2$ cells with lithium metal foil as anode and a $LiNi_xCo_{1-x}O_2$ film as cathode of 1.5 cm^2 active area using a Teflon home-made cell hardware. The silicon substrate was mounted on Ag wire with silver paint and covered by insulating epoxy leaving only the PLD film as active area. The electrolyte consisted of 1 M $LiClO_4$ dissolved in propylene carbonate. Cyclic voltammetry measurements have been carried out at sweep rate α = 1 mVs^{-1}. Electrochemical titration was made by charging and discharging the cells using the galvanostatic mode of a Mac-Pile system in the potential range between 2.0 and 4.2 V. Quasi open-circuit voltage profiles were recorded using current pulses of 5 μAcm^{-2} supplied for 1 h followed by a relaxation period of 0.5 h. Electrochemical potential spectroscopy (ECPS) was performed using 5 mV potential steps.

3. Results and discussion

Pulsed laser deposited $LiNi_xCo_{1-x}O_2$ films are pin-hole free as revealed from optical microscopy and well adherent to the substrate surface. The thicknesses of $LiNi_xCo_{1-x}O_2$ films are 250 nm. The influence of oxygen partial pressure (pO_2) and deposition temperature (T_s) on the microstructural properties were systematically studied. The chemical compositional studies made on $LiNi_xCo_{1-x}O_2$ films revealed that a minimum of 100 mTorr oxygen partial pressure is required to grow nearly stoichiometric films.

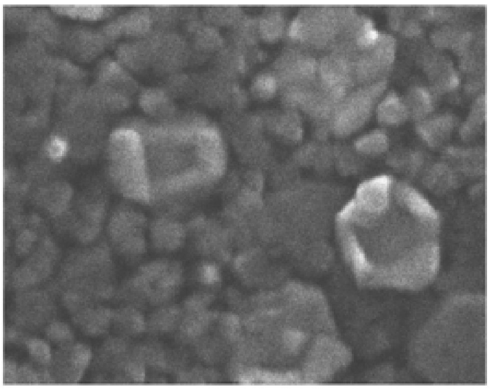
3. 1 Structure

A single-phase $LiNi_xCo_{1-x}O_2$ with an α-$NaFeO_2$ - type layered structure was obviously grown at 500 and 700 °C, in pO_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 $(Ni_xCo_{1-x}O_2)_n$ infinite slabs formed by edge sharing $(Ni_xCo_{1-x})O_2$. Hexagonal cell parameters of the oxide lattices are in good agreement with reported values in the literature [23].

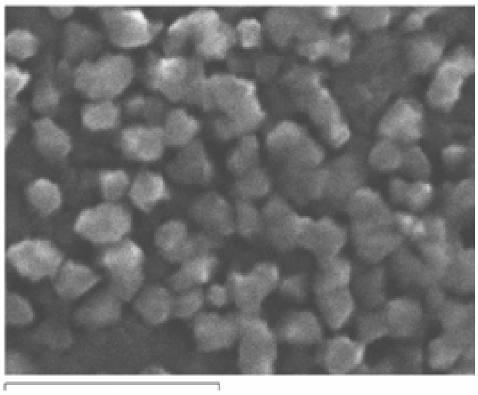
As the Nickel content increases in $LiNi_xCo_{1-x}O_2$, both the metal-metal intra sheet distance and the metal-metal interlayer distance decrease in an almost linear. The lattice vibrations are attributed to the difference in the size between the trivalent nickel and cobalt ions, and the increase of the $(Ni_xCo_{1-x}O_2)_n$ sheet covalency [23]. Constructing the crystallographic $LiNi_xCo_{1-x}O_2$ 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]. These XRD results confirm the formation of pure phase.

3.2 Surface morphology

The surface morphology and texture as well as particle sizes were observed by scanning electron microscopy. The scanning electron micrographs of pulsed laser deposited $LiNi_xCo_{1-x}O_2$ films grown in oxygen partial pressure pO_2 = 100 mTorr on silicon wafers maintained at 500 and 700 °C are shown in Fig. 1. The SEM micrograph of film grown at 500 °C exhibits a smooth surface roughness with spherical droplets related to the ejection of liquid material from the molten zone of the irradiated targets. The grain size of the films is found to be 146 nm. The crystallite sizes tend to increase as the deposition temperature increased, suggesting the formation of submicron sized particles with uniform grain size distribution. The grain size of the films formed at 700 °C is 195 nm.



$T_s = 500\ ^oC$



$T_s = 700\ ^oC$

Fig. 1. SEM images of $LiNi_xCo_{1-x}O_2$ thin films deposited at different substrate temperatures in pO_2 = 100 m Torr.

The morphological changes, grain size enhancement and their distribution characteristics as a result of increase in growth temperature can be explained on the basis of the difference in the mobility of ablated species on the substrate surface as follows. When the laser beam hits the target the ions or molecules or atoms of the target material are liberated. The ablated atomic or molecular or ionic species impinging on the substrate surface (which is at higher temperature) acquire a large thermal energy and hence a large mobility. This enhances the diffusion density of the ablated species. As a result, the collision process initiates the nucleation and enhances the island formation in order to grow a continuous film with larger grains. These results are suitable for the further utilization of PLD films because a fundamental role in terms of charge transfer capability and cycle life is played by the morphology of the films used as cathodes in lithium microbatteries [21].

3.3 Electrochemical properties

Fig.2 shows the cyclic voltammogram for a $Li//LiNi_xCo_{1-x}O_2$ cell with a film grown at temperature 700 °C in an oxygen partial pressure of 100 mTorr. There are two sets of well defined current peaks observed in the CV diagram corresponding to the oxidation and reduction reaction: they are located at 3.71 and 3.61 V for the $LiNi_xCo_{1-x}O_2$ film. These CV features are associated with the redox process of Co^{3+} to Co^{4+} and vice-versa, when lithium is extracted from, and inserted into the Li_xCoO_2 phase. The redox couple with a mid-peak potential of about 3.66 V is considered to be a single-phase insertion/deinsertion reaction of lithium ions in $LiNi_xCo_{1-x}O_2$.

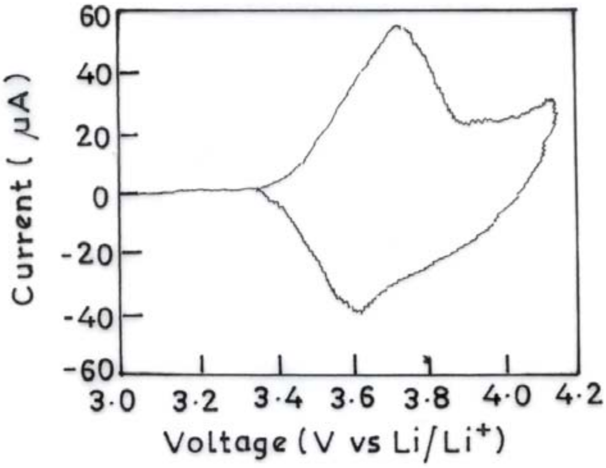


Fig. 2. Cyclic Voltammogram of $Li//LiNi_xCo_{1-x}O_2$ cells deposited at 700 °C

Fig. 3 shows the typical charge – discharge curves of $Li//LiNi_xCo_{1-x}O_2$ cells using pulsed laser deposited film grown at temperature 500 °C in an oxygen partial pressure of 100 mTorr. The electrochemical measurements were carried out on $Li//LiNi_xCo_{1-x}O_2$ cells with a lithium metal foil as anode and a polycrystalline film as cathode of 1.5 cm^2 active area using a Teflon home-made cell hardware. The silicon substrate was mounted on Ag wire with silver paint and covered by insulating epoxy leaving only the PLD film as active area. The electrolyte consisted of 1 M $LiClO_4$ dissolved in propylene carbonate. Electrochemical titration was made by charging and discharging the cells using the galvanostatic mode of a Mac-Pile system at a rate of C/100 in the potential range between 2.5 and 4.1 V, as such, the voltage profile should provide a close approximation to the open-circuit voltage (OCV). The initial open circuit voltage of the film is 2.5 V and it is cycled between 4.1 and 2.5 V. The voltage plateau at 3.65 V in the charge curve of $LiCoO_2$ disappears in the charge curve of $LiNi_xCo_{1-x}O_2$; this is the net result of the doping effect which cancels the semiconductor-metal like transition of the $LiCoO_2$ framework. This is mainly due to the presence of Ni^{3+} ions, which are preferentially oxidized to Ni^{4+} before cobalt in Ni-substituted compounds [26]. Thus, at low degree of Li extraction, the electrochemical features resemble those of Li_xNiO_2 with a stabilization of the 2D framework. Consequently, the charge-discharge profiles have a $LiNiO_2$ –like character without the disadvantages of the multiple-phase system exhibited by this compound. The $LiNi_xCo_{1-x}O_2$ film grown at 500 °C has interesting electrochemical properties for the microbattery application. In the high voltage region, such a cell delivered a specific capacity of 210 mC/μm cm^2.

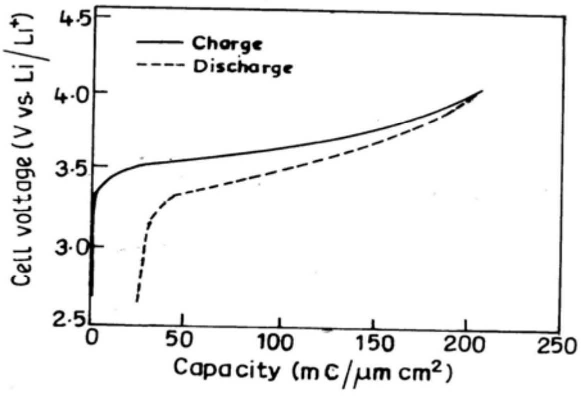


Fig. 3. Charge – discharge profile of Li//LiNi$_x$Co$_{1-x}$O$_2$ cells.

4. Conclusion

LiNi$_x$Co$_{1-x}$O$_2$ thin films were grown using the pulsed laser deposition technique, in which the control of the deposition parameters promotes the film stoichiometry. PLD films were found to be uniform with regard to the surface topography, thicknesses and well adherent to the substrate surface. The structural properties of the films have been investigated as a function of deposition conditions, which play important roles in the physical and chemical characteristics of the material. LiNi$_x$Co$_{1-x}$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. Cyclic voltammetry measurements have been carried out at sweep rate α = 1 mVs^{-1}. Electrochemical titration was made by charging and discharging the cells in the potential range between 2.5 and 4.1 V. Specific capacity as high as 210 mC/cm^{2}μm was measured for the film grown at 500 °C. This performance is due to the good crystallinity of the LiNi$_x$Co$_{1-x}$O$_2$ films grown by PLD technique. These results suggest that the open and porous structured LiNi$_x$Co$_{1-x}$O$_2$ PLD films find potential applications as binder free electrode in the fabrication of all solid state microbatteries.

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