Optical and electrical properties of laser ablated $LiNi_xCo_{1-x}O_2$ thin films

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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 optical absorbance of $LiNi_xCo_{1-x}O_2$ thin films have been studied in the vicinity of the fundamental absorption edge. A gradual increase of the optical transmission from 400 to 1000 nm with the appearance of a prominent dip at 750 nm is observed. This feature is more pronounced for the well-crystallized film grown at 700 ^{0}C. The variation of the optical absorption near the fundamental edge allows determining the energy gap between d-bands of $LiNi_xCo_{1-x}O_2$. Band gap energies of 2.39 and 2.15 eV for films grown at 500 and 700 ^{0}C, respectively, with accuracy $\pm$ 0.02 eV were measured. The electrical conductivity of $LiCoO_2$ varies from 10^{-9} to 10^{-4} S/cm in the temperature range from 180 to 500 K. Doping the oxide network with nickel oxide leads to an increase of the electrical conductivity of one order of magnitude from 6×10^{-7} S/cm for $LiCoO_2$ to 9×10^{-6} S/cm for $LiNi_xCo_{1-x}O_2$ at room temperature. The increase of electrical conductivity could be connected with either an enhancement in the effective carrier concentration or a decrease of the activation energy with substitution of Ni^{3+} ions for Co^{3+} ions. The activation energy decreases from 0.36 eV to 0.28 eV on nickel doping. These results suggest that the open and porous structured $LiNi_xCo_{1-x}O_2$ films find potential applications as binder free electrode in the fabrication of all solid state microbatteries.

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]. These LiCoO2 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. Hence in the present study the influence of deposition parameters on the optical and electrical 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. 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 ^{o}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 was10 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 optical properties of $LiNi_xCo_{1-x}O_2$ thin films are recorded using Hitachi U 3400 UV-VIS-NIR double beam

spectrophotometer with accuracy limits ± 0.2 nm in the UV- VIS region and ± 1 nm in the NIR region. The dc electrical conductivity measurements are made on the $LiNi_xCo_{1-x}O_2$ thin films employing the standard four-probe technique.

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 electrochemical 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 Optical properties

The optical absorbance of $LiNi_xCo_{1-x}O_2$ thin films have been studied in the vicinity of the fundamental absorption edge. Fig. 1 shows the transmission spectra of thin films in the wavelength range 300-1200 nm as a function of the growth temperature. We observed a gradual increase of the optical transmission from 400 to 1000 nm with the appearance of a prominent dip at 750 nm. This feature is more pronounced for the well-crystallized film grown at 700 ^{0}C. Plots of the optical absorbance, $(\alpha h v)^2$ versus photon energy for $LiNi_xCo_{1-x}O_2$ films are shown in Fig. 2. The variation of the optical absorption near the fundamental edge allows to determine the energy gap between d-bands of $LiNi_xCo_{1-x}O_2$. These plots gave the band gap energy of 2.39 and 2.15 eV for films grown at 500 and 700 ^{0}C, respectively, with accuracy ± 0.02 eV. These results are in good agreement with theoretical estimations [23, 24] and experimental data reported by Kushida and Kuriyama [25].

The electronic structure of the Co-3d bands of layered rock salt $LiCoO_2$ consists of three Co-t$_{2g}$ (valence bands) and two Co-e$_g$ (conduction bands). Theoretical investigations have shown that the Co-e$_g$ bands are empty and their peak position lies at around 1.7 eV above the top to the Co-t$_{2g}$ bands [23]. The density of states due to the Co-e$_g$ bands consist of a prominent peak at ~2.2 eV above the Fermi level E$_F$ in the Co-t$_{2g}$ band [24]. Recently, experimental data of optical absorption related to Co-3d bands in $LiCoO_2$ have been reported [25]. Excess of Li in $LiCoO_2$ increases the Co-O bond length leading to a small σ overlap between the O-2p and Co-3d orbitals, thereby pushing the antibonding bands (e$_g$ bands) down [24]. Thus the textured films allowed for investigation of the d-d electronic transition in $LiCoO_2$. Our experimental data that

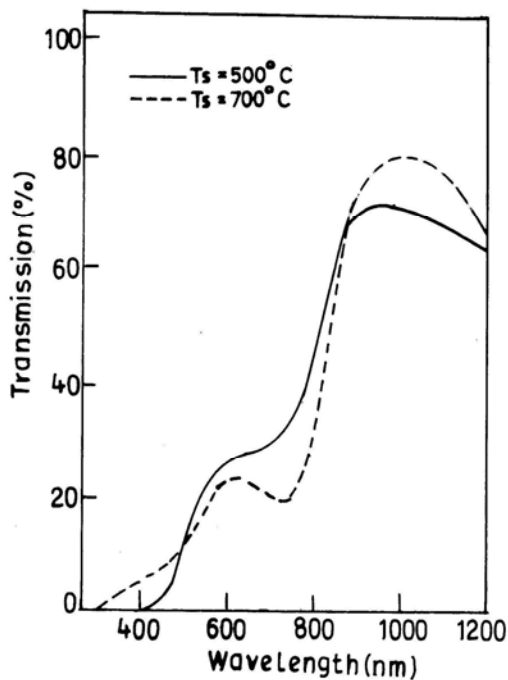is optical absorption support the above theoretical prediction.

Fig. 1. Optical transmission spectra of LiNi$_x$Co$_{1-x}$O$_2$ films deposited at different substrate temperatures in pO$_2$ = 100 mTorr
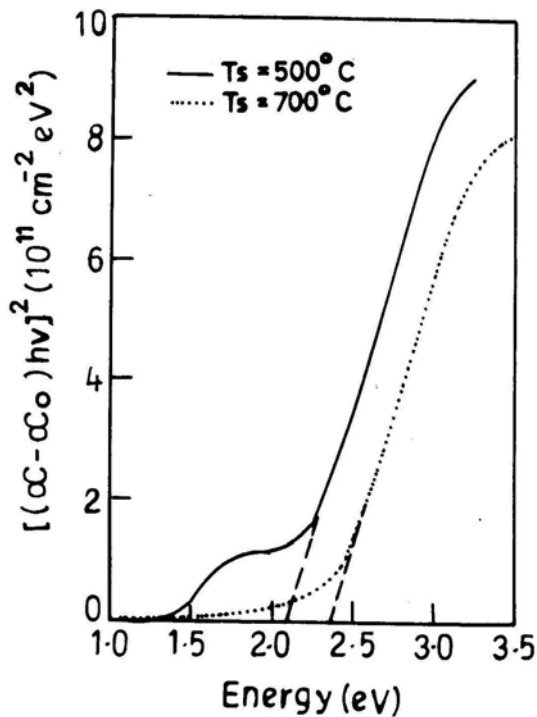

Fig. 2. Plot of the optical absorbance, (αhν)^2 vs. hν, for LiNi$_x$Co$_{1-x}$O$_2$ films deposited at different substrate temperatures in pO$_2$ = 100 mTorr

3.2 Electrical properties

Electrical transport plays an important role in the performance of the electrode in lithium microbattery. According to the electronic considerations [26], the small polaron semiconducting character of the LiCoO$_2$ compound is due to weak M-M interactions, which prevents an itinerant-electron bandwidth giving localized electronic configurations. Fig. 3 shows the temperature dependence of the dc conductivity for LiCoO$_2$ and LiNi$_x$Co$_{1-x}$O$_2$ thin films. These Arrhenius plots for the electrical conductivity showed that the conduction is thermally activated owing to the semiconducting character of these oxides. Upon nickel doping, we clearly observed a subsequent increase of the conductivity of LiCoO$_2$ film.
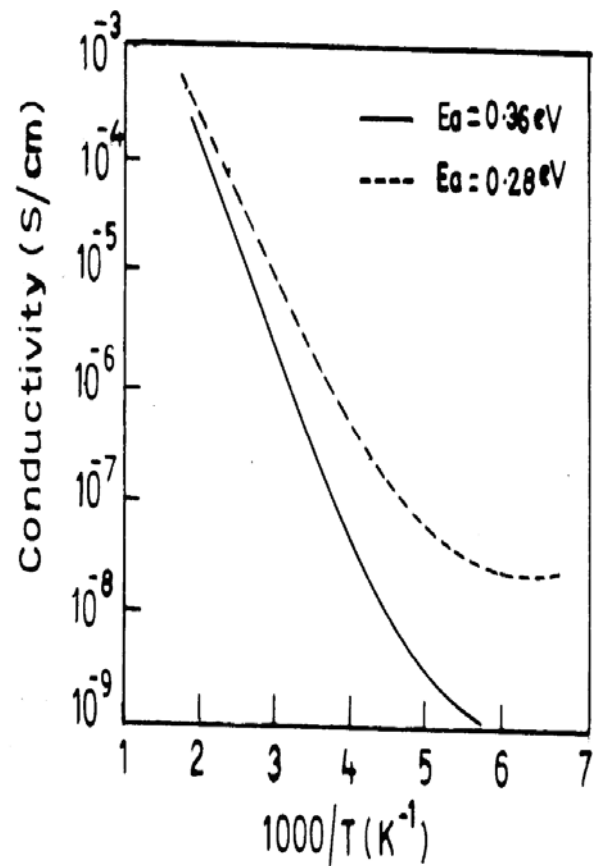

Fig. 3. Arrhenius plot of the electrical conductivity for (a) LiCoO$_2$ film and (b) LiNi$_x$Co$_{1-x}$O$_2$ thin film

The electrical conductivity of LiCoO$_2$ varies from 10^{-9} to 10^{-4} S/cm in the temperature range from 180 to 500 K. Doping the oxide network with nickel oxide leads to an increase of the electrical conductivity of one order of magnitude from 6 x 10^{-7} S/cm for LiCoO$_2$ to 9 x 10^{-6} S/cm for LiNi$_x$Co$_{1-x}$O$_2$ at room temperature. The increase of electrical conductivity could be connected with either

an enhancement in the effective carrier concentration or a decrease of the activation energy with substitution of Ni^{3+} ions for Co^{3+} ions. Examination of the data (Fig. 3) indicates that a noticeable change in the activation energy is observed in the temperature range 250–500 K. The activation energy decreases from 0.36 eV to 0.28 eV on nickel doping. These values are typical for small polaron conduction in a mixed valent system. In fact, the conduction in the semiconducting $LiCoO_2$ phase imposes Co^{4+} and Co^{3+} ions, which allows for facile transfer of charge carriers via hopping. Thus the electrical conductivity of lithium cobaltates with the layered structure ought to depend on the valencies of the cations and their distribution among the crystallographic positions in the framework. The curvature appearing in the Arrhenius plots of σ_{dc} at temperature around 280 K suggests the possibility of a variable range hopping mechanism for the small polaron transport [26].

4. Conclusions

$LiNi_xCo_{1-x}O_2$ 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 optical absorbance of $LiNi_xCo_{1-x}O_2$ thin films have been studied in the vicinity of the fundamental absorption edge. A gradual increase of the optical transmission from 400 to 1000 nm with the appearance of a prominent dip at 750 nm is observed. This feature is more pronounced for the well-crystallized film grown at 700 ^{0}C. Band gap energies of 2.39 and 2.15 eV for films grown at 500 and 700 ^{0}C, respectively, with accuracy $\pm$ 0.02 eV were measured. The electrical conductivity of $LiCoO_2$ varies from 10^{-9} to 10^{-4} S/cm in the temperature range from 180 to 500 K. Doping the oxide network with nickel oxide leads to an increase of the electrical conductivity of one order of magnitude from 6 x 10^{-7} S/cm for $LiCoO_2$ to 9 x 10^{-6} S/cm for $LiNi_xCo_{1-x}O_2$ at room temperature. The increase of electrical conductivity could be connected with either an enhancement in the effective carrier concentration or a decrease of the activation energy with substitution of Ni^{3+} ions for Co^{3+} ions. The activation energy decreases from 0.36 eV to 0.28 eV on nickel doping. These results suggest that the open and porous structured $LiNi_xCo_{1-x}O_2$ PLD films find potential applications as binder free electrode in the fabrication of all solid state microbatteries.

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