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Effect of doping on the electrochemical performance of LiCoO_2 thin films grown by pulsed laser deposition

M.C.Rao

Department of Physics, Andhra Loyola College, Vijayawada - 520 008, (INDIA)

E-mail: raomc72@gmail.com

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ABSTRACT

LiCoO_2 thin films were grown by pulsed laser deposition technique on silicon substrates. Two important deposition parameters such as substrate temperature and oxygen partial pressure during the thin film deposition were controlled. The electrochemical measurements were carried out on Li/LiCoO_2 cells with a lithium metal foil as anode and LiCoO_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. Electrochemical titration was made by charging and discharging the cells using the galvanostatic mode of a Mac-Pile single 608 electrochemical analyzer system in the potential range between 2.0 and 4.2 V. The Li/LiCoO_2 cells were tested in the potential range 2.6 – 4.2 V. Specific capacity as high as $205 \text{ mC}/\text{cm}^2\mu\text{m}$ was measured for the film grown at 700°C . The electrochemical measurements were also carried out on $\text{Li}/\text{LiTi}_x\text{Co}_{1-x}\text{O}_2$ and $\text{Li}/\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ cells. The $\text{Li}/\text{LiTi}_x\text{Co}_{1-x}\text{O}_2$ cell delivered a specific capacity of $225 \text{ mC}/\mu\text{m cm}^2$ and the $\text{Li}/\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ cell delivered a specific capacity of $220 \text{ mC}/\mu\text{m cm}^2$.

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KEYWORDS

LiCoO_2 ;
PLD films;
Electrochemical properties.

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 274 mAh/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 $\text{LiCo}_{1-x}\text{M}_x\text{O}_2$ oxides (M = Mn, Cr, Al, Ti, B, Mg, etc.), which show interesting structural and electrochemical properties^[3,4]. Doping with

non-transition metals such as titanium has gained increasing interest for the following reasons: (i) the low cost and low toxicity, (ii) the fact that titanium substitution for transition metal oxides leads to higher lithium intercalation voltages, (iii) the titanium doping stabilizes the layered structure and extends the cyclability and enhances the capability of the electrochemical cells. It is known that the electrochemical performance of the oxides is largely governed by the chemical stoichiometry, homogeneity, crystallinity and size of the particles. Preparation of titanium doped LiCoO_2 films may have advantages from a point of view of fundamental studies (because it is a binder free material with a well-defined interfacial area) and of the emerging field of microbatteries as well.

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 $x = 0.8$, resulting in improvements in the cycle life and rate of the electrodes^[5,6]. The substitution of nickel by cobalt 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 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 micro-crystallites. 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. A brief literature survey reveals that it is difficult to grow stoichiometric and stable c - axis oriented LiCoO_2 thin films by several physical vapour deposition methods due to many growth kinetic processes which occur in vacuum or at low oxygen partial pressures.

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. Another chief advantage is, PLD films crystallize at relatively low deposition temperatures than the other physical vapour deposited films. In addition, PLD is environmentally friendly. 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 $195 \text{ mC}/\mu\text{m cm}^2$ 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/SiO₂/Si (Pt) and Au/MgO/Si (Au) substrates, respectively. However the investigations on the microstructural features 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 electrochemical properties of pulsed laser deposited LiCoO_2 , $\text{Li}/\text{LiTi}_x\text{Co}_{1-x}\text{O}_2$ and $\text{Li}/\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ thin films were reported.

EXPERIMENTAL

LiCoO_2 films were grown by pulsed laser deposition technique on silicon substrates maintained at temperatures in the range 200 - 700 °C. LiCoO_2 target was prepared by sintering a mixture of high purity

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LiCoO_2 and Li_2O powders (Cerac products) with excess of Li i.e. $\text{Li/Co} > 1.0$ by adding Li_2O . The mixture was crushed and pressed at 5 tonns.cm^{-2} to make tablets of 3 mm thick and 13 mm diameter. To get quite robust targets, the tablets were sintered in air at 800°C . 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 $1 \times 3 \text{ mm}$ and the energy 300 mJ. 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 electrochemical measurements were carried out on Li//LiCoO_2 cells with a lithium metal foil as anode and LiCoO_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. Electrochemical titration was made by charging and discharging the cells using the galvanostatic mode of a Mac-Pile single 608 electrochemical analyzer system in the potential range between 2.0 and 4.2 V. Quasi open circuit voltage profiles were recorded using current pulses of $5 \mu\text{A cm}^{-2}$ supplied for 1 h followed by a relaxation period of 0.5 h. Electrochemical potential spectroscopy (ECPS) was performed using 5 mV potential steps.

RESULTS AND DISCUSSION

Pulsed laser deposited LiCoO_2 films are pin-hole free as revealed from optical microscopy and well adherent to the substrate surface. The thickness of LiCoO_2 films is 250 nm. The influence of oxygen partial pressure ($p\text{O}_2$) and deposition temperature (T_s) on the electrochemical properties of the films are systematically studied. The chemical compositional studies made on LiCoO_2 films revealed that a minimum of 100 mTorr oxygen partial pressure is required to grow nearly stoichiometric films.

The electrochemical measurements were carried out on Li//LiCoO_2 cells with a lithium metal foil as anode and LiCoO_2 film as cathode of 1.5 cm^2 active area. Typical charge discharge curves of Li//LiCoO_2 cells using pulsed laser deposited film grown at substrate temperature 700°C in an oxygen partial pressure of 100 mTorr are shown in Figure 1. Electrochemical measurements were carried out at a rate of C/100 in the potential range 2.0 - 4.2 V; as such, the voltage profile should provide a close approximation to the open circuit voltage (OCV). From the electrochemical features, we may make some general remarks that are (1) an initial voltage about 2.15 V versus Li/Li^+ was measured for LiCoO_2 thin film cathode cells, which is lower to that recorded in the galvanic cell using crystalline cathode, (2) the cell voltage profiles display the typical profile currently observed for Li_xCoO_2 cathodes, (3) the cell voltage is a function of the structural arrangement in the film and thus depends on the substrate deposition temperature. These potentials slightly increased for films grown at high substrate temperature.

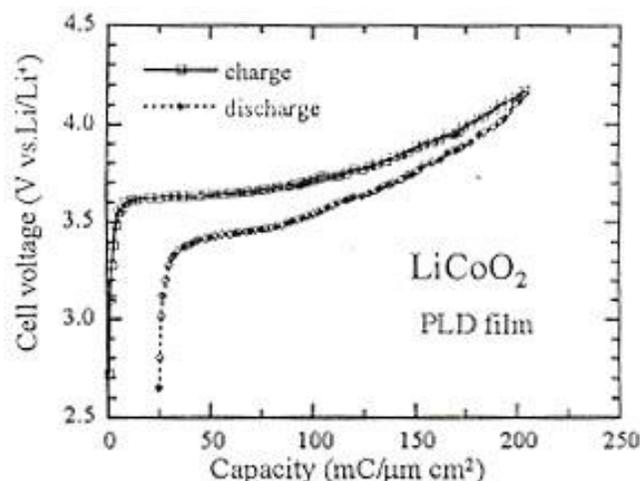


Figure 1 : Charge-discharge profile of Li//LiCoO_2 cell.

These results suggest that about 0.5 Li can be removed at charge potential up to 4.2 V. The PLD LiCoO_2 film grown at substrate temperature 700°C has interesting electrochemical properties for the microbattery application. In the high voltage region, such a cell delivers a specific capacity of $205 \text{ mC/cm}^2 \mu\text{m}^{[21]}$. This value could be compared with the theoretical specific capacity of a LiCoO_2 film $420 \text{ mC/cm}^2 \mu\text{m}$ ($116 \mu\text{Ah/cm}^2 \mu\text{m}$) assuming density of 4.28 g cm^{-3} and a theoretical gravimetric capacity 273 mAh g^{-1} for a total extraction

of Li^+ ions from the host matrix.

The electrochemical measurements were carried out on $\text{Li}/\text{LiTi}_x\text{Co}_{1-x}\text{O}_2$ cells with lithium metal foil as anode and a $\text{LiTi}_x\text{Co}_{1-x}\text{O}_2$ film as cathode of 1.5 cm^2 active area. 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. Figure 2 shows the charge discharge curves of $\text{Li}/\text{LiTi}_{0.05}\text{Co}_{0.95}\text{O}_2$ thin film cells. Electrochemical measurements were carried out at a rate of C/100 in the potential range 2.6–4.2 V; as such, the voltage profile should prove a close approximation to the open circuit voltage (OCV). The initial open-circuit voltage of the film is 2.7 V and it is cycled between 2.6 and 4.2 V. The voltage plateau at 3.65 V in the charge curve of LiCoO_2 is due to the semiconductor metal like transition of the LiCoO_2 framework. The voltage plateau at 3.65 V in the charge curve of LiCoO_2 disappears in the charge curve of $\text{LiTi}_{0.05}\text{Co}_{0.95}\text{O}_2$; this is the net result of the doping effect which cancels the semiconductor-metal like transition of the LiCoO_2 framework. On the other hand, the practical capacity for the $\text{Li}/\text{LiTi}_{0.05}\text{Co}_{0.95}\text{O}_2$ cell is larger than for the Li/LiCoO_2 cell because the slight lower averaged potential allows for deeper charge capacity in the same potential window.

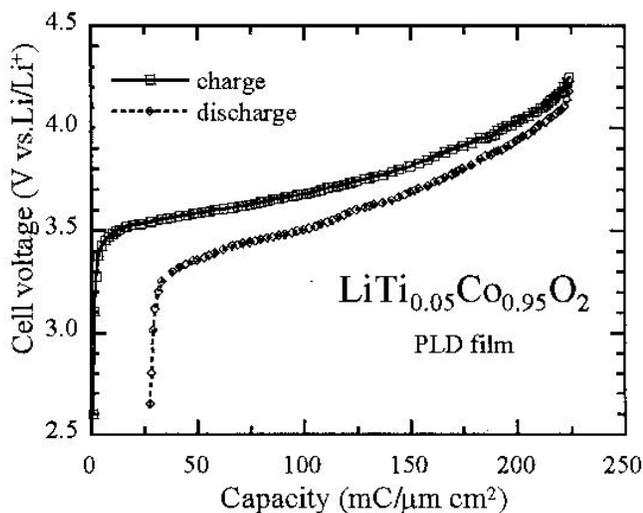


Figure 2 : Charge-discharge profile of $\text{Li}/\text{LiTi}_x\text{Co}_{1-x}\text{O}_2$ cell.

Considering the experimental error, these results suggest that about 0.5 Li can be removed at charge potential up to 4.2 V. The PLD $\text{LiTi}_{0.05}\text{Co}_{0.95}\text{O}_2$ film grown at 700°C has interesting electrochemical properties for the microbattery application. In the high voltage region,

such a cell delivered a specific capacity of $225 \text{ mC}/\mu\text{m}^2$. The capacities are observed to be retained even after 10 cycles. This result is interesting in view of the fact that we have obtained higher capacities for the titanium doped LiCoO_2 films than as deposited LiCoO_2 thin films. Thus titanium doped LiCoO_2 materials emerged as an improved active material for commercial use in lithium based batteries.

Figure 3 shows the typical charge–discharge curves of $\text{Li}/\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ cells using pulsed laser deposited film grown at temperature 700°C in an oxygen partial pressure of 100 mTorr. 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 2.4 V. The voltage plateau at 3.65 V in the charge curve of LiCoO_2 disappears in the charge curve of $\text{LiNi}_{0.2}\text{Co}_{0.8}\text{O}_2$; 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^[23]. 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 $\text{LiNi}_{0.2}\text{Co}_{0.8}\text{O}_2$ cell delivered a specific capacity of $220 \text{ mC}/\mu\text{m}^2$.

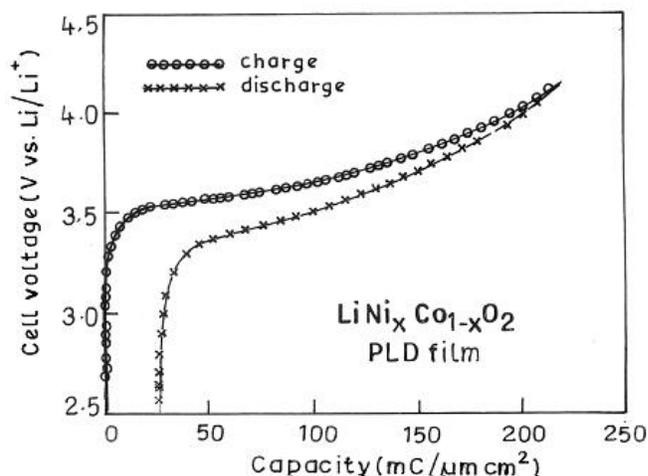


Figure 3 : Charge-discharge profile of $\text{Li}/\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ cell.

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CONCLUSIONS

LiCoO₂ thin films were prepared by pulsed laser deposition. The films were found to be uniform with regard to the surface topography and well adherent to the substrate surface. The Li/LiCoO₂ cells were tested in the potential range 2.6–4.2 V. Specific capacity as high as 205 mC/cm² μm was measured for the film grown at 700 °C. The electrochemical measurements were also carried out on Li//LiTi_xCo_{1-x}O₂ and Li//LiNi_xCo_{1-x}O₂ cells. The Li//LiTi_xCo_{1-x}O₂ cell delivered a specific capacity of 225 mC/μm cm² and the Li//LiNi_xCo_{1-x}O₂ cell delivered a specific capacity of 220 mC/μm cm². These results suggest that the open and porous structured LiCoO₂ PLD films find potential applications as binder free electrode in the fabrication of all solid state microbatteries.

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