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MICROFABRICATION OF $LiCoO_2$ THIN FILM CELL

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ABSTRACT

$LiCoO_2$ thin films were prepared by pulsed laser deposition technique on silicon substrates. 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. Cyclic voltammetry (CV) measurements have been carried out at sweep rate $\alpha = 1$ mVs^{-1}. Two sets of well defined current peaks observed corresponding to the oxidation and reduction reaction located at 3.74 and 3.64 V for the $LiCoO_2$ film. Electrochemical titration was made by charging and discharging the cells in the potential range between 2.0 and 4.2 V. Quasi open circuit voltage profiles were recorded using current pulses of 5 $\mu A\ cm^{-2}$. Electrochemical potential spectroscopy (ECPS) was performed using 5 mV potential steps. Specific capacity 180 $mC/cm^2\mu m$ was measured for the film grown at 300 mTorr.

Key words: $LiCoO_2$, Thin films, PLD, Oxygen pressure, CV.

INTRODUCTION

Advances in science and engineering related to the emerging technologies of lithium-ion batteries (LIBs) have been so spectacular in the past decade that they have become the most popular power source for portable computing, battery cars, microelectronics, biomedical implantable devices and telecommunication[1]. There is a growing interest in thin film batteries with smaller dimension. The cathode is one of the critical components of a lithium-ion battery and it determines the capacity, cyclic performance and thermal stability of the battery. In order to improve the electrochemical properties of the cathode material, researchers have attempted to modify the cathode surface by using stable materials[2]. 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[3]. $LiCoO_2$ crystallizes in the

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layered rock-salt α-$NaFeO_2$ type structure with hexagonal lattice parameters a = 2.815 Å and c = 14.049 Å. The rock salt $LiCoO_2$ lattice consists of a close packed network of oxygen ions with lithium and cobalt ions on alternating (111) planes of the cubic rock salt sublattice (Fig. 1). The Co and Li cations occupy the octahedral 3a and 3b sites, respectively, while oxygen anions are located on the 6c sites, The CoO_6 octahedra are shared edges to form CoO_2 sheets and Li ions can move in two dimensional (2-D) directions between the CoO_2 slabs.

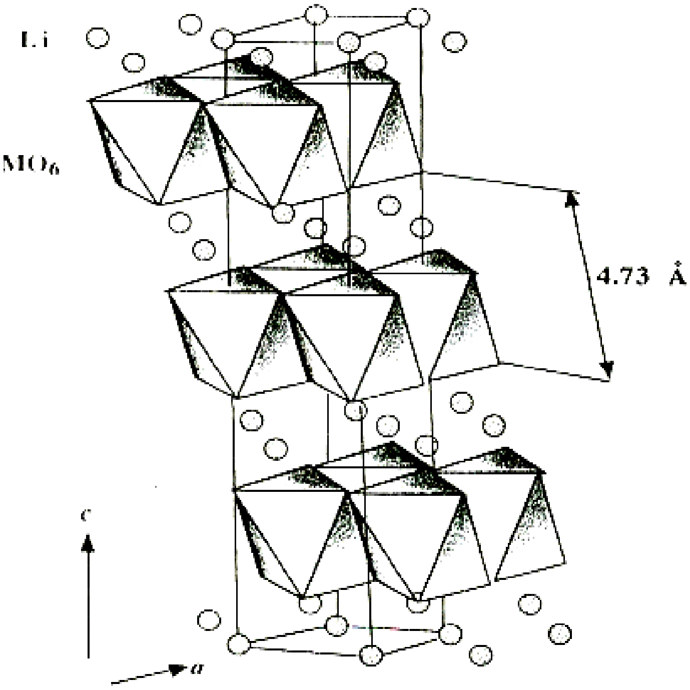

Fig. 1: The hexagonal unit cell of the α-$NaFeO_2$ structure

Thin films of $LiCoO_2$ have been synthesized by a variety of techniques including sputtering, spray deposition, reaction of metals and pulsed laser deposition. Various aspects of LiCoO2 thin films prepared by RF sputtering[3,4], pulsed laser deposition[4-7], electrostatic spray deposition[8] and chemical vapour deposition[9] 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[10]. 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. Iriyama et al.[5] prepared thin films of $LiCoO_2$ by PLD and studied the electrochemical performance. However the investigations on the electrochemical properties 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 oxygen pressure on the electrochemical properties of pulsed laser deposited $LiCoO_2$ thin films were reported.

EXPERIMENTAL

$LiCoO_2$ films were grown by pulsed laser deposition technique on silicon substrates. $LiCoO_2$ target was prepared by sintering a mixture of high purity $LiCoO_2$ and Li_2O powders (Cerac products) with excess of Li i.e. $Li/Co > 1.0$ 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^{o}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 x 3 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[11].

The electrochemical measurements were carried out on Li//$LiCoO_2$ cells. Cyclic voltammetry measurements have been carried out at sweep rate $\alpha = 1$ mVs^{-1}. 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 μA 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[12].

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 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. Fig. 2 shows the cyclic voltammogram for a Li//$LiCoO_2$ cell with a film grown at 400°C in an oxygen partial pressure of 300 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 3.74 and 3.64 V for the $LiCoO_2$ 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 3.69 V is considered to be a single-phase insertion/deinsertion reaction of lithium ions in $LiCoO_2$.

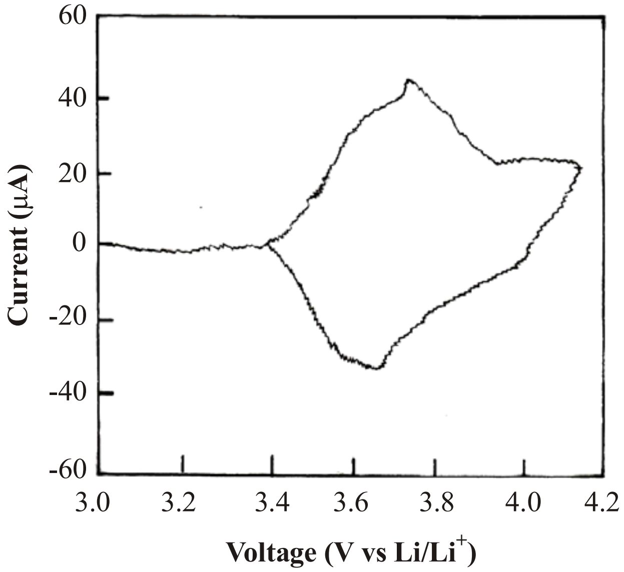

Fig. 2: Cyclic Voltammogram of Li//$LiCoO_2$ cells deposited at pO_2 = 300 mTorr

Typical charge discharge curves of Li//$LiCoO_2$ cells using pulsed laser deposited film grown at temperature 400°C in an oxygen pressure of 300 mTorr are shown in Fig. 3. 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[13,14], (2) the cell voltage profiles display the typical profile currently observed for Li_xCoO_2 cathodes. These potentials slightly decreased for films grown at higher oxygen pressures. The incremental capacity curve ($-\delta$ x /δV) versus cell voltage for the Li//$LiCoO_2$ thin film cell that is derived from the charge curve (Fig. 3) exhibits only one well defined voltage, which displays a peak centered at 3.64 V. The electrochemical process seems to be a classical intercalation mechanism for the lithium ions into the Li_xCoO_2 matrix as indicated by the peak. These results suggest that about 0.5 Li can be removed at charge potential up to 4.2 V. In the high voltage region, such a cell delivers a specific capacity of 180 mC/cm^2 μm[11-13].

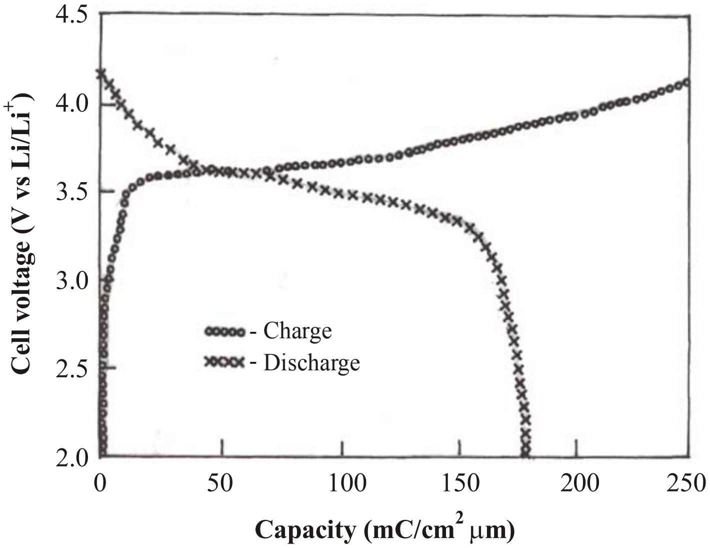

Fig. 3: Charge-discharge profile of Li//$LiCoO_2$ cells deposited at pO_2 = 300 mTorr

CONCLUSION

Thin films of $LiCoO_2$ were prepared by pulsed laser deposition. PLD films were found to be uniform with regard to the surface topography, thicknesses and well adherent to the substrate surface. Cyclic voltammetry measurements have been carried out at sweep rate $\alpha = 1$ mVs^{-1}. The redox couple with a mid-peak potential of about 3.69 V is considered to be a single-phase insertion/deinsertion reaction of lithium ions in $LiCoO_2$. The Li//$LiCoO_2$ cells were tested in the potential range 2.6 – 4.2 V. Specific capacity 180 mC/cm^2 μm was measured for the film grown at 300 mTorr. These results suggest that the open and porous structured $LiCoO_2$ PLD films find potential applications as binder free electrode in the fabrication of all solid state microbatteries.

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