



Trade Science Inc.

Materials Science

An Indian Journal

Full Paper

MSAIJ, 5(4), 2009 [451-454]

Electrochemical properties of pulsed laser deposited LiCoO₂ thin film cathodes

M.C.Rao

Department of Physics, Andhra Loyola College, Vijayawada – 520008, (INDIA)

E-mail : raomc72@gmail.com

Received: 12th June, 2009 ; Accepted: 22nd June, 2009

ABSTRACT

Thin films of LiCoO₂ 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. Electrochemical measurements were carried out on Li//LiCoO₂ cells with a lithium metal foil as anode and a LiCoO₂ film as cathode of 1.5 cm² active area. Cyclic voltammetry (CV) measurements have been carried out at sweep rate $\alpha = 1 \text{ mVs}^{-1}$. The Li//LiCoO₂ cells were tested in the potential range 2.6 – 4.2 V. Specific capacity as high as 205 mC/cm²μm was measured for the film grown at 700 °C. © 2009 Trade Science Inc. - INDIA

KEYWORDS

LiCoO₂ thin films;
PLD;
Electrochemical.

INTRODUCTION

Lithiated transition metal oxides such as LiMO₂ (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^[1]. Among these, the high cycling stability and high cell potential against lithium makes LiCoO₂ an attractive cathode material in the fabrication of all solid state rechargeable microbatteries^[2,3]. 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.

The layered LiCoO₂ consists of a close packed network of oxygen ions with Li and Co ions on alternative (111) planes of the cubic rocksalt sub-lattice. The edges of CoO₆ octahedral were shared to form CoO₂ sheets and lithium ions can move in two-dimensional direc-

tions between CoO₂ sheets. Thus the layered LiCoO₂ has an anisotropic structure and thereby electrochemical lithium insertion / extraction behaviour must depend strongly on the orientation of the microcrystallites. The growth of LiCoO₂ thin films with preferred orientation is known to be crucial. Several thin film deposition techniques such as RF sputtering^[2,4], pulsed laser deposition^[4-8], electrostatic spray deposition^[9] and chemical vapour deposition^[10] were employed for the growth of LiCoO₂ thin films. A brief literature survey reveals that it is difficult to grow stoichiometric and stable c - axis oriented LiCoO₂ thin films by several physical vapour deposition methods due to many growth kinetic processes which occur in vacuum or at low oxygen partial pressures.

Pulsed laser deposition (PLD) has been widely recognized as a very promising, versatile and efficient method for the deposition of metal oxide thin films^[11]. When PLD is carried out in the atmosphere of a chemi-

Full Paper

cally 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. Preliminary investigations on pulsed laser deposited LiCoO_2 thin films were carried out by Julien et al.^[5], Iriyama et al.^[6] and studied the electrochemical performance. They observed that the reactivity in single-phase region at potentials more positive than 4.0 V was lower than that of randomly oriented films. Poly-crystalline layered $R\bar{3}m$ phase thin films of LiCoO_2 were grown by PLD using Nd:YAG laser by Julien et al.^[12]. This LiCoO_2 cathode active films were found to deliver a specific capacity of $195 \text{ mC/cm}^2\mu\text{m}$ in the voltage range 2.0 - 4.2 V. In the present study the influence of deposition parameters 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 maintained at temperatures in the range 200 - 700 °C. 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. $\text{Li/Co} > 1.0$ 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 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. Figure 1 shows the cyclic voltammogram for a Li/LiCoO_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 3.73 and 3.63 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 3.68 V is considered to be a single-phase insertion/deinsertion reaction of lithium ions in LiCoO_2 . Figure 2 shows the cyclic voltammogram for a Li// LiCoO_2 cell with a film grown at temperature 300 °C in an oxygen partial pressure of 100 mTorr. The peaks are slightly shifted to lower potential due to the small grain size for the films grown at lower substrate temperature.

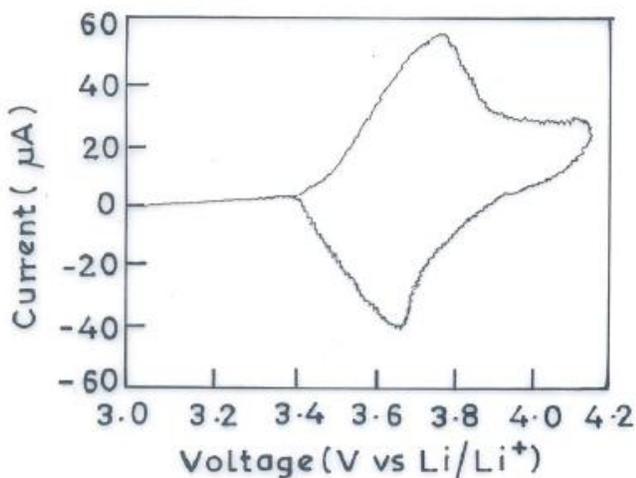


Figure 1 : Cyclic Voltammogram of Li// LiCoO_2 cells deposited at 700 °C

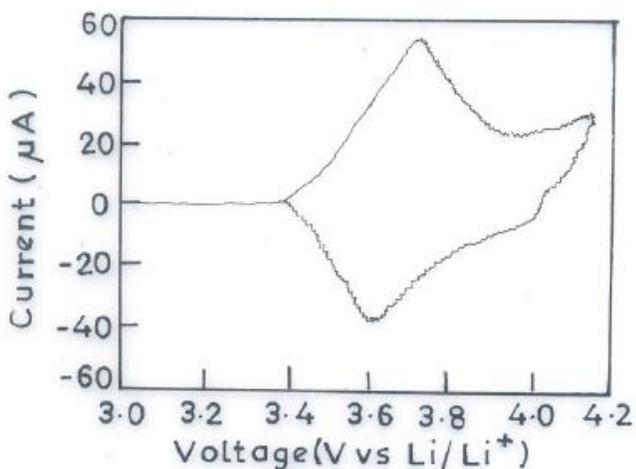


Figure 2 : Cyclic Voltammogram of Li// LiCoO_2 cells deposited at 300 °C

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 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], (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.

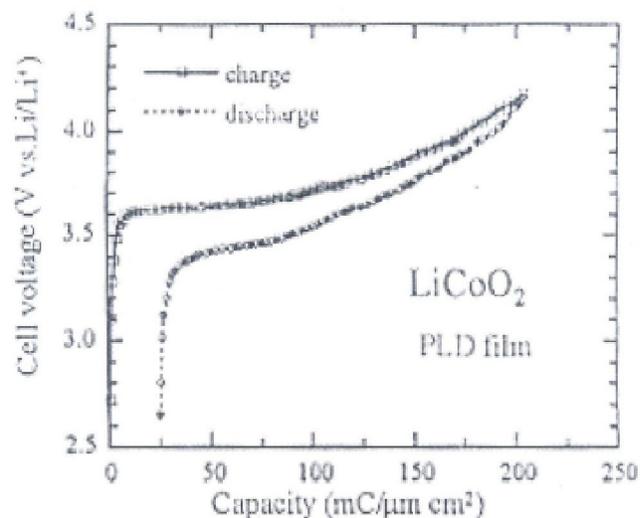


Figure 3 : Charge-discharge profile of Li// LiCoO_2 cells deposited at 700 °C

The incremental capacity curve ($-\delta x/\delta V$) versus cell voltage for the Li// LiCoO_2 thin film cell that is derived from the charge curve (Figure 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. 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 $\text{mC}/\text{cm}^2\ \mu\text{m}^2$ ^[12]. The potentials are slightly decreased for the films grown at 300 °C and the cell delivered a higher specific capac-

Full Paper

ity of $190 \text{ mC/cm}^2 \mu\text{m}$. 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.

CONCLUSIONS

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 (CV) measurements have been carried out at sweep rate $\alpha = 1 \text{ mVs}^{-1}$. The Li//LiCoO_2 cells were tested in the potential range $2.6 - 4.2 \text{ V}$. Specific capacity as high as $205 \text{ mC/cm}^2 \mu\text{m}$ was measured for the film grown at $700 \text{ }^\circ\text{C}$. This performance is due to the good crystallinity of the LiCoO_2 films grown by PLD technique. 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.

REFERENCES

- [1] T.Ohzuoku; 'Lithium Batteries, New Materials, Developments and perspectives', G.Pistoia, p.239, Elsevier, Amsterdam, (1993).
- [2] B.J.Neudecker, N.J.Dudney, J.B.Bates; J.Electrochem.Soc., **147**, 517 (2000).
- [3] J.B.Bates, N.J.Dudney, B.Neudecker, A.Veda, C.D.Evans; Solid State Ionics, **135**, 33 (2000).
- [4] P.J.Bouwman, B.A.Boukamp, H.J.M.Bouwmeester, P.H.L.Notten; Solid State Ionics, **152**, 181 (2002).
- [5] C.Julien, E.Haro-Poniatowski, O.M.Hussain, C.V.Ramana; Ionics, **7**, 165 (2001).
- [6] Y.Iriyama, T.Inabu, T.Abe, Z.Ogumi; J.Power Sources, **94**, 175 (2001).
- [7] H.Xia, L.Lu, G.Ceder; J.Power Sources, **159**, 1422 (2006).
- [8] S.B.Tang, M.O.Lai, L.Lu; J.Alloys and compounds, **449**, 300 (2008).
- [9] C.H.Chen, A.A.J.Buysman, E.M.Kelder, J.Schoonman; Solid State Ionics, **80**, 1 (1995).
- [10] W.-G.Chai, S.-G.Yoon; J.Power Sources, **125**, 236 (2004).
- [11] J.C.Miller, R.F.Haglmel Jr.; 'Laser Ablation and Deposition', J.C.Miller, R.F.Haglmel, Academic Press, New York, (1998).
- [12] C.Julien, M.A.Camacho-Lopez, L.Escobar-Alavcon, E.Haro-Poniatowski; Mater.Chem.Phys., **68**, 210 (2001).
- [13] E.A.Davis, N.F.Mott; Philos.Mag., **22**, 903 (1970).