CHAPTER - III

GROWTH AND CHARACTERIZATION OF LiCoO$_2$ THIN FILMS
3.1 Introduction

The high cycling stability and high cell voltage against lithium makes LiCoO$_2$ as an attractive cathode material in the fabrication of all solid state rechargeable microbatteries [1-3]. The deposition and characterization of LiCoO$_2$ in thin film form is very essential for their effective use as cathode materials in the cell fabrication since the growth of LiCoO$_2$ with preferred orientation is known to be crucial. Also LiCoO$_2$ is a complex material with highly volatile elements, maintaining the stoichiometry in the films is another difficult task. Several thin film deposition techniques [4-12] were employed for the growth of LiCoO$_2$ thin films. A brief literature survey mentioned in the introduction chapter reveals that it is difficult to grow stoichiometric single phase 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.

The pulsed laser deposition (PLD) has been widely recognized as a very promising, versatile and efficient method for the deposition of metal oxide thin films. PLD owes several advantages over the other techniques visually stoichiometric transfer of chemically complex materials, reactive deposition, growth of high quality films from an energetic beam, simplicity in the experimental design and process controls during multilayer growth and possible growth of meta stable phases. Hence in the present investigation thin films of LiCoO$_2$ were deposited using pulsed laser deposition technique. The films were grown at various substrate temperatures 100-700 °C and oxygen partial pressures 10-300 mTorr. The films were systematically characterized by studying their composition, structure, surface morphology, vibrational, optical and electrical properties and the deposition conditions were optimized. The electrochemical properties of these films were studied to understand the kinetics of lithium insertion in those films. The results of these investigations were systematically presented in this chapter.
3.2 Preparation of LiCoO₂ thin films

LiCoO₂ films were grown by pulsed laser deposition technique on silicon substrates maintained at temperatures in the range 100 - 700 °C. LiCoO₂ target was prepared by sintering a mixture of high purity LiCoO₂ and Li₂O powders (Cerac products) with excess of Li i.e., Li/Co > 1.0 by adding Li₂O to compensate the loss of lithium during the deposition [10]. The mixture was crushed and pressed at 5 tons.cm⁻² to make tablets 3 mm thick and 13 mm diameter. To get quite robust targets, the tablets were sintered in air at 800 °C. Highly polished and thoroughly cleaned silicon wafers were used as substrates. 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 power density at the target surface was 10 Jcm⁻². The target to substrate distance was maintained at 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 oxygen partial pressure was varied from 10-300 mTorr.

3.3 Results and Discussion

Pulsed laser deposited LiCoO₂ films are pin-hole free as revealed from optical microscopy and well adherent to the substrate surface as tested by scratch tape method. The good film integrity is favourable for electrochemical testing. The thickness of LiCoO₂ films is 250 nm. The structural and morphological properties of the films were found to be highly influenced by the process parameters (deposition temperature and oxygen partial pressure) during the film deposition. The influence of oxygen partial pressure (pO₂) and deposition temperature (Tₐ) on the properties of the films was systematically studied.
3.3.1 Structure

The X-ray diffraction pattern for LiCoO₂ powder synthesized at 800 °C is shown in Fig. 3.1. The pattern shows a random orientation of the LiCoO₂ structure with three major, well defined reflections of (003), (104) and (101). This indicates that the starting material is LiCoO₂ polycrystalline powder with R3m layered rock salt structure. The X-ray diffraction pattern of the films deposited at a substrate temperature < 200 °C was found to be broad and diffused indicating that the films are X-ray amorphous, whereas the films formed at higher substrate temperature were polycrystalline with predominantly (00l) orientation.

![X-ray diffraction pattern of LiCoO₂ target.](image)

Fig. 3.1. X-ray diffraction pattern of LiCoO₂ target.

Fig. 3.2 shows the X-ray diffraction patterns of LiCoO₂ films grown from pure and lithium rich targets on silicon wafers maintained at $T_s = 300$ °C in an oxygen partial pressure of 100 mTorr. The X-ray diffraction spectra of the films grown from pure LiCoO₂ target displayed (Fig. 3.2(a)) the presence of two additional small peaks at about $2\theta = 45$ and 59°, which are attributed to the presence of cobalt oxide impurity...
(namely the Co$_3$O$_4$ phase) due to lithium deficiency [10]. As the amount of Li$_2$O increased in the target, the XRD patterns develop features expected for the hexagonal LiCoO$_2$ phase. The X-ray diffraction pattern of the films (Fig. 3.2(b)) deposited from 15% excess Li$_2$O target exhibited predominantly (00l) orientations without the additive Co$_3$O$_4$ impurity phases indicating that the films are of single phase with hexagonal structure. These results indicate that an optimum of 15% excess Li$_2$O in the target is necessary to overcome lithium deficiency in the films.

Fig. 3.2. X-ray diffraction patterns of (a) thin film deposited from a LiCoO$_2$ target without Li$_2$O, and (b) thin film deposited from a LiCoO$_2$ target with 15% of Li$_2$O
The X-ray diffraction pattern of the films displayed only two sharp and intense peaks at $2\theta = 18.95$ and $38.48^\circ$, which are indexed as the (003) and (006) reflections, respectively, of hexagonal LiCoO$_2$. Other reflections such as (101), (012) and (104), which are usually observed for LiCoO$_2$ powder samples [14] were not observed in the XRD pattern. The absence of the reflection lines other than the (00l) lines indicated that the film had a preferred c-axis (003) orientation perpendicular to the substrate surface. In fact, this is the advantage of PLD for growing oriented films at low temperatures around 300 $^\circ$C when compared to other physical deposition methods like electron beam evaporation and sputtering. The observed c-axis orientation can be explained by the lowest surface energy of the (003) plane because it is the most closely packed plane of LiCoO$_2$, according to Braives's empirical law [15]. Bates et al. [16] reported that very thin LiCoO$_2$ films (0.1 $\mu$m or less) prepared by RF sputtering tend to have c-axis orientation. The thicknesses of the c-axis oriented films obtained in the present study were thicker (around 0.25 $\mu$m) than their criterion, but the tendency was in agreement with their results.

The X-ray diffraction patterns of LiCoO$_2$ thin films grown at different substrate temperatures using lithium rich target are shown in Fig. 3.3 and 3.4. In all the X-ray diffraction patterns, the (003) orientation was observed to be more predominant. The films deposited at substrate temperatures less than 500 $^\circ$C displayed only (003) and (006) orientations. Whereas the films deposited at higher substrate temperatures displayed (101), (012) and (104) orientations in addition to (003) and (006) reflections. The relative intensity of (104) orientation increased with the increase of substrate temperature. A slight shift is observed in the position of (003) orientation towards higher 2$\theta$ value with the increase of substrate temperature. The lattice parameters of LiCoO$_2$ films deposited at 700 $^\circ$C obtained from a least square fit of the reflections (003), (101), (006), (012) and (104) gave $a = 2.815$ and $c = 14.061$ $\text{Å}$. These results indicate that the films deposited at 700 $^\circ$C in an oxygen partial pressure of 100 mTorr has close reflection pattern to that of powder sample indicating that the film had practically no preferred orientation. The lattice parameter values are in good agreement with the powder file data. Higher deposition temperatures provide sufficient kinetic
energy for the rearrangement of lithium, cobalt and oxygen atoms to grow polycrystalline films with higher grain size. As the particle size increases, the lattice of the deposited film expands and the volume of the film increases and the film may be in nearly stress free state. The grain size decreased with the decrease of substrate temperature.

Fig. 3.3. X-ray diffraction patterns of LiCoO$_2$ thin films deposited at different substrate temperatures in pO$_2$ = 100 mTorr
During the film deposition process at lower substrate temperature \( (T_s \leq 400 \, ^\circ C) \) the film may grow with preferred orientation to minimize the surface energy in which the compressive stresses due to smaller grain size are predominant. It is believed that (003) plane has the lowest surface energy since it has highest atomic density of the planes. Therefore, the percentage of (003) oriented grains will increase at lower substrate temperatures.

![X-ray diffraction patterns of LiCoO\(_2\) thin films deposited at different substrate temperatures in pO\(_2\) = 100 mTorr](image)

**Fig. 3.4.** X-ray diffraction patterns of LiCoO\(_2\) thin films deposited at different substrate temperatures in pO\(_2\) = 100 mTorr
3.3.2 Composition

The X-ray photoelectron spectroscopic technique was used to determine the binding energies of the constituent elements. The sample was irradiated with soft monochromatic X-rays (Al K$_\alpha$ = 1486.6 eV). The ICP-AES (Perkin - Elmer plasma 40 emission spectrometer) was used to determine the composition. The X-ray photoelectron spectroscopic studies were performed on the films prepared at various substrate temperatures and oxygen partial pressures.

A typical X-ray photoelectron spectra of LiCoO$_2$ thin films deposited at 700°C and in an oxygen partial pressure of 100 mTorr is shown in Fig. 3.5. The binding energy peak position of lithium, cobalt and oxygen are evidenced in the XPS spectra. There is no sign of broadening or splitting of the peaks. The binding energy peaks of Co (2p$_{3/2}$) and Co (2p$_{1/2}$) are observed at 779.3 eV and 794.4 eV which can be attributed to the Co$^{3+}$ bonding state of LiCoO$_2$ and are in good agreement with the previous results [13]. The energy separation (ΔE) of the spin orbit splitting of Cobalt 2p levels is 15.1 eV. The binding energy of lithium is at 54.0 eV indicating that the lithium atoms are in an octahedral environment of oxygen atoms. The oxygen O(1s) core level was observed at 530.5 eV. The Li/Co ratio estimated from ICP-AES data for these films is found to be 1:1. The intensity of core level binding energy peak of Co (2p) decreased for the films deposited at lower substrate temperatures. However the peak positions are observed to be similar except the broadening of the binding energy peaks. These results indicate that there is no severe variation in the composition of the films deposited in the temperature range 300 - 700°C.

The composition of films was found to be a strong function of oxygen partial pressure. A shift in Co (2p$_{3/2}$) towards higher energy value was observed with a reduction in the energy separation (ΔE) of spin orbit splitting of Co (2p) levels was observed for the films formed at lower oxygen partial pressures (< 100 mTorr). The oxygen to cobalt ratio for the films deposited at lower oxygen partial pressures decreased and found to be 1.76 for the films formed at an oxygen partial pressure of
50 mTorr. The core level binding energy peak positions observed from XPS data and the estimated Li/Co ratio of the LiCoO$_2$ films deposited in an oxygen partial pressure of 100 mTorr and in the substrate temperature range 300-700 °C indicates that the films are nearly stiochiometric.

![XPS binding energy core levels](image)

**Fig. 3.5.** The XPS binding energy core levels of (a) Li (1s) (b) O (1s) (c) Co (2p$_{3/2}$) and Co (2p$_{1/2}$)
3.3.3 Surface morphology

The microstructural and surface morphological properties of laser ablated LiCoO$_2$ thin films grown at various deposition conditions were studied using atomic force microscopy (AFM) and scanning electron microscopy (SEM) techniques.

3.3.3(a) Atomic force microscopy

The atomic force microscopy data demonstrated that the pulsed laser deposited LiCoO$_2$ thin films are homogeneous and uniform with regard to the surface topography and thickness over an area of 1 cm$^2$. Fig. 3.6(a) shows the surface topography of LiCoO$_2$ films deposited for pure target on silicon substrates recorded by atomic force microscopy at $T_s = 300\,^\circ$C in $p_{O_2} = 100$ mTorr. The surface of the films is composed of irregular grains with high root mean square surface roughness of about 18 nm. The effect of target composition on the film morphology can be seen from the micrographs as long as the layer thicknesses are similar. The AFM picture of LiCoO$_2$ thin films deposited at $300\,^\circ$C in an oxygen partial pressure of 100 mTorr prepared from target with 15\% Li$_2$O (Fig. 3.6(b)) reveals that the film is composed of roughly spherical grains of varying sizes and the average grain size is estimated to be around 80 nm. The root mean square surface roughness of the films derived from AFM data is 8 nm. The individual grains are clearly visible and are seem to be in good contact with each other. The films exhibit characteristic open and porous structure with small grains at lower substrate temperature ($300\,^\circ$C). In fact this is the advantage of the PLD where nanocrystalline films can be grown at lower substrate temperatures compared to other physical vapour deposition methods. Because of the short distance between the target and the substrate in the PLD technique the films exhibit dense layers with small grains at lower substrate temperatures.
Fig. 3.6. AFM images of (a) thin film deposited from LiCoO$_2$ pure target, and (b) thin film deposited from LiCoO$_2$ target with 15% Li$_2$O.
Fig. 3.7. AFM images of LiCoO$_2$ thin films deposited at different substrate temperatures in $pO_2 = 100$ mTorr.
The increase in grain size with deposition temperature is clearly observed in AFM data and found to be around 210 nm for the films deposited at 700 °C (Fig. 3.7(b)) with a root mean square surface roughness of about 15 nm. The surface roughness increases due to the randomness of the grain distribution at higher substrate temperatures. Fig. 3.8 shows the variation of grain size with the rise in temperature. 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 [17]. The observed increase in grain size from AFM data with substrate temperature is in consistent with the XRD result.

Fig. 3.8. Variation of grain size of LiCoO₂ thin films with substrate temperature
3.3.3 (b) Scanning electron microscopy

The surface morphological features of pulsed laser deposited films grown at various substrate temperatures were also studied by scanning electron microscopy and the results are compared with AFM data.

Scanning electron micrographs of pulsed laser deposited LiCoO₂ films grown in oxygen partial pressure \( pO_2 = 100 \text{ mTorr} \) on silicon wafers maintained at 300 °C and 700 °C are shown in Fig. 3.9.

Fig. 3.9. SEM images of LiCoO₂ thin films deposited at different substrate temperatures: \( T_s = 700 \text{ °C} \) and \( T_s = 300 \text{ °C} \).
The SEM micrograph of LiCoO$_2$ thin film grown at 300 °C exhibits a smooth surface with small roughly spherical grains. For the films deposited at 700 °C the surface morphology appears to be slightly different. In this case, the film displayed a surface roughness with larger small grains of irregular shape. It was reported that high the substrate temperature, the less porous the layer [18, 19]. Therefore, the reaction between LiCoO$_2$ and Li$_2$O contributes to the formation of this dense morphology. These results are in consistent with the AFM data.

3.3.4 Vibrational studies

The Vibrational modes, which involve primarily atomic motion of cations against their oxygen neighbours, are sensitive to the crystal symmetry and cationic valence state and, consequently, frequency and strength of these oxides are very sensitive to the cationic local environment in the host matrix [20]. The purpose of this study is to investigate the local environment of cations in a cubic close-packed oxygen array of the LiCoO$_2$ lattice using Raman and FTIR spectroscopies. FTIR modes correspond to vibrations involving primary atomic motion of cations against their oxygen neighbours. Consequently these modes are very sensitive to the cationic local environment in the host matrix.

3.3.4(a) Raman studies

The Raman spectroscopic studies were performed on pulsed laser deposited films using the Raman-laser apparatus (Jobin-Yvon U1000) to understand the crystal system in the films. This system was equipped of holographic grating double-monochromator, an intermediate spatial filter and a computer-controlled photon-counting system. The emission from a laser (Spectra-Physics, 2020 argon-ion) with a wavelength of 514.5 nm was used. The frequency stability and the accuracy of the apparatus were checked recording the Raman spectrum of silicon. To avoid sample photo-decomposition or denaturation, the RS spectra were recorded using a low power density of 100 W/cm$^2$. LiCoO$_2$ possesses the R3m space group, D$^{3d}_{3d}$ spectroscopic
symmetry. According to the results of the theoretical factor-group analysis, two modes are active in the Raman spectrum \((A_{1g} \& E_g)\) of the LiCoO\(_2\) crystal [20]. Fig. 3.10(a-c) shows the unpolarized Raman scattering spectra of LiCoO\(_2\) films deposited on silicon maintained at 300 \(^\circ\)C in oxygen partial pressure \(pO_2 = 100\) mTorr as a function of the target composition.

![Raman spectra](image)

**Fig. 3.10.** Raman spectra of LiCoO\(_2\) thin films deposited from composite target with different concentrations of Li\(_2\)O: (a) without Li\(_2\)O (b) 10 wt.% , and (c) 15 wt.%

These spectra displayed the Raman active mode of the silicon wafer at 520 cm\(^{-1}\). The experimental Raman data consist of a series of broad bands located
between 400 and 700 cm\(^{-1}\). The RS peak positions at 484 and 592 cm\(^{-1}\) of PLD LiCoO\(_2\) films are in good agreement with those reported for the LiCoO\(_2\) crystal [21]. The vibrational signature of the LiCoO\(_2\) matches well the two allowed Raman modes. The peak located at 693 cm\(^{-1}\) in Raman spectra (Fig. 3.10(a) and (b)) indicates the presence of Co\(_3\)O\(_4\) impurities in the film [22]. The formation of Co\(_3\)O\(_4\) is related to lithium loss during the deposition process. In order to compensate this loss we have prepared films from lithium rich targets including addition of 10 and 15% of Li\(_2\)O concentration. The corresponding spectra are shown in Fig. 3.10(b-c). Upon addition of Li\(_2\)O, the peak at 693 cm\(^{-1}\) decreased substantially indicating the disappearance of Co\(_3\)O\(_4\) species as it is shown in the RS spectra (Fig. 3.10(c)). The optimum concentration of Li\(_2\)O to compensate the lithium loss must be 15% of Li\(_2\)O. LiCoO\(_2\) possesses the prototype symmetry R-3m of the rock-salt structure, where the cobalt cations reside on the octahedral 3a sites, the lithium ions occupy the octahedral 3b interstices, and the oxygen anions are in a cubic close-packing, occupying the 6c sites [22]. According to the results of the theoretical factor-group analysis, two modes are active (A\(_{1g}\) and E\(_g\)) in the Raman spectrum of the LiCoO\(_2\) crystal [23]. It is also convenient to analyze the RS spectrum in terms of localized vibrations, considering the rock-salt structure built of CoO\(_6\) and LiO\(_6\) octahedra [21]. The Raman band located at 592 cm\(^{-1}\) can be viewed as the symmetric Co-O stretching vibration of CoO\(_6\) groups. This band is assigned to the A\(_{1g}\) symmetry in the D\(^{5}_{3d}\) spectroscopic space group. Its broadening could be related with the cation-anion bond lengths and polyhedral distortion occurring in LiCoO\(_2\). The RS peak at 484 cm\(^{-1}\) derives from the E\(_g\) species. The Raman bands are likely lie to the motions involving mainly the Co-O stretching and O-Co-O bending, as the contributions of the Raman modes are only from the motion of the oxygen atoms.

The polarized scattering spectra show uniaxially (003) textured LiCoO\(_2\) thin films. Based on the intensity ratio of Raman spectra, the peaks situated at 484 and 592 cm\(^{-1}\) correspond to the E\(_g\) and A\(_{1g}\) optical modes of LiCoO\(_2\), respectively [21]. The polarization dependence of the recorded spectra is consistent with the prediction for phonon symmetries. These results show that, as expected, the A\(_{1g}\) stretching mode should be at higher energy than the E\(_g\) bending mode.
Information for the structural quality of the PLD LiCoO₂ films can be given considering the Raman data using the shape and the frequency of two peaks located in the low and high frequency region of the spectra. When the PLD films were grown from target with Li₂O ≤ 15%, the oscillator strength of the A₁₈ stretching mode of RS spectra rose with a narrow full width at half maximum (FWHM). This phenomenon is due to the well-defined rock-salt structure of the films and the regular distortion of CoO₆ octahedra. As the stretching mode is sensitive to the film morphology, low FWHM values provide evidence for the rock-salt-like structure for samples grown at a high substrate temperature. These spectroscopic results indicate that the conjunction of target composition (lithium-rich), substrate temperature (T, > 300 °C), and oxygen partial pressure (pO₂ = 100 mTorr) promotes reconstruction of the stoichiometric LiCoO₂ layered framework.

Fig.3.11. Raman spectra of LiCoO₂ thin films deposited at different substrate temperatures in pO₂ = 100 mTorr

Raman spectroscopy is also useful to distinguish between different symmetries in a given material. Fig.3.11 shows non-polarized Raman spectra of thin films deposited at different temperatures in pO₂ = 100 mTorr. The spectra are nonpolarized by the intensity of the A₁₈ peak at 592 cm⁻¹. I₄₈₄ and I₉₉₄ are referred as intensities of the E₉ and
A_{1g} bands respectively. The $I_{484}A_{594}$ increased with a decrease in the degree of the c-axis orientation of the films. The film deposited at 700 °C in $p_O_2 = 100 \text{ mTorr}$, indicating that the film had no preferred orientation. These results are in good agreement with the results reported by Iriyama et al. [9] and also in consistent with XRD data.

3.3.4(b) Fourier transform infrared (FTIR) spectroscopy

Experimental FTIR spectra of LiCoO$_2$ thin films have been recorded at various stages of pulsed laser deposition. LiCoO$_2$ possesses the R3m space group, $D_3^1$ spectroscopic symmetry. According to the results of the theoretical factor-group analysis, four modes are active in the infrared spectrum ($2A_{2u} & 2E_u$) of the LiCoO$_2$ crystal [20]. Fig. 3.12 shows the FTIR spectrum of LiCoO$_2$ thin films deposited on silicon substrate maintained at temperature 700 °C in an oxygen partial pressure $p_O_2 = 100 \text{ mTorr}$.

![FTIR spectrum of LiCoO$_2$](image)

**Fig. 3.12.** FTIR spectra of LiCoO$_2$ deposited at 700 °C in $p_O_2 = 100 \text{ mTorr}$

The spectrum displayed the characteristic IR dominant bands at 250 and 554 cm$^{-1}$ for LiCoO$_2$. The former is attributed to the asymmetric stretching mode of the octahedral LiO$_6$ units, while the latter is due to the asymmetric stretching vibration of
CoO$_6$ groups. FTIR features presented in Fig. 3.12 are in good agreement with elemental analysis.

### 3.3.5 Optical properties

The study of optical absorption, particularly the absorption edge, has proved to be very useful for elucidation of the electronic structure of the materials. It is possible to determine whether the optically induced transition is direct or indirect and allowed or forbidden by analysis of the absorption edge.

The optical absorption coefficient of the films is evaluated using the relation

$$\alpha = \frac{1}{t} \ln \left( \frac{T}{(1-R)^2} \right) \quad \text{(3.1)}$$

Where $T$ is the transmittance, $R$ is the reflectance and $t$ the thickness of the film.

For an incident photon energy greater than the band gap and above the exponential tail the optical absorption follows a power law [24] of the form

$$\alpha(h\nu) = B(h\nu - E_g)^n \quad \text{(3.2)}$$

Where $B$ is a constant, $E_g$ is the band gap of the material and $n$ is the exponent. The exponent $n$ determines the type of electronic transition causing the absorption and take the values 1/2, 3/2, 2 and 3 for direct allowed, direct forbidden, indirect allowed and indirect forbidden transitions respectively [25].

The optical absorbance of LiCoO$_2$ thin films have been studied in the vicinity of the fundamental absorption edge. 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 [26]. 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 [27].
Fig. 3.13 shows the optical transmission spectra related in the wavelength range 300-1200 nm for the films deposited at substrate temperatures 300 and 700 °C on quartz substrate. We observed a gradual increase of the optical transmission from 400 to 1000 nm with the appearance of a prominent step at 750 nm. This feature is more pronounced for the well-crystallized film grown at 700 °C. Plots of the optical absorbance, $(\alpha h\nu)^2$ versus photon energy for LiCoO$_2$ films are shown in Fig. 3.14.
1. The variation of the optical absorption near the fundamental edge allows to determine the energy gap between d-bands of LiCoO$_2$. These plots gave the band gap energy in the range 2.38 - 2.30 eV for films grown at temperatures in the range 300 - 700 °C, respectively, with an accuracy ± 0.02 eV. These results are in good agreement with theoretical estimations [26, 27] and experimental data reported by Kushida and Kuriyama [28]. The d-d transition from $E_F$ in the Co-t$_{2g}$ bands to the Co-e$_g$ bands in LiCoO$_2$ was observed at 2.1 eV. Intercalation of Li in LiCoO$_2$ increases the
Co-O bond length leading to a $\sigma$ overlap between the O-2p and Co-3d orbitals, thereby pushing the antibonding bands (e_g bands) down [27]. Thus the textured films allow for investigation of the d-d electronic transition in LiCoO_2. Our experimental data, that is optical absorption and FTIR spectra, support the above theoretical prediction.

3.3.6 Electrical properties

Electrical transport plays an important role in the performance of the electrode in the lithium microbattery. The electrical conductivity of LiCoO_2 thin films grown at various substrate temperatures were studied using a standard four probe technique in the temperature range 180-500 K. Fig. 3.15 shows the temperature dependence of the dc conductivity for PLD LiCoO_2 thin films. The electrical conductivity of the films showed that the conduction is thermally activated owing to the semiconducting character of these oxides. On increasing the temperature, we clearly observe a subsequent increase of the conductivity of LiCoO_2 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. 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 increasing substrate temperature. According to the electronic considerations [29], the small polaron semiconducting character of the LiCoO_2 compound is due to the weak M-M interactions, which prevents an itinerant-electron bandwidth giving localized electronic configurations. Examination of the data (Fig. 3.15) 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 0.26 eV. 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 plots of $\sigma_{dc}$ at temperature around 280 K suggests the possibility of a variable range hopping mechanism for the small polaron transport.
3.3.7 Electrochemical studies

The electrochemical measurements were carried out on Li//LiCoO₂ cells with a lithium metal foil as anode and LiCoO₂ film as cathode of 1.5 cm² 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 LiClO₄ 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 μA cm⁻² supplied for 1 h followed by a relaxation

Fig. 3.15. Arrhenius plots of LiCoO₂ thin film deposited at different substrate temperatures in pO₂ = 100 mTorr
period of 0.5 h. Electrochemical potential spectroscopy (ECPS) was performed using 5 mV potential steps. Cyclic voltammetry (CV) measurements have been carried out at sweep rate $\alpha = 1 \text{ mVs}^{-1}$. Fig. 3.16 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$_x$CoO$_2$ 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$_2$. Fig. 3.17 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.

![Cyclic Voltammogram](image)

**Fig. 3.16.** Cyclic Voltammogram of Li//LiCoO$_2$ cells deposited at 700 °C
Typical charge discharge curves of Li/LiCoO₂ cells using pulsed laser deposited film grown at substrate temperature 300 °C in an oxygen partial pressure of 100 mTorr are shown in Fig. 3.18. 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).

Fig. 3.17. Cyclic Voltammogram of Li/LiCoO₂ cells deposited at 300 °C

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 LiCoO₂ thin film cathode cells, which is lower to that recorded in the galvanic cell using crystalline cathode [30], (2) the cell voltage profiles display the typical profile currently observed for Li₂CoO₂ 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. This is consistent with many literature data [10] and ensures that, at substrate temperature 300 °C in an oxygen partial pressure of 100 mTorr, the material particles are electrochemically active.
Fig. 3.18. Charge-discharge profile of Li//LiCoO$_2$ cells deposited at 300 °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 (Fig. 3.18) 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$_x$CoO$_2$ 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 300 °C has interesting electrochemical properties for the microbattery application. In the high voltage region, such a cell delivers a specific capacity of 190 mC/cm$^2$ μm. 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 Fig. 3.19. The potentials are slightly increased from the films grown at 700 °C and the cell delivered a higher specific capacity of 205 mC/cm$^2$ μm. This value could be compared with the theoretical specific capacity of a LiCoO$_2$ film 420 mC/cm$^2$ μm
(116 μAh/cm² μm) assuming density of 4.28 g cm⁻³ and a theoretical gravimetric capacity 273 mAhr g⁻¹ for a total extraction of Li⁺ ions from the host matrix.

Fig. 3.19. Charge-discharge profile of Li//LiCoO₂ cells deposited at 700 °C
References


