Chapter – VI

Summary and Conclusions
Summary

Development of rechargeable lithium ion (Li' - ion) microbatteries has attracted considerable attention in the past few years, owing to its potential energy storage capacity even in small dimensions. The discovery of Li'-ion micro-batteries would find application in MEMS technology, integrated passive components like CMOS, analogous commercial, aerospace, and military applications. The basic working principle of such rechargeable batteries is the reversible electrochemical process i.e. the "lithium de-intercalation/intercalation" from/into the positive electrode host matrix. Therefore, intensive investigations are carried out on thin-film positive electrodes deposited on suitable substrates for their potential application in micropower sources. Generally, lithium transition metal oxides (LTMO's) such as layered LiCoO₂, LiNiO₂, spinel LiMn₂O₄ and olivine LiFePO₄ viz. have been widely recognized as most promising functional intercalation (positive electrode) compounds for their application in all types of Li-ion batteries. Among these LiCoO₂ has primarily been selected as unique intercalation host material with distinguished properties viz. high structural stability even after the phase transition that occurs upon cycling, complete reversibility, high energy density, high cycling stability even after several runs and has already proven its potentiality as intercalation electrode. All these practical applications of LiCoO₂ films are strongly depends upon microstructure, chemical composition, topographical features and relative packing density of the films, which in turn depend on the type of deposition technique and film processing parameters employed for the growth. RF magnetron sputtering technique is the most versatile and industrially viable for the synthesis of materials even dielectrics, insulator, semi-conductors in thin film form homogeneously along with good adhesion. Hence, investigations are performed on the fabrication of well-defined LiCoO₂ film cathodes using RF magnetron sputtering technique and studied the influence of process parameters on microcrystalline and electrochemical properties of the films, systematically.

The key feature of the thesis entitled the growth of layered crystalline LiCoO₂ films on different substrates viz. Au/Ti/SiO₂/(polished)Si, Au/Ti/SiO₂/(textured)Si and Au/polyimide (Kepton) maintained at a moderate temperature by varying the process parameters viz. oxygen to argon gas composition (1:1 - 1:9), RF power (20 - 200 W) and post deposition annealing (673 K to 1023 K, for 4 hours), systematically. In each set of
depositions, LiCoO\textsubscript{2} films were deposited systematically, by varying one deposition parameter each time and keeping the other parameters constant. The optimization of these process parameters has been carried out in relation with the characteristic microcrystalline and electrochemical properties of the LiCoO\textsubscript{2} films derived from XRD, Raman, SEM, XPS and galvanostat/potentiostat electrochemical experiments. The electrochemical measurements were made by designing two different test cells with a configuration i.e. (Pt/LiCoO\textsubscript{2}) and (Li/LiCoO\textsubscript{2}) compatible for aqueous and non-aqueous electrolytes, respectively. In addition, investigations are also aimed to fabricate high performance as-grown LiCoO\textsubscript{2} film cathodes, avoiding the unusual affects of high temperature annealing process. Studies are enumerated the endurance of substrate texturing and the nature of the substrate in getting the electrochemically active film cathodes compatible for the development of micro power generation which find their application in both silicon chip technology and flexible micro-electronics. In this section, the chapter wise important results are highlighted and scope for the future work is proposed.

**Microstructural and electrochemical properties of LiCoO\textsubscript{2} films - “Influence of process parameters”**

The LiCoO\textsubscript{2} films were deposited at various O\textsubscript{2} to Ar ratios in the range (1:1) - (1:9) keeping the sputtering pressure and RF power constant at 3 x 10\textsuperscript{-3} mbar and 100 W, respectively, by taking growth rate (12.5 nm.min\textsuperscript{-1}) into consideration. The films deposited on Au/Ti/SiO\textsubscript{2}(polished) Si substrates maintained at 523 K and at lower reactive gas composition [O\textsubscript{2} : Ar, (1:9)] exhibited randomly oriented layered crystalline phase (R\textbar m symmetry) along with a minute Co\textsubscript{3}O\textsubscript{4} additional impurity phase. These films delivered a specific discharge capacity of about 42.5 \(\mu\text{Ah.cm}^{-2}\mu\text{m}^{-1}\) and poor cycling stability with a chemical diffusion coefficient (D\textsubscript{Li}\textsuperscript{+}) of 1.5 x 10\textsuperscript{-11} cm\textsuperscript{2}s\textsuperscript{-1} which is attributed to the presence of minute spinel crystalline phase along with predominant hexagonal layered phase in the film. This ‘meta-stable’ film rapidly develops into poly-crystalline hexagonal layered structure during controlled heat treatment > 823 K. As grown films exhibited preferential (0 0 3) orientation, while the films annealed at higher temperatures lead to (1 0 4) and (1 0 1) preferential orientations. These textural transformations in the films are ascribed to the thermally stimulated reconstruction and agglomeration of the crystallites induced by the high temperature annealing process. All the microcrystalline studies demonstrating that the as-grown LiCoO\textsubscript{2} films subsequently annealed at 923 K in a
controlled O₂ ambient (5 x 10⁻⁶ mbar) exhibited (1 0 4) out of plane texture crystallizes in R₃m structural symmetry with an average grain size of 500 nm. The films were found to be near-stoichiometric and having uniform distribution of surface grains. The slow scan cyclic voltammetry (CV) and chronopotentiometry experiments were conducted on these films by designing aqueous Pt/LiCoO₂ and non-aqueous Li//LiCoO₂ electrochemical cells using these films. From the CV measurements, the presence of single redox couple at expected potentials confirmed the existence of single phase crystallography and electrochemical activity of the films. Both the electrochemical cells delivered the identical initial discharge capacity of 60 μAhcm⁻²μm⁻¹ when they are discharged with current density of 50 μAcm⁻². The estimated chemical diffusion coefficient is around 10⁻¹³ cm² s⁻¹ for Li⁺ ions. This low chemical diffusion coefficient parameter of cathode has led to high structural stability even after several numbers of cycles. The Pt//LiCoO₂ cell shown a faster capacity fading rate than the Li//LiCoO₂ organic cell and the capacity fade rates in average are 3.0 % and 0.15 % per cycle for the first 20 cycles, respectively.

An investigation has been made to avoid the high temperature annealing process and to enhance the microcrystalline and electrochemical properties of as-grown films by varying the applied RF powers to the LiCoO₂ target. The films prepared at low RF powers (≤ 50 W) representing the additional impurity phase (Li₂O and Co₂O₄) along with poor crystallographic order structure which results the insignificant electrochemical performance. Considerable increase in capacity with low chemical diffusion coefficients are noticed with the increase of ordered crystallography and grain size as a function of RF power. Here also, transformation of film texture from c-axis to a-c plane distribution has been observed and is attributed to the high rate of deposition induced by the increase of RF power. Particularly, the films deposited at RF power of 150 W exhibited preferential (1 0 4) orientation and high discharge capacity of about 54.5 μAh.cm⁻²μm⁻¹ with a good capacity retention. These films achieved low chemical diffusion coefficients (Dₐₚ) of about 7.3 x 10⁻¹³ cm²s⁻¹ and value is near comparable with the results on annealed LiCoO₂ films. However, the films deposited at RF power > 150 W demonstrates an increase in surface roughness provided with non-uniform distribution of distribution of crystallites with additional phases. This is may be due to impact of re-sputtering along with the target heating and is owing to high rate of deposition.
"Silicon substrate texturing influence on RF sputtered LiCoO₂ film cathodes"

The growth of HT-LiCoO₂ film formation is observed to have either an elevated deposition parameter (RF power) or a post - deposition annealing treatment at high temperature to improve the crystallinity of thin films and to enhance its electrochemical performance. However, such a high temperature and elevates processing steps are often not compatible for their integration with semiconductor, microelectronic device technology. Negative effects of high temperature annealing degrade the performance of devices to be integrated by thin film microbatteries. Hence, considerable interest has been developed on the fabrication of as-grown LiCoO₂ films with desirable properties and is become a challenging and dynamic objective for the researchers. The performance of a thin film positive electrode is mainly governed by the growth of the film electrode supported by the substrate and the film surface area. Surface roughening increases the surface area of the film and may enhance the flux of Li at the interface surface. By considering these introductory implications, the as - grown LiCoO₂ films were developed on a Au/Ti/SiO₂/(textured)substrates at an optimized deposition parameters i.e. RF power 100 W, substrate temperature 523 K and O₂ to Ar ratio 1:9. The films have the grains with c-axis (0 0 3) orientations along with enhanced surface area induced by high surface roughness of the base (textured Si) substrate. These films exhibited near comparable electrochemical performance with the annealed LiCoO₂ films developed on polished Si substrates in terms initial discharge capacity (57.5 μAhcm⁻² μm⁻¹) and \( D_{Li}^+ \) (6.5 × 10⁻¹³ cm²s⁻¹). These films delivered better capacity retention of about 0.07 % per cycle and is attributed to the increase of active surface area induced by the substrate texturing and the development of homogeneous c-axis oriented LiCoO₂ films.

"Growth and properties of RF sputter deposited LiCoO₂ film cathodes on flexible Au/polyimide substrates"

Growing world wide interest in the development of light weight, high compact, flexible solid state micro-power sources for bio-sensors, roll to roll devices and MEMS, the low temperature synthesis of HT-LiCoO₂ film cathodes onto flexible kepton substrates opens a comprehensive study of investigation. By considering the implication of flexible micro-power generation, LiCoO₂ films were deposited onto Au/polyimide flexible substrates and investigated their microstructural and electrochemical properties. The films deposited at optimized substrate temperature 573 K and in presence of reactive gas ratios \( O_2 \) to Ar) 1:9, respectively. The films deposited at RF power 150 W were found to be
comprises of large particles of target material with low amount of lithium loss exhibited well-structured polycrystalline with c-axis growth of the films perpendicular to the substrate surface in (0 0 6) preferred orientation. Cyclic voltammetry (CV) measurements shown one set of intercalation/de-intercalation current peaks located at 0.732 V and 0.653 V, respectively, with a peak separation of 79 mV for the LiCoO₂ film indicating the single phase transition reaction during charge/discharge reactions with a charge compensation of Co²⁺/Co³⁺ and vice versa. These films delivered a discharge specific capacity of about 53 μAh cm⁻²μm⁻¹ with a D_Li⁺ value of about 4.2 x 10⁻¹² cm²s⁻¹ and exhibited good cycling performance.

Conclusions

Intensive investigations are carried out to realize layered structure HT-LiCoO₂ films with good microstructural and electrochemical properties to find their potential application as binder free cathode in the fabrication of microbattery. The RF magnetron sputtering technique which is an industrially viable has been employed for the growth of the films. The relative physical and electrochemical properties of the grown films are thoroughly studied in relation with the process parameter and optimized the conditions.

The films grown on Au/Ti/SiO₂/Si substrates maintained at 523 K in an oxygen to argon ratio at 1:9 and at RF power 100 W were found to exhibit (0 0 3) orientation with an estimated discharge capacity of about 42.5 μAh cm⁻²μm⁻¹. The capacity and cycling stability of the films are found to be enhanced by subjecting the films for annealing at temperature 923 K in a controlled oxygen ambient. These films are exhibited (1 0 4) out of plane texture in the films crystallizes in R 3 m symmetry and delivered a discharge capacity of about 60 μAh cm⁻²μm⁻¹. However, the as-grown films fabricate at higher RF power (150 W) also delivered almost equal performance to that of annealed films with a discharge capacity of about 54.5 μAh cm⁻²μm⁻¹. On the other hand, the electrochemical properties of the as-grown LiCoO₂ films have been improved to 57.5 μAh cm⁻²μm⁻¹ by depositing c-axis oriented LiCoO₂ films on textured Si substrates where we could successfully avoid the negative affects of elevate processing parameters i.e. high temperature annealing and high RF power. An attempt has also been made by successfully depositing the HT-LiCoO₂ on Au/polyimide flexible substrates with a discharge capacity of about 53 μAh cm⁻²μm⁻¹ by considering their applications for bendable electronics.
Au/polyimide flexible substrates with a discharge capacity of about 53 µAh cm⁻²µm⁻¹ by considering their applications for bendable electronics.

The successful realization of crystalline LiCoO₂ films on various substrates with high electrochemical performance can be employable as binder free cathode in the fabrication of all types of solid state micro batteries.

The realization of the solid state microbattery using the same technology will revolutionarize the future micro/nano electronic devices. For this reason, some researchers feel that it is premature to describe the set-up as a battery. "Nonetheless, "it's a great lab experiment to design a microbattery. To be practical, some means of charging them, removing them from the template and connecting them to wires must be developed."
commented Charles Martin of the University of Florida in Gainesville, who is designing tiny batteries. Unfortunately, these microbatteries are expensive and their preparation is time consuming. To my teacher and to my opinion, the micro-power generation is highly essential and it could be highly possible with tiny secondary lithium cell match the energy requirements of the integrated electrical circuit, in other words.

**Future work**

The following work is recommended as a follow-up to this study:

LiCoO₂ as positive electrode is still stand as a sources to all type of Li-ion microbatteries, but commercially it is not viable because of high cost. Hence innovations have to be done by the substitution of nickel (Ni) or manganese (Mn) in place of cobalt to reduce the cost.

The intercalation mechanism of lithium in to the Li₂CoO₂ host matrix is still unrevealed. There are still some unanswered fundamental properties are to be solved.

Fabrication of all solid state thin film microbattery based on LiCoO₂ film cathodes using RF magnetron sputtering technique on Si chip employing thin film solid electrolyte is the ultimate goal.
RF Magnetron Sputter Deposited Nanocrystalline LiCoO₂ Film Cathodes on Flexible Substrates

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Nanocrystalline LiCoO₂ films were grown on gold (Au) coated flexible polyimide (Kapton) substrates by reactive rf magnetron sputtering technique. The growth, microstructural and electrochemical performance of the LiCoO₂ films are studied as a function of applied rf power. With the increase of rf power, the size of the nanocrystals was observed to be increased with low compressive microstress. Transformation of two phase domain structure to single phase hexagonal layered structure was noticed in the films with development of film thickness and the reasons were scrupulously discussed. The as-deposited LiCoO₂ films on flexible polyimide substrates grown at high RF power (150 W) exhibited predominantly (0 0 1) orientation representing single phase hexagonal structure (R3m space group) and the film surface is comprised of vertically aligned nanoparticulates with micro porous nature provided with high surface roughness and improved surface area. These films delivered an initial discharge capacity of about 53 mA h cm⁻², and low chemical diffusion coefficient (4 x 10⁻⁹ cm² s⁻¹) at aqueous electrode/electrode interface. These initial studies of LiCoO₂ films on flexible polyimide substrates have shown its promising application as a binder-free cathode in flexible lithium microbatteries.

KEYWORDS: LiCoO₂ Thin Films, Flexible Substrates, RF Magnetron Sputtering, Microstructure, Electrochemical Properties

1. INTRODUCTION

Advances in microelectronic industry, in particular, the development of micro-electro-mechanical systems (MEMS) technology, smart cards etc have reduced the current and power requirements to extremely low levels. Planar microbatteries made on metallized silicon wafer have successfully received as a choice of such requirements. 1,2 Whereas, the design of advanced portable and handheld electronic devices such as roll up displays and wearable devices requires the development of integrate batteries that are thin, light weight, flexible and manufactured at low cost. 3 Design of rechargeable lithium ion microbatteries on flexible substrates can accomplish the fore-discussed requirements and are identified as a new generation power sources for the today's information-rich, mobile society. 4 The fabrication of such microbatteries primarily comprises the selection of (i) ideal intercalation host material, (ii) compatible flexible substrates, and (iii) type of thin film deposition technique to lay-up the device.

Lithium transition metal oxides (LTO's) are the unambiguous choice of intercalation host, in which the guest species, Li⁺ ions, can be reversibly intercalated within or deintercalated from the van der Waals gap between transition metal oxide host frame works. The LTO's such as LiM₂O₃ (where M = Cu, Ni, Mn, Fe etc) have received considerable attention in recent years as high voltage positive electrode materials for use in all types of secondary Li⁺ ion batteries. 5,6 Despite considerable efforts made to investigate the best cathode material amongst, LiCoO₂ still remains as industrially viable positive electrode by its promising advantages like high structural stability, high theoretical capacity, high operating voltage, high energy density, and high cycling stability versus lithium. 7,8,9,10 It is well known that, the electrochemical properties of LiCoO₂ films primarily depend on their microstructural properties such as crystallinity, structure, stoichiometry and density of the films which in turn depend upon the type of thin film deposition technique. In addition, the development of electrochemically active LiCoO₂ films onto the flexible substrates at low processing temperatures is known to be crucial. The rf magnetron sputtering technique has been widely recognized as very promising, versatile and efficient plasma deposition method for the deposition of LiCoO₂ thin films. 11 The chief advantage is that rf magnetron sputtering activates broad ionization even at low sputtering powers and also allows the film crystallization at a moderate substrate temperatures, especially during long sputtering times.
Various flexible substrates were employed for the preparation of LiCoO$_2$ thin films. Song et al. used flexible mica sheet as a substrate to develop Li/LiFON/LiCoO$_2$ structure using sequential sputtering and evaporation techniques. TaHe et al. have grown LiCoO$_2$ thin films on flexible stainless steel substrates using sol-gel process and spin-coating technique. All these substrates are suitable for annealing at elevated temperature like Si and Al, to achieve LiCoO$_2$ thin film cathodes with good crystallinity. However, growing world wide interest in the development of light weight, high compact, flexible solid state micro-power sources for bio-sensors, roll to roll devices and MEMS, the low temperature synthesis of HT-LiCoO$_2$ film cathodes onto flexible kepton substrates opens a comprehensive study to investigate. Hence, the present investigations are aimed to grow LiCoO$_2$ films on flexible Polyimide substrates at moderate substrate temperature using rf magnetron sputtering technique. The work is focused on the study of microstructural properties of films in relation with the RF sputtering power using X-ray diffraction (XRD), Raman spectroscopy, and Atomic force microscopy (AFM). Further, the electrochemical behavior of LiCoO$_2$ thin films on flexible Polyimide substrates is studied in aqueous electrolyte media by investigating the cyclic voltammetry and the chronopotentiometry measurements.

2. EXPERIMENTAL DETAILS

2.1. Synthesis of LiCoO$_2$ Films

LiCoO$_2$ thin films were deposited by radio frequency magnetron sputtering of lithium rich (10%) LiCoO$_2$ target. The sputtering system was configured in sputter up geometry. Commercial gold (Au) plated polyimide sheets obtained from the Arthut Engineers, India were used as substrates for the deposition of LiCoO$_2$ films. The system is evacuated to a base pressure of less than 5 × 10⁻² mbar with a turbo molecular pumping system backed by rotary pump. Prior to the LiCoO$_2$ film formation, the target was pre-sputtered for 30 min at RF sputtering power 100 W under Ar environment alone. The rf sputtering power and substrate temperature are the prominent deposition parameters of magnetron sputtering process in the development of thin films on the flexible polymer substrates. Among these, the variation of rf sputtering power by maintaining a moderate substrate temperature is a prominent study of research for the low temperature synthesis of materials in thin film form. In case of polyimide substrates, the suggested substrate temperature$^{17}$ is near below its glass transition temperature and is maintained at 300 °C. The LiCoO$_2$ films were prepared at various rf sputtering powers ranging from 50 W to 150 W. The oxygen to argon flow ratio was maintained at 1:3 with a working pressure of 0.3 Pa. A rotary drive mechanism was used to rotate the substrate holder to obtain good uniformity of the films. The deposition time was maintained constant at 90 min.

2.2. Microstructural Characterization

The powder X-ray diffraction (XRD) pattern of the films were recorded with Stöber XRD Model 3000 TT grazing incidence X-ray diffraction (GIXRD) geometry using Cu Kα$_1$ ($λ = 0.15406$ nm) radiation. The angle of incidence of the X-ray beam is fixed at 3° and the measurements were recorded with a step size of 0.03° in the 10-70° range. Peak positions were determined precisely using RAYFLEX-Analyse software. The Raman spectra of LiCoO$_2$ films in the wave number region 200-1500 cm$^{-1}$ were recorded at room temperature with a Jobin Yvon (Model HR 800UV) Raman spectrometer using an excitation wavelength of 532 nm (Nd: YAG laser). The laser power on the sample was measured by a PM 100D console with a Co-series photodiode sensor (Thorlabs GmbH). Atomic force microscopy (AFM) (Digital instrument. Dimension 3100 series) was used to study the surface morphology of the films in a simple contact mode of operation. The morphological features of the thin films were also characterized by scanning electron microscope (Carl Zeiss, LEO MA 15). The LiCoO$_2$ film thickness was measured using Veeco-Dektak 150 stylus profilometer.

2.3. Electrochemical Characterization

The electrochemical experiments were carried out in saturated Li$_2$SO$_4$ aqueous electrolytes since the use of organic electrolytes may cause partial damage to the polyimide substrates. A three electrode electrochemical stainless prototype glass cell with LiCoO$_2$ flexible film working electrode, a platinum (Pt) metal strip counter electrode and a saturated calomel reference electrode (SCE) was employed for the electrochemical measurements. Potentiostatic cyclic voltammetry and Galvanostatic chropotentiometry electrochemical experiments were conducted using CHI 500E (CH Instruments Inc., USA) electrochemical analyzer equipped with a data acquisition system. Potentiostatic cyclic voltammogram was obtained for the film electrode in the potential range of 0.2-2.2 V versus Pt at a scan rate of 0.5 mV s$^{-1}$. Galvanostatic charge discharge experiments were conducted in cathodic-anodic current steps of 30 μA cm$^{-2}$.

3. RESULTS AND DISCUSSION

3.1. Microstructural Properties

3.1.1. GIXRD Measurements

GIXRD profiles of the as deposited LiCoO$_2$ thin films prepared at various rf sputtering powers i.e., 50 W, 80 W, 110 W, 120 W to 150 W are shown in Figure 1. All the measurements were recorded with a step size of 0.03° in the 10-70° range.

The enhancement in the crystallographic ordered structure of the grown films in accordance with the ion bombardment rate on the target surface which leads to the transformation of two phase domain structure [HT-LiCoO2 with Co3O4 impurity phase] to single phase structure of LiCoO2 in the as-grown films. Remarkably, enhanced (0 0 6) peak indicates that the film is oriented against the substrate surface.

Table 1 shows the structural parameters of the films deposited at various sputtering powers determined from the GIXRD patterns (Fig. 1). The lattice parameters, lattice constants and volume of the lattice were calculated using (0 1 8) and (1 1 0) Bragg's reflections. The average size of the crystallites (D) was calculated by employing Scherrer's formula considering the full width half maxima (FWHM) values of all lattice planes.

$$D = k \lambda / (\beta \cos \theta)$$

where 'D' is the crystallite size as measured perpendicular to the reflecting plane, 'K' the Scherrer's constant (0.9), 'λ' the wavelength of X-ray radiation (1.5406 Å), 'β(20)' the half intensity width measured in radians and 'θ' the Bragg angle. And, the micro-steps within the crystallite (ε) was examined considering the full width half maxima (FWHM) of predominant (0 0 6) orientation using the formula proposed by Li and coworkers.

$$\varepsilon = (\beta(2θ) \cos θ)/4$$

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**Table 1. Structural parameters of the LiCoO2 films as a function of applied rf sputtering power.**

<table>
<thead>
<tr>
<th>RF power</th>
<th>150 W</th>
<th>120 W</th>
<th>100 W</th>
<th>80 W</th>
<th>60 W</th>
</tr>
</thead>
<tbody>
<tr>
<td>FWHM (0 0 6)°</td>
<td>0.3867</td>
<td>0.4199</td>
<td>0.4232</td>
<td>0.4311</td>
<td>0.4913</td>
</tr>
<tr>
<td>Lattice parameters</td>
<td>a = 2.836</td>
<td>a = 2.836</td>
<td>a = 2.836</td>
<td>a = 2.842</td>
<td>a = 2.844</td>
</tr>
<tr>
<td>(0 1 1) and (1 1 0) Å</td>
<td>c = 14.112</td>
<td>c = 14.086</td>
<td>c = 13.989</td>
<td>c = 14.053</td>
<td>c = 13.943</td>
</tr>
<tr>
<td>Lattice constant (a/c)</td>
<td>4.976</td>
<td>4.970</td>
<td>4.963</td>
<td>4.956</td>
<td>4.656</td>
</tr>
<tr>
<td>Volume of the crystallite Å³</td>
<td>97.8</td>
<td>98.1</td>
<td>98.2</td>
<td>98.5</td>
<td>92.7</td>
</tr>
<tr>
<td>Crystalline size (D) Å</td>
<td>1.39</td>
<td>1.13</td>
<td>1.12</td>
<td>1.09</td>
<td>0.91</td>
</tr>
<tr>
<td>Micro-steps (ε) 10°</td>
<td>4.9</td>
<td>5.685</td>
<td>5.203</td>
<td>3.160</td>
<td>11.82</td>
</tr>
</tbody>
</table>

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**Fig. 1.** GIXRD patterns of LiCoO2 thin films deposited at various rf sputtering powers. (Inset: Magnified image representing the influence of rf power on the development of (1 0 4) peak.)
Figure 2 represents the variation of crystalline size and crystalline micro-strain versus applied RF power during the growth of the films. The estimated micro-strain component is observed to be decreased and the average crystalline size is increased correspondingly, which lead to development of single phase structure in the grown films, with the increase of applied rf sputtering power. The evaluated component value for the monocrystalline LiCoO$_2$ films grown at rf power = 150 W is found to be about 5 x 10$^{-3}$, which is observed to be slightly higher than that of the films grown on Aluminum films reported by Li et al.$^{16}$ and single crystalline Silicon substrates.

### 3.1.2. Raman Measurements

The Raman scattering measurements were carried out to understand the microstructural variations of the LiCoO$_2$ films as a function of rf sputtering power. According to Kang and co-workers,$^{20}$ four Raman-active $(A_g + E_g)$ and five IR-active $(F_g, F_u)$ vibrational modes are predicted for Li$_2$OCoO$_2$, and two Raman-active $(A_g + E_g)$ and four IR-active $(E_u, E_g + 2E_g)$ vibrational modes are predicted for HT-LiCoO$_2$. Figure 3 illustrates the Raman spectra recorded in the wave number range 450-700 cm$^{-1}$ for the films deposited at various powers in the range 50-150 W. For the films prepared at rf power < 50 W, the Raman spectrum demonstrated four noncharacteristic broad band in the wave number range 450-700 cm$^{-1}$ whose center of gravity are observed to be located around 410 cm$^{-1}$ $(A_g, 410)$, 590 cm$^{-1}$ $(A_g, 590)$ and 521 cm$^{-1}$ $(A_g, 521)$ and are attributed to the Raman active modes of Li$_2$OCoO$_2$ and Co$_3$O$_4$ crystalline phases in the films. Co$_3$O$_4$ crystallizes in the normal cubic spinel structure $\text{Co}_3(\text{Co}^{2+})_2\text{O}_4$ (space group Fd3m) with $\text{Co}^{2+}$ and $\text{Co}^{3+}$ placed at tetrahedral and octahedral sites, respectively.$^{21}$ The $A_g$ (410 cm$^{-1}$), $E_g$ (485 cm$^{-1}$) and their $F_g$ ($205, 326, 104$ cm$^{-1}$) modes are Raman active modes. The broad band is observed to be well resolved with the enhancement of rf power ≥ 80 W. The $\text{FWHM}$ of the Li$_2$OCoO$_2$ characteristic Raman active peaks $(A_g + E_g)$ is observed to be decreased with the increase of rf powers, and the peaks intensities of Co$_3$O$_4$ crystalline modes are decreased respectively. The films prepared at rf powers (100 W and 80 W showing Co$_3$O$_4$ symmetric signature with $A_g$ Raman active located at around 689 cm$^{-1}$ which is assigned to the Co-$\text{O}-\text{O}$ stretching vibrations. The films prepared at rf sputtering power of 150 W showed two well defined and sharper Raman bands located at 411 $(A_g)$ and 512 $(A_g)$ cm$^{-1}$. These bands are attributed to the characteristic $E_g$ and $A_g$ vibration modes of single phase hexagonal layered LiCoO$_2$ structure and respective hexagonal phase is belongs to R3m space group. These Raman bands are attributed to Co-$\text{O}-\text{O}$ bending mode vibrations in which vibration of oxygen atoms are coupled at the r axis ($A_g$ mode) of the LiCoO$_2$ in the hexagonal layered structure, respectively. The estimated intensities ratio $(\text{Co}-\text{O}2\text{Co}-\text{O})$ of $F_g$ is observed to be decreased from 1.89 to 1.31 with the increase of rf power from 100 W to 150 W resulting the increase in crystallinity in the films. These observations are in good agreement with the results of GIXRD measurements. The above extensive analysis demonstrates that the as grown LiCoO$_2$ films at rf power 150 W on flexible Polyethylene substrates are more suitable as an anode and cathode structure for the fast kinetics of lithium during intercalation-deintercalation charge transfer reactions.

### 3.1.3. Surface Morphology and Film Thickness

The surface morphological features of the LiCoO$_2$ films grown on flexible substrates are studied as a function of...
The RF sputter deposition of polycrystalline \( \text{LaCo}_3 \) film capacitors on flexible substrates improves the morphology of the films with sharp-headed nanograins of average domain size in the order of 50 nm. The morphological growth of \( \text{LaCo}_3 \) films is improved by the diminution of large size lattice particles with a high rate of deposition incurred by increasing rf power. Respective changes are associated with the size and shape of the grains. Particularly, at rf power 150 W, the film is composed of predominant surface grains and each grain is demonstrated as a combination of sub-grains. These grains are observed to be individual, bound tightly together with high density of interfaces, grain boundaries provided with incoherent and internal laminae as shown in Figure 4(b). The morphological characteristics of the films were examined by the SEM measurements. Figure 4(c) represents the 3D surface profile of the films grown at rf power 150 W, obtained from the image processing of SEM image using ‘’image’’ software (model L.446). The image processing of the SEM images were carried out in two steps: (1) De-noising using a medium filter of radius 9.3 nm (2 planes). (2) Quantification of grain surface area fraction and surface roughness using the ‘’2D’’ and ‘’roughness calculation’’ (v) plug-ins. Results concluded that the as-grown films on flexible substrates have shown improved surface area fraction of about 93.9% and giving strong support for the AFM observations. The evaluated particle size and surface roughness as a function of rf powers are shown in the Figure 5. The enhancement of crystalline size and the surface roughness with the increase of rf power of the films grown on flexible substrate is a positive observation for electrochemical research. This type of morphological features of \( \text{LaCo}_3 \) films comprises of nano-particles surface with micron pores nature and is the most preferable characteristics of positive electrodes in electrochemical. These surfaces can have the enhanced surface area and are well adaptable.
for efficient ion insertion-extraction process in an electrochemical system. The stylus profilometry recordings of LiCoO₂ films representing the material thickness deposited at various r.f. powers are shown in Figures 6(a-e). It should be mentioned that 1% error in thickness is expected from the stylus profilometry. Figure 7 shows the variation of deposition rate with sputtering power. Significant deposition rate (153 Å/min) was observed for the films at r.f. power 150 W. These results challenge the limiting choice of flexible polyimide substrates for the growth of LiCoO₂ film with higher thickness on polymer surfaces.

3.1.6. Nucleation Mechanism and Growth of LiCoO₂ Films on Flexible Au/Polyimide Substrates

The c-axis growth formulation mechanism of LiCoO₂ films on flexible Au/polyimide substrates is systematically proposed in Figure 8. Generation of stress component is the most significant parameter in the growth of films on the flexible polymer substrate. Surface nucleation and film formation density on these substrates is quite critical because of poor rate of adatom mobility induced by the lower aggregation energy of the sputter ejected particles onto the polymer surface. Generally, in reactive sputtering process, the sputtering yield (number of target atoms/molecules which are ejected from the target per incident high energetic ion) and deposition rate are mainly confined to the kinetic energy of incident positive ions and is a proportional function of applied sputtering power. With the increase of sputtering power, the kinetic energy of the incident ion increases and as such, the ion bombardment force on the target surface is also increases. This leads to the ejection of large particles from the target surface and reaches to substrate surface with greater kinetic energy by passing through the high-density plasma. At the substrate surface end, the impinging species are attracted to the surface by instantaneous dipole and quadrupole moments of substrate surface atoms and initiates the condensation of vapor species film growth.

During the deposition of LiCoO₂ films on Au/polyimide substrates using rf magnetron sputtering technique, the sputter ejected species reach the surface of substrate with greater kinetic energy by passing through the high-density plasma. At a substrate temperature (300 °C), the adatom mobility on surface of substrates is relatively constant for all sputtering powers. The rate of downward funneling of sputtered species onto the substrate surface is increases relatively with the increase of r.f. power. This process favors for the formation of a greater number of crystallite centers rather than coalescence of islands. Hence vertical growth of grains perpendicular to the substrate surface in (0 0 1) direction is observed and may be responsible for the existence of more stress and strain components in the films at low rate of deposition. The tensile and compressive stresses are generated during deposition of the films. The tensile stresses may be explained by the grain-boundary relaxation model and the strain is generated from the interatomic attractive forces along the constrained grains.

Sputtering at low powers, during the process of sputtered species transformation and their condensation onto the substrates, these small sized sputtered particles are possibly collides with the energetic particles within the plasma region. These collisions reduce the kinetic energy of the particles impinging on the substrates and leads to formation of the films having low thickness with lowest surface energy. In addition, the bombardment of energetic plasma particles possibly causes re-sputtering of loosely bonded lithium on the surface of sputter ejected particles, and make lithium deficient which leads to the development of Co₃O₄ phase in the films. On further condensation of such particles leads to formation of films with lithium deficient phase at low sputtering powers and is demonstrated in both GI-XRD and Raman measurements. On the other hand, the condensation of such small size of particles onto the substrate and further bombardment of energetic particle at film surface end leads to formation of the grains with nanocrystallites acquiring high compressive stress.

As high sputtering powers, large size of sputter ejected particles may start to condense on the substrate surface. The bombardment of high energetic particles on the film surface mostly lead to scatter the surface grains which initiates the process of diffusion and is mainly determined by the energy. In this case, the film surface may be more pronouced by the target particles that crystallize in (0 0 1) direction with low crystalline microcrystals, leading to hexagonal LiCoO₂ structure with R3̅m symmetry. Such type of c-axis orientation growth has been observed for the pulsed laser deposited LiCoO₂ thin films. Therefore, it can be seen that, at higher sputtering powers, film surface was dense with larger grain sizes. In addition, their thickness is different i.e., quite high due to the high sputtering yield at this point which induces high deposition rate although all films are grown for the same period (90 minutes).

In case of flexible substrates, augmentation of the films and deformation induced grain growth of material across the substrate surface are limited only by rupture of the polymer substrate. Hence, all the films are crystallized in (0 0 1) orientation i.e., perpendicular to substrate surface. Moreover, it is a parallel plane of (0 0 3) the most closely packed plane of LiCoO₂ has the lowest surface energy. As the degree of this orientation increases, the distortion in the space lattices parallel to this lattice plane are observed to be decreased resulting the reduction in micro-stress component of the crystallites. These observations show promising sign for the low temperature synthesis of LiCoO₂ film using rf magnetron sputtering process on flexible substrates.
3.2 Electrochemical Measurements

LiCoO₂ films onto flexible polyethylene substrates obtained at RF sputtering power 150 W were used as cathode materials and tested in saturated Li₂SO₄ aqueous electrolyte solution. This is an initial investigation to check the performance of films to be used as binder-free cathode material in flexible lithium batteries. Cyclic伏特ammometry (CV) measurements have been carried out at sweep rate 0.5 mV s⁻¹ during the potential scan ranging...
from 0.2-1.0 V and is shown in Figure 9. One set of smoothly-defined current peaks observed in the CV diagram which corresponds to the oxidation and reduction reactions of LiCoO₂ in the aqueous electrolyte. The presence of redox couple at expected potentials (vs. SCE) confirms the existence of single phase domain of LiCoO₂ which is in consistent with the microstructural properties of the film derived from the XRD and Raman measurements. The intercalation/de-intercalation current peaks are located at 0.732 V and 0.653 V, respectively, with a peak separation of 79 mV for the LiCoO₂ film. The oxidation peak at 0.732 V during anodic sweep corresponding to extraction of lithium from LiCoO₂ host, producing Li₁CoO₂ phase (x equals to 1.0-0.5) with a charge compensation of Co²⁺/Co³⁺. While in cathodic sweep, one reduction peak observed at 0.653 V is corresponding to the insertion of lithium into the same intercalated state of Li₁CoO₂ and producing original LiCoO₂ with a reverse charge compensation of Co²⁺/Co³⁺. Furthermore, the small peak separation between redox peaks indicates the fast change transfer reaction in the aqueous solution system and represents the fast kinetics of Li⁺ ions in the LiCoO₂ film with greater intercalation/de-intercalation rate. The redox couple mid-peak potential of about 0.69 V is considered to be as single phase i.e., hexagonal to hexagonal phase transition of LiCoO₂ during de-insertion/insertion reaction of lithium ions and is the characteristic feature of LiCoO₂. The kinetics of Li⁺ ion in the LiCoO₂ this film host structure is the key factors to understand the whole battery operation. The Li⁺ ion diffusion coefficient in insertion film electrodes have been calculated by the SSCV experiments for (Ptil/LiCoO₂) electrochemical cells. The average Li⁺ diffusion coefficient in the electrochemical reaction can be obtained by the following equation:28

\[ i = 2.69 \times 10^{9} C_{Li}^{1/2}D_{Li}^{1/2} \]  

(3)
Where, \( i_s \) is the peak current in the SSCV plot, \( A \) is the surface area of the anode, \( n \) is the stoichiometric number of electrons involved in this reaction, \( C \) is the Li\(^+\) concentration in the electrolyte, \( D \) is the diffusion coefficient of lithium ions and \( r \) is the scan rate. According to Eq. (1), the calculated Li\(^+\) diffusion coefficient for LiCOO\(_2\) thin films was around 1.3 x 10\(^{-7}\) cm\(^2\) s\(^{-1}\). These results indicate that, in the aqueous electrolyte, the diffusion of Li\(^+\) ions in the LiCOO\(_2\) host matrix does not differ much relative to its hexagonal framework in the film surface.

Figure 10 shows the typical charge-discharge curves of a PolLiCOO\(_2\) aqueous cell using a LiCOO\(_2\) film grown at substrate temperature 300 °C and RF sputtering power 150 W. The measurements were carried out at a current density of 30 μA cm\(^{-2}\) in the potential range from 0.2 to 1.0 V. Both the curves are exhibited only one smoothly-defined voltage plateau, which displays classical intercalation mechanism for the lithium ions into the LiCOO\(_2\) matrix. These voltage plateaus centered as potentials 0.65/0.72 V (vs. SCE) which is similar to those peak potential (0.63/0.72 V) observed in CV data. In the high voltage range (1.0 V) of this discharge curve, the cell delivers a specific discharge capacity of 53 μAh cm\(^{-2}\). This value could be compared with the theoretical specific capacity of a LiCOO\(_2\) film (116 μAh cm\(^{-2}\)) assuming a density of LiCOO\(_2\) as 4.98 g cm\(^{-3}\) and a theoretical gravimetric capacity 271.6 μAh g\(^{-1}\) for a total extraction of Li\(^+\) ions from the host matrix. By considering the experimental error including the utilization of Pt metal anode as anode, these results suggest that about 40% (≈ 64%) of Li\(^+\) ions can be removed at maximum charge potential up to 1.0 V (vs. SCE) from the LiCOO\(_2\) host matrix. The electrochemical performance of the LiCOO\(_2\) films deposited on flexible substrates at a power 150 W a

4. CONCLUSIONS

Cation-exchanged nanostructured LiCOO\(_2\) films were successfully grown on an inert polystyrene substrate by the concurrent RF ion-sputtering technique at a substrate temperature of 300 °C. The influence of applied RF sputtering power on the growth, microstructural and electrochemical properties of films were studied. The as-deposited LiCOO\(_2\) films on flexible polystyrene substrates exhibited prominent RF (13.56 MHz) hollow nanotubes in Raman spectroscopy. The size of the crystallites increased with the increase of RF power. The transformation of two phase domain structure in single phase hexagonal layered structure was noticed with the increase of power. The microstructural studies were supported by Raman, XPS and SEM observations. The as-deposited films grown at a power of 150 W exhibited single phase hexagonal layered structure and the film surface comprises of hexagonally aligned nanoparticles providing with high surface roughness and improved surface area. According to deposition rate (1.0 μm/min) was observed for the film grown at a power of 150 W. The results indicate that the films were on flexible substrates at a power 150 W. The films grown at a power 150 W exhibits single phase hexagonal layered structure and the film surface comprises of hexagonally aligned nanoparticles providing with high surface roughness and improved surface area. According to deposition rate (1.0 μm/min) was observed for the film grown at a power of 150 W. The results indicate that the films were deposited on flexible substrates at a power 150 W in comparison with the films deposited on highly oriented silicon substrates using pulsed laser deposition (PLD) technique. These nanostructured LiCOO\(_2\) films can be regarded as active negative electrodes in solid state flexible microbatteries.

Fig. 10: Typical charge-discharge curves of PolLiCOO\(_2\), aqueous lithium-ion chemical cell.