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Synthesis and Characterization of LiCoO₂ by Sol gel method

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Abstract: LiCoO₂ is the most widely utilized cathode material for lithium ion batteries. Lithium rechargeable batteries with LiCoO₂ cathodes and carbon anodes are currently used as the main rechargeable power sources in modern portable electronic devices such as cellular phones, PDAs, laptop computers and camcorders, due to their high output voltage, high specific energy and good cycling life. LiCoO₂ powders are synthesized by Sol gel method. The sol-gel method is well known as one of the promising thin-film preparation methods, which has good advantages such as low fabrication cost, relatively easy stoichiometry control, high deposition rate and also known as a low-temperature synthesis method for various ceramics. LiCoO₂ prepared by the sol-gel method exhibits interesting electrochemical properties. The material was subjected to a physical and chemical characterization using TG/DGA, X-ray analysis, SEM and UV Spectra. The peaks are identified with the reported values and the crystal structure found to be tetragonal. Morphological studies are done and uniform distributions of grains are observed. The crystalline size is found to be 0.8288 nm. The band gap of LiCoO₂ was found to be 2.3 eV. Films heat-treated under appropriate conditions exhibit high capacity and good crystalline so those films are considered to be candidates as cathodes for thin-film micro batteries.

Introduction

Advances in Science and Engineering related to the emerging technologies of lithium ion batteries have been so spectacular in the past decade that they have become the most popular power source for portable computing, battery cars, microelectronics, biomedical implantable devices and telecommunication^{1,2}. The sol gel method is used at large as a technique for both powders and films preparation, due to some well known advantages, a simple way to obtain homogeneous distribution of precursors, the possibility to introduce controlled amount of dopant chemical methods of reaction control, viscosity control as well as low process temperatures³. LiCoO₂ is the most widely used material for commercial lithium batteries due to its excellent electrochemical cycling stability. LiCoO₂ is a prominent material for energy storage. LiCoO₂ has found large scale potential applications in the commercial lithium ion batteries. Li based layered transition metal oxides such as LiMoO₂ where M is a 3d transition metal such as Ni, Co, Mn, Al, V have attracted great interest worldwide. Li⁺ ions can be deintercalated from LiCoO₂ down to Li_{0.5}CoO₂ with a very good reversibility and a high electrochemical potential, giving rise to batteries with good cyclability and high voltage⁴. LiCoO₂ samples were synthesized by sol gel technique with citric acid as a chelating agent. LiCoO₂ thin film prepared by sol gel method to serve as cathode in all solid state thin film microbatteries⁵. In the sol-gel process, synthesis of organic oxides is achieved from inorganic or organic precursors. The important features of sol-gel techniques

are better homogeneity, high purity, lower processing temperature, and more uniform phase distributions in multi component system, better particle size morphological control possibility of synthesizing new crystalline and Nano crystalline phase⁶. The LiCoO_2 had a structure similar to the layer structures of the dichalcogenides and showed that the lithium could be removed electrochemically, thus making its viable cathode material. LiCoO_2 has the alpha structure with oxygen's in a cubic closed-packed arrangement. On complete removal of the lithium the oxygen layers rearrange themselves to give hexagonal close packing of the oxygen in CoO_2 . The reason for making of lithium-ion batteries from fine particles is to achieve high power output⁷.

Experimental

Stoichiometric amounts of Lithium Acetate and Cobalt Acetate was dissolved in an appropriate quantity of distilled water at room temperature. Solution was stirred at 50°C and citric acid was added to the solution which acts as chelating agent. pH of the solution was adjusted to 8 by slowly dropping Ammonium hydroxide drop-wise and continued stirring for 4hrs. Temperature of the solution was raised to 80°C to 90°C and continued stirred still the solution turn into high viscous gel. Gel was dried in oven at 200°C for 2hrs. The samples were characterized by X-Ray diffraction. The particle morphologies of the as-synthesized materials were observed by Scanning Electron Microscope (SEM).

Results and Discussion

XRD

X-Ray Diffraction pattern of the sample was taken using XPERT-PRO Diffractometer. The XRD patterns of samples were shown in Fig1. It reveals sharp peak diffraction. The observed peaks for LiCoO_2 were compared with the JCPDS (37-1162) shows prominent peaks..From the XRD results shows one prominent peak having (1 0 1). The preferential orientation is found at (1 0 1). It forms a Tetragonal structure with the JCPDS value of $a = 2.809 \text{ \AA}$; $c = 9.942 \text{ \AA}$. One out of five observed peak matches with the JCPDS value.

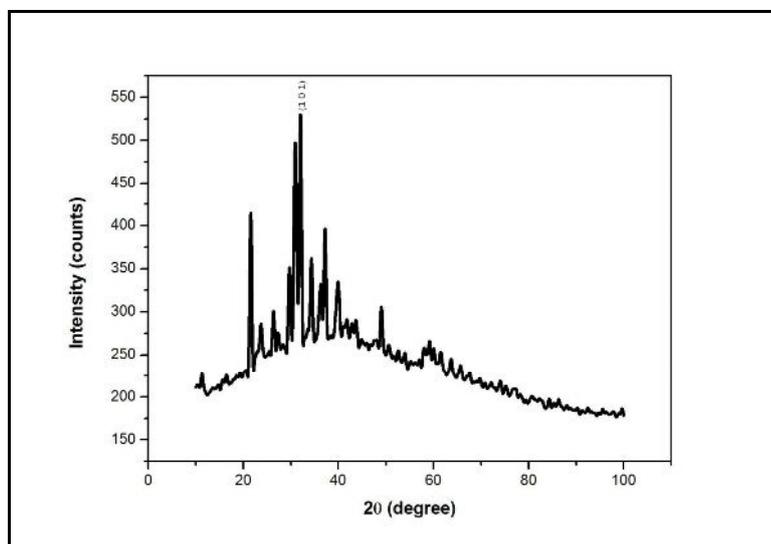
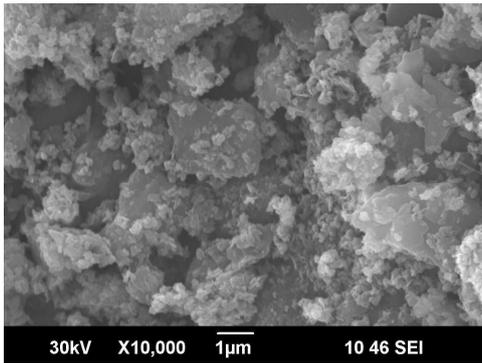
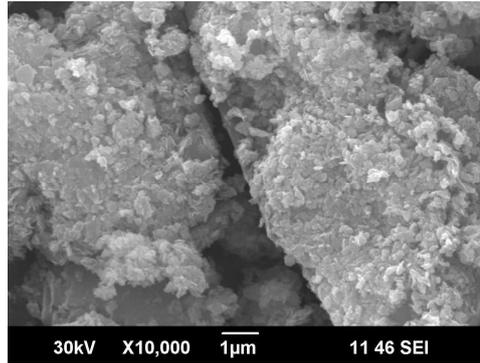


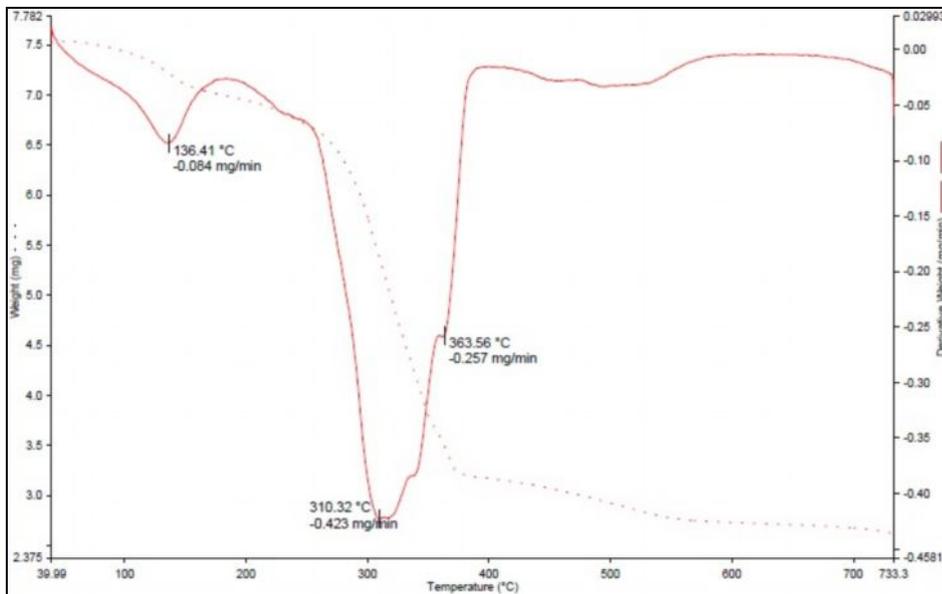
Figure 1: XRD Spectrograph of sample (Lithium Acetate: Cobalt Acetate)

SEM

The surface morphology of the films has been performed using scanning electron microscope (Philips XL30 ESEM) as shown in Fig 2. It shows the morphological pattern of the deposited film on ITO substrate. The particles are found to be well defined facets that have a wide range of distribution ranging from 100 to 200 nm. This show a much more compact surface morphology compared with those obtained at high temperature. It can be attributed to the calcinations of the particles at high temperature. The Morphological changes were noticed to be predominant at higher oxygen pressures and the changes are associated with the grain size and their shape distribution⁶.

At Low temperature**At High temperature(700°C)****Figure 2: SEM images of the sample (Lithium Acetate: Cobalt Acetate)****TG/DTA**

Thermo gravimetric Analysis (TG) determines the weight changes of a sample, whereas Differential Thermal Analysis (DTA) measures changes in temperature between a sample and a reference, as a function of temperature or time. TG/DTA was recorded by Perkin Elmer STA 6000, at 10°C/min. The complex chemical route LiCoO_2 preparation the DTA/TGA analysis was initially performed. The behaviour of the starting precursor during the thermal treatment is shown in Fig 3. TGA curve which exhibit three distinct weight loss steps and the DTA curve shows one endothermic peak and exothermic peaks. The first weight loss step in the temperature range about 150°C - 160°C is accompanied by an endothermic peak around 150°C on the DTA curve, which is due to the loss of residual water in the gel. The second weight loss step in the temperature range of 370-400°C is associated with the decomposition of chelating agent, citric acid. Third step conform the formation of the Nanocrystalline LiCoO_2 powder⁸.

TG/DTA**Figure 3: TG/DTA curve of sample (Lithium Acetate: Cobalt Acetate)****UV Studies**

The optical absorbance LiCoO_2 was recorded by using JASCO-V-530 model spectrophotometer. Optical absorption for the prepared LiCoO_2 was found to be 3.7 eV. The UV Spectra of LiCoO_2 was found for direct band gap, Direct Forbidden, Indirect Band Gap, Indirect Forbidden are shown in Fig 4. The UV spectra of LiCoO_2 shows three peaks, one intensive broad peak at 493 nm and two shoulders at 585nm and 634nm as shown in Fig. 5. The maximum 75% transmittance was observed for as deposited film. The PL spectrum of

LiCoO₂ film was given in Fig 6. The spectra exhibit a emission band peak around 341 nm for LiCoO₂ film as deposited on ITO Substrates.

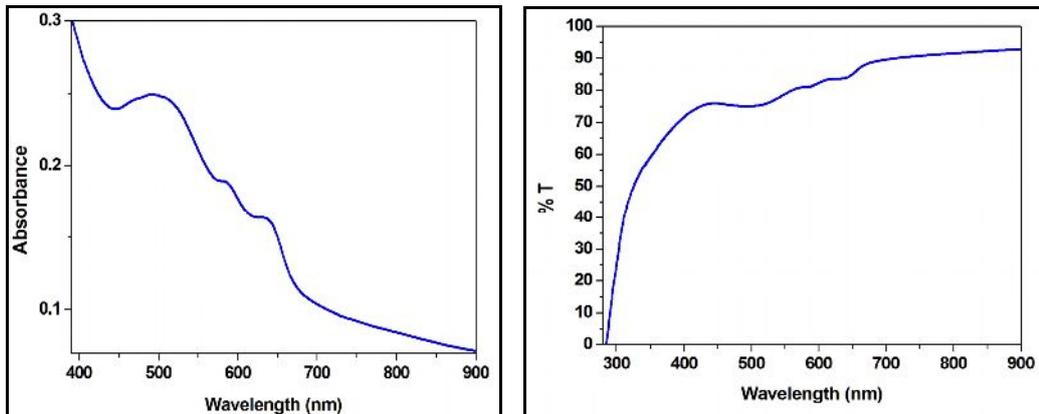


Fig5: Absorbance & Transmittance spectra for LiCoO₂ thin film

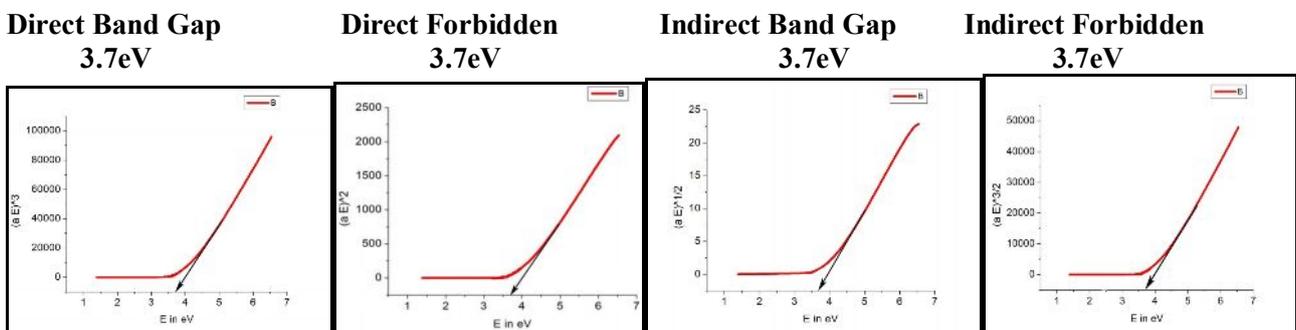


Fig 4: UV Spectra of LiCoO₂

PL Studies

The Photoluminescence spectrum of LiCoO₂ was recorded by ISS INC USA spectrophotometer. Figure.6 shows the photoluminescence spectra of LiCoO₂ being excited with 293 nm. The excitation of the material with 450nm wavelength generates a strong and broad emission in UV region i.e. 300 to 400 nm. The peak at 340nm shows that the emission wavelength of LiCoO₂. The band gap of the material was found to be 3.63eV using the relation $E = hc/\lambda$. The PL emission of LiCoO₂ is interesting in nature as it displays up-conversion.

PL Studies

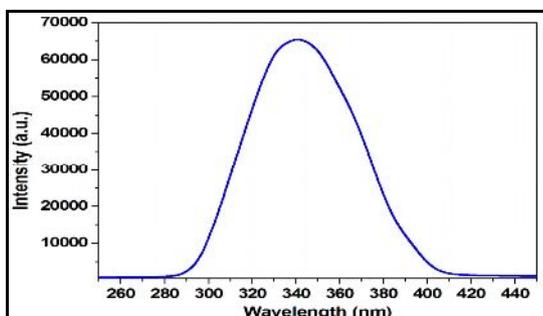


Fig 6 : The Photoluminescence Spectra for LiCoO₂ thin film

Discussion

Structural and microstructural properties were studied. Microscopy studies reveal that the particle size increases with the increase of dopant content. The relatively good electrochemical performances of the thus obtained active electrode material confirms that LiCoO₂ can be used as cathode in solid state batteries. The

peaks are identified with the JCPDS values and the crystal structure is found to be Tetragonal and the values are $a = 2.809\text{\AA}$; $c = 9.942\text{\AA}$. The Crystalline size is found to be 0.8288 nm. The band gap of LiCoO_2 is in good agreement with reported value and tabulated and the value is 3.7eV.

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