Original Research Article

J. Funct. Mater. Biomol. 8(2) (2024) pp 803 – 806

SACRED HEART RESEARCH PUBLICATIONS

Journal of Functional Materials and Biomolecules

Journal homepage: www.shcpub.edu.in

ISSN: 2456-9429

PREPARATION OF LITHIUM COBALT OXIDE NANOPARTICLES BY SOL-GEL METHOD USING TARTARIC ACID AS CHELATING AGENT

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Received on 20 August 2024, accepted on 8 September 2024,
Published online on December 2024

Abstract

Lithium ion batteries are one of the most commercially sought after energy storages today. Nanocrystalline Lithium cobalt oxide ($LiCoO_2$), one of the most promising cathode material for lithium ion secondary batteries were synthesized via sol-gel process using aqueous solution of metal nitrates. The chelating agent tartaric acid was assisted to get different size and morphology of particle. The optimized size may be achieved through sol-gel processing. The XRD, SEM, UV and FTIR characteristics were studied.

Keywords: Energy storage, Lithium Cobalt Oxide, morphology.

1 Introduction

In order to enhance the performance of lithium rechargeable batteries, it has become increasingly appealing to design nanostructured cathodes rather than using traditional materials. Because of its high specific energy, outstanding power rates, low self-discharge, long cycle life, and good capacity, lithium cobalt oxide ($LiCoO_2$) has been extensively researched as a cathode material for lithium ion secondary batteries [1]. $LiCoO_2$ comes in two different shapes: hexagonal and cubic. The spatial configurations of cations distinguish these structures, which are based on the sub lattice of certain oxides. $LiCoO_2$ can be made conventionally by a solid-state reaction at a high temperature [2]. However, the process could lead to inhomogeneity, which would cause aberrant grain development and inadequate stoichiometry control. Numerous sophisticated chemical techniques, including hydrothermal, co-precipitation, the sol–gel process, electrostatic spray deposition, the water-in-oil emulsion approach, etc have been created to create extremely pure and crystallinity-rich materials that are highly active [3].

Although these techniques have the advantage of operating at lower calcination temperatures and taking less time to calcinated, it is typically challenging to synthesize particles smaller than 100 nm because of the particles' propensity to aggregate. To achieve the fine and uniform dispersion of nanoparticles, new synthetic techniques or even adaptations of these current techniques must be developed [4-5]. $LiCoO_2$ nanoparticles using the co-precipitation method in ethanol with mechanical stirring that have a thin polygonal shape and range in size from 20 to 100 nm. The issue here is that the $LiCoO_2$ nanoparticles made using this technique aggregate, making it difficult to mix and distribute them with binder and carbon black to create the cathode [6]. As a result, a cathode employing these nanoparticles has a contact resistance that is significantly higher than the commercial one, which causes noticeable capacity fading. Particle size and the material's crystalline phase have an impact on the cathode performance in lithium batteries [7].

In this present work, we have prepared lithium cobalt oxide nanoparticles by sol-gel method. Here, we

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have used tartaric acid as chelating agent used to prepare the material to attain the morphology. The structural, optical studies are confirmed the $LiCoO_2$ nanoparticles.

2. Materials and methods

2.1 Materials

All of the Chemicals used in this work were analytical grade reagents and used without further purification. Lithium nitrate [Li NO3], Cobalt nitrate [$Co(NO_3)_2$], tartaric acid [$C_4H_6O_6$] were purchased from Merck company. Deionized water was used to prepare all solutions.

2.2 Synthesis of Lithium Cobalt Oxide Nanoparticles

Lithium nitrate and cobalt nitrate was used as reactants. 0.01 mol of lithium and 0.02 mol of cobalt nitrate mixture are dissolved in deionized water and done continuous stirring to get a homogenous solution. Chelating agent tartaric acid (0.03 mol) were also added in the dissolved solution and continued 30 minutes of stirring. Then the stirring is continued with heat for another 3 hours to remove water molecules in the dissolved solution and finally the viscous gel is formed. After that the viscous gel is placed into the hot air oven for 3 hours to get dry sample. The obtained pink color dried sample is calcined at 550oC for 3 hours. Similar procedure is followed for other samples of $LiCoO_2$.

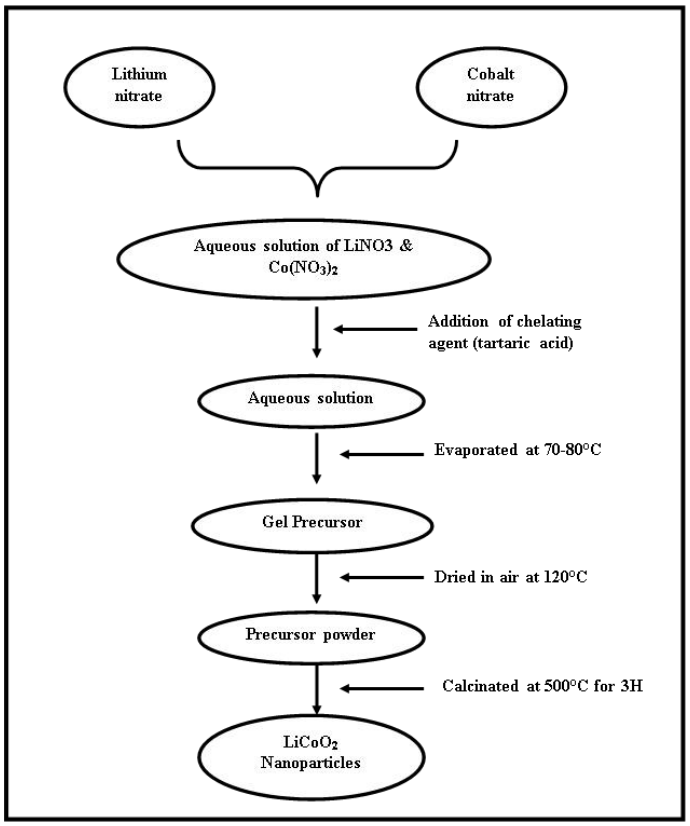

Fig 1: Flow chat of $LiCoO_2$ Nanoparticles

3. Results and Discussion

The samples of synthesized $LiCoO_2$ were characterized by powder XRD analysis, Scanning Electron Microscopy (SEM) morphological analysis, and Fourier transform infrared (FTIR) spectral analysis and UV-Vis spectral analysis.

3.1 Powder X-Ray Diffraction Analysis.

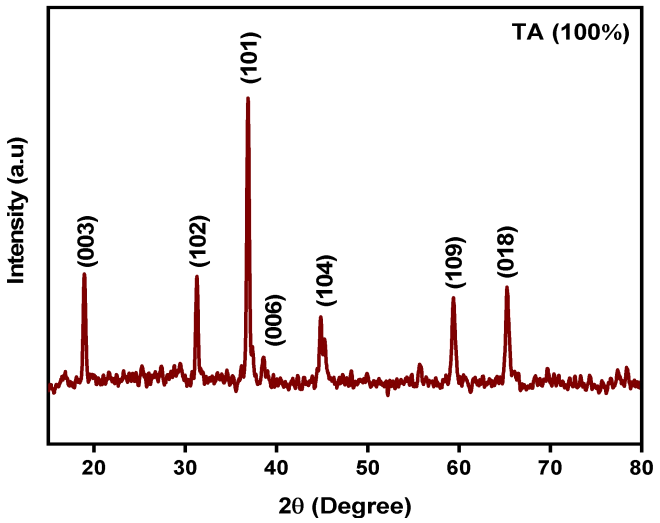

Fig. 2: XRD patterns of synthesized $LiCoO_2$ calcinated at 550°C, 3h using Tartaric Acid (TA) as chelating agents

The spectrum clearly reveals that there is increase in the intensity of peaks as the concentration of tartaric acid as a chelating agent increases. The miller indices (hkl) values of main diffracted peaks are compared and matched with JCPDF card #77-1370. The observed 2θ values are 18.96, 36.89, 44.91, 59.46, and 65.35 are associated with (003), (102), (101), (006), (104), (109), and (018) planes. From the analysis it shows that rhombohedral structures are observed. The crystallite size "D" is calculated using the Debye Scherrer formulae,

$$D = k\lambda / \beta \cos\theta \ldots\ldots\ldots nm$$

The average crystallite size was calculated using the above formula is 23 nm when tartaric acid as chelating

agent (TA 100%). The integrated intensity ratio of I (003) / (101) peaks has been considered to be a major part signifying the degree of cation ordering in the crystal structure of $LiCoO_2$. It has been proposed that electrochemical performance of cathode material is extremely improved when intensity ratio is higher than 1.2 [8]. It clearly reveals that the electrochemical performance of $LiCoO_2$ cathode material could be lesser for tartaric acid as chelating agents. The particle size and crystalline phase of material plays a major role in cathode performance of lithium batteries. Smaller size distribution resulted in better cycle stability [9].

3.2 UV-Vis Spectral analysis

The optical absorption spectrum is observed for $LiCoO_2$. The absorption spectrum ranges from 200 – 800 nm. From the absorption spectrum the conductivity band gap energy is calculated. The energy band gap is calculated using the formula

$$Eg=hc/\lambda \text{ (eV)}$$

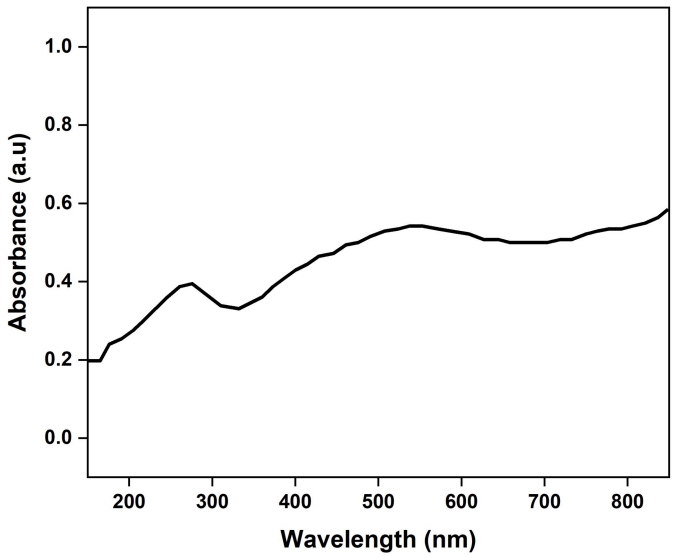

Fig. 3: UV-Vis spectrum of $LiCoO_2$ calcined at 550°C, 3h using tartaric acid as chelating agent

The Figure 3 shows the UV-Vis spectrum of $LiCoO_2$ with oxalic acid and tartaric acid as chelating agents. The band gap energy of $LiCoO_2$ using tartaric acid as chelating agent is 5.9 eV for the wavelength 207 nm.

3.3 FTIR Analysis

The vibrations in the chemical bonding of the sample are recorded through FTIR spectrum. Figure 4 shows FTIR spectra of $LiCoO_2$ prepared by sol-gel method using oxalic acid and tartaric acid as chelating agents. The spectra were recorded from 400 - 4000 cm^{-1} frequency. Functional group analysis predicts that there are two IR active bands. The FTIR bands of $LiCoO_2$ are 565, 663, 1397, 2928 and 3398 cm^{-1}.

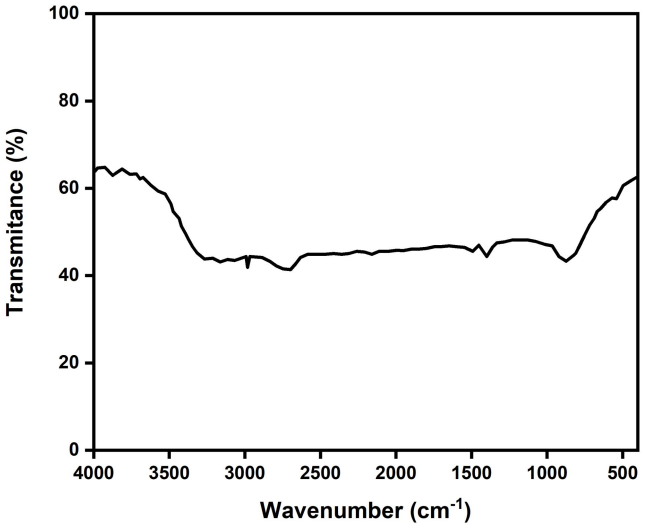

Fig. 4: FTIR spectra of $LiCoO_2$ prepared by sol-gel method using tartaric acid as chelating agent

The bands observed at 565 and 663 cm^{-1} frequency confirms the metal oxide peaks. The higher frequency band is located at 1397 cm^{-1} frequency attributed to asymmetric modes of CoO_2. The frequency band 2928 cm^{-1} is attributed to CH_3 stretching is attributed to organic impurity present in the sample. The band 3398 cm^{-1} is OH stretching vibration. The Vibrational bands are observed and matched with the literature.

3.4 Morphological analysis

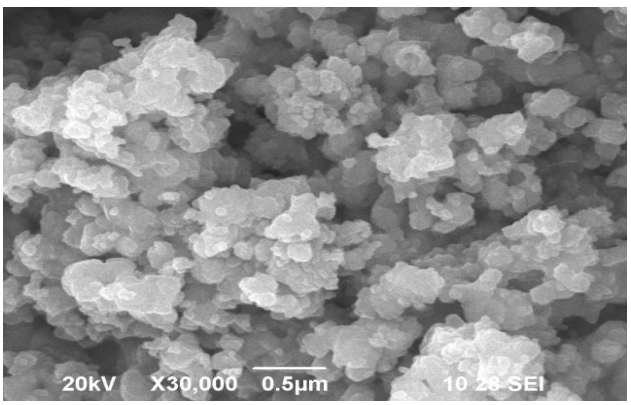

Fig. 5: SEM image of $LiCoO_2$ with tartaric acid (100%)

The morphology of $LiCoO_2$ calcinated at 550°C for 3hrs are analyzed with SEM images. The $LiCoO_2$ sample with tartaric acid as a chelating agent shows sphere like structure with little agglomeration. The average particle size is 300 nm under 0.5 µm.

Conclusion

$LiCoO_2$ Nanocrystalline has been successfully synthesized by sol-gel method. $LiCoO_2$ were prepared and verified the concentration of tartaric acid (TA 100%) as chelating agent. The dimensions of the $LiCoO_2$ Nanomaterials were calculated using Debye's- Scherrer formula and it was 23 nm and the structure was found to be Rhombohedral. The FTIR bands of $LiCoO_2$ are observed and confirmed the present of $LiCoO_2$ nanoparticles. The estimated band gap energy for the materials is found to be 5.9 eV. The SEM images shows sphere like structure formation with little agglomeration in it. From the SEM images the average crystallite size is found 300 nm.

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