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Research Article

Synthesis and physical characteristics of nano crystalline $LiMn_{2-x}Co_xO_4$ powder using combustion method

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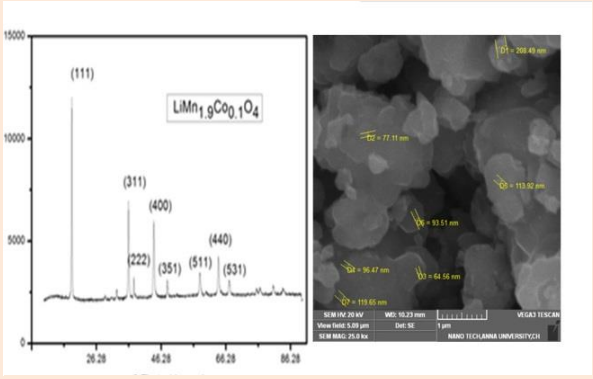
Abstract

Spinel $LiMn_{2-x}Co_xO_4$ powder with nano particle size powders were successfully synthesized by Solid state combustion method. Stoichiometric amounts of lithium nitrate, manganese nitrate and cobalt nitrate with urea as the igniter are ground well using mortar and pestle to get a homogeneous paste. Then the mixed product is heated to 100°C and kept for 1 hour in muffle furnace and then heated to 900°C for 12 hrs. The synthesized $LiMn_{2-x}Co_xO_4$ powder by combustion method were investigated by X-ray Diffractometer (XRD), Scanning Electron Microscope (SEM) and Fourier Transform Infrared Spectroscope(FTIR).The synthesis process of $LiMn_{2-x}Co_xO_4$ nano crystalline powder involved the combustion of redox mixture in which metal nitrate acted as an oxidizing agent and urea as a reducing agent. The crystallography of the synthesized powder was characterized using a X-ray powder diffractometer. The particle size is calculated using Scherrer formula which is found to be 50 nm and the lattice constant is 8.253 nm. The morphological characteristics of the synthesized material were studied using scanning electron microscope. The SEM image of $LiMn_{2-x}Co_xO_4$ confirmed the nanoparticles of the order of 100 nm. The FTIR spectrum of $LiMn_{2-x}Co_xO_4$ is taken. The bands observed at 511 cm^{-1} is assigned to the Li-O-H vibrations and the band at 2962cm^{-1} is attributed to the bending modes of Li-O-Mn. The synthesis method is very simple and novel.

Keywords: Spinel $LiMn_{2-x}Co_xO_4$, Solid state combustion method, X-ray Diffractometer (XRD), Scanning Electron Microscope (SEM) and Fourier Transform Infrared Spectroscope (FTIR)



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Introduction

For almost more than 20 years , spinel $LiMn_2O_4$ has been widely studied as a promising cathode materials for lithium-ion [1-3] on one aspect, because it has many advantages in view of low cost, low toxicity, high working voltages and high drawbacks such as severe capacity fading during charge-discharges cycles and low specific capacity. Also it has other advantages, such as high –rate capability, higher thermal stability and high power density. These have made it a hot topic of research and promising cathode materials usage in large scale lithium- ion batteries for Electric Vehicles (EV) or Hybrid Electric Vehicles (HEV) in recent years [4-7]. However its low specific discharge capacity, especially its fast capacity fading at high temperature limits its application in large scale. It has been agreed that there are three main reasons for the capacity fading (1) manganese dissolution from $LiMn_2O_4$ into electrolyte solution, (2) the Jahn-Teller effect out of the deep discharge to distort the crystal lattice, and (3) the decomposition of electrolyte solution in the higher voltage region. It has been verified by many researchers that single metal element doping is one good way to improve the cycling performance of $LiMn_2O_4$ [8].

It is believed that single-phase, homogeneity, uniform particle morphology with nanometer size distribution is the desired feature for achieving a higher electrode activity. Nanometer-scale structured electrode materials are of great interest as potential building blocks for future generation electronics devices with greatly reduced size, because they show higher capacity and better cycling performance than conventional electrodes composed of this kind of materials. There have been increased interests in synthesizing nanostructure and their derivative compounds for their diverse physicochemical properties and potential application as cathode materials for lithium ion batteries [9-11]

Experimental Method

Stoichiometric amounts of $LiNO_3$, Mn $(NO_3)_2$ and $Co(NO_3)_2$ were taken along with urea as the fuel and made into a homogeneous paste by adding few drops of glycerol as the binding material and then the product was heated to 100°C and kept for one hour in a muffle furnace and then slowly heated to 700°C and maintained in that temperature for ten hours. The dried mass from the furnace was ground well with the pestle and mortar to get a fine black nano powder. The synthesis procedure is given in the following **Figure 1**.

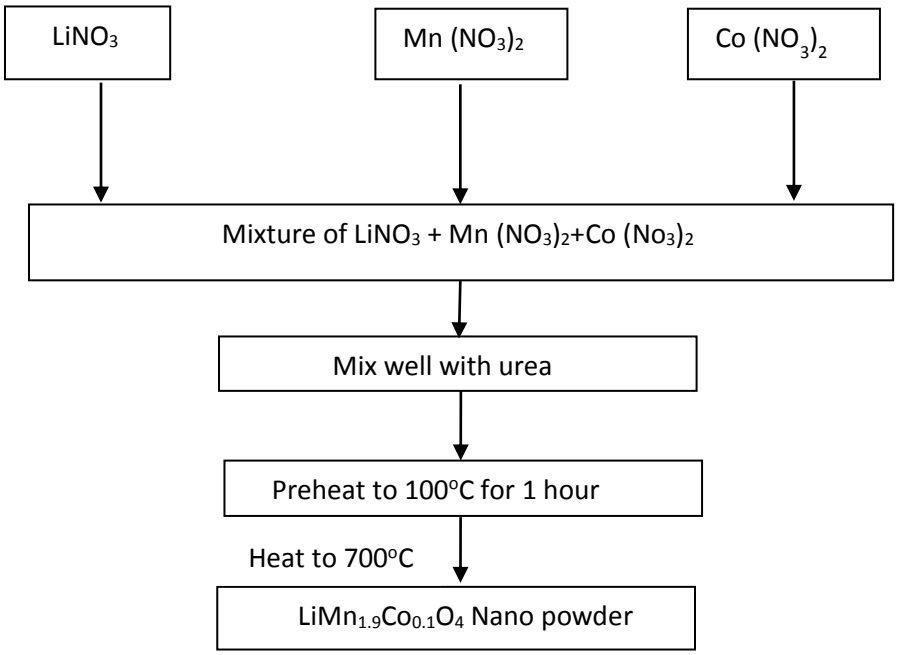

Figure 1 Synthesis procedure for Co doped $LiMn_2O_4$

Results and discussion

XRD analysis of Co doped $LiMn_2O_4$

The XRD patterns of $LiMn_{1.9}Co_{0.1}O_4$ calcined at 700°C is shown in **Figure 2**. The XRD patterns shows that the spinel $LiMn_{1.9}Co_{0.1}O_4$ as pure and crystalline in nature and the observed XRD pattern is in good agreement with the standard pattern of the $LiMn_2O_4$ (JCPDS card No.88-1026) and confirmed the formation of cubic spinel structure with space group Fd3m [12]. From the X-Ray data the particle size is calculated using Scherrer formula and is found to be 45nm.The calculated lattice constant value for of the synthesized $LiMn_{1.9}Co_{0.1}O_4$ powder is 8.272Å which is in good agreement with the reported value by Subramania et al. [13]. Because of the substitution of Mn atom with Co^{3+}, the lattice constant of $LiMn_{1.9}Co_{0.1}O_4$ is lower than that of $LiMn_2O_4$.The decrease in lattice constant lead to possible minimal Jahn-Teller distortion which enhances the structural stability.

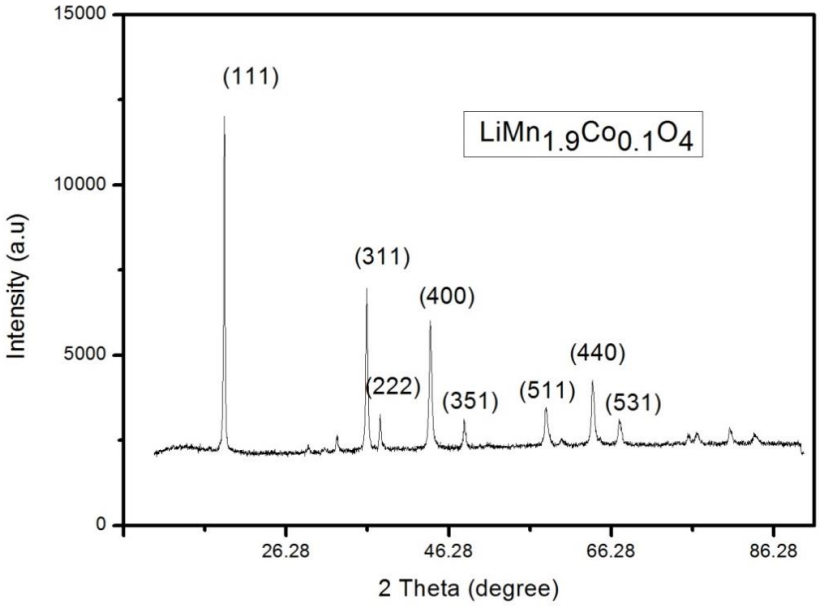

Figure 2 XRD patterns of $LiMn_{1.9}Co_{0.1}O_4$

Particle size and Morphological studies

SEM images of nanocrystalline $LiMn_{1.9}Co_{0.1}O_4$ are shown in **Figure 3**. The SEM photograph reveals the formation of uniform grains of nano particles size. The particles are uniformly distributed and there is little agglomeration. The average particle size of 70nm is observed from SEM image which is confirmed from [16-17].

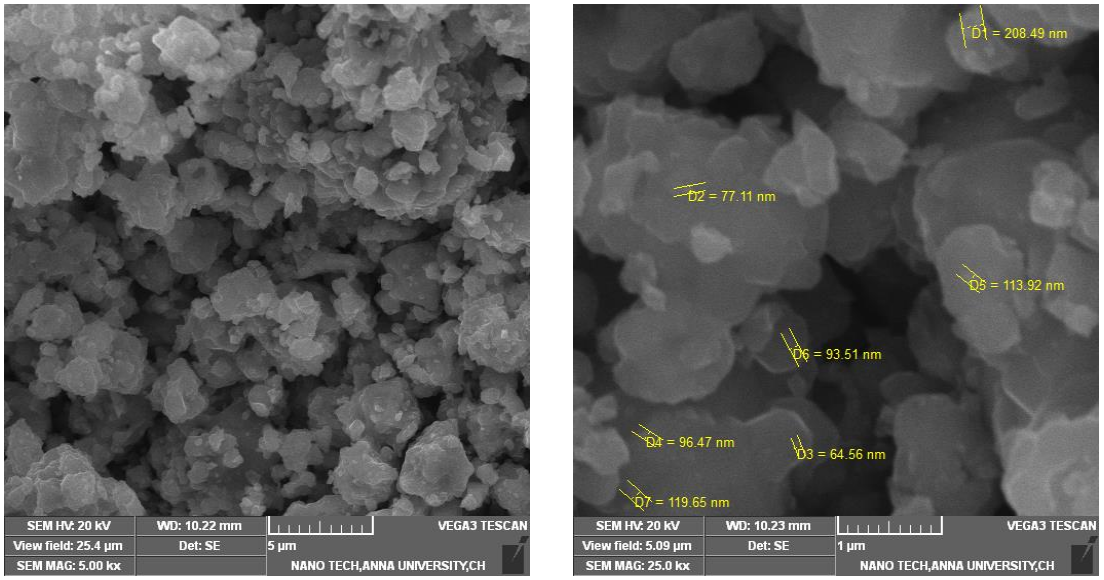

Figure 3 SEM image of $LiMn_{1.9}Co_{0.1}O_4$

FTIR studies

The FTIR spectra for Co doped $LiMn_2O_4$ are shown in **Figure 4**. The band observed at 511 cm^{-1} indicating the presence of Li-O-H bond. The band observed 2962cm^{-1} is due to Li-O-Mn. The peak around 3454 cm^{-1} indicates the presence of Li-Co-Mn-O. Thus all the vibrations of the bonds have been clearly investigated from FTIR studies [18-20].

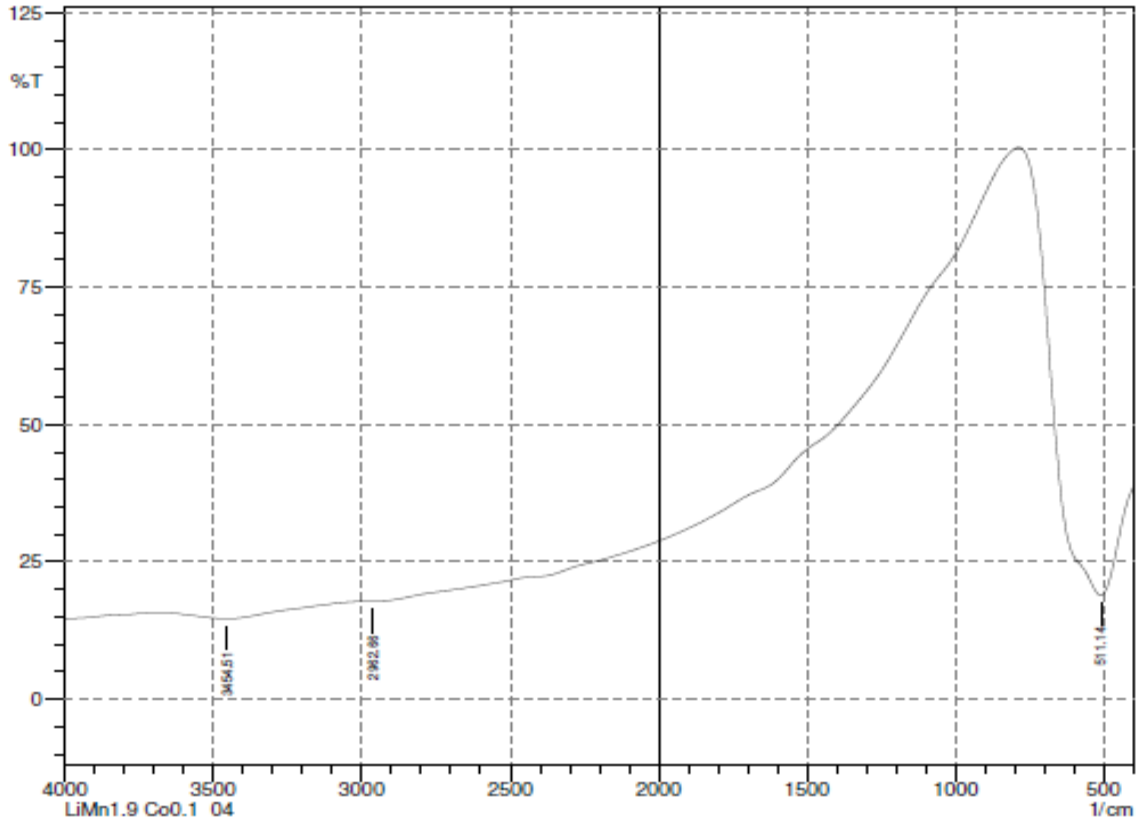

Figure 4 FTIR spectra for $LiMn_{1.9}Co_{0.1}O_4$

Conclusion

The solid state combustion method could be a promising method for synthesizing $LiMn_{1.9}Co_{0.1}O_4$ nano crystalline powder. The XRD results confirm the formation of cubic spinel structure. The SEM result reveals the formation of nano particle size morphology. The FTIR results confirm the formation of Li-Mn-O bond. The experimental condition can be modified to reduce the size of the nano particles and further physical characteristics can be carried out to establish the best cathode material for lithium ion batteries.

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