

Synthesis and Characterization of Nano Crystalline LiMn_2O_4 Powder for Lithium-Ion Batteries

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Abstract

A simple solid state combustion method has been tried for the preparation of nano particle sized LiMn_2O_4 powder with urea as the igniter and glycerol as the binding material. Nitrates of Li^+ and Mn^{3+} were mixed together to form a homogeneous paste. This paste was carefully heated to 100°C in the muffle furnace and then the product is heated to 800°C for 12 hrs. The obtained nano powder was subjected to XRD, TEM, and FTIR analysis. The particle size of the material was roughly calculated from the X-ray data using Scherrer equation. The TEM analysis was carried out in detail to confirm the particle size. The procedure is very simple and novel.

Keywords: *Nano particle, LiMn_2O_4 , transmission electron microscope, solid state combustion method, lithium batteries*

INTRODUCTION

Lithium-ion batteries have become major attractive power sources for modern portable electronic devices such as mobile phones, notebook computers and camera corders. They also very much useful for electric vehicles, hybrid electric vehicles and stationary power storage, which will bring a significant contribution to reduce green house gas emissions, global warming and climate change. Materials

research is a key role in the development of next generation of advanced lithium-ion batteries with high energy density, high power density and long cycle life. LiMn_2O_4 has been emerging as a new cathode material for lithium ion batteries with low cost [1–2].

LiCoO_2 is a commonly used cathode material in commercial lithium ion batteries. The high cost, toxicity and

limited abundance of cobalt have been recognized to be disadvantages. As a result, alternative cathode materials have attracted much interest. Spinel LiMn_2O_4 is considered as one of the most promising alternative cathode materials and investigated widely because of its low cost, good safety, environmental benign nature and high abundance [3–5].

Several synthesis processes, such as the sol-gel process, the Pechini process, and the emulsion-drying process have been investigated for obtaining LiMn_2O_4 with homogeneous composition, spherical grain shape [6–8]. However, most of these methods involve complicate treatment process or expensive reagent, which is time consuming and high cost for commercial applications [9]. In this work, a combustion process has been investigated for obtaining LiMn_2O_4 . This process uses the combustion reaction of some oxidizers and fuels, such as glycine and urea, which emits heat and promotes a chemical reaction to form rapidly oxide powders [10].

EXPERIMENTAL

Synthesis

Nano crystalline cathode material for lithium batteries are prepared by solid

state combustion method. Stoichiometric amounts of pure AR LiNO_3 and $\text{Mn}(\text{NO}_3)_2$ are taken along with urea as the fuel and made into a homogeneous paste by using a pestle and mortar arrangement. Then, the product was transferred to a ceramic crucible. This crucible was introduced into the muffle furnace and the furnace was initially heated to 100°C and kept for 1 h in a muffle furnace to remove any moisture and then slowly heated to 800°C and maintained in that temperature for 12 hrs. The product was cooled slowly to room temperature and the dried mass from the furnace was ground well with the pestle and mortar to get a fine powder. A small portion of the sample was examined for its purity and structure by X-ray.

XRD Studies

The purity, phase identification and evaluation of lattice parameters of the products are determined by JEOL X-ray diffraction analysis (JDX-8030) using $\text{Cu-K}\alpha$ radiation. The X-ray diffraction patterns of the Nano crystalline powder are obtained at 25°C in the range of 10° to 80° in step scans. The step size and scan size are fixed at 0.1 and 2° per minute respectively. The x-ray diffraction pattern for LiMn_2O_4 nanocrystalline powder is given in Figure 1.

The particle size of the material prepared is roughly calculated from the above X-ray data using Scherrer formula.

Average particle size $t = 0.9 \lambda / \beta \cos \theta$

Where, λ is the wavelength of the X-ray used, β is the full width at half maximum and θ is the Bragg angle. Using this formula, the calculated particle size of LiMn_2O_4 nanocrystalline powder is in the range of 30 nm. Such excellent nanoparticles will provide excellent cycle performance for Cathode Material of Lithium batteries [11].

The XRD pattern of LiMn_2O_4 calcined at 800°C shows high intensity spectral profiles such as (111), (311), (222), (400), (331), (551), (440) and (531) depict the phase pure structure and formation of a highly crystalline spinel, which is in good agreement with previous reports [12–15]. All these samples were identified as cubic spinel family with a space group $\text{Fd}\bar{3}\text{m}$ from JCPDS file (card no 35-0782). This means that lithium ions occupy tetrahedral 8a sites and manganese ions occupy 16d sites [16–18].

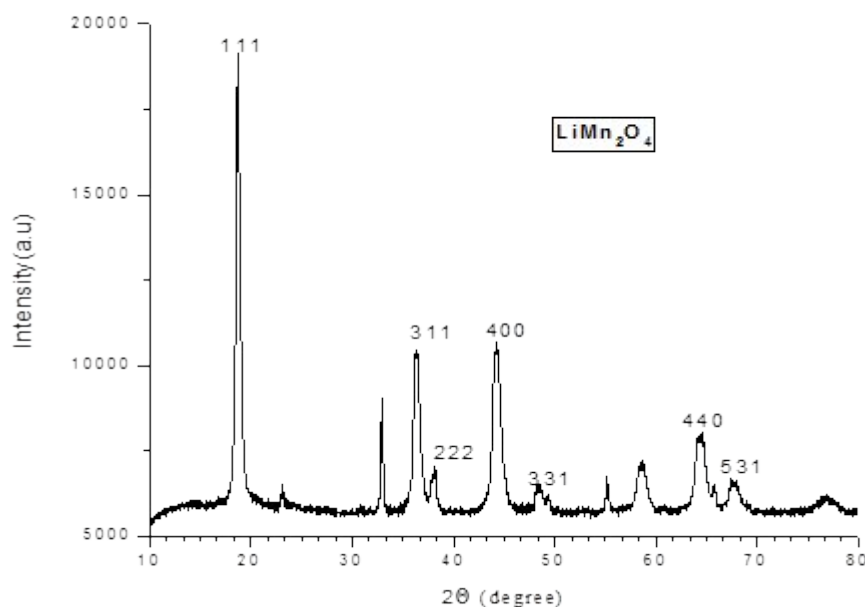


Fig. 1: XRD Pattern of LiMn_2O_4 Synthesised by Combustion Method.

TEM Analyses

To observe the powder morphology and size of the synthesized LiMn_2O_4 nano crystalline powder, TEM Photograph is taken by transmission electron microscope which is shown in Figure 2. The TEM image shows nano particles of the order of 50 nm with individual morphology.

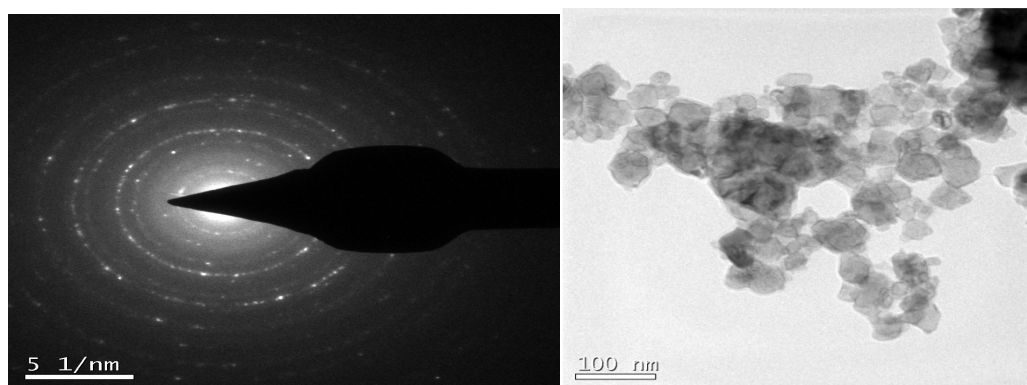


Fig. 2: Transmission Electron Micrographs of LiMn_2O_4 .

Spectroscopic Studies

The Fourier Transform Infrared [FTIR] spectra of the synthesized LiMn_2O_4 nano crystalline powder recorded at room temperature are shown in Figure 3. The low frequency absorption bands at 512, 619 cm^{-1} are attributed to asymmetric modes of Mn-O. The high frequency absorption bands at 2921 cm^{-1} are assigned to the bending modes of Mn-O. The peak around 617 cm^{-1} is assignable to the Li-Mn-O stretching vibration bond [19, 20].

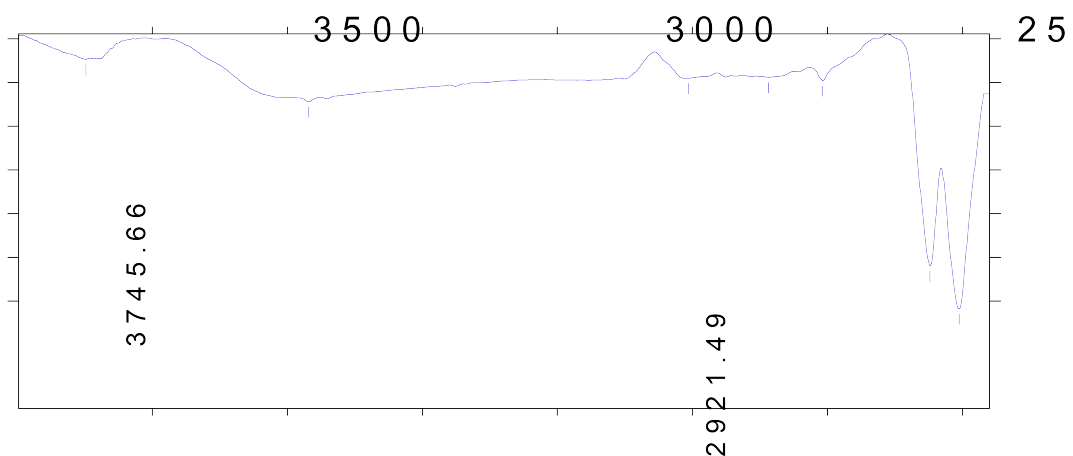


Fig. 3: FTIR Spectrum of LiMn_2O_4 .

RESULTS AND DISCUSSIONS

LiMn₂O₄ nano crystalline powder is synthesized by solid state combustion method. The X- ray diffraction analysis confirms the particle size of the synthesized material is in the range of 30 nm. The TEM analysis confirms the formation of uniform grains in the range of 50 nm. The FTIR Spectra shows the asymmetric stretching modes and bending modes of Mn-O.

CONCLUSION

Therefore this solid state combustion method could be a promising method for synthesizing LiMn₂O₄ nanocrystalline powder. The experimental conditions will be modified to reduce the size of the nano particles and further physical studies can be carried out to establish the best cathode material for Li- ion batteries.

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