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Synthesis and Characterization of Nano Crystalline $LiMn_2O_4$ Material by Solid State Combustion Method for lithium Batteries

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Abstract: A simple solid statecombustion 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 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, TGA 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 are also very much useful for electric vehicles, hybrid electric vehicles and stationary power storage, where they significantly contribute to the reduction of green house gas emissions, global warming and climate change. Material research plays 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. In particular $LiMn_2O_4$ has been emerging as a new cathode material for lithium ion batteries with low cost.

$LiCoO_2$ 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 [1,2].

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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 [3]. However, most of these methods involve complicate treatment process or expensive reagent, which is time consuming and expensive for commercial applications [4]. In this work, a combustion process has been investigated for obtaining nano crystalline $LiMn_2O_4$. This process uses the combustion reaction of some oxidizers and fuels, such as glycerol and urea, which emits heat and promotes a chemical reaction to form rapidly oxide powders .

2. Experimental

2.1. Synthesis

Nano crystalline cathode material for lithium batteries are prepared by solid state combustion method as given in flow chart figure 1.

Stoichiometric amounts of pure AR $LiNO_3$ and $Mn(NO_3)_2$ are taken along with urea as the self heating material and made into a homogeneous paste by using a pestle and mortararrangement. 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 hour in a muffle furnace to remove any moisture and then slowly heated to

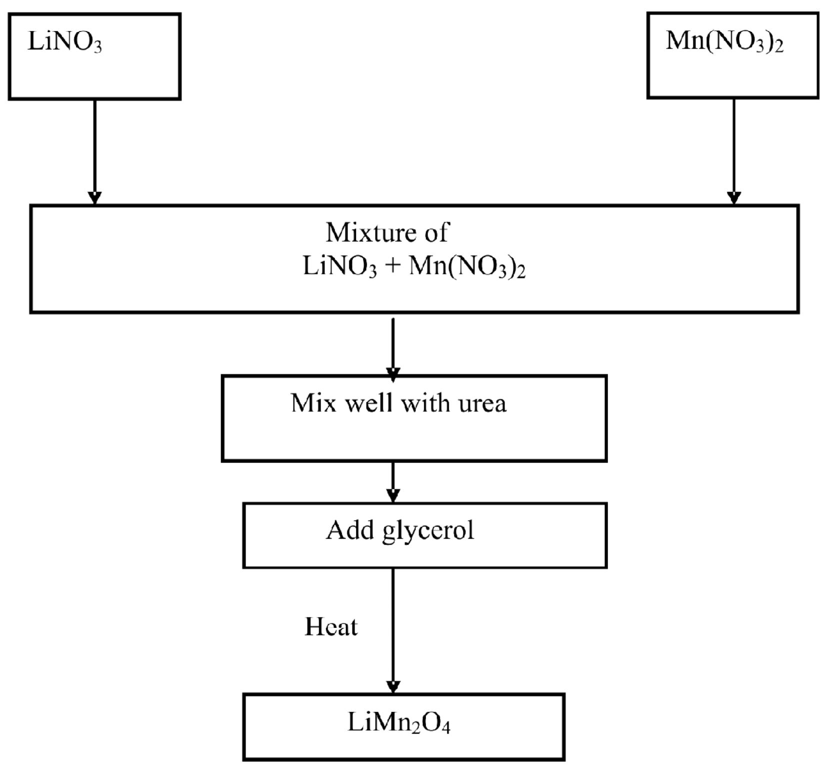

Figure 1: Synthesis procedure of $LiMn_2O_4$.

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[10]. A small portion of the sample was examined for its purity and structure by x-ray.

2.2. 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 Cu-Ká radiation. The x–ray diffraction patterns of the nano crystalline powder is 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°C per minute respectively. The x-ray diffraction pattern for $LiMn_2O_4$ nano crystalline powder is given in figure 2.

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 $LiMn_2O_4$ nano crystalline powder is in the range of 40 nm. Such excellent nanoparticles will provide excellent cycle performance for cathode material of lithium batteries [6, 7]. Also the x-ray

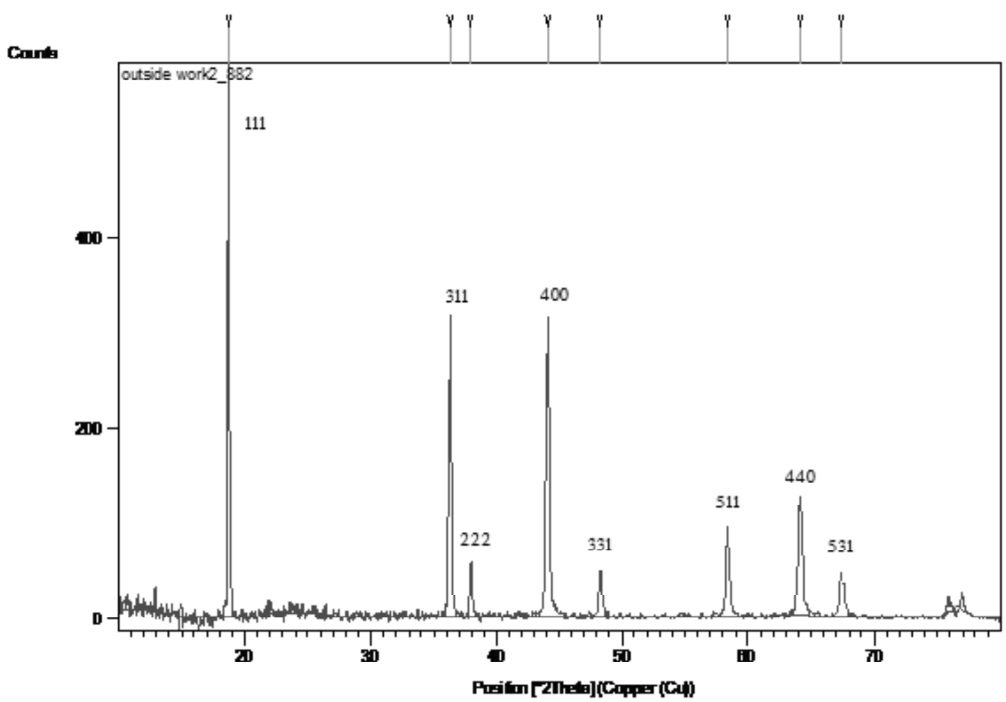

Figure 2: XRD Pattern of $LiMn_2O_4$ Synthesised by Combustion Method

reflection of $LiMn_2O_4$ at 850ºC shows high intensity spectral profiles such as (111), (311), (222), (400), (331), (551), (440) and (351) which depict the phase pure structure and formation of a highly crystalline spinel, which is in good agreement with previous reports [5,11]. All these samples were identified as cubic spinel family with a space group Fd3m from JCPDS file. This means that lithium ions occupy tetrahedral 8a sites and manganese also occupies 16d sites [9].

2.3. 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 fig. 3

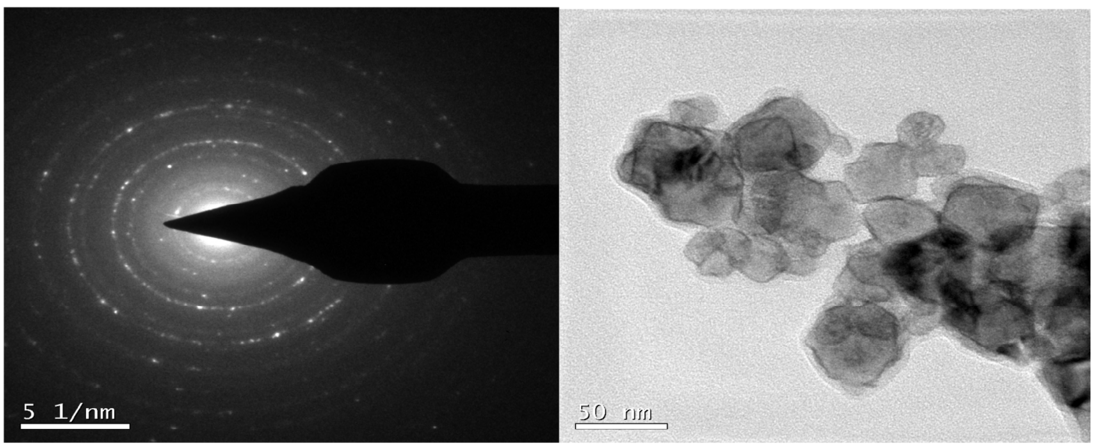

Figure 3: Transmission Electron Micrographs of $LiMn_2O_4$

2.4. Spectroscopic Studies

The Fourier Transform Infrared [FTIR] spectra of the synthesized $LiMn_2O_4$nano crystalline powder recorded at room temperature is shown in fig. 4. The low frequency absorption bands at 512, 619 cm^{-1} are attributed to asymmetric modes of Mn-O [9,12]. The high frequency absorption bands at 2921cm^{-1} are assigned to the bending modes of Mn-O. The peak around 617cm^{-1} is assignable to the Li-Mn-O stretching vibration bond [14,15].

2.5. TGA Studies

The thermal behavior of $LiMn_2O_4$ nano powders was analyzed by thermo gravimetric analysis. The TGA curves are given in the following figure 5.

3. Results and Discussions

$LiMn_2O_4$ 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 40nm. The $LiMn_2O_4$XRD showsthe features of the spinel structure with Fd3m

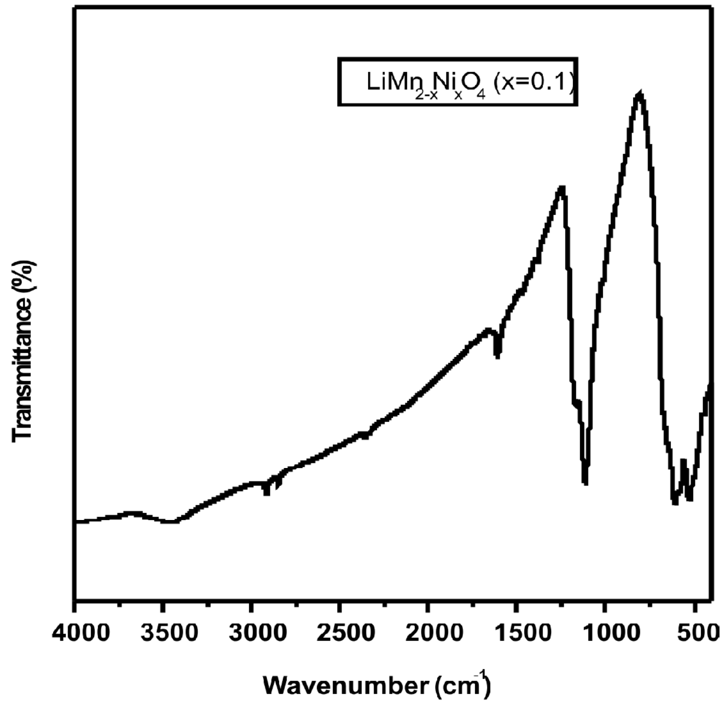

Figure 4: FTIR Spectrum of $LiMn_2O_4$

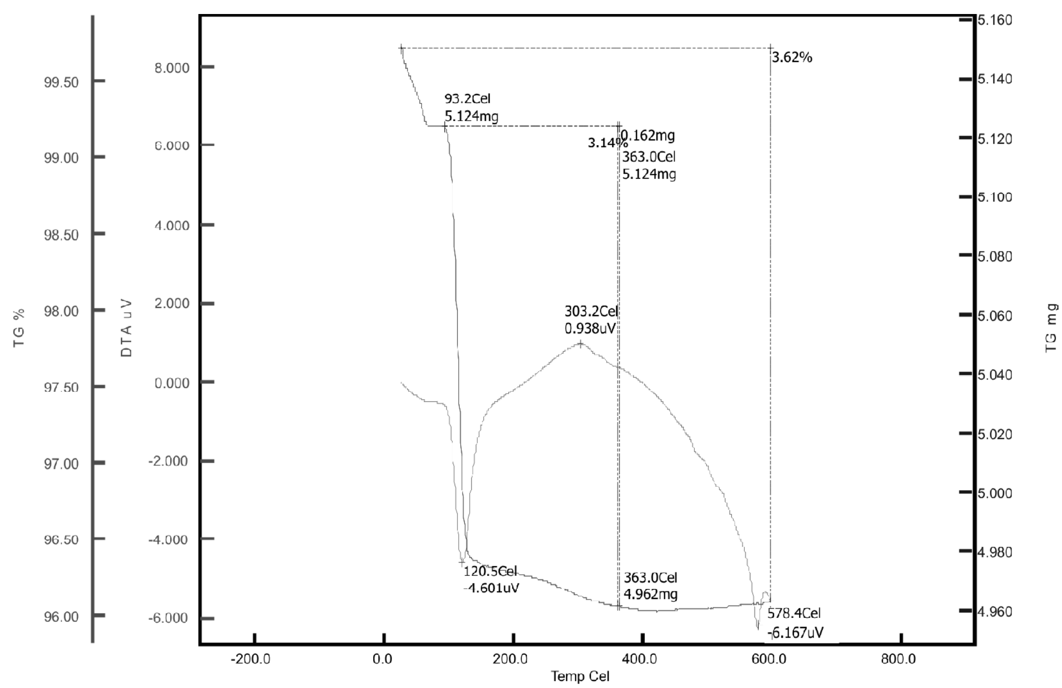

Figure 5: TG/TDA result of $LiMn_2O_4$

space group (JCPS card No. 35-782)[8,13]. The TEM analysis confirms the formation of uniform grains in the range of 50nm. The FTIRSpectra shows the asymmetric stretching modes and bending modes of Mn-O.Thermal analysis gives the exact phase formation and crystallization temperature of the sample. It is found that the product undergoes complete crystallization above 600 degree Centigrade.

4. Conclusions

Therefore this solid state combustion method could be a promising method for synthesizing $LiMn_2O_4$ nano crystalline 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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