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Synthesis and Characteristics of Nano Crystalline $LiAl_xMn_{2-x}O_4$ Cathode Material Using Solid State Combustion Method for Li-ion Batteries†

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Lithium-ion batteries are most advanced batteries used for modern portable electronic devices such as mobile phones, notebook computers and camera recorders. They are also big potential for lithium-ion batteries to be used for electric vehicles, hybrid electric vehicles and stationary power storage. In particular, the later 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. But it suffers from loss of capacity during cycling. To improve the cycle performance of spinel $LiMn_2O_4$, Al doped $LiMn_2O_4$ powders are synthesized. A simple solid state combustion method has been tried for the preparation of nano particle size $LiAl_xMn_{2-x}O_4$ powder with urea as the igniter and glycerol as the binding material. $LiNO_3$, $Al(NO_3)_3$ and $Mn(NO_3)_3$ were mixed together to form a homogeneous paste. This paste was carefully heated to 100 ºC in the muffle furnace and then the product is heated to 800 ºC for 12 h. The obtained nano powder was subjected to XRD, TEM, TG/DTA 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.

Key Words: Nano particles, $LiAl_xMn_{2-x}O_4$, Transmission electron microscope, Solid state combustion method, Li-ion batteries.

INTRODUCTION

Lithium-ion batteries have become major attractive power sources for modern portable electronic devices such as mobile phones, notebook computers and camera recorders. They are 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. $LiAl_xMn_{2-x}O_4$ 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 $LiAl_xMn_{2-x}O_4$ 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]. Several synthesis processes, such as the sol-gel process, the Pechini process and the emulsion-drying process have been investigated for obtaining $LiAl_xMn_{2-x}O_4$ with homogeneous composition, spherical grain shape[3]. However, most of these methods involve complicated treatment process or expensive reagent, which is time consuming and high cost for commercial applications[4]. In this work, a combustion process has been investigated for obtaining $LiAl_xMn_{2-x}O_4$. 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.

EXPERIMENTAL

Nano crystalline cathode material for lithium batteries are prepared by solid state combustion method as given in flow chart Fig. 1. Stoichiometric amounts of pure AR $LiNO_3$, $Mn(NO_3)_2$ and $Al(NO_3)_3$ are taken along with urea as the self heating material 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 ºC and kept for 1 h in a

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muffle furnace to remove any moisture and then slowly heated to 800 ºC and maintained the temperature for 12 h. 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[5].

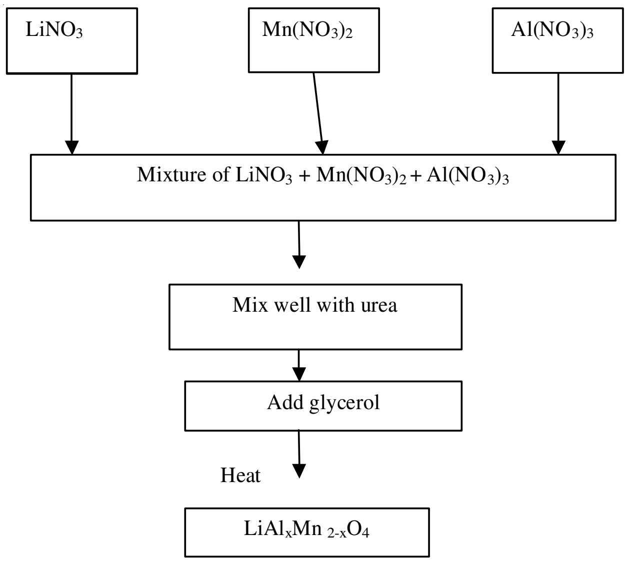

Fig 1. Synthesis procedure of $LiAl_xMn_{2-x}O_4$

The purity, phase identification and evaluation of lattice parameters of the products are determined by JEOL X-ray diffraction analysis (JDX-8030) using CuK_α radiation. The X-ray diffraction patterns of the nano crystalline powder are obtained at 25 ºC in the range of 10º to 80º in step scans. The step size and scan size are fixed at 0.1 and 2 ºC per minute respectively. The X-ray diffraction pattern for $LiAl_xMn_{2-x}O_4$ nano crystalline powder is given in Fig. 2.

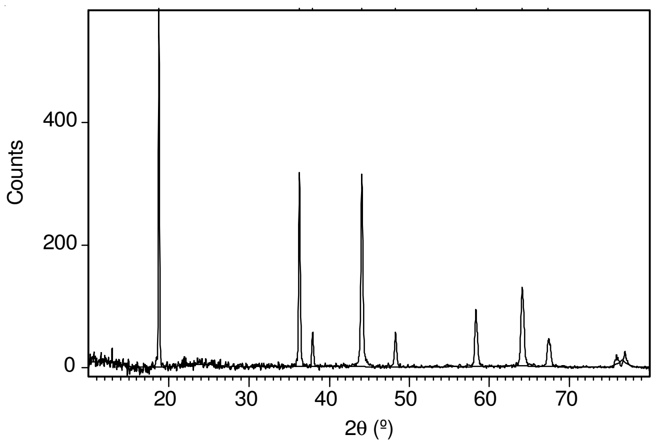

Fig. 2. XRD pattern of $LiAl_xMn_{2-x}O_4$ synthesized by combustion method

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 $LiAl_xMn_{2-x}O_4$ nano crystalline powder is in the range of 40 nm. Such excellent nanoparticles will provide excellent cycle performance for cathode material of lithium batteries[2]. Also the X-ray reflection of $LiAl_xMn_{2-x}O_4$ at 800 ºC shows high intensity spectral profiles such as (111), (311), (222), (400), (331), (551), (440) and (351) depict the phase pure structure and formation of a highly crystalline spinel, which is in good agreement with previous reports[6,7]. All these samples were identified as cubic spinel family with a space group Fd3 m from JCPDS file. This means that lithium ions occupy tetrahedral 8a sites and manganese also occupies 16 d sites[3].

To observe the powder morphology and size of the synthesized $LiAl_xMn_{2-x}O_4$ nano crystalline powder, TEM image is taken by transmission electron microscope (Fig. 3).

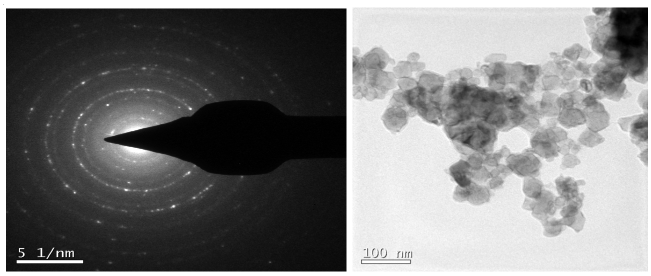

Fig. 3. Transmission electron micrographs of $LiAl_xMn_{2-x}O_4$

The Fourier transform infrared spectra of the synthesized $LiAl_xMn_{2-x}O_4$ 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. 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[7,8].

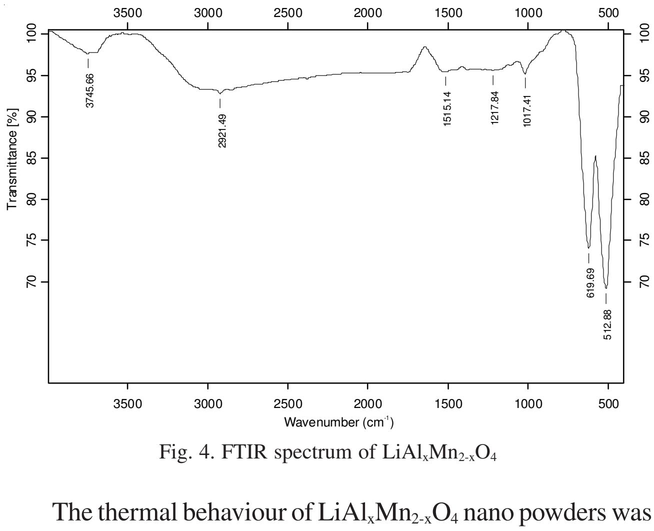

Fig. 4. FTIR spectrum of $LiAl_xMn_{2-x}O_4$

The thermal behaviour of $LiAl_xMn_{2-x}O_4$ nano powders was analyzed by thermo gravimetric analysis. The TGA curves are given (Fig. 5).

RESULTS AND DISCUSSION

$LiAl_xMn_{2-x}O_4$ 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 40 nm. The $LiAl_xMn_{2-x}O_4$ XRD shows the features of the spinel structure with Fd3 m space group (JCPS card No.35-

782). 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. Thermal analysis gives the exact phase formation and crystallization temperature of the sample. It is found that the product undergoes complete crystallization above 1000 ºC.

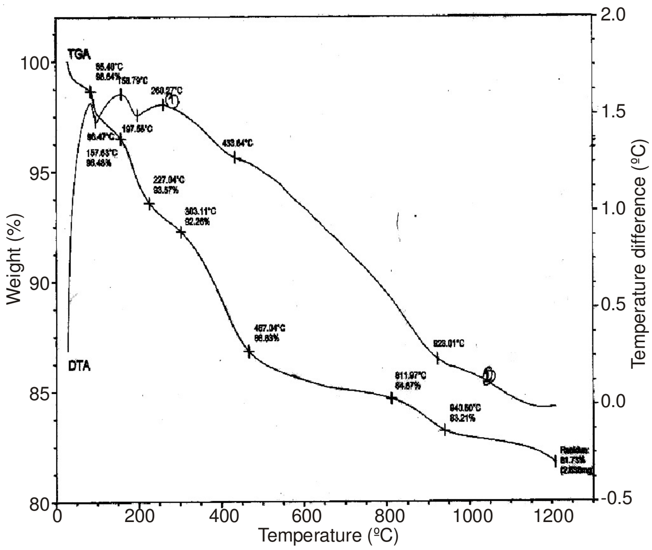

Fig. 5. TG/TDA result of $LiMn_2O_4$

Conclusion

Therefore this solid state combustion method could be a promising method for synthesizing $LiAl_xMn_{2-x}O_4$ 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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