Research Article

Effects of different metal ion doping on nano crystalline $LiMn_2O_4$ as cathodes for Lithium ions batteries

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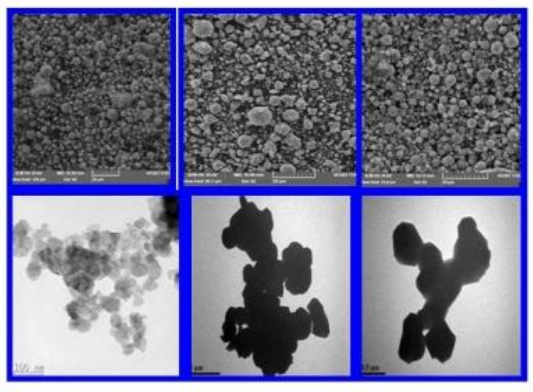
Abstract

The spinel $LiMn_2O_4$ is one of the most promising cathode materials due to its low cost, non-toxicity and improved safety compared with commercial $LiCoO_2$. Developing Nano structured electrode materials represents one of the most attractive strategies to dramatically enhance battery performance such as, capacity, rate capability, and cycling life. Currently extensive efforts have been devoted for developing nano structured $LiMn_2O_4$ to further improve the rate capability of lithium-ion batteries for high power applications.In spite of these advantages,$LiMn_2O_4$ has the problem of severe capacity fading during charge and discharge cycles which makes it unsuitable for commercial applications . Intensive research has particularly focused on the mechanism of capacity fading and has suggested numerous solutions. Among these methods doping is considered to be an effective path to improve the electrochemical performance of spinel $LiMn_2O_4$. So several attempts have been made for improving the lithium manganese spinel by doping various metals ions.In this paper, a solid state combustion method has been used to synthesize Al and Ni doped spinel $LiMn_2O_4$.



Keywords: Nano structured, Capacity fading, Lithium ion battery, Combustion method, Doped $LiMn_2O_4$

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Introduction

Due to the fast depletion of fossil fuels and the associated environmental problems, there has been a strong and ever increasing demand for renewable energy and reliable devices for energy conversion and storage. Lithium batteries, with their superior energy density, have become attractive energy –storage systems for portable electronic devices, such as cellphones, digital cameras, and laptops [1-2]. Currently the world wide marked for Lithium batteries is valued as 10 billion dollars per annum and it is still expanding. The emerging new technologies such as electric vehicles for transportation and smart glides for utilizing renewable energy sources will largely depend on the development and application of lithium-ion batteries for large scale energy storage [3-7].

Two methods are generally employed to increase the rate capability of the cathode materials. One method is to reduce the crystalline size and particle size of the cathode materials from micrometer to nanometer so that the electron and lithium ion diffusion paths can be shortened doping with metal ions like Al^{3+}, Ni^{2+}, Co^{2+}, Cu^{2+}, Cr^{2+} has been suggested to stabilize its structure[8-9].Among the studied cathode material the spinel $LiMn_2O_4$,with the theoretical storage capacity of $148mAhg^{-1}$,has been recognized the most potential candidate to replace $LiCoO_2$ in commercialized lithium ion batteries,because of its high abundance, cost effective, and environmental benign[10-11-12].

Experimental

The $LiM_{0.1}Mn_{1.9}O_4$ (M=Al, Ni) were prepared by combustion method using urea as the fuel. The Stoichiometric amounts $LiNo_3$, $Mn(NO_3)_2$ and $Al(NO_3)_2$ are mixed with were mixed with urea as the igniter and glycerol as the binding material to form a homogeneous paste. This paste was carefully heated to 100° C in the muffle furnace and then the product is heated to 900° C for15hrs, then cooled to room temperature naturally in the furnace. The synthesis procedure is given in the following **figure 1**

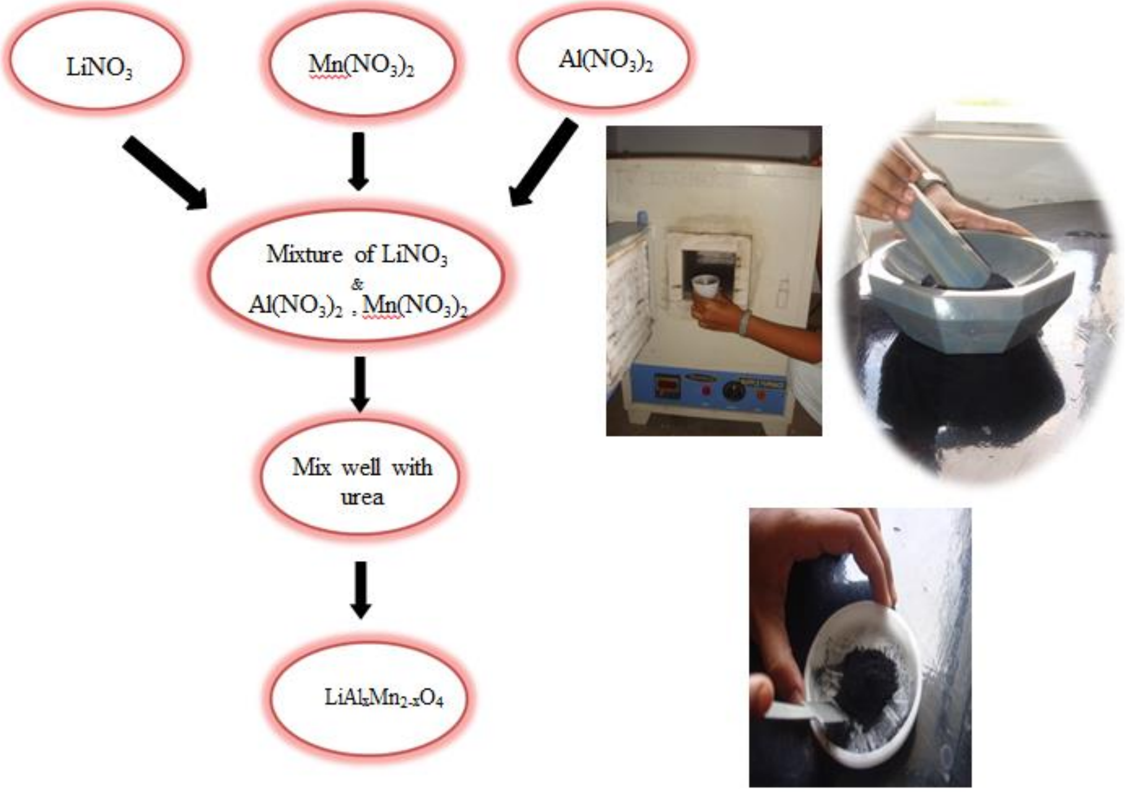

Figure 1 synthesis procedure

were mixed with urea as the igniter and glycerol as the binding material to form a homogeneous paste. This paste was carefully heated to 100° C in the muffle furnace and kept for one hour and then the product is heated to 900°C for12hrs.

Results and discussion

X-ray diffraction analysis:

X-ray diffraction patterns of undoped and Ni and Al doped LiMn2O4 samples are presented in **figure 2**. It could be seen that all the materials show single phase diffraction patterns. This could be indexed on the basis of the cubic structure. XRD peaks are (111)(311), (222), (400), (331), (551), (440), (531), and (222) respectively. These observations are in good agreement with the earlier reports [1-10]. $LiMn_2O_4$ spinel belongs to Fd3m symmetry, wherein manganese ions occupy 16d sites and oxygen ions occupy 32e sites [14]. The XRD patterns for $LiMn_2O_4$ and $LiAl_{0.1}Mn_{1.9}O_4$ confirms to JCPDS card no 35-78 corresponding to single phase spinel compound without any impurities. It is in good agreement with that of previous work. From the X-ray diffraction patterns it could be seen that the main diffraction peaks are not only strong and very sharp, but also very symmetrical, which shows that the synthesized samples have complete crystal structure and the arrangements of the internal sites are more regular and almost no cation mixing happens .Some crystal structure parameters for the materials are presented in **Table 1**.

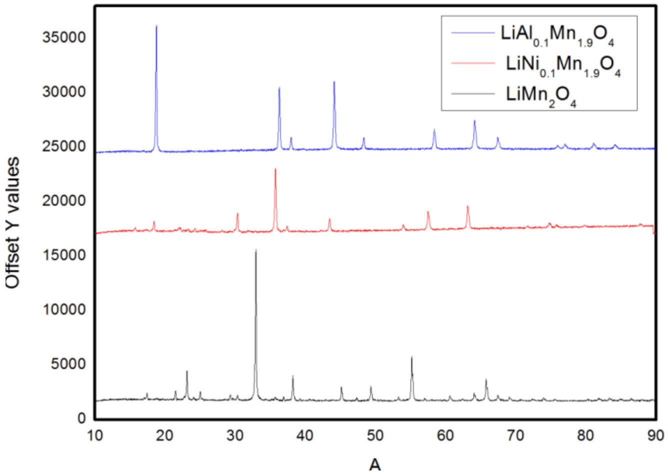

Figure 2 XRD patterns of a)$LiAl_{0.1}Mn_{1.9}O_4$ b)$LiNi_{0.1}Mn_{1.9}O_4$ c)$LiMn_2O_4$

Table 1 Lattice parameters and crystalline sizes of the prepared samples

Samples	**Lattice parameter (A°)**	**Volume size(A^3)**	**Crystallite size(nm)**
$LiMn_2O_4$	8.2136	554.1159	30
$LiNi_{0.1}Mn_{1.9}O_4$	8.1716	545.6589	23
$LiAl_{0.1}Mn_{1.9}O_4$	8.1681	544.9581	17

From the data in **Table1**, it can be proposed that the distances between different facts due to the decrease of crystal cell parameters for B and C samples compared to the un-doped sample and this is favourable for the quick and easy insertion -deinsertion for Li^+. Crystalline sizes have been obtained by Scherrer equation.

SEM analysis

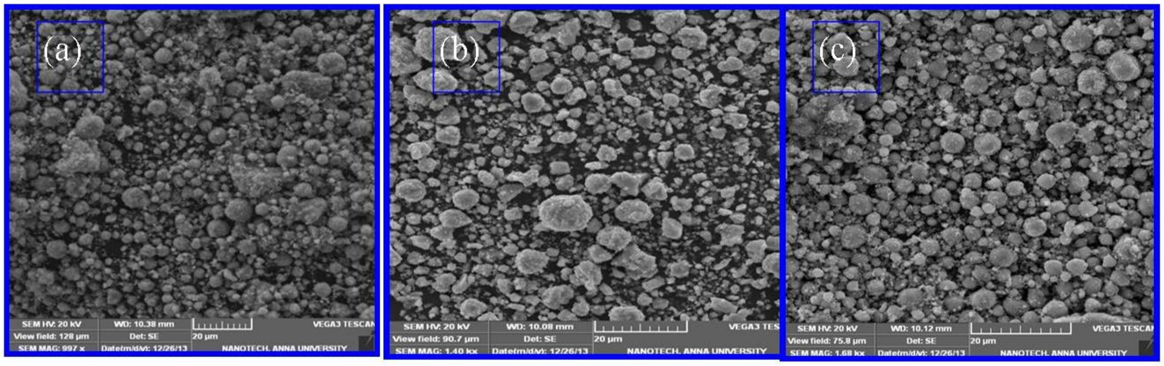

Figure 3 SEM image of a) $LiMn_2O_4$ b) $LiNi_{0.1}Mn_{1.9}O_4$ c)$LiAl_{0.1}Mn_{1.9}O_4$

SEM photos are presented in **Figure 3**. From the figure, it could be seen that all the samples have good morphologies, even particle sizes. The average diameter for each sample is smaller than 50nm, which indicates that the materials could be considered to be nano-materials. This can also be verified by the results in **Table 1** obtained from Scherrer equation. But agglomeration appears in some samples. Based on the particle size and morphology results, the prepared materials should have better electrochemical performances[13].

TEM analysis

To observe the powder morphology and size of the synthesized $LiMn_2O_4$ and doped $LiMn_2O_4$nano crystalline powder, TEM Photograph is taken by transmission electron microscope which is shown in figure 4

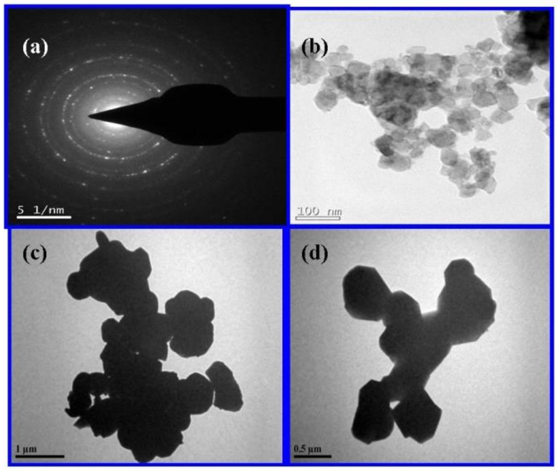

Figure 4 (a) SAED pattern of $LiMn_2O_4$ TEM images of (b) $LiMn_2O$ (c) Ni doped $LiMn_2O_4$ (d)Al doped $LiMn_2O_4$

Fourier Transform Infrared Spectroscopy(FTIR)

The Fourier Transform Infrared [FTIR] spectra of the synthesized $LiMn_2O_4$ and doped $LiMn_2O_4$ nano crystalline powder recorded at room temperature are shown in figure5. The low frequency absorption bands at 512, 619 cm^{-1} are attributed to asymmetric modes of Mn-O. The high frequency absorption bands at 2921cm^{-1} are assigned to the bending modes of Mn-O [14]. The peak around 617cm^{-1} is assignable to the Li-Mn-O stretching vibration bond.

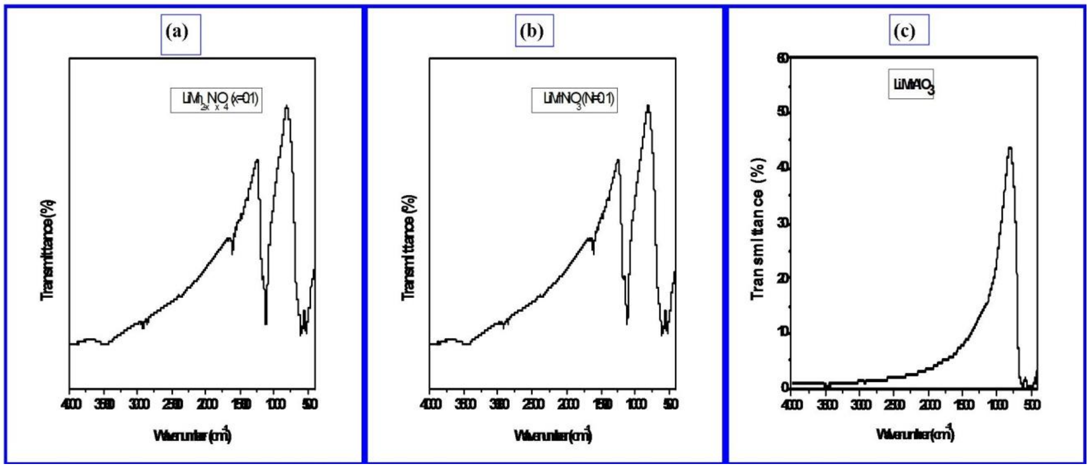

Figure 5 FTIR image of a) $LiMn_2O_4$ b) $LiNi_{0.1}Mn_{1.9}O_4$ c)$LiMnAlO_3$

Conclusions

The spinel $LiMn_2O_4$ and $LiM_{0.1}Mn_{1.9}O_4$(M=Ni,Al) materials were synthesized using combustion process, starting from metal nitrate, urea and glycerol. The synthesized material were subjected to XRD, SEM, TEM, and FTIR studies to ascertain the physical properties. The XRD patterns for $LiMn_2O_4$ and $LiAl_{0.1}Mn_{1.9}O_4$ confirms the single phase spinel compound without any impurities.The SEM and TEM studies confirm that the synthesized grains are of uniform regular surface morphology. FTIR studies confirm the stretching and bending vibration band of Li-O and Li-Al-Mn-O. Low doping (x=0.1) of Al is found to be beneficial in stabilizing this spinel structure.

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