EFFECTS OF Ni-ion DOPING ON NANO CRystalline SPINEL LiMn$_2$O$_4$ PREPARED BY SOLID STATE COMBUSTION METHOD

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Abstract- Spinel LiMn$_{2-x}$Ni$_x$O$_4$ compounds doped with a range of Ni were synthesized by combustion method. The structure and morphology characteristics are studied using X-ray diffraction, Scanning electron microscopy, Transmission electron microscopy and Fourier Transform Infra-Red Spectroscopy. The XRD data reveals that all the samples have well-defined spinel structure, but, with the increase in Ni content, the doped lithium manganese spinels have smaller lattice constant. The undoped and doped spinel LiMn$_2$O$_4$ particles are fine, narrowly distributed, and well crystallized. With the increase in the Ni content, the specific capacities of the samples decrease slightly, but their cyclic ability increases. The procedure is very simple and novel.

Keywords: LiMn$_2$O$_4$ powders. Ni-doped, Combustion method. Lithium- ion batteries.

1 INTRODUCTION

Lithium ion batteries have been studied extensively for the past 20 years due to their highest specific energy. In 1990, Sony energy technical used LiCoO$_2$, because of its high cost and environmental toxicity of cobalt, much effort has been done to develop alternatives[1]. At present, spinel LiMn$_2$O$_4$ is considered a promising and attractive cathode material for lithium ion batteries due to its high-reduction potential, low cost, and acceptable environmental impact as compared to LiCoO$_2$[1-2].

Unfortunately, LiMn$_2$O$_4$, used as a cathode in lithium ion batteries, exhibits capacity fading during cycling.After many studies, the capacity fading is mainly due to the following reasons:(a) the decomposition of the electrolyte at high-voltage region,(b) the dissolution of Mn$^{3+}$ ions into the electrolyte, and (c) the Jahn-Teller distortion.To improve the cycle performance of the spinelLiMn$_2$O$_4$,doping and coating of LiMn$_2$O$_4$ were considered to be the effective methods. Several attempts have been made for synthesizing improved lithium manganese spinel doped with various elements, such as Al, Ni, Mg, Co, Cr, Nd, and so on.

In this present work, an attempt was made for improving cycling ability of LiMn$_2$O$_4$ doped with Ni. Combustion method has its many advantages, including the fact that it is a simple system and its cost effectiveness, and it can be scaled up to ton quantities. Thus, the morphology, structure, and electrochemical characteristics of undoped and doped LiMn$_2$O$_4$ with different Ni content prepared by combustion method are investigated for comparison in detail.

2.0 EXPERIMENTAL TECHNIQUES

2.1 Synthesis of Ni doped Spinel LiMn$_2$O$_4$

Ni-ion-doped spinel LiMn$_2$O$_4$ was synthesized by combustion method. Stoichiometric amounts of nitrates of Li$^+$, Mn$^{3+}$ and Ni$^{2+}$ 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 850°C for15hrs. The obtained nano powder was characterized by powder X-ray diffractometry (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), and Fourier Transform Infrared Spectroscopy (FTIR).

2.2 Characterization of the materials.

2.2.1 XRD studies

The crystal structure of the powders were identified using X-ray diffractometry (XRD) analysis. The XRD patterns show that the spinel LiMn$_2$O$_4$ and LiNi$_{0.1}$Mn$_{1.9}$O$_4$ powders have pure and crystalline nature in all compositions. The peak planes are (111), (311), (222), (400), (331), (551), (440), (531), and (222) respectively. These observations are in good agreement with the earlier reports [2-4-10] LiMn$_2$O$_4$ spinel belongs to Fd3m symmetry.wherein manganese ions occupy 16d sites and oxygen ions occupy 32e sites [5-11]. In the combustion reaction, a Ni-cation with a similar ionic radius to Mn$^{3+}$ (0.66Å) can be incorporated into the spinel structure by substitution of Mn$^{3+}$ the ionic radii of Ni$^{2+}$(0.69Å) are similar to that of Mn$^{3+}$ [1-3].
The calculated lattice constant of LiMn$_2$O$_4$, LiNi$_{0.1}$Mn$_{1.9}$O$_4$ are 8.2136Å and 8.1716Å respectively. This lattice contraction indicates that successful substitution of Ni for Mn product [12].

Figure 1 XRD patterns of a) LiMn$_2$O$_4$ b) LiNi$_{0.1}$Mn$_{1.9}$O$_4$

2.2.2 SEM analysis
The following figure 2 shows SEM images of undoped and Ni-doped LiMn$_2$O$_4$ powders. These images exhibit typical morphologies for all the prepared powders. The particles have an average size of about 50nm and shows uniform particle size distribution.

Figure 2. SEM image of a) LiMn$_2$O$_4$ b) LiNi$_{0.1}$Mn$_{1.9}$O$_4$

The SEM photographs for undoped and doped well dispersed particles of final size with less agglomeration of particles [6-7] which are the result of combustion method. Such kind of morphology is very important to both the high specific capacity and good cycleability of the material[1]

2.2.3 TEM analysis
To observe the powder morphology and size of the synthesized LiMn$_2$O$_4$ nano crystalline powder, TEM Photograph is taken by transmission electron microscope which is shown in fig 3
2.2.3 Fourier Transform Infrared Spectroscopy (FTIR) studies:

The following fig 4 a) and b) shows that the FTIR spectrum of LiMn$_2$O$_4$ and LiNi$_{0.1}$Mn$_{1.9}$O$_4$. The Fourier Transform Infrared [FTIR] spectra of the synthesized LiMn$_2$O$_4$ nano crystalline powder recorded at room temperature is shown in fig.3. The low frequency absorption bands at 512, 619 cm$^{-1}$ are attributed to asymmetric modes of Mn-O [11]. The high frequency absorption bands at 2921 cm$^{-1}$ are assigned to the bending modes of Mn-O [8-9]. The peak around 617 cm$^{-1}$ is assignable to the Li-Mn-O stretching vibration bond.

3.0 RESULTS AND DISCUSSION

XRD patterns of the undoped and Ni-doped LiMn$_2$O$_4$ powders shows that all the samples can be identified as an ordered spinel structure with space group Fd3m. There is no significant difference in the crystal structure. This indicates the Mn site in LiMn$_2$O$_4$ is substituted fully by Ni, and no other phase is formed [6]. The lattice parameters and unit cell volumes of the samples are calculated from the XRD data. For the pure LiMn$_2$O$_4$ the lattice parameter and the unit cell volume are $a=8.2136\AA$ and $V=554.116.\AA^3$. The increase in the amount of nickel, the lattice parameter decreases gradually. According to the literature [11-13] this decrease is due to the increase in the concentration of Mn$^{4+}$ ions in the spinel structure as Mn$^{3+}$ ions are substituted by Ni$^{2+}$ ions.

4 CONCLUSIONS

This study is focused on modifying the spinel LiMn$_2$O$_4$. Using combustion method, doped and undoped LiMn$_{2-x}$Ni$_x$O$_4$ materials were synthesized. Pure single phase Ni-doped spinel LiMn$_2$O$_4$ is obtained with very good crystallinity. Therefore the solid state combustion method will be an attractive method for fabrication of the spinel LiMn$_{2-x}$Ni$_x$O$_4$ powders for lithium ion batteries.

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