

Synthesis of B-Site Substituted Cathode Material for Reduced Capacity Fading

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Abstract: LiMn_2O_4 (LMO) and Zn doped Lithium manganese oxide ($\text{LiZn}_x\text{Mn}_{(2-x)}\text{O}_4$) spinels were synthesized through solution combustion approach. Here, various amount of doping zinc in the manganese B site were studied by X-ray diffraction. The Zn doped spinels exhibit spherical morphology as like as LMO, which were observed using scanning electron microscope. Further, their particle sizes were found to be in micrometer range, which may help to reduce capacity fading. Thus, Zn doped Lithium manganese oxide spinels can be used as a substituent to replace commercial cathode.

Keywords: LMO, cathode, combustion, Raman spectroscopy.

1. Introduction

Lithium ion batteries (LIB) are used in almost all portable electronic devices such as mobile phones, laptops, and hybrid electric vehicles. LiMn_2O_4 is still considered as a good cathode material compared with LiNiO_2 and LiCoO_2 because of its easy availability, low cost, less toxicity, and high safety [1]. On the other hand, it suffers from capacity fading which arises owing to three main factors that are Jahn-teller distortion, Mn dissolution into electrolyte, and electrolyte decomposition at high voltage [2]. It has been reported that it is possible to suppress capacity fading by partially substituting divalent or trivalent cations in the Mn site [1, 3]. It has been found that Zn^{2+} addition improves the cycling stability of LiMn_2O_4 . Also, Zn^{2+} has preference for tetrahedral sites in LiMn_2O_4 which may produce very efficient spinels through the stabilization of the tetrahedral structure [4]. Moreover, doping protocol is also found to have a major role in determining the significance of the parent material. Solid state method is a tedious and time consuming process which also gives rise to non-stoichiometry and impurity formation in addition to its expensive cost [5]. However, solution combustion synthesis method (SCS) is found to be an effective, low cost for production of various industrial materials. Urea and glycine are most commonly used as fuel for the synthesis of ceramic powders with uniform structures and controlled stoichiometry [6]. To the best of our knowledge, combustion synthesis of Zn doped LiMn_2O_4 spinels were not significantly found in the literature. In this work, Zn modified LiMn_2O_4 materials were synthesized by solution combustion method using urea as fuel and their properties were investigated.

2. Experimental

Lithium nitrate (LiNO_3) (SDFCL, Mumbai), Manganese nitrate tetra hydrate ($\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) (Alfa Aesar, UK), Zinc nitrate hexa hydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) (Merck, Mumbai) were used as precursors to prepare spinel powders. Urea is used as a fuel. All the chemicals used were of analytical grade. Stoichiometric amount of precursors were taken and dissolved in required amount of double distilled water by continuous stirring in a magnetic stirrer. The aqueous solution was kept for combustion at 500°C in a muffle furnace which yielded a

black fine powder [5]. The powder was then calcined at 800 °C for 6 h to form pure spinel phase which was confirmed by XRD analysis.

3. Results and Discussions

3.1 Structural Analysis

3.1.1 XRD

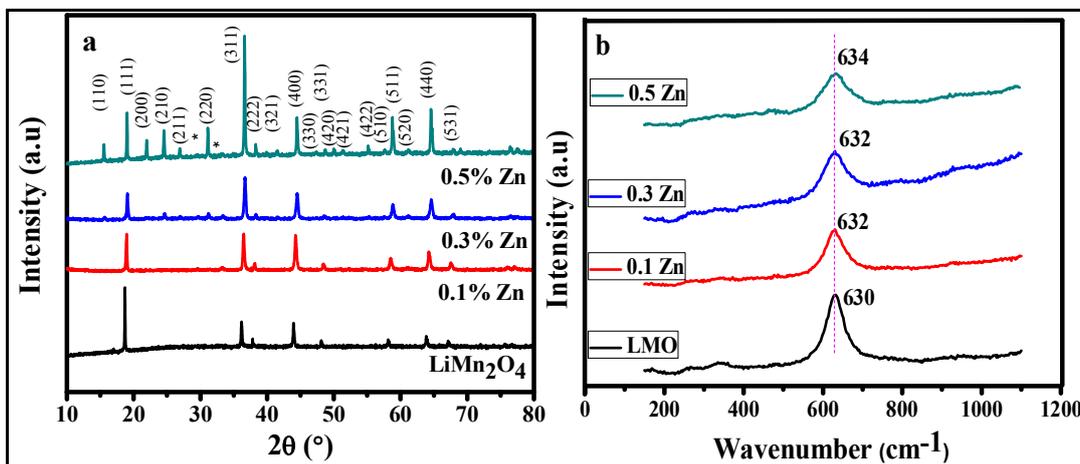


Fig.1. (a) XRD of synthesized materials; (b) Raman spectroscopy of synthesized materials

XRD patterns of the spinel powders with varying concentration of zinc doping ($x=0, 0.1, 0.3, 0.5$) is shown in Fig. 1(a). The observed sharp peaks indicate the crystallinity of the sample. The XRD pattern of LMO matches well with the standard pattern (PDF # 89-8325). The peaks at (111), (311), (222), (400), (331), (511), (440), and (531) designate the formation of the pure spinel phases without any secondary phases or impurities. It is observed that the intensity of peaks such as (110), (200), and (210) increases as the Zn content increases [7]. With increasing Zn content to 0.3%, (220) peak was observed which further increases in intensity when Zn content is increased to 0.5%. The XRD pattern of 0.5% Zn doped LMO also matches with its standard pattern (PDF # 32-0610). The XRD pattern of 0.5% Zn doped LMO is different from pure LMO with the former having more number of peaks than the latter. Small peaks were observed around 29.7° and 33.4° which might be owing to the presence of secondary ZnMn_2O_4 phase [8].

3.1.2 Raman Spectroscopy

To quantify the nature and amplitude of disorder in synthetic LiMn_2O_4 spinels from vibrational features, Raman spectroscopy was carried out on $\text{LiZn}_x\text{Mn}_{(2-x)}\text{O}_4$, where $x = 0.1, 0.3, 0.5\%$ using a laser light of 480nm between 150 and 1100 cm^{-1} at room temperature. A laser light of wavelength 480nm was used to illuminate the sample. In spinel oxides, energies of $600\text{--}650\text{ cm}^{-1}$ are characteristics of vibrations involving motion of oxygen inside the octahedral unit MnO_6 [9]. Raman spectrum of LiMn_2O_4 shows a strong band at 632 cm^{-1} , corresponds to the symmetric Mn-O stretching vibration of MnO_6 octahedra and the A_{1g} mode in O_h^7 symmetry. The charge disproportionation of $\text{LiMn}^{3+}\text{Mn}^{4+}\text{O}_4$, results in the formation of isotropic Mn^{4+}O_6 octahedra and locally distorted Mn^{3+}O_6 octahedra. Thus, the observed broadness of A_{1g} mode is because of the stretching vibrations of both MnO_6^{9-} and MnO_6^{8-} octahedral in spinel LiMn_2O_4 . The RS peak with medium intensity located at 471 cm^{-1} has $F_{2g}^{(2)}$ symmetry. The $F_{2g}^{(3)}$ mode corresponds to the Li-O vibrations, which has a connection to the tetrahedral cation movements. The low intensity band observed at 264 cm^{-1} because of Li-O vibration, might be related to the cationic disorder in the material [10, 11]. Increasing the concentration of zinc, shifted the bands towards higher frequency (Fig. 1b), implies the compression in the lattice structure created by the zinc, while occupying the Mn site, as the ionic radii of zinc is larger than manganese.

3.3 TGA and DSC

The thermal decomposition behavior of LMO powders combusted at 500 °C was studied using thermo gravimetric analysis (TGA) by heating the sample from room temperature to 900 °C at a heating rate of 10°C/min under the flow of N₂ gas.

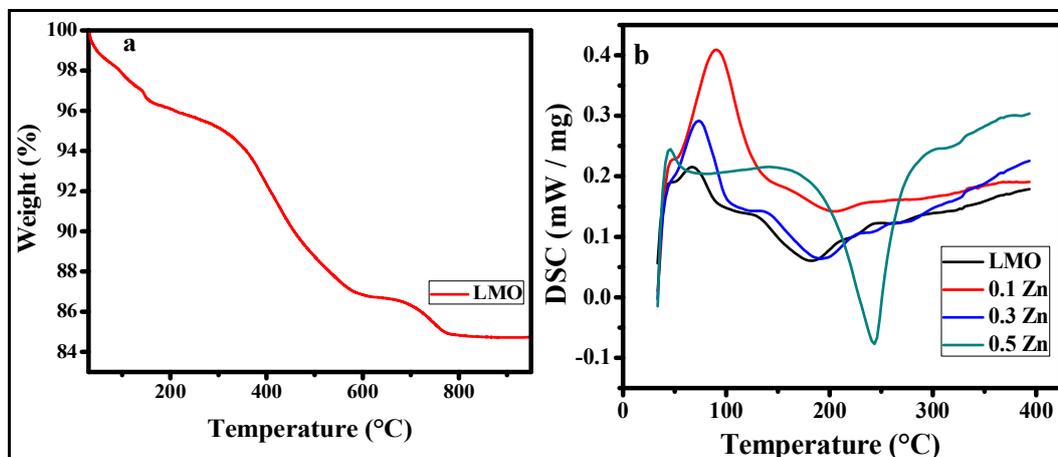


Fig.2. (a) TGA of LMO; (b) DSC curves of LMO, 0.1, 0.3, 0.5% Zn doped materials

From the Fig. 2(a), the TG curve shows an overall weight loss of 15% over three zones. In the first zone, 3% weight loss occurs till 130 °C because of the evaporation of physically absorbed water. The second zone of weight loss (10%) which occurs from 130 °C to 560 °C, might be due to loss of water of crystallization and decomposition of nitrates present in the sample [12,13]. The last zone of weight loss (2%) which initiates at 560 °C and continues up to 760 °C is owing to the gradual removal of remaining metal nitrates present in the sample. Above 760 °C, no loss was observed owing to the formation of stable LiMn₂O₄

phase.

From the DSC curves shown in Fig. 2(b), it can be observed that, for all the samples, the first exothermic peak observed at a range from 46 °C to 92 °C is because of the adsorbed and residual water loss of the as-prepared LiMn₂O₄ powders. From the Fig. 3(b), it can be clearly seen that, as the Zn content increases, the endothermic peak becomes more dominant which might be owing to the evaporation of large amount of chemically absorbed water from the precursors. The endothermic peaks observed at the temperature range from 181 °C to 241 °C are related to the loss of water owing to crystallization and decomposition of inorganic residues from the samples during combustion synthesis [14].

3.4 Morphological Studies

3.4.1 SEM Analysis

All the samples show spherical morphology with size distribution ranging from 1 μm to 5 μm. In the case of agglomerates, spheres between 10 μm and 11 μm are found. In Zn doped samples (0.1, 0.3, 0.5% Zn doped LMO), as Zn doping is increased between 0.3% and 0.5%, relatively more spherical particles could be seen with good agglomeration which is because, addition of Zn acts as a sintering aid and binds the particles together [6].

3.4.2 Particle Size Distribution Analysis (PSDA)

Fig. 3(e - h) shows the particle size distribution of the synthesized powders analyzed using particle size distribution analyzer. The D₅₀ values of the particles were found to be in the size range from 2.02 to 4.48 μm. This size range co-relates with the particle size observed through SEM analysis (Fig. 3 (a - d)). The values of LMO, 0.1%, 0.3%, and 0.5% Zn doped LMO powders were found to be 3.86 μm, 2.41 μm, 2.02 μm, and 4.48 μm respectively.

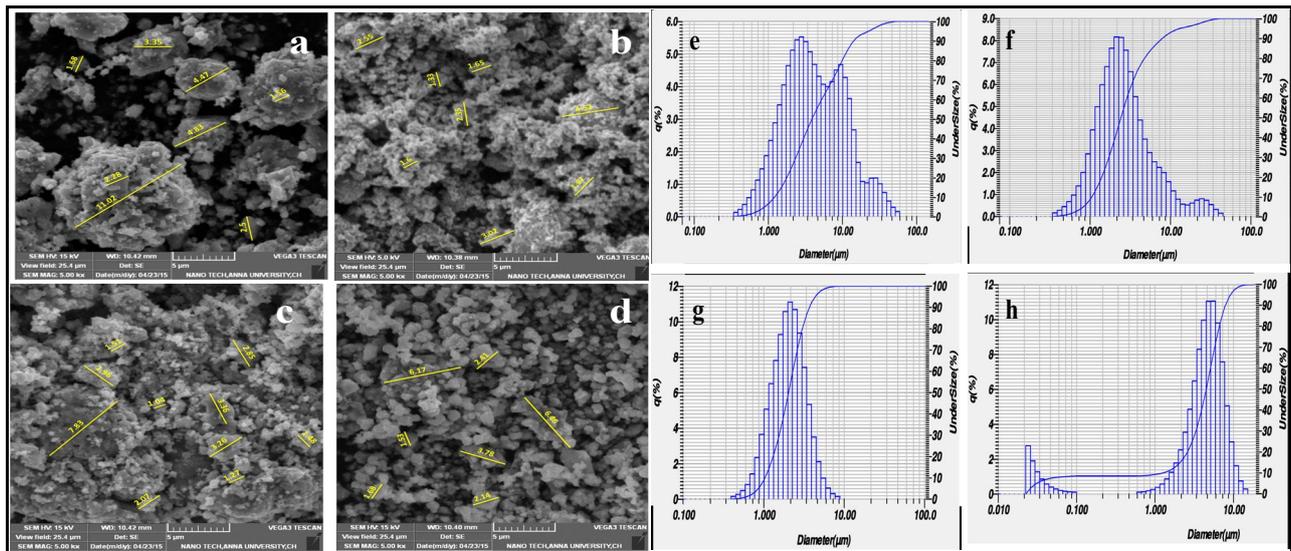


Fig. 3. (a) SEM image of LMO; (b) SEM image of 0.1% Zn doped LMO; (c) SEM image of 0.3% Zn doped LMO; (d) SEM image of 0.5% Zn doped LMO; (e) PSD of LMO; (f) PSD of 0.1% Zn doped LMO; (g) PSD of 0.3% Zn doped LMO; (h) PSD of 0.5% Zn doped LMO.

4. Conclusion

LiMn_2O_4 and Zn doped LiMn_2O_4 (0.1, 0.3, 0.5% Zn) spinels were successfully synthesized by solution combustion method. XRD pattern of the prepared powders matches well with the standard JCPDS pattern of LiMn_2O_4 and $\text{LiZn}_{0.5}\text{Mn}_{1.5}\text{O}_4$ respectively. The temperature of stabilization of spinel phase was found to be around 800 °C. The endothermic and exothermic peaks associated with the formation of LiMn_2O_4 powders were analyzed by DSC. The peak shift observed in Raman spectroscopy shows the change in lattice structure upon addition of zinc. The D_{50} values of the particles were found to be around 2.0 μm to 4.8 μm and the morphology of particles was found to be spherical. From the literature, it can be observed that these spherical particles having micron size diameters exhibit high power performances [15]. Thus, the synthesized spinels having micron sized spherical particles is also expected to perform better in battery applications.

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