

Synthesis and Structural Studies of $\text{LiMn}_{2-x-y}\text{Zn}_x\text{Mg}_y\text{O}_4$ ($x = y = 0.0, 0.02, 0.04$) Spinel As Cathode Materials For Lithium-Ion Batteries

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Abstract

The Spinel structure $\text{LiZn}_x\text{Mg}_y\text{Mn}_{2-x-y}\text{O}_4$ ($x = y = 0, 0.02, 0.04$) were being prepared by the sol-gel method. The physical properties of the synthesized materials were discussed in the structural (XRD, SEM and FT-IR) measurements. The X-ray diffraction (XRD) patterns possessed the spinel structure of the cubic space group ($Fd3m$) with no evidence of any impurities. Scanning electron microscopy (SEM) showed the phase morphological features and particle size distribution was in the range of 200 to 250 nm. The FT-IR spectroscopy revealed the spinel structure, built of MnO_6 octahedra and LiO_4 tetrahedra.

Keywords: Sol-gel process, spinel, XRD, SEM, FT-IR

1. Introduction

The present day lithium-ion batteries have been focused mainly on their harmlessness and high performance in daily life [1-3]. The cathode materials for lithium-ion batteries like layered structure LiMO_2 ($M=\text{Co}, \text{Ni}$ and Mn), Spinel structure LiMn_2O_4 and Olivine structure LiMPO_4 ($M=\text{Fe}, \text{Co}, \text{Ni}$ and Mn) were mostly studied in world wide [4-8]. In general, the spinel structure LiMn_2O_4 was taken as an attractive candidate for the cathodes of lithium-ion batteries due to its low cost, easy preparation and high environmental acceptability than other LiCoO_2 , LiNiO_2 and LiFePO_4 cathode materials [9]. Therefore, this does not allow its commercialization. This capacity fading was mainly due to 3 volts cycling phase transition, change of cubic to tetragonal phase. The spinel LiMn_2O_4 cathode material space group was $Fd3m$ and it consisted of a cubic close packed arrangement of oxygen ions at the 32e sites, Li-ions at the tetrahedral 8a sites and Mn ions at the octahedral 16d sites. Therefore, this showed a cubic spinel type structure [11]. Many researchers have studied spinel LiMn_2O_4 with various elements doped, such as Co, Fe, Ni, Cr, Ga, Ti and Al to reduce the capacity fading and improve the electrochemical properties [12-15]. Several preparation methods were developed, such as a solid state reaction, co-precipitation, pechini process, hydrothermal, combustion method, freeze during method and sol-gel methods. In this work, we have chosen sol-gel method and compared with the other methods, such as lower temperature processing, better control of material morphology, smaller and more uniform particles [16-20]. Mainly, the sol-gel method was also one of the most cost saving and time effective ways to produce doped metal nitrates in large quantities.

In this paper, we were studied $\text{LiZn}_x\text{Mg}_y\text{Mn}_{2-x-y}\text{O}_4$ ($x = y = 0, 0.02, 0.04$) cathode materials synthesized by sol-gel method using citric acid as a fuel at 800 °C for 8 hours. Therefore, we examined the structural and morphologies behaviors.

2. Preparation and Experimental Techniques

The spinel $\text{LiZn}_x\text{Mg}_y\text{Mn}_{2-x-y}\text{O}_4$ ($x = y = 0, 0.02, 0.04$) cathode materials were synthesized by the sol-gel method using citric acid as the chelating agent. The stoichiometric amounts of lithium nitrate, manganese acetate and citric acid were thoroughly mixed and dissolved in deionized water according to their molar ratio of 1:1. The solution is stirred continuously at 70°C for one hour, forming a homogeneous solution containing manganese and lithium. This solution was vaporized at 120°C till dry gel was formed, followed by the heat treatment in oven at 500°C for 4 h. The pH of the mixed solution was maintained by adding ammonia solution. The resulting gel was ground and calcinated at 750°C for 8h to decompose the nitrates. Thus, the powder was obtained and sintered at 850°C for 8 h.

The powder X-ray diffraction (XRD) data of the sample were collected on a Rigaku Cu-K α diffractometer with diffraction angles of 2θ and -80° in increments of 0.02° . The unit cell lattice parameter was obtained by the least square fitting method from the d-spacing and (hkl) values. Further, the crystallite size of the sample was obtained by applying Scherrer's equation from XRD pattern. The particle morphology of the powder was observed using a scanning electron microscope (SEM) with EDX image taken from CarlZeiss, EVOMA 15, Oxford Instruments, Inca Penta FETx3.JPG. Fourier transform infrared (FT-IR) spectra were obtained on a Shimadzu FT-IR-8900 spectrometer using a KBr pellet technique in the wave number range between 400 and 1500 cm^{-1} .

3. Results and Discussion

3.1. X-ray Diffraction Analysis

Figure 1 showed the XRD patterns of $\text{LiZn}_x\text{Mg}_y\text{Mn}_{2-x-y}\text{O}_4$ ($x = y = 0, 0.02, 0.04$) samples. It was seen that the cubic spinel lattice had Fd3m space group wherein lithium occupied the 8a tetrahedral sites, and manganese ions occupied the 16d sites perfectly matched with the joint committee on powder diffraction stranded card no 35-1782 [21].

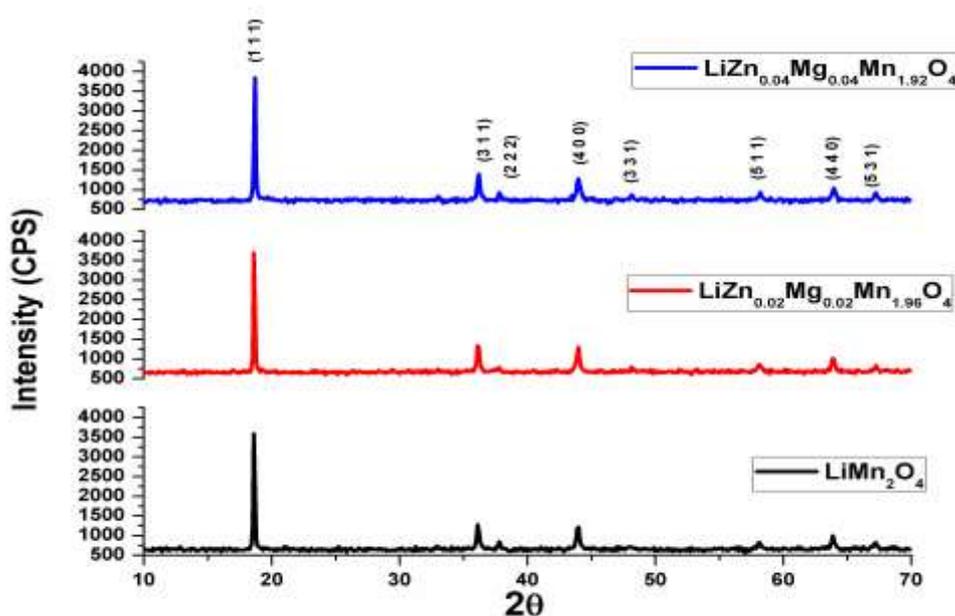


Figure 1. XRD Patterns of $\text{LiZn}_x\text{Mg}_y\text{Mn}_{2-x-y}\text{O}_4$ ($x = y = 0, 0.02, 0.04$)

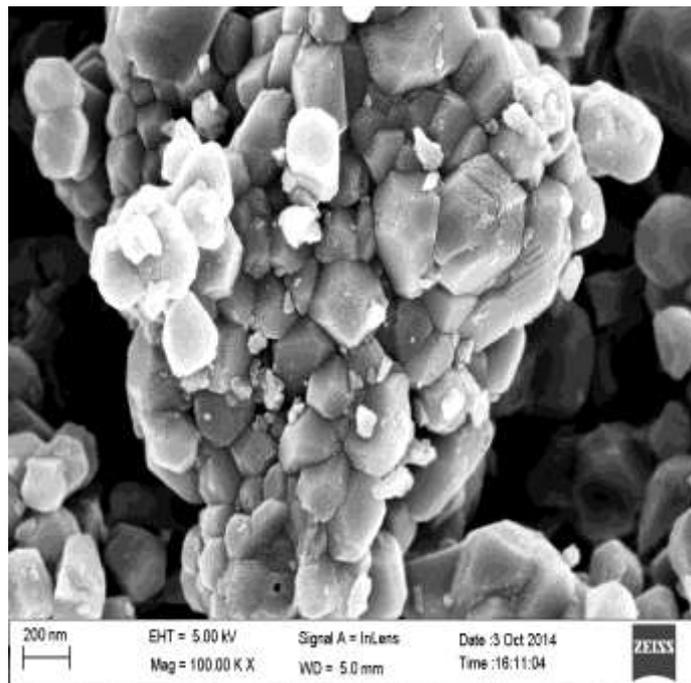
The lattice constant a and unit cell volume were calculated by the Unit-cell software (1995) using the XRD data and listed in Table 1 [22]. The lattice constant ' a ' slightly increased from 8.2275 to 8.2387 Å and also the unit cell volume increased from 556.9396 to 559.2139 (Å)³. The average crystallite size increased with $x=0.02$ then decreased for $x=0.04$. From XRD patterns, the most intense peak (111) was used to calculate the average crystallite size and it is listed in Table 1.

Table 1. Lattice Constant, Unit Cell Volume and Crystallite Size of $\text{LiZn}_x\text{Mg}_y\text{Mn}_{2-x-y}\text{O}_4$ ($x = y = 0, 0.02, 0.04$)

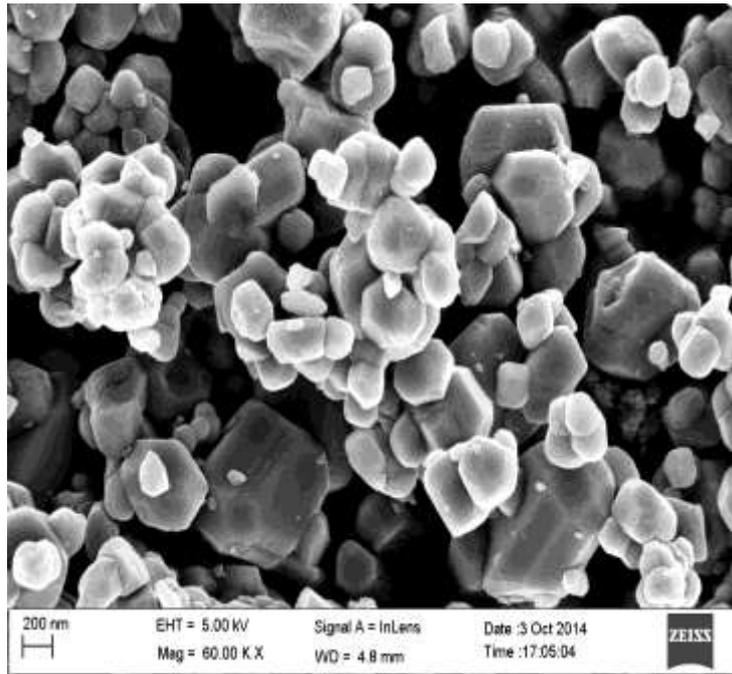
S.No.	Sample	a (Å)	Unit cell volume (Å) ³	Crystallite size (nm)
1	LiMn_2O_4	8.2275	556.9396	61.07
2	$\text{LiZn}_{0.02}\text{Mg}_{0.02}\text{Mn}_{1.96}\text{O}_4$	8.2387	559.2132	66.23
3	$\text{LiZn}_{0.04}\text{Mg}_{0.04}\text{Mn}_{1.92}\text{O}_4$	8.2316	557.7597	58.59

3.2. Scanning Electron Microscopy Study

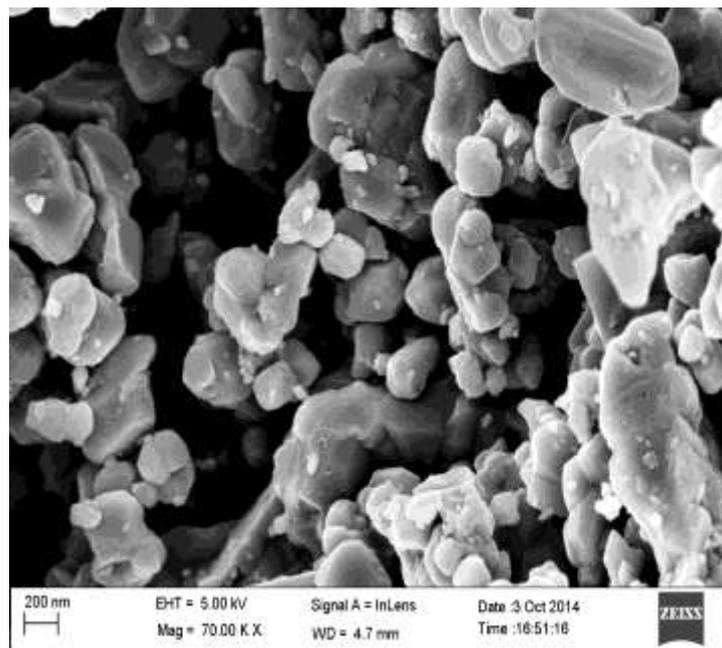
Figure 2 showed the shape, size and surface morphology of the grains in the $\text{LiZn}_x\text{Mg}_y\text{Mn}_{2-x-y}\text{O}_4$ ($x = y = 0, 0.02, 0.04$) cathode materials. These cathode materials were prepared by the sol-gel method at 850 C for 8 hours. The size of synthesized materials by route was about 200 to 250 nm. The particle uniform, nearly polyhedral structure, with narrow nano size distribution [23].



(a)



(b)



(c)

Figure 2. (a) to (c): SEM Images of $\text{LiZn}_x\text{Mg}_y\text{Mn}_{2-x-y}\text{O}_4$ ($x = y = 0, 0.02, 0.04$)

3.3. Fourier Transform Infrared Spectra Analysis

Figures 3 showed the FT-IR spectra of $\text{LiZn}_x\text{Mg}_y\text{Mn}_{2-x-y}\text{O}_4$ ($x = y = 0, 0.02, 0.04$) samples prepared by sol-gel method, sintered at 850 °C for 8 hours. In this spectra, which plotted transmittance versus wavenumber in the range 400 - 1500 cm^{-1} , two strongly prominent bonds were seen [24-25]. The bands found around 516.5302 to 518.2312 cm^{-1} were assigned to Li-O stretching vibration which indicated the formation of the LiO_6 octahedra group. The band around 617.1241 to 619.3145 cm^{-1} was assigned to Li-Mn-O

and Li-Zn-Mg-Mn-O stretching vibrations, which indicated the formation of MO_6 octahedra group. When compared with Zn and Mg doped sample, the better band shift towards higher wavenumber was observed in LiMn_2O_4 sample.

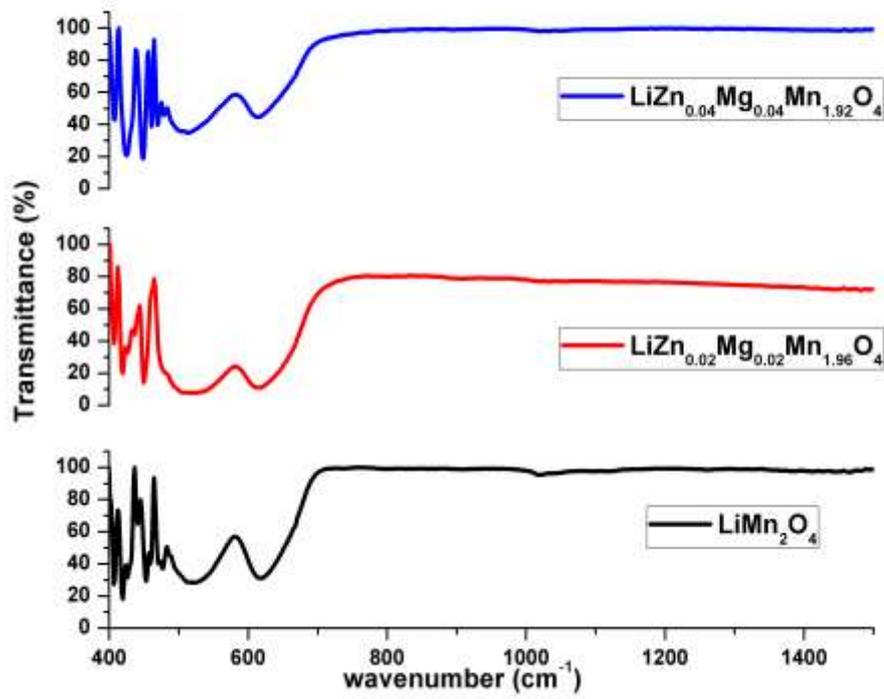


Figure 3. FT-IR Images of $\text{LiZn}_x\text{Mg}_y\text{Mn}_{2-x-y}\text{O}_4$ ($x = y = 0, 0.02, 0.04$)

Table 2. FT-IR Spectral Peaks Observed for $\text{LiZn}_x\text{Mg}_y\text{Mn}_{2-x-y}\text{O}_4$ ($x = y = 0, 0.02, 0.04$)

S.No.	Sample	Wave number (cm^{-1})	Assignments
1	LiMn_2O_4	516.5302 617.1241	Li-O Li-Mn-O
2	$\text{LiZn}_{0.02}\text{Mg}_{0.02}\text{Mn}_{1.96}\text{O}_4$	517.7304 618.3542	Li-O Li-Zn-Mg-Mn-O
3	$\text{LiZn}_{0.04}\text{Mg}_{0.04}\text{Mn}_{1.92}\text{O}_4$	518.2312 619.3145	Li-O Li-Zn-M-Mn-O

4. Conclusion

The Spinel structure $\text{LiZn}_x\text{Mg}_y\text{Mn}_{2-x-y}\text{O}_4$ ($x = y = 0, 0.02, 0.04$) was synthesized by sol-gel method using citric acid as the chelating agent to obtain micron-sized particles as cathode materials in lithium rechargeable batteries. The XRD peak reflections of $\text{LiZn}_x\text{Mg}_y\text{Mn}_{2-x-y}\text{O}_4$ ($x = y = 0, 0.02, 0.04$) calcined at 850 °C for 8 h reflected a high degree of crystallinity and phase purity of the synthesized materials. The SEM showed the decrease in particle size, enlargement of the specific surface area and the grain sizes,

whose values were found at 0.49, 0.48 and 0.46 μm . The FT-IR spectroscopy showed that for moderate Ce substitution in the local octahedral environment of Li-ions in $\text{LiMn}_{1.92}\text{Zn}_{0.04}\text{Mg}_{0.04}\text{O}_4$ material, were almost similar to that in LiMn_2O_4 material.

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