Synthesis and structural studies of Mg doped LiNi_{0.5}Mn_{0.5}O_{2} cathode materials for lithium-ion batteries

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Abstract: Layered Mg doped LiNi_{0.5}Mn_{0.5}O_{2} materials have been synthesized by sol-gel method. The physical properties of these materials were examined by XRD, FESEM and FT-IR studies. From XRD patterns, the phase formation of α-NaFeO_{2} layered structure with space group is confirmed. The surface morphology of the synthesized materials has been examined by FESEM analysis in which the average particle size is found to be about 2 - 2.5 µm. These materials show some changes in the local ion environment, as examined by FT-IR studies.

Keywords: X-ray diffraction; FESEM; FT-IR.

1. Introduction

The rechargeable lithium-ion batteries (LiCoO_{2}, LiNiO_{2}, LiMnO_{2} and LiNi_{0.5}Mn_{0.5}O_{2}) have a great impact on the electronic equipments like digital cameras, cell phones, etc. basing on their high energy density, volume and long life cycle. The volume of these rechargeable batteries is comparatively more than that of rechargeable batteries [1-5]. The similar sizes between Li^{+}, Ni^{2+/4+} and Mn^{4+} being exchanged between the Li (3a) and Ni/Mn (3b) sites due to the similar size of the Li^{+}, Ni^{2+} and Mn^{4+} cations (Li^{+} = 0.69 Å, Ni^{2+} = 0.76 Å and Mn^{4+} = (0.53 Å), there is the exchange between Li (3a) and Ni/Mn (3b) sites is made favorable [6]. Many studies have been done on the structural and electrochemical properties of the substituted LiNi_{0.5}Mn_{0.5}O_{2}, such as LiNi_{0.5}Mn_{0.5-x}Ti_{x}O_{2} and LiNi_{0.5-x}Mn_{0.5-x}Co_{x}O_{2} [7]. Many researchers have tried to overcome the disadvantages due to this cation exchange and the electrochemical properties are improved by doping various impurities with different metal ions such as Co, Fe, Ni, Cr, Ga, Ti and Al [8-9]. LiNi_{0.5}Mn_{0.5}O_{2} can be used as a potential cathode material for high rate applications if these doping can be proved to be successful [10]. To improve the electrochemical performance of LiNi_{0.5}Mn_{0.5}O_{2} different synthesis methods have been used, such as combustion process, molten salt method, solid state reaction method, co-precipitation, hydrothermal synthesis and sol-gel method [11]. Among these methods, sol-gel method is a widely used approach for preparing Mg doped LiNi_{0.5}Mn_{0.5}O_{2} material.

In the present work, we have studied the LiNi_{0.475}Mn_{0.475}Mg_{0.05}O_{2} and LiNi_{0.45}Mn_{0.45}Mg_{0.1}O_{2} materials synthesized by sol-gel method. The structure and morphological properties are examined.
2. Preparation and experimental techniques

LiNi_{0.475}Mn_{0.475}Mg_{0.05}O_2 and LiNi_{0.45}Mn_{0.45}Mg_{0.1}O_2 cathode materials are synthesized by sol-gel method, from the taken stoichiometric amounts of CH_3COOLi·2H_2O (AR), Ni(NO_3)₂·6H_2O (AR), Mg(NO_3)₂·6H_2O (AR) and C_6H_2MnO_4·4H_2O (AR) dissolved in distilled water. The aqueous solution of citric acid, acting as a chelating agent, is added to the mixture of the metal ion solution according to their molar ratio of 1:1. At the same time, an ammonia solution, as a precipitation agent is separately added. The reaction temperature is kept at 80 °C and pH was controlled by ammonia solution to the value of 8 to 9. The solutions are added together while stirring at 130 °C for 10 hours, forming sol solution. The sol solution is vaporized at 130 °C till the dry gel is formed, followed by the heat treatment at 500 °C for 6 h in air with a 5 °C/min heating rate to eliminate the organic residues. The powders are thoroughly grounded and then calcined at 850 °C for 20 hours in the air and required compounds are obtained.

The powder X-ray diffraction (XRD) data of the sample are collected on a Rigaku CuKα diffractometer with diffraction angles of 2θ from 20° to 80° in increments of 0.02°. The unit cell lattice parameter is obtained by the least square fitting method from the d-spacing and (h k l) values. Further, the crystallite size of the sample is obtained from the XRD pattern by applying Scherrer’s equation. The particle morphology of the powder is observed using a scanning electron microscopy image taken from Carl Zeiss, EVOMA 15, Oxford Instruments, Inca Penta FETx3.JPG. Fourier transform infrared (FT-IR) spectra is obtained on a Shimadzu FT-IR-8900 spectrometer using a KBr pellet technique in the wavenumber range between 400 cm⁻¹ and 1500 cm⁻¹.

Results and Discussion

2.1 X-ray Diffraction (XRD) Analysis

The XRD patterns of LiNi_{0.475}Mn_{0.475}Mg_{0.05}O_2 and LiNi_{0.45}Mn_{0.45}Mg_{0.1}O_2 compounds prepared by the sol-gel method are shown in Fig. 1. The compounds have a layered structure and all peaks can be indexed on the basis of the α-NaFeO₂ structure with space group (R-3m) [12] as hexagonal lattice. This XRD pattern identifies well with a typical hexagonal pattern and showed a clear doublet structure such as (0 0 6), (1 0 2) and (1 0 8), (1 1 0) as observed. A good resolution of the (0 0 6)/(0 1 2) and the (0 1 8)/(1 1 0) reflection pairs are typical of an ideal layered structure [13]. This is seen as a consecutive arrangement of lithium and transition metal ions in a close-packed oxygen array which lead to the formation of discrete lithium and transition metal layers [14]. From Table 1 the lattice parameter values are found to be \(a = 3.091\) Å and \(c = 13.971\) Å and \(a = 3.101\) Å, \(c = 14.042\) Å. The lattice parameter values increased slightly depending on the changes of the concentration and in comparison with other previous literature [15, 16].

| Sample                      | a (Å)  | c (Å)  | c/a   | Unit Cell Volume (Å³) | Crystallite size (nm) |
|-----------------------------|--------|--------|-------|-----------------------|-----------------------|
| LiNi_{0.475}Mg_{0.05}O_2    | 3.091  | 13.971 | 4.523 | 116.191               | 75.15                 |
| LiNi_{0.45}Mg_{0.1}O_2      | 3.101  | 14.042 | 4.532 | 117.102               | 82.02                 |
| LiNi_{0.475}Mg_{0.05}O_2 [15]| 2.885  | 14.223 | 4.931 | 102.481               | -                     |
| LiNi_{0.475}Al_{0.05}O_2 [16]| 2.879  | 14.341 | 4.997 | 102.998               | -                     |
Figure 1: XRD patterns of (a) LiNi<sub>0.475</sub>Mn<sub>0.475</sub>Mg<sub>0.05</sub>O<sub>2</sub> and (b) LiNi<sub>0.45</sub>Mn<sub>0.45</sub>Mg<sub>0.1</sub>O<sub>2</sub>

Figure 2: FESEM images of (a) LiNi<sub>0.475</sub>Mn<sub>0.475</sub>Mg<sub>0.05</sub>O<sub>2</sub> and (b) LiNi<sub>0.45</sub>Mn<sub>0.45</sub>Mg<sub>0.1</sub>O<sub>2</sub>
2.2 Field Effect Scanning Electron Microscopy (FESEM) Study:

The FESEM micrographs of LiNi$_{0.475}$Mn$_{0.475}$Mg$_{0.05}$O$_2$ and LiNi$_{0.45}$Mn$_{0.45}$Mg$_{0.1}$O$_2$ compounds are shown in Fig. 2. The images show that the samples have a spherical morphology in the primary particle. The particles with regular shapes, almost spherical shape are observed, indicating good crystallinity of the synthesized powders [17]. The morphological properties play a critical role in the performance of the battery, especially in high power applications [18]. The morphology of the particles becomes well shaped with an increase in its size. The average particle size is in the 2 - 2.5 µm.

2.3 Fourier Transform Infrared (FT-IR) Spectra Analysis:

Fig. 3 shows the mode of vibrations for LiNi$_{0.475}$Mn$_{0.475}$Mg$_{0.05}$O$_2$ and LiNi$_{0.45}$Mn$_{0.45}$Mg$_{0.1}$O$_2$ in the 400-1400 cm$^{-1}$ region that are associated with the vibrations of MO$_6$ and LiO$_6$ octahedral units. The peaks at 488, 518 and 792, 805 cm$^{-1}$ are the bending modes of MO$_6$. The band at around 431 cm$^{-1}$ can be assigned to the asymmetric stretching of Li-O in LiO$_6$ environments considering the structure built of MO$_6$ octahedra [19], and the stretching modes of (Ni, Mg and Mn)O$_6$ octahedra and occurring in the high frequency region (500–850 cm$^{-1}$) [20].

![Figure 3: FT-IR images of (a) LiNi$_{0.475}$Mn$_{0.475}$Mg$_{0.05}$O$_2$ and (b) LiNi$_{0.45}$Mn$_{0.45}$Mg$_{0.1}$O$_2$.](image-url)
3. Conclusion

Synthesis and structural properties of the LiNi_{0.475}Mn_{0.475}Mg_{0.05}O_2 and LiNi_{0.45}Mn_{0.45}Mg_{0.1}O_2 material are investigated by XRD, FESEM and FT-IR. XRD patterns confirmed that the synthesized samples belongs to the hexagonal structure with R-3m space group. It is also observed that with an increase of the Mg content, there is an increase in lattice parameter, unit cell volume and crystallite size. Pure phase of LiNi_{0.5}Mn_{0.5}O_2 is obtained when powders are heat treated at 850 °C for 20 h in air. The porosity nature of the samples is also observed from FESEM study, showing particle size around 2 – 2.5 µm and spherical in shape. The local structure is examined by FT-IR spectroscopy in both the samples.

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