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Impact of cerium doping on the structural and electrical properties of Lithium Nickel Manganese Oxide (LiNi_{0.5}Mn_{0.5}O₂)

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Abstract : The present work focuses on the influence of Cerium on the structural and electrical properties of LiNi_{0.5}Mn_{0.5}O₂ compound. Equivalent (LiNi_{0.475}Ce_{0.05}Mn_{0.475}O₂) and non-equivalent sites (LiNi_{0.45}Ce_{0.05}Mn_{0.5}O₂ and LiNi_{0.5}Ce_{0.05}Mn_{0.45}O₂) cerium doped LiNi_{0.5}Mn_{0.5}O₂ compounds were prepared by PVP assisted sol-gel method and was investigated by XRD and AC impedance analysis. The XRD analysis shows that Ce doping does not change the basic crystalline structure of LiNi_{0.5}Mn_{0.5}O₂. The appearance of new peaks at ~ 28 and 33 ° in the XRD pattern was consistent with the standard peaks of CeO₂. In addition, the intensity ratio (I₀₀₃/I₁₀₄) of planes (003) and (104) was decreased by doping, suggesting the undesirable cation mixing to be occurred at the lattice. By AC impedance analysis the total electrical conductivity of the pristine compound was found to be 2.57×10⁻⁷ S/cm. An effective improvement of the total electrical conductivity (order of 10⁻⁶ S/cm) was observed for the cerium doped LNMO compounds.

Keywords: LiNi_{0.5}Mn_{0.5}O₂, Sol-Gel, Poly(vinylpyrrolidone), Cerium doping, AC impedance

Introduction

In recent years, layered LiNi_{0.5}Mn_{0.5}O₂ (LNMO) has been rapidly popularized as a cathode material for lithium rechargeable batteries because of its high reversible capacity, good cyclic performance, higher specific capacity, excellent thermal stability as well as comparatively low cost and non-toxic nature than commercial LiCoO₂[1-2]. However its poor rate capability, difficulty in the preparation, cation mixing, low tapping density and poor electrical conductivity are the hurdles to overcome[3-4]. It is well known that, foreign metal ion doping or surface coating method is the effective way to improve the electrochemical performance of the cathode materials. Literature study shows that doping of foreign metal ions like Ti, Mg, Zr, Al, and Co etc. improves the structural stability, reduces the cation mixing and enhances the cyclic performance of LiNi_{0.5}Mn_{0.5}O₂. To the best of our knowledge the studies of Cerium (Ce) doped LiNi_{0.5}Mn_{0.5}O₂ is yet to be reported. In this study, LiNi_{0.475}Ce_{0.05}Mn_{0.475}O₂, LiNi_{0.45}Ce_{0.05}Mn_{0.5}O₂ and LiNi_{0.5}Ce_{0.05}Mn_{0.45}O₂ prepared by PVP assisted sol-gel method was investigated by means of XRD and AC impedance analysis to explore the changes in the structural and electrical properties of pristine LNMO compound by cerium substitution.

Experimental

LiNi_{0.475}Ce_{0.05}Mn_{0.475}O₂, LiNi_{0.45}Ce_{0.05}Mn_{0.5}O₂ and LiNi_{0.5}Ce_{0.05}Mn_{0.45}O₂ was prepared by sol-gel method using the raw materials Poly(vinyl pyrrolidone) PVPK-40, LiNO₃, MnNO₃.4H₂O, NiNO₃.6H₂O, and

Ce(NO₃)₃ from Sigma-Aldrich. The preparation procedure is reported elsewhere [5]. X-ray diffraction pattern of the prepared samples were obtained using SHIMADZU-XRD-6000 diffractometer with Cu-K α radiation ($\lambda = 0.1541$ nm) as the source at 40 KV. The AC impedance studies were carried out using computer controlled CH instrument (CHI-600E) in the frequency range of 40 Hz – 1 MHz at room temperature with 50 mV of fixed amplitude.

Results and discussion

The powder XRD patterns of pristine and cerium doped LiNi_{0.5}Mn_{0.5}O₂ compounds are shown in Figure 1 (a, b, c & d). All the main peaks in the XRD diffractogram of prepared compounds could be indexed on the basis of α - NaFeO₂ structure with space group R3-m. Moreover the clear splitting of (006/012) and (018/110) peaks indicates the formation of well ordered hexagonal layered structure. The peaks appeared at $2\theta \sim 28, 33, 47, 56$ and 58° (fig. 1 (b, c & d)) is attributed to CeO₂ phase (JCPDS: 89-8436), while all other peaks are consistent with the hexagonal layer structured LiNi_{0.5}Mn_{0.5}O₂ (JCPDS: 09-0063) [6]. Our XRD result implies that 0.05 M of Cerium doping doesn't change the basic crystalline structure of the LNMO compound.

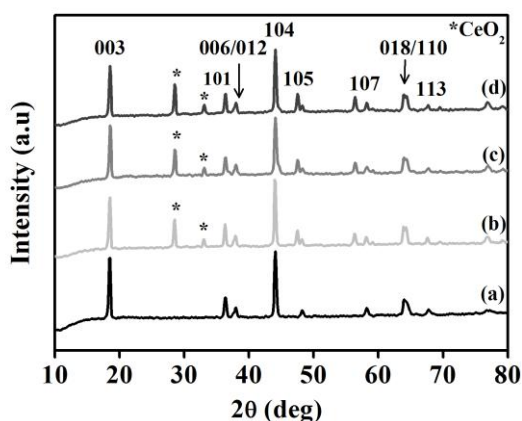


Fig.1 XRD patterns of the a) LiNi_{0.5}Mn_{0.5}O₂, b) LiNi_{0.5}Ce_{0.05}Mn_{0.45}O₂ c) LiNi_{0.45}Ce_{0.05}Mn_{0.5}O₂ & d) LiNi_{0.475}Ce_{0.05}Mn_{0.475}O₂ powders

The intensity ratio (I_{003}/I_{104}) was found decreased after doping (Pristine - 1.04, Mn site- 0.85, Ni site - 0.91 and both site -0.83), suggesting the undesirable cation mixing to be occurred at the lattice. Irrespective of dopant site, all the peaks corresponding to LNMO shifts to a higher angle, indicating that Ce doping shrink the lattice. This may be attributed to the substitution of larger Ce⁴⁺ ion ($r = 0.087$ nm) for smaller Ni²⁺ ($r = 0.069$ nm) and Mn⁴⁺ ($r = 0.053$ nm) ions.

The measured complex-plane impedance plot for the LiNi_{0.5}Mn_{0.5}O₂, LiNi_{0.5}Ce_{0.05}Mn_{0.45}O₂, LiNi_{0.45}Ce_{0.05}Mn_{0.5}O₂ and LiNi_{0.475}Ce_{0.05}Mn_{0.475}O₂ compound at room temperature are shown in Figure.2. The pristine LNMO and the cerium doped compounds shows the two overlapping semicircles related to the parallel combination of resistor with capacitor (both grain and grain boundary effect). But the width of the semicircles was reduced after doping. This indicates that the presence of CeO₂ phase in the LNMO compound reduces the overall resistance of the material.

The electrical conductivity of the all the prepared compounds was calculated using the following formula,

$$\sigma = l / RA \text{ --- Eq. (1)}$$

Where, l and A are the thickness and area of the sample respectively. R is the resistance, which can be calculated from the intercept of the low frequency spike on real axis. The electrical conductivity of the all the samples are tabulated in Table 1. The observed conductivity spectra (Figure.3 (a)) shows mid frequency plateau region followed by high frequency dispersion region, for all the samples. The conductivity value obtained from the low frequency plateau region all most matched with the value obtained from complex-plane impedance

spectra. Our result shows that Ce doping significantly increases the electrical conductivity by one order ($\sim 10^{-6}$ S/cm).

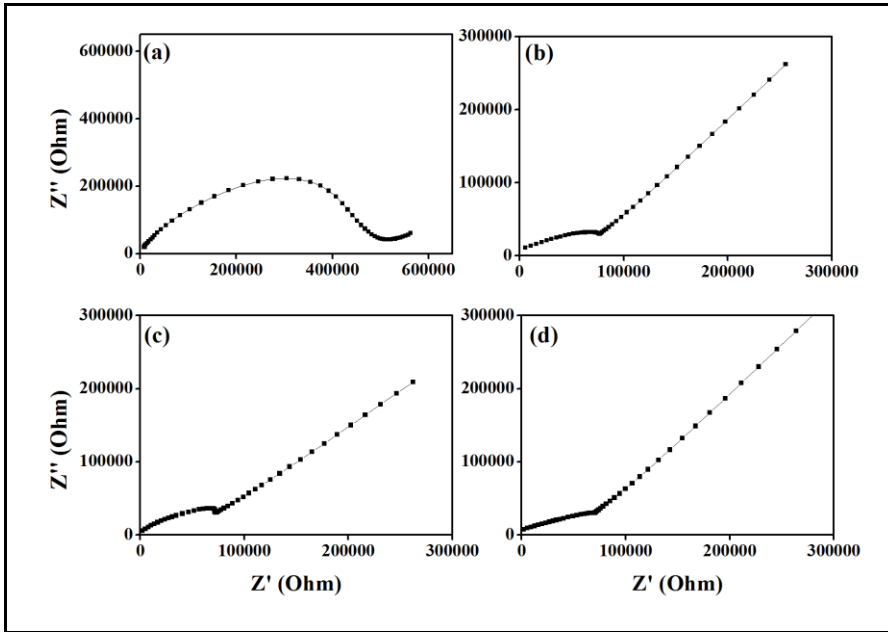


Fig.2 (a) Nyquist plot for the compounds (a) $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$, (b) $\text{LiNi}_{0.5}\text{Ce}_{0.05}\text{Mn}_{0.45}\text{O}_2$, (c) $\text{LiNi}_{0.45}\text{Ce}_{0.05}\text{Mn}_{0.5}\text{O}_2$ and (d) $\text{LiNi}_{0.475}\text{Ce}_{0.05}\text{Mn}_{0.475}\text{O}_2$

Table.1 Comparison of conductivity data

S.No	Compound	Conductivity (S/cm) From Nyquist plot	Conductivity (S/cm) From conductivity spectra
1	$\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$	2.57×10^{-7}	2.15×10^{-7}
2	$\text{LiNi}_{0.5}\text{Ce}_{0.05}\text{Mn}_{0.45}\text{O}_2$	1.29×10^{-6}	1.22×10^{-6}
3	$\text{LiNi}_{0.45}\text{Ce}_{0.05}\text{Mn}_{0.5}\text{O}_2$	1.34×10^{-6}	1.25×10^{-6}
4	$\text{LiNi}_{0.475}\text{Ce}_{0.05}\text{Mn}_{0.475}\text{O}_2$	1.52×10^{-6}	1.39×10^{-6}

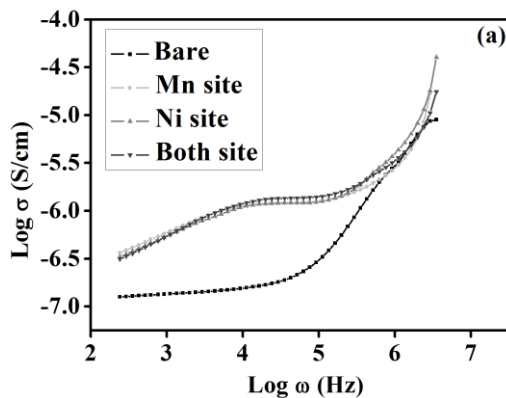


Fig. 3 (a) conductivity spectra of pristine $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ and cerium doped compounds

In the Modulus plot (Figure.3 (b)), for the pristine compound, the presence of peaks at low and high frequency region indicates the grain boundary and grain region, respectively, Interestingly, the absence of grain boundary peak in the modulus spectra of the doped compounds, suggest the reduced grain boundary thickness after doping, thereby decreasing the overall resistance of the material.

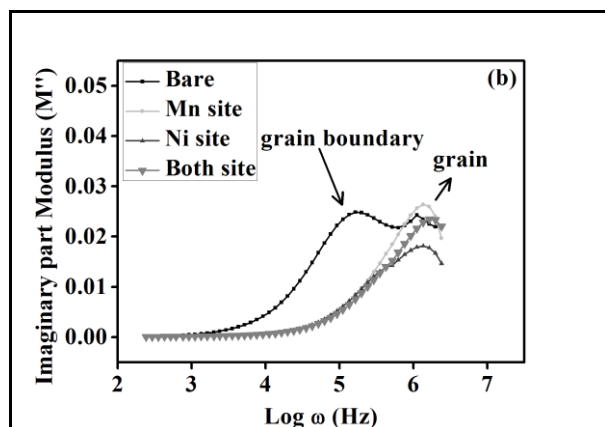


Fig. 3 (b) Modulus spectra of pristine $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ and cerium doped compounds

Conclusion

Pristine and 0.05 M of Ce doped lithium nickel manganese oxide were successfully prepared by PVP assisted sol-gel method. The XRD results indicate the presence of CeO_2 phase leading to slight increase in the cation mixing in the lattice. Electrical studies show the overall conductivity of the compound to be improved by one order after doping due to the reduction of grain boundary region by the presence of CeO_2 phase. With proper doping level of cerium and preparation methods, there is a scope for better performance of cerium doped lithium nickel manganese oxide cathode material.

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