

**A STUDY OF THE STRUCTURAL, MORPHOLOGICAL
AND ELECTROCHEMICAL PROPERTIES OF
LiLa_{0.01}Mn_{1.99}O₄ CATHODE MATERIAL****Paulos Taddesse Shibeshi¹ and Dr. V. Veeraiah²**¹M.Sc. Research Scholar, Department of Physics, College of Science and Technology,
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ABSTRACT

The La substituted LiMn₂O₄ cathode material is prepared by two steps solid-state reaction method. Structural identification, surface morphology and electrochemical performance of the material are studied by X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, scanning electron microscopy (SEM), and galvanostatic charge/discharge test. The XRD result shows that LiLa_{0.01}Mn_{1.99}O₄ powder sample keeps the structure of LiMn₂O₄. No additional phase or impurity is detected. The SEM study reveals that LiLa_{0.01}Mn_{1.99}O₄ has fairly uniform particle/grain size distribution and porous structure. Further the electrochemical cell formed from LiLa_{0.01}Mn_{1.99}O₄ cathode yields relatively high initial discharge capacity of 110.25 mAh/g close to 75% of its theoretical capacity. After 15 cycles, the electrochemical cell retains 94.3% of its initial capacity. As compared with LiMn₂O₄, the La substituted material yields better cyclability or capacity retention performance. The observed results confirm that substitution of La for Mn is an effective method in improving crystallinity, structural stability and capacity retention performance of LiMn₂O₄.

Keywords: Solid-state reaction, XRD, SEM, FT-IR Spectroscopy, Galvanostatic charge-discharge test.

INTRODUCTION

The spinel LiMn₂O₄ is the most widely studied cathode material for application of lithium-ion batteries, because of its high voltage source and high energy density [1-3]. However, LiMn₂O₄ suffers capacity fading during charge/discharge cycling [4-7]. The causes for the capacity loss of the material are also proposed by different researchers. The two basic factors which are responsible for the capacity loss of the material are Jahn-Teller distortion [8-10] due to the presence of high spin Mn³⁺ ions in the 3 V range and the manganese dissolution into the electrolyte [10,11]. To inhibit these problems, many efforts have been

made by the researchers. It has been shown that partial cation substitution for manganese in LiMn_2O_4 yields successful improvement of cycling performance. For instance, substitution of cations such as Co [11,12], Mg [13], Ni [14,15], Cr [16,17], Al [11,18], Fe [15] and Cu [17] for Mn exhibited greatly improved cycling performance of LiMn_2O_4 .

The primary objective of this study is to investigate the effect of partial substitution of La^{3+} for Mn^{3+} on the structural morphological and electrochemical properties of LiMn_2O_4 material. A comparative study on the electrochemical properties of $\text{LiLa}_{0.01}\text{Mn}_{1.99}\text{O}_4$ and LiMn_2O_4 is also performed.

Experimental

The pure $\text{LiLa}_{0.01}\text{Mn}_{1.99}\text{O}_4$ powder sample is synthesized by two-steps solid-state reaction method at high temperature. A mixture of stoichiometric Li_2CO_3 (99%, Merck), MnO_2 (99%, Hymedia) and La_2O_3 (99.99%, Sigma-Aldrich) is initially ground in agate mortar for about three to four hours. After thorough homogenizing with some methanol added, pre-calcination is done at 500 °C for 5 hours in air with heating and cooling rates of 5 °C/min to remove the CO_2 gas. Further, the obtained powder is ground again for three to four hours followed by calcination at 800 °C for 24 hours in air with heating and cooling rates of 5 and 1 °C/min, respectively.

The working electrode is made by dissolving 90 wt.% $\text{LiLa}_{0.01}\text{Mn}_{1.99}\text{O}_4$ active material, 7 wt.% carbon black and 3 wt.% polyvinylidene fluoride (PVDF) binder in n-methylpyrrolidone (NMP) solvent to form slurry. The slurry is then coated on an aluminum foil, followed by drying in vacuum oven at 110 °C for 24 hours. The electrochemical test cell is assembled in a glove box under a dry argon atmosphere. $\text{LiLa}_{0.01}\text{Mn}_{1.99}\text{O}_4$ electrode is used as positive electrode and lithium foil as negative electrode. The electrolyte is a solution of 1M of LiPF_6 dissolved in ethylene carbonate/dimethyl carbonate (EC/DMC) (1:1 volume ratio).

The X-ray diffraction (XRD) pattern of the powder sample is performed with X-ray Phillips XPERT-PRO diffractometer fitted with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54060 \text{ \AA}$) over a 2θ range from 10° and 90°. The particles morphology is observed by scanning electron microscopy (ZEISS SEM). Fourier transform infrared (FT-IR) spectroscopy of the sample is performed within wavenumber range from 400 to 4,000 cm^{-1} by using IRPrestige-21 instrument. Charge/discharge characteristics is tested by WonATech Potentiostat/galvanostat instrument in the range between 3.0 and 4.5 V at a charge/discharge rate of 0.1C.

RESULTS AND DISCUSSION

XRD Analysis

Fig. 1 shows the XRD pattern of $\text{LiLa}_{0.01}\text{Mn}_{1.99}\text{O}_4$ sample after heating at 800 °C for 24 hours in air. The synthesized sample shows a single-phase spinel structure with $\text{Fd}\bar{3}m$ space group (according to JCPDS card). This indicates that partial replacement of La^{3+} for Mn^{3+} does not change the basic crystal structure of LiMn_2O_4 . Also, highly intense sharp and narrow peaks are observed, which indicates the high crystallinity of the sample.

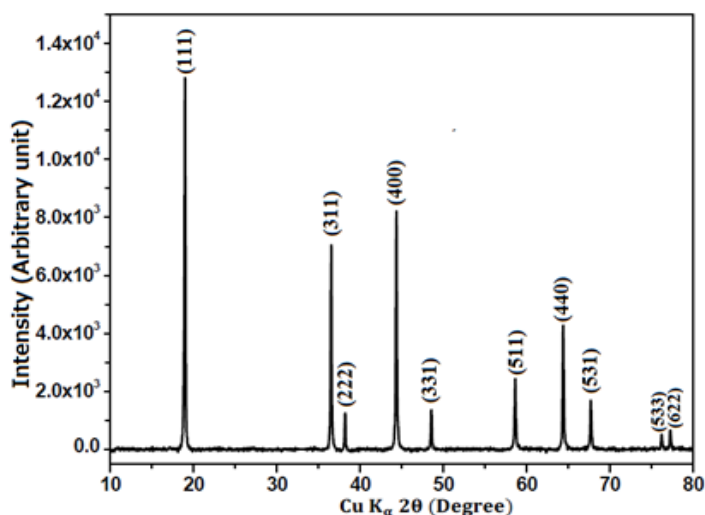


Fig. 1. XRD pattern of LiLa_{0.01}Mn_{1.99}O₄ powder sample

The unit cell lattice parameter (a) of the sample is calculating by the least square fitting method from the d-spacing and Miller indices, hkl values of (440) diffraction peaks using [19,20],

$$a = d\sqrt{h^2 + k^2 + l^2}$$

It is found to be 8.2311 Å, which is lower than the lattice parameter of LiMn₂O₄ (8.2314 Å) [21]. This is due to the stronger bond energy of Li³⁺- O (799 KJ mol⁻¹) [22] than Mn³⁺- O (402 KJmol⁻¹) [23]. On the hand the crystal size of LiLa_{0.01}Mn_{1.99}O₄ is also calculated using the relation [20],

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

where λ is the wavelength of X-ray, θ is the Bragg angle, and β is the full width at half maximum (FWHM) of (111) diffraction peak in the cubic lattice. It is found to be 95.35 nm, which is lower than the crystal size of LiMn₂O₄ (96.4 nm) [21].

SEM Study: SEM study is employed to investigate the surface morphology of LiLa_{0.01}Mn_{1.99}O₄ powder sample and the image at magnification of 100,000 X is shown in Fig. 2. As shown in the figure, the powder sample exhibits relatively uniform particle/grain size distribution, indicating the well developed crystallinity as confirmed by XRD pattern. In addition, the synthesized sample exhibited porous structure, which facilitates faster penetration of the electrolyte through the cathode materials.

FT-IR Spectroscopy Study: The room temperature FT-IR spectrum of LiLa_{0.01}Mn_{1.99}O₄ powder is shown in Fig. 3. As shown in the figure, the IR spectrum mainly consists of two frequency bands centered at wavenumbers of about 627.13 and 527.75 cm⁻¹, corresponding to the asymmetrical stretching modes of MnO₆. The obtained band at higher wavenumber

of 627.13 cm^{-1} is attributed to the asymmetric stretching modes $\text{Mn}^{3+}\text{-O}$ group [24]. Additionally, the band at lower number of 527.75 cm^{-1} is associated with the asymmetric stretching of $\text{Mn}^{4+}\text{-O}$ in the octahedral site [24]. As compared with LiMn_2O_4 [21], the observed bands of $\text{LiLa}_{0.01}\text{Mn}_{1.99}\text{O}_4$ material are shifted slightly towards higher wavenumber regions. This indicates that the substitution of La ions has led to the decrease in octahedral site radius by decreasing the concentration of Mn^{3+} into spinel lattice. The reason is the stronger bond energy between La and O as discussed above. This result is in good agreement with the smaller lattice parameter and crystal size obtained from the XRD pattern.

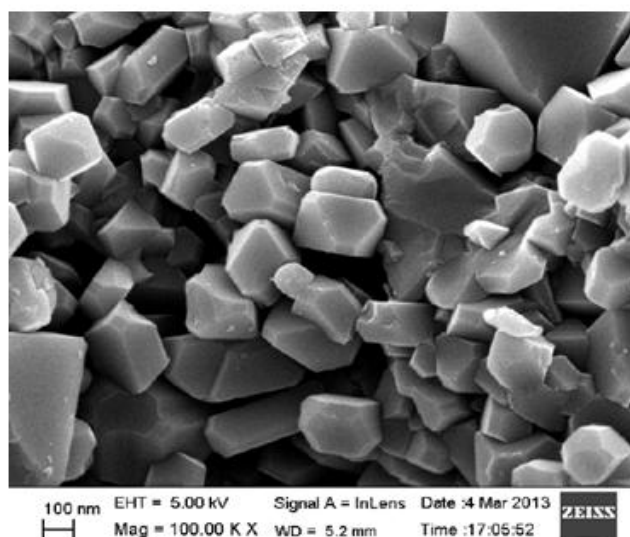


Fig.2. SEM image of $\text{LiLa}_{0.01}\text{Mn}_{1.99}\text{O}_4$ powder sample

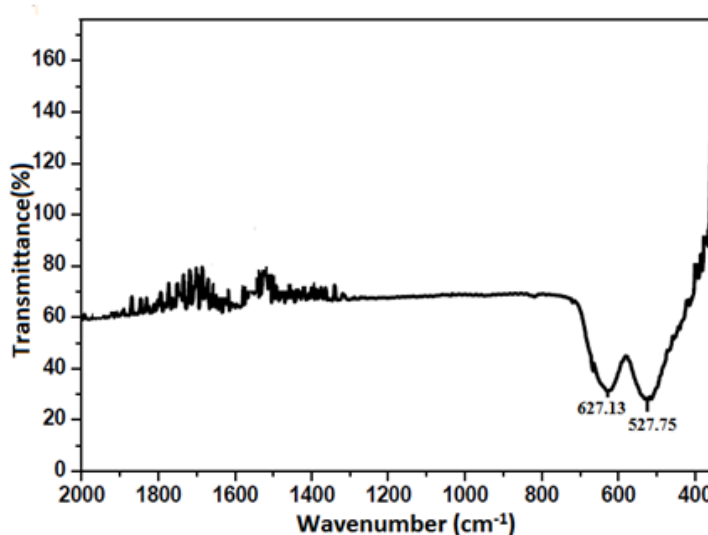


Fig. 3. FT-IR spectrum of $\text{LiLa}_{0.01}\text{Mn}_{1.99}\text{O}_4$ sample

Charge/Discharge Study: The first charge/discharge curves of Li/LiLa_{0.01}Mn_{1.99}O₄ electrochemical cell at constant current rate of C/10 between 3.0 and 4.5 V is shown in Fig. 4. It can be observed that the charge/discharge curves have two voltage plateaus at around 3.96 and 4.2 V. This indicates that both the insertion and extraction of lithium-ions proceed in two stages [25]. The first one is due to the removal of the lithium-ions from half of the tetrahedral sites and second plateau is due to the removal of the lithium ions from the other tetrahedral sites of LiLa_{0.01}Mn_{1.99}O₄ cathode [25]. Further, the initial discharge capacity of LiLa_{0.01}Mn_{1.99}O₄ obtained in this study is 110.25 mAh/g. However, LiMn₂O₄ is able to deliver the first discharge capacity of 121 mAh/g [21], which is greater than the La substituted sample. This is due to La substitution into the Mn site decreases the Mn³⁺ ions which contributes to the charge/discharge capacity.

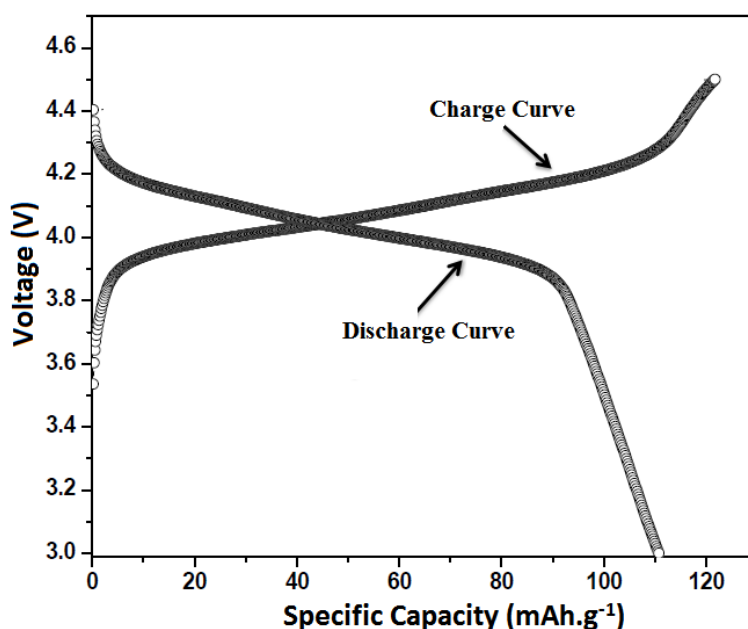


Fig.4. the charge/discharge curves of Li/LiLa_{0.01}Mn_{1.99}O₄ electrochemical cell

Cyclic Performance Study: Fig. 5 shows the cyclic behavior of Li/LiLa_{0.01}Mn_{1.99}O₄ electrochemical cell in the voltage range 3.0 to 4.5 V. It is found that the cyclability and the capacity retention performance of La substituted sample are better as compared with LiMn₂O₄. As discussed in the charge/discharge study, Li/LiLa_{0.01}Mn_{1.99}O₄ electrochemical cell is able to deliver the initial discharge capacity of 110.25 mAhg⁻¹. After 15 cycles, it is able to retain a discharge capacity of 103.97 mAhg⁻¹, which is 94.3% of its initial discharge capacity. However, LiMn₂O₄ is able to retain 92.2% of its initial capacity after 10 cycles [21], which is lower than that of La substituted sample. The reason for the improved capacity retention performance is that the substitution of La for Mn in the 16d octahedral sites decreases the unit cell volume of the sample and consequently enhances the structural stability of the sample during charge/discharge processes. Also, the substitution process reduces the Mn³⁺ concentration in the sample as a result the effect of Jahn–Teller distortion

is reduced. Finally, from this study it is observed that the partial substitution of La for Mn is effective in improving the cyclability and capacity retention performance of LiMn_2O_4 .

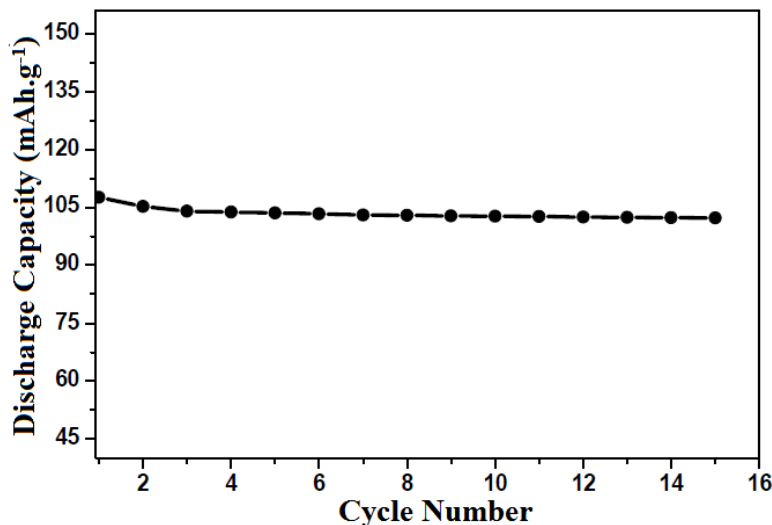


Fig. 5. Cycle performance of $\text{Li/LiLa}_{0.01}\text{Mn}_{1.99}\text{O}_4$ electrochemical cell

CONCLUSION

The La substituted LiMn_2O_4 cathode material is successfully prepared by two steps solid-state reaction method. The XRD analysis confirms that the synthesized sample belongs to $\text{Fd}\bar{3}m$ space group. Moreover, $\text{LiLa}_{0.01}\text{Mn}_{1.99}\text{O}_4$ sample has smaller lattice parameter and crystallite size than that of LiMn_2O_4 . Further, the uniform particles/grains size distribution and porous structure of the sample are confirmed by SEM. From the FT-IR study of the powder sample, two distinct strong absorption peaks which are associated with the asymmetric stretching modes of MnO_6 are detected. Comparing with LiMn_2O_4 sample, larger band shift towards higher wavenumber is observed in $\text{LiLa}_{0.01}\text{Mn}_{1.99}\text{O}_4$ sample. The electrochemical cell formed from $\text{LiLa}_{0.01}\text{Mn}_{1.99}\text{O}_4$ cathode exhibits $110.25 \text{ mAh.g}^{-1}$ discharge capacity during the first cycle. After 15 cycles, the cathode material is able to retain $103.97 \text{ mAh.g}^{-1}$ which is 94.3% of its initial capacity. From this study, it is observed that substitution of La for Mn into LiMn_2O_4 is very effective method in improving its crystallinity, structural stability and improving the capacity retention rate during cycling.

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