Electrochemical performances of Li-rich layered-layered Li$_2$MnO$_3$-LiMnO$_2$ solid solutions as cathode material for lithium-ion batteries

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ABSTRACT

In this work a series of Li-rich layered-layered solid solution of Li$_x$Mn$_2$O$_3$-LiMnO$_2$ [Li[Li$_{1-x}$Mn$_{2+x}$/3]$O_2$; $x$ = 0.0, 0.1, 0.3 and 0.5] nanocomposite structure were successfully synthesized using sol-gel technique. All the synthesized compositions exhibit the main characteristics peaks of m-Li$_2$MnO$_3$ and could be indexed to the C2/m space group except some weak diffraction peaks located around 20$^\circ$–30$^\circ$ which can be attributed to the superlattice structure originate due to the ordering of Mn ion into Li-Mn layers and are typically observed for Li-rich based materials. CV results show that pristine LMO possesses weak anodic peak around 4.7 V and no symmetric cathodic peak in the voltage window of 2.0–4.8 V. Among all the synthesized compositions, $x$ = 0.3 (LM03) delivers highest specific discharge capacity and best rate and cycling performances at all values of current densities. The LM03 composition delivers an initial discharge capacity of 177 $\pm$ 5 mAh g$^{-1}$ at a current density of 10 mA g$^{-1}$ in the voltage range of 2.0–4.8 V and holds nearly 97% of the initial discharge capacity after 120 charge/discharge cycles at the same current density.

1. Introduction

Single layered-type transition metal oxide cathode materials such as ABO$_2$/AB$_2$O$_3$, spinel-type cathodes such as ABO$_4$ and olivine-type cathodes materials such as ABO$_4$ (A = Li, B = transition metal, X = P, Si, etc.) have been extensively studied in order to have high energy density electrode material. Apart from advantages possesses by these materials their disadvantages are also evident. For ABO$_2$-type cathode materials such as LiCoO$_2$ and LiNiO$_2$, higher cost, toxic nature and poor thermal stability remain important points of concerns [1,2]. In ABO$_4$-type cathode materials such as LiMn$_2$O$_4$, capacity fading due to the dissolution of manganese ions and Jahn-Teller distortion hindered their widespread applications [3,4]. Furthermore, poor electronic conductivity and sluggish lithium ion diffusion in olivine-type cathode materials such as LiFePO$_4$ restrict their use in automotive industry [5–7]. Layered-layered solid solutions of type AB$_2$O$_3$-ABO$_2$ have become attractive cathode materials for lithium-ion batteries due to their high reversible capacity of 250 mAh g$^{-1}$ with lower cost, structural stability and better safety as compared to the currently used commercial LiCoO$_2$ cathode [8]. Layered oxide Li[Li$_{1/3}$Mn$_{2/3}$]O$_2$ (commonly written as Li$_2$MnO$_3$) possess AB$_2$O$_3$-type monoclinic structure (C2/m space group) and high theoretical capacity up to 458 mAh g$^{-1}$ [9–11]. However, it is electrochemically inactive in the typical voltage range 2.2–4.4 V vs. Li$^+$/Li as all Mn atoms exist in +4 valence. Due to this, it is hard to oxidize beyond Mn$^{4+}$ in an octahedrally coordinated environment and therefore, no lithium can be easily removed from the Li$_2$MnO$_3$ phase [2,3,8,9,11]. Furthermore, it requires a high cut-off voltage (~4.8 V vs. Li$^+$/Li) during the initial charging process to activate Li$_2$MnO$_3$ by removing Li$_2$O from the electrode active material according to the following reaction [2,9,12,13]:

$$\text{Li}_2\text{MnO}_3 \rightarrow x\text{Li}_2\text{O} + (1-x)\text{MnO}_2$$

(1)

Li$_2$MnO$_3$ also shows poor cycling performance which is due to the structural transition from layered structure to the spinel structure during charging/discharging process [14]. Therefore, rigorous research efforts are on-going to find optimized electrode materials containing Li$_2$MnO$_3$ along with two or three components [2,3,8–12,15–19]. In this work, Li$_2$MnO$_3$ has been integrated with another Mn-based layered cathode LiMnO$_2$ in order to have lithium rich layered-layered solid solutions. LiMnO$_2$ crystallizes in two
forms: orthorhombic (α-LiMnO₂, Pmmn Symmetry) and monoclinic (m-LiMnO₂, C2/m Symmetry) and has a high theoretical capacity of around 290 mAh g⁻¹ and better cyclability when operated between 2.0 and 4.5 V vs. Li⁺/Li [9,14,20].

The motive behind the present work is to study the physico-chemical and electrochemical performances of the lithium rich Mn-based layered-layered solid solutions of Li₂MnO₃-LiMnO₂. The research work reported on solid solution in this investigation has not been explored in the past. Although, there are reports on various solid-solution system which have been investigated previously like Li₂MnO₃-LiMO₂ (M = Ca, Sr, Ba) [21], Li₁₋ₓ(Ni0₂Mn0₇₋ₓTy)₁₋ₓLi₂O₂, 0 < x < 1/3, y = 0, 0.1, 0.2 [22], xLi₂MnO₃-(1-x) LiNi0.2Co0.8O₂ [23], 0.5Li₂MnO₃-0.5Li(Ni0.373Mn0.627O2) [24] etc. Apart from these reported works several attempts has also been made to synthesize and study electrochemical performances of some Li-rich manganese-based compositions using different methods [25,26] and morphology [27,29] etc. All the synthesized compositions in this work have been prepared using the sol-gel route and were examined using X-ray diffraction (XRD) for phase analysis, scanning electron microscopy (SEM) for microstructural investigation and Fourier-transform infrared spectroscopy (FTIR) for vibrational modes analysis. Electrochemical characterizations of as-prepared compositions were carried out to study electrochemical performance and lithium ion kinetics.

2. Experimental

2.1. Material preparation

Stoichiometric amounts of lithium acetate dihydrate (CH₃COO-Li₂H₂O, Sigma-Aldrich, ~99%) and Manganese acetate ([CH₃COO]₂Mn·4H₂O, Fisher Scientific, 99%) were used as precursors for the development of solid solutions of Li₂MnO₃-LiMnO₂ [Li[Li₁₋ₓMnₓ]₀.₃Mnₐ₋₀.₇O₂; x = 0, 0.1, 0.3 and 0.5] using sol-gel technique. Citric acid (Sigma-Aldrich, >99.9%) was used as a chelating agent. A dispersed solution of all the precursors in deionized water was prepared with continuous stirring and then added to citric acid solution one by one. The pH value of the resulting solution was maintained between 6 and 7 using ammonia solution. The resulting solution of citric acid and precursors was heated at 70 °C at 400 rpm with continuous stirring until a transparent gel was obtained. The gel thus obtained was dried at 120 °C for 5 h in a vacuum oven to obtain xerogel. The yielded powders were reground using pestle mortar and again heated at 600 °C for 3 h in air and then finally calcined at 900 °C for 12 h in air and then allowed to cool normally up to room temperature. The powders thus obtained for x = 0.0, 0.1, 0.3 and 0.5 were abbreviated as LMO, LMO1, LMO3 and LMO5, respectively. The heating rate of the furnace was kept at 5 °C min⁻¹.

2.2. Material characterization

Synthesized samples were characterized using RIGAKU make X-ray diffractometer coupled with CuKα radiation (λ = 1.540 Å) for quantitative analysis of crystal structure and phase composition of the synthesized structures. The XRD data was collected over an angular range of 10–70° with a step size of 0.02°. Rietveld refinement of LMO sample was performed using ‘X’pert high score plus’ software in order to obtain quantitative information about structural parameters. The microstructural characterization of the prepared samples was carried out using HITACHI make S-3700N scanning electron microscope working at 15 kV. The as-synthesized samples were mixed with 2.5 wt% of polyvinyl alcohol (PVA) binder, pressed into round pellets with 10 mm diameter by applying pressure of 5 tons using a hydraulic press and then heated at 250 °C for 2 h in air to remove PVA. In order to make electrical contacts, silver (Ag) paste was applied on both sides of pellets and then dried at 150 °C for 1 h in air to remove moisture content. A two-point probe setup (AGILENT 4284A) was used to calculate the electronic conductivity of the synthesized samples. Conductivity measurements were done at a bias voltage of 1.0 V and the frequency range was kept from 20 Hz to 1 MHz. The electronic conductivity (σ) can be calculated using the following equation;

\[
\sigma = \frac{1}{R} \left( \frac{L}{A} \right)
\]

where R is the resistance of the sample (Ω), L and A is thickness (cm) and cross-sectional area (cm²) of the circular disc, respectively.

2.3. Electrode preparation and electrochemical characterization

For the electrochemical studies, two electrode coin half-cells (CR2032) were assembled. The working electrodes were prepared by dissolving 70 wt% active material, 15 wt% super P as a conductive carbon and 15 wt% polyvinylidene difluoride (PVDF) as a binder in N-methyl-2-pyrrolidinone (NMP2) as a solvent. This results in the uniform mixing of the active materials which were stirred for 10 h. Thus obtained slurry was uniformly coated on Al foil current collector using the “doctor blade” technique and further dried out at 80 °C in a vacuum oven for overnight to evaporate the solvent. Then circular electrodes with diameter 19 mm were punched and weighed. The electrodes were then dried up under vacuum at 60 °C and finally brought inside the Mbraun make glove box having O₂ and H₂O level <0.5 ppm. The coin cells (CR2032) were assembled for electrochemical studies of the synthesized samples with metallic lithium as both counter and reference electrode and a microporous polypropylene sheet Celgard 2400 used as a separator. The electrolyte used was 1 M LiPF₆ in EC: DMC 1:1 v/v. Cyclic voltammetry (CV) experiments were carried out over the potential range of 2.0–4.8 V (vs. Li/Li⁺ metal). The galvanostatic charge/discharge (GCD) performance test, rate capability at different C-rates and Electrochemical Impedance Spectroscopy (EIS) using an AC voltage pulse of 5 mV in the frequency range of 10 mHz-10 kHz were performed. All the electrochemical tests were performed using EZstat-pro Nuvant systems Inc. (U.S.A) cell test system at 298 K.

3. Results and discussion

3.1. Structural and morphological analysis

The XRD patterns of the as-synthesized compositions are shown in Fig. 1. The pristine Li₂MnO₃ (LMO) shows diffraction peaks which correspond to the m-Li₂MnO₃ and could be assign to C2/m space group (Reference Code: 01-084-1634). The sharp and intense peaks indicate the crystalline nature of all the synthesized compositions. Even composite solid-solutions i.e. Li[Li₁₋ₓMnₓ]₀.₃Mnₐ₋₀.₇O₂ (x = 0.1, 0.3 and 0.5) still shows the main characteristics peaks of m-Li₂MnO₃ indicating that the layered structure of the synthesized samples is still preserved. The (001) diffraction peaks of the synthesized compositions (shown in the magnified XRD image) clearly shows slight shifts towards higher 2θ angle suggesting a minor shrink of the unit cell and decrease in lattice parameters. On the other hand, weak diffraction peaks located around 20–30° can be attributed to the superstructure ordering of the lattice which is caused by the arrangement of Mn ion into Li-Mn layers and are observed for Li-rich based materials [1,28,30–32]. However, the
The intensity of these superlattice peaks become weaker on changing the value of \( x \) from 0.1 to 0.5 which indicates that the local ordering of Li/Mn has been reduced. In addition, the peak around 37° splits into two peaks i.e. (Z01) and (130), which can also be indexed to C2/m space group with a high degree of crystallinity. Similarly, the peak around 45° also depicts the same results. However, the intensity of these doublets gets faded with an increase in \( x \). The splitting of peaks located at 59° and 65° for all values of \( x \) has also been noticed which indicates the presence of spinel phase [15].

Rietveld refinement was performed for the pristine LMO synthesized sample to obtain quantitative structural information of the crystal lattice structure using ‘X’pert high score plus’ software. The observed XRD pattern along with calculated and difference pattern for original LMO sample are shown in Fig. 2. No background subtraction and data smoothening were done before refinement. The starting atomic position coordinates for pristine LMO were taken from somewhere else [33]. The structural refinement results indicate that the goodness of fitting factor i.e. \( \chi^2 \) for primitive LMO is around 4.5% which demonstrates that the results are reliable. The crystal structure generated after refinement has been displayed in the inset of Fig. 2 where Li and Mn atoms are surrounded by O atoms to form LiO\(_6\) and MnO\(_6\) octahedra. The lattice parameters obtained from refinement for bare LMO are: \( a = 4.928 \) Å, \( b = 8.522 \) Å and \( c = 5.022 \) Å. The average crystallite size for pristine LMO was calculated to be 54 nm using Scherrer’s formula 
\[
d = \frac{k \lambda}{b \cos \theta},
\]
where \( d \) is the mean crystallite size, \( k \) is the constant parameter of shape factor (0.94), \( \lambda \) is the wavelength of X-ray (0.154 nm), \( b \) is the full-width half maximum corresponding to (001) peak and \( \theta \) is the corresponding angle of Bragg diffraction. These results suggest that the variation in \( x \) not only increase the crystallinity of the synthesized samples but also induce phase transformation to some extent.

The effect of variation in \( x \) value on the morphologies of Li
\[
[Li_{1-x/2}Mn_{x/2}]_2O_2 \text{ (} x = 0.0, 0.1, 0.3 \text{ and } 0.5 \text{)}
\]
composites are shown in Fig. 3(a)-(d). All prepared samples display nearly same morphology with plate-like and relatively spherical grains. The average grain size of LMO, LMO1, LMO3 and LMO5 composites were found to be around 0.45, 0.3, 0.5 and 0.45 μm, respectively. Therefore, the average grain sizes of the composites were distributed in a range of 300–450 nm. SEM images also show that the synthesized nanocomposites possess dispersed grains with little aggregation.

Among all synthesized samples, the pristine LMO and LMO3 compositions are chosen to investigate the morphological properties further. Fig. 4(A) and (B) shows the TEM/HRTEM images of the LMO and LMO3 synthesized samples. TEM image of pristine LMO (Fig. 4(A)) sample indicates that the particles are homogeneously
distributed with little agglomeration. It can also be observed from TEM image that the particles are nearly spherical and possess nearly uniform size. The average particle size was calculated using ImageJ software and observed to be 0.472 nm which corresponds to (001) plane of the monoclinic structure of synthesized LMO composition. Likewise, TEM image of LMO3 composition (Fig. 4(B)) also reveals the spherical morphology of the synthesized composition with slight agglomeration. The interlayer spacings of LMO3 composition were found to be 0.470 and 0.475 nm which again corresponds to (001) plane of the monoclinic structure. The obtained TEM/HRTEM results are well synchronized with XRD and SEM results.

3.2. Cation environment study-FTIR

FTIR spectroscopy proves to be an appropriate and dominant technique for the structural evaluation and to study local environment of the cations in the crystal lattice of close-packed oxygen atoms. Vibrational modes are generally assigned to the motion of cations with respect to an oxygen atom. The local cation environment of synthesized compositions in the range of 400−600 cm⁻¹ has been studied using FTIR spectroscopy and results are displayed in Fig. 5. It can be observed from FTIR graph that the spectrum of all synthesized samples shows nearly similar features. In the spectrum of LMO, four bands located around 520 cm⁻¹ (weak band), 465 cm⁻¹ (slightly broad peak), 430 cm⁻¹ (sharp band) and at 417 cm⁻¹ (less intense band) can be observed. These four IR active modes are assigned to the stretching and bending vibrations of octahedrally coordinated molecule of MnO₆ in Li[Li(1−x)/3Mn(x+2)/3]O₂ matrix [32,34]. The weak band located at 520 cm⁻¹ slightly moves towards higher wavenumber side for LMO1, LMO3 and LMO5 compositions which may be attributed to the variation in Li and Mn amount in Li[Li(1−x)/3Mn(x+2)/3]O₂ solid solution which induces a difference in the local cation environment. Similarly, the band at 412 cm⁻¹ shift towards lower wavenumber side for LMO3 and LMO5 which confirms that the local environment of the cations has been changed.

3.3. Electronic conductivity measurements

Electronic conductivity gives the direct measurement of the electron kinetics and hence, the electrochemical properties of the material. Fig. 6 displays the AC electrical resistance measurement for the as-synthesized compositions. The frequency range for the data collection was kept from 20 Hz to 1 MHz. From Fig. 6 it can be seen that all the compositions display depressed semicircle whose intercept at x-axis gives the AC resistance of the cathode active material. It can be seen that excluding LMO3 sample all the compositions have AC resistance in megaohm. The AC conductivity values for the samples LMO, LMO1, LMO3 and LMO5 were found to be 10.1 × 10⁻⁹, 10.8 × 10⁻⁹, 1.65 × 10⁻⁷ and 9.36 × 10⁻⁹ S/cm, respectively. Therefore, among all the synthesized samples LMO3 shows the highest AC conductivity and hence, superior electrochemical performances are expected from LMO3 composition as compared to other synthesized samples.

3.4. Electrochemical performance of Li₂MnO₃-LiMnO₂ solid solutions

Cyclic voltammetry measurements give an insight into the electrochemical reactions taking place during the charging-discharging process. Fig. 7 displays the CV results of the as-synthesized samples in the voltage window of 2.0−4.8 V. The data for the CV measurement was collected at a scan rate of 0.05 mVs⁻¹. It can be observed from Fig. 6 that pristine LMO possesses weak anodic peak around 4.7 V and no symmetric cathodic peak. It
indicates the loss of lattice oxygen along with lithium extraction from monoclinic crystal structure as given by eq. (1) [33]. Therefore, CV result indicates that the activation of primitive LMO will take place at 4.7 V and this process will not be reversible. However, for LMO1, LMO3 and LMO5 compositions the intensity of the peak at 4.7 V decreases significantly which indicates that the redox reaction mechanism is different from LMO. Moreover, MnO2 obtained in eq. (1) is assumed to be electrochemically active and formed spinel structure during Li-intercalation. The samples with x > 0 i.e. LMO1, LMO3 and LMO5 shows a redox couple around 3.0/2.8 V, 4.1/4.0 V and anodic peak around 2.1 V. The redox couple at 4.1/4.0 V can be attributed to insertion of lithium ion at vacant 8a tetrahedral sites of the spinel structure formed by MnO2 [9]. Likewise, the emergence of redox couple at 3.0/2.8 V is due to intercalation of Li-ion at 16c octahedral sites of the spinel structure [33]. The origin of anodic peak around 2.1 V can be attributed to structural modification of the material which generally take place due to high upper voltage limit and can be assigned to spinel Mn4+/Mn3+ redox couple [35].

When charged at higher voltage, transition metal dissociation takes place which leads to phase transformation from layered to spinel structure. However, the intensity of these redox couples was found to vary with x. This phenomenon may be correlated to the manganese dissolution which originated due to Jahn-Teller distortion and leads to change in oxidation state of Mn in the composition [9]. The average oxidation states of Mn in LMO, LMO1, LMO3 and LMO5 were calculated to be 4.0, 3.85, 3.61 and 3.40, respectively according to the redox titration method [27]. As average oxidation state of Mn changes from 4.0 to 3.4, Jahn-Teller distortion leads to dissociation of Mn4+ to Mn3+ and Mn2+ which results in active mass loss and a decrease in intensity [9]. This change of oxidation state is generally expressed in terms of the transformation of the layer-to-spinel structure as predicted by XRD (splitting of peaks at 2θ = 59° and 65°). The presence of shoulder peaks at 4.04, 3.98, 3.93 and 3.96 V also indicates the existence of small spinel phase due to electrochemical active MnO2. Therefore, the above results clearly indicate the coexistence of spinel structure along with layered structure while the redox process observed at 2.8 V and 4.1 V for LMO1, LMO3 and LMO5 samples will lead to stable capacity and cyclic performances.

Fig. 8 shows the initial charge-discharge capacity curves of Li [Li(1-x)/3Mn(x/2)/3]O2 (x = 0.0, 0.1, 0.3 and 0.5) solid solution at a current density of 10 mAg/g and in a voltage window of 4.8–2.0 V. The initial discharge capacities for composites LMO, LMO1, LMO3 and LMO5 were found to be 81 ± 5, 97 ± 5, 177 ± 5 and 71 ± 5 mAhg⁻¹, respectively. It can be observed that as x value increases capacity increases, goes maximum for LMO3 and then decreases for LMO5. For all composite samples, a sloping voltage plateau above 4.5 V can be seen in the charging curves. However, no discharge plateau was observed above 4.5 V for the composite samples which is associated with the oxidation of O2⁻ ions and electrochemical activation of Li2MnO3 by irreversible removal of oxygen from the lattice. Moreover, the charge-discharge profile of the LMO1, LMO3 and LMO5 samples exhibits three voltage plateaus around 4.25 V, 2.87 V and 2.25 V. The voltage plateaus around 4.25 V and 2.87 V originate due to change in oxidation state of Mn ion during charging-discharging. The length of voltage plateau at 4.25 V, 2.87 V and 2.25 V increases with increase in the value of x, reaching a maximum for LMO3 and then decreases for LMO5 which is possibly due to Jahn-Teller distortion as predicted in CV results. Among all the four samples, the LMO3 composition gives the highest discharge capacity and the composition LMO5 delivers the...
least charge-discharge capacity. These results indicate superior lithium ion kinetics and excellent reactivity for LMO3 sample. Fig. 9(a)-(d) shows the charge/discharge capacity curves of LMO, LMO1, LMO3 and LMO5, respectively for 1st, 2nd, 10th and 50th cycle at 10 mA/g. From Fig. 9(a), it can be observed that discharge capacity of LMO composition at the 50th cycle is much greater as compared to 1st cycle. This is due to activation of LMO compound due to the removal of O2 along with lithium extraction which causes an increase in the length of voltage plateau around 3.2 V.

However, for LMO1 (Fig. 9(b)), LMO3 (Fig. 9(c)) and LMO5 (Fig. 9(d)) compositions the charge/discharge profiles for 1st, 2nd, 10th and 50th cycle remains nearly same. These results indicate that the integrity of the synthesized compositions remains unchanged during cycling.

Fig. 10(a)-(d) shows the charge/discharge curves of the synthesized samples at different current densities (10–1000 mA/g) for the initial cycle. It can be observed from Fig. 10 that among all the synthesized samples LMO3 (Fig. 10(c)) delivers the highest specific
Fig. 9. Charge/discharge profiles of the prepared compositions for 1st, 2nd, 10th and 50th cycle at 10 mA/g: (a) LMO; (b) LMO1; (c) LMO3; (d) LMO5.

Fig. 10. Initial charge/discharge curves of the synthesized compositions at various current densities: (a) LMO; (b) LMO1; (c) LMO3; (d) LMO5.
discharge capacity at all current densities. LMO3 shows an initial discharge capacity of $177 \pm 5$ mAh/g at 10 mA/g and delivers nearly 37% of its capacity value even at the high current rate of 5C (1A/g). The loss of capacity at high current densities can be linked to the large polarization effects of the composites which hindered lithium ion kinetics. Fig. 11(b) displays the cycling stability of the synthesized composites at 10 mA/g current density for 120 charge-discharge cycles at room temperature. It is evident from Fig. 11(b) and Table 1 that except for LMO3 composite sample, discharge capacity at 120th cycle comes out to be more as compared to 1st cycle for LMO, LMO1 and LMO5 compositions. LMO3 shows an initial discharge capacity of $177 \pm 5$ mAh$^{-1}$ at 10 mA/g and retains nearly 97% of its capacity after 120 charge/discharge cycles at same current density.

Fig. 12 depicts the dependence of the rate performance on the variation of $x$. From the figure, it can be observed that at low C-rates, the difference in electrochemical properties is mainly due to the change in oxidation state of Mn ion which subsequently leads to manganese dissolution and inferior capacity performance. Under high C-rates, the alteration in discharge capacities is predominantly due to increase in polarization potential of the cathode active material which leads to poor discharge capacity values.

![Graph showing specific discharge capacity vs. number of cycles for different current densities](image1)

**Table 1**

<table>
<thead>
<tr>
<th>Samples</th>
<th>R (%)</th>
<th>0.05C ($\pm 5$) (mAh$^{-1}$)</th>
<th>0.1C</th>
<th>0.25C</th>
<th>0.5C</th>
<th>2.5C</th>
<th>5C</th>
<th>0.05C ($\pm 5$) (mAh$^{-1}$)</th>
<th>1st</th>
<th>120th</th>
<th>$R^\prime$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LMO</td>
<td>81</td>
<td>144.4</td>
<td>128.3</td>
<td>116.0</td>
<td>55.5</td>
<td>6.1</td>
<td>81</td>
<td>144</td>
<td>177.7</td>
<td>108.2</td>
<td></td>
</tr>
<tr>
<td>LMO1</td>
<td>97</td>
<td>84.5</td>
<td>81.4</td>
<td>72.1</td>
<td>32.9</td>
<td>20.6</td>
<td>97</td>
<td>105</td>
<td>108.2</td>
<td>97.1</td>
<td></td>
</tr>
<tr>
<td>LMO3</td>
<td>177</td>
<td>84.7</td>
<td>70.6</td>
<td>62.1</td>
<td>50.8</td>
<td>37.2</td>
<td>177</td>
<td>172</td>
<td>97.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LMO5</td>
<td>71</td>
<td>98.8</td>
<td>90.1</td>
<td>78.8</td>
<td>83.0</td>
<td>67.6</td>
<td>71</td>
<td>72</td>
<td>101.4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- $R^\prime$ is the capacity retention ratio at different C-rates as compared to 0.05C.
- $R^\prime$ is the capacity retention rate of samples compared to the 1st cycle at 0.05C.

![Graph showing rate performance as a function of x](image2)
EIS of the fresh cells was also performed to study the variation in electrode reaction impedance of the prepared composition. Fig. 13(a) demonstrated the EIS curves of Li[Li(1-x)/3Mn(x+2)/3]O2 compositions in the frequency range of 10 mHz-10 kHz using an AC voltage pulse of 5 mV amplitude. It can be observed from Fig. 13(a) that all the EIS curves of the composites samples enclose a depressed semicircle lies in the high-frequency region and a straight line falls in the low-frequency region. The intercept by the semi-circle at the real axis in the high-frequency region gives the ohmic resistance (R_s) of the cell which usually represents the resistance of the electrode material and the electrolyte. The part of semicircle lies in the middle-frequency range is mainly attributed to the electrochemical reactions taking place at the electrode and electrolyte interface and named as charge transfer resistance (Rct). The 45° inclined line with the x-axis in the low-frequency region signifies the Warburg impedance (Zw) which is related to Li-ion diffusion in the electrolyte solution. The values of lithium ion diffusion coefficient in the bulk electrode materials can be calculated using the following equation [38]:

\[
D = \frac{0.5R^2T^2}{A^2F^4C^2\sigma_W^2}
\]

where D is Li-ion diffusion coefficient, R is gas constant, T is absolute temperature, A is electrode area, C is the lithium-ion concentration, F is the faraday constant and \(\sigma_W\) is the Warburg factor which is given by the following equation:

\[
Z' = R_s + R_{ct} + \sigma_W\omega^{-0.5}
\]

4. Conclusions

A series of solid solution of layered-layered composites Li[Li(1-x)/3Mn(x+2)/3]O2 (x = 0.0, 0.1, 0.3 and 0.5) were successfully synthesized using sol-gel technique. XRD results confirm the coexistence of layered structure along with spinel structure. Microstructural investigations reveal that the average grain size of all the compositions lies in a range of 300-450 nm. Among all the synthesized compositions LMO3 shows the best rate and cycling performances. Also, the lithium-ion diffusion coefficient was found to be minimum for LMO5 composition and therefore, it possesses inferior electrochemical performances. The EIS results clearly indicate that the LMO3 composition possesses the lowest charge transfer resistance due to which it delivers the highest discharge capacities among all the synthesized samples.
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References

[9] W. West, R. Staniewicz, C. Ma, J. Robak, J. Soler, M. Smart, B. Ratnakumar, Implications of the first cycle irreversible capacity on cell balancing for LiMn2O4–LiMnO2–LiNi0.5Mn1.5O4 Li-ion batteries, J. Power Sources 196 (2011) 9696–9701.
[13] Z. Su, Z. Lu, X. Gao, P. Shen, X. Liu, J. Wang, Preparations of electrochemical performance of LiCoO2–LiNi0.5Mn1.5O4 blended with LiFePO4 to achieve high energy density and pulse power capability, J. Power Sources 196 (2011) 9702–9707.
[15] J. Shojan, V.R. Chitturi, J. Soler, O. Resto, W.C. West, R.S. Katiyar, High energy xLi2MnO3–(1−x)LiNi0.5Mn1.5O4–xLiNi0.5Mn1.5O4 composite cathode for advanced Li-ion batteries, J. Power Sources 274 (2015) 440–450.
[17] C. Hou, Y. Oaki, E. Hosono, H. Lin, H. Imai, Y. Fan, F. Dang, Bio-inspired synthesis of xLi2MnO3–(1−x)LiNi0.33Co0.33Mn0.33O4–LiNi0.33Co0.33Mn0.33O4 lithium-rich layered cathode materials, Mater. Des. 109 (2016) 718–725.
[20] B. Li, Y. Yu, J. Zhao, Facile synthesis of spherical xLi2MnO3–(1−x)LiMn0.5Co1.5O4–LiNi0.33Co0.33Mn0.33O4 electrochemical performance for lithium-ion batteries with improved electrochemical performance, J. Power Sources 275 (2015) 64–72.
[21] G. Xu, J. Li, X. Li, H. Zhou, X. Ding, X. Wang, F. Kang, Understanding the electrochemical superiority of 0.6Li1/3Li2/3MnO2–0.4Li[Ni0.1Co0.9]O2 nanofibers as cathode material for lithium ion batteries, Electrochem. Acta 173 (2015) 672–679.
[23] C. Miao, P. Bai, Q. Jiang, S. Sun, X. Wang, A novel synthesis and characterization of LiFePO4 and LiFePO4/C as a cathode material for lithium-ion battery, J. Power Sources 246 (2014) 232–238.
[28] J. Lin, B. Mu, Y. Jin, B. Wu, Y. Ma, F. Wu, Li-rich layered composite Li[Ni0.1Co0.9]O2 synthesized by a novel approach as cathode material for lithium-ion battery, J. Power Sources 230 (2013) 76–80.