CHAPTER - IV

RESULTS AND DISCUSSION

Preparation of LiMn$_2$O$_4$ thin film cathode materials by conventional spray pyrolysis and polymer spray pyrolysis methods are presented here. The best method was chosen for the preparation of metal cations doped LiMn$_2$O$_4$. The effects of metal cations such as Y$^{3+}$, Gd$^{3+}$ and Nd$^{3+}$ in the cubic spinel LiMn$_2$O$_4$ on physico (X-ray diffraction, Scanning electron microscopy, Atomic force microscopy) and electrochemical characterizations (charge-discharge and cycleability studies) are discussed in detail.

4.1. PREPARATION OF LiMn$_2$O$_4$ THIN FILM CATHODE MATERIAL BY SPRAY PYROLYSIS METHOD

4.1.1. Thermal analysis

The TGA curve for the precursor heated at a rate of 10°C/min is shown as Fig. 4.1. The curve indicates that a huge loss in weight between 40 and 120°C due to the removal of solvent. As the process of heating was continued, the weight loss increased, due to the combustion nature of the precursor. The weight loss in the temperature range of 240-320°C is associated with the decomposition of organic impurities. At higher temperatures, > 320°C there was no weight loss. This suggests that the decomposition temperature of precursor is 320°C. Hence, the temperature of the substrate was kept at 320°C for spraying the precursor solution for the preparation of LiMn$_2$O$_4$ thin films.
Fig. 4.1 Thermo-gravimetric analysis curve of LiMn$_2$O$_4$ precursor sample
4.1.2. X-ray diffraction analysis

The X-ray diffraction patterns of LiMn$_2$O$_4$ thin films calcined at different temperatures for 30 min. are shown as Fig. 4.2. For the sample sprayed at 320°C, the diffraction peaks appeared at $2\theta = 18.68$, $36.32$, $44.18$, $58.47$ and $63.79$ which corresponds to the (111), (311), (400), (511) and (440) planes of spinel LiMn$_2$O$_4$ lattice [1]. The changes in the relative X-ray line intensities may be attributed to a different cationic distribution in the film compared to the powder sample. The peak (400) overlapped with that of the substrate peak which could not be distinguished. The peaks related to the substrate are marked with an asterisk. This XRD pattern showed that the cubic spinel LiMn$_2$O$_4$ thin film was pure and crystalline in nature. Impurity phases such as Li$_2$CO$_3$ and Mn$_2$O$_3$ are not observed [2]. The observed peaks became sharper when the annealing temperature was increased to 700°C. It improved the crystal structure and increased the size of the crystallites. The observed diffraction lines are more intense and narrow. Annealing at 800°C for 10 minutes, there was no improvement in the intensity of observed peaks. This suggests that the optimum calcination temperature for the formation of well defined crystalline LiMn$_2$O$_4$ thin film is 700°C for 10 min. The crystalline size is calculated by Debye-Scherrer formula [3] (Table 4.1). According to the equation for cubic spinel structure

\[ d_{\text{ab}} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \]

the average crystal lattice parameter was calculated. All these values of the samples were calculated from XRD data [4].

\[ D = \frac{0.94}{\beta \cos \theta} \]
Fig. 4.2 X-Ray Diffraction patterns of LiMn$_2$O$_4$ thin films
(a) As-deposited at 320°C (b) Annealing at 500°C
(c) 600°C (d) 700°C (e) 800°C
Table 4.1

Grain size and lattice parameters of LiMn$_2$O$_4$ thin films calculated from Scherrer formula

<table>
<thead>
<tr>
<th>Annealing temperature ($^\circ$C)</th>
<th>Crystal size (nm)</th>
<th>Lattice parameter (Å)</th>
<th>Unit cell volume (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>450</td>
<td>40</td>
<td>8.1879</td>
<td>548.93</td>
</tr>
<tr>
<td>500</td>
<td>47</td>
<td>8.2142</td>
<td>554.23</td>
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<tr>
<td>600</td>
<td>52</td>
<td>8.2287</td>
<td>557.18</td>
</tr>
<tr>
<td>700</td>
<td>59</td>
<td>8.2319</td>
<td>557.83</td>
</tr>
<tr>
<td>800</td>
<td>62</td>
<td>8.2412</td>
<td>559.72</td>
</tr>
</tbody>
</table>
Where \( D \) is the crystallite size, \( \lambda \) is the radiation wavelength; \( \beta \) is the bandwidth at half-height and \( \theta \) is the diffraction peak angle. The calculated particles sizes of the prepared samples are in nanometer.

4.1.3. Scanning electron microscopy analysis

The surface of LiMn\(_2\)O\(_4\) thin film prepared by spray pyrolysis technique annealed at 700°C is shown in Fig. 4.3. The surface of the thin film had uniform particle size and well-defined edges with dense surface area and the average grain size was 434.3nm. It was porous in nature and it facilitated an easy access of battery electrolyte. This causes an increase with number of active sites. The deposited LiMn\(_2\)O\(_4\) thin film was grown at low temperature showed poor crystallization which was partially amorphous and the high crystallized LiMn\(_2\)O\(_4\) was developed by high temperature process.

4.1.4. Thickness measurement analysis

The film thickness verified with the Stylus thickness profiler was 0.421 \( \mu \)m.

4.1.5. Electrochemical characterization analysis

The electrochemical performance of the prepared thin film cathode materials was studied. The charge/discharge studies were carried out by fabricating electrochemical cell in the configuration of Li/LiMn\(_2\)O\(_4\) employing a Li\(^+\) ion conducting PVdF-HFP based micro porous polymer electrolyte. The charge and discharge cycling was performed galvanostatically at 0.2mA/cm\(^2\) within the voltages range of 3.0 - 4.5 V. The charge/discharge curves at the 1\(^{st}\) and 25\(^{th}\) cycle
Fig. 4.3 SEM photograph of LiMn$_2$O$_4$ thin film annealed at 700°C.
for Li//LiMn$_2$O$_4$ prepared are shown as Fig. 4.4. The initial discharge capacity of LiMn$_2$O$_4$ thin film was 137 mAh/g.

During charge-discharge, the change of manganese valence state occurs as follows:

$$\text{LiMn}^{3+}\text{Mn}^{4+}\text{O}_4 \leftrightarrow \text{Li}^+ + \text{e}^- + \text{Mn}^{2+}\text{O}_4$$

During the charge, the deintercalation of lithium ion from the spinel was accompanied by an oxidation of Mn$^{3+}$ to Mn$^{4+}$. More Mn$^{3+}$ existed in LiMn$_2$O$_4$ facilitate more lithium-ion to deintercalate from the host to offer higher capacity. The discharge capacity versus cycle number of Li//LiMn$_2$O$_4$ system is shown in Fig. 4.5. At 25th cycle, the capacity loss observed by the system was only 15%. LiMn$_2$O$_4$ thin film prepared by spray pyrolysis method exhibited very good reversibility. As the film is thin with small particle size, LiMn$_2$O$_4$ facilitated rapid diffusion of Li$^+$ ions which led to good battery performance [5].

4.2. EFFECT OF PEG FOR THE PREPARATION OF LiMn$_2$O$_4$ THIN FILM BY POLYMER SPRAY PYROLYSIS METHOD

4.2.1. Thermal analysis

TGA curve of LiMn$_2$O$_4$ precursor sample is shown in Fig. 4.6. It indicates that a continuous enormous weight loss. This started from 60°C to 430°C. It revealed that the solvent evaporation and decomposition of the intermediate complexes of the precursor sample such as carbonates, poly ethylene glycol etc., were completed below 430°C. This was due to the complete crystallization/phase formation temperature for LiMn$_2$O$_4$ active material (~430°C). The substrate temperature for
Fig. 4.4 Charge - discharge curves for the LiMn$_2$O$_4$ prepared by spray pyrolysis method.
Fig. 4.5 Relationship between the discharge capacity and cycle number of Li//LiMn$_2$O$_4$ thin film cell in the voltage range of 3.0 - 4.5 V at a current density of 0.2 mA/cm$^2$.
Fig. 4.6 Thermo-gravimetric analysis curve of LiMn$_2$O$_4$ polymeric precursor sample
spraying the precursor solution on the substrate was held at 430°C for the preparation of LiMn$_2$O$_4$ thin film active material.

4.2.2. X-ray diffraction analysis

X-ray diffraction patterns of LiMn$_2$O$_4$ thin film annealed at 450, 500, 600, 700°C for 30 min. are given in Fig. 4.7. The diffraction peaks of all the samples are identified as a single phase of cubic spinel structure with the space group Fd3m. It revealed that the films annealed at different temperatures have the same crystal structure. The intensity of XRD peaks increased with annealing temperature indicating that the crystallinity of thin film became enhanced and high phase purity was formed at 600°C. With further annealing at 700 & 800°C for 10 minutes, there was no difference in the observed peaks. It showed that the optimum calcination temperature for the formation of well defined crystalline LiMn$_2$O$_4$ thin film was 600°C. The product formation without polymer additive at 700°C was good, whereas the product formation with polymer additive was good even at 600°C. XRD data were interpreted with JCPDS data and the crystal structure of LiMn$_2$O$_4$ thin film was found to be a normal spinel [6]. It is possible that the changes in the relative X-ray line intensities may be attributed to a different cationic distribution in the films compared to the powder samples. The full width at half maximum (FWHM) of diffraction peaks is varied by the annealing. The Debye-Scherrer formula was used to calculate the average crystal size (Table 4.2). The peak (400) overlapped with that of the substrate peak which can not be distinguished. The peaks corresponding to the substrate are marked with an asterisk. High intense peaks corresponding to the reflections of (111) and (311) planes are characteristics of spinel structure. Low
Fig. 4.7 XRD patterns of LiMn$_2$O$_4$ thin films annealed at (a) 450 °C (B) 500 °C (C) 600 °C.
Table 4.2
Grain size and lattice parameters of LiMn$_2$O$_4$ thin films
Calculated from Scherrer formula

<table>
<thead>
<tr>
<th>Annealing temperature (°C)</th>
<th>Crystal size (nm)</th>
<th>Lattice parameter (Å)</th>
<th>Unit cell volume (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>450</td>
<td>37</td>
<td>8.1985</td>
<td>551.06</td>
</tr>
<tr>
<td>500</td>
<td>41</td>
<td>8.2252</td>
<td>556.47</td>
</tr>
<tr>
<td>600</td>
<td>45</td>
<td>8.2297</td>
<td>557.38</td>
</tr>
</tbody>
</table>
intense peaks of (333) and (311) planes are also observed around 58°. This suggests that the prepared thin films are of pure cubic phase LiMn$_2$O$_4$.

4.2.3. Scanning electron microscopy analysis

The scanning electron micrograph of LiMn$_2$O$_4$ thin film annealed at 600°C is shown as Fig. 4.8. The surface of the stainless steel substrate was found to be covered with fine crystals. No cracks were observed on the entire surface of the thin film. The grain size was small and uniform. The average grain size of the prepared thin film was 90.7nm. Compared with normal spray pyrolysis, it had very small grain size. The nanosized LiMn$_2$O$_4$ facilitated the rapid diffusion of Li$^+$ ions, which led to enhanced electrochemical performance [7,8].

4.2.4. Atomic force microscopy analysis

Fig. 4.9 presents the surface topography of the two dimensional view of the deposited LiMn$_2$O$_4$ thin film on stainless steel substrate as measured by atomic force microscopy. The image shows the uniformly distributed grains. The film consists mainly of nanocrystals with 85nm particle size. The surface of the thin film was not very dense and the root mean square roughness of the thin film is 26.7nm.

4.2.5 Thickness measurement analysis

The film thickness verified with the Stylus thickness profiler was 0.465 μm.

4.2.6 Electrochemical characterization analysis

Fig. 4.10 shows the electrochemical behaviour of rechargeable Li/polymer electrolyte/ LiMn$_2$O$_4$ thin film battery at 30°C. The thin film cell was cycled between
Fig. 4.8 SEM micrograph of nanocrystalline LiMn$_2$O$_4$ thin film annealed at 600°C.
Fig. 4.9 Surface topography of the LiMn$_2$O$_4$ thin film on stainless steel substrate measured by AFM, a) 2d image b) LFM image
3.0 and 4.5V at 0.2 mAcm⁻². Initial discharge capacity of LiMn₂O₄ thin film was 138mAhg⁻¹ against the theoretical value of 148mAhg⁻¹. During charge-discharge, the change of manganese valence state occurs as follows:

\[ \text{LiMn}^{3+}\text{Mn}^{4+}\text{O}_4 \leftrightarrow \text{Li}^+ + e^- + \text{Mn}^{2+}\text{O}_4 \]

During the charge, the deintercalation of lithium ion from the spinel is accompanied by an oxidation of Mn⁺⁺ to Mn⁺⁺. More Mn⁺⁺ that exists in LiMn₂O₄, the more lithium-ion can deintercalate from the host and more lithium-ion would intercalate into the host, resulting in higher capacity. The discharge capacity versus cycle number of Li/LiMn₂O₄ of both conventional and polymer spray pyrolysis system are shown in Fig. 4.11. The discharge capacity of the cell decreased slowly to 87.6% of its initial capacity in the 25th cycle and its average columbic efficiency was 92%. A lower capacity loss (12.4%) was at 25th cycle for the polymer spray pyrolysed material, whereas 15% capacity loss at 25th cycle for the conventional spray pyrolysed material. At 25th cycle, the percentage of capacity loss observed in both the conventional spray and polymer spray pyrolysis is shown in Fig. 4.12. Introduction of PEG on the preparation of nanocrystalline LiMn₂O₄ thin film causes a superior performance for Li-ion battery.
Fig. 4.10 Charge-discharge curves for LiMn$_2$O$_4$ prepared by polymer spray pyrolysis method
Fig. 4.11 Relationship between the discharge capacity and cycle number of
(a) Li/LiMn$_2$O$_4$ thin film cell obtained by polymer spray pyrolysis
(b) Li/LiMn$_2$O$_4$ thin film cell obtained by conventional spray pyrolysis
Fig. 4.12 Bar chart for % of capacity fading vs LiMn$_2$O$_4$ obtained by

(a) conventional spray pyrolysis method and

(b) the polymer spray pyrolysis method
4.3. EFFECT OF DOPING OF METAL CATIONS IN LiMn$_2$O$_4$

4.3.1. PHYSICAL AND ELECTROCHEMICAL CHARACTERIZATIONS OF Li$_{1-y}$Y$_y$Mn$_2$O$_4$ PREPARED BY POLYMER SPRAY PYROLYSIS

4.3.1.1. Thermal analysis

The TGA curve for Li$_{0.05}$Y$_{0.95}$Mn$_2$O$_4$ precursor sample is shown in Fig.4.13. The TGA curve may be divided into two regions. The initial weight loss is between 60°C and 150°C corresponded to the evaporation of solvent and the second weight losses from 280°C to 520°C, was due to the combustion nature of polyethylene glycol and to the decomposition of acetates, nitrates and intermediate compounds. In lost region, the curve became flat and no obvious change was observed above 520°C. Hence for spraying the precursor solution, the substrate was kept at 520°C for the preparation of Li$_{1-y}$Y$_y$Mn$_2$O$_4$ thin film active materials.

4.3.1.2. X-ray diffraction analysis

Fig.4.14 shows XRD patterns of Li$_y$Y$_{1-y}$Mn$_2$O$_4$ ($y=0.01, 0.03, 0.05$) samples calcined at 600°C for 30 min. In the XRD pattern, the peaks of the stainless steel substrate are also observed. All the peaks except those of the substrate peaks corresponded to the cubic spinel structure. The peaks corresponding to the substrate are marked with an asterisk. The crystallinity of the polycrystalline Li$_y$Y$_{1-y}$Mn$_2$O$_4$ was determined from the peak intensities and peak widths of the diffraction lines. Main peaks for these prepared materials were labelled with h,k,l indexes. The main diffraction peaks, such as (111), (311) and (400) were well developed as like cubic spinel space of LiMn$_2$O$_4$. The sample was identified as a pure spinel phase with a
Fig. 4.13 Thermo-gravimetric analysis curve of LiY_{0.05}Mn_{1.95}O_{4} polymeric precursor sample.
Fig. 4.14 X-ray diffraction patterns of Li$_x$Y$_{1-x}$Mn$_2$O$_4$ (y=0.01, 0.03, 0.05) thin film prepared by polymer spray pyrolysis method.
space group Fd3m where lithium ion occupy the tetrahedral (8a) sites; Mn\(^{3+}\), Mn\(^{4+}\) and Y\(^{3+}\) ions reside at the octahedral (16d) sites; and O\(^{2-}\) ions are located at (32e) sites\(^9\). There was no significant difference in the crystal structure after the doping compared to pure LiMn\(_2\)O\(_4\) which was identified as a spinel structure. It is evident that the spinel structure didn’t change due to small doping of yttrium in the octahedral site (16d) in the crystal lattice. The site occupancy of the dopant ions in the host matrix is an important factor, which determines the electrochemical properties of the system. Usually the occupancy of the dopant ions in the 8a lithium site will lead to unfavourable electrochemical results. But in XRD profiles, the Y\(^{3+}\) replaced manganese in the 16d octahedral sites and not lithium in the 8a tetrahedral sites, since the appearance of (220) Bragg plan (at ca. 20 = 30\(^\circ\)), which was extremely sensitive to the occupancy of the 8a tetrahedral sites was not observed \(^{10}\). If the dopant metal ionic radii was larger than Mn, the lattice constant increased by adding dopant. But the inverse behaviour for the case of yttrium takes place. As the bond energy of the Y-O (719.6 KJ/mol) is greater than that of Mn-O (402.9 KJ/mol), so it has higher octahedral site preference energy which resulted in diminution of the bond length. It increased the crystal stability of Li\(_y\)Mn\(_{2-x}\)O\(_4\) during intercalation and deintercalation process. The lattice parameter for Li\(_y\)Mn\(_{2-x}\)O\(_4\) was determined from the XRD patterns and it was smaller to that of pure LiMn\(_2\)O\(_4\). Doped Y\(^{3+}\) had substituted Mn\(^{3+}\) and existed in lattice structure. According to the equation for cubic spinel structure $d_0 = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$, the average crystal lattice parameter was calculated.

The crystal size was calculated by Debye-Scherrer formula is given in Table 4.3.
Table 4.3
Grain size of LiY$_{y}$Mn$_{2-y}$O$_{4}$ ($y = 0.01, 0.03, 0.05$) thin films calculated from Scherrer formula and its lattice parameters

<table>
<thead>
<tr>
<th>Compound</th>
<th>Crystal size (nm)</th>
<th>Lattice parameter (Å)</th>
<th>Unit cell volume (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiMn$_2$O$_4$</td>
<td>45</td>
<td>8.2297</td>
<td>557.38</td>
</tr>
<tr>
<td>LiY$<em>{0.01}$Mn$</em>{1.99}$O$_4$</td>
<td>47</td>
<td>8.2289</td>
<td>557.23</td>
</tr>
<tr>
<td>LiY$<em>{0.03}$Mn$</em>{1.97}$O$_4$</td>
<td>51</td>
<td>8.2283</td>
<td>557.10</td>
</tr>
<tr>
<td>LiY$<em>{0.05}$Mn$</em>{1.95}$O$_4$</td>
<td>55</td>
<td>8.2277</td>
<td>556.98</td>
</tr>
</tbody>
</table>
4.3.1.3. Scanning electron microscopy analysis

The SEM photographs were taken for LiY\textsubscript{0.05}Mn\textsubscript{1.95}O\textsubscript{4} thin films but only a representative surface morphology of SEM photographs for LiY\textsubscript{0.05}Mn\textsubscript{1.95}O\textsubscript{4} is given in Fig. 4.15. The influence of particle size plays a vital role on the electrochemical properties of the cathode material as the nanosize particle results in an improvement in the lithium ion intercalation kinetics [12]. This study revealed that the film consists of homogeneously well crystallized particle with small grain size and crack free distribution. The average particle size was 96.2nm.

4.3.1.4. Atomic force microscopy analysis

The AFM photographs were taken for the prepared LiY\textsubscript{0.05}Mn\textsubscript{1.95}O\textsubscript{4} thin films, but only a representative AFM photograph for LiY\textsubscript{0.05}Mn\textsubscript{1.95}O\textsubscript{4} and its corresponding two dimensional views and LFM image are given in Fig. 4.16. Uniformly distributed grain with an average grain size of 93nm may be seen. The surface of the thin film was not very dense and the root mean square roughness of the film was 23.4 nm.

4.3.1.5. Thickness measurement analysis

The film thickness verified with the Stylus thickness profiler was 0.476 \mu m.

4.3.1.6. Electrochemical characterization analysis

In order to know the electrochemical performance of the prepared LiY\textsubscript{0.05}Mn\textsubscript{1.95}O\textsubscript{4} thin film, the electrochemical charge/discharge studies were carried out by fabricating electrochemical cell in the configuration of Li//LiY\textsubscript{0.05}Mn\textsubscript{1.95}O\textsubscript{4} employing PVdF-HFP based microporous polymer electrolyte.
Fig 4.15 Scanning electron micrograph image of LiY_{0.05}Mn_{1.95}O_{4} thin film
Fig. 4.16. Surface topography of Li$_{0.05}$Mn$_{1.95}$O$_4$ thin film on stainless steel substrate measured by AFM, a) 2d image b) LFM image
The charge and discharge cycling was performed galvanostatically at the current density of 0.2 mA/cm² in the voltage range of 3.2 - 4.5 V. Fig. 4.17 (a-c) show the charge/discharge curves at the 1st and 25th cycle of Li//LiYₘMₙO₄ (y=0.01, 0.03, 0.05). The theoretical [11] and the observed initial discharge capacities of Li//LiYₘMₙO₄ (y=0.01, 0.03, 0.05) are given in Table 4.4. Charge/discharge studies showed that Li//LiY₀.₀₅Mₙ₀.₉₅O₄ gave initial cycle discharge capacity of 138 mAh/g, which faded to 127 mAh/g in the 25th cycle, registering the capacity retention of 92%. The corresponding values for Li//LiY₀.₀₃Mₙ₀.₇₇O₄ and Li//LiY₀.₀₅Mₙ₀.₆₅O₄ were 133 mAh/g, 120 mAh/g & 90.2% and 129 mAh/g, 116 mAh/g & 89.9%, respectively (Fig. 4.18). The initial discharge capacity came down with an increase in the substituent content due to decrease in Mn⁺⁺⁺ concentration and with an increase in y value of LiYₘMₙO₄. The capacity loss observed for Li//LiYₘMₙO₄ from y=0.01, 0.03, 0.05 are 8%, 9.8% and 10.1% respectively is shown in Fig. 4.19. Among the various compositions, LiY₀.₀₅Mₙ₀.₉₅O₄ showed very good electrochemical performance than the other compounds.

4.3.2. PHYSICAL AND ELECTROCHEMICAL CHARACTERIZATIONS OF LiGdₓMₙO₄ PREPARED BY POLYMER SPRAY PYROLYSIS

4.3.2.1. Thermal analysis

The TGA curve for LiGd₀.₀₅Mₙ₀.₉₅O₄ precursor sample is shown in Fig. 4.20. The initial weight loss observed between 30°C and 130°C corresponded to the evaporation of solvent. A second weight loss started from 230°C to around 450°C, was due to the combustion nature organic compounds such as poly ethylene glycol and the decomposition of acetates, nitrates and intermediate compounds. In last
Fig. 4.17(a) Charge-discharge curves for Li/Li$_{Y_1}$Mn$_{2-y}$O$_4$ (y=0.01) cell
Fig. 4.17(b) Charge-discharge curves for Li/Li$_y$Mn$_{2-y}$O$_4$ (y=0.03) cell
Fig. 4.17(c) Charge-discharge curves for Li/Li$_2$Mn$_{2-y}$O$_4$ (y=0.05) cell
Table 4.4

Theoretical and observed initial discharge capacities of LiY$_x$Mn$_{2-x}$O$_4$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Theoretical discharge capacity (mAh/g)</th>
<th>Practical discharge capacity (mAh/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$<em>{0.01}$Y$</em>{0.99}$Mn$_{2}$O$_4$</td>
<td>144.98</td>
<td>138</td>
</tr>
<tr>
<td>Li$<em>{0.05}$Y$</em>{0.95}$Mn$_{2}$O$_4$</td>
<td>138.54</td>
<td>133</td>
</tr>
<tr>
<td>Li$<em>{0.05}$Y$</em>{0.95}$Mn$_{2}$O$_4$</td>
<td>132.16</td>
<td>129</td>
</tr>
</tbody>
</table>
Fig. 4.18 Relationship between the discharge capacity and cycle number of Li//Li$_2$Y$_{2-y}$Mn$_{2+y}$O$_4$ cells

a) $y=0.01$  b) $y=0.03$  c) $y=0.05$
Fig. 4.19 Bar chart for % of capacity fading vs amount of Y$^{3+}$ doped in LiY$_x$Mn$_{2-y}$O$_4$. 

Amount of Y$^{3+}$ in LiY$_x$Mn$_{2-y}$O$_4$ 

% of Capacity Fading 

0.01 0.03 0.05
Fig. 4.20 Thermo-gravimetric analysis curve of LiGd$_{0.85}$Mn$_{1.95}$O$_4$ polymeric precursor sample
region, the curve became flat and no obvious change was observed above 450°C. Hence spraying the precursor solution on the substrate was kept at 450°C for the preparation of LiGd$_x$Mn$_2$O$_4$ thin film active materials.

4.3.2.2. X-ray diffraction analysis

Fig.4.21 shows XRD patterns of LiGd$_x$Mn$_2$O$_4$ ($x=0.01, 0.03, 0.05$) samples calcined at 600°C for 30 min. In the XRD pattern, the peaks of the stainless steel substrate are also shown. There was no significant difference in the crystal structure after the doping. The peaks corresponding to the substrate are marked with an asterisk. All the diffraction peaks except those of the substrate corresponded to the cubic spinel structure. There was no significant difference in the crystal structure after the doping compared to pure LiMn$_2$O$_4$ and it was identified as a group Fd3m. The main diffraction peaks, such as (111), (311) and (400) are well developed spinel structure. It was evident that the spinel structure didn’t change due to small doping of yttrium in the octahedral site (16d) in the crystal lattice. The spinel adopted the $[A]_8[B]_{16}O_4$ formula, with lithium and manganese occupying the tetrahedral (8a) and the octahedral sites (16d), respectively. The oxygen ion located to the (32e) sites. The interstitial space in the [Mn$_2$] O$_4$ framework represents a diamond - type network of tetrahedral (8a) and surrounding octahedral (16d) sites. The empty tetrahedral and octahedral sites, which were interconnected with one another by common faces and edges, formed a three-dimensional diffusion path way for Li$^+$ ions. The crystallinity of the polycrystalline LiGd$_x$Mn$_2$O$_4$ was determined from the peak intensities and peak widths of the diffraction lines. The volume of unit cell in doped materials decreased with increasing the dopant content. This decrease was
Fig. 4.21 X-ray diffraction pattern of LiGd$_x$Mn$_{2-x}$O$_4$ ($y=0.01, 0.03, 0.05$) thin film prepared by polymer spray pyrolysis method.
stronger in higher Gd$^{3+}$ dopant concentration. The ionic radius of Gd$^{3+}$ was higher than that of Mn. The strength of the Gd-O bond was higher than Mn-O bond. The integrated intensity ratios of the (400) /(311) and (220) /(311) peaks are indices of the extent of occupancy of the substituent ions in the 8a lithium lattice sites [10]. In the case of LiGd$_x$Mn$_{2-x}$O$_4$ samples, the integrated intensity ratio of (400)/(311) was not dropped when the Gd$^{3+}$ content increased. The (200) peak was not observed indicating the substituent Gd$^{3+}$ did not occupy 8a tetrahedral lithium lattice site. The substituent Gd$^{3+}$ occupied only 16d octahedral manganese lattice site. The crystal size calculated by Debye-Scherrer formula is given in Table 4.5.

4.3.2.3. Scanning electron microscopy analysis

The scanning electron micrographs were taken for LiGd$_x$Mn$_{2-x}$O$_4$ thin films, but only a representative SEM photograph for LiGd$_{0.05}$Mn$_{1.95}$O$_4$ is given in Fig. 4.22. The lithium insertion and reinsertion depended on the morphological structure. The SEM image showed dense particles uniformly distributed. The average particle size of the prepared thin film cathode material was 92.6nm.

4.3.2.4. Atomic force microscopy analysis

The AFM photographs were taken for the prepared LiGd$_x$Mn$_{2-x}$O$_4$ thin films, but only a representative AFM photograph for LiGd$_{0.05}$Mn$_{1.95}$O$_4$ and its corresponding two dimensional view and LFM images are given in Fig. 4.23. The image shows the uniformly distributed grain with an average grain size of 89 nm. The thickness of the thin film was around 500 nm. The root mean square roughness of the film was 24.4nm.
Table 4.5

Grain size of $\text{LiGd}_x\text{Mn}_{2-y}\text{O}_4$ ($y=0.01, 0.03, 0.05$) thin films calculated from Scherrer formula and its lattice parameters

<table>
<thead>
<tr>
<th>Compound</th>
<th>Crystal size (nm)</th>
<th>Lattice parameter (Å)</th>
<th>Unit cell volume (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiMn$_2$O$_4$</td>
<td>45</td>
<td>8.2297</td>
<td>557.38</td>
</tr>
<tr>
<td>LiGd$<em>{0.01}$Mn$</em>{1.99}$O$_4$</td>
<td>49</td>
<td>8.2289</td>
<td>557.22</td>
</tr>
<tr>
<td>LiGd$<em>{0.03}$Mn$</em>{1.97}$O$_4$</td>
<td>53</td>
<td>8.2282</td>
<td>557.08</td>
</tr>
<tr>
<td>LiGd$<em>{0.05}$Mn$</em>{1.95}$O$_4$</td>
<td>55</td>
<td>8.2276</td>
<td>556.95</td>
</tr>
</tbody>
</table>
Fig. 4.22 Scanning electron micrograph of LiGd_{0.05}Mn_{1.95}O_{4} obtained on stainless steel substrate by polymer spray pyrolysis.
Fig. 4.23. Surface topography of LiGd$_{0.05}$Mn$_{1.95}$O$_4$ thin film on stainless steel substrate measured by AFM, a) 2d image b) LFM image
4.3.2.5. Thickness measurement analysis

The film thickness verified with the Stylus thickness profiler was 0.498 μm.

4.3.2.6. Electrochemical Characterization

In order to know the electrochemical performance of the prepared LiGd$_y$Mn$_{2-y}$O$_4$ thin films, the electrochemical charge/discharge studies were carried out by fabricating cell in the configuration of Li/LiGd$_y$Mn$_{2-y}$O$_4$ employing PVdF-HFP based microporous polymer electrolyte. The charge and discharge cycling was performed galvanostatically at the current density of 0.2 mA/cm$^2$ in the voltage range of 3.2 - 4.5 V. Fig. 4.24 (a-c) show the charge/discharge curves at the 1st and 25th cycle of Li/LiGd$_y$Mn$_{2-y}$O$_4$ (y=0.01, 0.03, 0.05). The theoretical and the observed initial discharge capacities of Li/LiGd$_y$Mn$_{2-y}$O$_4$ (y=0.01, 0.03, 0.05) are given in Table 4.6. The initial discharge capacities for Li/LiGd$_{0.01}$Mn$_{1.99}$O$_4$, Li/LiGd$_{0.03}$Mn$_{1.97}$O$_4$ and Li/LiGd$_{0.05}$Mn$_{1.95}$O$_4$ were 137 mAh/g, 134 mAh/g and 126 mAh/g, respectively. This initial discharge capacity reduced with the amount of substituent ions as its value depends on the concentration of Mn$^{3+}$ in the lattice. At 25th cycle, the discharge capacities for Li/LiGd$_{0.01}$Mn$_{1.99}$O$_4$, Li/LiGd$_{0.03}$Mn$_{1.97}$O$_4$ and Li/LiGd$_{0.05}$Mn$_{1.95}$O$_4$ were 124 mAh/g, 123 mAh/g and 115 mAh/g, respectively. Substituted spinel electrode capacity versus cycle number plots for various Li/LiGd$_y$Mn$_{2-y}$O$_4$ cells are shown in Fig. 4.25. Its percentage of capacity fade vs amount of Gd$^{3+}$ in LiGd$_y$Mn$_{2-y}$O$_4$ plots is shown in Fig. 4.26. The capacity loss observed for Li/LiGd$_y$Mn$_{2-y}$O$_4$ from y=0.01, 0.03, 0.05 were 9.5%, 8.2% and 8.8% respectively. LiGd$_{0.01}$Mn$_{1.99}$O$_4$ showed slightly better capacity retention compared to others. The doping of Gd$^{3+}$ in LiMn$_2$O$_4$ suppressed the diffusion of manganese ions into the 8a-16c-8a-16c pathway and
Fig. 4.24(a) Charge-discharge curves for Li/LiGd$_x$Mn$_{2-y}$O$_4$ (x=0.01) cell
Fig. 4.24(b) Charge-discharge curves for Li/LiGd$_y$Mn$_{2-y}$O$_4$ (x=0.03) cell
Fig. 4.24(c) Charge-discharge curves for Li/LiGd$_3$Mn$_{2-x}$O$_4$ (x=0.05) cell
Table 4.6
Theoretical and observed initial discharge capacities of LiGd\textsubscript{3}Mn\textsubscript{2-y}O\textsubscript{4}

<table>
<thead>
<tr>
<th>Compound</th>
<th>Theoretical discharge capacity (mAh/g)</th>
<th>Practical discharge capacity (mAh/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiGd\textsubscript{0.1}Mn\textsubscript{1.9}O\textsubscript{4}</td>
<td>144.42</td>
<td>137</td>
</tr>
<tr>
<td>LiGd\textsubscript{0.03}Mn\textsubscript{1.97}O\textsubscript{4}</td>
<td>137.00</td>
<td>134</td>
</tr>
<tr>
<td>LiGd\textsubscript{0.05}Mn\textsubscript{1.95}O\textsubscript{4}</td>
<td>129.73</td>
<td>126</td>
</tr>
</tbody>
</table>
Fig. 4.25 Relationship between the discharge capacity and cycle number of Li/LiGd$_y$Mn$_{2-y}$O$_4$ cells

a) $y=0.01$  b) $y=0.03$  c) $y=0.05$
Fig. 4.26 Bar chart for % of capacity fading vs amount of Gd^{3+} doped in LiGd_{y}Mn_{2-y}O_{4}
4.3.3. PHYSICAL AND ELECTROCHEMICAL CHARACTERIZATIONS OF LiNd$_y$Mn$_{2-x}$O$_4$ PREPARED BY POLYMER SPRAY PYROLYSIS.

4.3.3.1. Thermal analysis

The TGA curve of the LiNd$_y$Mn$_{2-x}$O$_4$ precursor sample is shown as Fig.4.27. The TGA curve may be divided into two regions. The continuous weight loss was between 60°C and 455°C corresponding to the evaporation of solvent, combustion nature of polyethylene glycol and the decomposition of acetates, nitrates and intermediate compounds. In the final region, the curve became flat and no obvious change was observed above 455°C. For spraying the precursor solution on the substrate at 455°C was selected for the preparation of LiNd$_y$Mn$_{2-x}$O$_4$ thin film active materials.

4.3.3.2. X-ray diffraction analysis

Fig.4.28 shows XRD patterns of LiNd$_y$Mn$_{2-x}$O$_4$ ($y$=0.01, 0.03, 0.05) samples calcined at 600°C for 30 min. In XRD patterns, the peaks of the stainless steel substrate were also observed. All the peaks except those of the substrate peaks corresponded to the cubic spinel structure. The peaks corresponding to the substrate are marked with an asterisk. The peaks attributed to the spinel structure are clearly visible. Main peaks for these prepared materials are labelled with h,k,l indexes. The main diffraction peaks, such as (111), (311) and (400) are well developed as like cubic spinel LiMn$_2$O$_4$ space. The unit cell of the LiMn$_2$O$_4$ contained 56 atoms: 8 lithium,
Fig. 4.27 Thermo-gravimetric analysis curve of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ polymeric precursor sample
Fig. 4.28 X-ray diffraction pattern of LiNd$_x$Mn$_{2-y}$O$_4$ ($y=0.01, 0.03, 0.05$) thin film prepared by polymer spray pyrolysis method.
16 manganese and 32 oxygen. The crystal structure may be described as a closed-packed array of oxygen atoms (32e positions) with lithium atoms occupying tetrahedral 8a positions and manganese atoms occupying octahedral 16d positions in the oxygen framework. The objective of the present study is to partially replace the Mn ions in the 16d sites of the LiMn$_2$O$_4$ matrix with the substituent ions. Occupancy of the substituent ions in the 8a lithium sites would lead to unfavourable electrochemical results [13]. Nd$^{3+}$ replaced Mn$^{2+}$ in the 16d octahedral site and the strong Bragg plane (220) was not observed at $2\theta$=30°, which was extremely sensitive to the occupancy of the 8a tetrahedral site [14]. The volume of the unit cell in doped materials slightly decreased with dopant content compared with Y$^{3+}$ and Gd$^{3+}$ doping in LiMn$_2$O$_4$. The lattice parameters of this spinel calculated from the diffraction data are listed in Table 4.7.

4.3.3.3. Scanning electron microscopy analysis

The scanning electron micrographs were taken for LiNd$_x$Mn$_{2-x}$O$_4$ thin films, but only a representative SEM photograph for LiNd$_{0.05}$Mn$_{1.95}$O$_4$ is given in Fig. 4.29. The particles are uniformly distributed with dense particles. The lithium insertion and reinsertion is dependant on the morphological structure. The photographs showed that all the Nd doped thin film cathode materials are in nanosized. The average diameter of the particles of thin film sample is 94.4nm.

4.3.3.4. Atomic force microscopy analysis

The AFM photographs were taken for the prepared LiNd$_x$Mn$_{2-x}$O$_4$ thin films, but only a representative AFM photograph for LiNd$_{0.05}$Mn$_{1.95}$O$_4$ and its
Table 4.7

Grain size of LiNd$_x$Mn$_{2-y}$O$_4$ ($y=0.01, 0.03, 0.05$) thin films calculated from Scherrer formula and its lattice parameters

<table>
<thead>
<tr>
<th>System</th>
<th>Crystal size (nm)</th>
<th>Lattice parameter (Å)</th>
<th>Unit cell volume (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiMn$_2$O$_4$</td>
<td>45</td>
<td>8.2297</td>
<td>557.38</td>
</tr>
<tr>
<td>LiNd$<em>{0.01}$Mn$</em>{1.99}$O$_4$</td>
<td>51</td>
<td>8.2292</td>
<td>557.28</td>
</tr>
<tr>
<td>LiNd$<em>{0.03}$Mn$</em>{1.97}$O$_4$</td>
<td>55</td>
<td>8.2283</td>
<td>557.10</td>
</tr>
<tr>
<td>LiNd$<em>{0.05}$Mn$</em>{1.95}$O$_4$</td>
<td>61</td>
<td>8.2285</td>
<td>556.13</td>
</tr>
</tbody>
</table>
Fig. 4.29 Scanning electron micrograph of LiNi_{0.5}Mn_{1.95}O_{4} spinel obtained on stainless steel substrate by polymer spray pyrolysis
Fig. 4.30 Surface topography of LiNd_{0.05}Mn_{1.95}O_{4} thin film on stainless steel substrate measured by AFM, a) 2d image b) LFM image
corresponding two dimensional view and LFM image are given in Fig. 4.30. The particle size is 90 nm. The particle in surface is dense and uniformly dispersed. The root mean square roughness of the thin film is 23.9 nm.

4.3.3.5. Thickness measurement analysis

The film thickness was subsequently verified with the Stylus thickness profiler and it is 0.489 μm.

4.3.3.6. Electrochemical characterization analysis

In order to know the electrochemical performance of the prepared LiNd₉Mn₂₋ₓO₄ thin films, the electrochemical charge/discharge studies were carried out by fabricating cell in the configuration of Li/LiNdₓMn₂₋ₓO₄ by employing PVdF-HFP based microporous polymer electrolyte. The charge and discharge cycling was performed galvanostatically at the current density of 0.2 mA/cm² in the voltage range of 3.2 - 4.5 V. Fig.4.31(a-c) show the charge/discharge curves at the 1st and 25th cycles for Li/LiNdₓMn₂₋ₓO₄ (y=0.01, 0.03, 0.05). The theoretical and the observed initial discharge capacities of Li/LiNdₓMn₂₋ₓO₄ (y=0.01, 0.03, 0.05) are given in Table 4.8. The initial discharge capacity decreased with increase in the degree of substituent, Nd³⁺. So, the initial capacity of LiNd₉Mn₂₋ₓO₄ is limited by the initial amount of Mn³⁺ in the 16d sites. LiNd₀.₀₁Mn₁.₉₉O₄, LiNd₀.₀₃Mn₁.₉₇O₄ and LiNd₀.₀₅Mn₁.₉₅O₄ exhibit capacities at 25th cycle are 123mAh/g, 121mAh/g and 113mAh/g respectively were shown in Fig.4.32. The capacity loss observed for Li/LiNdₓMn₂₋ₓO₄ (y=0.01, 0.03, 0.05) were 9.6%, 9.1%, and 10.4% respectively (Fig.4.33). This can be achieved by the substitution of Nd⁻³ into the Mn site.
Fig. 4.31(a) Charge-discharge curves for Li/LiNd$_y$Mn$_{2-y}$O$_4$ (y=0.01) cell
Fig. 4.31(b) Charge-discharge curves for Li/LiNd$_y$Mn$_{2-y}$O$_4$ ($y=0.03$) cell
Fig. 4.31(c) charge/discharge curves for Li/LiNd$_2$Mn$_{2-y}$O$_4$ (y=0.05) cell
Table 4.8
Theoretical and observed initial discharge capacities of LiNd$_{x}$Mn$_{2-y}$O$_{4}$

<table>
<thead>
<tr>
<th>System</th>
<th>Theoretical discharge capacity (mAh/g)</th>
<th>Practical discharge capacity (mAh/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNd$<em>{0.00}$Mn$</em>{1.99}$O$_{4}$</td>
<td>144.52</td>
<td>136</td>
</tr>
<tr>
<td>LiNd$<em>{0.03}$Mn$</em>{1.97}$O$_{4}$</td>
<td>137.29</td>
<td>133</td>
</tr>
<tr>
<td>LiNd$<em>{0.05}$Mn$</em>{1.95}$O$_{4}$</td>
<td>130.18</td>
<td>126</td>
</tr>
</tbody>
</table>
Fig. 4.32 Relationship between the discharge capacity and cycle number of Li/LiNd$_y$Mn$_{2-y}$O$_4$ cells

a) $y=0.01$  
b) $y=0.03$  
c) $y=0.05$
Fig. 4.33 Bar chart for % of capacity fading vs amount of Nd\(^{3+}\) in LiNd\(_{y}\)Mn\(_{2-y}\)O\(_4\)
accompanied by the oxidation of Mn$^{3+}$ into Mn$^{4+}$ resulting in an increase in the average valency of Mn which suppressed the Jahn-Teller distortion. It also reported that the doped materials enhanced the stability of the octahedral sites in the spinel skeleton structure [15]. Hence, the electrochemical stability of LiMn$_2$O$_4$ is less than that of the Nd$^{3+}$ substituted LiMn$_2$O$_4$. Among the various compositions, LiNd$_{0.05}$Mn$_{1.95}$O$_4$ shows better reversibility.
REFERENCES