CHAPTER IV

Studies on $\text{LiCo}_x\text{Ni}_y\text{Mn}_{2-x-y}\text{O}_4$ spinel synthesized by sol-gel method as 5V cathode materials for use in rechargeable lithium batteries
4.1 Introduction

Miniaturization of electronics and the demand of effective electrochemical power sources necessitate high performing lithium secondary batteries. A major impetus is to find out cheaper cathode materials than LiCoO\(_2\) which is used in majority of commercial lithium batteries. Moreover, there is a strong initiative to develop materials of better rate capability and high voltage, than the existing available materials (LiCoO\(_2\), LiNiO\(_2\) and LiMn\(_2\)O\(_4\)). Towards this goal, recent investigations are focused on the development and characterization of cathode materials capable of working in the 5V zone [205,296]. The use of LiCoO\(_2\) delivers only 50% of its theoretical capacity (273.8 mAh g\(^{-1}\)) corresponding to 0.5 lithium extraction. Further, the toxicity of cobalt and since these cells does not work at high voltages (> 4.5V) thereby posing serious problem [297]. Pure phase LiNiO\(_2\) is difficult to synthesize because of its tendency to undergo non-stoichiometric reactions and structural instability leads to poor cycling performance and therefore is not the preferred material for commercialization [279]. LiMn\(_2\)O\(_4\) is considered as a prospective positive electrode material considering its ease of synthesis, low price, abundance and environmentally benign nature. However, the commercial utilization of LiMn\(_2\)O\(_4\) is hindered by capacity fade upon prolonged cycling especially at elevated temperatures [279,280,298,299]. The mechanism of capacity fade has been attributed to various factors viz., Jahn-Teller distortion [175,299,300], lattice instability, [231,300] manganese dissolution [300], lattice site exchange between lithium and manganese ions [301], oxygen rich spinels [293].
The systematic research has been revealed that partial substitution of Mn in LiMn$_2$O$_4$ with 3d transition elements like Ni, Co, Cr, Cu, Fe, Ti, Zn makes it as a 5V cathode material [206,302]. Several authors investigated single and multi doped manganese based spinels synthesized by using various chelating agents in order to improve the electrochemical performance [286,290-291,303-305]. Amdouni et al. [282] reported that Ni substitution in LiNi$_{0.5}$Mn$_{1.5}$O$_4$ for Mn was beneficial for improving the charge/discharge cycling performance in the cut-off voltage 3.5–4.9V. Gao et al. [306] found that lithium extraction from LiNi$_{0.5}$Mn$_{1.5}$O$_4$ takes place at 4.7V where Ni$^{2+}$ is oxidized to Ni$^{4+}$. The nickel in the LiNi$_{0.5}$Mn$_{1.5}$O$_4$ spinel can reversibly transform from Ni$^{2+}$ to Ni$^{4+}$ during cycling thereby making it possible to replace Mn$^{3+}$ with a small quantity of other transitional metals and elevate the operation potential of the material.

LiMn$_{1.5}$Ni$_{0.5}$O$_4$ improves the structure stabilization and capacity retention after prolonged cycling [308 rather than LiMn$_2$O$_4$. The strive for delivering a high voltage cathode material capable of reduced phase transition during charging and discharging so as to prevent cation disordering and better capacity retention entail partial substitution of Co$^{2+}$/Co$^{3+}$ in LiMn$_{1.5}$Ni$_{0.5}$O$_4$ [307-309]. The present work reports the synthesis, physical and electrochemical characterization of LiCo$_x$Ni$_y$Mn$_{2-x-y}$O$_4$ ($0 < x \leq 0.4$ and $0 < y \leq 0.4$) using chelating agents such as acetic acid, maleic acid and oxalic acid.
4.2 Experimental

The flow chart shown in Fig.4.1 presents the typical procedures followed for the synthesis of spinel LiCo\textsubscript{x}Ni\textsubscript{y}Mn\textsubscript{2-x-y}O\textsubscript{4} (0 < x \leq 0.4 and 0 < y \leq 0.4) by sol-gel method using acetic acid, maleic acid and oxalic acid as chelating agents. Stoichiometric proportions of high purity acetates of lithium, manganese, nickel, and cobalt were homogeneously stirred, mixed and dissolved in triple distilled water. The solution was stirred continuously with gentle heating and either of 1M acetic acid or 1M maleic acid or 1M oxalic acid as chelating agent is added drop wise to get a homogeneous solution. The pH of the solution was maintained between 5 and 7.5 and the solution was slowly heated until a viscous gel has been obtained. The gel mass was dried overnight in a hot air oven at 110°C to obtain a dried mass. A portion of the gel precursors were characterized by thermo-gravimetric and differential analysis (TG/DTA) [PL Thermal Sciences Instrument, model STA 1500] to ascertain the thermal behavior. About 50 mg of the samples were taken and heated in a heating ramp at 20°C/min in air. The dried mass was ground well and calcined at different temperatures viz., 250, 400, 600 and 850°C for 6 h in alumina crucibles and subjected to physical and electrochemical studies. The physical characterization of the synthesized samples were carried out by X-ray diffraction (XRD) [JOEL 8030 X-ray diffraction with nickel filtered Cu Kα radiation], Scanning electron microscopy (SEM) [Hitachi S- 3000 H], Fourier-transform infrared spectroscopy (FT-IR) [Perkin-Elmer, model Paragon-500 spectrophotometer] and finally electrochemical cycling studies.
Fig. 4.1 Flow chart for the synthesis of spinel LiCo\(_x\)Ni\(_y\)Mn\(_{2-x-y}\)O\(_4\) (\(x=0.1, 0.25, 0.4\)) and (\(y=0.4, 0.25, 0.1\)) by sol-gel method using acetic acid, maleic acid and oxalic acid as chelating agents.
4.2.1 Electrochemical Cell Assembly

The charge/discharge studies were carried out using 2016 coin cell [Hohsen Co., Japan]. Lithium foil has been used as anode, Celgard 2400 as separator and 1M LiPF₆ in 50:50 (v/v) mixture of ethylene carbonate (EC) and diethylene carbonate (DEC) as electrolyte. The cathode has been prepared by a slurry coating procedure. The cathode slurry consisted of 85% of the synthesized material, 10% conducting carbon and 5% polyvinylidenefluoride (PVdF) binder dissolved in n-methyl-2-pyrrolidone (NMP). The slurry was coated over aluminium foil and vacuum dried at 110° for 2 h. The dried coating was pressed under 10 tonnes load for 2 minutes, from which electrodes (16mm diameter) were punched for using as cathode. All cell assembly was done in an argon filled glove box [MBraun, Germany] with <2 ppm oxygen and moisture. The galvanostatic cycling studies were carried out between 3 and 5V at C/10 rate.

4.3 Results and discussion

4.3.1 Thermal Studies

TG/DTA curves are presented for the synthesis of LiCoₓNi₀.₄Mn₁.₅O₄ using acetic acid [Fig.4.2 (a-c)], maleic acid (Fig.4.2d) and oxalic acid (Fig.4.2e). Fig.4.2a shows three weight loss zones for LiCo₀.₁Ni₀.₄Mn₁.₅O₄ obtained by using acetic acid as a chelating agent. Ab initio, the first weight loss of about 20% up to 100°C may be ascribed to the
Fig 4.2   TG/DTA curves of the acetic acid assisted LiCo$_x$Ni$_y$Mn$_{2-x-y}$O$_4$ (a) Co–0.1; Ni–0.4, (b) Co–0.4; Ni–0.1, (c) Co–0.25; Ni–0.25, (d) Co–0.25; Ni–0.25 (maleic acid assisted), (e) Co–0.25; Ni–0.25 (oxalic acid assisted).
removal of water molecules whereas the second and third weight losses observed between 100–450 °C corresponding to a weight loss of 17% may be due to the combustion of chelating agent (acetic acid) and acetate precursors. DTA curve shows broad exothermic peak at 311°C indicating the formation of the compound. No weight loss is observed beyond 700 °C suggesting the completion of the thermal events. In the case of acetic acid assisted synthesized LiCo0.4Ni0.1Mn1.5O4 (Fig.4.2b), higher cobalt content shows similar trend of weight loss in all the three zones as observed in LiCo0.1Ni0.4Mn1.5O4. DTA of exothermic peak for the formation temperature of the compound is seen at ~291°C, which is slightly earlier than low amount of cobalt doped LiCo0.1Ni0.4Mn1.5O4. Finally, in Fig.4.2c, LiCo0.25Ni0.25Mn1.5O4 synthesized via acetic acid as a chelating agent depicts lower weight loss (15%) at the first zone up to100°C followed by high weight loss of 30% in the second zone which is greater than both 0.1 and 0.4 doped Co. A broad exothermic peak is observed at 311°C indicating the formation of the compound. Further, in the case of maleic acid assisted synthesized LiCo0.25Ni0.25Mn1.5O4 (Fig.4.2d), two weight loss zones corresponding to 40% up to 200°C is due to the removal of water molecules and precursors. DTA curve shows a very sharp profile centered at ~200°C which is the lowest temperature than in the case of acetic and oxalic acid for the equal stoichiometric dopant ratio of cobalt and nickel. The inactive thermal region is also seen after 200°C and is the lowest than all the above mentioned TG/DTA curves. It is interesting to observe that in the case of oxalic acid assisted LiCo0.25Ni0.25Mn1.5O4 (Fig.4.2e) possesses first weight loss zone (10%) up to 100°C and showing a broad exothermic peak at 363°C for the formation of spinel.
compound. In this case, further thermal reactions ceases beyond 500°C which is very high formation temperature compared to all the investigated chelating agents.

4.3.2 X-Ray Diffraction

Fig. 4.3 (a-c) shows XRD patterns of the acetic acid assisted LiCoₓNiᵧMn₂₋ₓ₋ᵧO₄ calcined at 850°C. It can be seen from these figures that all the signature peaks viz., (111), (311), and (400) are well-defined and are of high intensity suggesting the formation of spinel structure with high degree of crystallinity and phase pure. Furthermore, the equal stoichiometric composition of cobalt and nickel synthesized using either maleic or oxalic acid [Fig. 4.3 (d,e)] show similar trend and is in good agreement with previous researchers [310-312] and JCPDS card No.35-782. Therefore, as is evident from the above XRD patterns, the pristine spinel has an Fd3m space group wherein lithium occupies the 8a tetrahedral sites while manganese (Mn³⁺ and Mn⁴⁺), cobalt (Co²⁺) and nickel (Ni²⁺) ions occupies the 16d sites with O²⁻ in the 32e⁻ site [313]. The lattice parameters of LiCoₓNiᵧMn₂₋ₓ₋ᵧO₄ compounds are shown in table 2.
Fig. 4.3  XRD patterns of the acetic acid assisted LiCo$_x$Ni$_y$Mn$_{2-x-y}$O$_4$ calcined at 850°C. (a) Co–0.1; Ni–0.4, (b) Co–0.4; Ni–0.1, (c) Co–0.25; Ni–0.25, (d) Co–0.25; Ni–0.25 (maleic acid assisted), (e) Co–0.25; Ni–0.25 (oxalic acid assisted).
Table 2. Unit cell parameters of LiCo$_x$Ni$_y$Mn$_{2-x-y}$O$_4$.

<table>
<thead>
<tr>
<th>LiCo$_x$Ni$<em>y$Mn$</em>{2-x-y}$O$_4$</th>
<th>Chelating agent</th>
<th>a (Å)</th>
<th>V (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCo$<em>{0.1}$Ni$</em>{0.4}$Mn$_{1.5}$O$_4$</td>
<td>acetic acid</td>
<td>8.220</td>
<td>555.4</td>
</tr>
<tr>
<td>LiCo$<em>{0.4}$Ni$</em>{0.1}$Mn$_{1.5}$O$_4$</td>
<td>acetic acid</td>
<td>8.224</td>
<td>556.2</td>
</tr>
<tr>
<td>LiCo$<em>{0.25}$Ni$</em>{0.25}$Mn$_{1.5}$O$_4$</td>
<td>acetic acid</td>
<td>8.215</td>
<td>554.3</td>
</tr>
<tr>
<td>LiCo$<em>{0.25}$Ni$</em>{0.25}$Mn$_{1.5}$O$_4$</td>
<td>acetic acid</td>
<td>8.209</td>
<td>553.1</td>
</tr>
<tr>
<td>LiCo$<em>{0.25}$Ni$</em>{0.25}$Mn$_{1.5}$O$_4$</td>
<td>acetic acid</td>
<td>8.203</td>
<td>552.9</td>
</tr>
</tbody>
</table>
Fig. 4.4 FTIR spectra of the acetic acid assisted LiCo$_x$Ni$_y$Mn$_{2-x-y}$O$_4$ calcined at 850°C. (a) Co–0.1; Ni–0.4, (b) Co–0.4; Ni–0.1, (c) Co–0.25; Ni–0.25, (d) Co–0.25; Ni–0.25 (maleic acid assisted), (e) Co–0.25; Ni–0.25 (oxalic acid assisted).
4.3.3 FTIR Spectroscopy

Fig. 4.4 shows FTIR spectra of the synthesized LiCo$_x$Ni$_y$Mn$_{2-x-y}$/O$_4$ calcined at 850°C for (a) Co–0.1; Ni–0.4 (acetic acid), (b) Co–0.4; Ni–0.1 (acetic acid) (c) Co–0.25; Ni–0.25 (acetic acid) (d) Co–0.25; Ni–0.25 (maleic acid) and (e) Co–0.25; Ni–0.25 (oxalic acid). The synthesized samples were ground, mixed with KBr and pressed to pellets of 10mm diameter. The FTIR spectra reveal stretching and bending vibration of the spinel lithium manganese oxide. In the FTIR profile, three peaks are seen at around 418, 510, and 619 cm$^{-1}$ respectively. FTIR studies on cobalt, nickel, multi cations magnesium and nickel doped spinel had been investigated by several authors [282,292,314]. The IR spectral band seen at higher wave length between 619 – 625 cm$^{-1}$ which can be attributed to Co–O stretching vibration and another band at a wave number between 510 – 524 cm$^{-1}$ assigned to Ni–O. These observations are in good accordance with the earlier reports. Further, the FTIR profile seen at lower wave number around 418 cm$^{-1}$ can be assigned to Li–O bending vibration.

4.3.4 Scanning Electron Microscopy

Fig. 4.5 (a-c) shows SEM images of the acetic acid assisted LiCo$_x$Ni$_y$Mn$_{2-x-y}$/O$_4$ calcined at 850°C whereas the samples synthesized using maleic acid and oxalic acid are presented
Fig. 4.5  SEM images of the acetic acid assisted LiCo$_x$Ni$_y$Mn$_{2-x-y}$O$_4$ calcined at 850°C. (a) Co–0.1; Ni–0.4, (b) Co–0.4; Ni–0.1, (c) Co–0.25; Ni–0.25, (d) Co–0.25; Ni–0.25 (maleic acid assisted), (e) Co–0.25; Ni–0.25 (oxalic acid assisted).
in Fig.4.5(d,e). The surface morphology of LiCo_{0.1}Ni_{0.4}Mn_{1.5}O_{4} calcined at 850°C (Fig.4.5a) clearly depicts an average particle size of 1μm. Cobalt rich spinel (Fig.4.5b) enumerates particles with flakes like morphology having a particles size around 0.5 μm. In the case of equal dopant ratio LiCo_{0.25}Ni_{0.25}Mn_{1.5}O_{4} compound, spherical grain boundaries are seen with particle size of 1μm. Further, maleic acid assisted LiCo_{0.25}Ni_{0.25}Mn_{1.5}O_{4} have ice cube morphology and possesses particle size around 0.5μm. The difference in particle size of the samples is due to rich and low dopant ratio of spinel compound. Lastly, oxalic acid (Fig.4.5e) assisted LiCo_{0.25}Ni_{0.25}Mn_{1.5}O_{4}, depicts an average micron sized particles of less than 0.8μm, which is lower than that of the other two investigated chelating agents assisted particles and also possessing good agglomeration thereby enhancing the inter particle contact for easy lithium ion diffusion.

### 4.3.5 Charge-Discharge Studies

Fig.4.6(a-e) shows first cycle charge-discharge curves of sol-gel derived LiCo_{x}Ni_{y}Mn_{2-x-y}O_{4} calcined at 850°C using all the 3 chelating agents like acet acid, maleic acid and oxalic acid. The first charge-discharge curves of sol-gel derived acetic acid assisted LiCo_{0.1}Ni_{0.4}Mn_{1.5}O_{4}, delivers a discharge capacity of 65 mAh g^{-1} against the charging capacity of 145 mAh g^{-1} when cycled up to 5V. However, cobalt rich LiCo_{0.4}Ni_{0.1}Mn_{1.5}O_{4} delivers inferior discharge capacity of around 55 mAh g^{-1} owing to the high cation mixing of cobalt is not favour to stabilize the spinel structure. Also, the equal dopant ratio of LiCo_{0.25}Ni_{0.25}Mn_{1.5}O_{4}, exhibits a maximum discharge capacity of 80 mAh g^{-1} against the charging capacity of 110 mAh g^{-1}. Furthermore, maleic acid and oxalic acid assisted
Fig. 4.6  First cycle charge-discharge curves of sol-gel derived acetic acid assisted LiCo$_x$Ni$_y$Mn$_{2-x-y}$O$_4$ calcined at 850°C. (a) Co–0.1; Ni–0.4, (b) Co–0.4; Ni–0.1, (c) Co–0.25; Ni–0.25, (d) Co–0.25; Ni–0.25 (maleic acid assisted), (e) Co–0.25; Ni–0.25 (oxalic acid assisted).
spinels (LiCo_{0.25}Ni_{0.25}Mn_{1.5}O_4), deliver discharge capacities of 92 and 110 mAh g^{-1} respectively. Among all the three investigated chelating agents, oxalic acid contains two COOH groups leading to better chelation and active combustion which obviously facilitate high order of grain disintegration. These observations are well corroborated by the SEM image (Fig.4.5e) and higher formation temperature of the spinel in the TG/DTA curve (Fig.4.2e).

Fig.4.7 presents the cycling behaviour and corresponding columbic efficiencies (CE) of different dopant levels of sol-gel derived LiCo_{x}Ni_{y}Mn_{2-x-y}O_4 calcined at 850°C synthesized using different chelating agents. Cycling performance of acetic acid Fig.4.7 (a-c) assisted LiCo_{0.1}Ni_{0.4}Mn_{1.5}O_4 shows maximum discharge capacity of 60 mAh g^{-1} corresponding to 89% columbic efficiency over the investigated 15 cycles with a capacity fade of ~ 0.4 mAh g^{-1} (per cycle) and stabilizes at around 61 mAh g^{-1} after the 7th cycle. Very low capacity has been observed in cobalt rich LiCo_{0.4}Ni_{0.1}Mn_{1.5}O_4 (43 mAh g^{-1}) while the equal dual dopant ratio of acetic acid assisted LiCo_{0.25}Ni_{0.25}Mn_{1.5}O_4, (Fig.4.7.c) and maleic acid assisted LiCo_{0.25}Ni_{0.25}Mn_{1.5}O_4 (Fig.4.7.d), these cells deliver stable discharge capacities of around 84 mAh g^{-1} with capacity fade of 0.06, 0.5 mAh g^{-1} (per cycle) respectively. Several researchers [315] had already reported on synthesis of cobalt and nickel doped spinels but cycled only up to 4.4V delivering inferior capacities. Wu et al. [236] investigated LiMn_{1.5}Ni_{0.2}Co_{0.3}O_4 delivering capacity of 100 mAh g^{-1} with a capacity fade of 0.2 mAh g^{-1} (per cycle) over the investigated 15 cycles. Rojas et al. [316] reported that the cathode material LiNi_{0.25}Co_{0.5}Mn_{1.25}O_4 was synthesized through combustion method and delivered maximum discharge capacity of 98 mAh g^{-1} with a
Fig. 4.7 The Cycling behaviour of different dopant levels of sol-gel derived acetic acid assisted LiCo$_x$Ni$_y$Mn$_{2-x-y}$O$_4$ calcined at 850°C. (a) Co–0.1; Ni–0.4, (b) Co–0.4; Ni–0.1, (c) Co–0.25; Ni–0.25, (d) Co–0.25; Ni–0.25 (maleic acid assisted), (e) Co–0.25; Ni–0.25 (oxalic acid assisted).
Fig. 4.8 The differential capacity curve of sol-gel derived acetic acid assisted 
LiCo$_x$Ni$_y$Mn$_{2-x-y}$O$_4$ calcined at 850°C. (a) Co–0.1; Ni–0.4, (b) Co–0.4; Ni–0.1, (c) Co–0.25; Ni–0.25 (acetic acid assisted), (d) Co–0.25; Ni–0.25 (maleic acid assisted), (e) Co–0.25; Ni–0.25 (oxalic acid assisted).
capacity fade of 0.5 mAh g\(^{-1}\) (per cycle) over the investigated 15 cycles. It is interesting to observe that in the present case, oxalic acid assisted LiCo\(_{0.25}\)Ni\(_{0.25}\)Mn\(_{1.5}\)O\(_4\), delivers maximum discharge capacity of 110 mAh g\(^{-1}\) than other chelating agents with good capacity retention and very low capacity fade of 0.2 mAh g\(^{-1}\) (per cycle) corresponding to 96% columbic efficiency. The oxalic acid undergoes complete combustion for associating with two COOH group and preventing cationic disorder.

### 4.3.6 dQ/dE Vs Potential Curves

Fig. 4.8 depicts the differential capacity (dQ/dE) curves of the sol-gel derived LiCo\(_x\)Ni\(_y\)Mn\(_{2-x-y}\)O\(_4\) calcined at 850\(^\circ\)C using acetic acid Fig.4.8 (a-c), maleic acid (Fig.4.8d) and oxalic acid (Fig.4.8e) assisted chelating agents. It can be seen from (Fig.4.6 a) that the curve possesses three oxidative peaks occurs at around 3.8, 4 and 4.6V during lithium ion extraction and three reductive peaks at 3.8, 4, 4.6V for lithium insertion. These three peaks are attributed to Mn\(^{3+}/\)Mn\(^{4+}\), Co\(^{3+}/\)Co\(^{4+}\) and Ni\(^{2+}/\)Ni\(^{4+}\) couples respectively. These results are in good agreement with previous researchers [317]. It is quite interesting to note that maleic acid (Fig.4.8d) assisted LiCo\(_{0.25}\)Ni\(_{0.25}\)Mn\(_{1.5}\)O\(_4\) illustrates the three redox peaks centered at around 4, 4.2, 4.7V. Finally, oxalic acid (Fig.4.8e) associated spinel shows two broad oxidation and reduction peaks at 4 and 4.8V. All preliminary observations suggest that oxalic acid assisted LiCo\(_{0.25}\)Ni\(_{0.25}\)Mn\(_{1.5}\)O\(_4\), bestows enhanced electrochemical stability.
4.4 Conclusions

LiCo$_x$Ni$_y$Mn$_{2-x-y}$O$_4$ ($0 < x \leq 0.4$ and $0 < y \leq 0.4$) has been synthesized via sol-gel route using three chelating agents (acetic acid, maleic acid and oxalic acid) to obtain single phase micron sized (0.8$\mu$m) particles with enhanced electrochemical performance for use as an attractive 5V cathode material in lithium rechargeable batteries. Charge-discharge studies of LiCo$_{0.25}$Ni$_{0.25}$Mn$_{1.5}$O$_4$ spinels synthesized using oxalic acid delivers a stable discharge capacities of 110 mAh g$^{-1}$ when cycled from 3 to 5V over the investigated 15 cycles with very low capacity fade of 0.2 mAh g$^{-1}$ (per cycle) corresponding to 96% columbic efficiency. Therefore, we may conclude that oxalic acid assisted LiCo$_{0.25}$Ni$_{0.25}$Mn$_{1.5}$O$_4$ spinel could be an apt high voltage cathode material for delivering high discharge capacity with good capacity retention for use in lithium rechargeable batteries.