CHAPTER- III

NITRATE MELT DECOMPOSITION ROUTE: A RAPID METHOD TO SYNTHESIZE LAYERED CATHODE MATERIALS

3.1. Introduction:

With increasing demand of Li-ion batteries for various applications, layered transition metal oxides are extensively studied as cathode materials.\(^1\) Electrochemical performance of layered cathode materials strongly dependent on the physical (particle size, morphology, porosity, etc.) and chemical nature (composition, structure, crystallinity, etc.) which are indeed influenced by the preparative methods and conditions adopted for the synthesis.\(^2\) Therefore, synthesis method plays a critical role in Li-ion battery technology and development.

Cathode materials of the type LiMO\(_2\) are generally prepared by solid state method (ceramic method).\(^3\) But formation of required phase needs high temperature with extended heating cycles in addition to intermediate mixing by grinding due to slow diffusion of metal ions in solid reactants. This often leads to lithium loss, disordered structure (cation exchange) and impure products. In order to overcome these limitations various solution based synthesis methods such as oxalate method,\(^4\) hydroxide precipitation method,\(^5\) sol-gel method,\(^6\) molten salt method,\(^7\) hydrothermal method,\(^8\) spray pyrolysis,\(^9\) polymer pyrolysis,\(^10\) pechini process\(^11\) and combustion method\(^12\) etc, have been attempted in the literature for realizing electrochemically active LiMO\(_2\).

Here, we demonstrate a synthetic method viz., nitrate melt decomposition method; which has not been explored yet for the synthesis of electrochemically active LiMO\(_2\) cathode materials. The aforesaid method is simple, rapid and yet different from the nitrates solution method. Further, it gives highly homogeneous product with improved electrochemical performance. The method involves melting of metal nitrate precursor’s mixture that on decomposition yields crystalline LiMO\(_2\).
Metal nitrate mixture melts at a temperature much lower than the melting point of individual metal nitrates. The metal nitrate melt thus formed on decomposition yields nano-crystalline LiMO$_2$ with perfect layered-structure suitable to use as an active cathode material in a lithium-ion rechargeable batteries. The overall reaction can be written as follows,

\[
\text{LiNO}_3 + \text{Metal nitrate} \xrightarrow{\Delta} \text{Melt with } \text{Li}^+, \text{M}^{3+} \text{and NO}_3^- \text{ions} \xrightarrow{\Delta} \text{LiMO}_2 + \text{NO}_2/\text{NO}
\]

**Advantages of nitrate melt decomposition method:**

Nitrate melt decomposition method has following advantages over conventional synthetic processes.

(a) Phase formation is facilitated by the diffusion of ions in molten salt and therefore the final product is highly homogeneous.

(b) The melting of metal nitrates and decomposition happens at lower temperature compared to other precursors. The low temperature melt and decomposition often helps formation of product at lower temperatures.

(c) The synthesis of electrochemically active LiMO$_2$ through nitrate precursors followed by combustion, sol-gel or flame pyrolysis methods have been reported previously,\textsuperscript{6,12} these methods require a fuel or chelating agent in addition with metal precursors. Generally, the product obtained using these methods have residual carbonaceous matter which requires high-temperature heating for long duration. Besides, in many cases, the product formed is amorphous and requires further calcination for crystallization. In this context, the metal-nitrate-melt-decomposition route is attractive as it requires shorter duration of heating and there will not be any carbonaceous material. Nitrate melt decomposition method is effective for the synthesis of homogeneous pristine and doped LiMO$_2$ phases. Further, shorter reaction time and relatively lower temperature helps in formation of nano crystalline material.
The method is simple as well as cost effective for synthesizing battery grade LiMO$_2$ in bulk quantities.

Nitrates melt decomposition synthesis of following cathode materials and their electrochemical performances are demonstrated and discussed in this chapter.

(i) LiCoO$_2$  (ii) LiNi$_{0.8}$Co$_{0.2}$O$_2$  (iii) Mg and Al substituted LiNi$_{0.8}$Co$_{0.2}$O$_2$
(iv) LiNi$_{0.33}$Mn$_{0.33}$Co$_{0.33}$O$_2$ (LiNMC).

### 3.2. Experimental

#### 3.2.1. Synthesis:

Powder sample of LiMO$_2$ phases are prepared by heating the mixture of corresponding metal nitrate salts, viz., LiNO$_3$ and transition metal nitrate at appropriate temperature followed by sintering. The molar ratios of the metal nitrates were taken such that Li:M is 1.1:1. A 10 mole percent excess Lithium, i.e. lithium-to-transition-metals ratio of 1.1:1, was taken to compensate for any lithium loss during calcinations at higher temperatures.

##### 3.2.1.1. Synthesis of LiCoO$_2$:

In a typical preparation, 3.87 g of LiNO$_3$ and 14.87 g of Co(NO$_3$)$_2$.6H$_2$O were taken in a sintered alumina crucible and introduced to a preheated furnace at 350 °C. Subsequently, the furnace was programmed for rapid heating to 700 °C and held there for 1 h. The furnace was then fast cooled to 350 °C in about 10 min and the crucible removed from the furnace. The sample was crushed and ground well to obtain a fine powder of LiCoO$_2$.

##### 3.2.1.2. Synthesis of LiNi$_{0.8}$Co$_{0.2}$O$_2$:

6.543 g of LiNO$_3$, 3.567 g of Ni(NO$_3$)$_2$.6H$_2$O and 0.8234 g of Co(NO$_3$)$_2$.6H$_2$O were taken in a 120 cm$^3$ alumina crucible and introduced into a cubical muffle furnace pre-heated to 400 °C. The metal-nitrates melt and forms homogenized liquid which undergoes decomposition. The furnace temperature was maintained at 400 °C for 3 h to ensure the complete decomposition of metal nitrates to yield partially formed product which was heated at 800 °C for 3 h to obtain the final phase.
3.2.1.3. Synthesis of LiNi$_{0.8}$Co$_{0.15}$M$_{0.05}$O$_2$ ($M = Al^{3+}$/Mg$^{2+}$):

Powder sample of LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ and LiNi$_{0.8}$Co$_{0.15}$Mg$_{0.05}$O$_2$ were prepared by heating the mixture of corresponding metal nitrates, namely LiNO$_3$, Ni(NO$_3$)$_2$.6H$_2$O, Co(NO$_3$)$_2$.6H$_2$O and Al(NO$_3$)$_3$.9H$_2$O/ Mg(NO$_3$)$_2$.6H$_2$O at appropriate temperature followed by sintering. The molar ratios of the metal nitrates were taken such that Li:Ni:Co:Al/Mg is 1.1:0.8:0.15:0.05. In a typical synthesis, stoichiometric mixture of metal nitrates were taken in a 120 cm$^3$ alumina crucible and introduced into a cubical muffle furnace preheated to 400 °C. The metal-nitrates melt and forms homogenized liquid which undergoes decomposition. The furnace temperature was maintained at 400 °C for 3 h to ensure the complete decomposition of metal nitrates to yield partially formed product which was heated at 800 °C for 3 h to obtain the final phase.

3.2.1.4. Synthesis of LiNi$_{0.33}$Mn$_{0.33}$Co$_{0.33}$O$_2$:

Powder samples of LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ were prepared by rapidly heating the mixture of 7.2398 g of LiNO$_3$.H$_2$O, 9.6937 g of Ni(NO$_3$)$_2$.6H$_2$O, 8.367 g of Mn(NO$_3$)$_2$.4H$_2$O, 9.7013 g of Co(NO$_3$)$_2$.6H$_2$O to a preheated furnace at 500 °C. The furnace was rapidly heated to 800 °C with a heating rate of 50 °C/min and allowed to stay for 3 hours. Subsequently, the furnace was fast cooled to 350 °C and the crucible containing the product was taken out from the furnace. The powder thus obtained was used for further characterization.

3.2.2. Characterization:

Powder X-ray diffraction patterns for the prepared samples were recorded using X’pert PRO-PANalytical Diffractometer with CuK$_\alpha$ radiation. The crystal structure, lattice parameters and extent of Li/Ni cation mixing in the samples were determined by Rietveld refinement of powder X-ray diffraction data using General Structure Analysis System (GSAS) code.$^{13}$ The morphology of the powder samples were examined under a Scanning Electron Microscope (HITACHI Model S-3000H). Chemical analyses of the samples were carried out using Perkin-Elmer Atomic Absorption Spectrometer (AAS). Electrochemical tests were conducted using Swagelok-type™ cells assembled in an argon-filled glove box. The positive electrode comprised the ball-milled mixture of 85 wt. % active material with 15 wt. % Super-P
Li Carbon (Timcal Belgium) as the conducting additive. Lithium electrode was prepared by pressing a piece of lithium metal onto a thin stainless steel disc. Electrolyte used was 1M LiPF$_6$ solution in a mixture of ethylene carbonate and dimethyl carbonate in 1:1 ratio by volume. The cells were cycled potentiostatically and galvanostatically between various voltages. Impedance measurements were carried out using three electrode assemblies with lithium as reference and counter electrode. The impedance spectra were recorded at various state-of-charge values of the cell during galvanostatic cycling at 0.2C rate in the frequency range between 400 kHz and 2 mHz. The data were analyzed using ZSimpWin software with complex nonlinear-least-squares fit.

3.3. Results and discussions:

3.3.1. Nitrate melt decomposition synthesized LiCoO$_2$:

Electrochemical performance of LiCoO$_2$ greatly depends on its crystallographic structure as it exists in two different modifications, namely the high-temperature (HT) phase and low temperature (LT) phase. HT-LiCoO$_2$ crystallize in an ideal layered-structure isomorphic to $\alpha$-NaFeO$_2$ (space group: $R\overline{3}m$) with ordered cobalt and lithium ions resulting in hexagonal sheets of Li$^+$- and Co$^{3+}$- ions in alternate layers of (111) planes.$^{14}$ Whereas LT- LiCoO$_2$ crystallize in spinel-like structure (space group: Fd3m) with about 6% of Co$^{3+}$ ions located at lithium sites.$^{15}$ Unlike LT-LiCoO$_2$, HT-LiCoO$_2$ exhibits excellent electrochemical stability on prolonged cycling. The stability of HT phase originates from the structural durability of the material with the layered cation-ordering that remains well preserved even after repeated insertion and de-insertion of Li$^+$ ions during the charge-discharge processes of the lithium-ion cell. The structure and degree of cation ordering in HT-LiCoO$_2$ vary with the synthetic conditions and affect its electrochemical activity. Nitrate melt decomposition method was used here and optimized for synthesizing HT- LiCoO$_2$ with good electrochemical performance.
**Optimization of synthesis:**

Powder samples of LiCoO$_2$ prepared by heating stoichiometric amount of LiNO$_3$ and Co(NO$_3$)$_2$.6H$_2$O in a 1:1 molar ratio at varying temperatures between 600 °C and 900 °C for 4 h is structurally analyzed using powder x-ray diffraction (Fig. 3.1(a-d)).

![Figure 3.1](image)

**Figure 3.1**, Powder X-ray diffraction patterns for LiCoO$_2$ obtained by nitrate melt decomposition at varying temperatures (a) 600 °C (b) 700 °C (c) 800 °C (d) 900 °C. The peaks marked as (#) correspond to Co$_3$O$_4$ and (*) correspond to lithium-deficient phase, Li$_{0.115}$Co$_{0.885}$O (ICSD collection code: 029229).

The diffraction pattern for the product obtained at 600 °C comprised of HT-LiCoO$_2$ and LT-LiCoO$_2$ as shown in Fig. 3.1 (a). Diffraction peaks could be indexed on rhombohedral R$^3$m LiCoO$_2$ phase along with small amounts of lithium-deficient...
LiCoO₂ crystallizing in cubic Fd3m structure. X-ray powder diffraction pattern for the product obtained by heating at 700 °C (Fig. 3.1 (b)) shows single-phase LiCoO₂ as indexed on the basis of α-NaFeO₂ structure (space group: R̅3m). All diffraction patterns show clear (006)/(102) peaks and (018)/(110) split peaks indicating a perfect layered-structure for LiCoO₂.¹⁶ The diffraction patterns of samples prepared at 800 °C and 900 °C comprise a major LiCoO₂ phase crystallizing in rhombohedral structure with a small Co₃O₄ spinel phase marked with (*) in Fig. 3.1 (c) and (d); This is due to lithium evaporation from the parent compound at high temperatures and further decomposition to non-stoichiometric LiCoO₂ and Co₃O₄. The intensity ratio I(003)/I(104) is the measure of cation exchange between cobalt layer and lithium layer.¹⁷ Decrease in the intensity ratio with increasing calcinations temperature indicated significant site exchange in the material.

It is clear from the aforesaid X-ray diffraction studies that 700 °C is the optimal temperature for obtaining pure LiCoO₂ in ordered rock-salt superstructure. In order to determine the optimal duration, the synthesis was carried out with varying heating durations between 15 min and 4 h at 700 °C. The X-ray diffraction patterns for the products formed at different time intervals are presented in Fig. 3. 2 (a). It is seen from the diffractograms that the sample prepared at 700 °C for as low as 15 min matches well with HT-LiCoO₂ pattern with R̅3m space group; the intensity ratio of I(003)/I(104) <1.2 indicating a considerable extent of cation mixing in the crystal lattice. By contrast, the samples synthesized at 700 °C for 1 h (or more) exhibit I(003)/I(104) >1.2 indicating the absence of cation mixing. On increasing the heating duration beyond 1 h, little change is observed in the diffraction pattern with increase in overall peak intensity owing to the improved crystallinity of the sample. The increase in crystallinity of the sample with longer heating duration is further corroborated from morphological studies by scanning electron microscopy (SEM). The SEM image for the samples heated at 700 °C for 1 h shows agglomerates of smaller crystallites of ~1 μm (shown in Fig. 3.2 (b)); whereas the sample obtained by heating at 700 °C for 4 h shows well defined crystals of platelet-like morphology of ~50 μm (Fig. 3.2 (c)). The chemical compositions of the prepared samples obtained from AAS analysis of Li and Co suggest cation stoichiometry to be strongly dependent on the synthesis temperature. LiCoO₂ prepared at 600 °C shows a slight excess of lithium
stoichiometry corresponding to Li$_{1.09}$CoO$_2$ which is closer to the initial stoichiometry of nitrates taken, suggesting little loss of Li during heating. It is to be noted here that impurity peaks corresponding to lithium salts are absent in the X-ray diffractogram. The sample prepared at 700 °C has its nominal composition as LiCoO$_2$ while the samples prepared at 800 °C and above have Co$_3$O$_4$ as impurity in the diffractogram albeit the use of 10 mol % excess Li salt in the synthesis. This suggests substantial amount of Li loss at high temperatures.

Figure 3.2, (a) Powder X-ray diffraction patterns for LiCoO$_2$ obtained by heating nitrates at 700 °C for varying durations. (b) & (c) Scanning Electron Micrographs for HT-LiCoO$_2$ obtained by heating corresponding metal nitrates in air at 700 °C for (a) 1 h and (b) 4 h.

Chemical analyses of these samples were not possible owing to the insolubility of Co$_3$O$_4$ in acids. From the foregoing, it is clear that the synthetic
conditions have a crucial role in controlling structural as well as compositional aspects of LiCoO$_2$ that affect its electrochemical activity.

**Electrochemical performance of LiCoO$_2$:**

Electrochemical performances of all the LiCoO$_2$ samples, prepared at different temperatures, have been evaluated using Swagelok-type cells; the cells are subjected to galvanostatic cycling with 1 Li in 5 h rate in the voltage range between 3.5 V and 4.2 V. Fig. 3.3 shows the voltage versus composition profiles for LiCoO$_2$ samples prepared by nitrate-melt decomposition at different temperatures namely (a) 600 °C, (c) 700 °C and (e) 800 °C; the corresponding capacity retention plots are shown in (b) 600 °C, (d) 700 °C and (f) 800 °C. The smooth curves for charge-discharge processes for all samples show the absence of spinel-phase formation during cycling. The plateau around ~3.9 V is associated with Co$^{3+}$/Co$^{4+}$ redox process. As is seen from the Fig. 3.3 (c), the LiCoO$_2$ sample prepared at 700 °C shows highest reversible capacity and lower polarization. A maximum of about 0.5 Li$^+$ (= 0.5e$^-$) can be reversibly cycled with a stable capacity of 120 mAh.g$^{-1}$ (first cycle irreversibility is ~0.05).

The first charge/discharge capacities of the samples prepared at 600 °C, 700 °C and 800 °C are 106/91, 132/122 and 131/114 mAh.g$^{-1}$, respectively. As obvious from the charge/discharge capacity values, the sample obtained by heating at 600 °C shows lower capacity and retains only 92% of its initial capacity after 25 cycles (Fig. 3.3 (b)), presumably due to the absence of perfect-layered structure as revealed by its X-ray diffraction pattern. By contrast, the sample prepared at 700 °C shows a maximum capacity with an irreversible capacity loss of about 10 mAh.g$^{-1}$; the sample retains a capacity value of ~116 mAh.g$^{-1}$ after 25 cycles with a capacity loss of only ~5% (shown in Fig. 3.3 (d)). The initial charge capacity for the sample synthesized at 800 °C is comparable to the sample prepared at 700 °C but its irreversible capacity loss in the first cycle is 17 mAh.g$^{-1}$ that pushes its specific capacity to ~114 mAh.g$^{-1}$. This is due to the Li-deficiency in the sample brought about by lithium loss at higher temperature. Accordingly, the sintering temperature clearly affects electrochemical
behaviour of the samples. In this study, the optimum electrochemical performance is observed for stoichiometric LiCoO$_2$ prepared at 700 °C.

Figure 3.3, Electrochemical performance of LiCoO$_2$ prepared by nitrate melts decomposition method. (a), (c), (e) are the voltage-composition curve of Li/LiCoO$_2$ cells cycled between 3.5-4.2 V with LiCoO$_2$ prepared at (a) 600 °C (c) 700 °C and (e) 800 °C. The corresponding capacity retention plots are shown in the right (b) LiCoO$_2$-600 °C (d) LiCoO$_2$-700 °C and (f) LiCoO$_2$-800 °C.
3.3.2. Nitrate melt decomposition synthesized LiNi_{0.8}Co_{0.2}O_{2}:

Layered LiNi_{0.8}Co_{0.2}O_{2}, a solid solution of LiCoO_{2} and LiNiO_{2} could deliver a capacity of ~180 mAh.g\(^{-1}\) which is much higher than that of the end members. Here nickel presents in +3 oxidation state and presence of even small amount of Ni\(^{2+}\) leads to cation exchange due to similar ionic radii of Ni\(^{2+}\) and Li\(^{+}\).\(^{18}\) Thus Ni\(^{2+}\) should strictly be excluded from the system. In nitrate melt decomposition method, the oxidizing nature of nitrates stabilizes nickel mainly in Ni\(^{3+}\)-states preventing Ni from taking Li\(^{+}\)-sites in the structure. Further high homogeneity of the mixed-metal ions in the melt facilitates formation of pure compounds with perfectly-layered arrangement of atoms.

The sample was characterized using powder X-ray diffraction (XRD) which indicated absence of impurity phases corresponding to oxides of cobalt, nickel or lithium salts. The XRD pattern could be indexed with LiNiO_{2} (PDF No: 00-009-0063). The crystal structure was refined using GSAS Rietveld suite, and the Rietveld fit with experimental, calculated and difference pattern is shown in Fig. 3.4.

![Figure 3.4, Powder XRD Rietveld fit for LiNi_{0.8}Co_{0.2}O_{2} derived from nitrates-melt decomposition. Inset shows the clear splitting of (006)/(102) and (108)/(110) peaks.](image)
LiNiO₂ structure with $R\bar{3}m$ space group is used as initial structural model wherein Ni, Li and O are fixed at 3a, 3b and 6c sites, respectively. Refinement is carried out by fixing Co at the 3a sites while allowing Li and Ni to exchange its position between 3a and 3b sites. As seen in Fig. 3.4, the refinement converges with a good fit between the experimental and calculated patterns. The crystallographic parameters obtained using refined powder XRD pattern is presented in Table 3.1.

### Table 3.1. Refined crystallographic parameters for nitrate-melt synthesized LiNi₀.₈Co₀.₂O₂

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li1</td>
<td>0.0</td>
<td>0.0</td>
<td>0.5</td>
<td>0.98(2)</td>
</tr>
<tr>
<td>Li2</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.01(8)</td>
</tr>
<tr>
<td>Ni1</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.78(2)</td>
</tr>
<tr>
<td>Ni2</td>
<td>0.0</td>
<td>0.0</td>
<td>0.5</td>
<td>0.01(8)</td>
</tr>
<tr>
<td>Co1</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.20</td>
</tr>
<tr>
<td>O1</td>
<td>0.0</td>
<td>0.0</td>
<td>0.25(8)</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Lattice parameters: $a=b=2.868(1)$ Å, $c=14.173(1)$ Å; Space group: $R\bar{3}m$, $c/a=4.942$, $\chi^2=0.8259$.

Li/Ni disorder observed here is only 1.8 % and indicates a highly-ordered arrangement of metal cations in the sample. The low-cation mixing (< 2%) observed here is attributed to the stabilization of high concentration of Ni³⁺ in the sample owing to the oxidizing nature of nitrate flux used in the synthesis. Formation of perfectly-ordered-layered structure is obvious from clear splitting of the (006)/(102), (108)/(110) peaks shown as inset to Fig. 3.4. Furthermore, the intensity ratio $I_{(003)}/I_{(104)}$ is found to be 1.48 which indicates high cation ordering. The R-factor, described as the intensity ratio $I_{(102)}+I_{(006)}/I_{(101)}$, is also used as a measure for degree of cation mixing. The R-factor calculated from the intensities of the corresponding peaks is as low as 0.4658 that also suggests high hexagonal-ordering in the sample.
Particle-size distribution and morphological studies are carried out using scanning electron microscopy. The representative SEM image for LiNi\textsubscript{0.8}Co\textsubscript{0.2}O\textsubscript{2} synthesized by nitrate-melts decomposition is depicted in Fig. 3.5(a). The micrograph illustrates well developed and nearly-cubic crystallites with a narrow size-distribution typically ranging between 100 nm and 350 nm. The histogram for particles-size distribution derived from the SEM image is shown in Fig. 3.5(b). It is seen from the histogram that the maximum percentage of particles have size distribution between 200 nm and 250 nm.

![Figure 3.5 (a), Scanning electron micrograph for LiNi\textsubscript{0.8}Co\textsubscript{0.2}O\textsubscript{2}, and (b) histogram shows the particle-size distribution.](image)

Electrochemical performance of LiNi\textsubscript{0.8}Co\textsubscript{0.2}O\textsubscript{2} is analysed using (1) cyclic voltammetry (2) Galvanostatic charge-discharge studies (3) Electrochemical impedance spectroscopy.

**Cyclic voltammetry (CV):** The experiments were carried out in the voltage range between 3V and 4.3 V by applying a constant potential of (scan rate) 0.1 mV.s\textsuperscript{-1}. Cyclic voltammogram of LiNi\textsubscript{0.8}Co\textsubscript{0.2}O\textsubscript{2} vs. Li cell for the first three cycles is shown in Fig. 3.6. It is seen from the Fig. 3.6 that the cyclic voltammogram during the first cycle is different from the consequent cycles. During the first cycle, a peak at 4.1 V is observed which is associated with the co-existence of two hexagonal phases, H\textsubscript{1} and H\textsubscript{2}, related to Li\textsubscript{1-x}Ni\textsubscript{0.8}Co\textsubscript{0.2}O\textsubscript{2}.\textsuperscript{21} The corresponding reduction peak appeared at 3.6 V, large difference between oxidation/reduction peak position and intensity in the first cycle shows the irreversibility in the lithium intercalation/deintercalation...
process. Phase change during first cycle is already reported by Gross et al.\(^{21}\) They found the material is changing from one phase to another during first cycle and this phase transition is responsible for the irreversibility of about 0.1 Li in the first cycle. From next cycle onwards, the process is completely reversible and is shown by the small difference in the position of oxidation and reduction peak potentials. Therefore, irreversibility in material is associated only with first cycle and in concurrent cycles phase transition is not affecting reversibility of the redox process. Song et al. had reported that Li\(_{x}\)Ni\(_{0.8}\)Co\(_{0.2}\)O\(_2\) adopts monoclinic structure for \(0.5 \leq x \leq 0.7\) compositions while it crystallizes in rhombohedral structure for \(x \geq 0.8\) and \(x \leq 0.4\) compositions.\(^{22}\) Accordingly, the peaks observed here at 3.9 V and 3.6 V are attributed to the coexistence of rhombohedral/monoclinic and monoclinic/rhombohedral phases, respectively.

![Cyclic voltammograms for LiNi\(_{0.8}\)Co\(_{0.2}\)O\(_2\) vs. Li cells in the voltage range 3 V and 4.3 V with a scan rate of 0.1 mV.s\(^{-1}\).](image)

**Figure 3.6, Cyclic voltammograms for LiNi\(_{0.8}\)Co\(_{0.2}\)O\(_2\) vs. Li cells in the voltage range 3 V and 4.3 V with a scan rate of 0.1 mV.s\(^{-1}\).**

**Galvanostatic charge-discharge studies:** Fig. 3.7 (a) shows the voltage vs. composition curve derived from galvanostatic charge/discharge experiments for LiNi\(_{0.8}\)Co\(_{0.2}\)O\(_2\)/Li cell in the voltage range between 3 V and 4.3 V at 0.2C rate.
Figure 3.7, (a) Voltage vs. composition plot derived from galvanostatic charge/discharge experiments on LiNi$_{0.8}$Co$_{0.2}$O$_2$/Li cell in the voltage range between 3 V and 4.3V at 0.2C rate (b) discharge capacity as a function of cycle number.

About 0.1 lithium, corresponding to a capacity of 20 mAh.g$^{-1}$ is irreversible during the first cycle. This irreversibility could be attributed to the transformation of initial phase to a new Li-deficient phase together with formation of SEI during initial charge cycle. The irreversible loss during second cycle is small and the material exhibits good capacity retention during subsequent cycles as shown in Fig. 3.7 (b). The sample shows initial charge/discharge capacity of 204/185 mAh.g$^{-1}$. About 90% of initial capacity is retained even after 50 cycles. Low polarization observed
between the charge and discharge curves suggests smooth accommodation of lithium during intercalation/de-intercalation processes with good inter-particle contact.

**Electrochemical impedance spectroscopy:** To further comprehend the electrochemical data presented in Fig. 3.6 and 3.7, impedance measurements are carried out on LiNi_{0.8}Co_{0.2}O_{2}/Li cells in three-electrode assembly configuration with lithium counter and reference. The impedance data are collected at varying state-of-charge values during galvanostatic cycling between 3 V and 4.3 V at 0.2C rate. Impedance spectra for as fabricated cells along with impedance spectra for the cell after de-intercalation of 0.1 lithium are depicted in Fig. 3.8.

![Impedance spectra for fresh cell together with that after de-intercalation of 0.1 Li in the frequency range between 400 kHz-2 mHz in galvanostatic mode. Inset is the magnified image of higher frequency region.](image)

It is seen from the figure that impedance of the fresh cell is very high and hence not fully developed in the measured frequency region. For the cycled cell of composition Li_{0.9}Ni_{0.8}Co_{0.2}O_{2}, there is a drastic decrease in the resistivity of the material. This decrease in resistance is mainly associated with the LiNi_{0.8}Co_{0.2}O_{2} which is reported to undergo transition from semiconductor to metallic behaviour at the initial stages of lithium deintercalation.²³ This transition is supposedly
responsible for the reduction in resistance on de-intercalation of 0.1 lithium, anomalous behaviour of first cycle and consequent irreversible capacity loss.

Variation in impedance parameters during different levels of intercalation/deintercalation is further probed for one full charge and discharge cycle. Fig. 3.9 shows the Nyquist plots for LiNi$_{0.8}$Co$_{0.2}$O$_2$/Li cell during lithium de-intercalation (a-e) and lithium intercalation (f-j) at different potentials. Experimental values are shown as points and the respective fit using equivalent circuit model is depicted by solid line.

**Figure 3.9**, Nyquist plots for LiNi$_{0.8}$Co$_{0.2}$O$_2$/Li half cells during de-intercalation (a-e) and intercalation (f-j) of lithium.

The spectrum reveals two semicircular regions and a slopping line at a constant angle. The semicircle at high-frequency region (>50 Hz) is generally attributed to the Li-ion migration through the surface passive film, namely solid electrolyte interface
(SEI), present on the cathode active surface. The semicircle at middle frequency (40Hz-1Hz) is assigned to charge-transfer through the cathode/electrolyte interface, and the low-frequency line (lower mHz) to lithium-ion diffusion through bulk of the cathode.

Hence, the impedance spectrum shown here is fitted with Frumkin-Melik-Gaykazyan model where the equivalent circuit comprises electrolyte resistance, \( R_e \) in series with two RC networks in conjunction with \( Z_{FLW} \) element followed by intercalative capacitance. The model equivalent circuit is shown in Fig. 3.10.

![Equivalent Circuit Model](image)

**Figure 3.10, Equivalent circuit model used for fitting the impedance spectrum.** \( R_e \) is the Ohmic resistance due to electrolyte, \( R_{SEI} \) and \( R_{ct} \) are total resistance associated with solid electrolyte interface (SEI) and charge transfer. \( Q_{SEI} \) and \( Q_{ct} \) are constant phase elements for SEI and charge transfer. FLW is finite-length Warburg and \( C_{int} \) represents intercalative capacitance.

The constant-phase element \( Q \) \( (Q=1/j\omega^n) \) is used instead of a capacitor to explain the depressed semicircle. In intercalation compounds, solid-state diffusion is normally associated with accumulation of charge on the surface resulting in capacitive behaviour at low frequencies. Accordingly, finite length Warburg element \( (Z_{FLW}) \) in series with \( C_{int} \) is used in the circuit to represent diffusion and accumulation of lithium at the LiNi0.8Co0.2O2 electrode.

Fig. 3.11 shows the variation in resistive and capacitive components during lithium deintercalation (a-c) and lithium intercalation (d-f). Resistance of SEI film, denoted as \( R_{SEI} \) (a,d), and cathodic resistance, denoted as \( R_{ct} \) (b,e), are derived from equivalent circuit fit values. From the data, it is seen that resistance values associated with SEI film during first charge change only nominally due to the initial SEI formation on the cathode active surface in contact with electrolyte. During the
discharge process, resistance due to SEI gradually increases and reaches a maximum in the potential region between 3.5 V and 3.8 V. This increase is linked to creation of larger active surface during first discharge process. The change in cathodic resistance during charge-discharge shown in Fig. 3.11 (b) and (e) agrees well with the CV data. It is noteworthy that cathodic resistance, \( R_c \), is lower for peak potentials in the CV while it is comparatively higher at the other points.

\[ R_{SEI} \] (a,d) and charge transfer as \( R_{ct} \) (b,e). \( C_{int} \) is the intercalative capacitance.

Figure 3.11, Plots showing variation in resistive and capacitive components for the cell during lithium de-intercalation (a-c) and intercalation (d-f) as derived from impedance spectra. Resistance due to SEI is denoted as \( R_{SEI} \) (a,d) and charge transfer as \( R_{ct} \) (b,e). \( C_{int} \) is the intercalative capacitance.
By contrast, intercalative capacitance denoted as $C_{\text{int}}$ in Fig. 3.11 (c) and (f) is high at the observed peak potentials in CV. Intercalative capacitance, $C_{\text{int}}$ is calculated from:

$$C_{\text{int}} = -1/ \omega Z''_{\omega \to 0}$$

where $\omega = 2\pi \gamma$ with $\gamma$ as the linear frequency and $C_{\text{int}}$ is the capacitance due to accumulation of lithium into the host material and is analogous to pseudo-capacitance. Amount of accumulated lithium depends on the available lattice sites in the host material which in turn depends on the electrode potential. Since the amount of lattice positions available in the host material is higher at peak potentials, $C_{\text{int}}$ also happens to be high at this potentials.

### 3.3.3. Nitrate melt decomposition synthesized LiNi$_{0.8}$Co$_{0.15}$M$_{0.05}$O$_2$ ($M= \text{Al}^{3+}/\text{Mg}^{2+}$):

In LiNi$_{0.8}$Co$_{0.2}$O$_2$, formation of Ni$^{4+}$ ions while charging leads to oxygen evolution at elevated temperature and hence causing the safety problems. In order to improve the safety and electrochemical properties, samples with various dopants like Al, Mg, Ga, Zr, Ce for Ni/Co have been reported. Although substitution of electrochemically inactive element resulted in reduction of capacity, they are found to be effective in suppressing the cation mixing and increase the stability of the compound in the delithiated state by acting as a pillaring agent. Further there is less amount of Ni$^{4+}$ in the charged state reducing the evolution of oxygen. Among these dopants aluminium and magnesium are commonly studied. Chen et al. showed that the aluminium doping improves the power capability by suppressing the rise in cell impedance on cathode surface. Further it increase intercalation voltage for lithium. Aluminium substitution is also proved to be effective in reducing the cobalt dissolution at higher voltages. Similarly, magnesium doping increases the cycling efficiency of the sample. Doping of Mg$^{2+}$ for Co$^{3+}$ produce Co$^{4+}$, thereby increasing the electronic conductivity. Nitrates melt decomposition method was extended for the doping of small amount of aluminium and magnesium in LiNi$_{0.8}$Co$_{0.2}$O$_2$. High homogeneity of the precursors melt in nitrate melt decomposition smooth the progress of aluminium/magnesium substitution in the material.

Powder X-ray diffraction of the samples LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ and LiNi$_{0.8}$Co$_{0.15}$Mg$_{0.05}$O$_2$ synthesized by nitrates-melt-decomposition route are shown in
Fig 3.12 (a) and (b) respectively. X-ray diffraction patterns are indexed on α-NaFeO$_2$ type layered structure with space group: R$ar{3}$m. Further there were no impurity peaks corresponding to Al$_2$O$_3$/MgO. Formation of perfectly-ordered-layered structure is also obvious from clear splitting of the (006)/(102), (108)/(110) peaks. All this proves the formation of highly homogeneous solid solution of aluminium or magnesium substituted LiNi$_{0.8}$Co$_{0.2}$O$_2$ in nitrate melt decomposition method. Crystal structure of the samples LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ and LiNi$_{0.8}$Co$_{0.15}$Mg$_{0.05}$O$_2$ synthesized by nitrates-melt-decomposition route are also analyzed using Rietveld refinement using LiNiO$_2$ structure as model. Disorder in the material is calculated by fixing Co at 3a sites while allowing Li and Ni to disorder between 3a and 3b sites.

![Figure 3.12](image-url)

**Figure 3.12,** Rietveld fit for (a) LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ (b) LiNi$_{0.8}$Co$_{0.15}$Mg$_{0.05}$O$_2$ derived from nitrates-melt decomposition route.
The refined crystallographic parameters obtained using refinement of powder XRD are presented in Table 3.2. About 2% of lithium is present in transition metal layer in LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ and 5% in LiNi$_{0.8}$Co$_{0.15}$Mg$_{0.05}$O$_2$. This low cation mixing is due to the stabilization of Ni$^{2+}$ instead Ni$^{2+}$ by highly oxidizing nitrate flux.

**Table 3.2. Refined crystallographic parameters for nitrate-melt synthesized LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ and LiNi$_{0.8}$Co$_{0.15}$Mg$_{0.05}$O$_2$.**

<table>
<thead>
<tr>
<th>Atom</th>
<th>site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNi$<em>{0.8}$Co$</em>{0.15}$Al$_{0.05}$O$_2$</td>
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<td>3b</td>
<td>0.0</td>
<td>0.0</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>Li2</td>
<td>3a</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>Ni1</td>
<td>3a</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>Ni2</td>
<td>3b</td>
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<td>0.0</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>Al1</td>
<td>3a</td>
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<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
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<td>Co1</td>
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<td>0.0</td>
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</tr>
<tr>
<td></td>
<td>O1</td>
<td>6c</td>
<td>0.0</td>
<td>0.0</td>
<td>0.25(8)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>
| Lattice parameters: $a$=$b$= 2.869(6) Å, $c$= 14.191(4) Å; Space group: $R\bar{3}m$, $\chi^2 = 4.945$, $\chi^2 = 0.7969$

<table>
<thead>
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<th>Atom</th>
<th>site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNi$<em>{0.8}$Co$</em>{0.15}$Mg$_{0.05}$O$_2$</td>
<td>Li 1</td>
<td>3b</td>
<td>0.0</td>
<td>0.0</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>Li2</td>
<td>3a</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>Ni1</td>
<td>3a</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>Ni2</td>
<td>3b</td>
<td>0.0</td>
<td>0.0</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>Mg1</td>
<td>3a</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>Co1</td>
<td>3a</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>O1</td>
<td>6c</td>
<td>0.0</td>
<td>0.0</td>
<td>0.25(3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
| Lattice parameters: $a$=$b$= 2.876(2) Å, $c$= 14.204(6) Å; Space group: $R\bar{3}m$, $\chi^2 = 4.939$, $\chi^2 = 0.8710$
Morphological studies are carried out using scanning electron microscopy. The representative SEM image for LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ and LiNi$_{0.8}$Co$_{0.15}$Mg$_{0.05}$O$_2$ synthesized by nitrate-melts decomposition are shown in Fig 3.13 (a) and (b). Micron sized particles were seen in the micrographs. The micrograph illustrates well developed agglomerates of nearly-cubic crystallites.

**Figure 3.13, Scanning Electron micrographs of (a) LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ (b) LiNi$_{0.8}$Co$_{0.15}$Mg$_{0.05}$O$_2$ derived from nitrates-melt decomposition route**

**Electrochemical performance of LiNi$_{0.8}$Co$_{0.15}$M$_{0.05}$O$_2$ (M= Al$^{3+}$/ Mg$^{2+}$):**

Fig. 3.14 (a) and (c) shows the cycling performance of Al and Mg doped samples in the voltage range of 3 to 4.5 V at 0.2C rate. A well-defined plateau region is seen at 3.8 V in the first charge cycle and the lithium insertion is smooth from second cycle onwards. Nearly 0.2 Li, corresponding to a capacity of 50 mAh.g$^{-1}$, is irreversible in the first cycle. The irreversible loss during second cycle is small and the material exhibit good capacity retention during subsequent cycles as shown in Fig. 3.14 (b) and (d). The initial charge/discharge capacity of LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ is 225/174 mAh.g$^{-1}$ and for LiNi$_{0.8}$Co$_{0.15}$Mg$_{0.05}$O$_2$ is 191/150 mAh.g$^{-1}$. Though there is a large irreversible capacity loss in the first cycle, both samples showed high capacity retention. LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ showed 80% of its initial capacity while LiNi$_{0.8}$Co$_{0.15}$Mg$_{0.05}$O$_2$ showed 83% after 100 cycles. Good capacity retentions imply Al/Mg substitution assist stabilization of layered structure at higher voltages.
Figure 3.14, Voltage vs. composition plot for LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ (left) and capacity retention plot (right) for LiNi$_{0.8}$Co$_{0.15}$Mg$_{0.05}$O$_2$/Li cell in the voltage range between 3 V and 4.5 V. Figures 3.14 (a) & (b) for LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$, and 3.14 (c) & (d) for LiNi$_{0.8}$Co$_{0.15}$Mg$_{0.05}$O$_2$

3.3.4. Nitrate melt synthesis of LiNi$_{0.33}$Mn$_{0.33}$Co$_{0.33}$O$_2$:

LiNi$_{0.33}$Mn$_{0.33}$Co$_{0.33}$O$_2$ is one of the promising cathode materials due to its high reversible specific capacity at a quite high potential.\textsuperscript{40-41} However, electrochemical performance of LiNi$_{0.33}$Mn$_{0.33}$Co$_{0.33}$O$_2$ is strongly influenced by the preparative method and conditions followed for the synthesis.\textsuperscript{43} Low-temperature synthesis result in electrochemically less active spinel-like phase\textsuperscript{44} while high-temperature syntheses lead to excess lithium loss and cation mixing. Presence of Ni$^{2+}$ always leads to defective structure with certain extent of cation mixing. Degree of cation mixing can be reduced by carefully controlling the synthesis method and condition. Thus nitrate melt decomposition method was carefully applied for the synthesis of LiNi$_{0.33}$Mn$_{0.33}$Co$_{0.33}$O$_2$. Optimization of temperature had been carried out in order to synthesis the material with lowest cation mixing and the best sample obtained is analysed electrochemically vs. lithium.
X-ray diffraction patterns for the LiNi$_{0.33}$Mn$_{0.33}$Co$_{0.33}$O$_2$ synthesized by nitrate-melt decomposition at varying temperatures, namely 750 °C, 800 °C, 850 °C and 900 °C, are shown in Fig 3.15. All the patterns could be indexed on α-NaFeO$_2$ type layered structure with space group: R 3m.

![X-ray diffraction patterns](image)

**Figure 3.15, Powder X-ray diffraction patterns of LiNi$_{0.33}$Mn$_{0.33}$Co$_{0.33}$O$_2$ obtained by nitrates melt decomposition at (a) 750 °C, (b) 800 °C, (c) 850 °C and (d) 900 °C.**

Careful examination of the diffraction pattern for the sample heated at 750 °C (Fig. 3.15 (a)) shows the absence of splitting (doublet) for (006)/(012) and (018)/(110) reflections indicating lack of a perfectly-layered structure. All other samples obtained at temperatures >750 °C clearly exhibit splitting of these peaks in the XRD suggesting the formation of perfectly-layered structure (Fig. 3.15 (b-d)).
However, the integrated intensity ratio of peaks (003) and (104) is highest for the samples prepared at 800 °C indicating lower degree of cation mixing compared to the samples prepared at 850 °C and 900 °C. The sample synthesized at 800 °C is further analyzed by Rietveld analysis in order to quantify the amount of cation mixing in the sample. Fig. 3.16 shows the XRD Rietveld-fit patterns for the sample prepared at 800 °C with observed, calculated, difference patterns and Bragg reflections.

![Image](image.png)

**Figure 3.16, Powder XRD Rietveld fit for LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2 derived from nitrates-melt decomposition. Inset is the scanning electron microscopic image.**

During the refinement of the XRD data, occupancy of Co and Mn are fixed as 1/3 at 3b-sites. Initially, refinements are carried out assuming no exchange between Li and Ni cation sites, i.e. all Li atoms are kept at 3a-sites and all Ni atoms at 3b-sites. The refinement converged with higher agreement factors, for example, the $R_{wp}$ value obtained is 10.4. In the final stages of refinement, the distribution of Li- and Ni-sites between 3a-alkali metal sites and 3b-transition-metal sites is allowed to refine keeping total (Li + Ni) content as (1+1/3). This improves the fit substantially and gives better agreement values ($R_{wp}= 8.05$ and $\chi^2= 0.85$). The refinement shows Li/Ni disorder of about 5.39% cation mixing in the sample.
Table 3.3, Refined crystallographic parameters for nitrate-melt synthesized LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li 1</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.94(6)</td>
</tr>
<tr>
<td>Li2</td>
<td>0.0</td>
<td>0.0</td>
<td>0.5</td>
<td>0.05(3)</td>
</tr>
<tr>
<td>Ni1</td>
<td>0.0</td>
<td>0.0</td>
<td>0.5</td>
<td>0.27(9)</td>
</tr>
<tr>
<td>Ni2</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.05(3)</td>
</tr>
<tr>
<td>Co1</td>
<td>0.0</td>
<td>0.0</td>
<td>0.5</td>
<td>0.33</td>
</tr>
<tr>
<td>Mn1</td>
<td>0.0</td>
<td>0.0</td>
<td>0.5</td>
<td>0.33</td>
</tr>
<tr>
<td>O1</td>
<td>0.0</td>
<td>0.0</td>
<td>0.278(3)</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Lattice parameters: \(a=b=2.837(4)\ \text{Å}, c=14.296(6)\ \text{Å}, R_w=8.05, \chi^2=0.85.

Morphology of the Li_{0.33}Mn_{0.33}Co_{0.33}O_2 sample was examined by Scanning Electron Microscope and is shown as inset in Fig. 3.16. Nitrate-derived sample prepared at 800°C contains agglomerates of nanometric particles of 200-300 nm. Distribution of Co, Ni and Mn in the individual crystallites is probed using EDAX analysis. EDAX analysis confirms the sample is homogeneous and the transition-metal cations are in the expected ratio. Further, the actual concentration of metal ions in the sample is also confirmed by atomic absorption spectroscopy and the stoichiometries obtained is Li_{0.98}Ni_{0.32}Co_{0.33}Mn_{0.31}O_2 for as-prepared samples; these compositions are close to nominal stoichiometry.

**Electrochemical performance of LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2:**

Fig. 3.17 (a) shows the voltage versus composition profiles for optimized LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2 samples prepared by nitrate-melt decomposition (800 °C). The smooth curves for charge-discharge processes for all samples show the absence of spinel-phase formation during cycling. In the initial stages of lithium deintercalation, Ni^{2+} oxidizes to Ni^{3+} and subsequently to Ni^{4+}, \(45\) which is equivalent to a removal of 0.66Li (or 0.66e\^-) corresponding to the theoretical capacity of 184 mAh.g\(^{-1}\). On further deintercalation, only a fraction of Co^{3+} is oxidized to Co^{4+} extending the capacity value of Li_{1-x}Ni_{0.33}Mn_{0.33}Co_{0.33}O_2 to about 200 mAh.g\(^{-1}\). As is seen from the
data in Fig. 3.17 (a), a maximum of about 0.68 Li (=0.68e) is reversibly removed for the nitrate-melt-decomposition-derived sample during the first charge amounting to a charge capacity of 188 mAh.g\textsuperscript{-1}. About 25 mAh.g\textsuperscript{-1} is irreversible in the first discharge reducing the discharge capacity to 165 mAh.g\textsuperscript{-1}. Then the capacity is stable in the subsequent cycle and it retains 70 % of its initial capacity after 25 cycles.

Figure 3.17, (a) Voltage vs. composition plot for LiNi\textsubscript{0.33}Mn\textsubscript{0.33}Co\textsubscript{0.33}O\textsubscript{2} vs. Li\textsuperscript{+} and (b) capacity retention plot.
3.4. Conclusion

- Nitrate melt decomposition route was demonstrated successfully for the synthesis of electrochemically active pristine and doped LiMO$_2$.

- Layered transition metal oxides namely LiCoO$_2$, LiNi$_{0.8}$Co$_{0.2}$O$_2$ and LiNi$_{0.33}$Mn$_{0.33}$Co$_{0.33}$O$_2$ have been prepared by nitrate melt decomposition method.

- Electrochemically active HT-LiCoO$_2$ has been prepared by heating nitrate precursors for duration as short as 15 min. LiCoO$_2$ prepared using this method exhibits varying degrees of cation mixing and crystallinity depending on the synthetic conditions. The samples prepared at 700 °C for shorter durations are nano-crystalline in nature and exhibit increased rate capability. HT-LiCoO$_2$ obtained by nitrate-melt decomposition at 700 °C results in a superior cathode material for lithium-ion batteries.

- LiNi$_{0.8}$Co$_{0.2}$O$_2$ having ordered-layered structure and $R\bar{3}m$ space group with less than 2% cation mixing is synthesized by nitrates-melt-decomposition route. The process yields highly homogeneous powders having near-cubic morphology with maximum particle-size distribution between 200 nm and 250 nm. The cyclic voltammograms reveal that LiNi$_{0.8}$Co$_{0.2}$O$_2$ undergoes a phase transformation during first cycle. The impedance data on LiNi$_{0.8}$Co$_{0.2}$O$_2$ electrodes indicate that the phase transition observed during the first cycle is linked to occurrence of semiconductor-metal transition on deintercalation of 0.1 Li. The galvanostatic charge-discharge studies reflect improved electrochemical performance of nitrates-melt synthesized LiNi$_{0.8}$Co$_{0.2}$O$_2$ with a stable capacity of 175 mAh g$^{-1}$ during prolonged cycling.

- Substitution of aluminium and magnesium for cobalt in LiNi$_{0.8}$Co$_{0.2}$O$_2$ is successfully carried out by nitrate melt decomposition method. Process yields highly homogeneous powders of LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ and LiNi$_{0.8}$Co$_{0.15}$Mg$_{0.05}$O$_2$ having ordered-layered structure with less cation...
mixing; and they showed high-quality electrochemical performance with stable capacity during prolonged cycling

- \( \text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2 \) prepared by nitrate-melt decomposition method shows 5% of cation mixing and superior electrochemical behaviour.

- To conclude, the method yields highly homogeneous product with improved electrochemical performance and it is attractive for the preparation of Li-ion cathode materials in bulk quantities.
3.5. References:


