SYNTHESIS AND CHARACTERIZATION OF CATHODE MATERIALS FOR HIGH

ENERGY DENSITY AND HIGH RATE CAPABILITY LITHIUM-ION

RECHARGEABLE BATTERIES

By

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ABSTRACT

Lithium metal oxides are of special interest as cathode materials in rechargeable lithium-ion batteries, because of their inherent property of Li deintercalation/intercalation upon charging and discharging, without altering the main crystal structure. We have developed a novel solution-based route for the synthesis of $\text{LiMn}_{1.5}$ Ni_{0.5-x}Cr_xO₄ (x = 0.1 and 0.2) cathode materials. The cathode powders were annealed at 875 ^oC for 24 hrs in O₂. The synthesized materials were structurally characterized using X-ray diffraction, Scanning electron microscopy, Raman spectroscopy, X-ray photoelectron spectroscopy (XPS). The coin cells were fabricated for the electrochemical characterization of the cathode material. The coin cells were fabricated inside a Glove Box in an inert atmosphere using LiMn_{1.5} Ni_{0.5-x}Cr_xO₄ cathode, LiPF₆[dissolved in ethyl carbonate (EC) and dimethyl carbonate (DMC) in 1:1 wt ratio) as electrolyte and Li foil as anode. The electrochemical studies include cyclic voltammetry and charge-discharge behavior, carried out at various current 'C' rates. The obtained data for LiMn_{1.5}Ni_{0.4}Cr_{0.1}O₄ and LiMn_{1.5} Ni_{0.3}Cr_{0.2}O₄ cathode materials were compared with the data obtained earlier for LiMn₂O₄ and LiMn_{1.5}Ni_{0.5}O₄ cathode materials. It was found that LiMn_{1.5}Ni_{0.4}Cr_{0.1}O₄ cathode material had improved electrochemical performance, which is discussed in detail in the following dissertation.

RESUMEN

Los óxidos metálicos de Litio son de especial interés como materiales que sirven como cátodo en baterías recargables de ión de Litio, debido a sus propiedades inherentes durante la carga y descarga de la batería. Esto permite que el Litio pueda ser deintercalado o intercalado, sin cambiar la estructura del cristal. Hemos desarrollado una nueva ruta basada en la síntesis en solución de LiMn_{1.5}Ni_{0.4}Cr_{0.1}O₄ y LiMn_{1.5}Ni_{0.3}Cr_{0.2}O₄ Como materiales de cátodo. Los polvos de cátodo fueron calcinados a 875 °C por 24 horas en O₂. Los materiales sintetizados fueron caracterizados estructuralmente usando difracción de rayos X, microscopia electrónica de barrido, espectroscopia Raman, espectroscopia fotoelectrónica de rayos X (XPS). Las pilas tipo moneda fueron fabricadas para la caracterización electroquímica del material de cátodo. Las mismas fueron ensambladas dentro de una caja de guantes inerte usando LiMn_{1.5}Ni_{0.4}Cr_{0.1}O₄ como cátodo, LiPF₆ [disuelto en el carbonato de etilo (CE) y carbonato de dimetilo (DMC) en proporción de 1:1 en peso) como electrólito y una lamina de Litio metálico como ánodo. Los estudios electroquímicos incluyen voltametría cíclica, y comportamiento de la carga y la descarga de la pila a distintos cambios de corriente 'C'. Los datos obtenidos para los materiales LiMn_{1.5}Ni_{0.4}Cr_{0.1}O₄ y LiMn_{1.5}Ni_{0.3}Cr_{0.2}O₄ fueron comparados con los datos obtenidos anteriormente para LiMn₂O₄ y LiMn_{1.5}Ni_{0.5}O₄. Se encontró que el material de cátodo LiMn_{1.5}Ni_{0.4}Cr_{0.1}O₄ mostró mejores propiedades electroquímicas, lo cual se expone en detalle en la disertación siguiente.

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CHAPTER 1: INTRODUCTION

1.0. General Introduction:

A battery is a device that converts the chemical energy contained in its active materials directly into electric energy by means of an electrochemical oxidation-reduction (redox) reaction. In the case of a rechargeable system, the battery is recharged by a reversal process.

Lithium is the third lightest and most electropositive element in the periodic table, hence it contribute towards the high energy density Li ion rechargeable batteries. Figure 1.1 showed the comparison of gravimetric and volumetric energy densities of various battery systems [1]. It can be seen from the figure that the Li ion batteries have the highest gravimetric and volumetric energy density.



Figure 1.1 Comparison of the gravimetric and volumetric Energy Density of various rechargeable battery systems.

1.1 Cell vs. Battery:

A cell is the basic electrochemical unit providing a source of electrical energy by direct conversion of chemical energy. The cell consists of an assembly of electrodes, separators, electrolyte, container and terminals. A battery consists of one or more electrochemical cells, electrically connected in an appropriate series/parallel arrangement to provide the required operating voltage and current levels, including, if any, monitors, controls and other ancillary components (e.g. fuses, diodes), case, terminals and markings

1.2 The major components of a cell:

1. Anode or negative electrode, the reducing or fuel electrode, which gives up electrons to the external circuit and is oxidized during the electrochemical reaction.

2. Cathode or positive electrode, the oxidizing electrode that accepts electrons from the external circuit and is reduced during the electrochemical reaction. The cathode must be an efficient oxidizing agent, be stable when in contact with the electrolyte, and have a useful working voltage.

3. Electrolyte, the ionic conductor that provides the medium for transfer of charge as ions, inside the cell between the anode and cathode. The electrolyte is typically a liquid, such as water or other solvents, with dissolved salts, acids, or alkalies to impart ionic conductivity. Some batteries use solid electrolytes, which are ionic conductors at the operating temperature of the cell. The electrolyte must have good ionic conductivity but not be electronically conductive, as this would cause internal short-circuiting. Physically, the anode and cathode electrodes should be electrolyte. In practical cell designs a separator material is used to separate the anode and the cathode. The separator, however, is permeable to the electrolyte in order to maintain the desired ionic conductivity.

1.3 The Li-ion battery:

There are advantages with using metallic Li as anode in the battery: the redox potential becomes very low and the equivalent weight is also low. There are problems, however, associated with the use of metallic Li: e.g. corrosion of Li by reaction with electrolyte, safety aspects, where dendrite formation [1] can cause short-circuiting of the cell with a thermal runaway and possible explosion. The concept of Li ion transfer cells was proposed to solve these problems. In these cells, an insertion electrode, usually carbon-based, replaces the Li metal anode [2-6]. In this way, the active lithium is always present as an ion rather than as a metal. Metallic lithium is highly reactive with oxygen, nitrogen and moisture, making it a difficult material to handle; glove boxes or dry-rooms becomes a necessity for the production. Battery production can be simplified by using insertion electrodes as both anode and cathode, since the battery components can be produced in ambient atmosphere and then swelled with electrolyte in a controlled atmosphere. To make a complete Li-ion cell, one of the electrodes will have to contain Li-ions, which are then shuttled reversibly between the electrodes during charge/discharge.

A big problem with the Li-ion concept is that any Li consumed by secondary reactions cannot be retrieved, and the specific capacity is totally dependent upon the amount of Li available for the reversible redox process in the cell. Some of the processes, which known to lead towards the capacity loss in Li-ion cells are: Li deposition (cell over-charge), electrolyte decomposition, active material dissolution, phase changes in the insertion electrode materials, and passive film formation on the electrode and current collector's surfaces [7-9]. The distinguishing features of today's commercial Li-ion batteries are:

1.3.1 High operating voltage:

A single cell has an average operating potential of approx. 3.6 V, three times the operating voltage of both Ni-Cd and Ni-MH batteries and about twice that of sealed Pb-acid batteries. Compact, lightweight, and high energy density: the energy density is about 1.5 times and specific energy is about twice that of high-capacity Ni-Cd batteries. Fast charging potential; batteries can be charged to about 80-90% of full capacity in one hour.

1.3.2 High discharge rate: Up to 3C are attainable. Wide range of operating temperature: from -20 to $+60^{\circ}$ C.

1.3.3 Superior cycle life: Service life of a battery exceeds 500 cycles.

1.3.4 Low self-discharge: Only 8-12% per month

1.3.5 Long shelf life: No reconditioning required up to approximately 5 years (Ni-Cd: 3Months; Ni-MH: 1 month). No memory-effect: can be recharged at any time. On- polluting: does not use toxic heavy metals such as Pb, Cd or Hg.

1.4 Operation of a cell:

Lithium ion rechargeable batteries operate by the lithium ions intercalation/deintercalation among the cathode and the anode. It is fundamentally different from non-rechargeable lithium batteries, where the basic forms of the cathode and anode materials do not change.

When the battery is charged, the lithium ions in the cathode material (lithium compound) migrate via a separator towards the carbon/graphite/Li foil anode and a charging current flow. Figure 1.2 describes the basic principle of Li ion rechargeable battery.

Battery ionic equation (charging)

Cobalt type
$$LiCoO_2+C_n \rightarrow Li_{1-x}CoO_2+C_nLi_x$$

Manganese type $LiMn_2O_4+C_n \rightarrow Li_{1-x}Mn_2O_4+C_nLi_x$

When the battery is discharged, the lithium ions from the anode materials migrate towards cathode (lithium compound) via a separator, and discharging current flows



Figure 1.2 Operations of the Lithium Ions Rechargeable Battery

Battery ionic equation (discharging)

| Cobalt type | $Li_{1-x}CoO_2+C_nLi_x \rightarrow LiCoO_2+C_n$ |
|----------------|---|
| Manganese type | $Li_{1-x}Mn_2O_4+C_nLi_x \rightarrow LiMn_2O_4+C_n$ |

1.5 Insertion electrodes:

An insertion compound is a solid host network incorporating guest ions. It has two Specific properties which makes it different from a normal solid structure: the guest ions are mobile between sites in the host network, and the guest-ions can be removed from or added to the host network, thus varying the guest-ion concentration. An insertion compound is an ionic and electronic conductor, and the uptake or release of electrons compensates for a change in guest-ion concentration Figure 1.3.

In Li-ion batteries, Li⁺ is the guest ion and the host network comprises transition-metaloxides (TMO's), for transition-metal oxides, positive ions guests (like Li⁺) occupy sites surrounded by negative oxygen ions.



Figure 1.3 the discharge process in a rechargeable Li-ion battery.

The guest ions strive to stay as far away as possible from the positive transition-metal ions. This is mainly due to their higher potential vs. Li/Li^+ giving a high specific energy and their excellent reversibility. The term "intercalation" is sometimes used in the literature; it implies a special case where "insertion" occurs into a layered host matrix, which retains its structural integrity during the intercalation process. This is the case, for example, for graphite, LiCoO_2 and LiNiO_2 [10-15].

Three-dimensional framework host with cubic spinel AB_2O_4 (A is alkaline lithium, B is transition metal and O is Oxygen) spinel-type structure. The simplest and the most studied insertion-compound structures contain close-packed arrays of oxygen with the transition-metal

(M=Cr, Ni, Mg and Al) atoms occupying half of the octahedral sites. These compounds are either layered (LiMO₂) or spinel framework (LiM₂O₄).

The theoretical capacity of a material can easily be calculated from Faraday's first law of Electrochemistry, which states that 1-gram equivalent weight of a material, will deliver 96487 coulombs (or 26.8 Ah) charge[16]. In case of LiMn₂O₄, the equivalent weight (M) of LiMn₂O₄ is 180.8 g, giving a theoretical capacity of 26.8/180.8 (Ah/g) = 0.148 Ah/g or 148mAh/g. The total cell reactions to provide a high cell voltage are.

a) Minimal change in the host network to ensure good reversibility.

b) Light host structure that is able to accommodate a significant amount of Li to provide a high capacity.

c) Good electronic and ionic conductivity to provide high rate capability.

d) Chemically and structurally stable over the whole voltage range and insoluble in the electrolyte.

e) Inexpensive and non-toxic.

f) Low oxidation potential for a fully charged positive electrode (high voltage vs. Li/Li⁺); high oxidation potential for a fully charged negative electrode.

1.6 Spinel LiMn₂O₄ cathode:

Normal spinel structures are usually cubic closed-packed oxides with one octahedral and two tetrahedral sites per oxide[17]. The tetrahedral points are smaller than the Octahedral points. B^{3+} ions occupy the octahedral holes because of a charge factor, but can only occupy half of the octahedral holes. A^{2+} ions occupy 1/8th of the tetrahedral holes. This maximises the lattice energy if the ions are similar in size. A common example of a normal spinel is AB₂O₄.

Inverse spinel structures however are slightly different in that you must take into account the Crystal Field Stabilisation Energies (CFSE) of the Transition metals present. Some ions may have a distinct preference on the octahedral site which is dependent on the d-electron count. If the A^{2+} ions have a strong preference for the octahedral site, they will force their way into it and displace half of the B^{3+} ions from the octahedral sites to the tetrahedral sites. If the B^{3+} ions have a low or zero Octahedral Site Stabilisation Energy (OSSE), then they have no preference and will adopt the tetrahedral site. A common example of an inverse spinel is Mn_3O_4 , if the Mn^{2+} (A^{2+}) ions are d6 high-spin and the Mn^{3+} (B^{3+}) ions are d5 high-spin.



Figure 1.4 Structure of spinel (LiMn₂O₄) Octahedral and Tetrahedral Positions

A part of the Li-Mn-O phase-diagram is described in Fig. 1.5. It is seen to involve a multitude of structures and tie-lines; this is related to the nature of Mn, which can have oxidation states II-VII. The most important oxidation states are II, IV and VII, with II the most stable. For Mn compounds with oxidation states II-IV octahedral coordination are the most common. From

a battery viewpoint, the spinel structures of interest in the Li-Mn-O phase-diagram are located within the triangle of the MnO_2 -LiMn₂O₄- Li₄Mn₅O₁₂ tie-lines. A close-up of the Li₂MnO₃ -LiMnO₂ -MnO₂ part of the Li-Mn-O phase diagram. The phases of interest in this thesis, and which can be found in electrodes after prolonged cycling or storage, elevated temperature treatments or fast charge/discharge, are MnO₂, LiMn₂O₄, Li_{1+x}Mn_{2-x}O₄, Li₂Mn₂O₄, Li₂MnO₃, Li₂Mn₄O₉ and Li₄Mn₅O₁₂ These involve Mn³⁺, Mn⁴⁺ or an average valence state somewhere in between; The structures in the Li₂MnO₃-LiMnO₂-MnO₂ part of the phase-diagram are either spinel or rock-salt related. There are also substituted phases like Li_{1+x}Mn_{2-x}O₄ (0 < x <0.33), where extra Li occupies the Mn site, which may stabilize the structure by raising the average valence number

In the LiMn₂O₄ spinel structure (space-group: Fd3m), a cubic close-packed (ccp) array of oxygen ions occupy the 32e position, Mn ions are located in the 16d octahedral site, and Li in the 8a tetrahedra sites. The Mn ions have an octahedral coordination to the oxygen's, and the MnO₆ Octahedral share edges in a three-dimensional host for the Li guest ions (Fig. 1.4). The 8a tetrahedral site is situated furthest away from the 16d site of all the interstitial tetrahedral (8a, 8b and 48f) and octahedral (16c). Each of the 8a-tetrahedron faces is shared with an adjacent, vacant 16c site. This combination of structural features in the stoichiometric spinel compound constitutes a very stable structure.

1.7 Lithium extraction/insertion mechanism:

The compound LiMn_2O_4 is a stable phase in the middle of the discharge curve of MnO_2 . On further reduction, the material converts into $\text{Li}_2\text{Mn}_2\text{O}_4$. The phases and phase transitions during reduction from -MnO₂ to LiMn_2O_4 have been the focus of debate in many publications paper [18-20]. From LiMn_2O_4 to $\text{Li}_2\text{Mn}_2\text{O}_4$, there is a distinct first order phase transition. When Li ions are inserted into the spinel host structure, they occupy the octahedral 16c sites. Since this site is face-sharing with the 8a tetrahedral, the Li ions in the tetrahedral site are instantly displaced into the vacant 16c site, causing a first-order phase transition When the Mn^{3+} (d4) concentration increases, a Jahn-Teller (JT) distortion [21-26] also occurs with a gain in energy equal to (Fig. 1.5). The crystal symmetry decreases from cubic (c/a = 1.0) to tetragonal (c/a ~ 1.16); this imposes a large strain on the individual spinel particles, that ultimately results in electromechanical grinding; the reversibility of this phase transition is poor.



Figure 1.5 Schematic representation of the splitting of the Mn 3d orbital in Mn^{3+} (d₄).

The situation is quite different during the removal of Li from the LiMn₂O₄ structure; the unit cell volume decreases gradually and isotropically as the Li-ion concentration decreases. The removal of Li from LiMn₂O₄ occurs through a two-step reaction around 4V; two potential plateaus can be discerned in the charge curve, separated by 100-150 mV. Rigorous studies have also shown that the material goes through at least one two phase region during charge/discharge. The structures of these intermediate phases are not yet determined, but single-crystal studies have shown that superstructures may occur in the upper part of the potential curve. An ordered

 $Li_{0.5}Mn_2O_4$ phase has been proposed to correspond to the step in the potential curve, but neutron studies showed no evidence for this.

We see then that LiMn_2O_4 is, in principle, an excellent candidate as a cathode material in secondary Li-batteries. The theoretical capacity is competitive with existing materials and the 3-D host network should function well in the 4V region. However, there are some problems with the material that leads to a slow capacity loss and need to be solved; they will be reviewed in this section [27-31].

Several processes have been proposed as source of the room-temperature capacity fade in $LiMn_2O_4$ are:

a) Loss of Mn through disproportionation of trivalent Mn. Hunter discovered [27] this already in 1981, and proposed a disproportionation reaction:

 Mn^{3+} (solid) Mn^{4+} (solid) + Mn^{2+} (solution). This reaction is dependent upon the acidity of the electrolyte; the choice of solvent and salt is also important from this point of view. Jang and Oh [32] reported the amounts of solvent-derived acid and dissolved Mn as a function of storage time in different electrolyte systems. They found that the extent of spinel dissolution is salt dependent in the following decreasing order: LiCF₃SO₃ > LiPF₆ > LiClO₄ > LiAsF₆ > LiBF₄

b) The dissolution of divalent Mn will not only cause a loss of active cathode material but also affect the anode. The solvated Mn^{2+} will be transported through the electrolyte and ultimately plate onto the anode. This will deplete the Li content in the anode, since the reduction of Mn will oxidize Li from the anode:

c) Formation of a Li-rich surface on cycling – leading to a JT transformation to the tetragonal $Li_2Mn_2O_4$ phase and ultimately to Li_2MnO_3 by dissolution of MnO was proposed by Thackeray and co-workers [33] as a variation of mechanism[a]. The electrode would incorporate extra Li in

the outermost surface layer, through the over-potential driving the electrochemical reaction during cycling. Mn^{2+} is known to dissolve from the active electrode, here as MnO. On prolonged cycling, the combined effects of overcharge and dissolution transform a significant amount of the electrode into Li₂MnO₃; this phase was detected by XRD measurements.

d) Instability of the de-lithiated MnO_2 phase and self-discharge or loss of oxygen from the host structure, coupled to solvent oxidation in the high-voltage region.

e) Structural degradation during cycling over the high-voltage two-phase region (approx. Li_{0.5}Mn₂O₄-MnO₂). A solution to the room-temperature capacity fade problem is cation substitution. Solid solutions in which monovalent, divalent or trivalent cations substitute the Mn cation increase the average Mn oxidation state. This results in a reduction of the unstable Mn³⁺ cations and a material less susceptible to the disproportionation reaction. Substitution of Al, for example, also decreases the cell parameter of the pristine material; an important factor for a wellfunctioning spinel electrode. Al doping has also been shown to improve the layered 2D cathode materials [34]. Anionic doping is another way of improving the Mn spinel material. At slightly elevated temperatures (ET), the capacity fade in Mn spinel electrodes escalates. This is a problem that must be solved since the applications for Li-ion batteries contain electronic circuits that generates heat, e.g. cell-phones and lap-tops. Tarascon and co- workers [35], [1] have performed a thorough study of the ET problem. They conclude that the mechanisms responsible for this capacity fade are the same at ET's as at room-temperature. Evidence was presented for a failure mechanism originating in the lithiated state, and the cell parameter of the pristine material was found to be a crucial factor. The difficulties associated with the Mn spinel at ET can be connected with the presence of HF acids in the electrolyte, which causes a significant quantity of Mn dissolution. The surface area of the material can be related directly to capacity fade, as an

increased surface area also increases the area of electrolyte contact and thus the HF attack on the material. The surface area is also important for obtaining a good rate-capability as smaller grains, i.e. a larger surface area, will facilitate faster lithiation/de-lithiation.

1.8 Statement of research problem:

There has been significant interest in the synthesis, structure, and electrochemical properties of lithiated transition metal oxides due to their use as positive electrodes in lithium ion batteries. Such a materials characteristic is not fortuitous and usually requires a better understanding of materials issue, mainly at the level of mastering its physical characteristic, chemical/thermal stability and more specially its surface reactivity. Here, we will report the synthesis of spinel cathode materials by a chemical solution route. Better in terms of electrochemical performance does not always mean new materials. But also enlist known ones with enhanced performances obtained through morphology changes. The same approach applied whatever we are dealing with positive cathode or negative anode intercalation electrodes. Optimizing an electrode material is only the first step of the food chain process leading to its implementation in a practical cell. Mastering the chemical stability of the new electrode material with respect to its operating liquid electrolyte medium that require control of the electrode /electrolyte interface through surface chemical by means of chemical or physical is as important. Among the basic requirements for highly electrochemically performing solid state intercalation electrode materials are numerous with wide compositional range for guess species (large capacity),

i) High diffusion of guest species in the host together with the good electronic conductivity (high power rates),

- Minimal structural change and a high chemical stability with respect to the electrolyte medium (long lifetime),
- iii) Large free energy of reaction (high voltage).

The elaboration of insertion materials, reassembling all these figures of merits listed above, constitute the main target for solid state chemists searching for better positive or negative electrode materials.

1.9 Objectives:

Following are the objectives of the present study:

- To synthesize cathode materials for high energy density and high rate capability Li ion rechargeable batteries
- To reduce the toxicity of the cathode materials as compared with the commercially used LiCoO₂ cathode material.
- To reduce the capacity fading in spinel LiMn₂O₄ cathode material by the substitution of Mn with transition metal ions e.g. Ni and Cr.
- To optimize the synthesis conditions of the cathode materials
- It has been theoretically proven that Ni, Co, Cr substitution in LiMn₂₀₄ improves its operating voltage (up to 5V).b.

In the present studies we are going to synthesis and characterized $LiMn_{1.5}Ni_{0.5-x}Cr_xO_4$ (x=0.1 and 0.2) by sol-gel method for Cathode materials for high-energy density and high rate capability Li ion rechargeable batteries.

CHAPTER 2: LITERATURE AND SYNTHESIS OF CATHODE MATERIALS

Over the last two decades lithium intercalated compounds have been investigated as cathode materials of rechargeable Li-ion batteries. LiCoO₂ was already used in commercially available Li-ion batteries [36-39]. However, LiCoO₂ has low reversible capacity, high toxicity and it is quite expensive. The low reversible capacity of LiCoO2 was attributed to the dissolution of Co in the electrolyte at high voltages. It has been suggested by several authors that the dissolution of Co into electrolyte can be suppressed by doping with other transition metal ions into LiCoO₂ [40-43] or by coating of LiCoO₂ with metal oxides such as MgO [44,45] B₂O₃[46,47], SiO₂[48], Al₂O₃[49,50], and ZrO₂[51,52]. Recently, LiMn_{1/3}Ni_{1/3}Co_{1/3}O₂ has been reported as the most promising cathode material for Li-ion batteries because of its higher reversible capacity, lower cost, and less toxicity than LiCoO₂[53,54].

Cho and coworkers [55] compared the electrochemical and thermal properties of AIPO₄ and Al₂O₃ coated LiCoO₂ cathode. They found that cycling stability of Al₂O₃-coated cathode was similar to that of the AIPO₄-coated sample at 4.6 V, but Al₂O₃ coated cathode showed increased charge-cutoff voltage to 4.8V, which led to the rapid capacity decay, exhibiting approximately 20% larger capacity-fading than the AIPO₄-coated cathode. The irreversible capacity of the Al₂O₃-coated cathode (Approx 34mAh g–1) was also found to be larger than that of AIPO₄-coated cathode (Approx 24mAhg–1) at a charge-cutoff voltage of 4.8V. This was attributed to the increase in the amount of Co dissolution into the electrolyte at higher voltage.

LiNi_{0.8}Co_{0.2-x}Ga_xO₂ (x = 0.0 0.01, 0.03, 0.05) was synthesized [56] using a sol-gel method and the effects of gallium doping on the structure and electrochemical properties of LiNi_{0.8}Co_{0.2}O₂ were investigated by X-ray diffraction, cyclic voltammetry and charge-discharge tests. The particle size of LiNi_{0.8}Co_{0.2-x}Ga_xO₂ (x = 0.01, 0.03, 0.05) cathode materials were found less than 1µm in diameter. XRD results showed that gallium-doping had no effect on the crystal

structure (α -NaFeO₂) of the cathode material in the range x≤0.05. The initial discharge capacity of the bare LiNi_{0.8}Co_{0.2}O₂ was found to be about 181.94 mAg⁻¹, which was higher than the gallium doped LiNi_{0.8}Co_{0.2-x}Ga_xO₂. It was also reported that the initial capacity tends to decrease with gallium doping. However, the bare LiNi_{0.8}Co_{0.2}O₂ loses its discharge capacity earlier than the others and shows 49% loss in discharge capacity after 50 cycles. On the other hand, the capacity loss was restrained in the gallium doped LiNi_{0.8}Co_{0.2}O₂ and approximately 89% of the initial discharge capacity was maintained after 50 cycles in the case of LiNi_{0.8}Co_{0.15}Ga_{0.05}O₂.

Li and coworkers [57] have synthesized a series of $\text{LiNi}_{0.5}\text{Mn}_{0.5-x}\text{Co}_x\text{O}_2$ ($0 \le x \le 0.5$) compounds by a solid state reaction, and studied their structural, morphological and electrochemical characteristics. They found that the Co doping suppresses the formation of the impurity phase, NiO, and improves the crystallinity of the compounds. Moreover, the unequivalent substitution of cobalt for manganese improved electrochemical properties because of increased average valence of nickel, and thereby shrinkage in the lattice volume. $\text{LiNi}_{0.5}\text{Mn}_{0.2}\text{Co}_{0.3}\text{O}_2$ shows a high reversible capacity as well as an excellent rate capability in 3–4.6V.

Choi and Manthiram [58] synthesized $Li_{1-x}Ni_{1/3}Mn_{1/3}Co_{1/3}O_2$ and studied its chemical stability by monitoring the oxygen content along with the lithium content in chemically delithiated samples. They correlated these results with the charge-discharge characteristics of this material and found that the system is chemically stable without losing any oxygen from the lattice for (1-x)>0.35 and structurally stable for at least (1-x) > 0.23. Due to chemical and structural stability of $Li_{1-x}Ni_{1/3}Mn_{1/3}Co_{1/3}O_2$, its reversible capacity was found to be higher (180 mAh/g) than that of LiCoO₂ (140 mAh/g).

Park and coworkers [59] synthesized molybdenum doped layered Li (Ni_{1/3+x}Co_{1/3}Mn_{3-2x}Mo_x) O₂ cathode materials by spray pyrolysis method, and obtained discharge capacity of 175mAh/g from the cathode with x=0.01. Ramos and coworkers [60] synthesized LiMn₂O₄ and LiCoO₂ powders by solution route and prepared thin films of these materials by spin coating technique. They found that the polycrystalline phase of these materials could be obtained at about 650 $^{\circ}$ C.

Tomar and coworkers [61] successfully synthesized LiAl_xCo_{1-x}O₂ ($0.0 \le x \le 0.7$) cathode materials by chemical method and characterized this material using XRD and Raman spectroscopy. They found that E_g and A_{1g} modes were present in the Raman spectra, corresponding to the hexagonal structure of LiAl_xCo_{1-x}O₂ cathode material. The line width of E_g and A_{1g} modes increased with the substitution of Co in LiCoO₂ by Al, indicating lattice disorder after Al substitution. It was found that these disorders were normalized after annealing LiAl_xCo_{1-x}O₂ at high temperature (700 °C).

Ramos and Tomar [62] synthesized LiMn_2O_4 , LiCoO_2 and LiNiO_4 cathode materials by solution route and obtained pure phase cathode materials at 700 °C.

Singh and coworkers [63] performed first principle calculations using VASP on the cation substitution of 4d transition metals (Mo and Rh) in $LiMn_{1/3}Ni_{1/3}M_{1/3}O_2$ cathode materials. The density of states for fully lithiated and delithiated $LiMn_{1/3}Ni_{1/3}Mo_{1/3}O_2$ was found to be slightly positive, indicating that the stoichiometric ratio of this material is unfavorable. On the other hand, the density of states for fully lithiated and delithiated $LiMn_{1/3}Ni_{1/3}Rh_{1/3}O_2$ was found to be negative, indicating the energetically favorable form of these phases. They also calculated the metal oxygen bond lengths and concluded that Mn remains in +4 state and only Ni and Rh participate in the electrochemical reaction.

Majumdar and coworkers [64] studied the effect of simultaneous doping with Co and Al ions on the phase formation behavior and electrochemical properties of the solution derived lithium nickel oxide cathode materials for rechargeable batteries. They synthesized LiNi_{0.80}Co_{0.20}O₂ (LNCO) and LiNi_{0.80}Co_{0.15}Al_{0.05}O₂ (LNCAIO) powders via chemical solution route using lithium acetate, nickel acetate, cobalt acetate, and aluminum nitrate as the starting materials. The electrochemical characterization of the synthesized cathode powders was carried out using a two-electrode test cell kept inside a glove box. The cyclic voltammetric studies revealed that the charge-discharge process of LNCO and LNCAIO belongs to a single-phase reaction. The charge-discharge characteristics were carried out in 3.2-4.2 V range at a constant current density of 0.45 mA cm⁻². After 2nd cycle, the discharge capacities of LNCO and LNCAIO cathode materials were stabilized at about 100.05 and 135.91 mAh g⁻¹, respectively. The capacity retention after 20 cycles was about 63% and 82% for LNCO and LNCAIO, respectively.

To enhance the cycleability of LiCoO₂ cathodes, its surface modification was carried out by the coating of TiO₂ and ZrO₂, and their mixed oxide, ZrTiO₄, using sol–gel and mechanothermal processes [65]. The coating levels were 1.0wt. % for TiO₂ and ZrTiO₄ and 0.3wt. % for ZrO₂, the coating levels at which the R-factor values were the lowest. The cycling behavior of LiCoO₂ coated with ZrO₂, TiO₂ and ZrTiO₄ showed that the first-cycle capacities of the coated samples were 162, 160 and 156mAhg⁻¹ for coatings of ZrO₂, TiO₂ and ZrTiO₄, respectively. The cycleability of the respective materials (for an 80% cut-off value based on their first-cycle capacities) was 93, 64 and 117 cycles. These represent 8-, 5- and 10-fold improvement in the cycleability, compared to the bare LiCoO₂ (12 cycles; first-cycle capacity: 169mAhg⁻¹). It was reported that the reduced first-cycle capacities of the coated materials were due to the reduced number of active Co^{3+} ions in the cathode material, as well as to a slight decrease in the capacity utilization because of the insulating surface layer on the particles.

The powders of LiCoO₂/Ag composite were prepared [66] by thermal decomposition of AgNO₃ added to commercial LiCoO₂ powders and were examined on their electrochemical performance with particular attention to their high-rate charge–discharge cycling properties as cathode materials for lithium-ion batteries. The discharge capacity of the LiCoO₂/Ag composite was found to be much higher than the precursor LiCoO₂ especially at high discharge rate. For example, the discharge capacity of the LiCoO₂/Ag composite for the first cycle was 172.3 and 133.1mAhg⁻¹ at 1C and 10C, respectively, while for the precursor LiCoO₂ was 137.6 and 113.1mAhg⁻¹ at the corresponding discharge rates. Table 1 summarized the cycling performances of the LiCoO₂/Ag composite in comparison with the precursor LiCoO₂. It can be seen from the table that the reversible capacity of the LiCoO₂/Ag composite were found to be much higher than the precursor LiCoO₂ at high charge–discharge rates.

| Table 2.1 | l:: | Summarizat | ion o | f cycling | g performanc | e for precurs | or LiCoO ₂ | and the | e LiCoO ₂ | /Ag | composi | ite |
|-----------|-----|------------|-------|-----------|--------------|---------------|-----------------------|---------|----------------------|-----|---------|-----|
|-----------|-----|------------|-------|-----------|--------------|---------------|-----------------------|---------|----------------------|-----|---------|-----|

| | Charge-discharge rate | 1C | 2C | 4C | 8C | 10C |
|----------------------------------|--|-------|-------|-------|------------|-------|
| LiCoO ₂ /Ag composite | The second discharge capacity $(mAh g^{-1})$ | 172.3 | 149.5 | 148.5 | 135.6 | 133.1 |
| | The 50th discharge capacity $(mAh g^{-1})$ | 133.9 | 129.7 | 124.3 | 119.4 | 126.6 |
| | Capacity degradation (%)* | 22.29 | 13.24 | 16.3 | 16.3 11.95 | 4.88 |
| Precursor LiCoO2 | The second discharge capacity (mAh g ⁻¹) | 137.6 | 132.2 | 128.6 | 124.1 | 113.1 |
| | The 50th discharge capacity $(mAh g^{-1})$ | 124.7 | 120.7 | 109.1 | 88.1 | 75.8 |
| | Capacity degradation (%)* | 9.38 | 8.70 | 15.16 | 29.01 | 32.98 |

Kawamura and coworkers [67] investigated the electrochemical properties of nano-sized $LiCoO_2$ powders. They investigated a new excess lithium method of preparing nano-sized $LiCoO_2$ powders. Using this method, the size of nano-sized spherical $LiCoO_2$ particles were found to be about 25 nm in diameter or needlelike $LiCoO_2$ particles with a diameter of about 5

nm and a length of about 60 nm. The discharge capacity of a $\text{Li}/5\mu\text{m}$ LiCoO₂ cell was reported as 51mAhg^{-1} , on the other hand nano-sized LiCoO₂ cathode materials showed the capacity increased to about 100mAhg^{-1} at the same cycling condition as of LiCoO₂.

On the other hand, the spinel structured lithium manganese oxide ($LiMn_2O_4$) has been considered as an ideally suitable cathode material for Li-ion batteries because of its non-toxicity, cost effectiveness and environmentally friendly nature [68-72]. However, this material suffers from insufficient cycleability and structural instability due to the formation of impurity phases and John-Teller distortion in 3-4 V regions. It was suggested that the capacity and cycle performance of this material can be enhanced by doping it with other transition metal (TM) ions, such as Ni, Cr, or non-transition metal ions, such as Mg, Al etc [73-76].

Singhal et. al. [77] synthesized pure phase $LiMn_{1.5}Ni_{0.5}O_4$ powders by chemical synthesis method. The cyclic voltammetric experiments were performed between 3.5 V and 5.3 V at a scanning rate of 0.1 mV s⁻¹. The presence of both oxidation and reduction peaks in cyclic voltammogram revealed reversible insertion and extraction of Li⁺ ions in the spinel structure. The oxidation and reduction peaks in cyclic voltammogram well correspond to the redox reactions of spinel LiMn₂O₄ and Ni²⁺/Ni⁴⁺ couple. Since nickel in LiMn_{1.5}Ni_{0.5}O₄ is oxidized and reduced at higher voltage (5.05 V and 4.862 V, respectively), LiMn_{1.5}Ni_{0.5}O₄ would be suitable for the 5 V cathode. The charge-discharge tests of the coin cell were performed in the 5 V range. The initial discharge capacity was found to be ~ 140 mAh g⁻¹ and decline to ~ 130 mAh g⁻¹ after 50 cycles.

It has been reported that the electrochemical performance of pure $LiMn_2O_4$ cathode can be improved by small (1%) substitution of Mn by Nd [78]. The lattice parameter for $LiMn_{1.99}Nd_{0.01}O_4$ was determined by XRD patterns to be ~8.2539 Å. The cyclic voltammetric tests were performed at room temperature between 3.5 V and 4.5 V vs. Li⁺/Li. Two cathodic current peaks during discharging at 3.384 V and 4.015 V, respectively, correspond to the twostep Li+ intercalation into the cathode and two anodic current peaks during charging at 4.146 V and 4.284 V correspond to Li⁺ de-intercalation out of the cathode. The initial charge and discharge capacities of LiMn_{1.99}Nd_{0.01}O₄ cathode were found to be about 166 mAh g⁻¹ and 149 mAh g⁻¹, respectively. After 25 cycles, the discharge capacity was reduced to about 132 mAhg⁻¹. Based upon theoretical calculations by Singh et al., LiMn_{1.5}Ni_{0.46}Rh_{0.04}O₄ cathode material was synthesized by sol-gel method. The synthesized powder was used as the cathode material of Liion battery. The initial charge and discharge capacities for LiMn_{1.5}Ni_{0.46}Rh_{0.04}O₄ were found to be about 163 mAh g⁻¹ and 153 mAh g⁻¹, respectively. The discharge capacity after 50 cycles was found to be about 144 mAh g⁻¹.

Santander et al [79]. optimized the synthesis of LiMn_2O_4 by chemical route technique. They annealed the synthesized powder in the temperature range of 400-850°C and found that the lattice parameter increased with the annealing temperature. This is attributed to the increased amount of high spin Mn^{3+} in the synthesized powder caused by annealing treatment. The cyclic voltammetric studies revealed the reversible nature of the LiMn₂O₄ cathode synthesized by calcinations at 700°C.

Nieto and coworkers [80] synthesized LiMn₂O₄ and Al-doped LiMn₂O₄ cathode materials by solution route technique, in which aluminum nitrate was used as the precursor of Al dopant. These powders were calcined in a 600-850 °C temperature range. The materials annealed below 700 °C were found to contain Mn₂O₃ impurity phase while pure phase material was obtained at 800 °C. The transmission electron micrograph (TEM) image showed that the particle sizes of the LiMn₂O₄ powder were in the range of 60-100 nm. During discharging, all tetrahedral sites were filled with the Li⁺ ions and were inserted into octahedral sites at about 2.8 V at which the material underwent a cubic to tetragonal structure transition with a 6.5% volume expansion (John-Teller distortion). Keeping this in mind, the charge-discharge cycling was performed in the voltage range between 3.4 V and 4.2 V, where John-Teller distortion should not occur. Thus, the initial discharge capacities of LiMn₂O₄ and Li_{1.2}Al_{0.05} Mn_{1.75}O₄ cathode materials were found to be about 120 mAh g⁻¹ and 75 mAh g⁻¹, respectively. After 25 charge-discharge cycles, the discharge capacity of LiMn₂O₄ and Li_{1.2}Al_{0.05} Mn_{1.75}O₄ cathode materials were declined to about 15 mAh g⁻¹ and 72 mAh g⁻¹, respectively. The facts above indicate that the simultaneous substitution by Li and Al increases the average oxidation state of Mn in pure phase LiMn₂O₄ cathode material, and thereby alleviates structural transition from cubic to tetragonal (John-Teller transition).

It has been reported by several researchers that Cr doped spinels could be used for 5V application [81-83]. Rajakumar and coworkers [81] have synthesized multiple-doped spinels, LiM_{0.25}Ni_{0.25}Mn_{1.5}O₄ (M = Cr, Fe, and Co) via glycine assisted sol-gel method. The initial discharge capacity of LiCr_{0.25}Ni_{0.25}Mn_{1.5}O₄, LiFe_{0.25}Ni_{0.25}Mn_{1.5}O₄, LiCo_{0.25}Ni_{0.25}Mn_{1.5}O₄ was reported as 116, 120, 80 mAh/g, respectively. They reported that LiFe_{0.25}Ni_{0.25}Mn_{1.5}O₄ cathode materials showed the best electrochemical performance upon cycling, where the capacity fading was observed as 0.05mAh/g/cycles, for 20 charge-discharge cycles. Suryakala and coworkers [88] have synthesized LiMn_{2-x}Cr_xO₄ cathode materials by sol-gel method. They observed discharge plateau in 5 V regions and found the discharge capacity increases upon increasing Cr concentration. The initial discharge capacity for 0.1, 0.2, 0.3, 0.4 Cr doping was found to be about 128, 131, 140, 142 mAh/g, respectively. They didn't report any cycleability data. Yi and coworkers [89] have reported electrochemical performance of LiMn_{1.4}Cr_{0.2}Ni_{0.4}O₄ cathode

materials in 4V range. They found that at a charge-discharge rate of 0.2 C, the cathode materials showed an initial discharge capacity of about 130.8 mAh/g in the voltage range of 3.3 V to 4.95V. After 50 charge-discharge cycles the discharge capacity was found to be about 119.5 mAh/g.

Park et al [84] synthesized Cr-doped LiMn_{1.5}Ni_{0.5-x}Cr_xO₄ (x=0.00, 0.01, 0.03 and 0.05) by sol-gel method. The lattice parameter of LiMn_{1.5}Ni_{0.5}O₄ was decreased from 8.1785 Å to 8.1656 Å after Cr doping (x=0.05), because of much stronger bonding energy of Cr with oxygen as compared to Mn. It was reported that Cr^{3+} oxidized in the 4.9 V vs. Li⁺/Li regions and the Cr^{3+} substitution suppressed Mn³⁺ generation at higher temperature, both of which contributed to the structural stabilization of LiMn_{1.5}Ni_{0.5-x}Cr_xO₄. It was also reported that the initial discharge capacity of Cr-doped LiMn_{1.5}Ni_{0.5-x}Cr_xO₄ cathode was improved (137 mAh/g, remained a 97.5% of capacity retention after 50 cycles) as compared with the pure LiMn_{1.5}Ni_{0.5}O₄ (128.67 mAh/g, being 92% of capacity retention after 50 cycles).

Synthesis of Cathode Material:

The cathode materials were synthesized by the Sol-gel method and the stepwise procedure is as follows:

Step I: Lithium acetate dihydrate [Li(CH₃COO). 2H₂O, 99%], manganese(II) acetate tetrahydrate [Mn(CH₃COO)₂·4H₂O, Mn 22%], nickel (II) acetate tetra hydrate [Ni(CH₃COO)₂.4H₂O], and chromium acetate hydroxide (Cr 24%) [Cr₃ (OH)₂(OOCCH₃)₇] (all procured from Alfa Aesar, USA) were used as a precursor materials. All precursor materials were dissolved separately as per stiochiometry LiMn_{1.5} Ni_{0.5-x}Cr_xO₄ (x = 0.1 and 0.2) in 2-ethy hexanoicacid at 80^oC. After complete dissolution of the precursor materials, all of the solutions were mixed together, followed by heating at 80^oC and stirring for about 1 hour. The final solution was then dried to obtain powder.

Step II: The dry powder was put inside oven at 450°C for 4 hours for the organic solvent removal from the synthesized powder. After the complete organic removal the material were grounds for the calcinations at various temperatures for the getting pure phase of spinel structure. It was found at 875°C for 24 h in an oxygen atmosphere for the pure phase single phase LiMn_{1.5}Ni_{0.5-x}Cr_xO₄ (x=0.1 and 0.2) cathode materials.

Step III: The degree of crystallinity and single phase of the LiMn_{1.5}Ni_{0.5-x}Cr_xO₄ (x=0.1 and 0.2) cathode material were obtained using a Siemens D5000 X-ray powder diffractometer [Cu-K α radiation, 1.5405 Å]. The cathode was prepared by mixing the calcined powder (LiMn_{1.5}Ni_{0.5-x}Cr_xO₄ (x=0.1 and 0.2), carbon type black, and polyvinylidene fluoride (in the weight ratio of 80:10:10), Subsequently a slurry was produced mixing the above mixture in the

ratio at 4000 rpm 45-60 minutes for homogeneous mixing with n-methyl pyrolidone. The resulting paste was cast uniformly onto aluminum foil followed by drying at about 80 0 C in an oven overnight. The chemical compositions of the electrode were analyzed using energy-dispersive spectrometer (EDS). X-ray photoelectron spectroscopy (XPS) measurements of LiMn_{1.5}Ni_{0.5-x}Cr_xO₄ (x=0.1 and 0.2) cathodes were performed before and after charge-discharge cycle, using PHI ESCA system (Physical Electronics) using Al K α radiation. Curve fitting of the slow-scanned XPS spectra was carried out using a nonlinear least-squares fitting program with a Gaussian–Lorentz sum function. The coin cells were fabricated in an argon atmosphere, inside a Glove Box (MBraun Inc, USA), using LiMn_{1.5}Ni_{0.5-x}Cr_xO₄ electrode as cathode, Li foil as anode, and 1M lithium hexafluoride (LiPF₆), dissolved in ethyl carbonate (EC) and dimethyl carbonate (DMC) [1:2 v/v ratio] as electrolyte. The electrochemical behavior of the cells was studied at room temperature by cyclic voltammetry and charge-discharge characteristics, using Solartron battery tester, Model 1470E. The impedance measurements of the cells were carried out using Gamry Instruments potentiostat and EIS 300 electrochemical software.


Flow chart of the synthesis of $LiMn_{1.5}Ni_{0.5-x}Cr_xO_4$ (x = 0.1 and 0.2) cathode materials

CHAPTER 3: CHARACTERIZATION STUDIES

Characterizations of Cathode Materials:

The synthesized materials were characterized structurally and electrochemically. The structural characterizations were carried out X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photo electron spectroscopy (XPS) and micro-Raman spectroscopy. The electrochemical characterizations were carried out using cyclic voltammetry and charge-discharge characteristics. The following chapter describes the basic principle of the instruments, used for various characterizations.

3.1 X-ray Diffraction:

The three-dimensional structure of non-amorphous materials is defined by regular, repeating planes of atoms that form a crystal lattice. When a focused X-ray beam interacts with these planes of atoms, part of the beam is transmitted, part is absorbed by the sample, part is refracted and scattered, and part is diffracted at characteristic repeatable angles. X-rays are diffracted by each crystalline or polycrystalline material differently, depending on what atoms make up the crystal lattice and how these atoms are arranged [85-86].

In X-ray powder diffractometry, X-rays are generated within a sealed tube that is under vacuum. A current is applied that heats a filament of the tube; the higher the current the greater the number of electrons emitted from the filament. This generation of electrons is analogous to the production of electrons in a television picture tube. A high voltage, typically 15-60 kilovolts, is applied within the tube. This high voltage accelerates the electrons, which then hits a target, commonly made of copper. When these electrons hit the target, X-rays are produced due to rapid deceleration of the electrons. The wavelength of these X-rays is characteristic of the target material. These X-rays are collimated and directed onto the sample, which has been usually ground to a fine powder (typically to produce particle sizes of less than 10 microns). A detector

detects the diffracted X-ray signal; the signal is then processed either by a microprocessor or electronically, converting the signal to a count rate. Changing the angle between the X-ray source, the sample, and the detector at a controlled rate between preset limits is an X-ray scan.

When an X-ray beam hits a sample and is diffracted, we can measure the distances between the planes of the atoms that make up the sample by applying Bragg's Law. [87]

Bragg's Law is: $2d \sin \theta = n\lambda$ Eq [3.1]



Figure 3.1 Bragg's Law

Where, the integer n is the order of the diffracted beam, λ is the wavelength of the incident X-ray beam, d is the distance between adjacent planes of atoms (the d-spacing), and θ is the angle of incidence of the X-ray beam. Since we know λ and we can measure θ , we can calculate the d-spacing. The geometry of an XRD unit is designed to accommodate this measurement. The characteristic set of d-spacing generated in a typical X-ray scan provides a unique "fingerprint" of the material present in the sample. When properly and carefully

interpreted, by comparison with standard reference patterns and measurements, this "fingerprint" allows for identification of the material [88].

Knowledge of crystal structure is a prerequisite to understanding the phenomena such as plastic deformation, alloy formation, and phase transformations. The size a shape of a unit cell determines the angular positions of the diffraction peaks, and the arrangement of the atoms in the unit cell determines the relative intensities of the peaks. It is possible to calculate the size and shape of the unit cell indirectly from the intensities of the diffraction peaks. Complete determination of an unknown crystal structure consists of three steps are;

1. Calculation of the size and shape of the unit cell from the angular positions of the diffraction peaks,

2. Computation of the number of atoms per unit cells from the size and shape of the unit cell, the chemical composition of the specimen, and its measured density.

3. Deduction of the atom positions within the unit cell from the relative Intensities of the diffraction peaks. This paper only addresses and illustrates the procedures involved with the first step of this process. We know ahead of time but will verify the structure is cubic for the reader to begin learning the basic concepts of indexing, Bravais lattice identification, and lattice parameter calculation.

In our studies we have used Siemens D5000 X-ray powder diffractometer (XRD) (D5000Model.) with Cu K α radiation (λ) 0.15406 nm at 40 kV and 40 mA).



Figure 3.2 Siemens D5000 X-ray powder diffractometer

3.2 Scanning Electron Microscopy (SEM):

The primary use of SEM is to study the surface topography of solid samples. The resolution of these instruments is typically between 1.5 and 3.0 nm, approximately, two order of magnitude better than optical microscopes and one order of magnitude less than transmission electron microscopes, thereby bridging the gap between these related techniques. SEM imaging is often preferred in place of optical imaging because of the enhanced depth of field. Any solid material may be studied.

Electrically conductive materials may be examined directly; nonconductive materials may require a thin conductive coating to prevent electrical charging of the specimen. Sample size is limited to specimen less than about 10 cm in diameter [90].

In SEM an electron beam passing through an evacuated column is focused by electromagnetic lenses onto the specimen surface. The beam is then rastered over the specimen in synchrony with the beam of a cathode ray display screen. The (inelastically scattered)

secondary electron emission from the sample (determined to a large extent by the surface topography) is then used to modulate the brightness of the cathode ray display screen, thereby forming the image, the image contrast is determined largely by compositional differences of the sample surface rather than topographic features. In cases where the sample surface consists of both topographic and compositional features [100], image interpretation can become quite complex and a multi detector system may be required. SEM microstructures were investigated using JEOL 35 CF microscope in secondary electron mode at an accelerating voltage of 5 kV to image the surface of carbon –based films. The surface morphology was revealed from SEM images and the average grain size was estimated, albeit qualitative [91].

3.3 X-ray Photoelectron Spectroscopy (XPS):

X-Ray photoelectron spectroscopy (XPS), or electron spectroscopy for chemical analysis (ESCA), is a surface-sensitive spectroscopy tool that provides information about the chemical state and concentration of elements comprising the outermost surface layers of a solid. Any materials can be studied using XPS. All elements, with the exception of H and He, can be detected [92].

When a solid is exposed to a flux of X-ray photon of known energy, photo-electrons are emitted from the solid. These photoelectrons originate from discrete electronic energy levels associated with those atoms in the analysis volume. The energy of the emitted photoelectrons is given by

$$E_k = hv - E_b - vs$$
 Eq. [3.2]

Where hu is the characteristic photon energy of the excitation source, E_k and E_b are the measured photoelectron kinetic energy and binding energy of a specific core or valence level

electron, respectively, and vs. is a parameter that depends on the work function of the spectrometer being used Since ionization may occur in any shell for a particular atom (with varying probability), the spectrum for that element is usually composed of a series of peaks corresponding to electron emission from the different shells. This allows for unambiguous elemental identification, since the energy separation and relative intensities of the peaks for a given element are well known. Additionally, ionization for p, d, or f levels leads to doublet structure in the spectrum as a result of spin orbit interactions.

For example, as a consequence of spin orbit interactions, the 2p electronic energy levels associated with transition metals are split into distinct peak, i.e., $2p_{1/2}$ and $2p_{3/2}$. Elements with higher atomic numbers have peaks reflected the $3d_{3/2}$, $3d_{5/2}$, and $4f_{5/2}$, $4f_{7/2}$ spin orbit energy separation. Many of these transitions are characteristic of the element in a particular oxidation state [93].

Photoelectrons are generally characterized by very short mean free paths within a solid. Photo emitted electrons traveling through a solid have a relatively high probability of interacting with neighboring atoms and undergoing inelastic energy loss process before the leaving the sample surface. Those electrons that are able to escape without a loss in energy appear in XPS spectra at discrete energies above a smooth background of in elastically scattered electrons. The distance that an electron can traverse through the solid before experiencing inelastic scattering is defined as the mean free path or photoelectron attenuation length (λ).

XPS measurements for elemental analysis were taken using a physical electronic system (Model PHI5600 ESCA) at room temperature, which was operated in the constant pass energy mode using monochromatic Al K α X-radiation (hu=1486.6 eV) operating at 400 W (15kV and

27 mA). The monochromatic X-ray source is located perpendicular to the analyzer axis, and the standard X-ray source is located at 54.70 relatively to the analyzer axis. The spectra were analyzed at an electron take off angle 70° , measured with respect to the surface plane and stored using PHI ACCESSTM data system. To ensure the accuracy of the data, the instrument is calibrated with known conducting specimen, typically Au4f (84.00 eV), or Cu2p (932.66 eV), and Cu3p (75.13 eV), lines. Utilizing these standard energies establishes the linearity of the energy scale and its position, i.e. the location of the Fermi level. The resolution of the electron energy analyzer was about 0.25 eV. The elemental peaks were fitted using Gaussian profiles and a linear background using the software provided by Perkin-Elmer.



Figure 3.3 Perkin-Elmer PHI-5600 XPS (X-ray photo-electron spectrometer)

3.4 Raman Spectroscopy:

The Raman shift depends upon the energy spacing of the molecules. There are 3N-3 optical normal modes in any material where N is the number of atoms. However not all modes are "Raman active" i.e. not all modes appear in Raman spectra. For a mode to be Raman active it must involve a change in the polarisability, α of the molecule.

Polarisability of the molecule:

$$\alpha = \alpha_0 + \alpha_1 \sin(2\pi v_{vib}t)$$
 Eq [3.3]

There is an external oscillating electric field from the photon, with a frequency vp:

$$\mathbf{E} = \mathbf{E}_0 \sin \left(2\pi \mathbf{v}_{\mathrm{p}} \mathbf{t} \right) \qquad \qquad \mathbf{E}\mathbf{q} \ [3.4]$$

Therefore the induced dipole moment is:

 $P_{ind} = \alpha_0 E_0 \sin (2\pi v_p t) + \alpha_0 E_0 / 2\cos (2\pi (v_p - v_{vib})t) - \alpha_0 E_0 / 2\cos (2\pi (v_p + v_{vib})t) Eq[3.5]$

A dipole moment oscillating at frequency v results in a photon of frequency v. Therefore in this case there are photons scattered at frequency v_p (Rayleigh scattering), $v_p - v_{vib}$ (Stokes scattering) and $v_p + v_{vib}$ (anti-Stokes scattering). Of course if the polarisability is not changing then the dipole moment will simply oscillate at frequency v_p , and only Rayleigh scattering will occur. This is the origin of the spectroscopic selection rule for

In this chapter, we present the vibrational properties of some cathodes materials with either spinel-type or layered-type structure. Lattice dynamics is studied using either a classical group theoretical analysis or a local environment model. Raman bands are identified on the basis of vibrational modes of polyhedral units, which are building the structure. Structural modifications induced by intercalation-deintercalation process, cation substitution, and/or by room temperature preparation route are examined. First, we present some theoretical aspect about of the vibrational spectroscopy, and then the experimental results of Raman study of the cathode materials.



In Materials Science Raman techniques are more often used for solids, where molecules cannot be taken individually. In crystalline materials vibrations are quantized as phonons modes, determined by the crystal structure. The spectroscopic selection rules still apply, i.e. only phonons with a change in the polarisability are Raman active. Phonons in solids are generally of a lower frequency than the vibrations in gases, so result in lower wave number shifts. Structural information can, therefore, be determined from these shifts [94-96].

Crystal orientation can also be determined from the polarization of the scattered light



Octahedra Raman Modes (Mn-O)



Tetrahedra Raman modes (Li-O)



3.5 Potentiostat/Galvanostat:

The potentiostat is a device for controlling the potential between reference electrode (RE) and working electrode (WE) at a fixed and selected potential. The simplest set up, which is of little practical use but outlines the principle, is shown in Figure 3.4 where the cell has been approximated by a very simple equivalent circuit of a solution resistance in series with a double layer capacitance.

It can be seen that the device is simply a voltage follower maintaining the output voltage between reference electrode (RE) and working electrode (WE) at the programming potential E1. WE have a potential-E1 relative to RE, so that the input voltage is inverted in the cell. Also in this arrangement there is no device for measuring the current though the cell and the potentiostat is unable to apply more than a single potential at any one time.



Figure 3.4 Simple Potentiostat for maintaining a constant potential between RE and WE; Rs is the Solution resistance between the RE probe and the CE; Ru the un compensate resistance luggin tip and WE

The simplest way to obtain a constant current is to apply a voltage from low output impedance voltage sources across a large resistor in series with the cell, the current will be given by the ratio E_{in}/R (the provided resistance R is very large compared with the impedance of the cell).Several operational amplifier circuits are also available for galvanostat. Two of the simplest are shown in Figure 3.5. The circuit arrangement is that of the voltage follower with the cell in the feedback loop, and the current is again determined by the ratio Ein/R. The configuration in Figure 3.5 (a) has the advantage that working electrode (WE) is at virtual ground. Thus, the reference potential, E_{ref} , can be monitored using a voltage follower.



Figure 3.5 Two galvanostat circuits employing operational amplifiers.

However, the output impedance of the voltage source, Ein, must be able to supply the required current into the feedback loop. In the configuration of Figure 3.5(b) the current is supplied by the output of the operational amplifier, but the working electrode is not at virtual ground, so that R_{ref} has to be monitored with a differential voltmeter. Most potentiostats can be

converted to a galvanostat by inserting a standard resistor R between working and reference inputs of the instrument and then by connecting WE to RE input and CE in the normal configuration.

Galvanostatic cycling (or cycling chronopotentiometry [97]) is an important method for electrochemical evolution of battery materials. A constant current (I) is here applied to the cell, and the potential is monitored as a function of time (t). The total amount of charge passed per unit mass of electrode material, i.e. the specific capacity C, during complete discharge (or charge) is given by:

C=It/m Eq. [3.2]

Data from galvanostatic measurements are often displayed as cell voltage E as a function of C. The cycleability of the material is usually presented as the total charge or discharge capacity, C, as a function of cycle number. C will sometimes contain both irreversible, C_{irr} , and reversible, C_{rev} components, where C_{irr} is obtained from the discharge and charge capacity difference (C_{dch} - C_{cha}). The cycling rate is usually given as C/N; Where N is the time in hours for a full discharge or charge.

Pulsed galvanostatic techniques can be useful for determining kinetic (and thereby power) Characteristics of an electrode material or an entire battery. Here, a short current pulse between t_0 and t_1 is applied and the potential response is monitored. This is shown schematically in Fig, 3.6 from the potential response, a cell resistance (R) can be obtained according to:

$$R = (Vt_o - Vt_1) / (It_o - It_1)$$
 Eq. [3.3]



Figure 3.6 Schematic representation of the potential response to a current pulse

The area dependent resistance (ASI, Area Specific Impedance) is a better unit for comparison between cells and electrode materials [98, 99].

ASI = R.Material Area (cm2) Eq. [3.4]

R and ASI represent an overall cell impedance with the major contributions coming from:1) electron transfer from the cell terminals to the reaction sites,2) electrode reactions involving active material and electrons, and 3) charge and mass transport in the electrolyte and electrodes via ions and reactant molecules. The separation of various impedance components is a complicated matter and alternating current (AC) methods are needed (EIS). This technique has not been used in this study.

3.6 Cyclic Voltammetry:

Cyclic voltammetry is an attractive method for teaching a number of concepts in electrochemistry. Electrolysis, cyclic voltammetry, amperometry and several other techniques might be described as "active" electrochemical methods because the experimenter drives an electrochemical reaction by incorporating the chemistry into a circuit and then controlling the reaction by circuit parameters such as voltage. In typical cyclic voltammetry, a solution component is electrolyzed (oxidized or reduced) by placing the solution in contact with an electrode surface, and then making that surface sufficiently positive or negative in voltage to force electron transfer. In simple cases, the surface is started at particular voltage with respect to a reference half-cell such as calomel or Ag/AgCl, the electrode voltage is changed to a higher or lower voltage at a linear rate, and finally, the voltage is changed back to the original value at the same linear rate. When the surface becomes sufficiently negative or positive, a solution species may gain electrons from the surface or transfer electrons to the surface. This results in a measuring current in the electrode circuitry. However, if the solution is not mixed, the concentration of transferring species near the surface drops, and the electrolysis current then falls off. When the voltage cycle is reversed, it is often the case that electron transfer between electrode and chemical species will also be reversed, leading to an "inverse" current peak. These features are illustrated in Figure 3.7

The wave form of the voltage applied to the working electrode versus the reference electrode is triangular shaped. Since this voltage varies linearly with time, the slope is referred to as the scan rate (V/s). The peak shape of the oxidative and reverse current–potential (I-E) curve in figure 3.7 is typical for an electrode reaction in which the rate is governed by diffusion to a planar electrode surface. That is, the rate of the electron transfer step is relatively fast compared to that of diffusion. In such a case the peak current, I_p , is governed by the Randle-Sevcik relationship:

$$I_p = kn^{3/2}AD^{1/2}CV^{1/2}$$
 Eq [3.5]

Where the constant, k, has a value of 2.72*105; n is the mole of electrons transferred per mole electro active species; A is the area of the electrode in cm²; D is the diffusion coefficient in cm²/s; C is concentration, in mole/L; V is the scan rate of the potential in vol/s, the Ip is linearly proportional to the bulk concentration, C, of the electro active species and the square root of the scan rate, V^{1/2}, thus, an important diagnostic reaction is controlled by diffusion, which is mass transport of electroactive species to the surface of the electrode across a concentration gradient, the thickness, d, of the diffusion layer can be approximated by: d~[Dt]^{1/2}, where D is the diffusion coefficient and t is time in seconds, A "quiet" i.e. unstirred solution is required. The presence of supporting electrolyte is required to eliminate movement of the charged electroactive species due to migration in the electric field gradient [100].

3.6.1 Cyclic voltammogram of spinel structure electrodes:

The charge/discharge reaction for $LiMn_20_4$ in the high voltage plateau (4V) can be represented as show in Eq [3.6]

$$LiMn_2O_4 \rightarrow Li_{1-x}Mn_2O_4 + xLi^+ + xe^- (0 < x < 1) Eq [3.6]$$

Figure 3.7 show the cyclic voltammogram of LiMn_2O_4 electrodes in voltage range of 3.4 V to 4.3 V and at a scan rate of 0.1 mV/s. It can be seen from Figure that, two voltammetric waves are observed indicating that the material change phases during the intercalation process [101,102].

The lower potential wave (centered at 4.04V) corresponds to Li^+ insertion and removed over the x value range of 0<x<0.5 (Eq.) In $Li_xMn_2O_4$. The high potential wave (centered at 4.22V) corresponds to Li^+ insertion and removal over the x value range 0.5<x<1.



Figure 3.7 Cyclic Voltammogram of LiMn₂O₄ cathode

The anodic and cathodic peaks observed in the cyclic voltammogram of the $LiMn_2O_4$ sample reflect reversible oxidation and reduction reactions corresponding to lithium extraction and insertion [103]. Two separated pairs of electrochemical peaks are seen both oxidation and reduction, indicating that the insertion and extraction of lithium ions occur in two stages [104].

The first peak at about 4.12 V is attributed to the removal of lithium ions from half of the tetrahedral sites in which Li/Li⁺ insertions occur. The second peak observed at about 4.22 V is due to the removal of lithium ions from the other tetrahedral sites in which lithium ions do not have Li-Li interactions. The area of two oxidation and reduction peaks are essentially equal which indicates that in each stage lithium ions occupy half of the total available crystallographic

sites. Moreover, if the peaks are sharp and show well defined splitting, these are the characteristic of the materials with high degree of crystallinity [105].



Figure 3.8 Solartron Battery Tester at Speclab (Model 1470E)

In the present studies, the electrochemical testing of the cells were carried out by cyclic voltammetry and charge-discharge characteristics, using Solartron battery tester (1470E), with cell test software (Solarton Analytical).

3.7 Electrochemical Impedance Spectroscopy:

Electrochemical Impedance Spectroscopy (EIS) is an electrochemical technique with applications in corrosion, battery development, fuel cell development, physical electrochemistry. The reason for this popularity is the high information content of EIS. EIS provides a more thorough understanding of an electrochemical system than any other electrochemical technique. EIS experiment involves the application of a sinusoidal electrochemical perturbation (potential or current) to the sample that covers a wide range of frequencies. This multifrequency excitation allows (1) the measurement of several electrochemical reactions that take place at different rates and (2) the measurement of the capacitance of the electrode.

3.7.1 Li/Li_xMnO₂ Cells:

The impedance of Li electrodes in different electrolytes for Li accumulators has been studied by various authors [106-110]. The main objectives were to find out the correlation between the impedance parameters and the cycling efficiency of the Li electrode. A general interface model was applied in this thesis. It was analogous to the one used for passivated Li in some of electrolytes for primary Li cells, such as LiSOCl₂ [111-113]. Fig.3.9 shows a typical impedance plot of the Li electrode in a Li/Li_xMn₂O₄/LiPF₆ (1:1 v/v ratio) coin cell in a charged state (4.9 V).

The ac impedance measurements were performed at open circuit voltage in galvanostatic mode with ac current amplitude of $10 \,\mu$ A. In order to reach the steady-state condition,



Figure 3.9 Nyquist plot of an overcharged Li electrode on a Li/LixMn₂O₄ accumulator

Impedance measurements were carried out 45-60 minutes after the cycling was completed. The first loop at high frequencies is characteristic of the charge transfer process at the Li/electrolyte interface. A second inductive loop at low frequencies corresponds to the relaxation process involving adsorbed intermediates.

CHAPTER 4: RESULTS AND DISCUSSION

The synthesized material LiMn_{1.5}Ni_{0.4}Cr_{0.1}O₄ was structurally characterized using XRD, Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). The electrochemical characterizations were characterized in a coin cell configuration by cyclic voltammetry, chargedischarge characteristics, and impedance spectroscopic techniques. The cyclic voltammetric and charge-discharge studies were performed at room temperature using Solartron battery tester, Model 1470E. The impedance measurements of the cells were carried out using Gamry Instruments potentiostat and EIS 300 electrochemical software. For the comparison XRD and electrochemical performance of LiMn_{1.5}Ni_{0.3}Cr_{0.2}O₄ cathode material is also discussed.

The coin cells were fabricated in an argon atmosphere, inside a Glove Box (MBraun Inc, USA), using LiMn_{1.5}Ni_{0.5-x}Cr_xO₄ (x = 0.1 and 0.2) electrode as cathode, Li foil as anode, and 1M lithium hexafluoride (LiPF₆), dissolved in ethyl carbonate (EC) and dimethyl carbonate (DMC) [1:1 w/w ratio] as electrolyte[114]. The obtained data of structural and electrochemical behavior of LiMn_{1.5} Ni_{0.5-x}Cr_xO₄ (x = 0.1 and 0.2) were compared with earlier reported data by our group on LiMn₂O₄ and LiMn_{1.5}Ni_{0.5}O₄ cathode materials.

4.1 X-Ray Diffraction Studies:

Figure 4.1 showed the XRD pattern of LiMn₂O₄, LiMn_{1.5}Ni_{0.5}O₄, and LiMn_{1.5}Ni_{0.4}Cr_{0.1}O₄ LiMn_{1.5} Ni_{0.3}Cr_{0.2}O₄ cathode materials. All peaks were found corresponds to Fd3m spinel crystal structure. XRD pattern showed very high intensity of the peaks corresponds to (111), (311), and (400) plane, indicates the well crystalline nature of the materials and the occupancy of Li ions in tetrahedral (8a) sites. The manganese, chromium and nickel ions occupy octahedral (16d) sites and O²⁻ reside at the general positions (32e) [115]. The lattice parameter of LiMn₂O₄, LiMn_{1.5}Ni_{0.5}O₄, LiMn_{1.5}Ni_{0.4}Cr_{0.1}O₄, and LiMn_{1.5}Ni_{0.3}Cr_{0.2}O₄ were obtained using interactive powder diffraction data interpretation and indexing program POWDMULT [116] and were found as 8.2470 Å, 8.1835 Å, 8.1707 Å, and 8.1685 Å, respectively. The lattice parameters, unit cell volume and the standard deviations are given in Table 4.2.



Figure 4.1. Powder diffraction patterns of (a) LiMn₂O₄ (b) LiMn_{1.5}Ni_{0.5}O₄ (c) LiMn_{1.5}Ni_{0.4}Cr_{0.1}O₄ and (d) LiMn_{1.5}Ni_{0.3}Cr_{0.2}O₄ Cathode materials at 875°C for 24 hr ia O₂ atmosphere.

The lattice parameter of $\text{LiMn}_{1.5}\text{Ni}_{0.4}\text{Cr}_{0.1}\text{O}_4$ and $\text{LiMn}_{1.5}\text{Ni}_{0.3}\text{Cr}_{0.2}\text{O}_4$ cathode material was less than that of the lattice parameter of pure LiMn_2O_4 (8.247 Å) [117], and $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cathode materials, because ionic radii of Cr^{3+} (0.615 Å) is less than that of the ionic radii of Ni^{2+} (0.69 Å), and Mn^{3+} (0.66 Å) results strong bonding energy of Cr with oxygen than Mn or Ni [118].

| Material | Peak position of 400 peak (2θ) | Lattice Parameter (Å) | Unit cell volume (Å ³) | Standard Deviation (Å) |
|--|-----------------------------------|--------------------------|---------------------------------------|------------------------|
| LiMn ₂ O ₄ | 44.18 | 8.247 | 560.90 | 0.0111 |
| LiMn _{1.5} Ni _{0.5} O ₄ | 44.21 | 8.1835 | 548.04 | 0.0138 |
| $LiMn_{1.5}Ni_{0.4}Cr_{0.1}O_4$ | 44.26 | 8.1707 | 545.47 | 0.00206 |
| LiMn _{1.5} Ni _{0.3} Cr _{0.2} O ₄ | 44.44 | 8.1685 | 545.03 | 0.00189 |

Table4. 2: lattice parameters, unit cell volume and the standard deviations of various Cathode materials

Further, as confirm by XPS results, doping of Cr^{3+} and Ni^{2+} in $LiMn_2O_4$ consequences the formation of Mn^{4+} (ionic radii 0.60 Å) and the bond length of Mn^{4+} -O is less than that of the bond length of Mn^{3+} -O, resulting the decreased lattice parameter.

4.2 XPS studies:

XPS studies of cathode material were carried out to find out the oxidation states of the different element in the material. Figure 4.2 showed two peaks in the XPS spectra of Ni are found at 858.30 eV and 855.22 eV. The peak at 858.30 eV is corresponds to Ni³⁺ and the peak at 855.22 eV is due to Ni²⁺ oxidation states [119]. The peak obtained at 642.48 eV is corresponds



Figure 4.2 XPS spectra of LiMn_{1.5}Ni_{0.4}Cr_{0.1}O₄ cathode material.

to Mn⁴⁺ oxidation state and the satellite peak obtained at 654.22 eV is in agreement as reported in the literature [119]. There is no peak obtained at 641 eV, indicating that Mn is not

presented in Mn^{3+} state [120]. The Cr peak appears at 576.21 eV, indicates that the Cr is in 3+ state .The binding energy of the O1s is found as 529.74 eV.

4.3 Raman Studies:

Raman scattering is quite sensitive to changes in the local lattice distortions and change in polarizability arising due to delithiation process in lithium based rechargeable batteries. The LiMn₂O₄, LiMn_{1.5}Ni_{0.5}O₄, and LiMn_{1.5}Ni_{0.4}Cr_{0.1}O₄ are characterized by spinel structure with the space group (Fd3m) [121]. The Raman active modes can be classified as follows[122]: $\Gamma = Ag+$ Eg + 3F2g, The Raman scattering data of LiMn₂O₄, LiMn_{1.5}Ni_{0.5}O₄, and LiMn_{1.5}Ni_{0.4}Cr_{0.1}O₄ cathode materials were obtained by employing normal backscattering geometry and the results are presented in Fig 4.3 a and 4.3 b.



Figure 4.3 a: Micro Raman spectra of LiMn₂O₄, LiMn_{1.5}Ni_{0.5}O₄ cathode materials

Figure 4.3 a showed the Raman spectra of $LiMn_2O_4$ and $LiMn_{1.5}Ni_{0.5}O_4$ cathode materials. Figure 4.3 a shows the Raman spectra of pure $LiMn_2O_4$ and $LiMn_{1.5}Ni_{0.5}O_4$ cathodes both in virgin state and after 50 repeated cycles of charge discharge at $0.2mAcm^{-2}$. In case of

pure LiMn₂O₄, the A_{1g} mode appeared at 627.27 cm⁻¹ before charge – discharge and after 50 cycles it shifted to 628.06 cm⁻¹, indicating slight decrease in Mn-O bond length. Besides this, after 50 charge-discharge cycles of LiMn₂O₄, a new band appears at 658cm⁻¹, which may be due to further shortening and distortion of Mn – O bond as reported by Julian and Massot [42]. However, the broadness to intensity ratio remained unchanged before and after the electrochemically cycling. This suggested a little tetrahedral distortion in the sample. The $T_{2g}^{(3)}$ mode was not prominent in pure LiMn₂O₄ sample, indicating the mixed valence nature of Mn oxidation state. However, after electrochemical tests, a prominent band appeared around 342 cm¹, which may be assigned to Li-O vibration. In case of $LiMn_{1.5}Ni_{0.5}O_4$ sample, the A_{1g} mode appeared at 636.43 cm⁻¹ in the virgin sample, and it shifted to 638.51 cm⁻¹ after the chargedischarge tests, suggesting a decrease in the bond length compared to pure LiMn₂O₄. The Ni²⁺-O vibration band appears at 500 cm⁻¹ and it is shifted to 492 cm⁻¹ after 50 charge-discharge cycles, which may be due to Ni³⁺ - O stretching mode [35]. The appearance of $T_{2g}^{(3)}$ mode at 586 cm⁻¹ in the case of LiMn_{1.5}Ni_{0.5}O₄ confirmed the increased oxidation state of Mn towards +4. This is an important observation, as the presence of Mn⁴⁺ in the spinel lattice inhibits the dynamic Jahn-Teller transition during the electrochemical cycling.

This explains the improved electrochemical properties of the cells containing $LiMn_{1.5}Ni_{0.5}O_4$ cathodes. Additionally, we observed $T_{2g}^{(2)}$ mode in these samples, but their Raman shifts remained unchanged after Galvanostatic cycling. We observed instance Raman modes at 388, 496, 583 (Fig 4.3 b), which are comparable to the earlier reported Raman spectra of LiMn₂O₄ with the same cubic (Fd3m) symmetry [123-125].

These Raman modes also shows a systemic change in Raman intensity with electrochemical cycling process i.e. Raman intensity of all the MnO_6 generated optical modes decreases during charging process and vice versa during discharging process



Figure 4.3 b: Micro Raman spectra of LiMn_{1.5}Ni_{0.4}Cr_{0.1}O₄

It reveals that the polarizibily derivatives of the $LiMn_{1.5}Ni_{0.4}Cr_{0.1}O_4$ changes during Li deintercalation because the vibrational potential energy of the MnO₆ octahedra is affected by change in Li/Li⁺, Mn³⁺/Mn⁴⁺, Ni²⁺/Ni⁴⁺ and Cr³⁺/Cr⁴⁺, ⁺ ions during the Li deintercalation/ intercalation. From the Raman results, structural stability and electrochemical reversibility of LiMn_{1.5}Ni_{0.4}Cr_{0.1}O₄ was observed clearly during the charging and discharging process.

4.4 EDS Studies:

The EDAX spectra of $LiMn_2O_4$, $LiMn_{1.5}Ni_{0.5}O_4$, $LiMn_{1.5}Ni_{0.4}Cr_{0.1}O_4$, and $LiMn_{1.5}Ni_{0.3}Cr_{0.2}O_4$ cathode materials are given in Figure 4.4. All of the spectra showed peak correspond to oxygen, carbon and fluorine, which are due to the active material, carbon black

and PVDF binder, respectively, present in the cathode. Besides this, EDAX spectra of $LiMn_2O_4$, $LiMn_{1.5}Ni_{0.5}O_4$, $LiMn_{1.5}Ni_{0.4}Cr_{0.1}O_4$, and $LiMn_{1.5}Ni_{0.3}Cr_{0.2}O_4$ showed peak for Mn, Mn and Ni, Mn, Ni and Cr, respectively and there is no other impurity peak in the synthesized materials, indicate that the synthesized materials are free from any other impurity.



Figure 4.4. EDS spectra of various cathode materials.

4.5 Cyclic Voltammetric Studies:

The cyclic voltammetric studies of $LiMn_2O_4$ were carried out at room temperature in the voltage range of 3.4 V to 4.3 V and at a scan rate of 0.1 mV/S. The two oxidation peaks for pure

LiMn₂O₄ cathode materials (Fig. 4.5 a) were obtained at 4.12 V and 4.22 V, and the two reduction peaks were obtained at 3.90 V and 4.04 V that correspond to Mn^{3+}/Mn^{4+} redox couple.



Figure 4.5 b showed the cyclic voltammogram of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ / LiPF_6 +(EC+DMC)/Li coin cells at a voltage scan rate of 0.1 mV/sec. It can be seen from Figure that oxidation peak at 4.08 V and reduction peak at 3.91 V is due to $\text{Mn}^{3+}/\text{Mn}^{4+}$ oxidation and reduction, respectively. The oxidation peak at 4.83 V (with a shoulder at 4.74 V) and reduction peak at 4.58 V are corresponds to $\text{Ni}^{2+}/\text{Ni}^{3+}$ and $\text{Ni}^{3+}/\text{Ni}^{4+}$ redox couple, respectively, indicating the substitution of Mn by Ni in $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$.

Cyclic voltammetric studies of $LiMn_{1.5}Ni_{0.4}Cr_{0.1}O_4$ cathode material were carried out in $LiMn_{1.5}Ni_{0.4}Cr_{0.1}O_4/LiPF_6+(EC+DMC)/Li$ coin cells at room temperature and in the voltage range of 3.0 V to 5.0 V and at a scan rate of 0.1 mV/s. The cyclic voltammogram showed [Figure 4.5 c] three well defined oxidation peaks at 4.07 V, 4.76 V, and 4.87 V. The peak at 4.07 V is

due to Mn^{3+}/Mn^{4+} redox couple while the peaks at 4.76 V and 4.87 V is due to Ni^{2+}/Ni^{4+} , and Cr^{3+}/Cr^{4+} redox couple, respectively [126]. The oxidation peak at 4.87 V indicates that this material can be used for 5 V applications.



Figure 4.5 c. Cyclic Voltammogram of LiMn1.5Ni0.4Cr0.1O4 /LiPF6+(EC+DMC)/ Li coin cell in 3.0 V- 5.0 V range, at a voltage scan rate of 0.1mV/sec.

4.6 Charge-Discharge Characteristics:

Figure 4.6a shows the charge discharge characteristics of the $LiMn_2O_4$, obtained at room temperature in 4 V range (3.4 V – 4.3 V) at a charge-discharge current of C/5. Each chargedischarge curve showed two plateaus during charging and discharging. It can be seen from 1st charge-discharge of pure $LiMn_2O_4$ that the two plateau during charging were obtained between 3.9 V to 4.02 V and 4.12 V to 4.16 V and the two plateau during discharging were obtained between 4.14 V to 4.07 V and 4.0 V to 3.87 V corresponding to Mn^{3+}/Mn^{4+} redox couple. It can be seen from Figure 4.6a that pure $LiMn_2O_4$ showed initial discharge capacity of 128.75 mAh/g with 76.74% capacity retention after 50 charge-discharge cycles. This fading in the discharge capacity of $LiMn_2O_4$ may be due to the Mn dissolution in the electrolyte.



It can be seen from Figure 4.6b that Ni substituted $LiMn_2O_4$ cathode materials showed two plateau between 4.73 V to 4.5 V and 4.2 V to 3.9 V range, which correspond to Ni²⁺/Ni⁴⁺ and

 Mn^{3+}/Mn^{4+} oxidation and reduction, respectively. It shows that Ni substituted Li Mn_2O_4 cathode materials can be used up to higher discharge voltage of 4.8 V and hence as high energy density materials for Li ion rechargeable batteries.

The charge-discharge characteristics of LiMn_{1.5}Ni_{0.4}Cr_{0.1}O₄/LiPF₆ (EC+DMC)/Li coin cells were carried out at room temperature in 3.0V- 4.9 V range, at various current rate of C/5, C/2, and C, where C = 147 mAh/g. Figure 4.6c showed the charge discharge behavior of LiMn_{1.5}Ni_{0.4}Cr_{0.1}O₄/LiPF₆ (EC+DMC)/Li coin cells at a constant charge-discharge rate of C/5. It can be seen from figure that initial discharge capacity was 108 mAh/g, which increases gradually up to 10^{th} consecutive charge-discharge cycles and reached at a maximum value of 126 mAh/g. The electrode showed stable behavior upon cycling and after 50 charge-discharge cycles the discharge capacity was found to be about 123.7 mAh/g. Figure 4.6d showed the charge discharge rate of C/5. It can be seen from figure that initial discharge capacity coin cells at a constant charge-discharge cycles the discharge capacity was found to be about 123.7 mAh/g. Figure 4.6d showed the charge discharge rate of C/5. It can be seen from figure that initial discharge capacity was 84 mAh/g, which increases gradually up to 10^{th} consecutive charge-discharge cycles and reached at a maximum value of 88 mAh/g. The electrode showed stable behavior upon cycling and after 50 charge-discharge discharge discharge cycles the discharge capacity was found to be about 123.7 mAh/g. Figure 4.6d showed the charge discharge behavior of LiMn_{1.5}Ni_{0.3}Cr_{0.2}O₄/LiPF₆ (EC+DMC)/Li coin cells at a constant charge-discharge rate of C/5. It can be seen from figure that initial discharge capacity was 84 mAh/g, which increases gradually up to 10^{th} consecutive charge-discharge cycles and reached at a maximum value of 88 mAh/g. The electrode showed stable behavior upon cycling and after 50 charge-discharge cycles the discharge capacity was found to be about 83 mAh/g.b

4.7 Cycleablility Studies:

Figure 4.7a showed the cycleability behavior of LiMn_2O_4 and $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cathode materials. It can be seen from the figure that LiMn_2O_4 cathode material showed initial discharge capacity of about 128.75 mAh/g, with 76.74 % discharge capacity retention after 50 charge-discharge cycles. The maximum discharge capacity and discharge capacity retention of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cathode material was found to be about 140 mAh/g and 98%, respectively.



Figure 4.7b showed the cycleability of $\text{LiMn}_{1.5}\text{Ni}_{0.4}\text{Cr}_{0.1}\text{O}_4$ / $\text{LiPF}_6(\text{EC+DMC})$ /Li coin cells at various C rates (C, C/2, and C/5). The maximum discharge capacity at C, C/2, and C/5 current was found to be about 100, 110, and 126 mAh/g, respectively. Discharge capacity retention after 50 charge-discharge cycles at C/5, C/2, and C current rate was found as 98.5%, 97.2%, and 96%, respectively.

Figure 4.7c showed the cycleability of $\text{LiMn}_{1.5}\text{Ni}_{0.3}\text{Cr}_{0.2}\text{O}_4$ / $\text{LiPF}_6(\text{EC+DMC})$ /Li coin cells at various C rates (C, C/2, and C/5). The maximum discharge capacity at C, C/2, and C/5 current was found to be about 71, 73, and 88 mAh/g, respectively. Discharge capacity retention after 50 charge-discharge cycles at C/5, C/2, and C current rate was found as 94%, 97%, and 98%, respectively.

4.8 Impedance Spectroscopic Studies:

Figure 4.8 showed the impedance spectra of $LiMn_{1.5}Ni_{0.4}Cr_{0.1}O_4/LiPF_6+(EC+DMC)/Li$ coin cell before and after charge-discharge cycles The impedance spectra were obtained within the frequency range of 10mHz to 1 MHz. It can be seen from the figure that the charge-transfer resistance doesn't change upon cycling.



Figure 4.8. Impedance spectra of LiMn_{1.5}Ni_{0.4}Cr_{0.1}O₄ /LiPF₆+(EC+DMC)/ Li coin cell, before and after 50 charge-discharge cycles.
Before and after charge-discharge cycles, the charge-transfer resistance was found to be about 78 Ω , indicating that there is no SEI layer formation on the surface of cathode after chargedischarge cycling, which is the main cause of stable behavior of the cells. The slope of the inclined line at low frequency region is almost same, indicating that

the Warburg impedance in the low frequency region doesn't change, confirms that there is no change in Li⁺ activity upon cycling [127].

Summary:

It was reported earlier by our group that $LiMn_2O_4$ showed huge capacity fading upon cycling and after 50 charge and discharge cycles (in 3.4-4.3 V range), the capacity retention was found as 69.23%. Further, by replacing Mn with 25% Ni in $LiMn_2O_4$, i.e. $LiMn_{1.5}Ni_{0.5}O_4$, the cathode material showed an enhancement in working potential and cycleability. The charge-discharge behavior of $LiMn_{1.5}Ni_{0.5}O_4$ showed a plateau around 4.7 V and 90% capacity retention after 50 charge-discharge cycle with a maximum discharge capacity of 140 mAh/g. In order to improve working voltage range, we have synthesized phase pure $LiMn_{1.5}Ni_{0.5-x}Cr_xO_4$ (x=0.1 and 0.2) cathode materials by sol-gel method.

It was found that upon cycling the Raman peak shifted towards higher Raman modes (stretching modes A_{1g}), it means that structure deformed upon lithium extraction/insertion, may be due to the Mn dissolution in the electrolyte upon cycling. Table 4.3 showed the comparison of electrochemical performance of LiMn_{1.5}Ni_{0.5-x}Cr_xO₄, with the electrochemical performance of LiMn_{1.5}Ni_{0.5}O₄, and ZnO coated LiMn_{1.5}Ni_{0.5}O₄, reported earlier by our group.

| S. No | Material Name | Voltag e range | Discharge capacity | Maximum discharge | Charge /dischar | Discharge capacity |
|----------|--|-------------------|-----------------------|----------------------|--------------------|-----------------------|
| • | | (V) | after50cycle | capacity | ge rate | retention |
| 1 | LiMn ₂ O ₄ | 3.4-4.3 | 90 | 130 | C/5 | 69.23 |
| 2 | LiMn _{1.5} Ni _{0.5} O ₄ | 3.0-4.8 | 126 | 140 | C/5 | 90 |
| 3 | ZnO coated LiMn _{1.5} Ni _{0.5} O ₄ | 3.0-4.8 | 140 | 146 | C/5 | 96 |
| 4 | LiMn _{1.5} Ni _{0.4} Cr _{0.1} O ₄ | 3.0-4.9 | 124 | 126 | C/5 | 98.5 |
| | | | 107 | 110 | C/2 | 97.2 |
| | | | 96 | 100 | 1 C | 96 |
| 5 | LiMn _{1.5} Ni _{0.3} Cr _{0.2} O ₄ | 3.0-4.9 | 83 | 88 | C/5 | 94 |
| | | | 70.8 | 73 | C/2 | 97 |
| | | | 69.5 | 71 | 1 C | 98 |

Table 4.3: Comparison between the cyclic performance of $LiMn_{1.5}Ni_{0.5-x}Cr_xO_4$ cathode materials with earlier works inn our group

It can be seen from the table that $LiMn_{1.5}Ni_{0.4}Cr_{0.1}O_4$ could be a potential cathode material for high energy density Li ion rechargeable

Conclusions:

We have synthesized phase pure LiMn_{1.5}Ni_{0.5-x}Cr_xO₄ (x=0.1 and 0.2) cathode material by sol-gel method. The XRD data of the above materials showed the cubic spinel network (Fd3m). The redox voltage peaks in the cyclic voltammogram showed the reversible reactions involved in Li-ion intercalation and de-intercalation in to the structure. The charge-discharge characteristics at various C rate showed the stable behavior of the LiMn_{1.5}Ni_{0.5-x}Cr_xO₄ cathode materials, even at higher C rate of 1C. In the Table 4.4 we have presented a comparison between the cyclic performance of LiMn_{1.5}Ni_{0.5-x}Cr_xO₄ (x =0.1 and 0.2) cathode materials, synthesized by us and those reported earlier by various researchers. It can be seen from Table 4.3 that LiMn_{1.5}Ni_{0.4}Cr_{0.1}O₄ could be a promising cathode material for high rate capability applications.

Further investigation is going on in order to improve the discharge capacity of $LiMn_{1.5}Ni_{0.4}Cr_{0.1}O_4$ and $LiMn_{1.5}Ni_{0.3}Cr_{0.2}O_4$ cathode material by surface modification with ZnO, Al_2O_3 , and ZrO_2 .

| a | | T T 1 / | | | N T 0 | D1 1 | D 4 |
|------------|--|-----------------------|-----------------------|---------------|--------------|-------------|------------|
| S . | Material | Voltage | Charge/Disc | Maximum/Init | No. of | Discharge | Ref. |
| No. | | range (V) | harge C rate | ial discharge | Cycle | capacity | |
| | | | | capacity | | retention | |
| 1 | $LiCr_{0.5}Mn_{1.5}O_4$ | 3.5 - 5.0 | 0.65mA/cm^2 | 140 | 4 | 99 | 122 |
| | | | | | | | |
| 2 | LiMn _{1.95} Cr _{0.05} O ₄ | 3.0 - 4.5 | 0.1 mA | 130 | 30 | 91 | 123 |
| 3 | LiMn _{1.9} Cr _{0.1} O ₄ | 2.5 - 4.8 | C/10 | 138 | 10 | 100 | 124 |
| 4 | LiMn _{1.4} Cr _{0.2} Ni _{0.3} O ₄ | 3.3 - 4.95 | 0.15C | 130.8 | 50 | 94.1 | 125 |
| 5 | LiMn _{1.4} Cr _{0.6} O ₄ | 3.0 - 5.0 | C/10 | 142 | 1 | - | 126 |
| 6 | LiMn _{1.5} Ni _{0.4} Cr _{0.1} O ₄ | 3.0 - 4.9 | C/5 | 126 | 50 | 98.5 | Present |
| | | | C/2 | 110 | 50 | 97.2 | work |
| | | | | | | | |
| | | | 1 C | 100 | 50 | 96 | |
| | | | | | | | |

Table 4.4: Novelty LiMn_{1.5}Ni_{0.4}Cr_{0.1}O₄ cathode materials with comparison of other cathode materials, reported earlier.

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