

Literature Survey and Scope of Thesis Work

The chapter 2 emphasizes on literature survey and thesis scope. The section 2.1 gives the introduction about the chapter. The synthesis methods are discussed in section 2.2. The section 2.3 presents review on LiMn_2O_4 cathode materials. The section 2.4 explains the existing challenges of the cathode material and the scope of thesis is described in the section 2.5 and concluding remarks are presented in section 2.6.

2.1 INTRODUCTION

The literature survey is the first step to excavation about the field in detail. The importance, application and challenges are derived from literature survey. It is also helpful in identifying various contributing efforts, materials, methods, approaches, instrumentation, etc. which are developed by various contributors in the respective field. By reviewing the literature, one came to know about the current state of art and the challenges exist in the field of interest. It supports in channelizing the strategy to overcome these challenges and to identify problem for thesis or new research work also.

The brief summary about synthesis methods and elaborated review about cathode materials with special attention to rare earth doped LiMn_2O_4 (here after abbreviated as LMO) are described. The challenges and scope of thesis are also stated.

2.2 SYNTHESIS METHODS

The spinel cathode material, LMO, is synthesized by various methods. The synthesis method affects the structural phase purity, grain size, surface morphology, specific capacity, rate performance, etc. In search of commercial viable method, the different methods are proposed and adopted by researchers. These are fall into two broad categories namely: solid state reaction (SSR) method, and sol-gel method. The sol-gel is basically solution based method and requires low temperature compared to SSR. There are various sol-gel based synthesis methods such as chelating agent assisted method [Hwang et al, 2001], emulsion-drying method [Hwang et al, 1998], hydrothermal method [Feng et al, 1995], molten salt synthesis method [Helan et al, 2010], organic solvent based method [Singhal et al, 2006], pachini method [Liu et al, 1996], self-combustion method [Kovacheva et al, 2002], etc. The selection of suitable method is mostly depending on the merit of method and infrastructural suitability. Each method has its own merits and demerits. The synthesis methods of cathode material are described in brief in successive paragraphs.

2.2.1 Solid State Reaction Method

The solid state reaction method is one of the oldest methods for oxide synthesis. It is time consuming and less energy efficient. The $\text{Li}_x\text{Mn}_2\text{O}_4$ ($0.9 < x < 1.2$) spinel cathode was synthesized by putting reacting mixture of $(x/2) \text{Li}_2\text{CO}_3$ or $x \text{LiNO}_3$ and 2MnO_2 in $x:2$ at 800°C for 24 h followed by two successive steps of annealing and manual grinding. The cooling step was adopted as natural cooling by switching off the furnace [Guyomard and Tarascon, 1994]. The LMO and gallium doped LMO, $\text{LiGa}_x\text{Mn}_{2-x}\text{O}_4$ ($0 < x < 0.1$) cathode materials, were synthesized in single heating step 730°C for 72 h using the same starting materials (LiCO_3 and MnO_2) in stoichiometric ratio [Pistoia et al, 1995]. In this method, the heating treatment was bifurcated as low temperature prolongs time (550°C for 150 h) and high temperature short time (750°C for 24 h) [Manev et al, 1995]. It is difficult to control particle size in narrow range and uniform surface morphology. The oxygen loss from the lattice site during annealing more than

600 °C was reported during synthesis of $\text{LiCo}_{0.5}\text{Mn}_{1.5}\text{O}_4$ via solid state reaction method [Kawai et al, 1998]. The single step synthesis of LMO via solid state reaction was adopted with intermediate step of ball milling of powder before annealing treatment [Wang et al, 2005]. Later on, the method was modified with supersonic wave treatment. The Li_2CO_3 and MnO_2 were taken as starting material. The mixture was heated at 700 °C for 24 h in air atmosphere to obtain LMO. The two steps supersonic wave treatment in Zn aqueous solution (Zn : distilled water :: 4 : 96) were adopted to improve the performance of LMO. In first step, at low frequency (28 and 40 kHz) with two different powers (150 and 300 W) for 10 minutes duration was adopted. In second step, at high frequency (200 and 950 kHz) with equal powers (150 and 300 W) for 10 minutes was considered. After the supersonic wave treatment, the sample was dried at 100 °C for 24 h. This method revealed that the Zn substitution and surface coating both can be done simultaneously at low temperature. However, the quantity of Zn doping and contribution of surface coating were not clear. The sample treated with 28 kHz at 300W in first step and 200 kHz and 300 W in second step delivered the highest initial discharge capacity (92.2 mAhg^{-1}) and improved capacities retention 91.7% (84.7 mAhg^{-1}) [Kitamura et al, 2009]. Recently, the porous nano-particles-constructed granule LiMn_2O_4 derived via solid state reaction method [Zheng et al, 2013]. The hybrid solid state reaction method was adopted to reduce the calcination time and energy [Li et al, 2015].

2.2.2. Sol-Gel Method

The sol-gel method is the advance method over solid state reaction method for synthesis of LMO spinel cathode for lithium-ion battery application. The method is named after its liquid nature of solvent. The method has advantages such as effective control on stoichiometric, lower calcination temperature and time duration, more homogeneous particle surface morphology, narrow particle size distribution etc. The method can be further divided in two broad categories: aqueous sol-gel route and non-aqueous sol-gel route. The aqueous sol-gel route is based on the distilled water as a solvent whereas the non-aqueous route is using organic nature of solvent.

2.2.2.1. Chelate compound based method: This method is similar to other method except the addition of chelating agent addition and pH control. The analytical grade lithium acetate, manganese acetate and acetate or nitrates of doped element were taken as starting materials. These chemicals were dissolve into de-mineralized water to get ionic form of species. The pH was adjusted using ammonium hydroxide (NH_3OH). The different chelate compounds, also known as chelating agent, are citric acid [Hwang et al, 2001; Singh et al, 2009], apidic acid [Thirunakaran et al, 2004], oxalic acid [Sulochana et al, 2008], glutamic acid [Thirunakaran et al, 2011], etc. The synthesis process involves several steps. First step is to obtain wet gel chelate complex with controlled pH condition at 80 - 120 °C for ~ 4 h. The next steps is the decomposition of chelating complex at 200-300 °C for ~ 6 h and wash it to remove any trace of chelate complex and to ensure decomposition of chelating compound. The precursors are calcined at 800 °C in air at heating and cooling rate 1 °C/min. to get pure spinel phase LMO cathode.

2.2.2.2 Emulsion-drying method: The LMO cathode materials were prepared by adopting an emulsion-drying method [Hwang et al, 1998]. The acidic aqueous solutions of lithium carbonate and manganese nitrate hexa-hydrate were dropped into mixture of oil (kerosene) and emulsifying agent (Tween 85). The volumetric ratio of emulsifying agent, oil and aqueous solution was 15:30:55. The synthesis procedure includes several steps namely; mixture storing, 6 h, ultrasonic agitation, 10 min, for reduction the droplet size, drop wise addition into hot kerosene to recover precursor, washed with toluene to remove any oil phase, drying (100 °C for 5 h) in air atmosphere, calcining temperature 750 °C for 48 h. The method is cumbersome and need several precautions in each step including the excess lithium content. The process was modified by changing starting materials (Lithium hydroxide and Lithium nitrate in place of lithium carbonate), solvent (distilled water in place of dilute nitric acid) and omitting the

toluene washing stage [Myung and Chung, 1999]. The process requires large heating time (48 h) to obtain efficient phase. This method is time consuming and not energy efficient.

2.2.2.3 Hydrothermal method: The synthesis of LMO spinel cathode materials and its derivatives by hydrothermal route is an alternate method. This method offers low temperature synthesis in controlled high pressure. This method didn't require prolong heat treatment as solid state reaction and sol-gel method. It required prolong reaction time (24 days) to complete the reaction [Feng et al, 1995]. However, in search of simple and efficient method, the advancement in method has taken place such as using H_2O_2 [Zhang et al, 2003], glucose [Kanamaru et al, 2005] as chelating agent. Using starting materials as $LiOH \cdot H_2O$ (99% pure), MnO_2 (EMD, $\geq 97.5\%$) and $Mn(NO_3)_2$ (50% aqueous solution), the LMO cathode materials were synthesized without any additional additives. The solution was kept into autoclave and put at $280^\circ C$ for 36 h, followed by cooling to room temperature in air atmosphere. After the completion of hydrothermal reaction, the products were washed and dried overnight in air at $150^\circ C$ [Wu et al, 2006]. By adopting hydrothermal method, the synthesis of $LiMn_2O_4$ and carbon (C) composite [Yue et al, 2009] at reduced temperature $120^\circ C$ for 24 h, and microwave assisted for nano-regime grains [Ragupathy et al, 2010] have reported recently.

2.2.2.4. Molten salt method: This method is also known as flux growth method. It is favorable for oxide, carbonates and chloride reagents. The method is named after the solvent, which is a molten salt. The typical molten salts, lithium chloride ($LiCl$), lithium carbonate ($LiCO_3$), and manganese chloride ($MnCl_2$) were taken in 0.6:0.4:2.0 ratio. The stoichiometric mixture was dried at $110^\circ C$ for 24 h. The dry mixture was kept at $700^\circ C$ for 12 h into muffle furnace for attaining melting phase of salts and then cooled down to ambient temperature. The resultant precursors were washed with 1M acetic acid and de-ionized water remove free chloride ions. The final products were again heated at $120^\circ C$ for 2 h to obtain phase pure spinel phase LMO cathode materials [Helan et al, 2010].

2.2.2.5. Organic solvent method: The starting analytical reagents were acetates of Lithium, magnesium and neodymium. The stoichiometric ratios of these salts were dissolve separately in organic solvent (2-ethylhexanoic acid) at $50-100^\circ C$ with continuous stirring for 1 h. After homogeneous dissolution of each salt, all salt solutions were mixed and the final solution was dried at $100^\circ C$ for 4 h. The heat treatment were carried out in two separate steps at $400^\circ C$ for 4 h to remove organic contents and between $700-900^\circ C$ for 14 h to obtain phase pure materials [Singhal et al, 2006].

2.2.2.6. Pechini process: The LMO spinel cathodes were synthesized via pechini process [Liu et al, 1996] also called liquid mix process. This method is based on mixing of oxides or salt solution at low calcining temperature in multiple steps. In spite of low temperature and fine grain size, the method contains several steps and removal of excess ethylene glycol which made it less attentive. However, the modification in process was carried out using pre-ignition of precursors in open air followed by reduction in calcining temperature [Han and Kim, 1999] and by substitution of polyethylene glycol in place of ethylene-glycol [Subramania et al, 2005].

2.2.2.7. Self-combustion method: This is one of the methods for synthesizing nano size oxides materials. The oxidizers, carbonates and nitrates of reagents, are working as reacting species. The redactors, such as glycine, urea, citric acid, glucose, etc., are working as fuel. The fuel is used to provide sufficient heat energy to decompose the reactant precursors. The resultant new spinel phase material is formed [Kovacheva et al, 2002]. The advancement in method was adopted by using cheap organic fuel reagent (sucrose, $C_{12}H_{22}O_{11}$) [Gadjov et al, 2004]. The optimized thermal treatment condition for this method was $600-650^\circ C$ for 2 h in air atmosphere to obtain better phase pure and fine particle size.

2.3 CHALLENGES OF LiMn_2O_4 CATHODE MATERIAL

In spite of the advantageous features of spinel cathode LMO such as high power density, cheap raw material, non-toxicity, and abundance of the Mn element in the earth's crust; it is still facing challenges to make wide spread commercially. The major challenge is the capacity fading over long cyclability. This phenomenon is accelerated at high C-rate and at elevated temperature cycling. These issues are addressed here in brief:-

- (i) *Jahn-Teller distortion*: Due to high spin of Mn^{3+} , the Jahn-Teller distortion is appeared in the 4 V region. It is also speed-up at high C - rate charge-discharge performance [Gummow et al, 1999; Yamada et al, 1999]. Not only Jahn-Teller distortion, but growth of dendrites at the grain surface is another failure mode when cycled in a high C - rate or non-equilibrium conditions. The strategy to overcome these issues is to increase the average valency of Mn by surface modification of LMO by $\text{LiNi}_x\text{Mn}_{2-x}\text{O}_4$ solution or doping transition metal [Li et al, 2009].
- (ii) *Mn dissolution*: The slow dissolution of Mn^{3+} ion is the main cause of capacity fading. The dissolution of Mn-ion at elevated temperature is more severe than that at room temperature [Gao et al, 1996; Yoshio et al, 2001]. Due to Mn^{3+} dissolution, the lattice defects are induced in the spinel structure which produce the disorder in the spinel structure and resulted in path blockage of Li insertion-extraction [Inoue and Sano, 1998]. The decomposition of electrolyte at elevated temperature (ET), $>50^\circ\text{C}$, compared to room temperature (RT) is also another cause [Hong et al, 2004].
- (iii) *Oxygen Loss*: The other failure mode is oxygen loss from the spinel lattice during the calcining process which is responsible for lattice instability during cycling [Gao and Dhan, 1996; Kawai et al, 1998].
- (iv) *Other Phase formation*: The formation of other phases, Li_2MnO_3 and $\text{Li}_2\text{Mn}_2\text{O}_4$, were detected at the particle surface [Liu et al, 2009] and [Cho and Thackeray, 1999]. The fracturing of the grains from the spinel structure during each charge-discharge cycle is also favored mechanism.

The cationic substitution has improved the electrochemical performance significantly at room temperature, but the improvement is subjected to the amount of doped cation element. That is, the increase amount of doping is also improving the structural stability, but at the cost of specific capacity i.e. reduction in the specific capacity.

2.4 REVIEW OF SPINEL FRAMEWORK CATHODE MATERIALS

To overcome the Mn dissolution into electrolyte at high charge-discharge rate, to enhance the cyclability at room and elevated temperature, the researchers are making efforts from past two to three decades. The study revealed that the transition metal doped spinel cathode materials are studied frequently with varied combination. However, the efforts in the surface coating of spinel cathode, LMO, by various oxides such as ZnO [Liu et al, 2007; Sun et al, 2003;], SiO_2 [Arumugam et al, 2008, Kim et al, 2004, Fan et al, 2012], MgO [Lim et al, 2008; Gnanaraj et al, 2003], Al_2O_3 [Kim et al, 2004; Lee et al, 2004], aluminum phosphate, AlPO_4 , [Cho et al, 2003] and dual methods (surface coating and element doping) [Sun et al, 2009] were also remarkable. The reduction in the Mn dissolution and the increase in cyclability were reported. The literature on rare-earth element doped spinel cathode was come into picture in year 2000 onwards and less attention was given compared to transition metal doping and surface coating work.

In this review, the minor attention is given towards the doping of transition metal, alkaline earth metal whereas major attention is directed towards doping of the rare-earth element in the spinel cathode framework.

2.4.1 Transition Metal Dual and Ternary Doping

The zinc (Zn), aluminum (Al), manganese (Mg), copper (Cu), chromium (Cr) transition metals were used for dual and ternary doping. The dual and ternary doped, $\text{Li}_{1.3}\text{Mn}_{1.91}\text{M}_{0.06}\text{O}_4$ ($\text{M} = \text{Zn}_{0.03}\text{Mg}_{0.03}; \text{Al}_{0.03}\text{Zn}_{0.03}; \text{Al}_{0.03}\text{Mg}_{0.03}; \text{Al}_{0.03}\text{Zn}_{0.153}\text{Mg}_{0.015}$), spinel cathodes were synthesized via citric acid based sol-gel route by using analytical grade reagents of aluminum nitrates, magnesium acetate and lithium acetate in stoichiometric ratio. The phase purity was attained by calcined treatment in air atmosphere in two steps: first at 500 °C for 5 h to remove organic content and second step at 600 °C for 12 h duration to get phase purity. The x-ray diffractograms revealed that all cathodes have high degree of spinel phase crystalline structure without any impure phase. The average particle diameter was about to 100 nm. The tendency of agglomeration among smaller particles was also observed. Among the dual and ternary doped cathodes, the $\text{Li}_{1.3}\text{Mn}_{1.91}\text{Zn}_{0.03}\text{Mg}_{0.03}\text{O}_4$ cathode showed the highest (97.3 %) capacity retention after 40 cycles at C/3 rate. All the measurements were carried out at room temperature. However, the initial discharge capacity for $\text{Li}_{1.3}\text{Mn}_{1.91}\text{Zn}_{0.03}\text{Mg}_{0.03}\text{O}_4$ cathode was reported as 107.5 mAhg⁻¹ which was lower compare to 122.5 mAhg⁻¹ for pristine LMO cathode. The other doped cathodes were also having high capacity retention in range of 94 - 95 % while the un-doped LMO cathode showed lower capacity retention (92.4 %) [Tian et al, 2013].

The dual transition metal [Cu (0.50), Cr (0.05, 0.50)] doped spinel LMO cathodes were synthesized via aqueous sol-gel method using myristic acid as chelating agent. The particle morphology was reported in nano size. The initial specific discharge capacity was observed as 124 mAhg⁻¹ but capacity fading was not stable. The results revealed that Cu (0.5) and Cr (0.05) doped cathode delivered the better results compared to other cathodes [Thirunakaran et al, 2016].

2.4.2 Alkaline Earth Metal Doping

The second column elements of periodic table are known as alkaline earth elements. These elements have electronic valence +2 which is equal to +2 of Mn. The alkaline elements can be easily accommodated in place of Mn²⁺-ion. By taking virtue of it, the effects of doped element are described here. The magnesium metal doped spinel cathode, $\text{LiMn}_{1.96}\text{Mg}_{0.04}\text{O}_4$, was synthesized via solid state reaction method [Lei Hu et al, 2016]. The precursor powders were calcined at 500 °C for different time duration (1 h, 3 h, 6 h, 9 h and 12 h) in air atmosphere. The author studied the effect of calcining duration on crystallinity, microstructure, charge-discharge capacity and electrochemical impedance of cathodes. The outcomes of the study revealed that the cathode materials calcined up to 9 h and 12 h were showed the agglomerated non-uniform polyhedral particle size (0.5 - 1.9 μm) with high crystalline. The electrochemical parameters were reported as initial specific discharge capacities (120.2 and 118.6 mAhg⁻¹), better capacity retention (92.51% and 93%) after 40 cycles at C/5 rate. The electrochemical impedance spectroscopy (EIS) demonstrated that the $\text{LiMn}_{1.96}\text{Mg}_{0.04}\text{O}_4$ cathode calcined at 12 h showed lowest impedance (~140 ohm) in comparison to other cathodes. It is conclusive from the study that spinel cathode, $\text{LiMn}_{1.96}\text{Mg}_{0.04}\text{O}_4$, prepared by this method and 12 h calcined duration were delivered better results.

2.4.3 Rare-Earth Metal Doping

The effects of rare-earth (La, Er, Dy, Nd, Gd, Sm, Ce, Yb, and Tb) elemental doping in spinel LMO cathode are reviewed here.

Neodymium (Nd) doped LMO, $\text{LiMn}_{1.99}\text{Nd}_{0.01}\text{O}_4$, cathode and un-doped LMO cathode were synthesized using neodymium and manganese oxides and lithium hydroxide hydrate by aqueous sol-gel route. The precursors were obtained by microwave heating method. The XRD diffractograms revealed that the cubic spinel phase (Fd3m) formation was taking place without any additional phase. The lattice constants were larger than un-doped LMO material. The

surface morphology revealed that the homogeneous particle distribution was observed. The dispersed particle mean size was found in μm range. The cyclic voltammetry (CV) was carried out at different scan rates as 5, 10, 20, 50, 100 mV/min. between 3.0 - 4.8 V potential window. The CV observations confirmed the fast diffusion of Li-ion and improvement in reversibility. The chrono-coulombometry validated the fast lithium ion diffusion in Nd-doped LMO cathode compared to un-doped LMO cathode. The specific charge-discharge study revealed that the specific discharge capacity was more stable in Nd-doped LMO cathode. The capacity fading rate was lower in LMO-Nd compared to un-doped LMO which supported the improvement in capacity retention [Yang et al, 2003].

Neodymium doped, $\text{LiMn}_{1.99}\text{Nd}_{0.01}\text{O}_4$, cathode material was synthesized using metal acetates by adopting organic sol-gel route. The calcination of precursors was carried out at 400 °C for 4 h and 850 °C for 14 h. The XRD diffractograms revealed that the spinel phase formation takes place. The lattice constants were similar to un-doped LMO material. The surface morphology revealed that the agglomeration among particles was taking place to increase grain size and resulted grain mean size was observed in 0.5 - 1.5 μm range. The specific charge-discharge performance was carried out at room temperature in potential 3.5 - 4.3 V region by applying constant 0.2 mAcm⁻² current density. The initial specific charge and discharge capacities of Nd doped cathode were reported as 166 and 149 mAhg⁻¹, respectively. However, 10 % reduction in capacity observed in first cycle ascribed to formation of solid electrolyte interface (SEI). The capacity retention was observed as 135 mAhg⁻¹ (91 %) after 25 cycles [Singhal et al, 2007].

Neodymium doped, $\text{LiMn}_{1.7}\text{Nd}_{0.3}\text{O}_4$, was prepared using lithium and manganese acetates and neodymium oxide by citric acid modified microwave assisted sol-gel route. The acryl amide was used as gelling agent. The heat treatment in inert atmosphere was carried out at 100 °C for 12 h to eliminate water content by using microwave heating in oven at 100 % (650 W) for 20 min. duration and further calcined at 550 °C for 6 h in two steps. Thermal-gravimetric analysis (TGA) revealed that the spinel phase formation started after 300 °C and till 450 °C. The powder x-ray diffraction patterns revealed that the cubic spinel phase formation was taken place without impure phase. The surface morphology revealed that particles were less agglomerated and grain mean size in micrometer range. However, tunneling electron microscopy (TEM) study revealed that the small cluster formation tendency was observed in Nd doped LMO cathode. The specific charge-discharge study was carried out at room temperature in 3.0 - 4.5 V potential window by applying constant 0.1 mAcm⁻² current density. The values of initial charge-discharge capacity of Nd doped cathodes were not reported. However, the plotted figure showed that the initial discharge capacity was about to 120 and 140 mAhg⁻¹ for LMO and LMO-Nd cathodes, respectively. The capacity fading in LMO was more compared to LMO-Nd cathode. The capacity retention after 50th cycles claimed as 99.5 % and 83 % for LMO-Nd and LMO cathodes [Suryakala et al, 2008].

Erbium (Er) doped, $\text{LiMn}_{2-x}\text{Er}_x\text{O}_4$ (where $x=0, 0.01, 0.015, 0.020$ and 0.025), cathode materials were synthesized using lithium acetate, manganese acetates and erbium oxide via rheological phase reaction in air atmosphere in single heating step at 750 °C for 12 h duration. The crystal structure was confirmed as cubic spinel phase. However, the $x=0.025$ content of Er had few impure phase of erbium oxide (Er_2O_3). The lattice parameters were gradually decreased from 8.2398 Å to 8.2193 Å with increasing the Er elemental doping. The initial discharge capacities for $\text{LiMn}_{2-x}\text{Er}_x\text{O}_4$ cathodes were reported as 132.87, 130.89, 129.31 and 126.1 mAhg⁻¹ for $x=0, 0.010, 0.015$ and 0.020 , respectively. Although, the initial discharge capacity of Er doped cathode was lower compared to pristine LMO cathode. The Er (0.02) doped cathode had achieved better reversibility 120.73 mAhg⁻¹ (97.5%) compared to bare LMO cathode material, 114.35 mAhg⁻¹ (86.06%), after 50 cycles at 0.5 mAcm⁻² current density. This was attributed to more binding energy, 615 kJ/mol, for Er-O bond at octahedral site [Liu et al, 2005].

The samarium (Sm) doped cathodes, $\text{Li}_x\text{Mn}_{2-y}\text{Sm}_z\text{O}_4$ ($0.95 \leq x \leq 1.2$, $0 \leq y \leq 0.3$, $0 \leq z \leq 0.2$), were synthesized using manganese and lithium carbonates in stoichiometric ratio by adopting mechano-chemistry fluid activation method. The calcination of precursors was carried out in two steps as at 600 °C for 8 h and 800 °C for 18 h. The XRD diffractograms revealed that spinel phase remains ultra pure. The lattice constants were decreased with increase in doping concentration. The surface morphology was similar as un-doped. The agglomerated grain mean size was found in μm range. The charge-discharge study was performed in 4 V region at C/10 rate in two temperature range. The specific discharge capacity of Sm doped cathodes was more than 130 mAhg^{-1} and comparatively high than un-doped LMO. The discharge capacity retention was measures as 80 % after 400 cycles at 1C rate [Peng et al, 2005].

The derivatives of samarium doped $\text{LiMn}_{2-x}\text{Sm}_x\text{O}_4$ ($x = 0.0, 0.05$ and 0.10) cathode materials were synthesized using metal nitrates and adopting double stage co-precipitation method followed by microwave calcination. The powder was pelletized and calcined at 500 °C for 10 min. and at 800 °C for 20 min. in two steps. The XRD diffractograms revealed that the spinel phase formed with few impurity peaks of SmMnO_3 in $x=0.10$ samples. The lattice constants were decreased with increase in doping concentration. The mean size of grains was found in the range of $1.5 - 0.8 \mu\text{m}$ with $\pm 0.2 \mu\text{m}$ accuracy. The porosity was observed $0.311 - 0.120$ with ± 0.001 . The grains were agglomerated to make large grains with lower surface roughness. The specific charge and discharge study were carried out at C/5 rate in 4 V potential window. The specific discharge capacities of un-doped LMO and LMO-Sm doped cathodes; $\text{LiSm}_{0.05}\text{Mn}_{1.95}\text{O}_4$ and $\text{LiSm}_{0.10}\text{Mn}_{1.90}\text{O}_4$; were $134, 132, 126 \text{ mAhg}^{-1}$ with capacity retention 78.4% 93.2%, and 88% after 100 cycles respectively [Balaji et al, 2012].

Gadolinium (Gd) doped, $\text{LiMn}_{1.99}\text{Gd}_{0.01}\text{O}_4$, was synthesized using lithium carbonate and chlorides of lithium, manganese, and gadolinium by molten salt solid state route. The salts were mixed in stoichiometric ratio and kept for heating to form spinel phase. The heating was done in programmable furnace at 700 °C for 8 h in single steps with $3.3 \text{ }^\circ\text{C}/\text{min}$. step. The TGA analysis revealed that the spinel phase formation started after 418 °C to till 551 °C with evolution of CO_2 . The powder x-ray diffraction patterns revealed that spinel phase formation without impurity. The surface morphology showed that particles were agglomerated with grain mean size $5-10 \mu\text{m}$ range. The electrochemical performance was not reported at all. However, Raman spectroscopy and electron paramagnetic resonance spectroscopy (EPRS) studies were carried out. The Jahn-Teller effect was not observed in EPRS which evidenced for the reduction in Jahn-Teller distortion by Gd doping in LMO cathodes. Raman study reported that the 3 cm^{-1} shift towards lower wave-number in A_{1g} mode [Helan et al, 2011].

Gadolinium doped spinel cathode materials, $\text{LiGd}_x\text{Mn}_{2-x}\text{O}_4$ ($x = 0, 0.02, 0.04, 0.08$), were synthesized using metal acetates by citric assisted sol-gel method. The pH was maintained 7.0 during reaction using ammonium hydroxide solution. The heating was done in double steps at 450 °C for 2 h and at 800 °C for 16 h to attain phase purity. Powder x-ray diffractograms revealed that Gd doping didn't affected the formation of cubic spinel phase. However, low amount impure phase of GdMn_2O_5 was observed clearly. The reduction in lattice parameters was evidenced for ensuring the Gd doping. The surface morphology through FESEM showed that the grains average size was in range of $150 - 200 \text{ nm}$. The atomic concentration of Mn (98.4 %) and Gd (1.6 %) was confirmed through x-ray photoelectron spectroscopy (XPS) elemental analysis. The specific charge-discharge performance at room and elevated temperature were carried out at three different C-rates (1 C, 5 C and 10 C), successively. The initial specific discharge capacities were observed as $126.6, 116.0, 103.7, 83.3 \text{ mAhg}^{-1}$ for $\text{LiGd}_x\text{Mn}_{2-x}\text{O}_4$ ($x = 0, 0.02, 0.04, 0.08$) at C/5 rate. The capacity fading was more in un-doped LMO cathode (83.3 mAhg^{-1} ; 66 % reduction) compared to $\text{LiGd}_{0.02}\text{Mn}_{1.98}\text{O}_4$ cathode (91.5 mAhg^{-1} ; 21 % reduction) at high 10 C-rate. However, capacity reduction in $\text{LiGd}_{0.04}\text{Mn}_{1.96}\text{O}_4$ and $\text{LiGd}_{0.08}\text{Mn}_{1.92}\text{O}_4$ cathodes were reported as 8.1 % and 10.3 %, respectively, at different discharge rates from 0.2 - 10 C rate.

The capacity fading for $\text{LiGd}_x\text{Mn}_{2-x}\text{O}_4$ ($x = 0.02, 0.04, 0.08$) cathodes was observed as 17 %, 14 % and 8 %, respectively, after 70 cycles at 1 C-rate. However, at 5 C-rate, capacity fading for LMO and $\text{LiGd}_{0.02}\text{Mn}_{1.98}\text{O}_4$ cathodes were reported as 22 % and 15 %, respectively. At 10 C-rate, capacity fading for $\text{LiGd}_x\text{Mn}_{2-x}\text{O}_4$ ($x = 0.02, 0.04, 0.08$) cathodes were assessed as 15 %, 12 % and 8 %, respectively. The specific charge-discharge study carried out at the elevated temperature (60 °C) also evidenced the severe capacity fading in LMO (45%) cathode compared to $\text{LiGd}_x\text{Mn}_{2-x}\text{O}_4$ (21 %, 17 %, and 15 % for $x = 0.02, 0.04, 0.08$) cathodes at 1 C-rate after 70 cycles [Han et al., 2012].

The derivatives of dysprosium (Dy) doped, $\text{LiMn}_{2-x}\text{Dy}_x\text{O}_4$ ($x = 0.0, 0.05, 0.10, 0.15$ and 0.20), were synthesized using metal nitrates and adopting double stage co-precipitation method followed by microwave heat treatment. The calcination was carried out in two steps at 500 °C for 10 min. and at 800 °C for 20 min. The XRD diffractograms revealed that the spinel phase formation taken place with additional impure phase of DyMnO_3 in $x=0.10, 0.15$ and 0.20 samples. The lattice constants were decreased with increase in doping concentration. The grain mean size was found in the range of 1.5 - 4.0 μm with $\pm 0.1 \mu\text{m}$. The grains were observed as agglomerated nature with lower surface roughness. The specific charge-discharge analysis were carried out in 4V region. The specific discharge capacities were 134, 127, 117, 107, 98 mAhg^{-1} and the capacity retention was as 82 %, 95 %, 95%, 91% and 88%, respectively, for un-doped LMO and Dy (0.05, 0.10, 0.15 and 0.20) doped cathodes. The information about cyclability and C-rate at which charge-discharge performed were not mentioned [Balaji et al, 2012].

Cerium (Ce) doped spinel cathode materials, $\text{LiCe}_x\text{Mn}_{2-x}\text{O}_4$ ($x = 0.0, 0.01, 0.03, 0.05$, and 0.10) were synthesized using manganese acetates, cerium and lithium nitrates by aqueous sol-gel method with succinic acid as chelating agent and pH was maintained in range of 2 - 2.5 during reaction period. The heating was done in single step at 900 °C for 12 h duration. Powder x-ray diffractograms revealed that the Ce doping didn't disturb the cubic spinel phase formation. However, the increase in lattice parameters was reported after Ce doping. The surface morphology Figure out through SEM/TEM showed that the grain average size is in 80-100 nm range. The specific charge-discharge performance at room and elevated temperature (60 °C) were performed at different C-rates (0.5 C, 1 C, 5 C, 10 C and 15 C). The initial specific discharge capacity was obtained as 137, 135, 130, 126 and 119 mAhg^{-1} for $\text{LiCe}_x\text{Mn}_{2-x}\text{O}_4$ ($x = 0.0, 0.01, 0.03, 0.05, 0.10$) cathodes, respectively, at C/2 rate. The capacity fading was more in LMO cathode (81 mAhg^{-1} ; 41% reduction) compared to 96, 106, 117, and 108 mAhg^{-1} (capacity reduction 29%, 19%, 8%, 10%) for $\text{LiCe}_x\text{Mn}_{2-x}\text{O}_4$ ($x = 0.01, 0.05, 0.05$, and 0.10) cathodes after 100 cycles. However, the capacity reduction for $\text{LiCe}_{0.05}\text{Mn}_{1.95}\text{O}_4$ cathode was 92 %, 91 %, 85 %, 79 % and 87 % at 0.5 C, 1 C, 5 C, 10 C and 15 C, respectively. The charge-discharge study carried out at the elevated temperature (60 °C) in potential window 2.75 - 4.5 V. The initial specific discharge capacities for $\text{LiCe}_{0.05}\text{Mn}_{1.95}\text{O}_4$ were reported as 101, 89, 69, 53 and 53 mAhg^{-1} at 0.5 C, 2 C, 5 C, 10 C and 15 C, respectively. The capacity fading was linear with low rate of decrement for few cycles and then becomes stable. The capacity retention was observed as 66, 71, 46, 24 and 15 mAhg^{-1} after 100 cycles at 0.5 C, 2 C, 5 C, 10 C and 15 C, respectively [Arumugam et al, 2010].

Terbium (Tb) doped spinel cathode materials, $\text{LiTb}_x\text{Mn}_{2-x}\text{O}_4$ ($x = 0.0, 0.01, 0.02$ and 0.04), were synthesized using lithium, manganese and terbium metal acetates by citric assisted sol-gel method. The pH at 7.0 was maintained during reaction using ammonium hydroxide solution. The heating was done in double steps with at 450 °C for 2 h and 800 °C for 16 h to attain pure cubic spinel phase. The x-ray diffraction patterns revealed that Tb doping didn't alter the formation of cubic spinel phase. However, low amount of impure phase of TbMn_2O_5 (ICSD No. 500294, orthorhombic Pbam), was observed. The reduction in lattice parameters was evidenced for Tb element doping. Surface morphology through FESEM showed that the grain average size was in 150 - 200 nm range. The atomic percentage of Mn and Tb was confirmed by XPS elemental analysis. The charge and discharge performance were analyzed at room temperature

and elevated (60 °C) temperature at three different C rates (0.1 C, 1 C and 10 C), successively. The initial specific discharge capacities were obtained as 122.1, 122.1, 117.0, 102.8 mAhg⁻¹ for LiTb_xMn_{2-x}O₄ (x = 0.0, 0.01, 0.02 and 0.04) at 1 C-rate. The capacity retention after 50 cycles at 1 C-rate was found less in LMO (86.4 %) cathode compared to LiTb_xMn_{2-x}O₄ (95.1 %, 94.6 % and 94.8 % for x=0.01, 0.02 and 0.04) cathodes. The charge-discharge study was also carried out at the elevated temperature (60 °C) which evidenced the severe capacity fading 62 % in LMO cathode compared to LiTb_xMn_{2-x}O₄ (81.9 % for x = 0.01) cathodes after 50 cycles [Lee et al.; 2012].

Lanthanum (La) doped spinel cathode, LiLa_{0.01}Mn_{1.99}O₄, and LMO cathode materials were obtained using lithium carbonate, electrolytic manganese dioxide and lanthanum acetate by solid state reaction route. The mixture was calcined in single step at 750 °C for 20 h to ensure spinel phase formation. Powder x-ray diffractograms revealed that the La doping didn't disturb the formation of a cubic spinel phase. The shrinking in lattice parameters evidenced that La doping didn't add any additional stress on spinel structure. The surface morphology obtained on FESEM showed that the grain average size was in order of 100 nm for LMO material and 200 nm for LiLa_{0.01}Mn_{1.99}O₄ material. The galvanostatic charge-discharge investigation at room temperature was performed. The initial specific discharge capacity was obtained as 126.8 and 116.06 mAhg⁻¹ for LMO and LiLa_{0.01}Mn_{1.99}O₄, respectively. The capacity retention was reported 105 mAhg⁻¹ (capacity fading 9.5%) for LiLa_{0.01}Mn_{1.99}O₄ cathode after 300 cycles whereas 100.3 mAhg⁻¹ (capacity fading 20.9%) for LMO cathode after 100 cycles. The EIS study revealed that the growth of solid electrolyte interface (SEI) layer in LiLa_{0.01}Mn_{1.99}O₄ was low compared to LMO cathode [Tu J. et al, 2006].

Lanthanum (La) doped spinel cathode materials, LiLa_xMn_{2-x}O₄ (x = 0.0, 0.01, 0.03, 0.05 and 0.10), were synthesized using metal nitrates by aqueous based sol-gel method. The pH was maintained between 2.0-2.5 during reaction using succinic acid. The dry gel was heated in single step at 900 °C for 12 h duration in air atmosphere to get phase pure material. The x-ray diffractograms revealed that low amount La doping didn't have influence on the formation of cubic spinel phase. However, low impure phase of LaMn₂O₅ (ICSD No. 500294, orthorhombic Pbam) was observed in x=0.10. The exterior morphology through SEM showed that grain average size was in between 0.1-2.0 μm range. The galvanostatic charge-discharge study was performed at different C-rates to access the electrochemical parameters at room temperature. The initial specific discharge capacities were obtained as 143 and 127 mAhg⁻¹ for LMO and LiLa_xMn_{2-x}O₄ (x=0.05) cathodes, respectively, at C/10 rate. However, the capacity was reduced for few initial cycles and becomes almost stable. The capacity retention for LiLa_xMn_{2-x}O₄ (x=0.05) cathode after 50 cycles was 115, 112, 106, 103 and 87 mAhg⁻¹ at C/10, C/2, 1 C, 2 C and 5 C rates, respectively, whereas in the case of LMO cathode, capacity retention was 80 mAhg⁻¹ (58%) after 30 cycles at C/10 [Arumugam et al, 2008].

2.4.4 Rare-Earth and Transition Metal Dual Doping

The transition metal Zinc (Zn) and rare earth metal Cerium (Ce) dual doped LiZn_xCe_yMn_{2-x-y}O₄ (x= 0.01-0.10; y= 0.10-0.01) cathodes were synthesized by taking stoichiometric ratio of cerium oxide, lithium nitrate, acetates of manganese and zinc via sol-gel route using p-amino benzoic acid as chelating agent. The phase purity was attained by calcined treatment in air atmosphere in single step at 850 °C for 4 h. The x-ray diffractograms revealed that all cathodes had high degree of spinel phase crystalline without any impure phase after calcined at 850 °C for 4 h. The geometry of particles was in spherical nature with particle size was in order of 0.5 μm. The grain size increased as increase in doping level. The electrochemical performance of LiZn_xCe_yMn_{2-x-y}O₄ (x= 0.01 - 0.10; y= 0.10 - 0.01) and LMO cathodes were compared at room temperature in voltage range 3.0 - 4.5 V at C/10 rate. The initial specific discharge capacity of LiZn_{0.01}Ce_{0.01}Mn_{1.98}O₄ and LMO cathodes were reported as 124 and 122 mAhg⁻¹. The discharge capacity retention after 10th cycle at room temperature was 122 and 112

mAhg⁻¹. The capacity fading was 0.2 mAhg⁻¹ and 1.0 mAhg⁻¹ for LiZn_{0.01}Ce_{0.01}Mn_{1.98}O₄ and LMO cathodes, respectively [Thirunakaran et al, 2009].

The transition metal cobalt (Co) and rare earth metal gadolinium (Gd) dual doped Li_{1.15}Mn_{1.96}Co_{0.03}Gd_{0.01}O_{4+δ} spinel cathodes were prepared in stoichiometric ratio. The reagent grade oxides of gadolinium (Gd₂O₃), manganese (MnO₂), cobalt (Co₃O₄), lithium carbonate (Li₂CO₃) were taken in account and synthesized via solid state route. The phase purity was achieved by calcined treatment in air atmosphere in two steps: first at 850 °C for 5 h for removal of organic content and second at 600 °C for 10 h for getting phase purity. The x-ray diffractograms revealed that all cathodes had high degree of spinel phase crystalline without any impure phase. The particle average size was in micron range and uniformly distributed. The electrochemical performance of Li_{1.15}Mn_{1.96}Co_{0.03}Gd_{0.01}O_{4+δ} and LMO cathodes were compared at room (25 °C) and elevated (50 °C) temperatures at C/2 rate. The specific discharge capacity at initial and after 100th cycle was reported as 126 and 124.4 mAhg⁻¹ at room temperature for Li_{1.15}Mn_{1.96}Co_{0.03}Gd_{0.01}O_{4+δ} whereas initial discharge capacity was observed as 128.1 mAhg⁻¹ at 50 °C temperature. The capacity fading was 0.017% and 0.079% per cycle for room and elevated temperature cycling for dual doped cathode [Sun et al, 2009].

The simultaneously dual doping of transition metal Zn and rare earth metal La spinel cathode materials, Li_xMn_{2-x-y}Zn_xLa_yO₄ (x=y=0.01-0.05), was synthesized in stoichiometric ratio using oxides of lanthanum, zinc nitrate, manganese and lithium acetates via aqueous sol-gel route using citric acid as chelating agent. The pH at 6.0 was maintained using ammonium hydroxide solution. The calcined treatment in air atmosphere was performed in two steps: first at 450 °C for 5 h for undesired organic content removal and second at 750 °C for 10 h for getting phase purity. The x-ray diffractograms revealed that all cathodes had high degree of spinel phase crystalline with trace amount of impure phase. The particles average size was obtained in between 42 - 140 nm range. The cyclic voltogram scanned over potential range 3.2 - 4.8 V with sweep rate 0.01 mV/sec. The electrochemical performance of Li_xMn_{2-x-y}Zn_xLa_yO₄ (x=y=0.01-0.05) and LMO cathodes were compared at room (25 °C) temperature at different C rates; 0.1C, 0.3C, 0.5C, 1C, 2C, and 5C; over potential range 3.0-4.6 V. The initial specific discharge capacity of LMO and La-Zn doped LMO cathodes were reported as 122 and 118, 111, 108, 106, 105 mAhg⁻¹ for x=y=0.01, 0.02, 0.03, 0.04 and 0.05, respectively. The capacity fading per cycle in La-Zn doped LMO cathodes was observed such as 0.34, 0.18, 0.22, 0.187, 0.165 and 0.26 mAhg⁻¹. The doped sample, x=y=0.01, showed the higher stable cyclability compared to all others. But at high C rate (at 5 C) capacity fading was also higher but less compared to bare LMO cathode [Azhar et al, 2012].

The transition metal chromium (Cr) and other metal [TM-Sc (Scandium); RE-Ce, Pr (Promitium) and Tb] dual doped LiCr_xRE_yMn_{2-x-y}O₄ (x = 0.01 - 0.03; y = 0.05) spinel cathodes were synthesized in lithium excess ratio using metal nitrates via aqueous sol-gel route. The phase purity was attained by calcined treatment in air atmosphere in two steps at 400 °C for 14 h and 750 °C for 24 h. The x-ray diffractograms revealed that all cathodes had high degree of cubic spinel phase crystalline nature without any impurity phase after calcined at 850 °C for 4 h. The particle average size was not determined due to particles wide size 100-300 nm. The electrochemical performance of Li_{1.05}Cr_xRE_yMn_{2-x-y}O₄ (RE: Ce, Pr and Tb x= 0.01; y=0.05) and LMO cathodes were compared at room temperature in potential range 3.0 - 4.4 V at C/3 rate. The initial specific discharge capacity of Li_{1.05}Ce_{0.01}Cr_{0.01}Mn_{1.98}O₄ cathode was measured as 96 mAhg⁻¹ and after 30th cycles capacity retained as 56.0 mAhg⁻¹. The Li_{1.05}Pr_{0.01}Cr_{0.01}Mn_{1.98}O₄ and Li_{1.05}Tb_{0.01}Cr_{0.01}Mn_{1.98}O₄ had similar discharge capacity. However, the specific discharge capacities didn't have plateau at low capacity compared to LMO cathode and showed continuous fading. The discharge capacity retention after 30th cycles at room temperature was obtained as 88 % for Li_{1.05}Sc_{0.01}Cr_{0.01}Mn_{1.98}O₄; 96 % for Li_{1.05}Sc_{0.01}Cr_{0.03}Mn_{1.96}O₄; 93 % for Li_{1.05}Sc_{0.01}Cr_{0.05}Mn_{1.94}O₄; 92.6 % for Li_{1.05}Sc_{0.01}Cr_{0.07}Mn_{1.92}O₄ and 84 % for Li_{1.05}Sc_{0.01}Cr_{0.1}Mn_{1.89}O₄.

However, initial discharge capacity for $\text{Li}_{1.05}\text{Sc}_{0.01}\text{Cr}_{0.03}\text{Mn}_{1.96}\text{O}_4$ cathode was obtained 113.8 mAhg^{-1} . The capacity retention was 91% after 80 cycles [Xie et al, 2007].

2.5 SCOPE OF THESIS WORK

From the above review study, it is concluded that the different synthesis method, different calcining temperature and varied amount of doping are affecting the cathode material electrochemical performance. The efforts are made to synthesize the different rare-earth doped spinel LMO cathode for 4 V potential window by adopting a single method, equal amount of doping of rare-earth elements, single organic sol-gel method, and compare the various physical and electrochemical properties. The optimum amount of doping is to be figured out. The effects of rare-earth elemental doping on 5 V cathodes ($\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$) are also explored. The various synthesized cathode materials and their code names are given in Table 2.1.

The main objective of thesis work is summarized as follows:

- Synthesis and characterization (physical and electrochemical) of rare-earth metal elemental doped spinel cathode, $\text{LiMn}_{2-x}\text{RE}_x\text{O}_4$ (RE: Gd, Dy, Tb, Yb, X=0.05), for lithium ion battery application.
- Optimization the Gd and Dy elements doping amount for the best performed cathodes.
- Synthesize and characterization (electrochemical and Physical) of rare-earth metal elemental doped spinel cathode, $\text{LiMn}_{1.5-x}\text{RE}_x\text{Ni}_{0.5}\text{O}_4$ [RE: Gd (X=0.02, 0.04), Nd (x=0.04, Dy (X=0.04)], for lithium ion battery application.

Table 2.1: Cathode Description and Its Code Names

SN	Cathode Description	Code Name
1	LiMn_2O_4	LMO
2	$\text{LiMn}_{1.95}\text{Gd}_{0.05}\text{O}_4$	LMO-Gd05
3	$\text{LiMn}_{1.95}\text{Dy}_{0.05}\text{O}_4$	LMO-Dy05
4	$\text{LiMn}_{1.95}\text{Tb}_{0.05}\text{O}_4$	LMO-Tb05
5	$\text{LiMn}_{1.95}\text{Yb}_{0.05}\text{O}_4$	LMO-Yb05
6	$\text{LiMn}_{1.99}\text{Gd}_{0.01}\text{O}_4$	LMO-Gd01
7	$\text{LiMn}_{1.96}\text{Gd}_{0.04}\text{O}_4$	LMO-Gd04
8	$\text{LiMn}_{1.99}\text{Dy}_{0.01}\text{O}_4$	LMO-Dy01
9	$\text{LiMn}_{1.98}\text{Dy}_{0.02}\text{O}_4$	LMO-Dy02
10	$\text{LiMn}_{1.97}\text{Dy}_{0.03}\text{O}_4$	LMO-Dy03
11	$\text{LiMn}_{1.96}\text{Dy}_{0.04}\text{O}_4$	LMO-Dy04
12	$\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$	LMNO
13	$\text{LiMn}_{1.48}\text{Ni}_{0.5}\text{Gd}_{0.02}\text{O}_4$	LMNO-Gd02
14	$\text{LiMn}_{1.46}\text{Ni}_{0.5}\text{Gd}_{0.04}\text{O}_4$	LMNO-Gd04
15	$\text{LiMn}_{1.46}\text{Ni}_{0.5}\text{Nd}_{0.04}\text{O}_4$	LMNO-Nd04
16	$\text{LiMn}_{1.46}\text{Ni}_{0.5}\text{Dy}_{0.04}\text{O}_4$	LMNO-Dy04

2.6 CLOSING REMARK

This chapter is presenting an overview of different synthesis methods, challenges, scientific contribution in spinel cathode material field with special attention towards LiMn_2O_4 cathode for Li-ion battery application. The scope and aims of the thesis have also discussed.

