CHAPTER II

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2.1 LITERATURE SURVEY

Since the introduction by Sony of its rechargeable lithium ion battery in 1990[1], more effort has been directed to this development of lithium ions systems by several research laboratories in order to meet the demands of a reliable safe and higher energy density and environmental friendly portable power sources. Commercial Li-ion cells have been an active area in recent years [2-10]. Heterekat et al [11] has reviewed the development of lithium batteries in the past few years. In this the authors have indicated the extensive research in various countries on the development of lithium primary and secondary batteries. The major area of research is towards the development of new materials with intercalation for positive and negative electrodes, new electrolytes, safety improvement, cost reduction and Cycleability and in the case of Li polymer electrolyte batteries the improvement of conductivity of the electrolyte, search for newer materials for positive and negative electrodes. Siapkas [12] has indicated that since lithium ion batteries find extensive application in portable consumer electronics, more attention has been diverted in lithium ion cells (with cathode materials with one of the high voltage oxides like lithium manganate, lithium nickelate, lithium cobaltate) and anode materials of come from carbon.

The practical use of lithium cells in electronic devices such as Li/(CF)n and Li/MnO₂ has been expanded widely. Later layered transition metal dichalcogenides, such as TiS₂ [13] MnO₂ [14] chain chalcogenide (NbSe₃) [15] or amorphous solids (MOS₂) [16] vanadium oxides etc. were used as
positive electrodes versus lithium foil as negative electrode in several prototype and commercial products. However, the use of lithium metal as anode materials in rechargeable batteries was finally rejected due to safety reasons. Scrosati et al [17, 18] have introduced the term 'rocking – chair batteries in the 1980's hence forth, this idea has been of the frequent use as a prelude to the pioneering concept of intercalation / deintercalation of lithium ions during cell charge and discharge.

Recently, an innovative secondary lithium cell technology has been proposed [19-23] leading to the fabrication of a 4V secondary lithium ion cell. The possible candidates for 4V Li-ion cathode materials are LiCoO₂ [19,24,25], LiNiO₂ [20], Li(Ni₁₋ₓCoₓ)O₂ [21], LiMn₂O₄ [22,26]. LiMn₂O₄ has a spinel-framework structure and other materials are iso-structural as that of α-NaFeO₂. LiMn₂O₄ have been intensively developed on account of its inexpensive materials cost, environmentally more friendly, and better safety compared with layered LiCoO₂ and LiNiO₂ [27-29]. Much research has been focusing on the application of several lithium manganese oxides to lithium ion batteries [30-32] particularly the spinel LiMn₂O₄. Therefore, the spinel LiMn₂O₄ cathodes have become appealing for lithium – ion batteries. The extraction/insertion of two lithium ions from/into the Li[Mn₂]O₄ spinel framework occurs in two distinct steps [33]. While the lithium extraction /insertion from into the 8a tetrahedral sites occurs 4V with the maintenance of the initial cubic spinel symmetry and that from/into the 16c octahedral sites occurs at around 3V by a two – phase mechanism involving the cubic spinel Li[Mn₂]O₄ and the tetragonal lithiated spinel Li₂[Mn₂]O₄. Although both involve the same Mn³⁺/Mn⁴⁺ couple, the 1V difference between the two processes
was a reflection of the differences in the site energies [34]. The theoretical capacity of LiMn$_2$O$_4$ was 148mAh/g. But can only store a capacity of 110-120 mAh/g in practice [35] To improve the cycleability of the LiMn$_2$O$_4$ spinel the modification or coating of its surface with other oxides such as LiCoO$_2$, V$_2$O$_5$, Al$_2$O$_3$ or MgO [36-39] are used with an aim to suppress the dissolution of manganese in contact with the electrolyte. The modified samples exhibit improved cycleability at both ambient and elevated temperature. This suggests that (i) a diffusion of the coating or modifying oxides M$_2$O$_3$ into LiMn$_2$O$_4$ is essential to achieve good cycleability and (ii) the improved cycleability need not be simply due to the protection of the cathode surface from the electrolyte and the consequent suppression of manganese dissolution. Clearly, additional factors than manganese dissolution could be playing a role in improving the cycleability on coating/modifying the LiMn$_2$O$_4$ cathodes.

Extensive research has been made by various research groups on the crystal chemistry, magnetic, electrochemical and several other important aspects of both doped LiMn$_2$O$_4$ to have an insight on the correlation between physical and electrochemical properties of this material and obtaining cathode materials with superior performance for lithium – ion cells when compared to undoped LiMn$_2$O$_4$ material. Few results on the above subjects have been furnished here for better understanding and to envisage the importance of further studies with these advanced cathode materials.
2.1.1 Co as substitute in LiMn$_2$O$_4$

The electrochemical properties of spinel LiMn$_2$O$_4$ are highly dependent on the synthesis route, composition, and thermal history of the samples. LiMn$_{2-x}$M$_x$O$_4$ spinels (M: Li, Co, Cr, Ni, Fe, Zn, Mg, Al and Ti) [40-43] have been shown to have better cyclic performance at around 4V than the parent LiMn$_2$O$_4$

Nevertheless, cobalt seems to be one of the most promising dopants investigated so far [41-48]. The presence of Co in the spinel inhibits the passivation process occurring on the surface of the cathode [44], increases the exchange current density [44, 48] and facilitates the charge-transfer reaction of the active material. Wu et al [54] reported the Co-substituted LiMn$_2$O$_4$ cathode materials exhibited improved cycling performance over the un-substituted spinels. Chang et al. [55] had reported that LiMn$_{1.8}$Co$_{0.2}$O$_4$ showed best cycling performance among LiMn$_{2-y}$Co$_y$O$_4$ spinels ($y = 0.0-0.5$) by conventional solid state method. Different optimum Co-contents had been suggested in preparing Co-substituted spinels via various preparation methods [56-61]. Shen et al. [60] reported that sample with amount of Co substitution $y=0.1$ exhibits the best cycling performance among samples with $0 \leq y \leq 0.5$ with the initial specific discharge capacity of 105.4 mAh/g and capacity loss of 0.48 % after 20 cycles.

But in the present investigation we have suggested a new method called low temperature CAM microwave assisted sol-gel method.
2.1.2 Cr as substitute in LiMn$_2$O$_4$

For the development of lithium–carbon batteries spinel type LiMn$_2$O$_4$ has been considered as a promising positive electrode material for the rechargeable batteries due to low cost, environmental acceptability, more abundance in nature, and high capacity retention [62-67, 49]. But LiMn$_2$O$_4$ shows unacceptable fading of capacity [68, 69]. This phenomenon has been attributed to several factors such as electrolyte decomposition, slow dissolution of LiMn$_2$O$_4$ [70], unstable two-phase reaction, i.e., Jahn-Teller distortion [71], lattice instability [72], and particle disruption [73]. Ohzuku et al. [74] have studied a series of 5-V positive – electrode materials obtained by substituting the Mn in LiMn$_2$O$_4$ with third transition metals such as Co, Cr, Cu, Fe, Ni, Ti and Zn which are effective in suppressing capacity fading on cycling. These materials have operating voltages above 4.8V, as also reported by Lee et al. [75]. The electrochemical behaviour of the material also depends upon the method of synthesis. In recent years, several low-temperature preparation methods, such as sol-gel [76, 77], precipitation [78], the pechini process [79] and hydrothermal method [80] have been used to prepare LiMn$_2$O$_4$.

Y.P. Fu et al. reported the LiMn$_{2-x}$Cr$_x$O$_4$ was used as cathode materials for lithium ion battery, whose discharge capacity and electrochemical characteristic properties in terms of cycle performance were also investigated. The results revealed that the Li/LiMn$_{2-x}$Cr$_x$O$_4$ cell synthesized by microwave – induced combustion had a high initial capacity and much better reversibility than one formed in a solid – state reaction [81]. Thirunakaran et al. reported the effect of chromium is more pronounced in reducing the capacity fade. On
the other hand, the cycleability of undoped LiMn$_2$O$_4$ decreases drastically. Undoped LiMn$_2$O$_4$ delivers an initial capacity of 120 mAh/g whereas 0.01 Cr gives a constant capacity of 110 mAh/g [82]. Many researchers reported the Cr doped LiMn$_2$O$_4$ [83-87] results revealed that a lower capacity fade and improve the electrochemical performances.

2.1.3 Sr as substitute in LiMn$_2$O$_4$

At present, the materials most likely to succeed in future commercial applications are LiMn$_2$O$_4$ and related derivatives due to low cost and nontoxicity of manganese, so an intensive research of that has been underway in recent years [88, 68] Although LiMn$_2$O$_4$ has some merits, it still has difficulty for practical application, owing to severe capacity fading. The reason why spinel LiMn$_2$O$_4$ shows capacity loss during cycling is not identified clearly yet, and several possible sources are suggested [88,68,57,89], such as Jahn-Teller distortion, lattice instability, manganese dissolution, electrolyte decomposition and so an. To defeat capacity fading, previous reports by Tarascon et al. [90] and Thackarey and Co-workers [40] demonstrated that addition of excess Li to the spinel (Li$_{1+x}$Mn$_{2-x}$O$_4$) improves the cathode cycle life, along with a concomitant decrease in the observed capacity. The capacity loss was reported to be 148 (1-3x) mAh/g [40]. Detailed analysis of this effect in the context of Li-Mn-O phase diagram related to LiMn$_2$O$_4$, Li$_4$Mn$_5$O$_{12}$, Li$_2$Mn$_4$O$_9$ cathode materials has been also reported by Xia et al. [91]

Another approach involves the substitution of second transition element instead of Mn in the spinel oxide matrix, obtaining a general composition of LiM$_x$Mn$_{2-x}$O$_4$. Attempts to substitute Mn with elements such as
Co, Mg, Cr, Ni, Ti, and Zn have been reported previously [29, 92, 44]. Hence the present, studies includes Sr doping in to LiMn$_2$O$_4$ matrix.

2.1.4 Mg as substitute in LiMn$_2$O$_4$

Lithium manganese oxides (LiMn$_2$O$_4$) are inexpensive cathode materials with a high energy density for Li-ion batteries. Although the reversible specific capacities for LiMn$_2$O$_4$ are lower than the theoretical specific capacity of the best cobalt and nickel LiMO$_2$ (M = Co, Ni) compounds [42, 49, 93-96]. An obvious obstacle of the application of LiMn$_2$O$_4$ is its poor cycling performance. A very effective way for improving the cycling performance of LiMn$_2$O$_4$ is to synthesize magnesium-substituted LiM$_x$Mn$_{2-x}$O$_4$ spinel phase by doping with divalent or trivalent ions.

Stoichiometric spinel phases LiM$_x$Mn$_{2-x}$O$_4$ is prepared to improve the electrochemical behaviour of LiMn$_2$O$_4$. Magnesium was selected as substitute material because of it low atomic weight compared with LiMn$_2$O$_4$ [97]. Many researchers reported the Mg doped LiMn$_2$O$_4$ [71, 97, 98]. G.M. Song et al. reported that the LiMg$_{0.1}$Mn$_{1.9}$O$_4$ powder with a narrow particle size has the best electrochemical performance, which delivers the discharge capacity of 119 mAh/g and exhibited good cycle stability [99]. I. S. Jeong et al. reported the charge –discharge capacity of Mg substituted spinel is higher than that of pure spinel, even on the first cycle. The discharge capacity of LiMg$_{0.1}$Mn$_{1.9}$O$_4$ on the first and 70$^{th}$ cycles is about 120 and 105 mAh/g respectively. The cell retains about 88% of the initial capacity at the 70$^{th}$ cycle [97].

Various electrochemical and physical properties of novel LiM$_y$Ni$_{0.5-y}$Mn$_{1.5}$O$_4$ (0.0-0.4) compounds have been investigated and their
improved performances were reported [100]. According to authors, simultaneous substitution of Mg and Fe, Cu, and Al enables one to obtain good cycling stability.

This present investigation is to synthesize the Mg doped LiMn$_2$O$_4$ by a new method called CAM microwave assisted sol-gel method and improve the capacity retention of the Mg doped material.

2.1.5 Nd as substitute in LiMn$_2$O$_4$

In the ideal spinel oxide LiMn$_2$O$_4$ structure, oxygen atoms form a face-centered cubic packing and occupy 32e sites of space group Fd3m. In LiMn$_2$O$_4$ spinel lithium ions occupy the tetrahedral (8a) sites and the transition-metal ions reside at the octahedral (16d) sites [101].

The electrochemical behaviour of LiMn$_2$O$_4$ is strongly influenced by the method of preparation, as well as the precursors and heat treatment protocols. Synthesis parameters determine the crystallinity, phase purity, particle morphology, grain size, surface area, and cation distribution in the spinel structure, all of which can impact on the electrochemical performance of the spinel [102, 103]. The cation dopants of Magnesium, Nickel, aluminium, Titanium, Cobalt, Chromium, have been studied recently. Such cation doping is found to improve the cycling performance [49, 29,104-106].

S.T. Yang et al. [107] have studied the effect of Nd substitution for Mn, for the development of LiMn$_2$O$_4$ cathode material through microwave method. The present study is to make further investigation with Nd substitution in LiMn$_2$O$_4$.
2.2 SCOPE OF THE PRESENT INVESTIGATION

From the thorough literature survey, the following points are noted. The cubic spinel LiMn$_2$O$_4$ cathode materials offer considerable advantages over the other cathode materials. But LiMn$_2$O$_4$ suffers from capacity fading that limits its reversibility. In order to overcome this problem, substitution of some of the manganese with additional lithium or metal cations has been explored. Many researchers have pointed out that the substitution of metal cations for Mn enhances the stability of spinels. This is due to the stronger M-O bonding of the MO$_6$ octahedron of partially substituted Li$_x$Mn$_{2-x}$O$_4$ in comparison with that of the M-O in the parent LiMn$_2$O$_4$. The electrochemical behaviour of these materials also depends upon the method of synthesis.

Several techniques such as sol-gel, self-propagating combustion, precipitation and emulsion drying have been adopted for the synthesis of nano-crystalline materials. Among these, self-propagating combustion synthesis is the most widely used materials. Nevertheless, this method has drawback of producing highly agglomerated particles. To remove this drawback, a low temperature pechini process has been introduced and yields a phase pure product with controlled stoichiometry. But the steps involved in this method are very tedious and must be performed carefully. In order to overcome the drawbacks of the above methods, a novel Citric acid modified microwave assisted sol-gel method to be introduced for the synthesis of cubic spinel LiMn$_2$O$_4$ based cathode materials. This method employs citric acid as a chelating agent and acryl amide as a gelling agent. This soft chemistry
technique offers many advantages such as better homogeneity, low calcination temperature, shorter heating time, and regular morphology, nano-sized particles, less impurities, large surface area, and good control of stoichiometry. Hence, in the present investigation, the CAM microwave assisted sol-gel method to be adopted for the synthesis of LiCo\textsubscript{x}Mn\textsubscript{2-x}O\textsubscript{4}, LiCr\textsubscript{x}Mn\textsubscript{2-x}O\textsubscript{4}, LiSr\textsubscript{x}Mn\textsubscript{2-x}O\textsubscript{4}, LiMg\textsubscript{x}Mn\textsubscript{2-x}O\textsubscript{4} and LiNd\textsubscript{x}Mn\textsubscript{2-x}O\textsubscript{4} (x = 0.0, 0.1, 0.2, 0.3 and 0.4). Among the above compositions, the best optimum composition was chosen for the synthesis of LiCo\textsubscript{x}Mn\textsubscript{2-x}O\textsubscript{4}, LiCr\textsubscript{x}Mn\textsubscript{2-x}O\textsubscript{4}, LiSr\textsubscript{x}Mn\textsubscript{2-x}O\textsubscript{4}, LiMg\textsubscript{x}Mn\textsubscript{2-x}O\textsubscript{4} and LiNd\textsubscript{x}Mn\textsubscript{2-x}O\textsubscript{4} (x = 0.0, 0.1, 0.2, 0.3 and 0.4). The following physical and electrochemical characterizations are to be carried out for the synthesized products.

- The phase formation and/or complete crystallization of the precursors are to be studied by thermal analysis.
- The structural properties of the synthesized samples are to be characterized by X-ray diffraction studies.
- The particle sizes of the synthesized products are to be conformed by transmission electron microscopic (TEM) studies.
- The electrochemical cyclic voltammetry studies of the synthesized powders are to be examined by EG&G electrochemical analyzer. The electrode was cycled between 2.5 and 4.5 V and 3.0 and 4.5V with a scan rate of 0.1mV/sec.
- The electrochemical charge-discharge studies of the synthesized powders are to be examined by fabricating 2016 coin type electrochemical cell in the configuration of C/synthesized cathode materials employing Li\textsuperscript{+} /LiClO\textsubscript{4}
electrolyte. The charge and discharge studies are to be then performed galvanostatically at the current density of 0.1 mA/cm$^2$ in the voltage range of 3.5 - 4.5V.
References


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