CHAPTER 2

OVERVIEW OF LITERATURE

2.1 POSITIVE ELECTRODES FOR LI ION BATTERIES

There has been considerable research and development activity targeted towards the commercialization of battery systems based on lithium insertion cathodes and metallic lithium anodes. This effort has been primarily driven by the desire for inexpensive high energy density rechargeable batteries, which could be utilized in various applications ranging from cellular telephones to electric vehicles. Lithium batteries without lithium metal anode are known for several years, and were originally termed as "Rocking chair" batteries (RCB) (Amatucci 1996). Shortly after the establishment of RCB concept, Di Pietro et al (1982) have demonstrated batteries with transition metal oxide based anodes and cathodes. Later this technology was named as Lithium ion (Whittingham 1976), Shuttlecock (Sawai et al 1994), Swing Electrode System (Bittihn 1993), etc., but the fundamental concept remained the same.

2.1.1 Layered Metal Oxide

The first generation Li ion cells used Lithium metal oxide as cathode, graphite/hard carbon as anode and Li salt dissolved in non aqueous solvents as the electrolytes. The charge and discharge cycles of this battery are merely extraction and insertion of the Li ions from or into the stable crystal lattice of the electrode. The performance of the Rocking chair Li ion battery mainly depends on the property of the cathode materials. The Lithium
Cobalt Oxide, LiCoO$_2$ with rock salt structure and rhombohedral R3m space group is the most extensively used cathode material for rocking chair batteries (Ohzuku 1994). Removal of lithium corresponding to $x = 1$ in Li$_x$CoO$_2$, is equivalent to a theoretical capacity of about 274 mAh/g.

The LiCoO$_2$ is the prominent cathode material because of its high theoretical capacity and long cycle life. Though the current predominant cathode material is LiCoO$_2$, it is very expensive and possesses limited practical capacity ($<140$ mAh$^{-1}$) (Delmas 1989). Moreover it suffers from stability problems at elevated temperatures in the common electrolyte solutions (e.g., a LiPF$_6$ salt in a mixture of alkyl carbonate solvents) resulting in capacity fading after several cycles. The main cause for the poor performance of the battery has been attributed to the instability of the electrode materials. The reasons for such instability are (i) In-homogeneity in the compound formation (i.e.) existence of two or more compound phases resulting in cation ordering (Nobuo Ishizawa 2003, Won-Sub Yoon 2004), (ii) slow dissolution of the cathode material into the electrolyte (Gadjov 2004) and (iii) high value of the relative volume changes accompanying charge/discharge cycling (Rodríguez-Carvajal 1998).

Lithium de-intercalation from LiCoO$_2$ has been investigated in detail by Mizushima et al (1980) and the report envisages the structural changes involved during de-intercalation. Lithium de-intercalation in LiCoO$_2$ has been identified to take place in several steps. The first step involves a monoclinic phase transition of Li$_{0.5}$CoO$_2$ (Arai 1995) and the second phase involves another monoclinic phase formation with lesser Lithium content. The formation of second monoclinic phase with low Li content has not been observed by Mc Breen et al (2001), instead these authors have observed a hexagonal phase formation. Similarly Chen and Dahn (2002) have found that
the hexagonal O3-compound formation with formula Li$_{0.12}$CoO$_2$. This observation also coincides with Vander ven et al (1998).

Removal of Li in Li$_x$CoO$_2$ form $x = 1$ to $x = 0.1$ was expected to yield a capacity value of 274 mAh g$^{-1}$. But, in practice, delithiation in LiCoO$_2$ is restricted to $x = 0.5$, corresponding to 4.2 V vs. Li/ Li$^+$ (Ozawa 1994) and hence the experimental capacity is always lesser than 274 mAhg$^{-1}$. In the report of Ozawa et al (1994) it has been shown, that Li removal up to $x = 0.5$ has resulted in an increase in interlayer distance. But it has been reported that CoO$_2$ structure can accommodate lithium up to 90-95 % by electrochemical reduction at a low rate (Vaughan 1999), suggesting the reversible nature of both the phases and volume changes as a result of delithiation. However, the dissolution of cobalt at high potentials in the electrolyte resulting in structural change is irreversible and results in capacity fading upon cycling above 4.2 V. Therefore, cycling of LiCoO$_2$ cathode has been generally restricted only up to 4.2 V.

There are several methods demonstrated by many authors to mitigate the instability of the LiCoO$_2$ in the electrolyte. Recent studies make use of oxide coatings on LiCoO$_2$ and high-temperature annealing to prevent cobalt dissolution (Cho 2001). Similarly in a review by Chen and Dahn (2003), the capacity fading in LiCoO$_2$ cathode has been attributed to the increase in impedance at the LiCoO$_2$ surface in LiPF$_6$-based electrolytes. The impedance at the LiCoO$_2$ surface could be suppressed by (a) metal oxide coating, (b) grinding to create fresh LiCoO2 surface and (c) heat treatment in air at 550°C (Chen 2004).

Thermal stability is another important factor concerned with the electrodes and electrolytes. The thermal stability of Li$_x$CoO$_2$ in electrolyte has been observed to decrease with increasing $x$. This problem has been studied and reported in detail by Cho et al (2001).
Apart from the feasibility to check the capacity fading of LiCoO$_2$ by various ways, the environmental hazardous nature of the Cobalt species and its cost have been considered as the impeding factor in wide spread commercialization. As an alternative to this material many materials have been suggested and LiNiO$_2$ is one such material with the same R3m structure as that of LiCoO$_2$. The lesser cost of Ni and its environmental harmlessness when compared to cobalt species has driven the researchers to investigate the compatibility of this material. Both LiCoO$_2$ and LiNiO$_2$ have layered crystal structure and thus provides Li ions to reside (intercalate/de-intercalate) in the in between layers. Because of the excessive spacing for the Li ion passage during charging and discharging, the structural distortion has comparatively lesser effect in this kind of electrode materials. Even then the main issues relating to these materials are the precise control of stochiometry, difficulty in the synthesis of the materials with intended layered structure and its instability at low lithium content (Riemers 1996).

2.1.2 Lithiated Spinel Material

LiMn$_2$O$_4$ material with cubic spinel structure has been identified as an alternative to the layered metal oxide, owing to its cost effectiveness, non toxicity, higher abundance of Mn in the earth and easy disposal. LiMn$_2$O$_4$ has been known to crystallize in space-group Fd3m with Li occupying 8a tetrahedral and Mn residing in the 16c and 16d octahedral sites of the cubic-close-packed oxygen array as shown in Figure 2.1 (Im 2003). In the structural framework, MO$_6$ octahedra share edges to build a rigid 3-dimensional network with open interconnected channels in the <110> directions. Li$^+$ ions are mobile within these channels along the 8a-16c-8a path.
A reversible extraction of Li from LiMn$_2$O$_4$ has been identified to occur in two steps around 4.05 V, 4.15 V respectively and results in delithiated MnO$_2$ crystal lattice (Ozhuku 1990). Operating voltage is larger for LiMn$_2$O$_4$ when compared to LiMO$_2$ (M = Co, Ni). Though the LiMn$_2$O$_4$ has many advantages rather than conventional LiCoO$_2$, the extensive usage of LiMn$_2$O$_4$ as cathode material is impeded due to its structural instability leading to capacity fading on extensive cycling.

The performance of the LiMn$_2$O$_4$ electrode mainly depends on the stochiometry and its lattice structure and hence there is a need to synthesize LiMn$_2$O$_4$ with average oxidation state of Mn higher than 3.5 to get good electrochemical performance, which in turn depends on O and Li stoichiometry (Gummov 1994). Accordingly, most of the researchers have focused on the preparation of spinels with formulations close to Li$_{1+x}$Mn$_{2-x}$O$_4$ with low x (= 0.05) to achieve 4 V capacity window (Yamada 1995).

Conventionally, the LiMn$_2$O$_4$ are synthesized by sintering the corresponding oxides (or) carbonates, in the approximate temperature range...
of 700 to 900°C. Inspite of the wide spread adoption of solid state reaction, it possess certain disadvantages like

- Difficulty in controlling particle size
- High operating cost - due to high temperature processing
- Repeated heat treatment followed by intermittent grinding leading to high processing time
- In homogeneous compound formation with irregular morphology
- Poor control of stochiometry

In order to overcome these disadvantages, various preparative techniques known as “soft-chemistry” methods have been developed. Such techniques are based on the processes of co-precipitation (Hui Cao 2004), ion-exchange or thermal decomposition at low temperature of appropriate organic precursors obtained by sol–gel (Kang 2000), xero-gel (Prabhaharan 1995), Pechini (Liu 1996), freeze-drying (Zhecheva 1999) and emulsion-drying (Hwang 1998). Among the different processing technologies being adopted for the synthesis of the electrode materials, the microwave processing attracts great deal of attention due to its advantages such as higher synthesis rate, the reduction of grinding steps during the synthesis process and the peculiar property of the microwaves to heat a system “from the inside”.

In conventional thermal processing, energy is transferred to the material through convection, conduction, and radiation of heat from the surfaces of the material. In contrast, microwave energy is delivered directly to materials through molecular interaction with the electromagnetic field. In heat transfer, energy is transferred due to thermal gradients, but microwave heating is the transfer of electromagnetic energy to thermal energy and is energy
conversion, rather than heat transfer. Since microwaves can penetrate materials and deposit energy, heat can be generated throughout the volume of the material. The transfer of energy does not rely on diffusion of heat from the surfaces and hence it is possible to achieve rapid and uniform heating of thick materials. For polymers and ceramics, which are materials with low thermal conductivities, this can significantly reduce the processing time. Thus, there often is a balance between processing time and product quality in conventional processing. As microwaves can transfer energy throughout the volume of the material, the potential exists to reduce processing time and enhance overall quality (Thostenson 1999).

Harish Bhat et al (2000) have reported the Microwave synthesis of electrode materials and has attempted in synthesizing LiMn$_2$O$_4$, LiCoO$_2$, CuBi$_2$O$_4$ and Bi$_4$B$_2$O$_9$. The microwave preparation of lithium manganate has been first attempted with Li$_2$CO$_3$ and MnO$_2$ as reactants. But the expected cubic spinel phase of LiMn$_2$O$_4$ has not formed. Instead a mixed phase of defect spinel (Li$_{2-y}$MnO$_2$) has been formed. The observed results are quite interesting because the defect spinel has been observed to be stable only below 400°C and upon heating above 400°C, it transformed into the cubic spinel. Therefore, the metastable phase seems to get stabilized easily in microwave preparation. This may be due to low microwave susceptibility of MnO$_2$, which does not enable the system to attain high (> 400°C) temperature. An alternate reaction scheme has been used for the microwave preparation of the cubic spinel phase. An intimate mixture of LiI and MnO$_2$ has been irradiated by microwaves. It has been found that cubic spinel formed directly in a single heating step of 6 min. The authors have also investigated on the effect of starting compounds and their susceptibility in achieving the final crystalline compounds and it has been conceded that at least one of the reactants should have high microwave susceptibility to achieve good crystallinity.
Hanxing Liu et al (2004) have investigated Solid chemical reaction in microwave and millimeter-wave fields for the syntheses of LiMn$_2$O$_4$ compound. They have presented in detail the influence of warm-up, soaking time, and coupled agent addition in the microwave field to increase the ability of absorbing electromagnetic energies. The method yielded powders of good crystallinity and phase purity. Generally in solid state reaction the final LiMn$_2$O$_4$ results after many intermediate products like LiMnO$_2$ and LiMn$_2$O$_3$. During the solid state reaction the intermediate grinding is necessary because of the self impediment effect. The self impediment is inevitable for the intermediate products because the newly formed LiMn$_2$O$_4$ surrounds them and hinder the intermediate products changing into final product. But in the microwave field, the diffusion speed of Li$^+$ ion has been increased greatly. The diffusion will accelerate the reaction speed of intermediate products changing into LiMn$_2$O$_4$. As the ion diffusion movement has been enhanced, the self-impediment of the intermediate products will be relaxed. This could accelerate the reaction so greatly that the intermediate products could not change into final product completely. Hence the preheating of the low loss material before calcinations would improve the compound formation. The authors have also investigated the dependence of crystallinity with soaking time and it has been identified that at lower reacting temperature (600°C), the longer soaking time would help to improve the crystalline phase.

Though the microwave synthesis has many potential advantages, there are still some factors that should be considered before commercialization of this technology. Main concern about using Microwave furnaces is the operating frequency. Usually the microwave ovens operate at 2.45 GHz with multimode cavity. The calcination carried out in multimode cavity result in the lack of uniform heating in the compounds. Several authors have expressed their serious concerns regarding this (Hongwei Yan 2004, Hu Guo Rong 2004). To overcome this bottle neck problem some authors
have proposed using of single mode cavity operating at same frequency. An interesting report made by Bousquet-Berthelin et al (2005) on Flash microwave synthesis of Mn$_3$O$_4$ -Hausmannite nano particles suggest a design of an original microwave reactor, the RAMO system (French acronym of Reacteur Autoclave MicroOnde. Compared to domestic ovens, this microwave oven allows higher electric field strengths for heating samples. By varying the position of a plunger, the resonant frequency of the cavity could be controlled and the effective cavity power could be increased by three orders of magnitude.

Though the LiMn$_2$O$_4$ has many advantages over the conventional LiCoO$_2$, the extensive usage of LiMn$_2$O$_4$ as cathode material is impeded due to its capacity fading on extensive cycling. The possible reasons that has been attributed for the fading effect are the manganese dissolution into the electrolyte (Xia 1997), Jahn teller distortion due to Mn$^{3+}$ ions (Kyung Yoon Chung 2004), change in crystal lattice arrangement with cycling (Park 2001), the disproportionation reaction of Mn$^{3+}$ (Strobel 2004) and so on. It has been successfully proved that the capacity fading can be reduced by partially replacing the Mn$^{3+}$ ions with other cations. Yen-Pei Fu et al (2006) have demonstrated the synthesis of LiMn$_{2-y}$M$_y$O$_4$ (M =Cr, Co) cathode materials by the microwave-induced combustion for lithium ion batteries.

Heavily-substituted Mn-spinels, namely LiM$_y$Mn$_{2-y}$O$_4$ (M = Fe, Cr, Ni, Co, Cu and their mixtures), may offer high output voltages by taking advantage of the redox couple of the substituted cation. Kawai et al (1999) have examined substituted spinels and found some of the cobalt substituted spinels, namely Li$_2$Co$_{0.8}$Mn$_{3.2}$O$_8$ and LiCoMnO$_4$ to be attractive. In these compounds, Co$^{3+}$/Co$^{4+}$ couple creates a discharge plateau at about 5 V along with the 4 V plateau for the Mn$^{3+}$/Mn$^{4+}$. The capacities obtained for these
materials are 135 and 105 mAh$^{-1}$, respectively, with a moderate capacity fading after 35 cycles at a load current-density of 0.5 mA cm$^{-2}$.

Ohzuku et al (1999) have investigated substituted spinels, such as Li[M$_{1/2}$Mn$_{2/3}$]O$_4$ ($M = \text{Ni, Co, Fe, Cr, Cu}$), and found initial capacities of 120 to 125 mAh$^{-1}$ for the Fe and Ni substituted samples. Interestingly, Nickel substituted compound provides most of its capacity in a single 4.5 V plateau. XPS results exhibit divalent nickel in the compound and its oxidation to tetravalent state results in a high voltage peak at 4.5 V with high capacity (Hernan 2002). Thackeray et al (1999) studied the spinel LiNi$_y$Cu$_{0.5-y}$Mn$_{1.5}$O$_4$ ($0 \leq y \leq 0.5$) and found that, with increasing Nickel content, the capacity increases and the upper plateau potential decreases. LiNi$_{0.5}$Mn$_{1.5}$O$_4$ synthesized by Sol-Gel route (Wu 2002, Sun 2002) exhibits a capacity of about 125 mAh g$^{-1}$ up to 60 charge - discharge cycles at a load current-density of 0.5mAcm$^{-2}$. Yoshio et al (2002) have investigated the influence of ZnO thin layer coating over LiNi$_{0.5}$Mn$_{1.5}$O$_4$, which on cycling at C/3 rate at 55°C has given a stable capacity value of 137 mAh g$^{-1}$.

As a new advancement in the field the introduction of the trace amount of rare earth materials have drawn the attention of few researchers. Though the usage of the rare earth doping is increasing linearly but it is likely to climb exponential statistics in the near future due to its unassailable advantages in checking the capacity fading and improving cycle life.

Chuanqi Feng et al (2003) have first reported the partial replacement of Mn$^{3+}$ ion with yttrium ion. The research paper investigates the non stochiometric formation of the LiY$_{0.02}$Mn$_{1.93}$O$_4$ compound through rheological phase method. The ideated compound has been prepared from citric acid assisted Sol-gel method. The XRD pattern has been observed to illustrate the cubic spinel phase with trace amount of Y$_2$O$_3$ phase on calcination, but the same phase has been observed to disappear on sintering.
On further doping the impurity phase could not be controlled. The intention of replacing Mn\(^{3+}\) ions with Y\(^{3+}\) ions has been observed to be successful and which has been clearly elucidated by the decrease in Mn\(^{3+}\) content through the XPS analysis. Similar observation has also been reported by Tian wen et al (2008). The electrochemical analysis measured Vs Li anode has resulted in the initial capacity of 126 mAhg\(^{-1}\), which has remained unaltered even after 35 cycles. The capacity retention after 50 cycles is 95.2%. The capacity retention has been observed to be as much better than the parent LiMn\(_2\)O\(_4\). The possible reasons for the increase in the rechargeability of the rare earth doped samples have been conceived as follows.

- The higher bond enthalpy of rare earth -oxygen bond rather than Mn\(^{3+}\)-O bond.
- The increase in the valency of Mn and resulting in crystal stabilization

The elements of 4f inner transition series have also been investigated as prospective dopant in ameliorating the capacity of the LiMn\(_2\)O\(_4\) in high temperature and longer cycle operations. The Lanthanum being first element of the inner transition series, it has been proposed by many researchers as potential dopant in checking the capacity fading. The works contributed by Tu et al (2006) clearly depict the influence of La\(^{3+}\) ion dopant in to the LiMn\(_2\)O\(_4\) lattice. The shrink in the lattice parameter on lanthanum doping has been observed, which has evidenced non stress inclusion on doping. Moreover from morphological analysis the authors have envisaged the reduction in surface area and increasing in particle size on doping. This effect has been considered to be significant in improving the capacity retention in both room and elevated temperature operations. The charge-discharge efficiency on doping has been observed to increase from 85.5% for LiMn\(_2\)O\(_4\) to 94.4% for La\(^{3+}\) doping. LiLa\(_{0.01}\)Mn\(_{1.99}\)O\(_4\) sample has exhibited
excellent capacity retention ability at room temperature with only 9.5% capacity loss after nearly 300 cycles. The authors have concluded that the improvement in electrochemical cycle life is possible only at the expense of the initial reversible capacity. The studies made by Chanyun Wan et al (2008) have also briefed extensively the influence of rare earth ion like La$^{3+}$, Pr$^{3+}$, Nd$^{3+}$, Eu$^{3+}$, Y$^{3+}$ and Sm$^{3+}$ in LiMn$_2$O$_4$. The authors have synthesized the stochiometric lanthanum doped compounds. In concurrence with the observation of other research reports the rare earth elements has demonstrated negative effect in the initial discharge capacity. Of all the rare earth dopants, the Lanthanum ion being bigger has low capacity values due to the hindrance offered by it for Li extraction and insertion. On the other hand the all the dopants have appreciable effect in improving the cycle life (Meng Chen et al 2008).

On studying the influence of dopant in structural modification and efficiency improvement, the sound speculation of the underlying physical and chemical effects should be accomplished. The work accomplished by Mohammed Javed Iqbal et al (2008) has thrown light in the influence of doping rare earth elements like La$^{3+}$, Ce$^{3+}$ and Pr$^{3+}$ in the structural, electric and dielectric properties of the LiMn$_2$O$_4$. The general trend of decrease in lattice parameter has been observed with increasing rare earth dopant concentration. The reason for this trend has been ascribed to the increase in binding energy when compared with Mn$^{3+}$ ion. The electrical resistivity measurement performed has clearly depicted the slight increase in resistivity with the substitution. As the conduction mechanism in LiMn$_2$O$_4$ is through small polaron hopping mechanism between octahedral site occupied Mn$^{3+}$ and Mn$^{4+}$ ion. The substitution of rare-earth ions tends to decrease the Mn$^{3+}$ concentration at the octahedral sites and as a result the frequency of hopping of electron decreases. It has also been suggested that exceeding the specific
limit of the dopant concentration may cause the transfer of Mn$^{3+}$ from the octahedral site to the tetrahedral and may result in a decrease in resistivity.

Substitutions of rare-earth elements like Neodymium often play major role in controlling the cationic in most perovskite structures (Melgarejo 2002, Tomar 2003). The investigation of Nd dopant in LiMn$_2$O$_4$ has been carried out extensively by Rahul Singhal et al (2007) in the hope to stabilize and improve the electrochemical performance of the LiMn$_2$O$_4$. They have reported that the small dopant concentration of Nd$^{3+}$ has not much altered the spinel cubic lattice of the LiMn$_2$O$_4$. The initial discharge capacity of the doped samples has been observed to be as high as 149 mAh$^{-1}$ than pure LiMn$_2$O$_4$ (125 mAh$^{-1}$) and the capacity retention of 91% of the initial capacity has been observed at 25 cycles. The improvement in the cycleability has been imputed to the structural stability due to Nd doping. Similar investigation has also been performed by Yang et al (2003) on LiNd$_{0.01}$Mn$_{1.99}$O$_4$ cathode material and Suryakala et al (2008) on series of concentration of Nd$^{3+}$ doped LiMn$_2$O$_4$.

As the multi ion substitution in the LiMn$_2$O$_4$ lattice is well known to stabilize the spinel frame work with good capacity retention, Yanting Xie et al (2007) have carried the co-doping of Sc, Ce, Pr, Tb with Cr$^{3+}$ in Li$_{1.05}$RE$_x$Cr$_y$Mn$_{2-x-y}$O$_4$ through soft chemical method. The co-doping of substituent has altered the spinel structures. But the appearance of some other phase corresponding to CeO$_2$, Pr$_{6}$O$_{11}$, TbLiO$_2$ has been observed. For the Sc$^{3+}$ doped samples, the increment in lattice parameter has been observed which has confirmed the solid solution formation in Sc doped compounds. The transmission electron microscopy studies have exhibited homogeneous and narrow particle size distribution. This narrow size distribution has been considered as influential parameter of the electrochemical capacity. The galvanostatic charge/Discharge studies of the Sc$^{3+}$ doped compounds have
demonstrated plateaus near 4.2 and 3.8V typical to that of LiMn$_2$O$_4$. The pattern of discharge curve has not altered even after 48 cycles.

On the other hand for the other rare earth dopants, the absence of plateaus in the first discharge cycles has been observed. The initial capacity of all the Rare earth doped materials has been observed to be smaller than that of Cr doped spinels; the reason has been attributed to the increasing repulsive interaction between lithium positive – positive ions in the oxide lattice. As far as the cyclability is concerned, the invariable valence Sc$^{3+}$ has positive effect, but for the variable valence rare earth metal including Ce$^{3+/4+}$, Tb$^{3+/4+}$, Pr$^{3+/4+}$ with Cr$^{3+}$, the co substituted compound exhibited poor stability and Sp. Capacity still decay quickly. The above observation of the authors evince that instead of increasing the concentration of both dopants in parent lattice, the fixing of single dopant concentration as constant and varying the other dopant concentration has commendable effect in improving the capacity retention. The authors have observed that of all dopants the Li$_{1.05}$Sc$_x$Cr$_y$Mn$_{2-y}$O$_4$ spinels have demonstrated improved capacity retention on cycling than single doped spinel phase.

An interesting study by Peng Zhong-dong et al (2005) regarding the influence of rare-earth Sm$^{3+}$ doping on performance and structure of spinel LiMn$_2$O$_4$. As per the crystal field theory, the d-electrons of transition cation split to three low energy orbitals and two high energy orbitals in the symmetrical octahedron crystal fields and the f orbital split in to 7 orbitals as shown in Figure 2.2.
In general the rare earth ion has higher ionic radius than Mn$^{3+}$ ion, at the same time, the ion of rare earth has quite strong affinity to oxygen, and has strong octahedral site preference in the spinel crystal lattice. From the crystal field theory it could be ascribed that the electrons in the $f_1$ orbit may occupy the empty $e_g$ orbit of Mn$^{3+}$, and cause the spherical, half filled distribution of d-electrons of Mn$^{3+}$ in the octahedral crystal fields and thus weaken the Jahn-Teller effect of Mn$^{3+}$ ion. The structural characterization of the LiSm$_{0.2}$Mn$_{1.8}$O$_4$ has illustrated the decrement in the lattice parameter values, which has clearly pictured the stronger affinity between rare earth Sm$^{3+}$ ion and oxygen leading to stronger bonding. The electrochemical charge discharge have demonstrated excellent capacity retention nearly about 80% even after 400 cycles and commendable improvement in high temperature cycling has also been observed. The results have clearly testified the conclusion drawn from crystal field theory.
An yet another dopant Erbium and its influence has been reported by Liu et al (2004). The structural investigations have shown the decrement in lattice parameter values which is an indicative of the strong bond formation in Er$^{3+}$-O rather than Mn$^{3+}$-O and stable cubic frame work of LiMn$_2$O$_4$. The charge/dis-charge studies have shown the decrease in initial capacity with increasing doping concentration. But the reversibility has been observed to increase with Er$^{3+}$ dopant. The capacity retention of LiMn$_{1.98}$Er$_{0.02}$O$_4$ has been observed to be around 118.03 mAh$^{-1}$. Only 6.4% of the initial capacity has been reduced. But for the un-doped compound the capacity retention has been observed to be as poor as 15%.

Altogether a collective influence of rare earth dopants in the capacity retention of LiMn$_2$O$_4$ has been presented in Figure 2.3. From the figure it could be observed that the capacity retention of most of the rare earth dopants lie between 80% to 99%. Hence based on the above observations, it could be inferred that the rare earth dopants could aid in improving the shelf life of the battery.

![Figure 2.3 Capacity retention due to Rare earth doping in LiMn$_2$O$_4$](image-url)
2.1.3 Other Cathode Materials

The spinel LiCo$_2$O$_4$ reported by Choi et al (2007) has been identified to be stable up to 200°C and disproportionate above 200°C into LiCoO$_2$ and Co$_3$O$_4$. This compound has delivered a capacity of 80mAh$^{-1}$ above 3V. The extraction of lithium from 8a-sites has occurred around 3.9 V and the insertion of additional lithium into 16c-sites has occurred around 3.5 V. However, LiCo$_2$O$_4$ has exhibited a huge polarization-loss. Attempts to synthesize LiNi$_2$O$_4$ spinel by chemically extracting 50% Ni from LiNiO$_2$ followed by heating at ≤ 200°C has resulted in a spinel-like cubic phase, with Ni$^{3+}$ and Ni$^{4+}$ ions distributed over both the 16c and 16d sites (Ronci 2000). LiTi$_2$O$_4$ (Murphy 1983) and LiV$_2$O$_4$ (Picciotto 1985) with the normal spinel structure have also been attempted by many researchers.

In recent years, LiFePO$_4$ (lithium iron phosphate) with a phospho-olivine structure has emerged as a promising cathode material for lithium-ion batteries. Its high theoretical specific capacity (280 mAh$^{-1}$), flat voltage at 3.4 V, low-cost and safety make it a promising material for lithium ion cells. Padhi et al (1997) have shown the possibility of chemically removing lithium from LiFePO$_4$ leaving behind FePO$_4$ lattice, which is iso-structural with Fe$_{0.65}$Mn$_{0.35}$PO$_4$. Electrochemical extraction of Li from LiFePO$_4$ proceeds through double step process, during which FePO$_4$ structure has been obtained with a minimal displacement of the ordered phospho-olivine framework. However, extraction of Li is limited to 0.6 Li$^+$ mol$^{-1}$ even at low rates. Ravet et al (2003) have renewed the interest in LiFePO$_4$ by improving its electrochemical behaviour by a new synthetic route. These authors have added sucrose to the precursors to act as a source of carbon during the thermal synthesis at 700°C. This material possesses high cycle life even at high discharge rates. Andersson et al (2000) have investigated the electrochemical
extraction and insertion of Li in thermally-synthesized, additive-free LiFePO₄ by \textit{in-situ} X-ray diffraction and Mössbauer spectroscopy.

2.2 NEGATIVE MATERIALS FOR LI ION BATTERIES

Graphitic carbons are currently the most often employed material for the negative electrode due to their low cost, excellent cyclability and reliability (Owen 1997, Winter 1998, Tarascon and Armand 2001). The compounds for negative electrodes are generally divided into two major categories (i) the carbonaceous and (ii) non carbonaceous based materials. Most of the present research is moving towards replacing carbonaceous anode with non carbonaceous one. The driving force behind this current research trend is to obtain a new generation anode materials with higher specific capacities (>372 mAhg⁻¹), along with the good properties of carbonaceous materials such as cyclability, cost and safety features.

2.2.1 Carbonaceous Materials

Carbonaceous-based materials are the most attractive and widely investigated materials for use as anode in Li ion batteries. This has been mainly used due to the following reasons.

- Low cost
- High safety for people
- Low Li ion insertion potential (~ 0.1V Vs Li/Li⁺), which is very close to that for metallic lithium
- Good cycling stability due to high mechanical integrity (compared to metal alloys)
In half cell reactions against metallic lithium, lithium-ion intercalation into carbon is referred to as the discharge step, while the de-intercalation process is the charge step.

\[ \text{C}_n + x\text{Li}^+ + xe^- \xrightarrow{\text{ discharged}} \text{Li}_x\text{C}_n \]  

At ambient temperature, graphitic carbon intercalates one lithium atom per six carbon atoms to form the compound, \( \text{LiC}_6 \) (Winter 1998). The maximum attainable specific charge capacity of the \( \text{LiC}_6 \) electrode is 372 Ah-kg\(^{-1}\) (based on the carbon weight only). Particularly during the first charge step of graphite electrodes, some amount of charge is consumed in an irreversible way. It is caused by the decomposition of the electrolyte, which induces the formation of a solid-electrolyte interphase (SEI) on the electrode surface (Peled 1979). The SEI prevents further electrolyte decomposition and allows the transfer of ions from the electrolyte into the electrode (Besenhard 1995, Aurbach 1999, Xu 2004).

Recently, with the discovery of new crystalline forms of carbon, i.e. the single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs), with dimensions of less than 100 nm have been carried out. These one dimensional carbon materials have attracted considerable attention, because they exhibit an increased capacity as an active material (Che 1998, Gao 1999, Leroux 1999, Claye 2000, Endo 2000).

### 2.2.2 Lithium Metal Alloys

Due to their much high theoretical specific charge capacities compared to graphite, binary or ternary lithium metal alloys with metals such as tin (Winter and Besenhard 1999, Tirado 2003), aluminium (Lindsay 2003), lead (Martos 2001), antimony (Tirado 2003), Silicon (Wilson and Dahn 1995) and copper-tin (Jiangua Ren 2007) are the most well investigated classes of
materials. However the main problem associated with these alloys is the high volume changes due to lithium insertion or extraction. (Besenhard 1997). As a result, mechanical stress and cracks occur during cycling, which leads to electrochemically inactive particles and thus quite poor cycle stabilities.

Today, the use of metal oxide such as lead oxide and tin based oxides attract considerable attention due to their low cost and commercial significance. Several research groups have attempted to use Sn, SnO or SnO$_2$ in conjunction with a carbonaceous material to ease the capacity fading (Courtney 1997). It is believed that both the particle size and size distribution are important factors that affect the material performance. Wet chemical and Microwave syntheses have been increasingly used in the preparation of oxide nano particles (e.g., SnO$_2$, CeO$_2$ and ZrO$_2$) (Zhu 2002, Liao 2001).

### 2.2.3 Transition Metal Oxides

One of the main challenges in the design of Li-ion batteries is to ensure that the electrodes maintain their integrity over many discharge-charge cycles. Although promising electrode systems have been proposed (Shodai 1996, Idota 1997, Kepler 1999), their life spans are limited by Li alloying, agglomeration (Courtney 1999) or the growth of the passivation layers which prevent the fully reversible lithium insertion into negative electrodes (Denis 1997).

Transition metal oxides with a layered structure favor easy lithium intercalation or de-intercalation. Nevertheless, the potentials at which this process takes place, often occurs in a region far above the Li/Li$^+$ couple and much lower than the 4V positive electrode material. Therefore a reduced voltage is obtained when these materials are combined in the cell, resulting in low energy and power densities for these systems (Winter 1998).
Poizot et al (2000) were the first to report that electrodes made of nano particles of transition-metal oxides (MO, where M is Co, Ni, Cu or Fe) demonstrate electrochemical capacities of 700 mAh\textsuperscript{-1}, with 100% capacity retention up to 100 cycles and high charging rates. In this material, the mechanism of Li reactivity differs from the classical Li insertion/De-insertion or Li-alloying processes. It involves the formation and decomposition of Li\textsubscript{2}O, which accompany the reduction and oxidation of metal nano particles. (in the range from 1-5nm). It has also been expected that the transition-metal nano particles would enhance surface electrochemical reactivity and thus would lead to further improvements in the performance of lithium ion batteries.

2.3 REVIEW ON ADVANCEMENT OF ELECTRODE MATERIALS FOR MICRO BATTERIES

The advancement evidenced in the portable electronics industry has resulted in equipments that require low power for operation. Therefore the development of miniaturized power sources with high volumetric energy density is highly anticipated to meet the demand of microelectronic components. Among the present day batteries, the energy requirements of most of the electronic components could only be satisfied with rechargeable type of batteries. Though there are many rechargeable/secondary batteries, the feasibility for miniaturization and compatibility with the micro components is the major criteria in selecting the battery type. The vast majority of solid state Micro batteries enlist some combination of lithium anode, oxide intercalation compounds as cathodes including V\textsubscript{2}O\textsubscript{5}, LiCoO\textsubscript{2}, LiMn\textsubscript{2}O\textsubscript{4} and solid state electrolytes composed of a glassy lithium ion conductor. This electrolyte imparts a long calendar life to the cells (when compared to traditional liquid electrolytes) (West 2001).
The present day state-of-the-art in battery chemistries have achieved the near-term power and energy density goals in their unpackaged form. However, fabrication, processing and integration present major challenges toward the achievement of the required energy density in micro batteries. Although the present day developments in the intercalation cathodes in powder form have evidenced remarkable growth, the performance need not be the same in thin film form. In light of this, lot of works are being carried out to re-examine the reversibility and the optimization of traditional chemistries when practiced in the nano scale. The development of micro batteries has witnessed considerable growth due to the research efforts carried with different perspective in different ways. The most of the publications have highlighted the dependence of the performance of the cell to certain processing parameters and henceforth the identification and control of the parameters could aid in achieving set goals in the development of micro batteries.

The research over the last decade at Oak Ridge National Laboratory (ORNL) has led to the development of solid state thin-film lithium and lithium-ion batteries using LiCoO$_2$ electrodes. (Bates 1994). The cell has been fabricated over Silicon substrate with Lithium, LiPON as anode and electrolyte respectively. The Lithium has been covered with protective parylene and Titanium as outer shields. The LiCoO$_2$ has been fabricated using RF sputtering method. The texturing of the films along (003) orientation has been observed for lower thickness films. The texturing has been attributed to the tendency to minimize Surface energy for thin films and volume strain energy for thicker films. (Bates 1993). Similar observation has been made by Nancy Dudney et al (2003), Jang (2001). In their observation, film of 4.2 µm thickness has yielded 1120 mWhr/Cm$^2$, whereas 1.0 µm thick film has yielded only 280 mWhr/Cm$^2$. But it has also been observed that the thin electrode has exhibited almost same capacity in all current densities. The
discharge curve of thinner electrodes have exhibited finite slope near 3.8V and this is because of the faster lithiation in the electrode but whereas this is not the case for thicker electrode and this has been attributed to the rate limiting diffusivity in thick electrodes.

Though the LiCoO$_2$ is widely used, it suffers from limitations like capacity fading after extended cycling when Li ions become de-intercalated above 4.2 V. This has been reported to be due to anisotropic expansion and contraction during cycling (Whitacre 2001, Wang 1999). In an attempt to overcome the problem, Cho et al (2000, 2001) have reported that thin film metal-oxide coating Al$_2$O$_3$, ZrO$_2$, etc., on the powder surface improved the capacity retention of LiCoO$_2$ cathodes. These metal-oxide coated powders exhibited no deterioration in their initial capacities, and also excellent capacity retention above 4.2 V relative to the uncoated cathodes. This phenomenon has been attributed to a suppression of expansion of the lattice constant (Tucker 2002).

2.3.1 Thin Film Cathodes of LiMn$_2$O$_4$ and Substituted Compounds

Lithium manganese oxides thin films have been prepared by various methods. Due to the ease in fabrication with correct stoichiometry, the solution routes of preparation like electrostatic spray deposition, spin coating are widely been carried out.

Shui et al (2004) have reported the electrostatic spray deposition of LiMn$_2$O$_4$ reported by from acetate precursors. The initial solutions have been utilized with Li to Mn ratio 1.2:2 and 1.3:2 respectively. The 20% excess lithium solutions on deposition and annealing at 800°C have been observed to possess Mn$_2$O$_3$ impurity peak. Whereas for the 30% excess films the Lithium loss due to evaporation at high temperature has been compensated. The fractal type morphology has been obtained and it has been shown that the tailoring of
morphologies is also possible by selecting suitable chelating agent. A mixed ethanol-mixed carbitol solvent has yielded sponge porous morphology. The normalized capacity for the film at C/6 rate is about 120mAh/g. The sponge-like porous LiMn$_2$O$_4$ electrode has greater active area for charge-transfer at its interface with electrolyte than the dense LiMn$_2$O$_4$ electrode and thus results in a smaller charge-transfer resistance. Similar attempts with ESD method have also been reported by Kyung Yoon Chung et al (2004).

In general, LiMn$_2$O$_4$ possess certain issues like dissolution of manganese into the electrolyte (Shokoohi 1992) and onset of Jahn Teller distortion at deep discharge due to Mn$^{3+}$ ion (Gummow 1994). The possible solution suggested for this is partially replacing Mn$^{3+}$ ion by some other element (Robertson 1997) and to induce surface modification by providing inert surface coating like Al$_2$O$_3$, MgO, ZrO$_2$ and so on (Hosoya 1998). Many doping elements have been studied by many authors in powder form. But there are very few publications dedicated to the doping of Mn$^{3+}$ ion in LiMn$_2$O$_4$ thin film. The Hee-Soo Moon et al (2003) have proved the improvement in cyclability by doping transition metal (Co$^{3+}$) instead of Mn$^{3+}$ ion. The deposition has been carried out using Co-sputtering of LiMn$_2$O$_4$ and Co$_3$O$_4$ in Ar/O2 plasma. The crystal structures of the undoped and doped films have been observed to be iso structural. Both films possess preferred orientation of <1 1 1> direction. In the half-cell test, the LiCo$_{0.26}$Mn$_{1.74}$O$_4$ film exhibited lower discharge capacity than that of the LiMn$_2$O$_4$ film. However, the capacity retention of the LiCo$_{0.26}$Mn$_{1.74}$O$_4$ film is better than that of the LiMn$_2$O$_4$ film. Thus the cobalt ions has modified the spinel thin films effectively and improved the electrochemical properties of the LiMn$_2$O$_4$ thin films for micro batteries.

In checking the capacity fading, the surface modification has played an influential role. The Influence of Al$_2$O$_3$ in LiMn$_2$O$_4$ has been
demonstrated by Ali eftekari (2004). The influence of Al₂O₃ has been studied as a multifunction agent for (i) surface modification of current collector, (ii) as an incorporating agent in LiMn₂O₄ and (iii) as a surface coating. In all the cases the Al₂O₃ incorporation has been observed to be beneficial. It has been observed that the mechanical and thermal stability of the thin films on the Al₂O₃ coated substrate is superior over film in bare substrate. In continuation with the surface modifiers, Ali Eftekhari (2003) has suggested the feasibility to fabricate the surface modified electrode film in relatively commercially viable electroplating method. In his accomplishment, Mixed-metals co-deposition has been introduced as an efficient method for the deposition of cathode materials onto substrate surfaces. The approach proposed has been typically used for the deposition of LiMn₂O₄ with co-deposition of mixed gold-cobalt. The annealing in oxygen atmosphere has resulted in fine Co₃O₄ films, which acts as the surface modification agent and improves the electrochemical performance of the LiMn₂O₄.

More and more publications with the objective of improving the performance of Li ion batteries and thin film batteries are upcoming. So it is widely been believed that in a not too distant future, this technology would witness tremendous growth.