CHAPTER-II
LITERATURE SURVEY

2.1 Introduction

Lithium cobalt oxide (LiCoO₂) is the most widely studied cathode material for lithium-ion batteries due to its superior electrochemical performance in terms of high discharge capacity and excellent cycleability. Several reviews and conference proceedings are published to improve the performance of LiCoO₂. To give a quantitative report on the state of art of LiCoO₂ is quite difficult and exhaustive. Still an attempt has been made to survey the pristine and metals doped LiCoO₂ system that is relevant to this work in this chapter.

2.2 Survey on Combustion Method

Rodrigues et al. [1] have synthesized LiCoO₂ cathode material by novel solution-combustion method. In this synthesis, a solution mixture of Co(NO₃)₂, Li₂CO₃ and diformyl hydrazine fuel is heated to ignite at 350 ºC, which is annealed at 850 ºC for 6 hrs to obtain an ordered-crystalline layered compound. The compound is found suitable for reversible positive electrodes with discharge capacities between 110 and 120 mAh g⁻¹.

Kalyani et al. [2] have synthesized LiNiVO₄, a high voltage lithium intercalated cathode by adopting starch-assisted combustion method. Using nitrates as the starting materials, different heat treating conditions were employed with varying amounts of starch, which serves as fuel.
Kalyani et al. [3] have synthesized commercially important, high-voltage LiCoO$_2$ from nitrates using starch as the combustion-assisting component. The simplicity and flexibility of this approach towards the synthesis of various other cathode materials is also discussed. Santiago et al. [4] have prepared LiCoO$_2$ powders by combustion synthesis, using metallic nitrates as the oxidant and metal sources and urea as fuel. The single rhombohedral structure for LiCoO$_2$ was obtained after post-heat treatment at 600 °C. The maximum energy capacity in the first discharge was 136 mA g$^{-1}$ for the composite electrode based on LiCoO$_2$ obtained after heat treatment at 700 °C. Kalyani et al. [5] have synthesized a set of LiNiM$_x$V$_{1-x}$O$_4$ compounds with M= Co, Mg and Al and x = 0.0, 0.1, 0.3 and 0.5 by adopting Starch-Assisted Combustion (SAC) method. The resultant mixture was oven dried initially at 110 °C (24 hrs) to get the precursor in the form of foam. The dried foam was furnace heated at 300 °C for 3 hrs followed by a thermal treatment at 700 °C for 3 hrs for better crystallinity.

Ghosh et al. [6] have synthesized nanocrystalline LiCoO$_2$ powders (10–50 nm) by a citrate-nitrate combustion process followed by calcination at different temperatures (300–800 °C) in air. Annealing at 500 °C produced mixed phases of cubic and rhombohedral LiCoO$_2$, annealing at 800 °C resulted in single-phase rhombohedral LiCoO$_2$. Vivekanandhan et al. [7] have synthesized nanocrystalline LiCoO$_2$ powders by combustion process using three different ammonium carboxylates named ammonium acetate (AA), ammonium citrate (AC) and ammonium tartarate (AT) as fuels and metal nitrates as the source of metal ions as
well as oxidants. Effect of three different ammonium carboxylates on the synthesis of nanocrystalline LiCoO$_2$ powders was investigated.

Ghosh et al. [8] have prepared nanocrystalline (~50 nm) LiCoO$_2$ powders containing 0–10 mol% of Ag by combustion synthesis using citrate–nitrate combustion route. Thermal analyses show a sharp decomposition of the gel at ~177 °C for pristine LiCoO$_2$. With addition of silver, the decomposition becomes sluggish and it completes only above 430 °C. Song et al. [9] have synthesized LiNi$_{0.975}$M$_{0.025}$O$_2$ (M = Ga, In and Tl) by the combustion method (by preheating at 400 °C for 30 min in air and then calcining in an O$_2$ stream at 750 °C for 36 h). This may lead to good crystallinity and homogeneous particle size when the sample is synthesized. Ragavendran et al. [10] have prepared two batches of poly-crystalline lithium manganate by a fuel assisted solution combustion method. LiMn$_2$O$_4$ (S) was prepared using starch as the fuel and LiMn$_2$O$_4$ (P) was prepared using polyvinylalcohol (PVA) as the fuel. They observed a huge lattice contraction in LiMn$_2$O$_4$ when PVA is used instead of starch as the fuel.

2.3 Survey on LiCoO$_2$

Czyzyk et al. [11] have studied the electronic properties of LiCoO$_2$ based on destiny-functional calculation. It was suggested that Li- doped Li$_x$Co$_{1-x}$O$_2$ system exhibits a transition from high-spin Co ions in CoO to low-spin Co ions in LiCoO$_2$. Antolini et al. [12] have observed the phase evolution and the sintering process of Co/Li$_2$Co$_3$ mixtures following thermal treatment at 1200°C in air. The sintering
constant n varied from 0.27 to 0.37, which suggested that grain-boundary diffusion was the primary mechanism for material transport.

Rabou et al. [13] have studied the aging of Li/LiCoO$_2$ cells with LiPF$_6$ in propylene carbonate electrolyte during cycling between fixed voltage limits. Reduction of the maximum voltage from 4.3 to 4.1 V results in a lower initial capacity, but also in a higher remaining capacity after 100 cycles. Zhecheva et al. [14] have observed that the loss of cell capacity is limited in electrodes prepared at 400 °C from citrate precursors as compared with products of low-temperature synthetic procedures previously reported.

Amatucci et al. [15] have established a direct correlation between the percentage capacity loss and percentage cobalt loss. For voltages greater than 4.2 V, the capacity fading scaled with the measured amount of cobalt dissolution which was found to correlate with structural changes. Amatucci et al. [16] have prepared LiCoO$_2$ powders at temperatures as low as 100 °C through the use of a two days ion exchange reaction between CoOOH and an excess of LiOH. H$_2$O. Low-temperature fabricated LiCoO$_2$ powders were well crystallized with lattice parameters agreeing with 850 °C prepared samples. Fey et al. [17] have prepared ultrafine LiCoO$_2$ powders by a sol-gel process. The purity and grain size of LiCoO$_2$ powders was dependent upon the pH value of the sol-gel process. Compared with grains synthesized using a solid-state high temperature method, which ranged from 5 to 20 μm.
Pyun et al. [18] have discussed the exact opposite dependencies of the lithium-ion diffusivity on the lithium charging potential during the intercalation and de-intercalation in terms of the phase-boundary movement which is caused by the intercalation-induced stress gradient developed across the $\alpha/\beta$-phase boundary. Sheu et al. [19] have studied LiCoO$_2$ of different particle-size distributions, in the Li/LiCoO$_2$ rechargeable battery system. The particle size influences the cycle stability. Upon cycling, the voltage drop contributed to the ohmic and polarization of charge/discharge processes were evaluated by current interrupt method.

Boyle et al. [20] have developed a nonaqueous coprecipitation process to prepare controlled stoichiometry lithium cobalt oxide precipitates. When electrochemically cycled, the material exhibited an initial capacity of $\sim$133 (mA h)/g with a fade of 0.02% in capacity per cycle. Choi et al. [21] have investigated lithium transport through a porous Li$_{1-x}$CoO$_2$ electrode during lithium intercalation and deintercalation using the current transient technique. From the appearance of such transients, it was inferred that lithium transport through the oxide electrode is mainly enhanced by the lithium ion diffusivity term during lithium intercalation, but it is mainly impeded by the electric field term during lithium deintercalation.

Jeong et al. [22] have prepared a LiCoO$_2$ cathode by a complex formation reaction for a lithium-ion rechargeable battery. 100 charge/discharge cycles were achieved for a cell composed of a LiCoO$_2$ cathode and graphite (MCMB 6-28) anode. The diffusivity of lithium ions, $D_{Li^+}$, as determined by ac impedance, is $5.2 \times 10^{-12}$ m$^2$ s$^{-1}$. Nakamura et al. [23] have prepared LiCoO$_2$ cathode materials with uniform grain size using fine grained Co$_3$O$_4$ particles. The effects of the molar ratio
of Li/Co and the sintering temperature on the microstructure (the grain size and its
distribution) and the electric properties were studied.

Layered LiCoO$_2$ was synthesized by Kim et al. [24] using an oxidation of
Co$^{2+}$ ions in aqueous solutions by lithium peroxide in the presence of excess lithium
hydroxide, followed by firing at 400–900 °C. The samples fired at low temperatures
($T \leq 700°C$) exhibited lower capacity and poor electrochemical cyclability in the
lithium cells, due to a disordering of the Li$^+$ and Co$^{3+}$ ions, and poor crystallinity.

Yoon et al. [25] have synthesized LiCoO$_2$ powders by the sol–gel process at
various temperatures using acrylic acid as a chelating agent. The change of the main
peak potentials and currents in cyclic voltammograms with increasing calcination
temperature could be explained by the effect of particle size. Yang et al. [26] have
observed a new intermediate phase H2a was observed in addition to the two expected
hexagonal phases, H1 and H2 in the composition range of $x = 0$ to $x = 0.5$. In the
region very close to $x = 0.5$, some spectral signatures for the formation of a
monoclinic phase M1 were also observed. Furthermore, in the $x = 0.8$ to $x = 1$ region,
the formation of a CdI$_2$ type hexagonal phase has been confirmed. However, this new
phase originates from a CdCl$_2$ type hexagonal phase, rather than from a monoclinic
phase M2. Venkatachalapathy et al. [27] have investigated the thermal behavior of
LiCoO$_2$ and LiNi$_{0.8}$Co$_{0.2}$O$_2$ cathodes in fully charged Li-ion cells. The net heat
transferred out of the cell fabricated with a LiNi$_{0.8}$Co$_{0.2}$O$_2$ cathode was found to be
51% higher than the net heat transferred out of the cell fabricated with LiCoO$_2$. 
Itoh et al. [28] have observed the nature of the changes in interfacial structure between LiCoO₂ and organic solutions propylene carbonate and ethylene carbonate containing 1M LiClO₄. As organic compounds fluoresce by visible light, the increased background is ascribed to the formation of a film on the LiCoO₂ electrode surface in organic solutions. Antolini et al. [29] have determined lithium loss from LiCoO₂ following isochronal thermal treatment for 5 h in the temperature range 850–1300 ºC. At 1050 ºC a change in the mechanism of lithium and oxygen evaporation was observed.

Jang et al. [30] have studied mass transport and thermodynamic properties of LiₓCoO₂ by the potentiostatic intermittent titration technique. They determined the chemical diffusion coefficient (D⁻ Li) and the thermodynamic factor (Θ) of Li in the region 0.45 < x < 0.7. Lu et al. [31] have investigated the surfactant effects on the microstructure and electrochemical properties of lithium cobalt oxide (LiCoO₂) powders prepared from emulsion-derived precursors. The LiCoO₂ powders prepared from the emulsion with a small amount of the surfactant added exhibit high discharge capacity and high coulomb efficiency, as well as good cyclability. Chen et al. [32] have synthesized nanoparticled lithium cobalt oxides by coprecipitation in ethanol. The controlled grain size was below 100 nm with a narrow distribution. On hand of an experimental cell it appears that the novel material has an exciting high charge and discharge rate: the capacity is 100 mAh/g for a 50 C rate and 130 mA h/g for a 10 C rate.

Lu et al. [33] have synthesized lithium cobalt oxide (LiCoO₂) powders, through the emulsion process. Compared to the traditional solid-state reaction, the
emulsion process not only significantly curtails the reaction time to prepare LiCoO$_2$, but also reduces the particle size.

Aurbach et al. [34] have studied the electrochemical behavior and surface chemistry of LiCoO$_2$ intercalation cathodes as a function of cycling and storage at 25, 45, and 60 ºC. The apparent capacity fading of the LiCoO$_2$ electrodes is attributed mostly to changes on their surface, rather than to bulk degradation. Shlyakhtin et al. [35] have observed the influence on the micromorphology of precursors during preparation of lithium cobaltate powders by chemical synthesis methods. Localization of melting during thermolysis by mixing acetate precursors with foaming agents promotes the reduction of grain.

Lala et al. [36] have studied the preparation of LiCoO$_2$ powder using the metallo organic decomposition route in air. The MOD route produced LiCoO$_2$ (R-3m) at 700 ºC with specific surface area 1.7 m$^2$g$^{-1}$. The MOD method yields LiCoO$_2$ agglomerated particles with size distribution and porosity that facilitate lithium diffusion in the composite electrode. Konstantinov et al. [37] have prepared LiCoO$_2$ cathode materials by a spray-drying technique. The changes of Li content in materials were monitored by ICP spectrometry.

Liang et al. [38] have investigated nanoparticled lithium cobalt oxides (LiCoO$_2$) using low-melting KNO$_3$ as reaction media. Due to the shorter diffusion pathways and the larger surface area, the discharge capacity of this sample maintains 97 mAh/g in the 30th cycle at charge–discharge rate of 30 C, which is corresponding to a current density of about 15 mA/cm$^2$. Lu et al. [39] have synthesized lithium
cobalt oxide powders by a developed microemulsion process. Nanosized and well dispersed LiCoO₂ powders are obtained. The electrochemical analysis reveals that the discharge capacity of LiCoO₂ significantly depends on the particle size and agglomeration state of the synthesized powders.

Chen et al. [40] have confirmed that 30% higher energy density than that accessed by LiCoO₂ normally used in a commercial cell. Good capacity retention cannot be attained for cycling LiCoO₂ above 4.5 V with respect to Li metal, presumably because of the structural changes between the O3 phase and the H1-3 phase that occur near 4.55 V. Li et al. [41] have investigated the dispersion property of aqueous lithium cobalt oxide (LiCoO₂) slurries and the corresponding cell performance of LiCoO₂ electrodes with and without dispersant additions. For the as-prepared LiCoO₂ electrode without PAA-NH₄ addition, the LiCoO₂ powder agglomerates and the binder accumulates around the powder.

Gu et al. [42] have prepared nanostructured LiCoO₂ fibers by the sol-gel related electrospinning technique. The cyclic voltammogram curves indicated faster diffusion and migration of Li⁺ cations in the nanostructured LiCoO₂ fiber electrode. Alcantara et al. [43] have analyzed layered particles of LiCoO₂ using rotor blade grinding. Reannealing improved the electrochemical behaviour of both ground and unground LiCoO₂. The best electrochemical behaviour was observed after grinding for 60 min and then reannealing at 850 °C which is linked with a low charge transfer resistance.
Shao et al. [44] have prepared LiCoO₂ nano fibers with a diameter of 100–150 nm using a sol–gel processing and electrospinning technique. They observed a strong correlation between crystalline phase and morphology of the fibers and calcinations temperature.

Kuepper et al. [45] have measured the valence band and core levels for Li_{x}CoO₂ (0.6 ≤ x ≤ 1.0). Resonant O Ka x-ray emission spectra of LiCoO₂ showed localized excitonic states due to a dd transition between unoccupied and occupied Co 3d states. He et al. [46] have successfully prepared LiCoO₂ from spherical basic cobalt carbonate via a simple uniform-phase precipitation. In the voltage range 2.8–4.2, 2.8–4.3, and 2.8–4.4V, the discharge capacities of LiCoO₂ electrode were 153, 159, and 168 mAhg⁻¹, respectively, with better cyclability.

Choi et al. [47] have investigated the effect of the particle size of LiCoO₂ on the operating temperature-dependent performance of lithium batteries. It is found that the discharge capacity of a cell made with the nanocrystalline powder is slightly lower than that of cells made with micronsized powders. Predoana et al. [48] have observed LiCoO₂ material is an excellent candidate as active compounds for high capacity cathode materials for rechargeable lithium batteries. The correlation between the structure of the obtained powders, determined by the applied thermal treatment, and the electrochemical behavior was established.

Kishida et al. [49] have investigated the effects of the LLT/LiCoO₂ interface structure on the electrochemical properties of the two different types of lithium lanthanum titanate (LLT)/LiCoO₂ assemblies. LiCoO₂ is formed epitaxially on LLT
with the orientation relationships for both assemblies, but amorphous regions are
formed at the interface for the assembly produced with polished LLT. Yang et al.
[50] have investigated cycle performance and high rate capability of LiCoO₂ cathode
at room temperature. After 300 cycles its capacity still retained 0.54 mAhcm⁻².

Lee et al. [51] have evaluated the dispersion, adhesion strength, electrical and
electrochemical properties of LiCoO₂ cathodes in lithium-ion batteries with the
addition of a new composite binder. Khomane et al. [52] have synthesized uniformly
distributed nanoparticles of LiCoO₂ through the simple sol–gel method in presence of
neutral surfactant (Tween-80). The particle size is reduced in presence of surfactant
as compared to normal sol–gel method. Ensling et al. [53] have delivered detailed
information about different lithium phases contributing to the complex surface
chemistry of active electrodes in lithium ion batteries.

Ruffo et al. [54] have observed that LiCoO₂ electrodes can be reversibly
cycled in LiNO₃ aqueous electrolytes for tens of cycles at remarkably high rates with
impressive values specific capacity higher than 100 mAh/g, and with a coulomb
efficiency greater than 99.7%. Wang et al. [55] have studied the thermal stability of
Li₀.₅CoO₂ in the presence of solvents/electrolyte and LiPF₆ salt by using C80 micro-
calorimeter. Thermal stability of two kinds of electrolytes with Li₀.₅CoO₂ was
explored.

Fu et al. [56] have applied molten salt method to prepare LiCoO₂ powder. It
shows that the LiCoO₂ samples obtained are homogenous and the particle size can be
easily controlled by preparation temperature. Okubo et al. [57] have investigated the
electrochemical properties including the Li-ion chemical diffusion coefficient of nano sized cathode material. Li-ion deintercalation/intercalation experiments suggested an extreme small amount of cation mixing between Li\(^+\) and Co\(^{3+}\) within a layered structure of LiCoO\(_2\). Zhang et al. [58] have investigated the electrochemical performance of the LiCoO\(_2\) composite cathode dispersed with BCA. The possible mechanism is that the MC in BCA can adsorb and retain electrolyte solution, which allows an intimate contact between the lithium ions and the cathode active material LiCoO\(_2\) due to its large mesopore specific surface area.

Mukai et al. [59] have carried out powder X-ray diffraction measurements using a synchrotron radiation source in the T range between 300 and 90 K. The x = 1.02 and 0.60 samples are in a rhombohedral phase (R–3m) in the whole T range measured. Burba et al. [60] have observed porous LiCoO\(_2\), exhibit improved electrochemical performance compared to the non-porous LiCoO\(_2\) analogue. Shin et al. [61] have investigated production of high temperature lithium cobalt oxide (HT-LiCoO\(_2\)) particles by continuous hydrothermal synthesis. The experiments were carried out in both subcritical and supercritical water, at temperatures ranging from 300 to 411 °C, with residence times less than 1 min in all instances.

2.4 Survey on Doped-LiCoO\(_2\)

Huang et al. [62] have observed a spinel structure with the space group Fd3m is unambiguously assigned to LiCoO\(_2\). Although solid solutions could be prepared for HT-LiCo\(_{1-x}\)M\(_x\)O\(_2\) (M = Ni, 0 < x < 1; M = Ti, x < 0.2) and LT-LiCo\(_{1-x}\)Ni\(_x\)O, (x < 0.2) some impurities were observed in LT-LiCo\(_{1-x}\)Ti\(_x\)O\(_2\). Stoyanova et al. [63] have used
to investigate the electronic structure and ion distribution of Li$_{1-x}$Ni$_x$Co$_{1-y}$O$_2$ ($y = 0.13$ and $0.8 \leq y \leq 5.1.0$) solid solutions prepared between 450 and 800 °C. The results show that a transition from non-random to a random Ni/Co distribution in the Ni$_x$Co$_{1-y}$O$_2$ slabs occurs between 650 and 750 °C.

Obrovac et al. [64] have prepared LiMO$_2$ ($M=Ti,Mn$ and Fe) by ball milling mixtures of lithium transition metals and transition metal oxides. During milling these samples lost lithia and oxygen to form Li$_x$M$_{1-x}$O ($0.25 \leq x \leq 0.5$). The electrochemical performance of the milled samples as cathodes in lithium batteries was poor, presumably due to the disorder of the cation lattice. Alcantara et al. [65] have synthesized new cathode materials for lithium-ion batteries. The introduction of nickel in the composition of these solids may be useful to improve the electrochemical performance of the solid solutions. Ternary systems show an improved electrochemical behaviour.

Ehrlich et al. [66] have prepared LiNi$_x$Co$_{1-x}$O$_2$ mixed metal oxide based cathode materials for Li-ion batteries. The most energy dense material evaluated, LiNi$_{0.8}$Co$_{1.2}$O$_2$ ($x=0.82$) offered 206 mAh/g on the first charge and was cycled at the C/2 rate at 157 mAh/g in prototype 3 Ah cells with rate capability comparable to similar cells which used a LiCoO$_2$ material. Julien et al. [67] have synthesized substituted lithium cobaltates LiCo$_{0.8}$M$_{0.2}$O$_2$ (where $M=\text{Ni, Mg, Mn, Zn}$) by the combustion method. Performances of lithiated oxides as cathode materials in lithium batteries and substitutive effect on electrochemical properties have been investigated. Holzapfel et al. [68] have prepared LiCo$_{1-x}$Fe$_x$O$_2$ compounds ($0 \leq x \leq 1$) with ordered rock salt structure of $\alpha$-NaFeO$_2$ type by ion exchange reaction in a molten eutectic.
Dupin et al. [69] have investigated the lithium deintercalation and the lithium intercalation processes, respectively, in LiCoO₂ and in MO₃ compounds (M= W, Mo). The changes occurring in metal and oxygen core-electron spectra as in valence spectra have been analysed. Madhavi et al. [70] have synthesized LiCo₁₋₃yCr₃O₂ (0.0 ≤ y ≤ 0.20 and y =1.0) compounds by high temperature solid-state reaction. Hexagonal a and c lattice parameters increase with increasing y as expected from ionic size effects. Cation mixing occurring in the layered structure could be the reason for their poor electrochemical performance. Kim et al. [71] have studied the discharge capacity and storage characteristics of Ag/LiCoO₂ and Cu/LiCoO₂ cells. The discharge capacity of the Ag/LiCoO₂ cell is better than that of the Cu/LiCoO₂ cell. The Ag/LiCoO₂ cell gives a maximum discharge capacity of 190 mAhg⁻¹.

Kajiyama et al. [72] have obtained layered LiₓCo₀.₅Mn₀.₅ by optimized synthesis conditions. The specific capacity of the layered LiₓCo₀.₅Mn₀.₅ was increased with an increase in a Li⁺ content of the products and showed a maximum with a composition of Li₀.₈Co₀.₅Mn₀.₅O₂. Gendron et al. [73] have measured susceptibility, electron-spin resonance, magnetization and electrical conductivity of LiCo₁₋₁.₃Ni₃O₂ powders. In the temperature range 120–300 K, the unique ESR line centered at 315 mT is the paramagnetic signal with a gyromagnetic factor g = 2.12.

Gopukumar et al. [74] have reported performance of Titanium-doped lithium cobalt oxides in a lithium rechargeable cell. It has been observed that single-phase materials were below 10% of Ti doping whereas impurity spinel phases were detected at higher concentrations. Han et al. [75] have prepared HT-LiCo₀.₈M₀.₂O₂
(M = Al, Ni), by molten salt synthesis (MSS) method. Among them, HT-LiCo0.8Al0.2O2 showed an inferior cyclic performance and a smaller discharge capacity than HT-LiCo0.8M0.2O2, even though the former is more structurally stable than the latter.

Caballero et al. [76] have prepared LiCo1-xMnxO2 mixed oxides (x = 0, 0.2) by using a sol–gel. Substitution of Co by Mn ions has the following favorable effects on the electrochemical properties. Aldon et al. [77] have observed the electronic changes occurring upon electrochemical delithiation of the LiCo1-γFe2O2 solid solution. The first one, with an isomer shift of 0.32–0.33 mms⁻¹, is ascribable to Fe³⁺ replacing Co³⁺ in the octahedral sites of the CoO₂ layer. Xu et al. [78] have synthesized a new class of LiCo1-γZrx/2Mgx/2O2 materials using a solution–combustion. It is found that the maximum doping level (x) is around 0.06, above which Li2MgZrO4 is formed as an impurity phase.

Suresh et al. [79] have synthesized Manganese-substituted lithium–cobalt oxides, LiCo1-xMnxO2 (0 ≤ x ≤ 0.5) by a solution combustion method. Specific capacity of the compound with x=0.2 has been found to be about 138 mAh g⁻¹. Needham et al. [80] have prepared layered intercalation compounds LiM₀.₀₂Co₀.₉₈O₂ (M=Mo⁶⁺, V⁵⁺, Zr⁴⁺) using a simple solid-state method. Charge–discharge cycling of the cells indicated first cycle irreversible capacity loss in order of increasing magnitude was Zr (15 mAh g⁻¹), Mo (22 mAh g⁻¹), and V (45 mAh g⁻¹). Ma et al. [81] have synthesized LiNi₀.₈Co₀.₂O₂ and Sn-doped LiNi₀.₈Co₀.₂O₂ cathode materials are via a rheological phase reaction method. The effects of Sn doping on the structural
and electrochemical properties are investigated. Alcantara et al. [82] have examined the distribution of Fe$^{3+}$ and Ni$^{3+}$ impurities and the electrochemical performance of LiCoO$_2$ electrodes. After rotor blade grinding of LiCoO$_2$, isolated Fe$^{3+}$ ions display a tendency to form clusters, while isolated Ni$^{3+}$ ions remain intact.

Carewska et al. [83] have synthesized the battery cathode material LiCoO$_2$, with a deliberate excess of Li, according to Li$_{1+y}$CoO$_2$. Electrical conductivity measurements of the stoichiometric material, without Mg, as functions of oxygen partial pressure and temperature exhibit p-type semiconducting behaviour. Alcantra et al. [84] have assessed boron environment by spectroscopic analysis, which showed a distorted tetrahedral coordination. Step potential electrochemical spectroscopy and galvanostatic cycling revealed that boron dopants improve the reversibility of the lithium deintercalation–intercalation process and favor lattice adaptation to lithium order–disorder in the depleted LiO$_2$ layers.

Tukamoto et al. [85] have observed LiCoO$_2$ cathode material in lithium batteries, associated with the presence of a small concentration of Co$^{4+}$ ions. Its conductivity at room temperature can be increased by over two orders of magnitude, to $\sim$0.5 Scm$^{-1}$, by partial substitution of Co$^{3+}$ by Mg$^{2+}$ and compensating hole creation. Wang et al. [86] have investigated microstructural damage and cation disorder due to changes in lithium concentration. Many particles exhibit severe strain, high dislocation densities, and localized fracture. Moreover, in particles that are severely strained, electron diffraction reveals two types of cation disorder brought about by electrochemical cycling.
Huang et al. [87] have prepared nominal LiAl\textsubscript{x}Co\textsubscript{1-x}O\textsubscript{2} with x ranging from 0.1 to 0.3. The effect of substitution of non-transition metal, Al, in LiCoO\textsubscript{2} is investigated as a 4 V cathode for lithium ion. Julien et al. [88] have investigated electrochemical performances of substituted layered oxides LiM\textsubscript{1-y}M’\textsubscript{y}O\textsubscript{2} (M= Ni, Co and M’= Mg, Al, B) as cathode materials in lithium batteries. The overall capacity of the oxides have been reduced due to the sp metal substitution. Coppola et al. [89] have investigated three different cathodes. The analysis of the diffraction data by means of Rietveld refinement (space group R-3 m) shows that, at the two investigated temperatures, increasing the Li content increases lattice parameter \(a\), while both \(a\) and \(c\) increase when Mg is added.

Mladenov et al. [90] have synthesized Mg-doped and MgO coated LiCoO\textsubscript{2} powders for enhancement of cycling behavior. Substitution of Co by Mg in the CoO\textsubscript{2} layers was found to have positive effect on the cycling stability, while Mg dopants in Li\textsubscript{2}O layers did not influence the capacity fade. Yoon et al. [91] have achieved a significant improvement in capacity and cyclability of Al-doped LiCoO\textsubscript{2}. The capacity fading of the Al-doped LiCoO\textsubscript{2} electrodes greatly reduced as the calcination temperature decreased. Yoon et al. [92] have examined structure and electrochemical properties of LiAl\textsubscript{y}Co\textsubscript{1-y}O\textsubscript{2} cathodes. Aluminium and cobalt ions were statistically distributed in octahedral 3b sites of the ordered \(\alpha\)-NaFeO\textsubscript{2} structure. Al-doped LiCoO\textsubscript{2} shows the good thermal stability of the cathode and reduction of the heat of the reaction.

Myung et al. [93] have studied microstructure of LiCo\textsubscript{1-x}Al\textsubscript{x}O\textsubscript{2} powders by the emulsion drying method. The substitution of Al was effective on suppressing
cobalt dissolution at 4.5 V versus Li/Li⁺ and on diminishing changes in a- and c-axes during lithium intercalation. Imanishi et al. [94] have examined the electrochemical behavior of LiₓCoO₂ (x > 1.0) and its high pressure oxygen-treated. The high oxygen pressure treatment reduced the number of oxygen defects and enlarged the interlayer distance. Levasseur et al. [95] have prepared HT-Li₀ₓCo₁₋₀ₓMgₓO₂ materials via a solid-state reaction. Mg doping in LiCoO₂ always leads to the simultaneous presence of Co⁴⁺ ions (sharing an itinerant electron hole with neighboring Co³⁺ ions) and, to a smaller extent, of intermediate spin Co³⁺(IS) ions trapped in a square based pyramidal environment because of an oxygen vacancy.

Fey et al. [96] have reported oxalic acid assisted sol–gel synthesis of Sr²⁺-doped LiNi₀.₈Co₀.₂O₂. Of all the doped compositions with dopant mole ratios ranging from 10⁻⁸ to 10⁻⁴, the compound with a dopant mole ratio of 10⁻⁶ showed improved capacity and cyclability with a first cycle discharge capacity of 173 mAh⁻¹ and 10th cycle of 167 mAhg⁻¹. Kim et al. [97] have carried out chemical Li ion extraction process for pristine LiCoO₂, LiCo₀.₉Ga₀.₀₅O₂ and LiCo₀.₉Ga₀.₁O₂ compounds. The Ga- substituted compounds are more stable against acid treatments than the LiCoO₂, since more basic Ga³⁺ ions retards the structural distortion of the CoO₆ octahedra against Li ion extraction. Levasseur et al. [98] have performed a detailed characterization of the structural modifications and redox processes occurring upon lithium deintercalation of Liₐ₀Co₁₋₀ₓMgₓO₂ materials. The study shows that the structural defects are present in the starting Mg-doped phases govern the electronic properties upon lithium deintercalation.
Frangini et al. [99] have investigated the effect of Mg-doping and Li overstoichiometry on the structural stability of LiCoO₂. The concomitant presence of Mg and Li excess in the structure is important for obtaining small particle sizes. Amdouni et al. [100] have prepared LiAl₀.₃Co₀.₇O₂ (0.0 ≤ y ≤ 0.3) oxides by the citrate route. The electrochemical capacity of the LiAl₀.₃Co₀.₇O₂ oxides have been reduced due to the sp metal substitution. García et al. [101] have prepared LiCo₁₋₀.₃Al₀.₃O₂ and LiNi₀.₃₋₀.₃Al₀.₃Co₀.₃O₂ (0 ≤ y ≤ 0.3) powder samples by a low temperature sol–gel method. At 4.2 V cut-off, the charge capacity of the Li/LiNi₀.₃₅Al₀.₁₅Co₀.₅O₂ cell is ca. 115 mAh/g. However, more stable charge–discharge cycling performances have been obtained as compared to those displayed by the native oxides.

Julien et al. [102] have presented the structural and electrochemical properties of LiCoO₂ and doped LiCo₁₋₀.₃MₙO₂ (M = Al, B, Mg) oxides prepared by various methods. It is shown that synthesis procedures of LiCoO₂ cathode materials greatly affect the electrochemistry and cycle life characteristics of their layered structure. Nobili et al. [103] have investigated ac impedance spectroscopic study of LiMg₀.₀₅Co₀.₉₅O₂, by sol–gel process. The intercalation/deintercalation reaction occurs through two-step processes involving an adatom mechanism that may be described in terms of partially desolvated lithium ions adsorbed/desorbed from the electrode surface. Jin et al. [104] have synthesized LiCo₁₋₀ₓSiₐO₂ (x =0, 0.01, 0.05, 0.10, 0.35) by a co-precipitation method. Iodine titration method was also employed to measure the average valence of cobalt ions. It is found that the Si-doping results in the decrease of cobalt valence and the crystallite size. H.J. Kim et al. [105] have synthesized LiCo₁₋₀ₓMgₓO₂ by the solid-state reaction method. With the increase in
Mg content in LiCo$_{1-x}$MgxO$_2$, distances between CoO$_2$ slabs were increased. The electrical conductivities of LiCo$_{1-x}$MgxO$_2$ increased with Mg content.

Shi et al. [106] have investigated the electronic structures of Mg-doped LiCoO$_2$ by the first-principle pseudopotential method. The effect of Mg-doping content on the band structure and structural stability of LiCoO$_2$ is presented. However, the doping magnitude should be controlled within 15 mol % of LiCoO$_2$ in order to keep its crystalline structure unchanged. Sathiyamoorthi et al. [107] have synthesized undoped LiCoO$_2$ and doped LiCo$_{0.8}$M$_{0.2}$O$_2$ (M = Mg, Ca, Ba) layered oxide materials by a low temperature solid-state reaction. LiCo$_{0.8}$Mg$_{0.2}$O$_2$ has better cycling results compared to all other materials. Zaheena et al. [108] have synthesized LiMg$_{0.1}$Co$_{0.9}$O$_2$ using microwave assisted solution technique. The LiMg$_{0.1}$Co$_{0.9}$O$_2$ delivers an average discharge capacity of ~135mAh$^{-1}$ over the investigated 20 cycles.

Yang et al. [109] have synthesized LiMn$_2$O$_4$ and rare earth elements doped LiNd$_{0.01}$Mn$_{1.99}$O$_4$ by microwave method. The introduction of Nd$^{3+}$ ion into the unit cell, the lattice parameter of the Nd-doped spinel was larger than that of the undoped one. Liu et al. [110] have synthesized erbium-doped spinels LiMn$_{2-x}$Er$_x$O$_4$ by rheological phase reaction method. The lattice parameters of the Er-doped spinel were smaller than that of the undoped compound. Tu et al. [111] have synthesized LiMn$_2$O$_4$ spinel and LiLa$_{0.01}$Mn$_{1.99}$O$_4$ cathodes. La doping can protect the spinel structure against electrochemical lithiation/delithiation and slows down the increase of electrode impedance, and thus improves the electrochemical properties greatly.
Xie et al. [112] prepared the spinel phases of \( \text{Li}_{1.05}\text{RE}_x\text{Cr}_y\text{Mn}_{2-x-y}\text{O}_4 \) (RE = Sc, Ce, Pr, Tb; \( 0 \leq x \leq 0.05; 0 \leq y \leq 0.1 \)) by a soft chemical method. Rare earth element-Sc and transition metal-Cr as co-substituents stabilize the spinel framework and improve charge–discharge performance. Sun et al. [113] have synthesized \( \text{Li}_{1.15}\text{Mn}_{1.96}\text{Co}_{0.03}\text{Gd}_{0.01}\text{O}_{4+\delta} \) by high temperature solid-state reaction method. The initial special capacity was 126.5 and 128.1 mAhg\(^{-1}\) at 25 and 50 °C.

2.5 Conclusion

The review clearly shows that several researches are involved in this system worldwide because of its potential as a future battery material. The interest in the materials is due to significant improvements expected by altering synthesis method, dopants etc. This study is aimed at using a low cost combustion route to prepare high quality pristine and doped electrodes.
References


