CHAPTER I

BASICS OF ELECTROCHEMICAL POWER SOURCES
1.1 Introduction

In his endeavours towards development, man has been in need of several entities, the pivotal among this being energy. Though various forms of energy are in use today, energy storage would be the gist of planning. Research in storage of energy helps not only in transporting energy in a convenient form but also in buffering load fluctuation. With the slow and steady depletion of the most widely used form of energy (i.e.) fossil fuels, energy storage should definitely be given a serious thought and energy source would be incomplete sans energy storage.

A battery is a device that converts the chemical energy contained in its active materials directly into electric energy by means of an electrochemical oxidation-reduction (redox) reaction. A battery consists of a group of interconnected electrochemical cells. How these are connected and packaged depends upon the specific application for which they are designed. The elemental building block of a battery, the electrochemical cell, interfaces the world through two posts: one is anode (negative electrode) and the other is cathode (positive electrode). The ionic current within an electro chemical cell is carried between the electrodes by an electrolyte, which is ideally an electronic insulator and a good conductor of the working ion of the cell [1].

1.2 Battery Development And Its Classification

The groundwork for battery began with Galvani’s frog leg experiment followed by Alessandro Voltas experiments in the University of Pavia [2]. Voltas discoveries were
phenomenal. Compared to the electrostatic generator in use those days, which could
deliver current to the order of milliamperes, Voltas cell could deliver current in the order
of amperes. Voltas cell was the prototype and many modifications were made on it
thereafter. The chronological order of battery development is outlined in Table 1 [1, 3-7].

1.2.2 Primary Batteries

Primary batteries are single use batteries and can not be recharged as only the conversion
of chemical energy to electrical energy takes place. The converse is not possible. Once
they have delivered all their electrical energy, their usefulness is lost. They come mostly
in prismatic and button type constructions. Typical examples of primary batteries are
Leclanche cells, zinc/silver oxide, zinc/mercuric oxide and lithium/manganese dioxide.
Generally they have good energy densities and shelf life. Common primary battery
anodes are metals like zinc, magnesium and lithium.

1.4.2 Secondary Batteries

Secondary batteries are those where the conversion of chemical energy to electrical and
vice-versa takes place. After discharge the secondary cells may be rejuvenated to the
fully charged state by the passage of an electric current through the cell in a direction
opposite to that of discharge. The electrochemical reactions at the electrode surface are
reversible. Common examples are lead-acid, alkaline nickel/cadmium, nickel/iron and
non-aqueous lithium ion or polymer batteries.
1.4.3 Reserve Batteries

Reserve cells are those from which a key component, usually the electrolyte, is kept aside from the system and made active by adding that key component at the time of necessity. The absence of such a component ensures long shelf life for the battery. Such cells find applications mainly in defence and meteorological areas. Examples are magnesium/silver chloride (sea water activated) and magnesium/meta-dinitrobenzene (electrolyte activated) Batteries.

1.4.4 Fuel Cells

Fuel cells are power sources in which the active materials are continuously fed into systems and whose depletion in an electrochemical reaction yields power. Active materials are mostly gases, e.g. hydrogen and oxygen.

1.4.5 Thermal Batteries

In thermal batteries, the electrolyte is present as an inactive solid. When the electrolyte is heated and brought to a molten state, a sufficiently large number of ions are provided between the anode and the cathode to activate the system, e.g. Sodium/Nickel chloride (ZEBRA cell).
1.4.6 Solid State Batteries

As the name indicates all the cell components are in the solid state. The electrolyte in these batteries is a substance that conducts ions in the solid state. They are mainly used in low drains and long-life applications. Example: Lithium/Iodine systems for pacemakers.

1.4.7 Hybrid Batteries

These batteries have a cathode, which consumes a gas while the anode used is itself consumed. A candidate system is the zinc/bromine cell.

1.3 Basic Components Of Batteries

A battery consists of one or more of cells, connected in series or parallel, or both, depending on the desired output voltage and capacity. The cell consists of four major components as below

a) **The cathode or positive electrode**: It is a good oxidizing agent which accepts electrons from the external circuit and is reduced during the electrochemical reaction. The cathode must be stable when in contact with the electrolyte, and have a useful working voltage. However, many of the cathode materials are metallic oxides, while other cathode materials are used for advanced battery systems giving high voltage and capacity.
b) **The anode or negative electrode:** It is a good reducing agent which gives up electrons to the external circuit and is oxidized during the electrochemical reaction. In a realistic system, the anode should possess high columbic output (A h/g), good conductivity, stability, ease of fabrication, and low cost.

c) **The electrolyte:** It is an ionic conductor which provides the medium for transfer of electrons, as ions, inside the cell between the anode and cathode. The electrolyte must have good ionic conductivity and but should not be an electrical conductor, as this would cause internal short circuiting. Other important characteristics are non reactivity with the electrode materials, little change in properties with change in temperature, safeness in handling, and low cost.

d) **The Separator:** It prevents internal short circuiting, but is surrounded by the electrolyte. In practical cell designs a separator material is used to separate the anode and cathode electrodes mechanically. The separator, however, is permeable to the electrolyte in order to maintain the desired ionic conductivity. In some cases the electrolyte is immobilized for non spill design.

The electrochemistry includes the study of chemical properties and reactions involving ions either in solution or in solids. In order to study these properties, generally electrochemical cells are constructed. Typical cell consists of two solid electrodes, the cathode and anode, in contact with an ionic conducting electrolyte. To prevent cell self-dicharge, an electronically insulating material that is permeable to the working ions
Fig. 1.1 Electrochemical Cell
physically separates the electrodes. The two electrodes are put in electrical contact by an external electronically conductive wire. Two different types of electrochemical cells can be defined: electrolytic cells, and galvanic cells. In electrolytic cells an applied electrical current causes the active material to undergo decomposition; a process corresponding to the conversion of electrical energy to chemical energy. Galvanic cells, however, are capable of converting chemical energy into electrical energy. Galvanic cells generate electrical energy by the spontaneous electrode reactions that give rise to electrical current.

The reaction for a cell with a negative Li-metal electrode and a positive tin (Sn) electrode is presented below. The discharge of a Li-Sn cell involves two half cell reactions. During discharge of a lithium cell, Li$^+$ ions are generated at the anode/electrolyte interface, and Li$^+$ is inserted into the cathode structure at the cathode/electrolyte interface. The electrode reactions are given below.

\[ \text{nLi} \rightarrow \text{nLi}^+ + \text{n e}^- \quad \text{(Negative - Oxidation Reaction)} \]

\[ \text{nLi}^+ + \text{Sn} + \text{n e}^- \rightarrow \text{Li}_n\text{Sn} \quad \text{(Positive - Reduction Reaction)} \]

The full cell reaction is:

\[ \text{nLi} + \text{Sn} \rightarrow \text{Li}_n\text{Sn} \quad \text{(Full Cell)} \]
The difference in chemical potential ($\mu$) of Li in the negative electrode compared to the positive electrode drives the reaction. The voltage difference between the electrodes is given by

$$V = \frac{(\mu_{\text{positive}} - \mu_{\text{negative}})}{e}$$

where ‘e’ is the magnitude of the charge on an electron. To charge the cell the reaction must be reversed. Energy is required to remove Li from Sn and re-deposit it onto the negative electrode, recharging the cell. The roles of the cathode and anode are reversed when the battery is being charged.

1.3.1 Thermodynamic Background

In a cell, reactions essentially take place at two areas or sites in the device. These reaction sites are the electrodes. In generalized terms, the reaction at one electrode (reduction in the forward direction) can be represented by

$$aA \, + \, ne \quad \leftrightarrow \quad cC \quad (a)$$

where a molecule of A take up n electrons e to form c molecules of C. At the other electrode, the reaction (oxidation in forward direction) can be represented by

$$bB \, - \, ne \quad \leftrightarrow \quad dD \quad (b)$$
The overall reaction in the cell is given by addition of these two half cell reactions

\[ aA + bB \leftrightarrow cC + dD \]  \hspace{1cm} (c)

The change in the standard free energy $\Delta G^\circ$ of this reaction is expressed as

\[ \Delta G^\circ = - nFE^\circ \]  \hspace{1cm} (d)

Where, ‘F’ is constant known as Faraday (96,487 C)

$E^\circ$ is standard electromotive force

n is number of electrons involved in stoichiometric reaction

When conditions are other than in the standard state, the voltage $E$ of a cell is given by the Nernst equation,

\[ E = E^\circ - \frac{RT}{nF} \ln \left( \frac{a_C a_D}{a_A a_B} \right) \]  \hspace{1cm} (e)

where ‘$a_i$’ = activity of relevant species

R = gas constant

T = absolute temperature

The change in the standard free energy $\Delta G^\circ$ of a cell reaction is the driving force which enables a battery to deliver electric energy to an external circuit. The measurement of the electromotive force, incidentally, also make available data on changes in free energy,
namely, entropies and enthalpies together with activity coefficients, equilibrium constants, and solubility products. Direct measurement of single (absolute) electrode potentials is considered practically impossible. To establish a scale of cell or standard potentials, a reference potential “Zero” must be established against which single electrode potentials can be measured. By convention, the standard potential of the H₂/H⁺ (aq) reaction is taken as zero and all standard potentials are referred to this potential.

1.3.2 Theoretical voltage

The standard potential of the cell is determined by its active materials and can be calculated from free energy data or obtained experimentally. The standard potential of a cell can also be calculated from the standard electrode potentials as follows (the oxidation potential is the negative value of the reduction potential)

Anode (oxidation potential) + cathode (reduction (potential)) = standard cell potential.

For example, in the reaction

\[
\begin{align*}
\text{Zn} + \text{Cl}_2 & \rightarrow \text{ZnCl}_2 \\
\text{Zn} & \rightarrow \text{Zn}^{2+} + 2e^- & (-0.76V) \\
\text{Cl}_2 & \rightarrow 2\text{Cl}^- - 2e^- & 1.36V \\
\end{align*}
\]

The cell voltage is also dependent on other factors, including concentration, temperature, etc.
1.3.3 Theoretical capacity

The capacity of a cell is expressed as the total quantity of electricity involved in the electrochemical reaction and is defined in terms of coulombs or ampere-hours. The “ampere-hour capacity” of a battery is directly associated with the quantity of electricity obtained from the active materials. Theoretically 1 gm-equivalent weight of material will deliver 96,487C or 26.8A h. (A gram-equivalent weight is the atomic or molecular weight of the active material in grams divide by the number of electrons involved in the reaction). The theoretical capacity of a battery system, based only on the active materials participating in the electrochemical reaction, is calculated from the equivalent weight of the reactants. Hence the theoretical capacity of the Zn/Cl2 system is 0.394 A h / g, that is,

\[
\begin{align*}
\text{Zn} + \text{Cl}_2 & \rightarrow \text{ZnCl}_2 \\
0.82 \text{ A h / g} & \rightarrow 0.76 \text{ A h / g} \\
1.22 \text{ g / A h} & = 1.32 \text{ g / A h} = 2.54 \text{ g / A h} = 0.394 \text{ Ah / g}
\end{align*}
\]

The capacity of battery is also considered on energy (Watt hour) basis by taking the voltage as well as the quantity of electricity into consideration,

\[
\text{Watt hour (W h) = voltage (V) \times ampere-hour (Ah)}
\]
In the Zn / Cl₂ cell example, if the standard potential is taken as 2.12V, the theoretical watt hour capacity per gram of active material (theoretical gravimetric energy density) is

Watt hour / gram capacity = 2.12V × 0.395 A h/g = 0.838 W h /g

Similarly, the ampere-hour or watt hour capacity on a volume basis, can be calculated by using the appropriate data for ampere-hours per cubic centimeter.

1.3.4 Free energy

Whenever a reaction occurs, there is a decrease in the free energy of the system, which is expressed as

$$
\Delta G^\circ = - nF \bar{E}^\circ
$$

Where,

‘F’ = constant known as Faraday ( 96,487 C or 26.8 A h)

n = number of electrons involved in stoichiometric reaction

E° = standard potential, V

1.4 Lithium Batteries

Lithium metal, the lightest of all metals possesses high voltage, high electrochemical equivalence (3.86 Ah g⁻¹, 0.259 gA⁻¹h⁻¹, 2.08Ah cm⁻³) high electrode potential (-3.05V) and good conductivity, which in turn made this metal a promising electrode material in primary as well as secondary batteries[8]. A number of materials with the ability of insertion and/or extraction of lithium have been investigated for practical application to electrode material for primary and secondary batteries. The application of Lithium
Table 1. Chronological order of battery development

<table>
<thead>
<tr>
<th>Scientific Development</th>
<th>Battery Development</th>
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<tbody>
<tr>
<td>1791 Galvani Frog Leg Experiment</td>
<td>1792 Volta Pile</td>
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<tr>
<td>1834 Faraday Laws Of Electrochemical Reactions</td>
<td>1836 Daniell Cell</td>
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<tr>
<td>1839 Grove Fuel Cell</td>
<td>1859 Plante Lead-Acid</td>
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<td>1860 Leclanche</td>
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<tr>
<td>1836 Daniell Cell</td>
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<tr>
<td>1839 Grove Fuel Cell</td>
<td>1866 Siemens Dynamo</td>
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<td>1873 Edisons First Battery Patent</td>
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<tr>
<td>1875 Edison Primary Cell</td>
<td>1875 MnO₂ Dry Cell</td>
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<tr>
<td>1899 Jungner Alkaline Accumulators</td>
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<tr>
<td>1891 Nernst Thermodynamics of Galvanic Cells</td>
<td>1895 Tafel Electrochemical Kinetics</td>
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<td>1905 Edison Nickel-Iron Battery</td>
<td>1927 Andre Silver-Zinc</td>
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<tr>
<td>1929 Vosburgh Mechanisms of Lead Acid Batteries</td>
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<td>1939 Harned and Hamer Mechanisms Of Lead Acid Batteries</td>
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<td>1951 Lander Mechanisms Of Lead Acid Batteries</td>
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<tr>
<td>1954 Deck and Wynne-Jones Mechanisms Of Lead Acid Batteries</td>
<td>1956 Bacon Alkaline Fuel Cells</td>
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<tr>
<td>1966 Sodium Sulfur Battery</td>
<td>1968 Lithium Sulfur</td>
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<tr>
<td>1970 Tobias Aprotic Solvent Research</td>
<td>1970 Bipolar dry cell, battery cameras</td>
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<tr>
<td>1972 Lithium primary Batteries</td>
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<td>1979 Practical</td>
<td></td>
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<td>1980 Zinc-Bromine Secondary Batteries</td>
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<tr>
<td>1980 Sealed Lead Acid Batteries Become Common</td>
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</tr>
<tr>
<td>1990 Lithium-ion Batteries</td>
<td>1997 Lithium Polymer Batteries</td>
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batteries varies from toys, computers, cameras, memory backup circuits, security devices, calculators and watches to standby power in missile silos. Based on electrochemical activity, lithium batteries are classified into three types Viz., Lithium Primary Batteries, Lithium Reserve Batteries and Lithium Secondary Batteries.

1.4.1 Lithium Primary Batteries

Lithium primary battery is a convenient, light weight source of packaged electrochemical power source for portable electronic devices and electric vehicles. Lithium metal is used as anode. Based on the type of cathode and electrolyte used they are classified [9] as

- soluble cathode (SO2, SOCl2, SO2Cl2),
- solid cathode (V2O5, AgV2O5.5, Ag2CrO4, MnO2, Cu4O(PO4)2, (CF)n, CuS, FeS2, FeS, CuO),
- solid electrolyte (PbI2, PbS)

The advantages over conventional batteries are its high voltages up to about 4V, compared with 1.5V for most other primary battery systems, of course depending on the choice of cathode material. The specific energy and energy density of a lithium battery (over 200 Whkg⁻¹ and 400 Whl⁻¹) is 200% to 400% more than that of conventional zinc anode batteries. These batteries can be operated over a wide temperature range and possess high power density. Lithium batteries can be stored for long periods, for up to 10 years at room temperature.
1.4.2 Lithium Activated Batteries

The lithium anode electrochemical system is also being developed in reserve configurations to take advantage of its high energy density and good low temperature performance. These batteries use either an organic electrolyte or a non aqueous inorganic electrolyte because of the reactivity of lithium in aqueous electrolytes. Even though the active lithium primary batteries are noted for their excellent storability, the reserve structure is used to provide a capability of essentially no capacity loss even after storage periods in the inactive state of 10 years or more. The performance characteristics of the reserve battery, once activated, are similar to those of the active lithium batteries, but with a penalty of 50% or more in specific energy and energy density due to the need for the activation device and the electrolyte reservoir. Lithium is also being considered as an anode in aqueous reserve batteries for high-rate applications in a marine environment.

1.4.3 Lithium Secondary Batteries

Secondary lithium batteries have the same components as primary ones but both electrodes function as secondary lithium electrodes, for example by lithium intercalation in the electrode material on either side. In the early 1970s, research carried out on rechargeable lithium batteries at the Exxon Laboratories in the US established that lithium ions can be intercalated electrochemically into certain layered transition-metal sulphides, the most promising being titanium disulphide [3]. It was discovered that lithium could be inserted or intercalated reversibly in several compounds, which makes it
possible to use these compounds as insertion cathodes in rechargeable lithium batteries. The choice of materials that can be used for the insertion cathode is relatively wide. The best cathodes for secondary lithium batteries are those where bonding with lithium occurs at low energy levels and the structural modification of the active materials during lithium insertion/extraction is minimal.

The first rechargeable lithium cell was commercialized in late 1980s by Moli Energy Corporation in Canada. The cell comprised a spirally wound lithium foil as the anode, a separator and MoS₂ as the cathode [10]. The cell had a nominal voltage of 1.8V and an attractive value of specific energy, which was 2 to 3 times greater than either lead acid or nickel-cadmium cells. However, the battery was withdrawn from the market after safety problems were experienced. This paved way for the discovery of lithium-ion battery.

1.4.3.1 Lithium Ion Battery

In lithium-ion batteries, the metallic lithium anode is replaced with carbon and tin based alloys. The introduction of carbon as an anode material and the development of insertion type cathode materials have made substantial improvements in energy density, cycle ability, cost and safety of secondary lithium batteries. A very large research effort continues in this field, after the first generation of lithium-ion batteries. The origin of lithium-ion battery lies in the discovery that Li⁺ ions can be reversibly intercalated within or de-intercalated from the Van der Wals gap between graphene sheets of carbon materials at a potential close to the Li/Li⁺ electrode. Thus, lithium metal is replaced by
carbon as the anode material for rechargeable lithium-ion batteries, and the problems associated with metallic lithium is mitigated. Complimentary investigations on intercalation compounds based on transition metals resulted in establishing LiCoO$_2$ and LiNiO$_2$ as promising cathode materials [11]. By employing the aforesaid intercalation materials, namely carbon and LiCoO$_2$, respectively, as negative and positive electrodes in a non-aqueous lithium-salt electrolyte, a Li-ion cell with a voltage value of about 3.5V resulted. These findings led to a novel rechargeable battery technology.

Commercial Lithium-ion batteries were first introduced by the Sony Corporation, Japan in 1991 [12]. Other Japanese manufacturers soon entered the market, followed closely by American and European companies. The subsequent growth in sales of the batteries was truly phenomenal because the Li-ion battery has many advantages over the rechargeable batteries viz., lead-acid battery (Pb-Acid), nickel-cadmium battery (Ni-Cd), nickel metal-hydride batteries (NiM-H) battery.

a) Two to three times higher voltage per single cell
b) Two to five times higher specific energy, i.e., watt-hours per kilogram (Wh/kg) of battery weight, and two to four times higher energy density, i.e., watt-hours per liter (Wh/l) of battery volume.
c) Low self-discharge and long shelf life, i.e., the battery does not lose a significant amount of its capacity while sitting idle on the shelf.
d) No memory effect, i.e., the available capacity in a fully charged Li-ion battery is independent of its operational history, unlike the Ni-Cd system.
e) Long charge-discharge cycle life. Li-ion batteries are capable of 500-1000 cycles at full depth of discharge. Due to these advantages Li-ion batteries are increasingly becoming the battery of choice for portable consumer products such as cellular telephones and notebook computers.

1.6.3.2 Operation of a Lithium-ion Cell

In the lithium-ion cell both the anode and cathode comprise intercalation materials with layer structure in which guest species are inserted and extracted without much structural modification of the host. The fully-charged negative plate is made of lithiated carbon, which is about 15 % lithium by weight and has about the same electrochemical potential as metallic lithium. The discharged positive plate employs intercalation compounds, such as LiCoO₂, LiNiO₂, LiMnO₂ and LiMn₂O₄.

Lithium-ion cells are based on non-aqueous electrolytes comprising a salt dissolved in an organic solvent. The main issues in selecting an electrolyte are compatibility and thermal stability up to 80°C. If the negative electrode consists of lithiated graphite then the choice of electrolyte is restricted to systems based on ethylene carbonate because those based on propylene carbonate cause the exfoliation of graphite due to co-intercalation. [13]. The use of lithiated coke for the negative plate provides a much wider choice with diethyl carbonate, propylene carbonate, dimethyl carbonate and many other solvents that may be used singly or in combination. The favourite solute is lithium hexafluorophosphate (LiPF₆) but other lithium salts may be used as well. The ionic conductivity of these mixtures is
about two orders of magnitude lower than that of aqueous alkaline electrolytes but is high enough to make practical batteries for use at or above room temperature. Actually, even at 0°C the ionic conductivity of $10^{-3}$ ohm$^{-1}$ cm$^{-1}$ for these electrolytes suffices for practical batteries. The conductivity however varies a bit with temperature and ranges from $0.23 \times 10^{-3}$ ohm$^{-1}$ cm$^{-1}$ at $-40$°C to $1.46 \times 10^{-2}$ ohm$^{-1}$ cm$^{-1}$ at 40°C for LiPF$_6$ dissolved in 1:1 volume mixture of ethylene carbonate and propylene carbonate [14]. As mentioned above, lithium-ion batteries combine highly energetic materials in contact with a flammable electrolyte based on organic solvents.

Accordingly, lithium-ion batteries can suffer premature failure if subjected to conditions for which they are never designed. Any abuse, including disposing in fire, overcharging, external short-circuiting or crushing can trigger spontaneous heat-evolving reactions, which can lead to fire and explosion. Lithium-ion batteries must pass a number of safety tests before they can be certified for use by a consumer. These battery tests include electrical tests such as external short-circuit, mechanical tests such as nail penetration, crushing, dropping to ground, and environmental tests such as heating in microwave oven, throwing into a hot liquid, and leak tests in vacuum. Several techniques have also been devised to improve safety such as use of safety vents, positive temperature coefficient elements, shutdown separators, more oxidation-tolerant or less flammable electrolyte-constituents, and redox shuttle mechanisms [15].

In operation, lithium ions move back and forth between two plates across the electrolyte as the cell is alternatively charged and discharged. The half-cell reactions at the two
Fig. 1.2 Operation of a lithium-ion cell
electrodes during the charge-discharge cycles of a lithium-ion cell can be represented as follows. The operating principle of a lithium-ion cell is depicted schematically in Fig.1.2

At the positive electrode:

\[ \begin{align*} 
\text{discharge} & : \quad x \text{Li}^+ + xe^- + \text{Li}_{1-x}\text{CoO}_2 \quad \rightleftharpoons \quad \text{LiCoO}_2 \quad (E_c = 0.6V \text{ vs. SHE}) \\
\text{charge} & : 
\end{align*} \]

At the negative electrode:

\[ \begin{align*} 
\text{discharge} & : \quad \text{LiC}_6 \quad \rightleftharpoons \quad \text{Li}_{1-x}\text{C}_6 + x\text{Li}^+ + xe^- \quad (E_a = -3V \text{ vs. SHE}) \\
\text{charge} & : 
\end{align*} \]

Accordingly, the net cell reactions during its charge-discharge process are:

\[ \begin{align*} 
\text{discharge} & : \quad \text{LiC}_6 + \text{Li}_{1-x}\text{CoO}_2 \quad \rightleftharpoons \quad \text{Li}_{1-x}\text{C}_6 + \text{LiCoO}_2 \quad (E_{cell} = 3.6V) \\
\text{charge} & : 
\end{align*} \]

Lithium-ion cell is also named as “swing cell”, “rocking chair cell”, or “shuttle-cock cell” [16].
1.7 Anode For Lithium Secondary Battery

The renowned anode materials for lithium secondary batteries are metallic lithium and tin- based alloys. Lithium-ion cells marketed by Sony used petroleum coke at the anode. Coke-based anodes offer a stable specific capacity of 180 mAh g⁻¹. By contrast, hard-carbon materials offer specific capacities over 1000 mAh g⁻¹ but have not achieved broad acceptance due to their instability and irreversibility on cycling [17]. Anodes with metallic lithium can store about 10 times more energy per unit weight than lithiated carbon [18]. However, the trouble is that the lithium electrode has a tendency to grow as dendrites across the cell, which shortens the cell life. Efforts are therefore being expended to prevent dendrite growth of lithium to provide new anode materials for lithium cells [19-21].

1.8 Cathode Materials For Lithium Battery

The considerations for a cathode material are high energy density, good rate capability, better electrochemical reversibility, high electrochemical equivalence, good electronic conductivity, high reactivity, high voltage, non-toxic, low cost, easy synthesis, rapid recharge, long cycle-life and long shelf-life. In addition to the aforesaid characteristics, the cathode materials for rechargeable batteries are those where there is little bonding and structural modification of the active materials during the discharge-charge reaction. In these intercalation compounds, a guest species such as lithium can be inserted interstitially into the host lattice (during discharge) and subsequently extracted during
recharge with little or no structural modification of the host. The intercalation process involves three principal steps

a. Diffusion or migration of solvated Li\(^+\) ions
b. Desolvation and injection of Li\(^+\) ions into the vacancy structure
c. Diffusion of Li\(^+\) ions into the host structure

The wide spectrum of cathode materials include halogens [22,23], halides [24], chalcogenides [25], sulphur [26], conducting polymers [27] and their composites with oxides[28], polyanionic compounds [29], layered oxides, spinel oxides and olivines. The removal and insertion of the lithium ion for the three lithiated transition metal oxides are

\[
\begin{align*}
\text{LiCoO}_2 & \quad \leftrightarrow \quad \text{Li}_{1-x}\text{CoO}_2 + x \text{Li}^+ + x \text{e}^- \\
\text{LiNiO}_2 & \quad \leftrightarrow \quad \text{Li}_{1-x}\text{NiO}_2 + x \text{Li}^+ + x \text{e}^- \\
\text{LiMn}_2\text{O}_4 & \quad \leftrightarrow \quad \text{Li}_{1-x}\text{Mn}_2\text{O}_4 + x \text{Li}^+ + x \text{e}^-
\end{align*}
\]

The reversible value of x for LiCoO\(_2\) and LiNiO\(_2\) is less than or equal to 0.5, and the value is greater than or to 0.85 for lithiated manganese oxide. Thus, although the theoretical capacity of LiCoO\(_2\) and LiNiO\(_2\) (274 mAh g\(^{-1}\)) is almost twice as high as that of LiMn\(_2\)O\(_4\), the reversible capacity of the three cathode materials is about the same (135 mAh g\(^{-1}\)). In the long run it is expected that the manganese based compounds will
become the material of choice as they are more abundant, less expensive, and non-toxic. Here we confine ourselves to the layered oxides, spinel oxides and olivine compounds used as cathode material lithium secondary batteries. These compounds are briefly reviewed and segregated on basis of operating voltage.

1.6.1 3V Cathode Materials

Most important compounds used as cathode candidates for 3V Lithium cells are manganese oxides, lithiated manganese dioxides [30,31], vanadium [32], chromium [33] and iron oxides [34]. Among these, Mn-based compounds remain the most studied oxides for cathodes in Li-rechargeable cells. There are different forms of MnO₂, namely α, β, γ-MnO₂. γ-MnO₂ material needs to be dehydrated at 250°C - 400°C prior to its use in Li rechargeable cells [35]. Upon heat treatment, γ-MnO₂ evolves towards β-MnO₂ and the material is called γβ-MnO₂. In this material, Li intercalation between 3.3V and 2V leads to an irreversible capacity higher by 30-50% in relation to γ-MnO₂. But, irreversibility is minimized by charging up to 3.8V. Apart from this, cycle-life is reportedly poor except for a recent report where a high surface-area HT-manganese dioxide is used [36]. β-MnO₂ is electrochemically inactive and transforms to spinel upon lithiation above 0.2 Li/Mn.

Ramsedellite-like Rγ-MnO₂ is synthesized by acid digestion of Li₂Mn₄O₉ at 95°C followed by dehydration at 200°C. This material provides an initial capacity of 190 mAh g⁻¹ and a reversible capacity of 120 mAh g⁻¹[37]. α-MnO₂ is most suitable for Li
intercalation [38] and is stabilized by NH4⁺, K⁺, Rb⁺ cations within 2×2 tunnels. Li intercalation in such compounds occurs with initial capacity of about 200 mAh g⁻¹ but with a poor cyclability and rate capability.

There have been reports of synthesis of MnO₂ by acid leaching of Li₂Mn₂O₃ at 90⁰C [39]. This compound exhibits a high initial capacity but poor cycling behavior. Pre-lithiated MnO₂ phases are synthesized, characterized and studied for lithium intercalation. It is reported to exhibit improved cyclability and a specific capacity of 160-200 mAh g⁻¹ in the voltage range between 3.6V and 2V [40]. δ-MnO₂ or phyllosilicate phases are known for their ion exchange properties and their structural chemistry is reviewed in the literature [41]. δ-MnO₂ is synthesized by low-temperature techniques, such as air oxidation of Mn(OH)₂ in LiOH solution [42], hydrothermal and molten-salt reactions [41], reduction of permanganate solution at 60⁰C [43] and hydrothermal reaction of K-, Na- and Li permanganates at 170⁰C [44]. δ-MnO₂ intercalates Li giving initial specific capacity as high as 200-230 mAh g⁻¹ but it loses its capacity very fast.

Good capacity retention is obtained with low-surface-area samples that deliver a capacity value of only 120 mAh g⁻¹ at C/6 rate over 50 charge-discharge cycles [45]. Lithium-ion cells with lithiated MnO₂, namely Li₀.₃₃MnO₂, cathode were commercialized in the early 90’s by Tadiran Battery due to the efforts of Aurbach et al. [46]. The performance of these cells was found to be satisfactory at low rates but is limited at high rates. A 29 single phase orthorhombic Li₀.₃₃MnO₂ is obtained by heating LiNO₃/MnO₂ at 350 °C for about 30 h. This compound delivers a capacity of 180 mAh g⁻¹. A better performance is
reported by Nakamura et al. [47] for orthorhombic Li_{0.5}MnO_2 obtained by lithiating MnO_2 with LiI at 150 °C - 200 °C. These authors report a capacity value of 250 mAh g\(^{-1}\) during cycling in the voltage range between 4.5V and 2V at a load current-density of 0.4 mA cm\(^{-2}\). Recently, Li- and O-rich spinels are also studied as 3V cathodes. Manthiram et al. [48] have examined the Li-rich spinel while Kilroy et al. [49] have examined the O rich compounds. These materials cycle well with a specific capacity of about 200 mAh g\(^{-1}\).

Recently, stable 3V cycling behavior for the LiMn_2O_4 prepared by sol-gel synthesis with a particle size of 0.8 μm has been reported by Goodenough et al. [50]. These authors report excellent cyclability in 3V range and conclude that the Jahn-Teller distortion responsible for the capacity fade could be accommodated by strained nano-sized particles.

Li-intercalation properties of o-Na_{0.44}MnO_2 [51] have also been studied recently [52]. Reversible intercalation of 0.55-0.6 Li/Mn resulting in specific capacities between 160-180 mAh g\(^{-1}\) is reported with moderate capacity-fade over 90 cycles. V_2O_5, V_6O_{13} and LiV_3O_8 are investigated as cathodes for 3V batteries with Li anode.

Vanadium bronzes, namely M=V_2O_5 (M=Li) with M= Na, K, Cu, Ag, Ca, Cd and Pb, are also studied as cathode materials [53-57]. Most vanadium-based oxides are easy to prepare and exhibit higher capacities in relation to MnO_2 with the operating voltages between 2.3V and 2.7V. Many compounds, such as V_6O_{13}, LiV_3O_8, V_2O_5, Xerogel-V_2O_5,
AyV$_2$O$_5$ (A=Li, Na, K) bronzes and MyV$_2$O$_5$+$z$ (M=Cr, Fe), also offer good electrochemical behavior but studies on long-term cycling behavior and storage behavior are lacking in literature.

Various chromium oxides, such as Cr$_2$O$_3$, CrO$_2$, Cr$_5$O$_{12}$, Cr$_2$O$_5$, Cr$_6$O$_{15}$, Cr$_7$O$_8$ and MCr$_3$O$_8$ (M=Li, Na, K, Ag), are examined as cathode materials in Li-batteries [58,59]. Although these exhibit a high capacity at around 3V, the poor cycling behavior and the toxicity of Cr have restricted their industrial utilization. A new amorphous oxide, a-CrO$_2$-$\delta$ ($\delta \leq 0.5$), prepared by aqueous reduction of K$_2$Cr$_2$O$_4$ with KBH$_4$ [60], exhibits the specific capacity value of about 180 mAh g$^{-1}$ at an average discharge voltage of 2.8V with good capacity retention of up to 30 cycles. Iron oxides, like Fe$_2$O$_3$ [61] and Fe$_3$O$_4$ [62] insert Li$_3$O at voltages as low as 2V but are attractive because of their cost and lower toxicity.

Some iron hexacyanides, like Fe$^{3+}$_4[Fe$^{2+}$(CN)$_6$]$_3$. 14 H$_2$O [63], are reported to deliver a specific capacity value of 100 mAh g$^{-1}$ at an average voltage > 3V. A Ni-based oxide, namely Ni$_{0.92}$Co$_{0.08}$OOH, is recently proposed as a cathode for Li-batteries [64]. It exhibits a high and reversible specific-capacity value of about 250 mAh g$^{-1}$ at an average discharge voltage of 2.7V.
1.6.2 4V Cathode Materials

The promising cathode materials for lithium batteries are strongly oxidizing agents in nature and have a high reversible lithium intercalation voltage around 4.0V vs. Li are dealt in this section. They may be divided in three big groups: LiMO$_2$ types of oxide i.e., bare and doped LiCoO$_2$, LiNiO$_2$ and LiMnO$_2$ compounds, lithiated manganese oxides (i.e., LiMn$_2$O$_4$) and other materials. Subsequent to the discovery of LiCoO$_2$ by Mizushima et al. [65] LiCoO$_2$ was used in the first commercial lithium-ion battery (Sony), and currently is used by most lithium-ion battery manufacturers as a cathode material. It is preferred for its electrochemical properties, although it is relatively expensive and toxic. Nickel compounds are relatively inexpensive but much more difficult to synthesize. For future lithium batteries, the LiMn$_2$O$_4$ compounds are favored over the other two compounds, based on availability, ease of synthesis, low cost, and environmental benign nature. The properties of aforesaid bare and doped materials are conferred in the subsequent segment.

1.6.2.1 LiCoO$_2$ and substituted LiCoO$_2$

The report of layered LiCoO$_2$ by Mizushima et al.[65] cyclable up to 4V received only limited attention due to the non-availability of appropriate electrolytes. However, even today, despite the high cost and toxicity of the cobalt, LiCoO$_2$ is used in many commercially available Li-ion batteries. LiCoO$_2$ is easily synthesized by solid-state reaction in the temperature range between 850°C and 1000°C over several hours. LiCoO$_2$
is isostructural to $\alpha$-NaFeO$_2$ [66]. It has a rhombohedral structure where Li and Co fill alternative layers of edge-sharing octahedral sites in a close-packed oxygen array (Li in 3b, Co in 3a and O in 6a sites) with R3m space-group [65]. Such a structure provides a two-dimensional diffusion path for Li$^+$ ions in the LiCoO$_2$ framework [66,67]. Lithium deintercalation from LiCoO$_2$ has been reported by Mizushima et al. [65] and the structural changes involved during deintercalation have been studied. Lithium deintercalation in LiCoO$_2$ involves several two-phase and one-phase regions [69], with a monoclinic phase at Li$_{0.5}$CoO$_2$. The second monoclinic phase with low Li content obtained is not observed by McBreen et al. [70], instead these authors have observed a 8 hexagonal phase.

At full delithiation, CoO$_2$ with O1-structure is obtained as reported by Yang et al. [71], and Amatucci et al. [72]. But, Venkatraman and Manthiram [73] contradict this and according to them CoO$_2$ has P3 structure. These authors observed the formation of P3-phase for Li$_{0.45}$CoO$_2$, which coexists with O$^3$-phase in the range $0.2 \leq x \leq 0.45$ in Li$_x$CoO$_2$ and are characterized by fast contraction of c-axis with decrease in x. P3-phase losses oxygen more easily in relation to O3-phase due to which a higher capacity fade results for LiCoO$_2$ cathodes on charging to potentials higher than 4.2V vs. Li/Li$^+$. Removal of Li in Li$_x$CoO$_2$ form $x = 1$ to 0.1 yields a capacity value of 274 mAh g$^{-1}$. But, in practice, delithiation in LiCoO$_2$ is restricted to $x = 0.5$, that corresponds to 4.2VVs. Li/Li$^+$ [74]. These authors report, that Li removal up to $x = 0.5$ results in an increase in interlayer distance and a decrease thereafter. Complete delithiation in LiCoO$_2$ brings
about 6-8 % reduction in unit cell volume, which is detrimental to electrode reversibility. It is however, reported that CoO₂ structure can accommodate lithium up to 90-95 % by electrochemical reduction at a low rate [75], suggesting both the phase and volume changes to be reversible. Hence, dissolution of cobalt at high potentials in the electrolyte and the resulting structural changes cause capacity fade upon cycling above 4.2V. Therefore, cycling of LiCoO₂ cathode is generally restricted to only up to 4.2V. However, several efforts to cycle LiCoO₂ cathode beyond 4.2V are being expended to extract extra capacity from LiCoO₂ so as to increase the energy density of the Li-ion cells.

Lee et al. [76] synthesized solid solutions of LiCoO₂ and Li₂SnO₃, and Aurbach et al. [77] used boron-based additives in LiCoO₂ to mitigate cobalt dissolution at high potentials. Recent studies make use of oxide coatings on LiCoO₂ and high-temperature annealing to prevent cobalt dissolution [78-80].

Cho et al. [78] reported that the poor structural stability of LiₓCoO₂, when cycled to x < 0.5, i.e. above 4.2V, could be improved by coating a metal oxide on the surface of LiCoO₂. These authors report that the metal-oxide coated LiCoO₂ exhibits a high reversible capacity of 170 mAh g⁻¹ with improved cycling behavior between 2.75 and 4.4V. According to them [78], LiCoO₂ coated with metal oxides of large fracture toughness have better cycling behavior. For example, the fracture toughness of metal oxides used by Cho et al. [78] decreased in the order: ZrO₂ > Al₂O₃ > TiO₂ > B₂O₃. This indicated that ZrO₂-coated LiCoO₂ performs better than the other oxides. It is suggested
that the metal-oxide layer serves as a mechanical constraint to prevent Li$_x$CoO$_2$ lattice from expanding and contracting during battery charge-discharge reactions. This eliminates the structural instability and provides good capacity retention. Subsequent to these studies, several authors have reported improvements in capacity retention of metal-oxide coated cathode materials.

According to Chen et al. [81], the annealing step involved in the surface coating of LiCoO$_2$ particles removes the surface species, such as Li$_2$CO$_3$ or LiOH, formed during the exposure of LiCoO$_2$ to air. These surface species are detrimental to capacity retention during cycling up to 4.5V. Dahn et al. [81] report that the capacity retention in LiCoO$_2$ annealed at the temperature used for Al$_2$O$_3$ or SiO$_2$ to be similar to LiCoO$_2$ coated with Al$_2$O$_3$ or SiO$_2$.

In a review by Chen and Dahn [82] that describes coating methods and their influence, it is inferred that the prime reason for capacity fade of LiCoO$_2$ cathode when cycled up to 4.5V is the increased impedance at the LiCoO$_2$ surface in LiPF$_6$-based electrolytes. The impedance at the LiCoO$_2$ surface is suppressed: (a) by metal oxide coating, (b) by grinding to create fresh LiCoO$_2$ surface, and (c) by heat treatment in air at 550°C. An improvement in cycle-life of LiCoO$_2$ cathode charged up to 4.5V is also reported by replacing LiPF$_6$ with lithium bis(oxalato) borate electrolyte [82]. This suggests that the impedance growth mechanism involves LiPF$_6$. Hence, by coating or by using proper electrolyte or by annealing LiCoO$_2$, it should be possible to cycle LiCoO$_2$ cathode up to 4.5V with only a marginal decrease in its capacity. Thermal stability is another important
factor as the thermal stability of Li$_x$CoO$_2$ in electrolyte is observed to decrease with an increasing of $x$. This problem is studied by Cho et al. [79] by coating AlPO$_4$ on LiCoO$_2$ and it is demonstrated that after AlPO$_4$ coating on LiCoO$_2$, the cell does not experience short-circuit on charging up to 12V for 2 h and no explosion is observed. By contrast, the cell without AlPO$_4$ coating on LiCoO$_2$ caught fire and exploded when charged to 12V. LiCoO$_2$ is generally prepared at high temperatures (HT) but low-temperature (LT) methods are also reported. The structure of LT-LiCoO$_2$ differs from HT-LiCoO$_2$ [83]. HT-LiCoO$_2$ shows better electrochemical activity but its commercial production involves high cost. The more affordable alternative, LT-LiCoO$_2$ fails to maintain the cell performance over initial (first few) charge-discharge cycles. This is mainly due to the difference in structures of HT-LiCoO$_2$ and LT-LiCoO$_2$ [84]. But, the analysis of the crystal structure is not possible for the LT-LiCoO$_2$ by XRD and neutron diffraction due to the structural anomaly at $c/a = 4.9$ [83]. It is proposed that LT-LiCoO$_2$ has a structure intermediate to ideally-layered and ideally-lithiated spinels [85]. Several authors have used Li-MAS NMR, IR and Raman spectroscopy to determine the crystal structure of LT-LiCoO$_2$ [84, 86] and inferred it be modified spinel structure that differs from the normal spinel with Li at 16c octahedral position compared to 8a tetrahedral positions in the normal spinel. LiCoO$_2$ synthesized by low-temperature route and then annealed at 800°C showed structure analogues to HT-LiCoO$_2$ with good electrochemical activity [87]. Generally, all high-temperature methods produce LiCoO$_2$ with O$_3$-structure. But synthesis of LiCoO$_2$ with O$_2$-structure is also reported. In 1982, Delmas et al.[88] first reported O$_2$-LiCoO$_2$. It is found that O$_2$-LiCoO$_2$ has slightly larger inter-layer spacing of 4.76 Å than conventional O$_3$-LiCoO$_2$ (4.69 Å) with a slightly smaller lattice constant
[59]. Accordingly, better electrode performance, namely fast and reversible intercalation, is expected for O$_2$-LiCoO$_2$. However, the electrochemical study by Delmas et al. [88] suggests that O$_2$-LiCoO$_2$ has smaller reverse cycling capacity than O$_3$-LiCoO$_2$. Only up to 0.38 lithium could be removed from the O$_2$-LiCoO$_2$ if charged to 4.4V corresponding to a capacity value of 105 mAh g$^{-1}$. Later, Dahn et al. [89] showed that achievable capacity for O$_2$-LiCoO$_2$ happens to be larger than 105 mAh g$^{-1}$, if it is cycled above 4.4V. They showed that 0.9 Li can be removed by charging O$_2$-LiCoO$_2$ up to 4.8V providing a high capacity value of 260 mAh g$^{-1}$. They concluded that the electrochemical performance of O$_2$-LiCoO$_2$ is comparable to O$_3$-LiCoO$_2$ as both yields the same capacity, high-rate capability and same capacity fade, with similar thermal stability in electrolyte. However, commercial utilization of O$_2$-LiCoO$_2$ is not feasible due to the difficulties involved in its synthesis.

Efforts have been made to successfully synthesize Li$_{M_y}$Co$_{1-y}$O$_2$ (M = metal) isostructural with LiCoO$_2$ to develop safe cathode materials with low-cost, high energy-density, and improved cycle-life. To this end, several substituent metals such as Ni [90-92], Al [93, 94], Mg [95], Fe [96], Mn [97, 98], Ti [99,100], Zn [98], Cr [101], B [102] and Rh [103], are reported in literature.

The efficacy after substituting Ni in LiCoO$_2$ has been studied by several authors using different methods, due to its significance in increasing the capacity. Substituting Ni metal in LiCoO$_2$ is found to favor its electrochemical performance up to $y = 0.2$. But, a high level of substitution is found to degrade its electrochemical performance due to cation
mixing, i.e. Ni occupying some of the Li sites in the Li layer. Even the rapid synthetic methods like solution-combustion method [104] and microwave method [105] suggest $y = 0.2$ sample to exhibit optimum performance.

Al-substitution in LiCoO$_2$ helps improving the effective capacity window for the lithium ion battery [93,106]. Jung et al. [93] observed that with increasing $y$ in Li$_x$Co$_{1-y}$Al$_y$O$_2$, the OCV of the cathode increases at all $x$ values. For LiAl$_{0.25}$Co$_{0.75}$O$_2$, both charge and discharge voltages are higher by 0.15 to 0.2V than that for LiCoO$_2$. But the cycle-life of the Al-substituted compound is poor and the cause for its capacity fade is not established.

Studies done by Yoon et al. [94] also suggest similar behavior for the Al-substituted LiCoO$_2$. It is suggested that a higher capacity fade in Al-substituted samples in relation to LiCoO$_2$ is due to a larger local structural-distortion during Li deintercalation. Hence, Al substitution into LiCoO$_2$ is interesting because of its higher potential even if capacity fade is lower in LiCoO$_2$.

Mg-substitution in LiCoO$_2$ is studied by Tukamoto et al. [95]. It is found that Mg substitution decreases the conductivity of LiCoO$_2$ at low concentrations when Li vacancies are occupied by Mg. But, the conductivity increases substantially at higher Mg concentrations where Mg$^{2+}$ ions occupy Co$^{3+}$sites. Mg-substituted compounds exhibit electrochemical properties similar to bare compound in terms of reversibility, but their capacity values are lower due to the lower Co$^{3+}$ concentration. Also, Mg substituted compounds exhibit single phase during the charge-discharge cycles, which is essential for
long-term performance. Substitution of Mg into LiCoO$_2$ (i.e. LiCo$_{1-y}$Mg$_y$O$_2$) by microwave method is also reported by Elumalai et al. [107]. These authors obtained single phase up to $y = 0.2$ but at $y > 0.2$ some MgO impurity is formed. Julien et al. [98] have reported the synthesis of 50% Mg-substituted LiCoO$_2$ by solution-combustion method with small amounts of impurities. Accordingly, solid-solution formation seems to depend on the method of synthesis. Gopukumar et al. [336] synthesized Mn, Cu, Fe, and Zn doped LiCoO$_2$ and the physical and electrochemical characterization of the synthesized materials for use in lithium rechargeable cells and firstly reported that the material, LiMn$_{0.05}$Co$_{0.95}$O$_2$ delivered a capacity of 158 mA h/g at a C/5 rate when cycled in the narrow range between 3.5 and 4.5V.

Fe-substitution in LiCoO$_2$ is reported by Kobayashi et al. [96]. It is interesting to substitute Fe for Co because Fe is cheaper and environmentally friendly while Co is both toxic and costly. But, Fe-substitution degrades the electrochemical activity of LiCoO$_2$ due to its tendency to occupy Li-sites in the Li-layer.

Mn-substitution in LiCoO$_2$ is attractive as Mn is both cheaper and safer. Mn-substitution for Co in LiCoO$_2$ has been studied by several authors [97, 98]. For the first time in literature, it was reported by Stoyanova et al. [97] that Mn-substitution for Co in the LiCoO$_2$ is possible up to $y = 0.2$ with the layered structure; when $y > 0.2$, the compounds exhibit a modified spinel structure equivalent to LT-LiCoO$_2$. This finding is also supported by synthesizing LiCo$_{1-y}$Mn$_y$O$_2$ using low-temperature solution-combustion method [104]. The sample with $y = 0.2$ composition shows good electrochemical activity with an optimum capacity of 138 mAh g$^{-1}$. B, Zn, Cr and Ti [99-101] substitution in
LiCoO$_2$ is also reported and observed to be beneficial at low concentrations. Gopukumar et al. [337] synthesized LiCoO$_2$ involving Bi, Cr, Sn, and Zr as dopant ions and studied the physical and electrochemical performance of the synthesized materials for use in lithium rechargeable cells. They showed for the first time that LiZr$_{0.05}$Co$_{0.95}$O$_2$ delivered a capacity of $\sim155$ mAh g$^{-1}$ when cycled in the voltage range between 3.5 and 4.5 V at C/5 rate. The enhanced performance could be ascribed to the presence of some Co$^{2+}$ ions due to charge compensation effect.

Subsequent to the synthesis of LiRhO$_2$ by Mendiboure et al. [108], Rh-substitution in LiCoO$_2$ is reported by Madhvi et al. [103]. These authors show that solubility of Rh in LiCoO$_2$ is lesser than 20 at %. Rh-substituted LiCoO$_2$ delivers similar capacity as LiCoO$_2$ but the phase transition occurring in Li$_x$CoO$_2$ at $x > 0.5$ is suppressed, which improves the capacity retention even at rates as high as 0.14C as compared to undoped LiCoO$_2$.

1.6.2.2 LiNiO$_2$ and Substituted LiNiO$_2$

LiNiO$_2$ is cheaper and less toxic than LiCoO$_2$. The specific capacity obtained for LiNiO$_2$ is also higher than LiCoO$_2$. However, LiNiO$_2$ needs to be synthesized carefully owing to the difficulties involved in oxidation of Ni$^{2+}$ to Ni$^{3+}$. The structural aspects and the electrochemical behavior of LiNiO$_2$ are reviewed in the literature [109,110].

Stoichiometric LiNiO$_2$ is a layered compound like LiCoO$_2$. In Li$_{1-x}$Ni$_{1+x}$O$_2$ (0 ≤ $x$ ≤ 1) for 0 ≤ $x$ ≤ 0.2 compositions, the structure is isostructural to LiCoO$_2$ (R3m space-group) with
[Li$_{1-x}$Ni$_x^{2+}$] in 3b and [Ni$_{1-x}^{3+}$Ni$_x^{2+}$] in 3a and O in 6c sites [111]. Ni$^{2+}$ concentration in the Li-layer varies depending on the synthesis procedure and conditions, [112-114]. By using high oxidizing conditions, Ni$^{3+}$ is stabilized in preference to Ni$^{2+}$, thus decreasing $x$. A lower value of $x$ is desirable from the electrochemical point of view since a higher amount of Ni$^{2+}$ in Li-layer decreases the capacity [115]. Hence, the $x$ values lower than 4% are desirable to achieve good electrochemical performance.

It is worth mentioning that the determination of $x$ value with accuracy is difficult. There are some methods reported in the literature to evaluate $x$. The intensity ratio of the XRD lines(I(003) / I(104)) [116] or (I(006)+I(102-)) / I(101) [117] provides an approximate estimation of $x$.

Rietveld refinement [118] is used by several authors to determine the $x$ value. Since the magnetic properties are also sensitive to the $x$ value, magnetic measurements of the sample and comparison with the magnetic behaviour of the sample with known $x$ value are also employed [111].

The structural chemistry of Li$_x$NiO$_2$ is complex like Li$_x$CoO$_2$ [119]. Solid solution with rhombohedral symmetry exists within the composition ranges $0.85 \leq x \leq 1$ and $0.32 \leq x \leq 0.43$. When $x = 0.5-0.75$, a single monoclinic phase is obtained. Delmas et al. [120] report that the amount of lithium extracted during first charging from LiNiO$_2$ cannot be inserted completely and the capacity loss is significant in the first cycle. In compounds with low $x$ values, reinsertion is possible only up to Li$_{0.85}$NiO$_2$. According to these
authors, at high degree of deintercalation, \( \text{Ni}^{2+} \) in the Li-layer oxidizes to \( \text{Ni}^{3+} \) and subsequently the structure collapses around \( \text{Ni}^{3+} \). Hence, it is desirable to keep the \( x \) value as low as possible. But, \( \text{Li}_x\text{NiO}_2 \) with low \( x \) values are sensitive to air and need proper care in handling [121].

\( \text{LiNiO}_2 \) is attractive because of cheaper Ni but the safety due to thermal instability of fully-charged \( \text{LiNiO}_2 \) is a concern. In order to overcome this problem, substitution of Ni by other ions, such as Co [122], Al [123], Fe [124], Ti [125], Cr [126], Mg [127], B [128], Ba [129], Ga [130], Ca [131], Sr [132], and Mn [124,133], are reported.

Co-substitution in \( \text{LiNiO}_2 \) has been studied extensively because these materials combine the properties of \( \text{LiCoO}_2 \) and \( \text{LiNiO}_2 \), namely, the high stability of \( \text{LiCoO}_2 \) and the high capacity of \( \text{LiNiO}_2 \). The presence of 30 % Co is mandatory to stabilize the layered structure with no \( \text{Ni}^{2+} \) in the Li-layers [122], in order to facilitate good electrochemical behavior with first discharge capacity nearly equal to \( \text{LiNiO}_2 \) and the cyclability comparable to \( \text{LiCoO}_2 \). But, cobalt substitution lowers the sensitivity of \( \text{LiNiO}_2 \) to moist air [121]. \( \text{LiFe}_y\text{Ni}_{1-y}\text{O}_2 \) (0 ≤ \( y \) ≤ 0.23) [124,134], \( \text{Li}_x\text{Mn}_y\text{Ni}_{1-y}\text{O}_2 \) (0.9 ≤ \( x \) ≤ 1.2, 0 ≤ \( y \) ≤ 0.5) [124,133,135], \( \text{LiAl}_y\text{Ni}_{1-y}\text{O}_2 \) (0 ≤ \( y \) ≤ 0.3) [123], \( \text{LiTi}_y\text{Ni}_{1-y}\text{O}_2 \) (\( y \) ≤ 0.3) [125] are also reported. A compromise between reversible capacity fade and thermal stability improvement is reached for \( \text{LiM}_y\text{Ni}_{1-y}\text{O}_2 \), where \( M = \text{Mn, Ti} \) are at low-substitution level (\( y = 0.10 \)). By restricting the extraction of Li from \( \text{LiNiO}_2 \) to \( 3/4 \)-Li per formula unit, the formation of poorly cyclable R3-phase can be avoided. Accordingly, \( \text{LiAl}_{1/4}\text{Ni}_{3/4}\text{O}_2 \) is synthesized and found appropriate to avoid overcharge with increased safety.
LiAl$_3$Ni$_{1-y}$O$_2$ solid solutions are also reported by Zhong et al. [136]. Mg-substitution in LiNiO$_2$ increases its conductivity by about two orders due to hole formation [127]. Single-phase deintercalation is reported to favor high-rate capability and good cyclability with a specific capacity value of 152 mAh g$^{-1}$. Substitution of Li in Ni sites with concomitant partial-replacement of O with F results in Li$_{1-x}$Ni$_{1-x}$O$_{2-y}$F$_y$ ($0 \leq x \leq 0.15$, $0 \leq y \leq 0.25$) compounds [137]. These compounds perform well. Mn, Al and Ti substitutions also provide structural stability to LiNiO$_2$.

Substitution of Co and Li for Ni with concomitant partial-replacement of O by F results in Li$_{1.075}$Ni$_{0.755}$Co$_{0.17}$O$_{1.9}$F$_{0.1}$, which exhibits a stable specific capacity of 182 mAh g$^{-1}$ with a capacity fade of only about 2.6 % after 100 cycles [138]. Similarly, substitution of Ti and Mg at Ni sites in LiNiO$_2$ results in LiNi$_{1-y}$Ti$_{y/2}$Mg$_{y/2}$O$_2$, with progressive disappearance of exothermic peak in differential scanning calorimetry with increasing $y$ [139]. For $y = 0.3$, no exothermic peak is obtained indicating the compound to be safer than LiNiO$_2$. However, these compounds show high irreversible capacities. There are also reports in the literature where O is substituted by S [140] or F [141]. Sulphur substitution is found to stabilize the capacity. For example, Li$_{1.05}$Ni$_{1.98}$S$_{0.02}$ exhibits a specific capacity of 140 mAh g$^{-1}$ over 100 cycles [140].

1.6.2.3 LiMnO$_2$ and Substituted LiMnO$_2$

LiMnO$_2$ is a material of interest for Li-ion cells because Mn is both cheaper and safer in relation to Co in LiCoO$_2$. LiMnO$_2$ based compounds, which yield high, stable and
consistent specific capacities over prolonged charge-discharge cycles, is difficult to obtain. Theoretical capacity expected for the layered LiMnO₂ is 285 mAh g⁻¹ [142]. However, LiMnO₂ is thermodynamically unstable in the layered structure [143] and high-temperature methods of synthesis result in orthorhombic LiMnO₂ (o-LiMnO₂). Initially, only medium- and low-temperature synthesized o-LiMnO₂ materials are reported to exhibit electrochemical activity [144,145] but, later, it has been realized that high-temperature synthesized samples with structural defects are also electrochemically active [146,147].

The electrochemical behavior of the o-LiMnO₂ has been reported by several authors [144-147]. It is known that the structural transformation takes place during cycling in the voltage range between 2V and 4.3V. It is difficult to determine the structure of new Li₁ₓMnO₂ obtained after cycling because of the c/a ratio being 4.9 by virtue of which cation arrangements in both cubic and hexagonal structures cannot be distinguished by XRD[149]. But, the voltage profile of the phase agrees fairly well with the partially-distorted spinel LiMn₂O₄ [148]. The structural transformation may take place during the very first cycle or it may take few cycles depending on the synthesis conditions. A recent study on the structural defects in o-LiMnO₂ suggests the spinel structure formed after cycling to retain some of the defects present initially [150]. Accordingly, the performance of the o-LiMnO₂ depends upon the synthesis condition even though all of these show the structural-transition during cycling. Coating of o-LiMnO₂ by oxide has been used to prevent the transition during cycling and it is inferred that coating can indeed increase the performance of the o-LiMnO₂ [151].
Although o-LiMnO$_2$ is thermodynamically more stable than the layered structure, it is possible to synthesize the layered LiMnO$_2$ by soft chemical-routes, namely by ion-exchange, as reported by Armstrong et al. [142]. But, the material does not crystallize with $\alpha$-NaFeO$_2$ structure akin to LiCoO$_2$ and results in a monoclinic symmetry with the space-group: C2/m. This is because the Jahn-Teller Mn$^{3+}$ ion causes a distortion of the MnO$_6$ octahedron.

Ammundsen et al. [152] summarizes different kinds of LiMnO$_2$ reported in the literature. LiMnO$_2$ reported by Armstrong et al. [142] has O3-structure but its electrochemical stability is poor due to the transition of the structure to spinel during cycling. Ceder and Mishra [153] predict that a partial substitution of Mn$^{3+}$ with non-magnetic ions would stabilize the layered structure. This is demonstrated by Robertson et al. by substituting LiMnO$_2$ with Co [154] and Ni by Quine et al.[155]. To address this problem, Paulsen et al. [156-157] synthesized O2-LiMnO$_2$, which differs from O3-LiMnO$_2$ as it contains two MnO$_2$ units in the unit cell rather than three for O3-LiMnO$_2$. The conversion of O2-structure into spinel is difficult as it requires rearrangement of oxygen lattice that is quite unlikely at room temperature. Accordingly, O2-LiMnO$_2$ is expected to provide stabler specific capacity than O3-LiMnO$_2$. But, the specific capacity is lower for O2-LiMnO$_2$.

Substitution of Mn by Co [154] and Ni [155] is reported to stabilize the capacity of layered-LiMnO$_2$. Both Co- and Ni-substituted layered LiMnO$_2$ samples perform better than LiMnO$_2$ with specific capacities higher than 200 mAh g$^{-1}$. 
Quine et al. [155] studied the effect of ion-exchange on the performance of the substituted samples and showed that the compounds exchanged in hexanol at 160 °C give higher capacity while the compounds exchanged in ethanol at 80 °C are stabler. This is because the defects in the samples exchanged in hexanol are lesser and the compounds do not restrict the strain due to Jahn-Teller distortion of MnO6 octahedra. It is reported that Co and Ni-substituted compounds retard the transition to spinel during cycling [154,155].

Al- [158] and Cr- [159] substitutions are also reported for LiMnO2. Al-substituted compounds transform into spinel during cycling but Cr-substituted compounds do not exhibit the transformation. Specific capacities as high as 160-190 mAh g⁻¹ are obtained with Cr-substituted compounds, which are higher than the capacities reported for Al substituted compounds. A reason for Cr-substituted compounds not being susceptible to conversion to spinel during cycling may be the strong octahedral-site-stabilization-energy of Cr. But these compounds show two voltage plateaus separated by 1V in the discharge curve. LiMn₀·₅Ni₀·₅O₂ [160,161] is studied by many authors because of its stable and high capacity. Ohzuku et al. [160] reported the synthesis of this compound by the ceramic method. This material provides a stable capacity value of 200 mAh g⁻¹ when cycled at low rate in the voltage range between 2.5V and 4.5V. Dahn has reported Co and Ni substituted O2-LiMnO₂ compounds that exhibit stable capacity value between 150-180 mAh g⁻¹ at low discharge-rates.

Bimetallic substitution into LiMnO₂ is also reported by Ohzuku et al. [162]. These authors used Ni- and Co-substituents resulting in Li[Co₁/₃Ni₁/₃Mn₁/₃]O₂ compound, which
has also studied by several others [163,164]. This material shows a zero volume change upto a deintercalation of 0.67 Li\(^+\) mol\(^{-1}\). Hence, this material is promising for advanced Li-ion cells. Sun et al. [165] reported Li[Li\(_{0.13}\)Ni\(_{0.3}\)Mn\(_{0.57}\)]O\(_2\), which gives a stable capacity of 190 mAh g\(^{-1}\) when cycled between 2V and 4.6V. Recently, LiMn\(_{0.9}\)Ni\(_{0.05}\)Fe\(_{0.05}\)O\(_2\) is reported to exhibit a stable specific capacity of 250 mAh g\(^{-1}\) at low discharge-rate (C/10) without much capacity fade up to 30 cycles [166]. Other promising materials being Li[Li\(_{0.15}\)Ni\(_y\)Al\(_{0.55-2y}\)Mn\(_{0.3+y}\)]O\(_2\) [167] and Li[Li\(_{0.2}\)Cr\(_{0.4}\)Mn\(_{0.4}\)]O\(_2\) [168]. Recently, both cation and anion substitutions in LiMnO\(_2\) are reported by Kim et al.[169]. These authors synthesized Li (Ni\(_{1/3}\)Co\(_{1/3}\)Mn\(_{(1/3-y)}\)Mg\(_y\))O\(_2\)\(_2\)F\(_z\) by co-precipitation method. This compound exhibits a specific capacity of 180 mAh g\(^{-1}\) and sustains excellent cycling behavior with almost 100 % capacity retention even after 30 charge discharge cycles.

Of late, S H Hut et al. [170] have reported ZrO\(_2\)-coated LiNi\(_{1/3}\)Co\(_{1/3}\)Mn\(_{1/3}\)O\(_2\) material exhibited an improved rate capability and cycling stability under a high cut-off voltage of 4.5V and they attributed the improved performance is due to the ability of ZrO\(_2\) to scavenge the HF species from the conventional lithium battery electrolytes hence the decomposition reaction.

The surface modified LiNi\(_{1/3}\)Co\(_{1/3}\)Mn\(_{1/3}\)O\(_2\) with Al\(_2\)O\(_3\) mechano-thermal coating process is reported by G T Fey et al. [171] and obtained first- cycle discharge capacity of 195 mAh g\(^{-1}\) when cycled between 2.5 to 4.5V at C/10 rate.
1.6.2.4 LiMn$_2$O$_4$

LiMn$_2$O$_4$ is extensively studied because of its lower cost, lower toxicity and higher thermal stability in relation to LiCoO$_2$. LiMn$_2$O$_4$ was first introduced into the commercial cells as early as in 1996. But the poor performance of LiMn$_2$O$_4$ directed research and development efforts in improving its characteristics. LiMn$_2$O$_4$ crystallizes in space-group Fd3m with Li and Mn, respectively, occupying 8a tetrahedral sites and 16d octahedral sites of the cubic-close-packed oxygen array [172]. In the framework, MO$_6$ octahedra share edges to build a rigid 3-dimensional network with open interconnected channels in the <110> directions where Li$^+$ ions are present. Li$^+$ ions are mobile within these channels along the 8a-16c-8a path. A reversible extraction of Li from LiMn$_2$O$_4$ in two steps at 4.05V and 4.15V results in delithiated MnO$_2$ [173]. Operating voltage is larger for LiMn$_2$O$_4$ as compared to LiMO$_2$ (M = Co, Ni). However, the achievable capacity is lower and the cyclability is poor. The method of synthesis plays important role in the electrochemical performance of LiMn$_2$O$_4$. This is mainly because the stoichiometry of the compounds obtained by different methods is different [174].

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. Hence, Li-rich and substituted cation-deficient spinels show better performance [175]. Accordingly, most of the research is focused on the spinels with formulations close to Li$_{1+x}$Mn$_{2-x}$O$_4$ with low x (= 0.05) to achieve 4V capacity window [176]. Capacity fade in LiMn$_2$O$_4$ is proposed to be due to the Mn dissolution into the
electrolyte, essentially in the case of fluorinated salts, which generate HF [177] Mn dissolution is proposed to originate from the dis-proportionation of Mn$^{3+}$ [175] as follows.

$$2\text{Mn}^{3+} (\text{solid}) \rightarrow \text{Mn}^{2+} (\text{solution}) + \text{Mn}^{4+} (\text{solid})$$

However, this mechanism seems inconsistent with the observed fast Mn dissolution rates in the sample with Mn average-oxidation-state close to 4. The amount of Mn released in electrolytes of various compositions is analyzed quantitatively using differential pulse polarography [178,179]. It is found that Mn dissolution is strongly dependent on the oxidation of the solvent molecules and presence of acid traces, which is attributed to the oxidation of the solvent molecules or the reaction of the fluorinated salts with trace amounts of water. The first step of the acid attack is considered as extraction of Li and Mn, while the oxygen loss from the lattice occurs in the second step. Charging of LiMn$_2$O$_4$ to high voltages also results in the formation of a resistive surface layer, which increases the cell resistance and decreases the utilization capacity window [178]. Recent results show that thermally-activated dissolution of Mn occurs in the discharged state of LiMn$_2$O$_4$ [180,181]. Such a process lowers the open-circuit voltage of LiMn$_2$O$_4$ below 3V. A mechanism proposed for Mn$^{2+}$ dissolution with concomitant Mn$^{2+}$/2Li$^+$ ion-exchange at the particle surface is shown below [181].

$$\text{Li}(\text{Mn}_2)\text{O}_4 + 2x\text{Li}^+ \rightarrow \text{Li}_{1+x}(\text{Mn}_{2-x}\text{Li}_x)\text{O}_4 + x\text{Mn}^{2+}$$
This leads to an oxidized-lithiated-spinel with increased Mn average-oxidation-state giving a decreased open-circuit voltage (< 3V). Many authors have addressed this capacity fade and have attempted to mitigate Mn dissolution by surface coating of LiMn$_2$O$_4$ particles with different oxides [182-186]. Li$_{1+x}$Mn$_{2-x}$O$_{4-δ}$ spinels, which exhibit capacity, cyclability and storage properties nearly similar to LiCoO$_2$, are potential materials to replace LiCoO$_2$ in futuristic lithium-ion cells [178].

1.6.2.5 LiFePO$_4$

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 g$^{-1}$), flat voltage at 3.4V, low-cost and safety make it a promising material for lithium ion cells. Ravet et al. [188] showed the possibility of chemically removing lithium from LiFePO$_4$ leaving behind FePO$_4$, which is iso-structural with Fe$_{0.65}$Mn$_{0.35}$PO$_4$.

Electrochemical extraction of Li from LiFePO$_4$ proceeds through a bi-phasic process during which FePO$_4$ structure is 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. [188] renewed the interest in LiFePO$_4$ by improving its electrochemical behavior by a new synthetic route; these authors added sucrose to the precursors to act as a source of carbon to be formed during the thermal synthesis at 700°C. This material cycles well even at high rates.
Andersson et al. [189] investigated the electrochemical extraction and insertion of Li in thermally-synthesized, additive-free LiFePO₄ by in situ X-ray diffraction and Mössbauer spectroscopy. These authors found that 20-25% of LiFePO₄ remains unutilized depending on the particle size and surface area of the material. Effect of synthesis temperature on the electrochemical properties of LiFePO₄ is reported by Sony Research Corporation [190,191] and it is found that reduction in temperature decreases the particle size, increases the specific surface-area and enhances the electrochemical performance. Prosini et al. [192,193] synthesized LiFePO₄ in presence of high surface-area carbon that performs better even at high discharge rates. Accordingly, the rate limitation of LiFePO₄ could be due to both the poor electronic-conductivity and poor lithium-diffusion. Accordingly, the presence of carbon facilitates the high-rate performance. The effect of particle-size reduction is studied by Goodenough et al. [194] on hydrothermally synthesized LiFePO₄. Croce et al. [195] have attempted to disperse the metal particles in LiFePO₄ to improve its electronic conductivity. Nano-crystalline LiFePO₄ is reported by Prosini et al. [196], which exhibits a capacity value of 162 mAh g⁻¹ at a load current-density of 17 mA g⁻¹. Huang et al. [197] studied the effect of both addition of carbon and particle size by synthesizing LiFePO₄/C composite with active material particles at nano-scale using sol-gel method, which delivered 90% of the theoretical capacity at high rate (C/2) at ambient temperature and also showed good cycle-life. When used at 5 C rate, the material is able to deliver 70% of the theoretical capacity up to about 800 cycles. Thus, a decrease in particle size and increase in electronic conductivity will enhance the performance of the material.
Substituted Li$_{M}Fe_{1-y}$PO$_4$ (M = Mg, Zr, Ti) synthesized by sol-gel method [198] have been reported recently. Although the specific capacity did not improve much, the rate capability of the substituted samples are found to be far more superior to unsubstituted compounds.

1.6.3 5V Cathode materials

The market prognosis in hand with technological escalation paved way for advanced lithium rechargeable batteries with high energy density, power density, good reversibility, safety, environment benign and low cost. Improved performance is achieved through improved anodes, electrolytes and cathodes [199]. To gratify to the demands of larger scale batteries improvement in energy density is crucial and it can be achieved by either increasing the capacity or raising the operating voltage. With the advent of electrolytes capable of operating in 5V zone, cells with high operating voltage cathode materials have been investigated and reported.

Lithium batteries have the highest energy density of all rechargeable batteries and are favoured in applications where low weight or small volume is desire [200]. Even though Lithium batteries can theoretically hold up to 6Volts of energy (e.g., an Li/F$_2$ battery); however, no mass-produced rechargeable battery has yet been able to surpass more than 4V till mid 1990. GTK Fey et al.[201], K. Amine et al. [202], C. Sigla et al. [203], Y. Elin-Eli et al. [204] found ways to engineer a 5V battery to have consistently high
capacity for multiple cycles but the reversible lithium extraction from the cathode (versus Li/Li\(^+\) couple) were around 5V. In 1999 H. Kawai et al. [205] reported the first single cell lithium battery systems to operate over 5V. Ozhuku et al. [206] substituted transition metal ions (Ti, Cr, Fe, Co, Ni, Cu and Zn) in place of manganese ions at the 16-d sites and carried out a series of experimental and theoretical studies to determine the solid-state electrochemistry of these lithium insertion materials for advanced lithium batteries.

### 1.6.3.1 Olivine structure 5V cathode materials

The LiMPO\(_4\) series (M= Mn, Fe, Co and Ni) have olivine structure and the operating potential is found to be around 5V only for Co and Ni. It is 4.8V for LiCoPO\(_4\) and for LiNiPO\(_4\) it is probably much higher for which absolute potential is not known for lack of electrolyte stable in such conditions[207]. Owing to these properties of the four olivine type materials LiCoPO\(_4\) have attracted much attention as the next generation 5V cathode material.

The theoretical specific capacity of LiCoPO\(_4\) is of 167 Ah kg\(^{-1}\). It crystallizes in the olivine structure; usually described in terms of a hexagonal close-packing of oxygen with Li and Co ions located in half of the octahedral sites and P in one eight of the tetrahedral positions. The [Co–O6] octahedra share four corners in the \(cb\)-plane being cross-linked along the \(a\)-axis by the PO\(_4\) groups, whereas Li ions are located in rows, running along \(a\), of edge-shared LiO\(_6\) octahedra which appear in between two consecutive [CoO\(_6\)]\(_{x}\) layers
Fig. 1.3 Olivine Structure
lying on the cb-plane. The electrochemical characteristics of LiCoPO$_4$ could be greatly improved (i) using a material of small particle size and (ii) producing a carbon/LiCoPO$_4$ composite prior to the conformation of the electrode. For most type of materials mechanical grinding (MG) leads to materials in fine particle form, resulting in the modification of the electrochemical performance of electrode material for lithium batteries. To have better capacity retention with cycling, LiCoPO$_4$ was mechanically grinded with conductive carbon. The presence of carbon additives in the grinding media enables a good carbon coating that enhances the electrical conductivity of the electrode. At a $C/5$ in the cycle 20 the specific capacity of the milled material (40 Ah kg$^{-1}$) doubles that of the fresh material (20 Ah kg$^{-1}$) and the electrolyte decomposition is certainly more effective at low than at high current rates. [208]. P. Deniard et al. [209] reported LiCoPO$_4$ exhibited first cycling capacity of 110 mAh g$^{-1}$ when used in an optimized electrode with particles small enough (about 1 mm) to allow Li diffusion within the core but its cyclability has to be improved.

S. Okada et al. [210] investigated LiCoPO$_4$ and also its relative, fluoride phosphate Li$_2$CoPO$_4$F, as high voltage cathodes and metal dissolution of cathodes into electrolytes and oxygen release from cathodes in cells at elevated temperature were studied . The LiCoPO$_4$ exhibited the highest 4.8V discharge plateau without aCo$^{4+}$ anomalous valence state. The energy density was comparable to that of layered rocksalt LiCoO$_2$ (120 mAh g$^{-1}$ ×4V= 480mWhg$^{-1}$). The open circuit voltage of Li$_2$CoPO$_4$F is slightly higher than that of LiCoPO$_4$. The theoretical capacity of Li$_2$CoPO$_4$F is almost twice as large as that of
LiCoPO₄ and the both polyanionic high-voltage cathodes, LiCoPO₄ and Li₂CoPO₄F, showed better stability than the traditional oxide cathodes, LiCoO₂ and LiMn₂O₄.

Of late, K. Nagata et al. [211] reported that Li/ LiCoPO₄ showed capacity of 136 mAh g⁻¹ using phosphate solid electrolyte Li₁₃Al₀₃Ti₁₇(PO₄)₃. However the practical use of LiCoPO₄ is precluded by its the oxidation of Co²⁺ to Co³⁺ (4.8–5.1V) overlaps with the stability limit of the most used and stable liquid electrolytes for lithium batteries (LiPF6 based) [212] and in addition to that poor rate cyclability related to a electronic conductivity, which is the common limitation for olivine LiMPO₄ compounds.

### 1.6.3.2 Inverse structure 5V cathodes materials

LiMVO₄ series materials ( M= M =Cu, Ni, Co, Zn, Cd, Mg, and Be) have been the focus of research as 5V cathode material since early 1960. GTK Fey et al. [213] are the first to show that both LiNiVO₄ and LiCoVO₄ were actually inverse spinels which were considered for decades to be spinel. In an inverse spinel, such as LiNiVO₄, the cations are arranged as V_{tetra}(LiNi)_{octa}O₄. The Li and Ni atoms are believed to be distributed equally and randomly in the octahedrally coordinated interstices and the V atoms are believed to occupy the tetrahedrally coordinated interstices. The LiNiVO₄ is the first material with an inverse spinel structure to be patented as a potential cathode material for rechargeable lithium cells and also the first known Li intercalation reaction observed near 5V.
Alternating $A_4O$ and $AO_4$ units in the (001) plane of the rocksalt structure.

Fig. 1.4 Inverse spinel structure
Among the two inverse spinels, LiNiVO$_4$ and LiCoVO$_4$, the former is bestowed with a high voltage of 4.8V vs Li$^+$ and the latter is found to exhibit only 4.2V. P. Kalyani et al. [214] used soft chemistry approach to synthesize LiNiVO$_4$ and obtained Li/ LiNiVO$_4$ the first discharge cell capacity of 90 mAh g$^{-1}$ against the theoretical value of 148 mAh g$^{-1}$. A significant irreversible capacity decline was observed owing to the oxidation of and loss of structural integrity.

The electrochemical properties can be improved by new synthesis strategies and partial replacement of nickel or vanadium by suitable metal cations such as Ni, Co and Mn. The inverse spinel LiNiVO$_4$ nano-particles was prepared by combustion process using gelatine as the new fuel by A. Subramania et al. [215]. The initial capacity of LiNiVO$_4$ was 102 mA h g$^{-1}$ and retaining almost 65% of its initial capacity at the 20th cycle. With regard to LiNiVO$_4$, Co, Mg and Al as dopants for Ni and V sites were attempted by several authors. Out of these partial substitution of V by Al (10%) in the LiNiM$_x$V$_{1-x}$O$_4$ recorded a moderate initial capacity of around 120 mAh g$^{-1}$ from the first discharge, against the theoretical capacity of 148 mAh g$^{-1}$ [216]. X. Li et al. [217] showed Li-extraction from LiNiVO$_4$ had little effect on the material’s crystal structure, but introduced extra defects in the material lattice. Li-extraction from LiNiVO$_4$ led to a decreased electronic conductivity to the material, as well as significant changes in the material’s local structure properties. However, the practical capacity is rather low (about 45mAh g$^{-1}$) many works such as synthesis, cationic doping, structural changes have been done to improve the electrochemical properties of LiNiVO$_4$. Also bare and doped LiNiVO$_4$ suffers capacity retention upon prolonged cycling.
1.6.3.3 Spinel 5V cathode materials

High voltage, hence high energy density cathode material is possible with LiMn$_2$O$_4$, when manganese atoms are partially substituted by 3d- transition elements. It has been established that cathodes based on these materials show reversible redox couple around 5V (versus Li/Li$^+$). Various cations, namely, Li$^+$ [218], Mg$^{2+}$ [219], Cu$^{2+}$ [220], Ni$^{2+}$ [221,222], Zn$^{2+}$ [223], B$^{3+}$ [224], Al$^{3+}$ [224,225], Cr$^{3+}$ [226,227], Fe$^{3+}$ [228,229], Co$^{3+}$ [230-232], Ga$^{3+}$ [224], Ti$^{4+}$ [223,224], Ge$^{4+}$ [223], Sn$^{4+}$ [224] and V$^{5+}$ [233] have been studied as substitutents to Mn in LiMn$_2$O$_4$ to enhance its cyclability. Substitution with cations of oxidation states $\leq 3$ results in a decreased 4V-capacity window due to decrease in the Mn$^{3+}$ content but improves the cyclability. Hence, an optimum amount of substitution is desired to provide high capacity with good cyclability.

Improved cyclabilities are obtained for Li[Li$_x$Mn$_{2-x}$]O$_4$ spinels for compositions with $0.05 \leq x \leq 0.15$ [218]. Partial substitution of Mn with M$^{3+}$ cations (M= Cr, Fe, Co, and Ga) gives the best result. LiMn$_{2-y}$M$_y$O$_4$ (M=Cr, Co) with 0.15 $\leq y \leq 0.25$ exhibits good cyclability together with an increased diffusion rate.

Double substitutions, such as M= Co+Ga [224], Cr+Ga [224], Al+Cr [234], B+Cr [234], B+Co [234], Cr+Ni[235], Co+Ni[236], Fe+Ni[237], are also found beneficial to the cycling behavior. Partial F-substitution for O in LiMn$_2$O$_4$ results in a single phase solid solution Li$_{1+x}$Mn$_{2-x}$O$_{4-\delta}$F$_\delta$ ($0 \leq \delta \leq 0.5$) with a wide range of initially possible average oxidation-states for Mn. The electrochemical activity of these compounds is less
attractive [238]. Both cation and anion substitution are studied by Park et al. [239] to obtain \( \text{Li}_{1.02}\text{Al}_{0.025}\text{Mn}_{1.75}\text{O}_{3.97}\text{S}_{0.03} \), which delivers a stable capacity of 196 mAh g\(^{-1}\).

Heavily-substituted Mn-spinels, namely \( \text{Li}_{M_y}\text{Mn}_{2-y}\text{O}_4 \) (\( M = \text{Fe, Cr, Ni, Co, Cu} \) and their mixtures), may offer high output voltages by taking advantage of the redox couple of the substituted cation. H. Kawai et al. [240] examined substituted spinels and found some of the Co-substituted spinels, namely \( \text{Li}_2\text{Co}_{0.8}\text{Mn}_{3.2}\text{O}_8 \) and \( \text{LiCoMnO}_4 \), to be attractive. In these compounds, \( \text{Co}^{3+}/\text{Co}^{4+} \) couple creates a discharge plateau at about 5V along with the 4V plateau for the \( \text{Mn}^{3+}/\text{Mn}^{4+} \). At a load current-density of 0.5 mA cm\(^{-2}\) the capacities obtained for these materials are 135 and 105 mAh g\(^{-1}\) respectively and with a moderate capacity fade after 35 cycles.

Ohzuku et al. [206] investigated substituted spinels, such as \( \text{Li}[(\text{M}_{1/2}\text{Mn}_{2/3})\text{O}_4 \) (\( M = \text{Ni, Co, Fe, Cr, Cu} \)), and found initial capacities of 120-125 mAh g\(^{-1}\) for the Fe- and Ni substituted samples. Luo et al. [241] investigated on low temperature fluorine doping to the already formed is a viable method to achieve good cyclability and rate capability. Interestingly, Ni-substituted compound provides most of its capacity in a single 4.5V plateau. XPS results exhibit divalent nickel in the compound and its oxidation to tetravalent state results in a high voltage peak at 4.5V with high capacity [242]. Ein-Eli et al. [243] studied the spinel \( \text{LiNi}_y\text{Cu}_{0.5-y}\text{Mn}_{1.5}\text{O}_4 \) (\( 0 \leq y \leq 0.5 \)) and found that, with increasing Ni content, the capacity increases and the upper plateau potential decreases \( \text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4 \) synthesized by sol-gel route [244,245] exhibits a capacity of about 125 mAh g\(^{-1}\) up to 60 charge-discharge cycles at a load current-density of 0.5 mA cm\(^{-2}\).
Fig. 1.5 Spinel Structure
Sun et al. [246] coated the sol-gel synthesized LiNi_{0.5}Mn_{1.5}O_{4} with nano-sized ZnO, which on cycling at C/3 rate at 55 °C gave a stable capacity value of 137 mAh g\(^{-1}\). These authors propose ZnO as HF scavenger that helps stabilizing the capacity. Subsequently, Lee et al. [247] have reported a composite carbonate process for synthesizing LiNi_{0.5}Mn_{1.5}O_{4}, which shows excellent capacity retention at high temperatures without ZnO coating. LiNiVO\(_4\) and LiCo\(_y\)Ni\(_{1-y}\)VO\(_4\) are also reported in the literature, which are found to operate above 4.2V [248]. LiCr\(_{0.4}\)Ni\(_{0.2}\)Mn\(_{1.4}\)O\(_4\) delivers a capacity of 110 mAh g\(^{-1}\) when charged above 4.5V [249].

1.6.3.4 Other spinels

The spinel LiCo\(_2\)O\(_4\) reported by Choi et al. [250], is stable up to 200 °C but disproportionates above 200 °C into LiCoO\(_2\) and Co\(_3\)O\(_4\). This compound delivers a capacity of 80 mAh g\(^{-1}\) above 3V. The extraction of lithium from 8a-sites occurs around 3.9V and the insertion of additional lithium into 16c-sites occurs around 3.5V. However, LiCo\(_2\)O\(_4\) exhibits 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 results in a spinel-like cubic phase, with Ni\(^{3+}\) and Ni\(^{4+}\) ions distributed over both the 16c and 16d-sites [251]. This compound also disproportionates to LiNiO\(_2\) and NiO above 200 oC. LiTi\(_2\)O\(_4\) and LiV\(_2\)O\(_4\) crystallize in the normal spinel structure. LiTi\(_2\)O\(_4\) inserted with an additional lithium into the empty 16c octahedral sites gives lithiated spinel (Li\(_2\))\(_{16c}\) (Ti\(_2\))\(_{16d}\)O\(_4\) that exhibits a flat discharge-curve at a much lower voltage of around 1.5V [252]. Hence, it is more attractive as anode than cathode. LiV\(_2\)O\(_4\)also takes additional
lithium into 16c-sites with extractable lithium ions at 8a-tetrahedral sites. However, LiV$_2$O$_4$ suffers from migration of vanadium ions during these processes, which leads to poor capacity retention [253, 254]. LiCr$_2$O$_4$ and LiFe$_2$O$_4$ are not known.

1.7 Present study

From the review of literature on electrode materials for lithium-ion batteries, it is clear that investigations on electrode materials for rechargeable Li-ion batteries are seminal to further their performance. In view of ease of synthesis, low price, abundance and environmentally benign nature, substituted LiMn$_2$O$_4$ is considered as a prospective high voltage positive electrode material. Despite such advantages, the commercialization of LiMn$_2$O$_4$ spinel oxide has been limited by some serious defects such as capacity fading on extended cycling. The capacity fading of the material has been attributed to several factors, such as (i) dissolution of manganese into the electrolyte and decomposition of the electrolyte, (ii) cation mixing between Li and Mn ion in the spinel lattice, (iii) oxygen loss from the spinel lattice and (iv) break down of the spinel lattice.

Moreover systematic research on spinel LiMn$_2$O$_4$ reveals the insertion of lithium ion occurs at unoccupied tetrahedral and octahedral sites. The filling and emptying of these sites is the discharge/charge of a battery. Correspondingly, the Mn$^{3+}$ sites switch from cubic to tetragonal symmetry, and the lithium insertion capacity is decreased This is caused by a Jahn-Teller cooperative distortion of the Mn$^{3+}$O$_6$ octahedra.
The Jahn-Teller Theorem (1937) states “any non-linear molecular system in a degenerate electronic state will be unstable and will undergo distortion to form a system of lower symmetry and lower energy thereby removing the degeneracy”. J. Carvajal et al.[255] and V. Massarotti et al. [256 ] have found that the stoichiometric LiMn$_2$O$_4$ goes through a cubic-to-orthorhombic transition. For this reason, we need to suppress the Jahn- Teller transition to achieve a long battery life and good performances. Doping with cations substituted into the 16d-spinel site provides one effective way of suppressing the J-T distortion. D. Capsoni et al. [ 257] have reported Cr$^{3+}$ and Ni$^{2+}$ form stable, undistorted and homogeneously distributed [MnO$_6$] octahedra when substituted in the spinel lattice In an ideal case, Jahn-Teller active Mn$^{3+}$ ions should not be present to avoid the structural and chemical instabilities by partially substituting manganese with metal cations thereby enhancing the structural stability.

In order to circumvent the capacity fade, the formation of Mn$^{3+}$ due to oxygen deficiency at high temperatures, the researchers correlated the bond dissociation energies between transition metal (M) and oxygen (O) ions in the compound. The greater the M–O bond energies than that of Mn–O bond make the material structurally stability with enhanced electrochemical activity. This could be achieved by appropriate double doping with elements like chromium, iron and cobalt which have larger bonding energy than that of Mn–O bimetal doping involving Cr, Co, Ni, Fe into spinel LiMn$_2$O$_4$ is carried out in the present study. The optimization in stiochiometric amounts of the dopants is undertaken which resulted in enhanced extended cycling performance. In addition, a sol-gel synthesis technique is used to prepare novel kinds of electrode materials. Further development and
application of sol-gel synthesis techniques shall bring about new and high performance electrode materials, thereby creating a new class of lithium batteries