CHAPTER 1

INTRODUCTION
1.1 General Introduction

Energy is the fundamental component in the daily lives of human society, and it can be used in different forms in our day-to-day activities. Nowadays, energy consumption is seen as a measure of a country’s economic growth and development. Accordingly, adequate availability and reliable supply of energy is a key for economic development which in turn results in improved standards of living. In recent years, energy demand has increased due to the high energy consumption in different fields such as electricity generation, industry, transportation and household. Conventional energy sources based on fossil fuels (oil, coal, and natural gas) have served and fulfilled almost all human needs for long era. However, the present energy economy based on fossil fuels is at a serious risk due to the continuous increase in the demand for oil, the political instability of oil producing countries, continuous increase in air pollution that threatens human health, and global warming associated with carbon dioxide (CO$_2$), sulphur dioxide (SO$_2$) and nitrogen oxides (NO$_x$) emission [1,2]. Further, the prices of these energy sources increased in the recent past and it is expected to rise further in the coming years [3,4]. Moreover, the fossil fuel resources are limited in amount, and it is widely accepted that most easily extracted reserves will be exhausted after some years [5]. All these challenges have become major political issues and subjects of international debate and regulation. Towards this end, several progresses have been made in the previous years to overcome the problems. For instance, renewable energy sources, such as solar energy, wind energy, bio energy, geothermal energy, tidal energy, and hydropower have been developed, and most countries are increasingly trying to replace fossil fuel energy sources with renewable energy sources [6]. However, almost all the renewable energy
resources are hampered by their high cost [3], as a result the technology has not reached widespread use up until now. Moreover, solar energy, wind energy and tidal energy are characterized by their intermittent nature, as they are not available all the time. These challenges have led to increased efforts in finding suitable and environmentally friendly alternative energy sources. From this perspective, the interest in energy storage technology and conversion systems which include batteries, super capacitors, and fuel cells, is on the rise as a means of alternative energy sources [7].

In this context, Li-ion battery technology currently plays an important role in producing alternative energy storage devices, because of its inherent outstanding characteristics. The technology offers the greatest development potential for automobile industries particularly for electric vehicles (EV) and hybrid electric vehicles (HEV), which substitute electricity for a portion of the petroleum used to power the vehicles [8,9]. Further, it is attractive for its potential to reduce greenhouse gases emission and also dependence on oil [10]. Analysis showed that HEV reduce greenhouse emissions by 32 % compared to conventional gasoline vehicles [11], but they still emit global-warming pollutants. However, pure electric vehicles are considered to produce almost zero carbon emissions during the use phase [12].

Now a days, Li-ion batteries have become part of the most successful technology to assist in the development of portable consumer electronic devices around the world. The outstanding growth is noticed in portable electronic devices such as, digital camera, video camera (camcorder), laptop, personal digital assistant (PDA), and cellular phone which are widely used as information disseminating devices for today’s information rich and mobile society [9,13-16]. As a matter of fact, there is an increasing demand for
development of Li-ion batteries with high performance characteristics, such as high energy density, long cycle life, high cell voltage, environmental friendly and extremely safe. The performance of this type of battery is mainly dependent on the physicochemical and the electrochemical properties of electrode materials used inside them.

1.2 Theoretical Background

In the following sections, the theoretical backgrounds of different materials are reviewed in order to understand the results presented in the subsequent chapters. After explaining the concept of battery, major properties of non-rechargeable and rechargeable types of batteries are discussed. General introduction to Li-ion batteries and their major components are also described. Finally, there is a brief review on common intercalation positive cathode materials.

1.2.1 Batteries

Batteries, which consist of one or more cells connected in series or parallel or both to achieve the desired capacity and voltage, are one of the energy storage devices that store chemical energy in their active materials and convert it into electrical energy by means of an electrochemical reaction taking place at the electrodes [17,18]. The reaction taking place in batteries is an oxidation-reduction (redox) reaction. One part of the electrodes (the anode) in a battery (cell) oxidizes thereby giving up the electron which is used to reduce the other part (the cathode) in the cell. When the two electrodes are connected through an external circuit, the reaction proceeds spontaneously and the electrons flowing in the external circuit provide a current that can be used to power a
resistive load. Simultaneously, the electrolyte also participates in the reaction by shuttling ions between active materials.

Batteries play an important role in everyday human life as they supply energy to many kinds of portable electric and electronic devices such as digital cameras, telephones, radios, video cameras, computers, cordless tools, military devices, implantable medical devices, flashlights, and even electric and hybrid cars [18,19]. Depending on the reversibility of the electrochemical processes involved, batteries are commonly categorized into primary and secondary batteries (non-rechargeable and rechargeable types, respectively) [18].

1.2.1.1 Primary Batteries

Primary batteries are any kind of combination of cells in which the electrochemical reaction is generally not reversible. The chemical energy cannot be restored once it has been converted to electrical energy [18,20]. Due to the non-reversibility of the chemical reactions inside the cell, primary batteries are generally used once and then replaced with new ones. In general, these types of batteries have fixed amount of energy stored in them during manufacture, and once that energy has been used up the batteries are simply thrown away and replaced. However, these types of batteries such as Leclanché Cells, Alkaline Cells, Mercury Oxide Cells, Lithium Cells, Zinc-Silver Oxide cells have advantages in respect of acceptable cost, long service life, flexibility, reasonable energy and ease for use.

A primary battery cell consists of three main parts: cathode (positive electrode), anode (negative electrode) and an electrolyte. When the two electrodes are connected to
an external load, electrons flow from the negative electrode through the external load to the positive electrode. In this process, the active material in anode gets oxidized and releases electrons to the external circuit whereas the active material in the cathode gets reduced by accepting the electrons to keep the charge balance during electrochemical reaction. The electric circuit is completed in the cells by the flow of ions between cathode and anode electrodes. The electrolyte, which is the ionic conductor and electronic insulator, provides the medium for the ions traveling between the anode and cathode inside the battery.

1.2.1.2 Rechargeable Batteries

Rechargeable batteries, also referred to as secondary batteries, are electrochemical devices that can be charged or discharged again for many times over a long period [18,21]. The reactions which take place in rechargeable batteries are not the same, and they are dependent on charge or discharge process. In the rechargeable batteries, the electrochemical reaction can be reversed by passing current through them in the direction opposite that of discharge. This gives the new life or an extended life of the batteries. To recharge this type of batteries, an external electrical power source is required with a constant voltage higher than that of the batteries to compensate the self-discharge. During charging process, the cathode material is oxidized and the electrons flow to the anode through the external circuit. The anode gets reduced by accepting the electrons. The electric circuit is completed in the battery by the flow of ions between cathode and anode electrodes [18]. During discharging, the process is reversed, and oxidation and reduction reactions take place on anode and cathode, respectively.
Rechargeable batteries are more environmentally friendly than primary batteries, because they can be charged and discharged numerous times before losing their standard performance abilities [7,10]. This reduces the amount of battery waste ending up in landfills. Rechargeable batteries have very wide applications which include home appliances, cordless tools (such as drills and screwdrivers), portable telecommunication devices, and portable computers [18,21]. They also have industrial applications including emergency lighting, military and space applications (such as missiles, launchers, and satellites), and aeronautics applications including on-board safety as well as turbine and jet starting. Other transportation applications of rechargeable batteries include railway uses (such as diesel engine starting, lighting and signaling systems), electric and hybrid vehicles [18,21]. Further, they are also used in power systems such as reserve power supply for industrial processes, refineries, thermal and nuclear power stations.

There are different kinds of commercialized rechargeable batteries. The most common ones are: Lead-Acid (Pb-acid), Nickel Cadmium (Ni-Cd), Nickel-Metal Hydride (Ni-MH), and Lithium ion (Li-ion) batteries.

**Lead-acid battery** is first invented 154 years ago by French physicist Gaston Planté in 1859, and it is well known and common one among the available rechargeable batteries [22,23]. Pb-acid battery contains lead (Pb) and lead dioxide (PbO₂) as negative and positive electrodes respectively [24], and a solution of sulfuric acid (H₂SO₄) in distilled water as an electrolyte. The electrolyte not only serves as an ionic conductor, but also serves as an active-material. Accordingly, the electrolyte is consumed and produced during discharge and charge reactions respectively [17, 24].
When Pb-acid battery is discharged, the electrons flow from the negative electrode through the external load to the positive electrode. Hence, Pb is oxidized and becomes Pb\(^{2+}\), and PbO\(_2\) reduced and turn out to be Pb\(^{2+}\). Also, lead sulphate (PbSO\(_4\)) is produced at both electrodes [21,25], accordingly the electrolyte loses sulfuric acid and increases its water content. On the other hand, during charging process, electrical energy is converted to chemical energy and oxidation takes place at the positive electrode and reduction at the negative electrode. For this process, PbSO\(_4\) is converted to Pb on the battery’s negative plate and PbO\(_2\) on the positive plate, thereby the sulfate present in the electrodes return to the electrolyte, which recovers its sulfuric acid nature. The active materials and chemical reaction taking place in Pb-acid batteries are shown in Table 1.1.

Pb-acid battery has some advantages such as relatively inexpensive (due to low cost manufacturing processes, and availability of the raw materials lead and sulfur), and the battery components are easily recycled [18,26]. It is also widely used in the automobile field (as starter battery, ignition, and lighting cars, trucks, and buses) and in electrical backup power [18,23,24]. Even though Pb-acid battery has very low energy-to-weight ratio and a low energy-to-volume ratio, it is still widely used in different types and diversity of applications compared to other available rechargeable batteries [17,18, 27].

**Nickel-Cadmium battery** with potassium hydroxide electrolyte was first invented by a Swedish scientist Waldemar Jungner in 1899 (40 years after lead-acid batteries). The electrode materials in this type of battery are metallic Cd as negative electrode and nickel oxyhydroxide (NiOOH) as positive electrode [22,28]. The electrodes are submerged in alkaline electrolyte, i.e., an aqueous solution of potassium hydroxide (KOH) containing small quantities of lithium hydroxide (LiOH), or sodium hydroxide
(NaOH) to improve the cycle life and high operation temperature. The electrolyte provides the means of charge carrier, and doesn’t involve in the discharge reaction as the acid does in the Pb-acid battery [22]. When Ni-Cd battery is discharged, Cd is oxidized by combining with two OH ions to form cadmium hydroxide Cd(OH)$_2$ and releasing two electrons. At the anode, NiOOH takes up an electron to form nickel hydroxide (Ni(OH)$_2$) and to release OH ions [22,28,29]. During charging, the reverse electrochemical reaction happens until cell potential rises to a level where hydrogen is evolved at the negative plate and oxygen at the positive plate which results in water loss. List of active materials and the electrochemical reactions of Ni-Cd battery are shown in Table 1.1.

Ni-Cd battery offers longer service life than Pb-acid battery, which means that it can be charged/discharged more times before battery cell failure occurs [30]. Moreover, Ni-Cd batteries store a much greater amount of energy in a smaller area than Pb-acid battery (Figur 1.3). However, Ni-Cd battery is expensive, and it is environmentally less friendly, health risks associated with Cd, and suffers from a "memory effect" if they are not fully charged/discharged over several cycles [17,28-32]. The symptom of “memory effect” is that the battery remembers the point in its charge cycle where recharging began and during subsequent use suffers a sudden drop in voltage (V) at that point, as if the battery had been fully discharged [29,32]. Ni-Cd battery is also used in different applications, such as electronic devices (cellular phones, cordless phones, notebook computers), emergency lighting, remote controls & security systems, vacuum cleaners, power tools, electric bicycles, memory back-up, aircraft engines starting, heavy-duty industrial applications (materials-handling trucks, mining vehicles, railway signaling, emergency or standby power, and diesel engine starting), etc. However, the importance
of the Ni-Cd battery has been reduced by the development of the new battery technologies, like Ni-MH, Li-ion, Li-polymer, which all have superior storage capacities and an increasing number of applications [18, 23,31].

**Nickel metal-hydride battery** has been developed as possible replacement for Ni-Cd battery in the fields of consumer and transportation applications, and it joined the commercial market in the early 1990s. The chemistry of Ni-MH battery is very similar to that of Ni-Cd battery [27]. The electrode materials in Ni-MH battery are NiOOH as positive electrode, which is the same composition as the positive electrode in a Ni-Cd battery, and hydrogen storing metal alloys as negative electrode [17,22,27,29]. Like Pb-acid and Ni-Cd batteries, Ni-MH battery operates on the principle that electrochemical reactions at each of the electrode are reversible. This enables energy to be stored during charging and released during discharging. Further, the reaction that occurs at the positive electrode of Ni-MH battery is the same as that for Ni-Cd batteries. In Ni-MH battery, hydrogen bond in a water molecule is the energy carrier between the electrodes. The chemical energy is stored in the oxygen-hydrogen bond in Ni-MH electrode. During discharge, the negative electrode (the metal alloy) releases hydrogen into the electrolyte to form water, and is inserted into NiOOH electrode in the form of hydrogen ion with associated reduction of the nickel ions from a trivalent to divalent state to form Ni(OH)$_2$. Consequently, NiOOH is reduced to Ni(OH)$_2$, releasing the stored chemical energy as electrical energy [18,19,22]. During charging, electric energy provided from the external power source break the oxygen-hydrogen bond in the Ni(OH)$_2$, and with the help of an OH ion from the electrolyte, NiOOH and water molecule are formed. In this process, the lower energy Ni(OH)$_2$ is converted to the
higher energy NiOOH, as a result, the electrical energy provided from an external power source is stored in the form of chemical energy in the battery [18]. Similarly, water molecules are split into an $\text{OH}^-$ ion and hydrogen on the metal hydride electrode, which is intercalated into the metal lattice to form the metal hydride. The electrolyte in Ni-MH cell is an aqueous solution of KOH which has a very high conductivity. The solution does not enter into the Ni-MH cell as the acid in the Pb-acid battery (Table 1.1). It is found that the electrolyte concentration remains almost constant over the charge/discharge cycle. The active materials and chemical reaction taking place in Ni-MH battery are shown in Table 1.1.

Ni-MH battery is the most widely used rechargeable battery until the introduction of Li-ion battery. However, it is still used in application for consumer electronics, portable devices, power tools and transportation (i.e., for electric and hybrid vehicles) [29]. The advantages of Ni-MH battery over Ni-Cd battery include, higher specific energy, higher practical energy density, more environmental friendly, longer cycle life, rapid charge capacity, significantly lower manufacturing cost, and reliable without memory effects [18,27,29,31,33]. Moreover, it stores greater amount of energy in a smaller area or it has higher energy density per volume and per weight than Ni-Cd battery (Figure 1.3). However, Ni-MH battery does not perform well at high temperatures, is less tolerant of overcharge, and has high self-discharge rate [17,27].

**Li-ion battery**, the most popular type of rechargeable battery, was first successfully commercialized by Sony in 1991 by adopting LiCoO$_2$ as the cathode material and carbon as the anode material [34,35]. It transports Li-ions between anode and cathode with the simultaneous oxidation or reduction of the host electrodes respectively. This type of
battery has the highest energy density than Pb-acid, Ni-Cd and Ni-MH batteries for the same size and weight (Figure 1.3) [16,36]. This will be discussed in detail in the next sections.
**Table 1.1** Characteristics of Rechargeable Batteries [17-19,18, 21-25,28,29].

<table>
<thead>
<tr>
<th>Battery Name</th>
<th>Cathode</th>
<th>Anode</th>
<th>Electrolyte</th>
<th>Discharge Cell Reaction</th>
<th>Over All Discharge / Charge Cell Reaction</th>
<th>Normal Voltage (V)</th>
<th>Specific Energy (Wh/kg)</th>
<th>Energy Density (Wh/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Lead-acid</strong></td>
<td>PbO₂</td>
<td>Pb</td>
<td>H₂SO₄ (aq)</td>
<td>Pb(s) + SO₄²⁻ (aq) → PbSO₄(s) + 2e⁻</td>
<td>Pb(s) + PbO₂(s) + 2H₂SO₄(aq) → 2PbSO₄(s) + 2H₂O(l)</td>
<td>2.0</td>
<td>35</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>NiOOH(s) + H₂O(l) + e⁻ → Ni(OH)₂(s) + OH⁻ (aq)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>NiOOH(s) + H₂O(l) + e⁻ → Ni(OH)₂(s) + OH⁻ (aq)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Cd(s) + 2OH⁻ (aq) → Cd(OH)₂(s) + 2e⁻</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nickel-cadmium</td>
<td>NiOOH</td>
<td>Cd</td>
<td>KOH (aq)</td>
<td>NiOOH(s) + H₂O(l) + e⁻ → Ni(OH)₂(s) + OH⁻ (aq)</td>
<td>Cd(s) + 2NiOOH(s) + 2H₂O(l) → Cd(OH)₂(s) + 2Ni(OH)₂(s)</td>
<td>1.2</td>
<td>35</td>
<td>100</td>
</tr>
<tr>
<td>Nickel-metal hydride</td>
<td>NiOOH</td>
<td>Metal hydride</td>
<td>KOH (aq)</td>
<td>MH(s) + OH⁻ (aq) → M(s) + H₂O(l) + e⁻</td>
<td>NiOOH(s) + H₂O(l) + e⁻ → Ni(OH)₂(s) + OH⁻ (aq)</td>
<td>NiOOH(s) + MH(s) → Ni(OH)₂(s) + M(s)</td>
<td>1.2</td>
<td>75</td>
</tr>
<tr>
<td>Li-ion battery</td>
<td>LiCoO₂</td>
<td>LiₓC₆</td>
<td>Lithium salts dissolved in organic solvent</td>
<td>LiₓC₆ → 6C + xLi⁺ + xe⁻</td>
<td>LiₓC₆ + Li₁₋ₓCoO₂ + xLi⁺ + xe⁻ → LiCoO₂</td>
<td>LiₓC₆ + Li₁₋ₓCoO₂ → LiCoO₂ + 6C</td>
<td>3.6</td>
<td>150</td>
</tr>
</tbody>
</table>
1.2.2 Lithium-ion Batteries

1.2.2.1 Introduction to Lithium-ion Batteries

The development of Li-ion batteries was motivated by the fundamental properties of lithium element. Lithium is the most electronegative or a highly reducing element (-3.04 V vs. the standard hydrogen electrode) as well as the lightest (specific density = 0.53 g/cm³ at 20 °C) electrochemically active metal with very high electrical conductivity [18,37]. This means that lithium metal can store more energy or provide the largest energy content. Lithium metal is also a highly reactive element, which means that a lot of energy can be stored in its atomic bonds (Table 1.2). All these properties make lithium metal to be used as an electrode material. In the view point of reversibility, it is believed that the lithium secondary battery with lithium metal anode is capable of very long cycle life and supplies a fairly stable operating voltage and capacity. However, practical cyclability of the battery is limited due to lithium dendrites growing during repeated charge/discharge cycling, which causes short circuit and short cycle life (Figure 1.1) [37,38]. The problem related to the lithium metal as anode leads to the development of new technology Li-ion batteries. This technology solved the problem due to lithium dendrites growth, because Li-ion batteries contains no lithium in a metallic state, instead use Li-ions that shuttle back and forth between the electrodes of the battery during charge/discharge processes [38,39].

Portable electronic devices have been widely used as information disseminating devices for today’s information rich and mobile society. From customers around the world, a need exists for electronic devices to be smaller, lighter, cheaper, and which can
be used with confidence. As a matter of fact, the weight and compactness of these high technology devices are tightly related to the battery performances. In response to these, Sony Corporation successfully manufactured the first Li-ion battery in 1991 by adopting LiCoO$_2$ as the cathode material and carbon as the anode material [38]. Today, the Li-ion battery is the fastest growing and the most promising battery because of its high working voltage, high energy density and good cyclability. Extensive researches still continue to achieve much improved performance of Li-ion battery. So, there is much hope for improvement of Li-ion battery technology for the next generation.

The basic functional components in Li-ion battery are electrodes, electrolyte, separator, and current collectors. The electrode (anode and cathode) materials are intercalation materials. They are also ionic and electronic conductors. An electrolyte composed of an organic solvent and dissolved lithium salt provides the medium for Li-ion transport between the electrodes. Separator prevents the two electrodes from contacting each other. Both electrolyte and separator also provide the separation of ionic transport and electronic transport so that electricity can be utilized by the outer circuit.
The current collectors are electrically conducting materials. Their role is to provide mechanical support for active materials, and to provide a point of mechanical connection to transfer current to the external circuit. Now a days, Li-ion battery cell uses carbon based materials as anodes and lithium transition metal oxide as the cathodes [16,18].

**Figure 1.1** Schematic representation and operating principles of Li batteries:

a) Rechargeable Li-metal battery, b) Rechargeable Li-ion battery [37].

The word intercalation refers to a guest material entering and leaving a host structure by a diffusion reaction without causing a major disturbance of the host material. In Li-ion battery, Li-ions are the guest ions and the host materials are the electrodes. Li-ions intercalation into the host leads to a change in the electronic properties of the transition metal oxide and its anion framework. This is the case, for example, in graphite anode and conventional cathode materials: layered compounds LiMO$_2$ (M = Co, Ni, Mn), spinel compound LiMn$_2$O$_4$, olivine compounds LiMPO$_4$ (M = Fe, Mn, Ni, Co), and their derivative compounds [40]. Also, intercalation materials have open one, two, or three dimensional channels through which guest ions are removed and inserted into compounds. For instance, LiMPO$_4$ (M = Fe, Mn, Ni, Co) materials possess one-
dimensional channel, and LiMO₂ (M = Co, Ni, Mn) and LiMn₂O₄ possess two and three
dimensional cross linked channels, respectively [40].

Li-ion batteries, with high energy density and long cycle life, have been
successfully used in various applications (such as portable electronic devices, renewable
energy storage devices, backup power source, power tools, remote control toys, etc.).
They are also attractive for high power applications for instance electric vehicles, hybrid
electric vehicles, air crafts, space crafts and satellites [9,13,37,41].

1.2.2.2 Working Principles of Lithium-ion Batteries

Inside Li-ion batteries, the Li-ions move through the electrolyte whereas the
equivalent numbers of electrons generated from the reaction go through the external
circuit to do work. Moreover, the electrode materials of Li-ion batteries allow for the
flow of both Li-ions and electrons, which means that they are both ionic and electronic
conductors [34]. Cathode material also has a capability to accept Li-ions and store them
until recharging the battery. Storing Li-ions in such type of battery provides a convenient
way of storing electricity and then making it to do work in an external circuit connected
to the battery.

Charging and discharging processes in Li-ion batteries are carried out by oxidation-
reduction reactions that occur at each of these two electrodes. During charging, Li-ions
are deintercalated from the cathode host, then move through the non-aqueous electrolyte,
and intercalate into the anode host and remain there [42]. The battery stores chemical
energy during this process. Whereas in the discharge process, the anode is
electrochemically oxidized, which results in the release of deintercalation of Li-ions into
electrolyte and again intercalated into the cathode as indicated in the Figure 1.2 [42]. The driving force for this process is the difference in the electro-chemical potential experienced by the Li-ion in the anode and the cathode materials. In both charge and discharge processes, equivalent number of electrons moves through the external circuit to compensate for the Li-ions flowing through electrolyte or to complete the electrochemical reaction. The movement of Li-ions through the electrolyte and electrons around the external circuit are interconnected processes and if any one of them stops and the other one also stops. In this mode of operation, Li-ion batteries are also referred to as rocking-chair batteries to describe the two way movement of Li-ions between the anode and cathode during the charge/discharge processes [43,44].

To charge a Li-ion battery, external applied voltage higher than the terminal voltage of a battery needs to be applied with the same polarity as the polarity of the battery. Li-ions in the cathode are now repelled by the positive charges supplied by the external applied voltage, so they tend to diffuse out of the cathode into the electrolyte, then the separator membrane and back into the anode material. At the same time the charger (an external voltage source) is supplying electrons to the anode, replacing the electrons lost from the anode to cathode while the battery was being utilized.

For Li-ion batteries fabricated from cathode material LiCoO$_2$ and anode material graphite, the occurring chemical processes are described below [18,21,22,38].

**Cathode reaction:** the Li-ions are extracted from LiCoO$_2$ by electrochemical oxidation during charging and are inserted into LiCoO$_2$ by electrochemical reduction during discharging, as indicated in Eq. 1.1.
Anode reaction: the graphite is reduced by electrochemical intercalation with Li-ions during charge and is electrochemically oxidized by Li-ions deintercalation during discharging. The process is shown in Eq. (1.2) below.

The above two equations indicate that LiCoO$_2$ cathode material and the graphite anode materials can be cycled upto $x = 0.5$ and $x = 1$, respectively.

Overall reaction: the overall reaction of the system is described in Eq. (1.3).
1.2.2.3 Advantages of Lithium-ion Batteries

In battery technology, the most basic factors for comparing the performance and success of any type of battery system are:

1. Energy (high energy content with respect to weight and volume),
2. Economics (low manufacturing costs, low maintenance during use and long service life),
3. Environment (free of toxic materials, safe, low energy consumption during manufacture and use, long service life, high reliability and easy to recycle).

Li-ion batteries exhibit the following advantages over other types of rechargeable batteries [18,22,38,43-46]:

Figure 1.2 Schematic description of the electrochemical process of a Li-ion cell [45].
1. Much lighter as compared to other types of rechargeable batteries of the same weight,
2. High energy density. As shown in the Figure 1.3, Li-ion batteries provide much higher volumetric as well as gravimetric energy densities,
3. High power density,
4. High operating voltage,
5. Fast charge rate,
6. High efficiency,
7. Long cycle-life,
8. Not suffering from memory effects,
9. Operates over a wide temperature range with little loss in performance,
10. Far good structural and chemical stability,
11. Long shelf life (low self-discharge rate),
12. Environmental friendly, and
13. Safe in use.

These outstanding characteristics brought Li-ion batteries their success in large applications. These beneficial properties have also established Li-ion batteries as leading candidate for the next generation.
As mentioned earlier in section 1.1.1, lithium-ion battery consists of one or more cells connected in series or parallel or both to achieve the desired capacity and voltage. Each electrochemical cell in Li-ion battery contains four fundamental parts, namely anode, cathode, electrolyte and separator. The basic components are discussed in detail in the next sections.

1.2.3.1 Cathode Materials

Common cathode materials are typically lithium transition metals oxides (TMO) which undergo oxidation to higher valances when lithium ions are removed. They are usually produced in the lithiated form and act as an initial source of Li-ions when coupled with anode materials. Along with this property, other electrochemical reactions such as
the formation of a surface layer/membrane on cathode material occur, which is called cathode-electrolyte interface (CEI) [48]. This layer is formed mainly in the first cycle of electrochemical reaction [48], and the CEI layer is thin, porous, and stable to provide a barrier between the electrolyte and electrode while allowing the passage of Li-ions. Moreover, the layer is basically a part of traditional Li-ion batteries and acts as a safety feature by maintaining a protective barrier between the cathode and the electrolyte.

In TMO cathode materials, the strong electronegativity of oxygen guarantees a highly ionic character of the materials which in turn is associated with a high potential. TMO cathode materials are basically classified into three categories: layered oxides such as LiCoO₂, LiNiO₂, and LiMnO₂, olivine structures such as LiFePO₄, and spinel structures such as LiMn₂O₄ [16,21]. These materials are characterized as strongly oxidizing in nature and as such reversibility intercalate Li-ions above 3 V versus Li⁺/Li can be obtained. Their details are found in section 1.1.4.1.

Cathode electrode is one of the key components in any type of batteries. More importantly, it affects the energy capacity, voltage, cycle life, safety and other basic physicochemical and electrochemical properties. Thus, the characteristics of the materials used as the active cathodes are one of the decisive factors to affect the performance of a Li-ion battery. The basic requirements for a material to be used as cathode in Li-ion battery are as follows [18,49]:

1. Structurally stable for repeated charging/discharging processes (long cycle life),
2. Capable of accommodating large quantities of Li-ions per formula unit (high capacity),
3. High gravimetric energy density (the amount of energy contained by the Li-ion batteries per weight),
4. High volumetric energy density (the amount of energy contained by the Li-ion batteries per volume),
5. Sustain high rates of Li intercalation/deintercalation (high charge/discharge rates),
6. High oxidation potential,
7. Stable in contact with the electrolytes,
8. Adequate electronic and ionic conductivity,
9. Low cost,
10. Non-toxic (environmentally friendly),
11. Easily prepared, and

However, all the existing cathode materials cannot meet all the above requirements at one time. Thus, research and development of new types of cathode materials with better electrochemical characteristics has been a hot topic in Li-ion battery research field.

1.2.3.2 Anode Materials

Anode (or negative electrode) materials are part of the main components in Li-ion batteries. Different types of materials such as metallic lithium, carbonaceous materials, and lithium metal alloys (example, LiAl, Li9Al4, Li4.2Si, Li17Sn4, Li22Si5, Li17Ge4) [50,51] have been proposed as anode for rechargeable Li-ion batteries. As discussed in section 1.1.3.1, the use of lithium metal as anode in Li-ion batteries has proved risky [21].

Carbon is the most widespread element in nature. There are also different kinds of carbon materials which are used for the anode electrode in battery technology. These
materials can be generally classified into three structural classes: graphitic, graphitizable (soft) and non-graphitizable (hard) carbons [52]. Considering its cost, stability, cycling performance, low Li-ion insertion potential and availability, graphite is extensively used as the anode material for commercial rechargeable Li-ion batteries production for many years [39,44]. For Li-ion battery containing graphite as anode, a maximum of one Li-ion per six carbons (Li:C = 1:6) can be inserted into each hexagon to form LiC₆, yielding a maximum theoretical capacity of 372 mAhg⁻¹ [18]. However, the graphite carbon cannot meet the capacity requirement of batteries due to its lower theoretical capacity of 372 mAhg⁻¹ corresponding to LiC₆. In recent years, lithium alloy materials have been studied extensively as alternative anode materials for application of Li-ion battery technology. They provide higher specific capacity or volumetric and gravimetric energy densities than graphite. For instance, Li₄.₄Si, Li₂.₂₅Al and Li₄.₄Sn provide theoretical specific capacities of 4212, 2235 and 992 mAhg⁻¹, respectively [53,54]. However, this type of anode materials suffer severely from huge volume variation during Li-ions insertion/extraction cycle, which leads to cracking and pulverization of the electrode and results in very rapid decline in capacity. Therefore, although greatly appealing in terms of storage capacity, lithium alloy electrodes are difficult to use in practice. In fact, even if improvement has been obtained by controlling the morphology and the metallurgical structure of the alloys, the cycling behavior is still unsatisfactory.

Like the formation of surface layer on cathode materials, a solid electrolyte interface (SEI) is also formed on the surface of carbon electrode. The SEI layer is formed mainly in the first cycle of electrochemical reaction, and it enhances battery life by preventing carbon exfoliation and direct reaction with the electrolyte, which mean that
it protects the decomposition of the electrolyte on the anode surface [55]. This process plays a fundamental role in assuring long life and cyclability [56]. It is generally accepted that the SEI layer is basically a part of traditional Li-ion batteries and acts as a safety feature by maintaining a protective barrier between the graphite electrode and the electrolyte. This layer is also conductive for Li-ions but electronically insulating.

As discussed previously, various carbonaceous and non-carbonaceous compounds are presently under study for application of anode materials. However, their performances are still to be fully ascertained, so that graphite is likely to be popular choice for the next few years [18,21].

Like cathode materials, anode materials should have also the following basic conditions [57-60]:

1. Structurally stable for repeated charging/discharging processes,
2. High capacity,
3. High gravimetric and energy densities,
4. Low potential,
5. Stable in contact with the electrolytes,
6. Adequate electronic and ionic conductivity,
7. Inexpensive,
8. Non-toxic (environmentally friendly), and
1.2.3.3 Electrolytes

Electrolytes are chemical compounds which can be dissociated into free ions. They are also ionic conductors in the form of a liquid solution or a solid. The main task of the electrolytes in Li-ion batteries is to continuously carry Li-ions between anode and cathode during charge/discharge processes. Electrolytes with high ionic conductivity over a wide temperature range, very poor electronic conductivity (high internal resistance), low melting point, high boiling point, high chemical stability, wide electrochemical voltage window (0 to 5 V) and good safety [18], are suitable for well performing Li-ion batteries. Moreover, the electrolytes have to be compatible with positive and negative electrodes, current collectors, and separator. There are different types of electrolytes which can be used in Li-ion batteries: liquid, polymer, gel polymer, and ceramic electrolytes [18]. Liquid electrolytes are solutions of a lithium salt such as, lithium hexafluorophosphate (LiPF₆), lithium perchlorate (LiClO₄), lithium hexafluoroarsenate (LiAsF₆), lithium tetrafluoroborate (LiBF₄), etc., in organic solvents, typically carbonates [18,61,62]. There are different types of organic solvents, but the most common solvents used in Li-ion batteries are ethylene carbonate (EC), dimethyl carbonate (DMC) and diethyl carbonate (DEC) [63]. The reason for using organic solvents is to decrease the electrolyte’s viscosity and increase solubility of lithium salts, to provide easier movement for Li-ions. Since Li-ion batteries are designed to operate between -20 °C and 60 °C, solvents with low melting point, high boiling point and low vapour pressure are highly required.

The choice of the proper electrolyte is an important task in the Li-ion battery technology. Among all the liquid electrolyte materials, LiPF₆ solutions in EC and DMC
(LiPF$_6$/EC + DMC) exhibit high ionic conductivity, good electrochemical stability (extending to 5.1 V vs. Li/Li$^+$), and excellent cyclic performance at room temperature [63-65]. For these reasons, LiPF$_6$ based liquid solutions are still the electrolytes of choice for most commercial Li-ion batteries [65]. However, if LiPF$_6$ is mixed with water or exposed to moisture, it will decompose to form hydrofluoric acid (HF), which can directly affect the capacity of battery [63-65]. So, electric cell assembly is conducted in dry environment to avoid the HF formation. The most recent development in the Li-ion battery technology is directed to the replacement of the liquid electrolyte with a polymer electrolyte which is a liquid and solvent free material. A polymer electrolyte is referred to as a solvent free material in which an ionically conducting phase is caused by dissolving salts in a high molecular weight polymer [27]. The potential advantages of polymer electrolytes include improving safety properties resulting from their low volatility and high viscosity, lighter weight, and design flexibility (no rigid cell-can is required) [27,28]. However, these types of electrolytes have lower conductivity and cannot deliver high power at room temperature, particularly in lower temperature region [37]. In the case of gel-type polymer electrolyte materials, an ionically conducting phase is formed by introducing small polar molecules into polymer electrolytes [27]. A possible advantage of these types of electrolytes is that the liquid phase is absorbed within the polymer, and thus resulting in less leakage from a battery. Gel-type polymer electrolytes entered in the market, known as polymer electrolytes or Li-polymer. Ceramic electrolytes are referred to as inorganic solid-state ionic conducting materials. They are more suitable for high temperature or other aggressive environments [18].
1.2.3.4 Separators

Separators are other important components of Li-ion batteries, and their key role is to keep the two electrodes apart to prevent electrical short circuits and at the same time allow rapid transport of Li-ions through the permeated electrolyte in the microporous, but insulates electronic flow [27,66]. The separators themselves do not participate in any electrochemical reactions, however, their properties affect the energy density, power density, cycle life and safety of the Li-ion batteries. Therefore, selection of an appropriate separator is critical to the battery performance. The separators are required to be chemically and electrochemically stable towards the electrolyte and electrode materials. They are also required to be mechanically strong to withstand the high tension during the battery assembly operation, wetted quickly by the electrolyte, offered almost no resistance to ionic transport in electrolytes and provide large resistance to electronic conductivity for isolation of electrodes [27,66]. They must also have appropriate melting point for safety concern, and sufficient porosity for free ion flow [18, 27,66].

For battery safety, the separator should be able to shut the battery down when accidentally overheating occurs, so that thermal runaway can be avoided [27,67]. Once shutdown occurs, ionic transport between the electrodes is effectively stopped and current ceases to flow. However, due to thermal inertia, there is a possibility that the temperature can continue to rise even after shutdown. Under such conditions the separator would melt and short the electrodes, leading to violent reactions and heat generation. This phenomenon is called “meltdown” or “breakdown” of the separator. Therefore, in order to ensure safety of the cell, the difference between the shutdown and meltdown temperatures should be as large as possible [67]. The shutdown function can be obtained
through a multilayer design of the separator, in which at least one layer melts to close the pores below the thermal runaway temperature and the other layer provides mechanical strength to prevent physical contact of the electrodes. Once the separator melts, the cell is destroyed.

According to their structure, composition and related properties, separators for battery can be divided into three major types: microporous polymer membranes, non-woven fabric mats, and inorganic composite membranes [68]. These three types of separators are, respectively, featured by the thinness, high porosity and excellent thermal stability. Among them, the microporous separator, which is fabricated from polyethylene and polypropylene, as well as various combinations of the two, have been widely used in commercially available liquid electrolyte Li-ion batteries due to their good mechanical strength, electrolyte permeability, safety and cost [18,27,67].

1.2.3.5 Safety Devices

Li-ion battery packs contain Li-ion cells connected in parallel and/or series, battery monitoring system and protection circuitry sealed in a plastic container. The battery packs have the potential to be dangerous if they are not carefully designed or if they are abused. Improper use may cause in product damage, electrolyte leaks, serious injury, and fire hazard. Unlike the aqueous electrolytes in Pb-acid, Ni-Cd, and Ni-MH batteries, Li-ion electrolytes use flammable organic solvents [69]. Therefore, battery safety is a matter of crucial importance to the Li-ion battery industry. Safety devices along with good electrode design can reduce the risk of fire or explosion. In large size batteries, the safety problems are more serious as compared to the small size batteries. Accordingly,
batteries for EV and HEV would have more risk of catching fire or explosion as compared to batteries for laptops and cell phones.

The safety issues of Li-ion batteries are mainly related to overcharging/discharging and overheating [70,71]. There are also situations such as physical abuse (crushing or penetration) that can also lead to overheating [46]. Over-discharge can lead to the dissolution of the copper current collector. As a result, the decomposition of copper on the electrolytes and separators can lead to a short circuit [70]. Overcharging is also hazardous because the charged positive electrode material can react with the electrolyte, resulting in electrolyte venting, smoke, fire, or explosion. Thus, bypass protection circuits controlled by a microchip offer protection from abuse by opening a switch before they are discharged/charged to a potentially hazardous level [70]. Therefore, the cell controller senses voltage and activates the bypass circuit on and off when the cell reaches near full charge or discharge. If the function of the circuit fails and the battery continues to charge, a safety vent, which is a part of a cell opens to release the pressure in the battery. The vent is designed to break the circuit in order to protect the battery from further overcharging or overheating. Once the vent opens, the battery is destroyed.

When a Li-ion battery exceeds a critical temperature, exothermic chemical reactions are initiated between the electrodes and the electrolyte, which cause raising the cell’s internal pressure and temperature [46,71]. The increased temperature accelerates the chemical reactions, producing more heat through a dangerous positive feedback mechanism that leads to thermal runaway. The possible processes contributing to self-heating include the thermal decomposition of the electrolyte solution due to reactions between salt and solvent, reactions between the electrolyte and electrodes, and the
thermal decomposition of the anode as well as the cathode materials [46,70]. For instance, the decomposition of high voltage lithium transition metal oxide cathode releases oxygen at elevated temperatures [70]. This has the effect of increasing the internal pressure of the cell. Safety vents open in response to a sudden increase in cell pressure, allowing gases to escape in a controlled way [18]. As discussed in section 1.1.3.4, separators are also used as safety devices in battery technology. They melt when the internal temperature of the cell exceeds a certain limit, thus closing the micropores and preventing ionic exchange, effectively shutting the cell down [70].

As discussed above, apart from damage from overheating, a battery may be damaged from excessive currents as well as from over and under voltage. A polyswitch or positive temperature coefficient (PTC) material [18], which consists of a blend of special polymers and conductive components that exist in a crystalline structure with low electrical resistance at room temperature, can be used for high current safety. At high currents, the crystallites in the polymer melt and become amorphous. The increased volume during melting of the polymer increases the internal resistance, thus rapidly controlling the high current. However, once the PTC device cools, it again becomes conductive.

1.2.4 Cathode Materials for Lithium-ion Batteries

In Li-ion batteries, cathode materials are the key components, and they are mainly identified to improve the performance of the batteries. Among the known cathode materials, layered LiCoO$_2$, LiNiO$_2$, and LiMnO$_2$, spinel LiMn$_2$O$_4$, and olivine LiFePO$_4$ have been studied extensively. The following sections present a brief description of these basic common cathode materials.
1.2.4.1 Lithium Cobalt Oxide

Lithium cobalt oxide (LiCoO₂), which was first proposed by G.B. Goodenough et al in 1980 and the first commercial successful cathode material for Li-ion battery, is still the most extensively used cathode material in commercial Li-ion battery production by virtue of its high working voltage (~3.6 V), structural stability, long cycle life, and easy synthesis [44,72,73]. However, this cathode material is associated with some drawbacks which include high cost due to limited sources of Co, toxicity, structural deformation when more than 0.5 Li is removed from it, and safety risks in large scale applications [72,73].

In terms of the processing methodology and the resulting structure, two distinct phases of LiCoO₂ are known: high temperature LiCoO₂ (HT-LiCoO₂) and low temperature LiCoO₂ (LT-LiCoO₂) [74]. The commonly used HT-LiCoO₂ has a layered α-NaFeO₂ [73,75] type rhombohedral or trigonal structure with space group R₃m [75], and lattice parameters a = 2.816 Å and c = 14.08 Å in a hexagonal cell setting [44,76]. As shown in Figure 1.4, the structure consists of layers of edge-sharing Li and Co octahedral sites stacked alternatively between ABCABC cubic-close packed oxygen planes along the c-axis with a Li-CO-O-etc. stacking order [77]. This structure has definite parallel planes containing Li-ions at much lower mass than the Co and oxygen rich planes. Because of the high electronegativity of oxygen, the Co and oxygen ions are arranged in strongly bonded planes. During charge/discharge cycling, Li-ions diffusion takes place in the lithium layer by hopping from one octahedral site to another octahedral site through an intermediate tetrahedral site. On the other hand, LT-LiCoO₂ has a spinel structure of composition Li₂Co₂O₄ with space group Fd₃m [74]. This structure is
distinguished from the ideal spinel (MgAl$_2$O$_4$ structure) by the amount of lithium stored in the crystal. The structure of LT-LiCoO$_2$ form contains cubic close-packed oxygen ions in 32e sites, Li-ions in the 16c sites, and Co ions in the 16d sites. Both HT and LT-LiCoO$_2$ forms are distinguished by the spatial arrangement of cations (i.e., about 6 % of Co ions located at lithium sites of LT-LiCoO$_2$) [74], but they have the same oxygen sub-lattice. Also, LT-LiCoO$_2$ processes poor electrochemical properties due to cation disorder, which limits its practical application.

The removal of lithium corresponding to \( x = 1 \) in Li$_x$CoO$_2$ (complete removal of Li-ions from LiCoO$_2$) is equivalent to a theoretical capacity of about 274 mAh$^{-1}$ [77,78]. However, the practical lithium reversible storage capacity of the LiCoO$_2$ cell is around 140 mAh$^{-1}$ [67,73], which is roughly half of its theoretical capacity. This practical value is indicating that only half of the Li-ions (0.5 Li/Co) can be used during the charge/discharge process. Complete removal of lithium from LiCoO$_2$ cannot be accomplished due to a series of phase transformations between hexagonal and monoclinic structures [73,76].

In order to improve the electrode performance, partially replacing Co with Mg, Al, Fe, Ni, Cr, Mn and Li in LiCoO$_2$ [21,79], and metal oxide coating on surface of LiCoO$_2$ with Al$_2$O$_3$, AlPO$_4$, ZrO$_2$, AlF$_3$, SiO$_2$, TiO and ZnO [21,38,77] have been studied. And significant improvements in cycling as well as structural performances have been obtained. However, as noted above, the recognized disadvantages of high cost, high toxicity, and limited abundance of cobalt created a paramount need for an alternative cathode candidate.
1.2.4.2 Lithium Nickel Oxide

Lithium Nickel Oxide (LiNiO$_2$) cathode material was first developed by Moli Energy Co in 1990 [80]. It also adopts layer structure like LiCoO$_2$ (Figure 1.4), with lattice parameters $a = 2.88$ Å and $c = 14.20$ Å [81]. LiNiO$_2$ is of great interest as a candidate for Li-ion batteries application since it is cheaper than LiCoO$_2$ and offers higher practical capacity (upto 200 mAhg$^{-1}$) and high energy density [76]. But, its theoretical capacity is 275 mAhg$^{-1}$ [81,82].

![The structure of layered LiMO$_2$ (M = Co, Ni, Mn) materials](image)

**Figure 1.4** The structure of layered LiMO$_2$ (M = Co, Ni, Mn) materials [41,83].

Most researchers suggest that LiNiO$_2$ requires utmost care in the synthesis process [84], due to the difficulty of obtaining stoichiometric LiNiO$_2$. During the synthesis process, excess nickel is found in the lithium layer, which leads to a composition of Li$_{1-x}$Ni$_{1+x}$O$_2$ ($x > 0$) [44,84]. This causes structural instability. In order to synthesize structurally stable materials, many researchers reported partial substitution of Co, Mn, Al,
Mg, Fe, Zn, etc. for Ni in LiNiO$_2$ [67,75]. Significant improvements in structural performances have been obtained.

1.2.4.3 Lithium Manganese Oxide

Lithium manganese oxide (LiMnO$_2$) has the same layered structure as LiCoO$_2$ and LiNiO$_2$ (Figure 1.4) [40]. Layered LiMnO$_2$ has two main crystal structures: orthorhombic and monoclinic [85]. LiMnO$_2$ in monoclinic form is not thermodynamically stable but the orthorhombic phase is more stable [40]. Although, orthorhombic LiMnO$_2$ (o-LiMnO$_2$) exhibits thermodynamic stable phase, the synthesis technique, firing temperature, oxygen partial pressure have significant influence on its electrochemical performance [86]. From the firing temperature point of view, o-LiMnO$_2$ has been synthesized by a conventional high-temperature solid-state reaction method. However, low-temperature synthesis methods such as ion-exchange and hydrothermal reactions are not suitable for preparation of o-LiMnO$_2$, but suitable for synthesis of m-LiMnO$_2$ [87].

The o-LiMnO$_2$ cathode material for Li-ion batteries has rock salt structure in which LiO$_6$ and MnO$_6$ octahedral are arranged in corrugated layers [88]. Its space group is Pmnm [82,88]. It also offers higher practical capacity of about 160-200 mAh$^{-1}$. Theoretically, it can deliver a specific capacity of about 285 mAh$^{-1}$ based on the Mn$^{3+}$/Mn$^{4+}$ redox couple [86,88]. On cycling process, o-LiMnO$_2$ is gradually converted into spinel structure like Li$_x$Mn$_2$O$_4$, with consequent decay in electrode performance [86,88]. However, many researchers have been trying to control this problem by a partial substitution of Mn by other metal elements such as Co, Ni, Al, Cr, Fe, etc. [40,75].
m-LiMnO$_2$ cathode material has $\alpha$-NaFeO$_2$ type of cation ordering in which Li-ions are located in octahedral sites between MnO$_6$ sheets. It also belongs to C2/m space group [85]. As discussed above, m-LiMnO$_2$ material was successfully synthesized by low temperature method. However, the material shows relatively large capacity loss in cycling. In order to improve its performance, different researchers have used partial substitution of Mn by other metal elements such as Co, Al, Cr, etc., [74].

1.2.4.4 Spinel Lithium Manganese Oxide

Spinel lithium manganese oxide (LiMn$_2$O$_4$), used as cathode material for Li-ion batteries, was originally proposed by Thackeray et al. in 1983 [48]. Its structure is the same as that of the original mineral MgAl$_2$O$_4$ which is called “Spinel”. The spinel LiMn$_2$O$_4$ material belongs to Fd$\overline{3}$m space group [40,73], and it contains three types of cations: Li$^+$, Mn$^{3+}$ and Mn$^{4+}$, and one type of anion O$^{2-}$. As shown in Figure 1.5, the structure consists of cubic close-packed oxygen ions in 32e sites, Li-ions in the 8a tetrahedral sites, and manganese ions (Mn$^{3+}$ and Mn$^{4+}$) in the 16d octahedral sites [40]. Also, the Li-ions and manganese ions occupy 1/8 and 1/2 of the tetrahedral and octahedral sites, respectively [75,89]. Furthermore, the spinel LiMn$_2$O$_4$ contains empty tetrahedral 8b and 48f, and octahedral 16c sites. In the spinel structure, the 8a tetrahedral sites are situated farthest from the 16d octahedra sites, and these two sites share each of their four faces with adjacent vacant 16c octahedra. This arrangement provides a three dimensional pathway for Li-ion diffusion along the 8a–16c–8a path (Figure 1.5 c) [40], or the diffusion process takes place from one 8a site to another 8a site through the intermediate 16c site. On the other hand, LiMn$_2$O$_4$ has a theoretical capacity of 148 mAhg$^{-1}$ [90], but its practical specific capacity is about 120 mAhg$^{-1}$ [18,90] when
cycled between 3.5 and 4.3 V. This means that about 80% of Li-ions can be 
de-intercalated from LiMn$_2$O$_4$ lattice.

Spinel LiMn$_2$O$_4$ is an attractive cathode material that attracts much attention due to 
low raw materials cost, low toxicity, high voltage source, high rate performance because 
of its three dimensional pathways for diffusion of Li-ions, easy preparation, and good 
safety compared with the LiCoO$_2$ [40,75]. However, it suffers severe capacity fade on 
cycling particularly at elevated temperature (above 40 °C) at which most electronic 
devices operate [91]. This capacity fade is associated with the dissolution of manganese 
into electrolyte, Jahn–Teller distortion due to Mn$^{3+}$ ions, decomposition of electrolyte 
solution on the electrode, and occurrence of lattice parameter difference between two 
cubic phases formed during charge–discharge process [18,48,73].

In order to improve the performance of LiMn$_2$O$_4$ related with surface morphology, 
many attempts were made to directly prepare spinel with surface coating (surface 
modifications) with MgO, Al$_2$O$_3$, SiO$_2$ and TiO$_2$ [92,93]. Moreover, in order to enhance 
the structural stability and electrochemical properties of LiMn$_2$O$_4$, partial substitution of 
cations such as Co$^{3+}$, Ni$^{2+}$, Fe$^{2+}$, Cr$^{3+}$, Al$^{3+}$, Mg$^{2+}$, Ga$^{3+}$ into Mn sites is widely reported 
[18,48]. However, the cationic replacement into the spinel lattice has the effect of 
lowering its initial reversible capacity [94], which may make this type of spinel 
unattractive for practical application. In order to improve the initial discharge capacity of 
the spinel LiMn$_2$O$_4$, nowadays partial substitution of anion such as F$^-$, Cl$^-$, S$^{2-}$, Br$^-$ for O$^{2-}$ 
has been reported. For instance, Chen Zhao-yong et al. [48] demonstrated that the 
substitution of F$^-$, Cl$^-$ and Br$^-$ for O$^{2-}$ leads to an increase of the reversible capacity.
Li-ions can be inserted into or extracted from spinels by electrochemical redox reactions. Different studies showed that, the discharge of $\text{Li}_x\text{Mn}_2\text{O}_4$ proceeds in predominantly two steps, one around 4 V in the range $0 \leq x \leq 1$ and the other around 3 V in the range $1 \leq x \leq 2$ [40,95].

![Schematic of the spinel structure](image)

**Figure 1.5** Schematic of the spinel structure showing: (a) the three dimensional framework (b) the connection between LiO$_4$ tetrahedra and MnO$_6$ octahedra (c) the location of different sites in the crystal structure of LiMn$_2$O$_4$ [96].

At 4 V, the Li-ions are extracted from the tetrahedral sites of LiMn$_2$O$_4$ (Mn$^{3+}$, Mn$^{4+}$), and another spinel phase $\lambda$-MnO$_2$ (Mn$^{4+}$) is formed. During this process, the Li-ions move from one 8a tetrahedral into another 8a site through the intermediate 16c octahedron, the cubic symmetry is maintained consequently leading to good recharge.
ability and cycling stability [40]. However, LiMn$_2$O$_4$ tends to exhibit capacity fade even in the 4V region, particularly at elevated temperatures. At 3 V, Li-ions are inserted into spinel LiMn$_2$O$_4$. During this process, Li-ions occupy both the tetrahedral 8a and octahedral 16c sites of the spinel structure, because the 16c octahedra share faces with the 8a tetrahedral. Electrostatic interactions between the Li-ions on these two sets of sites cause an immediate displacement of Li-ions in the tetrahedral site into the neighboring vacant 16c octahedra. This intercalation process induces a Jahn-Teller distortion, as a result, the crystal structure changes from the cubic spinel LiMn$_2$O$_4$ (Mn$^{3+}$, Mn$^{4+}$) to the tetragonal spinel Li$_2$Mn$_2$O$_4$ (Mn$^{3+}$) [75]. This leads to severe capacity fade [96]. The intercalation process can be described by the electrochemical reactions as follows.

$$\text{LiMn}_2\text{O}_4 (\text{cubic}) \rightleftharpoons 2\lambda\text{MnO}_2 (\text{cubic}) + \text{Li}^+ + e^- \quad \text{(at 4 V)}$$

$$\text{LiMn}_2\text{O}_4 (\text{cubic}) + \text{Li}^+ + e^- \rightleftharpoons \text{Li}_2\text{Mn}_2\text{O}_4 (\text{tetragonal}) \quad \text{(at 3 V)}$$

### 1.2.4.5 Lithium Iron Phosphate

Lithium iron phosphate, LiFePO$_4$, is one of the most interesting materials used as cathode in Li-ion batteries. It was first reported as a cathode material for rechargeable Li-ion battery in 1997 by Goodenough and his co-workers [75,97]. LiFePO$_4$ cathode material has olivine structure [75,97] with space group Pmna in which Li and Fe ions occupy octahedral 4a and 4c, respectively, and P ions occupy tetrahedral 4c sites [75,98]. Also, Li and Fe ions occupy 1/2 of the octahedral sites and P ions occupy 1/8 of tetrahedral sites. Moreover, the oxygen ions create strong covalent bonds with phosphorous ions to form the PO$_4$ tetrahedral polyanion and stabilize the entire three dimensional frameworks which provide improved stability and extreme safety. As shown
in Figure 1.6, FeO$_6$ is a corner shared octahedron and PO$_4$ is an edge-shared tetrahedron, and they form the zigzag skeleton by sharing oxygen [98]. All the PO$_4$ tetrahedra do not touch each other. However, the corner shared FeO$_6$ octahedra of LiFePO$_4$ which are separated by the oxygen atoms of the PO$_4$ tetrahedra cannot form a continuous FeO$_6$ network, which results in the poor electronic conductivity of LiFePO$_4$. Moreover, as discussed above, Li-ions in LiFePO$_4$ form LiO$_6$ octahedra, which share corners along the b-axis. These corner-sharing octahedra are separated by vacant tetrahedra, so no atoms separate Li-ions in adjacent sites along this direction to screen the electrostatic interaction. This leads to one dimensional Li-ions movement.

LiFePO$_4$ cathode material has attracted the wonderful attention of researchers due to its high energy density, high practical theoretical capacity (170 mAhg$^{-1}$ at steady voltage of around 3.4 V vs Li$^+/\text{Li}$). It is also attractive due to its low raw material cost (because, iron is the fourth most abundant element in the earth’s crust next to aluminum, silicon and oxygen), low toxic as well as environmental friendly nature, good thermal stability at fully charged state, very stable during charge/discharge process, and high safety [48,67,75,97]. However, the problem for this type of material is low electronic and ionic conductivity [48,67,97]. For instance, the electronic conductivity of LiFePO$_4$ is only $10^{-9}$-$10^{-10}$ Scm$^{-1}$, which is much lower than that of LiCoO$_2$ (~$10^{-3}$ Scm$^{-1}$) and LiMn$_2$O$_4$ (2$\times$10$^{-5}$ - 5$\times$10$^{-5}$ Scm$^{-1}$) [75,98]. The low conductivity has been attributed to different material properties including the coexistence of Li$_x$FePO$_4$ and Li$_{1-x}$FePO$_4$ phases during charge/discharge processes and one dimensional ionic diffusion. Different experimental approaches have been proposed to solve the problems, including partial substitution of Fe by other metal elements, like Mn, Co, Ni, etc., coating with conductive
substance such as Ag, Cu, conductive carbon during the synthesis process, reduction of grain size so as to shorten the Li-ion diffusion length and synthesis of particles with well-defined morphology [48,98].

Figure 1.6 Schematic diagram of the crystal structure of the LiFePO₄ olivine with Pnma space group along the c-axis [37].

1.3 Objectives of the Present Study

Recent studies of Li-ion batteries focus on improving electrochemical performance of electrode materials and lowering the cost. Considerable improved electrochemical performance of the electrode materials has been achieved. There are still problems needing further investigation. The nature of the active materials is of primary importance because the resulting cell energy density depends on them. The main features of the active materials which determine cell energy are the number of ions they can store per
unit volume or weight (volumetric capacity or specific capacity), and the electrochemical potential they provide.

The extensive literature survey reveals that the synthesis of spinel cathode materials by solid state reaction method and fabrication of cation substituted spinel cathode materials have been attempted by a number of researchers. Moreover, few studies have been reported regarding the synthesis and fabrication of anion substituted particularly fluoride substituted spinel cathode materials. Also, very few studies have been reported regarding synthesis and fabrication of simultaneous anion and cation substituted spinel cathodes. However, synthesis of fluorine substituted spinels $\text{LiLa}_x\text{Mn}_{2-x}\text{O}_{3.85}\text{F}_{0.15}$ ($0.5 \leq x \leq 0.01$), $\text{LiLa}_x\text{Cr}_y\text{Mn}_{2-x-y}\text{O}_{3.85}\text{F}_{0.15}$ ($0.01 \leq x \leq 0.05$ and $y = 0.15 - 2x$) and $\text{LiMn}_{2-x-y}\text{Li}_x\text{Cr}_y\text{O}_{3.85}\text{F}_{0.15}$ ($0.02 \leq x \leq 0.1$ and $y = 0.15 - x$); and non-fluorinated spinel $\text{LiLa}_x\text{Cr}_y\text{Mn}_{2-x-y}\text{O}_4$ ($0.01 \leq x \leq 0.05$ and $y = 0.15 - 2x$) materials with three steps solid-state reaction method have not yet been reported according to our knowledge. Hence, this study has mainly focused on fabricating alternative cathode materials that meet the requirements of low cost, good cyclability and high discharge capacity. In this regard, the electrochemical properties of the spinel cathodes are investigated by pursuing cationic substitutions for manganese and/or anionic substitutions for oxygen.

1.4 Thesis Outline

This dissertation is structured as follows:

Chapter 2 gives detailed information of materials and chemicals used in this work, followed by the brief description of synthesis, cathode fabrication and cell assembly procedures employed. Different techniques for characterization used in this study including TG/DTG, XRD, SEM, EDS, FT-IR spectroscopy, redox titration, specific
surface area and porosity measurements, CV and galvanostatic charge/discharge cycling are fully described.

**Chapter 3** reports the influence of fluorine substitution on the physiochemical and electrochemical properties of spinel LiMn$_2$O$_4$ cathode material for Li-ion batteries synthesized by one step solid state reaction method. The physiochemical properties of the synthesized materials are investigated by TG/DTG, XRD, SEM, EDS and FT-IR spectroscopy. For comparison, a study on fluorine substituted spinel LiMn$_2$O$_4$ synthesized by a low temperature solid-state reaction method is also mentioned in this chapter. Different characterization techniques, including TG, XRD, redox titration, SEM, specific surface area and porosity measurements are also described. Moreover, the electrochemical performance of the prepared cells is investigated by galvanostatic charge/discharge cycling.

**Chapter 4** explores a comparative study on lanthanum substituted LiLa$_x$Mn$_{2-x}$O$_{3.85}$F$_{0.15}$ and LiLa$_x$Mn$_{2-x}$O$_4$ (0.01 ≤ x ≤ 0.05) cathode materials for Lithium-ion batteries synthesized by three steps solid-state reaction method. Different methods including XRD, EDS, SEM, FT-IR spectroscopy, redox titration, specific surface area and porosity measurements as well as EIS, CV and galvanostatic charge/discharge cycling are carefully conducted.

**Chapter 5** reports a comparative study on the lanthanum and chromium substituted LiLa$_x$Cr$_y$Mn$_{2-x-y}$O$_{3.85}$F$_{0.15}$ and LiLa$_x$Cr$_y$Mn$_{2-x-y}$O$_4$ (0.01 ≤ x ≤ 0.05 and y = 0.15 - 2x) cathode materials for lithium-ion batteries. Different characterization techniques including XRD, SEM, EDS, FT-IR spectroscopy and redox titration are applied to the
synthesized materials. Moreover, ac conductivity, EIS and galvanostatic charge/discharge cycling are carefully conducted.

**Chapter 6** discusses synthesis and characterization of LiMn_{2-x-y}Li_xCr_yO_{3.85}F_{0.15} (0.02 ≤ 0.1 and y = 0.15-x) cathode materials

Finally, general conclusions of the study and plans for future work are also proposed in **chapter 7**.
References


