CHAPTER – I

INTRODUCTION

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1.1 General Introduction

The exponential growth in portable electronic devices such as cellular phones, laptop computers, etc., has motivated enormous interest in developing safe, compact, light weight and high energy density batteries with better cycle life [1-4]. Also, growing environmental concerns around the globe are driving the development of advanced batteries for electric vehicles [5-7]. The lithium ion batteries are more suitable to meet the above mentioned applications, since they provide high energy density compared to other available rechargeable batteries, such as lead acid, nickel- cadmium, nickel- metal hydride, etc., as shown in fig. 1.1 [8-10].

In recent years, the rechargeable battery market further expanded and tends to increase continuously [11]. The world wide sales for Li ion portable batteries is 63% and it is larger than those of Ni-Cd (23%) and Ni-MeH (14%), which indicates that lithium battery technology receives most attention [12]. Ever growing demand for batteries lead the industry and government liberally invest in battery research and development. The investment of industry is focused on improving battery technology for communication, mobile electronics and computer technology, whereas majority of government funded research is for military, spacecraft, transportation, etc. [13]. Requirement for improving the battery properties included cycleability, reversibility, high energy, power density, safety, environmental impact, lower cost, etc. [14]. Hence, a wide range of materials (anodes, cathodes and electrolytes) have been developed and investigated for the improved lithium battery technology [15-17].

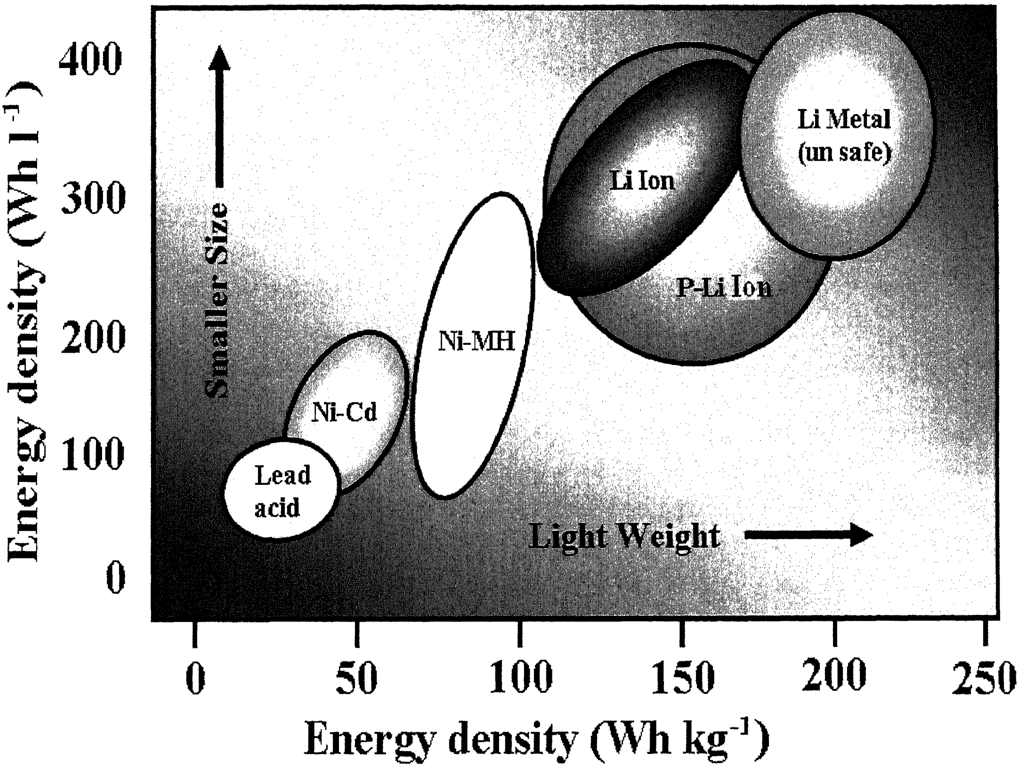


Fig. 1.1 Comparison of different types of secondary battery technologies in terms of volumetric and gravimetric energy density.

Most of the commercial lithium batteries are based on the lithium carbon (anode) / lithium cobalt oxide (cathode) chemistry [18]. In order to develop high energy density batteries with extended cyclic life, it is necessary to find the electrode materials with high specific charge as well as more structural stability. Most of the efforts are concentrated on developing new cathode materials not only to improve the cell voltage but also the specific capacity of lithium batteries, which are much depend on their intercalation behavior during charge / discharge cycles [19, 20]. Among them, lithium transition metal oxides have been studied as promising positive electrode materials (cathode), since it shows large stability region with respect to lithium content than other class of intercalation compounds [21-22].

Layered $LiCoO_2$, $LiNiO_2$ and $LiMnO_2$, spinel $LiMn_2O_4$, inverse spinel $LiNiVO_4$ and olivine $LiFePO_4$ are the most studied cathode materials in the last two decades [23-30]. Although, numerous classes of cathode materials were studied, only 40 to 65 % of the theoretical capacity of the cathode materials could be practically utilized due to the chemical and structural instabilities due to the lithium intercalation during the charge and discharge process [31]. Recently, it is found that the nanocrystalline cathode materials exhibit high storage capacity, voltage and charging / discharging rates due to much shorter diffusion paths for Li^+ diffusion and the smaller dimensional change during intercalation and deintercalation processes [32-36]. Synthesis process plays major role in the development of nanocrystalline cathode materials with desired physiochemical properties [37-40]. Wet chemical routes such as sol gel, combustion, hydrothermal, etc., are intensively used for this purpose [41-48].

Present chapter starts with an introduction and classification of batteries and also provides a brief description on the materials aspect of secondary lithium batteries with special emphasize towards cathode materials. Finally, aims of the present investigation are presented.

1.2 Batteries (Cells)

A battery is a device that converts the chemical energy into electrical energy by means of an electrochemical reaction called oxidation – reduction (redox) [49]. Each oxidation and reduction reactions are associated with the standard cell potential E^o, which can be calculated from the thermodynamic information as follows,

$$E^o = \frac{-\Delta G^o}{zF}$$

Where, ΔG^o standard Gibbs free energy, z – number of electrons exchanged and F- faraday constant. The overall theoretical cell voltage ΔE^o is obtained by subtracting the negative electrode potential $E^{o(-)}$, from the positive electrode potential, $E^{o(+)}$.

$$\Delta E^o = E^{o(+)} - E^{o(-)}$$

Although the term "Battery" often used, the basic unit is called electrochemical cell. Battery can consists of one or more electrochemical cells connected in series or parallel or both to provide the required operating voltage and current [50].

1.2.1 Components of Batteries

A battery / cell consist of three major components and they are cathode, anode and electrolyte.

1.2.1.1 Anode (Negative Electrode): The anode is an electrode, where the oxidation reaction occurs, which releases electrons to the external circuit and reduced during the electrochemical reaction. In practical, anode is selected based on their efficiency as a reducing agent, high coulombic output (Ah/g), good conductivity, etc. The following materials can be used for the negative electrode in batteries [50],

(i) Metals: Li, Na, Zn, Cd, Pb, etc.

(ii) Metal alloys (for example, lithium alloys, where the alloying elements can be Al, Sn, Si, etc.) and metal hydrides ($LaNi_5H_x$, $ZrMn_2H_x$, Mg_2NiH_x, etc.).

(iii) Carbons (for example graphite carbons, non-graphite carbons).

(iv) Redox polymers with negative redox potentials.

1.2.1.2 Cathode (Positive Electrode): The cathode is an electrode where the reduction reaction occurs, which accepts electrons from external circuit and oxidized during the electrochemical reaction. The cathode must be an efficient oxidizing agent, high stability when it is in contact with the electrolyte with use full working voltage. The following are the commonly used cathode materials in batteries [50, 51],

(i) Metal oxides (such as MnO_2, PbO, etc.) and metal sulfides (such as TiS_2, NbS_3, MoS_2, etc)

(ii) Insertion or host materials like metal oxides (for example; $LiMO_2$, where M= Co, Ni, Cr, Fe, V and Mn).

(iii) Metal oxyhydroxides (NiOOH, PbOOH and MnOOH).

(iv) Redox polymers with positive redox potentials.

1.2.1.3 Electrolyte: The electrolyte is an ionic conductor with negligibly small electronic conduction, which provides the medium for transfer of ions from one electrode to another electrode and also prevent short circuit. Important properties of the electrolyte are non reactivity with electrode materials, small property change with respective to temperature variation, safety in handling, etc. In majority of conventional batteries, the electrolytes are aqueous solutions such as $ZnCl_2$, KOH, etc., but some advanced batteries are fabricated with non aqueous solutions, ion conducting solids or polymers as electrolytes [50].

1.2.2 Classification of Batteries

Batteries are identified as primary (non rechargeable) and secondary (rechargeable) depending on their capacity of being electrically recharged.

1.2.2.1 Primary Batteries

In primary batteries, the electrode reactions are not reversible, i.e., applying the external energy will not reconstruct the electrodes, hence, the cells are not rechargeable. After the discharge, they are discarded. Some of the important primary batteries are briefly explained below,

(i) Zinc - Carbon Battery (Leclanche Cell)

The zinc - carbon battery uses a zinc anode, a manganese dioxide cathode, and an electrolyte of aqueous ammonium chloride and /or zinc chloride. Powdered carbon is used in the cathode mix, usually in the form of carbon black to improve conductivity of the mix [52, 53]. In zinc chloride cell, NH_4Cl is completely replaced by $ZnCl_2$ and the electrochemical reactions of the zinc- carbon battery are given in the table 1.1

(ii) Alkaline Manganese Battery

Compared to the zinc – carbon battery, the alkaline battery is more reliable, since it has better performance i.e., up to ten times of Ah capacity than zinc – carbon battery at higher discharge currents, which is required for advanced portable electronic devises. The principal difference between zinc – carbon and alkaline manganese battery is electrolyte, i.e., concentrated potassium hydroxide (KOH) solution and the electrochemical reactions of the alkaline manganese battery are given in the table 1.1

Table – 1.1
Various primary batteries and their characteristics

S. No	Battery System	Cathode	Electrolyte/ Reaction	Anode	Nominal Voltage (V)	Specific Energy (Wh/Kg)	Energy Density (Wh/l)
1	Zinc Carbon (Leclanche Cell)	MnO_2	Aqueous NH_4Cl and/ or $ZnCl_2$ $Zn \longrightarrow Zn^{2+} + 2e^-$ (Anode) $MnO_2 + H_2O + 2e^- \longrightarrow MnOOH + OH^-$ (Cathode) $Zn + 2MnO_2 + 2H_2O \longrightarrow 2MnOOH + Zn(OH)_2$ (Total reaction)	Zn	1.55	65	100
2	Alkaline Manganese	MnO_2	Aqueous KOH Solution $Zn + 2OH^- \longrightarrow ZnO + H_2O + 2e^-$ (Anode) $2MnO_2 + H_2O + 2e^- \longrightarrow Mn_2O_3 + 2OH^-$ (Cathode) $Zn + 2MnO_2 \longrightarrow ZnO + Mn_2O_3$ (Total reaction)	Zn	1.50	95	220
3	Lithium Manganese Dioxide	MnO_2	Ion Conducting Organics $Li \longrightarrow Li^+ + e^-$ (Anode) $2MnO_2 + Li^+ + e^- \longrightarrow MnO_2{}^-(Li^+)$ (Cathode) $MnO_2 + Li \longrightarrow MnO_2{}^-(Li^+)$ (Total reaction)	Li	3.60	200	400

(iii) Primary Lithium Battery

Primary lithium batteries become popular because of their high voltage as well as high energy density [52-54]. These lithium batteries employ a lithium foil as anode, different cathode active materials such as CuO, CuS, CF, MnO_2, etc., with lithium ion conducting organic electrolytes. Commercially, the most widely adopted positive electrode materials are CF and MnO_2. There are several other types of primary lithium batteries, which find specialized application. Among them, important primary batteries are lithium / iodine battery, lithium manganese dioxide battery and lithium – lithium thionyl chloride [55]. The electrochemical reactions of the primary lithium battery with MnO_2 cathode are described in table 1.1.

1.2.2.2 Secondary Batteries

In secondary batteries, the electrode reactions are reversible, i.e., applying the external voltage to reconstruct the electrodes to their original state, hence, the batteries can be rechargeable. Thus, the rechargeable batteries act as energy source as well as energy storage systems. The capacity, rate capability, cycling performance, environmental health and safety issues are few of the significant performance characteristics, which are concern in rechargeable batteries [56]. Some of the important common secondary batteries are briefly discussed in this section.

(i) Lead – Acid Battery

Lead - acid battery is well known and common one among the available rechargeable batteries, which is based on the chemistry of lead [57]. The electrode and the cell reaction are shown in table 1.2. In this battery, lead serves as the anode and lead dioxide serves as the cathode, which are dip into an electrolyte solution of sulfuric acid [8].

Table – 1.2
Various secondary batteries and their characteristics

S. No	Battery System	Cathode	Electrolyte/ Reaction	Anode	Nominal Voltage (V)	Specific Energy (Wh/Kg)	Energy Density (Wh/l)
1	Lead Acid	PbO_2	H_2SO_4 aqueous Solution $Pb + SO_4^{2-} \rightleftharpoons PbSO_4 + 2e^-$ (anode) $PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightleftharpoons PbSO_4 + 2H_2O$ (cathode) $PbO_2 + 2PbSO_4 + Pb \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} PbSO_4 + 2H_2O$ (total reaction)	Pb	2	35	80
2	Ni- Cd	NiOOH	KOH aqueous Solution $Cd + 2OH^- \rightleftharpoons Cd(OH)_2 + 2e^-$ (anode) $2NiOOH + 2H_2O + 2e^- \rightleftharpoons 2Ni(OH)_2 + 2OH$ (cathode) $2NiOOH + Cd + 2H_2O \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} Ni(OH)_2 + Cd(OH)_2$ (total reaction)	Cd	1.2	50	100
3	Ni – MH	NiOOH	KOH aqueous Solution $H_2 + 2OH^- \rightleftharpoons 2H_2O + 2e^-$ (anode) $2NiOOH + 2H_2O + 2e^- \rightleftharpoons 2Ni(OH)_2 + 2OH$ (cathode) $2NiOOH + H_2 \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} 2Ni(OH)_2$ (total reaction)	Hydrogen Adsorbed Alloy	1.2	80	300
4	Lithium Ion	$LiCoO_2$	Organic Electrolyte + Lithium Salt $Li (C) \rightleftharpoons Li_{(1-x)}(C) + x Li^+ + xe^-$ (anode) $xLi^+ + xe^- + Li_{(1-x)}CoO_2 \rightleftharpoons LiCoO_2$ (cathode) $Li (C) + Li_{(1-x)}CoO_2 \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} LiCoO_2$ (total reaction)	C+Li / Li	3.7	165	420

During the discharge, the formation of water changes the electrolytic activity, which affects the open circuit voltage. Also, the formation of $PbSO_4$ during the discharge caused the passivation of cathodes and reduces the practical capacity. Considering the limited mass utilization and the necessity of inactive compounds such as grids, separators, cell containers, etc., the practical value of specific energy (Wh/Kg) is only ~25% of the theoretical one. To enhance the ionic conductivity in the charged and discharged states, an excess acid is necessary. Because of the limitations, such as short life, high maintenance and inadequate energy density, manufacturers of rechargeable batteries are exploring other technologies [58].

(ii) Nickel - Cadmium Battery

Nickel - Cadmium (Ni-Cd) is the first small sealed rechargeable battery [59]. In alkaline (KOH) electrolyte, the Cd negative electrode functions reversibly according to a solution precipitation mechanism with $Cd(OH)_2$ being the discharge product. The positive electrode is $Ni(OH)_2$, which is able to reversibly de- insert / insert protons during discharge / charge. The electrochemical reactions of Ni-Cd battery are shown in table 1.2. Ni-Cd batteries exhibit long cycle life, high rates of charge and discharge with constant discharge voltage and also better low temperature performance [52, 53]. However, the cost of the nickel - cadmium battery construction, healthily risks associated with the manipulation of cadmium and also the memory effect lead to the search of alternate secondary battery system [52, 53].

(iii) Nickel-Metal Hydride Battery

Nickel-Metal Hydride is one of the most advanced commercially available rechargeable systems and an environmentally friendlier than the nickel- cadmium battery

[60]. The electrochemical reactions of Ni-MH battery are shown in table 1.2. The hydrogen storage alloy is a proton inserting negative electrode material that replaces the environmentally threatened cadmium negative electrode in the Ni-Cd battery. The positive electrode is $Ni(OH)_2$ and electrolyte is KOH. Ni-MH quickly replaced the Ni-Cd for electronic applications because of its significantly higher energy storage capability and an extensive research is moving to develop the multicomponent, multiphase alloys for high hydrogen storage capacity, oxidation and corrosion resistance, fast gas recombination kinetics and lower cost [61-62]. The major issues to be solved for Ni-MH are poor low temperature capability, limited high rate capability and also high self discharge.

(iv) Secondary Lithium Battery

Among the available secondary battery systems, rechargeable lithium batteries exhibit highest specific energy and energy density. Another advantage of lithium batteries is its highest individual cell potential over others [63, 64]. One great advantage of Li-ion batteries is their low self-discharge rate of only approximately 5% per month, compared with over 30% per month and 20% per month respectively in nickel - metal hydride batteries and nickel - cadmium batteries [65]. The electrochemical reactions of secondary lithium battery are shown in table 1.2. Various aspects of rechargeable lithium batteries are well discussed in following sections.

1.3 Rechargeable Lithium Batteries

For fast 20–25 years an enormous activity has been motivated through out the world in the development of both primary and secondary lithium batteries [66]. The interest stems from the low atomic mass of lithium (6.94), its high specific capacity about 3860 Ah / Kg in comparison with Zinc (820 Ah / Kg) and lead (260 Ah / Kg) and its high electrochemical reduction potential of -3.045 V, which contribute to a high specific energy for lithium cells [67]. Present section briefs historical account of the developments of secondary lithium battery technology.

1.3.1 Development of Lithium Batteries

In 1980's, first commercial rechargeable batteries with lithium metal were introduced using TiS_2 as positive electrode but failed in the market due to safety concerns associated with the Lithium metal [68]. Later, researchers overcome this problem by using lithium aluminum (Li-Al) alloys [69]. There after, many lithium alloys have been developed as alternative anode materials, however it exhibits reduced energy density, compared to the pure lithium metal [70]. The major disadvantage of lithium metal alloy anode materials is the volume change during insertion and deinsertion of Li ions from the alloy matrices, which caused the disintegration of the alloy anodes by cracking and crumbling [71]. Disadvantages of metal alloy anode lead to the invention of graphite carbon as anode material, which exhibits high structural stability during the insertion and deinsertion of Li ions [72-74]. Intercalation of lithium ions corresponding to the composition of LiC_6 results in only about a 10% increase in the lattice distance [75]. Hence, graphite becomes the better anode material of choice for the lithium ion battery replacing lithium metal and lithium alloy. Similarly, noticeable development has been made on the intercalation cathode materials of lithium transition metal oxides such as Li_xMO_2 (where M is Co, Ni, and Mn) to replace the chalcogenides [76-80].

The combination of intercalation positive and negative electrode materials with suitable electrolytes has been emerging as lithium – ion battery technology and its principle was first demonstrated by Murphy et al [81] and also Scrosati group [82]. Eventually, rechargeable Li-ion batteries were commercialized by Sony corporation in

1991 and this technology is still used by manufacturers of secondary lithium batteries, which have proven to be extremely safe [18]. These cells contain carbon based negative electrode instead of metallic lithium and a lithium transition metal oxide as positive electrode [83]. This technology is called Li- ion rocking chair batteries.

1.3.2 Principle of Lithium Battery

The lithium battery is constructed by coupling positive electrode with negative electrode in ion conducting electrolyte [52, 53]. The lithium ions move back and forth between the positive and negative electrodes through electrolyte during charge and discharge process. The positive electrode accommodates Li ion during the discharging of the battery and the negative active materials accommodates during the charging. The cell is activated by charging. There are two kinds of rechargeable lithium batteries based on the lithium chemistry and they are (a). lithium metal and (b). lithium ion battery [84]. In both, cathode is a lithium insertion material, whereas, anode in the lithium metal battery is metallic lithium and the anode in lithium ion battery is lithium insertion host. Schematic representation of both types of lithium batteries are shown in fig. 1.2.

1.3.2.1 Lithium - Metal Batteries

Lithium - metal batteries exhibit unique advantages, such as, higher specific energy and energy density, due to the high theoretical specific capacity of lithium metal, which is used as positive electrode. The strong reducing power of lithium metal makes it highly unstable in most of the electrolytes. Charge and discharge processes of the lithium result in the formation of passivating film over the lithium surface. This passivating layer is made up of various inorganic and organic compounds formed due to the reaction of lithium with electrolytes [52, 53]. The formed dendrites can grow and penetrate the separator and caused the internal short circuit, which give rise in the internal temperature and results in the accidental fire or explosion [52, 53]. Schematic of the lithium - metal battery is shown in fig. 1.2a. The cell configuration for the lithium - metal battery is given below,

$$Li(s) \mid \text{Solvent, lithium salt} \mid LiC_OO_2(s)$$

1.3.2.2 Lithium- Ion Batteries

The problem related to the lithium metal (anode) lead to the invention of lithium intercalated materials as negative electrodes. Comparing to lithium metal, lithium intercalating compounds improves the cycle life as well as safety but lowers the cell voltage and the charge transfer rate [52, 53]. During the operation, lithium ions are shuttle between the electrodes through the electrolytes, while electrons are driven through the external electrical circuit by the electrochemical potential [52, 53]. Fig. 1.2b shows the schematic representation of lithium ion battery, which is also called "rocking chair battery" with anode and cathode lithium insertion materials [52, 53, 84]. The cell configuration of the lithium- ion battery is given below,

$$LiC_6(s) \mid \text{Solvent, lithium salt} \mid LiC_OO_2(s)$$

1.3.3 Applications of Lithium Batteries

Lithium battery technology found wide range of applications due to its enhanced performance than other available energy technology and few of them are given below.

Mobile Electronics: Lithium ion rechargeable batteries are the best choice for many of portable devices, such as, camera, laptop, camcorder, i-pod, etc., because of the light weight and enhanced over all performance [85-88].

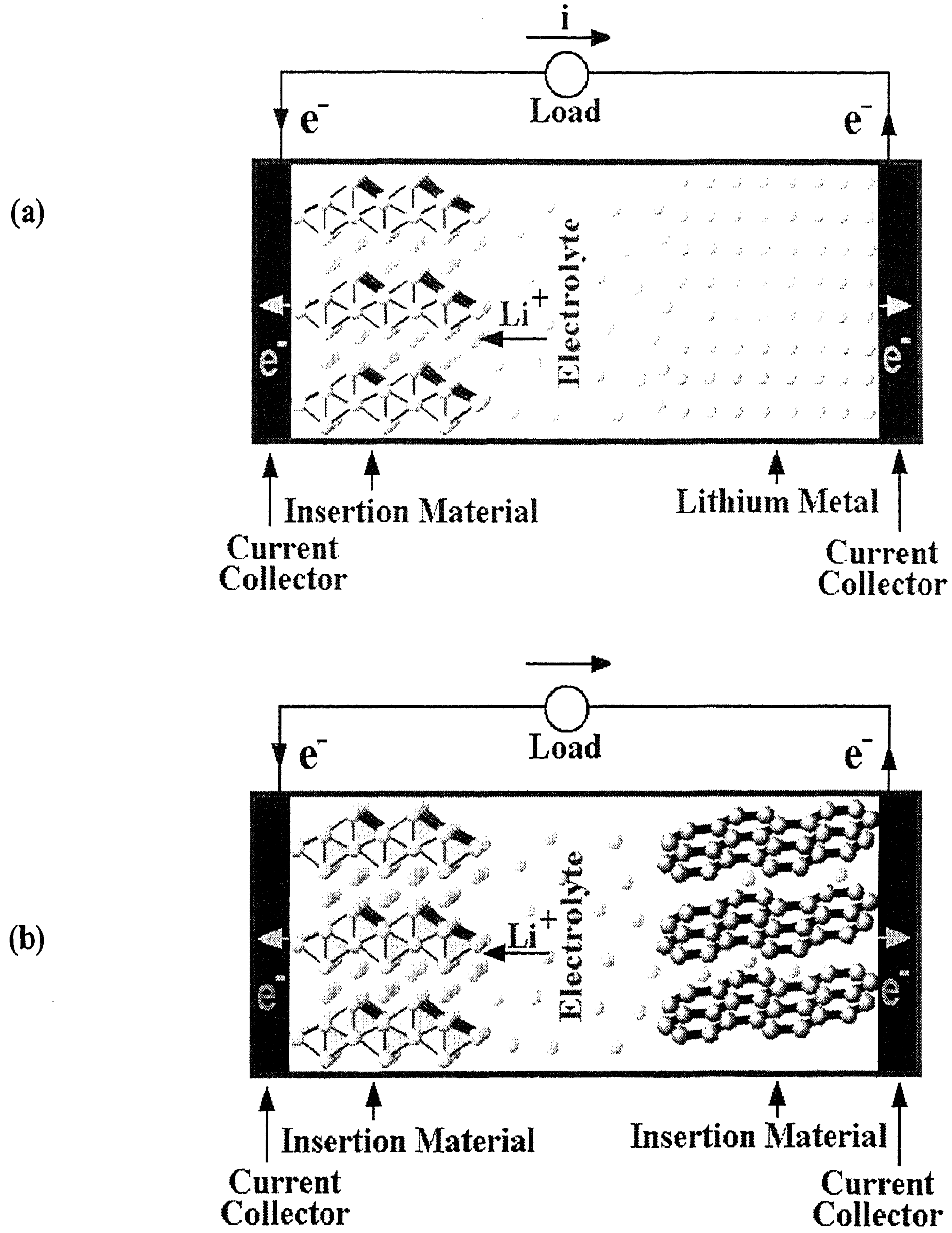


Fig. 1.2 Schematic of (a) lithium metal and (b) lithium ion batteries.

Nanotechnology: Lithium battery technology exhibits a promising application as a power source in the emerging nanotechnology. Nano battery technology is the recent hot topic, which is essential for the growing nano size devices as power source [89-90].

Medical Tool Kits: Advances of lithium batteries, such as higher specific energy and energy density make them potential candidates for power source in implantable devices [91-95].

Space Applications: Space mission also requires batteries, which can provide maximum electrical energy with minimum weight and volume. Since lithium batteries are very much satisfying the above requirements, it is an improved as well as alternate technology for conventional batteries, which are widely used in space applications [96-98].

Military Applications: Lithium batteries are found wide range of applications in military equipments including communications, thermal imaging, night vision, surveillance, chemical detection, search & rescue, undersea mines, etc [99-101].

Hybrid Vehicles: Lithium batteries are most promising for hybrid electric vehicles due to its highest specific energy, energy density and have very long cycle life [102-105].

1.4 Components of Rechargeable Lithium Battery

1.4.1 Insertion Electrode Materials

There is wide choice of materials, which can be selected for the electrodes of rechargeable lithium batteries. Performances of these materials are mainly based on the structural stability as well as reversibility of lithium ions during the charge and discharge processes. In these aspects, insertion or intercalation compounds are most useful for the cathode as well as anode (in the case of lithium ion battery) applications [106-108]. An insertion compound is a host, where the guest species may be topotactically and reversibly inserted / extracted over a finite range of solid solution. In topotactic reaction, the structure of the host is changed only by atomic displacement and the reaction does not involve a diffusive rearrangement of the host atoms. Lithium batteries are based on a wide range of insertion / intercalation materials such as metal chlorides, sulfides, selenides, oxides, etc., which have been proposed and examined for positive as well as negative electrode (in the case of lithium ion battery) of secondary lithium batteries. Based on the redox potential for the insertion of lithium ions into hosts shown in fig. 1.3, it is possible to determine which compound will suitable for positive electrode and which is for negative [109-115].

1.4.1.1 Basic Requirements for the Application of Insertion Materials in Batteries

- Insertion / extraction of the mobile guest species, which are normally the working cations, must be reversible.
- Large free energy of cell reaction to provide high cell voltage for high energy density.
- Wide composition range for high cell capacity i.e., maximum number of lithium ions to be available for intercalation without changing the compound structure.
- Minimum structural change as a function of composition to ensure good reversibility of the insertion process.
- High diffusivity of lithium into the host matrix to enable high current density and power density.
- Suitable electrode morphology to enhance electrochemical performance. Small particle size increases the lithium ion diffusion can enhance the insertion materials capacity
- High electronic conductivity to avoid the addition of conductive materials in the electrode.
- Insolubility of lithium in the electrolyte medium to eliminate self discharge.

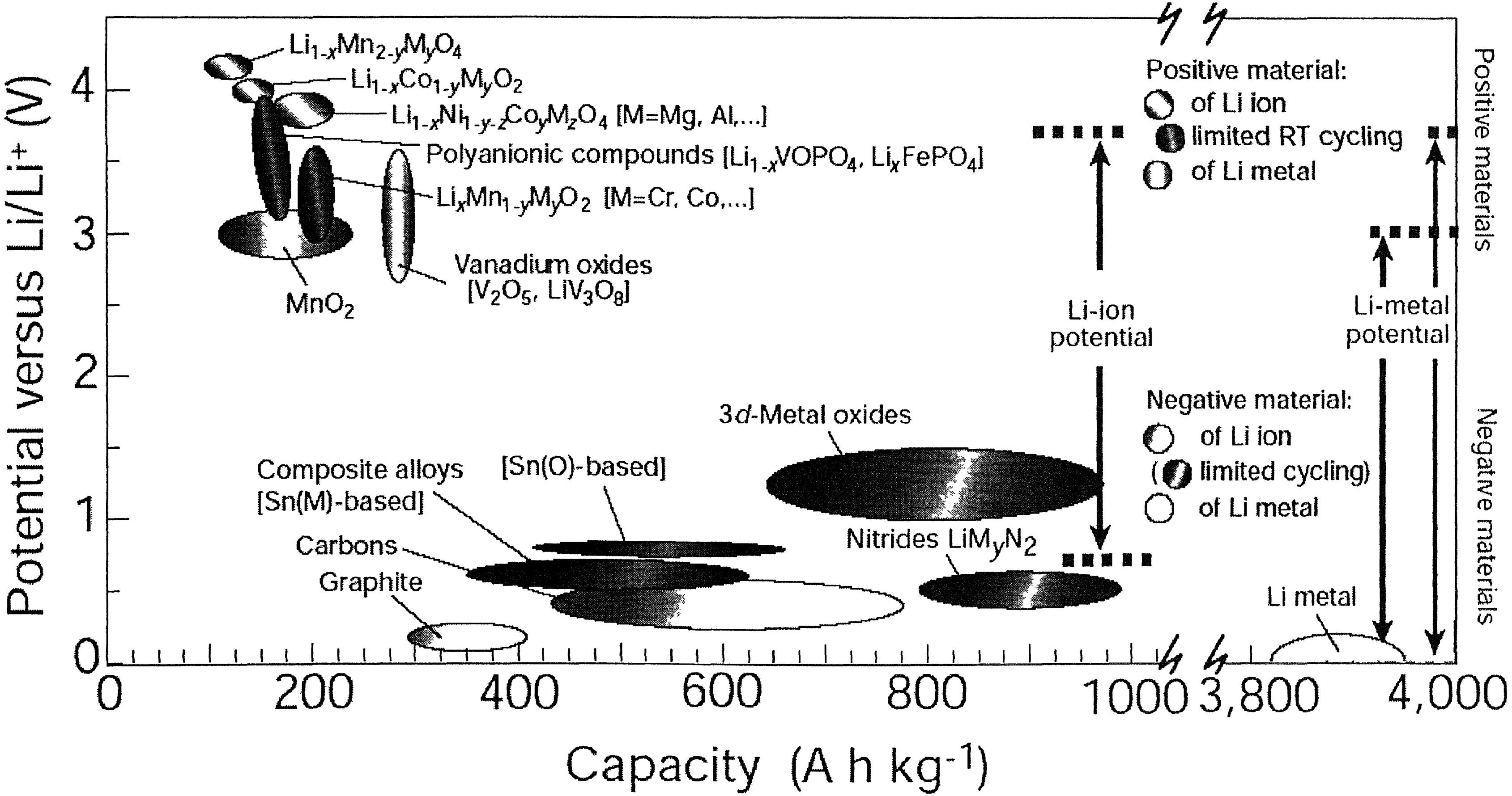


Fig. 1.3 Voltage versus capacity for positive and negative electrode materials [12].

1.4.1.2 Classification of Insertion Compounds

Based on the void space available for lithium insertion, shown in fig. 1.4, lithium insertion materials are classified as one, two and three dimensional hosts [116].

(i) One Dimensional System

One dimensional system is the simplest configuration with drain like tunnels, which exhibits one dimensional migration path for guest ions. Examples of this series of compounds are $NdSe_3$, MoS_3 and TiS_3 [116].

(ii) Two Dimensional System

Many layered compounds are made of close packed anions (X) with transition metals (M) in octahedral or trigonal prismatic sites. In these systems, the guest ions can intercalate between the X-M-X sandwich. The most important compounds of this family for the Li- ion batteries are $LiCoO_2$, $LiNiO_2$ and $LiMnO_2$ for positive electrode and graphite for the negative electrode [116, 117].

(iii) Three Dimensional Systems

In these systems, the guest ions are inserted into a three dimensional network consisting of cross linked channels. The size of the channels must be sufficiently large to accommodate the ions. The advantage of three dimensional frameworks over two dimensional layered structures are,

(i) the possibility of avoiding the co-insertion of bulky species such as solvent molecules

(ii) the smaller degree of structural change during lithium insertion / de-insertion.

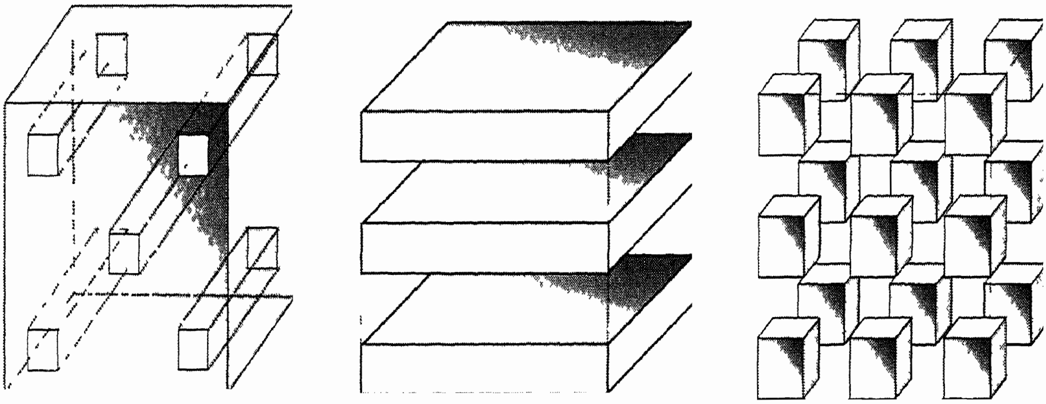


Fig. 1.4 Schematic representations of lithium ion paths in insertion materials

Examples for three dimensional systems are zeolites or spinels (e.g. $LiMn_2O_4$) with a cubic framework. In spinel, the available sites for both transition metal and guests are either octahedraly or tetrahedrally co-ordinated by oxygens [118].

1.4.2 Cathode Materials

Wide range of intercalation compounds have been studied as cathode materials for rechargeable lithium batteries [119-122]. Among them, lithium based transition metal oxides ($LiMeO_2$, where Me- Metal ions such as Ni, Co, etc.) exhibit better performances, since it has very high volumetric capacity, higher chemical and structural stability and favorable electrical properties than others. Based on the structure, lithium based transition metal oxide cathode materials are classified as follows,

1.4.2.1 Layered Compounds

Layer structured α-$NaFeO_2$ type (shown in fig. 1.5) of $LiMeO_2$ (Me = Ni, Co, Mn, V, etc.,) compounds have been widely investigated as cathode materials for rechargeable lithium batteries. The layered structure exhibits two dimensional interstitial site, which allows the extraction and insertion of lithium ions in simple way. Among the available layered intercalation compounds, $LiCoO_2$, $LiNiO_2$, and their mixed oxides $Li(Ni,Co)O_2$ are used for commercial application due to their durability. $LiCoO_2$ is first introduced by Min et. al, [123-125] and it was extended to commercial rechargeable batteries by SONY in 1980s. Still it retains as a dominant cathode material in commercial lithium batteries. Even the theoretical capacity of the $LiCoO_2$ is about 275 mAh/g, it exhibits only 150 mAh/g by charging up to 4.20- 4.25 V versus Li/Li^+.

Apart from $LiCoO_2$, another layered compound, $LiNiO_2$, is also obtained an intensive interest by several researchers due to its economic advantage as well as more

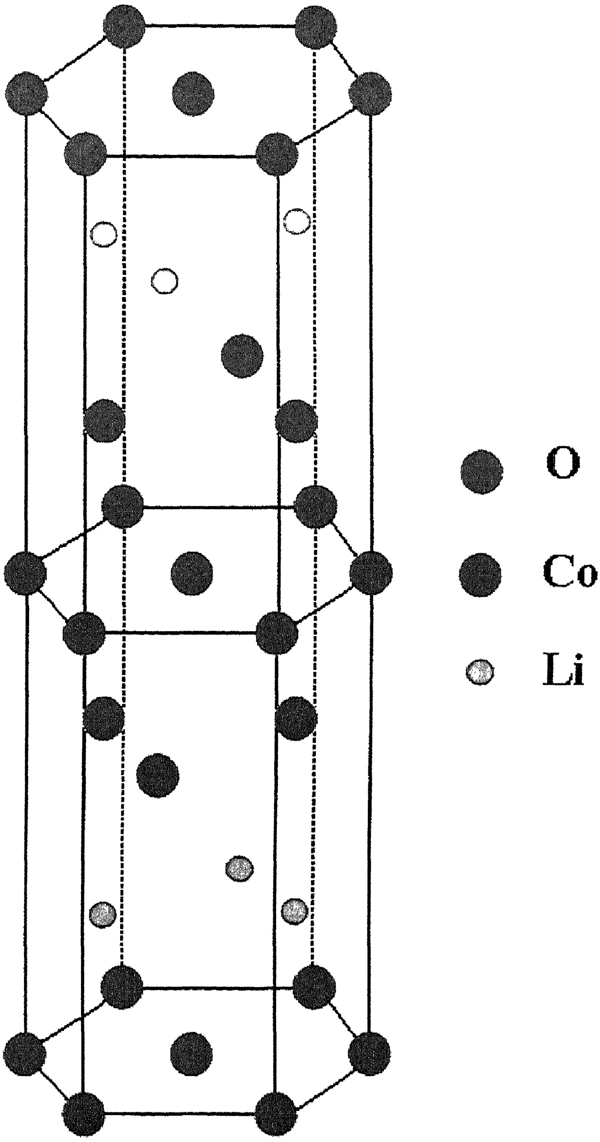


Fig. 1.5 Layer structure (α-NaFeO$_2$ type).

negative than $LiCoO_2$. The theoretical capacity of $LiNiO_2$ is 275 mAh/g, which is very closer to the theoretical capacity of $LiCoO_2$. Also. $LiNiO_2$ delivers the specific capacity about 180 to 210 mAh/g by charging up to 4.10- 4.20 V versus Li/Li^+, which is much higher than $LiCoO_2$. Though, it shows higher specific capacity than $LiCoO_2$, it exhibits higher capacity fading, poor thermal stability and difficult in the preparation (structurally ordered phase). To enhance the electrode performance, a partial substitution of nickel in $LiNiO_2$ with Co, Mn, Mg, Fe and Al has been investigated and it is found that such a substitution stabilizes the structure during de insertion of lithium ions.

Another layered compound of interest, $LiMnO_2$, has been widely investigated because, it shows significant technological advantages than $LiCoO_2$ and $LiNiO_2$ systems due to its cost, safety and low toxicity. The theoretical capacity of $LiMnO_2$ is 285mAh/g, and delivers 190 mAh/g in the potential interval between 2.00 and 4.25 V versus Li/Li^+. However, de-lithiation process caused the gradual phase transition of orthorhombic $LiMnO_2$ into tetragonal lithiated spinel compound, which results poor cycleability and hence it requires further optimization to achieve better results [119, 106, 107].

1.4.2.2 Spinel Compounds

Spinel $LiMn_2O_4$ system is most attractive cathode material for secondary lithium batteries, in terms of cost, material abundance, nontoxicity, etc., [119, 126]. The spinel $LiMn_2O_4$ belongs to the cubic system with closed - packed (ccp) oxygen array as shown in fig. 1.6 [127]. The spinels are more tolerant of cycling because the volume variation in the cubic unit cell is less than 1 % in optimum composition limits [128]. The theoretical capacity of $LiMn_2O_4$ is 148 mAh/g and it delivers the specific capacity about 100 to 120 mAh/g by charging up to 4.10- 4.20 V versus Li/Li^+ [119, 129]. The electrochemical Li^+ de- insertion is reversible as given below,

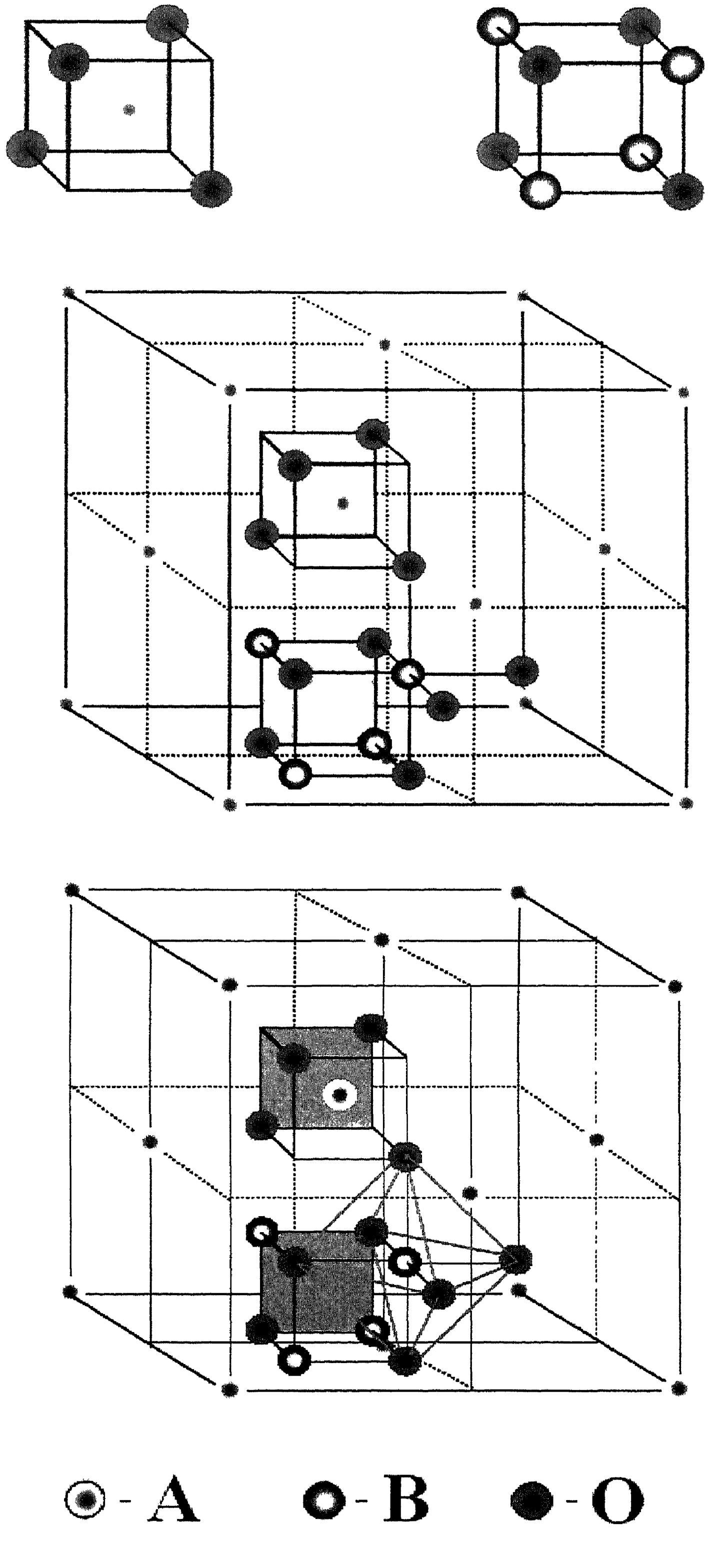


Fig. 1.6 Spinel structure (AB_2O_4).

$$LiMn_2O_4 \rightleftharpoons xLi^+ + Li_{1-x}Mn_2O_4 + x\ e^-$$

and offers 4 V versus lithium in the composition range of $0 < x < 1$ in $Li_xMn_2O_4$. During the charge and discharge process at 4 V range $LiMn_2O_4$ undergo phase transition at $Li_{0.5}Mn_2O_4$, which lead to the minimal unit cell contraction over a wide composition range. Additional lithium ions can also be inserted into $LiMn_2O_4$ in 3 V domain vs. lithium as follows.

$$LiMn_2O_4 + xLi^+ + x\ e^- \rightleftharpoons Li_{1+x}Mn_2O_4$$

Lithium ion insertion into $LiMn_2O_4$ spinel structure results in the transition of cubic $LiMn_2O_4$ into tetragonal $Li_2Mn_2O_4$, which is accompanied by the Jahn – Teller distortion due to the reduction of an average oxidation state from 3.5 to 3.0 [130]. The cycleability of $LiMn_2O_4$ spinel electrode can be improved by over coming the Jahn – Teller effect and it is achieved through the replacement of Mn with different metal ions such as M^+ (Li^+), M^{2+} (Zn^{2+}, Mg^{2+}), M^{3+} (Co^{3+}, Cr^{3+}, Al^{3+}) and M^{4+} (Ti^{4+}) etc. Improvement of an electrochemical performance is not only due to the suppression of Jahn – Teller distortion but also due to the enhancement of structural stability, since M-O (M= Cr and Co) are much stronger than the Mn-O bond. However, the capacity decreases with the increased concentration of substitution metal.

1.4.2.3 Inverse Spinels

The new classes of materials with inverse spinel structure such as $LiNiVO_4$, $LiCoVO_4$, $LiCo_{(1-x)}Ni_xVO_4$ (where x = 0.5), etc., are interesting candidates as cathode materials for lithium ion batteries because of their high voltages of 4.3 - 5.0 V vs. Li/Li^+, with the capacity of 148 mAh/g [131]. However, these inverse spinel cathodes suffer from lower capacity, compared to other potential cathodes and hence, attempts were made to improve an electrochemical characteristics of those materials through the partial replacement of transition metal ions by suitable metal cations [132].

1.4.2.4 Olivine Compounds

Recently, lithiated transition metal phosphates ($LiFePO_4$, $LiCoPO_4$, etc.) exhibit superior thermal and chemical stability, which provide better safety characteristics than those of lithium-ion technology made with other cathode materials [133]. This allows the voltage as well as the specific capacity of these active materials respectively to be 2.1 to 5 Volts and 271 mAh/g [134]. However these materials can not be charged and discharged at high rate. Their key limitation has been extremely low electronic conductivity, which can overcome by doping of metals supervalent to Li^+ [134]. The resulting materials show close to theoretical energy density at low charge / discharge rates and retain significant capacity with little polarization at rates as high as 6,000 $mAhg^{-1}$ [135].

1.4.2.5 Other Oxides

Among the available transition metal oxides, different types of vanadium oxides such as V_2O_5, $Li_6V_{10}O_{28}$, V_2MoO_8, LiV_3O_8, etc., were investigated as cathode materials with an average discharge voltage of ~ 2.5V, but show capacity fading during cycling. Hence, these materials are not exploited further in lithium battery industry [136-138].

1.4.3 Anode Materials

Metallic lithium has been used as negative electrode material for rechargeable lithium batteries, however, it shows an un-favor performance during the reiterative cycles due to its high reactivity [139]. Limitations of lithium metal, as negative electrode, lead to the development of different types of intercalated anode materials as described below.

1.4.3.1 Lithium Metal

Lithium metal has been used as anode with intercalation cathodes, which exhibits an attractive energy densities, excellent storage characteristics and reasonable cycle life. The limitations concern with the use of metallic lithium is it's reactivity with electrolyte during the charge discharge process. Using metallic lithium as anode, caused the formation of passivating layer at the electrode electrolyte interface, which decreases an over all ionic diffusion coefficient. The above effects are responsible for an increased interfacial impedance of the lithium electrode. The presence of passivating layer promotes the growth of dendrites at the electrolyte and electrode interface. Accumulation of dendrites reduces the amount of lithium metal available for cycling and increases the probability of cell failure [139].

1.4.3.2 Insertion Anode Materials

The limitation concern with the metallic lithium is overcome by an insertion material such as lithium metal alloys, carbon materials, etc., which are the best alternate for lithium metal with an improved safety and electrochemical performance.

(i) Metal Alloys

Extensive work has been carried out on the investigation of metal alloys as negative electrode for lithium batteries, due to their high specific capacity and acceptable lithium mobility at room temperature [113, 140]. The advantage of using metal alloys as anode electrode is that the reactivity of lithium towards the electrolyte can be decreased, leading to a reduction of the dendrite formation [141]. However, it exhibits the huge volume change during the intercalation of lithium ions, which is the major negative aspect of such alloy compounds [113].

(ii) Intercalated Carbon Materials

The lamellar structure of graphite allows the intercalation of Li ions between the layers with out major structural changes, which is considered to be an advantage for the reversibility of the reaction. Intercalation of lithium corresponding to LiC_6 (max. intercalation degree) results in only about 10% increase in layer distance [142, 143]. Hence, lithiated graphite is suitable for anode materials and also an alternate to metallic lithium. Apart from that, intercalated carbon materials are emerged as most attractive anode materials due to the following reasons too,

- Low cost and high safety
- The Li insertion potential, which is very close to the one for metallic lithium
- Good cycleability because of high mechanical stability (compared to alloys)
- Higher specific charges

According to the structural aspects, carbon intercalation materials are classified into two categories such as graphite and non-graphite. The schematic representations of graphitic and non-graphite carbonaceous structure are shown in fig. 1.7. Non-graphite carbon materials do not show a crystallographic order, which is further classified into soft and hard.

(iii) Metal Oxide Anodes

Fujifilm Celtec has proposed new negative electrode materials, which are tin based amorphous oxides containing elements of groups III, IV and V, such as boron, gallium, phosphorus, etc., in commercial batteries with excellent electrochemical properties. These materials show high specific capacity, up to 600 $AhKg^{-1}$ and $2200AhL^{-1}$ [144]. Recently, $Li_4Ti_5O_{12}$ intercalation compounds have been extensively investigated as anode material

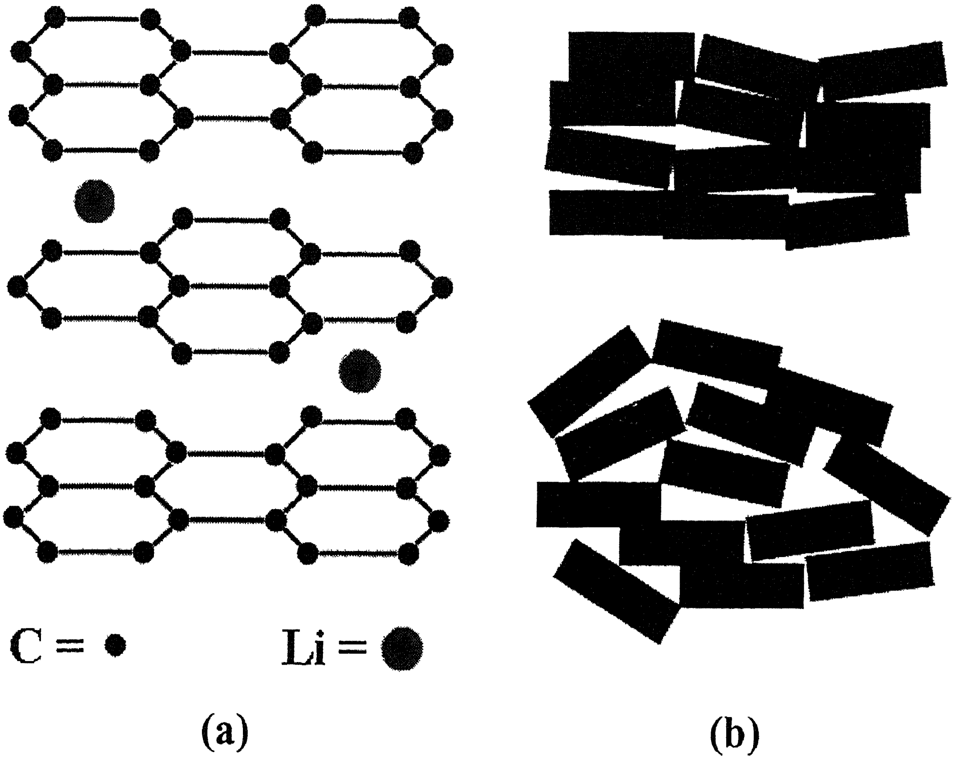


Fig. 1.7 (a) Graphite and (b) non-graphite carbonaceous structure.

for lithium secondary batteries. Intercalation and deintercalation processes accompanied by a very little change in lattice dimension in this compound is as follows,

$$Li_4Ti_5O_{12} + 3Li \rightleftharpoons Li_7Ti_5O_{12}$$

The absence of structural deformation makes $Li_4Ti_5O_{12}$ an almost zero strain electrode material, which exhibits very less capacity fading during the cycling process [145].

1.4.4 Electrolytes

The electrolyte plays an important role in the determination of electrochemical performance of lithium ion cell. Preparation of electrolyte system is usually dissolving the lithium salts in an organic solvent. The lithium salts also have to fulfill certain criteria, such as low price, high performance (i.e., thermally, chemically and electrochemically stable) and non toxic nature. Further, requirements for lithium salts are sufficiently high solubility in dipolar solvents and compatibility with cell compounds. The most frequently used lithium salts are $LiClO_4$, $LiAsF_6$, $LiBF_4$, $LiPF_6$ and $LiNi(SO_2CF_3)_2$ [146]. The choice of proper electrolyte is an important task in the lithium ion battery technology. Some important criteria that the electrolytes have to fulfill are given below

- Thermodynamically stable.
- Higher ionic conductivity, which minimize the internal resistance.
- Good compatibility with the other components of the cell
- Low cost, reliable, safety and minimum environmental impact.

The most recent development in the lithium ion battery technology is directly to the replacement of liquid electrolyte with polymer membrane capable of operating both as the separator as well as electrolyte [147]. According to the chemical and physical nature electrolytes used in lithium battery technology are classified as follows.

1.4.4.1 Liquid Organic and Inorganic Electrolytes

Liquid organic electrolytes consisting of pure or mixture of appropriate organic solvents with a lithium salt dissolved in it. In particular, organic carbonates such as propylene carbonate (PC), ethylene carbonate (EC), dimethyl carbonate (DMC) and diethyl carbonate (DEC) are in the center of interest [148].

1.4.4.2 Polymer Solid Electrolytes

Much interest has been devoted to solving a safety problem on rechargeable lithium batteries concern with the usage of liquid electrolyte. Hence, research on non-liquid electrolyte systems, such as gel-polymer electrolyte, polymer electrolyte and nanocomposite polymer electrolyte, have been performed. Also, it acts as a separator as well as a medium for ion transport between anode and cathode during charge / discharging process [149]. Numerous polymer electrolytes have been developed as well as characterized and they are based on polyethylene oxide (PEO), polyacrylonitrile (PAN), Polymethyle methacrylate (PMMA), polyvinyl chloride (PVC) and polyvinylidene fluoride (PVdF) [150]. All the above mentioned polymer based electrolytes are categorized as (i) polymer solid electrolytes (ii) plasticized or gel polymer solid electrolytes [151] and (iii) nano composite polymer solid electrolytes [152, 153].

1.4.4.3 Solid Electrolytes (SEs) or Superionic Solids (SICs) or Fast Ion Conductors (FICs)

Much effort has made for the development of lithium based fast ion conducting solids to produce all solid state batteries with high safety and reliability, special attention towards the development of thin film batteries. Although two types of solid inorganic electrolyte, crystalline and glass have been investigated, most of recent progresses have focused on glass electrolytes due to many advantages over crystalline solids such as isotropic ionic conduction, no grain boundaries, easy fabrication, etc. The ionic conductivity of glassy materials is, in general, higher than that of the corresponding crystals [154]. For example, in $AgI–Ag_2O–P_2O_5$ system, the ambient temperature conductivity of glasses is 10^{-2} S cm^{-1}, which is higher by 1–2 orders of magnitude than the conductivity of crystals. Hence, wide ranges of lithium ion conducting glassy electrolytes are investigated for the battery applications. However, it has not used in the commercial battery system, because solid electrolyte has not completely satisfied the requirements for practical application such as high ionic conductivity as well as chemical, thermal and electrochemical stability [155].

1.4.5 Other Components

1.4.5.1 Separator: The separator plays major role in lithium batteries as following ways (a) to avoid the direct contact of an anode with cathode while allowing the free mass transfer of the electrolyte and (b) Shutter action to stop the mass transfer in the case of accidental heat generation [156]. The important characteristics of the separator are given below,

(i) The materials should be soft and flexible.

(ii) The materials should be stable (chemically and physically) for a long time.

1.4.5.2 Binders: Binders are used for the fabrication of composite electrodes using active materials. Two types of binders are widely used for this purpose and they are (a) polyvinylidenefluoride (PVdF) and (b) olefin elastomer.

1.5 Issues and Challenges for Cathode Materials

For an application point of view an improvement in the rate capabilities of lithium batteries are required. Also, it is well established that the limitations related with the rate capabilities are due to the mass-transfer effects caused by the slow solid state diffusion of Li^+ with in the electrode materials [157]. The lithium-ion battery performance is dramatically affected by the particle size of the intercalation materials used to prepare the electrodes. Specifically, when large particles were used, the experimental capacity of the electrode was significantly lower than the theoretical capacity. Capacity is lost when large particles are used to make the electrode because concentration polarization occurs within the particle before the entire capacity can be utilized [158].

In addition to that major issue in the lithium battery technology is capacity fading, which is mainly accompanying with the structural deformation due to the insertion and deinsertion of lithium ions during the electrochemical cycles. This non uniform dimensional change occurs most of the insertion materials [159]. The main reason for the poor electrochemical performance including capacity fading in $LiCoO_2$, $LiMn_2O_4$ and $LiNi_{0.5}Co_{0.5}VO_4$ cathode materials are given below.

$LiCoO_2$: In $Li_{1-x}CoO_2$ the structural stability is maintained only for a limited composition range of $0 < x > 0.5$. Excess removal of Li ions (i.e., $x > 0.5$) lead to the structural change from hexagonal to tetragonal and caused the capacity fade [160].

$LiMn_2O_4$: *Dissolution of Mn^{3+}*- at discharged state, the Mn^{3+} at the surface may disproportionate as, $Mn^{3+} \rightarrow Mn^{4+}(solid) + Mn^{2+}(Solution)$, where Mn^{2+} ions from the disproportionation dissolve in the electrolyte solution [161].

Jhan-Teller effect- Lithium insertion into $LiMn_2O_4$ results in the transition of the structure from cubic to tetragonal $Li_2Mn_2O_4$, which is accompanied by a Jahn- teller distortion due to the reduction of the average oxidation state of Mn from 3.5 to 3.0. [162]

$LiNi_{0.5}Co_{0.5}VO_4$: Harmful interaction of $LiNi_{0.5}Co_{0.5}VO_4$ with the electrolyte at the surface deteriorates the performance of the cathode materials. Also, caused the huge heat generation, which lead to the explosion [163].

In order to face the above challenges, following effort has made for the lithium based cathode materials and succeeded to meet the requirement for an enhanced lithium battery technology.

1.5.1 Nano Crystallinity in Cathode Materials

In order to enhance the rate capabilities, tremendous effort has been made through out the world; as a result, nanostructued cathode materials mitigate the problem of slow diffusion of lithium ions during the charge and discharge process [157, 158, 164-167]. Nanoscale materials are simply defined as any material with a physical length scale in at least one dimension less than 100 nanometers (nm), corresponding to either the diameter of a particle, thickness of a film layer or fiber, or the average grain size in a poly crystalline materials [168]. When the physical dimensions of a material are below this threshold, its physical properties are greatly altered including mechanical, optical, electronic and magnetic, etc. [169].

The use of nanomaterials for energy storage and conversion in electrochemical power sources is a rapidly growing field with tremendous potential [170]. Even though the use of nano materials in power sources is not a new, the science at the nano scale has still not been fully exploited [171-173]. The challenges and opportunities for nano science in power sources lie in the understanding, control and fabrication of complex structure at nano scale [174-176]. An improved rate capacity and cyclic ability are obtained in secondary lithium batteries while using nano structured cathode materials. In addition to small size, narrow particle size distribution also an important [173]. Hence, nanocrystalline materials contribute to improved batteries in several ways as follows,

Small Particle Size: The size and surface area of nanocrystalline materials allow faster, more efficient diffusion of lithium ions, leading to enhanced power and greater accessible capacity. These stable and robust materials lead to superior cycling performance.

Uniform Morphology: The morphology of nanocrystalline materials allows electrode fabrication with exceptionally smooth and regular layers, which enable to use thinner separator membranes without danger of breakage.

Crystallinity: Single-crystal grains of active material show greater stability through multiple charging cycles. Without this stability, the microstructure of a polycrystalline grain is damaged with repetitive cycles, leading to degraded capacity over time.

For these reasons, nanocrystalline cathode active materials in lithium rechargeable batteries are expected to create a new generation of products offering higher power, capacity and cycling behavior than the products on the market today [177]. For example nano sized V_2O_5 (~94nm) exhibits the capacity of 410 mAh/g, which is very close to the theoretical value of 420 mAh/g [178]. Apart from the above, nanocrystalline $LiCoO_2$, $LiMn_2O_4$, $LiNiVO_4$, etc., also synthesized and showed an enhanced electrochemical performance [178, 179].

1.5.2 Metal Ion Doping in Cathode Materials

The more efficient rechargeable lithium battery can be achieved only by the zero strain cathode materials. Many attempts have been made to stabilize the initial structure of cathode materials (such as $LiCoO_2$, $LiMn_2O_4$, etc.) during the charge and discharge process by doping the metal ions such as Al, Mg, Co, etc. in cation sites and stabilized the structure, which showed an improved electrochemical performance (capacity retention) than the bare cathode materials, however it exhibits initial capacity loss [180-184].

1.5.3 Surface Modified Cathode Materials

In 1996, G. G. Amatucci and J. M Tarascon were patented that the coating of Al_2O_3, B_2O_3 and SiO_2 on $LiMn_2O_4$ to suppress Mn dissolution from $LiMn_2O_4$ [185]. They proved that the surface modification of cathode materials suppresses the structural change during charge and discharge process and hence, improves the performance of batteries. The coatings prevent the direct contact with the electrolyte solution, suppress phase transition, improve the structural stability, and decrease the disorder of cations in crystal sites [186]. Overall, these studies revealed that the physical morphology of the coating materials significantly influenced the electrochemical properties. Hence, numerous research works has been carried out on the surface modification of cathode materials using inert oxides to achieve zero strain cathode materials [186]. Recently, surface modifications of cathode materials using metals, metal oxides (MgO, Al_2O_3, SiO_2, etc.), metal phosphates ($AlPO_4$, $LaPO_4$, $CePO_4$, etc.) and intercalation materials ($LiMn_2O_4$ and $LiCoO_2$) [187-190] have been proved as a successful route for improving the cycling stability.

1.6 Review of Literature and Current Status of Surface Modification

Recent research findings confirm the importance of surface modifications for the structural stability of cathode materials for their enhanced electrochemical performance. Surface modification of the cathode materials including $LiCoO_2$, $LiNiO_2$, $LiMnO_2$, $LiMn_2O_4$ and $LiNi_{0.5}Co_{0.5}VO_4$ is performed by coating of various oxides such as MgO, Al_2O_3, SiO_2, TiO_2, ZnO, SnO_2, ZrO_2 and metal phosphates such as, $AlPO_4$, $FePO_4$, $CePO_4$

and other materials ($LiCoO_2$ and $LiMn_2O_4$). Further more, surface modifications of cathode materials with Ag thin layer also come into the picture in order to enhance their electronic properties. Modification by coating is an important method to achieve improved electrochemical performance and the latest progress is reviewed here [190-193].

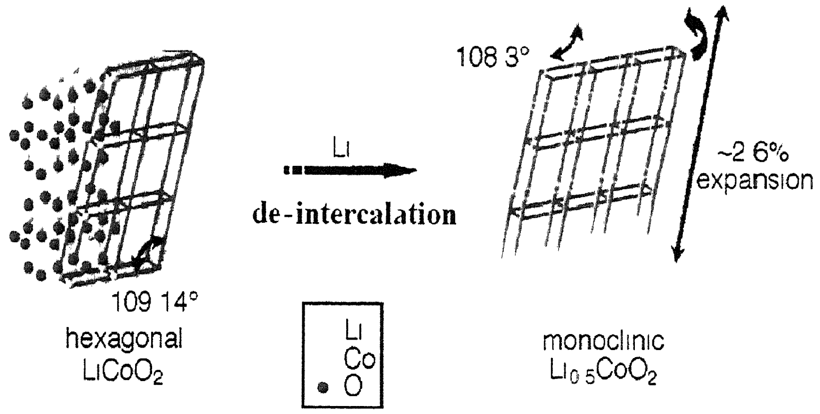
1.6.1 Metal Coating

High lithium ion and electronic conductivity are essential for the better performance of cathodes in rechargeable lithium batteries [194]. In order to enhance the electronic conductivity as well as full electrode utilization, it is necessary to add an electronically conductive phase such as carbon to the cathode materials. Recently, J. T. Son et. al., found a new approach that the surface coating of cathode materials with Ag metal and enhanced the cell performance [195-196].

1.6.2 Metal Oxide Coating

Wide range of metal oxides such as MgO, Al_2O_3, SiO_2, TiO_2, ZnO, SnO_2, ZrO_2, B_2O_3, etc., were coated over $LiCoO_2$, $LiMn_2O_4$ and $LiNi_{0.5}Co_{0.5}VO_4$ related compounds to improve the cycling capacity [197-216]. Recently, Cho *et. al.,* reported that the $LiCoO_2$ coated with metal oxides having larger fracture toughness have better cycling behavior also concluded that ZrO_2-coated $LiCoO_2$ was the best among the other metal oxides Al_2O_3, TiO_2, B_2O_3, which exhibit the lower fracture toughness than ZrO_2. Deintercalation process of the bare and coated $LiCoO_2$ structure is schematically shown in fig. 1. 8. The cycle-life performances for ZrO_2, Al_2O_3, TiO_2, B_2O_3 coated, and uncoated (bare) $LiCoO_2$ are shown in fig. 1.9 [197-210]. Also, coating of Co_3O_4 thin layer over $LiMn_2O_4$ spinel completely block the Mn^{3+} dissolution enhanced the cyclic performance. Consequently, marked improvement of electrochemical performance of electrode materials including reversible

Without coating



With coating

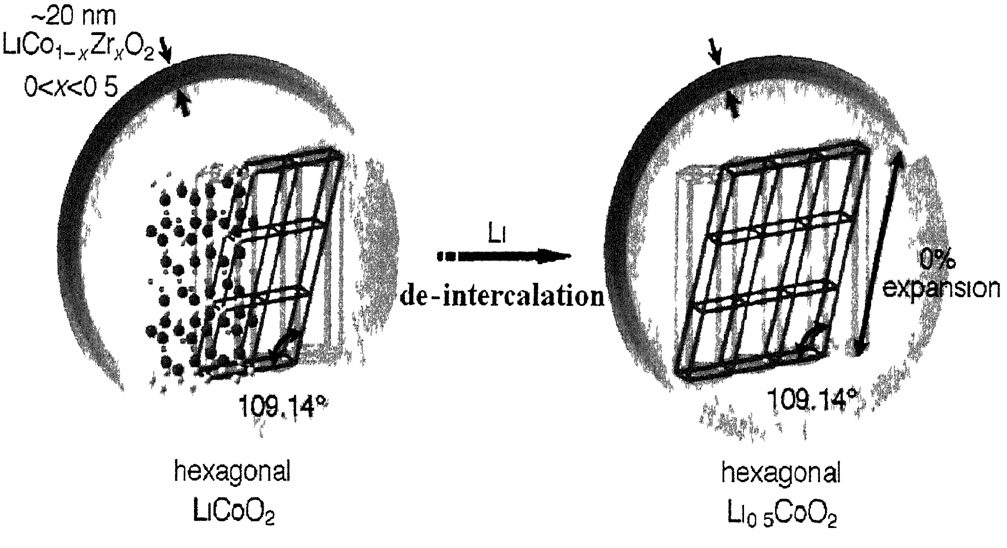
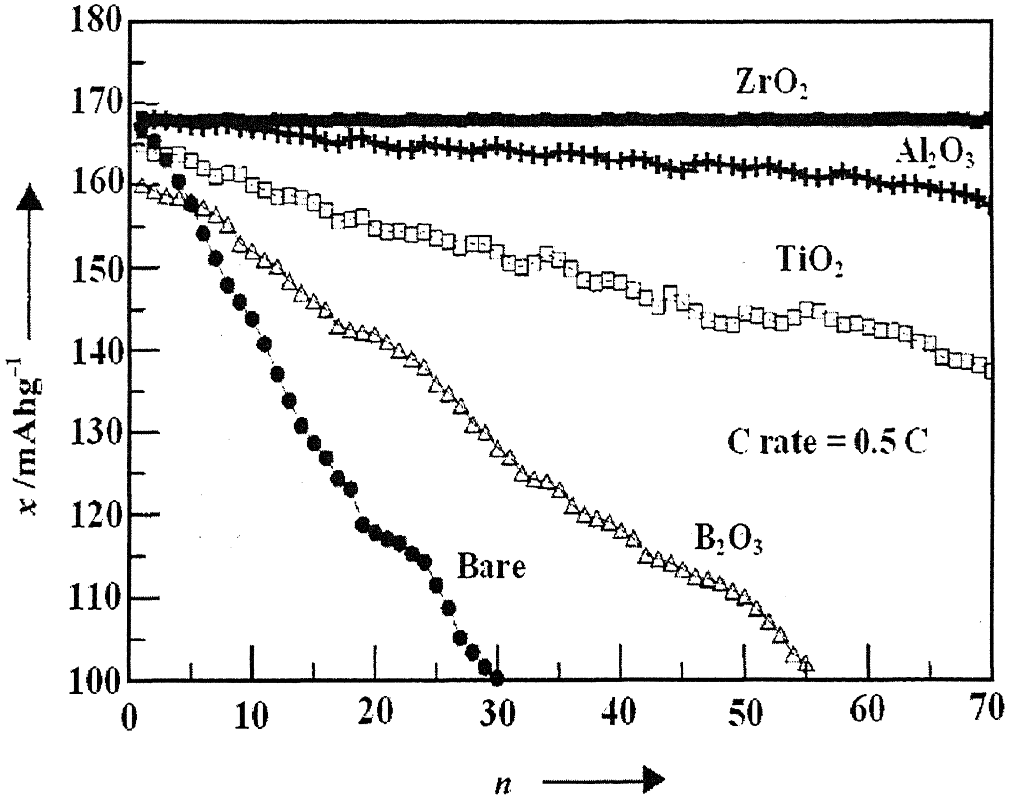


Fig. 1.8 Schematic representation of the de- intercalation process of bare and coated $LiCoO_2$ structures.



(χ – discharge capacity, n – number of cycles)

Fig. 1.9 Cycle life performances of ZrO_2, Al_2O_3, TiO_2, and B_2O_3 coated and uncoated $LiCoO_2$ (bare) [198].

capacity, coulombic efficiency in the first cycle, cycling behavior, rate capability and overcharge tolerance has been achieved [211-215]. $LiNi_{0.5}Co_{0.5}VO_4$ cathode material exhibits higher voltage than $LiCoO_2$ and $LiMn_2O_4$ but its harmful interactions with electrolyte at the surface, hinders its practical use in Li-ion cells. Coating of metal oxides is an effective way to improve its performance. L-Q. Mai et. al., has reported SiO_2 coating over $LiNi_{0.5}Co_{0.5}VO_4$ powders noticeably increasing the specific capacity and cycling performance [163].

1.6.3 Metal Phosphate Coating

Recently, it is found that metal phosphate coated cathode powders ($LiCoO_2$ and $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$), improved the cycling property [216, 226]. J. Kim *et al.*, reported that the $LiCoO_2$ coated with different metal phosphates such as $AlPO_4$, $FePO_4$, $CePO_4$, etc., have better cycling behavior also reported that $AlPO_4$, coating with a particle size and coating thickness <3 nm and <10-15 nm, showed the best electrochemical performance [219]. Coating of metal phosphates behave as a protective layer and is quite effective to prohibit the chemical reactions between the electrolyte and the cathode [217]. As a result, the $AlPO_4$ coated cathodes does not exhibit thermal runaway, which controls the overall safety of the Li-ion cells, and is quite effective in improving the capacity retention over the bare cathodes [220-221].

In conclusion, further directions are suggested for the surface modification of electrode materials. With further understanding of the effects of the surface structure of cathode materials on lithium intercalation and de-intercalation, better and / or cheaper cathode materials from surface modification will come up in the near future.

1.7 Present Work

The literature survey in the field of cathode materials for lithium battery technology inspired to develop the various wet chemical processes (combustion) for the synthesis of nanocrystalline cathode materials. Hence, in the present investigation $LiCoO_2$, $LiMn_2O_4$ and $LiNi_{0.5}Co_{0.5}VO_4$ cathode systems are taken for the synthesis by combustion process using various fuels as well as fuel combinations. Also, present investigation deals with the optimization of suitable fuel and synthesis conditions for the preparation of cathode powders with desired properties, i.e., lower crystallite size, pure phase and absence of organic residuals. The combustion process for the synthesis of nanocrystalline cathode materials was monitored using various techniques such as FTIR, XRD, SEM, TG/DTA and TEM

Apart from that, from the literature, it is found that coating of various metal oxides such as ZrO_2, Al_2O_3, TiO_2, and B_2O_3 over cathode particles enhance the electrochemical performance. Also, it is found that there is a remarkable relation between the fracture toughness and capacity retention. The invariability of c-axis dimension correlates extremely well with the fracture toughness of the coated oxides, in the order $ZrO_2 > Al_2O_3 > TiO_2 > B_2O_3$. Also, G. T. K. Fay et. al., investigated that the oxides of the lanthanide series possess excellent thermal stability, increase the maximum current carrier capacity and support high voltages. Dy_2O_3 is well known material in lanthanide series with high transformation toughness, which is also investigated as an alternate to ZrO_2. Hence, in the present investigation, Dy_2O_3 has selected for the surface modification of nanocrystalline cathode materials ($LiCoO_2$, $LiMn_2O_4$ and $LiNi_{0.5}Co_{0.5}VO_4$). Novel polymeric resin route using polyacrylic acid (PAA) and ethylene glycol (EG) was first investigated for the surface modification of cathode materials by nano-layer of Dy_2O_3.

Also, surface the modifications of other ceramic particles are carried out for a myriad of reasons such as to protect the core materials from aggregation and acid leaching, enhance the structural, tuning the optical properties, functionalizing surface (coating of SiO_2, Citric acid, etc., over Fe_2O_4 for biocompatibility), etc. Engineering the surface of nanostructured particles enhances the physical and chemical properties over their individual counterparts and found to have many applications, including analytical chemistry (chromatography), separation technology (ion exchange), ceramic industries, biochemistry, medicine, etc. Hence, the present investigation deals with the synthesis of two different types of metal oxides ($NiFe_2O_4$ and ZrO_2) and their surface modification (respectively with SiO_2 and MoO_3) for different applications.

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