Chapter 1

Introduction

The present chapter gives a general introduction to the subject matter contained in this thesis. It includes a chronological description of the development of batteries, commonly used battery terminology, description of the lithium battery concept, the significance of the materials selected for the present investigations and a brief description of the various synthesis and characterization techniques employed.

1.1 A Brief History of Development of Batteries

Among all the power sources that man has invented, batteries find a commendable position owing to their versatile applications ranging from medical implants to space applications. Aiming at better power and life for batteries, researchers all over the globe are searching for newer and newer materials for battery developments. The invention of the battery in 1800 paved the way for major advances in the theories of electric current and electrochemistry. This invention resulted in the rapid development of both science and technology, making the 19th
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century, the age of electricity. Italian physicist Alessandro Volta gave the first authenticated description of an electrochemical cell. It was the introduction of telegraphy that increased the demand of reliable commercial batteries, capable of sustaining a substantial flow of electric current, with out much loss in cell voltage.

![Fig.1.1 The Voltaic pile](image)

Following the earlier work of his compatriot Luigi Galvani, Volta performed a series of experiments on electrochemical phenomena during the 1790s. By about 1800 he had built his simple battery, which later came to be known as the “Voltaic Pile” (Figure-1.1) This device consisted of alternating zinc and silver disks separated by layers of paper or cloth soaked in a solution of either sodium hydroxide or brine.

Experiments performed with the voltaic pile eventually led Faraday to derive the quantitative laws of electrochemistry (about 1834). These laws, which established the exact relationship between the quantity of
electrode material and the amount of electric power desired, formed the basis of modern battery technology. Various commercially significant primary cells were produced on the heels of Faraday's theoretical contribution. In 1836 John Frederic Daniel, a British chemist, introduced an improved form of electric cell consisting of copper and zinc in sulfuric acid. The Daniel cell was able to deliver sustained currents during continuous operation far more efficiently than Volta's device. Further advances were effected in 1839 by William Robert Grove with his two-fluid primary cell consisting of amalgamated zinc immersed in dilute sulphuric acid, with a porous pot separating the sulphuric acid from a strong nitric acid solution containing a platinum cathode. The nitric acid served as an oxidizing agent, which prevented voltage loss resulting from an accumulation of hydrogen at the cathode. The German chemist Robert Wilhelm Bunsen substituted inexpensive carbon for platinum in Grove's cell and thereby helped to promote its wide acceptance.

In 1859 Gaston Plante (1) of France invented a lead-acid cell, the first practical storage battery and the forerunner of the modern automobile battery. Plante's device was able to produce a remarkably large current, but it remained a laboratory curiosity for nearly two decades. Georges Leclanché's prototype of the zinc–manganese dioxide system paved the way for the development of the modern primary cell. The original version of the Leclanché cell was "wet," as it had an electrolyte consisting of a solution of ammonium chloride. The idea of employing an immobilized electrolyte was finally introduced in the late
1880s leading to the launching of dry-cell industry, which continues to flourish, even today. The invention of alkaline electrolyte batteries (specifically storage batteries of the nickel–cadmium and nickel–iron type) between 1895 and 1905 provided systems that could furnish much-improved cycle life for commercial application. The 1930s and '40s saw the development of the silver oxide–zinc and mercuric oxide–zinc alkaline cells, systems that provided the highest energy yet known per unit weight and volume.

Shortly before the Second World War mercury primary cell invented by Samuel Ruben was introduced in the market. At first, mercury cells were expensive, and due to their small size, they weren’t used in many applications. With the invention of the transistor in the 1950s, mercury cells found their way into hearing aids and transistor radios. In the 1950s, the alkaline manganese cell was further refined. At the same time, small cameras with built in flash units were developed that required high power in a small package. Alkaline cells worked in this and other new consumer applications so well that, they gained tremendous popularity. They remain one of the largest portions of revenue for portable battery sales to this day. Development of the nickel metal hydride rechargeable cell began in the 1970s, but it was a long time before hydride alloys could perform well enough to begin production. Since the late 1980s, the performance of nickel metal hydride cells has steadily improved, and there may still be room for further performance enhancement.
Since mid-century, advances in construction technology and the availability of new materials have given rise to smaller, yet more powerful batteries suitable for use in a wide array of portable equipments. The latest developments in batteries, both primary and rechargeable, have centered on the use of lithium. Lithium is the lightest of all metals, has the greatest electrochemical potential, and provides the maximum energy. Lithium primary batteries were popularized in the 1970s and 80s. They have replaced the alkaline cell in most photovoltaic applications and are better suited to military and scientific applications than any other type. Attempts to make lithium rechargeable batteries go back to the 1980s. Problems with safety prevented the commercial use of the technology at that time. Finally rechargeable cells that use lithium metal were abandoned. Investigations were shifted to the use of lithium ions containing oxides and phosphates such as LiMn$_2$O$_4$, LiCoO$_2$, LiFePO$_4$, LiNiPO$_4$ etc. Since then lithium-ion batteries have become the most popular choice for use in high tech applications such as cellular phones and laptop computers.

What's next? Lithium polymer batteries are already being produced in a small scale, and offer the high performance of lithium combined with unparalleled packaging flexibility. Growing demands for development and introduction of battery-powered electric vehicle to keep cleaner environments have greatly stimulate the research on lithium insertion materials for high-volume, high-energy density, lithium ion batteries.
1.2 Battery

A battery is a device that converts the chemical energy contained in its active materials directly into electric energy by means of an oxidation-reduction reaction. In the case of rechargeable system, the battery is recharged by a reversal of the process. This involves the transfer of electrons from one material to another through an electric circuit. While the term "battery" is often used, the basic electrochemical unit being referred to as the "cell" (A cell is the basic electrochemical unit providing a source of electrical energy by direct conversion of chemical energy. The cell consists of an assembly of electrodes, separators, electrolyte, container and terminals) A battery consists of one or more of these cells, connected in series, parallel or the combinations of these, depending on the desired output voltage and capacity. Batteries, therefore, are capable of having higher energy conversion efficiencies.

1.3 Basic Components of an Electrochemical Cell.

Each cell consists of a positive and a negative electrode separated by an electrolyte solution containing dissociated salts (Figure1.2), which enable ion transfer between the two electrodes [2]. Once these electrodes are connected externally, the chemical reactions proceed in tandem at both the electrodes, thereby liberating electrons and enabling the current to be trapped by the user. The electrode materials and electrolyte are chosen and arranged so that sufficient electromotive force (voltagge) and electric current (amperes) can be developed between the terminals of a battery to operate electrical gadgets. Since
an electrode contains only a limited number of units of chemical energy convertible to electrical energy, it follows that a battery of a given size has a certain capacity to operate devices and will eventually become exhausted. The active parts of a battery are usually encased in a box (or jacket).

![Electrochemical operation of a cell](image)

**Fig.1.2.** Electrochemical operation of a cell

Battery usefulness is limited not only by capacity but also by how fast current can be drawn from it. The salt ions chosen for the electrolyte solution must be able to move fast enough through the solvent to carry chemical matter between the electrodes in accordance with the rate of electrical demand. Battery performance is thus limited by the diffusion rates of internal chemicals as well as by capacity. The voltage of an individual cell and the diffusion rates inside it are both reduced if the temperature is lowered from a reference point. If the
temperature falls below the freezing point of the electrolyte, the cell will usually produce very little useful current and may actually change internal dimensions, resulting in internal damage and diminished performance even after it has warmed up again. On the other hand, if the temperature is raised deliberately, faster discharge can be sustained, but this is not generally advisable because the battery chemicals may evaporate or react spontaneously with one another, leading to early failure. Beyond the technical factors so far discussed, it must be recognized that commercially available batteries are designed and built with market factors in mind. The quality of materials and the complexity of electrode and container design are reflected in the market price sought for any specific product. As new materials are discovered or the properties of traditional ones improved, however, the typical performance of even older battery systems sometimes improves by large percentages.

Batteries are divided into two general groups: (1) primary batteries and (2) secondary, or storage, batteries. Primary batteries are designed to use until the voltage is too low to operate a given device and then discarded. Secondary batteries have many special design features, as well as particular materials for the electrodes, that permit them to be reconstituted (recycled). After partial or complete discharge, they can be recharged to their original state by dc voltage and current. While this original state is usually not restored completely, the loss per cycle in commercial batteries is only a small fraction of 1 percent even under varied conditions.
1.4 Principles of Operation of an Electrochemical Cell.

The anode of an electrochemical cell (Figure 1.2) is usually a metal that is oxidized (gives up electrons) at a potential between 0.5 volt and about four volts above that of the cathode. The cathode generally consists of a metal oxide or sulfide that is converted to a less-oxidized state by accepting electrons, along with ions, into its structure. A conductive link via an external circuit (e.g., a lamp or other device) must be provided to carry electrons from the anode to the cathode. Sufficient electrolyte must be present as well. The electrolyte consists of a solvent (water, an organic liquid, or even a solid) and one or more chemicals that dissociate into ions in the solvent. These ions serve to deliver electrons and chemical matter through the cell interior to balance the flow of electric current outside the cell during cell operation. The fundamental relationship of electrochemical cell operation put forth by Faraday in 1834 is that for every ampere that flows for a period of time, a matching chemical reaction or other change must take place. The extent of these changes is dependent on the molecular and electronic structure of the elements comprising the battery electrodes and electrolyte. Secondary changes may also occur, but a primary pair of theoretically reversible reactions must take place at the electrodes for electricity to be produced. For a cell with electrodes of zinc and manganese dioxide (e.g., the common flashlight dry cell), one finds that a chemical equivalent of zinc weighs 32.5 grams and that of manganese dioxide about 87 grams. The discharge of one equivalent weight of each of these electrodes will cause 32.5 grams of zinc to dissolve in the electrolyte to produce Zn ions and 87 grams of manganese...
dioxide to change into a different oxide containing more hydrogen and zinc ions. Some of the electrolyte also will be consumed in the reaction. One chemical equivalent of each electrode produces one faraday, or 96,500 coulombs of current equal to 26.8 amperes per hour. There are a large number of elements and compounds from which one can select potentially useful combinations for batteries.

1.5 Battery terminology

The following are the commonly used terms used while dealing with batteries [2,3].

1.5.1 Active material

Active materials are the chemically reactive materials at the positive or negative electrodes that engage in the charge and discharge reactions.

1.5.2 Ampere-hours

It is a measure of cell capacity. It is the product of current in amperes and by the discharge time.

1.5.3 The anode

The electrode at which oxidation reaction occurs is the anode. In secondary cells, either electrode may become the anode, depending upon direction of current flow.

1.5.4 The cathode

An electrode at which reduction reaction occurs is the cathode. The positive electrode is the cathode on discharging and the negative electrode is the cathode on charging.
1.5.5 Electrolyte

The medium for movement of ions within the cell is the electrolyte.

1.5.6 Electrodes

Parts of the cell where the electrochemical reaction occurs are called electrodes. They normally consist of the active material and the current collector.

1.5.7 Theoretical capacity

The ability of the battery or cell to supply current to an external circuit is termed as the theoretical capacity. It is determined by the amount of active materials in the cell. It is expressed as the total quantity of electricity involved in the electrochemical reaction and is defined in terms of coulombs or ampere-hours.

1.5.8 Cycle

In a rechargeable battery a cycle consists of a charge followed by a discharge.

1.5.9 Duty cycle

The pattern for using a battery including charge, overcharge, rest and discharge is commonly known as duty cycle.

1.5.10 Theoretical energy density

The energy stored in a cell or battery as a function of the weight or volume is termed as energy density [2,4]. It is often expressed as the ratio of its power to weight or size. The preferred terminology for this
ratio on weight basis is Watt-hour/kilogram (Wh/kg) or on volume basis is Watt-hour/litre (Wh/L)

\[
\text{Energy density} = \frac{1000E}{W} \text{Wh/kg}, \quad \text{where } W \text{ is the equivalent weight of anode and cathode and } E \text{ the cell emf which is related to free energy, } \Delta G, \text{ of the cell reaction by}
\]

\[
\Delta G = -nEF
\]

where \(n\) is the number of electrons passed per mole of reactant and \(F\) is Faraday constant.

1.5.11 Shelf life

The length of acceptable performance received from a battery, measured in years or in charge/discharge cycles.

1.5.12 Open circuit voltage

The voltage of a battery with no load applied to it is referred to as Open circuited voltage.

1.5.13 Operating voltage

Voltage of a battery under load is its operating voltage.

1.5.14 Primary cell

A cell designed to be used only once, and then discarded.

1.5.15 Secondary cell

A cell capable of repeated use as it uses chemical reactions that are reversible, i.e., supplying electrical current to recharge the cell may restore the discharge energy.
1.6 Different Nomenclature Representing Voltage of a Battery

a. The theoretical voltage is a function of the anode and cathode material parameter, the composition of the electrolyte and the temperature (usually stated at 25°C).

b. The open-circuit voltage is the voltage under a no-load condition and is usually a close approximation of the theoretical voltage.

c. The closed-circuit voltage is the voltage under a load condition.

d. The nominal voltage is one that is generally accepted as typical of the operating voltage of the battery as, for example, 1.5 V for a zinc-manganese dioxide battery.

e. The working voltage is more representative of the actual operating voltage of the battery under load and will be lower than the open-circuit voltage.

f. The average voltage is the voltage averaged during the discharge.

g. The midpoint voltage is the central voltage during the discharge of the cell or battery.

h. The end or cut-off voltage is designated as the end of the discharge. Usually it is the voltage above which most of the capacity of the cell or battery has been delivered. The end voltage may also be dependent on the application requirements.
1.7 Thermal Runaway

The loss of the gas barrier in one or more cells of a vented nickel-cadmium battery can lead to thermal runaway [1]. Loss of this function allows oxygen, generated in overcharge, to reach the negative plate and recombine on it. This generates heat. The temperature increase, which follows, causes the internal cell voltage to decrease. Charge current then increases exponentially to increase cell voltage to match the charger voltage. Thermal runaway occurs with the use of a voltage-regulated charge source on a battery containing cells with a failed gas barrier. Thermal runaway begins when the failed cells approach overcharge following recharge. The over-charge current may reach a minimum and then gradually increases. Voltage inequities may exist at this point unless all cells are experiencing similar recombination (gas barrier damage). Oxygen recombination heats up, and begins to increase the temperature of the failed cell or cells and thus their neighboring cells also unless the battery is effectively air-cooled. The resulting temperature increase, however, proceeds slowly due to the large thermal mass involved. It may take 2 to 4 hours of (nearly) consecutive overcharging for a cell to reach boiling temperature. If the boiling phase continues long enough, or is repeated, and the failed cell becomes dry, large inequities in cell voltage will appear. The voltage across the cell that has boiled dry will increase, thereby decreasing the charge current and the voltage across the cells that are still wet with electrolyte. The next event probably will be internal short-circuiting of the dried-out cell due to very high temperatures and voltage at the last remaining damp spots with consequent burning of the
electrical separator insulation. The over-charge current then increases sharply due to cell loss, and the process repeats itself with the next cell to go dry. Because of extensive heating and boil away times, thermal runaway may go undetected for many hours following the onset of gas barrier failure if the use of the system is not consecutive or continuous. This can confuse the perceived connection between the cause of the gas barrier damage and the resultant thermal runaway.

1.8 Memory Effect in Batteries

The gradual reduction of both power and capacity of a battery with cycling in a battery especially in Ni-Cd cell is an added disadvantage. This effect, sometimes referred to as ‘memory effect,’ ‘fading,’ or ‘voltage depression,’ results from charging following repetitive shallow discharges where some portion of the active materials in the cell is not used or discharged, such as in a typical engine-start use [1]. This effect is noticed when the previously undischarged material is eventually discharged. The terminal voltage during the latter part of that full discharge may be lowered a little (i.e. a depression of voltage). The total capacity is not reduced, however, if the discharge is continued to the lower voltages. This effect is completely reversible by a maintenance cycle consisting of a thorough discharge followed by a full and complete charge-overcharge.

1.9 Classification of Batteries

Electrochemical cells and batteries are identified as primary or secondary depending on their capability of being electrically recharged. Primary batteries are not capable of being easily or effectively recharged electrically and, hence, are used once and discarded. Many primary cells in
which there are no liquid electrolytes are termed ‘dry cells.’ The primary battery is a convenient, usually inexpensive, lightweight source of packaged power for portable electronic and electric devices, lighting, photographic equipments, toys, memory backup, and a host of other applications, giving freedom from utility power. The general advantages of primary batteries are good shelf life, high energy density at low to moderate discharge rates, little, if any, maintenance, and ease of use. Although large high capacity primary batteries are used in military applications, signaling, standby power, and so on, the vast majority of primary batteries are the familiar single cell cylindrical and flat button batteries or multicell batteries using these component cells.

![Fig. 1.3 Classifications of Battery](image-url)
1.9.1 Comparison Data among Various Lithium based Batteries

<table>
<thead>
<tr>
<th>Battery</th>
<th>LiFePO₄</th>
<th>LiCoO₂</th>
<th>LiMn₂O₄</th>
<th>LiNiPO₄</th>
<th>Li(NiCo)O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Safety</td>
<td>Safest</td>
<td>Not stable</td>
<td>Acceptable</td>
<td>Safe</td>
<td>Not stable</td>
</tr>
<tr>
<td>Environmenta l Concern</td>
<td>Most Environmentally friendly</td>
<td>Very dangerous</td>
<td>Green</td>
<td>Environmentally friendly</td>
<td>Very dangerous</td>
</tr>
<tr>
<td>Cycle life</td>
<td>Excellent</td>
<td>Acceptable</td>
<td>Acceptable</td>
<td>Better</td>
<td>Acceptable</td>
</tr>
<tr>
<td>Power/weight density</td>
<td>Acceptable</td>
<td>Good</td>
<td>Acceptable</td>
<td>Acceptable</td>
<td>Best</td>
</tr>
<tr>
<td>Long term cost</td>
<td>Most Economic</td>
<td>High</td>
<td>Acceptable High</td>
<td>High</td>
<td>High</td>
</tr>
<tr>
<td>Temperature Range</td>
<td>Excellent (-20°C to 70°C)</td>
<td>Decay beyond (-20°C to 50°C)</td>
<td>Decay extremely fast over 50°C</td>
<td>Excellent (-20°C to 70°C)</td>
<td>-20°C to 55°C</td>
</tr>
</tbody>
</table>

1.10 Ion Conductors and their Classifications

According to the ability of carrying electric current at room temperature solid materials can be classified into (1) metals (conductivity $\sigma = 10^4$- $10^6$ S/cm) (2) insulators ($\sigma < 10^{-10}$ S/cm) and (3) semiconductors ($10^4 > \sigma > 10^{-10}$ S/cm). Solids having mainly electronic conductivity are the first type; where as solids having ionic conductivity predominance is the second type. The solid conductors, having electrons and ions contributing equally to conductivity, are mixed conductors. The high ion conductivity in certain solids approach similar values ($\sigma = 1-10^{-3}$S/cm) as in liquid salt solutions or melted salts. Therefore, such materials are called
solid electrolytes. Their conductivity is caused by a delocalization of metal ions over an excessive number of free interstitials in an immobile sublattice. Most of the solids show certain ion localization. However, in some compound at a certain temperature, a phase transition is possible, where the localized cation sublattice gets disordered over numerous interstitials. The conductivity spontaneously increases by several orders upon the melting of cation sublattice. Therefore, the term “solid electrolyte” can rather be used for the identification of a particular state of solid material. However, many other materials being ion conductors with a lower conductivity are also often referred to as solid electrolytes. According to Ratner et al. a solid electrolyte exhibits a characteristic ionic conductivity in the range $10^{-6}$ S/cm to $10^{-1}$ S/cm near ambient temperature. A more general approach is to use the term of “ion conductor” instead of using “solid electrolyte”. A schematic representation of the classification of ion conductors according to chemical composition, polarity of mobile ions and morphology of solids are shown in Figure-1.4. The scheme comprises of a wide spectrum of solids starting from crystalline and ending with amorphous ones.
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Fig. 1.4 Types of solid ion conductors

1.11 Properties of the Components of a Battery

A solid-state battery consists of three active components as shown below. The anode is the electropositive half of the cell, typically a metal, and the cathode the electronegative half. The electrolyte must
be able to transport only a single ionic species, and at the same time be an electronic insulator so that self-discharge is minimized.

1.11.1 The Anode

The requirement of high energy density demands a high voltage, that is, a high-energy change during the anode- cathode reaction. Thus materials required as the anode are the most electro positive elements such as alkali metals.

1.11.2 The Cathode

Following are desired characteristics of a cathode material.

a. High energy density
b. High oxidizing power
c. High Electronic conductivity
d. A long cycle life
e. Low equivalent weight
f. Ability to form product reversibly
g. No reactivity with electrolyte
h. No solubility in electrolyte
i. Low corrosive properties.

More over it is desired that the material be easy to handle chemically stable, non-toxic and cost effective. The cathode must be capable of cycling daily with high efficiency for several years. This
dictates that the cathodic reaction must be readily reversible. This in turn demands that the cathode structure must maintain its structural integrity in low temperature systems.

1.11.3 The Electrolyte

The electrolytes for use in batteries must exhibit the following properties.

a. High ionic conductivity
b. Low electronic conductivity
c. Extreme chemical inertness

1.12 Renaissance in the Battery Development

In a society progressively relying more on electricity it is necessary to have a convenient way of storing this energy. Batteries are the predominant means used today; where the electrical energy is readily mobile and is stored as chemical energy. Until recently the conventional batteries using solid electrodes and aqueous electrolytes have proved satisfactory for the majority of common applications. For most portable electrical equipments the traditional primary systems such as Leclanché and mercury cells have been successful as power sources. In rural areas, in railways and in telephone systems the well-established rechargeable batteries such as those based on the lead-acid or nickel–cadmium batteries have long been employed as sources or auxiliary power sources. Research and developments in this direction has been taking place for improvements in efficiency, energy density and cyclability.
In the last two decades, however, the situation has changed considerably. Many advances have been made in the battery technology in recent years both through continued improvement of a specific electrochemical system and through the development and introduction of new battery chemistry. However batteries are not keeping pace with developments in electronic technology, where performance doubles every 18 months, phenomenon known as Moore’s law. Micro electronic components are inexpensive and are widely used in the production of pocket calculators, electric watches, computers, mobile phones etc. Development of such miniature electronic instruments demands the evolution of miniature power supplies, which can offer a much higher energy density and superior discharge characteristics as compared with those of traditional batteries.

The most important factor affecting the demand for new battery systems is the shift towards the exploitation of alternating energy sources to replace the fossil fuel, which is progressively getting exhausted from the earth. To meet with the constantly increasing energy needs of the developed countries of the world, the utilization of discontinuous energy sources such as solar power, wind power etc requires batteries as a storage facility. For this application, batteries should have the ability to undergo large number of deep charge/discharge cycles with high efficiency.

Batteries, unlike electronic devices, consume materials when delivering electrical energy and there are theoretical limits to the amount of electrical energy that can be delivered electrochemically by
the available materials. Recognizing the limitations of the battery materials researchers are focusing on reducing the ratio of inactive to active components to improve energy density, increasing conversion efficiency and rechargeability, maximizing performance under stringent operating conditions and enhancing safety.

1.13 Thin Film Batteries - A Trendsetter in Miniature Power Sources

The trend of power sources, in accordance with the shrinkage in the size of electronic devices have shifted from city line to regular batteries, and the final goal may be miniature power sources. By preparing electrochemical cells with thin-film architecture, extensive opportunities arise for their utilization in extremely diverse fields of technology, where small dimensions, high specific-energy ratings, reliable performance and long shelf life are required. The main advantages of thin film battery technology can be listed as follows.

a. Thin films are well accepted for device design,

b. The thinning of layers gives a lower resistance in the transverse direction in the case of poorly semi conducting materials,

c. The formation of a thin layer of electrolyte allows us to use glassy materials with a low ionic conductivity,

d. Some of the main difficulties in the behaviour of the electrolyte-electrode interface can be avoided,
e. Thin film batteries are manufactured by the same technique as currently used in microelectronics industry,

f. The micro battery is manufactured in almost any two-dimensional shape.

Thin film rechargeable lithium batteries have potentially many uses as low-current active or standby power supplies. A micro battery is a system, which can deliver energy in the range of few hundreds of μAh and can be used as a micro-power source applied to various devices. The most interesting application of solid-state micro batteries is in the field of electronic systems.

1.14 Major Events in Secondary Battery Development

Figure-1.5 shows a comparison of the different battery technologies in terms of volumetric and gravimetric energy density. The share of worldwide sales for Ni-Cd, Ni-MeH and Li-ion portable batteries is 23%, 14% and 63% respectively. The use of Lead-acid batteries is restricted mainly to SLI (starting, lighting and ignition) in automobiles of standby applications, while Ni-Cd batteries remain the most suitable technology for high-power applications (for example, power tools).
Fig. 1.5 Comparison of the different battery technologies in terms of volumetric and gravimetric energy density

### 1.15 The Concept of Flexible Paper Battery

Victor L. Pushparaj (Rensselaer Nanotechnology Center, NY, USA), Pulickel M. Ajayan (Rensselaer Polytechnic Institute Troy, NY, USA) et al. have recently demonstrated the design, fabrication, and packaging of flexible carbon nano tube (CNT)–cellulose–RTIL (room temperature ionic liquid) nanocomposite sheets, which can be used in configuring energy-storage devices such as super capacitors, Li-ion batteries, and hybrids [9,10]. The intimate configuration of CNT, cellulose, and RTIL in cellulose helps in the efficient packaging, operation, and handling of these devices. The discharge capacity and performance observed here compare well with other flexible energy-storage devices reported. The robust integrated thin-film structure allows not only good electrochemical performance but also the ability to function over large
ranges of mechanical deformation and record temperatures and with a wide variety of electrolytes. These self-standing flexible paper devices can result in unprecedented design ingenuity, aiding in new forms of cost-effective energy storage devices that would occupy minimum space and adapt to stringent shape and space requirements.

Uniform films of vertically aligned thin-walled multiwalled nanotubes (MWNT) are grown on silicon substrates by using a thermal-chemical vapor-deposition method. Unmodified plant cellulose dissolved in RTIL is infiltrated into the MWNT to form a uniform film of cellulose and 1-butyl, 3-methylimidazolium chloride ([bmIm][Cl]) embedding the MWNT. After solidification on dry ice, this nanocomposite is immersed in ethanol to partially or completely extract excess RTIL and dried in vacuum to remove residual ethanol. The resulting nanocomposite paper that forms the basic building unit is peeled from the substrate for use as the super capacitor. The nanocomposite paper (CNT cellulose–RTIL) shows excellent mechanical flexibility. The paper can be rolled up, twisted, or bent to any curvature and is completely recoverable. The nanocomposite paper, which can be typically a few tens of microns thick, contains MWNTs as the working electrode and the cellulose surrounding individual MWNTs, as well as the extra layer as the spacer and the RTIL in cellulose as the self-sustaining electrolyte. Two of the nanocomposite units bonded back-to-back make a single super capacitor [11,12] device. The thin lightweight (15mg/cm²) design of the device results from avoiding the use of a separate electrolyte and spacer, generally
used in conventional super capacitors. The use of RTIL electrolyte (3 wt/wt % of cellulose in RTIL) makes the device environmentally friendly. In a final package, operating devices can be fabricated by laminating multiple stacks of individual nanocomposite layers.

Postage -stamp sized super capacitor has a voltage of almost 2.5 V. Stacking sheets of the paper increases the voltage, and increasing its size increases the power stored. The paper battery has enough power to light LED and is extremely biocompatible, so it could be used as power supplies for devices implanted in the human body.

The fabrication of the flexible Li-ion battery based on the nanocomposite paper consists of RTIL-free nanocomposite as cathode and a thin evaporated Li-metal layer as anode with Al foil on both sides as current collectors. Aqueous 1 M LiPF6 (lithium hexafluoro phosphate) in ethylene carbonate and dimethyl carbonate (1:1 vol/vol) is used as the electrolyte. As with the super capacitor, this battery also uses the excess cellulose layer in the nanocomposite cathode as the spacer, without the use of any stand-alone spacer. The charge-discharge cycle voltages of the battery are measured between 3.6 and 0.1 V, at a constant current of 10 mA/g. A large irreversible-capacity (~430 mAh/g) is observed during the first charge–discharge cycle and further charge–discharge cycles resulted in a reversible capacity of 110-mAh/g. The battery devices operates under full mechanical flexibility.

In recent years, super capacitors coupled with batteries have been considered as promising hybrid devices (82,83) to combine with the
best features of a battery and a super capacitor. This battery and super capacitor devices could be integrated in parallel to build hybrids, as reported for conventional hybrids. In this case, the battery segment of the hybrid is used to charge the adjoining super capacitor.

1.16 Rechargeable Lithium- ion Battery Concept

For today's information rich, mobile society rechargeable Li-ion cells are indispensable as they are the key component in the portable, entertainment, computing telecommunication equipments. In most of the modern electronic equipments Li-ion batteries are the systems of choice, offering high energy density, flexibility and lightweight design. The motivation for using this technology is the fact that Li is the most electropositive as well as the lightest metal that facilitates the design of storage systems with high energy density. The most advanced batteries available in the market today are Li-ion and Li-ion polymer batteries \[1,13,14\]. The advantage of using Li metal was demonstrated in the year 1970 with assembly of primary Li cells. Owing to their high capacity and variable discharge rates, they could rapidly find applications as power sources for portable electronic devices such as watches, calculators and even in implantable medical equipments. Originally, lithium metal foil was used as anode in the secondary Li-batteries, and an inorganic intercalation compound as cathode, thus exploiting the low weight and high reactivity of lithium. (Metallic lithium is highly reactive with oxygen, making it a difficult material to handle). Safety concerns have led, however, to the replacement of metallic lithium by a Li-insertion compound. The discovery of such
IntrOduction

materials was crucial in the development of rechargeable Li systems. By 1972 the concept of intercalation compounds and its potential use were clearly defined [2,3,4]. Thus the concept of Li-ion transfer cells was proposed to solve the problem of corrosion and thermal run away and possible explosion.

The invention of a new type of electrolyte based on lithium compounds dissolved in an ion conducting polymer cast as thin film made it possible to make all-solid state electrochemical batteries. This was the trigger for the lithium-polymer concept [13]. Today, these batteries generally incorporate a carbon based Li-compound or polymer-gel electrolyte. In this way active lithium is always present as an ion rather than as a metal.

1.17 Material Strategy for the Rocking Chair Battery

A lithium ion battery is comprised of three main components, a cathode, an anode and the electrolyte. The cathode material is a lithium metal oxide, while the anode is usually carbon. The electrolyte material can be an organic liquid containing dissolved electrolyte salts or a polymer electrolyte. Research is being carried out globally on developing all these three components. The present work however is focused on cathode materials and their innovations.

A lithium ion rechargeable battery is known as a rocking chair battery due to the two-way motion of lithium ions. The lithium ions are transported between the anode and the cathode through the electrolyte. During charging the lithium ions undergo deintercalation from the
Cathode in to the electrolyte, simultaneously lithium ions intercalate from the electrolyte in to the anode. Intercalation is the process of inserting lithium ions into the structure of the electrodes. (Electrochemical reactions consisting of electron and lithium ion insertion into/extraction from a solid matrix without much destruction of the core structure are called topotactic reactions and the materials for which such reversible reactions proceed are called insertion compound). During discharge the intercalation and deintercalation, reverse. The shift in charge, due to Li⁺ movement during charging and discharging is compensated by electron flow through the external circuit. The topotactic Li-intercalation mechanism is the basis for the material’s application as an electrode in a rechargeable battery. It is believed that Li is fully ionized in most lithium-metal oxides and donates its electron to the host without much affecting them. This substantial charge transfer to the anion is responsible for the voltage difference between oxides and sulphides. This makes it possible to control the band filling of the host material by varying the Li content electrochemically. In electrochromic applications, band filling is used to adjust the electronic and optical properties. Ionic relaxation, as a result of Li interaction, causes non rigid-band effects in density of states (DOS) of these materials [1-3,74]

Figure (1.6) shows schematically an electrochemical lithium cell. Two electrodes, the anode and cathode, are separated by an electrolyte. The electrolyte allows transfer of Li ions between the anode and cathode but does not allow for any electron transport. In most
applications the electrolyte is liquid, although glasses and solid polymers are being investigated as more versatile alternatives. The equilibrium voltage difference between the two electrodes, also referred to as the open circuit voltage (OCV), depends on the difference of the Li chemical potential between the anode (here Li metal) and cathode

$$V(x) = -\frac{\mu_{\text{Li}}^{\text{cathode}}(x) - \mu_{\text{Li}}^{\text{anode}}}{zF}$$

$F$ is the Faraday constant and $z$ is the charge transported by lithium in the electrolyte. In most nonelectronically conducting electrolytes $z=1$ for Li intercalation. For a battery, a large chemical-potential difference between cathode and anode is desirable as this leads to a high OCV.

![Fig.1.6 Dynamics of the Li-ion rocking chair battery](image-url)
1.17.1 Reaction Mechanism

In lithium ion cells metallic lithium is substituted by insertion materials so that the safety and cycle life of the cells are remarkably improved. The reactions at both positive and negative electrodes consist of electron and lithium ion insertion in to/extraction from solid matrices with out the destruction of the core structure. The cathode materials are air stable 3d-transition metal compounds (say LiMn$_2$O$_4$) and anodes are usually carbon materials. The cells are fabricated in discharged state, so that the freshly prepared cells cannot deliver electricity. On charging, electrons and Li- ions move from positive to negative electrode storing electricity in the solid matrix. After charging the cells can deliver electricity while moving back the lithium ions. In other words, the cells are operated with lithium-ion shuttling between positive and negative electrodes. Hence the insertion materials are extremely important in developing the Li-ion batteries.

Lithium has got low density (0.53 g cm$^{-3}$), lightweight, low electro negativity, good conductivity, high electrochemical equivalence and high electron /atom mass ratio. Because of these features, lithium has become the preferred choice for the active element of anode, which, on discharge functions as an electron donor.

**Anode:**

\[ x \text{Li} \Rightarrow x \text{Li}^+ + x e^- \]  \hspace{1cm} \text{(Discharge)}

where Li$^+$ enters the electrolyte, and the electron exits the anode to the external circuit to power the load.
Ideally, an electrolyte would have electrical properties of a liquid and mechanical property of a solid. Such a material would serve both as electrolyte and separator and endow the battery with mechanical flexibility, a property unattainable in cells with conventional liquid electrolytes. So in this case, electrolyte must be an ionic conductor capable of solvating Li$^+$ ions. Because lithium is more electropositive than hydrogen, electrolyte must be non-aqueous and aprotic. A representative formulation is a solution (1:1 by volume) of ethylene carbonate and propylene carbonate containing a suitable lithium salt (at a concentration of about 1M) such as lithium hexafluorophosphate (LiPF$_6$) i.e. electrolyte must be a lithium salt dissolved in liquid/polymer gel. Non-aqueous phosphate electrolytes have to be employed since Li decomposes water. For safety, a separator made of a polyolefin such as micro-porous polypropylene is placed between the electrodes. If the electrolyte temperature exceeds a certain value, separator melts closing the pores, and current ceases to flow.

**Cathode:**

At the cathode, Li$^+$ engages in an electron transfer reaction that decreases the chemical potential of lithium relative to its value in the anode: on discharge, the cathode functions as an electron acceptor. In commercial cells, cathode active material is a lithiated transition metal oxide (TMO) such as lithium manganese oxide, which reacts according to

\[
x \text{Li} + x e^- + \text{LiMn}_2\text{O}_4 \rightarrow \text{Li}_{1+x}\text{Mn}_2\text{O}_4 \quad \text{(Discharge)}
\]
If the battery is to be rechargeable, the reactions must be reversible; i.e., if the load in the external circuit is replaced with a power supply, it should be possible to run the reaction at the cathode and anode in reverse.

1.18 General Characteristics of Lithium Rechargeable Batteries

Rechargeable lithium batteries operating at room temperature offer several advantages compared to conventional aqueous technologies, including

a. Higher energy density (up to 150 Wh/kg, 400 Wh/L)
b. Higher cell voltage (up to about 4 V per cell)
c. Longer charge retention or shelf life (up to 5 to 10 years)

These advantageous characteristics result in part from the high standard potential and low electrochemical equivalent weight of lithium metal [1]. Ambient-temperature lithium rechargeable batteries, on the other hand, do not have the high-rate capability (because of the lower conductivity of the aprotic organic or inorganic electrolytes that must be used because of the reactivity of lithium in aqueous electrolytes) and in some instances, the cycle life of conventional rechargeable batteries. In addition, rechargeable lithium batteries that use lithium metal as the negative electrode present potential safety problems, which are more challenging than those with primary lithium batteries. This is due to a three- to five-fold excess of lithium, which is required for these types of cells in order to obtain a reasonable cycle life, and to the reactivity of the high-surface-area lithium that is formed during cycling.
There is another type of rechargeable "lithium" battery, however, which uses a lithiated carbon or other intercalation material for the negative electrode in place of lithium. The absence of metallic lithium in these lithium-ion batteries minimizes these safety concerns.

1.19 Advantages and Disadvantages of Rechargeable Lithium Batteries Operating at Ambient Temperature

The advantages and disadvantages of rechargeable lithium batteries operating at ambient temperature are summarized as follows.

1.19.1 Advantages

a. High energy density and specific energy
b. High voltage
c. Good charge retention, low self-discharge rate

1.19.2 Disadvantages

a. Low cycle life with metallic lithium systems
b. Relatively poor high-rate performance (compared to conventional aqueous rechargeable batteries)
c. Relatively poor low-temperature performance (compared to conventional aqueous rechargeable batteries)
d. Capacity fading (with some systems)
e. Potential safety problems with metallic lithium systems

A number of different battery systems have been investigated by various teams all over the world for the development of lithium rechargeable batteries in order to achieve the high specific energy and
charge retention that lithium batteries can offer without sacrificing other important characteristics, such as specific power and cycle life, while maintaining safe and reliable operation [1]. The rechargeable lithium batteries are generally characterized by a high cell voltage, good charge retention, higher specific energy but poorer high-rate performance, and poorer cycle life than conventional aqueous rechargeable batteries. Rechargeable lithium metal batteries, because of their many potential advantages, have been considered for use in a wide variety of applications. Because of the reactivity of lithium and the possibility of safety problems, emphasis also has been placed on achieving safe operation under normal and abusive conditions. For these reasons, too, commercialization of rechargeable lithium batteries has been limited. They have been introduced into the market only on a limited scale and in small cell sizes. Coin-type batteries have been commercially available for use in low power portable applications and as memory backup. Small cylindrical cells, using a lithium metal anode, have been marketed briefly for consumer electronic applications but were withdrawn when safety problems arose. Rechargeable lithium metal batteries (including ambient-temperature as well as high-temperature types), because of their high energy density, have been investigated for applications requiring larger size cells and batteries as, for example, electric vehicles. More recently, the lithium-ion type battery has been introduced into the consumer market, again in small cylindrical and prismatic sizes for camcorders, cell phones and other portable electronic devices. The lithium ion battery became the dominant rechargeable lithium system during the 1990s.
1.20 Lithium Insertion Compounds

An insertion compound is a host structure that can accommodate mobile guest ions together with their charge compensating electrons. These guest species can be added or removed (i.e. the concentration of the guest in the insertion material can vary) in conjunction with redox processes normally involving a change in oxidation-state of transition metal ions [4]. Under alkali metal insertion, the alkali metal ions donate their outer s-electron to the electronic energy levels of the host. Here two factors are to be considered. (1) The availability of sites in the host and (2) the positions of the energy levels in the host. Several structure types can serve as host materials, typically 2-D hosts like LiCoO$_2$ and 3-D hosts like LiMn$_2$O$_4$, LiFePO$_4$, and LiNiPO$_4$. In a topotactic reaction, the structure of the host is changed only by atomic displacement; the reaction does not involve a diffusive rearrangement of the host atoms. Moreover, the guest species in such a reaction may be neutral, an electron donor, or an electron accepter. In other words, an insertion compound is an ionic and electronic conductor, and the intake or release of electrons compensates for a change in guest-ion concentration.

In a Li-ion battery Li$^+$ is the guest ion and a transition metal-Oxide (TMO) is the most attractive candidate as the host. Phosphates, sulphates and arsenates of transition metals are also suitable as host material in the intercalation process. The alkali metal ions donate their s-electrons to the electronic energy level of the host. Here the
availability of the sites in the host and the position of the energy levels in the host must be taken into account.

Fig. 1.7 (a). Two-dimensional layered host with -NaFeO$_2$ -type structure.
(b). Three-dimensional framework host with cubic spinel AB$_2$O$_4$ -type structure.

For transition -metal oxides the positive guest Li$^+$ occupy sites surrounded by negative oxygen ions. The guest ions strive to stay as far as possible from the transition metal ions. The sites available to the Li-ion are determined by the host structure. Due to the higher potential vs. Li/ Li$^+$ ratio giving a high specific energy and excellent reversibility, TMO's are found to be the most attractive candidate for insertion electrode (15).

1.21 Classification of Insertion Compounds

Insertion compounds can be classified according to their crystal structure, chemical composition and morphology. The composition of the host lattice consists of transition metal Chalcogenides; spinel related, layered and 3D. There are numerous transition metal oxides that exist as separate group of Chalcogenides; layered and tunnel type,
three dimensional, spinel type Li\textsubscript{x}M\textsubscript{2}O\textsubscript{4} (M=Ti, V, Mn), layered Li\textsubscript{x}MO\textsubscript{2} (M=Co, Ni, Mn) and so on. Several conjugated organic polymers have been found to have good electronic conductivity. They can exhibit host properties. Examples of such conducting type polymers are thin electro-polymerized electrode films of polyaniline and polypyrrole [16]. Lithium forms alloys with carbon (graphite, coke), Al, Sn etc., which can also be treated as intercalation compounds. Since 1990, such alloys have found application as anode materials in lithium ion (rocking chair) rechargeable batteries. Use of insertion material for negative electrode solves the problems connected with the appearance of lithium dendrites (due to reactivity with electrolyte) and subsequent degradation of lithium electrode during cycling. However, due to the application of carbon morphology, a fraction of 20-40% of lithium, located at the cathode (e.g. LiMn\textsubscript{2}O\textsubscript{4}) irreversibly reacts in the passivation layer formed on the carbon anode surface. A scheme of classification of insertion compounds is shown in Figure-1.8.
Fig. 1.8 Scheme of classification of insertion compounds

1.22 Properties Expected for Insertion Electrodes in a Li-Ion Cell

The following are the criteria required for intercalation compounds to be chosen as electrodes for a Li-ion battery [16].

a. Must be an intercalation host for lithium

b. Large value of Gibbs free energy ($\Delta G$) for the total cell reaction to provide a high voltage.
c. Limited change in $\Delta G$ over the useful range of inserted Li-ions to ensure a stable operating voltage.

d. Low Fermi level and Li+ site energy which enable high open-circuit voltage

e. Low molar volume to get high volumetric energy density

f. Electrode potential should not vary significantly with lithium content (i.e. cell voltage varies little with state of charge)

g. Minimal changes in the host network to ensure good reversibility (i.e. to sustain high rates of lithium intercalation and deintercalation)

h. Light host structure, which is able to accommodate a significant amount of Li-ions to provide a high capacity

i. Good electronic and ionic conductivity to provide high rate capability.

j. Chemically and structurally stable over the whole voltage range and insoluble in the electrolyte (i.e. to avoid co-intercalation of solvent)

k. Non-toxic and inexpensive

l. Easily fabricated into electrode

m. Intrinsic safety and environmental acceptability (green nature).

1.23 Distinguishing Features of Li-ion Batteries

The overwhelming need for lightweight and compact sources of portable electricity has resulted in a massive international effort for the
development of radically new rechargeable batteries. The considerable technological impetus in this area comes from three main sources; consumer electronics (e.g. mobile telephones), electric vehicles and implantable medical devices (e.g. the artificial heart). The introduction of the world's first commercially successful rechargeable lithium battery represented (by Sony in 1990) a revolution in the power source industry. Following are the essential features of Li-ion cell [17].

a. High operating voltage.
b. Compact, light weight and high energy density.
c. Fast charging potential.
d. High discharge rate.
e. Wide range of operating temperature.
f. Superior cycle life.
g. Excellent safety.
h. Low self discharge.
i. Long shelf life.
j. No memory effect.
k. Non-polluting.

1.24 Phospho Olivines-A Breakthrough in Lithium ion Battery Technology

The standard Li-ion battery has been the leading energy storage material since the mid 1990’s but a new breed of lithium ion batteries is
being investigated, with a view to producing batteries that are cheaper, less toxic and electrochemically superior. The conventional nickel cadmium/cobalt batteries are toxic and they experience a detrimental memory effect. Cobalt is one of the primary constituents of standard cathodes for lithium batteries. Cobalt has a low abundance leading to high cost. Metals such as Mn could provide a cheaper alternative. Cobalt is also a heavy metal that can cause cumulative poisoning. Lithium cobalt batteries have an extra cost associated with a necessary protection circuit to ensure safety. Thus there is a significant drive in industry and research, to develop batteries with materials that are non-toxic and less expensive.

Possible alternative to lithium cobaltate include LiNiO₂, LiMn₂O₄, LiFePO₄ and other oxides. LiNiO₂ is a layered compound that has been investigated as a possible cathode material. This compound has the same structure as the lithium cobaltate compound, but due to its poor thermal stability it undergoes a structural change on heating, which causes an undesired reduction in its conductivity. Therefore, LiNiO₂ is not currently practical as battery material.

LiMn₂O₄ system undergoes structural change upon cycling [18]. The capacity fading of the lithium manganese oxide system is prominent. It is reported that this compound has an initial capacity of 120mAh/kg, but by the 100th cycle the capacity falls to about 60%. The resulting capacity fade can be improved by partial substitution with cobalt. A lithium manganese cobalt oxide [Liₓ (Mn₁₋ₓCoₓ) O₂] has been practiced but is difficult to prepare and also have a poor cycle life. Thus
these compounds are not at the forefront of the new generation of lithium battery cathode materials.

The recent developments in the Li-ion battery technology include the introduction of newer cathode materials such as the conductive lithium Phospho-olivines LiFePO$_4$, LiNiPO$_4$ etc by Padhi, Nanjudaswamy and Goodenough [19]. The lithium transition metal phosphates are emerging as materials of interest due to their low material cost, high energy density, safety and non-toxicity. But these materials have low electron conductivity. A dramatic increase in conductivity can be achieved through structure control [20]. This new breakthrough in identifying electrically conductive and "environmentally green" Phospho-olivines has evoked great interest in the research world.

The electrically conductive Phospho-olivines can be used for applications in safer and high power rechargeable Li-ion batteries [21]. The applications include power sources for hybrid and electric vehicles and implantable medical devices as well as back-up power.

1.25 Multi Walled Carbon Nano Tube (MWNT) as Additives

One of the drawbacks in Li-ion battery hindering the widespread applications is the insufficient electric capacity. Carbon materials such as carbon micro beads (MCMB) and graphite have been used for the anode instead of lithium metal foil mainly due to safety considerations although the theoretical capacity (372mAh/g) of carbon-based secondary Li ion battery is much lower than lithium metal. A host of
experiments have been conducted to enhance the capacity by adopting hard carbon, modified graphite carbon and metal oxide compounds as the anode electrode. Although the electric capacity increased to a certain extent, some obstacles such as irreversibility and constant discharge voltage still need to be overcome.

The very good electronic conductivity, mechanical and thermal stability of carbon nano tube can be exploited for enhancing the performance of lithium ion batteries. The unique properties of carbon nano tubes include, one dimensional, and well-graphitized structure with a central hollow core. Thus, it is expected that the discovery of MWNTs provide an opportunity to improve the electrochemical properties of the secondary Li ion battery. Since their discovery in 1991 by Iijima carbon nanotubes have been of great interest, both from a fundamental point of view and for future applications [22]. The most eye-catching features of these structures are their electronic, mechanical, optical and chemical characteristics, which open a way to future applications. These properties can even be measured on single nanotubes. For commercial application, large quantities of purified nanotubes are needed.

1.25.1 Fullerenes

Fullerenes are large, closed-cage, carbon clusters and have several special properties that were not found in any other compound before. As is the case with numerous, important scientific discoveries, fullerenes were accidentally discovered. In 1985, Kroto and Smalley found strange results in mass spectra of
evaporated carbon samples [23,24]. Herewith, fullerenes were discovered and their stability in the gas phase was proven. The search for other fullerenes had started. Since their discovery by Iijima and coworkers, many researchers all over the world have investigated carbon nanotubes. Their large length (up to several microns) and small diameter (a few nanometers) result in a large aspect ratio. They can be seen as the nearly one-dimensional form of fullerenes. Therefore, these materials are expected to possess additional interesting electronic, mechanic and molecular properties. Especially in the beginning, all theoretical studies on carbon nanotubes focused on the influence of the nearly one-dimensional structure on molecular and electronic properties.

Many exotic structures of fullerenes exist: regular spheres, cones, tubes and also more complicated and strange shapes. Single Walled Nanotubes (SWNT) can be considered as long wrapped graphene sheets (Figure-1.9). As stated before, nanotubes generally have a length to diameter ratio of about 1000 so they can be considered as nearly one-dimensional structures. Multi Walled Nanotubes (MWNT) can be considered as a collection of concentric SWNTs with different diameters. The length and diameter of these structures differ a lot from those of SWNTs and, of course, their properties are also very different.
1.25.2 Special Properties of Carbon Nanotubes

Electronic, molecular and structural properties of carbon nanotubes are determined to a large extent by their nearly one dimensional structure. The most important properties of CNTs and their molecular background are stated below.

a. Chemical reactivity. The chemical reactivity of a CNT is, compared with a graphene sheet, enhanced as a direct result of the curvature of the CNT surface [25]. Carbon nanotubes reactivity is directly related to the pi-orbital mismatch caused by an increased curvature. Therefore, a distinction must be made between the sidewall and the end caps of a nano tube. For the same reason, a smaller nanotubes diameter results in increased reactivity. Covalent chemical modification of either sidewalls or end caps has shown to be possible. For example,
the solubility of CNTs in different solvents can be controlled this way. Though, direct investigation of chemical modifications on nanotubes behaviour is difficult as the crude nanotubes samples are still not pure enough.

b. **Electrical conductivity.** Depending on their chiral vector, carbon nanotubes with a small diameter are either semiconducting or metallic. The differences in conducting properties are caused by the molecular structure that results in a different band structure and thus a different band gap. The differences in conductivity can easily be derived from the graphene sheet properties [26]. The resistance to conduction is determined by quantum mechanical aspects and was proved to be independent of the nanotubes length [27,28].

c. **Optical activity.** Theoretical studies have revealed that the optical activity of chiral nanotubes disappears if the nanotubes become larger [29]. Therefore, it is expected that other physical properties be influenced by these parameters too. Use of the optical activity might result in optical devices in which CNTs play an important role.

d. **Mechanical strength.** Carbon nanotubes have a very large Young’s modulus in their axial direction. The nanotubes as a whole is very flexible because of the great length. Therefore, these compounds are potentially suitable for applications in composite materials that need anisotropic properties.
1.25.3 Potential Applications of CNTs

a. **Energy storage.** Graphite carbonaceous materials and carbon fiber electrodes are commonly used in fuel cells, batteries and other electrochemical applications. Advantages of considering nanotubes for energy storage are their small dimensions, smooth surface topology and perfect surface specificity. The efficiency of fuel cells is determined by the electron transfer rate at the carbon electrodes, which is the fastest on nanotubes following ideal Nernstian behaviour [28] Electrochemical energy storage and gas phase intercalation will be described more thoroughly in the following chapters of the report.

b. **Hydrogen storage.** The advantage of hydrogen as energy source is that its combustion product is water. In addition, hydrogen can be easily regenerated. For this reason, a suitable hydrogen storage system is necessary, satisfying a combination of both volume and weight limitations. The two commonly used means to store hydrogen are gas phase and electrochemical adsorption. Because of their cylindrical and hollow geometry, and nanometer-scale diameters, it has been predicted that carbon nanotubes can store a liquid or a gas in the inner cores through a capillary effect. It is reported that SWNTs were able to meet and sometimes exceed this level by using gas phase adsorption (physisorption). Another possibility for hydrogen storage is electrochemical storage. In
this case not a hydrogen molecule but an H atom is adsorbed. This is called chemisorptions.

c. **Lithium intercalation.** The basic principle of rechargeable lithium batteries is electrochemical intercalation and deintercalation lithium in both electrodes. An ideal battery has a high-energy capacity, fast charging time and a long cycle time. The capacity is determined by the lithium saturation concentration of the electrode materials. For Li, this is the highest in nanotubes if all the interstitial sites (inter-shell van-der-Waals spaces, inter-tube channels and inner cores) are accessible for Li intercalation. SWNTs have shown to possess both highly reversible and irreversible capacities. Because of the large observed voltage hysteresis, Li-intercalation in nanotubes is still unsuitable for battery application. This feature can potentially be reduced or eliminated by processing, i.e. cutting, the nanotubes to short segments.

d. **Electrochemical super capacitors.** Super capacitors have a high capacitance and potentially applicable in electronic devices. Typically, they are comprised two electrodes separated by an insulating material that is ionically conducting in electrochemical devices. The capacity of an electrochemical super cap inversely depends on the separation between the charge on the electrode and the counter charge in the electrolyte. Because this separation is about a nanometer for nanotubes in electrodes, very large capacities result from
the high nanotube surface area accessible to the electrolyte. In this way, a large amount of charge injection occurs if only a small voltage is applied. This charge injection is used for energy storage in nanotubes super capacitors [30].

e. **Conductivity in CNTs.** Electron transport in metallic CNTs is ballistic of nature, which means that electrons move with a much higher speed than expected on the ground of thermal equilibrium. Ballistic transport can only occur in strictly confined semi-conductor regions and is totally determined by material properties. Electron transport in semi-conducting CNTs is far more complicated due countermand scattering, influences of charges at the electrode interface and adsorbed gasses. Therefore, conductivity in semi-conducting CNTs is usually described in classic physical laws of diffusivity [26]. Diffusive charge transport means that electron motion can be described with an effective mobility \( \mu \). In case of ballistic transport, the average free path \( l \) of an electron is relatively short (\( \sim 2 \) nm.) compared with the ballistic transport situation (\( l \sim 10 \mu m \)).

1.26 Methods of Synthesis of Experimental Samples

1.26.1 Hand mortaring

The most commonly used approach to reduce particle size is to grind the substance using mortar and pestle, but mechanical mills also do a fine job. Mortar and pestles are usually made from agate or ceramics. Agate is suitable for grinding hard materials. When
aggregation effects are severe, adding a chemically inert liquid such as acetone, which does not dissolve the material may help to prevent excessive conglomeration.

In the present work grinding of material by hand with an agate mortar and pestle has been used for mixing and particle size reduction of small amounts of materials (less than 20 g). For getting homogeneity in mixing acetone is used as a mixing medium. For many small- scale studies, hand- mortaring is perfectly adequate for reducing the particle sizes of powder samples. The successive grinding and mixing are done for a maximum of two hours for each batch of samples. Usually two stages of hand mortaring are adequate for the synthesis of the material. A facemask should be worn to prevent fine dust inhalation.

1.26.2 Solid-state reaction

Solid-state reaction is done by mixing the pre-dried precursors in the exact (stoichiometric) ratio to get a desired target product. To get the starting materials close to each other for mixing a homogeneous phase of final product, it is common to grind the and mix using mechanical milling techniques first. Alternatively, the precursors may be dissolved to give a homogeneous solution, which is stirred continuously and evaporated to dryness. Then the solid remaining is mechanically milled to yield a very homogeneous powder ready for conversion in to a final product.

Once the homogeneous precursor is obtained, it is placed into a furnace and heated to a suitable temperature for hours. Waste gases will
be generated and released. Chemicals will interact to form final product. Commonly, this material may be ground finely again and then put into the furnace a second time. The second sintering allows the crystals to form and grow in size. Sometimes powder materials are hydraulically pressed into pellets to increase the interactivity between the powder grains and form a higher quality final product.

The spinel LiMn$_2$O$_4$ is prepared and sintered in a muffle furnace in air. While the phospho olivines LiMPO$_4$ (M=Fe,Ni) are prepared in a specially designed tubular furnace as shown in Figure 1.10 for thermal decomposition under inert atmosphere.

**Fig.1.10.** Arrangement for the synthesis of LiMPO$_4$(M=Fe,Ni) in an inert atmosphere
1.26.3 Sintering

Sintering commonly refers to processes involved in the heat treatment of powder compacts at elevated temperature, in the temperature range where diffusion mass transport is appreciable. Successful sintering usually results in a dense polycrystalline solid. However sintering can proceed only locally, (i.e. at contact points of grains), without any appreciable change in the average overall density of a powder compact. The principal goal of sintering is the reduction of compact porosity. The sintering process is usually accompanied by other changes within the material, some desirable and some undesirable.

On sintering the largest changes occur in
a. Strength, elastic modulus
b. Hardness, fracture toughness
c. Electrical and thermal conductivity
d. Permeability of gases and liquids
e. Average grain number and size
f. Average pore size and shape
g. Chemical composition and crystal structure

Sintering is a very widely used, but complex phenomenon.

1.27 Characterization Techniques
127.1 X-Ray Diffraction analysis

X-ray diffraction is an extremely important technique in the field of material characterization to obtain information on atomic scale from
crystalline and amorphous materials. The discovery of X-ray diffraction by crystals in 1912 by Max von Laue and its immediate application to structure determination in 1913 by W.L Bragg and his father W.H Bragg paved the way to determine crystal structures of metal and alloys, minerals, inorganic compounds, polymers and organic materials. When materials are irradiated with X-rays they get diffracted and the manner of diffraction reveals the structure of the crystal [75,76]. At first this tool was used only for the determination of crystal structure. Today the method is applied not only to crystal structure determination, but also to such diverse problems as chemical analysis and stress measurement, to the study of phase equilibrium and measurement of particle size, to the determination of orientation of one crystal or the ensemble of orientations in a polycrystalline aggregate.

Many factors affect the quality of powder diffraction data and the quality of the specimen used in a powder diffraction experiment is one of them. Poorly prepared samples will inevitably lead to additional efforts to repeat from the beginning. On the other hand, a high quality sample for powder diffraction may take longer to prepare, but this will be time well spent. The true powder diffraction pattern can only be obtained from specimen containing an infinite number of individual particles realizing an infinite number of orientations in the irradiate volume. In other words, the particles in the specimen should have a completely random distribution of crystallographic orientations of grains with respect to one another. This is usually achieved by reducing the average particle size. Another very effective approach to increase both the number of particles in the irradiated
volume and the randomness of their orientations is to spin the specimen continuously during data collection.

1.27.2 Electron beam techniques for characterizations

When a sample is irradiated with electrons the incident electrons are absorbed, emitted, reflected or transmitted and can, in turn cause light or X-ray emission. An electron of energy $E_i$ incident on a sample (figure 1.11) surface causes emission of electrons from surface over a wide range of energies. Usually three groups of electrons are distinguished. First group shows a maximum electron yield. The interaction of an electron beam with a solid can lead to the ejection of loosely bound electrons from conduction band. These are the secondary electrons with a lower range of energies. Auger electrons are emitted in an intermediate energy range. Back-scattered electrons that have undergone large angle elastic collisions leave the sample with essentially the same energy as the incident electrons. These electrons can be focused, deflected, and accelerated by appropriate potentials. They can be efficiently detected and counted. Their energy and angular distributions can be measured, and they do not contaminate the sample or the system. An electron microscope utilizes an electron beam to produce a magnified image of the sample [77-81]. There are three principal types of electron microscopes

a. Scanning
b. Transmission and
c. Emission.

All analytical techniques are based on similar principles. A primary electron, ion, or photon beam causes backscattering or transmission of the
incident particles or the emission of secondary particles. The mass, energy, or wavelength of the emitted entities is characteristic of the target element or compound from which it originated. The distribution of the unknown parameter can be mapped in the x-y plane and frequently also in depth. Each of the techniques has particular strengths and weaknesses, and frequently more than one method must be used for unambiguous identification. Differences between the various techniques include sensitivity, elemental or molecular information.

In the scanning and transmission electron microscope, an electron beam incident on the sample produces an image, while in the field-emission microscope the specimen itself is the source of electrons. Scanning electron microscopy (SEM) is similar to light microscopy with the exception that electrons are used instead of photons and the image is formed in a different manner. A detailed description of this method is given in Chapter-2.

![Electron beam characterization techniques](Fig. 1.11 Electron beam characterization techniques)
In the present work SEM images are obtained using JEOL JSM - 6380 LV (JEOL Inc., Tokyo, Japan), operating at a voltage of 30 KV. TEM images are acquired using JEOL JEM 1200 EX 11 (JEOL Inc., Tokyo, Japan), maintained at a voltage of 120 KV.

1.27.3 Photoacoustic technique as a characterization tool
1.27.3.a Photothermal science

Photothermal (PT) science encompasses a wide range of techniques and phenomena based upon the conversion of absorbed optical energy into heat. Although the initial absorption processes in many materials are very selective, it is common for atoms or molecules in excited electronics states to lose their excitation energy by a series of non-radiative transitions that result in a general heating of the material. The main components of a photothermal system are an excitation source, a modulator, a detector and a signal processor with a display system. The modulated light beam absorbed by the sample generates modulated heating in and around the sample, giving rise to the various PT effects such as temperature rise, pressure change, refractive index gradient etc. Depending on the specific PT effect being probed [31], PT techniques are classified into Photopyroelectric (PPE) technique or Calorimetric technique (temperature rise) [32-45], Photoacoustic technique (pressure change) [46-48), Probe beam deflection or Mirage technique (Refractive index gradient) [49-51], Photothermal Radiometric technique (infrared emissions) [50-51] etc. The PPE signal (PT signal in general) not only carries information regarding the absorbed light energy which is the basis of their application in
absorption spectroscopy, but also contains details regarding the thermal properties of the sample

1.27.3 b. Thermal, Electronic and Optical Characterization using PA Technique.

For the past few decades, photoacoustic technique has been emerging as a powerful tool in the thermal, electronic and optical characterization of materials whether solids, liquids or they are gases [52-66]. Photoacoustic technique is based on an effect originally discovered by Bell in 1880, where a chopped light impinging on a solid surface enclosed in a cell produces an acoustic signal within the cell. The reason for this acoustic signal generation is the fact that after the absorption of light by the sample, non-radiative de-excitation processes convert a part or all of the light absorbed by the sample into heat. Hence, a periodic or chopped excitation results in a periodic heat generation in the sample, which diffuses into the surrounding gas. This periodic flow of heat into the gas produces pressure fluctuations in it resulting in periodic sound or acoustic signal. This periodic acoustic signal can be detected by a microphone and the signal output from the microphone can be recorded as a function of the wavelength of light used or as a function of the chopping frequency depending on the application [52-66].

It is being extensively used as a spectroscopic tool because of its relative advantage over other conventional spectroscopic techniques, in that it can be applied to any type of sample in general. This is due to the fact that scattering poses less difficulties in Photoacoustic Spectroscopy
(PAS) unlike other conventional spectroscopic techniques since the amount of signal generation is directly dependent on the amount of light absorbed. Due to the same reason, absorption spectra of opaque samples can also be accurately obtained. The PA signal recorded, as a function of wavelength will be the optical absorption spectra of the sample under investigation because the magnitude of the acoustic signal produced in the photoacoustic cell is proportional to the amount of heat emanating from the solid absorber, provided that non-radiative processes dominate in the dissipation of the absorbed light energy. Suitable normalization procedures remove the spectral characteristics of the excitation light source [52-65].

On the other hand, the PA signal obtained as a function of the chopping frequency is used in obtaining the thermal and electronic parameters like carrier diffusion coefficient, surface recombination velocity etc of the materials since the chopping frequency is related to the heat generation and propagation. In the case of semiconductors, heat generation under the irradiation with an intensity modulated light beam arises due to three processes namely thermalisation due to intra band transitions of photo-generated carriers, nonradiative bulk recombination and surface recombination due to inter band transitions of photo-generated carriers. All these different mechanisms finally result in the creation of heat energy, which is then transferred to the lattice through the creation of phonons, and which of these generation mechanisms is dominant in a PA signal depends on the frequency of excitation and de-excitation i.e. the chopping frequency [61,62]. The
heat propagation is described in terms of the thermal wave propagation having a wavelength $2\pi\mu$ where $\mu$ is the thermal diffusion length given by $\sqrt{\frac{\alpha}{2\pi f}}$, $\alpha$ being the thermal diffusivity and $f$ the chopping frequency.

1.28 Portable Radiometer for Band Gap Measurement

Portable spectroradiometers or radiometers, as they are generally known, are extensively and commonly used instruments in studying Earth Science, especially vegetation, soil, minerals, etc [67] Due to these applications, the radiometers are made compact with accessories for in situ measurements, such as different fields of view lenses from 1 degree to 10 degrees and/or a fiber-optic bundle with a 25 degree field of view. Besides these lenses, there are also other fore-optic accessories such as reduction tubes and remote cosine receptors in order to increase the freedom of collecting the light reflected from the object under investigation. This gives the added advantage of choosing the area of light collection, helping to perform in situ measurements, and making the measurement precise. These measurements are often done with the sun/halogen lamp as the excitation source, and the reflected light from the object under investigation is collected. This collected light from the object is projected on to a holographic diffraction grating where the wavelength components are separated and measured by detector(s). The detectors commonly used to detect the visible and near-infrared (Vis-NIR) portion of the collected light are 512-channel silicon photodiode arrays with an order separation filter or 1024 x128 (or 64) charge-coupled device (CCD) arrays, and the short-wave infrared (SWIR)
portion of the spectrum is acquired using two scanning spectrometers in the ranges 900–1850 nm and 1700–2500 nm, with the controlling software accounting for this wavelength overlap. Unlike the Vis-NIR, each SWIR spectrometer has only one detector, which is exposed to the different wavelengths of light as the grating oscillates (at a period of 200 ms, i.e., 100 ms/scan). Data is recorded and saved very quickly (in less than one second).

The radiometer gives flexibility in the size of the samples to be studied since there is no restriction on the upper limit and the lower limit can be down to as little as 1 mm × 1 mm in size. Temperature dependence of the band edges in semiconductors is of great interest in electronic and opto electronic applications. [68-70] However, the shift is small and can be observed only with high resolution techniques; for example, the shift in band gap of silicon when the temperature changes from 300 K (room temperature) to 370 K is about 0.01 eV and so the shift occurring in the band edges will be very small for small temperature changes. Although the spectrophotometers available have a spectral resolution of 1 nm, the use of a radiometer that has the same spectral resolution will give the added advantage of in situ measurements. Hence, another way of rating the performance of a radiometer is by looking at the accuracy and resolution of the spectra while looking for shifts in band edges of semiconductors with change in temperature. In this regard, the advantage of varying the temperature during measurements is that the temperature of the sample can be varied easily (for example, coarse measurements can be done by
placing the sample in an ice bath or on a hot plate) as the size of the sample holding apparatus or heating/cooling apparatus does not matter since the sample is placed outside the instrument, contrary to the other techniques in which the sample is mounted inside a sample holder in the instrument. Band gap measurement of semiconductor nano particles is of immense interest due to their structural and electronic information carrying capability. This technique can act as a powerful tool for this application [71-73].

1.29 Motivation for the present investigation

The work presented in the thesis is centered around two important types of cathode materials, the spinel structured Li$_x$Mn$_2$O$_4$ ($x = 0.8$ to $1.2$) and the phospho-olivine structured LiMPO$_4$ (M=Fe and Ni). The spinel system Li$_x$Mn$_2$O$_4$, especially LiMn$_2$O$_4$ corresponding to $x=1$ has been extensively investigated to understand its structural electrical and electrochemical properties and to analyse its suitability as a cathode material in rechargeable lithium batteries. However there is no reported work on the thermal and optical properties of this important cathode material. Thermal diffusivity is an important parameter as far as the operation of a rechargeable battery is concerned. In Li$_x$Mn$_2$O$_4$, the electronic structure and phenomenon of Jahn-Teller (J.T) distortion have already been established theoretically and experimentally. Part of the present work is an attempt to use the non-destructive technique (NDT) of photoacoustic spectroscopy to investigate the nature of the various electronic transitions and to unravel the mechanisms leading to the phenomenon of J.T distortion in Li$_x$Mn$_2$O$_4$. 
The phospho-olivines LiMPO₄ (M=Fe, Ni, Mn, Co etc) are the newly identified, prospective cathode materials offering extremely high stability, quite high theoretical specific capacity, very good cyclability and long life. Inspite of all these advantages, most of the phospho-olivines especially LiFePO₄ and LiNiPO₄ show poor electronic conductivity compared to LiₓMn₂O₄, leading to low rate capacity and energy density. In the present work attempts have been made to improve the electronic conductivity of LiFePO₄ and LiNiPO₄ by adding different weight percentage MWNT. It is expected that the addition of MWNT will enhance the electronic conductivity of LiFePO₄ and LiNiPO₄ without causing any significant structural distortions, which is important in the working of the lithium ion battery.

References


Introduction


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Chapter-1


