

CHAPTER 1

INTRODUCTION

1.1 NEED FOR BATTERIES

Technological improvement in the field of batteries has progressed to a significant extent in the past decades due to the increasing demand for power sources in transportation vehicles, portable electronic equipments and so on. The batteries are primarily an electrochemical power source (EPS), that converts the chemical energy in to electrical energy. An EPS comprises one or several galvanic cells. In each such cell, a comparatively low voltage is generated, typically 0.5 to 4 V depending upon its cell chemistry. Whenever higher voltage is required, the necessary numbers of cells are connected in series to form a galvanic battery.

Batteries have a major role to play in the cleaner energy economy. Recent summit of international energy agency (IEA) has expressed its concern on climate change mitigation due to green house gas emissions and it has predicted that by 2020 the crude oil supply will cease to exist, as demand will outstrip the supply (IEA 1998). A recent survey of IEA suggests that as the world's population may climb from six billion as of today to 7.5 billion in two decades, the green house gas emission will also alleviate exponentially. Now the challenge before the world is to adopt affordable and profitable electric power source for vehicles that are safe, effective and environmentally sustainable.

There are probably two dominant types of energy storage systems required for the new energy economy, one related to static load leveling of renewable energy and the other related to transport applications. For both, the cost and reliability are extremely important; energy and power density are also important, although to differing degrees. For energy storage related to transport, high power batteries are required for Hybrid electric vehicles. The Table 1.1 illustrates the most common specification of various batteries and their applications.

Table 1.1 Specification and application of various battery types

Battery type	Voltage (V)	Specific energy (Wh)	Energy density (Wh/g)	Life cycles	Applications
Li-ion batteries	3.6	150	350	>1000	Cellular telecom, Smart cards and Hybrid energy Vehicles.
Ni/ metal hydride, Batteries	1.2	90	300	>1000	Domestic timers, special MBU (memory backup applications), automotive
Ni – Cd batteries	1.2	70	180	1500	Electronic gadgets
Small Lead acid battery	2.0	30	80	500	Transport applications

1.2 HISTORICAL BACKGROUND OF BATTERIES

Although the earliest electric cells (such as the so-called "battery of Baghdad") were in existence over 2,000 years ago, the history of the battery

really started in the period, when electricity was discovered and started being widely used in the 17th and 18th centuries. People like Alessandro Volta (1745 – 1827) and Luigi Galvani (1737 – 1798) carried out the groundwork that led to an electrochemical energy storage device, and their names live on in terms like "volts" and "galvanic cell".

Around 1800, Volta's greatest and most successful discovery, the voltaic column arrived as the world's first working battery. It consisted of alternate copper and zinc plates saturated with acid and separated from one another with scraps of cloth. Volta discovered that certain liquids initiate chemical reactions between metals, thereby generating electrical energy. During the industrial revolution the development of electrochemical energy storage devices gathered pace. Large-scale production of rechargeable lead batteries started around 1880, when Emile Alphonse Fauré developed a process in which the lead battery reached a high capacity after just a small number of charging cycles (forming). Meanwhile Fauré covered both sides of a lead sheet with a paste consisting of powdered lead and sulphuric acid, by which he achieved a high battery capacity immediately after the first charge. (Linden 2003).

There are numerous existing battery types that vary with respect to size, structural features and nature of the chemical reactions. Accordingly they vary in their performance and parameters. In general, all batteries are based on a specific electrochemical system consisting of specific a particular set of oxidizer, reducer, and electrolyte. In terminology, an electrochemical system is written as oxidizer | electrolyte | reducer. Often, the oxides of certain metals are used as the oxidizers. The electrochemical systems and batteries are generally named after these oxidizer metals. (E.g. lead acid battery, Lithium battery, nickel -cadmium battery etc...).

Based on the principles of functioning, batteries can be classified as follows:

(i) Primary (single-discharge) batteries

A primary battery contains a finite quantity of the reactants participating in the reaction; once this quantity is consumed (on completion of discharge), a primary battery cannot be used again (“throwaway batteries”).

(ii) Secondary (rechargeable) batteries

On the completion of discharge, a storage battery can be recharged by forcing an electric current through it in the opposite direction, this will regenerate the original reactants from the reaction (or discharge) products. Therefore, electric energy supplied by an external power source (such as the grid) is stored in this battery in the form of chemical energy. During the discharge phase, this energy is delivered to a consumer independent of the grid. Good rechargeable batteries or cells will sustain a large number of such charge–discharge cycles (hundreds or even thousands).

1.3 SIGNIFICANCE OF THE LI ION BATTERY

Amongst the available energy storage systems, lithium ion-based rechargeable battery system is of particular interest for hybrid electric vehicle application. The usage of lithium ion battery has progressed to a significant extent in the past decade because of its following advantages over other contemporary battery technologies

- Two-three times of higher voltage per single cell.
- Two-five times higher specific energy, i.e., watt-hours per kilogram (Wh/kg) of battery weight, and two-four times higher

energy density, i.e., watt-hours per liter (Wh/l) of battery volume.

- Low self-discharge and long shelf life, i.e., the battery does not lose a significant amount of its capacity while sitting idle on the shelf.
- No memory effect, i.e., the available capacity in a fully charged Li-ion battery is independent of its operational history, unlike the NiCd system.
- Long charge/discharge cycle life.

The Figure 1.1 shows a comparison of the different battery technologies in terms of volumetric and gravimetric energy density (Manthiram.A 1998). Because of these advantages Li ion Batteries are preferred for portable consumer products such as cellular telephones and laptops. As a result of proliferation in usage, the Li ion battery business is expected to generate tens of billions of dollars in sales in the not too distant future.

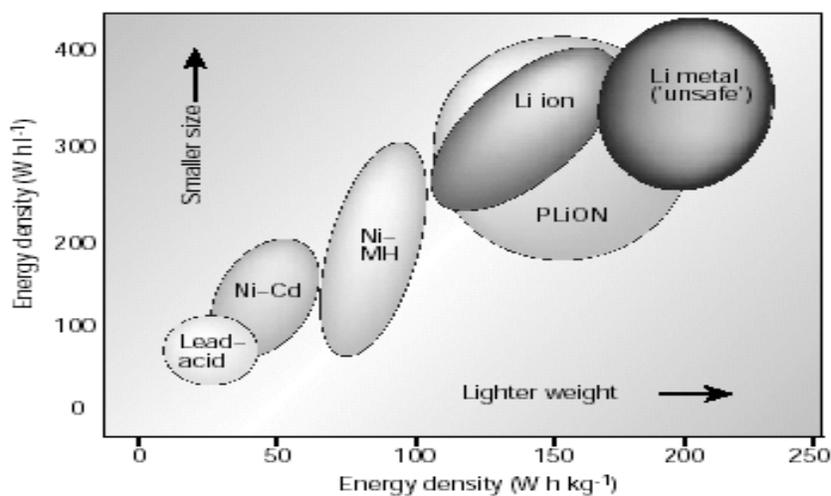


Figure 1.1 Comparison of Different battery technologies

1.4 WORKING PRINCIPLE OF BATTERY

Li-ion batteries are composed of two Li insertion electrodes in which the battery voltage is obtained by the difference between the redox potentials of the positive electrode (cathode) and the negative electrode (anode). The batteries with the two intercalation electrodes are generally called as Rocking chair battery. The typical commercial Li-ion battery has a graphite anode (represented as C_6) and a $LiCoO_2$ cathode as shown in Figure 1.2. The charge/discharge reaction of this battery is shown in equation 1.1, where forward reaction corresponds to charging and reverse reaction corresponds to discharging.

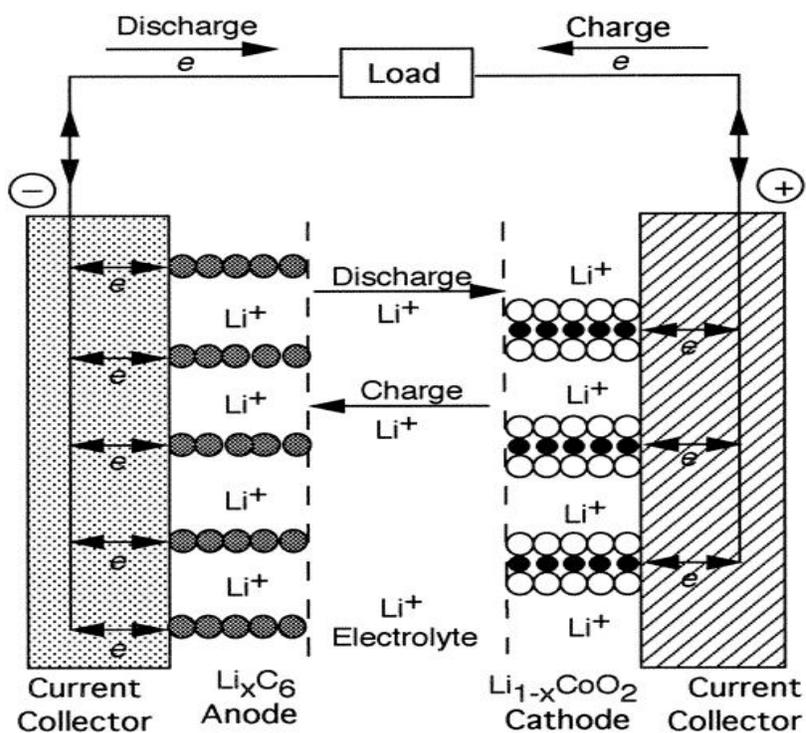


Figure 1.2 Working Principle of Li ion battery

The specific capacity of LiCoO_2 is ~ 140 mAh/g (milli-ampere hour per gram) and that of graphite is 372 mAh/g. However, a practical Li-ion battery contains few more components in addition to the electrode materials such as, electrolyte solution, a porous separator, metal foil current collectors and a metal can container with current feed-through. The weights of these components decrease the practical specific capacity. In other words, a practical Li-ion battery can be expected to deliver about 40% of its theoretical specific capacity calculated from electrode reactions. Similarly, the Li-ion battery yields a practical energy density (energy per unit volume) of approximately 350 Wh/l versus a theoretical value of 1330 Wh/l, or about 26% of the theoretical value.

1.5 BACK GROUND AND OBJECTIVES OF THE THESIS

High energy density rechargeable lithium ion batteries are presiding candidates in secondary batteries with innumerable applications due to their excellent properties such as good capacity retention, wide range of operating temperatures and fair degree of safety in operation (Kannan 2006). In recent years, the enhanced application of Li ion batteries in electronic industry and hybrid electric vehicle has led to increasing demand for cheaper and less toxic electrode materials with excellent capacity. However, the technological development of batteries has been criticized for not keeping pace with the rate of the progress of electronic industry. In spite of the advantages of the Li ion Batteries, the issues that limit the technology from the many possible applications are the poor shelf life, Instability of the electrode and toxicity of the electrodes and electrolytes. There is a world-wide effort to improve the specific energy, energy density and specific power (current drain rate) of Li-ion batteries. The performance of the battery mainly rely on the electrochemical performance of the cathode material.

1.5.1 Significance of Cathode Materials

The correct choice of the materials, the suitable design and the compatible methodology can aid the technology to witness new heights with superior efficiency. The extensive works are being accomplished by several research groups on the primary basic rate studies in the Materials Science, Synthesis Methodology, Surface Sciences, Crystallography, Electro chemistry and spectroscopy involved in the Li ion battery field. Of all the possibilities being explored for the improvement of the battery performance, the exploration of the new materials and novel processing techniques play a predominant role. Hence technologies being pursued to achieve these performance improvement include usage of alternative electrode materials, new electrolytes and improved cell design and packaging.

In order to achieve the near term goals in battery development the cathode materials are expected to possess certain stringent requirements like

- High Energy density
- High Rate capability
- High Electrochemical reversibility
- High Electronic conductivity
- Low Reactivity with electrolyte
- Non toxic and Safe
- Lower Cost
- Feasibility for fast synthesis
- Long cycle-life and Shelf life

Based on the afore mentioned considerations, this work has been dedicated to develop electrode materials for Li ion batteries through rapid and

reproducible synthesis methodologies with the inherent possibility of scaling up to bulk quantities for wider commercialization.

The first generation Li ion cells used LiMO_2 ($M = \text{Co}, \text{Ni}$) as cathode, graphite/hard carbon as anode and Li salt dissolved in non aqueous solvents as the electrolytes. The charge and discharge cycles of this battery are merely extraction and insertion of the Li ions from or into the stable crystal lattice of the electrode (Amatucci 1996). The main cause for the poor performance of the battery could be attributed to the instability of the electrode materials. The reasons for such instability could be summarized due to (i) Inhomogeneity in the compound formation (i.e.) existence of two or more compound phases resulting in cation ordering (Kobayashi 1969, Arun Patil 2008), (ii) slow dissolution of the cathode material into the electrolyte and (iii) high value of the relative volume changes accompanying charge/discharge cycling (Park 2001).

Apart from the shortcomings listed above, the environmental hazardous nature of the cobalt species and its cost have been considered as the impeding factor for wide spread commercialization. As an alternative to this material many materials have been suggested and LiNiO_2 is one such material with the same R3m structure as that of LiCoO_2 (Mizushima 1980). Both LiCoO_2 and LiNiO_2 have layered crystal structure and thus provide Li ions to reside (intercalate/ de-intercalate) in the inbetween layers. Because of the excessive spacing for the Li ion passage during charging and discharging, the structural distortion has comparatively lesser effect in this kind of electrode materials. The lesser cost of Ni and environmental harmlessness when compared to cobalt species has driven the researchers to investigate the compatibility of this material. Even then the main issues relating to this material are the precise control of stoichiometry and the difficulty in synthesis

of the materials with intended layered structure. The practical delithiation in this electrode material is very limited (i.e $\text{Li}_{1-x}\text{MO}_2$ ($x \sim 0.5$) (Delmas 1989).

Hence this thesis lays emphasis on the development of another material LiMn_2O_4 as an alternative to conventional LiMO_2 materials. The LiMn_2O_4 with cubic spinel has gained striking importance in the last decade due to its cost effectiveness, non toxicity, higher abundance of Mn in the earth and easy disposal. LiMn_2O_4 has been known to crystallize in space-group $\text{Fd}\bar{3}m$ with Li and Mn occupying 8a tetrahedral sites and 16d octahedral sites respectively of the cubic-close-packed oxygen array (Im 2003). In the framework, MO_6 octahedra share edges to build a rigid 3-dimensional network with open interconnected channels in the $\langle 110 \rangle$ directions for the passage of Li^+ ions (Figure 1.3). Li^+ -ions are mobile within these channels along the 8a-16c-8a path. Moreover the operating voltage is also larger for LiMn_2O_4 as compared to LiMO_2 ($M = \text{Co}, \text{Ni}$) (Koksbang 1996).

Though the LiMn_2O_4 has many advantages over conventional LiCoO_2 , the extensive usage of LiMn_2O_4 as cathode material is impeded due to its structural instability leading to capacity fading on extensive cycling. Upon several efforts to check the capacity fading, the act of reducing the concentration of the Mn^{3+} ion prone to Jahn teller distortion has been identified as suitable solution. The reducing of Mn^{3+} ion could be carried out easily by partially replacing the Mn^{3+} ions with other cations such as Co (Mandal 2002), Ni (Guohua 1996), Cr, Fe, Cu (Molenda 2004) and Al (Teruaki Kakuda 2007). As a new advancement in the field, the introduction of the trace amount of rare earth materials has drawn the attention of few researchers. Interesting properties on rare earth doping witnessed by the research groups has attracted remarkable attention of many researchers and commercial sectors. Though the usage of the rare earth doping is increasing linearly but it is likely to climb exponential statistics in the near future due to

its unassailable advantages in checking the capacity fading and improving cycle life.

1.5.2 Significance of Synthesis Methodology

The stoichiometry, crystal structure and morphology of the active material (electrodes) are essentially important for battery's electrochemical properties and in turn all these factors are closely related to the method of synthesis. To enhance the battery performance, the homogeneous and phase pure materials are highly needed. In the synthesis of uniform, phase pure and homogeneous material, selecting synthetic method is the key step to obtain final products.

The conventional Solid state reaction method has been widely utilized by commercial sectors due to the easier preparative procedures. But this method needs intermittent grinding in order to obtain homogeneous product and to reduce the grain boundary resistivity. Some inherent disadvantages like coarse grain size, loss of Lithium during evaporation resulting in unbalanced stoichiometry have been observed by many researchers. Although the solutions to these problems have been addressed by many research groups, the alternative synthesis procedures are attracting great deal of attention. Of the alternative synthetic procedures, wet chemical procedures like Sol gel, Co-precipitation, Combustion, hydrothermal and ion exchange have been exercised widely due to the promising advantages such as lesser reaction time, lesser processing sequence, good control over the stoichiometry and reduced grain size.

Among the different processing technologies being adopted for the synthesis of the electrode materials, the microwave processing attracts great deal of attention due to its advantages such as higher synthesis rate, the reduction of grinding steps during the synthesis process and the peculiar property of the microwaves to heat a system "from the inside".

1.5.3 Step towards Miniaturization

The advancement evidenced in the portable electronics industry has resulted in equipments that require low power for operation. Therefore the development of miniaturized power sources with high volumetric energy density is highly anticipated to meet the demand of microelectronic components such as small sensor nodes, active smart labels and MEMS components. Micro batteries are now viewed as the quintessential application specific device owing to their unique advantages like enhanced battery safety, absence of electrolyte leakage, extraordinary cycle life, fabrication into any shape and so on.

Recent studies of lithium ion batteries focus on improving electrochemical performance of electrode materials and lowering the cost. Considerable improvement in electrochemical performance of the electrode materials has been achieved. Among several methodologies being adopted for making Thin film cathode materials, RF sputtering has attracted greatest deal of attention because of the possibility to achieve repeatability, possible scaling for bulk production (Fragnaud 1995). But it needs high voluminous cathode target materials and sophisticated vacuum arrangements. As an alternative to this, Electron Beam assisted evaporation has widely been practiced in the fabrication of thin films (Shokoohi 1992). In micro battery applications, electron beam assisted evaporation has been adopted due to the merits such as

- Excellent control over the stoichiometry
- Easy control of crystallinity, density and microstructure
- Easy to be doped in order to produce better properties
- High deposition rate

1.6 ORGANISATION OF THESIS

The research effort accomplished by several researchers on (a) different electrode materials, (b) influence of various dopants in the structure, morphology and electrochemical performance of the electrode materials and (c) the influence of synthesis methodology in the specific power capacity of the electrode has been discussed in detail in Chapter 2. This chapter has been completely dedicated to the present state of art in the Li ion batteries technology and also highlights varying degree of complexity in electrode processing. Chapter 3 describes the experimental methodology adopted to synthesize electrode materials through Co-Precipitation method and Micro wave calcinations method. The chapter also discusses various techniques utilized for characterizing the electrode materials.

Chapter 4 describes influence of rare earth dopant Nd^{3+} , Pr^{3+} in the LiMn_2O_4 synthesized by Double hydroxide co-precipitation method. Chapter 5 describes the synthesis of Sm and Dy doped LiMn_2O_4 and the influence of the Sm and Dy in the capacity retention has been investigated in detail. Chapter 6 pertains to the thin film formation of the LiMn_2O_4 , $\text{LiNd}_y\text{Mn}_{2-y}\text{O}_4$ ($y = 0.05, 0.1$), $\text{LiSm}_z\text{Mn}_{2-z}\text{O}_4$ ($z = 0.05, 0.1$) through electron beam evaporation over the platinum and ITO coated glass substrates. Chapter 7 deals with the Synthesis and characterization of Sn substituted Nickel Ferrite as alternative anode for Li ion Batteries.