

CHAPTER – 1

INTRODUCTION

1.1 Introduction to Li- ion batteries:

Demand of energy and its supply is the most important issue for the quality enhancement of human life. With the development of electronic vehicles in recent years, the lithium –ion batteries as the energy storage device are gaining more and more attention due to its inherent benefits of high energy and power density. Low self-discharge rate and long life span are guarantee the battery safety, performance, reliability and life. There are many source of electrical energy such as wind, solar, tidal, nuclear, etc. Some of these energy resource such as solar and winds needs to store energy, so that the stored energy may be used in practical life. Where batteries have an important role in the efficient use of energy produced by these renewable energy source. Batteries are through to be a collective arrangement of the cell which can store and produce electrical form of energy and chemical reaction .The release and storage of energy is done by electrons and ions. The modern battery was developed by Italian physicist Alessandro Volta in 1800. It had a series of Cu and Zn disc and they are separated by card board [1]. Since then after 200 years of enhancement, battery technology is now have an era that batteries are safe now and can be used in many applications such as laptop, mobile, coin cells and in various transports.

There are two type of batteries :

- 1) Non chargeble batteries/ Primary batteries
- 2) Chargeble batteries/ Seondry batteries

Primary / Non chargeble batteries are disposable because of their electrochemical reaction. Seondry batteries are rechargeble batteries. Their electrochemical reaction can be reversed on applying a certain voltage to the battery in the oppostie direction of discharge. In rechargeable batteries electrochemical reaction is reversibile in nature [2]. In this general, a rechargeable battery can be charged and discharged number of times. These batteries have good cell voltage, capacity and better energy densities and long life comparing to primary / non rechargeable batteries. Among rechargeable batteries, Li-ion batteries are most useful because of very high capacity, energy density and excellent cyclabiility.

1.2 History:

The periodic table symbol is Li. Atomic number is 3. So it is light in weight. Lithium is an alkali metal. Lithium is highly reactive with high energy density. Lithium is used for the treatment of manic depression because it is particularly effective at calming a person in a manic state. In 1800 Alessandro Volta invented the first true battery. The name of the battery is the voltaic pile. The voltaic pile is constructed by two metals, copper and zinc, which are separated by a layer of cloth. The voltaic pile produces a continuous stable current. Alessandro Volta experimented with various metals and found that zinc and silver gave the best results [3].

1.3 Need for Lithium-ion batteries:

In the 21st century, the role of energy has been assuming increasing significance in recent times with the growing concern for the country's energy security. Energy self-sufficiency was the major driver for new and renewable energy in the country. The wake of the two oil shocks of the 1970s, the sudden increase in the price of oil, uncertainties associated with its supply, and the adverse impact on the balance of payments position led to the establishment of the Commission for Additional Sources of Energy in the Department of Science & Technology in March 1981. In this time, the energy economy is based on non-renewable resources, and the demand for energy is increasing continuously. The emission of CO₂ from fossil fuels is the main reason for global warming [4].

In March 1981, the commission was charged with the responsibility of formulating policies and their implementation programs for the development of new and renewable energy, apart from coordinating and intensifying R&D in the sector. In 1982, a new department, "Department of Non-Conventional Energy Sources," was established. In 1992, the Department of Non-Conventional Energy Sources became the Ministry of Non-Conventional Energy Sources [5].

The establishment of the Ministry of Non-Conventional Energy Sources has a main objective to reduce the emission of CO₂ and increase the renewable energy sources worldwide. Batteries are a source of energy storage mechanism and they work without pollution. Batteries convert chemical energy into electrical energy directly. They are also used in large-scale applications (e.g., portable radios & TVs, pagers, etc.). Lead-acid and nickel-cadmium batteries are being replaced by lithium-ion batteries. The main objective of replacing lithium is that it is the most electropositive and lightest metallic element. The stability of a lithium-ion battery is 500 cycles. Lithium-ion batteries are used in many devices, such as calculators, cardiac pacemakers, and implantable devices.

Features of commercial lithium- ion batteries:

1. These batteries have high energy density. The energy density 1.5 times of the Ni-Cd batteries.
2. These batteries are light in weight and compact.
3. They have high cell voltage approx. 3.6 V. Who is twice of the Ni-Cd and Ni-MH batteries.
4. Excellent cycle life the number of cycle approximate 500 and Service life of a battery exceeds.
5. These batteries have no memory effect .It can recharged at any time.
6. The operating temperature range of Li- ion batteries is -20 to + 60°C.
7. The Department of transportation United States harm full materials declared li-ion batteries exempt from dangerous materials safety issue.
8. Lithium- ion batteries have low self- discharge rate nearly 8% to 10% per month.
9. Lithium –ion batteries have fast charging potentials .They can charge 80% to 90% of full capacity in one hour duration.
10. High discharge rate are attainable.

Table 1.4 Comparison of various batteries:

Nickel-cadmium (Ni-Cd)	Nickel Metal hydride (Ni-MH)	Lithium –ion (li-ion)
Rechargeable	Rechargeable	Rechargeable
Memory effect	No memory effect	No memory effect
1.2 Volt/second	1.2 Volt/second	3.7 Volt/second

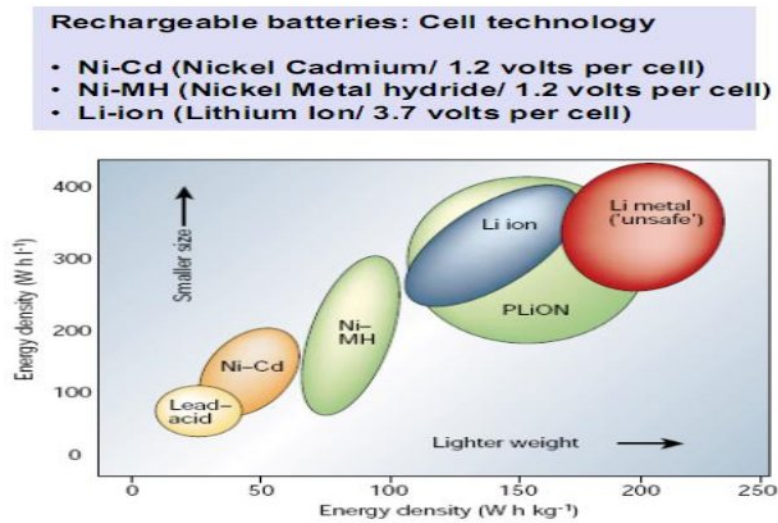


Figure 1.1: Comparison of various battery technology [6]

1.5 Battery technology:

1) Recharge - ability:

Basically, when the direction of electron discharge or negative to positive reversed restoring power.

2) Memory effect:

Generally when a battery is repeatedly recharge before it has discharged more than half of its power. It will forget its original power capacity.

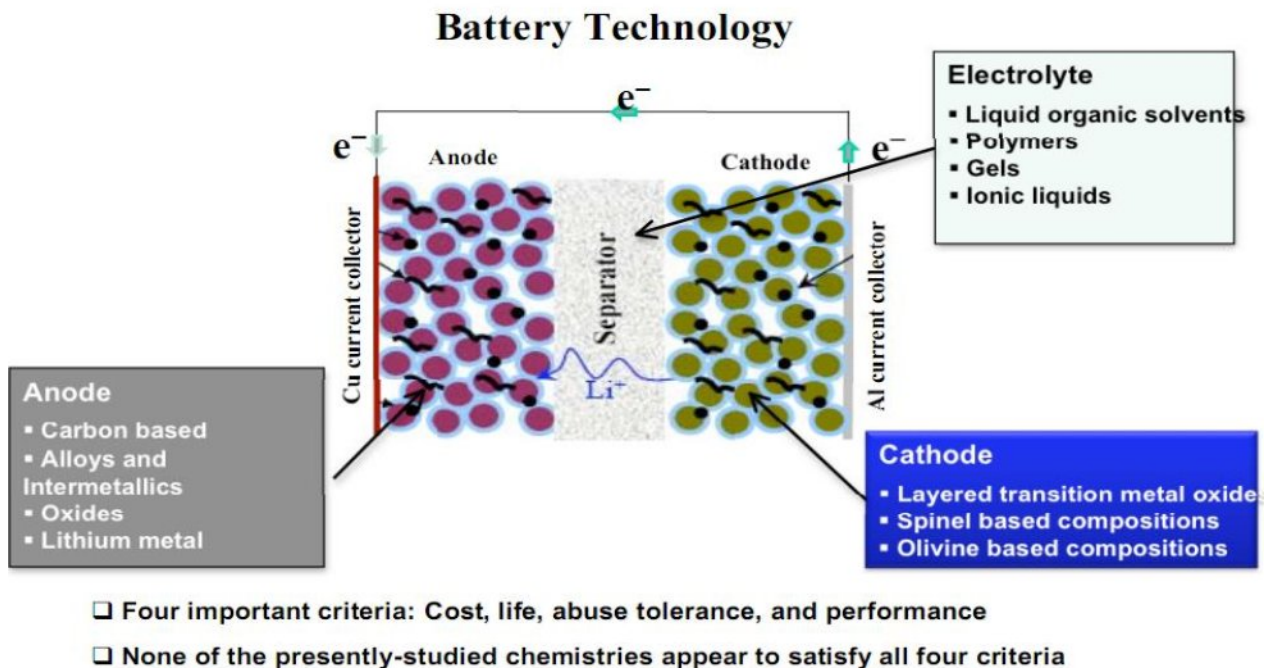


Figure1.2: Battery Technology [7]

1.6 Challenges:

There are number of factors that pose challenges to lithium ion batteries. There are no single lithium – ion battery.

There are variety of materials are present in market and many application of different materials. Observation of voltage, life time needs, and safety selection of specific electrochemical are very difficult.

- Variety of anode materials, research of new anode material is driven important role. The main challenges observation of reversible discharge capacity, surface area, density, mechanical strength.
- Balancing of material in cell, lithium ion batteries are made of layer of porous electrodes on aluminum and copper current collector foils. The capacity of each electrode pair needs to be balanced to ensure battery safety and avoid risk of overcharge of the anode.
- Cost challenges in manufacturing of lithium –ion batteries, the cost of lithium –ion batteries is much higher than the market.

1.7 Motivation:

Even – increasing attention has been paid to the development of large – scale energy storage system with a growing concern about environmental issue. Lithium –ion batteries have achieved great success as portable power sources for personal electronic over the past decades, and they have also been seriously considered as one of the most inspiring storage systems for the development of alternative anode materials for lithium –ion battery . During the past few years, spinel –type $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has received tremendous attention as an alternative anode material for large scale lithium –ion battery.

1.8 Features:

There are many features of commercial lithium –ion batteries.

- High operating potential, a single cell has average operating voltage of approximate 3.6 V.
- These batteries are compact, lightweight, and high energy density. They have fast charging potential, high discharge rate.
- They have excellent cycle life, excellent safety, low self-discharge, long self-life.
- Lithium –ion batteries has no memory effect and non-polluting.

1.9 Scope of thesis:


This work represents a simple solid state route method followed by a two stage thermal treatment for large scale production of a spinal type of lithium titanium oxide. Further, the enhancement in the electrochemical properties has been performed to test as alternate anode material for lithium – ion batteries in place of carbon based graphitic / MCMB electrode materials for anode.

CHAPTER - 2

LITERATURE REVIEW

2.1. Introduction of lithium metal:

Periodic table symbol is Li. lithium atomic number is 3. It is light in weight. It has high energy density, highly reactive. It has high voltage, very long cycle life so charging discharging rate is better. It is used to treatment of manic depression. It is particularly effective at calming a person in manic state.



Periodic Table of the Elements

1 H																	2 He														
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne														
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar														
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr														
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe														
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn														
87 Fr	88 Ra	89 Ac	104 Unq	105 Unp	106 Unh	107 Uns	108 Uno	109 Une	110 Uun																						
																		58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
																		90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

A lithium-ion battery is member of a family of rechargeable battery types. Lithium ions move from the negative electrode to the positive electrode during discharge, and back when charging. Lithium-ion

batteries use an intercalated lithium compound as the electrode material compound to the metallic lithium used in the non- rechargeable lithium battery.

2.2) Working of lithium –ion batteries:

The three functional components of a lithium –ion battery are the negative electrode, positive electrode, and electrolyte. Electrolyte is a separator .A negative electrode of a conventional lithium –ion cell is made from carbon. The positive electrode is a metal oxide, and the electrolyte is a lithium salt in an organic solution [6]. The electrochemical roles of the electrodes change between anode and cathode, depending on the direction of current flow through the cell. The most commercially popular negative electrode material is graphite .the positive electrode is generally one of three materials.

- 1) A layered oxide (such as lithium cobalt oxide)
- 2) A poly anion (such as lithium iron phosphate)
- 3) A spinel (such as lithium manganese oxide)

The electrolyte is typically a mixture of organic carbonates such as ethylene carbonate or diethyl carbonate containing complex of lithium ions. These non- aqueous electrolyte generally use non-coordinating anion salt such as lithium hexafluorophosphate (LiPF₆), lithium hexafluoroarsenate monohydrate [8]. Depending on materials choices, voltage, capacity, life and safety of lithium –ion battery can change dramatically. Recently, novel architectures using nanotechnology have been employed to improve performance. Pure lithium is very reactive .It reacts vigorously with water to form lithium hydroxide and hydrogen gas. Thus, a non –aqueous electrolyte is typically used, and a sealed container rigidly excludes water from the battery pack. Lithium –ion batteries are more expensive than Ni-cd batteries but operate over a wider temperature range with higher energy densities is harmful. [9].

Working of lithium –ion batteries is explained using Co based cathode (LiCoO₂) and graphite used as anode (Li_xC) with the reaction occurred at both the electrodes during charging/discharging process. During charging process, Li⁺ moves from cathode to anode through the electrolyte and results in oxidation of Co₃⁺ to Co₄⁺ .While in discharge process exactly the reverse process happens. The role of electrolyte is as a medium between anode and cathode to transfer the Li⁺ ions [10].

Lithium- ion battery system:

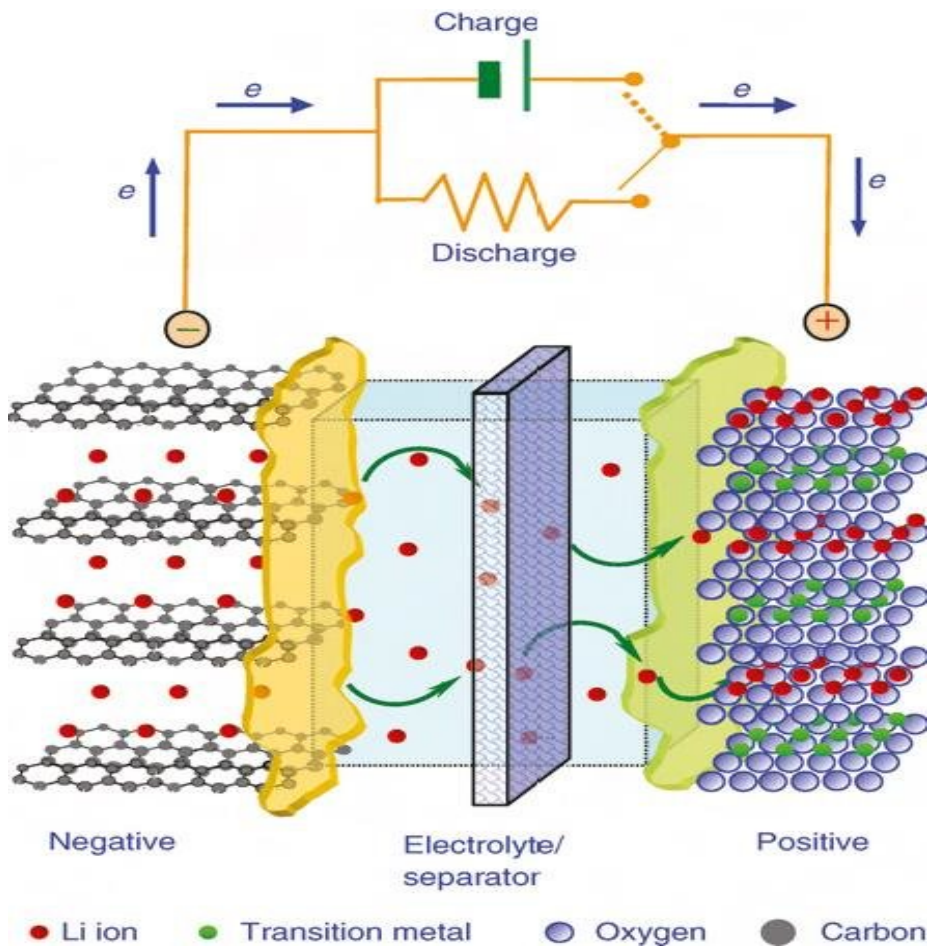


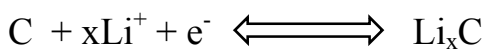
Figure 2.1: Schematic illustration of a rechargeable lithium battery[11]

Electrochemical Reactions :

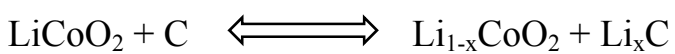
Cathode



Anode



Over all



2.3) Charging and discharging procedure

Lithium –ion batteries have three part.

1)Cathode

2)Anode

3)Seperator (made of polymer)

Negative electrode is electron doner ,and postive electrode is acceptor as like LiMo_2 ($M = \text{co}$, Ni , Mn) . Postive electrode is strong electronigative and negative electode is strong electropostive .In discharge process, negative electrode releases electron and shows its oxidised. The relased electron moves towards the postive electrode. The postive electrode accepted the outer circuit electron and showing reduction on this electrode. Charging process, lithium- ion moves from cathode to anode through electrolyte results in oxidation of Co_3^+ to Co_4^+ . Discharging process is exactly the reverse process.

2.7) ANODE MATERIALS:

2.7.1) Lithium metal as anode material:

Commercially, lithium metal is used as anode material of lithium-ion batteries. The first lithium-ion battery anode material is lithium metal. Lithium-ion is most electronegative ion. Lithium weight is 6.94 g/mol. So it is the lightest element of the periodic table.

Lithium metal specific gravity is 0.53 g/cm and specific capacity is 3.68 Ah/g [11].

2.7.2) History of anode material development:

In 1995, major anode material is graphite and hard carbon. In this time anode material in graphite, either mesophase graphite or systematic graphite is popular. Mesophase graphite is more costly in this time. In 2010 the shipment of anode material grew and reached 27000 t. In time of 1995 the anode material shipped approximately 450t. In this time natural graphite is most expensive. Technology of coating the graphite surface with a thin carbon layer has become widely used, modified graphite is replacing the mesophase graphite. The modified graphite is now the leading graphite anode material [12].

2.7.3) Recent research on anode materials:

There is a little scope to increase the capacity of graphite anode. Research has turned some new materials including oxides such as Co_3O_4 , CuO , and FeO , and lithium metal alloys such as Si-c-Li, Cu-Sb, Si-Li. Lithium metal has higher capacity than graphite [13].

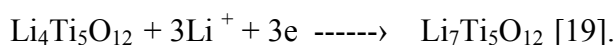
2.8) Introduction to $\text{Li}_4\text{Ti}_5\text{O}_{12}$:

The increased concern on environmental pollution from fossil – fuel consumption and the rapid depletion of fossil fuel demand the development of clean, efficient and sustainable energy –storage systems for applications including portable electronic devices and electronic vehicles. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has been demonstrated as a promising alternative of graphite anode materials for high power applications. The spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has proven to be a promising alternative anode material that can safety concern . It exhibits a flat charge /discharge plateau at a potential of approximately 1.55 V[15]. Lithium titanium oxide has excellent cycle life due to its negligible volume change and high thermal stability. The spinel structure of lithium titanium oxide produces a three dimensional network –like channel .For lithium ion diffusion and thus renders excellent reversibility for lithium ion insertion and extraction, as well as structural stability.This mainly lithium titanium oxide exhibits excellent Li^+ insertion/ extraction reversibility with zero structural change and a relatively higher operating voltage (1.55vs Li/Li^+) to ensure battery safety. Lithium titanium oxide present poor rate capability due to the poor electrical conductivity and sluggish Li^+ diffusion[16]. Thus some strategies have been proposed to overcome the significant drawbacks, by reducing the particle size, doping and surface modification. Reducing the particle size can shorten the Li^+ diffusion distance, and hence improve the rate capability of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Modifying the surface by coating of conductive material such as Ag, Sn and carbon could enhance the electronic conductivity and electronic inter connection between the particles resulting leading to improve electrochemical performance.The cost of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ will be pretty high [17].

2.9) Key feature of $\text{Li}_4\text{Ti}_5\text{O}_{12}$:

Lithium titanium oxide exhibits excellent Li^+ insertion/extraction reversibility with zero structural change and a relatively higher operating voltage (1.55 vs Li/Li^+) to ensure the battery safety .

- The theoretical capacity of spinel lithium titanium oxide is 175 mAh/ g .
- Spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ can be synthesized by different synthesis techniques including solid state reaction, sol-gel, high –energy ball milling etc. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ have extraordinary structural stability, low toxicity, very high rate capability, better promising safety, long cycle life. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is an significant candidate of anode material of future lithium ion battery[18].
- The electrochemical reaction on $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode with Li takes



2.10) Structure of $\text{Li}_4\text{Ti}_5\text{O}_{12}$:

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ has cubic spinel structure. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ spinel structure consist of lithium and titanium atoms randomly distributed on one half of the octahedral sites and lithium atoms filling one –eight of the tetrahedral sites with in the oxygen close packed lattice. Three –fourth lithium –ions are occupy 8a tetrahedral postion other Li^+ and Ti^{4+} are statically distributed over 16d octahedral postion . The ratio of Li^+ and Ti^{4+} is 1:5 and represented by the formula of compound $\text{Li}(\text{Li}_{1/3} \text{Ti}_{5/3})\text{O}_4$. Ohzuku and veda [20] analysis showed that the IR and Raman spectra of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ indicate the titanium and lithium ion on octahedral and tetrahedral postions.

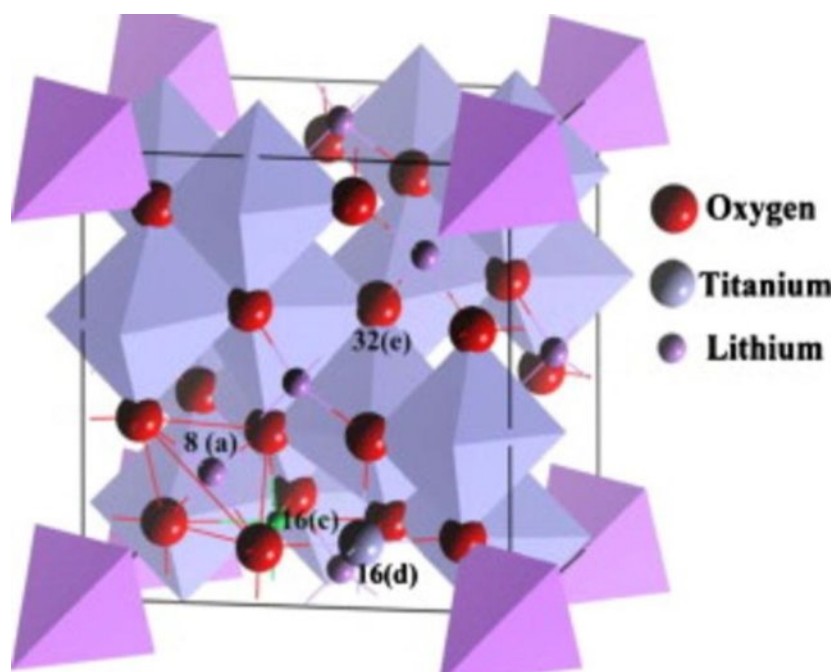


Figure 2.2: Structure of spinal type of $\text{Li}_4\text{Ti}_5\text{O}_{12}$

2.11) Structure position during charge and discharge:

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ exhibits excellent Li^+ insertion/extraction reversibility with zero structural change and a relatively higher operating voltage to ensure battery safety. Lithium is electrochemically active. Lithium insertion takes place in lithium titanium oxide. The spinel LTO is changed into a rock salt LTO [21].

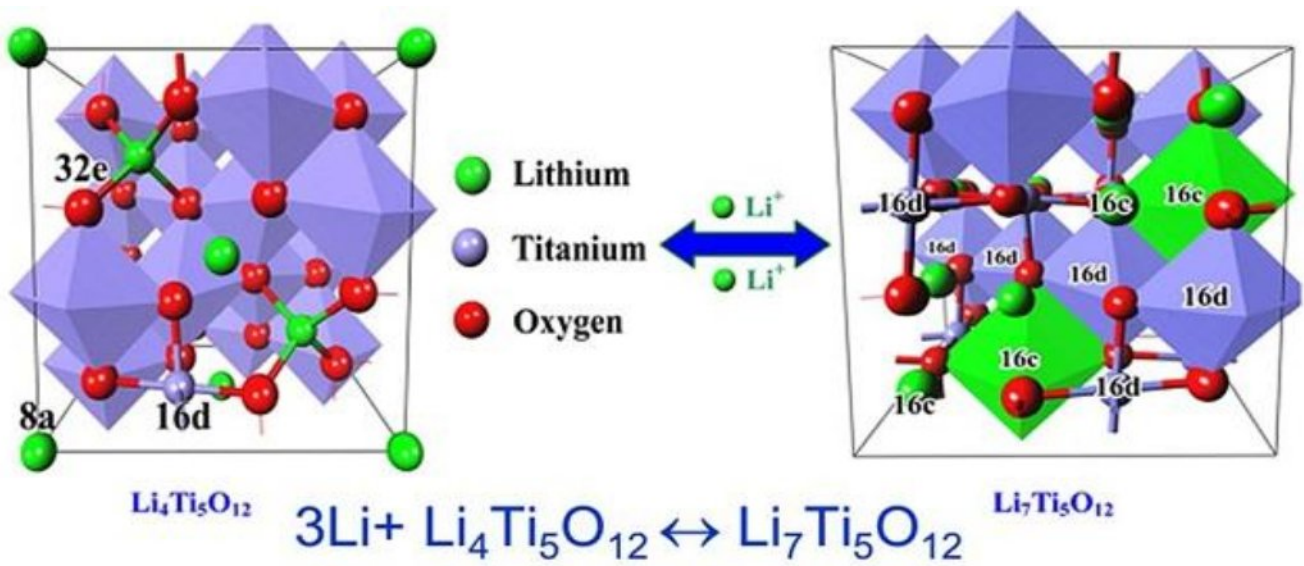


Figure 2.3: Change in the structure during charging and discharging

CHAPTER – 3

SYNTHESIS AND CHARACTERIZATION OF $\text{Li}_4\text{Ti}_5\text{O}_{12}$

3.1) Introduction:

Nanostructured electrode materials are commonly used in lithium –ion batteries due to their high specific and high rate capacities. Among many candidates, spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has been considered as an ideal anode material for long –life. Lithium batteries because of its negligible volumetric change during the insertion /extraction of the lithium ion. Compared to commercial carbon anode, S- LTO is a safer material because of its high thermal stability, the relatively fast transfer of lithium –ion, and enhance safety due to high discharge – plateau (at about 1.5 v) which prohibits the formation of metallic Li dendrites on the electrode which limits the cycling reaction rate. Its power density various approaches have been explored applying a conductive surface – coating, doping with elements (e.g. Mg, Zn, Ni), making composite electrode, or using thermal nitration .Reducing the particle size can shorten the Li^+ diffusion distance, and hence improve the rate capability of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Modifying the surface by coating conductive material such as Ag, Sn, and carbon could enhance the electronic conductivity and electronic inter connection b/w particles, further improve electro chemical performance. Nano structured $\text{Li}_4\text{Ti}_5\text{O}_{12}$, such as Nano particles, Nano wires, Nano tubes, Nano plates, and other three dimensional architectures have been prepared as they can contribute to improved kinetics and performance by effectively reducing lithium –ion diffusion distance [22].

LTO is highly safe anode material for lithium- ion batteries because it has sufficiently high operating potential (1.55v) than that for lithium plating .Most of these LTO films have sufficiently high crystallinity via high temperature treatment and show similar charge discharge properties and cycle stability and conventional LTO electrode with conducting additives and binder coated on metal foil. The cost of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ will be pretty high if we use these raw materials, industrial titanyl sulfate solution is an intermediate product in the commercial preparation of TiO_2 by sulphate route, which is obtained by acidulating ilmenite with sulphuric acid that can solubilize titanium to form its sulphate [24].

A large number of different synthesis methods have been preferred to obtain single –phase LTO powder. Among them solid state method of synthesis is considered as one of the efficient and simple way for the large scale production of LTO. Spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ can be synthesized by different synthesis techniques including solid- state reaction, sol-gel, high –energy ball milling etc [23].

Hence the synthesis of spinel LTO as anode material solid state reaction method is used applying two stage thermal treatments .Main aim of synthesis to remove the lower electronic conductivity and higher activation energy problem .Acetylene gas exposure of LTO resulting in terms of inclusion of carbon in the structure/ coating of LTO. The characteristics of two different samples are measured and compared to know the effectiveness of carbon treatment of LTO as anode material [25].

3.2) Experimental work

3.2.1) Synthesis procedure:

Solid state reaction method is one of an old and most common technique to produce polycrystalline and inorganic materials. Solid state reduction at low temperature or even room temperature has been developed as an effective approach of synthesizing metal alloy, inorganic oxide or coordinate compound compared to solid state reaction at high temperature and the solution reaction, this approach has several distinguishing features:

- 1) It is simple and convenient.
- 2) It involves less solvent and reduces contamination.
- 3) It gives high yield product.

Generally solid state reaction process, metal alloys are prepared with the assistance of ball milling. The obtained metal alloys often have micro scale sizes, leading to a low surface area of the final products. It is still a challenge to prepare metal alloys with large surface area of final products. It is still a big challenge to prepare metal alloys with large surface area by solid state reaction with room temperature. Solid state reaction method depends on the condition of reaction structural specifications of reactants, surface area of the material, their reactivity and thermodynamic change in terms of free energy associated with the reaction. In synthesis of spinel LTO, Titanium dioxide (TiO_2 with 99% purity) and lithium carbonate (Li_2CO_3) material mixed with help of motor and pestle. The molar ratio of titanium and lithium is 5:4. Motor and pestle were washed and cleaned with acetone and tissue paper. The grinding of the mixed material was carried out for 7 hour with acetone. In this process two stage thermal treatment was attempted. Initially annealed at 500°C for 6 hours and then further calcined at 800°C for 20 hours. After annealing the calcined mixture, fine powder form of LTO was observed.

Calculation:

Molar ratio of Ti: Li to be 5:4

Molecular weight of $\text{TiO}_2 = 79.90 \text{ g}$ (purity 99%)

Molecular weight of $\text{Li}_2\text{CO}_3 = 73.89 \text{ g}$ (purity 99%)

For one mole of TiO_2 weight is equal to $(79.90/99) \times 100 = 80.707 \text{ gm}$ (M)

For one mole of Li_2CO_3 weight is equal to $(73.89/99) \times 100 = 74.636 \text{ gm}$ (N)

Total sample will be perfect if Li and Ti mixture 6 gm then calculation.

Required $\text{TiO}_2 = 5M / (2N + 5M) \times 6 = 4.3798 \text{ gm}$. Required $\text{Li}_2\text{CO}_3 = 2N / (2N + 5M) \times 6 = 1.6201 \text{ gm}$

Total sample = 5.8287 gm.

Steps followed during the synthesis of LTO:

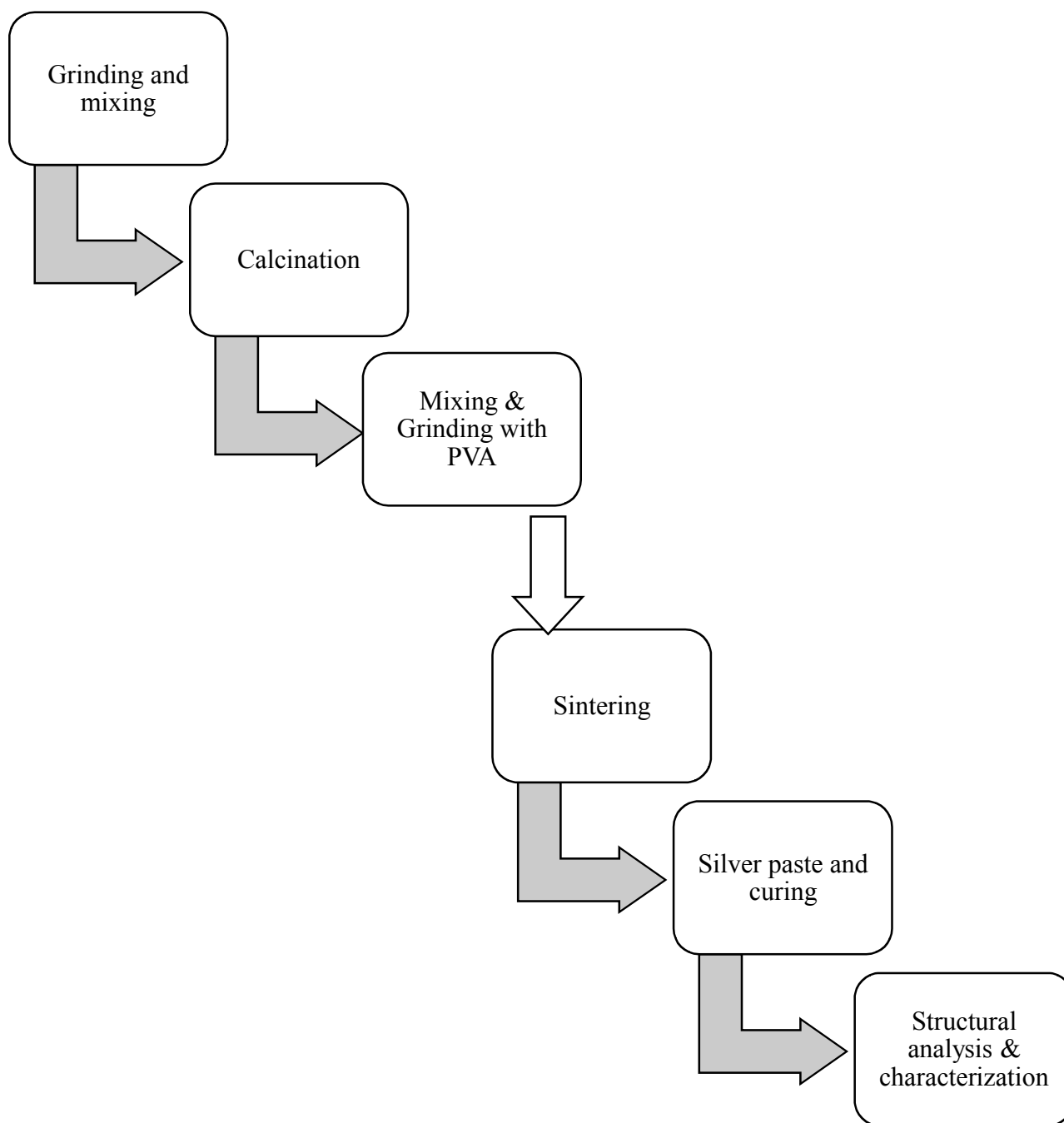


Figure 3.1 Solid State Reaction Method

3.3) Characterization

3.3.1) X-ray diffraction technique:

X-rays are highly penetrating electromagnetic (EM) waves. The range of waves lies in the range of 0.1nm -10 nm. When matter is irradiated by a beam of high energy charged particles such as electrons. Filament heated to produce electrons which are accelerated in vacuum by high electric field in range 20 - 60 KV towards a metal target. Positive plate / terminal is called anode. Corresponding electronic current is in the range 5-100 mA. A continuous spectrum produced when electrons hit the target, which is referred as “bremsstrahlung” or braking radiation. It is produced by stopping electrons [28].

However, when applied voltage is raised above a critical value, characteristic of the target metal, sharp intensity maximum appears in the spectrum which is used to characterize the material property and it is unique for all elements and compounds.

Analysis of XRD:

Structural analysis could determine the following structural details.

- 1) Lattice parameters: lattice parameter and constant “a” can be calculated by indexing. Indexing will let “w” know the miller indices. h , k, l, for a particular plane giving. The intercepts and the lattice constant can be obtained using following equations.

$$n \lambda = 2d \sin \theta \quad : \text{Bragg's law}$$

- 2) Phase identity: Identity of a particular phase, both peak position and relative intensities must fit in accordance to the standard data available for the element or compound. All peaks with relative intensity presents pure phase identity for a compound, if some major peaks are absent in impurity or absence of some element in it [29].
- 3) Accounted peak present in a pure sample impurity.
- 4) For a particular compound, try all the possible phases that could be fitted in the curve.
- 5) In a sample, more than one phase of the same element compound could be present. If the major peaks are fitting, then addition phases should also be taken in account.
- 6) Phase purity: XRD can also indicate whether or not the sample is single or multiphase. If the major peaks of only a single phase are indexed, it indicates that the sample has pure single phase.

3.3.2) Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) is used for inspecting topographies of specimens at very high magnifications. SEM magnifications can go to more than 300,000 X but most semiconductor manufacturing applications require magnifications of less than 3,000 X only. SEM inspection is often used in the analysis of die/package cracks and fracture surfaces, bond failures, and physical defects on the die or package surface [30]. In SEM, a beam of electrons is focused on a spot volume of the specimen, resulting in the transfer of energy to the spot. These bombarding electrons, also referred to as primary electrons, dislodge electrons from the specimen itself. The dislodged electrons, also known as secondary electrons, are attracted and collected by a positively biased grid or detector, and then translated into a signal. To produce the SEM image, the electron beam is swept across the area being inspected, producing many such signals. These signals are then amplified, analyzed, and translated into images of the topography being inspected. Finally, the image is shown on a CRT. The energy of the primary electrons determines the quantity of secondary electrons collected during inspection. The emission of secondary electrons from the specimen increases as the energy of the primary electron beam increases, until a certain limit is reached [31]. Beyond this limit, the collected secondary electrons diminish as the energy of the primary beam is increased, because the primary beam is already activating electrons deep below the surface of the specimen. Electrons coming from such depths usually recombine before reaching the surface for emission. Aside from secondary electrons, the primary electron beam results in the emission of backscattered (or reflected) electrons from the specimen. Backscattered electrons possess more energy than secondary electrons, and have a definite direction. As such, they cannot be collected by a secondary electron detector, unless the detector is directly in their path of travel. All emissions above 50 eV are considered to be backscattered electrons. Backscattered electron imaging is useful in distinguishing one material from another, since the yield of the collected backscattered electrons increases monotonically with the specimen's atomic number. Backscatter imaging can distinguish elements with atomic number differences of at least 3, materials with atomic number differences of at least 3 would appear with good contrast on the image. For example, inspecting the remaining Au on an Al bond pad after its Au ball bond has lifted off would be easier using backscatter imaging, since the Au is left would stand out from the Al background. A SEM may be equipped with an EDX analysis system to enable it to perform compositional analysis on specimens. EDX analysis is useful in identifying materials and contaminants, as well as estimating their relative concentrations on the surface of the specimen.

CHAPTER – 4

RESULT AND DISCUSSION

4.1 XRD Results:

The XRD patterns of LTO sample synthesized by solid state route method followed by grinding of the precursors for 7 hours is shown in fig 4.1. The two stage thermal treatments at 500 C for 6 hours and calcination at 800°C for 20 hours has been carried out. The XRD pattern of pure LTO sample shows the material has single –phase spinal LTO with cubic symmetry and Fd3m space group.

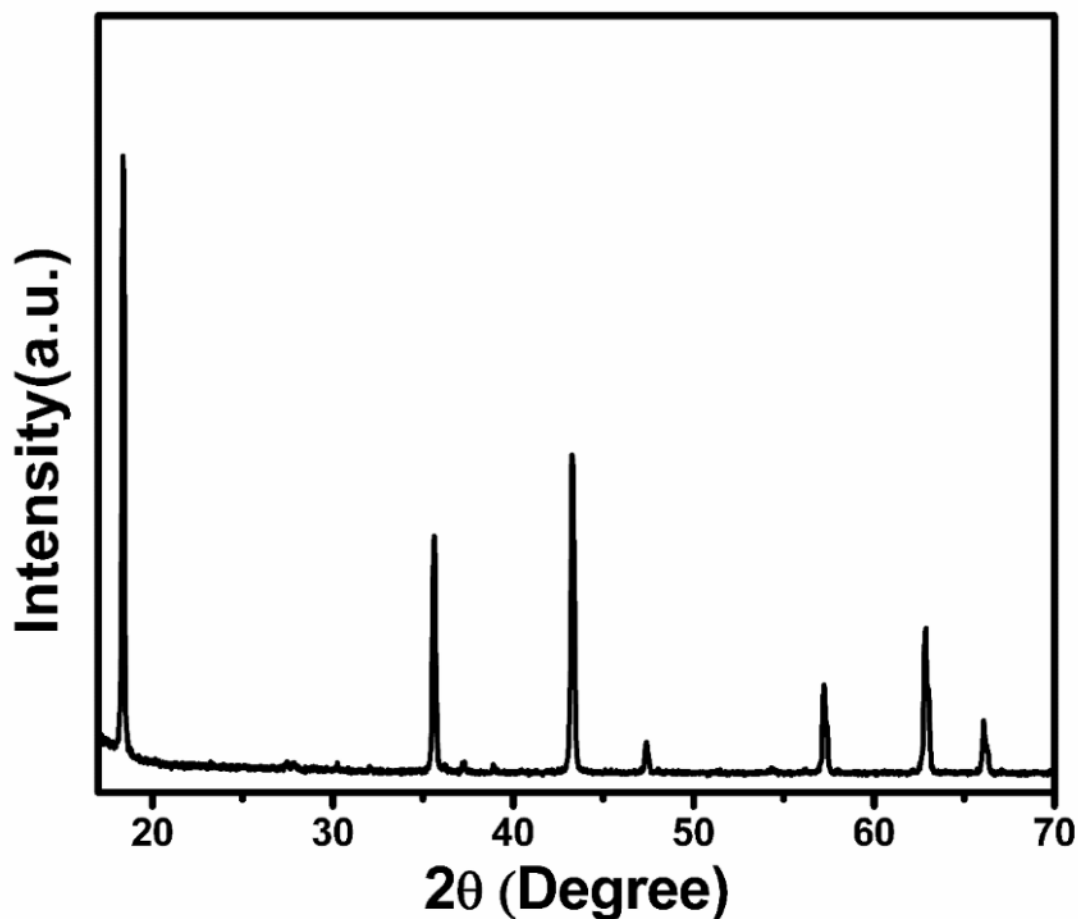


Figure 4.1: XRD pattern of LTO synthesized Solid state route

SEM images for pure LTO

In order to make a insight into the effect of particle size on the electrochemical performance of material electrode, sample LTO was annealed at 500°C for 6 hours and then calcined at 800°C for 20 hours, respectively and the micrographs are shown in Figure 4.2. The cubic shape type particles are bit distorted and have homogenous distribution showing the regular in arrangement as can be seen in fig (A and B). The average particle size of the prepared pristine LTO samples are in the range of 200 nm to 500 nm. SEM images indicate that LTO shows slight agglomeration.

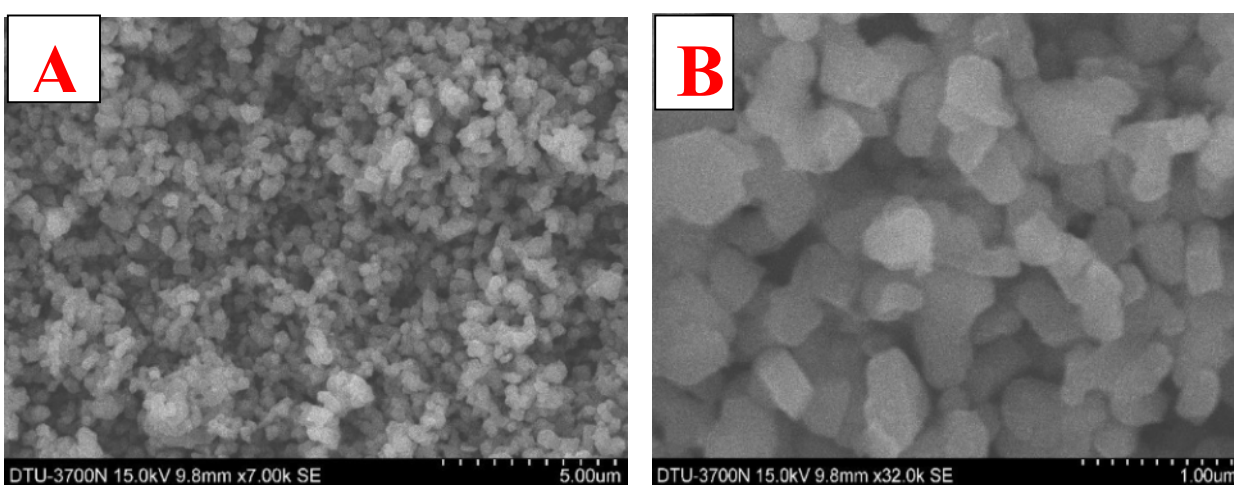


Figure.4.2 SEM images of pure LTO material synthesized by solid state methode (A) At magnification of 5 μm and (B) At magnification 1μm.

Electrochemical performance

Fig.4.3 shows the initial discharge –charge curves of the sample at 0.1C ,0.5C, 1C and 2C rates as shown, sample exhibits an initial discharge specific capacity of 149.1 mAh/g at 0.1C and 111.4 mAh/g at 0.5C, and 78.4mAh/g at 1C and 30mAh/g at 2C, respectively. The initial discharge specific capacity of the 0.1C is obviously higher than that of 0.5C,1C and 2C. The enhancement of the discharge specific capacity of sample can be attributed to improvement of the conductivity of material. The decrease of crystal size of sample shortens the diffusing path. From the shape of discharge profiles, sample exhibits longer and stable plateau around 1.55 V, indicating less polarization.

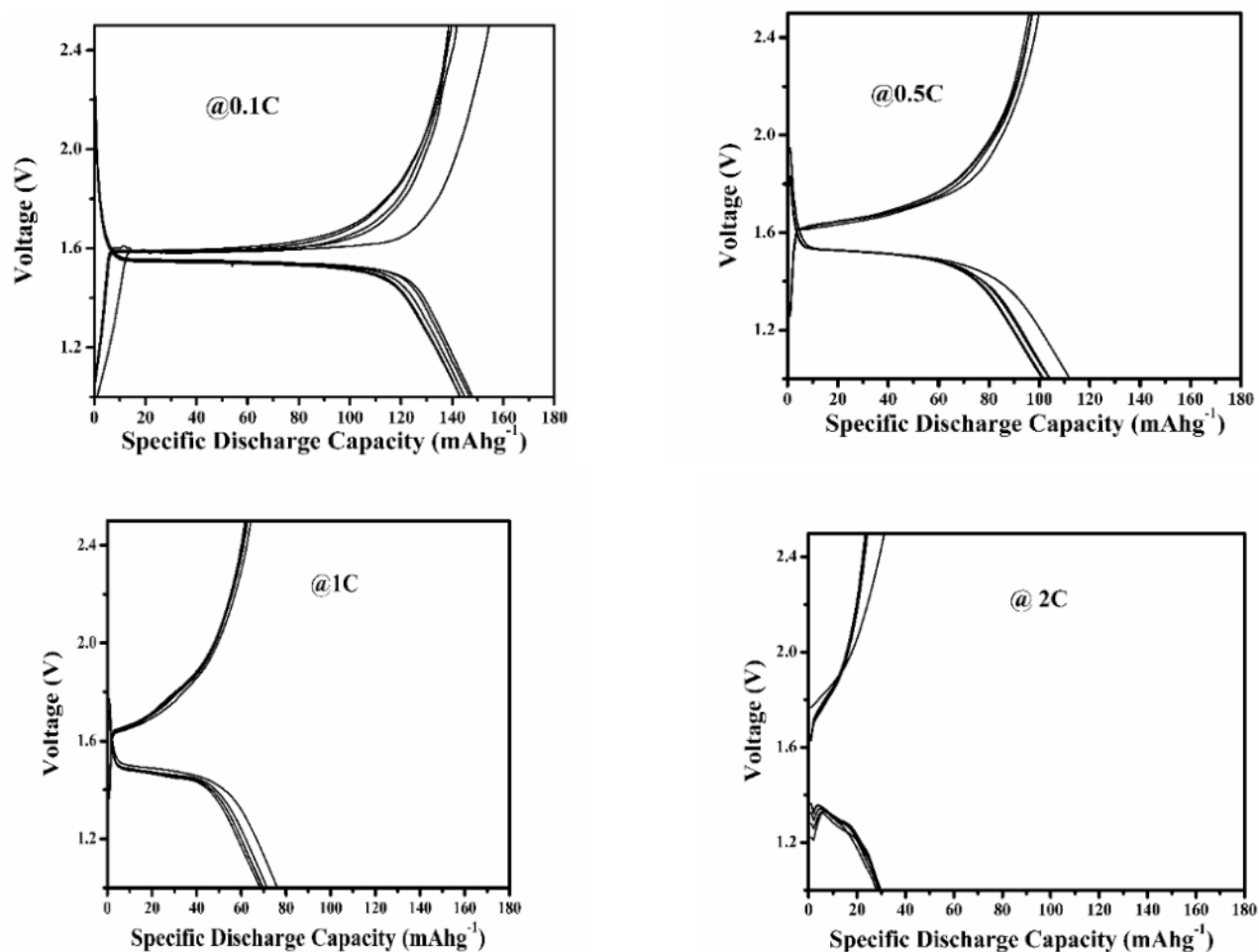


Fig.4.3 Initial discharge-charge curves of pure LTO

Fig.4.4 shows the cycling performance of the specimens at different rates from 0.1 to 2C. Figure 4.5 shows the EIS spectra of the pure LTO sample electrodes, which were measured at the stable voltage 5mV, and EIS spectra are tilted using an equivalent circuit. The total impedance 350 Ω .

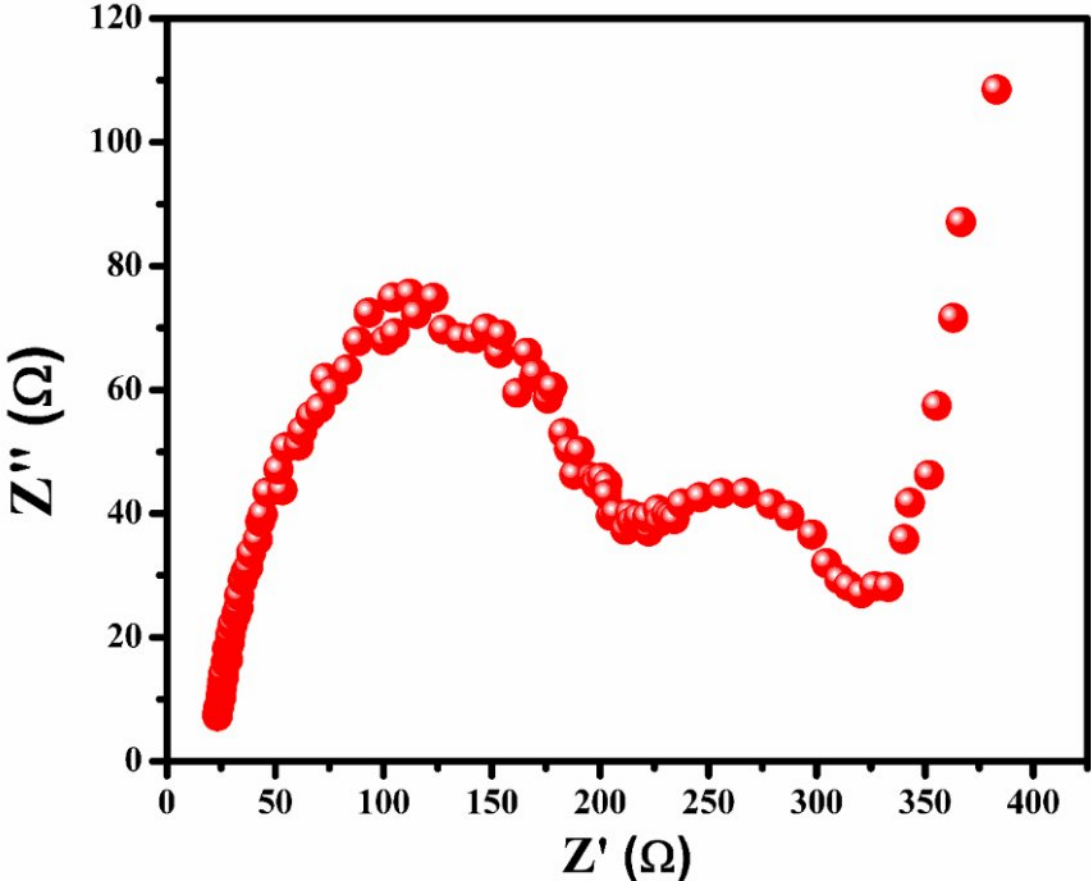


Figure 4.4 EIS spectra of pure LTO at an AC voltage pulse of 5mV

The cyclic voltammogram of synthesized sample of LTO is shown in Fig.4.5 in a range of 0.6 V -2.4 V verses Li/Li⁺ electrode. As shown in fig.(4.5) two pair of reversible redox peak can be clearly seen. As noticed, the sample contains redox peaks of Ti⁴⁺/Ti³⁺ in the range of 1.4 -1.8 V. For the discharge and charge cycle, the curve shows that the one cathodic peak located at 1.4V corresponds to the voltage platu of first discharge process. This is the process of Li insertion in Li₄Ti₅O₁₂ and there is also another anodic peak at 1.78 V that corresponds to the voltage platu of the first charge process, this is the process of Li -intecalation and de intercalation from Li₄Ti₅O₁₂.

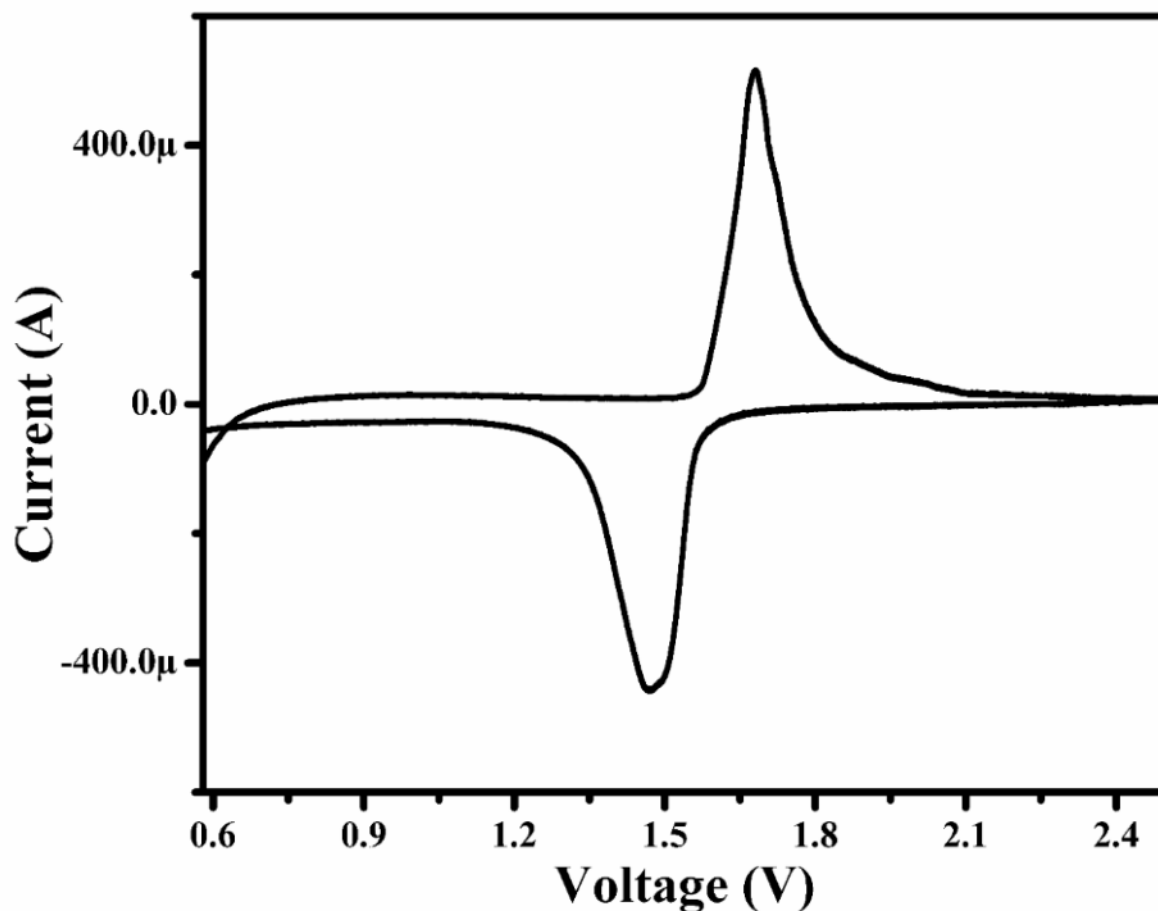


Fig. 4.5 Cyclic voltammograms of pure LTO scanning rate 0.05 mVs⁻¹ in the voltage window of 0.6–2.4 V.

CHAPTER -5

Summary and Conclusion

A novel ball-milling assisted solid-state reaction route has been designed successfully to prepared mesoporous $\text{Li}_4\text{Ti}_5\text{O}_{12}$. XRD analysis shows the proper formation of LTO spinel cubic crystal structure on optimized calcining temperature. Electrochemical performance of as-prepared $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has been investigated. The fine particles of around 200 nm to 500 nm in diameter support to attain good capacity and reversibility of lithium ion on charging and discharging. A electrochemical capacity of 149.1 mAh/g has been obtain at 0.1C rate.

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REFERENCES

1. M. Armand, J.-M. Tarascon, *Nature*, 451 (2008).
2. M. Winter, R. J. Brodd, *Chem. Rev.*, 104 (2004).
3. J.-M. Tarascon, M. Armand, *Nature*, 414 (2001).
4. J. B. Goodenough, Y. Kim, *Chem. Mater.*, 22(3) (2010).
5. M. S. Whittingham, *MRS Bulletin*, 33(2008).
6. J. M. Tarascon and M. Armand. *Nature* 414, 359-367(2001)
7. http://berc.lbl.gov/venkat/main_files/batteries-for_vehicles.pdf
8. K. Xu, *Chem. Rev.*, 104(2004).
9. K. Naoi, S. Ishimoto, Y. Isobe and S. Aoyagi, *J. Power Sources*, 2010.
10. Xiangcheng Sun, Pavle V. Radovanovic and Bo Cui, 2015.
11. K. Xu. *Encyclopedia of power sources*, Elsevier, 2010.
12. Wei Kong Pang, Vanessa K. Peterson, Neeraj, Je – Jang Shui, She-huangwu, 2014.
13. T. Ohzuku, A. Ueda and N. Yamamoto, *J. Electrochem. Soc.* 1995, 142, 1431.
14. J. Shu, *J. Solid State Electrochem.*, 2009.
15. X. Yao, S. Xie, C. Chen, Q. Wang, J. Sun, Y. Li and S. Lu, *Electrochim. Acta*, 2005, 50, 4076.
16. P. P. Prosini, R. Mancini, L. Petrucci, V. Contini and P. Villano, *Solid State Ionics*, 2001, 144, 185.
17. X. Yao, S. Xie, H. Nian and C. Chen, *J. Alloys Compd.*, 2008, 465, 375.
18. Y. Hao, Q. Lai, Z. Xu, X. Liu and X. Ji, *Solid State Ionics*, 2005, 176, 1201.
19. M.-H. Oh, H.-J. Kim, K. J. Kim and S.-G. Park, *ECSTrans.*, 2007, 3, 101.
20. N. Alias, M. Kufian, L. Teo, S. Majid and A. Arof, *J. Alloys Compd.*, 2009, 486, 645.
21. R. B. Khomane, A. Prakash, K. Ramesha and M. Sathiya, *Mater. Res. Bull.*, 2011, 46, 1136.
22. M. Venkateswlu, C. Chen, J. Do, C. Lin, T.-C. Chou and B. Hwang, *J. Power Sources*, 2005, 146, 204.
23. N. Zhang, Z. Liu, T. Yang, C. Lia, Z. Wang and K. Sun, *Electrochem. Commun.*, 2011, 13, 654.
24. Y.-J. Hao, Q.-Y. Lai, J.-Z. Lu, D.-Q. Liu and X.-Y. Ji, *J. Alloys Compd.*, 2007, 439, 330.
25. M. Mohammadi and D. Fray, *J. Sol-Gel Sci Technol.*, 2010, 55, 19.
26. Y. H. Rho and K. Kanamura, *J. Solid State Chem.*, 2004, 177, 2094.
27. G. Yan, H. Fang, H. Zhao, G. Li, Y. Yang and L. Li, *J. Alloys Compd.*, 2009, 470, 544.
28. C.-M. Shen, X.-G. Zhang, Y.-K. Zhou and H.-L. Li *Mater. Chem. Phys.*, 2003, 78, 437.
29. S. H. Ju and Y. C. Kang, *J. Phys. Chem. Solids*, 2009, 70, 40.
30. S. Yin, L. Song, X. Wang, M. Zhang, K. Zhang, *Electrochim. Acta*, 2009, 54, 5629.
31. Monika Michlskaa, Michalkrajewski, Dominika Ziolkowska, Bartosz Hamankiewicz, Mariusz Andrzejczuk, Ludwika Lipinska *Powder Technology* 266(2014).
32. Park YJ, Kim JG, Kim MK, Chung HT, Kim G (2000) *Solid State Ionics* 130:203.
33. Y. S. Lee, Y. K. Sun, K. S. Nahm, *Solid Ionic State* 109(1998)285.
34. J. M. Tarascon, W. R. Mckinnon, T. N. Bowmer, et al. *J. Electrochem. Soc.* 141 (1994).

