Synthesis and characterization of Antimony based nanostructured composite as anode material for Li–ion batteries

A dissertation submitted in partial fulfillment of the requirement for the award of the degree of

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In

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By

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CERTIFICATE

This is to certify that the dissertation entitled on **"Synthesis and characterization of Antimony based nanostructured composite as anode material for Li–ion batteries"** submitted to Delhi Technological University (formerly Delhi College of Engineering) by **Vaibhav Dadheech (2K15/NST/10)** in the partial fulfillment of the requirements for the award of the degree of **Master of Technology** in **Nano Science and Technology (Applied Physics Department)** is a bona fide record of the candidate's own work carried out under the supervision of **Dr. Amrish K. Panwar**. The information and data enclosed in this thesis is original and has not been submitted elsewhere for honoring any other degree.

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Candidate Declaration

I hereby declare that the work which is being presented in this thesis entitled **"Synthesis and Characterization of Antimony based nanostructured composite as anode material for Li-ion batteries"** is my own work carried out under the guidance of **Dr. Amrish K. Panwar**, Assistant Professor, Department of Applied Physics, Delhi Technological University, Delhi.

I further declare that the matter embodied in this thesis has not been submitted for the award of any other degree or diploma.

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ABSTRACT

Lithium-ion batteries have an outstanding combination of good power density and high energy, which ultimately makes it the technology of choice for portable electronics, power tools, and hybrid/full electric vehicles. There are exciting developments in new negative electrode (Anode) materials which are based on antimony(Sb) based nanostructured composite for use in the lithium-ion batteries (LIBs) over the past decade. In this study, preparation of antimony (Sb) based nanostructured composite(Sb/TiO_2/C) is done by Ball milling method. The influences on the sample are investigated by X-ray diffraction (XRD), Scanning electron microscope (SEM). X-Ray Diffraction technique result shows the proper thermodynamically stable phase formation of Sb/TiO_2/C composite. The Scanning electron microscopy (SEM) shows the regular shape & distribution of fine particles along with their dense and smooth surface. Electrochemical performances for this antimony(Sb) based nanostructured composite are further analyzed.

CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION – Li-ion Batteries

Demand of energy and supply of the same always play a very important role in enhancing quality of human life. Along with the development of electronic vehicles in past few years, the lithium–ion batteries, as the versatile energy storage device, are attaining enormous attentions due to its inherent benefits of power density and high value of energy, low value of self discharge rate and fair lasting life span to assure the battery safety, reliability, performance and life. Many sources of electrical energy are there such as tidal, wind, solar, nuclear etc. Some of them like solar and wind needs to store energy, in order to use that stored energy in practical life[1]. Batteries play an important role in the optimum use of energy produced by such renewable energy sources. Batteries are considered as collective arrangement of cell which is capable of storing and producing electrical form of energy and able to perform some chemical reactions. The process of storage and release of energy is done through use of electrons and ions[1]. The development of modern battery is done by Italian physicist Alessandro Volta in the year 1800. It contains series of Zn & Cu disc which are separated by help of card board. After 200 years of Enhancement, now there is an era of battery technology and batteries are much safe now and they can be used in various applications such as mobile, laptop, coin cells and in various other transports. hybrid electric vehicles (HEVs) due to their outstanding performances: high specific energy density, low weigh, long calendar life.

Batteries can be categorized in two forms:

1. Re-chargeable batteries
2. Non Re-chargeable batteries

Here, Non Re-chargeable batteries are considered as disposable batteries. Since their electrochemical reaction cannot be inverted. This is unlike the case of Re-chargeable batteries where nature of electrochemical reaction is reversible[2]. Thus, In this nature given battery could be charged and discharged enormous number of times. Very good capacity, Higher cell voltage, maximum specific energy are contained in Li-ion batteries. Li-ion batteries are extremely popular because of their highest capacity.Also, Secondary batteries are considered as rechargeable batteries as their electrochemical reaction can be inverted by applying a fixed voltage to the battery in the direction opposite of discharge.

1.2 STANDARD BATTERIES

Various standard batteries are as follows :

A. ALKALINE:

The electrodes being used are zinc & manganese oxide, along with alkaline electrolyte. They are thus commonly used in common Duracell and the Energizer batteries.

B. ZINC-CARBON:

Here electrodes being used are zinc & carbon, which contain anodic paste among them which also serves as an electrolyte.

C. LEAD ACID:

The electrodes being utilised are lead and the lead oxide, along with an acidic electrolyte. These can be used in transport vehicles like cars etc. Also, Lead – acid batteries are the example of re-chargeable batteries.

1.3 BATTERY TYPES:

A) NICKEL- CADMIUM:

Nickel –Cadmium is a kind of re-chargeable battery .Also, It has memory effect.

B) NICKEL-METAL HYDRIDE:

Nickel – Metal hydride is a kind of re-chargeable battery and it has no memory effect.

C.) LITHIUM-ION:

Li-ion is a kind of re-chargeable battery. Also, similar to Ni-Cd battery, It also has no memory effect.

1.4 MEMORY EFFECT AND CONCEPT OF RE-CHARGEABLILITY

The concept of memory effect comes into action generally when a given battery is recharged over and over again before it gets discharged more than to half of its power, it will lose its default power capacity. Recharge ability comes into consideration when the direction of electron discharge which goes from negative to postive, is inverted. Due to this, it also restores power.

1.5 HISTORY

The periodic table symbol of lithium is Li. Atomic weight of the same is 3. Thus, it is light-weighted. Lithium is also an alkali metal which is like sodium and potassium . It is highly reactive with enormous energy density . Lithium is commonly used in the treatment of manic depression since it is extremely effective at calming down a person during his/her manic state. In the year 1800, Alessandro volta, invented the first true battery. Name of that battery was given voltaic pile. The voltaic pile then, was constructed by two metals zinc and copper disc . Both are disparated by a layer of cloth[3]. Voltaic pile produces continuous & stable current. Alessando, at that time, experimented with several metals and ultimately found silver and zinc giving optimum results.

1.6 LI-ION BATTERY NEED:

In the era of 21st century, energy is playing a crucial role and significance in recent times since there is growing concern of energy security in country. Becoming energy sufficient was major need for country after wake of 2 oil shocks in year 1970. The abrupt growth in the prices of oil, dilemma connected by its supply and unfavorable influence on the balance of payments position ultimately led to formation of commission for extra source of energy in department of science & technology during march 1981.At that time, energy economy was based on non–renewable resources and demand of energy was growing continuously. Also, the emission of Co_2 along with fossil fuels is the main reason of increasing global warming[4].

Thus, during march 1981, the commission was finally given charge of applying policies and the implementation programs for the same so as to promote development of renewable energy aside to coordinating R&D in the sector .In 1982, a fresh department, which was named as "Department of non–conventional energy sources" was started. Then, again during 1992 this "department of non–conventional energy sources" upgraded to the "Ministry of non-conventional energy sources"[5].

Objective behind the inception of this ministry was to lessen the emission of Co_2 and expand sources of the renewable energy across the globe. Batteries can be considered as sources of energy storage and most importantly, it works without polluting the environment. Batteries are capable of converting chemical energy to electrical energy in one go. Therefore, they are also used at large scale in various applications like portable radios and televisions, pager etc. Nickel-cadmium & lead-acid batteries are nowadays replaced by lithium ion batteries. The main objective of this replacement is the most electropositive nature of lithium and also lithium is the lightest metallic element. The Stability of lithium ion battery is excellent(500 cycles). Lithium-ion batteries are thereby used in many devices which includes calculations, implantable devices and cardiac pacemakers.

There are many features of Li-ion batteries. Some commercial features are listed below:

1. Light weighted and compact.
2. High cell voltage (about 3.6volts), which is twice of the Ni-Cd & Ni-MH battery.
3. High energy density, which is approximately 1.6 times of Ni-Cd battery.
4. No memory effect.
5. Can be recharged anytime.
6. Operating temperature range is from -20 to + 60˚C.
7. Excellent life cycle of the battery.
8. Safety issues in transportation (Department of transportation in US exempts these batteries from dangerous materials).
9. Low self-discharge rate(8-10% per month).
10. Fast charging potentials i.e. they can charge upto 90% of their capacity in one hour duration.
11. Attainable high discharge rates.

1.7 COMPARISION AMONG VARIOUS BATTERIES

The comparison table is shown below, which also provides details of their recharge ability and memory effect.

Nickel-cadmium (Ni-Cd)	Nickel Metal hydride (NiMH)	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

TABLE 1.1 – COMPARISION AMONG VARIOUS BATTERIES

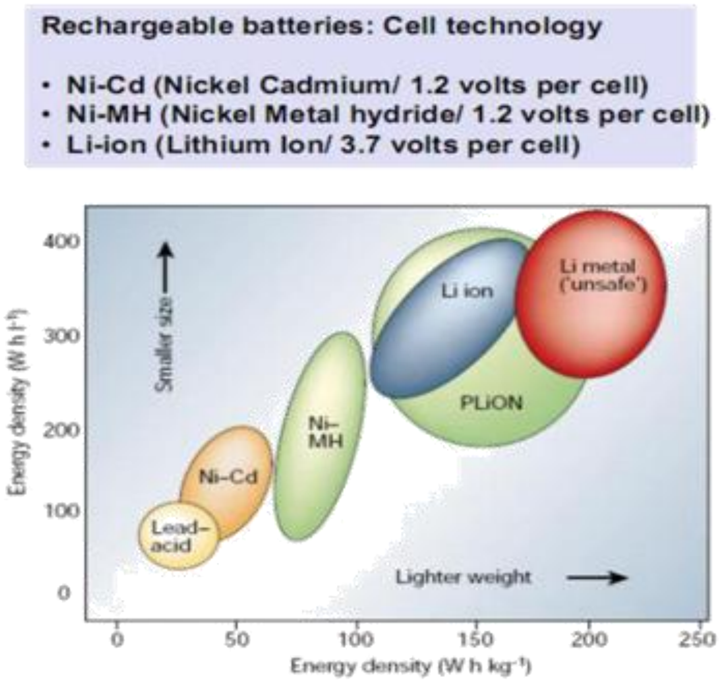

Figure 1.1: Resemblence of several battery technologies[6]

1.8 BATTERY TECHNOLOGY

1. ABILITY TO RECHARGE:

   Here, the direction of the electronic discharge is from negative to positive. It is reversed in order to restore power.

2. EFFECT OF MEMORY:

   Normally, when a battery is recharged over and over again before it gets discharged more than 50% of its power, it will lose its usual default power capacity.

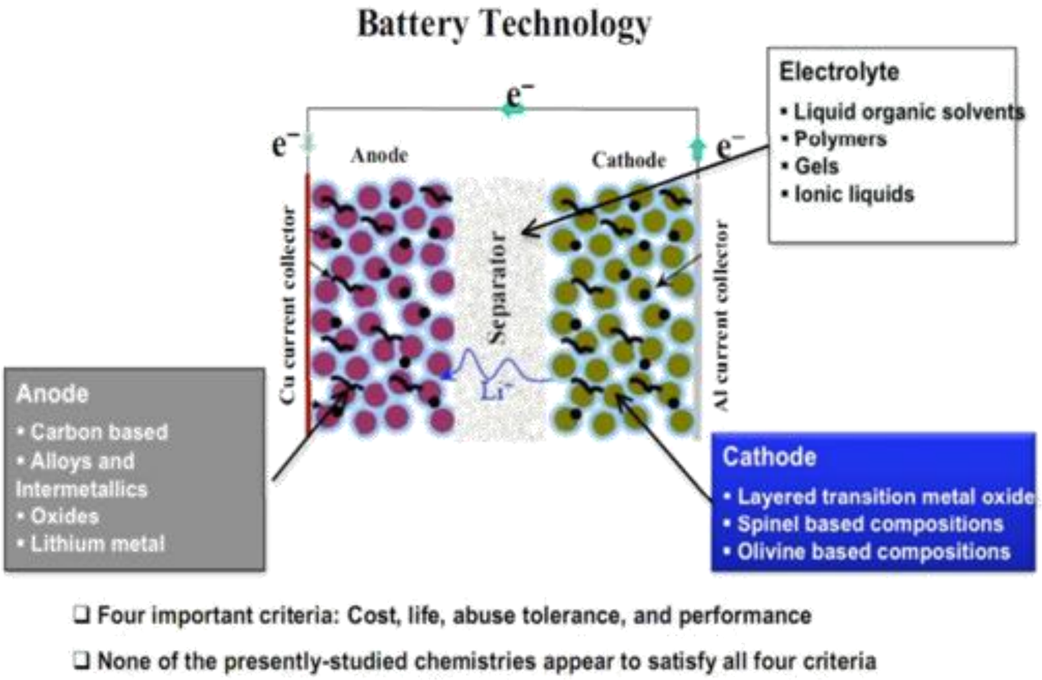

Figure1.2: Battery Technology[7]

1.9 CHALLENGES TO LI-ION BATTERIES

There are number of factors that pose challenges to lithium ion batteries.

A) There is not availability of single Li–ion battery.

B) There are diversified materials which are present in market and much application of different materials. Observation of voltage, life time needs, and safety selection of specific electrochemical are very difficult.

C) 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.

D) Making the balance of material in the cell is again a challenge. Capacity in each of the electrode pair is needed to be balanced.

E) Cost of the manufacturing of Li-ion batteries also is major issue. Cost of these batteries is much higher in the market.

1.10 MOTIVATION FOR ITS USAGE

Nowadays, increasing attention is being paid to the evolution of large– scale energy depositing systems with the increasing concerns about environmental issues. Li–ion batteries have successfully achieved enormous success as movable power sources for the personal electronics during the past decades, and thus, they also have been seriously thought as one of the most inspiring depository systems for the evolution of substitute anode materials for Li-ion battery. In the past years, Amorphised Sb-based Nano-composite has received massive attention as the substitute anode material for Li-ion batteries.

1.11 FEATURES - LI-ION BATTERIES

There seems a lot of features of the Li-ion batteries. Some of them being featured below:

- Giant operating potential range. Here, single cell is having mean operating voltage of approximately 3.6 volts.
- The Li-ion batteries are compact, light-weighted and possess high energy density. They also have very fast charging potential and high value of discharge rate.
- Li-ion batteries also have brilliant cycle life, extreme safety, low value of self-discharge and a high value of self-life.
- Li –ion batteries have as such no memory effect and also they are non-polluting.

1.12 EXTENT OF THESIS

The work here depicts formation of Antimony(Sb) based nanostructured composite through High energy mechanical milling process to make it available as an alternative anode material for lithium ion battery. Further enhancement in the properties which includes charge/discharge capacities need to be done so that its electronic conductivity can also be increased.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION TO LITHIUM METAL

Periodic table image is Li. lithium nuclear weight is 3. It is light in weight like sodium and potassium .it has high energy density, exceptionally reactive. It has high voltage, long cycling life so charging releasing(discharging) rate is better. It is utilized to treatment of manic depression in light of it is especially viable at quieting a man in hyper state.

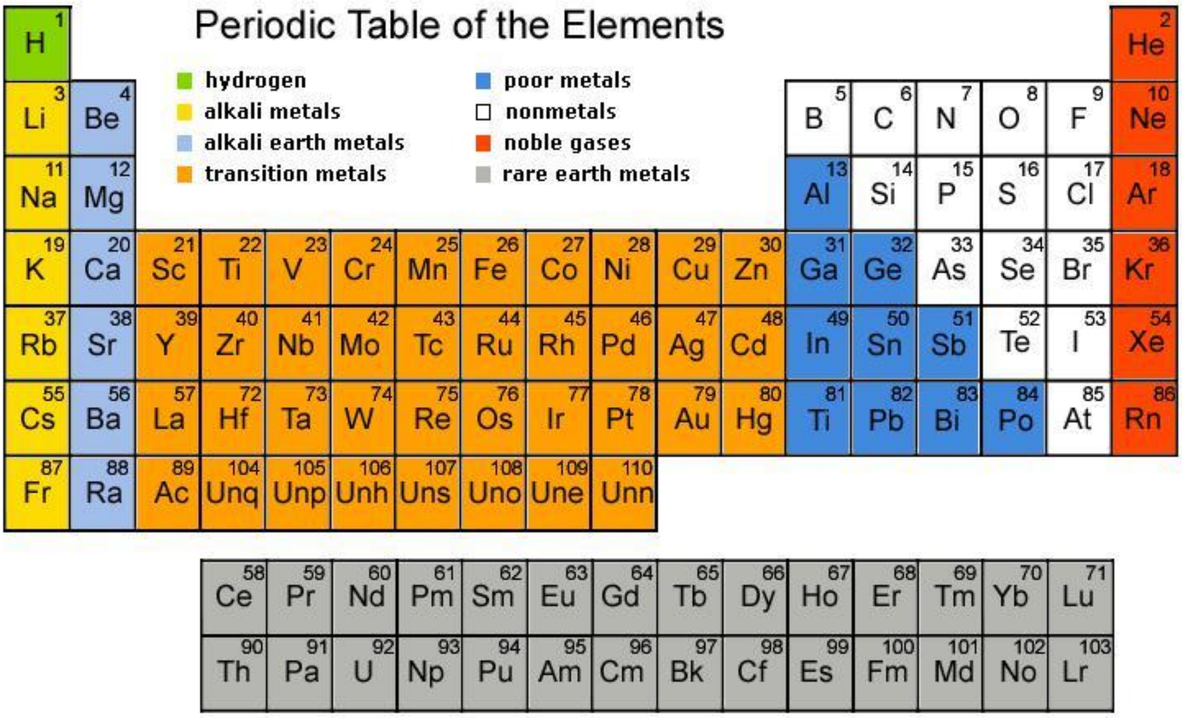

FIGURE 2.1 PERIODIC TABLE MENTIONING LITHIUM METAL[7]

A lithium–ion battery is an individual from a group of rechargeable battery sorts in which lithium particles move from the negative terminal to the positive anode amid release, and back while charging. Lithium–ion batteries utilize an intercalated lithium compound as the cathode material compound to the metallic lithium utilized as a part of the non-rechargeable lithium battery.

2.2 WORKING OF LITHIUM ION BATTERIES

The three practical segments of a lithium –ion battery are the negative terminal, positive terminal, and electrolyte. Electrolyte is a separator.

A negative terminal of a regular lithium –ion cell is produced using carbon[6]. The positive terminal is a metal oxide, and the electrolyte is a salt of lithium in a natural arrangement. The electrochemical parts of the terminals change amongst anode and cathode, contingent upon the heading of current course through the cell. The most economically well known negative cathode material is graphite .The positive anode is for the most part one of three materials.

1) A layered oxide, (for example, lithium cobalt oxide)

2) A poly anion, (for example, lithium press phosphate)

3) A spinel, (for example, lithium manganese oxide)

The electrolyte is ordinarily a blend of natural carbonates, for example, ethylene carbonate or diethyl carbonate containing complex of lithium particles. These non-fluid electrolytes for the most part utilize non-planning anion salt, such as lithium hexaflurophosphate ($LiPF_6$), lithium hexafluoroarsenate monohydrate[7]. Contingent upon materials decisions, the voltages, limit, life and security of lithium –ion battery can change drastically. As of late, novel models utilizing nanotechnology have been utilized to enhance execution since immaculate lithium is extremely responsive[7]. It responds energetically with water to frame lithium hydroxide and hydrogen gas. In this way, a non –aqueous electrolyte is ordinarily utilized, and a fixed holder inflexibly rejects water from the battery pack. Lithium –ion batteries are more costly than Nickel-cadmium batteries however work over a more extensive temper goes with higher vitality densities, defensive circuit to constrain peak voltages[8].

Working of lithium–ion batteries is clarified utilizing Cobalt based cathode ($LiCoO_2$) and graphite utilized as anode (Li_xC) with the response happened at both the terminals amid charging/discharging procedure. Amid charging process, Li^+ moves from cathode to anode through the electrolyte and results in oxidation of Co^{3+} to Co^{4+}, while in discharging, prepare precisely the reverse process happens. The part of electrolyte is as a medium amongst anode and cathode to exchange the Li^+ particles.

Lithium ion battery system

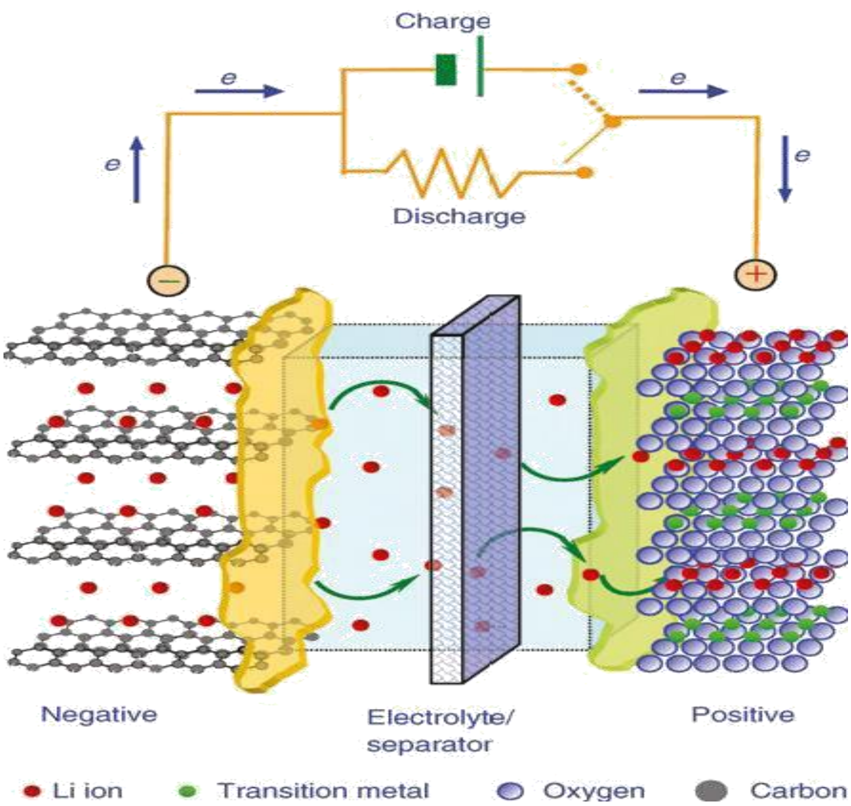

Fig2.2 - **Schematic illustration – Li-ion battery**[8]

Electrochemical Reactions :

Cathode :

$$LicoO_2 \Longleftrightarrow Li + CoO_2 + e^-$$

Anode:

$$C_6 + Li + e^- \Longleftrightarrow LiC_6$$

Over all

$$LicoO_2 + C_6 \Longleftrightarrow Li_{1-x}coO_2 + Li_xC$$

2.3 PROCEDURES: CHARGING AND DISCHARGING

Lithium –ion batteries have three sections

- Cathode
- Anode
- Separator (which is made of polymer)

Negative terminal is electron donor, and positive electrode is acceptor just like $LiMo_2$ (M = Co , Ni , Mn) .Positive cathode is solid electronegative and negative electrode is solid electropositive . In process of discharge, negative anode discharges terminal and demonstrates its oxidized. The released anode moves towards the positive terminal. The positive terminal acknowledged the external circuit electron and demonstrating diminishment on this cathode.Charging process includes lithium-particle moving from cathode to anode through electrolyte results. Also in oxidation of Co^{3-} releasing procedure is precisely the invert procedure.

2.4 ADVANTAGES OF UTILIZING LITHIUM ION BATTERY

1) **Power**:

Lithium–ion batteries have high vitality density. The vitality is around 1.5 times and specific energy is about twice when contrasted with the high limit Ni-Cd batteries. High vitality thickness implies awesome power in a littler bundle. Lithium–ion is 160% greater than NiMH and 220% more noteworthy than Ni-Cd batteries.

2) **Higher voltage**:

A little cell has a working voltage of inexact 3.6volt. A solid current enables it to control complex mechanical gadget.

3) **Long –Self life** :

Lithium particle battery have just 5% release misfortune for every month in look at of NiMH battery 10% release misfortune .Ni-Cd battery have 20% of discharge misfortune for each month. So no reconditioning required up to surmised 5 year .In Ni-Cd battery reconditioning time is almost 3 months. NiMH battery reconditioning time is also around 1 month.

4) **Non –polluting** :

Lithium –ion is not contaminating as a direct result of not utilization in lethal overwhelming metals. For example- Pb, Cd or Hg.

2.5 ENVIRONMENTAL IMPACT – LITHIUM ION BATTERY

Lithium–ion battery life is expected inexact 10 year. Cathode with nickel and cobalt, having most astounding potential for environmental impacts, these impacts are reason of an Earth-wide temperature boost, natural toxicity, and human well being impacts. Rechargeable batteries are regularly recyclable. Oxidized lithium is toxic, and can be removed from the battery, neutralised, and utilized as feedstock for new lithium particle batteries(source : Joined states enviromental security office).

2.6 BATTERY SAFETY

"Flexibility from chance is meaning of safety. Lithium metal have inborn shakiness amid charging, put a damper improvement. The temperature would quickly ascend to the dissolving purpose of the metallic lithium and caused a savage response. An extensive amount of rechargeable lithium batteries must be reviewed in 1991 after the pack in cellular telephone discharged hot gasses and incurred copies to a man face. The Catastrophe theory, the issue is that of finding hazardous, as opposed to asafe, working region. Taking these ideas as abases ,we will utilize comparable approach. We characterize safety in a way that is contrarily relative to the idea of "abuse"

$$\textbf{Safety} \quad \alpha \quad \textbf{1/abuse}$$

2.7.1 MECHANICAL ABUSE

Mechanical mishandle is from infiltration of cells, amid entrance of cell happen hamper. This exists amid transportation and installation. As we probably are aware, a large portion of lithium–ion batteries are transported in charged condition. Mechanical manhandle are additionally appear in administration of completely charged batteries. Mechanical manhandle is qualified by the strain ε of the battery, that is, contrasting a deformed measurement with its unique measurement, or by measuring the anxiety σ that would create such strain. The reason for strain might be because of normal extension amid intercalation, in light of maturing and lithium plating, or in view of compassion or outside impacts.

2.7.2 OVERCHARGING

Lithium-particle batteries control numerous compact buyer electronic gadgets. To enhance the execution of these batteries for existing and developing applications, an essential comprehension of the stage advancement of cathodes inside lithium-particle batteries amid charge and release is important. A comprehension of the basic advancement of anodes amid operation increased through non-damaging investigations will direct adjustments to battery structure and utilize that are gone for enhancing battery execution. Specifically, the investigation of cathodes working at the furthest points of true conditions, for example, amid cheating, can uncover the underlying driver of battery disappointment from which better materials can be composed, bringing about more secure batteries.

2.7.3 OVER TEMPERATURE

Over temperature in a lithium ion cell is likewise a fundamental issue. In lithium–ion cell, inside created warm shapes to a short–circuit cell disappointment. Interior temperature surpasses over temperature (100 c) SEI layer and the dynamic material will begin breaking down, bringing about exothermic responses and probability of warm runway, which could additionally prompt fire and blast. Also, on the off chance that it goes beneath under temperature the response rate is significantly diminished and endeavoring to charge or release may bring about, metallic lithium storing on negative anode, prompting irreversible loss of limit and danger of inward short-circuits.

2.8 ANODE MATERIALS

2.8.1 LITHIUM AS AN ANODE MATERIAL

Commercially, lithium metal is utilized as an anode material of lithium–ion batteries. The primary lithium–ion battery anode material is lithium metal. Lithium–ion is most electronegative particle which shows 3.4volts. Lithium weight is 6.94 g mol. So, it is the lightest component of intermittent periodic table.

Lithium metal's specific gravity is 0.53 gcm and specific limit is 3.68Ahg[11].

2.8.2 HISTORY : ANODE MATERIAL DEVELOPMENT

In 1995, noteworthy anode material was graphite and hard carbon. In this time, anode material in graphite, either mesophase graphite or precise graphite is prominent . meso-phase graphite is all the more exorbitant in this time. In 2010 the shipment of anode material is developed and achieved 27000t. In time of 1995, the anode material delivered approximately 450t. In this time natural graphite is most costly. Innovation of coating the graphite surface with thin carbon layer has turned out to be broadly utilized, modified graphite is supplant the meso-phase graphite .This Modified graphite is currently the main graphite anode material[12].

2.8.3 RECENT RESEARCH ON ANODE MATERIALS

There is a little degree to build further the limit of graphite anode. Research has turned some new materials including oxides as like Co_3O_4 , CuO, and FeO. Also, lithium metal compounds as Si-c-Li, Cu-Sb, Si-Li, lithium metal have higher limit than the graphite[13].

2.9 INTRODUCTION TO $Sb/TiO_2/C$

Usually graphite is used as anode material for lithium ion batteries but now a days, focus has been shifted towards alloy based anode materials which includes Sn(tin), Sb(Antimony), Si(silicon), P(phosphorus). These are used because they possess great hydrometric and volumetric capacities. They experience the ill effects of poor cycling conduct since a substantial volume change happens amid release/charge. As of late, composite materials which are nanostructured arranged by different manufactured devices have been considered as possibility for the alloy-based anode materials in lithium auxiliary batteries[15]. The usage of Nanostructured composite materials provides

a) a full hypothetical limit by their capacity to give a high interfacial range.

b) a quick rate capacity by expanding the lithium-ion dispersion rate.

c) large cycling conduct by pleasing the strain produced amid the cycling.

Nanostructured composites consist of accurately distributed Active & Inactive nano-crystallites. The expanded worry on environmental contamination from fossil – fuel utilization and the fast exhaustion of petroleum derivative requests the advancement of clean, productive and manageable vitality–storage frameworks for applications including

convenient electronic gadgets and electronic vehicles[16]. The Sb based nanostructured composite has turned out to be a promising option anode material that can ease the security worry as noted above in light of the fact that it shows a level charge/release level.

2.10 KEY FEATURES OF Sb/TiO_2/C

Among alloy based elements, Lithium addition/extraction in Sb-based frameworks has been explored as a conceivable contender for anode materials in Li-particle batteries. With a specific end goal to ease the issue of volume extension, Sb-based intermetallics else nanocomposites have been considered. In spite of the fact that these materials display improved limit maintenance, their cycle exhibitions or Coulombic productivity for the principal cycle are as yet poor[17]. Although electrode of Pure Sb depicts high initial charge capacities and high initial discharge capacities. They possess values of 627 $mAhg^{-1}$ and 724 $mAhg^{-1}$. But after some cycles, they shows very poor electrochemical behavior.

Sb based nanostructured composite can be synthesized by different mechanisms. These includes high energy ball milling method, Sol-gel method, solid-state method etc. $Sb/TiO_2/C$ have uncommon basic steadiness, low poisonous quality, high rate ability, better encouraging security long cycle life. Thus it is a critical hopeful of anode material of future lithium particle battery.

The following electrochemical reaction is used while forming Sb based nanostructured composite.

$2Sb_2O_3 + 3Ti \rightarrow 4Sb + 3TiO_2$

Also, Standard free energy of this reaction is -337.353 KJ mol^{-1} at standard 298 kelvin[17].

Here mechanochemical reduction process is used to prepare Sb based nanostructured composite with embedded titanium oxide.

2.11 STRUCTURE OF $Sb/TiO_2/C$

Nanocomposites offer a promising way to deal with fuse nanostructured constituents to mass thermoelectric materials. These materials possess extended capacity retention. But, their performances after many cycles or in other words, coloumbic efficiency for 1st cycle is not good[18]. The nanocomposite structures are powerful in diminishing warm conductivity more than electrical conductivity, consequently in enhancing the thermoelectric execution.

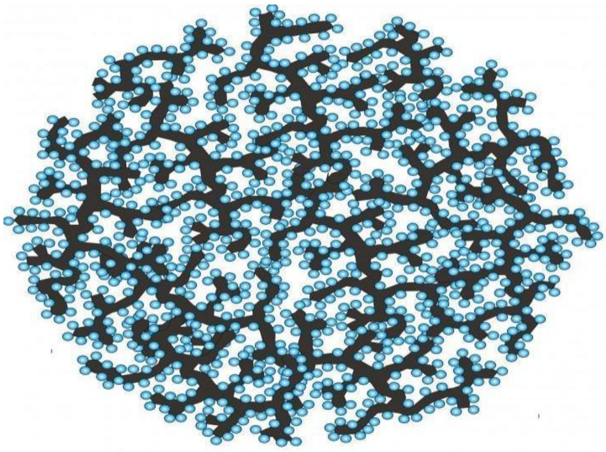

Figure 2.3 - SCHEMATIC – NANOCOMPOSITE[source : Wikipedia]

CHAPTER 3

CHARACTERIZATION

CHARACTERIZATION OF Sb/TiO_2/C COMPOSITE

Various techniques are used in characterization of Li-ion battery. These include “X-Ray Diffraction” technique (XRD) and “Scanning Electron Microscopy” (SEM).

3.1 **X-RAY DIFFRACTION TECHNIQUE** :

X-Ray beams are exceptionally infiltrating EM waves. The scope of waves is in between 0.1nm-10nm. At the point when matter is illuminated by a light emission vitality charged particles, for example, electrons, Fiber warmed to deliver electrons which are then quickened in vacuum by high electric field in extend 20-60Kv towards a metal target , which being certain is called anode comparing electronic current is ranged 5-100ma[19]. A ceaseless range delivered when electrons hit the objective, which is alluded as "bremsstrahlung" or braking radiation as it is created by halting electrons.

Notwithstanding, when connected voltage is raised over a basic valve, normal for the objective metal, sharp force most extreme shows up in the range which is a material property and is special for all components and mixes[20].

In single XRD measurement, crystal is being placed on goniometer. This goniometer is used to place crystal at the given orientations. This crystal is enlightened with focused monochromic ray of light. This produces a pattern of diffraction which are termed as reflections. This 2-D image is then converted into 3-D image of density of the electrons.

Here poor resolutions can be obtained if crystals are very small or in case, they are non-uniform in their internal structure.

Figure 3.1 – Schematic of XRD machine[21]

Investigation of XRD:

Auxiliary investigation could decide the accompanying basic points of interest.

1. Lattice parameters: cross section parameter and consistent "a" can be computed by ordering. Ordering will tell "w" the miller indices records h, k, l, for a specific plane giving the captures and afterward, lattice constant can be gotten by utilizing following conditions[21].

$$N \lambda = 2d \sin \theta \qquad \text{which is Bragg's law}$$

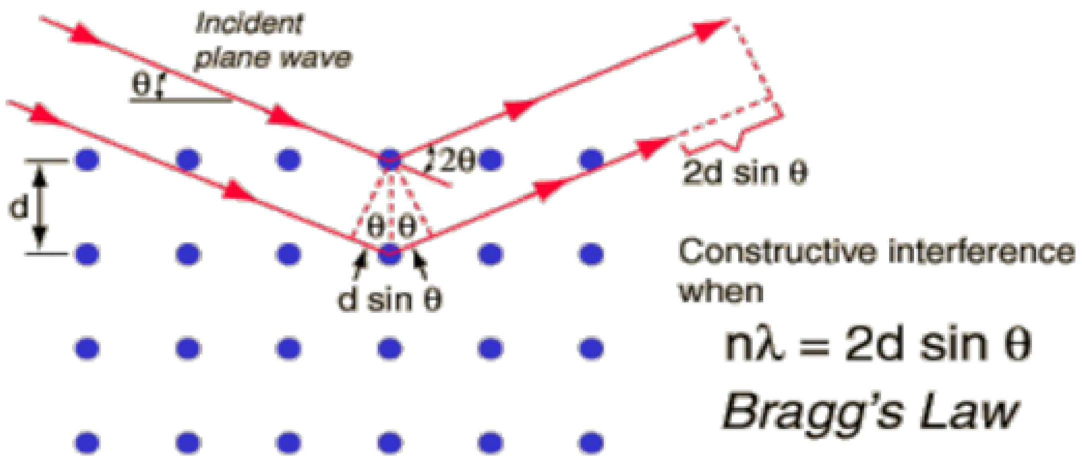

Figure3.2 – Schematic of Bragg's law[22]

2. Phase personality: character of a specific stage, both pinnacle position and relative forces must fit in understanding to the standard information accessible for the component or compound. All tops with relative power presents immaculate stage character for a compound, if some significant pinnacles are missing in contamination or nonappearance of some component in it.
3. Accounted pinnacle display in an unadulterated specimen pollution.
4. For a specific compound, attempt all the conceivable stages that could be fitted in the bend.
5. In a specimen, more than one period of a similar component compound could be available. In the event that the major pinnacles are filling, at that point expansion stages ought to likewise be considered.
6. Phase immaculateness(Purity): XRD can likewise show regardless of whether the example is single or multiphase. On the off chance that the major pinnacles of just a solitary stage are recorded, it shows that the example has immaculate single stage[22].

3.2 **SCANNING ELECTRON MICROSCOPY:**

Scanning electron microscopy is utilized for reviewing geographies of examples at high amplifications utilizing a bit of hardware called the Scanning electron microscope. SEM amplifications can go to more than 300,000 X yet most semiconductor producing applications require amplifications of under 3,000 X as it were. SEM investigation is regularly utilized as a part of the examination of die/package cracks and crack surfaces, bonds disappointments, and physical deformities on the pass on or package surface. Amid SEM assessment, a light emission is centered around a spot volume of the example, bringing about the exchange of energy to the spot. These barraging electrons, likewise alluded to as primary electrons, unstick electrons from the example itself. The unstuck electrons, otherwise called secondary electrons, are pulled in and gathered by a decidedly one-sided lattice or identifier, and after that converted into a signal.

Figure3.3 – Schematic of Scanning Electron Microscope[23]

To create the SEM picture, the electron bar is cleared over the zone being examined, delivering numerous such signals. These signs are then opened up, examined, and converted into pictures of the geography being reviewed. At long last, the picture is appeared on a CRT. The vitality of the essential electrons decides the amount of secondary electrons gathered amid review. The outflow of secondary electrons from the example increments as the vitality of the essential electron shaft increments, until the point that a specific utmost is come to.

Past this point of confinement, the gathered secondary electrons lessen as the energy of the essential bar is expanded, in light of the fact that the essential pillar is as of now initiating electrons far beneath the surface of the example. Electrons originating from such profundities as a rule recombine before achieving the surface for outflow. Beside auxiliary electrons, the essential electron shaft brings about the emanation of backscattered (or reflected) electrons from the example. Backscattered electrons have more vitality than secondary electrons, and have a distinct course. In that capacity, they can't be gathered by an optional electron identifier, unless the locator is specifically in their way of travel. All discharges over 50 eV are thought to be backscattered electrons. Backscattered electron imaging is helpful in recognizing one material from another, since the yield of the gathered backscattered electrons increments monotonically with the example's nuclear number. Backscatter imaging can recognize components with nuclear number contrasts of no less than 3, i.e., materials with nuclear number contrasts of no less than 3 would show up with great difference on the picture. For instance, investigating the rest of the Au on an Al bond cushion after its Au ball bond has lifted off would be less demanding utilizing backscatter imaging, since the Au islets would emerge from the Al foundation. A SEM might be furnished with an EDX investigation framework to empower it to perform compositional examination on examples. EDX examination is valuable in distinguishing materials and contaminants, and additionally assessing their relative fixations on the surface of the example.

CHAPTER 4

EXPERIMENTAL WORK

EXPERIMENTAL WORK

Ball-milling strategy is one of an old and most normal method to deliver polycrystalline and inorganic materials. Ball-milling at low temperature or even room temperature has been created as a compelling methodology of blend metal amalgam, inorganic oxide or arrange compound.

Its other critical components incorporates

> It is straightforward and helpful.

> It includes less dissolvable and decreases sullying.

> It gives high return item.

For the most part with ball-milling technique, metal combinations are readied. The acquired metal composites regularly have small scale sizes, prompting a low surface region of the last items. It is as yet a test to get ready metal amalgams with huge surface zone of conclusive items.

In synthesis of $Sb/TiO_2/C$ nanocomposite through High energy mechanical milling process. Compositions of Sb_2O_3(purity>99%), Ti(purity > 99.98%) and Carbon(Super P) are placed in apposite concentrations[25,26]. The calculations were made to predict the amount of concentrations to be mixed in pestle and mortar.

These are as follows –

Molar weight of Sb_2O_3 (with purity 99%) = 291.52 $gmol^{-1}$

Molar weight of Ti (with purity 99%) = 47.867 $gmol^{-1}$

Molar weight of Carbon (with purity 99%) = 12.0107 $gmol^{-1}$

Actual Molecular weight to be considered,

Sb_2O_3 = 291.52*100/99, Which is equal to 294.464 $gmol^{-1.}$

TiO_2 = 79.866*100/99, Which is equal to 80.672 $gmol^{-1}$

C = 12.0107*100/99, Which is equal to 12.132 $gmol^{-1}$

Therefore, total actual molecular weight is addition of above all, i.e. 387.268 $gmol^{-1}$.

Ball weight(used in ball milling) is 3.903gram.

Also, taken ratio of Ball : Sample(powder) is 20 : 1

Therefore, amount of Sb in final mixture will be (294.464/387.26)*8 = 6.083 grams.

Also, amount of Ti in final mixture will be (80.672/387.26)*8 = 1.666 grams.

And amount of C ultimately will be (12.132/387.26)*8 = 0.2506 grams.

We can also observe that 6.083 + 1.666 + 0.2506 = 8 grams(approx)

Thereby, we took 8 gram powder of Sb/TiO_2/C nanocomposite.

The sample was characterized by X-Ray Diffraction technique(XRD) followed by Scanning electron microscopy(SEM).

ELECTROCHEMICAL EVALUATION

For electrochemical evaluation, We need to use four things.

Active material (Sb/TiO_2/C nanocomposite)

N-methyl pyrrolidinone(NMP) as solvent

Polyvinylidene fluoride(PVDF) as binder

Super P/Carbon black

In order to make total 0.25gm of slurry, apposite composition of above mentioned are used, i.e. active material(80% by wt), PVDF(15% by wt), super P(5% by wt). Each component was mixed well in order to form a slurry[27]. This is then coated on a copper foil substrate

which is done by pressing followed by drying at 120°C for 5 hours under vaccum. Used concentrations are

Active material = 0.20 grams

PVDF = 0.0375 grams

Super P = 0.0125 grams

Figure 4.1 Sb/TiO_2/C nanocomposite(sample)

CHAPTER 5

RESULTS AND DISCUSSIONS

RESULTS AND DISCUSSIONS

XRD result: Figure below show the XRD pattern of $Sb/TiO_2/C$ composite. Here all of the peaks of $Sb/TiO_2/C$ composite correspond to Sb with no other phases detected. Through this XRD pattern, phase of TiO_2 was not detected. We can also deduce that small nanocrystalline TiO_2 are embedded in the composite.

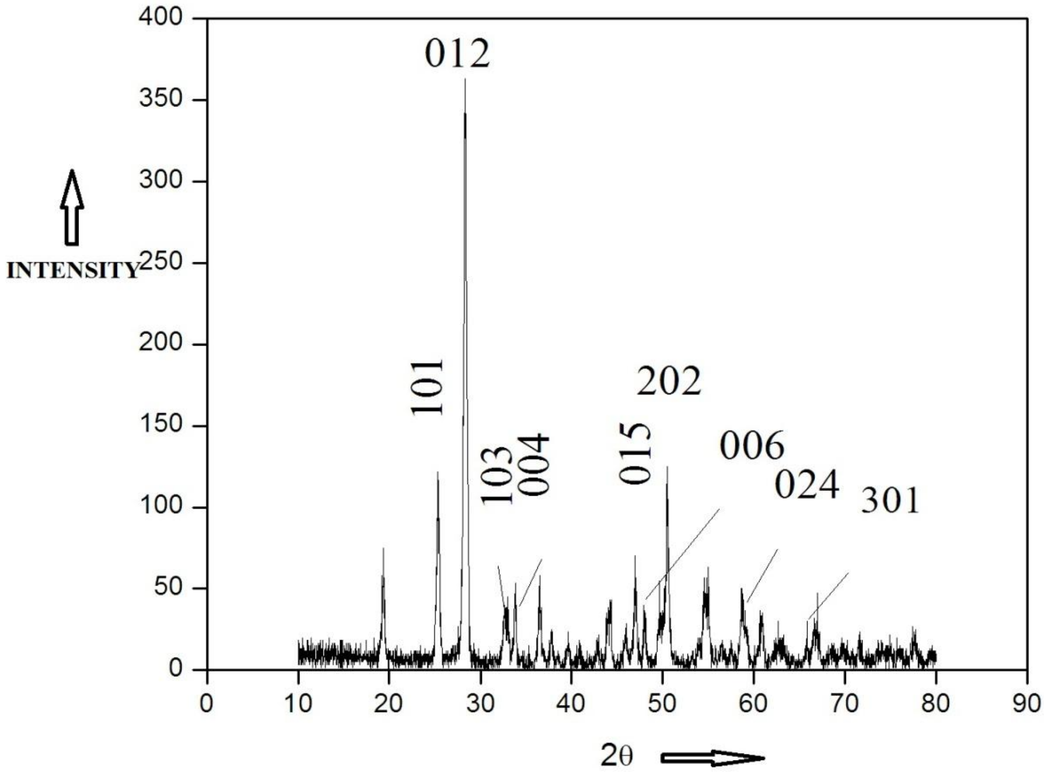

Figure 5.1 – XRD data

Highest peak is with (012) pair which is around 28^{o} which confirms the presense of antimony(Sb) in it.

SEM result: The following Image data are obtained by SEM for $Sb/TiO_2/C$ composite.

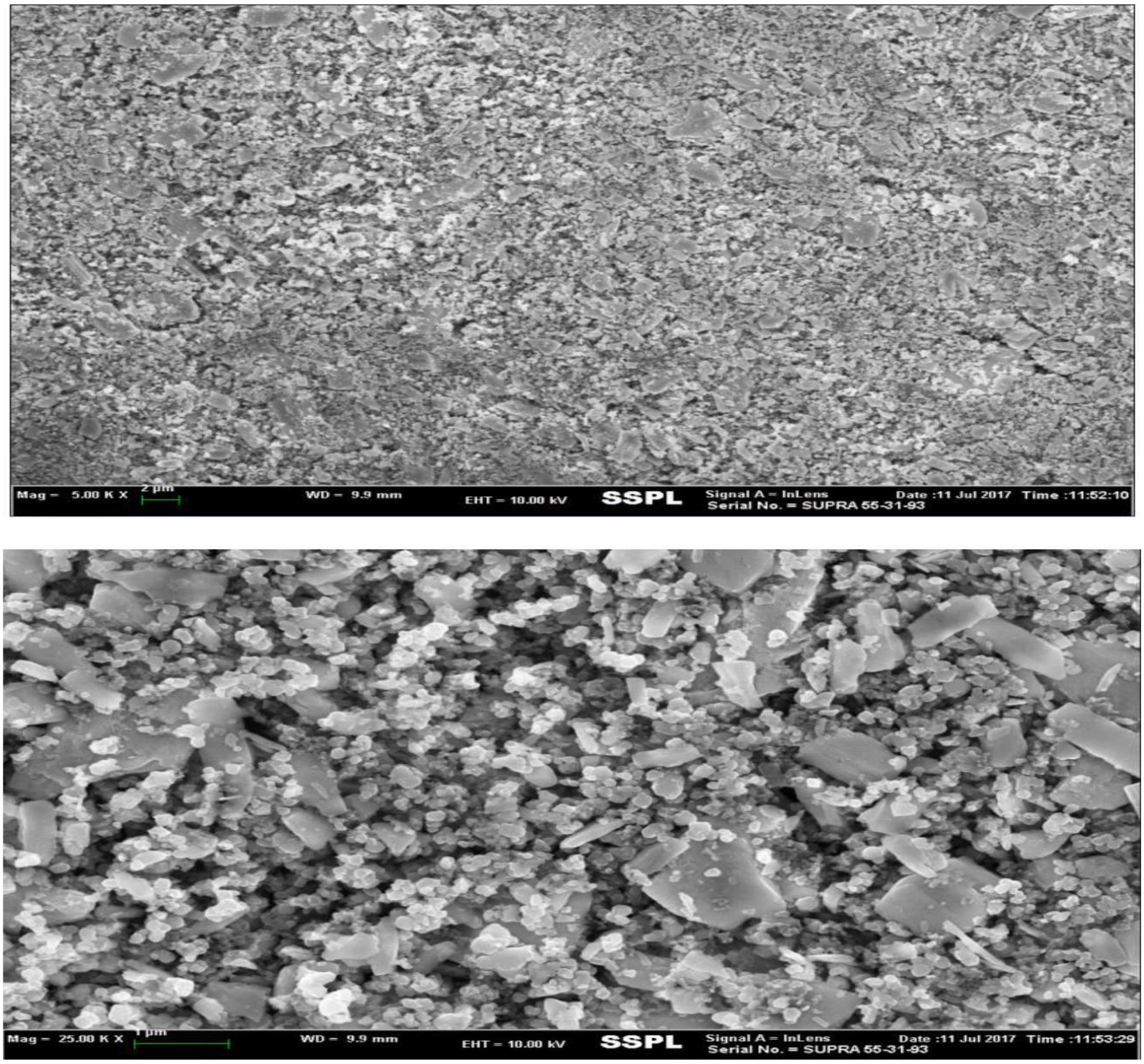

Figure 5.2(a) magnified at 2pm scale and (b) magnified at 1pm scale – SEM Images

The SEM image data of the given sample of antimony(Sb) based nanostructured composite are regular and compact in size. With different magnifications, SEM data are taken to provide this aspect in a broader manner. SEM data assures that the provided sample consists TiO_2 in it. This $Sb/TiO_2/C$ nanocomposite provides a better cyclability and good discharge and charge capacities.

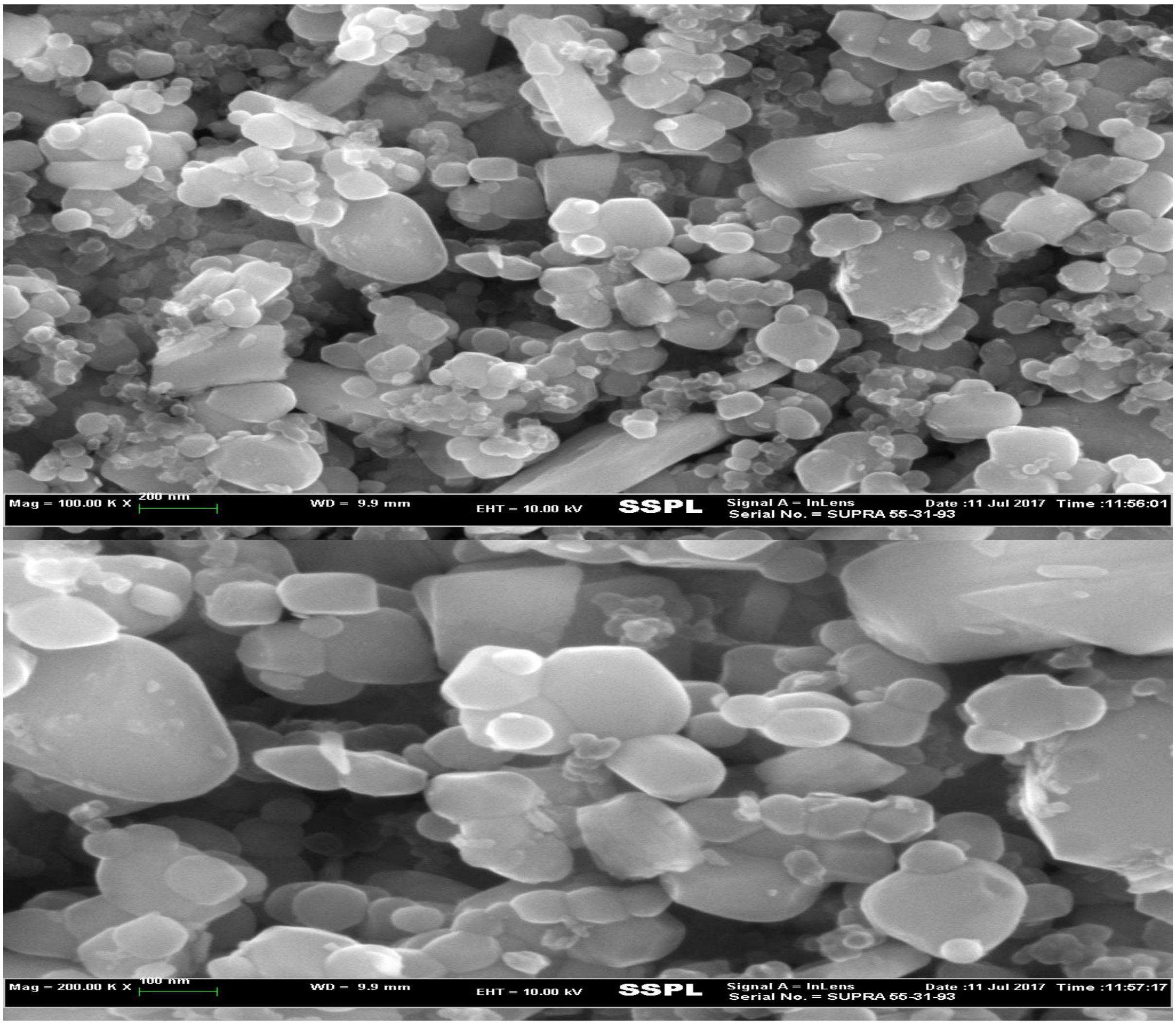

Figure 5.2 – SEM image data. (c) – magnification at 200 nm scale and (d) – magnification at 100 nm scale.

Here in above figures, 5.2(c) and 5.2(d) , SEM data are taken with a magnification of 200nm scale and 100 nm scale respectively which clearly depicts the uniform structure of the antimony(Sb) based nanostructured composite.

CHAPTER-6

CONCLUSION

CONCLUSION

In outline, we have successfully prepared antimony based nano-structured composite($Sb/TiO_2/C$) by Ball milling technique in order to enhance the electrochemical properties of Sb, when used as an potential anode material for lithium ion batteries. This nanostructured composite showed enhanced electrochemical behavior with a good cyclability. This large capacity and very high value of cyclability of $Sb/TiO_2/C$ nano-composite electrode are attributed to a new kind of nanostructure consisting of acive nanocrystallites (Sb)/ active ceramic(rutile TiO_2)/ Buffer matrix(carbon) against the volume expansion during cycling.

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.Whittinggham, MRS Bulletin., 33(2008).
6. K.Xu,Chem.Rev.,104(2004).
7. K. Naoi,S.Ishimoto,Y.Isobe and S.Aoyagi,J. Power Sources,2010.
8. Xiangcheng Sun,Pavle V.Radovanovic and Bo Cui,2015.
9. Wei Kong Pang, Vanessa K.Peterson,Neeraj, Je–Jang Shui, She-huangwu,2014.
10. T.Ohzuku,A Ueda and N.Yamamoto, J. Electrochem.Soc.1995,142,1431.
11. J.Shu,J.Solid State Electrochem.,2009.
12. X.Yao,S.Xie,C. Chen, Q.Wang, J.Sun,Y.Li and S.Lu,Electrochim.Acta, 2005,50,4076.
13. P .P.Prosini, R. Mancini, L.petrucci, V. Contini and P.Villano, Solid State Ionics,2001,144, 185.
14. X.Yao, S.Xie,H.Nian and C. Chen,J. Alloys Compd.,2008,465,375.
15. Park YJ,Kim JG,Kim MK,Chung HT,Kim G(2000) Solid State Ionics 130:203
16. S.Lee ,Y.K. Sun,K.S Nahm,Solid Ionic State109(1998)285.
17. Ji Hyun Sung, Cheol-Min park, feburary 2013, 704-230.
18. Huggins RA. J Power Sources 1999;81:13–9.
19. Bruce PG, Scrosati B, Tarascon J-M. Angew Chem Int Ed 2008;47:2930–46.
20. Park C-M, Kim J-H, Kim H, Sohn H-J. Chem Soc Rev 2010;39:3115–41.
21. Larcher D, Beattie S, Morcrette M, Edstrom K, Jumas J-C, Tarascon J-M. J Mater Chem 2007;17:3759–72.

22. Gleiter H. Prog Mater Sci 1989;33:223–315.
23. Park C-M, Yoon S, Lee S-I, Sohn H-J. J Power Sources 2009;186:206–10.
24. Jeong G, Kim Y-U, Krachkovskiy SA, Lee CK. Chem Mater 2010;22:5570–9.
25. Yang J, Winter M, Besenhard JO. Solid State Ionics 1996;90:281–7.
26. Park C-M, Sohn H-J. Adv Mater 2010;22:47–52.
27. Fransson LML, Vaughey JT, Benedek R, Edstrom K, Tomas JO, Thackeray MM. Electrochem Commun 2001;3:317–23.
28. Park C-M, Sohn H-J. Chem Mater 2008;20:3169–73.
29. Armstrong AR, Armstrong G, Canales J, Garcia R, Bruce PG. Adv Mater 2005;17:862–5.
30. Yang X, Wen Z, Xu X, Lin B, Huang S. J Power Sources 2007;164:880–4.
31. Hu Y-S, Kienle L, Guo Y-G, Maier J. Adv Mater 2006;18:1421–6.
32. Suryanarayana C. Prog Mater Sci 2001;46:1–184.