Synthesis and characterization of Li_2MnO_3 as an alternative cathode 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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By

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CERTIFICATE

This is to certify that the dissertation entitled on **"Synthesis and characterization of Li_2MnO_3 as an alternative cathode material for Li–ion batteries"** submitted to Delhi Technological University (formerly Delhi College of Engineering) by **Navneet Goyal (2K15/NST/05)** 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 Li_2MnO_3 as an alternative cathode 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.

Date: 27-07-2017 **Navneet Goyal**

Place: New Delhi **Roll No. 2K15/NST/05**

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ABSTRACT

Lithium ion batteries provides un-matched blend of high capacity and energy density, that is why this technology is highly portable for compact gadgets, power devices, control apparatuses, and electric vehicles(full/hybrid). There are vital improvements in latest positive terminal electrode (cathode) materials to substitute the well developed $LiCoO_2$ as cathode material for using in lithium-ion battery (LIBs). In this research work alternative cathode material Li_2MnO_3 (LMO) nano fibers has been investigated by electro- spinning technique. Physiochemical characterization of LMO nano fibers are performed by XRD (X-rays diffraction), scanning electron microscope (SEM). Electrochemical performance of LMO nano fibers will be investigated to check the capacity, cyclic performance, power density and energy density of the sample which definitely will be used in the lithium-ion batteries in the near future.

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Chapter-1

INTRODUCTION

1.1 History - Battery

In 1979, Benjamin franklin, the U.S. polymath, used term “Battery”. Battery then was to explain a group of capacitors linked together [1]. Alessandro Volta, in 1800, discovered primary model of battery known by voltaic pile. Voltaic pile consist piled discs of Copper and Zinc separated by electrolyte saturated cardboard. Volta experimented with numerous types of metal and found lastly that the best results were given by zinc and silver. There were some technical faults in voltaic pile for example electrolytic leakage, short circuit, etc. Figure 1.1 shows basic model of Zn–Copper voltaic pile.

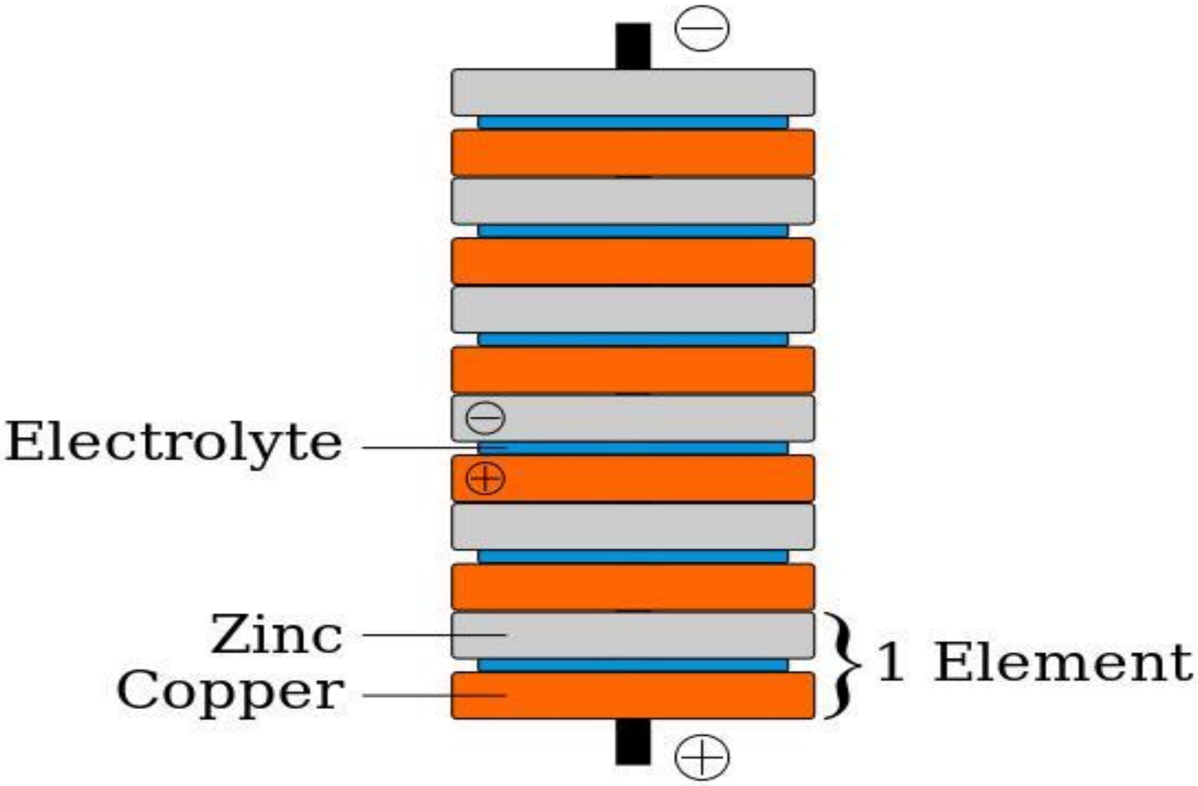


Fig 1.1 Zn–Copper voltaic pile [2]

Four decades after voltaic cell was invented Daniel cell was fabricated which performed better than Volta’s cell thus eliminating few faults shown by voltaic pile. And the time passes by and advancement of electronic industry took place and fabrication of various types of electronic goods increased and therefore products with higher and higher electro-chemical potential and also higher energy were required. Lithium – ion battery has higher energy density also high power density then Ni–Cadmium and Ni–Metal Hydride batteries. That was the most important reason behind using Li–ion battery [3]. Sony Corporation (Japan), in

1991-1992, brings up an abstract idea of first commercialized lithium–ion battery [4]. Li–ion batteries which were being used in ipod, laptops, cellular phones, personalized computers, etc since they are very small in size.

1.2 Battery Definition

A battery is an electrochemical transducer cell (one or many enclosed cell) which can be charged electrically in order to provide static potential through internal electrochemical redox reaction in which electrical and chemical energies changes back and forth when needed.

Batteries are classified into two groups as primary and secondary ones.

Primary Battery:

These kind of batteries are easily manageable voltaic cells where both electrode reactions are irreversible, which makes it non rechargeable. Therefore these cells are used only once. Zn/air, Alk. MnO_2 are some of the examples related to primary batteries.

Secondary Battery:

These kind of batteries are easily manageable voltaic cells where both electrode reactions are reversible, which allows them to be recharged many times. Ni-Cadmium, Lead acid, Li–ion battery are some examples of these secondary batteries.

1.3 Lithium–ion Batteries

Lithium–ion battery (secondary type batteries) has capability to be charged as many times. Li–ion battery has excellent cell voltage, specific energy, cycling capacity and exceptional power density. Because of these outstanding properties they are being used in portable electronics, vehicles, and very power tools [5].

Following factors contribute to the development of Li–ion battery:

1. Battery management system
2. Electrolyte Anode and Cathode
3. Shape / orientation of the batteries.

The most popularly available anode material are graphite (carbon) and Lithium Titannate ($Li_4Ti_5O_{12}$), Li_2Sn_5, LiB, Li_3Sb etc. few examples regarding anode materials. Whereas in Cathode material there are layered oxide for example Li_2MnO_3 (lithium manganese oxide), $LiCoO_2$ (lithium cobalt oxide) and lithium iron phosphate also there is an electrolyte which is a fine mixture of organic carbonate like ethylene carbonate comprising lithium ion complex. When talking about Cathode material, some very important factors which depend upon cathode material are specific capacities, cycling capacities, discharging potential etc. [6].

Table 1.1 Characteristic and comparisons of globally used re-chargeable batteries [6].

S. No.	Battery Parameter	Ni- Cd	Lead Acid	Ni- MH	Li- ion
1	Commercial use	1950	1970	1990	1991
2	Load Current(peak)	20C	5C	5C	>2C
3	Energy Density (Wh /kg)	45 -79	28 - 50	60 - 121	111-160
4	Cell Voltage	1.25V	2V	1.25V	3.6V
5	Fast Charge Time	1h typical	8-16h	2-4h	2-4h
6	Cycle Life	2000	500-800	500-1000	400-1200
7	Operating Temperature(only discharge)	-40 to 60°C	-20 to 60°C	-20 to 60°C	-20 to 60°C
8	Internal Resistance in mΩ	100 to 200	<100	200 to 300	150 to 250
9	Maintenance	30 to 60 days	3 to 6 months	60 to 90 days	negligible.

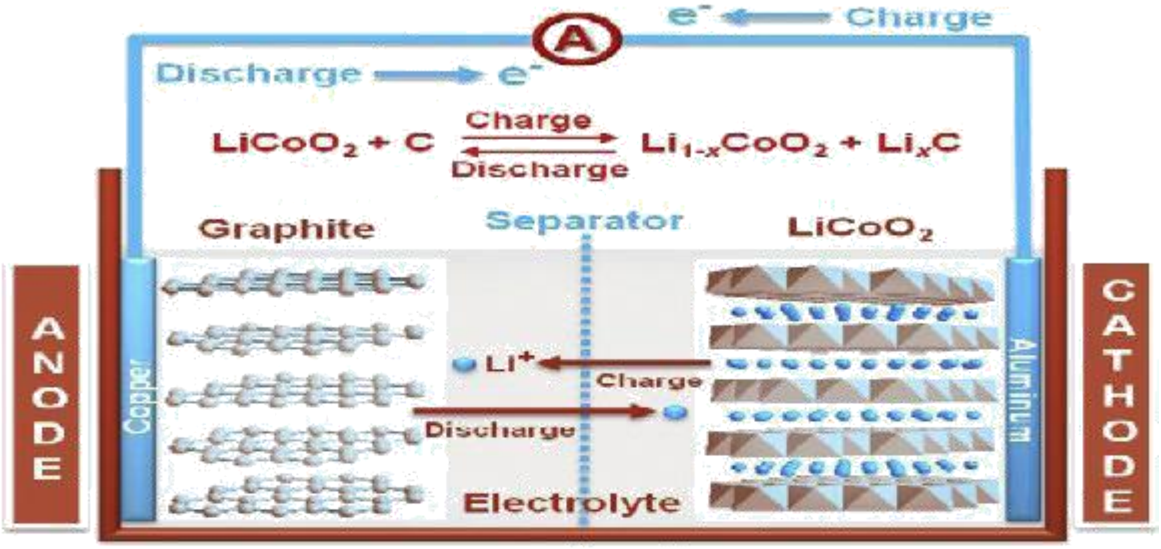


Fig 1.2 Schematic diagram of lithium-ion battery [8]

1.3.2 Construction

Lithium-ion cell consist of four layered structure. First is Cathode (positive electrode) that is fabricated from $LiCoO_2$ having a collector of current made by thin Aluminium foil. Second is Anode (negative electrode) fabricated from carbon having a collector of current made of thin copper foil. Third is a separator fabricated from porous fine polymerized film. Fourth is an electrolyte that is formed of lithium containing salt within organic solvent [7].

Very first generation Li- ion batteries is shown below in figure 1.2 where $LiCoO_2$ is taken to act as cathode material, whereas organic solvent consisting $LiPF_6$ is taken as an electrolyte and lastly graphite acting as anode material [8-10].

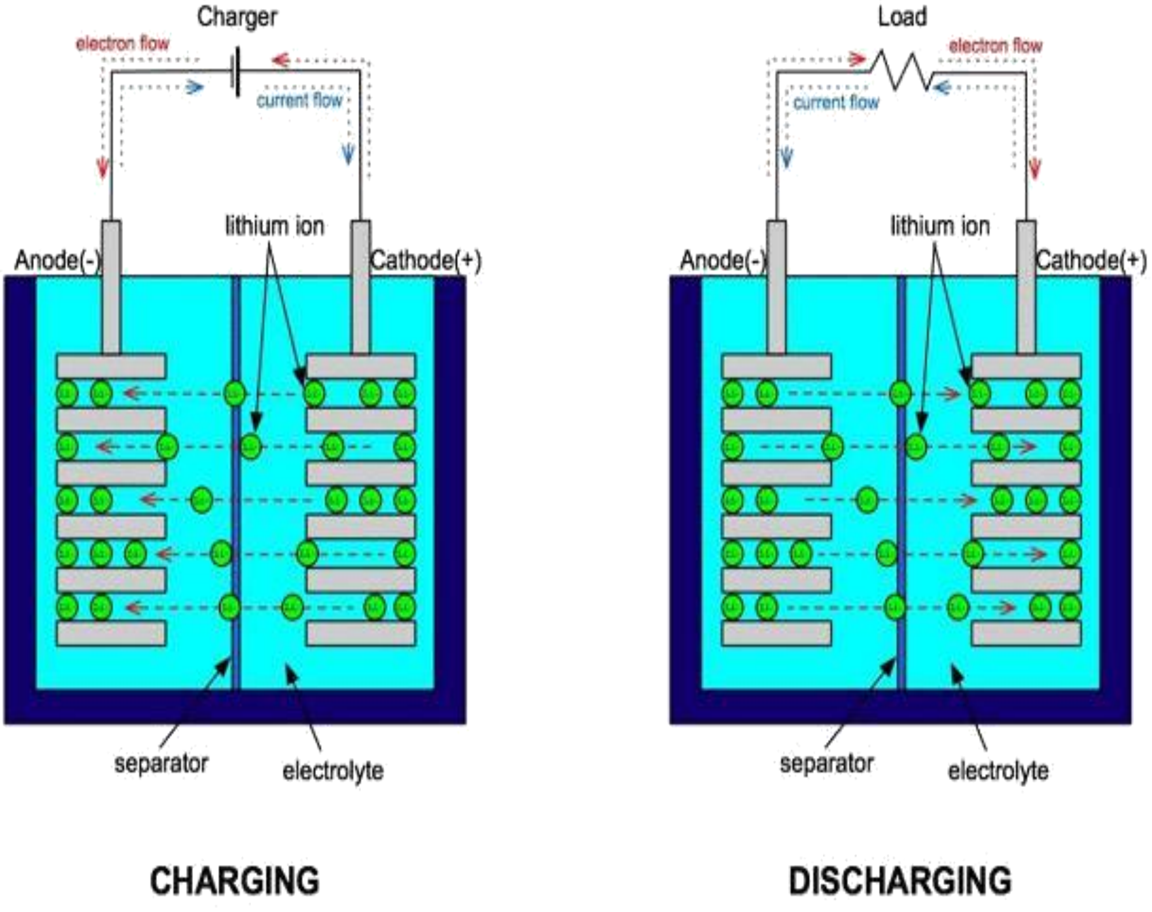
1.3.3 Principle

During charging operation, lithium ions charged positively (Li^+) moves towards anode terminal from cathode via an electrolyte but negatively charged electron moves along opposite direction across the external circuit. Battery is considered fully charged whenever ions are not moving and battery is up for usage. While the battery discharges, ions movement takes place towards cathode terminal from anode terminal. That literally means, lithium ion, after segregating from anode gets transferred via the electrolyte and get inserted onto the cathode. Lithium–ion battery got to be known as Rocking chair and also as swing cells owing to the cycle of charging and discharging. Figure 1.3 show the clear charging and discharging operation of a rechargeable lithium-ion battery [8].

At anode $6C + Li^{+} + e^{-}$ LiC_6

At cathode $LiCoO_2 - Li^{+} - e^{-}$ $Li_{0.5}CoO_2$

Overall: $C + LiCoO_2$ $LiC_6 + Li_{0.5}CoO_2$



CHARGING

DISCHARGING

Fig 1.3: Lithium-ion batteries (Charging and Discharging process) [11]

1.4 Reason why we are using Lithium-ion battery

Technological enhancement made environmental and toxicity based issue a main areas of concern, since these factors are primarily related to technological advancement. Following are the reasons that are responsible for the increased usage of Lithium-ion batteries.

- Lithium is lightest alkali metal element.

- Lithium-ions batteries are friendly to the environment.
- No matter of toxicity.
- Too high operation potential.
- Lithium-ions battery is portable, light weighted and very compact.
- Lithium-ions battery has too high energy density.
- No memory effect.
- Fast Charging capabilities of Lithium ion batteries.

1.5 Challenges

Lithium ion batteries have following limitations.

- Problem of short circuiting while transportation.
- Reversed capacity of discharge
- Limited mechanical strength
- Cell material balancing, batteries made of layered porous electrodes over current collector of aluminium and copper foils. Battery safety is ensured if these electrode pairs have balanced capacity in order to avoid risk relating overcharged anode.
- Ageing issues.
- Costing issues.
- Protective circuitry requirements i.e. lie under safety operating limit.

1.6 Motivation

Lithium-ions particle assumes an enormously critical role in our lives. Not exclusively will it be utilized to power the mass of digital gadgets that make up our current digital lives however progressively lithium-ions will turn into the gold standard for rechargeable batteries. The pocket rechargeable batteries which we as of now utilize, for example nickel-cadmium (NiCd) and nickel-metal-hydride (NiMh) batteries, will turn into a thing about the past. Indeed, nickel-cadmium has as of now had its day, essentially because of environmental worries around the utilization of cadmium. What's more, nickel-cadmium is progressively be replaced by a similarly priced yet more intense lithium-ions. Further, the enrichment in properties of lithium – ion batteries is ultimately required as electronic conductivity, activation energy of cathode is a requirement and better alternate for electro-conductive Cathode material in lithium – ion related batteries.

1.7Objective

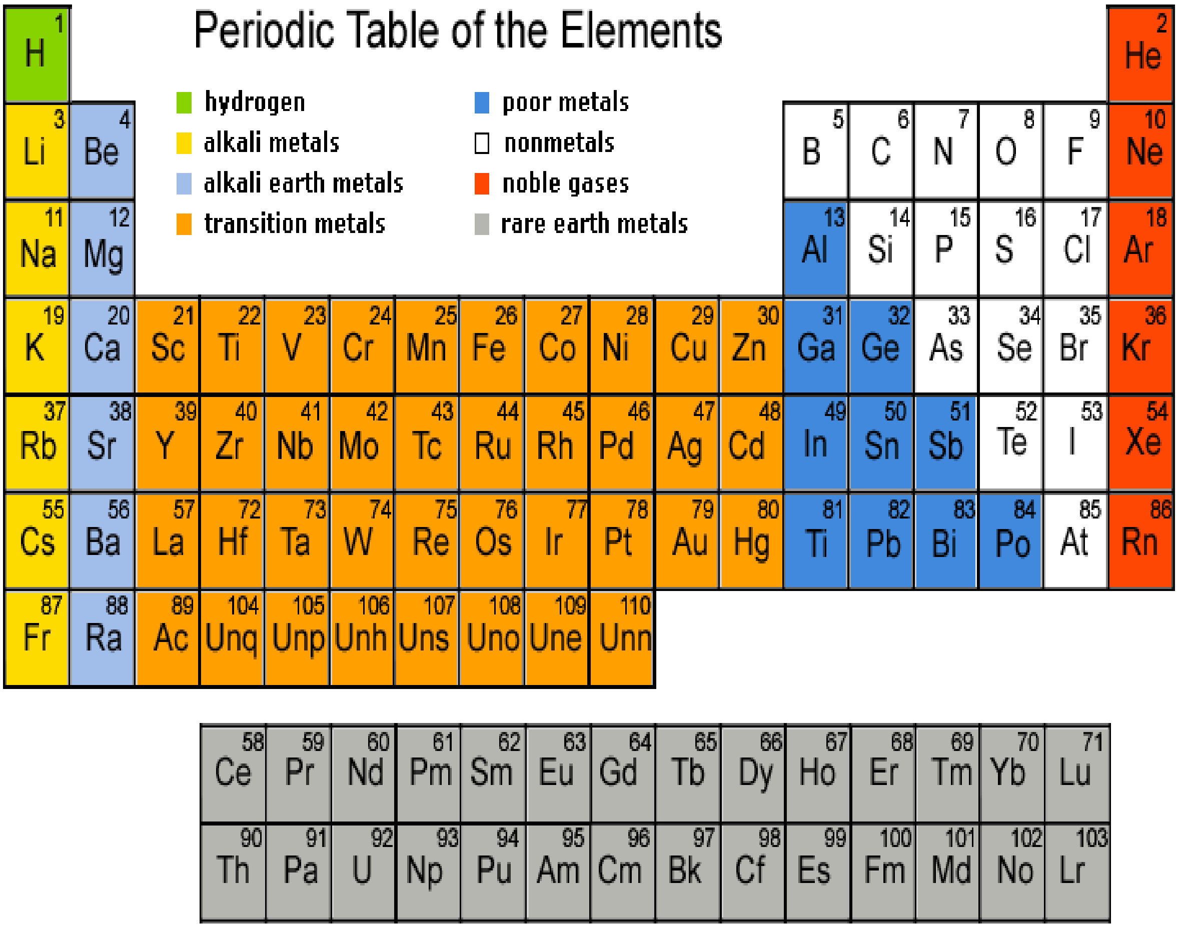
As it is already revealed that the currently used cathode material $LiCoO_2$ is risky in nature and poisonous too, so instead of utilizing it, another cathode material is required to be supplanted in lithium-ion batteries. The aim of this research is to conceive nano fibers of Li_2MnO_3 and to utilize them as alternative cathode material by a unique method i.e. electro-spinning strategy and to portray the fabricated material of its physiochemical and electrochemical properties. The phase development of Li_2MnO_3 with electro-spinning route has been affirmed by XRD outcomes and elemental stoichiometric and morphological examination is further carried out by SEM.

Chapter-2

LITERATURE REVIEW

2.1 Lithium metal

Lithium, an element with symbol Li, having atomic number 3, is very soft, silvery-white alkali metal. Under ideal conditions, lithium is lightest of all the metals and the lightest solid element. Like all other alkali metals, lithium is exceedingly reactive and combustible, and is put away in mineral oil for safety. Lithium is very reactive having large sp. capacity (3840 Ah/Kg), lower density (0.535 g/cm^3), and higher energy density (0.9-2.64 MJ/L), Higher reduction potential (- 3.05 V), lower density (0.533 g/cm^3), and high electro-negativity **[12]** which requires soft handling.



Periodic Table of the Elements

🟩 hydrogen
🟨 alkali metals
🟦 alkali earth metals
🟧 transition metals
🟦 poor metals
☐ nonmetals
🟥 noble gases
▨ rare earth metals

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 Ti	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 Unn								

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

Fig 2.1 Periodic table of elements

Late in the twentieth century, lithium turned into an imperative part of battery electrolytes and electrodes, in view of its high reduction potential. Due to its low atomic mass, lithium has a higher charge- and power to- weight proportion. Lithium-ion batteries, which are rechargeable having higher energy density, should not be mistaken for lithium batteries, as they are primary disposable batteries having anode of lithium or its compounds. Other batteries (rechargeable) that utilizes lithium ions include the lithium-ions polymerized battery, lithium iron phosphate batteries, and the nano-wired battery.

2.2 Working of lithium –ion batteries:

The basic functional parts of the lithium –ion battery are the electrodes (cathode and anode), and the electrolyte where electrolyte acts a separator and carbon is utilized to act as a negative terminal of a conventional lithium –ion cell. The positive terminal comprises a metal oxide material, whereas the electrolyte is a solution that consist lithium salt [13].The direction of current flow in a cell governs the electrochemical role of the terminals that changes amongst anode and cathode. Graphite is famous and used extensively as a negative electrode terminal whereas the positive cathode usually is one of the following three material.

1) A layered oxides (for e.g. lithium cobalt oxide)

2) A poly anion (e.g. lithium iron phosphate)

3) A spinel structure (e.g. lithium manganese oxide)

Organic carbonates mixture for example ethylene carbonate and diethyl carbonate incorporating complex of lithium ions typically represents the “electrolyte”. Non-coordinating anionic salts viz. lithium hexaflourophosphate ($LiPF_6$), lithium hexaflouroarsenate monohydrate are by and large utilized by non- aqueous electrolyte [14]. The voltages, battery life, capacities and safety of and from lithium –ion battery can be altered drastically depending upon the material choice and for this, as of now, noble designs are utilized with the help of nanotechnology in order to improve performance of these batteries. Lithium in its pure form is extremely reactive and its reaction with water is very vigorous to produce lithium hydroxide with hydrogen gas. In this scenario, a non –aqueous electrolyte is preferably utilized and a sealed compartment keeps away water from the cell. Lithium –ion batteries costs more than Ni-Cd batteries however they work for more wide temperature range having higher densities, safe circuits to restrict top peak voltages [14].

Lithium –ion batteries working is clarified using Co related cathode ($LiCoO_2$) and a graphite which is utilized as an anode (Li_xC) also with the help of reactions occurring at the electrode terminals while charging/discharging of battery. When charging takes place, Li+ ions travels from cathode towards anode via electrolyte and which results in oxidation of Co^{3+} to Co^{4+}. Whereas, exactly reverse phenomenon occurs during discharging. Electrolyte acts as a medium in between anode terminal and cathode one to exchange Li^+ ions [15].

Lithium- ion battery schematic:

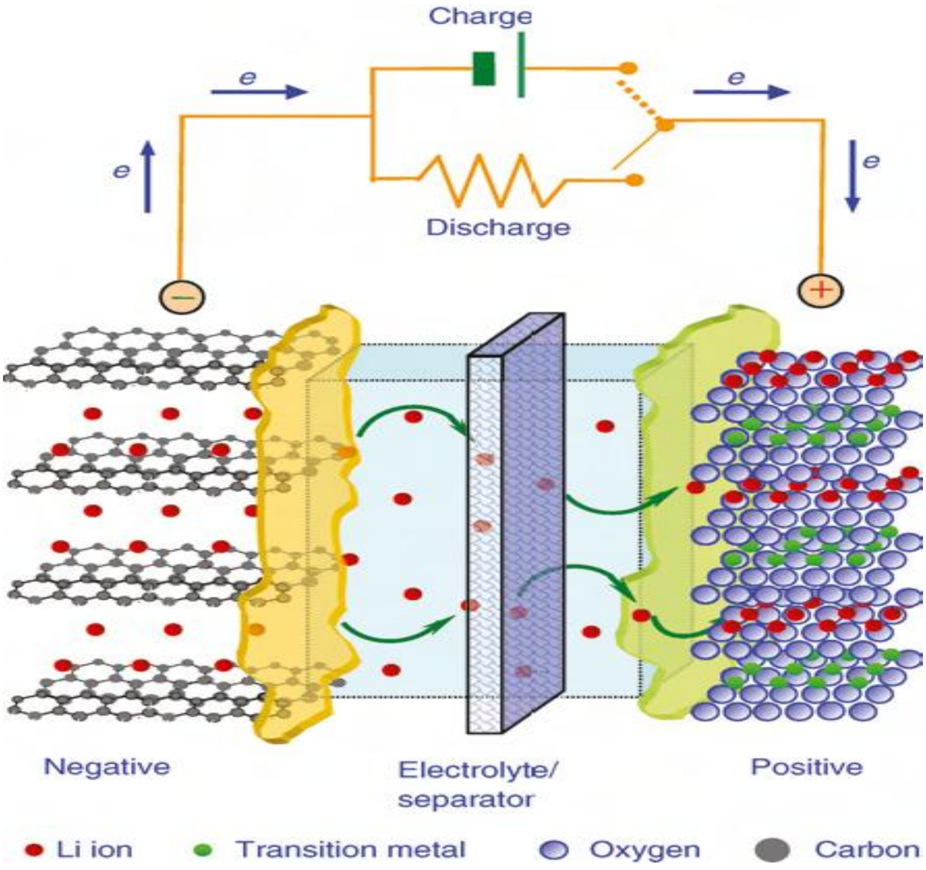


Figure2.2: Schematic of a rechargable lithium ion battery

Electrochemical Reactions :

Cathode

$$LiCoO_2 \Longleftrightarrow Li^+ + CoO_2 + e^-$$

Anode

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

Over all

$LiCoO_2 + C_6 \Longleftrightarrow CoO_2 + LiC_6$

2.3) Charging and discharging procedure

There are three parts in Lithium ion batteries

1. Cathode
2. Anode
3. Seperator (made out of polymer)

Negative electrode, which is highly electropositive acts as a electron donor whereas the cathode i.e. positive terminal which is highly electronegative acts as electron acceptor.

During discharging of battery, electrons are released from negative electrode which is referred to as oxidation. The movement of released electrons towards the postive electrode takes place. Reduction occurs at the postive electrode(cathode) while it accepts the external circuit electrons.

Now during charging , electrolyte acts as a medium for lithium- ions transport from cathode towards anode internally that results in oxidative change of Co^{3+} into Co^{4+} .

2.4) Benefits of using lithium – ion battery:

1) **Power**:

High energy density is an attribute of lithium ion batteries. When contrasted with the highly capacitative Ni-Cd batteries, the sp.energy of lithium ion batteries is almost twice and energy is around 1.5 times. Higher power in little pack of battery is directly related with higher energy density. Also it is that the energy density of lithium –ion battery is somewhat 160% higher than NiMH type and also 220% higher than NiCd.

2) **Higher voltage**:

A basic small battery operates over the voltage of around 3.6 V. and a strong current enable a battery to power complicated electro-mechanical gadgets.

3) **Longer – shelf life**:

When compared with other battery types such as NiMH which discharges itself upto 10% per month without a usage, lithium ion cell has only about 5% discharging loss per month.Also there is no need for reconditioning of lithium batteries up to almost 5 years. Reconditioning time in NiCd battery is around 3 months.On the same note reconditioning time related to NiMH battery comes after every 1 month.

4) **Non –polluting**:

Metals such as Pb,Cd, Hg which are toxic in nature are not at all utilized in a lithium ion battery thus they are highly safe from environmental point of view.

2.5) Impact of lithium-ion batteries on enviromental:

Expected life of lithium ion battery is around 10 year. Cathode made out of nickel and Co, poses higher enviromental threats, some of the issues are toxicity of biopshere,global warming and health effects on human.Often rechargeable batteries are recyclable but oxidized lithium has a issue that it is toxic in nature,so it is required to removed it from the battery, reduced and be utilized for other lithium batteries.

2.6) Safety of battery:

"Freedom from hazard is the meaning of safety". Natural unsteadiness is the inherent property of lithium during charging process which poses a damper in battery development. Tempreraturе ascends quickly upto the melting point of lithium metal that used to cause a violent response. In 1991, a big lot of lithium rechargeble batteires are called off since it causes severe burn to the people's face as hot gases were released out of the batteries. after the pack in celleur telephone discharged hot gasses and exacted copies to a man face. As Catastrophe theory states that the hazardous range must be found first rather than the safe region. We move ahead keeping in mind the similar approach which is defined as " concept of "abuse" is inversly proportional to the safety. [16]

$$\text{Safety} \;\alpha\; 1/\text{abuse}$$

2.6.1) Mechanical abuse :

Shortcircuit occurs amid infiltration of cell which is referred to as mechanical abuse and this happens during instillation and transport. Mechanical abuse is more pronounce in completely charged lithium ion batteries and we know that they are dispatched in mostly charged condition.Mechanical abuse is calculated by measuring original dimentions with the deformed ones and is denoted by strain ε of the battery, or it is also being calculated by meauring stress σ which creates such strain. Regular expansion amid intercalation causes the main strain in the battery. External impacts ,lithium plating and lithium battery ageing and compression are the other factors [17].

2.6.2) Over charging :

A variety of electronic gadgets are now-a-days powered by lithium batteries. It is crucial to understand the phase development and evolution of battery electrodes while discharging and charging process in order to enhance the performance of currently used batteries for them to be used in various emerging applications. Comprehending the evolution of structure, during battery operation that is attained via non- destructive studies will allow the alterations of battery composition thereby utilizing it to enhance performance of battery. Specifically, the operation of electrode under extreme conditions posed by real world, for example overcharging phenomenon can uncover the main cause of failure of battery so that best materials can be conceived, which helps in creating safer batteries.

2.6.3) Over temperature:

One important issue with the batteries made of lithium ions is their overrated temperature. Internal short circuit occurs when the battery generates internal heat. The moment when Internal temperature surpasses hundred degree centigrade, the material (active) within the battery begins breaking down, ultimately leading towards an exothermic response that may cause thermal runaway and can further creates explosion in the battery. Under temperature condition also affects battery performance as rate of reaction becomes undesirably low and at that moment if discharging or charging occurs in battery ,metal lithium starts depositing over anode which promotes irreversible losses in capacity and poses a danger of internal short circuits.

2.7) ANODE MATERIALS :

2.7.1) Lithium as negative electrode material:

Lithium metal is being commercially utilized to act as anode material for rechargeable batteries. In the firstly made basic lithium –ion battery, lithium metal is used as anode material. It has a useful property that its electronegativity is -3.05 V.Atomic weight of lithium is 6.94 $gmol^{-1}$. That is why lithium element is the lightest of elements in periodic table. Specific gravity of Li is 0.53 g/cm and its sp. capacity is $3.68Ahg^{-1}$ [18] .

2.7.2) Development History of anode material:

During 1995, important anode materials were graphite(hard carbon). At that time most popular graphites were mesophase and systematic graphite but then the cost of mesophase is more than systematic one. Requirement of anode material grown in 2010 and it reached upto 27000T but in 1995 the requirement of anode material was only aproximate 450T. when natrural graphite was mostly expensive. Coating surface of graphite with thin hard carbon layer was used widely and mesophase graphite was replaced by modified graphite and which has now arisen as the top leading anode material of recent times [19].

2.7.3) Recent research on anode materials:

Increasing capacity of graphite made anode has a little scope. So, research has focusd towards incorporating latest materials that inculds oxides for example Co_3, O_4, CuO, and FeO.and furthermore alloys of lithium metal such as Cu-Sb,Si-C-Li, Si-Li et cetera. Graphite has lower capacity than lithium [20].

2.8 Various methods of synthesis

Various methods of synthesis greatly influence capacity of charging and discharging and LMO’s cyclic performances. Various synthesis methods include sol – gel methods, electro-spinning methods, solid state methods, micro- wave helped method, sprayed pyrolysis, hydro thermal methods et cetera. Some of over techniques are clarified below.

2.8.1 Sol-gel method [21-22]:

The sol- gel might be depicted as “Oxide networks formation by poly-condensation reaction of a precursor in a fluid.” A sol is a steady scattering of colloidal particle in solvent. Particle of sol may be crystalline or amorphous form. A particle of aerosol is in a gas state, whereas a sol is particle in a fluid. Three dimensional continuous networks enclosing a liquid phase is referred to as gel. Network build from colloidal particle agglomeration is called colloidal gel.

- The thought behind sol-gel method is to “break down” the component in a fluid keeping in mind the end goal to bring back the component is controlled way.
- By blending sols of various components in a controlled stoichiometry a multi component compound may be synthesized.
- The sol – gel strategy keeps the issue of co- precipitation away, which might be in homogenous weather it is gelatin reaction.
- Enable blending at atomic level
- Resulting minute particles are effectively sintered.

2.8.2 Solid state technique [23]:

Ceramics are prepared commonly by solid state method since this strategy is simple for industrialization and making process is quite simple. In this method ball mill is used to ground solid precursor followed use of furnace for heat treatment. The primary disadvantage of this strategy is that it takes long duration for synthesis and also that synthesized product is not uniform and also non crystalline. Properties of LMO are greatly affected by the sintering temperatures which not just influence the purity but also capacity of discharge of LMO materials. All in all, appropriate temperature range is 700-800 °C. Due to high temperatures, Long time of processing, repeated grinding and higher energy, production cost turns out to be high.

2.8.3 Hydrothermal technique [24-25]:

Synthesis of LMOs through hydrothermal technique is done in autoclave. This strategy is carried in fluid medium so it needs exceptionally exact control of pressure and temperatures. This technique is suitable for fine particles synthesis. Homogenous product is the main feature of this preparation technique which is also very fast, simple and allows better controllability of morphology. This strategy has turned critical for electrode formation of various types in lithium ion battery.

2.8.4 Spray pyrolysis [26-27]:

For creating great quality ceramic particles with immaculate crystallized state in single state inside a brief span spray pyrolysis method is used. Aside from this, this strategy can possibly create high purity, round morphology, synthetically homogeneous powder (fine sized) and agglomerated particles that are not agglomerated. Spray pyrolysis technique is made out of a quartz reactor, a powder collection material and generator of droplets. Droplets are conveyed into higher temperature tubular reactors utilizing transporter gas. Powder and droplets, after this, are evaporated, and crystallized in quartz reactor. It is a proper strategy for preparing spherical LMO.

2.8.5 Electro spinning method

Electro-spinning is a prominent methodology for amassing nano-fibers utilizing an energized stream of a polymeric liquid. The stringy, nonwoven fiber mat that usually comes to fruition on account of electro-spinning finds applications in a broad assortment of industries. Although settling an electro-spinning experimental apparatus is for the most easier, but controlling the attributes of the last outcomes, for instance, the width and morphology of formed fiber, the orientation of the produced fibers, also the porosity, and the surface features of resultant mat, etc. is altogether all the more troublesome. For preparing higher performance nano fiber anode, nano-sized separator and nano fiber cathode which can conceivably replace Lithium ion batteries, electro-spinning is incorporated. LMO/PAN nano fiber separator has huge electrolyte take-up, higher conductivity (ionic) and lower inter-facial barrier with lithium, thereby increasing cyclic stability of Lithium-ion batteries.

Chapter-3

EXPERIMENTAL PROCEDURE

3.1 Synthesis of LMO by electro-spinning method

Stoichiometric quantity of manganese acetate Mn($C_2H_3O_2$).4H_2O (0.1 mol) was added in 5ml distilled water, stirred (RPM 400) for 30 minutes and named solution A. Stochiometric quantity of lithium acetate Li($C_2H_3O_2$).2H_2O (0.2 mol) was also added to 5 ml distilled water ,stirred (RPM 400) for 30 minutes and named as solution B. Solution A and solution B were mixed together for another 30 minute and named as solution C. Typically, 1 g PVA (sigma Aldrich wt. 1,30,000) was mixed into above solution C @ 70ºC and stirred for 12 hours (RPM 350) thus the precursor was prepared for further electro-spinning process.

This precursor was then fed into the plastic syringe of 10 ml volume having a steel needle(stainless) and being connected to very high voltage supplier. Syringe pump controlled the flow rate at 1.6 ml/h with voltage of 16.8 kV applied to it. A collector (aluminum foil feet) was placed on the drum having diameter 0.5 mm which is 12 cm away from the needle pointed. Drum speed was 260 RPM. Further, as-spun Li2MnO_3 nano fibers were dried for 12 hours at 50ºC. the fibers are then scratched out on a petri dish and further calculation is done at 500ºC for another 12 hours.

Fig.3.1 synthesized LMO nano material by electro-spinning

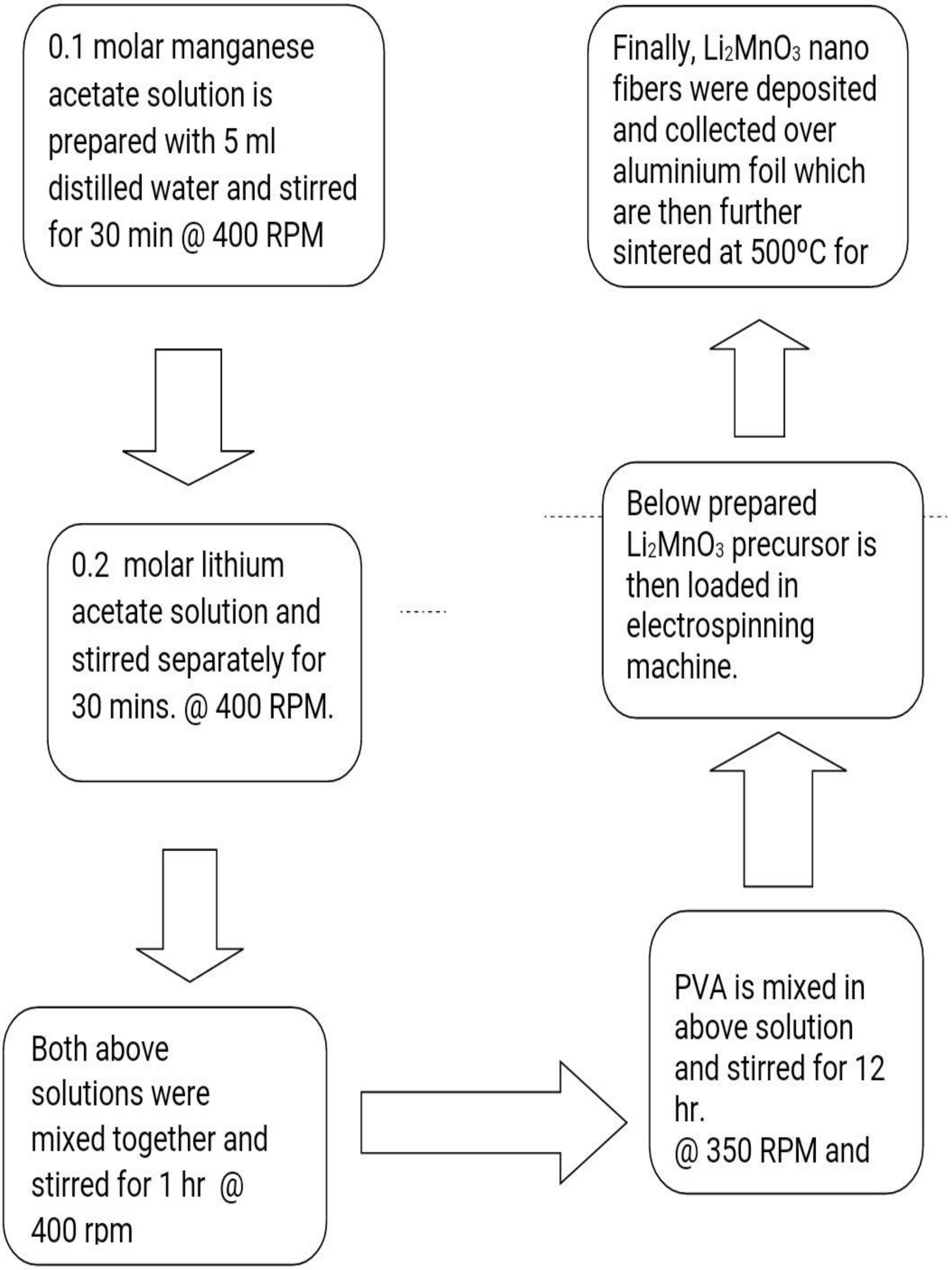


Fig. 3.1 Block diagram of synthesis of LMO by electro- spinning method

Chapter-4

CHARACTERIZATION METHODS

Characterization methods

Procedures of characterization referred to the technique with the help of which we can, without much stretch, distinguish arranged specimen concerning its surface topology, inward structure, morphology and so on. These strategies were utilized to ponder the features, resilience of sample to the forced environment so that amid the procedure, no harm will be caused to the specimen either inside or externally. Following methods are devised for characterization.

4.1 X-rays Powder Diffraction (XRD)

X-ray diffraction system is utilized to get data about phase identification, sample crystal size and unit cell's miller planes measurements. It utilizes the idea of spatial dispersion of X-rays that sample scatters and intensities of them. Natural diffraction gratings are contained in a crystal for X-rays and having strong periodicity in structure. At the point when X-ray beams colloid with the sample's particles, X-ray beam are diffracted by electron and x-ray impact. X-ray diffraction pattern is greatly affected by wavelength of sample and its structure.

Crystal are by and large regular array of atomic particles arranged periodically. At the point X-rays waves colloid with the regularly arranged molecules then a wave scatters in the regressive direction (back scattering). X-rays striking electrons will deliver secondary waves (spherical) rising up out of the electron. This is referred to as elastic scattering, the electron is referred as the scattering electron. Atoms of a specimen produces patterned array of spherical waves. The constructive interference of forwarding and in reverse wave is in charge of getting the data about XRD which can be computed by Bragg's law. At the point X-rays with wavelength λ of magnitude (1–100 Å) and test sample crystal spacing d in between will gives off the diffraction pattern.

. Bragg law states,

$$2d\sin\theta = n\lambda$$

θ = scattering angle.

n = integer.

Here approaching x-ray beam wavelength (λ) is related with planar separation of the crystal (d) is depicted in figure underneath. XRD is a non-destruction strategic tool for distinguishing orientation and also phase, nanoparticles size estimation, depict the basic structural features and to calculate thin film thickness.

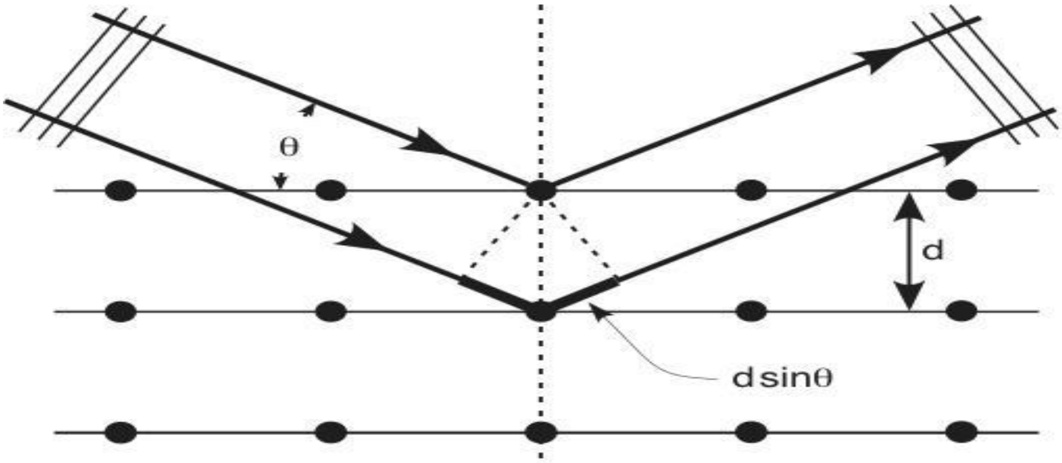


Fig 4.1 Bragg diffraction [28]

Fig 4.2 X-ray diffraction equipment used in the XRD characterization of LMO

4.2 Scanning Electron Microscopy (SEM)

SEM is a kind of microscopy, using electrons, which creates sample's image with the assistance of centered beams of electrons while scanning the sample. It creates diverse sorts of signals when electrons colloid with the atoms of sample that is detectable and collects the data about the specimen's surface topography and composition. The electrons beam is by and large scanned in a raster sort scanned pattern thereby creating a pictures, detected signal is converged with the beam positioning. The auxiliary (secondary) electrons are energized by these electrons beam from the specimen surface which is to a great extent identified by SEM. The point at which beam falls upon the specimen surface (i.e. on sample topography) affects the amount of released secondary electrons. In a SEM, to gather the released secondary electrons, there is an uncommon kind of detector which can be utilized to identify these auxiliary electrons through scanning the specimen. Consequently a picture showing the topographical points of interest of the upper surface is made, thus showing shape and size of specimen which has minute attributes less than 1 nanometre in measure.

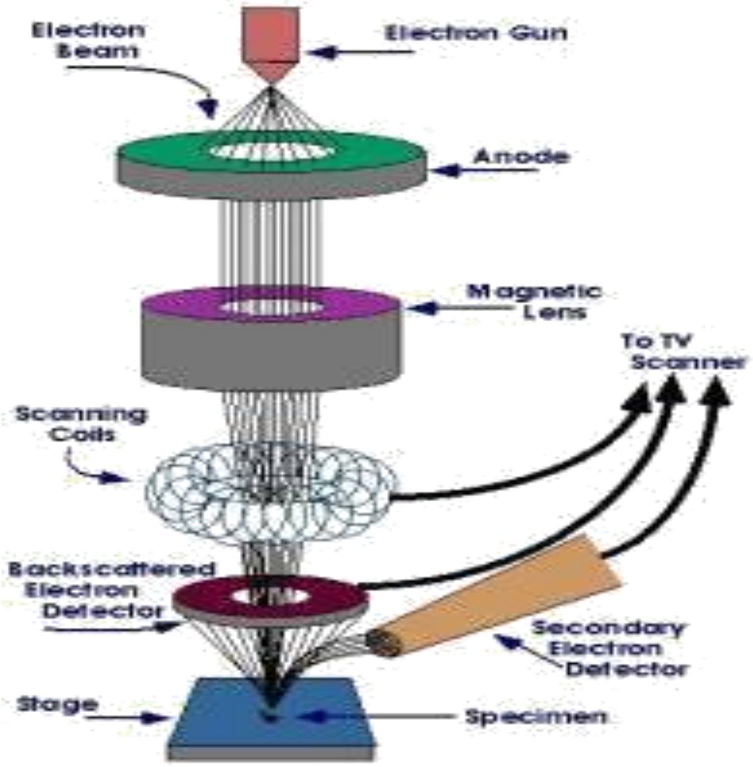


Fig 4.3 Schematic of SEM apparatus [29]

SEM has typically following features:

- A gun of electron (source) which emits the electron rays that is accelerated to the down column.
- A arrangement of focal lenses that are objective and condenser that controls the width of the beams and in addition focusing beams on a sample.
- A arrangement of gaps that are miniaturized scale openings in metal films which allows the beams to be passed through and which influences beam’s property.
- Control over position of sample (x, y, z) and also orientation (tilt, rotation).
- All the parts were kept up at high vacuum level.

An electron gun emits thermionic beams of electron in SEM which is prepared from a cathode of tungsten filament. Energy of the electron rays by and large extends from 0.2 to 40 KeV, the beam is concentrated by a couple of condenser focal lenses for a spot with diameter extends from 0.4 nm to 5 nm. At that point the beams is gone through sets of redirector plates or two or more of scanning loops that exists in electron segment, and ultimately through deflector focal lenses, which deflects the beams out and scanning in a raster approach is done to cover a rectangular zone in x and y axes of the sample's surface.

Fig 4.4 Scanning electron microscope equipment used in the SEM characterization of LMO

This procedure begins at the top towards bottom and from leftward to rightward. Raster design is utilized to deliver the image over screen. The assortment of pixels in each line yet as aggregate number of columns of the scanned spaces was laid low with image resolution selected. At the point when beams of electrons(primary) going through focal lenses interfaces with the specimen, the energy of electrons is lost by ceaseless irregular absorption and dissipating interaction volume at intervals, that is by and large however 100 nm to 5 µm into the sample surface. Distinctive sorts of signals delivered by a SEM incorporate auxiliary i.e. secondary electrons (SE), Augers electrons, characteristics X-ray beams, back-scattered electrons (BSE), and light (cathode luminescence) (CL).

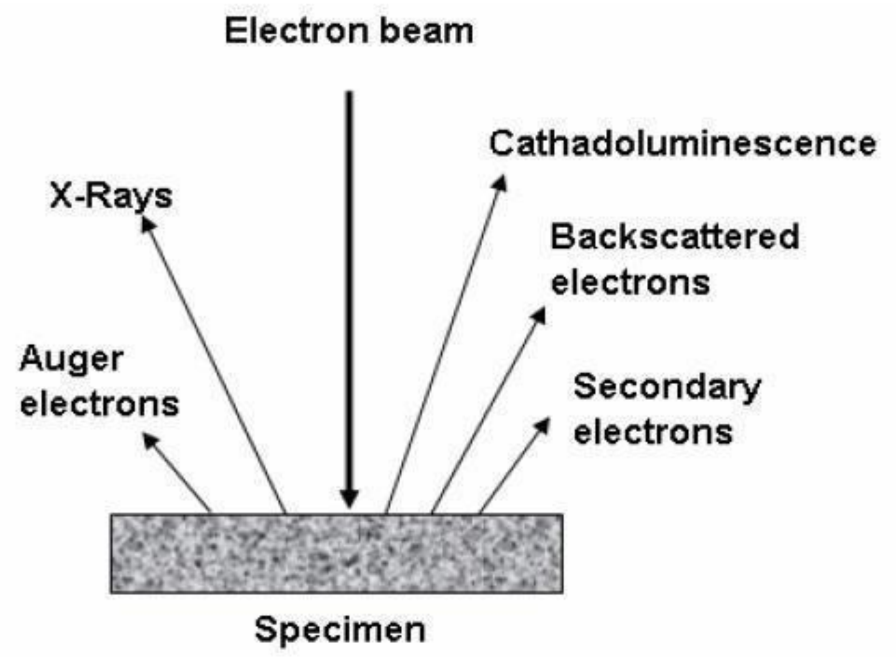


Fig 4.5 Different types of electrons released during SEM imaging [30]

Secondary Electrons:

Electron will be thumped out from its orbital shell of sample surface when the incident electron crashes into an electron in sample atom, and it is changed over into ionized form. Multiple crashes may be conceivable since the approaching electron loses just a little measure of energy amid each impact. Subsequently, such process proceeds until the point that the event electron has no extra vitality to remove secondary electrons. Each liberated auxiliary electrons have a little kinetic energy (<50 eV), which do not depend upon incident electron energy.

These secondary electrons which escape from specimen surface can be gathered by the detector. Subsequently, specimen topography can be viewed through imaging secondary electrons.

Backscattered Electrons

In the event that an electron interacts with the core of a surface particle, at that point the electron will swing back or scatter "backward" out of specimen which is referred to as backscattered electron (BSE). These backscattered electrons range in high energy, ordinarily in the extent of 50 eV. Amount of BSE electrons are influenced by atomic number of the sample thus these BSE electrons changes clearly according to atomic number and to perceive difference in specimen atomic number, backscattered electron pictures can be used.

Auger Electrons

A vacancy is made in an ionized molecule's electron shell on account of production of secondary electron. Keeping in mind the end goal to fill these vacancies, a higher energy external shell electron can dropped down in order to fill the vacancy. On account of this surplus energy of the atom, an external electron is radiated which is known as an Auger electron. Auger electrons are produced from shallow specimen depths (<3 nm) since it has a comparatively little kinetic energy. These electrons can be utilized to give compositional data about the objective sample.

Chapter-5

RESULTS AND DISCUSSION

5.1 X- ray Diffraction Characterization

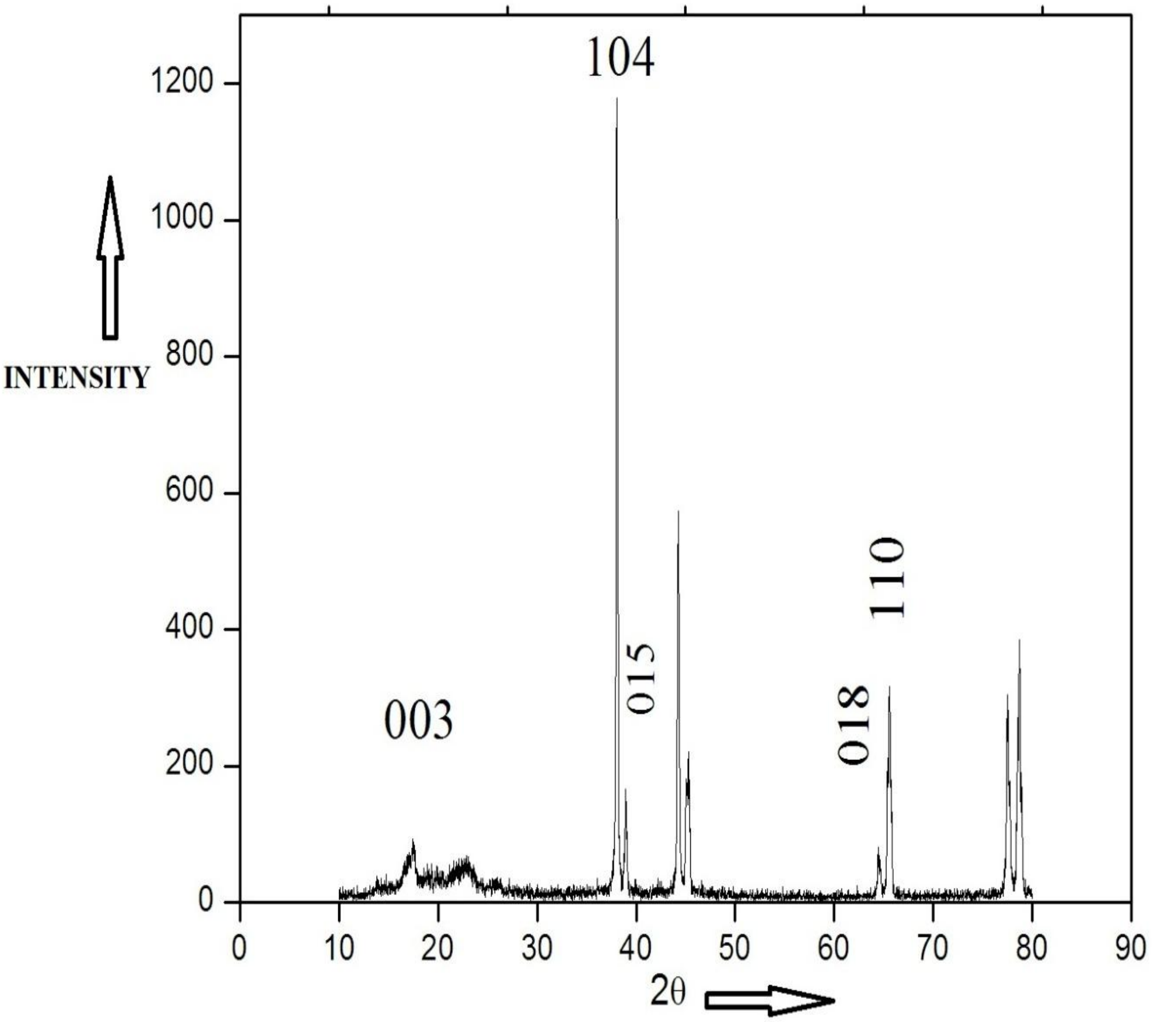


Fig 5.1 XRD pattern of LMO

XRD patterns of Li_2MNO_3 fiber film in Fig. 5.1 shows that it had been fabricated using electro spinning method. Here in XRD pattern highest peak is obtained [104] plane which signifies the formation of impure form of Li_2MnO_3 that will be further investigated to check the capacity, cyclic performance, power density and energy density of the sample which definitely will be used in the lithium-ion batteries in the near future.

5.2 Scanning Electron Microscopy Characterization

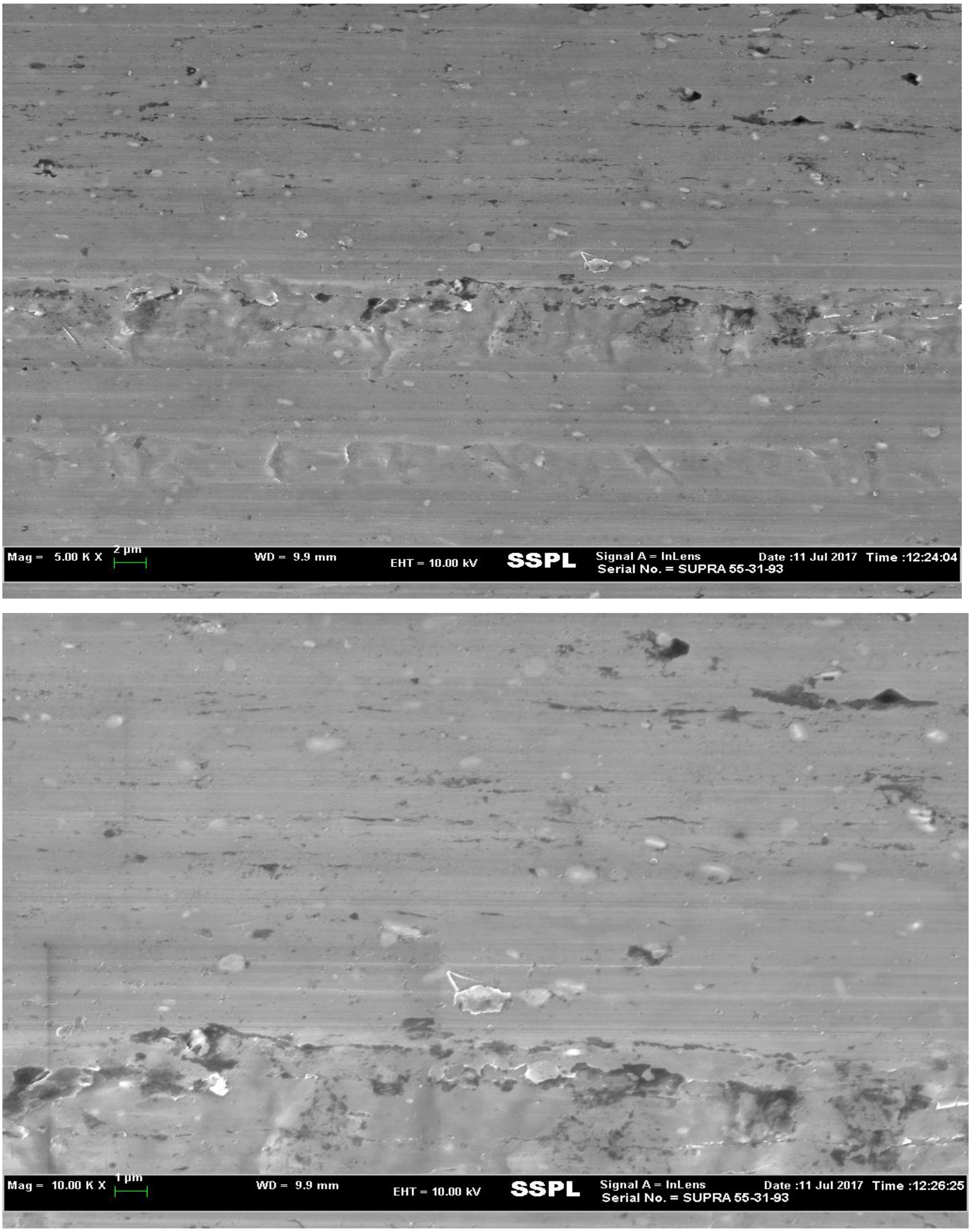


Fig 5.2 SEM images of LMO at different magnifications

Fig 5.2 shows SEM images of LMO fibers that are synthesized by using electro spinning route. To order to evaluate the size of particles, their shape and their morphology, the scanning electron microscopic (SEM) is being performed. Figure 5.2 (A) shows the SEM images of LMO, which has the irregular shape and also has agglomerated morphology having the size of particle of about. Mean while, shape of sample (irregular) shows higher extent homogeneity. Synthesized LMO material can be considered to be suitable for better electrochemical performances as the cathode material. As the size of particle and its morphology do have a important effect on electro chemical characteristics of LMO.

Chapter-6

CONCLUSION

Conclusion

The fabrication of LMO fibers using electro-spinning method has been carried out. The temperature during sintering process and the route of fabrication played an eminent role in deciding the crystal structure, morphology of particles and its physiochemical purity. The fabricated Li_2MnO_3 nano fibers will be investigated to check the capacity, cyclic performance, power density and energy density of the sample which definitely will be used in the lithium-ion batteries in the near future.

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