

Project Report On
Synthesis and Characterization LiFePO_4 as cathode
materials for lithium ion batteries

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IN
NANOSCIENCE AND TECHNOLOGY

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CANDIDATE'S DECLARATION

I, Himanshu Singh Vishen, Roll No. 2K18/NST/03 of M.Tech. Nanoscience and Technology, hereby declare that the project Dissertation titled "**Synthesis and Characterization LiFePO_4 as cathode materials for lithium ion batteries**" which is submitted by me to the Department of Applied Physics, Delhi Technological University, Delhi in partial fulfillment of the requirement for the award of the degree of Master of technology, is original and not copied from any source without proper citation. This work has not previously formed the basis for the award of any Degree, Diploma Associateship, Fellowship or other similar title or recognition.



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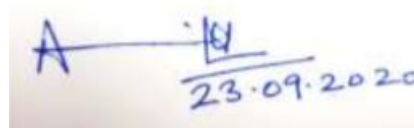
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CERTIFICATE

I hereby certify that the Project Dissertation titled “**Synthesis and Characterization LiFePO₄ as cathode materials for lithium ion batteries**” by **Himanshu Singh Vishen**, Roll No. **2K18/NST/03**, Department of Applied Physics, Delhi in partial fulfilment of the requirement for the award of the degree of Master of Technology, is a record of the project work carried out by the student under my supervision. To the best of my knowledge, this work has not been submitted or full for any Degree or Diploma to this University or elsewhere.

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ABSTRACT

Rechargeable Lithium ion batteries are one of the prominent alternative source of energy storage. The applications of these batteries from smaller electronic product to heavy duty applications such as electric vehicles, energy storage back-ups etc. are being extensively explored. But still there is need to improve energy density, power density, long cyclability and development of environment friendly and cost-effective cathode material in these batteries. Usually, the conduct of rechargeable Li-ion battery succumb on cathode material. The deintercalation and intercalation of Lithium in various layered structured of cathode has been reported for many materials that are in transition group of the periodic table and have been investigated. In this study, synthesis and characterization of olivine type LiFePO_4 has been carried out using the sol-gel route, Further, physiochemical characterization such as XRD and thermal behaviour TGA of synthesized material has been performed. For confirming the formation of the LiFePO_4 , characterization by X-ray diffractometer (XRD) is undertaken to confirm the proper phase formation and TGA technique are using for variation in mass of a sample undergoing temperature scanning in a controlled atmosphere (air and N_2). However, the electrochemical analysis of the synthesized LiFePO_4 could not be perform due to closing of laboratory in lockdown for COVID-19 pandemic

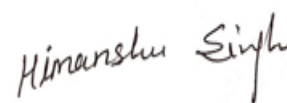
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Himanshu Singh Vishen

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List of Abbreviation

- LIB- Li-Ion battery.
- LFP-LiFePO₄
- XRD- X-ray diffraction
- SEM -Scanning Electron Microscope.
- TEM: Transmission electron microscopy
- AFM-Atomic Force Microscopy.
- HEV: Hybrid Electric Vehicles
- PHEV: Plug-In Hybrid Electric Vehicles.
- NPs: Nanoparticles
- DOD: Depth of Discharge
- TGA: Thermogravimetric Analysis
- NPs=Nanoparticles
- °C=Degree centigrade
- DI=Deionized water
- pH=Power of hydrogen
- FWHM =Full Width Half Maxima
- HCP=Hexagonal closed packed

List of Symbol

σ =electronics conductivity(s/cm)

R=Resistance of the sample(Ω)

V=voltage(V)

L=Thickness and Diffusion Length

A=Cross-sectional Area of The Circular Disc (Cm^2)

E_a = Activation Energy(eV)

K_B = Boltzmann Constant(j/k)

T= Temperature(k)

D= Diffusion Coefficient

τ =diffusion time

λ =Wavelength

I =Intensity

\sim =Approximately

/ =Per

CHAPTER-1

Introduction

1.1 Overview

Incredible tension on non-renewable electricity resources like charcoal, petroleum, and also problems associated along with their usage like sky contamination, ejection of greenhouse fuels, global warming has forced the researcher/ scientists to seek the alternative power resources which are eco-friendly as well as much less hazardous to individual wellness. Therefore, various renewable energy resources have been developed along with their storage energy system in recent past. Usually, energy storage system are categories by the different area like mechanical, electro-chemical, chemical etc. Most promising areas of the energy storage devices are batteries, capacitors, flywheel compressed air energy storage, thermal and hydro-power as shown in fig1. The critical abuse of inexhaustible and practical vitality sources, for example, wind and sunlight based vitality has been incited by ecological concerns identified with the non-stop utilization of non-renewable assets and the expanding multifaceted nature of intensity dispersion frameworks. Proficient utilization of these new vitality sources is urgent concerning their nonconstant power age [1]. Among numerous energy storage sources rechargeable batteries like Pd-acid, Ni-Cd and lithium ion are prominent source of energy storage devices. In all rechargeable system, lithium ion battery has been considered more useful due to high energy density, large power density and cyclic performance over other rechargeable batteries. The development of alternative cathode materials is essential requirement for Li- ion batteries keeping the view of improvement of various properties like capacity, cyclability, energy and power density, environmentally friendliness and inexpensive. Among various developed cathode materials olivine type LiFePO_4 is most important cathode materials during its excellent electrochemical properties and capacity. Lithium iron phosphate (LiFePO_4) have orthorhombic crystal structure [2]. LiFePO_4 have good theoretical capacity approximately 170 mAh/g better cycling stability, inexpensive material, nontoxicity and enhanced safety. Hence, its significant consideration for the application of Li- ion battery which are considered as one of the most auspicious power sources for HEVs [3]. LiFePO_4 batteries shows low high-rate performance because of its lower conductivity. Therefore, to increase the intrinsic drawback of LiFePO_4 , numerous ways have been adopted like the doping with different cations and particles coated by electronic conductive materials [4-6]. In addition to these, changing of the

grain size is likewise a successful method to reduce the dispersion separation for lithium ion inside the electrode [7-9].

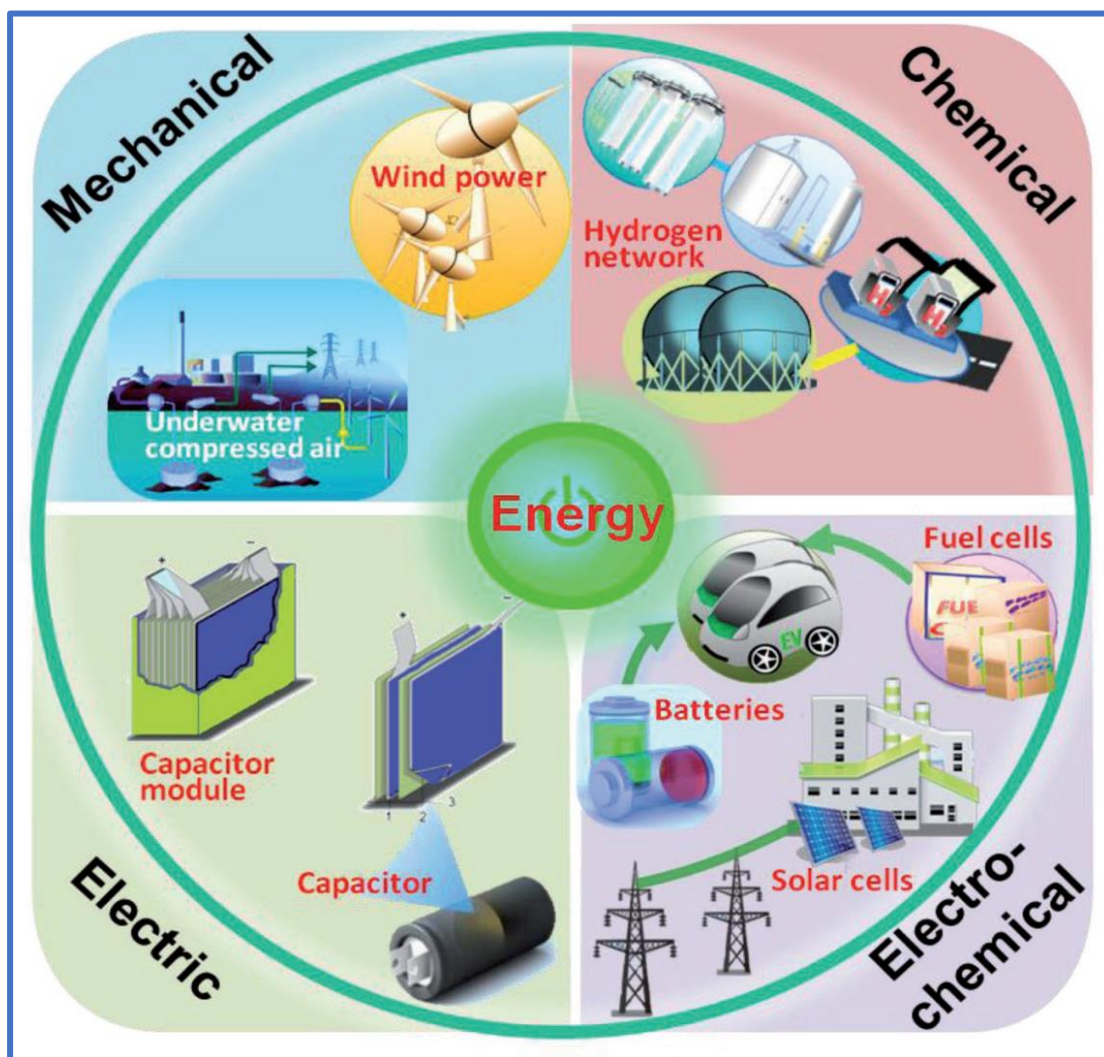


Fig 1: Energy Storage System ^[1]

Recently researchers developed a new method to modify the surface structure of the electrode which are improved the high-rate performance of the LiFePO_4 based batteries [10-12]. Olivine type LiFePO_4 meets utmost of the criteria desired olivine material such as large theoretical capacity (172 mAhg^{-1}), cheap, structural stability through brilliant retention capacity and, environmentally friendly because of non-toxicity [13-23]. It holds steady voltage elevation approximately 3.45 V vs. Li^+/Li due to 2-phase redox reaction consistent of transition metal $\text{Fe}^{2+}/\text{Fe}^{3+}$. Low conductivity ($10^{-9} - 10^{-11} \text{ S/cm}$) and inactive kinetics diffusion of lithium-ion

($\sim 10^{-18}$ cm²/s) has limited detailed usage of automobiles as well as hybrid vehicles [24-26]. Many techniques of enhancing the surface and electronic conductivity of excellent LFP material, featuring carbon coating [27,28] layer as well as lithium (M1) or even iron (M2) cation doping [29,30] have been reported so far. Carbon dioxide finishing, having said that, boosts the faucet thickness of the LiFePO₄ cathode product as well as thereby reduces the electric density. Hu et al [31] were actually analysing the study of ZnO-doped LiFePO₄ made from hydrothermal Method and organize the ZnO-doped sample send the capacity 132.3mAhg⁻¹ and 80 mAhg⁻¹ discharge capacities at 0.10C and 1.0C, correspondingly. The pristine LiFePO₄ and ZnO-doped LFP/C [32] sample are mixing 2.5-2.6 wt.% PVA, pressurised to circular disks with a dia. of 10mm by using a hydraulic press to apply pressure of 7 tons then after heated to 250-270 o C for 2h-3h in the air to remove PVA. Ag paste has placed on two way of the pellets to made a electrical contacts , subsequently, dry up 150°C for 1-1.5 hrs in the open environment to eliminate humidity. A two-point probe setup usually using for to measuring for the electronic conductivity. Measurements of conductivity have made bias voltage of 1Volts, the frequency ranges of LFP material is 10kHz-10mHz [32].

1.2 Working of rechargeable li-ion battery

In periodic table lithium is 3rd lightest material and which have highest oxidation potential among all periodic table elements. Generally, third generation rechargeable lithium ion batteries contains mainly four components such as cathode, anode, electrolyte and separator as shown in Table 1 and briefly explained there also;

Table 1: Components of rechargeable lithium ion battery

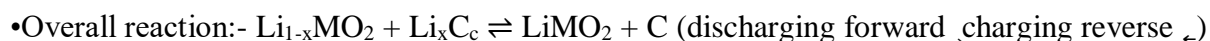
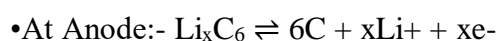
Component	Functions	Materials
CATHODE	Emit Li-ion to anode, during charging and Receives Li-ion during the discharging.	Cathode portion of the LiFePO ₄ , which is made up of lithium metal oxide powder.

ANODE	The anode portion of the battery receives Li- ion to anode, during charging and Emits Li-ion during the discharging.	Graphite powder
ELECTROLYTE	allows the transfer of the Li-ion between anode and cathode portion of battery.	the electrolyte portion of the battery, which is made up of lithium salts and organic solvents.
SEPARATOR	separator are using for prevention of short-circuit between anode and cathode and Transfer Li-ion through pores in separator.	Micro-porous membranes.

Lithium ion batteries work by utilizing the exchange of lithium ions and electrons from the anode to the cathode as shown in figure 2. Lithium having high tendency to lose electron if we placed lithium-ion to metal-oxide, lithium ion is quite stable with metal oxide.

During charging lithium ion from oxide ($\text{Li}_{1-x}\text{MO}_2$) based cathode moves through electrolyte and porous separator (PP) towards anode (graphitic, C) and the equal number of electrons flow through the external circuit (power source) due to oxidation process at cathode towards anode also. Both the lithium ions and electrons reach at the anode (graphite) due reduction to process at this electrode. Hence, charge is balanced at anode and stored there and make lithium with carbon make phase Li_xC_6 .

During discharging oxidation takes place at anode therefore the lithium ion stored at anode side in graphitic layers (Li_xC_6) return to cathode through the separator and electrolyte while same number of electrons move through external circuit /applied power load. During discharging process electron occupy its position to make again metal oxide (LiMO_2). Both the oxidation and reduction reaction occurred during discharging of Li-ion;



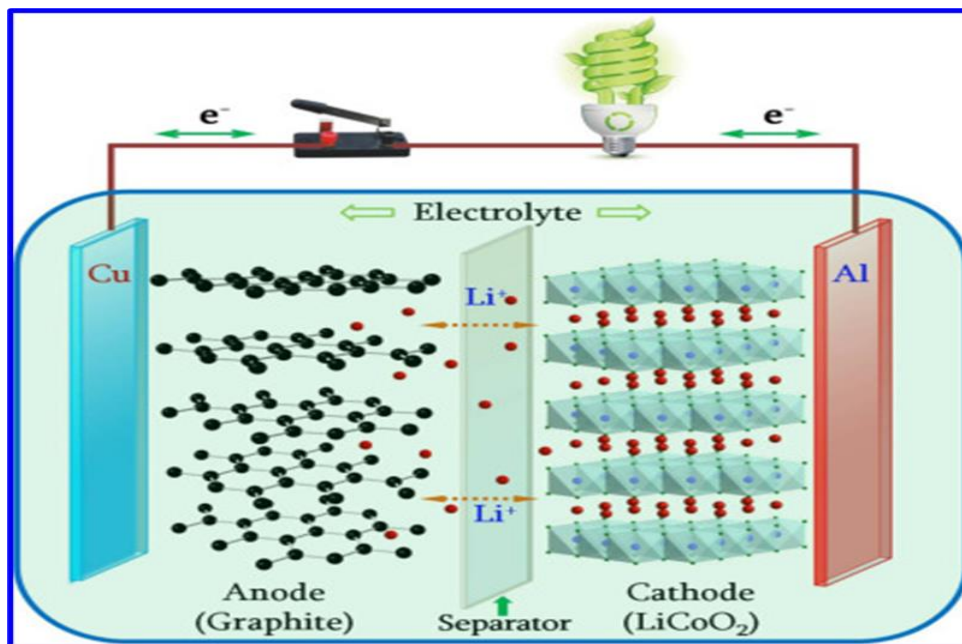


Fig 2: Working of Rechargeable Li-ion battery ^[33]

1.3 Applications

Lithium Iron Phosphate LiFePO₄ (LFP) cathode materials are being used to prepare lithium ion batteries at commercial scale. The application of lithium ion batteries made of LFP based cathode is prominently working in all sizes of batteries like small electronic devices, medium portable and heavy-duty applications by various commercial organizations /companies. Some of the application examples are as following;

Communications Equipment consisting of Ham Radio: The company is utilizing LFP electric batteries to substitute lead-acid and also Ni-Metal hydride electric batteries for broadcast interaction tools including pork broadcast. In add-on, the electric batteries are much less than half the bodyweight of traditional lead-acid electric batteries.

General Purpose Equipment/ Instrumentation: LFP based lithium batteries supply incredible conveniences for powering as well as billing several standard objectives and also machinery tools. The basic reason devices feature audio amps, cell phones so on.

Batteries for e-bikes/e-scooters to substitute lead-acid electric batteries. Since LFP based electric batteries supply tremendous conveniences consisting of higher particular capability and also considerably boosted pattern lifestyle, as well as really reduced body weight, these

electric batteries are actually suitable for e-bike/ e-scooter uses.

Electric Golf Caddy: LFP electric batteries could be made use of to energy electrical golf caddies which are actually utilized to lug golf clubs around greens. LFP electric batteries are actually less than half the bodyweight of conventional lead-acid electric batteries producing all of them best for electricity golf caddies, along with greatly improved

Energy Storage: LFP based lithium ion batteries when incorporated along with inverters as well as converters may be utilized as a power storing answer which may energy lots of forms of power lots in atmospheres where there is actually no accessibility to electric power.

Numerous transportable electronic devices can easily be actually billed utilizing LiFePO_4 electric batteries consisting of laptops pc and also wise phones.

Boats/Kayaks: LFP electric batteries provide remarkable perks for powering little watercraft and also kayak electric motors. LiFePO_4 electric batteries are actually less than half the bodyweight of typical lead-acid electric batteries and also give significantly improved pattern lifestyle that makes all of them suitable for utilizing all of them in little watercraft and also kayak electric motors.

Solar: LiFePO_4 electric batteries could be blended along with solar power as well as solar energy controller. The photovoltaic panel may bill the LiFePO_4 electric battery while concurrently deliver electrical power to an electric load. Contrasted to lead-acid electric batteries, LiFePO_4 electric batteries use an exceptional pattern lifestyle.

CHAPTER-2

Literature Survey

The commercialization of first generation of lithium-ion cell was done by Sony in the year 1990-1991. Lithium ion cell was made of $\text{Li}_{1-x}\text{CoO}_2$ and Li_xC_6 as cathode and anode electrode materials, respectively. The theoretical discharge capacity of $\text{Li}_{1-x}\text{CoO}_2$ is estimated as ~ 274 mAh/g while experimentally it was observed ~ 140 mAh/g. The reversible cyclability LiCoO_2 allows only half of lithium ions upto the voltage range 2.8 - 4.20 V vs. Li^+/Li . LiCoO_2 is a well established rechargeable lithium ion battery cathode material following the layered structure. But its limitation of capacity, toxicity due to cobalt and unsafety at high temperature leads to develop alternative olivine materials. Alternative cathode materials have developed to improve the battery performances like energy density, power density, rate capability, cyclability and reduced cost, toxicity as well as hazardless. LiCoO_2 was first generation cathode with the generalize formula ABO_2 . All alternative cathodes of layered type structure are shown in Table 2 with their specific capacity (theoretical/observed) and available voltage with reference to lithium metal as anode. Further, the second and third generations of alternative cathode materials is given in table 3. Spinel-type cathodes allow the lithium intercalation pathways in all three dimensions. The general formula of spinel structure is AB_2O_4 ($A = \text{Li}$, $B = \text{Mn}$, Ni). LiMn_2O_4 is the most common studied material in this category. Other spinel-type transition metal oxides commonly called spinel-ferrites/ ferro spinels with general formulation MFe_2O_4 ($M = \text{Ni}$, Co , Zn).

Table 2: Layered-type cathode materials (2-D) [34]

Chemical formula	Specific capacity (mAh/g) (Theoretical/observed)	Potential vs, Li^+/Li
LiCoO_2	274/147	3.9
LiNiO_2	274/180	3.6
$\text{LiNi}_x\text{Co}_y\text{Mn}_2\text{O}_2$	270/150-180	3.8
LiMnO_2	290/100-150	4.1/3.0
Li_2MnO_3	460/50-100	4.7

Table 3: Spinel-type cathode materials (3-D) [34]

Chemical formula	Specific capacity(mAh/g) (Theoretical/observed)	Potential vs Li ⁺ /Li
LiMn ₂ O ₄	148/130	4.1
LiMn _{1.5} Ni _{0.5} O ₄	146/130	4.7

Olivine-type cathode materials (1-D)

The third generation of alternative cathode of intercalation type cathode materials are shown in table 4. The olivine type of cathode belongs to polyanion compounds that contain “(XO₄)ⁿ⁻ (X = P, S, As, W or Mo)” tetrahedral anion structural units. In all phosphor-olivines, a strong covalent bond exists between all oxygen ions and P⁵⁺ to form tetrahedral PO₄³⁻ structural unit. Generally, the formula of LiMPO₄ (M = Fe, Mn, Co, Ni, etc.) known as natural mineral triphylite.

Table 4: Various Olivine Type Cathodes materials for LIBs [34]

Chemical formula	Specific capacity (mAh/g) (Theoretical/observed)	Potential vs, Li ⁺ /Li
LiFePO ₄	170/160	3.45
LiMnPO ₄	171/80-150	4.1
LiNiPO ₄	166	5.1
LiCoPO ₄	166/60-130	4.8

2.1 Development of Intercalation Type Cathodes Materials

There are four type of alternative intercalation cathode materials developed and being used Li-ion batteries. The structural formula and position of lithium atom in the structure of different cathodes are shown in figure 3. These four types of cathode materials belong to layered, spinel, olivine and tavorite type structures.

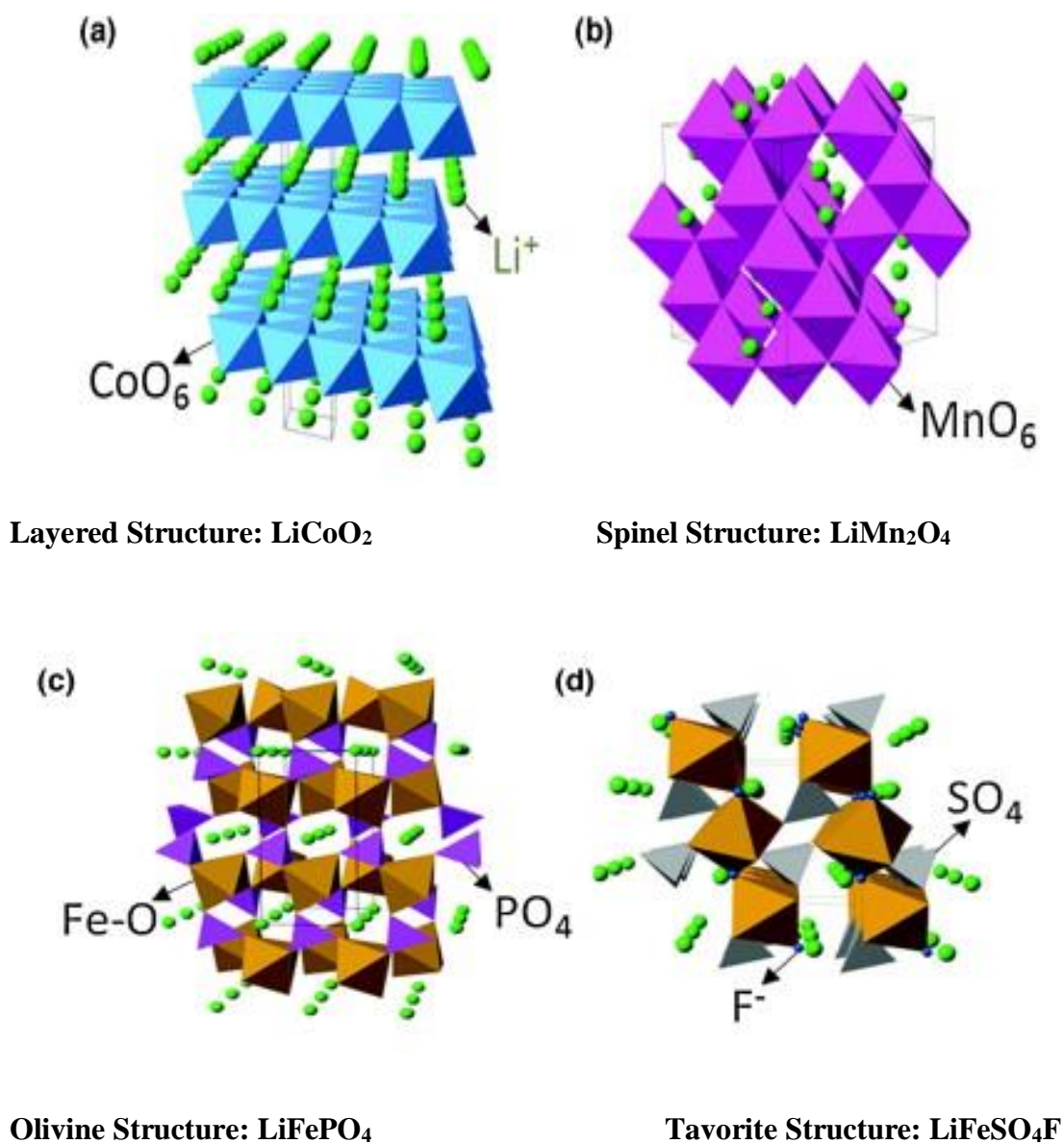


Fig 3: Position of lithium in intercalation type cathode materials ^[35]

2.2 Feature of LiFePO₄

Crystal structure of LiFePO₄

LiFePO₄ has an ordered structure of olivine, Pnma orthorhombic space group, the crystal constant of LiFePO₄ of a,b and c are 10.35 Å, 6.11 Å and 4.65 Å and volume is 294.05 Å³ [36]. Fig 5 and Fig 6 shows the olivine structure of LiFePO₄ of ideal and actual structure. LFP comprises of FeO₆-octahedral and PO₄-tetrahedral. FeO₆-octahedral and PO₄-tetrahedral reach separately by allocate oxygen vertices in b-c plane. The FeO₆-octahedral connections another PO₄-tetrahedral due to sharing a corner. All PO₄-tetrahedral do not contact one another. Li-ions are arranged in interstitial voids, framing infinite chains sideways the c-axis in another a-c plane [36]. Li possesses the M1 site and Fe M2 site. Fe atom possess zigzag chain of corner-shared octahedral corresponding to the C-axis in parallel planes of ac-planes. oxygen arranges as far as HCP structure with less distortion. Not every single PO₄-tetrahedral touches each other.

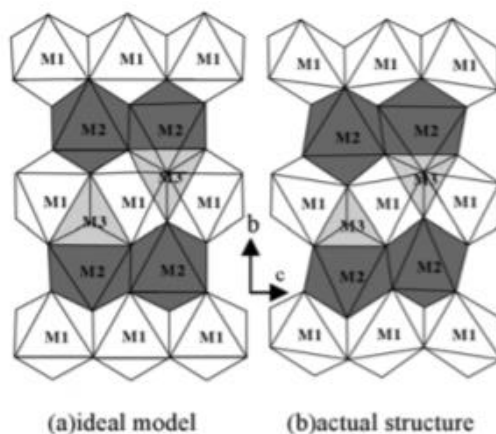


Fig 4: structure of LiFePO₄ (a) ideal model and (b) actual structure [36]

The lithium ions are situated in the framework's interstitial-voids, making unlimited chains laterally the c-axis in an alternating a-c plane. Li ions occupy the M1 site and Fe atoms filled with the “M2 site”. In the other ac planes, the Fe atoms occupy zigzag chains of corner-shared octahedra consecutively parallel to the c-axis [36]. Oxygen arranges with slight distortion in terms of the hexagonally close-packed (HCP) structure

The covalent P-O connection develops the delocalizing chemical connect in 3D, through which LFP is thermodynamically and also dynamically stable at temperature levels above 200°C. A.K.Padhi et al. kept in mind that LiFePO_4 , as well as FePO_4 , had practically the same construct, each orthorhombic. Small variation in between the two substances induces merely a mild adjustment in quantity, So that's not most likely to result in damage to the crystal construct in the course of releasing and also asking for. LiFePO_4 's one-of-a-kind olivine construct may ensure exceptional reliability certainly not like various other cathode materials, as a result, its own life is much higher. Focus on the academic LiFePO_4 installation/ removal process that is various coming from other processes [36]. The area region of the bits comes to be lithiated during the attachment of lithium ions into a cathode bit (discharge), And also between two unique phase locations surfaces a period user interface (a lithiated phase as well as a delithiated phase region). The user interface minimizes along with the procedure of asking for until the particle comes to be a single stage area.

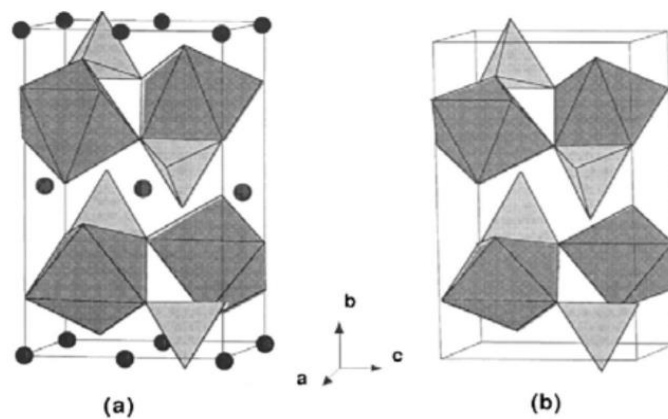


Fig 5: Crystal structure of (a) LiFePO_4 and (b) FePO_4 [36]

CHAPTER – 3

Experimental

Experimental methods and materials

3.1 Material synthesis

Preparation to synthesis of olivine LiFePO_4 , stoichiometric amounts of $\text{LiOH}\cdot\text{H}_2\text{O}$ (Sigma-Aldrich, ~99%), $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ (CDH, 98%) and $\text{H}_9\text{N}_2\text{O}_4\text{P}$ (Sigma-Aldrich, ~99%) were using as a precursors. Citric acid made use of a chelating substance. A different service was prepared with constant mixing of overall forerunners in de-ionized water and then incorporated individually to the citric acid solution. The leading remedy of pH market value was actually maintained in between 6 to 7. The ratio of metal ion and the citric acid proportion was actually 1:1. The Citric Acid and Precursor service were warmed at 70°C at 400 rpm along with continual rousing till a straight forward green gel was gotten. The gel hence obtained have broken down at 350°C for 5 hours in a tubular heating system beneath lessening air. Disintegration creates elimination of raw material as well as inconsistent contaminations in the form of gasoline depending on to the adhering to reaction. Fig 6 shows how to form LiFePO_4

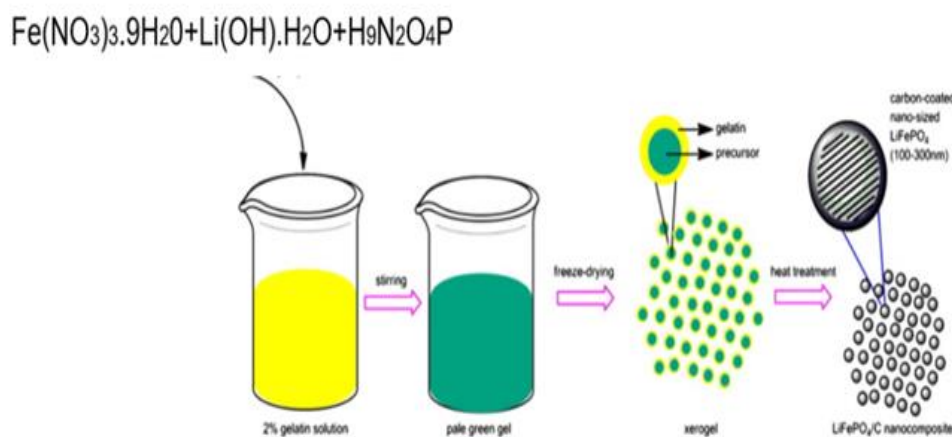


Fig 6: Step by Step Process to form LFP/C NPs

by sol-gel method, we are using the precursor to form a gelation after that the mixture was kept at particular temperature and stirrer at 350 rpm and put 3-4 drops of ammonium hydroxide as reducing agent are mixing together to form yellow colour to pale greenish gel shows in Fig 7 and Fig 8. When we get the pale greenish gel, we need to dry it to make xerogel after becoming

xerogel, we have to do heat treatment and after that we get LiFePO_4 material. stirrer are using for proper mixing of material and measure the temperature through thermometer.

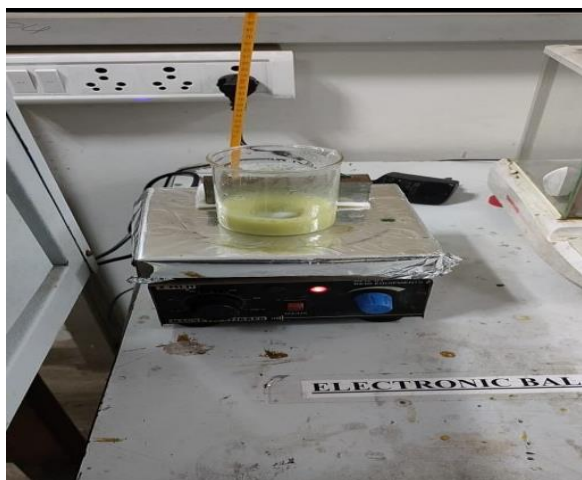


Fig 7: Stirrer and Thermometer



Fig 8: Prepared Material



In this flow chart (Fig 7) we are making separate solution of 10ml of distilled water with $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$, $\text{LiOH}\cdot\text{H}_2\text{O}$ and $\text{H}_9\text{N}_2\text{O}_4\text{P}$ respectively after making separate solution we need to mix each solution in a beaker and then continuous stirring at 400 rpm and maintain the PH value through reducing agent (NH_4OH). when we are using ammonium hydroxide (NH_4OH) colour changes from yellowish to transparent greenish gel (Fig 8) and then prepared material placed in vacuum oven to form xerogel (gel to powder) after making xerogel we need to heat treatment with the flow of Ar/N_2 in tubular furnace at 350°C for 5 hours.

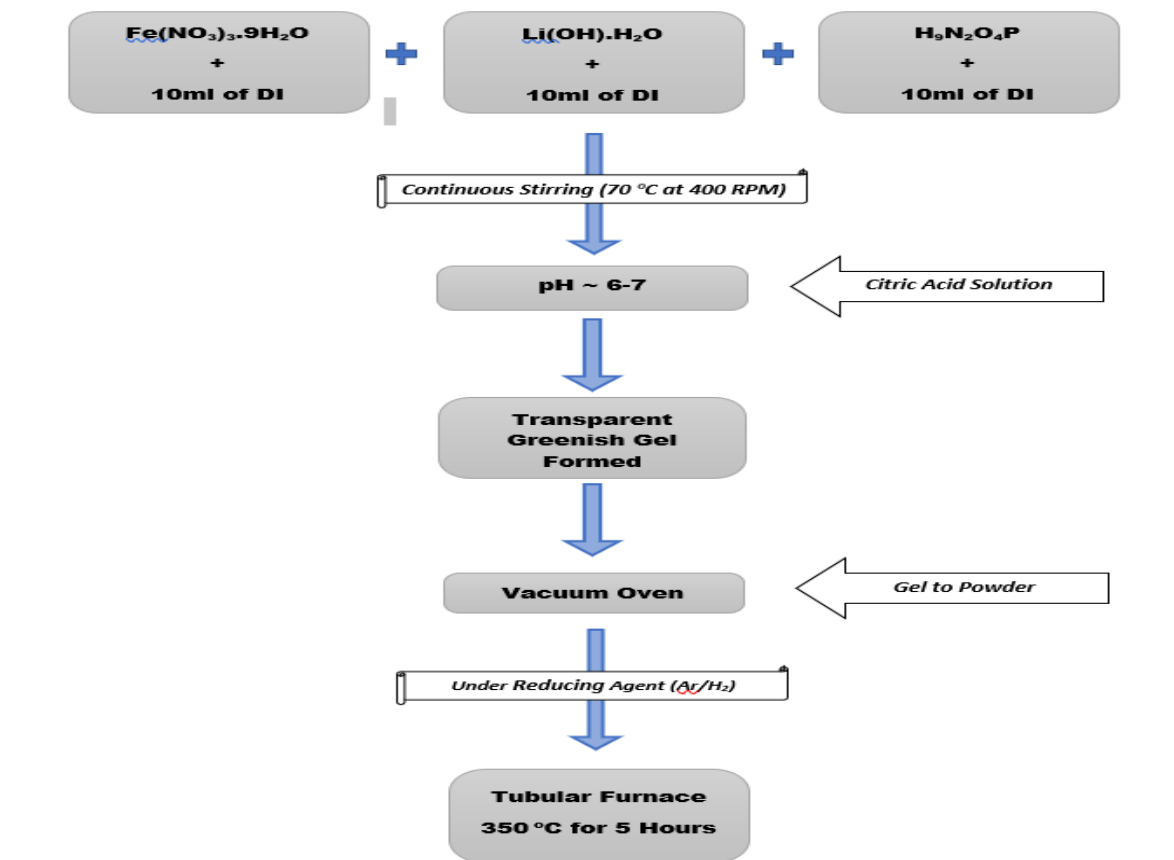


Fig 9: Flowchart for Preparing Cathode (LFP)Material

3.2 Liquid state and solid-state synthesis method

3.2.1 High-temperature solid-state method

This process adheres to: mix the precursor-salts as well as lithium salt with a certain proportion, sinter the mix first at a much-reduced temperature level (300 ~ 400°C) to extract volatiles 2nd at a higher temp (500 ~800°C) to take shape LiFePO_4 , then refreshing, fit together as well as grind to prep the product. The procedure of strong state response has been developed as well as Used frequently for automation as well as simple to manufacture [36]. Regrettably, the need for heat upgrades costs, what is actually additional, the dimension of the product can not constantly be actually tiny. So various other actions are contributed to steer clear of those issues, including a little lowdown temp or even including carbon dioxide granules.

3.2.2 Co-precipitation method

Mix the soluble precursor salts and lithium salt in water, readjust the PH worth in N_2 setting with stirring till $LiFePO_4$ precipitates into the blend. Filter, washout, and also dry out $LiFePO_4$ therefore at that point dispose it under excessive temperature. The temp won't usually influence the microstructure as too much temperature dependable empire technique does. This science desires a shorter response opportunity and also reduced temperature level in contrast along with solid nation response [36]. The fragment dimension can easily obtain the nanometer level as well as this reduced size can aid to enrich the charge-discharge functionality particularly unconfined current problems. The inadequacies hindering assembly-line production are a complicated way and gigantic electricity usage.

3.2.3 Sol-gel method

The Li^+ , Fe^{2+} and PO_4^{3-} compounding agent improves In a water remedy, to develop a sol. Dross sol-crystal rain to $400 \sim 900^\circ C$. Ultimately, the consistent circulation of ions in solution impersonates even item in measurements of a nanometer [36]. Keeping an eye on the procedure is basic yet this strategy is hard to mechanize as the system is structure. A lot of wastewater is also produced.

3.3 Material Characterization

Characterized the synthesized sample by the usage of RIGAKU make XRD with $CuK\alpha 1$ radiation ($\lambda=1.550 \text{ \AA}$) for significant focus of crystal structure. Section arrangement of the prepared samples [36]. XRD statistics used to be accumulated angular range of $11-70^\circ$, a step size of $.021^\circ$. Electrochemical properties are defined in terms of cyclic voltammograms (CVs), galvanostatic charge/discharge(GCD), electrochemical impedance spectroscopy (EIS), rate capability, and cycling stability, gathering coin cells in setup of Li metal(-)/electrolyte/LFP/C(+) with organic electrolyte, utilizing microporous polypropylene film as separator. TGA is a thermal analysis process in which a mass is deliberate time as the temperature increases. This study provides information on physical phenomenon such as phase transitions, absorption, adsorption and desorption, and chemical phenomenon like

chemisorptions, thermal decomposition, and reactions to solid gas. Most of the case of thermal behaviour is same for N₂ as well as air. TGA graph shows weight loss plot at 100°C, 195°C, 280°C, 400°C and 680°C, with an overall weight loss. The response pathways in the development of LiFePO₄ nanoparticles are resolved with the thermal analysis related to X-ray.

3.3.1 X-ray Diffraction:

XRD is an instrumental that is utilized to examine/distinguish tests XRD can give the examination researcher a quick apparatus for routine example ID. X-beam diffraction is a long-run request procedure which is touchy to the intermittent structure of a strong material X-beam diffracting method is significant method that is accustomed to recognizing the clear stage presents inside the example and to compute the auxiliary boundaries (like grain size, stage organization, strain state, deformity structure, and favoured directions). A lattice of crystal is supposed to be made up of systematic layer of planes containing atoms of identical separation afar [37]. As x-ray wavelength is close to the inter-atomic spacing, Laue scientist in 1912 recommended that whichever crystal may acts like grating for x-ray diffraction. Thus if x-ray beam is permitted to drop on a crystal then a immense no. of different intensity images are created. whether the wave which are diffracted are in a similar phase as that of incident then they strengthen each other so that a pattern of bright shiny is formed on the photographic sheet, put down in their way.[1 2 3] When X-ray radiations are moves through material, the radiations interact by electrons of atoms, which results in scattering of light radiations. And when these atoms are arranged in the planes (that is the substance is crystalline in nature) and distance in the middle of these atoms are of equal extent(value) as that wavelength of X-beams used, alternating progressive & reductive interferences may be produced [38] diffracted X-rays were emitted at particular angles, depended on interlayer spacing in the middle of atoms present inside the crystal planes. Each and every atom belongs to numerous pairs of crystal planes. Every pair of plane has a particular inter-planar separation & may gave arise to a specific angle of diffracted X-rays. William Henry Bragg & William Lawrence Bragg in 1913, played out a scientific count to discover entomb nuclear good ways from the X-beam diffraction, the connection is called as Bragg's law [39].

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

Here, λ = Incident x-ray wavelength n = Diffraction order d = Inter-planar distance θ (theta) = Bragg's angle

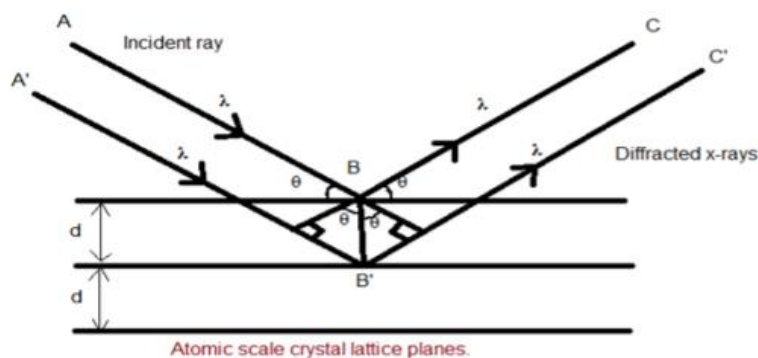


FIG 10: Bragg's law

X-rays diffracted from atoms inside crystalline plane follows the reflection laws.

The 2-rays are reflected from the continuous planes, may be in phase when the additional path covered by 2nd -ray is integral count of wavelengths. When the wavelength illuminated is familiar & the angle could be calculated, there the inter-planar spacing can be easily calculated. A set of inter-planar spacing will be get through an individual compound, representing pair of planes which may go through from atom & it may be utilized for compare with the other pair of inter-planar spacing's get by the general results Condition for the reflection (that is Bragg's condition) can be fulfilled for some arrangement of planes whose between planar dispersing will be more prominent than half of the frequency of X-beams utilized (when $d < \lambda/2$ at that point $\sin \theta > 1$, which is absurd) [1 2 3]. This trial comprises of examining two X-beam films uncovered in a powdered diffraction camera. In the powder X-beam procedure, the x-beam falls on an aggregate mass of little precious stones having direction every which way, and the diffracted bar will frame h,k,l shaping a cone. Bends of these cones are caught by a film which is encircled by the specimen [40]. X-beams pillar goes through a collimator and strikes the example. A film strip which is put along the round and hollow camera divider would be uncovered by dispersed radiations and show, after adequate improvement and time, the diffraction design.. The un-dispersed radiation will leave the camera through the leave port. The Scherrer eqn., it is a equation which related with the dimension of nanoparticles, or crystallites, in a strong to widening of top in diffraction design. scherrer eqn. can be utilized for the assurance of the size of particle of the crystals in the powder structure. It is broadening strip at middle of the maxim intensity, Subsequently removing instrumental broadening strip, measured in radians. It may sometimes have written as $\Delta = (2\theta)$, $\theta =$ Bragg's angle. There are

3 basic parts of X-rays diffractometers: an Ex: - holder , x-beam tube, xbeam indicator . Number of X-rays are shaped in cathode flash tube by heating fiber to liberate number of electrons, these electrons are quickening towards an object with apply adequate measure of voltage, & the target material is bombarded by electrons. At the time where the electron has a sufficient measure of energy to break inner shell of electrons then x-ray range is delivered. This range comprises of different parts, α_1 and α_2 [41]. The α_1 has insignificantly lower frequency yet force is twice as α_2 has. These particular frequencies are relying upon the trademark target material. Normally α_1 and α_2 are adequately near the frequency with the final aim that usual load of the two is employed. Cu is normally utilized objective for individual-valuable stone diffraction with Cu α illumination (light) equivalent to 1.54 angstroms [42]. The X-ray beams is coordinated & collimated on the Ex. At point when the example and locator are pivoted then The power of X-ray beams were recorded when the X-ray episode on the example fulfill the Bragg's condition then productive impedance design happens and a force top shaped.[1 2 3] Detector is utilized to record and to process these X-ray signals and it convert sign to a tally rate that is yield of a gadget like printer or PC screen etc[43].



Fig 11: Bruker's X-ray Diffractometer [Model: D8 ADVANCED]

configuration of X-rays beam diffractometer is with the aim that the example pivots inside the direction towards particular point (collimated) X-ray beams pillar at a pillar of θ , although X-ray beam indication device (detector) is linked with a branch for gathering the diffracted X-rays & thus turns at a point 2θ . The apparatus or device which is utilized for maintaining the edge and used to pivot the example is called as Goniometer.

3.3.2. TGA (thermogravimetric analysis)

TGA is a thermal analysis process in which a sample 's mass is deliberate time as the temperature increases. This analysis provides information on physical phenomena such as phase transitions, absorption, adsorption and desorption, and chemical phenomena such as chemisorptions, thermal decomposition, and reactions to solid gas. A normal thermogravimetric analyzer contains a preciseness equilibrium along with an example pot consisting of a programmable management temperature level inside a heating system. Generally, the temp is actually enhanced at continuous pace (or even the temperature level is actually controlled for a steady mass reduction for sure programs) to create a thermic response. The thermic response might take place in a range of airs consisting of: background air, suction, passive fuel, corroding/ minimizing gasoline, acrid fuels, carburizing gasoline, liquefied water vapors, "self-generated atmosphere".

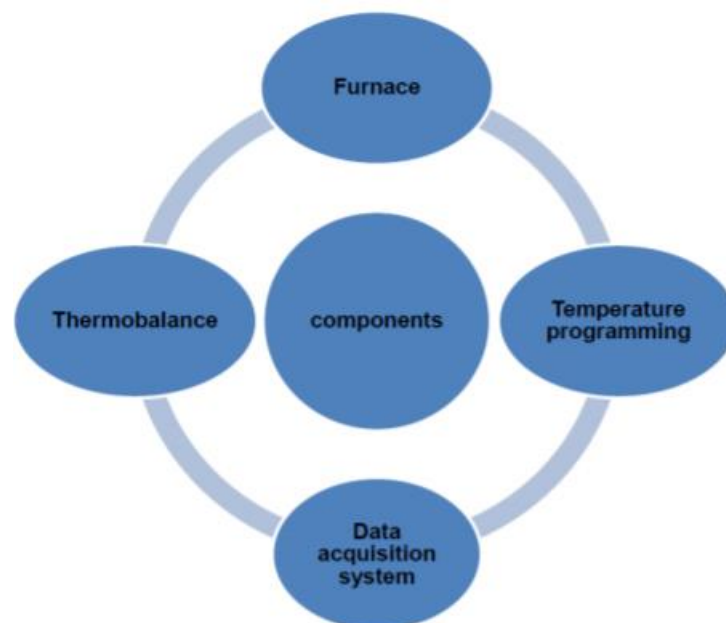


Fig 12: General conformation of Thermal Analysis Apparatus

BASICS OF TGA

Amounts improvements in body weight in connection with improvements in temp.

The measure weight reduction curve offers info on:

- variation in example composition
- thermal stability
- kinetic criteria shows the chemical reactions in the sample.

A derivative weight reduction curve might be made use of to figure out the aspect at which weight-loss is highly appropriate . Mainly two types of TGA analysis shows:-

- Dynamic TGA
- Isothermal TGA

CHAPTER-4

4.1. Characterization and thermal analysis of LiFePO₄

4.1.1 TGA Analysis (thermogravimetric analysis)

The decay of the prepared powder and its auxiliary developments has been concentrated by thermogravimetric and differential thermal analysis. TGA curves of thermal degradation of iron (III) nitrate nonahydrates, lithium hydroxide monohydrates, diammonium phosphate precursor powder are shown in the fig15 and fig16. The significant decomposition of the decay happen between 180°C to 750°C. Most of the case of thermal behaviour is same for N₂ as well as air. TGA graph shows weight loss plot at 100°C, 195°C, 280°C, 400°C and 680°C, with an overall weight loss. The response pathways in the development of LiFePO₄ nanoparticles are resolved with the thermal analysis related to X-ray. Along these lines the calcination temperature required for nanostructured material is lower contrasted with that of mass material. As indicated by the XRD result the crystallization happens after this calcination temperature 650°C. The feeble exothermic top at 650°C with no comparing mass misfortune is required to be the crystallization change in which the indistinct oxide powder becomes nanocrystallites with the arrival of cross section vitality. The huge exothermic pinnacle is probably going to be the consequence of a stage progress to the oxide stage. In this manner, the initial three weight reduction steps can be ascribed to the vanishing of physiosorbed water, interlayer water, structural water, CO₂ and NH₃ from the interlayer. Above 750°C there were no loss of weight which have absorbed in the graphical data. Faster the heating rate, higher decomposition temperature.

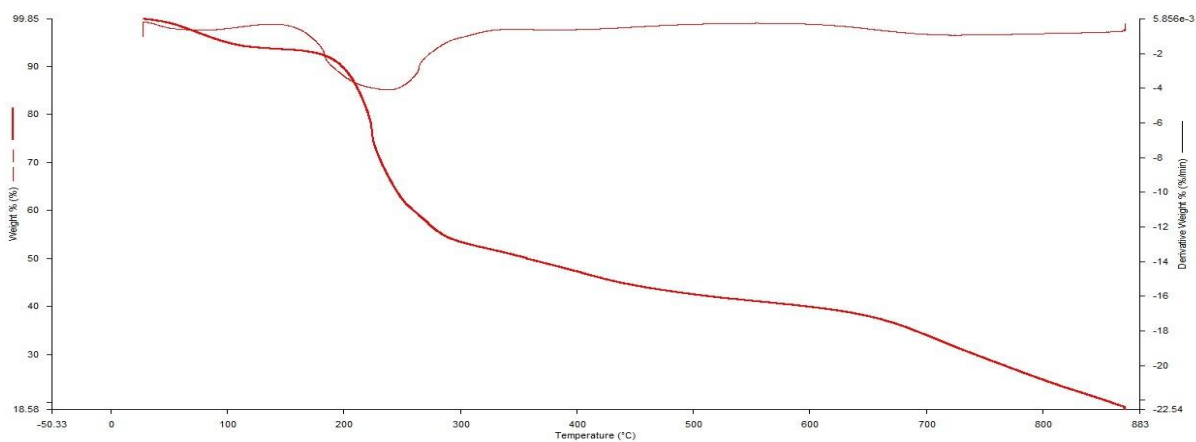


Fig 13: TGA analysis of LFP-AIR

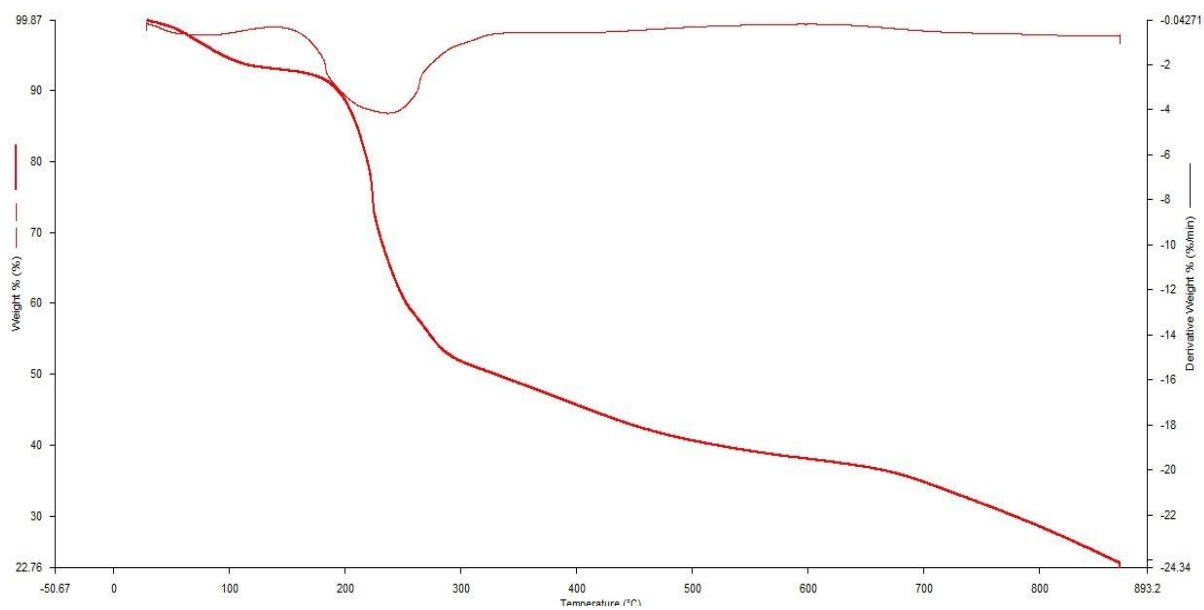


Fig 14: TGA analysis of LFP-N₂

4.1.2 XRD Analysis

Lithium iron phosphate (LiFePO_4) is a olivine type structure i.e. orthorhombic crystal structure with Pnma space group, which consist of hexagonal closed-packed (hcp) of oxygen atom with Li^+ and Fe^{2+} cations located in half of the cell. Fig shows the average XRD graph of LiFePO_4 prepared by the sol-gel method strategy depicted previously. This synthesis was finished utilizing citric acid as chelating agent and procedure include two heat treatment at 350°C for 5hr and 750°C for 12hr in reduced environment (H_2 and N_2). Prior to each toughening, the powder is squashed to protect the best homogeneity. The final product is a contamination free olivine structure with lattice parameter $a=10.2638 \text{ \AA}$, $b=5.9718 \text{ \AA}$, $c=4.6920 \text{ \AA}$ and $V=287.6 \text{ \AA}^3$ which are in acceptable concurrence with the writing esteems [45].

XRD pattern is used to analyse the crystalline size in the range of 20 to 60 degrees. All the XRD diffraction pinnacles can be filed to a olivine structure of LiFePO_4 , which is acceptable concurrence with the writing esteem JCPDS card number 81-1173. The intense peak of LiFePO_4 were observed at 40.28° and 44.97° relative to (410) and (221) with H.C.P structure, which shown the crystalline behaviour.

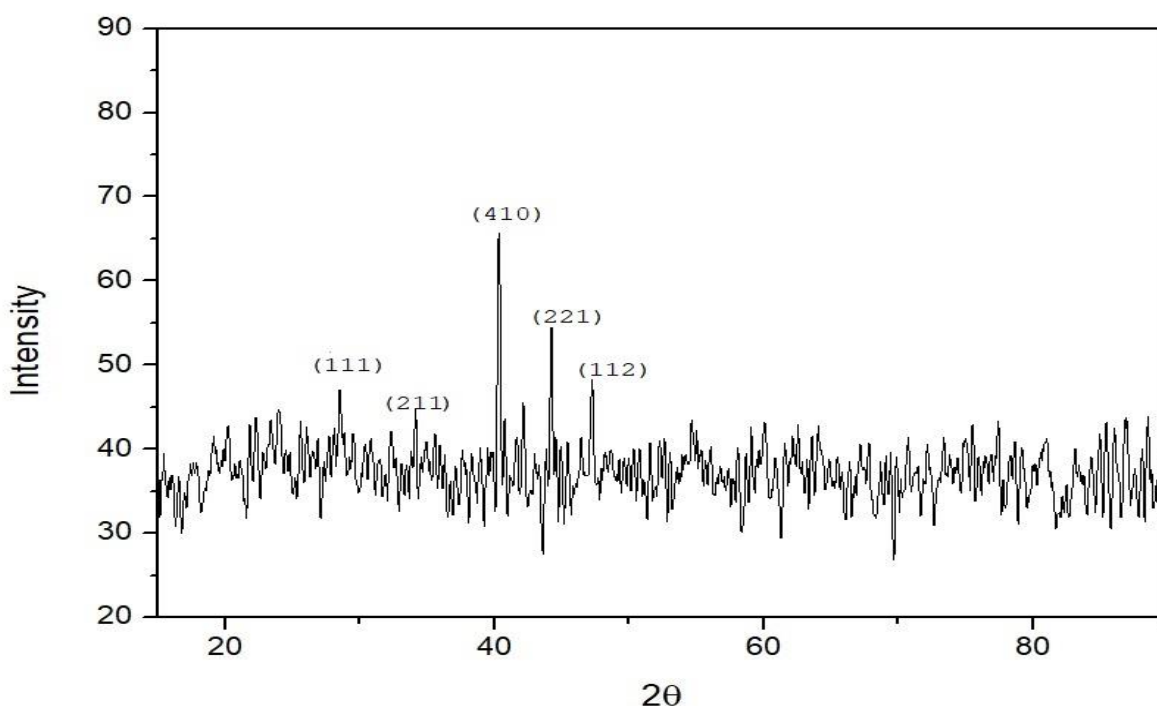


Fig 15: XRD pattern of LiFePO_4 prepared using citric acid assisted sol-gel method

All the structural parameters can be calculated from the xrd peak as shown in above figure 17. The mean size of LiFePO_4 formed was calculated by the FWHM of (410) diffraction reflection adopting Scherrer equation.

$$D = k\lambda/\beta\cos\theta$$

Where, D=particle size, λ =wavelength of x-rays (1.54\AA), θ = Bragg's angle corresponding to a peak, β = full-width half maxima measured (radians), k=Scherrer constant (0.94),and the particle size of LiFePO_4 was found around 0.04nm as observed from the main peak shown in the table 4

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

By using the above formula, the inter-planer spacing between the atomic layers are found to be 0.08 nm shown in Table 4 (as observed from the main peak 1 at $2\theta = 40.28$).

and the lattice parameter 'a' is determined from the equation:

$$a = d\sqrt{h^2 + k^2 + l^2}$$

So for the main peak 1 the value of the lattice parameter comes equal to 3.29\AA , which is given in table 5.

The atomic radius of the HCP structure is calculated from:

$$r = a / 2$$

So the value of atomic radius of HCP structure is calculated from the above relation and it is equal to 0.1645nm given in table5. All the structural parameters can be calculated from the peak represented in figure15. A slight variation in the diffraction peak positions with the concentration represents the strain in the lattice of crystal. The XRD pattern shows to exhibit a orthorhombic structure, all the peaks are slightly match from JCPDS pattern No: 81-1173. the diffraction pattern of prepared material shows the broad peaks centered around $2\theta \sim 40.28$ and 44.97 corresponding to the (410) and (221) planes are summarized table

Table 5: XRD data of LiFePO₄

Sample	Peak No.	2 θ (degree)	θ (degree)	h k l (planes)
LiFePO ₄	1	40.28	20.14	(410)
	2	44.97	22.48	(221)
	3	47.24	23.62	(112)

Table 6: Various parameter of LiFePO₄

Sample	LiFePO ₄
FWHM (radian)	0.21597
D (nm), Crystalline size	0.04
a (Å), lattice parameter	3.29
r (Å), atomic radius	1.645
d (Å), inter-planer spacing	0.80
a ³ (Å ³), Volume	35.611

Overall, from the calculation it has been observed that for LiFePO₄ (prepared by sol-gel method) exhibit many peak but we are taking only one sharp peak for calculation 40.28^o and the miller indices is (410) and the corresponding value of FWHM is 0.21597. From this data, we calculate different parameters like particle size, lattice parameter, atomic radius, inter-planer spacing, etc. and the corresponding value of these are 0.04nm, 3.29Å, 1.645Å and 0.80Å, respectively.

4.2 Conclusion

In this study, synthesis of LiFePO_4 as cathode material has been attempted using sol-gel route of material synthesis. Thermogravimetric analysis of dry gel estimated from sol-gel process was performed to analysis the thermal behavior of material and phase transitions. Thermogravimetric (TGA) was performed in air and inert (N_2) atmosphere up to $900\text{ }^\circ\text{C}$. TGA curve shows the decomposition and calcination temperatures of material are lying between $180\text{ }^\circ\text{C}$ to $750\text{ }^\circ\text{C}$. Which indicates that the weight loss percentage is about 19-26%, and the calcination temperature of material is $750\text{ }^\circ\text{C}$. XRD measurement of synthesized material was also carried out. XRD confirms the proper phase formation of LiFePO_4 . Orthorhombic type crystal structure of LiFePO_4 of intense peaks corresponds to diffraction angle at 40.28° and 44.97° relative to (410) and (221) are observed. Further, the electrochemical analysis of the prepared sample is in progress.

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