Effect of Organic Acids on Selective Lithium Recovery from Spent $LiFePO_4$ Cathode Scraps

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Session 2021-23

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THESIS ACCEPTANCE CERTIFICATE

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Dedication

This thesis is dedicated to my parents who have supported me throughout my life. Thanks for making me see this adventure through to the end.

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I would like to thank **Allah Almighty** for letting me through all the difficulties. I have experienced your guidance day by day. You are the one who let me finish my degree. I will keep on trusting you for my future.

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Abstract

The increasing energy storage demand for electric vehicles and renewable energy technologies, as well as environmental regulations demanding the reutilizing of LIBs. The issue of depleting resources, particularly Li, is a major issue. To lessen the environmental risks brought on by the mining of the metals and spent lithium-ion batteries, efforts should be done in the field of recycling lithium-ion batteries. To regain Li and $FePO_4$ from spent LFP lithium-ion batteries, an organic acid-based leaching approach has been developed in this work. This investigation used organic acids, such as acetic acid and succinic acid, as the leaching agents. In comparison to another organic acid, succinic acid has the highest leaching efficiency and the best leaching effects on the reaction system when used with an oxidizing agent. The leaching conditions were optimized by varying the acid concentration, solid-to-liquid ratio, and the concentration of the oxidizing agent. Under the optimal condition of the 1.5 M succinic acid, 4 vol % H_2O_2, 15 $g{\cdot}L^{-1}$ at 70 ℃ for 40 min Li and Al leaching efficiency is 98.7 % and 95.3 % respectively. However, the loss of Fe and P was only 6.5% and 4.3 %, respectively. The lithium carbonate was recovered using leachate. The suggested organic-based recycling strategy is environmentally benign and produces less secondary trash for the environment.

Keywords: Hydrometallurgy, $LiFePO_4$, Leaching, Organic acids, Recycling, Spent lithium ion batteries

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1. **Maryam Ali**, Naseem Iqbal, Tayyaba Noor "Effect of the Organic Acids on Selective Lithium Recovery from Spent $LiFePO_4$ Cathode Scraps"
   Journal: Separation and Purification Technology, 2023 **(Under Review)**

List of Abbreviations

LIB	Lithium-Ion Batteries
LIBS	Laser Induced Breakdown Spectroscopy
EV	Electric Vehicles
EU	European Union
LCO	$LiCoO_2$
NMC	$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$
LFP	$LiFePO_4$
NCA	$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$
LMO	$LiMn_2O_4$
PLS	Pregnant Leach Solution
DMF	Dimethylformamide
NMP	N-methyl-2-pyrrolidone
UN	United Nations
PVDF	Polyvinylidene Fluoride
EDTA	Ethylenediaminetetraacetic acid
XRD	X-ray Diffraction
FTIR	Fourier Transform Infrared Spectroscopy
CAM	Cathode Active Material

Chapter 1 Introduction

1.1 Background

As the energy usage rises day by day, changing lifestyles and more awareness have reduced the use of fossil fuels, which has increased reliance on renewable energy resources. The sole drawback of renewable energy is the erratic electricity production, which is a lifesaver for the world's mounting environmental issues. To avoid this problem energy must be stored properly to account for variations in the supply of power. Lithium-Ion Batteries are the standard energy storage technology due to their high specific density, high energy density, and high theoretical capacity. Due to its appealing energy storage capabilities, it is used in modern gadgets like mobile phones, laptops, tablets, and electric/hybrid vehicles. The usage of LIB is expanding in industrial and private applications as well due to its stationary storage solutions. [1]

Between 2005 and 2015, the market for lithium-ion batteries had an increase of up to 15%, and in 2015, China manufactured 15.7 GWh of electric vehicle (EV) cells whereas the $LiFePO_4$ occupied 69.9%. The analysis published by Avicenne Energy Worldwide predicts that by 2030, the demand for LIB will have increased from 282 GW/h in 2020 to more than 2600 GW/h. it is predicted that at the end of 2023, 11 million tons of LIB will be dumped globally, and by 2030, the market for recycling LIB is expected to recover up to €555 million in valuable materials. [2, 3]

Numerous electronic gadgets require enormous volumes of LIB, which adds to the LIB waste stream once those devices have reached to their end lives. Because they contain heavy metals that can leach out into the soil after disposal and harm the ground and surface water, spent LIBs are too dangerous for the environment. Every 4000 tons of spent lithium-ion batteries contains more than 200 tons of toxic electrolytes and 1100 tons of heavy metals [3]. To reduce the risk to the environment and human health, certain precautions should be implemented. Spent LIBs must either be processed before disposal or dumped in designated dumpsites to prevent an explosion or environmental harm. However, the capacity of the specialized dumpsites will be constrained, and as the demand for LIB rises, the amount of used LIB will also rise over time and could eventually surpass the capacity of designated dumpsites. According to the statistics, China generated over 500,000 tonnes of wasted LIBs in 2020, totaling about 2.5 billion. [4]. Additionally, this will increase the expense of disposing of the used LIBs. Resource depletion is another issue caused by the increased demand for LIBs. Since lithium is a crucial component of LIBs, greater LIB production has led to increased lithium use, which is depleting the world's lithium resources. Additionally, the demand for LIBs is driving up the price of lithium compounds regularly. For instance, the cost of Li_2CO_3 increased from 4256 $/ton in 2012 to 25,300 $/ton in 2017 [5]. In light of all these factors, LIBs require end-life management.

The recycling of LIBs is the best solution to all of these issues because it has numerous advantages, including a reduction in the risk that discarded LIBs pose risks to the environment and to people's health. , as well as a financial gain from the recovery of metals from discarded LIBs that are of a standard purity and can be used to make new LIBs. Recycling will enable us to recover all the metals, including cobalt, lithium, manganese, nickel, and aluminum, which are essential to manufacturing LIB. Recycling the LIB will lessen resource depletion and the reliance on raw metals for its production, as well as the pollution caused by the extraction of these metals from their ores and the production of waste. It will enable the circular economy; lessen the environmental damage caused by wasted LIB after their end of life.

The LIB's cathode contains the majority of the precious metals. According to the cathode material, the LIB is divided into subcategories called $LiCoO_2$ (LCO), $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NMC), $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA) and $LiFePO_4$ (LFP). LCO was once the most widely used cathode in industry, however, it is no longer preferred due to high cobalt prices and depleted cobalt deposits. NMC, NCA, and LFP are the three most widely used active materials for cathodes. However, the LIB with diverse cathode chemistry and more metals can complicate recycling. Separating more metals is challenging, and saving money will not have a positive economic impact. As a result, it may be more cost-effective to recycle LIB using cathodic active material, which comprises expensive metals or fewer components [6].

Olivine-type $LiFePO_4$ (LFP) batteries, first created in 1996, have gained popularity in a variety of applications, including energy storage devices, electronic devices, and electric vehicles (EVs), thanks to their low cost of raw materials, long lifespan, thermal stability, non-toxicity, low fire risk, and superior electrochemical performance. Due to the inclusion of lithium, graphite, and phosphorus in LFP batteries, they are a source of strategic materials. [6]. Federica Forte evaluated the LIB recycling availability as shown in Figure 1.1.

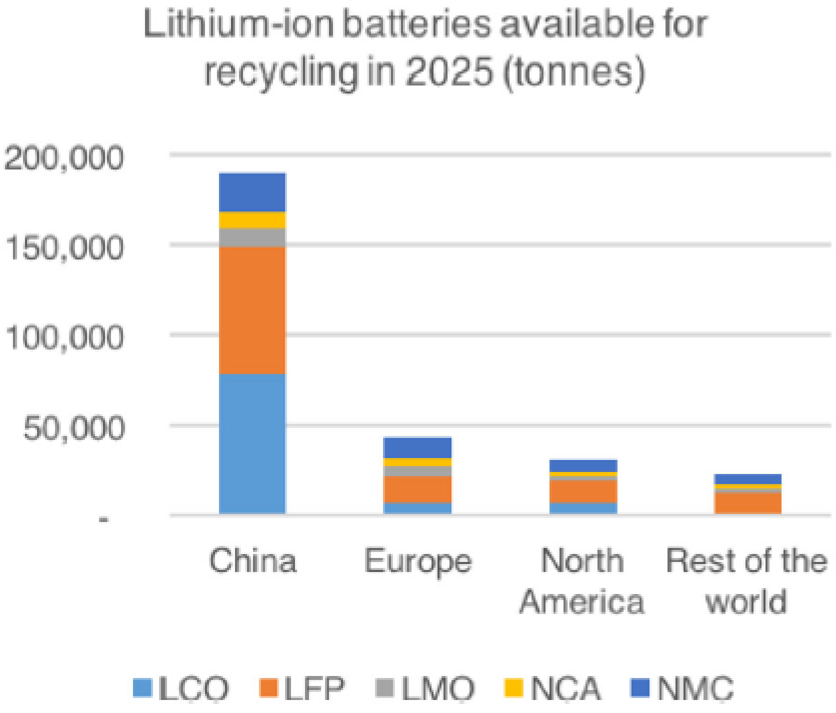

Figure 1.1 LIBs are available for Recycling in 2025 [7].

The most common batteries used in EVs are LFP and NMC. The condition of spent LFP batteries around the world is shown in Figure 1.1. The demand for lithium has surged because of the rising demand for LIB. Because it is a special metal ion with electrochemical activity, low density (0.534 g/cm-3), a high charge-to-weight ratio, the highest redox potential of any solid element, and the largest specific heat capacity, lithium is essential to the LIBs [8]. Due to its special characteristics, lithium accounts for 50% of the cathode metals on a mole basis. The recovery of lithium, the LIB's primary component, and other precious metals must be the focus. Several studies on the end-life management of LIBs have been reported, which are lithium reservoirs. According to studies, recycling and recovering at least 90% of the lithium could stop a future disaster [9]. Therefore, it is crucial that we create a circular economy and ensures sustainable management of natural resources for lithium by assisting the supply of raw materials with recycled lithium reserves like those found in spent LIBs.

Pyrometallurgy and hydrometallurgy are the two main methods used to recycle LIB. Hydrometallurgy is the best method for the selective recovery of metals from spent LIBs, while many recycling plants in various nations use pyrometallurgy. These procedures frequently involve manual dismantling, physical separation, size reduction, leaching, solvent extraction, and precipitation. Precipitation is the process of separating metal in the form of solids (precipitates), whereas solvent extraction is the process of separating metal in the form of layers within the solution [10]. Leaching is the key process in hydrometallurgy, and the most popular leaching agents for recycling LIBs are hydrochloric acid and sulphuric acid. These leaching agents emit poisonous fumes that are risky for the environment and human health. Because of this, recent research has turned to the use of organic acids as leaching agents to lessen the dangerous effects of inorganic acids on the environment and can achieve a similar leaching efficiency to that of the inorganic acids.

Economic issues are currently present, coupled with environmental issues. The secondary waste is growing because of the lengthy series of procedures needed to recycle LIBs, which require a massive quantity of various chemicals. Additionally, the usage of various chemicals leads to high expenses that are financially viable. Research is required to ascertain whether organic acids may take the place of inorganic acids and to build a recycling method that is safe for the environment, practical from an economic standpoint, and does not generate any secondary waste.

1.2 Problem Statement

Pyrometallurgy is an energy-intensive process that requires a temperature of up to 1450℃. This LIB recycling process is limited to the recovery of transition metals. The pyrometallurgy requires sophisticated calcination equipment. The lightest metals such as lithium and aluminum are lost to the slag phase and cannot be recovered easily in this process. This process is not very efficient for the selective recovery of lithium, which is the key element of LIBs. In addition, this process generates a lot of secondary waste and releases toxic gases into the environment.

Due to lower operating temperatures, the hydrometallurgical process uses less energy, but it also uses more chemicals, which raises the cost. This method maximizes transition metal recovery while lithium selective recovery is given top priority. Hydrochloric acid and sulfuric acid are the leaching agents used in leaching, which is the key phase in hydrometallurgy. By using inorganic leaching agents, poisonous gases are released into the air, endangering both human health and the environment.

Research is currently being done to determine whether organic acids, which are safe for the environment and human health, can be used as leaching agents to recover valuable metals. However, the organic pregnant leach solutions are likely to complicate the recovery of the precious metals but the separation and recovery of metal from organic acid solutions needs more study.

1.3 Objectives and Aim

This project examined the recovery and separation of the metals leached from the cathode active powder extracted from the spent LFP LIBs into the solution of organic acids i.e. acetic acid and succinic acid. The project's primary aim is to separate the key metal lithium from spent LFP LIBs for battery remanufacturing, with the secondary aim of separating the precious metal by generating less secondary waste using an environmentally friendly procedure.

The research goals were to:

1. Confirm the effectiveness of the organic acids as a leaching agent to recover the key metal lithium from spent LFP LIBs.
2. Select the organic acid, from the current literature, which is capable of extracting the lithium from spent LFP LIBs.
3. Determine which organic acids have the highest leaching efficiency when it comes to selectively extracting lithium from spent LFP LIBs.
4. Optimize the leaching efficiency of the recycling process for recovery of the lithium by generating the least amount of secondary waste to the environment.
5. Compare the effectiveness of the leaching process and suggest a more effective organic leaching agent for hydrometallurgical processing.

6. Create a strategy for the selective recovery of lithium from LFP LIBs that is ecologically benign.

1.4 Research Approach

As shown in Fig. 1.2, this project's experimental work was divided into five phases. The cathode active material was chipped off the cathode after the LFP LIBs had been manually disassembled. The spent LFP cathode active material was analyzed to ascertain its composition before being transformed into cathode active powder, which was subsequently leached into the organic acids acetic acid and succinic acid.

The fourth stage involved screening several leachate samples from various organic acids' leachate to ascertain the amount of recovered metal. The experiments' results, which revealed the most promising organic leaching agent, were optimized to guarantee the highest metal recovery. The separation of the metal into solid form was a part of the last stage.

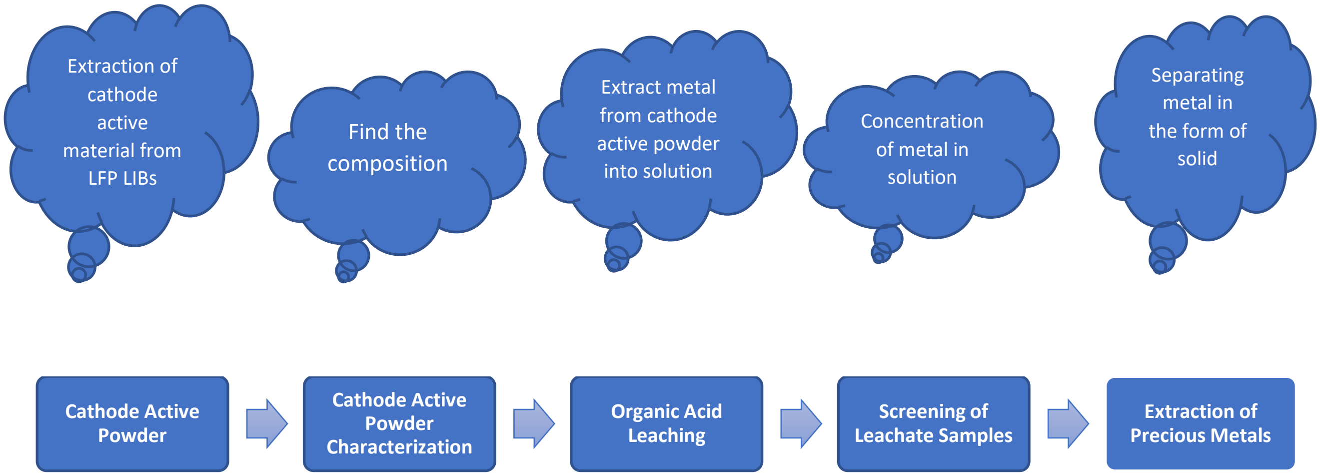

Figure 1.2 Summary of Research Approach

1.5 Unique Research Contributions

This study's unique contributions are:

1. Identification of the best organic leaching agent to extract valuable metal from cathode active powder of LFP LIBs.
2. Analysis of the leaching effectiveness and effects of various organic acids on acid leaching.

3. Demonstration of feasible organic acids as leaching agents as opposed to the strong mineral acids commonly used for the recovery of valuable metals.
4. Synthesis of a process for selective recovery of lithium from succinic acid to enable environmentally friendly recycling of lithium-ion batteries.
5. Demonstration of the lithium recovery process, which produces the least secondary waste to the environment.

Summary

This chapter addresses the background, lithium-ion battery demand, market share, resource depletion, and solutions to all the issues that have arisen because of the escalating demand for lithium-ion batteries. The goals and approach of this research, as well as its distinctive contributions, are further covered in Chapter 1.

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Chapter 2 Literature Review

2.1 Background

Rechargeable battery requirements with lower weight, reduced size, and higher capacity has increased along with the prevalence of electronic and portable gadgets including laptops, watches, cameras, portable appliances, smartphones, tablets, etc. There are numerous conventional rechargeable batteries on the market, including aqueous electrolyte-based lead-acid, nickel-cadmium, and nickel-metal hydride batteries. The energy density and ability to minimize battery size and weight were constrained by the aqueous electrolyte. Lithium-ion batteries are therefore the greatest option for meeting the demand for compact, lightweight rechargeable batteries.

Lithium-ion battery development was started in the beginning of the 1980s; it was commercialized in 1991. The introduction of various kinds of electric vehicles contributed to an escalation in the demand for lithium-ion batteries, as the LIB market has continued to expand because of its special characteristics [1]. The issue over LIB waste has increased due to the LIB market's rapid expansion. According to the statistic, China generated over 2020 will see 2.5 billion LIBs consumed, with a mass of roughly 500,000 tonnes. [2]. Studies have also looked into the possibility of LIBs in current EVs taking the place of conventional batteries like nickel-metal hydride batteries. As a result, there will be less demand for the rare components necessary to make nickel metal hydride batteries. However, the demand for the elements utilized in LIBs, such as lithium, nickel, magnesium, iron, and phosphorus, will rise shortly [3]. This could lead to an increase in price of these elements as well as the depletion of resources.

As mentioned in the previous section, recycling LIBs is essential. and the recycling is mainly focused on LCO LIBs due to the high cost of cobalt and its lucrative properties. The modern LIBs changed their chemistry to materials with less carbon content like NCA, NMC, and LFP. Due to the limited availability of cobalt, lithium-ion batteries (LIBs) will need to adapt to other metals like lithium, manganese, and nickel. Resource depletion is now seriously threatened by the rising demand for lithium [4].

For the production of LIBs, lithium is shipped throughout the world from Chile, Australia, and Argentina. Lithium is mined from ores in these nations. Statistics [1] show that 90 percent of lithium-ion batteries must be reprocessed to satisfy rising lithium demand [5]. Because smart devices and electric vehicles are widely used throughout the world. A lithium-ion battery also serves as the brain of these gadgets. A cathode, anode, and electrolyte make up the bulk of a lithium-ion battery, and the cathode material in LIBs consumes roughly 68 percent of the battery's total lithium content. LCO used to be the most used LIB in commercial applications, but it no longer is because of the exorbitant cost and dearth of cobalt resources. The majority of devices employ NMC; however, because of its low-value metal content and the inclusion of several components that make it difficult to separate the various metals, it is not appropriate for recycling. The LFP is utilized in EVs because of its low density and distinct electrochemical characteristics [6].

Lithium and cobalt are key components needed to make lithium-ion batteries, but these metals' supplies are running out quickly. As a result, there is a significant demand for lithium-ion battery recycling to protect the environment from the hazardous effects of lithium-ion batteries' end-of-life and to prevent resource depletion. A circular economy can be facilitated by recycling LIBs.

2.2 LIB Chemistry and Working

LIBs are generally made up of a cathode, anode, current collectors, a separator, a liquid electrolyte, a container, and sealing parts. Graphite, a conductor, a binder made of polyvinylidene fluoride (PVDF), and the electrolyte typically cover the anode. Similarly, the PVDF binder with fluoride salt is added to aluminum foil that has been covered with cathode materials, a conductor, and the $LiFePO_4$ cathode. Between the electrodes, a separator made of polypropylene (PP) or polyethylene is placed that serves to avoid any short circuits between the cathode and anode (PE) [6].

To ensure that the powder sticks to the aluminum foil, the cathodic material is combined with a polyvinylidene fluoride (PVDF) binder or a poly tetra-fluoro-ethylene (PTFE) binder. The battery is subsequently filled with multi-layer electrode coils. Lithium hexafluorophosphate $LiPF_6$ is often used as the electrolyte, and it is normally dissolved in an organic solvent such as ethylene carbonate (EC), diethyl-carbonate (DEC), dimethyl carbonate (DMC), or a combination of these. The LIB's structure is displayed in Figure 2.1.

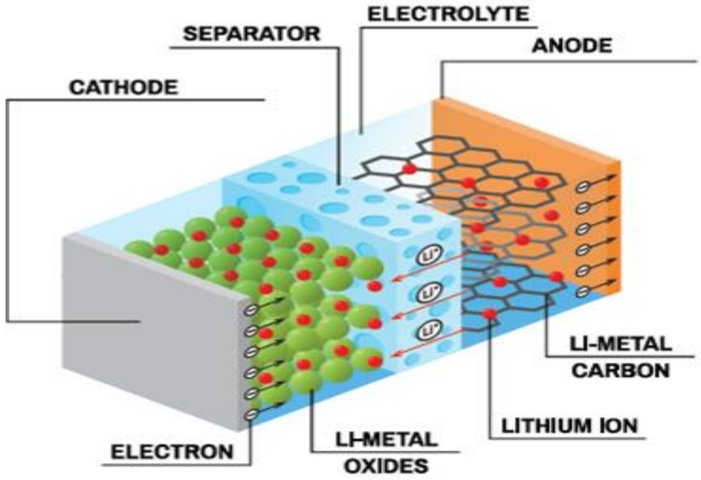

Figure 2.1 Structure of Li-Ion cell [7]

When the LIB is completely discharged, the cathode is the only place where all the Li atoms are present. Because during the discharging of the LIB, the Li-ion migrates from the anode to the cathode and is intercalated into the empty spaces in the voids of the cathode. Additionally, during the charging period, Li ions travel backward. The microporous separator serves as a membrane of around 20 to 30μm thick. Under high temperatures, the micro pores melt and close, disabling all battery functions [6]. The charging and discharging process is clarified in Figure 2.2.

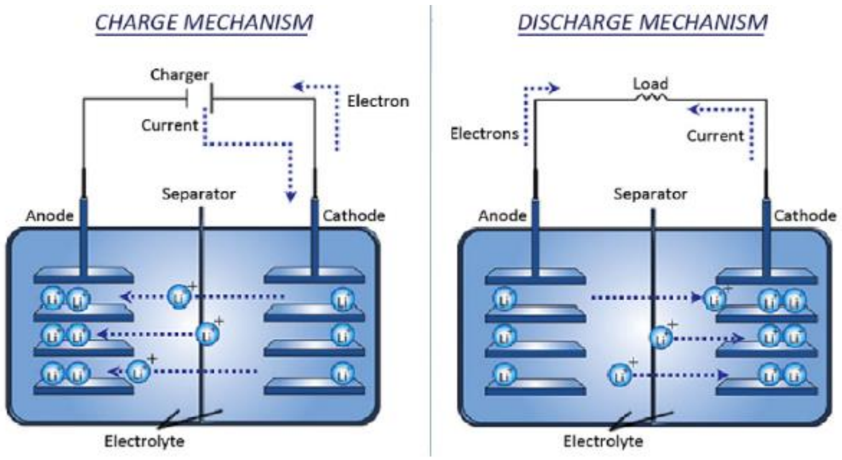

Figure 2.2 Charging and Discharging Mechanism of LIB [8]

Table 2.1 provides a summary of the LFP LIB's average composition, and Figure 2.3 displays it.

Material	**Weight%**
Cathode active material	25%
Anode Cu foil	10%
Anode active material	13%
Electrolyte	16%
Housing	27%
Separator	3%
Cathode Al foil	6%

Table 2.1 Weight% composition of LFP LIB [9]

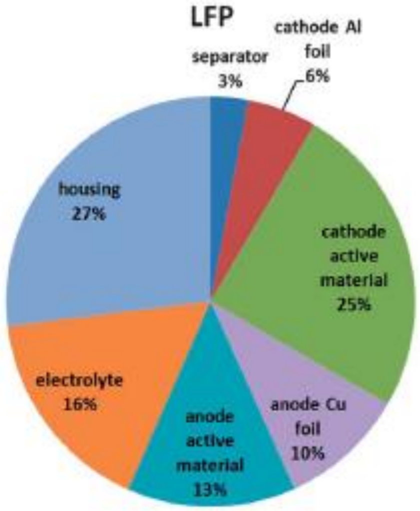

Figure 2.3 Composition of LFP LIB [9]

2.3 LIB Recycling

Recycling LIB is crucial because the growing amount of waste LIB could harm the environment. Dead lithium-ion batteries are discarded on the ground, which can cause the soil and groundwater to become contaminated with metals from the ground. The largest benefit of recycling is the decrease of organic, inorganic, and reactive components, which helps to lessen the impact of LIBs during their entire life cycle [10]. A large number of

LIBs are employed in stationary energy storage systems in homes, businesses, even electrical grids , which are crucial for the development of renewable energy. The rise in end-life management has dramatically decreased the cost of second-life LIBs thanks to the reuse of LIBs in stationary energy storage systems [11].

Recycling has the advantage of reducing CO_2 emissions, which are produced during the mining of raw materials, in addition to toxic waste. Since the European Union (EU) collects 85 percent of its LIBs, it has been determined that more than 218 000 tonnes of CO_2 can be reduced through LIB recycling by the year 2030 [12]. Toxic metals, PVDF binder, and other compounds present in the LIB make it difficult to separate and extract the metals. However, mining the new metals is more expensive than obtaining lithium, copper, cobalt, nickel, and iron. Low-cost components have been included in LIB chemistries, resulting in lower grades of cobalt and nickel.

It has been predicted that the rapid increase in demand for LIB may increase future requirements for lithium. This will increase the price of lithium and can cause resource depletion. Due to the specific geographic region, lithium and cobalt are considered scarce. The instability of resources is sometimes due to the conflict in the nations that control these little reserves, which supply the globe with a significant amount of lithium and cobalt.

The aim of recycling LIBs is not only the recovery of valuable metals but also the improvement of their cost-effectiveness if it is implemented. Economic feasibility is one of the important reasons why very few LIBs are recycled. Profitable recycling can create many job opportunities for different operations like the collection, dismantling, and recycling of LIBs. However, the processing cost needs to cover the labor costs, transport, discharging, smelting, and purification. The profitable process will lead to the successful recycling of LIBs.

There are two approaches to reducing resource depletion. Increased mining activity is the first way to meet raw material demand; however, this will ultimately deplete the available metal resources. The another option is to meet the need for raw materials by recovering valuable metals required for the production of LIBs while recycling the majority of spent LIBs. Recycling LIBs will not only meet the demand for precious metals but also help to prevent resource depletion and the environmental concern that toxic waste poses.

Lithium demand is rising quickly, while nickel, copper, and aluminum recycling demand have increased relative to other metals because their recycling fractions only have a small impact on the total mass mined [13]. In contrast, cobalt recycling mass is 10% greater than the total mass mined. Now, though, attention is being paid to cobalt-free cathodes such as NCA, LFP, and NMC rather than cobalt electrodes.

Since lithium is a crucial metal for transferring across electrodes, it is an vital component of lithium-ion batteries. It is a better substitute for sodium because of its high charge-to-weight ratio, high specific heat capacity, and maximum redox potential. The European Commission recently added lithium to the list of essential elements [14]. The recycling of lithium from spent lithium-ion batteries is necessary due to the demand for lithium and its importance. Due to the substantial lithium content in used LIBs, the fact that less than 1% of lithium is currently reprocessed raises serious concerns.

The development of electrodes and the use of less expensive metals make it unprofitable to recycle lithium-ion batteries. The price of recycling batteries will have to be incorporated into the battery pricing. This should be due to the LIB recycling laws and regulations of countries that have become strict as the LIBs wastage is increasing and pose a serious environmental threat due to its toxic component [15].

There should be no difficulty in collecting spent LIBs. The proper collection system must make it possible to collect the used LIBs so that recycling businesses can access them more easily. This is made possible by various collection points at various battery disposal or retail locations, such as electronic shops or dealerships. Storage of the spent LIBs must be secure and free from any hazards to the environment or public health. To process spent batteries for secondary use, they must first be inspected.

The advancement and creation of future LIB technologies may change the standardization and design of recycling. The sorting of the various LIBs would be simple and would allow the recycling firms to handle them appropriately if the batteries were identified with their restrictions and the cathode chemistry on each cell. Additionally, since the system will be created and tuned for cathode chemistry, recycling processes will be more under control and work better.

An important consideration is whether the active cathode material is appropriate for recycling or not is a factor when deciding whether to recycle it directly. The material of the spent LIBs after stationary storage could be recycled or not. The recovered metals may be able to meet the requirements of the LIBs due to the ongoing development and innovation in the spent LIBs. Another issue that was brought up was whether the batteries' cycle performance would be able to meet expectations after being remanufactured [16]. To create an effective system, it is essential to standardize the recycling operations at every stage, including identification, sorting, labeling, marking, and production.

2.4 Metal Extraction from Spent LIBs

There are different techniques used for recycling LIBs. The reprocessing of the LIBs requires the blend of the different steps due to the diversity of chemicals and materials used for the manufacturing of the LIBs. The main processes used for recycling LIBs are pyrometallurgy and hydrometallurgy. LIBs are dismantled through mechanical processing to separate the different components of LIBs like cathode, anode, separator, and casing. The separation of the different components helps to achieve accuracy and purity for the abstraction of valuable metals from spent LIBs.

2.4.1 Mechanical Processing

The disassembly procedure used to separate the various parts of the spent LIBs is known as mechanical processing. Mechanical processing is utilized to produce the active cathode powder used in the recycling of LIBs. To separate the various parts that make up LIBs, the used LIBs are chopped, shredded, and crushed into little pieces. It is not safe to open the LIBs until they have not been completely discharged or deactivated. Make sure the expended LIBs are fully discharged before disassembling them; otherwise, they may explode violently and risk short-circuiting or fire. They contain poisonous and combustible electrolytes, thus the crushing and separation must be done in an inert environment.

After the batteries are cut open, crushed, or shredded the components are separated because of the physical properties like density, weight, magnetic properties, or chemical composition The LIBs are crushed using machinery that has blade crushers installed to do so at a particular rate and duration. By dry sieving, the crushed bits are divided into various categories. Al, Cu, and the big plastic particles are separated. Using floatation, the layer of hydrocarbon, cathode material, and graphite could be separated [10]. Zhang et. al. 2014 investigated the separation of the crushed particles of the spent LIBs where selective crushing was performed between the cobalt, copper, and aluminum [17]. The second way of dismantling the spent LIBs is cutting the casing of the LIBs and then removing all accessories and uncurling the cathode, anode, and separator manually.

2.4.2 Pyrometallurgical Processing

The recycling of LIBs uses Pyrometallurgical processing, which employs heat treatment to induce the material's physical and chemical changes that then permit the retrieval of the valuable metals. High temperatures are needed for this process, which burns polymers, electrolyte solvents, cathode, anode, and graphite, producing hazardous fumes as a result [10]. This procedure makes it simple to recover metals like cobalt, copper, and nickel, but it is ineffective for recovering the lightest metals like aluminum and lithium. The lightest metal's phase shifts because of the high temperature, turning it into slag [18]. The lightest metal will therefore be recovered in the form of slag through this procedure and could be included as a concrete additive [16]. This technique has a significant disadvantage because lithium is a crucial component of LIBs and was added to the list of important components by the European Union [14].

Pyrometallurgical operations require a lot of heat and complex heating apparatus, such as ovens and special heat furnaces, which may achieve temperatures of up to 1450°C. To avoid the emission of harmful halogen chemicals, Fluorides that are usually boiled at high temperatures, this procedure may need a gas cleaning system [19]. Because recycling at high temperatures is more expensive, it requires many batteries for recycling to be cost-effective [16].

The smelter is used to melt the raw materials, which are then compelled to matte or transform into slag. In this procedure, the organics and polymers that produce toxic gases in the smelter are burned off in oxygen-free furnaces. These gases include lithium salts dissolved in the organic solvents, polymers from the separator, and organic solvents utilized in the electrolyte. A calcination step has been used in numerous investigations to get rid of the carbon and PTFE or PVDF binders in a muffle furnace before hydrometallurgical metal extraction of the active cathode material [18].

2.4.3 Hydrometallurgical Processes

The most popular process for extracting lithium is the hydrometallurgical process. Lithium is ionized using acids and bases. The substance must be dissolved because this process is carried out in an aqueous environment. Through this method, metals are transferred from the solid phase to the liquid phase. The contaminants in the solution can be removed and the metals concentrated using a variety of reagents. Metals could be separated via precipitation or solvent extraction after being extracted from the solid into the aqueous phase. The best method for effectively purifying metals is solvent extraction. This approach is more practical for the laboratory because it does not require any extra tools. At various pH of the leaching solution, metals including nickel, manganese, and cobalt are removed. The final product may be a pure lithium solution if all the metals have been removed from the solution. Lithium must be precipitated from its solid state using the precipitating agent, Na_2CO_3 to produce Li_2CO_3 in the end. However, solvent extraction may need a significant amount of acid for leaching, which may increase the cost. The precipitate is also necessary to remove the metals in solid form [10].

The most common method for separating metals is precipitation; however, This procedure utilizes the different solubility of the metals, which are more sensitive to temperature and pH. Precipitation is an opportunity for substances with limited solubility, including transition metals, hydroxides, and oxalate. This approach is the most straightforward and is most researched, but to achieve the perfect material profile, it requires precise operating conditions including pH, Li concentration, and temperature [10]. The majority of hydrometallurgical processes use an initial mechanical step, such as grinding or shredding, to provide sample sizes that improve the dissolution process. Several recycling plants use the hydrometallurgical process because it is efficient at recovering light metal and requires little energy. One such general stage is pre-treatment is pre-treatment, leaching, solvent extraction, and precipitation, various recycling factories use it. Due to the cathode active powder's high solubility in the acidic solution, the hydrometallurgical process is significantly more efficient than the Pyrometallurgical process.

The crucial factor to keep in mind is that the chemicals used for the hydrometallurgical process could be toxic or dangerous, endangering both the health of people and the environment. To lessen the threat to human health and welfare, the liquid waste created during this procedure needs to be treated properly. The comparison of the benefits and drawbacks of these metal extraction strategies outlined in section 2.4 is shown in Table 2.2.

Extraction Techniques	**Disadvantages**	**Advantages**
Mechanical Process	• High risk of explosions • High energy requirement • Time-consuming • Uniform feed composition	• Simple operation • Accuracy in dismantling • Constant material composition
Pyrometallurgical Process	• High energy requirement • Lithium to slag • Toxic emissions	• Simple operation • Economical • Large fee volumes
Hydrometallurgical Process	• Secondary waste • Complex operations • Expensive chemicals	• Low energy requirement • Minimum toxic emissions • Highly efficient • Purity of product stream

Table 2.2 Comparison of Metal Extraction Techniques

The LIB active cathode material is recycled in this work using a hydrometallurgical method. Because this procedure is what makes recycling profitable and because it is the most effective way to recover the most important and lightest metals from spent cathode active material. The cathode active material was first properly separated from the cathode via mechanical treatment. This procedure aids in separating the cathode, anode, and separator from the LIBs. This method provides active cathode material, which is then utilized as feedstock for the hydrometallurgical process to recover valuable metals from the wasted cathode active material.

2.5 LIB Pre-Treatment

The cathode, anode, and separators are manually separated during battery disassembly, as was previously covered. The individual LIB cells are cut and shredded, and the bits of various components are then sorted according to their weight, density, physical characteristics, and chemical composition. If the LIB cells are not properly discharged before being dismantled, the manual disassembly process could result in an explosion. Liquid nitrogen should be used to discharge LIB batteries and cool them before opening, according to Dorella and Mansur (2007) [20]. When the LIB is discharged appropriately, the flammable hazard is reduced. To neutralize the cell, LIBs are commonly discharged in a salt solution; this releases oxygen gas, which needs to be adequately vented to prevent any risks.

Musariri 2019 concluded that liquid nitrogen steps are unnecessary if the battery is properly discharged below 0.5V [21]. To ensure the batteries are discharged to below 0.5V, the LIBs are typically discharged in a 5-weight percent NaCl solution for 48 hours, dried, and then measured for voltage using a multimeter [17]. The components like the cathode, anode, and separator can be separated by hand, and batteries below 0.5V are inactive and can be cut with a handsaw. However, since discharged batteries might release some harmful fumes from the electrolyte, it is preferable to carry out the disassembly procedure in a space that is adequately aired.

By carrying out the NaOH leaching, the cathode active material can be separated from the aluminum foil [21]. When treated with a 10-weight percent NaOH solution at a concentration of 100 g/L for two hours [18]. The NaOH dissolves the aluminum foil and causes the cathode scraps to sink to the bottom of the beaker. Lithium can be lost from the cathode if it is exposed to a solution of NaOH that contains more than 10% by weight.

2.6 Leaching

The removal of metal from a solid into an aqueous solution is known as leaching. Leaching is frequently used to remove the valuable metals from the ores—metals that are found in minute amounts in massive volumes of material—that are present in the ore. To extract the metals, a leaching agent is employed. It helps to penetrate the material's pores and cracks that are difficult to access and dissolves the precious metals in an aqueous solution.

Leaching can size-reduce the cathode active material, which will enhance the dissolution process. The procedure is more effective since the leaching agent aids in shrinking the size of the active powder, which increases surface area. The principal method of recycling spent lithium-ion batteries, this one is also the most expensive. To avoid incurring needless costs, this procedure should be used appropriately if necessary. The undesirable solids won't be impacted by the leaching agent and will continue to exist as solids unreacted. The necessary metal will dissolve in the aqueous solution, and the undesirable solid can be filtered out. Additional treatment might be applied to the pregnant liquid solution (PLS) to produce the desired result. Thermodynamic phase diagrams can create the leaching conditions for a particular metal.

The fundamental issue with the leaching procedure is that it necessitates the use of abrasive leaching agents to extract the metals from the ore. Inorganic acids and cyanide are both employed to extract precious metals. In earlier investigations, precious metals were recovered using hydrochloric and sulfuric acids [10].

Table 5.1 provides a summary of the literature review on the recycling of spent LIBs. The literature review made it evident that a lot of work had been done on the LCO cathode material using inorganic acids such as sulphuric acid, hydrochloric acid, etc., along with some experiments on NMC and LMO. Furthermore, little in the way of thorough research has been done on LFP cathode material. Inorganic acids like sulfuric acid and hydrochloric acid are frequently employed as leaching agents to recover the metals from the ore. These leaching agents are effective at removing metals from ores, but they also discharge hazardous gases into the environment, such as Cl_2 and SO_3. The release of poisonous gases harms the environment, and if they are not handled or stored correctly, they can represent a serious threat to the people around them.

Because it produces toxic gases like Cl_2 when it performs leaching, hydrochloric acid is toxic to the environment; therefore, organic acids and sulphuric acid are preferred because they produce fewer toxic gases. Equipment that is resistant to corrosion is necessary for the generation of Cl_2 gas, which adds additional expenses to the budget. However, recent literature has examined the potential of organic acids for acid leaching. Although sulphuric acid is preferred due to its economic viability, the emission of SO_3 gases is still a serious threat to the environment. According to the literature shown in Table 5.1, leaching environmentally beneficial agents include succinic acid, citric acid, tartaric acid, etc. Although organic acids are less powerful than inorganic acids, they are more cost-effective and pose less of a threat to the environment, which has increased the motivation to use them as leaching agents.

2.7 Solvent Extraction

The two immiscible liquid phases of metals are separated using the solvent extraction method. The organic extractant and the metal species undergo a chemical reaction. The loaded organic phase can then be retrieved after allowing the separation of the aqueous and organic phases. The necessary metals loaded in the loaded organic phase are subsequently stripped out of it into another aqueous phase, which regenerates the organic phase and enables its recovery.

To increase the physical qualities of the extractant, such as density and viscosity, an inexpensive organic solvent known as the diluent is used. The requirement that the diluent be insoluble in the organic solvent is the most crucial one. The diluent is inert and unable to extract metals; instead, it only affects how the extractant and the diluent interact for the metal extraction to occur.

Any solid particles in the aqueous solution must be removed before performing solvent extraction since they could prevent phase separation. Because it can be implemented with continuous operation, the use of solvent extraction in industrial settings is extremely desirable. because it enables processes with large capacities. A large variety of metals can be purified and enhanced via solvent extraction. Due to its ecologically favorable behavior and excellent recovery rate the solvent extraction technology has come into greater prominence due to the increased demand for pure metals. The use of solvent extraction has become widespread in commercial plants since it is suitable for industrial-scale applications and does not require lengthy precipitation stages [10].

2.8 Precipitation

The recovery of the metals in solid form from the solution depends critically on precipitation. Metals must be recovered in their solid form if they are sold to a customer for remanufacturing because manufacturers utilize solid metals. The most popular technique for concentrating the metal content, removing impurities from solutions, and recovering the metals from solution is precipitation.

The precipitation process consists of two stages: crystal growth and nucleation [22]. The precipitation agent and solvent molecules interact during nucleation to create the new substance. Using a higher concentrated solution will increase agitation speed, which will enhance nucleation growth [23]. Due to the following reasons, fast precipitation creates fine particles while slow precipitation creates huge particles.

Fast precipitation produces amorphous crystals that are challenging to separate using the filtration process because the precipitates are created incorrectly. The solution can be heated to speed up the aging process even more [23]. With an aging process that allows the precipitate to remain in contact with the solution, repeatedly leave it, and redeposit back into it, the process of separating the solution from the precipitate can be improved [22] to reduce co-precipitation, it is preferable to add only one precipitating agent per component in the solution. When many compounds are insoluble at the temperature and pH of the precipitation conditions, co-precipitation results. The unwanted material's precipitation can be reduced by choosing just one precipitating agent. The occlusion may be brought on by co-precipitation. The contaminants are trapped in the layer of crystals around it via occlusion [23].

The majority of metal hydroxides precipitate as the pH of the solution rises, hence raising the pH causes precipitation. This enables the various metals to precipitate at various pH levels. Because lithium hydroxide does not exist and requires a large amount of precipitating agent and an extremely high pH, it precipitates out as lithium carbonate.

2.9 Research Gap

Currently, the techniques that are widely commercialized or researched are also environmentally harmful due to use of inorganic acids. Lithium recycling technology should not only mitigate lithium scarcity but also reduce waste to prevent environmental pollution. The use of inorganic acids and organic solvents produces harmful gases and many pollutants which also leads to additional expenses. This work is focused on an organic acid based recycling technique for $LiFePO_4$ lithium-ion batteries to recover mainly the lithium.

Summary

This chapter discusses a quick overview of lithium-ion batteries, their chemistry, and how they operate. Additionally, what are the reasons for reprocessing lithium-ion batteries and the methods that are used, such as mechanical processing, Pyrometallurgical processing, and hydrometallurgical processing? A detailed analysis of the methods utilized for extracting metals, including pros and cons. The research gap after conducting a healthy literature review that the use of inorganic acids for the recovery of the lithium is hazardous for environment as it releases toxic gases in environment.

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Chapter 3 Review of Characterization Techniques

3.1 X-ray Diffraction (XRD)

This is one of the most crucial and popular methods for characterizing materials since it tells you about the shape, constituents, and crystallite size of the substance. It employs X-ray radiations that strike the substance at an angle from the source and pass through it. The intensity is measured and the diffraction angle is computed. The number of radiations that a material deflects from a particular plane at an angle reveals details about the structure and morphology of the material.

The double particle/wave character of X-rays is used to gather information on the configuration of crystalline materials during X-ray diffraction (XRD). The main applications of the technique are material identification and characterization based on their X-ray form. The first thing that happens when a monochromatic X-ray incident beam interacts with an object material is that the target substance's atoms scatter the incident X-rays, as depicted in Figure 3.1. Diffraction is the term for the destructive and constructive interference that the dispersed X-rays cause in solids with correct structure (i.e., crystalline). Bragg's Law describes how crystals deflect X-rays.

The directions of expected diffractions are determined by the size and form of the material unit cell. The diffracted wave intensities depend on how the atoms are arranged in the crystal structure. Many substances are made up of numerous, tiny crystallites arranged in all conceivable directions; this type of material is known as polycrystalline powder or aggregate. The X-ray beam will examine all accessible interatomic planes when it is directed at a material with randomly focused crystallites. All the material's diffraction peaks will be detected if the experimental angle is scientifically changed [1].

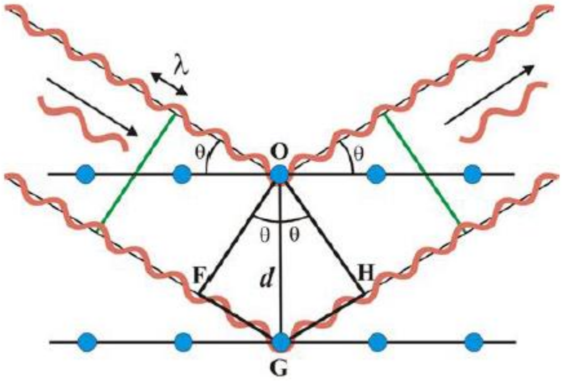

Figure 3.1 Crystallography, Scattering and Diffraction. The Bragg’s Law [2]

3.2 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier-transform infrared spectroscopy (FTIR) can be used to precisely identify the chemical bonds that are present in the particle that has been removed from water. The analysis is accessible for the transmission, reflectance, and attenuated total reflectance (ATR) modes. For micro plastics with erratic spectra, the ATR mode offers stable spectra. [3].

FTIR offers quantitative and qualitative studies for samples that are both organic and inorganic. Fourier Transform Infrared Spectroscopy (FTIR) may determine the chemical bonds of a molecule by generating an infrared absorption spectrum. The spectra produce a sample profile, or particular molecular fingerprint, that can be used to screen and scan samples for a number of constituents. When presenting information about covalent bonds and identifying functional groups, FTIR is a helpful analytical technique. [4].

FTIR is only very helpful for verifying the identity of pure compounds when used to identify chemical combinations. The approach is based on identifying molecules' functional groups that vibrate in response to specific light wavelengths (either through stretching or bending in different ways). Plotting the frequency of light (cm-1) that the material is exposed to against the intensity of the vibrations results in an FTIR spectrum (percent transmission). Parts of the FTIR spectrum that are particular to the chemical under test are present (this is called the fingerprint region). Because the majority of samples seized are mixtures of chemicals, FTIR has extremely limited utility in the investigation of street samples of drugs of abuse. However, the advantages of not requiring derivatization and being non-destructive outweigh these. [3].

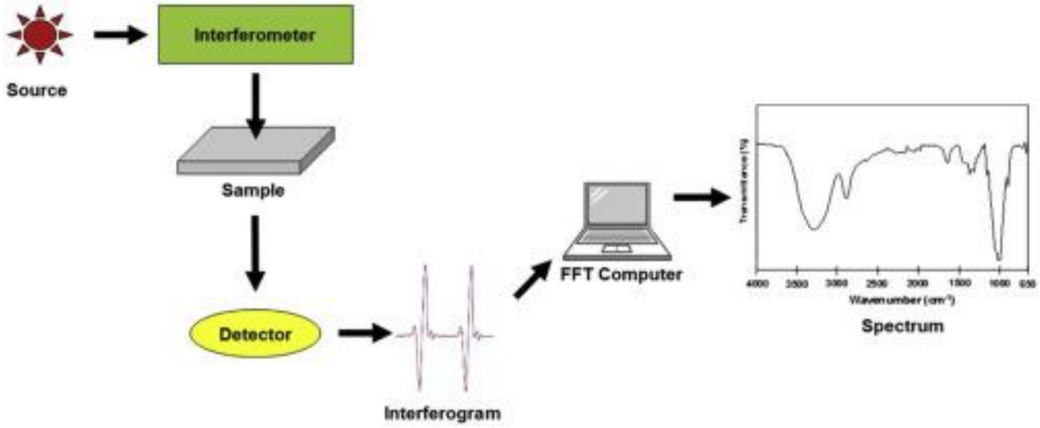

Figure 3.2 FTIR Spectroscopy [5]

3.3 Laser Induced Breakdown Spectroscopy (LIBS)

A technique for sensitive elemental analysis that has recently been improved to be suitable for industrial use laser-induced breakdown spectroscopy (LIBS). With its high sensitivity, good lateral resolution, and quick processing durations, LIBS is a nearly non-destructive measurement technique. Quantification is feasible with the right reference materials. LIBS provides a special opportunity for inline monitoring of process stability and/or product quality as a result. [6].

One of the simplest analytical techniques for displaying the cathode reaction distribution is LIBS. An analytical method called LIBS is used to capture the optical spectrum released by atoms that evaporated from a sample after being exposed to a pulsed laser with a high power density. When evaporated atoms in a plasma created by pulsed laser irradiation are de-excited, light is released. Without pretreatment of the sample, LIBS can be carried out in a lab (and does not require large-scale equipment like a synchrotron radiation facility); nonetheless, LIBS is a destructive analysis and is challenging to carry out in situ. Additionally, the sample's form and thickness are not constraints on LIBS measurements. Unlike XAS, Raman spectroscopy, XRD, and X-ray tomography, LIBS can directly detect lithium signals, that is, light associated with the de-excitation of lithium atoms in a plasma created with a strong laser pulse.

Laser-induced breakdown spectroscopy is an efficient analytical technique for locating and classifying materials (LIBS). For LIBS, it is simple to focus a very strong laser pulse onto a solid or liquid's surface, or onto a sample volume of a liquid, gas, or cloud of aerosolized particles. In the resulting micro plasma, along with ablated particles, are excited molecular and atomic species from the bulk material. Different light wavelengths are produced by these excited-state organisms. After collecting this light with a spectrometer, a computer may analyze it. Since each element has a unique emission spectrum, all elements may be found using LIBS. Remote and real-time LIBS can be performed with little or no human interaction. [7].

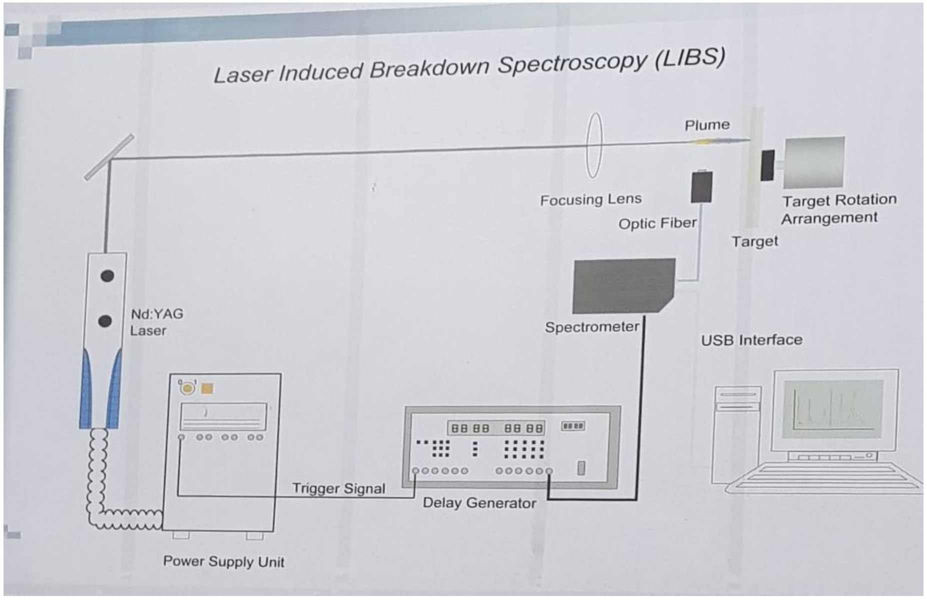

Figure 3.3 Experimental setups of LIBS

Summary

The methods of characterization employed in this work are discussed in this chapter. laser-induced breakdown spectroscopy, Fourier transform infrared spectroscopy and X-ray diffraction. X-ray diffraction is used to study the structure of the samples. The Fourier transform infrared spectroscopy was used to analyze the chemical bonding of the sample. To find out the composition of the leached residue and the cathode active material laser induced breakdown spectroscopy was used which also provides the qualitative analysis along with the quantitative analysis.

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Chapter 4 Experimentation

4.1 Discharging and Dismantling of LIB

The spent lithium-ion batteries that have been collected from nearby businesses and industries will be fully discharged before being separated from their lithium-ion battery components to prevent any accidents. Lithium-ion cell discharge has been completed. Then, for 48 hours, the discharged lithium-ion batteries are submerged in a solution of 5-weight sodium chloride [1]. After 48 hours, the lithium-ion cells are taken out of the NaCl solution and left to dry at ambient temperature. When the voltage from a multimeter is checked to be below 0.5 V, it is confirmed that all lithium-ion cells have been discharged properly.

The lithium-ion batteries were discharged, and the voltage of the batteries was checked using a multimeter. The batteries were then disassembled using a handsaw and pliers, and the plastic and casing were taken off with a plier. The cathode film of the batteries was further processed for the cathode active material after the anode, cathode, and separator were uncoiled.

4.2 Extraction of Cathode Active Material

The cathode of the lithium-ion cells was cut into squares using scissors before treating it further. The NaOH leaching is used to dissolve the aluminum foil of the cathode and to extract the cathode’s active material. The cathode film squares were added to the 10 wt. percentage NaOH solution at room temperature with a solid-to-liquid ratio of 100 g L^{-1}, and 300 rpm for 2 hours to dissolve the aluminum foil in it and keep the cathode active material as solid particles [1].

After 2 hours of leaching, the solution was filtered using vacuum filtration. The black mass that remained on the filter paper was washed properly through the deionized water before being dried at room temperature. The black mass cathode active material was weighed after being dried at room temperature. The black mass was calcined at 700 ℃ to remove the carbon and the binder. Lastly, the cathode active material was finely ground to reduce the particle size. The finely grounded samples are then used as the feed material for the cathode active material characterization and the leaching.

According to Section 3.1, the cathode active material was separated from the lithium-ion cells. Lithium-ion batteries contain cathodes of various compositions and employ various binders during production. The polar binder can be dissolved using dimethylformamide (DMF) and N-methyl-2-pyrrolidine (NMP) at 100 °C. These solvents are expensive and present a major risk to both human health and the environment. To eliminate the carbon and binder that were present in the cathode active material, the cathode active material was calcined at a high temperature instead of using these solvents in this study.

4.3 Cathode Active Material Characterization

The cathode active material was analyzed using the x-ray powder diffraction (XRD) analysis to determine the cathodic material present in the LIB. After leaching, the leached residue was vacuum filtered, dried, and analyzed using the XRD analysis, and the leachate was analyzed using the flame photometer to determine the elemental composition of the sample. The laser-induced breakdown spectroscopy (LIBS) was used for the quantitative and qualitative analysis of the cathode active material and the leached residue.

To ascertain the cathodic material present in the LIB, the x-ray powder diffraction (XRD) examination was used to examine the cathode active material. After leaching, the leached residue was vacuum filtered, dried, and subjected to XRD examination; the leachate underwent flame photometer analysis to ascertain the sample's elemental composition. The cathode active material and the leached residue were analyzed quantitatively and qualitatively using laser-induced breakdown spectroscopy (LIBS).

4.4 Materials and Reagents

$\mathrm{LiFePO_4}$ Lithium-ion cells were collected from the local region industry and pretreated. The $\mathrm{LiFePO_4}$ cells were discharged and dismantled to recover the spent $LiFePO_4$ cathode powder. The anode, cathode, and separator were separated. By using NaOH leaching, the cathode active material was detached from Al foil reported by Tiaan Punt et al. [1]. The wrapped Al foil was scrapped clean of the cathode powder. The powder was ultimately ground for the fine results. Table 1 lists the elemental composition of the spent $\mathrm{LiFePO_4}$ cathode powder. The chemicals and reagents i.e., acetic acid (CH_3COOH), succinic acid ($C_6H_6O_4$), hydrogen peroxide (30%) (H_2O_2) sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3) used in this study were of company Sigma Aldrich. All chemicals were analytical-grade reagents, and they were used exactly as they were received. The solutions were prepared with deionized water (DI) and a dilute NaOH solution was used to regulate the pH throughout the experiments.

Element	**Fe**	**Li**	**Al**	**Na**	**P**
Composition (wt. %)	32.1	3.7	0.9	0.5	12.8

Table 4.1 Elemental composition of spent $LiFePO_4$ cathode active material

4.5 Methodology

To investigate the impact of organic acids on acid leaching for the selective retrieval of the Lithium from spent LFP lithium-ion cells, the strategy prepared to convert the spent into reuse is shown in Fig 1. For acetic and succinic acid, a series of experiments were conducted using the same strategy.

The acid leaching was performed in the (500 ml) round bottom flask with a magnetic stirrer. Several sets of experiments were conducted, and leaching parameters were adjusted to maximize leaching efficiency. to optimize the leaching parameters according to the leaching efficiency, including the acid concentration (0-3 M), solid-to-liquid ratio (0-20 $g \cdot L^{-1}$), and amount of oxidizing agent (0-6 vol %) H_2O_2.

The scale-up experiment began from the 5 g of spent LFP cathode powder and the optimized results were achieved for succinic and acetic acid are:

Parameters	**Acetic Acid**	**Succinic Acid**
Acid Concentration	1.5 M	1.5 M
Solid-to-Liquid Ratio	20 $g \cdot L^{-1}$	15 $g \cdot L^{-1}$
Oxidizing Agent (H_2O_2)	4 vol %	4 vol %

After leaching, the residue was filtered. Fe and Al were removed by purifying the leachate with the addition of the NaOH solution. The refined Li solution was filtered and analyzed. A saturated Na_2CO_3 solution in a stoichiometric amount was used to treat the Li solution. The solution will then be heated at 90 ° C for three hours. The white precipitates that formed at the bottom after heating, were separated and dried in the oven.

Leaching efficiency is calculated by using the obtained data. The leaching efficiency is calculated according to the given Eq. 1

$$\text{Leaching Efficiency \%} = \frac{\text{concentration of element} \times \text{volume of leachate}}{\text{mass of raw material(g)} \times \text{wt(\%)of element in raw material}} \times 100$$

(1)

4.6 Acid Leaching of Ideal Leaching Agent

The group of experiments was performed under different conditions by varying the acid concentration, solid-to-liquid ratio, and the concentration of the hydrogen peroxide. The group of experiments was conducted to find the optimal conditions as displayed in Table 4.1.

Acid Concentration	1.5 M
Solid-to-liquid ratio	15 gL^{-1}
Hydrogen Peroxide	4 vol %
Temperature	70 ° C
Rpm	300
Time	40 min

Table 4.2 Optimal Condition of Acid Leaching for succinic acid

The succinic acid solution was prepared by dissolving the succinic acid powder in the deionized water at 600 rpm and 60 ° C until all the crystals of the succinic acid are not dissolved properly and the solution will turn into a transparent solution. The acid solution was then added into the leaching vessel, closed the lid, and placed on a hot plate. The cathode active material was added when the temperature reached 70 ° C after which the hydrogen peroxide was poured dropwise into the leaching solution. After 40 min, the hot plate was turned off and then the leaching solution was vacuum filtered to separate the leached residue from the filtrate. The filtrate and the leached residue were then analyzed. The filtrate was then further purified by adding the dilute NaOH solution and the impurities of aluminum, iron, and copper were precipitated out. After this, the pure transparent lithium solution was achieved.

4.7 Metal Extraction

A stoichiometric amount of Na_2CO_3 is added to the lithium solution after it has been thoroughly cleaned of all contaminants to precipitate out the lithium compound. At a temperature of 90°C, the solution was heated for three hours. The white precipitate will begin to form at the bottom of the beaker after a short period of heating. Let the solution cool down after three hours of heating to allow precipitates to form, then filter the precipitates using vacuum filtration and dry them in an oven.

Summary

This chapter includes the overall strategy proposed for the recycling of the lithium ion batteries. The process of how the spent lithium-ion batteries are discharged properly before dismantling. The extraction of the cathode active material for the recovery of the metals and the conditions of the acid leaching and precipitation to precipitate the lithium carbonate.

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Chapter 5 Results and Discussion

5.1 Laser-Induced Breakdown Spectroscopy

Laser Induced Breakdown Spectroscopy (LIB) is used to examine the LFP cathode active powder and the leached residue; Figure 5.1 displays the qualitative spectra for cathode active material and the leached residue of succinic acid. For the solid-state elemental investigation of battery materials, laser-induced spectroscopy is a beneficial method [1]. The laser utilized in this technique was an Nd YAG laser with a wavelength of 532 nm. The pulsed laser's energy that was applied to the samples was 20 mJ per pulse and the duration was 0 µs to 50 µs. For each measurement point, the samples were exposed to a single laser pulse. Using a Plano-convex lens with a focal length of 10 cm, the laser was focused on the samples and sent via optical fiber to spectrometer equipment, including an ICCD detector and a spectrograph for LIB measurement. The laser activated the ICCD detector's gate, and the digital delay generator built inside the ICCD detectors regulated the relative delay. The height of the samples was altered by rotating the sample stage in the sample chamber. The spectrum demonstrates the numerous, clearly differentiated emission lines. A careful examination of the spectrum at different wavelengths using the NIST (National Institute of Standard and Technology) atomic spectral database confirms the presence of Al, Fe, Li, and Na [2]. Furthermore, the analysis was verified when the LIBS spectra of the cathode active powder and the leached residue is equated with the individual LIBS spectra of the authentic elements [3]

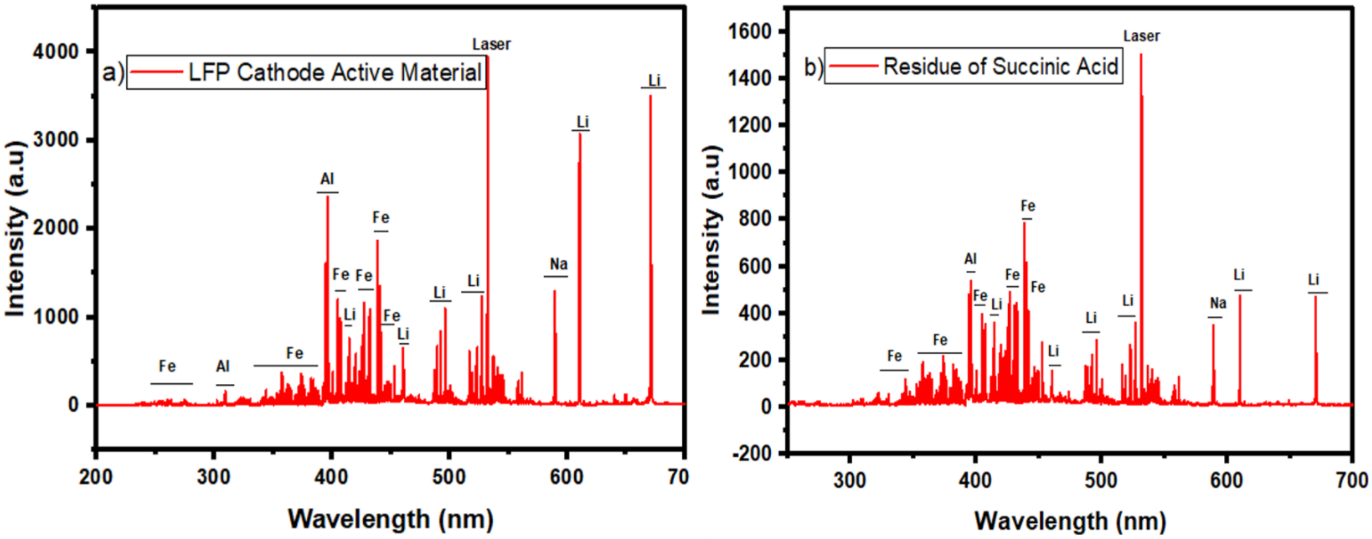

Figure 5.1 LIBS Qualitative Spectrum a) Cathode Active Material b) Leached Residue of Succinic Acid

5.2 Leaching of Lithium Iron Phosphate with Acetic Acid

The acid leaching was performed in the round bottom flask with a magnetic stirrer. The spent lithium iron phosphate powder was added to the acetic acid solution prepared in DI water, and the oxidizing agent was dropped into the solution once the temperature reached 70°C for 40 minutes. The optimal leaching conditions were created by adjusting the acetic acid concentration, H_2O_2 volume fraction, and the solid-to-liquid ratio.

A typical weak organic acid is acetic acid. One carboxyl is present in each CH_3COOH molecule, and 1 mol of acetic acid should theoretically create 1 mol of H^+ upon dissociation in pure water. However, in reality, not all of the H^+ is liberated into the solution [4]. Following is the possible way to express how acetic acid dissociates:

$$\mathrm{CH_3COOH} \rightarrow \mathrm{CH_3COO^-} + \mathrm{H^+}$$

After the spent lithium iron phosphate powder interacts with the leaching solution, allowing the metal to enter the solution, the leaching residue contains unreacted metal oxides and contaminations. When leachate is tested using flame photometry the results show that most of the lithium enters into the solution. Lithium carbonate was precipitated from the pure lithium leachate after further processing it with diluted NaOH solution to eliminate any remaining contaminants in the solution.

To explore the impact of acetic acid concentration, solid-to-liquid ratio, and volume fraction of oxidizing agent on the leaching of lithium, a series of experiments were conducted, by varying the acid concentration from 0 M to 3 M, solid-to-liquid ratio from 5 gL^{-1} to 25 gL^{-1}, and volume fraction of H_2O_2 from 0 vol % to 6 vol %.

5.3 Analysis of Dissolution of the Lithium Using Acetic Acid

5.3.1. Effect of Acetic Acid Concentration on Leaching Efficiency

To investigate the effect of acetic acid concentration (0 M-3 M) on the leaching efficiency of lithium from spent lithium iron phosphate cathode material the experiments were conducted at solid-to-liquid ratios of 15 gL^{-1} and 4 vol % H_2O_2 with different concentrations of the acid (0 M-3 M) at 70℃ for 40 min. To determine the leaching efficiency, samples were taken from each experiment, and the leachates were then tested using flame photometry. The fluctuation in leaching efficiency with acid concentration is depicted in Figure 5.2a. The leaching efficiency is almost negligible between 0 M and 1 M of acid. When the acetic acid concentration is raised to 1.5 M, the leaching efficiency rises; however, it then starts to fall and shows no clear increase after the 1.5 M concentration shown in Figure 5.2b. The maximum lithium leaching efficiency is attained at 1.5 M acetic acid concentration i.e. 98.2 %. As a result, the ideal acid concentration was determined to be 1.5 M.

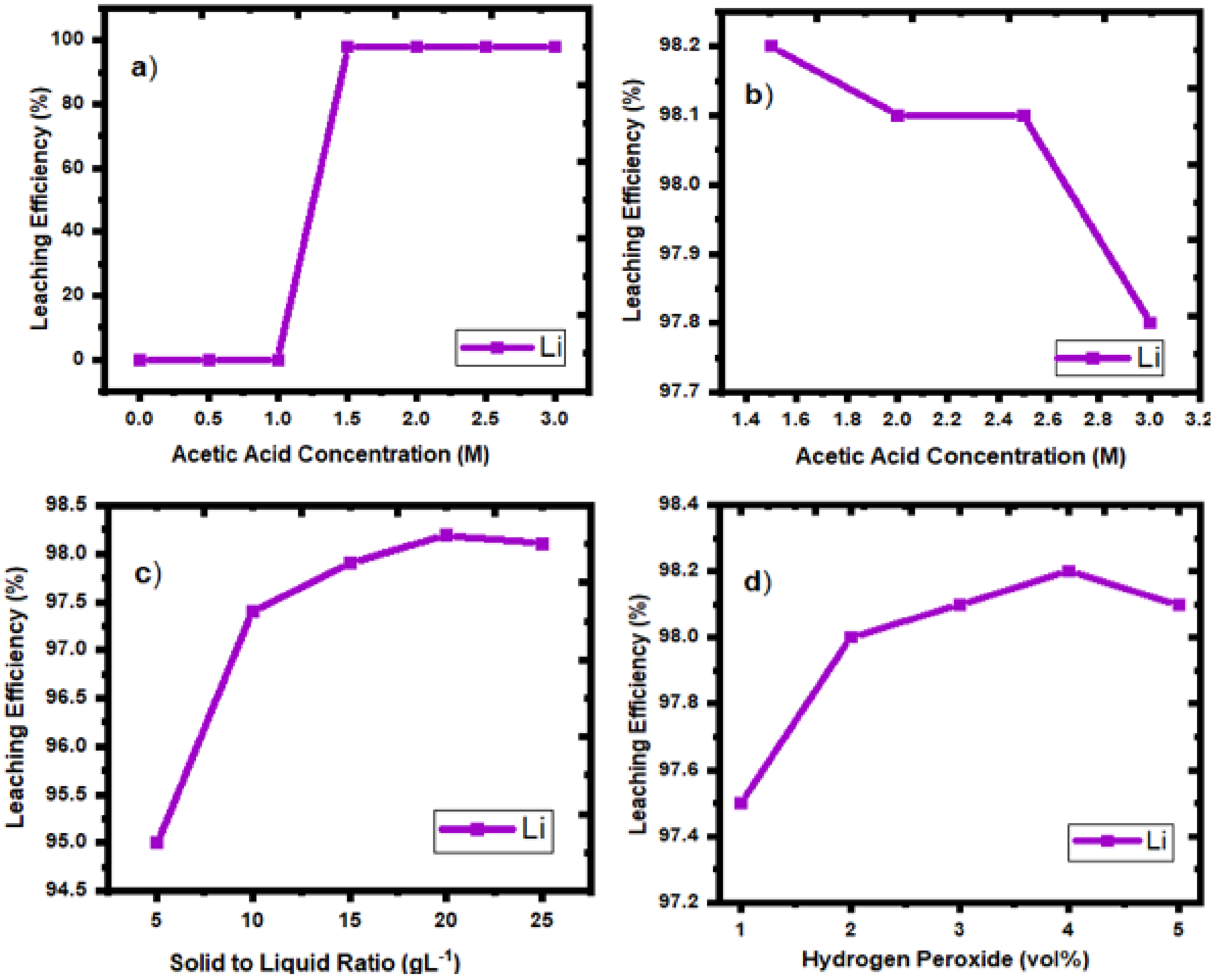

Figure 5.2 Effect of different parameters of acetic acid on leaching efficiency a) effect of varying acid concentration between 0 M to 3 M b) effect of varying acid concentration between 1.5 M to 3 M c) effect of varying solid to liquid ratio from 5-25 gL^{-1} at an acid concentration of 1.5 M and H_2O_2 4 vol % d) effect of varying Hydrogen Peroxide concentration form 0-6 vol % at an acid concentration of 1.5 M and S:L ratio of 15 gL^{-1}

5.2.2. Effect of Solid-to-Liquid Ratio on Lithium Leaching

To investigate the impact of the solid-to-liquid ratio on the leaching efficiency of the lithium, experiments were conducted under the following conditions: 1.5 M acetic acid concentration, 4 vol % H_2O_2 with solid-to-liquid ratio 5 gL^{-1} to 25 gL^{-1} at 70°C for 40 min. Figure 5.2c shows the variation of the leaching efficiency with the solid-to-liquid ratio. The lithium leaching efficiency increase clearly from 5 gL^{-1} to 20 gL^{-1} after which there is an obvious decrease from 20 gL^{-1} to 25 gL^{-1}. The maximum leaching efficiency is achieved at 20 gL^{-1}, so this is considered the optimal solid-to-liquid ratio for lithium leaching.

5.2.3 Effect of Hydrogen Peroxide Volume Fraction on Lithium Leaching

To investigate the impact of the volume fraction of H_2O_2 on the leaching efficiency of the lithium, experiments were conducted under the following conditions: 1.5 M acetic acid concentration, solid to liquid ratio 20 gL^{-1} with volume fraction of H_2O_2 from 1 vol % to 6 vol % at 70℃ for 40 min. Figure 5.2d explains that the maximum lithium leaching efficiency is achieved at 4 vol % H_2O_2 after which there is not any obvious increase in leaching efficiency making it an optimal volume fraction of H_2O_2 for leaching of lithium from spent lithium iron phosphate material.

5.3 Leaching of Lithium Iron Phosphate with Succinic Acid

The solid-liquid heterogeneous reaction occurs when LFP cathode powder and organic acid are combined. Succinic acid is an effective leaching agent for valuable metals. Succinic acid has two $C_4H_4O_4$ molecules. Succinic acid has pK_a values of 4.102 and 5.408. The LFP cathode powder was mixed with the oxidizing agent (H_2O_2) and the leaching agent. Li is liberated in the solution in the form of $C_4H_4O_4Li_2$ along with Fe^{+2} in $LiFePO_4$ and is oxidized into Fe^{+3} as the product of $FePO_4$ as demonstrated in Eq. (2). The little quantity of $LiFePO_4$ dissolved in the acidic solution will probably lead to the loss of P and Fe. Under an acidic condition with an appropriate concentration of ions, $LiFePO_4$ can directly be transmuted into the $FePO_4$ without converting into any Fe species. Under the achieved pH of the reaction system, it holds the leading species Li^+, $FePO_4$, and $LiFePO_4$ [5]. However, the case of not appropriate pH for the reaction system will lead to the production of more Li^+ and Fe^{+2} , which is an unfavorable way for selective recovery of Li.

$$2\ C_6H_6O_4 + 3\ H_2O_2 + 6\ LiFePO_4 \longrightarrow 6\ FePO_4 + 3\ Li_2\,(C_4H_4O_4) + 3\ H_2O \qquad (2)$$

The acid leaching was performed in the round bottom flask with a magnetic stirrer. The spent LFP powder was added to the succinic acid solution prepared in DI water, and the oxidizing agent was dropped into the solution once the temperature reached 70°C for 40 minutes. The optimal leaching conditions were created by adjusting the succinic acid concentration, H_2O_2 volume fraction, and the solid-to-liquid ratio.

After the spent LFP powder interacts with the leaching solution, allowing the metal to enter the solution, the leaching residue contains unreacted metal oxides and contaminations. When compared the LIBS spectra of the spent lithium iron phosphate powder with the LIBS qualitative spectra of the leached residue given in Figure 5.1 demonstrates that the spectral peaks of lithium declined and disappeared in residue spectra, and there were practically the spectral lines of the iron which shows that most of the lithium enters into the solution. Lithium carbonate was precipitated from the pure lithium leachate after further processing it with diluted NaOH solution to eliminate any remaining contaminants in the solution.

To explore the effect of acid concentration, solid-to-liquid ratio, and volume fraction of oxidizing agent on the leaching of lithium, a series of experiments were conducted, by varying the succinic acid concentration from 0 M to 2.5 M, solid-to-liquid ratio from 5 gL^{-1} to 20 gL^{-1}, and volume fraction of H_2O_2 from 0 vol % to 6 vol %.

5.4 Analysis of Dissolution of Lithium Using Succinic Acid

5.4.1 Effect of Acid Concentration on Lithium Leaching

To examine the effect of succinic acid concentration on the leaching of lithium from spent LFP powder, a series of experiments were conducted by rising the acid concentration from 0 M to 2 M, the solid-to-liquid ratio of 15 gL^{-1} with 4 vol % H_2O_2 at 70℃ for 40 min. The leaching efficiency of lithium shoot up from 0 to 98.7 % and then started decreasing as presented in Fig. 5.3a. The leaching efficiency of P and Fe was maintained at 6.5 % and 4.3 %. Maximum lithium leaching efficiency of 98.7 % with acceptable Fe and P loss was achieved at 1.5 M succinic acidic concentration, which was considered as ideal succinic acid concentration for leaching of lithium from spent LFP cathode powder.

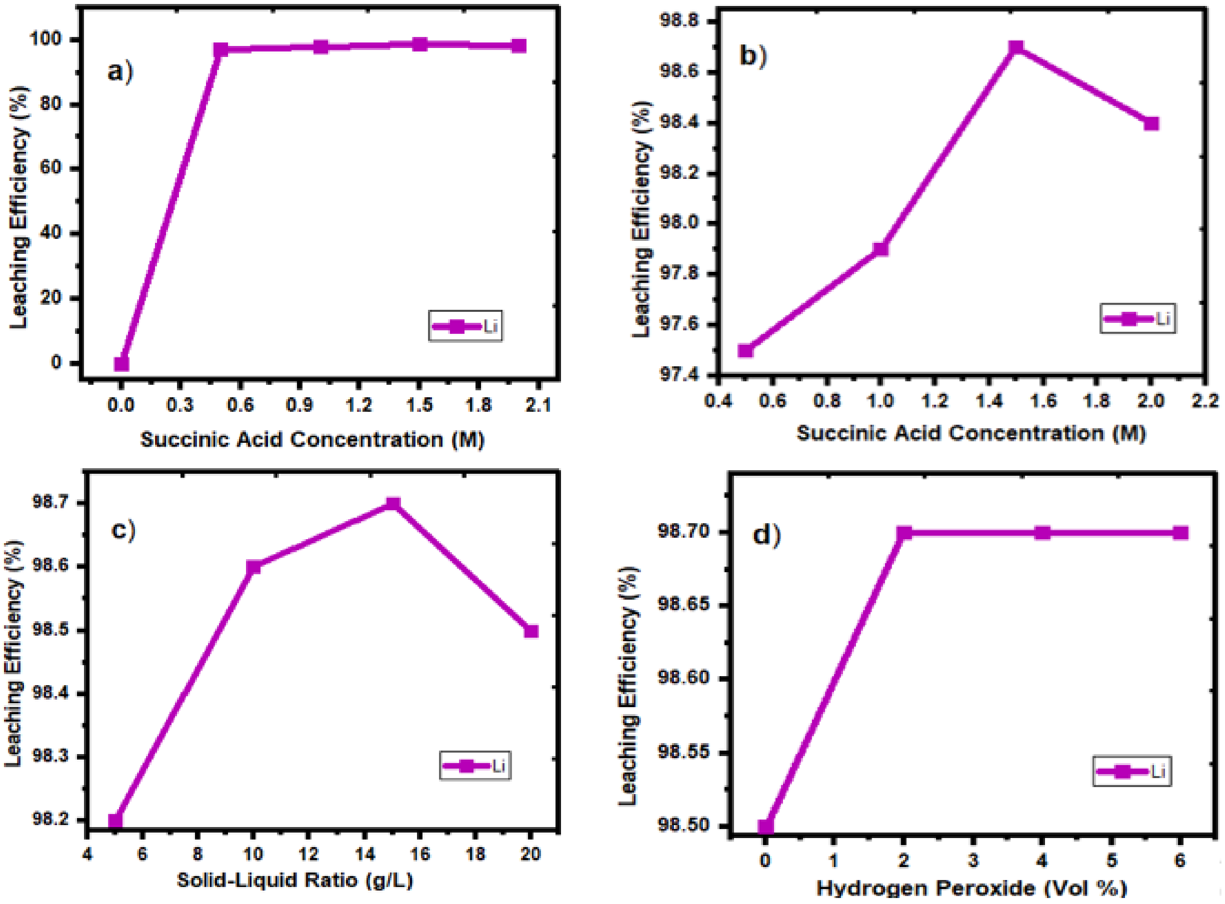

Figure 5.3 Effect of different parameters on leaching efficiency a) effect of varying acid concentration between 0 to 2M b) effect of varying acid concentration between 0.5 M to 2M c) effect of varying solid to liquid ratio from 5-20 gL^{-1} at an acid concentration of 1.5 M and H_2O_2 4 vol % d) effect of varying Hydrogen Peroxide concentration form 0-6 vol % at an acid concentration of 1.5 M and S:L ratio of 15 gL^{-1}

5.4.2. Effect of Solid-to-Liquid Ratio on Lithium Leaching

The group of experiments was conducted to examine the impact of the solid-liquid ratio on the leaching efficiency. The solid-liquid ratio was varied from 0 to 20 gL^{-1} with 1.5 M acid concentration, 4 vol % H_2O_2 at 70℃ for 40 min. The leaching efficiency of the Li increased firstly and then started declining as displayed in Figure 5.3c. The solid-liquid ratio was tuned to 15 gL^{-1}, and further experiments were conducted under these circumstances, to achieve the maximum leaching efficiency with acceptable Fe and P loss.

5.4.3 Effect of Hydrogen Peroxide Volume Fraction on Lithium Leaching

To evaluate the effect of the H_2O_2 on leaching efficiency a series of experiments were conducted by varying the amount of the oxidizing agent from 0 to 6 vol % while maintaining the optimal conditions. Increasing the concentration of the oxidizing agent did not significantly affect the leaching efficiency; instead, it merely resulted in a cost increment. The maximum leaching efficiency was attained at 4 vol % H_2O_2. The leaching efficiency first increased and then remained constant by increasing the amount of oxidizing agent as illustrated in Fig. 5.3d.

5.5. Comparison Leaching Efficiency of Different Organic Acids

The leaching efficiency of the lithium from spent $LiFePO_4$ cathode active powder was compared using different organic acids, including acetic acid and succinic acid. The maximum lithium leaching efficiency of 98.2% was attained at optimal conditions of 1.5 M acetic acid, solid to liquid ratio 20 gL^{-1} with 4 vol % H_2O_2 at 70℃ for 40 min for acetic acid. However, the maximum lithium leaching efficiency of 98.7 % is attained at optimal conditions of 1.5 M succinic acid, solid to liquid ratio 15 gL^{-1} with 4 vol % H_2O_2 at 70℃ for 40 min for succinic acid.

Fig. 5.4 displays the leaching efficiency of acetic acid and succinic acid. The leaching rate of Li for acetic acid, and succinic acid is 98.2 % and 98.7 % respectively. Hence, succinic acid is considered the ideal leaching agent for lithium leaching from spent LFP cathode active material because it can achieve the highest lithium leaching efficiency with a lower solid-to-liquid ratio at the same optimal conditions. With this leaching efficiency, succinic acid outplays another organic acid with a Li leaching efficiency of 98.7 %.

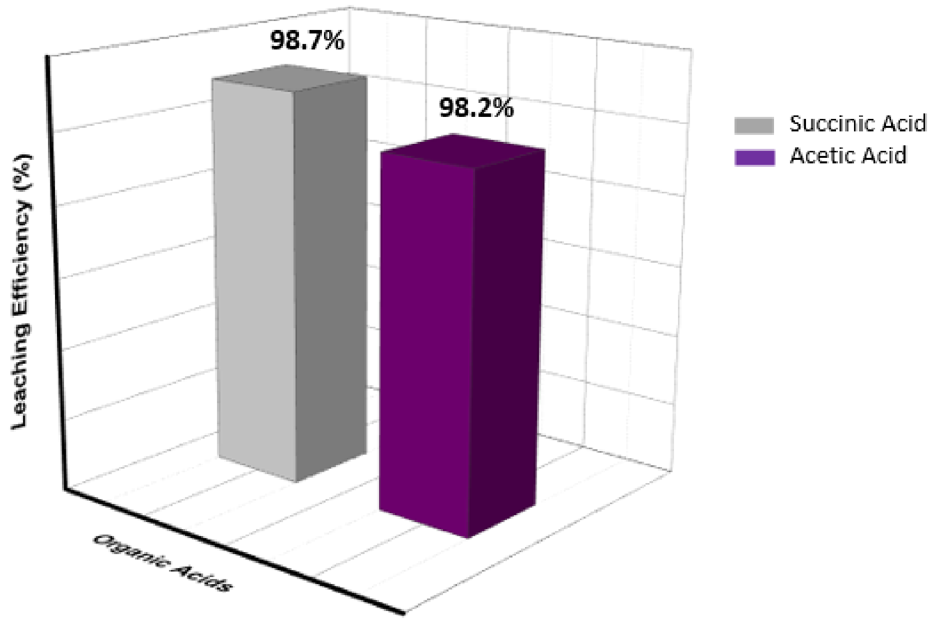

Figure 5.4 Leaching efficiency for different organic acids with an acid concentration of 1.5 M, S:L ratio of 15 gL^{-1}, 4 vol % H_2O_2, and leaching time 40 min

To get the product $FePO_4$ after acid leaching and enhance the mechanochemical reaction, adding the oxidant during the delithium process of the $LiFePO_4$ is necessary [6] [7]. Hydrogen peroxide H_2O_2 is the best oxidant to enhance the mechanochemical reactions because its reduction products are O_2 and H_2O which have no adverse effect on the environment. To determine the impact of the H_2O_2 on leaching efficiency, experiments were conducted with and without the H_2O_2 for both acetic and succinic acid under their optimal conditions as shown in Figure 5.5.

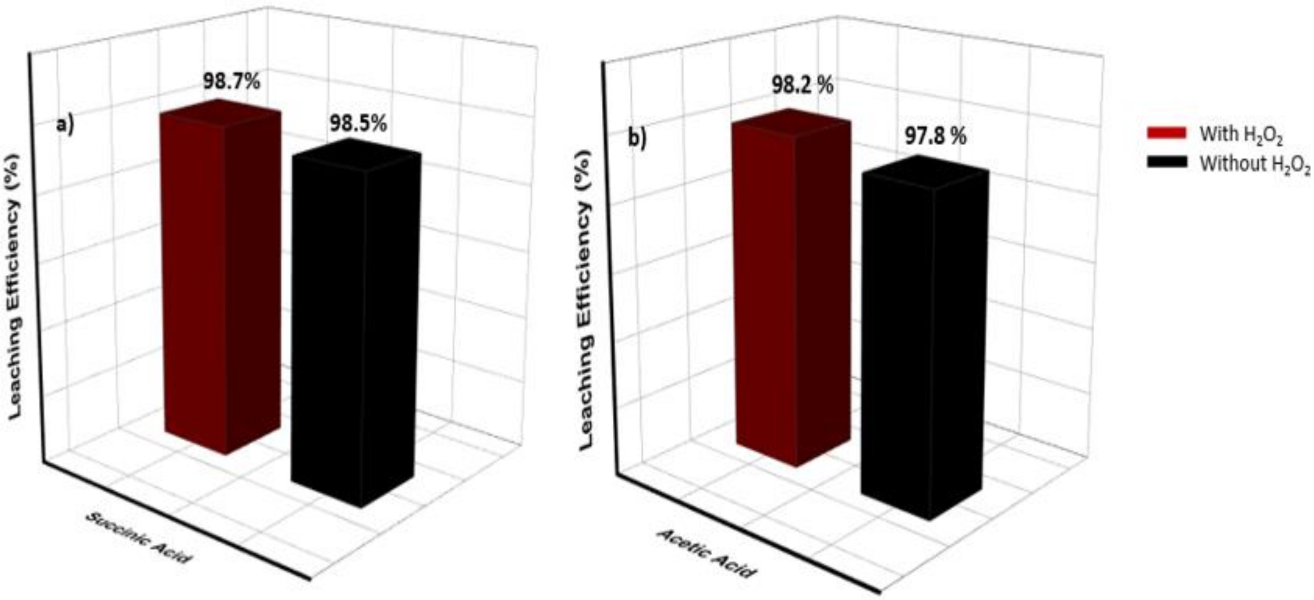

Figure 5.5 Comparison of leaching efficiency with and without H_2O_2 a) Succinic acid concentration of 1.5 M and S:L ratio of 15 gL^{-1} b) Acetic acid concentration 1.5 M and S:L ratio of 20 gL^{-1}

However, without the oxidizing agent H_2O_2, the achieved Li leaching efficiency is 98.5 % for succinic acid and 97.8 % for acetic acid. Thus, succinic acid is the recommended ideal leaching agent for selective lithium recovery from spent $LiFePO_4$ cathode active material.

3.6. Extraction of Fe/P and Li in bulk for Ideal Leaching Agent

The scale-up experiment was carried out under optimal conditions, based on the results and discussion above for succinic acid. In the beginning, 5 g spent cathode active powder was used. After acid-based leaching, the solution is filtered the residue and leachate were separated. Table X2. shows the composition of the residue and the 250 ml leachate for the ideal leaching agent i.e. succinic acid, which was analyzed using a laser-induced breakdown spectroscopy and flame photometer. The calculated residual rates of P and Fe from the leached residue were 95.62 % and 93.45 % respectively, and the calculated Leaching efficiency of Li, Al, and Na was 98.7 %, 95.37 %, and 92 % respectively. The reported literature, as given in Table 5.1. was contrasted with the calculated leaching efficiency of the Li. The succinic acid's leaching effectiveness was discovered to be equivalent to sulfuric acid [8], formic acid [9], lemon juice [10], acetic acid [11], and tartaric acid [12]. Indeed, the proposed organic acid-based strategy for the selective recovery of the Li from spent LFP cathode scrap is effective.

To attain the desired purity, the leachate was treated with the diluted NaOH solution to remove the contaminants, i.e., Fe, and Al. The leachate was first treated with a sufficient amount of NaOH solution, to modify the pH of the leachate to precipitate $Fe(OH)_3$ and $AL(OH)_3$. These precipitates were filtered. The elimination of Fe and Al was confirmed by analyzing the leachate using a flame photometer. NaOH solution was additionally introduced to purge the solution of any remaining contaminants. The shade of the solution will change into a transparent solution once more NaOH is added, and the impurities will precipitate out and be removed by filtration. The pure lithium solution will be achieved at the end and confirmed by flame photometry tests. Under specific circumstances, the lithium solution was further treated with a stoichiometric dosage of precipitating agent to produce the required lithium compound [13].

Furthermore, the remaining solution can be processed using other techniques, such as crystallization, for later use, and all of the aforementioned elements can be recovered without producing any secondary waste

Leaching Reagents	**Cell Type**	**Leaching Conditions**	**Leaching Efficiency**	**References**
Sulfuric Acid (H_2SO_4)	LNCMO	1.5 M sulfuric acid, 30 % H_2O_2 or glutaric acid	Li 99.91% Co 87.85% Ni 91.46%	[8]
Succinic Acid ($C_4H_6O_4$)	LCO	1.5 mol·L^{-1} succinic acid, 15 g·L^{-1}, 4 vol % H_2O_2 , 40 min, 70 ° C,	Li 96% Co 100%	[5]
Ascorbic Acid ($C_6H_8O_6$)	LCO	1.25 mol·L^{-1} ascorbic acid, 25 g·L^{-1}, 70 ° C, 20 min	Li 98.5% Co 94.8%	[14]

Phosphoric Acid (H_3PO_4)	LCO	1.5 mol·L^{-1} phosphoric acid, 0.02 mol·L^{-1} glucose, 80 °C, 2hr	Li 100% Co 98%	[9]
Lemon Juice ($C_6H_8O_7$)	LFP	100 % lemon juice, 6 vol % H_2O_2, 67 g·L^{-1}, 90 min	Li 94.8% Cu 96.92% Al 47.24%	[10]
Acetic Acid (CH_3COOH)	LCO	1.7 M acetic acid, 6 vol % H_2O_2, 8 g·L^{-1}, 60 min, 330 rpm, 75 ° C	Li dissolution 100% 90% cobalt oxalate, 92% lithium carbonate.	[11]
Tartaric Acid ($C_4H_6O_6$)	NMC	2 M tartaric acid, 4 vol % H_2O_2, 17 g·L^{-1},30 min, 70 ° C	Li 99.07% Mn 99.31% Co 98.64%	[12]
Formic Acid (CH_2O_2)	LCO	10:1 acid concentration, 60 ° C, 20 g·L^{-1}, 20 min	Li 90.90% Co 99.96%	[15]
Sulfuric Acid (H_2SO_4)	NMC	1 mol·L^{-1}, S/L 1:10, 90 ° C, 1hr	Ni, Co, Mn 90%	[16]
Acetic Acid (CH_3COOH)	LFP	1.5 M acetic acid, 4 vol % H_2O_2 15 g·L^{-1}, 40 min, 70 ° C	Li 98.2%	In this work
Succinic Acid ($C_4H_6O_4$)	LFP	1.5 M succinic acid, 4 vol % H_2O_2 15 g·L^{-1}, 40 min, 70 ° C	Li 98.7%	In this work

Table 5.1 Summary of Literature Review

5.7 Materials Characterization

Figure 5.6 depicts the XRD spectrum of the cathode active material and lithium carbonate recovered. The spectrum of cathode active material displays peaks that resemble the JCPDS no. 40-1499 and the peaks of lithium carbonate resemble reference data JCPDS no. 80-1307. According to the XRD spectra, which reveal that carbon and binder are removed from the cathode active material after calcination, no carbon phase was presumably present.

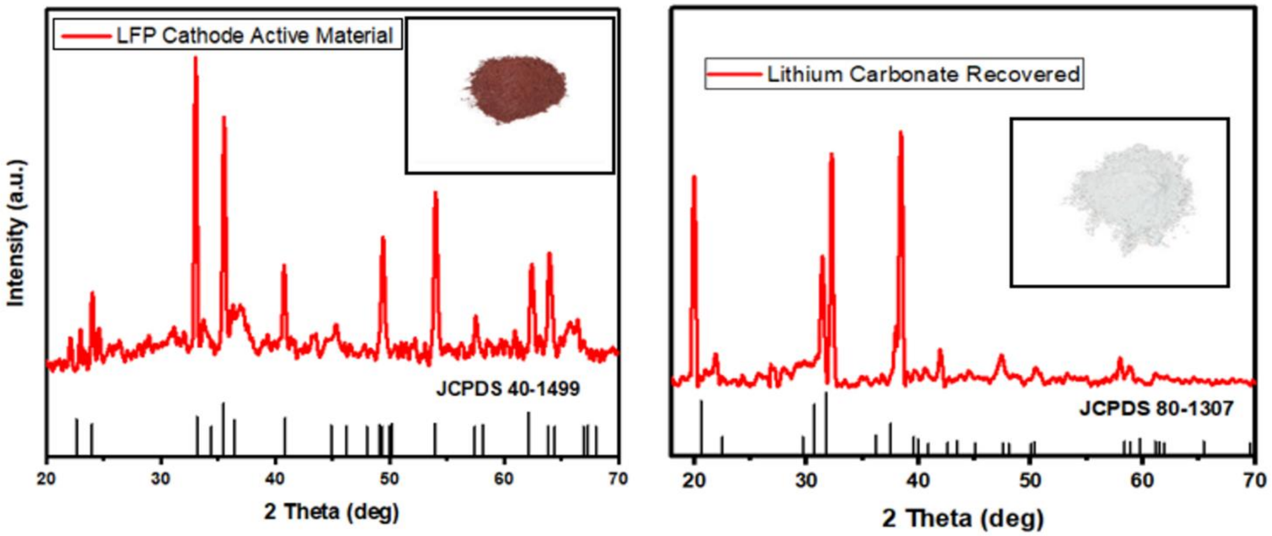

Figure 5.6 XRD a) Cathode active material b) Lithium carbonate recovered

The FT-IR spectrum of the $LiFePO_4$ cathode active material is shown in Figure 5.7. The olivine phosphate group's P-O antisymmetric stretching vibrations are visible in the broad bands about 1053, 1098, and 1140 cm^{-1}. The presence of O-P-O symmetric and antisymmetric vibrations was seen in the bands at 550 and 578 cm^{-1}. The vibrations of the lithium ions present in the olivine $LiFePO_4$ cathode active material can be attributed to the bands 468 and 501 cm^{-1}. Due to the carbon that is present on the surface of the $LiFePO_4$ cathode active material, the region 1400-2000 cm^{-1} revealed the presence of the C=C bond. The presence of the -OH, COOH, and H_2O bonds is indicated by the band at 3430 cm^{-1} [17]. The recovered lithium carbonate's FT-IR spectrum is consistent with the transmittance spectra on the NIST database and the FTIR spectra reported by Steven Renault et. al and Stefan A. Freunberger et.al [18] [19].

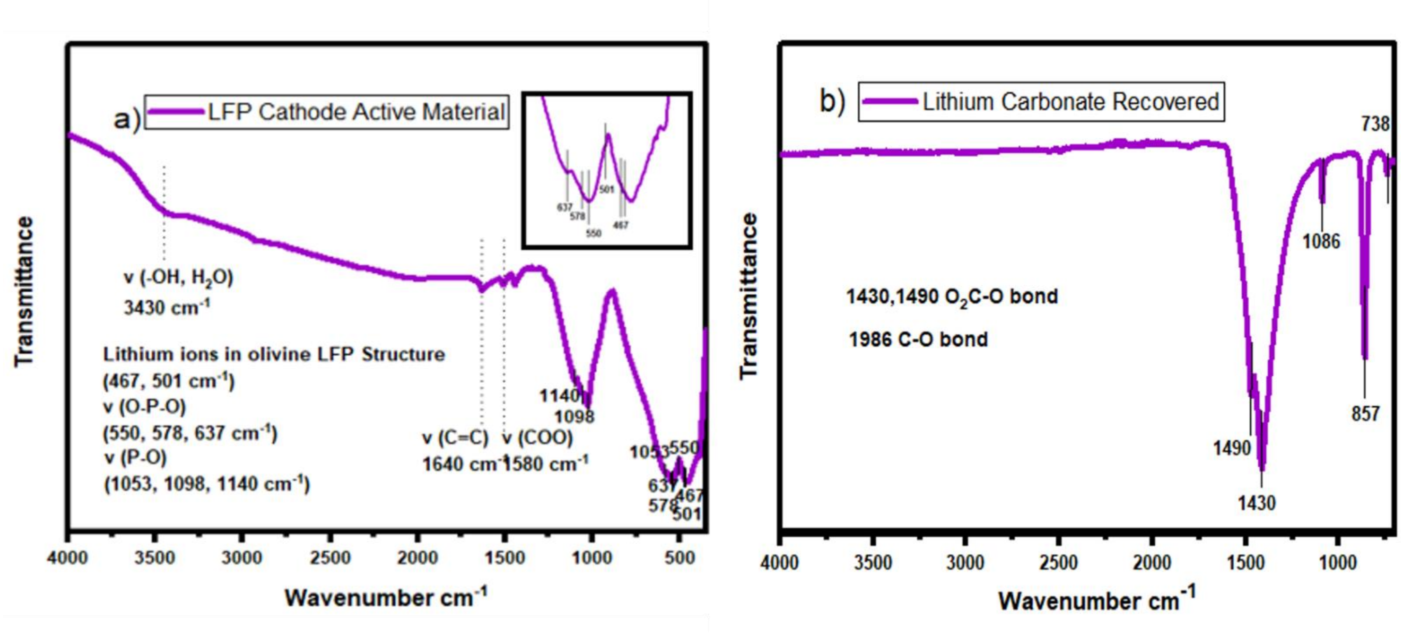

Figure 5.7 FTIR of a) $LiFePO_4$ cathode active material b) Lithium carbonate recovered

Summary

The cathode active material, leached residue, and recovered lithium compound are all characterized in this chapter. The crystal structure of the cathode active material and the recovered lithium compound was analyzed using the X-ray diffraction analysis. The composition was analyzed using the laser induced breakdown spectroscopy. The leaching experiment results are discussed here, and the chosen leaching conditions are supported by previously published research.

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Chapter 6 Conclusion and Recommendation

6.1 Conclusion

Spent lithium-ion batteries are the major source of lithium, iron, phosphorus, and aluminum. Reusing all of these materials not only helps the environment but also reduces global consumption. For the recycling of spent $LiFePO_4$ cathode powder, a straightforward and environmentally beneficial organic-based leaching technique has been put forth in this work. In this study, a method for recovering lithium from used $LiFePO_4$ batteries is devised. Mineral acids were replaced with mixtures of organic acids as the leaching agent for recovering lithium from depleted $LiFePO_4$ batteries. To determine the best agent for leaching lithium from used $LiFePO_4$ batteries, acetic acid, and succinic acid are put side by side. This study optimizes the leaching conditions for both acetic and succinic materials. By utilizing 1.5 M acetic acid at a solid-to-liquid ratio of 15 gL^{-1}, 4 vol % H_2O_2, for 40 min, 98.2 % lithium leaching efficiency is attained. However, at 1.5 M succinic acid with a solid-to-liquid ratio of 15 gL^{-1}, 4 vol % H_2O_2, for 40 min, 98.7 % of Li extracted selectively along with a residual rate of 95.62 % and 93.45 % of P and Fe respectively. When compared to acetic acid and published data, succinic acid has the highest lithium leaching efficiency from the used LFP cathode material, as demonstrated in Table 5.1. The leaching residue can be used to recover the $FePO_4$. The mechanism for leaching demonstrates an excellent $FePO_4$ recovery rate and high leaching efficiency. Leachate was treated to achieve Li_2CO_3 as a product, by altering pH and removing other components like Al, and Fe with NaOH. The currently suggested method for recycling spent $LiFePO_4$ powder is very safe, highly effective, and has a promising future for use. In the following work, organic acids like succinic and acetic acid extract the lithium from the spent $LiFePO_4$ cathode material.

In both research and Industry, the sustainable recycling of used lithium-ion batteries continues to be a difficult problem. The objective of additional research activities must be the continued development of recycling processes, particularly with regard to ecologically benign and climate-neutral ways. Since the framework conditions in this context are continually changing, economic efficiency calculations may only be secondary at this time. Profitability for similar tonnages can be expected thanks to the procedures used, which are also used in the industry. Currently, the emphasis must be placed on the efficient recycling and recovery of essential raw materials from these waste streams, as this can foster political independence and sustainably maintain the environment.

6.2 Recommendations

During sample preparation, aluminum electrodes were dissolved using a selective alkaline leach of NaOH. When the NaOH leach filtrate was tested, it was shown to have a relatively high aluminum concentration. It is suggested that this solution be treated to recover the aluminum since the alkaline leach filtrate may be a significant source of exceptionally pure aluminum. This is important since metallic aluminum is currently the cathode electrode material of choice, therefore it will be necessary for procedures that use a similar sample preparation method in the future.

The amorphous structure of the lithium compound may be caused by impurities, an inappropriate pH of the solution during precipitation, or the environment, so it is advised to try precipitating the lithium compound in any other form, such as LiOH or Li_2SO_4. This was observed during the precipitation of the lithium carbonate, and it may be the problem that despite our best efforts we are unable to precipitate the lithium compound in the crystalline form. Other methods, such as solvent extraction or metal sieving, can also be used to remove metal. Additional work on the mixing of various acids could be done to attain the necessary leaching efficiency.

Appendix-1 Publications

The increasing energy storage demand for electric vehicles and renewable energy technologies, as well as environmental regulations demanding the reutilizing of LIBs. The issue of depleting resources, particularly Li, is a major issue. To lessen the environmental risks brought on by the mining of the metals and spent lithium-ion batteries, efforts should be done in the field of recycling lithium-ion batteries. To regain Li and $FePO_4$ from spent LFP lithium-ion batteries, an organic acid-based leaching approach has been developed in this work. This investigation used organic acids, such as acetic acid and succinic acid, as the leaching agents. In comparison to another organic acid, succinic acid has the highest leaching efficiency and the best leaching effects on the reaction system when used with an oxidizing agent. The leaching conditions were optimized by varying the acid concentration, solid-to-liquid ratio, and the concentration of the oxidizing agent. Under the optimal condition of the 1.5 M succinic acid, 4 vol % H_2O_2, 15 $g \cdot L^{-1}$ at 70 ℃ for 40 min Li and Al leaching efficiency is 98.7 % and 95.3 % respectively. However, the loss of Fe and P was only 6.5% and 4.3 %, respectively. The lithium carbonate was recovered using leachate. The suggested organic-based recycling strategy is environmentally benign and produces less secondary trash for the environment.

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