*Review*

# Lithium Iron Phosphate Battery Regeneration and Recycling: Techniques and Efficiency

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**Abstract:** This study investigates advanced strategies for r regenerating and recycling lithium iron phosphate ($LiFePO_4$, LFP) materials from spent lithium-ion batteries. Recovery techniques are categorized into direct regeneration, which restores positive electrode materials with high electrochemical performance, and recycling, which produces intermediate compounds such as lithium carbonate and iron phosphate. Additionally, resynthesis methods are explored to convert recovered precursors into high-quality LFP materials, ensuring their reuse in battery production. Innovative approaches, including carbothermic reduction, doping, and hydrothermal resynthesis, are highlighted for their ability to enhance material properties, improve energy efficiency, and maintain the olivine structure of LFP. Key advancements include the use of eco-friendly reagents, automation, and optimization strategies to reduce environmental impacts and costs. Regenerated and resynthesized positive electrodes demonstrated performance metrics comparable to or exceeding commercial LFP, showcasing their potential for widespread application. This work underscores the importance of closed-loop recycling systems and identifies pathways for scaling, improving economic feasibility, and minimizing the ecological footprint of the lithium-ion battery lifecycle.

**Keywords:** lithium iron phosphate; direct regeneration; recovery; resynthesis; recycling; spent lithium-ion battery

## 1. Introduction

Currently, the global community faces the pressing issue of climate change. In December 2015, the UN Paris Climate Agreement established a target to limit global warming to a maximum of 2 °C above pre-industrial levels, ideally keeping it within 1.5 °C [1]. Numerous countries have committed to achieving net-zero carbon emissions by the second half of the 21st century. Carbon dioxide is only one of the greenhouse gases that have intensified climate impact, largely due to the widespread use of fuel-powered vehicles [2]. Greenhouse gases in the atmosphere absorb part of the infrared radiation and re-emit it in all directions, including back to Earth's surface. This emphasizes the need for the development of environmentally friendly, renewable energy sources. However, solutions such as solar, hydroelectric, and wind power are not consistently reliable due to their dependence on weather conditions, while energy storage through lithium-ion batteries (LIBs) shows promise [3,4].

One potential solution to this issue is the shift to electric transportation, replacing fossil fuel-based vehicles. Many countries are advancing electric vehicle (EV) initiatives, with lithium-ion batteries as the primary power source due to the advantages of LIBs, such

as high specific energy, functionality across a range of temperatures, and fast charging capabilities [5,6]. It is also worth noting that lithium-ion batteries can be charged from renewable energy sources. For the efficient and safe charging of lithium-ion batteries from "green" energy, it is necessary to choose the components correctly—the batteries themselves, the BMS, the charge controller/inverter—and to ensure the correct operating conditions. If everything is performed correctly, it makes it possible to significantly save on electricity, increasing energy independence and reducing the negative impact on the environment. Modern electric vehicles use several types of lithium-ion batteries, differing in characteristics, lifespan, and cost. Although NCA and NMC batteries are the most popular in EV applications, Tesla shifted back to lithium iron phosphate (LFP) battery chemistry in 2022 [7], primarily due to the lower cost of LFP technology.

The rapid growth of electric transportation, however, raises important questions about recycling lithium-ion batteries, particularly with LFP positive electrode material due to finite resource availability and increasing environmental concerns associated with end-of-life LIB disposal. It is estimated that the volume of waste requiring recycling could reach 11 million tons by 2030, given the 3–6 year lifespan of high-capacity batteries [8,9]. It is notable that in 2020, LFP batteries accounted for 51.7% of all installed vehicle batteries in the Chinese market [10]. However, LFP recycling is less developed than NMC recycling, as NMC batteries offer higher energy density, and their contents of Ni, Co, Mn, and Li represent greater value as recycled and regenerated end-products than Fe. Additionally, LFP recycling involves certain challenges, such as lithium loss during hydrometallurgical and pyrometallurgical processes [11].

Although LFP recycling has received comparatively less attention, this does not diminish its importance, given the volume of decommissioned LFP batteries. Furthermore, LFP batteries have some notable differences from NCM batteries: LFP offers robust safety characteristics, partly due to its olivine structure, which provides good thermal stability, unlike the layered structure of NCM batteries [12]. Nonetheless, recent recycling efforts have focused more on NCM and LTO positive electrode materials [13–15]. Lithium iron phosphate batteries contain a higher proportion of electrolytes compared to NCM batteries, which presents additional challenges during the recycling process. The increased electrolyte content complicates the separation and recovery of valuable components and can lead to higher volumes of hazardous waste, thus impacting the overall efficiency and environmental sustainability of the recycling process. Electrolytes in lithium-ion batteries, including LFP types, typically consist of a lithium salt, such as lithium hexafluorophosphate ($LiPF_6$), dissolved in a mixture of organic solvents (e.g., ethylene carbonate, diethyl carbonate). These organic electrolytes are flammable and pose safety risks, such as fire and explosion, during both the use and recycling of batteries. In the recycling process, the handling of these electrolytes requires careful management to prevent environmental contamination and ensure worker safety. The approximate composition of LFP battery components by percentage is as follows: positive electrode material (LFP): 30–40%, electrolyte: 15–25%, separator: 5–10%, negative electrode material: 15–25%, casing and other components: 10–15%.

In contrast, NMC batteries typically have a lower electrolyte content, which simplifies the recycling process to some extent. Given these differences, it is crucial to develop specialized recycling methods for LFP batteries that effectively manage the higher electrolyte content. These methods should prioritize the safe removal and neutralization of electrolytes to mitigate environmental hazards and improve the overall efficiency of the recycling process [16,17].

Unlike NMC batteries, lithium iron phosphate LFP batteries have a lower intrinsic value due to the absence of expensive metals like cobalt and nickel. This lower value significantly influences the driving forces and focus of LFP recycling efforts.

In NMC battery recycling, the recovery of high-value metals such as cobalt and nickel is a primary economic driver. These metals are scarce and expensive, making their recovery not only economically viable but also critical for resource sustainability. Consequently, the recycling processes for NMC batteries are designed to maximize the recovery of these valuable metals, often justifying the costs associated with complex and energy-intensive recycling technologies.

In contrast, the economic incentive for recycling LFP batteries is less driven by the value of recovered materials. Instead, the focus shifts toward environmental sustainability, regulatory compliance, and the efficient management of end-of-life battery waste. The primary materials recovered from LFP batteries, such as lithium and iron phosphate, have lower market values. Therefore, the recycling processes for LFP batteries must be cost-effective and efficient to justify their implementation. This fundamental difference necessitates a distinct approach in LFP recycling, emphasizing the development of economically sustainable methods that minimize costs while achieving high material recovery rates [18–21].

Therefore, this paper aims to direct our research towards a comprehensive review and systematization of methods for the recycling and regeneration of LFP positive electrode materials, and should thoroughly discuss these differences, highlighting the challenges and opportunities in LFP recycling. An important aspect of the novelty of our article is the unique approach to categorizing existing methods for recycling lithium iron phosphate (LFP) batteries based on the type of final products obtained. While some methods focus on a closed-loop system that restores the LFP structure using direct regeneration approach, other processes aim at extracting decomposition products of this olivine structure, such as lithium carbonate or iron phosphate, which are then used in other processes. Additionally, these products may be used in the following processes of LFP resynthesis. This categorization allows for a deeper analysis of each method's efficiency and sustainability. From our point of view, our research emphasizes the importance of distinguishing these methods to understand their role in the regeneration and recycling approaches of spent LFP batteries.

## 2. Lithium-Ion Battery, LFP Structure and Its Degradation

A lithium-ion battery (LIB) consists of four main components: the positive electrode, negative electrode, electrolyte, and separator.

- Positive electrode: Typically made from lithium oxides, such as lithium cobalt oxide ($LiCoO_2$), lithium iron phosphate ($LiFePO_4$), lithium manganese oxide ($LiMn_2O_4$), lithium nickel cobalt aluminum oxide (NCA, $LiNiCoAlO_2$), or lithium nickel manganese cobalt oxide (NCM or NMC, $LiNiMnCoO_2$). During charging, the positive electrode releases lithium ions, which it then reabsorbs during discharge.
- Negative electrode: Usually made from graphite or other carbon-based materials, except in lithium-titanate (LTO) batteries. During discharge, lithium ions move from the negative electrode to the positive electrode.
- Electrolyte: A substance containing lithium ions that facilitates ion transfer between the negative electrode and positive electrode. It is typically an organic solvent, such as a lithium salt dissolved in carbonates.
- Separator: A thin porous material positioned between the negative electrode and positive electrode. It prevents electrode contact and short-circuiting while allowing lithium ions to pass through. Separator materials: polyethylene (PE) and polypropylene (PP) are the most common polymer materials for the manufacture of separators. Multilayer

structures are often used, such as PP/PE/PP. Cellulose, polyamide, ceramic coatings, or gel polymers are found as alternatives, less frequently in mass production, but are in demand in specialized solutions (for example, to increase thermal stability or improve electrolyte properties).

- Current collectors in lithium-ion batteries (Li-ion) are important components that ensure the collection and transfer of charge from the material of the active electrode to the external circuit. Current collectors are usually made of metals that have high permeability, corrosion resistance, and chemical stability in the electrolyte environment. In lithium-iron-phosphate (LFP) batteries, as in most other lithium-ion systems, two basic metals are usually used as current collectors (metal foil serving as a "base" for the active material). Aluminum (Al) is used for the positive electrode (in this case, it is a layer of $LiFePO_4$ active material), and copper (Cu) for the negative electrode (most often graphite-based).

In terms of crystal structure, LIB positive electrodes can exhibit layered structures (e.g., $LiCoO_2$) or spinel structures (e.g., $LiMn_2O_4$) [22]. In 1997, a new olivine structure ($LiFePO_4$) was introduced [23]. $LiFePO_4$ operates at a lower voltage compared to traditional LCO-type lithium-ion batteries, with a fully charged voltage of about 3.65 V per cell and a fully discharged voltage of around 2.5 V per cell, which affects its energy density. However, $LiFePO_4$ batteries are safer due to their reduced risk of thermal runaway. Notably, replacing iron with other trivalent transition metal ions could result in new materials with voltages exceeding 4 V while retaining the thermal stability typical of phosphate-based positive electrode materials [24,25].

The properties of $LiFePO_4$ also include durability and stable discharge voltage (around 3.2 V). Batteries based on $LiFePO_4$ can withstand thousands of charge–discharge cycles with minimal capacity loss. However, after approximately 3000 cycles, battery capacity decreases to around 80% of its nominal value, indicating battery degradation [26].

*Degradation Aspects and Mechanisms of LFP Battery Failure*

The primary factor in battery capacity decline is the loss of active lithium. As charge–discharge cycles progress, lithium-ion loss accumulates, primarily due to positive electrode degradation. The crystal structure of the positive electrode gradually loses its ability to retain lithium ions, with iron ions potentially occupying the vacant sites, creating antisite defects [27]. The main mechanism of lithium loss, however, is associated with the formation of a solid electrolyte interphase (SEI) on the negative electrode, particularly in the early stages of battery use [28]. SEI formation consumes lithium ions, permanently trapping some within the layer. Over time, the SEI breaks down and reforms, further depleting lithium and increasing internal resistance [29].

Additionally, metallic lithium deposition can lead to dendrite formation, potentially puncturing the separator and causing short circuits [30]. Electrolyte degradation contributes to capacity loss by forming insulating layers on the positive electrode surface, reducing lithium availability and capacity. During extensive cycling, lithium ions shuttle between the negative electrode and positive electrode, causing irreversible lithium depletion, electrode–electrolyte interface formation, and iron phosphate phase development, ultimately leading to capacity reduction [31,32].

Despite these losses, the strong P-O bond in the LFP structure helps maintain its integrity [33–35]. This resilience highlights the potential for direct LFP regeneration. Successful regeneration depends on effectively replenishing lithium, typically sourced from compounds such as $Li_2CO_3$, LiOH, lithium halides, and polycyclic aryl-lithium organic compounds.

Figure 1 demonstrates a scheme of the degradation process of the lithium iron phosphate (LFP) positive electrode material. Figure 1a shows the initial crystalline structure of LFP. In this structure, lithium (Li) ions are located in the channels between the octahedra formed by oxygen (O), iron (Fe), and phosphorus (P) atoms. This structure stably holds lithium during cycling. Figure 1b displays the structure after a certain number of cycles, illustrating the following changes that occurred due to degradation:



(**a**)  (**b**)
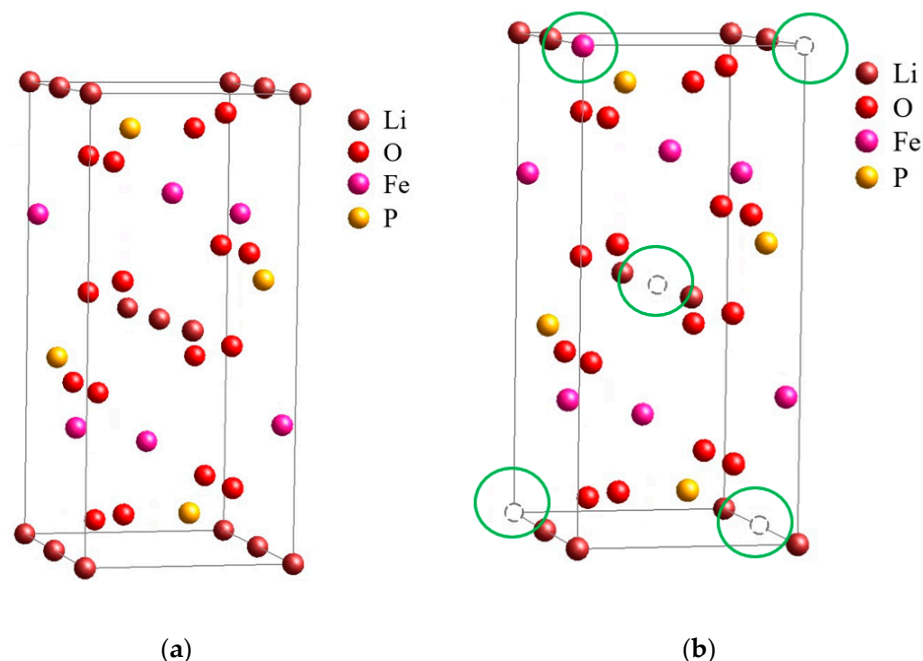
**Figure 1.** The scheme of LFP degradation process, (**a**) LFP before degradation, (**b**) LFP after degradation.

Anti-site defects: The diagram shows iron (Fe) ions occupying the positions of lithium (Li) ions, indicated by green circles. This is one of the main degradation mechanisms, as such defects hinder lithium movement, reducing the material's capacity.

Oxygen release: Some oxygen atoms may shift or even leave the structure, which also contributes to the breakdown of the crystalline lattice.

The loss of lithium: In the figure, this can be shown by a decrease in the number of lithium ions in the channels of the structure or their disappearance from the material, which also contributes to the degradation of the electrochemical properties of LFP.

These changes in the crystalline structure lead to a decrease in the material's electrochemical activity and capacity, which is typical for degradation processes in LFP batteries.

## 3. Pretreatment

To improve the efficiency of recovery, ensure the purity of the resultant materials, and reduce energy consumption and overall costs during the regeneration and recycling processes of lithium iron phosphate (LFP), it is critically important to implement an effective procedure for the pretreatment of spent lithium-ion batteries (LIBs). Typically, the primary stages of pretreatment encompass deactivation, disintegration, and the separation of the desired materials [36–38]. Currently, at the lab scale, manual separation methods have demonstrated high efficiency; nevertheless, it is hardly sufficient to apply to industrial-scale processing [39]. One of the main problems in large-scale recycling is how to sort the various types of chemical compositions of EoL batteries without dismantling. Mostly, the industrial recycling processes include sorting based on the technical documentation provided by the last usage of the batteries. Thus, mechanical treatments such as milling, grinding, and shredding in automatic and semi-automatic installations are preferably used in order to

obtain the maximum efficiency. As the processes of disintegration and dismantling of spent LIBs may cause overheating, combustion, and explosion due to the residual energy, it is highly important to discharge and deactivate the batteries beforehand [40–42].

Commonly used deactivation and discharging approaches can be divided into four types: thermal deactivation [43,44], liquid nitrogen freezing [45], solid conductors [46,47], and electrolytic discharging [48–50]. The thermal and liquid nitrogen methods are often used in industrial settings due to their simplicity [51,52]. Recently, the recycling companies Umicore and Retriev started to integrate the liquid nitrogen technique into their process flows. The notably low cryogenic temperatures, ranging from −175 to −200 °C, achievable through the use of liquid nitrogen, may result in the electrolytes freezing. Consequently, this can lead to battery deactivation, as lithium-ion batteries may become non-conductive and metallic lithium may also become inactive [38]. Thermal deactivation was successfully integrated into the Accurec process [53]. This procedure entails the application of vacuum heating at temperatures not exceeding 250 °C to spent lithium-ion batteries, which effectively facilitates the removal of organic components, such as electrolytes, plastic films, and binders, through a series of thermal decomposition reactions. And as a result, without the electrolytes, it becomes impossible to discharge cells.

The utilization of various solid conductors, such as copper and graphite powder, may result in the induction of external short circuits, subsequently leading to battery discharge. However, this path exhibits a significant drawback in terms of rapid heat generation. To resist this undesirable effect, it is essential to integrate some cooling equipment. One scientific group have put forth a methodology for LIB deactivation through the incorporation of graphite powder to discharge the batteries. Additionally, copper has been utilized as a discharge medium [46].

Extensive research has been conducted on electrolyte solution usage in battery deactivation, mostly with sodium chloride due to its low cost and widespread availability. A comparative evaluation of various salt solutions' effectiveness was conducted by a research group [46]. NaCl, $MnSO_4$, and $FeSO_4$ were analyzed based on their environmental influence and discharge efficiency of spent 18650 batteries. The findings indicate that both NaCl and $FeSO_4$ solutions demonstrated commendable discharge efficiency; however, the process utilizing the $FeSO_4$ solution exhibited greater environmental sustainability. This superiority is attributed to the fact that discharging with NaCl solution can lead to the emission of organic gases, particularly short-chain hydrocarbon compounds containing up to four carbon atoms.

Battery disintegration represents the next stage in the pretreatment process for lithium-ion batteries (LIBs). As noted previously, in laboratory settings, the liberation of target materials is predominantly achieved through manual dismantling due to its simplicity and the high purity of the resulting powders. However, this method presents a significant drawback; the generation of hydrofluoric acid (HF) vapor occurs when lithium hexafluorophosphate ($LiPF_6$) reacts with air, posing potential health risks [36,54].

In industrial applications, dismantling is typically conducted through a series of crushing and sieving procedures to obtain separated fractions of LIB scrap. Based on the physical properties of LIB components, such as magnetic characteristics, wettability, and density, further separation is achievable through techniques such as gravity separation, pyrolysis, magnetic separation, and flotation [55,56]. Following crushing, the shredded particles from aluminum (Al) and copper (Cu) foils form coarse particles, while the "black mass"—a term for the fine particulate matter consisting primarily of active materials—can be separated by sieving [57]. Additionally, due to the hydrophilic properties of the positive electrode material and the hydrophobic nature of the graphite negative electrode, these

materials can be separated effectively via flotation [58]. The schemes of both lab- and industrial-scale pretreatment approaches are presented in Figure 2.
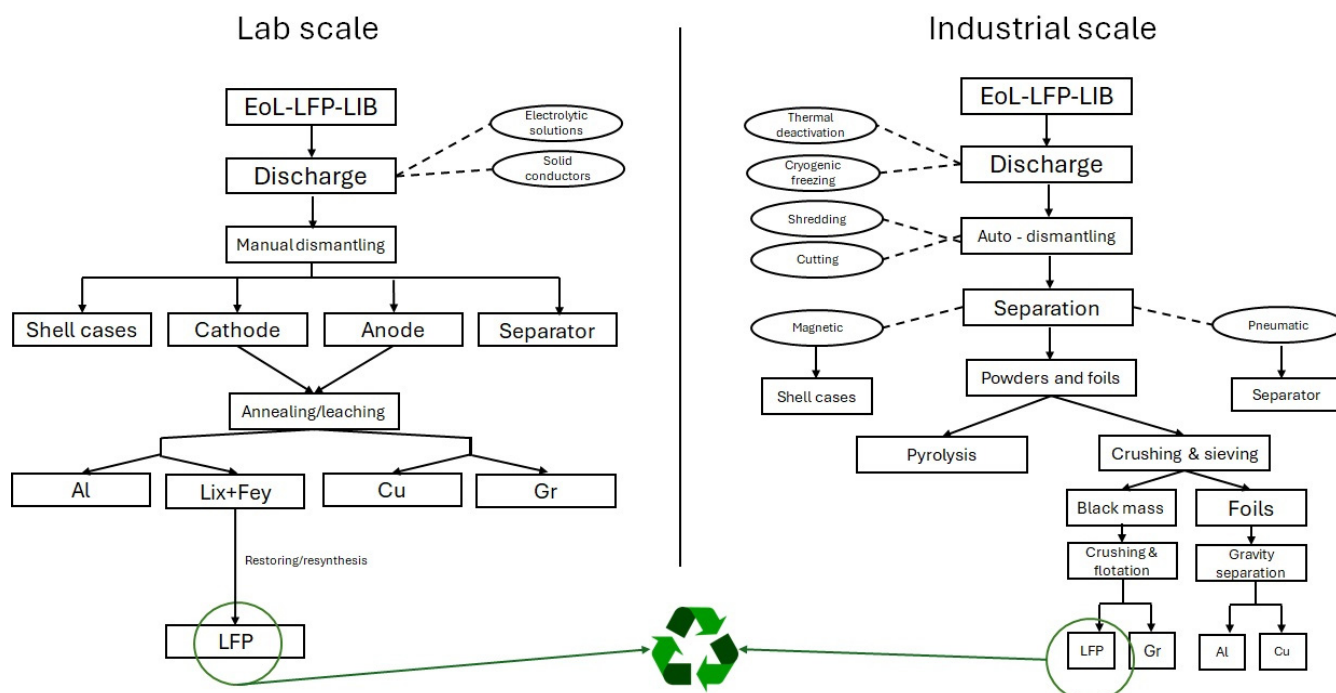


**Figure 2.** Scheme of the LIB pretreatment approaches.

The liberated positive electrode material, specifically lithium iron phosphate (LFP), undergoes various regeneration and recycling processes, which are discussed comprehensively in the subsequent sections. The direct regeneration approach encompasses methods that restore spent LFP material to its original state, making it suitable for reuse in LIBs. In contrast, the recycling approach is subdivided into two categories: the first involves technologies that recover various compounds and convert them into different useful materials, while the second includes technologies that produce new LFP material through intermediate processes and analyze its electrochemical properties.

## 4. Direct Regeneration

The direct regeneration of recovered LFP mass from retired batteries presents a sustainable strategy for restoring their electrochemical performance. The primary cause of LFP degradation is lithium depletion, which is effectively addressed through lithium replenishment. This approach reinserts lithium ions into the crystal lattice of spent LFP, thereby re-establishing their electrochemical functionality [59]. By circumventing labor-intensive processes—concentration, leaching, purification, precipitation, and resynthesis—lithium replenishment significantly streamlines regeneration, reducing both the energy consumption and processing time [60].

LFP regeneration relies on the precise incorporation of lithium compounds in carefully controlled stoichiometric ratios, with spent LFP serving as the raw material. A reductant is often introduced to create reducing conditions, facilitating the conversion of Fe(III) to Fe(II) and enhancing $Li^+$ reintegration while maintaining the structural stability of the LFP [61]. Regeneration methodologies are broadly categorized into solid-state, liquid-state, and electrochemical approaches, each offering distinct mechanisms for restoring electrochemical functionality.

The direct regeneration of LFP, akin to its synthesis, frequently involves various techniques such as surface design (e.g., carbon coating) and lattice substitution (e.g., doping).

In addition to serving as reductants, organic carbon sources also contribute to the formation of a highly uniform coating of carbon during direct regeneration, thereby enhancing conductivity. Furthermore, organic carbon helps alleviate problems such as uncontrolled growth and particle aggregation in LFP.

### 4.1. Solid-State Methods

The solid-phase approach utilizes LFP direct regeneration in elevated temperatures to sinter spent LFP with fresh lithium precursors in a reductive environment. This process promotes the reintegration of $Li^+$ ions in the lattice structure of lithium-iron phosphate at elevated temperatures, restoring its capacity and cycling properties. The presence of a reductant actively drives the reduction of Fe(III) to Fe(II) in the structural defects of LFP. To maintain charge balance, each Fe(III) ion reduced to Fe(II) requires the incorporation of a monovalent lithium ion ($Li^+$), which inserts into the lattice of the spent LFP. This effectively replenishes the lithium vacancies, thereby restoring the electrochemical performance of the material.

Lithium sources commonly employed for direct regeneration include $Li_2CO_3$, $CH_3COOLi$, $LiNO_3$, and LiOH [56–58]. Organic carbon sources such as glucose, ascorbic acid, and sucrose are also utilized. To further optimize electrochemical performance, doping with additional elements for lattice substitution, such as Mg, Ti, and N, may be incorporated [54,59,60]. Ideally, the LFP regeneration process is carried out in an inert or mildly reducing atmosphere (e.g., nitrogen, argon, hydrogen) to mitigate oxidation during the reaction, akin to the synthesis of new LFP via high-temperature solid-phase methods. There is more detailed information about some of the direct regeneration investigations below.

Lithium carbonate was utilized in Song and colleagues' investigation [62] as a lithium precursor, glucose served as both a reducing component and an organic carbon source, and carbon nanotubes were incorporated to modify the regenerated LFP surface, thereby decreasing the resistance and enhancing the diffusion of $Li^+$ for superior electrochemical performance. A mix consisting of 5% carbon nanotubes by weight, 15% glucose by weight, and 5% $Li_2CO_3$ by weight was combined with LFP waste using a 1:1 water–ethanol solution as a dispersant and subsequently processed via ball-milling. The mixture was then heated in a tube furnace in Ar atmosphere at elevated temperature for 2 h, followed by 650 °C for 12 h. The refurbished LFP achieved a discharge capacity of 155.47 mAh/g at 0.05 C, corresponding to 99% of the capacity of pristine LFP at just 33.7% of the production cost of new material. This underscores the economic efficiency and significant potential of this regeneration approach.

In turn, another science group [63] employed a solid-phase method for direct regeneration, incorporating copper doping simultaneously. $Li_2CO_3$ was utilized as a lithium precursor, 5% glucose as a reducing agent and a source of organic carbon, and $Cu(NO_3)_2 \cdot 2.5\,H_2O$ as an additive for alloying with copper, along with ethanol as a dispersant. The mixture was ground in a ball mill and dried, and then sintering was carried out at 350 °C for 2 h, followed by a second step at 650 °C for 12 h. The study revealed that copper doping enhances the physical and conductive properties of the regenerated material, expands the paths for lithium-ion diffusion, and consequently significantly improves the electrochemical performance of the regenerated LFP positive electrode. The regenerated material demonstrated a capacity of 160.15 mAh/g at a current rate of 0.05 C, representing 97.65% of the capacity of new positive electrode material. Remarkably, even after 1000 cycles at a 1 C rate, the regenerated LFP retained 81.19% of its initial performance, underscoring its durability and potential for long-term application.

Liang et al. [59] conducted a study on the elemental speciation of waste LFP. They supplemented the waste with salts of various elements, including lithium, iron, and phos-

phor in order to restore the LFP and achieve a balanced 1:1:1 molar ratio of these elements. The resulting LFP demonstrated a capacity of 139 mAh/g and an improved ion diffusion coefficient.

Furthermore, Liu et al. [64] investigated the simultaneous restoration of both lithium and iron-phosphate in LFP by doping with vanadium during annealing at elevated temperatures. They used $Li_2CO_3$, $V_2O_5$, $NH_4H_2PO_4$, and glucose in a specific stoichiometric ratio to achieve V-doping. The restored LFP doped with 3 mol.% vanadium displayed a discharge capacity of 134.3 mAh/g after 200 cycles at a current density of 1 C, with a capacity retention of 99.1%. Under higher current densities of 2 C, 5 C, and 10 C, the corresponding discharge capacities were 134 mAh/g, 124.1 mAh/g, and 111.5 mAh/g, respectively.

Zou et al. [65] proposed a fabrication method for carbon-coated lithium iron phosphate (LFP), using recycled LFP as the precursor. The process incorporated 1 wt.% $Li_2CO_3$ as the lithium source, 30 wt.% ascorbic acid as a reductant and carbon-coating agent, a minor quantity of graphene for enhanced conductivity, and sodium dodecyl benzene sulfonate as a surfactant. The regenerated LFP demonstrated a remarkable specific capacity above 160 mAh/g at 0.1 C rate and retained approximately 80% of its initial capacity after 800 charge–discharge cycles at 1 C, highlighting its excellent electrochemical performance and long-term stability.

The solid-phase methods for LFP regeneration share significant similarities with the synthesis of new LFP. Both processes use pre-treated waste LFP, supplemented primarily lithium, with occasional additions of iron and phosphorus. The process involves the addition of a reducing agent and dispersant, followed by ball-milling. The mixture is then pre-sintered at 350–400 °C to eliminate moisture and volatile components and subsequently sintered at 650–700 °C to restore the LFP structure. While this process takes place, ions $Fe^{3+}$ are reduced to $Fe^{2+}$, while lithium ions replenish vacancies in the crystal lattice. To further enhance electrochemical performance, some studies incorporate elemental doping, which improves material properties without altering the core regeneration process.

Solid-phase methods present notable benefits, such as straightforward operation, minimal reagent consumption, cost-effectiveness, and suitability for large-scale applications. However, they face critical limitations in achieving a homogeneous distribution of lithium ions and in regulating particles' morphology, size and crystallinity. Furthermore, the requirement for sustained high temperatures leads to substantial energy consumption. These methods can also generate greenhouse gases and toxic emissions, contributing to environmental pollution [66–68].

### 4.2. Liquid-State Methods

The liquid-state direct regeneration of retired LFP entails immersing the spent LFP powder in a solution with a calculated lithium content and re-lithiating it under reducing conditions. The hydrothermal method is the most frequently used liquid-phase technique. After the reaction, crystallinity can be enhanced through annealing, typically performed at temperatures between 400 and 800 °C for 2 to 10 h, within an inert atmosphere [69]. Commonly used lithium sources are water-soluble compounds, such as LiOH, $CH_3COOLi$, and $Li_2SO_4$ [67,70,71]. Reagents such as sodium sulphite, hydrogen peroxide, ethanol, malic acid, ascorbic acid, and tartaric acid are widely employed as reducing agents in the liquid-state approach [69,72–75].

Some representative examples of liquid state methods are described in more detail below.

Yang et al. [71] utilized $Li_2SO_4$ as the source of Li and $Na_2SO_3$ as the reduce component. They combined these with waste LFP, subjected the mixture to high-pressure conditions at 200 °C for 6 h, and subsequently dried the product to obtain restored LFP. The regenerated powder displayed an exhibited capacity of 145.1 mAh/g at 0.1 C current density, 142.7

at 0.2 C, 139.9 at 0.5 C, 135.9 at 1 C, 129.3 at 2 C, and 115.0 mAh/g at 5 C. Notably, after 100 cycles at 1 C, the retained capacity exceeded 99%, indicating exceptional restoration efficiency and robust cycling stability.

Jing et al. [74] employed $Li_2SO_4 \cdot H_2O$ as the Li precursor and $N_2H_4 \cdot H_2O$ as the reducing instrument. They combined waste LFP with a $Li_2SO_4 \cdot H_2O$ solution and $N_2H_4 \cdot H_2O$, stirred the mixture for 10 min, and then subjected it to high-pressure conditions at 200 °C for 3 h. The restored LFP demonstrated capacity values varying from 146.2 to 128.2 mAh/g at 0.2 C and at 5 C, respectively. Notably, its capacity retention reached 98.6% after 200 cycles at 1 C, highlighting its outstanding stability and superior electrochemical performance.

Jiang et al. [67] proposed a microwave-assisted hydrothermal technique for restoring LFP. Lithium hydroxide and L-ascorbic acid were combined with LFP material in a ratio of 1:1:0.5, mixed for one hour, and processed in a sealed microwave reactor. To enhance conductivity, graphene was incorporated using PDDA-assisted electrostatic self-assembly. The LFP/MWrGO composite, containing 5 wt% graphene, achieved an electrochemical output of 161.4 mAh/g and maintained 94.9% retention after 100 cycles at 0.2 C, showcasing excellent durability and improved material properties.

Similarly, Chen et al. [68] employed a high-pressure synthesis technique involving $LiOH \cdot H_2O$ and tartaric acid to restore LFP material. A blend of 3 g of LFP, 20 mL of Li hydroxide solution, and 30 mL of tartaric acid solution was subjected to high-pressure treatment at 200 °C for 3 h. The treated material was then filtered, dried, and annealed in an inert argon atmosphere at 700 °C for 2 h. The restored material demonstrated a discharge output of 145.92 mAh/g at 1 C and retained 99.1% of its capacity after 200 cycles. At higher rates of 2 C and 5 C, it exhibited retention rates of 96.3% and 94.7%, respectively, underscoring its stability and high-rate capabilities.

Compared to solid-state methods, the liquid-state direct regeneration of LFP via various hydrothermal techniques generally yields superior morphology and enhanced electrochemical performance. This improvement stems from the uniform distribution and free diffusion of lithium ions in the solution, which mitigates the lithium supplementation imbalances often encountered in solid-state processes. Additionally, unreacted lithium sources can be recovered, as they do not interact with the reducing agent. Despite these advantages, liquid-state methods necessitate the use of sealed, high-temperature, high-pressure equipment and require the waste LFP to be of high purity. Furthermore, challenges related to the toxicity and cost of certain reducing agents remain unresolved.

### 4.3. Electrochemical Methods

The direct regeneration of $LiFePO_4$ via electrochemical methods is similar to the discharge procedure of LFP positive electrode, with the key difference being the need for an extra power supply from an external circuit. Unlike batteries, electrochemical approaches typically employ cost-effective and ecological solutions as the electrolytes, replacing organic components. This process often necessitates the use of specific electrodes and electrolytic cells in research settings. Compared to the previously discussed methods, the electrochemical approach is less studied due to its complexity. The following examples illustrate some distinctive features of this method.

In research by Shiyu Zhou et al. [76], a specially engineered H-type electrolytic cell was employed, incorporating an anion exchange membrane that effectively prevents cation migration while ensuring unrestricted anion mobility. They employed 1 M solution of $Li_2SO_4$ as the electrode medium on the positive electrode side, dispersing positive electrode waste in the electrolyte on the negative electrode side under continuous agitation. Graphite felt served as the positive electrode, and a zinc plate acted as the negative electrode in the 0.1 M $ZnSO_4$ electrolyte. Upon connection to an external circuit, zinc from the negative

electrode plate oxidized to divalent zinc ions, while lithium ions from the positive electrode integrated into the depleted LFP structure. Concurrently, Fe(III) ions within lithium vacancy defects were reduced to divalent ferrous ions, completing the electrochemical restoration of LFP. The regenerated LFP achieved optimal performance under a 5 mA current and 150% TIA, displaying an initial discharge capacity of 134.0 mAh/g at 1 C and maintaining an 85.5% capacity retention rate after 300 cycles.

Yang et al. [72] developed an in situ approach for the simultaneous extraction of lithium and to restore the LFP structure, leveraging innovative electrode materials. Both electrodes were made of waste LFP, with lithium detaching from the negative electrode, migrating through the electrolyte, and reintegrating into the positive electrode, effectively restoring its functionality. This method achieved a 92% lithium removal rate, high lithium utilization, and allowed for further recovery through hydrometallurgical processes. The process eliminates the need for additional lithium input, and the electrolyte remains reusable. The restored LFP demonstrated an initial discharge capacity of 136.5 mAh/g at 1 C and maintained 95.32% capacity retention after 300 cycles at 5 C. While clean and environmentally friendly, the method's complexity limits large-scale application, though it holds promise for future competitiveness amid rising environmental demands.

The direct regeneration of LFP from retired batteries is a sustainable approach to restore its electrochemical properties by replenishing lithium. This process simplifies regeneration by bypassing complex steps like leaching and purification, reducing time, cost, and energy usage. Various methods such as solid-state, liquid-state, and electrochemical approaches have been developed, each with unique benefits and challenges. Solid-state methods offer simplicity and cost-efficiency but face issues with uniform lithium distribution and high energy consumption. Liquid-state methods provide better morphology and performance but require high-purity LFP and complex equipment. Electrochemical methods, while less studied due to complexity, show promise with eco-friendly and efficient lithium utilization. These advances in direct regeneration hold significant potential for sustainable battery recycling and environmental conservation. A comparative analysis of the direct regeneration methods is presented in Table 1.

**Table 1.** Comparative analysis of the direct regeneration methods.

| Method | Key Characteristics | Advantages | Challenges |
|---|---|---|---|
| Solid-state | High-temperature sintering with lithium sources and reducing agents under reducing conditions | Simple, cost-effective, suitable for large-scale production, enhanced with doping options | High energy consumption, non-uniform lithium distribution, potential toxic emissions |
| Liquid-state | Hydrothermal treatment with lithium-containing solutions under reducing conditions | Superior morphology, enhanced performance, uniform lithium distribution | High energy consumption, non-uniform lithium distribution, potential toxic emissions |
| Electrochemical | Utilizes electrochemical cells with external energy input, uses inorganic salt solutions as electrolytes | Eco-friendly, high lithium utilization, recyclable electrolytes, potential for clean regeneration | Complex operation, less studied, requires specialized equipment, not yet suitable for large-scale application |

## 5. Recycling

### 5.1. Material Recovery Methods

This section reviews various methodologies for recovering materials from spent LFP, focusing on processes that do not culminate in positive electrode material synthesis or final electrochemical testing. Despite this, these approaches provide foundational techniques

for the subsequent regeneration of lithium iron phosphate (LiFePO$_4$) positive electrodes, thereby contributing to the broader goal of creating a closed-loop recycling system for lithium-ion batteries.

### 5.1.1. Hydrometallurgy

In one study [77], an effective redox-based leaching process was employed, utilizing hydrochloric acid (HCl) and sodium hypochlorite (NaOCl) as the leaching agents. This process enabled the oxidation of Fe(II) ions to Fe(III), resulting in the formation of FePO$_4$. The leaching was conducted under mild conditions, offering significant advantages by achieving efficient metal dissolution at relatively low temperatures and in a short time frame. Structural analysis, including scanning electron microscopy (SEM), revealed that the olivine structure of the residual material remained intact, indicating minimal structural degradation. Lithium carbonate (Li$_2$CO$_3$) was subsequently precipitated using sodium carbonate, thus producing high-quality precursors for further positive electrode regeneration.

Another innovative approach was detailed [78], which employed a two-phase aqueous system incorporating ionic liquids for the selective separation of lithium and iron from leachates. The system, comprising tri-n-butyl tetradecyl phosphonium chloride and salting agents (HCl or NaCl), facilitated efficient metal extraction without the use of additional oxidizing agents. By adding an aqueous ammonia solution, iron was precipitated as Fe(OH)$_2$ and Fe(OH)$_3$, while lithium phosphate (Li$_3$PO$_4$) was recovered for subsequent reuse. The process demonstrated exceptional efficiency in separating and recovering both metals, underscoring its potential for industrial applications in LFP recycling.

Selective lithium extraction using a combination of formic acid and hydrogen peroxide (H$_2$O$_2$) was highlighted in [79]. This process involved two-stage lithium precipitation at controlled temperatures and pH levels, ultimately yielding high-purity lithium phosphate. Structural analysis via X-ray diffraction (XRD) confirmed the complete removal of lithium and the oxidation of Fe(II) to Fe(III). The study identified optimal conditions, such as a molar ratio of formic acid to lithium and a specific concentration of H$_2$O$_2$, which significantly enhanced leaching efficiency. Despite using formic acid in low concentrations, the method demonstrated substantial promise for sustainable recycling.

In [80], the proton circulation technique was introduced, employing monocarboxylic acids as both leaching agents and precipitants. The process relied on the proton exchange mechanism to achieve efficient lithium leaching and the precipitation of FePO$_4$. The study examined the relationship between acid structure, acidity constants, and leaching performance, concluding that acids with lower pKa values exhibited superior leaching capabilities. This stable and scalable method highlights a viable route for the regeneration of LFP precursors.

Finally, ref. [81] described acid-free methods involving iron(III) sulfate and hydrogen peroxide. Lithium carbonate was precipitated, and iron was recovered as hydroxides and phosphates. XRD analysis confirmed the oxidation of Fe(II) to Fe(III), and the method's eco-friendliness and efficiency highlight its potential for sustainable LFP processing.

### 5.1.2. Electrochemical Approach

The electro-oxidation method using the Fenton process was detailed in [82]. The electrochemical oxidation of Fe$^{2+}$ ions and subsequent lithium-ion release were facilitated by the in situ generation of hydroxyl radicals (OH$^-$). The influence of critical parameters, including pH, voltage, and carbon black modification, was examined, revealing that optimal conditions led to a 98% lithium leaching efficiency. The method's reliance on environmentally benign reagents and its high efficiency underscore its applicability for large-scale recycling.

In [83], an electrolysis system using sodium carbonate ($Na_2CO_3$) as the electrolyte demonstrated a highly efficient process for lithium extraction. Lithium ions were dissolved into the solution, leaving $FePO_4$ intact at the negative electrode. The process produced lithium carbonate, hydrogen gas, and sodium hydroxide as by-products, offering an acid-free and environmentally friendly alternative. The method achieved a 99% lithium extraction rate, verified through photoelectron spectroscopy, and highlighted the feasibility of industrial-scale adoption. The scheme is presented in Figure 3.
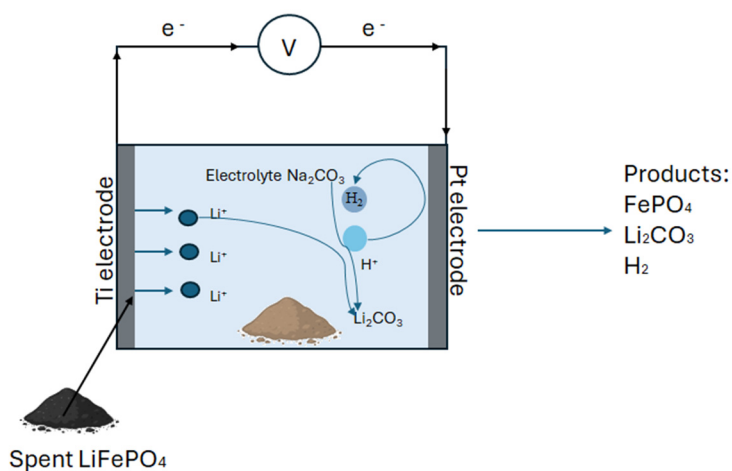


**Figure 3.** The scheme of the material recovery process [76].

A combined electrochemical and leaching method was explored in [84]. Using sulfuric acid as the leaching agent, lithium ions were efficiently extracted while $FePO_4$ remained as a stable by-product. The study demonstrated that variables such as pH and applied voltage significantly influenced reaction kinetics and overall leaching efficiency. The process achieved near-complete lithium recovery, with minimal environmental impact due to reduced by-product formation.

### 5.1.3. Pyrometallurgy

Thermal methods, including carbothermic reduction, were investigated in [85]. High-temperature roasting using sodium carbonate or sodium hydroxide facilitated the conversion of LFP into lithium phosphate and metallic iron. Magnetic separation and subsequent precipitation processes yielded high-purity lithium carbonate. The method demonstrated an extraction efficiency of 99.2%, supporting its industrial scalability and environmental sustainability.

Ammonium sulfate-assisted roasting was investigated in [86] as a selective recycling method for degraded $LiFePO_4$ positive electrodes. High-temperature roasting with ammonium sulfate facilitated the extraction of lithium by breaking down the $LiFePO_4$ structure. Subsequent processes yielded high-purity lithium products, demonstrating significant efficiency and selectivity. The method's rapid reaction time and minimal environmental impact highlight its potential for industrial scalability and sustainability in recycling lithium-ion batteries.

These studies collectively underscore significant advancements in the recovery of lithium and iron from LFP materials. The diverse methodologies, each with distinct advantages, offer a roadmap for achieving efficient, eco-friendly, and scalable recycling solutions for lithium-ion batteries, fostering a circular economy for critical battery components. The key factors are summarized in Table 2.

**Table 2.** Summary of methods for lithium and iron recycling from spent LFP positive electrodes.

| Method | Key Reagents | Process Overview | Products | Outcomes | Environmental Impact | Ref. |
|---|---|---|---|---|---|---|
| Redox Leaching | HCl, NaOCl | Oxidation of Fe(II) to Fe(III); leaching at low temperatures | $FePO_4$, $Li_2CO_3$ | High leaching efficiency; preservation of olivine structure | Mild conditions; minimal degradation | [77] |
| Ionic Liquid Extraction | [P44414]Cl, HCl/NaCl, $NH_3$ | Two-phase system for selective metal separation; Fe precipitation | $Li_3PO_4$, $Fe(OH)_2$, $Fe(OH)_3$ | High selectivity for Li and Fe | No oxidizers; eco-friendly separation | [78] |
| Acid and Oxidizer Leaching | HCOOH, $H_2O_2$ | Two-stage Li precipitation; oxidation of $Fe^{2+}$ | $Li_3PO_4$, $FePO_4$ | Optimized leaching conditions; high purity | Low formic acid usage; eco-friendly | [73] |
| Proton Circulation | Monocarboxylic acids | Leaching Via proton exchange; $FePO_4$ precipitation | $Li_3PO_4$, $FePO_4$ | Stable, scalable method | Acid-based; stable recycling method | [80] |
| Acid-Free Leaching | $Fe_2(SO_4)_3$, $H_2O_2$ | $Fe^{3+}$ and Li leaching; NaOH precipitation | $FePO_4$, $Li_2CO_3$ | High Fe oxidation; lithium recovery | No harmful by-products | [81] |
| Electro-oxidation (Fenton) | $H_2O_2$, $OH^-$ | $Fe^{2+}$ oxidation; Li release Via hydroxyl radicals | $FePO_4$, $Li^+$ | 98% lithium leaching | Mild reagents; low waste | [76] |
| Electrolysis | $Na_2CO_3$ | Li extraction Via negative electrode oxidation; $FePO_4$ retention | $Li_2CO_3$, $H_2$, NaOH | 99% leaching efficiency | Acid-free; eco-friendly | [83] |
| Electrochemical and Leaching | $H_2SO_4$ | Negative electrode oxidation; $FePO_4$ as by-product | $FePO_4$, $Li^+$ | Near-complete Li recovery | Minimal by-products | [84]. |
| Carbothermic Reduction | $Na_2CO_3$/NaOH, C | High-temperature roasting; Fe reduction | $Li_3PO_4$, Fe | 99.2% efficiency | Scalable; low carbon use | [79] |
| Pyrometallurgy | $(NH_4)_2SO_4$ | Firing under oxygen or vacuum; $FePO_4$, Li leaching | $FePO_4$, $Li(NH_4)SO_4$ | Rapid, simple process | Few reagents; suitable for industry | [80] |

The reviewed methods for recovering materials from spent LFP batteries offer various advantages and challenges. Hydrometallurgical methods are efficient under mild conditions, have high selectivity, are easily scalable, and environmentally friendly. On the other hand, this approach requires precise control over reactions and parameters, complex handling, and dependency on specific conditions. In turn, electrochemical methods are also environmentally friendly, with high lithium extraction rates, but need careful optimization for scalability. Pyrometallurgy offers high extraction efficiency and scalability methods, but has strong drawbacks, such as high energy consumption and dependence on specific oxidizing agents. Each method contributes to sustainable, closed-loop recycling processes for lithium-ion batteries. Hydrometallurgical methods are versatile, pyrometallurgical approaches are scalable, and electrochemical methods offer eco-friendly alternatives, all supporting a circular economy for battery components.

### 5.2. LFP Resynthesis Methods

The resynthesis and regeneration of lithium iron phosphate (LiFePO$_4$) positive electrodes have garnered significant attention due to the increasing demand for sustainable energy storage solutions. Recent studies have focused on innovative methodologies for the regeneration of LiFePO$_4$/C (carbon-coated) materials and restoring of LiFePO$_4$, emphasizing environmentally friendly processes and enhanced electrochemical performance. This section summarizes key findings from various studies, highlighting their contributions to closed-loop regeneration, improved material properties, and practical scalability. For better understanding, all of the discussed methodologies are divided into pyrometallurgy, hydrometallurgy and solvometallurgy categories.

#### 5.2.1. Pyrometallurgy

Doucheng Bian and colleagues [87] investigated a carbothermic reduction method to resynthesize LiFePO$_4$/C from FePO$_4$·2H$_2$O microflowers. The microflowers were synthesized through an intermediate process involving the dissolution of LiFePO$_4$ in phosphoric acid, followed by filtration and drying. Lithium dihydrogen phosphate (LiH$_2$PO$_4$) was extracted using ethanol rinsing and subsequent drying at 80 °C. The resynthesized material was mixed with acetylene black and polyvinylidene fluoride (PVDF) to fabricate electrodes. X-ray diffraction (XRD) patterns revealed sharp peaks characteristic of the olivine structure without any detectable carbon peaks, confirming the structural integrity of LiFePO$_4$ and the absence of carbon-related interference. Electrochemical testing demonstrated a capacity retention of 93.7% at 0.1 C relative to theoretical values, indicating high cyclic stability. This highlights the viability of carbothermic reduction for producing high-performance LiFePO$_4$/C materials.

Godong Wen et al. [88] examined oxidative roasting's role in enhancing lithium and iron leaching. The process was optimized at 500 °C, where lithium extraction exceeded 99%, while graphite oxidation was minimal. Sintering temperatures around 800 °C were found to be effective for graphite removal but risked sintering Li$_3$Fe$_2$(PO$_4$)$_3$. The study emphasized maintaining a balance between temperature and reaction kinetics to maximize material recovery.

The following paper [89] studied the effect of roasting by sulfation with the addition of sodium salt on the further leaching of Li and Fe from spent LFP material in order to further regenerate the positive electrode material. The mixture of LFP/C and NaHSO$_4$·H$_2$O was mixed in a planetary mill and heated at temperatures from 500 °C to 700 °C in an oxygen atmosphere. X-ray diffraction analysis of annealed material at 500–700 °C demonstrated that all products consisted of lithium sodium sulfate (LiNaSO$_4$), iron phosphate (FePO$_4$), and iron oxide (Fe$_2$O$_3$), and the optimal temperature for sintering was 600 °C. During further leaching, it was found that an increase in the addition of NaHSO$_4$·H$_2$O in annealing leads to greater leaching of Li$^+$ ions. The addition of a Na$_3$PO$_4$ solution makes it possible to obtain precipitated lithium. The reconstituted white powder in the form of Li$_3$PO$_4$ fully complies with the standards, which has been proven by the XRD study. Leachate residues consist mainly of FePO$_4$ and Fe$_2$O$_3$, which are used to produce FePO$_4$. Positive electrode material was obtained from recycled Li$_3$PO$_4$ and FePO$_4$, and X-ray diffraction images met the standards for positive electrode material. The discharge specific capacity of the obtained R-LFP material was 162.25 mAh/g at a current density of 0.1 C, and the sample was also tested at higher current densities and showed good results. When the current was restored to 0.1 C, the capacity was almost equal to the original one. As a result, we can say that the article describes an eco-friendly method with good practical results.

5.2.2. Hydrometallurgy

A novel hydrometallurgical route [90] for synthesizing $FePO_4 \cdot 2H_2O$ involved leaching iron phosphate residues with phosphoric acid ($H_3PO_4$) without the need for alkali. This process eliminates wastewater discharge, enhancing its environmental sustainability. The positive electrode material produced via carbothermic reduction exhibited a discharge capacity of 157.6 mAh/g at 0.1 C and maintained 100% capacity retention over 100 cycles at 1 C. The combination of high performance and eco-friendliness positions this method as a promising candidate for industrial adoption. The leaching reaction is presented in Equation (1).

$$3LiFePO_4 + 2H_3PO_4 + 3H_2O_2 = 2Li_3PO_4 + 2FePO_4 \cdot 2H_2O \tag{1}$$
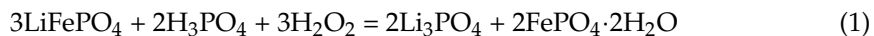
In another approach [91], $LiFePO_4$ was subjected to leaching in a buffered solution containing $NaH_2PO_4$ and $H_2O_2$. The buffering action stabilized the solution, enabling efficient Li-ion extraction without compromising the olivine structure. $Li_3PO_4$ was subsequently crystallized via evaporation, and the solution was reused by replenishing phosphoric acid. The resulting RLFP material, synthesized through grinding, calcination, and sintering, demonstrated superior initial specific capacities and high retention (99.2% after 200 cycles at 0.5 C). This closed-loop recycling approach underscores the potential for resource-efficient battery regeneration. The leaching reaction is presented in Equation (2).

$$LiFePO_4 + 3NaH_2PO_4 + 2H_2O_2 = Li_3PO_4 + 3Na_3PO_4 + FePO_4 \cdot 2H_2O \tag{2}$$

In the previously discussed articles, phosphoric acid was used in the leaching process with various additions; now, let us consider a combination of organic and inorganic acids as a leaching solution using the example of phosphoric and oxalic acids. Mixed acid leaching using phosphoric acid ($H_3PO_4$) and oxalic acid ($H_2C_2O_4$) [92] provided an effective mechanism for Li and Fe extraction. Oxalic acid facilitated Fe(III) chelation, destabilizing the LFP structure and enabling precursor adjustment through lithium carbonate, iron(III) nitrate, and ammonium dihydrogen phosphate. Spray drying yielded well-crystallized LFP with an olivine Pnmb space group structure. Morphological analysis revealed spheroidal particles, which enhance lithium-ion diffusion, thereby improving electrochemical performance. The leaching reaction is presented in Equation (3). The scheme of the process is demonstrated in Figure 4.

$$LiFePO_4 + 3NaH_2PO_4 + 2H_2C_2O_4 = 3Li_3PO_4 + 3FeC_2O_4 + 3H_2O \tag{3}$$
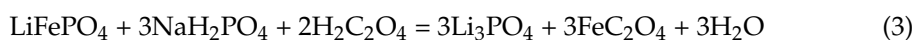


**Figure 4.** The scheme of the resynthesis process [86].

An innovative approach using weak organic acids such as methyl sulfonic acid (MSA) and p-toluene sulfonic acid (TSA) [93] achieved metal ion leaching at room temperature instead of the usual strong acids. MSA demonstrated superior efficiency in recovering $FePO_4 \cdot xH_2O$ and lithium carbonate. Despite lower initial capacities (93 mAh/g at 0.2 C),

stability during high-rate cycling was notable. The carbon content, however, exceeded commercial standards, suggesting that further refinement is needed for practical applications. The leaching reactions are presented in Equations (4) and (5).

$$LiFePO_4 + 3CH_3SO_3H + 2H_2O_2 = LiCH_3SO_3 + FePO_4 \cdot 2H_2O + O_2 \tag{4}$$

$$LiFePO_4 + CH_3C_6H_4SO_3H + 2H_2O_2 = LiC_7H_6SO_3H + FePO_4 \cdot 2H_2O + O_2 \tag{5}$$

In this investigation [94], lemon fruit juice—the juice of lemons, oranges, and apples—was used as a leaching solution. The efficiency of leaching with lemon juice and the effect of crystalline carbon on the resulting material were studied after leaching with lemon juice and 6% hydrogen peroxide; $FePO_4$ was obtained in the residue after filtration, and sodium hydroxide was added to the remaining solution to remove metals. Next, sodium carbonate was added to the purified lithium solution, mixed, and heated, and lithium carbonate was obtained. Regenerated LFP material was obtained from the obtained substances by adding 20% glucose as a carbon source and calcining in an argon atmosphere. Iron phosphate was used as a precursor, which was obtained after 5–7 h of annealing at 700 °C; this was necessary to remove crystalline carbon and obtain a pure powder. The restored lithium cell showed the results of a capacity of 155.3 at 0.1 C and a capacity retention of 98.30% after 100 cycles at 1 C. This technology can be attributed to green chemistry because it does not use strong inorganic acids; in turn, theoretically, it is possible to prepare solutions from waste from food enterprises to produce juices. The leaching reactions are presented in Equations (6) and (7). The scheme is presented in Figure 5.
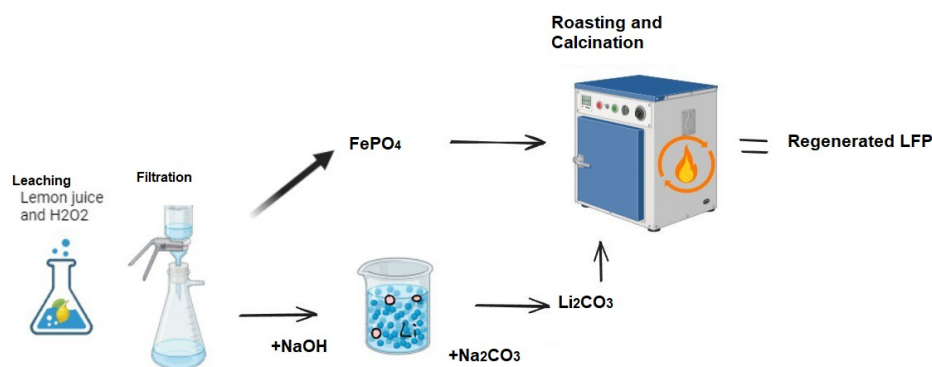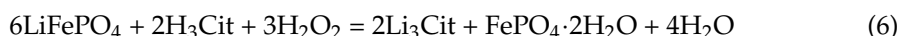
$$6LiFePO_4 + 2H_3Cit + 3H_2O_2 = 2Li_3Cit + FePO_4 \cdot 2H_2O + 4H_2O \tag{6}$$

$$3LiFePO_4 + 3H_3Cit = 2Li_3Cit + Fe_3(Cit)_2 + Li_3Cit + 3H_3PO_4 \tag{7}$$



**Figure 5.** The scheme of the resynthesis process [88].

In the study [86], the leaching of retired LFP powder was carried out in a solution of ammonium persulfate; the solution was filtered and dried, and $FePO_4$ was obtained. When the solution heated after the previous leaching was heated and saturated sodium carbonate was added, a powder precipitates, and by filtering and drying they obtained lithium carbonate. Glucose was added as a reducing agent and alcohol was added at the ball mill stage, and by mixing lithium carbonate and iron phosphate, carbothermic reduction was performed. The morphology of the particles and the XRD peaks of the obtained material correspond to $LiFePO_4$ with high crystallinity. It is noted that the application of a carbon coating improves and increases the specific charging capacity of the sample. For example, the obtained specific discharge capacity of LFP-G12 at 0.1 C is 161.9 mAh g$^{-1}$. With a

mass fraction of the carbon coating equal to 12% by weight, the sample presents the best electrochemical properties. The leaching reaction is presented in Equation (8).

$$2LiFePO_4 + 3(NH_4)S_2O_8 + 6H_2O = 2Li_2SO_4 + 2Fe_2(SO_4)_3 + 4(NH_4)_3SO_4 \tag{8}$$

5.2.3. Solvometallurgy

In the study [95], a new technology was proposed using a new carbon source and a polyvinyl acetate alcoholysis reaction. A mixture of a carbon source (PVAc), $Li_2CO_3$, $FeC_2O_4$, and $NH_4H_2PO_4$ was dispersed in a solution containing methanol and ammonia water; then, the mixture was sintered for the resynthesis of the LFP material. A part of the polyvinyl acetate undergoes an alcoholysis reaction during high-temperature regeneration under the action of methanol and an alkaline medium. Methanol and ammonia water evaporate during sintering, which does not lead to the appearance of impurities. Next, a positive electrode was manufactured and studied, the electrochemical properties of which turned out to be very encouraging. Discharge capacities of 163.2, 154.8, 142.1, 129, 116.6, and 94.6 mAh·g$^{-1}$ were obtained at 0.1 C, 0.2 C, 0.5 C, 1 C, 2 C, and 5 C, respectively. The method is simple in its application, but the required amount of PVAc needs to be clarified.

The summary of the above reviewed regeneration and resynthesis approaches are presented in Table 3.

To sum up all the above discussion methods of LFP resynthesis, the pros and cons are presented below.

*Pros*

1. High Performance and Stability:

The carbothermic reduction method for resynthesizing $LiFePO_4/C$ from $FePO_4·2H_2O$ demonstrated excellent capacity retention (93.7% at 0.1 C) and cyclic stability, confirming the feasibility of this approach for high-performance positive electrode material production. Hydrometallurgical methods, such as leaching with phosphoric acid and oxalic acid, exhibited high discharge capacities (up to 157.6 mAh/g at 0.1 C) and 100% capacity retention over multiple cycles, underscoring their effectiveness.

2. Eco-Friendliness and Sustainability:

Several methods, such as using lemon juice and weak organic acids, highlight a move towards greener chemistry, reducing the reliance on strong acids and minimizing waste discharge. The closed-loop recycling process using buffered solutions showed the potential for resource efficiency, enhancing environmental sustainability.

3. Innovative Techniques:

The introduction of novel approaches, like using methyl sulfonic acid and p-toluene sulfonic acid at room temperature, demonstrates innovation in reducing process complexity and energy consumption. The use of food industry waste products, such as fruit juices, as leaching solutions presents a unique way of integrating waste reuse into the recycling process.

**Table 3.** The summarized pathways of LFP resynthesis methods.

| Method | Key Processes | Outcomes | Advantages | Challenges | Ref. |
|---|---|---|---|---|---|
| Carbothermic Reduction | $FePO_4 \cdot 2H_2O$ microflowers synthesized; $LiFePO_4$/C mixed with acetylene black and PVDF. | High structural integrity confirmed via XRD. Discharge capacity 150–160 mAh/g at 0.1 C; 93.7% capacity retention at 0.1 C. | Simple method; good electro-chemical performance. | Carbon interference needs further study. | [87] |
| Oxidative Roasting | Roasting at 500 °C; minimal graphite oxidation. | >99% lithium leaching; optimal graphite removal at 800 °C. | High lithium extraction efficiency. | Balancing temperature for graphite removal and sintering. | [88] |
| Sulfation Roasting | $NaHSO_4 \cdot H_2O$ used; sintering at 600 °C. | $Li_3PO_4$ with high purity; 162.25 mAh/g at 0.1 C. Discharge capacities R-LFP and F-LFP after 200 cycles 140.99 and 144.78 mAh/g; retention rates of 96.57% and 97.83% | High purity and performance; eco-friendly. | Optimization of sodium salt addition. | [89] |
| Hydrometallurgical Approach | $FePO_4 \cdot 2H_2O$ leached with $H_3PO_4$; no alkali used. | Discharge capacity of 157.6 mAh/g at 0.1 C; 100% capacity retention after 100 cycles at 1 C. | Eco-friendly, no wastewater discharge. | Requires further scalability. | [90] |
| Buffered System Leaching | $NaH_2PO_4$ and $H_2O_2$ used for leaching; $Li_3PO_4$ crystallized via evaporation. | Capacities of the order of 150–160 mAh/g; superior initial capacity; 99.2% retention after 200 cycles at 0.5 C. | Closed-loop recycling; high efficiency. | Buffer optimization needed. | [91] |
| Mixed Acid Leaching and Spray Drying | $H_3PO_4$ and $H_2C_2O_4$ used; spray drying employed. | Well-crystallized LFP; improved ion diffusion. | Enhanced lithium-ion diffusion; good morphology. | No electro-chemical tests performed. | [92] |
| Weak Organic Acids Leaching | MSA and TSA used at room temperature. | Initial capacity of 93 mAh/g at 0.2 C; stable at high rates. | Green chemistry approach. | Carbon content higher than commercial standards. | [93] |
| Fruit Juice Leaching | Leaching with lemon, orange, and apple juices. | Discharge capacity of 155.3 mAh/g at 0.1 C; 98.3% retention after 100 cycles. | Green chemistry using food by-products. | Scaling up for industrial use. | [94] |
| Ammonium Persulfate Leaching | Ammonium persulfate used; carbothermic reduction with glucose. | 161.9 mAh/g at 0.1 C; enhanced crystallinity. The storage capacity of the LFP-G12 reaches 97.9%. | High crystallinity and performance. | Requires fine-tuning of carbon coatings. | [86] |
| Alcoholysis and High-Temperature | PVAc as carbon source; sintering in methanol–ammonia solution. | Discharge capacity of 163.2 mAh/g at 0.1 C. Capacity retention is 97.08% at 0.5 C after 100 cycles. | Simple, impurity-free process. | Requires optimization of PVAc dosing. | [95] |

*Cons*

1.  Lower Initial Capacities:

Some methods, like those involving weak organic acids, resulted in lower initial discharge capacities (e.g., 93 mAh/g at 0.2 C), which could be a drawback for high-performance applications.

2.  Complexity and Refinement Needs:

Techniques such as oxidative roasting and roasting with sulfation require a careful balance and optimization of temperature and reaction kinetics to avoid undesirable by-products or incomplete reactions. The need for further refinement is evident in some methods, like the one using weak organic acids, where the carbon content exceeded commercial standards, suggesting additional processing steps.

3.  Process Specificity and Optimization:

Methods like those using polyvinyl acetate require precise conditions and amounts, indicating that scalability and repeatability may be challenging without extensive process control. The carbothermic reduction and specific carbon coating ratios for optimal electro-chemical properties highlight the need for precise material engineering and quality control.

The reviewed methodologies for recycling and resynthesizing $LiFePO_4/C$ positive electrode materials demonstrate a wide range of innovative approaches, each with its advantages and limitations. High performance, eco-friendliness, and novel processing routes characterize the current advancements. However, challenges related to initial capacities, process complexity, and the need for further refinement must be addressed to ensure industrial scalability and commercial viability. The diverse strategies indicate a robust research trajectory aiming to optimize both the economic and environmental aspects of $LiFePO_4$ battery recycling, positioning it as a sustainable alternative to conventional methods.

## 6. Conclusions and Perspectives

This review underscores the significant advancements in lithium iron phosphate (LFP) battery regeneration and recycling, emphasizing the need for scalable, eco-friendly, and economically feasible solutions. Cutting-edge methods like direct regeneration and innovative recycling approaches successfully address challenges such as lithium depletion, positive electrode degradation, and environmental sustainability. Techniques such as carbothermic reduction, redox leaching, and ionic liquid extraction achieve high recovery efficiencies and excellent electrochemical performance, enabling regenerated materials to meet or exceed commercial standards. Additionally, the focus on green chemistry through the use of weak acids, ionic liquids, and acid-free processes minimizes the ecological footprint of these technologies.

Future efforts should prioritize optimizing closed-loop systems to ensure complete material recovery while reducing resource loss. Integrating automation and artificial intelligence in battery sorting and recycling workflows can enhance efficiency and cost-effectiveness, making large-scale adoption feasible. Furthermore, developing greener chemistry solutions and leveraging bio-based leaching agents will align these technologies with stringent environmental regulations. Policy incentives, coupled with industry–academia collaborations, will accelerate the transition to sustainable battery recycling practices. Advanced material designs, including novel coatings and formulations, hold the potential to simplify recycling and improve battery performance, ensuring the long-term viability of lithium-ion battery technologies.

In conclusion, the ongoing innovation in LFP battery regeneration and recycling offers promising pathways for creating a sustainable, closed-loop energy storage ecosystem.

These advancements will be instrumental in addressing the rising demand for lithium-ion batteries while significantly reducing their environmental impact.

*6.1. Perspectives*

The future of lithium iron phosphate (LFP) battery recycling and regeneration lies in addressing both technical and economic challenges to meet the growing demand for sustainable energy storage solutions. Significant strides have been made, but further developments are essential to maximize the potential of recycling, regeneration, and resynthesis methodologies.

### 6.1.1. Optimization of Closed-Loop Recycling

Closed-loop systems should be further refined to minimize resource loss and achieve full material recovery. Technologies that allow for direct lithium replenishment and the reuse of recovered precursors will contribute to this goal.

### 6.1.2. Integration of Automation and AI

Automation in the disassembly and sorting of end-of-life (EoL) batteries, combined with artificial intelligence (AI)-driven process optimization, can enhance efficiency and reduce labor costs, making recycling more viable at scale.

### 6.1.3. Development of Green Chemistry Solutions

Expanding the use of green chemistry in recycling processes, such as bio-based leaching agents and low-temperature methods, will mitigate environmental impact and comply with stricter regulations.

### 6.1.4. Economic Feasibility and Policy Support

Government incentives and policies promoting battery recycling infrastructure and circular economy practices will be crucial. Establishing partnerships between industry and academia can drive innovation and lower costs.

### 6.1.5. Advanced Material Design

Future research should explore new LFP formulations and coatings that enhance battery performance and simplify recycling, such as coatings that prevent dendrite formation or enable easier lithium recovery.

In summary, the continuous development of innovative LFP recycling and regeneration techniques holds significant promise for addressing environmental challenges and resource constraints in the energy storage sector. Achieving sustainable, closed-loop recycling systems will play a pivotal role in meeting the global demand for lithium-ion batteries while minimizing their ecological footprint.

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