Recycling of Spent Lithium Iron Phosphate Cathodes: Challenges and Progress

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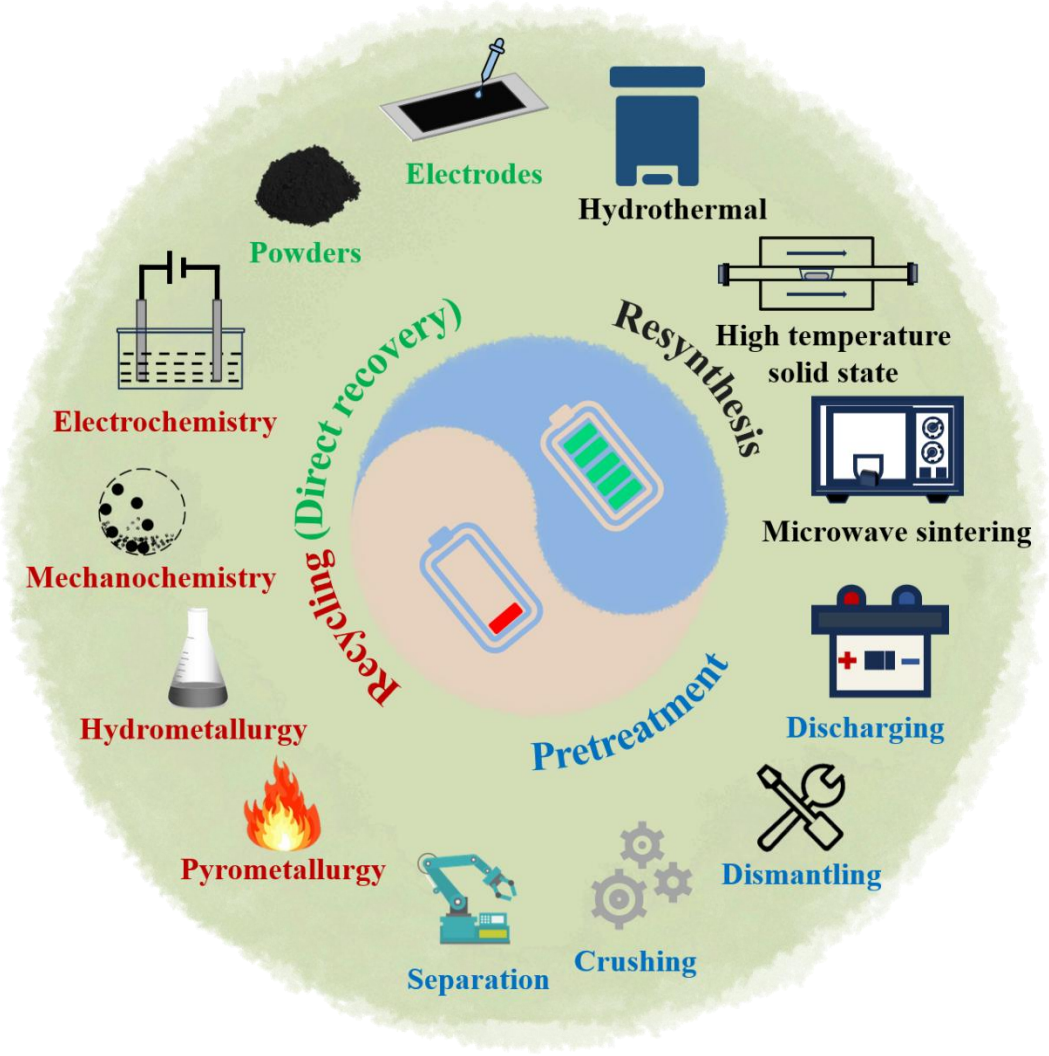
Abstract: The number of spent lithium iron phosphate (LFP) batteries will increase sharply in the next few years owing to their large market share and development potential. However, recycling of spent LFP batteries is necessary and urgent from both resource utilization and environmental protection standpoints. In this review article, the significance of pretreatment for LFP recycling is firstly underscored, and its technical challenges and recent advancements are presented. Following that, the current recycling methods for spent LFP cathode are outlined in terms of the respective approach process, advantages and disadvantages. Additionally, the preparation methods of LFP cathode material are reviewed to guide the resynthesis of LFP that using salts obtained from spent LFP, which are beneficial for closed-loop recycling of LFP batteries. Lastly, we explore the future development direction of spent LFP battery recycling, highlighting the importance of technological innovation to advance the sustainable growth oft of the LFP battery industry.

Keywords: lithium iron phosphate, recycling of spent battery, pretreatment, recycling method, resynthesis



1. Introduction

Global warming has attracted widespread attention on the international level because it will result in ecological environment deterioration.[1-2] Many countries have joined in constructing an energy-saving and emission-reducing society. Europe, for instance, aims to substantially lower greenhouse gas (GHG) emissions by 2030 and achieve GHG neutrality by 2050.[3] Similarly, China has pledged to reach a carbon peak by 2030 and achieve carbon neutrality by 2060.[4] A significant contributor to carbon dioxide emissions is the use of fuel vehicles, which has propelled electric vehicles (EVs) as the primary developmental direction for the automotive industry globally.[5] Governments and automakers worldwide are making substantial investments in EV research and infrastructure to mitigate climate change effects.

As the electrochemical energy storage device with the best comprehensive performance, lithium-ion battery (LIB) is one of the core components of EVs, and plays a pivotal role in promoting their application and development.[6] Consequently, the global demand for LIBs has been increasing steadily year by year.[7] In 2022, the global installed capacity of power batteries reached 517.9 GWh, and the year-on-year growth rate was as high as 71.8%.[8] It is easy to surmise that the number of retired power batteries will increase rapidly in the next 5–8 years, the effective disposal of these batteries is necessary and urgent.[9-13] Therefore, the recycling of electrode material for spent LIBs is an important part of the development of the EV industry that influences its long-term stable development. On the other hand, lithium (Li) resources are mainly distributed in South America, of which Chile accounts for approximately 55% of the global Li production.[14-15] The rapid development of the LIB and EV industries will lead to a further wide supply-demand gap for Li resources. Considering that the Li and other metal elements in spent batteries are far more than the natural ores, its recycling utilization has high economic value compared with mining ores.[16-19] Importantly, the spent LIBs contain organic solvents and Li salts with high toxicity ($LiPF_6$, HF, etc.), direct stacking or discarding will result in serious environmental pollution.[20-25] Therefore, the recycling of spent LIBs is imperative from both environmental and

economic perspectives, which is beneficial for the sustainable development of human society.[26-29]

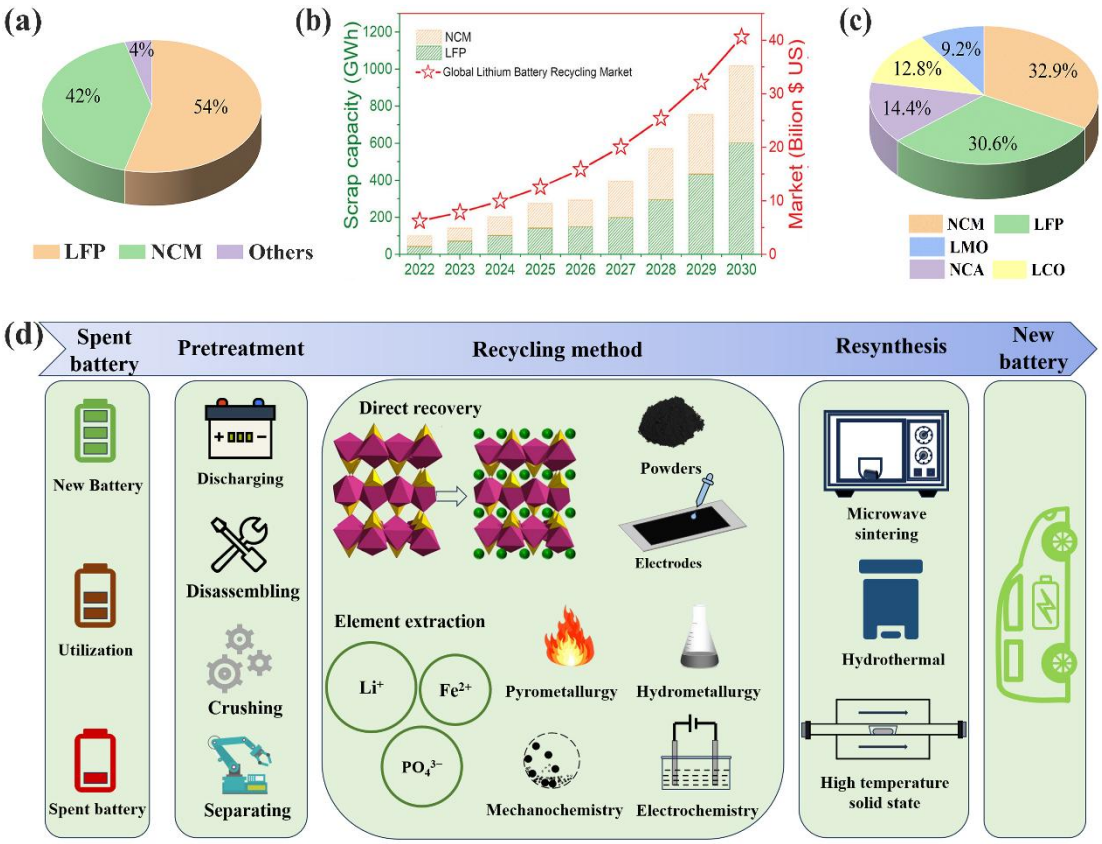


Figure 1. Analysis of the market, economic environment and recycling process for spent LFP batteries. (a) Proportion of LFP, NCM and other cathode power batteries of China in 2021[30] (Copyright 2021 Elsevier. Reproduced with permission from ref 30.). (b) Bar plot showing the estimated global market size of power and energy storage batteries from 2022 to 2030[31] (Copyright 2024 Wiley. Reproduced with permission from ref 31.). (c) Proportion of publications on five cathode materials for recycling of LIBs in the past five years (Data source: Web of Science). (d) Utilization process and recycling methods of spent LFP batteries (Copyright 2020 Elsevier. Reproduced with permission from ref 32.).

Currently, the cathode materials for commercial LIBs mainly include lithium iron phosphate ($LiFePO_4$, LFP), lithium cobalt oxide ($LiCoO_2$, LCO), lithium manganate ($LiMn_2O_4$, LMO), and ternary material system ($LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$, NCM).[33] The proportion of different cathode power batteries of China in 2021 as shown in Figure 1a. Among these, LFP batteries have long attracted particular attention from both academia

and industry because they do not use expensive metals such as Co and Ni.[34] Meanwhile, the olivine structure of LFP incorporates strong oxygen-containing covalent bonds, which endow these batteries with exceptional cyclic stability, superb thermal properties, and high safety levels.[35] [35, 36] Moreover, LFP batteries becomes competitive in terms of energy density with the development of cell-to-pack (CTP) technology.[36] As summarized in Table 1, when LFP individual cells are assembled into batteries packs, the energy density of LFP packs is close to that of the well-known high-energy NCM ($LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$) batteries.[37] Owing to the low cost, exceptional stability, high safety, and competitive energy density, LFP batteries have increasingly captured a larger market share. In China, the largest LIB and EV markets in the world, the total output cathode materials reached 1.65 million tons in 2023, of which LFP cathode material accounted for 66%, a significant increase of 48.65% compared to 2022.[38] The installed capacity of LFP batteries reached 103.9 GWh in the first half of 2023, which exceeded twice that of NCM ($LiNi_xCo_yMn_{1-x-y}O_2$) batteries (48.0 GWh).[39-40] The declaration from the Trend Force predicts that the global recycling market size of power and energy storage batteries will exceed 1000 GWh by 2030, of which the market share rate of LFP reach 58% (Figure 1b).[31] It is predicted that the global Li battery recycling market will reach 41.3 billion by 2030 form 6.2 billion of 2022. The recycling of spent LFP batteries was first reported as a scientific research topic in 2014, it has received increasing attention with the increase of LFP battery market share.[41] In the publications for the recycling of LIBs, proportion of LFP reached about 30.6%, which indicates its importance (Figure 1c). Therefore, it is very necessary to review the research progress to promote the sustainable development of the LFP batteries recycling industry.

Table 1. Comparison of NCM and LFP at theoretical, cell and pack levels.

	Performance testing	Specific energy/Wh kg^{-1}	Energy density/Wh L^{-1}
Theory	NCM	700	2400
	LFP	350–370	1100
Cell	NCM	250	700
	LFP	160–180	330–380
Pack	NCM	130	250

	LFP	130–140	210–230

The general rule is that LIB power batteries should be retired when their capacity decays to 80% of the rated value.[42-44] In order to realize the high-effective utilization of energy and resources, these retired power batteries firstly need to experience cascade utilization (Figure 1d). According to the residual capacity of the batteries, they can be reused for communication base stations, low-power electric vehicles, grid energy storage, etc. and then should be disassembled and handled as solid waste.[45-48] Generally, when the capacity of the battery decays to 40% of its rated value, it becomes a spent battery because it does not meet the standards for LIB battery cascade utilization.[49] The recycling process of these spent batteries includes the pretreatment and direct/indirect recovery.[50] To be specific, the pretreatment process includes the discharge, disassembly of batteries, and separation of corresponding components.[51-52] The recycling processes mainly include direct recovery, pyrometallurgy, hydrometallurgy, mechanochemical, electrochemical, and deep eutectic solvent methods.[21, 31, 53]

The aim of this article is to highlight the significance of spent LFP battery recycling from both resource utilization and environmental protection perspectives, and to guide the high-effective recycling in actual research by integrating the advantages of each recycling method. The significance of pretreatment is firstly highlighted, the recent advancements and technical challenges are summarized. Following that, the different recovery methods are itemized and reviewed to comprehensively uncover their principles, advantages, and challenges. In the end, the preparation methods of LFP are conducted to guide the resynthesis of LFP using salts obtained from spent LFP, which has significance for closed-loop recycling of LFP batteries. The recycling of spent LFP batteries holds great promise for addressing environmental challenges, optimizing resource utilization, and promoting the sustainable development of the LIBs industry.

2. Pretreatment of spent LFP batteries

The pretreatment for spent LIBs is an essential procedure, which includes the discharge, disassembly, and component separation.[54] If there is a residual charge in the spent LIBs, it is easy to cause a fire or even an explosion when the batteries are disassembled and broken.[55] Therefore, the spent LIBs need to be fully discharged to prevent the safety hazard before disassembly. Typically, the discharge process is carried out by placing the spent LIBs into the salt solution or using a specific discharge device to realize the full discharge of batteries.[56] Among them, using the NaCl solution is the most efficient, adaptable, and stable route.[29] The fully discharged batteries are disassembled into individual components like as positive, negative, shells, etc.[57] or directly mechanical pulverized into black powders composed of cathode, anode, Al foil, Cu foil, etc..[58] There are various subsequent recycling methods for different pretreatment processes.[59] The common of laboratory-scale pretreatment process includes complete discharge, disassembly, separation, and material sorting for batteries.[60] Despite achieving promising experimental results, the careful and slow process poses a formidable challenge in meeting large-scale industrial applications.[61] In industry, batteries are mechanically crushed to product the black powders containing electrode materials, current collectors, conductive carbon, etc. after completely discharging in a salt solution.[26, 61] These black powders are then sieved and separated based on corresponding material characteristics.[62] The mechanical grinding technology is an efficient way for industrial production to obtain black powders.[26] However, this process may bring about fire, explosion, and generation of toxic gases, which require specialized equipment to avoid the production risk and suppress the environmental pollution.[63]

The simpler the composition of the mixture, the more conducive it is to later separation and recovery.[64] Therefore, magnetic separation is developed and used for the separation of black powders. Magnetic separation is that utilizing magnetic field gradients generated from magnetic materials to achieve the separation of substances and it has been widely applied in mineral processing, solid-state chemistry, biomedicine, etc..[65] Magnetic separation has advantages like simple operation, high efficiency, low cost, and environmental friendliness.[66] As shown in Table 2, all the usual cathode

materials are strongly paramagnetic, except for $LiCoO_2$.[67] Additionally, C and Cu foils are weakly antimagnetic, which is very close to non-magnetic. $LiCoO_2$ and Al foil are weakly paramagnetic, which can be treated as non-magnetic. The high specific susceptibility of LFP (741×10^{-9} m^3 kg^{-1}) indicates the great potential of the magnetic separation method for the pretreatment of LFP batteries. Hu et al.[67] successfully separated LFP and graphite from the spent LFP black powders by using a high gradient magnetic separator (HGMS) and an inductive roll magnetic separator (IRMS). For HGMS, the concentrate grade and recovery of LFP were 74.54% and 96.60% under magnetic field strength of 1 T (Tesla), respectively. For IRMS, the concentrate grade and recovery of LFP cathode pieces were 93.30% and 98.69% under magnetic field strength of 1 T, respectively. Although research on the recovery of spent LFP batteries by magnetic separation is still in the initial stage, it has shown great potential in meeting industry development demands. In the future, with the continuous progress of the technology, the application of magnetic separation methods in the field of LIBs recycling will be more extensive and comprehensive.

Table 2. Specific susceptibility of electrode materials in LIBs[67] (10^{-9} m^3 kg^{-1}).

Material	Specific susceptibility
$LiFePO_4$ (LFP)	741
$LiMnO_2$ (LMO)	574
$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NCM)	331
$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA)	251
$LiCoO_2$ (LCO)	17
C	−84
Cu	−1.12
Al	8.15

The separation of Al foil from spent LFP electrodes is a key step for recycling LIBs because it avoids the influence of Al foil on the purity of the recycled products.[68-69] LFP cathode materials are usually composed of LFP powders, conductive black, Al foil, and polyvinylidene fluoride (PVDF) binder.[70] The binder can maintain the tight bonding between electrode materials and Al foil after the long cycles. Importantly, the

separation of metallic Al from the black powders is difficult owing to the high stability and strong binding capacity of PVDF.[70-71] Therefore, whether through manual dismantling or mechanical grinding processes, the effective separation of the Al foil and electrode materials is critical for recycling LFP. The main methods can be mainly categorized into liquid-phase separation, physical separation, and annealing separation (Figure 2a).

(1) Liquid-phase separation involves using a specific solvent to dissolve the PVDF binder, thereby separating the cathode material from the Al foil.[72-74] Strong acid and strong alkali solutions have been investigated as straightforward and viable liquid-phase separation reagents.[75-77] For example, a solution of citric acid and methanol has shown its effectiveness in separating cathode materials and collectors.[75] For alkali solution, Li et al.[76] successfully demonstrated that separated the LFP powders and Al foil by immersing the electrode in a NaOH aqueous solution of 10 mol L^{-1} with ultrasound assistance to realize the separation of cathode materials and Al foil. However, strong acid and alkali solutions with high concentration can result in the dissolution of Al foil, raising challenges for subsequent separation processes.[77] Also, the use of strong acid or strong alkali brings about the increase of costs and environmental problem of wastewater pollution.[71] Conversely, low concentration can't effectively realize the separation of LFP material from the Al foil. Another reported strategy is that using organic solvents to dissolve PVDF binder and realize the separation of electrode material and Al foil. N-methyl-2-pyrrolidone (NMP) is one of the most widely used chemical reagent for dissolving PVDF, which exhibited high efficiency and recyclability (Figure 2b).[71, 78] Nevertheless, most of organic solvents have disadvantages of volatility, toxicity and high price compared with inorganic acid and alkaline solution, which hinder their practical application. Therefore, numerous efforts have been devoted to explore new separation solvents in meeting the demand of industry development. For instance, the electrolytic approach could be completely stripped LFP materials for the spent electrode within 15 minutes in sodium sulfate solution of 3 g L^{-1} under electrolytic voltage of 10 V.[79] The hydrogen peroxide system was also found to be effective in completely stripping the cathode materials.[79] When

separation conditions were identified as a hydrogen peroxide concentration of 0.2%, a rotary speed of 400 rpm, a reaction time of 4 minutes, and a solid-liquid ratio of 14.2 g L^{-1}, the loss of Al foil was less than 0.4%. Morphological and crystal structure analysis revealed that the stripped cathode materials were completed and the Al foil was uncorroded. Li et al.[80] used a novel solvent with both environmental sustainability and highly efficient, 1,2-dichloroethane (ChCl-EG), to rapidly degrade the PVDF binder and facilitate the separation of Al foil under microwave heating approach. The separation efficiency of Al foil can reach 100% in the solution with a molar ratio of ChCl:EG of 1:2 at 120 ºC for 8 minutes. Liquid-phase separation methods have demonstrated their efficacy in the laboratory; however, further investigation is necessary to verify their suitability for industrial applications. The cost and environmental influence are unavoidable issues that must be addressed. The consideration of solvent reuse merits attention in light of its potential environmental and economic benefits.

(2) Physical separation involves the detachment of LFP powders from the surface of Al foil using mechanical forces, including mechanical pulverization and separation.[81] This method exploits the mechanical force to exfoliate LFP material from the Al foil, often resulting in the curling of the foil.[82] Given the granular nature of the LFP material, it can be effectively separated from mixture containing Al foil by sieving treatment. As depicted in Figure 2c, Bi et al.[81] developed a gas splitter to separate LFP from a mixture composed of Al foil and LFP powders. Although the efficiency of this method is suboptimal, it presents economic advantages over manual separation, which shows great promising for industrial-scale applications. In a report conducted by Bruno et al.[83], the influence of ultrasonic, ball milling, and heat treatment that combinates with ball milling on the separation of LFP powders and Al foil were investigated, in which production scraps and end-of-life cathode materials were used as target materials. The findings revealed that all methods demonstrated superior performance in the separation of end-of-life (EOL) cathode samples compared to production scraps (PS). It is noted that ultrasound was unable to separate the electrode material from the Al foil surface in PS samples. The separation efficiency was as high as 95 ± 5% for Li, 99 ± 6% for Fe,

and 80 ± 3% for P in production scraps under 200 ºC for 30 min and ball milled at 840 rpm for 5 minutes. The separation efficiency of 93 ± 15% for Li, 97 ± 21% for Fe, and 82 ± 20% for P in EOL cathodes, which had been treated at 250 ºC for 30 minutes and ball milled at 840 rpm for 5 minutes. Although relevant literature reports are scarce, the straightforward and facile characteristics of this method make that it has promising potential for industrial applications. However, several challenges must be addressed for physical separation to become viable for industrial applications. Firstly, the toxic and harmful gases rooted in the decomposition of organic components are inevitable during the mechanical crushing process. Moreover, residual small Al foil fragments within the LFP powders could potentially compromise the recovery of other metal elements.

(3) Annealing separation involves the thermal decomposition of PVDF to weaken the bonding between Al foil and LFP powders, thereby obtaining separated LFP powders without Al foil and PVDF binder.[84-86] The melting point of PVDF is approximately 350 ºC, which indicates that annealing separation is an effective method.[84] Annealing separation is characterized by its simplicity and convenience, making it potentially applicable in industrial settings. The ANVIIL (adhesion neutralization via incineration and impact liberation) method was introduced by Hanish's group (Figure 2d)[84]. This method involves the calcination of PVDF and then using a newly designed jet separator to exfoliate electrode materials from the collector surface. In this experimental setup, a calcination time of 90 minutes resulted in a compound separation efficiency of 97.1% w/w after an air impact stressing time of 1 minute. The advantage of the ANVIIL process is that the purity of recycling material is close to that of raw materials. However, dioxins, hydrogen fluoride (HF), phosphorus pentoxide (P_2O_5), and other toxic compounds are possibly generated during the heat treatment process, posing risks of equipment corrosion and atmospheric pollution.[87] Therefore, specialized equipment is necessary to collect gases and fumes generated during combustion. Elevated temperatures also can lead to the structural collapse of LFP, thereby potentially hindering the recovery of metal elements. Moreover, interactions between substances at high temperatures can cause Li loss, reducing Li recovery efficiency. The energy consumption associated with high temperatures is a

substantial economic burden, diminishing the overall benefits of the recovery process. Li's group[88] successfully separated cathode materials and Al foil by mechanical crushing after annealing treatment under 300 ºC. The binder will not be pyrolyzed to produce toxic gas when the heat treatment temperature is below its heat decomposition temperature. Additionally, lower pretreatment temperature can reduce the energy consumption of recycling process and corresponding equipment requirements. The annealing method with a lower temperature is an efficient and environmentally friendly method for recovering spent LFP batteries.

In conclusion, effective separation of the cathode material from the Al foil is essential for the recovery of valuable materials from spent LFP batteries. Each separation method has its advantages and limitations, and the choice of method depends on the specific requirements and constraints of the recycling process. Considering the loss of Li during high-temperature annealing and liquid-phase treatment, the physical separation method may be more suitable for industrial applications. Furthermore, a combination of methods can be used to realize the separation of electrode material and Al foil.

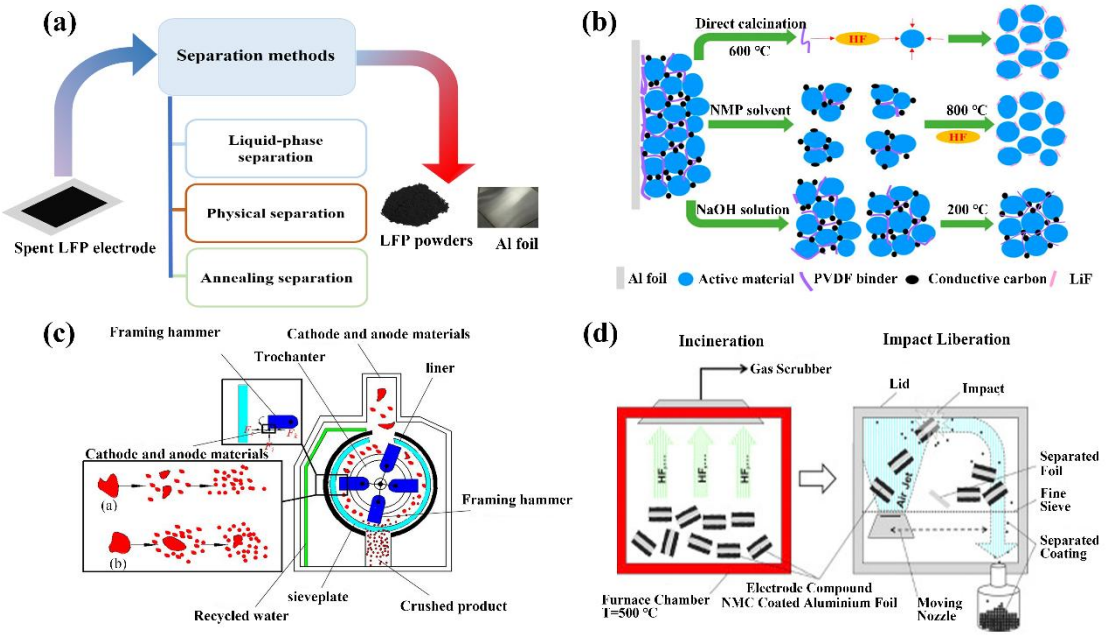


Figure 2. (a) The schematic diagram of cathode materials and Al foil separation. (b) Three separation methods of Al foil (including liquid-phase separation)[78] (Copyright 2016 American Chemical Society. Reproduced with permission from ref 78.). (c) The

schematic diagram of physical separation device and precess[81] (Copyright 2021 Sage Journals. Reproduced with permission from ref 81.). (d) The schematic diagram of annealing separation process[84] (Copyright 2015 Elsevier. Reproduced with permission from ref 84.).

3. Direct recovery

Generally, the main strategies for spent LFP recycling can be divided into three categories: direct recovery, element extraction, and other new methods.[25, 52]The direct recovery is reconditioning electrochemical performances of electrode materials for reuse.[61] Compared with other methods, direct recovery has lower energy consumption and reagent cost, which is an economical and environmentally friendly approach for recycling of LIBs.[89-91] However, this method involves manual disassembly of batteries, and the batteries must be lie good condition[92].

The degeneration of the electrochemical performance of LFP electrode is mainly attributed to the loss of active Li.[93] The extracted Li-ions (Li^+) during the charge process are fully unable to reinsert into the structure of $FePO_4$ and form LFP during the discharge process, resulting in the accumulation of the $FePO_4$ phase and containing Li side products.[40, 94] Due to the similar structure of $FePO_4$ and LFP, spent LFP can be directly regenerated to restore its electrochemical performances by electrochemical,[95] sintering,[96] and hydrothermal[96] methods.

3.1 Direct regeneration of LFP powders

The direct regeneration of LFP powders has been regarded as a promising recycling method. The lithiation approach based on solution has been demonstrated to be an effective approach to fully restore the electrochemical performances of LFP.[97] Typically, the LFP powders were placed into a 100 mL aqueous solution consisting citric acid of 0.08 M of 20 mL and LiOH of 0.2 M of 80 mL under 60 ºC for 17 hours or 70 ºC for 10 hours to realize their lithiation. Subsequently, the lithiated LFP powders after washing with deionized water and drying were mixed with an excess of Li_2CO_3 of 4% and then annealed under 600 ºC in a nitrogen atmosphere for 2 hours to realize the recycling of spent LFP powders. Ouaneche et al.[98] successfully recovered the

electrochemical properties of LFP materials by dissolving LFP powders in the ethanol solution consisting of LiI. The regeneration LFP cathode exhibited a high reversible capacity of ~168 mA h g^{-1} with a stable Coulombic efficiency (> 98%) for 25 cycles in a half cell. Additionally, its displayed superior rate performance with a specific discharge capacity of 160 mA h g^{-1} at the current density of 1 *C*, while the spent LFP cathode only reached about 30 mA h g^{-1} under the same current density. Song's group et al.[99] reported that ascorbic acid-assisted ultrasonic reaction to repair the defect of spent LFP to recover its electrochemical performance (Figure 3a). To be specific, LFP powders of 1 g were added into LiOH solution of 0.25 M of 20 mL, in which ascorbic acid of 1 mL was introduced as reducing agent. The mixed solution was then subjected to supplement Li in an ultrasonic environment under conditions of 500 W for 1 hour at room temperature. The regenerated LFP can still maintain a discharge capacity of 132.89 mA h g^{-1} with a retention rate of 93.56% after 200 cycles at the current density of 1 *C*. Moreover, Wang et al.[100] reported the successful lithiation of spent LFP cathode via $LiNO_3$-assisted annealing spent LFP under the 300 ºC for 30 minutes (Figure 3b). The recovered LFP exhibited a high reversible capacity of 162 mA h g^{-1} with capacity retention of ~90% after 500 cycles at a current density of 0.5 *C*. As can be seen from the above discussion, the replenishment approach of Li and the construction of reaction condition are of great importance for restoring the structure and properties of LFP during the recovery process. The direct recovery method minimizes the emission of secondary pollutants and the consumption of energy. However, direct recovery methods often require pretreatment for the spent batteries before recovery, leading to increased recovery costs. The meticulous separation of battery components undoubtedly enhances efficiency and economics in direct recycling. Therefore, the transfer of promising outcomes achieved from laboratory to industry necessitates further exploration.

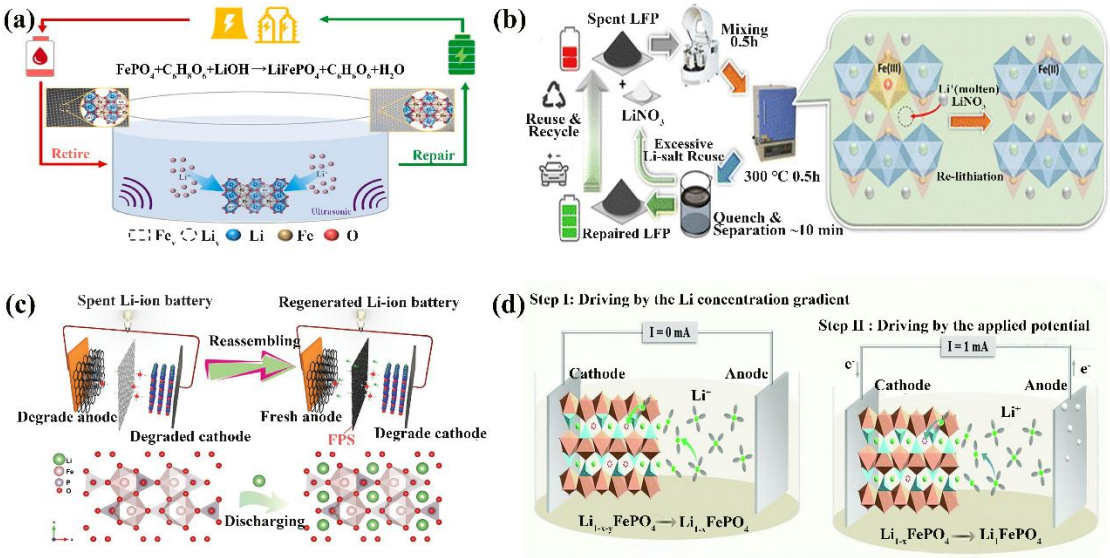


Figure 3. (a) The schematic diagram of high-power ultrasound facilitation of the generality for LFP regeneration[99] (Copyright 2024 Elsevier. Reproduced with permission from ref 99.). (b) The schematic diagram of repairing spent LFP black mass by recrystallization100 (Copyright 2023 Royal Society of Chemistry. Reproduced with permission from ref 100.). (c) The schematic illustration of the direct regeneration strategy based on FPS[101] (Copyright 2022 Wiley. Reproduced with permission from ref 101.). (d) The schematic diagram of resting-output current lithiation for regenerating retired LFP batteries[95] (Copyright 2022 Royal Society of Chemistry. Reproduced with permission from ref 95.).

3.2 Direct regeneration of LFP electrode

Considering the difficulty of LFP powders separated from the spent electrodes, direct regeneration for LFP electrodes sheets without removing Al foil collector has been regarded as a promising technology. In situ electrochemical process is effective approach for the direct regeneration of LFP electrode (Figure 3c).[101] Due to its cheapness, air-stability, and high irreversible capacity ($>$ 500 mA h g^{-1}), Li oxalate ($Li_2C_2O_4$) as the sacrificial agent is coated on the commercial separator to form the functionalized prelithiation separator (FPS). As a result, the specific capacity for the regeneration cell is 146.7 mA h g^{-1} along with a high-capacity retention of 90.7% after 292 cycles. This direct regeneration process is facile and does not change the existing

process during battery assembly. As shown in Figure 3d, Peng et al.[95] reported an efficient method to directly regenerate LFP cathodes by a consecutively spontaneous and electrically-driven lithiation process in Li_2SO_4 solution. Li-ions (Li^+) are spontaneously inset into the spent LFP ($Li_{1-x-y}FePO_4$) to form $Li_{1-x}FePO_4$, and finally obtaining $LiFePO_4$ by applying an electric field. Kinetic analysis showed that the embedding rate of Li^+ in the spontaneous process is related to the concentration of Li_2SO_4 and the Li deficiency of $LiFePO_4$. The applied electric field is only related to the Li deficiency of the material. The regenerated $LiFePO_4$ electrode delivered a discharge capacity of 135.2 mA h g^{-1} with a capacity retention of 95.30% after 500 cycles at the current density of 1 *C*. The direct recovery of electrodes removes the Al separation and the LFP resynthesis processes, which can reduce the energy consumption and environmental pollution resulting from these processes. However, adjusting the parameters to avoid the erosion of Al foil remains a problem that needs to be solved during the experiment. Additionally, the influence of impurities on the performance of the recovered electrodes poses challenges to their large-scale application.

4. Extraction of elements

Extracting valuable elements from spent LFP batteries is the dominant production route in industry. These elements can be collected by pyrometallurgy,[71] and hydrometallurgy,[102] mechanochemistry,[103] electrochemistry[104] approaches to form salts containing corresponding elements as shown in Figure 4. It is noted that these recycled products can serve as raw materials for the resynthesis of LFP, which promotes the cyclic utilization of resources.[105] Pyrometallurgy is converting metal elements in active materials into metals or metallic compounds by high-temperature annealing.[29, 106] Hydrometallurgy is using acid or alkali solutions to extract and separate the valuable elements in the spent LIBs.[62, 92] Although pyrometallurgy has more flexibility and selectivity for raw battery materials, but hydrometallurgy is the most popular recovery method due to its lower fixed investment.[54, 87, 106] Moreover, hydrometallurgy has higher recovery efficiency for metals and other organic components in spent LIBs

compared with pyrometallurgy[62]. Therefore, a recovery strategy combined with hydrometallurgy and pyrometallurgy is widely used in the industry, which integrates the strengths of both methods.[107] Apart from chemical separation and metallurgical extraction, emerging strategies such as mechanochemical,[108] electrochemical,[32] and deep eutectic solvent methods[109] have attracted widespread attention in recycling LFP batteries. These strategies are based on the unique properties of LFP batteries and corresponding materials.[110]

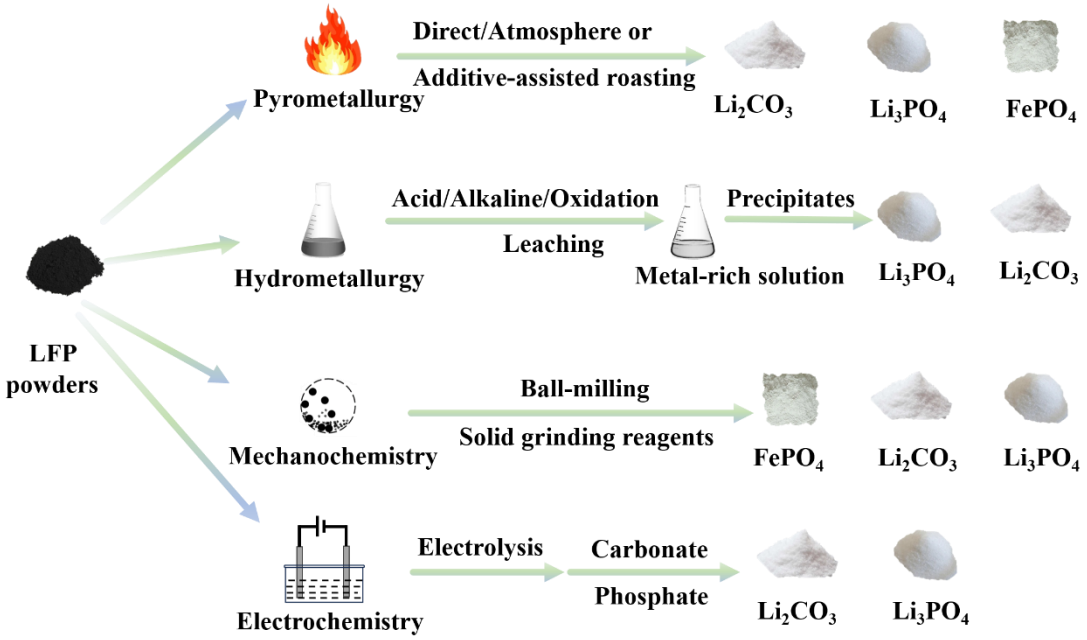


Figure 4. The schematic diagram of element extraction methods.

The element Li is one of the most valuable elements in spent LFP batteries due to its scarcity of resources in the earth's crust.[111-112] Therefore, extracting Li has become the main purpose of LFP battery recycling, which is the focus of current enterprise production. From the perspective of industry development, the recovery of all elements is very necessary, which not only can enhance the efficiency of resource utilization, but also is beneficial for the protection of ecological environment. For example, the disposal of heavy metals and phosphorus (P) will cause serious pollution to the soil[24].

4.1 Pyrometallurgy method

Pyrometallurgy extracts and recovers metal elements from minerals or materials via high-temperature calcination. Despite its high energy consumption, the advantages

of a simple recovery process, high applicability, and high processing capacity have made it became widely used method in the industry.[106] Pyrometallurgy methods can be subdivided into direct roasting (Figure 5a),[85] atmosphere-assisted roasting (Figure 5b and Figure 5c),[113-114] and additive-assisted roasting (Figure 5d).[115]

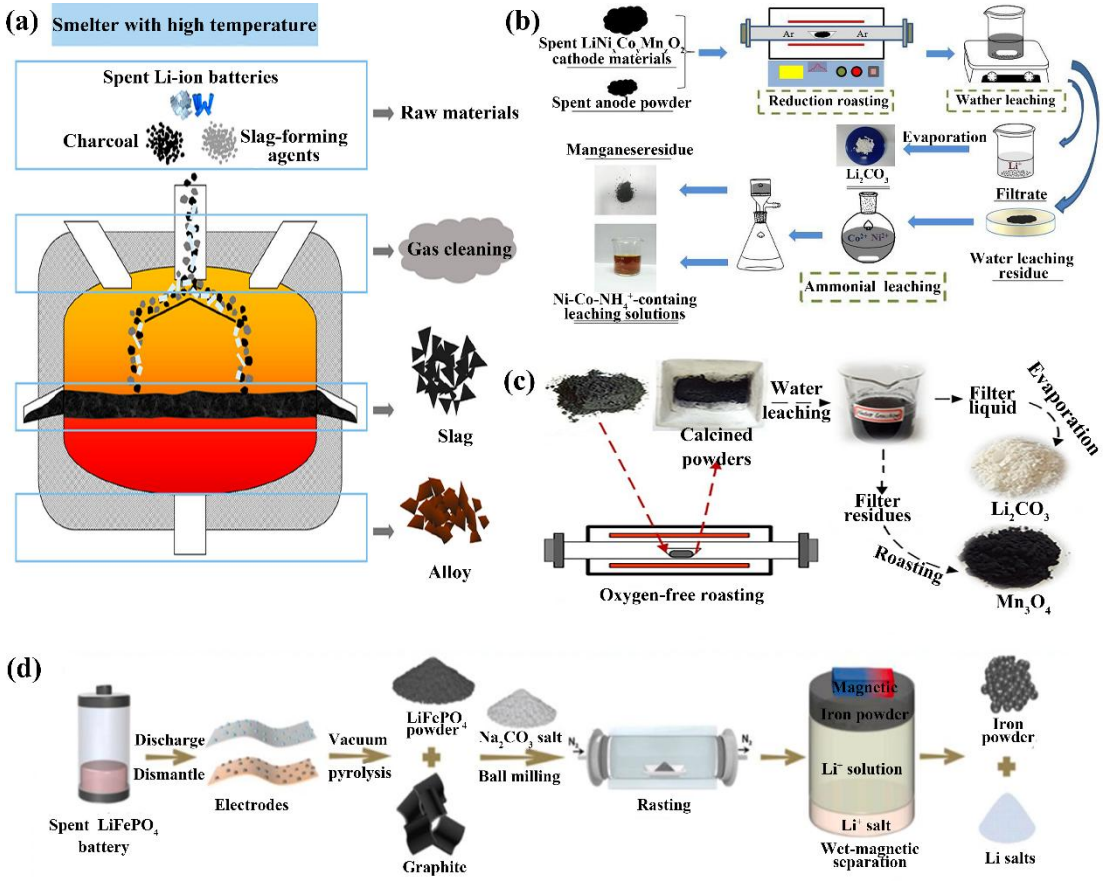


Figure 5. (a) The schematic diagram of typical pyrometallurgical treatment process for spent LIBs[106] (Copyright 2021 American Chemical Society. Reproduced with permission from ref 106.). (b) The schematic diagram of Ar atmosphere assisted roasting[113] (Copyright 2021 Elsevier. Reproduced with permission from ref 113.). (c) The schematic diagram of roasting under vacuum condition[114] (Copyright 2017 Elsevier. Reproduced with permission from ref 114.). (d) The schematic diagram of Na_2CO_3 salt assisted-roasting approach followed by acid leaching[115] (Copyright 2021 Elsevier. Reproduced with permission from ref 115.).

The principle of direct roasting primarily uses reductants (such as carbon or Al) to reduce cathode materials and produce metal alloys under high temperature environment.[106] In the early stage, this process is applied primarily in recovering the

metallic cobalt (Co) and nickel (Ni) from spent LCO and NCM batteries, in which Li and other components are discarded with the slag.[116] With the rapid development of EVs and rapid consumption of Li resources, Li has become most valuable recycling element for spent LIBs.[117] Therefore, optimizing the recycling process to realize the efficient recovery of Li element is the current focus of pyrometallurgy for recycling of spent LIBs. Dang et al.[116] and Li et al.[118] demonstrated that 90% of Li can be successfully recovered by introducing calcium chloride and sodium sulphate into slag and roasting it under 800 ºC for 1 hour. Although direct roasting has been rarely reported in the literature for the recycling of spent LFP, it should attract enough attention as an alternative. Atmosphere-assisted roasting technology utilizes a vacuum environment or an inert atmosphere to regulate the thermodynamic equilibrium between carbothermic reduction and Al thermal reduction, thereby allowing their conversion in an oxygen-free environment.[106] The advantage of atmosphere-assisted roasting is can effectively reduce the reaction temperature and corresponding energy consumption of the recovery process compared with direct roasting, as verified by the reports of Shao's group[119]. Moreover, additive-assisted roasting technology primarily involves the use of inorganic salts or acid additives in the roasting process, it can significantly reduce the wastewater volume. Li et al.[120] reported a pre-oxidation regeneration strategy for LFP. To be specific, $Li_3Fe_2(PO_4)_3$ and Fe_2O_3 were firstly produced by direct roasting of LFP powders under 550 ºC. Then, Li_2CO_3 was added and roasted at 700 ºC under a nitrogen atmosphere to regenerate LFP. The regenerated LFP exhibited a specific capacity of 144.1 mA h g^{-1} at the current density of 0.1 *C*. Yin's group et al.[115] reported that Li_3PO_4 and Li_2CO_3 were obtained from spent LFP cathode materials by $NaCO_3$-assisted roasting at 900 ºC. Magnetic Fe_3O_4, $NaLi_2PO_4$, and $NaLi_5(PO_4)_2$ were obtained by NaOH-assisted roasting. Similarly, Zhang et al.[121] reported that using $NaHSO_4$ instead of $NaCO_3$ to obtain Li_3PO_4 and $FePO_4$ form spent LFP materials by direct roasting at 600 ºC. The regenerated LFP exhibited a higher reversible specific capacity of 146 mA h g^{-1} at the current density of 1 *C*.

It is important to note that excessively high roasting temperatures will cause the volatilization of active Li and destroy the original crystal structure of $FePO_4$ (FPO),

resulting in the degeneration of electrochemical properties. Additionally, the high energy consumption of pyrometallurgy significantly increases recovery costs, and the subsequent recovery process often needs the auxiliary process of hydrometallurgy. Therefore, pyrometallurgy may not be the most suitable choice for large-scale industrial applications.

4.2 Hydrometallurgy method

Hydrometallurgy is another widely used method for extracting target metal elements from minerals or materials[87]. Its typical processes include leaching, solid-liquid separation, solution purification, metal extraction, and wastewater treatment as shown in Figure 6a. One notable advantage of hydrometallurgy is that it can be carried out in normal temperature and pressure, and has high selectivity for valuable metal elements. The hydrometallurgy for spent LFP batteries can be mainly categorized into acid[122], alkaline[123], and oxidation leaching[124].

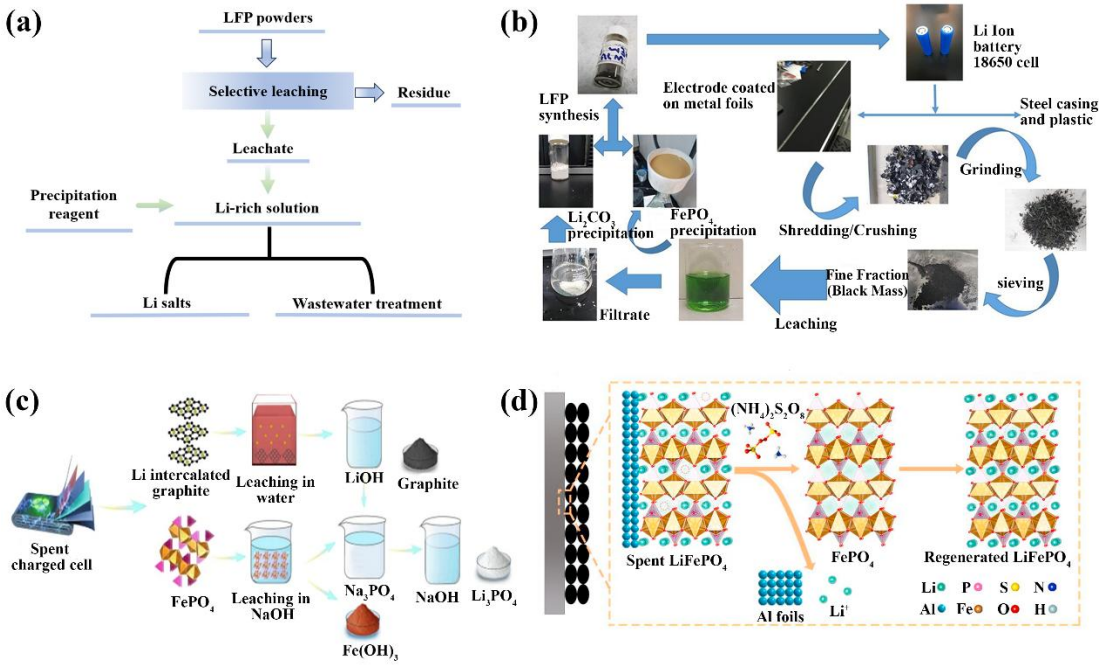


Figure 6. (a) The schematic diagram of hydrometallurgical recovery process for spent LFP batteries. (b) The schematic diagram of recycling of acid leaching[125] (Copyright 2020 Elsevier. Reproduced with permission from ref 125.). (c) The schematic diagram of alkaline leaching[123] (Copyright 2022 Springer Link. Reproduced with permission from ref 123.). (d) The schematic diagram of oxidation leaching of LFP (Copyright 2021 Elsevier. Reproduced with permission from ref 126.).

(1) Acid leaching: Acid leaching mainly involves the use of inorganic acids (e.g., phosphoric acid, sulfuric acid, nitric acid, and hydrochloric acid) and organic acids in recycling the metal elements of spent LIBs[127]. For instance, H_2SO_4 can effectively facilitate the leaching of Li and iron (Fe) from spent LFP materials[128]. Under leaching conditions characterized by a liquid-solid ratio of 20:1, H_2SO_4 of 2 mol L^{-1} under 70 ºC for 2 hours, the leaching efficiency of Li^+ and Fe^{2+} reached 96.67% and 93.52%, respectively. Unfortunately, the use of inorganic acids may produce toxic gases, which proposes a higher demand for recycle conditions[129-130]. Therefore, organic acids are more widely used to recycle spent LIBs. To be specific, Yang et al.[19] successfully extracted Li of 95.05% from spent LFP cathodes under 120 g L^{-1} solid-liquid ratio for 30 minutes using a mixture solution composed of 0.8 mol L^{-1} acetic acid and 6 vol% H_2O_2. Hua et al.[131] introduced an oxalic acid/H_2O_2 leaching process based on thermodynamic calculations to eliminate impurities and extract object elements from spent LFP electrodes. Under ideal experimental conditions (room temperature of 25 ºC, solid-liquid ratio of 100 g L^{-1}, the oxalic acid of LFP powders mass ratio of 3~ 4, LFP powder of 1 g corresponded to H_2O_2 of 30% of 2mL), the leaching efficiency of Li remained stable at 96%. Prasad et al.[125] realized a leaching efficiency of 95% for Li and Fe from LFP cathode materials under experimental condition characterized by methyl sulfonic acid (MSA) of 0.4 mol L^{-1}, liquid to solid ratio of 1:60, and H_2O_2 of 18 vol% (Figure 6b). Although using organic acids can effectively realize the extraction of metal elements, these processes usually need to add the reductive agent due to their weak acidity and difficulty in separating metal-ligand complexes.[132] Moreover, organic acids have higher prices compared with that of inorganic acids. Therefore, organic acids are rarely used as leaching reagents for Li. In industrial applications, controlling acidity to reduce the consumption of chemicals and improve the purity of recovered products remains a huge challenge.

(2) Alkaline leaching: To solve the problems of acid leaching like as toxic gas generation and high cost, alkaline reagents are used to recycle the metal elements in spent LFP batteries, namely alkaline leaching.[129-130] Currently, alkaline leaching methods based on the amino compounds have been intensively explored in recycling

LIBs[133-137]. In alkaline solution, the Li^+ and Fe^{2+} in $LiFePO_4$ is converted to $Fe(OH)_3$ and Li_3PO_4 precipitation, respectively (Figure 6c).[123] Fan et al.[123] proposed an economical and environmental-friendly recycling approach that is using water and NaOH as leaching agents to recover the elements in the LFP materials at room temperature. The deep charge for spent LFP batteries was carried out to obtain $FePO_4$ and lithiated graphite before leaching. Water is used to leach Li^+, as shown in equation (1), the lithiated graphite spontaneously reacted with water to form LiOH. Meanwhile, the replacement reacted between $FePO_4$ and NaOH to produce $Fe(OH)_3$ precipitate as shown in equation (2), which is realized the extraction of Fe. Na_3PO_4 solution, another reaction product, was transferred and mixed with as-formed LiOH solution to form Li_3PO_4 precipitate as shown in equation (3). This approach not only realized the complete extraction of $LiFePO_4$ components, but also established a recycling system for the atomic economy owing to the regeneration of NaOH. Under the optimal leaching conditions, the leaching efficiency of 99.7% for Li, 89.1% for Fe, and 99.2% for P were achieved, respectively.

$$2LiC_x + 2H_2O \rightarrow 2LiOH(aq) + 2xC + H_2 \uparrow \quad (1)$$

$$FePO_4 + 3NaOH \rightarrow Na_3PO_4 + Fe(OH)_3 \downarrow \quad (2)$$

$$Na_3PO_4 + 3LiOH \rightarrow 3NaOH + Li_3PO_4 \downarrow \quad (3)$$

The alkaline leaching method show great promising, but generation of H_2 make it difficulty in industry application. Moreover, the alkaline leaching process is like the acid leaching process, it also produces waste solutions. These waste liquids require additional treatment, consequently increasing overall recovery cost and limiting its application prospects.

(3) Oxidation leaching: Using oxidizing agents as leaching reagents can reduce the generation of wastewater as well as ensure high efficiency, which makes it more practical than acid and alkaline leaching treatments.[138] Furthermore, oxidation leaching is beneficial for reducing corrosion of equipment and facilitating the element recovery of closed loop.[132] To promote the removal of Li in LFP cathode materials, Fe^{2+} in LFP is oxidized to Fe^{3+} in the presence of an oxidizing agent. H_2O_2 has been recognized as a promising oxidation leaching reagent for the recycling of spent LIBs due to its strong

oxidizing property, low cost, and clean reduction product.[139-141] According to the report of Jing et al.[142], using H_2O_2 of 2.7 mol L^{-1} with PH of 7 can be extracted Li of 95.4% in LFP at room temperature for 4 hours. To reduce the cost of oxidation agents, Jin et al.[143] also proposed a new recovery strategy for recycling of Li from LFP by aqueous leaching using air as the oxidizing agent. 99.3% of Li was leached under optimal conditions (pH of 3.5, air flow rate of 600 mL min^{-1}, 25 ºC, liquid-solid ratio of 10 g L^{-1}, reaction time of 5 hours), whereas the leaching efficiency of Fe and P was only 0.02%. The rapid and efficient leaching process is of vital importance in industrial production. Therefore, $(NH_4)_2S_2O_8$ is one of the strong oxidizing anions, which can react quickly during the oxidative leaching process. As shown in Figure 6d, Peng et al.[126] used $(NH_4)_2S_2O_8$ as an oxidant to leach LFP, and the leaching efficiency of Li is more than 98% under the optimal conditions (leaching time of 30 minutes, solid-liquid ratio of 50 g L^{-1}, the theoretical amount of oxidizing agent of 1.4 times at 30 ºC). Zhou et al.[144] innovatively proposed a self-activated advanced oxidation process with peroxyacetic acid (PAA) for recycling of spent LFP, in which Li^+ in the PAA is selectively released to convert $FePO_4$. To be specific, PAA prepared by a mixture of H_2O_2 and CH_3COOH with 1:1 volume ratio stood for 24 hours was used to leach Li^+ from the mixed slurry of LFP powder and HCl solution. Under an optimized condition, *i.e.,* reaction temperature of 25°C, PAA concentration of 0.6 vol%, slurry density of 80 g L^{-1}, and leaching time of 15 minutes, the leaching efficiency of Li reached 99.02%. However, most of the oxidants are very expensive, so not only their oxidation efficiency but also their cost should be considered in large-scale industrial applications.

4.3 Mechanochemical method

The mechanochemical method is to induce the recovery of material structure by mechanical force, thereby regaining its physical and chemical properties (Figure 7a).[20] Compared with the pyrometallurgy and hydrometallurgy methods, the mechanochemical process can reduce the activation energy of materials and improve the reaction activity without the use of solvents, which provides an alternative method for recycling the valuable metals from LFP.[145-146] The mechanical force commonly generated by ball-milling transfers energy to the powder, reducing its particle size and

disrupting its crystal structure. The solid grinding reagents (oxalic acid,[103] NaCl,[147] Na_2EDTA,[148] $Na_2S_2O_8$,[108] etc.) are used to assist the recovery. Solid materials under mechanical forces produce local collision points, which can spur instantaneous local high temperatures and induce thermochemical reactions at the nanoscale.[149] The high collision force results in the formation, diffusion, and local atom rearrangement of defects in both LFP and NaCl crystals, promoting local atomic rearrangement and leading to the isomorphic substitution of Li with Na (Figure 7b).[147] As shown in Figure 7c, Yang et al.[148] used Na_2EDTA as co-grinding agent to successfully recover Fe of 97.67% and Li of 94.29% under a recycling condition characterized by activation time of 2 hours, cathode powder-Na_2EDTA mass ratio of 3:1, H_3PO_4 of 0.6 M, solid-liquid ratio of 50 g L^{-1} and leaching time of 20 minutes.

Considering the influence of grinding agent on energy consumption and reaction time, Liu et al.[108] designed a $Na_2S_2O_8$-assisted solid-phase oxidation route (Figure 7d). This method successfully extracted Li of 99.7% after the ball-milling time for 5 minutes as well as maintained the olive structure of $FePO_4$. Obviously, the solid-phase oxidation design greatly improves the mechanochemical extraction efficiency of Li for spent LFP. However, it is worth noting that the energy consumption of the mechanochemical approach is higher than that of hydrometallurgy due to its low energy conversion efficiency. Therefore, the energy cost is still a problem that needs to be solved for industrial applications[150].

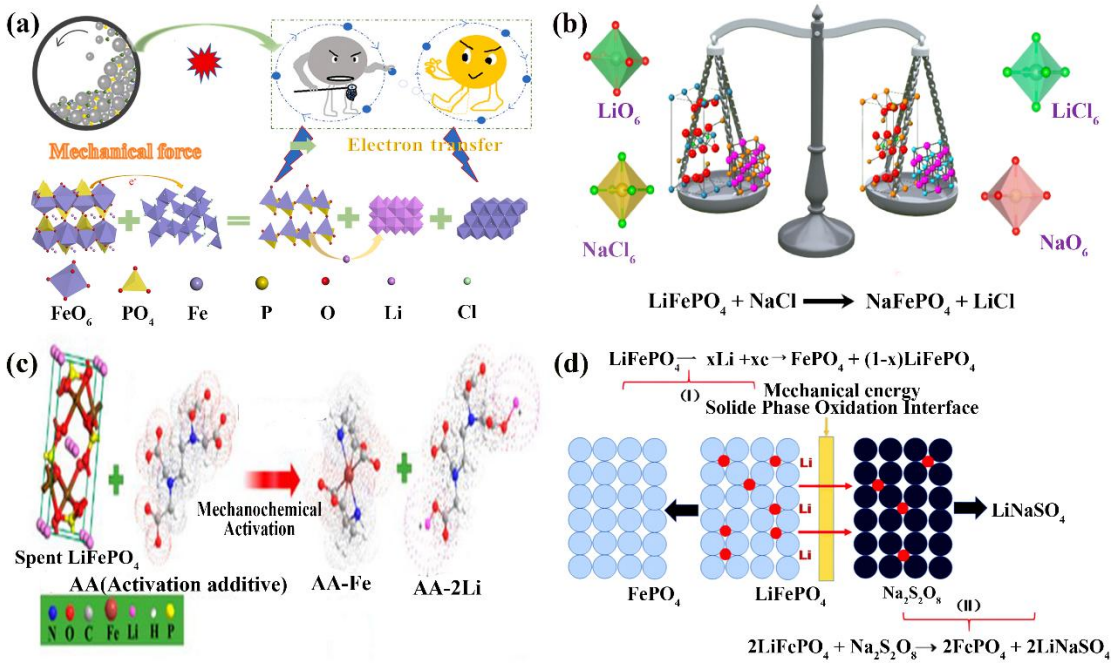


Figure 7. (a) The schematics for the recycling of spent LFP by mechanochemical method[20] (Copyright 2023 Elsevier. Reproduced with permission from ref 20.). (b) The schematics for selective extraction of Li from spent LFP batteries via a mechanochemically induced isomorphic substitution[147] (Copyright 2019 American Chemical Society. Reproduced with permission from ref 147.). (c) The schematics for recycling of spent LFP batteries by mechanical activation method[148] (Copyright 2017 American Chemical Society. Reproduced with permission from ref 148.). (d) The schematics for selective extraction of Li from a spent LFP batteries by mechanochemical solid-phase oxidation[108] (Copyright 2021 Royal Society of Chemistry. Reproduced with permission from ref 108.).

4.4 Electrochemical method

Electrochemical method has commonly attracted attention for the recovery of liquid Li^+ due to their applicability in low-concentration solutions, which reduces cost and improves economic efficiency.[151] As shown in Figure 8a, Li in the $LiFePO_4$ olivine structure can be extracted and Fe^{2+} is oxidized to Fe^{3+} ($FePO_4$) by electrolysis process.[32] Electrochemical methods can dissolve or deposit specific elements by controlling voltage, current, and electrolyte conditions to achieve the purpose of separating various

elements, which has a good prospect in LIBs recycling.[152] He's group et al.[153] utilized the characteristics of slurry electrolysis and the LFP battery charge to design an electrodialysis process that separates Li and $FePO_4$ in slurry electrolysis without any chemical reagents (Figure 8b). Under optimal conditions characterized by a reaction time of 8 hours, current density of 80 mA cm^{-2}, NaCl of 50 g L^{-1}, and LFP of 50 g L^{-1}, more than 98% Li was leached into the electrolyte and over 96% Fe was recycled as $FePO_4$/C. Qin et al.[154] reported a method to achieve selective recovery of Li from spent LFP by anode electrolysis in LiCl electrolyte (Figure 8c). The Li, Fe, and P leaching rates were 96.31%, 0.06% and 0.62%, respectively, under a current density of 15 mA g^{-1}, electrolyte concentration of 0.5 mol L^{-1} with pH of 5~8 for 12 hours. The traditional electrolysis method cannot completely recover the metal elements in LFP. Studies have shown that using ion exchange membranes for selective Li recovery can enhance the recovery efficiency of LFP. Inspired by the above progress, Li et al.[17] used acid-assisted suspension electrolysis to selectively recover Li^+ from LFP powders (Figure 8d). This process achieved a Li leaching efficiency of 99% under optimal conditions (pH of 1.7, voltage of 4.2 V, electrolyte concentration of 0.05 M, temperature of 70 ºC and the solid-liquid ratio of 13 g L^{-1}), resulting in the formation of high-purity Li_3PO_4 with an efficiency of 88.46% for the Li^+. Additionally, the membrane-free and high-temperature molten salt treatment can obviously reduce the cost and energy consumption of recovery process. Electrochemical method avoids the disadvantages originating from the use of strong acids and alkalis compared with hydrometallurgy and holds promise for eco-friendly processes. However, its high energy consumption drives up recovery costs, limiting its broad application.

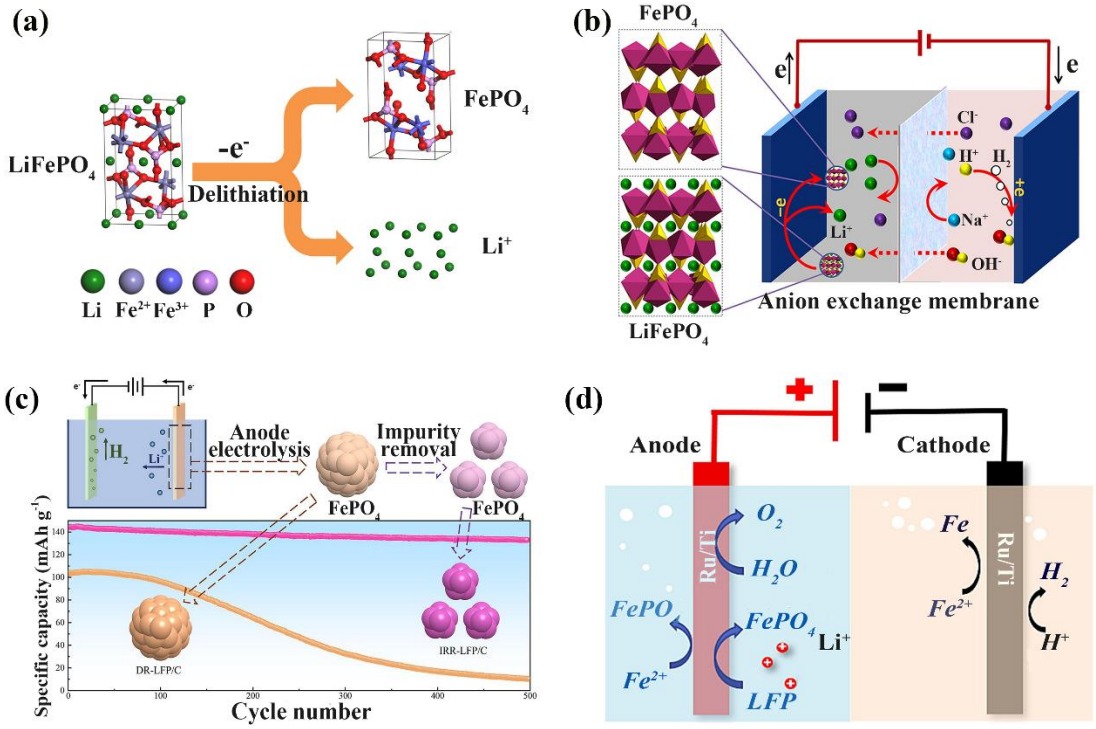


Figure 8. (a, b) The schematic diagram of the electrolysis principle for the recycling pent LFP[32] (Copyright 2020 Elsevier. Reproduced with permission from ref 32.). (c) The schematics for selective recovery of Li from spent LFP by anodic electrolysis[154] (Copyright 2024 Elsevier. Reproduced with permission from ref 154.). (d) The schematics for acid-assisted electrochemical method recovers the Li^{+} and Fe^{2+} from LFP powder[17] (Copyright 2023 Elsevier. Reproduced with permission from ref 17.).

Additionally, Deep eutectic solvents (DESs) have been received widespread attention in the field of LIBs recycling due to its strong solubility, high thermal stability, and low vapor pressure.[155] DESs are generally formed by intermolecular hydrogen bond association melting between hydrogen bond acceptors (usually choline chloride) and hydrogen bond donors (e.g., organic acids, polyols, and urea).[156] Wang et al.[109] successfully employed DESs to recover the spent LFP powders, where DESs were synthesized using choline chloride ($C_5H_{14}CINO$) and oxalic acid dihydrate ($C_2H_2O_4{\cdot}2H_2O$). The leaching efficiency of Li and Fe reached 95.3% and 85.2% under the solid-liquid ratio of 0.02 at 106 °C for 110 minutes, respectively. Chen et al.[157] found that natural DESs containing glucose and lactic acid showed a high leaching efficiency of 96.5% for Li from spent LFP at a mild temperature. Recently, Cheng's group[158] proposed an upcycling strategy for mixed failure cathode materials (LFP+LMO) in

which using green DESs as media by structural regulation and transition metal replacement to transform them into higher energy density polyanionic cathode materials. This strategy can realize full element recovery and solvent recycling in the mixed positive electrode and expand the resynthesis of other high-voltage phosphate materials, which provided a new idea for recycling low-value mixed cathode materials to upgrade to the next generation of positive electrode materials. Although DESs have achieved good results in recycling LIBs, problems like the long reaction time and the high reaction temperature limit their industrial application.

5. Resynthesis

The recycling and reuse of resources is the eternal theme in promoting the sustainable development of the economy and society. Utilizing recycled salts to synthesize LFP with high electrochemical performance is considered as most effective route for the recovery and utilization of spent LFP batteries (Figure 9a).[159-160] For instance, Zhou's group[161] proposed that using components of failed materials to directly achieve self-sufficiency in the recycling process without additional input from foreign precursor salts, which in line with the current trend of closed-loop battery recycling. To ensure the sustainable development of the LFP battery industry, the substances containing Li, Fe, and P obtained from spent LFP by pyrometallurgy and hydrometallurgy need to serve as raw materials to again prepare LFP cathode materials using various synthesis methods, namely as the resynthesis of LFP. Actually, the resynthesis of LFP is an integral part of the recycling process, in which the importance of raw material purity and quality control need to be emphasized.

Currently, the resynthesis of LFP is based on synthetic methods of LFP, including high-temperature solid-phase,[162-164] carbothermal reduction,[165-166] microwave sintering,[167-168] and hydrothermal synthesis.[147-148] methods. The raw materials include Li sources (LiOH, Li_2CO_3, $LiNO_3$, etc.), Fe sources (Fe_2O_3, $FeSO_4$, $FeCl_3$, FeC_2O_4, etc.), and P sources ($NH_4H_2PO_4$, $(NH_4)_2HPO_4$, $FePO_4$, etc.)[169-172]. The high-temperature solid-phase method involves annealing of homogeneous raw materials in a reducing atmosphere at temperatures in the range of 350 to 900 °C to obtain LFP powders.[173]

Although the high-temperature solid-phase method is widely applicable and cost-effective, it consumes more energy and is prone to uneven crystal growth, which affects product quality.[174] The carbothermal reduction method is an extension of the high-temperature solid-phase method, therefore, the reaction conditions and the selection of Li, Fe and P sources are essentially identical.[175] Carbothermal reduction does not require reducing atmosphere, but an additional carbon source (such as acetylene black and glucose) is introduced as a reducing agent.[166] These introduced carbons not only serve as reducing agents but also form a coating layer of LFP particles.[176] Chen et al.[105] used recycled $FePO_4$ as both Fe and P sources, recycled Li_2CO_3 as Li source, alcohol as dispersant, and glucose as C source to synthesize LFP, as shown in Figure 9b. It showed superior cyclic properties at the current density of 1, 2, and 5 *C*. The carbothermal reduction method has a relatively low reaction temperature, minimal energy consumption, and various carbon source options. However, the reaction process generates numerous environmental pollutants, necessitating meticulous control over carbon selection and quantity.[177] To address the high energy consumption associated with high-temperature sintering using the aforementioned methods, Higuchi et al.[167] firstly applied microwave sintering to synthesize single-phase LFP, in which Li_2CO_3 was usually chosen as the Li source, $NH_4H_2PO_4$ as the P source, and FeC_2O_4 as the Fe source. Unlike other methods, the microwave sintering method realizes rapid sintering and crystal growth by microwave energy input. However, it requires high equipment costs and advanced operational technology. The hydrothermal method involves a liquid-phase reaction, which has the advantages of simplicity, low energy consumption, and prevention of structural damage caused by high temperature.[153-154] The selection of raw material for the hydrothermal reaction is largely similar to that of other methods. The synthesis process may involve the addition of surfactants or template reagents to regulate the crystal growth direction, morphology, and purity of the LFP.[165, 178] However, the extended reaction duration and the requirement for high-pressure equipment result in high costs. Song et al.[128] used acids to recycle spent LFP, and then synthesized LFP cathode material by adding $FeSO_4$, H_3PO_4, LiOH and glucose through a hydrothermal reaction (Figure 9c). The LFP electrode exhibited good cyclic performance at the

current density of 1 *C*. The future development of these methods should prioritize low energy consumption, improved efficiency, and reduced costs to facilitate the industrialization and scalability of LFP recovery and resynthesis.

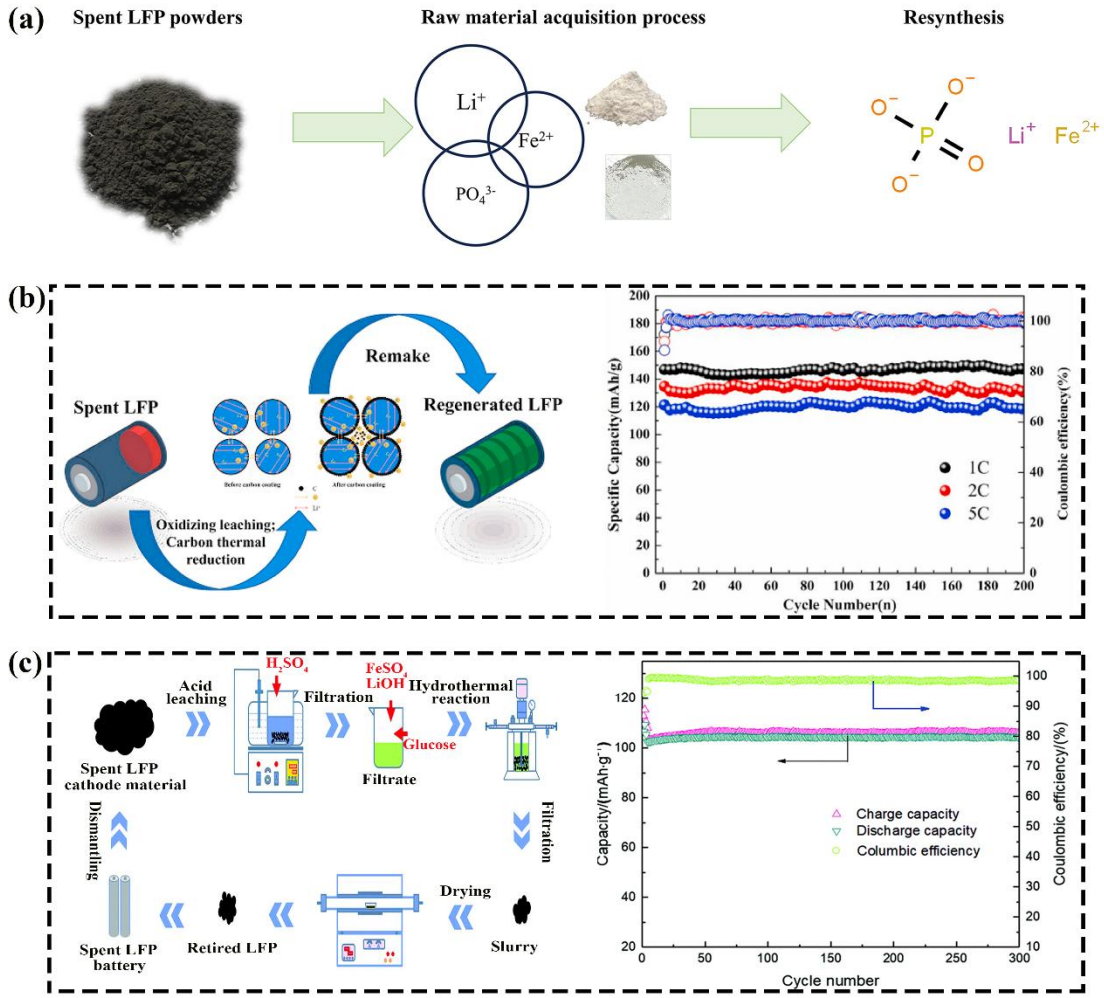


Figure 9. (a) The brief schematic diagram of LFP resynthesis. (b) The schematics for the resynthesis process of LFP by carbothermal reduction method after oxidizing leaching and corresponding cycling performances[105] (Copyright 2022 Elsevier. Reproduced with permission from ref 105.). (c) The schematics for resynthesis process of LFP by hydrothermal method after acid leaching and corresponding cycling performance[128] (Copyright 2021 Royal Society of Chemistry. Reproduced with permission from ref 128.).

It is noted that element doping can be carried out in the synthesis phase to alleviate Li^+ diffusion resistance for the purpose in improving the electrochemical properties of LFP during the mentioned above methods.[179-180] Due to the comparable ionic radii of

Mn^{2+} (0.083 nm)[181] and Fe^{2+} (0.076 nm)[182], they can be blended in any proportion. Consequently, Mn-doped result in the occupation of Fe sites by Mn^{2+} and forming $LiMn_xFe_{1-x}PO_4$.[164] Given that Ti^{4+} (0.061 nm)[166] has a similar ionic radius with Li^+ (0.068 nm)[168] and is smaller than that of Fe^{2+} (0.076 nm), Ti^{4+} tends to occupy Li sites, forming $Li_{1-x}Ti_xFePO_4$. It is noted that the purity of these raw materials significantly impacts the electrochemical performance of LFP electrode.[183] Impurities in the raw materials can cause lower battery efficiency, reduce cycle life, and compromise safety. Therefore, the resynthesis of LFP needs to enhance the purity of raw materials obtained by spent LFP.

Commonly applied techniques for resynthesis of LFP include high-temperature solid-phase method, carbothermal reduction method, microwave sintering method, and hydrothermal synthesis method. Each of these methods has its advantages, and the future development of these methods should prioritize low energy consumption, improved efficiency, and reduced costs to facilitate the industrialization and scalability of LFP recovery and resynthesis.

6. Challenges and prospect

The environmentally friendly recycling of spent LFP batteries, which serve as a core component of EVs, plays a crucial role in achieving the sustainable development of automotive industry and carbon neutrality. To enable efficient and sustainable recycling LFP batteries, significant efforts have been made by academia and industry over the past few years to optimize the recycling process, including battery pretreatment, direct recovery of spent LFP electrode materials, indirect extraction of elements, as well as resynthesis of LFP.

The quality of the battery pretreatment, especially the separation process assumes a key role in determining the effectiveness of subsequent LFP materials recovery processes. Magnetic separation is highlighted as a simpler, more efficient, cost-effective and environmentally friendly method to separate cathode materials and current collectors from dismantled spent LPF batteries. However, its separation efficiency is related to the magnetic susceptibility of the materials. The separation methods of Al foil

are outlined in terms of the respective approach process, advantages and disadvantages, highlighting the application potentiality of physical separation in industry.

Regarding the direct recovery of spent LPF cathodes, we accentuate the research progress in lithium replenishment at the material scale and electrode scale. While these direct recovery technologies have economic and environmental advantages, the stringent requirements for pre-treatment and poor recovery effectiveness greatly limit their application in the industry.

The extraction of elements from spent LFP is the mainstream method in the industry, which mainly includes pyrometallurgy, hydrometallurgy, mechanochemical methods, and electrochemical leaching. Pyrometallurgy, while effective in decomposing batteries materials, is characterized by high energy consumption and significant environmental pollution. Hydrometallurgy, which involves dissolution and extraction processes, is expensive and requires wastewater treatment, despite its relatively low environmental disruption. Mechanochemical method do not require high-temperature treatment and solvent addition, which makes them more environmentally friendly. However, their recovery efficiency for chemical components is lower than those of other methods, and require equipment with high cost. Electrochemical method avoids the disadvantages resulting from the use of strong acids and alkali. However, the higher significant energy consumption drives up its recovery costs and limits its application field. Therefore, a recovery strategy combined with two or more of the methods mentioned above is widely used in the industry, which integrates the strengths of these methods.

Using recycled salts or compounds containing P, Li and Fe obtained by element extraction as raw materials to synthesize LFP with high electrochemical performance represents the most effective route for the utilization of spent LFP.

Although considerable progress has been achieved in the field of LIBs recycling, the LFP recycling industry has not reached the ideal degree of the industry, and is still full of challenges and opportunities. If we want to achieve the development of LFP integrated recycling methods and promote the sustainable development of the LFP batteries industry, we could focus on the following goals:

(1) The current recycling methods have one or more drawbacks such as high energy consumption, low recycling efficiency, high cost, etc., which can't meet the development demands of the LFP recycling industry. Therefore, it is necessary to explore and develop advanced recycling methods to overcome these challenges. The recycling process should aim to shorten the recovery steps and reduce the use of expensive reagents as much as possible, thus maximizing the economic benefits of recovery. Moreover, energy consumption is one of the main problems faced by various recycling methods, it not only affects recovery costs, but also impacts the environment. Therefore, it is necessary to reduce energy consumption as much as possible in the production process.

(2) Formulating and completing relevant standards for the assembly of batteries, and unifying the shape of the batteries as much as possible to promote the development of mechanical automatic disassembly technology. Assembling batteries with eco-friendly and non-toxic electrolytes to minimize the environmental impact caused by electrolyte volatilization during the battery disassembly process. Furthermore, the current recycling of LFP primarily focuses on the recovery of Li, overlooking the retrieval of other valuable resources. Therefore, popularizing the importance of closed-loop recycling for industrial development and resource utilization, and increasing recycling of components other than Li and precious metals.

(3) While the laboratory-scale process shows promise, industrial-scale recycling of LFP batteries requires further refinement to address safety, environmental, and efficiency concerns. Moreover, the performance issues of resynthesized materials also need to be improved. The majority of LFP recycling research is an urgent need to develop cost-effective energy-saving, green, and sustainable closed-loop recycling technologies to facilitate the transition of LFP recycling from laboratory research to industrial applications.

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Conflict of interest

The authors declare no competing financial interests.

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