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Recycling technologies of spent lithium-ion batteries and future directions: A review

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Abstract: Lithium-ion batteries (LIBs) are the most popular energy storage devices due to their high energy density, high operating voltage, and long cycle life. However, green and effective recycling methods are needed because LIBs contain heavy metals such as Co, Ni, and Mn and organic compounds inside, which seriously threaten human health and the environment. In this work, we review the current status of spent LIB recycling, discuss the traditional pyrometallurgical and hydrometallurgical recovery processes, and summarize the existing short-process recovery technologies such as salt-assisted roasting, flotation processes, and direct recycling. Finally, we analyze the problems and potential research prospects of the current recycling process, and point out that the multidisciplinary integration of recycling will become the mainstream technology for the development of spent LIBs.

Key words: spent lithium battery; short-process recycling; secondary resources; pretreatment; metal recovery

1 Introduction

Energy is the key driver of human social development and technological progress. The tightening of the global energy supply chain has highlighted the issues caused by mankind's reliance on fossil energy and unequal energy distribution. According to the report of the International Energy Agency (IEA), oil topped the energy consumption list in 2022 and accounted for a proportion of 25.7%. Meanwhile, coal, natural gas, hydro-energy, renewable energy, and nuclear energy accounted for 24.4%, 18.3%, 7.0%, 11.0%, and 6.4%, respectively (Fig. 1(a)). Renewable energy types have grown rapidly in the last decade, and their global consumption increased from 9.63 EJ in 2010 to 48.66 EJ in 2022 (Fig. 1(b)). Solar and wind energy are becoming the primary ways of generating electricity. However, because long-distance power transmission unavoidably results in large losses, an effective and dependable energy storage system must be developed.

The greenhouse effect caused by the excessive consumption of fossil energy has become the most serious environmental problem to be solved worldwide. The IEA report shows that the concentration of CO_2 in the atmosphere increased from 32877 to 36930 mT between 2010 and 2022, showing an increase of 17.6% (Fig. 1(c)). Transport has been emitting the most CO_2 since 2000. Increasing the use of new energy technologies in the transportation industry will considerably reduce its negative environmental impact [1]. Currently, electric vehicles (EVs) and new power batteries are eliciting increased attention. LIBs play a huge role

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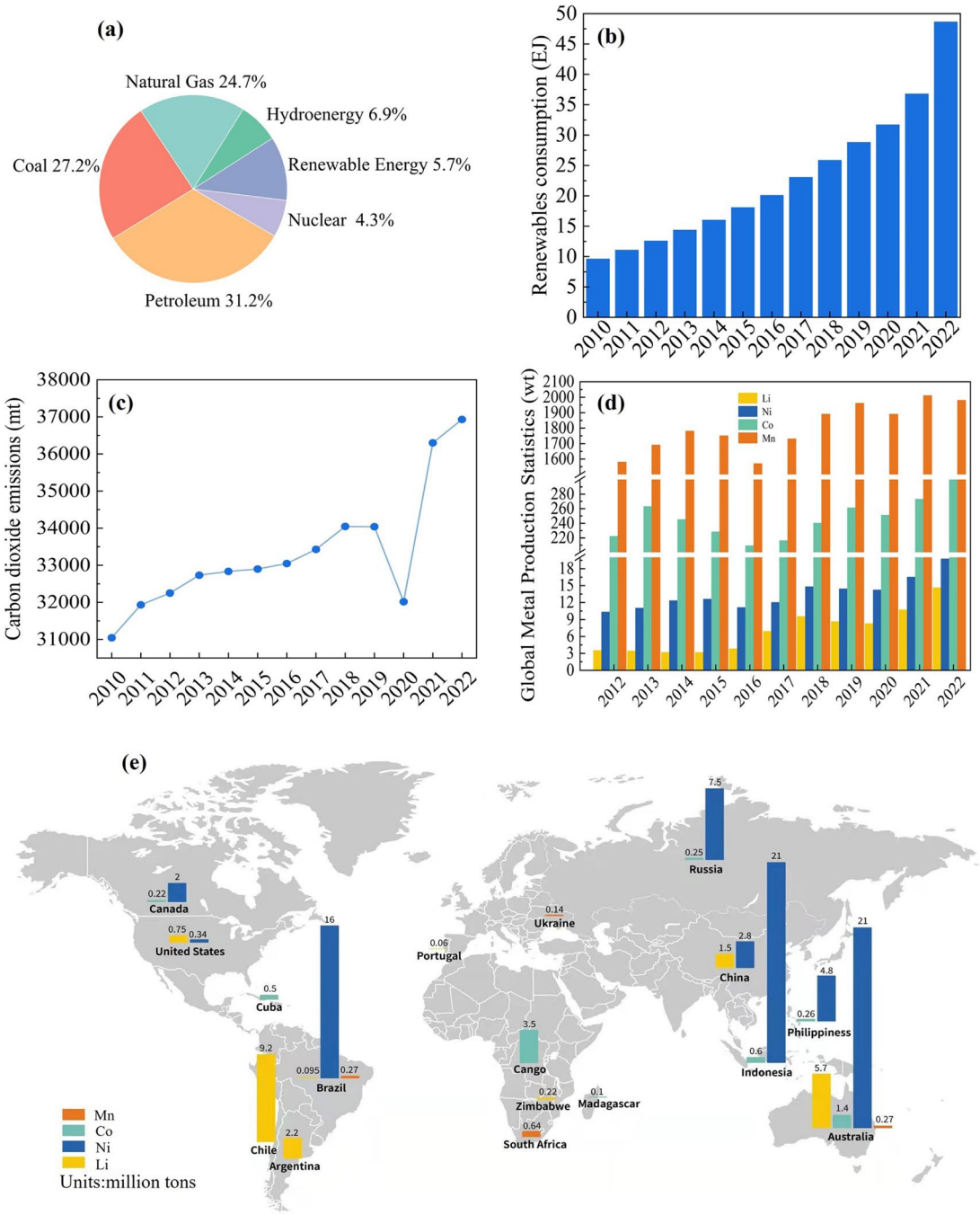

Fig. 1 Global energy consumption in 2022 (a); Renewable energy consumption from 2010 to 2022) (b); Global carbon dioxide emission from 2010 to 2022 (c); Global production of Li, Ni, Co, Mn metals in 2022 (d); Global storage distribution map of Li, Ni, Co and Mn in 2022 (e)

in electrified transportation and large-scale power storage because of their high specific energy and power density, simple operation, safe use, and long storage life.

In 1985, LIBs, which were first developed by Sony employees [2], came into commercial use. LIBs have been used in various applications, such as EVs, light electronics, and energy storage. The export of LIBs increased remarkably in the first half of 2022; it totalled RMB¥74.3×10^{10} in the first half of this year and increased by roughly 70% year on year, according to Industry Statistics [3]. Although LIBs have a long storage life, they generally last for eight years [4]. In 2016, the first batch of LIBs installed and used in China began to be decommissioned, and the number of spent LIBs gradually increased over the next year.

LIBs are more environmentally friendly than

dry cells, but they can cause extremely serious environmental pollution if spent LIBs are not recycled properly. Some rechargeable batteries contain heavy metals, such as Pb, Hg, Cd, and Ni. Pb is known to have adverse effects, including mental retardation and cognitive impairment. Ni can enter the body through the skin and cause allergic dermatitis and other negative symptoms. The cathode-active materials (CAMs) in LIBs also contain toxic elements. Spent LIBs can release heavy metal elements after decomposition, causing severe land and water pollution. In addition, the Li contained in spent LIBs is a chemically reactive element that can cause digestive and nervous system disorders if ingested [5].

Furthermore, the electrolyte released by spent LIBs is a major cause of pollution, and the electrolyte is typically made up of three categories of chemicals: (1) Organic solvents include propylene carbonate (PC), vinyl carbonate (EC), diethyl carbonate (DEC), dimethyl sulfoxide (DMSO), dimethyl carbonate (DMC), methyl ethyl carbonate, and others. (2) Lithium salts are used as electrolytes, such as lithium hexafluoroarsenate ($LiAsF_6$), lithium perchlorate ($LiClO_4$), lithium tetrafluoroborate ($LiBF_4$), and others. (3) Additives are commonly used to improve electrolyte performance, such as by increasing electrolyte conductivity and improving battery safety and stability. These three types of compounds are simple to make but difficult to retrieve, and when exposed to air, they emit an unpleasant, irritating stench. Furthermore, when hydrolyzed, electrolyte lithium salt produces poisonous arsenide and phosphide, aggravating environmental pollution [6]. Table 1 gives the chemical characteristics and potential risks of several lithium-ion battery materials.

The demand for Li, Ni, Co, and Mn is on the rise due to the rapid development of LIBs and the power vehicle industry. The global production of Li, Ni, Co, and Mn metals is shown in Fig. 1(d), and the global distribution of Li, Ni, Co, and Mn resources is presented in Fig. 1(e). Currently, dozens of countries in the world have abundant Li resources [15]. However, most Li mines are not in China, resulting in China's import of large quantities of ore every year. Spent LIBs contain abundant Li and are considered a high-Li secondary resource. According to LARCHER and TARASCON [16], 1 t of Li can be extracted from 14 t of spent LIBs, but it takes 250 t of Li ore or

Table 1 Main components and potential hazards of lithium-ion batteries

Component	Composition	Hazard
Cathode	Lithium cobaltate (LCO)	Affect human respiratory system and cause congestion, edema, and pulmonary bleeding [7]
	Lithium manganate (LMO)	Damage to human lungs [8]
	Lithium nickel−cobalt manganate	Cause human skin cancer [8]
	Aluminum foil	Inhalation lung injury [9]
Anode	Copper foil	Copper dust and smoke can cause harm to human stomach and intestine [10]
	Graphite	Cause irritation to human eyes and mucous membranes [8]
Electrolyte	$LiPF_6$	React easily with water in air to produce white fumes, and have strong erosive effect on human eyes, skin, and especially lungs [11]
	$LiBF_4$	Very polluting to water bodies, cause strong skin irritation in small amounts, and serious eye health hazard [11]
	$LiAsF_6$	Serious pollution of water resources
Electrolyte solution	Ethylene carbonate Dimethyl carbonate (DMC) Diethyl carbonate	Organic pollution [12]
Separator	Polypropylene (PP) Polyethylene (PE)	Organic pollution [13]
Binder	Polyvinylidene fluoride Partial chloroethylene	Organic pollution [14]

750 t of Li-containing brine to extract 1 t of Li via the conventional process. If green, efficient recycling of spent LIBs is implemented, the country's dependence on imported Li resources can be alleviated, and green and healthy development of the LIB industry can be realized.

The recycling of spent LIBs has recently emerged as a research hotspot in the resource and environment field, and due to the tireless effort of many academics, two types of recycling technologies, namely, pyrometallurgy and hydrometallurgy, have been introduced. Pyro-metallurgical processes recover valuable metals, such as Ni, Co, and Cu, through high-temperature reduction melting, a simple process with a large processing capacity but with a substantial loss of valuable components and high energy consumption. Hydrometallurgy has a high metal recovery rate and a broad application range, but it suffers from a lengthy pretreatment procedure and problematic metal element separation. Although the spent LIB recycling market is still in its infancy, competition is tough. In recent years, the short-process recycling of spent LIBs has gained popularity. This process attempts to obtain a high recovery rate for each important metal whilst simplifying the recycling process and enhancing the industry's economy and environmental friendliness. Few reviews, however, have thoroughly explored these recycling processes for spent LIBs. In this review, the authors elaborate on the present recycling process by examining the structure of LIBs, outlining the current short-process recycling technology, and forecasting the future development of recycling technology.

2 Structure of LIBs

LIBs can be cylindrical, button-shaped, thin plate-shaped, or cubic [17,18]. They are composed of cathode, anode, electrolyte, and separators [19−22]. The cathode of LIBs is made of aluminum foil coated with CAMs such as $LiCoO_2$, $LiMn_2O_4$, Li−Fe−phosphate (LFP), and Ni−Co−Mn (NCM). The anode material can be carbon, graphite, or Li titanate [23]. Polyvinylidene difluoride (PVDF) is the most commonly used positive binder, and styrene butadiene rubber and carboxymethyl cellulose are the most commonly employed negative binders. Acetylene black is commonly utilized as a conducting agent. The electrolyte is a mixture of Li salts and organic solvents [24,25].

LIBs rely on Li^+ to move between positive and negative electrodes and complete charging and discharging. In the case of common lithium cobalt oxide batteries (LCOs), the electrode response during charging and discharging is as follows:

Cathode:

$$LiCoO_2 \underset{\text{Dicharge}}{\overset{\text{Charge}}{\rightleftharpoons}} Li_{1-x}CoO_2 + xLi^+ + xe \quad (1)$$

Anode:

$$nC + xLi^+ + xe \underset{\text{Dicharge}}{\overset{\text{Charge}}{\rightleftharpoons}} Li_xC_n \quad (2)$$

Reaction:

$$LiCoO_2 + nC \underset{\text{Dicharge}}{\overset{\text{Charge}}{\rightleftharpoons}} Li_{1-x}CoO_2 + Li_xC_n \quad (3)$$

When the battery is charged, the Li^+ on the positive electrode comes out under an external electric field, reaches the negative electrode through a separator in the electrolyte, and acquires electrons on the negative electrode, forming a detachment compound. The negative material acquires negative electrodes and forms a Li-embedded compound. When the battery is discharged, the opposite reaction occurs. The previously formed Li compound loses electrons, allowing Li^+ to escape, travel through the electrolyte to the positive electrode, and embed itself into the cathode materials. Outside the cell, the negative electrode loses electrons, and the positive electrode gains them.

3 Recycling technologies of spent LIBs

3.1 Echelon utilization of LIBs

The explosive growth of EVs has increased the consumption of LIBs. LIBs are subject to aging due to their battery pack mode, usage environment, charging and discharging frequency, and depth [26]. The aging of LIBs or the decline of their capacity is the result of various chemical reactions, and the mechanism is complex. Previous studies have suggested that the failure mechanisms of LIBs include high battery self-discharge, electrolyte loss and decomposition, CAM consumption, and crystal structure change in CAMs [27−29].

Given that the average life of LIBs is about five years [30], the first batch is now approaching the limit of use. Traditional disposal methods, such as landfills and incineration, cause severe damage to soil, air, and water environments. The recovery

process of LFP and NCM, which dominate almost the entire market, is shown in Fig. 2. The first step is echelon utilization when the capacity of the LIB is reduced. When the battery cannot be used, the metal in the electrodes can be recovered by pre-processing, fire processing, and hydrometallurgy.

Currently, three performance evaluation indexes are used for LIBs: battery state of charge (SOC), battery state of health (SOH), and battery state of function (SOF) [31]. Accurate evaluation of SOC is crucial for the service life and usage of LIBs and the development of the power vehicle industry. SOC evaluation methods include traditional ampere−hour integration [32,33], open-circuit voltage [34,35], model-based [36], and data-driven methods [37,38]. SOC evaluation methods based on deep learning are being updated as AI continues to evolve.

SOH is a parameter used to detect whether the state of batteries is reliable and safe [39]. In the testing process, SOH parameters can control the charge storage capacity inside the battery and regulate the charge−discharge voltage, current, and heating efficiency of the battery management system through SOH adjustment to prolong the service life of LIBs. SOH can be calculated with battery capacity, internal resistance, and number of cycles [40]. CHEN et al [41] reported that SOH can be defined by the capacity-related parameters of LIBs as follows:

$$\mathrm{SOH}=\frac{C_{\mathrm{bat}}}{C_{\mathrm{norminal}}}\times 100\% \tag{4}$$

where C_{bat} is the current capacity and C_{norminal} is the rated capacity. This approach is relatively simple when used to define the battery's health state, but the determination of the battery's current capacity in real-world operation is cumbersome and requires a large amount of data. The change in internal resistance seriously limits the charge and discharge currents of LIBs.

DAI et al [42] proposed the use of internal resistance to define SOH, and its calculation formula is as follows:

$$\mathrm{SOH}=\frac{R_{\mathrm{EOL}}-R}{R_{\mathrm{EOL}}-R_{\mathrm{NEW}}}\times 100\% \tag{5}$$

where R_{EOL} is the internal resistance of the battery

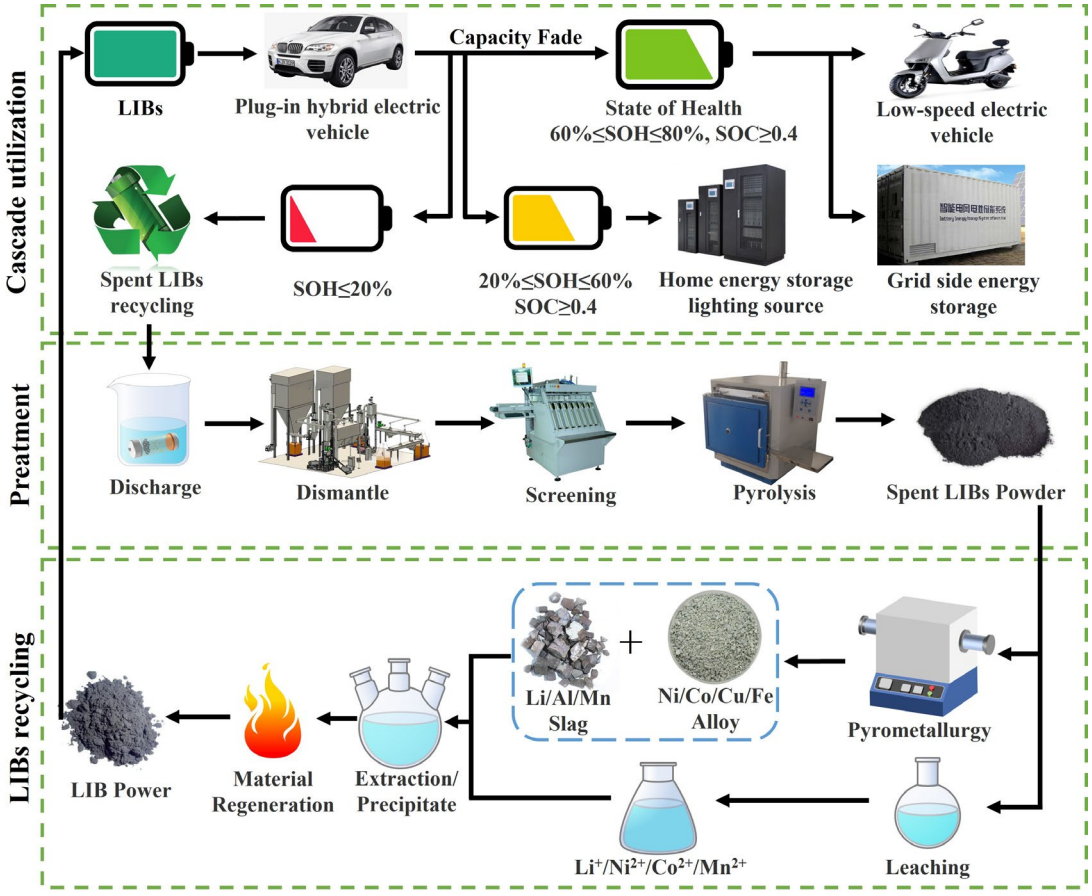

Fig. 2 Flow chart of LIB recycling

when it is retired, R is the current internal resistance of the battery, and R_{NEW} represents the internal resistance when the battery is assembled.

In addition, ZHANG et al [40] stated that the number of remaining cycles can be used to define battery SOH, and the formula is as follows:

$$SOH=\frac{C_{remain}}{C_{total}}\times 100\% \quad (6)$$

where C_{remain} is the number of remaining cycles of LIBs and C_{total} is the total number of cycles. The total number of cycles is marked by the manufacturer when batteries leave factories; thus, defining SOH in terms of the cycle number is simple.

SOH can be easily and accurately obtained by the method of definition, but the results obtained by this method are not exact because SOH is an estimated value. The problem of battery aging is difficult to avoid during the life of LIBs. As the usage time continues to increase, the external temperature, storage conditions, charge and discharge rates, and current and voltage of the batteries cause the battery SOH value to deviate from the predicted value.

To accurately estimate SOH, researchers have begun to study in detail the mechanism of battery operation and the effects of external environmental factors to ensure that SOH errors are minimized. CHENG et al [43] used empirical mode decomposition combined with neural networks to predict SOH. The model established by this method has a simple structure and high accuracy, and the average error of SOH estimation is 0.02, which effectively improves prediction accuracy. To accurately describe SOH, MA et al [44] established a multi-battery sharing framework combined with a long short-term memory neural network. The combined error of this method is only 0.0831 compared with that of the conventional prediction method. However, capacity performance continues to degrade due to the different usage environments and application methods of LIBs in real-world applications [45]. LIBs need to be retired from EVs when their capacity decreases to 80%. When the capacity is between 80% and 30%, decommissioned LIBs can be used for secondary purposes in the energy storage industry. When it drops to below 30%, the LIBs must be dismantled and recycled.

At present, many problems still exist. For example, although the technologies for detecting the SOC and SOH of spent LIBs are mature, research on battery SOF is scarce. Moreover, different industries have different technical standards for batteries. The technical standards of power and energy storage batteries are independent; that is, they comply with the guidelines in their respective industries, making the promotion of gradual utilization difficult.

3.2 Pretreatment process

LIB electrodes are often assembled using PVDF as the electrode binder [46]. The disassembled spent LIB cathodes have complex compositions and need to be pretreated to improve the efficiency of subsequent pyrometallurgical or hydrometallurgical processing [47−49].

Conventional pretreatment methods involve mechanical treatment, dissolution, separation, and other steps [50,51]. Pretreatment is crucial for the subsequent recovery of anode and cathode materials. DIEKMANA et al [52] reported that in industrial production, three problems related to spent LIBs are encountered due to the nature of LIBs; the three problems are electrical, fire, and chemical hazards. These problems increase with battery capacity and energy density [53−56].

3.2.1 Discharge process

Spent LIBs still have remaining charges. If the discharging operation is not implemented effectively before a crushing operation, experiments and industrial production will face serious safety risks. At present, the common discharge methods for spent LIBs are soaking batteries in conductive salt solution [54], short-circuiting with conductor metal powder or semiconductor graphite [57], and discharging by extrusion [58].

The direct compression method short-circuits the cathode and anode of the battery, and the compressed battery is then placed in water for rapid discharge. KIM et al [59] placed a disassembled battery in distilled water. Its voltage dropped rapidly within 10 min, and it was fully discharged within 70 min. To improve battery discharge speed, OJANEN et al [60] introduced NaCl, Na_2SO_4, $FeSO_4$, and $ZnSO_4$ salt solutions into distilled water, measured the evolution of battery voltage in each solution, and studied the influence of soaking in conductive salt solutions on battery discharge (Fig. 3). Among the four conductive salt solutions,

NaCl is the most efficient conductor, and the discharge time decreases with increasing NaCl concentration. The conductive metal powder discharge method and the semiconductor graphite discharge method are physical discharge approaches that produce a large amount of heat in the discharge process and require timely heat dissipation. In industrial production, physical discharge is limited by device performance. Therefore, the procedure for addressing the safety issues of physical discharge needs to be developed further.

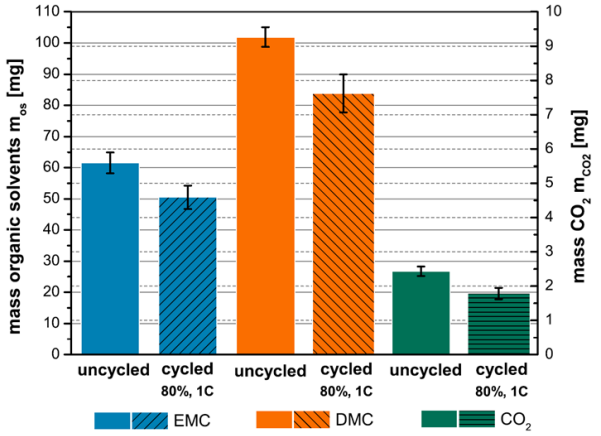

Fig. 3 Gas mass released during crushing of spent lithium-ion batteries [52]

3.2.2 Mechanical pretreatment

Dismantling is the first step in mechanical pretreatment. In laboratories, the number of LIBs that need to be disassembled and broken is small, so manual disassembly can be used. In industrial production, however, as the amount of spent LIBs increases, manual disassembly is no longer feasible, and workers use only relatively simple protective measures during disassembly [61]. LI et al [54] found that disassembled batteries contain dimethyl carbonate and tert-butylbenzene, which pose a great threat to the health of factory workers. In general, activated carbon and alkaline solutions are used to treat the exhaust gases generated during battery disassembly. The disassembly of large quantities of spent LIBs requires the use of mechanical devices instead of manual manipulation.

Crushing is necessary to enrich the valuable parts of the disassembled material and allow the battery components to separate. Crushing may cause a short circuit due to the need for compression treatment of spent LIBs, and the high-speed operation of machinery makes the temperature in the crushing chamber reach 300 °C [62]. The battery must be discharged before disassembly to prevent spontaneous combustion caused by the short-circuiting of spent LIBs. PINEGA and SMITH [63] invented a crushing process under inert gas with two stages of crushing implemented by a low-speed rotary mill and a high-speed impact mill, which enable the disassembled LIBs to be crushed safely and the electrode material of the spent LIBs to be adequately separated. The extreme temperature generated in the crushing chamber also causes the remaining electrolytes in the electrode material to evaporate, producing toxic gases [62].

Depending on the type of LIB, the gas decomposed from the electrolyte considerably varies, with DMC, EMC, and CO_2 being the main components. In industrial production and laboratories, filters are commonly used for the absorption of volatile gases from electrolytes. DIEKMANA et al [52] investigated the release of gases from the crushing of spent and normal LIBs and found that the release of DMC and EMC from spent LIBs is much higher than that from fresh batteries. They concluded that prolonged charge and discharge are the main causes of anode aging in LIBs.

Spent LIB crushing can be classified as dry or wet crushing, depending on the crushing environment. ZHANG et al [64] used dry and wet crushers to crush spent LIBs from different mobile phones. Their results showed that the dry crushing of spent LIBs is selective, and the particle size of most of the products is >2 mm and < 0.25 mm. The crushed fine products mainly contain Co, O, and C, with trace amounts of F, P, Cu, and Mn. Owing to the influence of water in wet crushing, the chemical reaction of LiF_6 hydrolysis in the electrolyte results in the loss of F, P, Cu, Mn, and other elements, and other impurities are mixed. A comparison of the fragmentation of LIBs under different conditions showed that wet crushing of LIBs results in fine particle size and easy separation of components; dry crushing allows for selective separation depending on the physical properties of the crushed components. ZHANG et al [65] conducted a re-study of dry crushing cells to determine the optimal conditions for the crushing of electrode materials. The crushing results showed that spent LIBs have excellent selective crushing performance,

and specific elements can be enriched by controlling the particle size of the crushed products. In addition, the crystal form and chemical properties of CAMs are not changed by crushing, but the residual organic matter on the plate needs to be removed before subsequent flotation.

Dry and wet crushing require discharge preparation, which increases the cost and complexity of recycling, and standard discharge technology creates a huge volume of contaminated waste salt solution that is difficult to handle. The crushing of spent LIBs is the most essential step in the pretreatment process because it defines the degree of separation of each valuable component in the crushed product and the difficulty of subsequent recycling of valuable components. ZHONG et al [66] discovered that temperature and atmosphere are the main causes of safety accidents in the crushing process; they revealed the causes of ignition and explosion phenomena in the dismantling process and innovatively developed the technology and equipment for charged crushing. This technology ensures safe implementation, greatly simplifies the pretreatment process, achieves harmless treatment of electrolytes while crushing efficiently, and provides a new direction for the future short-process recycling of spent LIBs.

After crushing, the separation of the different components of the crushed cell can be realized by sieving. Based on the different properties of broken cells, the approximate size range for screening has been determined to be 1−50 mm [67]. SHIN et al [68] divided crushed materials into three classes with different particle sizes after crushing. Experimentally, plastic casings of Al and Cu can be sifted through a coarse particle-size sieve. By regrinding the metal fraction to <0.075 mm, GRANATA et al [69] found that the particle size of Li, Co, and Ni to be recovered in the metal fraction is less than 1 mm, whereas the particle size of Cu and Al is larger than 1 mm; the materials to be recovered can be separated by this particle size distribution. WANG et al [53] used a fine sieve to separate four types of broken spent LIB plates into different grain sizes and studied the distribution of elements in the different grain sizes (Figs. 4(a−d)). The results showed that the distribution of elements varies considerably amongst spent LIBs. Therefore, in the recovery of spent LIBs, the broken plate should be sieved to enrich the valuable metal.

Sieving can also be divided into dry and wet sieving, depending on the crushing method. ZHANG et al [64] compared the contents of crushing products with three size classifications of <0.25 mm, 0.25−2 mm, and >2 mm under different crushing conditions and found that wet sieving is more advantageous than dry screening in obtaining fine-grained products. Afterward, to determine the content of each metal under different separation size conditions, ZHANG et al [65] divided the crushing products into eight size intervals. The experimental results revealed that Cu and Al are mainly concentrated in coarse-grained products with recovery of 94.14%, and Co is mainly concentrated in fine-grained grades below 0.25 mm with recovery of 94.39%.

After sieving crushed products, the impurities can be further removed by various separation methods, such as magnetic separation and flotation, depending on the different physical properties (such as density, magnetism, and wettability) of the screened products. Pneumatic separation, which relies on the difference in density of sifted products, has been widely adopted in agriculture because of its economic feasibility, greenness, and simplicity [70]. In spent LIB recycling, the pneumatic separation method allows the complete separation of the separator and aluminum and copper foils. The Z-shaped pneumatic separator designed by ZHONG et al [71] can recover 98.64% of the separator and 99.23% of the collector fluid at gas flow rates of 6.96−7.8 m/s and material sizes of 3−4 cm. The trajectory gap between the collector and separator increases as the airflow velocity increases from 5.94 to 8.9 m/s, and the theoretical recovery rate is predicted at different airflow velocities.

Magnetic separation is also a common decontamination technique in the recycling process. The magnetic separation method, through the application of a magnetic field in space, enables the screening of products based on their magnetic differences to achieve separation of components; the magnetic component, which is mainly derived from iron-based materials, can be effectively separated with magnetic Co-based materials. QIU et al [72] used fluid magnetic separator to recover magnetic Co particles from spent LCO and successfully recovered 99% of the Co particles at 35 °C and a liquid-to-solid ratio of 500 mL/g.

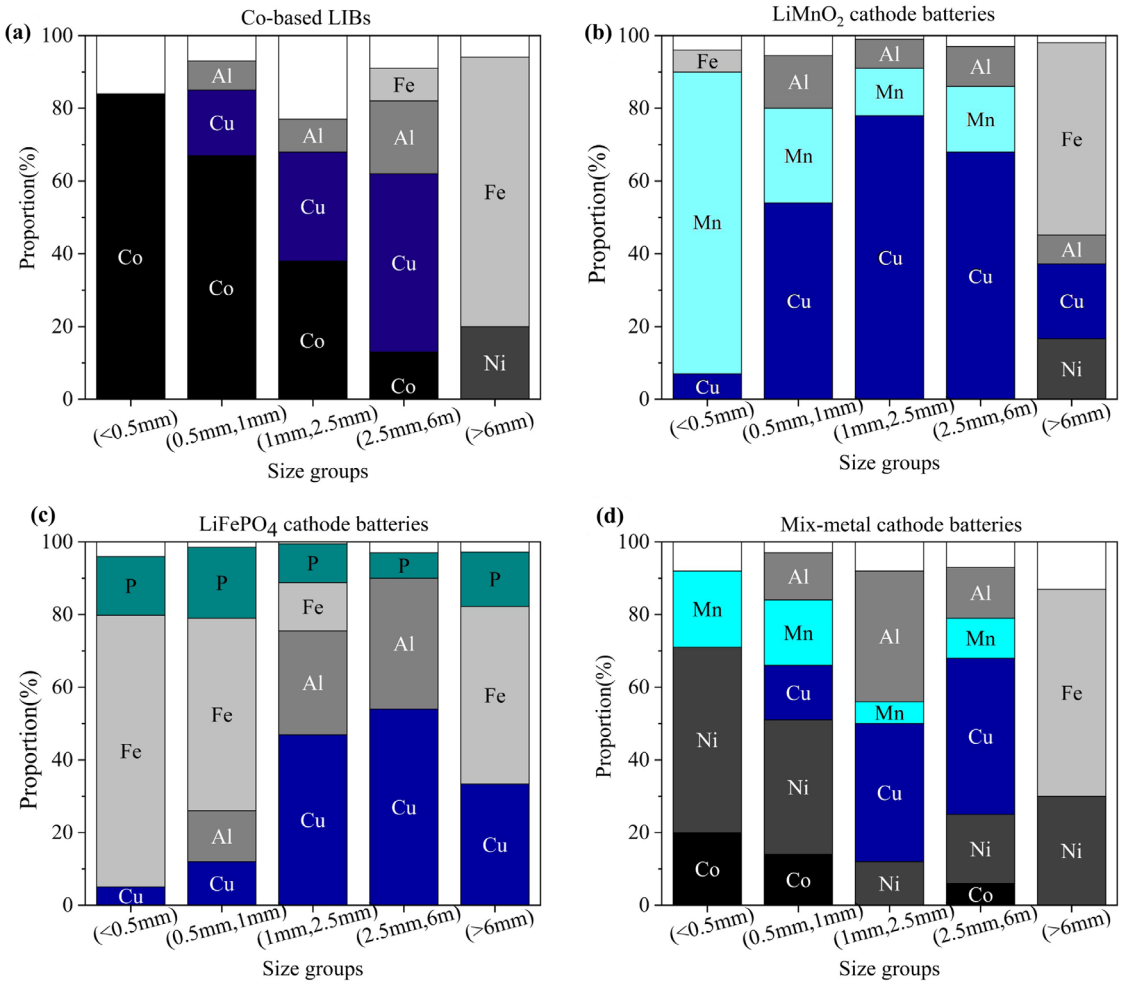

Fig. 4 Metal proportion in crushing products of various types of LIBs [53]: (a) LCO; (b) LMO; (c) LFP; (d) NCM

3.3 Pyrometallurgical recycling

Pyrometallurgy here refers to the pyrolysis of spent LIBs and the reduction melting process. Reduction melting primarily extracts precious metals, such as Ni, Co, and Cu, from spent LIBs. The technique has a simple procedure and a large processing capacity, but its growth in the field of LIB recycling is hampered by drawbacks, such as high energy consumption and substantial secondary contamination [73].

The use of the pyrolysis technique to create high-purity battery powder has attracted much attention [74]. The presence of organic materials, such as PVDF, in crushed plates can interfere with the subsequent recovery of CAMs. Thermal treatment can remove organic impurities, including binder, conductive carbon, and electrolytes, adhering to the plates, and the valence state of CAMs can be premediated by regulating the atmosphere during pyrolysis to reduce the difficulty of subsequent leaching. Additional attention needs to be paid to the pyrolysis temperature when stripping CAM from aluminum foil by pyrolysis. An extremely low pyrolysis temperature (<600 °C) cannot remove the residual organic matter from the electrode sheet, and an extremely high temperature leads to oxidation of the aluminum foil, which forms aluminum oxide in CAM and hinders subsequent leaching.

To determine why valuable materials are difficult to separate, some researchers employed the first nature principle to calculate the bonding process amongst the cathode material, PVDF, and aluminum foil. The findings indicated that the bonding between LFP and PVDF is stronger than that between PVDF and Al [46]. LFP bonds to PVDF only at the surface, and the surface chemistry does not change upon pyrolysis. Based on ensuring effective stripping of CAM while reducing the pyrolysis temperature, ZHONG et al [49] developed a method that uses dimethylformamide (DMF)-assisted pyrolysis to achieve a high CAM stripping

rate (98.93%) with a reduced pyrolysis temperature (450 °C) (Figs. 5(a, b)). The addition of DMF can accelerate the detachment between $LiFePO_4$ and the filter due to the generation of microbubbles consisting of CH_4, CO_2, H_2O, HF, and CO during pyrolysis (Figs. 5(c−e)). After analyzing and testing the pyrolysis products, the researchers proved that DMF-assisted pyrolysis of spent LIBs results in almost no Al CAM (Fig. 5(f)), and it can be used for subsequent regeneration treatment. The subsequent analysis also showed that DMF can accelerate the decomposition of electrolytes to nontoxic substances during pyrolysis, revealing the green and environmentally friendly characteristics of the technology.

Because of its ultra-fast, controllable, and energy-saving electrical heating, the flash Joule heat (FJH) process has found increasing applications in the recycling of used lithium-ion batteries in recent years, in addition to reduction smelting and pyrolysis [75,76]. CHEN et al [77] found that, compared with conventional leaching, the FJH activation process of used lithium batteries was able to heat the reaction temperature to >2100 K in a few seconds, which greatly enhanced the leaching kinetics, and the leaching rate of all the metal fractions reached 98% when using 0.01 mol/L HCl leaching. At the same time, the fast electrothermal process mitigates the diffusion loss of volatile metals (e.g., lithium) compared to the continuous melting process in pyrometallurgical methods.

3.4 Hydrometallurgical recycling

Hydrometallurgy mixes CAMs and leaching agents in solutions to recover the metals via chemical reactions, followed by precipitating the products from the liquid phase. Compared with pyrometallurgy, hydrometallurgy for recovering spent LIBs has simpler operation, lower energy consumption, faster reaction, and wider range of recovered metals. However, the large amount of effluent generated by hydrometallurgy and the relatively cumbersome operation process limit the development of hydrometallurgical recovery. The main hydrometallurgical recovery process consists of leaching, extraction, and precipitation techniques to obtain the final product, as illustrated in Fig. 6 [78,79].

3.4.1 Leaching

Depended on the reagent, leaching can be divided into acid and alkaline leaching. Alkaline leaching is achieved with the use of ammonia and other alkaline substances with different Ni, Co, and Li selectivities, resulting in the formation of stable metallic ammonia complexes [80].

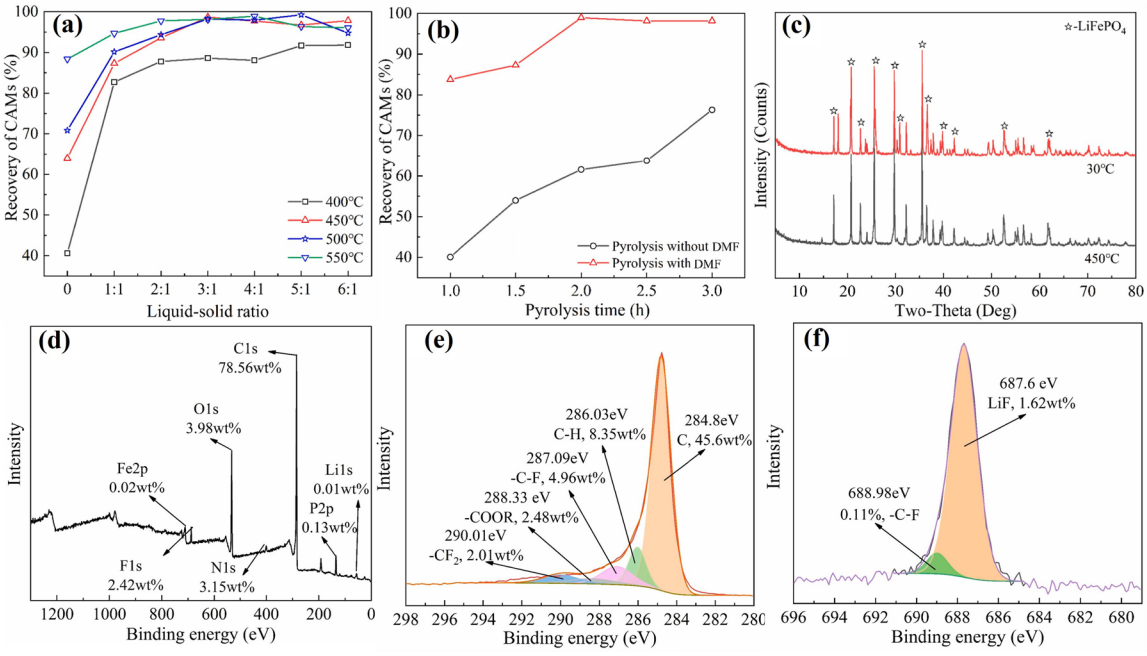

Fig. 5 Relationship between DMF supplemental levels and CAMs recovery (a); Relationship between pyrolysis time and CAMs recovery (b); XRD patterns of pyrolysis products at 30 and 450 °C (c); XPS diagram of thermal products (d); C 1s spectra of thermal products (e); F 1s spectra of thermal products (f) [49]

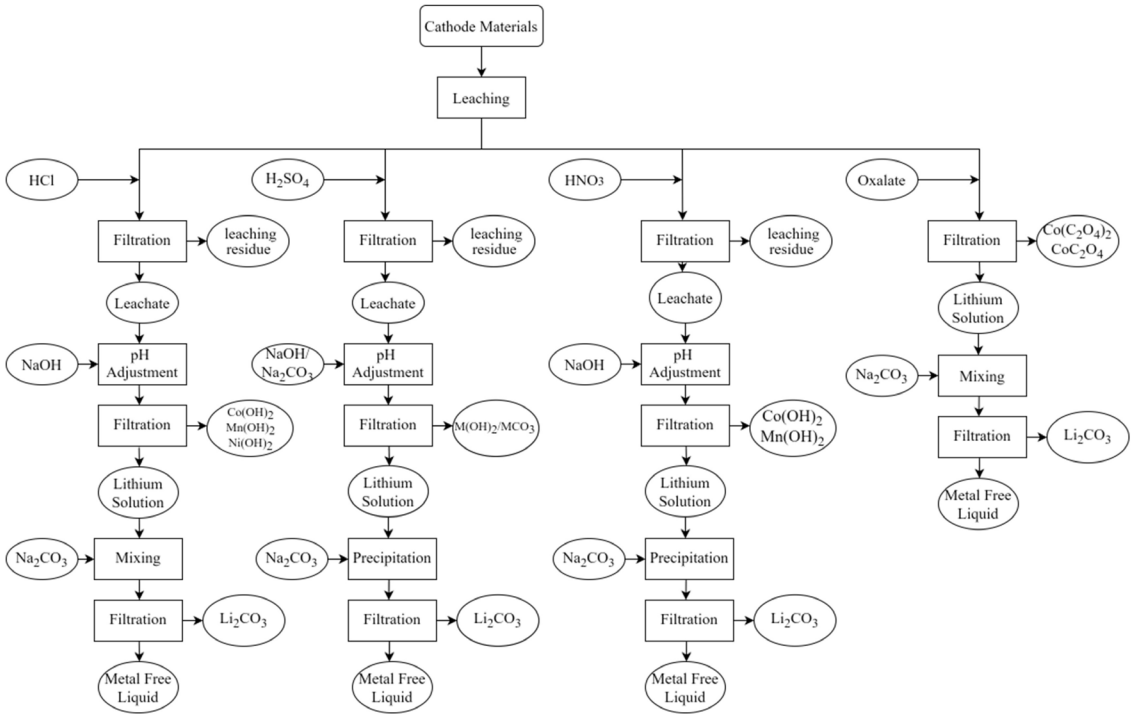

Fig. 6 Hydrometallurgy leaching flow chart [78]

However, in the alkaline leaching process, the recovery is limited by the reaction between the metal and the alkali solution. Acid leaching ensures that most of the metals and their oxides can be dissolved in the solution. In accordance with different kinds of acids, acid leaching can be divided into inorganic and organic acid leaching. HCl, H_2SO_4, and HNO_3 are the most widely used chemicals in inorganic acid leaching [81]. ZHANG et al [82] and CONTESTABILE et al [83] studied the recovery of spent LCO by HCl and found that Co and Li can be completely recovered when acid leaching is performed at 80 °C by using 2 mol/L and 4 mol/L of HCl, respectively. CASTILLO et al [84] proposed the use of nitric acid to leach $LiMnO_4$ from LIBs. The final recovery rates of Li and Mn are 100% and 95%, respectively, after 2 h of leaching at 80 °C by using 2 mol/L nitric acid solution. LEE and RHEE [85], and LI et al [86] discovered that the addition of H_2O_2 considerably improves the leaching of Co and Mn by reducing Co^{3+} and Mn^{3+} to Co^{2+} and Mn^{2+}, respectively, through the use of low concentrations of nitric acid combined with H_2O_2. SUN and QIU [87] achieved a final leaching efficiency of 76% by using 2 mol/L of H_2SO_4 at 70 °C.

Inorganic acid leaching produces a large amount of wastewater that, if not treated and discharged directly, will cause damage to the environment. Organic acid reactions are milder and more environmentally friendly than inorganic acid reactions. Commonly used organic acids for leaching include oxalic acid, citric acid, malic acid, and ascorbic acid [88]. SUN and QIU [89] leached Co and Li from the solution by using oxalic acid. During the reaction, CO_2 precipitates from the solutions and lowers the valence state of Co ions, resulting in enhanced leaching. LI et al [88] attempted to leach LCO by using malic acid, which is a natural organic acid and well suited for leaching because it decomposes easily under aerobic and anaerobic conditions. They found that the ideal leaching conditions for LCO are 1.5 mol/L malic acid, 3% H_2O_2, 90 °C, and solid-to-liquid ratio of 20 g/L; all of Li and 90% of Co can be recovered.

In addition to leaching using inorganic and organic acids, bioleaching is another effective approach. Bioleaching is different from acid- and alkaline-leaching. It uses the acid produced in the metabolism of microorganisms to dissolve the metals in the CAMs of spent LIBs. A few species of bacteria can be used to leach electrode materials. MISHRA et al [90] and XIN et al [91] employed an acidophilic bacterium and *Thiobacillus ferrous*

oxide for the bioleaching of spent LCO. *Thiobacillus ferrous* oxide uses ferrous ions for metabolism in leaching and produces sulfuric acid and iron ions to accelerate the leaching of CAMs. The Fe^{3+} produced by bacteria through metabolism can induce a series of redox reactions in leaching, with Fe^{2+} acting as a strong reducing agent that induces the reduction of Co^{3+} to Co^{2+}. Bioleaching has milder reaction conditions and is relatively less dangerous to operators than other processes. However, the industrial application of bioleaching still requires substantial research due to the difficulty of growing strains for bioleaching, the lengthy reaction time, and the treatment capacity limited by the biological properties of the strains.

3.4.2 Solvent extraction

The solvent extraction method is based on the selective adsorption of different ions by the extractor, which enables the separation and extraction of different mixed ions in solutions. Commonly used extractants include 2-ethyl phosphoric acid, trimethyl phosphonic acid, trioctylamine, diethyl hexanoic acid, and diethyl phosphoric acid mono-2-ethyl ester [92]. To describe the process of solvent extraction of electrode materials accurately, VASILYEV et al [93] developed a different mechano-mathematical model that microscopically reveals the extraction of Co, Ni, and Li from sulfate solutions via Cyanex 272 (Fig. 7). The model maps the interfacial ion exchange extraction reactions, in which the aqueous phase competes with the cations and forms different complexes in the organic phase. The model consists of nonlinear algebraic equations for all liquid-phase reactions in the extraction reaction. The nonlinear algebraic equations for the equilibrium constants and the current equilibrium equations are converted into a system of ordinary differential equations on the basis of the rates. The model was constructed, solved using MATLAB, and calibrated with the data provided by VIROLAINEN et al [94]. The simulated values are in excellent agreement with the experimental data of INOUE et al [95], demonstrating the accuracy of the method in extracting metallic elements from the electrode materials of spent LIBs.

Solvent extraction methods can be used not only for the recovery of metallic elements from spent LIBs but also for the extraction and treatment of spent LIB effluent. Spent LIB leaching is frequently performed by adding Na_2CO_3 to precipitate Li as Li_2CO_3. However, a small amount of Li^+ remains in the solution due to the solubility of Li_2CO_3. ZHANG et al [96] proposed a technique to recover Li from spent LIB recycling effluent. The effects of pH, extraction time, degree of saponification, and initial Li in the aqueous phase on extraction were investigated. More than 90% of Li in the effluent was recovered under a three-stage counterflow extraction condition with O/A of 1:1.

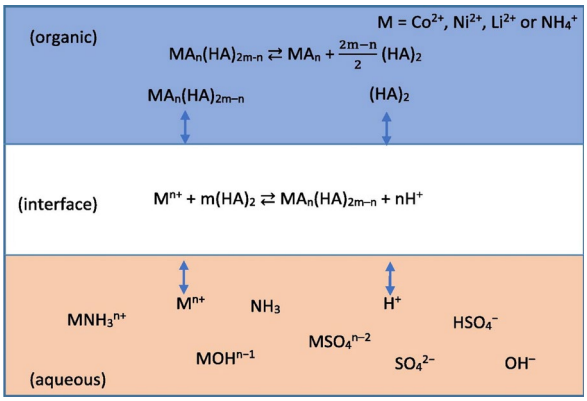

Fig. 7 Mechano-mathematical model of solvent extraction by Cyanex 272 [93]

3.4.3 Chemical precipitation

The chemical precipitation method relies on the different solubility of metal compounds under different pH conditions. The impurity elements, such as Fe^{3+}, Al^{3+}, and Cu^{2+}, contained in spent LIBs precipitate under low-pH conditions [67,97]. After removing these impurities, valuable metals, including Li, Ni, Co, and Mn, can be precipitated to settle the separation. Common precipitants include NaOH, Na_2CO_3, $H_2C_2O_4$, $(NH_4)_2C_2O_4$, and $NH_3{\cdot}H_2O$. Li, Co, Ni, and Mn can be easily recovered by adding these reagents to the leaching solution to produce insoluble materials. When the precipitation is performed, various factors, such as leaching temperature, leaching time, solution equilibrium pH, and precipitant concentration, often influence the leaching efficiency of metal element. ZHU et al [98] used H_2SO_4 mixed with H_2O_2 to leach the CAMs of spent $LiCoO_2$, which were then dissolved using $(MH_4)_2C_2O_4$ and H_2CO_3 to precipitate Li and Co, respectively. The obtained recovery rates for Co and $LiCoO_2$ were 94.7% and 71.0%, respectively, with 2 mol/L H_2SO_4 and 2.0% H_2O_2 (Figs. 8(a−c)).

To minimize environmental pollution during

recovery of electrode materials, CHEN et al [67] utilized citric acid as a chelating agent and ascorbic acid as a reducing agent to ensure a gentle and environmentally friendly leaching process. 80% of Co and all of Li were leached, confirming the feasibility of the experimental design. Cobalt oxalate and lithium fluoride, which can be used to prepare precursors for LCO, were obtained by the addition of $H_2C_2O_4$ and NH_4F to allow Co and Li precipitation.

4 New techniques for spent LIB recycling

Although extensive research has been conducted on the recycling of spent LIBs, pyro-metallurgical and hydrometallurgical techniques still have drawbacks. When hydrometallurgical technology is used in the leaching of the CAMs of spent LIBs, although all the metallic elements can be recovered, Li tends to precipitate in the end during industrial production, resulting in a low recovery rate for Li. Pyrometallurgical technology is mature, but the large loss of Li in smelting slag and the high energy consumption limit its development [99]. Hydrometallurgy consumes large amounts of acid and alkali when it is utilized to leach spent LIBs and produces a large amount of waste liquid that, if not treated in a green and clean manner, can cause great damage to the environment [100]. The advantages and disadvantages of the two methods are given in Table 2. With the ongoing research in the field of LIB recycling, the comprehensive utilization of multiple methods has become a promising research direction.

4.1 Reduction roasting

Reduction roasting was initially applied in industrial settings due to the technique's simplicity. Graphite, hydrogen, and biomass are often used as reducing agents. Actually, the typical reducing agent is carbon. The cathode material gradually transforms into Li oxide, Li carbonate, and transition metal oxides or metals over time at high temperatures (600−1000 °C), after which various metal components are successfully separated by straightforward water leaching or weak acid leaching.

HU et al [101] observed the synthesis of NCM valuable materials and proposed a new process that combines pyrometallurgy and hydrometallurgy, that is, the combined use of reduction roasting and acid leaching to recover spent LIBs. After mixing and grinding a sample of cathode powder containing a certain amount of coal, the roasted product was subjected to a rapid quenching process. The Li in NCM was successfully converted to Li_2CO_3 by roasting at 650 °C for 3 h at 19.9% carbon, and the product was obtained by water leaching. Similarly, GU et al [102] proposed a reduction roasting–sulfuric acid leaching technique to solve the current scientific challenges in NCM recycling. The original roasting could destroy the original lattice in CAMs and reduce the valence state of each metal in NCM, and H_2SO_4 could fully dissolve the NCM

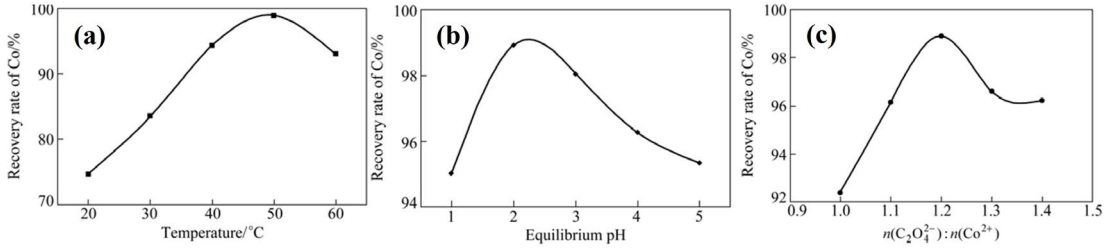

Fig. 8 Variation of recovery rate of Co with course of temperature (a), equilibrium pH (b) and ammonium oxalate concentration (c) [98]

Table 2 Advantages and disadvantages of pyro- and hydrometallurgy in spent LIBs recycling

Recycling method	Advantage	Disadvantage
Pyrometallurgy	Chemical solution free; Simple procedure; Large processing capacity; Wide applicability	High loss of Li and Mn; High energy needs; High carbon emission; Severe environmental pollution
Hydrometallurgy	High metal recovery; Production flexibility	Long pretreatment process; Complex separation of metal elements; High losses of lithium in full flow

crushing products. Afterward, the process of reduction roasting was studied thermodynamically and kinetically to reveal the principles of reduction roasting and sulfuric acid leaching from the spent NCM battery (Fig. 9).

NCM with α-$NaFeO_2$ structure is a complex compound composed of several metallic elements, and the reaction is extremely complicated during the reduction roasting process. To reveal the effect of roasting conditions on leaching, GU et al [102] leached roasted samples under different conditions and found that the metal leaching rate in NCM increases when the amount of carbon in reduction roasting is increased. They successfully leached 98.2% Li, 97.5% Ni, 98.6% Co, and 95.3% Mn at 10% carbon addition.

Another excellent additive for reduction roasting is hydrogen. As the global demand for the decarbonization of industrial production grows, the need to recover graphite or other carbon sources for high-value products is increasing. As a reducing agent for the reduction of metal oxides in a high-temperature process, hydrogen is less energy-demanding, more recyclable, and more ecologically benign than carbon [103−107]. PINEGAR et al [104] discovered that by reducing Li cobaltate with hydrogen, Li cobaltate can be converted to Co with Li oxide at a considerably low temperature (600 °C), and metal separation can be accomplished by simple water leaching with magnetic separation.

LCO is a α-$NaFeO_2$ hexagonal crystal system with high structural stability, but hydrogen can disrupt its lattice structure at low temperatures. The final form of Co is largely dependent on the amount of hydrogen injected due to the differences in the nature of the metals, but the roasting temperature determines Li. Co-production begins at 400 °C and continues until 1200 °C. At 600 °C, Li is transformed into LiOH and eventually decomposes to Li_2O at 1000 °C [105]. If the reactants are mixed with a carbon source, the carbon will convert LiOH to Li_2CO_3. From a thermodynamic standpoint, hydrogen can convert Ni, Co, and Mn oxides at high temperatures into NCM with complex elemental compositions. However, because the decomposition of NCM is a heat-absorbing reaction, the reduction reaction requires a high temperature. When the temperature is raised to 600 °C, layered NCM begins to convert into a spinel structure and releases Li_2O; at 710 °C, a considerable amount of Ni, Co, and Mn is generated [107]. After water leaching, the roasted product can recover 99.92% of Li in the form of LiOH−H_2O. After regeneration, the developed high-Ni cathode material has good electrochemical characteristics [103].

4.2 Salt-assisted roasting

Because of its simple process, high reactivity, and low pollution, salt-assisted roasting has been widely used in recent years to extract valuable components from solid wastes and refractory minerals, particularly the destruction of complex insoluble structures. Salt-assisted roasting can achieve a good deconstruction of the positive electrode materials of the waste lithium battery and convert valuable metal elements into compounds with different properties, whether it is LCO, LMO, and NCM with layered structure for the LIBs' positive electrode or LFP with olivine structure [108,109].

In comparison to pyrometallurgical technology, the salt-assisted roasting process can achieve priority extraction of lithium in electrode materials,

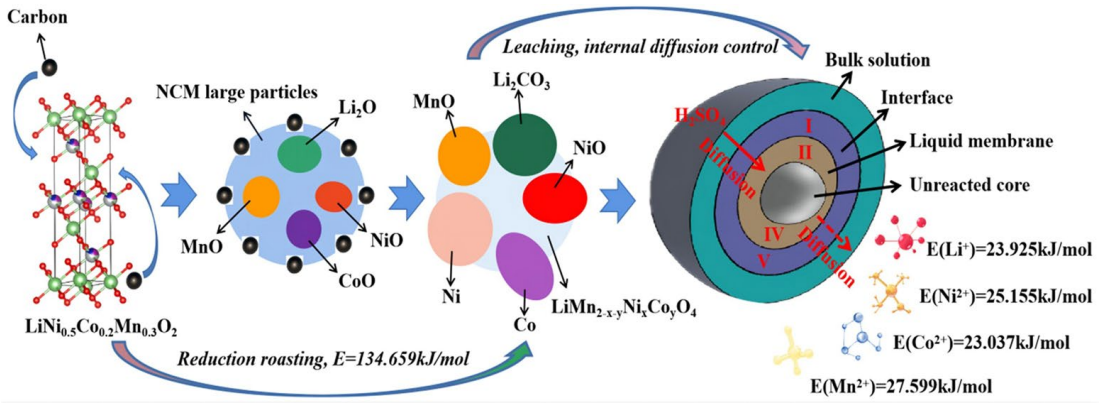

Fig. 9 Mechanism of NCM reduction roasting−sulfuric acid leaching [102]

avoiding the fact that lithium and manganese compounds cannot be recovered as a result of the lithium and manganese compounds entering the smelting slag during the process of reducing and smelting spent LIBs. In comparison to the hydrometallurgical process, salt-assisted roasting technology allows the lithium element to be extracted preferentially through water leaching in the subsequent leaching process, avoiding the loss of lithium element during the extraction and counter-extraction of nickel, cobalt, and manganese elements.

4.2.1 Sulfate roasting

Sulfuric acid is used in the sulfation roasting of battery powders at a reaction temperature lower than that of reduction roasting [110−115]. During the reaction, sulfuric acid reacts with Ni, Co, and Mn to form metal sulfates, and the cell powder, whose laminar structure is destroyed, starts to release Li^+ and form Li_2SO_4; when the temperature rises, the transition metal sulfates begin to decompose and eventually form CoO, NiO, and MnO [110,111]. Unlike in traditional roasting, sulfur is recycled as SO_4^{2-} rather than SO_x by managing the amount of sulfuric acid, thus avoiding the problem of environmental pollution [112]. The various constituents can be separated by water leaching and acid washing of the roasted product. However, the Al and F impurities contained in the powder easily produce $LiAlO_2$ and LiF with Li, lowering the rate of Li recovery. Furthermore, the lack of C makes it difficult to convert Ni, Co, and Mn in the powder into low-valence metal oxides and sulfates, thereby reducing the metal recovery rate [114].

Similarly, sulfate-assisted roasting extracts precious metal components from powder by using SO_4^{2-} in the salt [109,116−119]. Sodium sulfate, sodium bisulfate, sodium thiosulfate, and ammonium sulfate are now used in sulfate-assisted roasting. CHANG et al [117] employed anode graphite and Na_2SO_4 as additives to induce the decomposition of NCM to Li_2CO_3, NiO, CoO, and MnO at high temperatures. Li is transformed into soluble $LiNaSO_4$ by adding a small amount of sodium sulfate, followed by the recovery of valuable components by using water leaching and low-concentration acid leaching without reducing agents. Sulfation roasting with the addition of $NaHSO_4$ uses the SO_3 produced by the salt decomposition during the heating process to change the morphology of Li, Ni, Co, and Mn in NCM. CHEN et al [118] discovered that the addition of $NaHSO_4$ exerts a considerable effect on the final phases of precious metal elements (Fig. 10). During the process, Li is removed from the lamellar structure, and the other elements exist as metal oxides and trace sulfates with varying salt addition. Ni is changed to NiO, $Na_2Ni(SO_4)_2$, and $Na_6Ni(SO_4)_4$, and Co is converted to $CoMn_2O_4$ and $Na_2Co(SO_4)_2$. Mn is transformed to $CoMn_2O_4$. Approximately 99.3% of Li may be recovered at a water-leaching temperature of 60 °C, a leaching period of 30 min, and a liquid-to-solid ratio of 25:1.

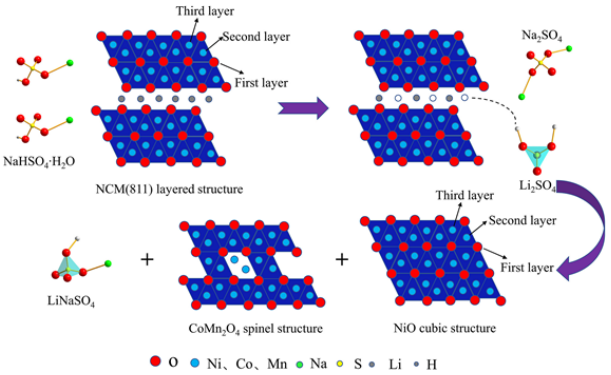

Fig. 10 Phase transition model of NCM (m_{NCM}: $m_{NaHSO_4\cdot H_2O}$=1:1.4, 600 °C) [118]

SO_x emissions can be minimized, and valuable metal resources can be recovered efficiently by limiting the quantity of roasting additives. Thermodynamic stress converts the laminar electrode material into soluble lithium sulfate and insoluble transition metal oxides. The structural thermal stability of the cathode material is critical to selective sulfation, allowing for effective Li leaching and the complete use of other metals via sulfation roasting.

4.2.2 Chlorine roasting

Chlorination roasting is a conventional pyrometallurgical technique that extracts metals from ores or solid waste by using chlorine gas (Cl_2), HCl, inorganic chloride salts (NaCl and $CaCl_2$), and organic chlorides (PVC and CCl_4) [120,121]. Given that the properties of Li and transition metal elements differ, chlorination roasting enables the selective recovery of Li from spent Li-ion batteries. Several reports have mentioned the use of Cl_2 [122], $CaCl_2$ [123−125], NH_4Cl [126,127], $SiCl_4$ [128], and PVC [129] as chlorinating agents. Cl_2 tends to

accelerate the transformation of CAMs into soluble LiCl and refractory transition metal chlorides at high temperatures because gas−solid interactions are likely to occur. With regard to the recovery of spent LCO, BARRIOS et al [122] discovered that the chlorination process of chlorine gas has three steps, as shown by the reaction equations:

$$LiCoO_2+1/2Cl_2(g)\rightarrow LiCl+1/3Co_3O_4+1/3O_2(g) \quad (7)$$

$$1/3Co_3O_4+Cl_2(g)\rightarrow CoCl_2+2/3O_2(g) \quad (8)$$

$$LiCoO_2+3/2Cl_2(g)\rightarrow LiCl+CoCl_2+O_2(g) \quad (9)$$

The change in Gibbs free energy reveals that three reactions may occur within a temperature range of 20−1000 °C. Energy change is reduced, and the reaction is accelerated when the reaction temperature surpasses the melting points of LiCl and $CoCL_2$. Roasting studies have revealed that the chlorination temperature of Li in spent LIBs is 400 °C, whereas the chlorination temperatures of Ni and Mn are 500 and 600 °C, respectively (Figs. 11(a−d)). Furthermore, the recovery of Li, Co, Ni, and Mn increases dramatically when roasting is performed at 900 °C for 30 min.

The high-temperature reaction of the solid chlorinated agents is more difficult to achieve than the high-temperature reaction of gases. HUANG et al [123] calculated NCM crystal structures and discovered that the interatomic distances of Li—O, Co—O, Ni—O, and Mn—O are 2.190, 1.926, 2.025, and 1.923, respectively (Fig. 11(e)). Existing theories suggest that the longer the interatomic chemical bonds are, the less stable the structures will be and the more likely the corresponding thermodynamic reactions will occur. Furthermore, the high-temperature reaction of $CaCl_2$ with NCM is regulated by a mild reduction driving force, which allows for the selective extraction of Li. When the reaction temperature is controlled to be 600 °C, the roasting time is 30 min, $CaCl_2$:NCM= 2:1, and the leaching solid-to-liquid ratio is 8 g/L, 98% of Li can be recovered.

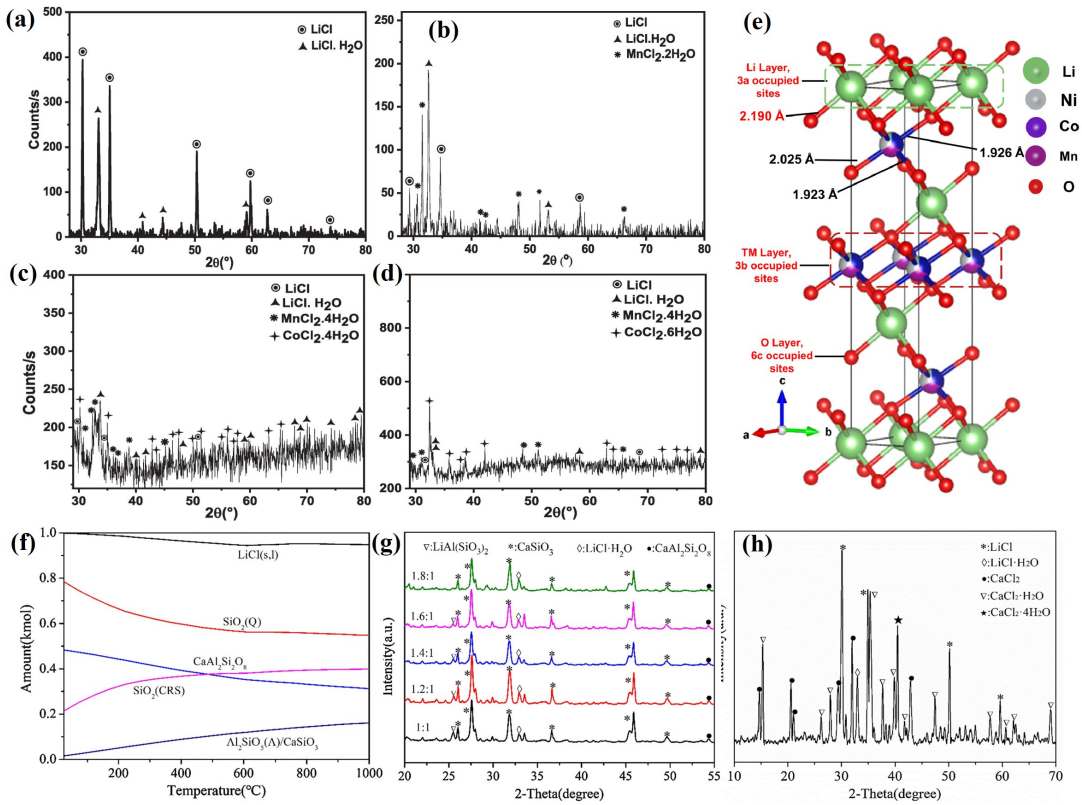

Fig. 11 XRD patterns of leachate of chlorinated roasting products at 400 °C (a); XRD patterns of leachate of chlorinated roasting products at 500 °C (b); XRD patterns of leachate of chlorinated roasting products at 800 °C (c); XRD pattern of volatiles of chlorinated roasting products at 800 °C (d) [122]; NCM crystal structure, atomic arrangement of each element and chemical bond length of metal ion with oxygen (e) [123]; Equilibrium composition of Si−Al−Li−O−Ca−Cl (CRS: cristobalite; A: andalusite; Q: quartz) (f); XRD patterns of roasted products under different Cl:Li molar ratios (roasting temperature 800 °C, 60 min) (g); XRD pattern of chlorination roasting desiccative leached solution (h) [125]

Chlorination roasting can also be used to recover Li from pyrometallurgical slag. On the basis of early research, DANG et al [125] modeled smelting slag and the interaction between the slag and $CaCl_2$ in the temperature range of 0−1000 °C. HSC simulations demonstrated that beyond 500 °C, $CaCl_2$ and $LiAl(SiO_3)_2$, the primary components of smelting slag, may combine to generate LiCl. At 800 °C, when the amount of added $CaCl_2$ is increased, the diffraction peaks of slag drop continually, and the distinctive peaks of LiCl become increasingly visible, suggesting that the Li in slag can be selectively extracted by chlorination roasting (Figs. 11(f–h)).

4.3 Roasting–flotation process

Even though current recovery technologies can be simplified by combined pyrometallurgical and hydrometallurgical processes, the various elements still need to be separated. After analyzing existing recycling methods, several researchers have proposed recovering the CAMs in spent LIBs from the material level to simplify the present recycling process. ZHONG et al [66] comprehensively examined the discharge and pyrolysis behaviors of spent LIBs, the recovery of electrolytes from spent LIBs by low-temperature volatilization, and the recovery of important chemicals from pyrolysis residue by physical separation. Spent LIBs were recovered by pyrolysis, color separation, high-pressure water cleaning, and flotation processes, and eventually, around 99.34% of Al, 96.25% of Cu, and 49.67% of CAM were recovered. CAM acquired with this method can be regenerated.

To further improve the recovery of the positive active material, ZHONG et al [81] improved the flotation process. They found that adding caustic starch as a depressant can considerably improve the recovery and quality of LFP. An LFP concentrate with a grade of 84.33% was effectively recovered from the pyrolysis slag via a closed-circuit flotation process with a recovery of 91.57% after calculating the ideal flotation process index. Scanning electron microscope plots of the flotation concentrate and tailings are shown in Figs. 12(a−f). The electrode materials regenerated by the doped metal oxide treatment exhibited good electrochemical properties because the flotation process did not change the crystal structure of LFP. This was the first time that spent LIBs were recovered while avoiding damage to their crystal structure, allowing the recovered products to be immediately regenerated and processed. Furthermore, this technique is much less expensive than the current recycling process. It minimizes environmental damage and has a quick procedure, so it is an economical and ecologically safe approach for recycling spent LIBs.

4.4 Direct recycling

Because positive active material in spent LIBs has the highest recycling value, determining how to achieve green and efficient recycling of positive

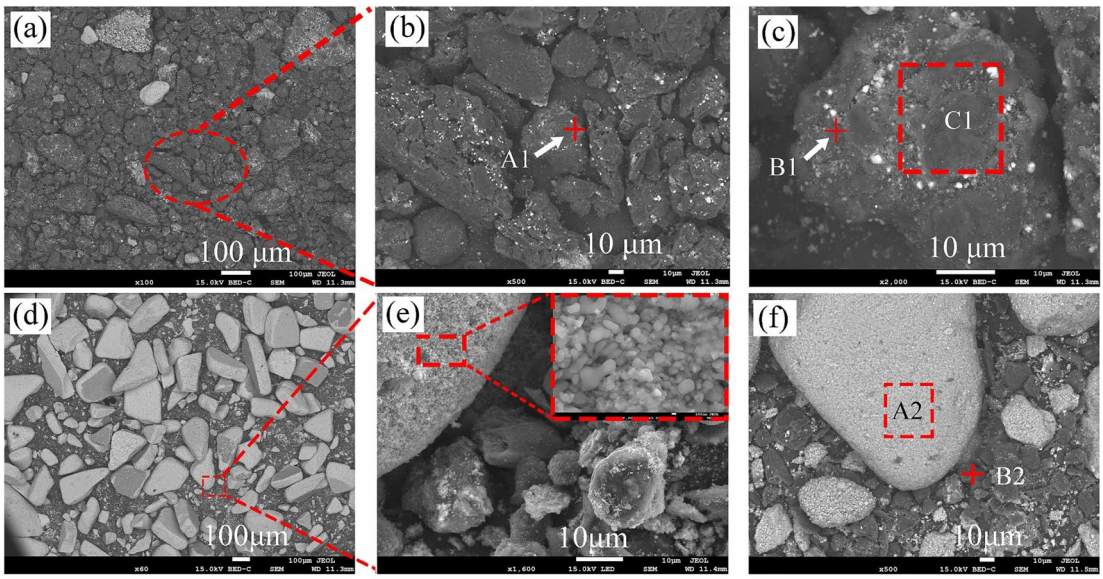

Fig. 12 SEM image of LFP flotation tailings (a); Enlarged view of marked area (b) in (a); SEM image of LFP flotation tailings (c); SEM image of LFP concentrates (d); Enlarged view of marked area (e) in (d); SEM image of LFP concentrates (h) [81]

active material is a critical step in determining whether the entire recycling of spent LIBs can generate enough economic value. Many academics have advocated in recent years that the direct recycling process can best optimize the economic advantages [130−133].

However, when compared to pyrometallurgical and hydrometallurgical processes, direct recycling of cathode active material is extremely difficult because the layered structure of LCO/NCM gradually changes into a spinel structure with a strong electrostatic repulsive force after a long period of cyclic charging, obstructing normal Li^+ transport [134]. Olivine-structured LFP undergoes an irreversible phase transition due to Fe^{2+} migration and Li^+ diffusion after a long time of cycling. Therefore, the key to direct recycling of used LFP is to fix Fe atoms in the crystal lattice to improve the Li^+ migration efficiency [135].

The direct recovery of cathode active materials mainly includes molten salt repair regeneration, the solid-phase lithium replenishment method, and hydrometallurgy-precursor regeneration. In conventional solid-state sintering, an external lithium source is required to regenerate the cathode active material. To achieve closed-loop recycling of used lithium batteries, WANG et al [136] recovered lithium sources from lithiated graphite and prepared Li_2CO_3 using CO_2 from the air for regeneration of spent LCO and NCM. After regeneration, the deteriorated LCO with varying residual capacities exhibited comparable electrochemical performance to the pristine LCO, and all of them recovered to 140 mA·h/g (Figs. 13(a−d)). The multiplicative capacity of regenerated LCO was likewise equivalent to that of the virgin LCO (Figs. 13(e, f)). In contrast to solid-phase remediation, the molten salt regeneration process not only offers an excess of lithium but also enhances ion diffusion. MA et al [137] created a lithium-rich molten environment by using a LiI−LiOH salt with a low eutectic point. A mixture of highly deteriorated NCM (HD-NCM523) and LiI−LiOH was heated to 200 °C for 4 h and then cooled to 850 °C for 3 h. The regenerated NCMs (R-NCM523) all had *R*−3*m* space group structural patterns and discharge point capacities equivalent to commercial NCMs (C-NCM523).

Co-precipitation is often used for the re-synthesis of multi-elemental materials, and the use of hydrometallurgy in conjunction with co-precipitation technology can be utilized to achieve short-flow recycling of spent lithium battery cathode actives at the molecular level. Typically, co-precipitation is carried out in hydroxide or carbonate systems with an optimal pH of 11 or 8, respectively [138]. SA et al [139] used the co-precipitation technique to successfully resynthesize high-performance $Ni_{1/3}Mn_{1/3}Co_{1/3}(OH)_2$ precursors from the leach solution of the spent LIB cathode materials when the pH of the leach solution was controlled to be 11, and there were almost no metal ions remaining in solution.

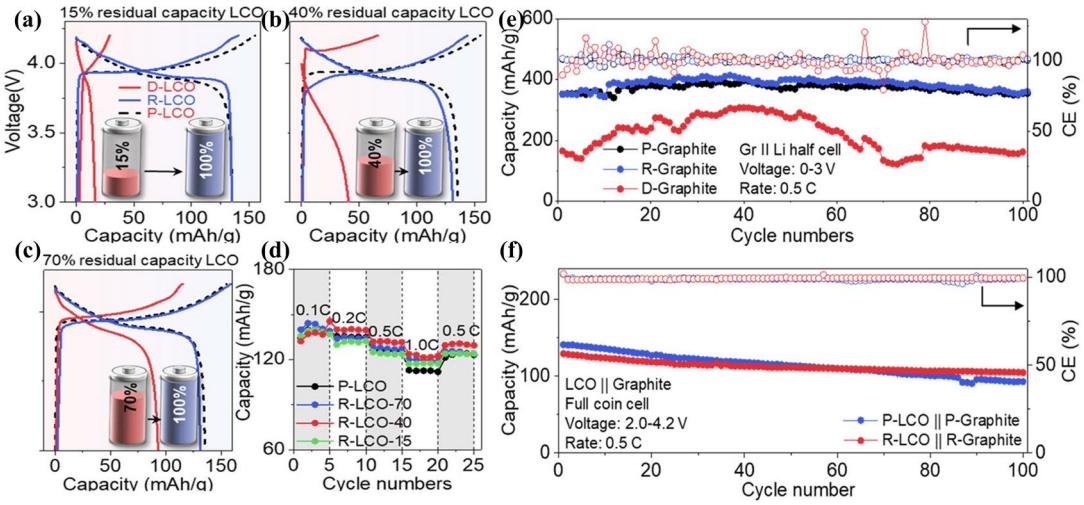

Fig. 13 Charge−discharge curves of D-LCO and R-LCO at different SoCs of 15% (a), 40% (b) and 70% (c); Rate capability of all R-LCO and P-LCO samples (d); Cyclic properties of graphite (D), graphite (R) and graphite (P) (e); Cycle performance of commercial electrode materials and recycled electrode materials for full batteries (f) [136] (Reprinted with permission from Ref. [136], Copyright 2024 American Chemical Society)

The final cathode material synthesized has a uniform size distribution. The electrochemical performance demonstrated an initial discharge capacity of 158 mA·h/g at 0.1*C* and an approximately 95% capacity retention rate after 50 cycles.

5 Challenges and future prospects

(1) There is still a risk of combustion and explosion in the waste lithium-ion battery pretreatment process, which necessitates the dismantling and crushing process of combustion and explosion in the formation of the mechanism, as well as the effective prevention and control mechanisms to be studied.

(2) The production of poisonous gases and waste liquids during recycling should be avoided, as well as the migration patterns of phosphorus, fluorine, and other dangerous elements should be identified.

(3) Many scholars have proposed various technologies to implement short-flow recycling, but it has to be seen whether laboratory-scale technology can be scaled up to industrial production.

(4) At the moment, there are several technologies engaged in the cathode active material, and there is very little electrolyte recycling. From the standpoint of environmental protection, they need to grow better. They should be appropriately processed and recycled to protect the environment.

(5) The recycling standard for spent lithium-ion batteries has not been standardized, and the legal framework surrounding it has not been perfected.

(6) The necessity to foster the growth of green economy in the industry has become increasingly pressing as people's environmental awareness has grown. Scholars should not only focus on metal recycling in future studies but also design or examine the environmental and economic benefits of recycling spent LIBs and investigate the industrial recycling technology of multidisciplinary knowledge unions.

6 Conclusions

The energy security and the environmental conservation are critical challenges to human society's progress. Li-ion batteries, as an outstanding energy storage technology, contribute considerably to the long-term development of the renewable energy sector. However, the amount of spent LIBs is increasing rapidly every year, necessitating the development of a green and effective recycling procedure. Echelon utilization can delay the end of the life of LIBs, but scientific and rapid detection and classification means are still lacking. The pyrometallurgical method can handle vast amounts of materials and is straightforward, but it has high energy consumption and results in a massive Li loss. Hydrometallurgy, with its high metal extraction rate and flexible production, has become the standard technology for recycling old Li batteries. The primary disadvantage of this technology is its lengthy pretreatment process and the difficulty of separating comparable metals. Although the spent LIB market is still in its infancy, competition is strong, and a quick recycling process is urgently needed to maintain environmental protection while enhancing the economic efficiency of recycling process.

To realize the short-process recovery of spent LIBs, some scholars proposed a combined process of pyrometallurgy and hydrometallurgy to modify LIBs via low-temperature roasting and extract valuable components from them by using an acid or an alkaline solution. Good recovery effects were obtained. Although the economic evaluation of the method is lacking, most academics are enthusiastic about it. A design at the material structure level combined with low-cost green recycling is obtained to realize healthy, sustainable recycling. The reviewed technology, which combines pyrolysis and flotation to achieve economy and environmental friendliness, offers novel insights into battery recycling for the future progress.

CRediT authorship contribution statement

Xue-song GAO: Writing − Original draft, Methodology, Data curation, Formal analysis; **Meng WU:** Data curation, Formal analysis, Writing − Review & editing; **Guang-jin ZHAO:** Methodology, Writing − Review & editing; **Kun-hong GU:** Data curation, Writing − Review & editing; **Jia-jia WU:** Supervision, Writing − Review & editing; **Hong-bo ZENG:** Data curation, Formal analysis; **Wen-qing QIN:** Supervision, Project administration; **Jun-wei HAN:** Methodology, Conceptualization, Writing − Review & editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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废旧锂离子电池回收技术及发展方向综述

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摘 要：锂离子电池(LIBs)因其高能量密度、高工作电压和长循环寿命而成为最受欢迎的储能设备。然而，由于锂离子电池中含有 Co、Ni、Mn 等重金属和有机化合物，严重威胁人体健康和环境，需要绿色高效的回收方法。作者对废旧锂离子电池回收的现状进行综述，讨论了传统的火法冶金和湿法冶金回收工艺，总结了现有的盐辅助焙烧、浮选、直接回收等短流程回收技术。最后，分析了目前回收工艺存在的问题和潜在的研究前景，并指出多学科融合的回收方法将成为废旧锂离子电池回收的主流技术。

关键词：废旧锂电池；短流程回收；二次资源；预处理；金属回收

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