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Valuable metals recovery from spent ternary lithium-ion battery: A review

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Abstract: Ternary lithium-ion batteries (LIBs), widely used in new energy vehicles and electronic products, are known for their high energy density, wide operating temperature range, and excellent cycling performance. With the rapid development of the battery industry, the recycling of spent ternary LIBs has become a hot topic because of their economic value and environmental concerns. To date, a considerable amount of literature has reported on the recycling of spent ternary LIBs designed to provide an efficient, economical, and environmentally friendly method for battery recycling. This article examines the latest developments in various technologies for recycling spent ternary LIBs in both research and practical production, including pretreatment, pyrometallurgy, hydrometallurgy, pyro-hydrometallurgy, and direct regeneration. Suggestions for addressing challenges based on the benefits and disadvantages of each method are made. Finally, through a comparison of the feasibility and economic benefits of various technologies, the challenges faced during battery recycling are summarized, and future development directions are proposed.

Keywords: spent ternary LIBs; recycling technologies; valuable metals; economic analysis

1. Introduction

As electric vehicles advance and electronic devices proliferate, lithium-ion batteries (LIBs) are under increasing scrutiny as energy storage systems [1–2]. Among them, ternary LIBs have become a primary power source for electric vehicles because of their high energy density, wide operating temperature range, and excellent cycling performance. The global electric vehicle market is projected to hit $221 billion by 2024 [3]. LIBs typically last 3–8 years, with either stepwise reuse or disposal once capacity decreases to 80%. By 2025, nickel–cobalt–manganese (NCM) battery scrap is expected to reach 100 GW·h [4].

On the one hand, spent batteries contain large amounts of valuable metals, including lithium (Li, 5wt%–8wt%), nickel (Ni, 15wt%–48wt%), cobalt (Co, 5wt%–20wt%), and manganese (Mn; 5wt%–19wt%), with a mass ratio exceeding 30% [5–7]. Their contents have higher grades than the original ores. China has low reserves of Li, Ni, Co, and Mn, with external dependence reaching 55%, 70%, 86%, and 90%, respectively. On the other hand, spent ternary LIBs contain a substantial amount of toxic substances, such as electrolytes and binders, improper discharge of which can cause severe environmental pollution [8–10]. From both economic and environmental perspectives, recovering valuable metals from discarded LIBs ensures a stable supply of raw

metal materials and mitigates the environmental pollution issues associated with landfilling and incineration of spent ternary LIBs [11–12].

Currently, a considerable amount of literature has reported on recycling technologies for spent batteries, primarily involving pyrometallurgy, hydrometallurgy, and direct regeneration. Pyrometallurgy is commonly used globally, enriching valuable metals in alloy formed at high temperatures [13–14], with major companies, such as Umicore in Belgium and Sony in Japan, leading the way [15]. However, at high temperatures, some valuable metals, such as Li and Mn, are lost in the slag and are difficult to retrieve. In China, hydrometallurgical technologies are widely employed in companies. Hydrometallurgy typically includes three steps, namely, pretreatment, leaching, and separation of valuable metals [16–19]. Although hydrometallurgy can yield high-purity products, the complex recovery process leads to the loss of some metals, such as Li, and gives rise to large amounts of wastewater, increasing subsequent treatment costs. To recover Li efficiently, researchers have explored a combined approach using pyrometallurgy and hydrometallurgy to leach Li selectively [20–21]. Subsequently, other valuable metals are recovered through acid leaching. However, combined recovery should involve cost-effective and environmentally friendly reducing agents and precise control of roasting conditions to dismantle the cathode materials into low-value

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metal oxides rather than elemental metals.

In recent years, direct regeneration of LIBs has garnered increasing attention as a next-generation research technology. This approach involves the direct restoration of the Li-deficient portion of the cathode materials without compromising their internal structure by selecting different Li sources and Li replenishment methods [22–25]. Direct recycling mitigates the challenges related to traditional recycling methods, such as pollution and significant metal losses, while maximizing the efficiency of the recycling process and increasing recovery profits.

Therefore, this paper begins by presenting an overview of ternary LIBs and reviewing the pyrometallurgical, hydrometallurgical, pyro-hydrometallurgical, and direct regeneration methods for recycling spent ternary LIBs, along with methods for recovering toxic substances from spent batteries. This paper considers the advantages and disadvantages of various recycling methods and assesses their economic benefits and feasibility. Finally, this paper offers prospects for the further development of recycled ternary LIBs in the future.

2. Ternary LIBs

Ternary LIBs typically include cathode and anode sheets, electrolytes, separators, and a shell (Fig. 1(a)) [26]. The cathode sheet consists of cathode material, binder, conductive agent, and aluminum (Al) foil collector. The cathode material is Ni–Co–Mn ternary material, and the binder is polyvinylidene fluoride (PVDF) or polytetrafluoroethylene (PTFE). The anode sheet consists of anode material, binder, conductive agent, and copper (Cu) foil collector. The anode material is graphite, the binder is PVDF, and the conductive agent is acetylene black [27]. The electrolyte consists of solute, solvent, and additives. The solute is soluble Li salt (i.e., $LiPF_6$, $LiBF_4$, or $LiClO_4$). The solvent is ether, ester, or carbonate, such as dimethoxyethane (DME), ethylene carbonate (EC), methyl carbonate (EMC), dimethyl carbonate (DMC), or propylene carbonate (PC). The additives are vinylidene carbonate (VC) or fluorinated vinyl carbonate (FEC). The diaphragm is polyethylene (PE) or polypropylene (PP). The casing is aluminized or Ni-plated steel [28].
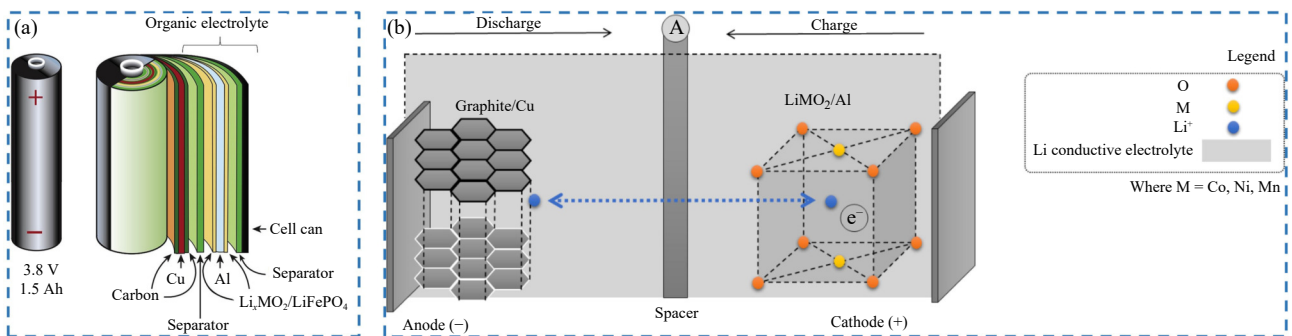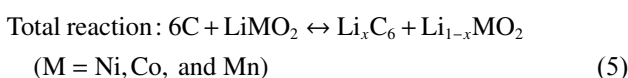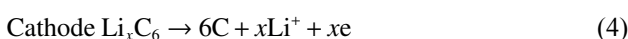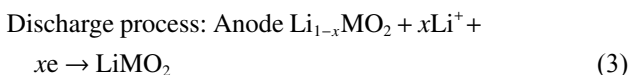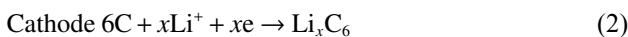

Fig. 1. **(a) Typical structure and (b) working principle of LIBs. (a) Reprinted by permission from Springer Nature:** *Nature*, **Issues and challenges facing rechargeable lithium batteries, J.M. Tarascon and M. Armand, Copyright 2001; (b) Reprinted from** *J. Energy Chem.*, **79, V.M. Leal, J.S. Ribeiro, E.L.D. Coelho, and M.B.J.G. Freitas, Recycling of spent lithium-ion batteries as a sustainable solution to obtain raw materials for different applications, 118–134, Copyright 2023, with permission from Elsevier.**

Ternary LIBs are charged and discharged through the embedding and detachment of Li ions in the anode and cathode materials, resulting in electron gains and losses. The operating principle is shown in Fig. 1(b) [29]. The reaction equations of the anode and cathode inside the cell and the total reaction equation are expressed as follows:

Charging process: Anode $LiMO_2 \rightarrow$
$$Li_{1-x}MO_2 + xLi^+ + xe \tag{1}$$

Cathode $6C + xLi^+ + xe \rightarrow Li_xC_6 \tag{2}$

Discharge process: Anode $Li_{1-x}MO_2 + xLi^+ +$
$$xe \rightarrow LiMO_2 \tag{3}$$

Cathode $Li_xC_6 \rightarrow 6C + xLi^+ + xe \tag{4}$

Total reaction: $6C + LiMO_2 \leftrightarrow Li_xC_6 + Li_{1-x}MO_2$
$$(M = Ni, Co, and Mn) \tag{5}$$

As LIBs undergo 800–1000 charge–discharge cycles, their capacity gradually declines because of various factors, including solvent molecule decomposition on the negative electrode, formation of a solid electrolyte interface passiva-

tion film, Li metal deposition causing membrane blockage and increased internal resistance, micropore blockage from oxidation–reduction reactions between cathode and anode by-products, and dissolution of electrode active materials. When battery capacity decreases to less than 80% of the rated capacity, the battery needs to be either used stepwise or disposed.

Spent ternary LIBs contain a large amount of toxic metals and corrosive electrolytes. Approximately every 4000 t of spent ternary LIBs contains approximately 1100 t of heavy metals and 200 t of toxic electrolytes [30–31]. If disposed of in landfills, these toxic materials can leach into the soil, causing significant damage to the environment and water quality. Moreover, $LiPF_6$ in the electrolyte can produce harmful compounds, such as hydrogen fluoride (HF) and other fluorine-containing substances, when exposed to water, posing health risks upon human exposure and endangering public health.

Efficient recycling of spent ternary LIBs not only helps alleviate potential supply tensions and price fluctuations of raw materials, which addresses resource shortages in China but also reduces environmental pollution caused by their dispos-

al. Consequently, recycling spent ternary LIBs has emerged as a key focus of research, with significant implications for resource sustainability and environmental preservation.

3. Pretreatment of spent ternary LIBs

Because of their complex internal structure, LIBs need to be pretreated to safely disassemble them and improve component recovery rates [32–33]. The pretreatment process includes discharge, crushing, and separation of cathode materials (Fig. 2(a)) [34–38].

To prevent battery short-circuiting from residual electricity, waste batteries need to be discharged to less than 2 V. Common methods include sodium chloride solution, metal powder, and low-temperature discharge [39]. The sodium chloride solution method is widely used because of its simplicity of operation. After waste batteries are fully discharged, they can be crushed and sorted to preliminarily sep-
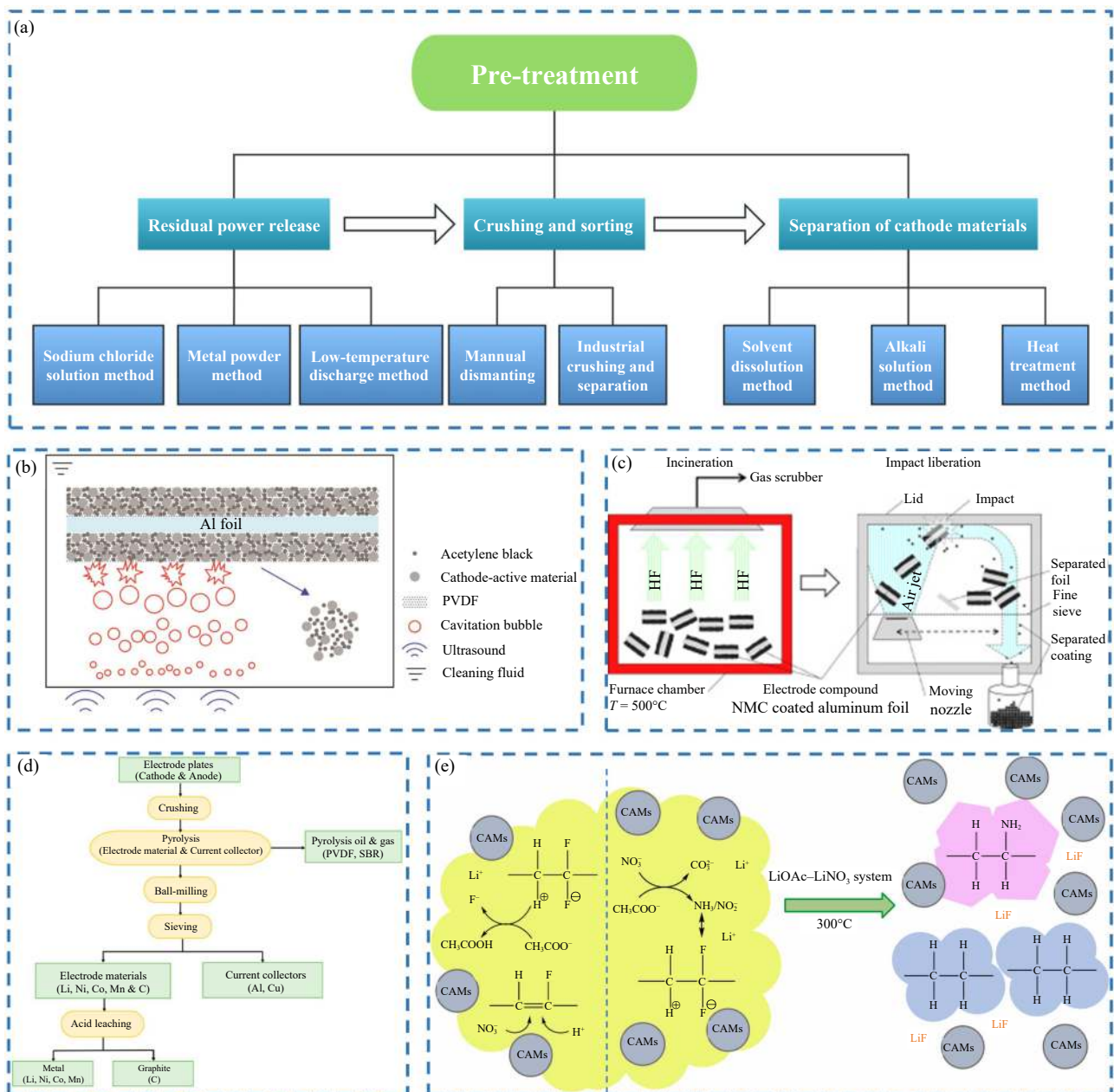

Fig. 2. (a) Pretreatment flowchart, (b) ultrasonic-assisted solvent dissolution method, (c) separation of aluminum foil and cathode by heat treatment, (d) pyrolysis-coupled mechanical milling method, and (e) eutectic molten salt method. (b) Reprinted from *Waste Manage.*, 46, L.P. He, S.Y. Sun, X.F. Song, and and J.G. Yu, Recovery of cathode materials and Al from spent lithium-ion batteries by ultrasonic cleaning, 523–528, Copyright 2015, with permission from Elsevier; (c) Reprinted from *J. Clean. Prod.*, 108, C. Hanisch, T. Loellhoeffel, J. Diekmann, K.J. Markley, W. Haselrieder, and A. Kwade, Recycling of lithium-ion batteries: A novel method to separate coating and foil of electrodes, 301–311, Copyright 2015, with permission from Elsevier; (d) Reprinted with permission from L. Zhao, X.Y. Zhang, Y.Y. Lu, *et al.*, *Energy Fuels*, 38, 1310–1318 (2024) [57]. Copyright 2024 American Chemical Society; (e) Reprinted from *J. Clean. Prod.*, 367, Y. Ji, C.T. Jafvert, N.N. Zyaykina, and F. Zhao, Decomposition of PVDF to delaminate cathode materials from end-of-life lithium-ion battery cathodes, 133112, Copyright 2022, with permission from Elsevier.

arate their components [6,40]. Component separation is typically based on discrete particle sizes, employing manual disassembly or crushing and sorting. Although manual disassembly is frequently used in experimentation, crushing and sorting are commonly used in industrial production.

After disassembly or crushing and sorting, the cathode material tightly bonds to the current collector via a binder. To facilitate subsequent recycling, separating the cathode material from the current collector is crucial. Primary separation methods include solvent dissolution, heat treatment, eutectic molten salt, and alkali dissolution [27,41–55]. He *et al*. [56] proposed a new pretreatment process (Fig. 2(b)). Initially, the battery is discharged in salt water, followed by manual disassembly for component separation to obtain the cathode material. The cathode material is soaked in the organic solvent N-methylpyrrolidone and subjected to ultrasonic treatment at 70°C. After 90 min, 99% separation between the cathode material and the collector is achieved. Although the solvent dissolution method exhibits superior separation performance using organic solvents, challenges related to these solvents include toxicity and high costs.

In addition to solvent dissolution, heat treatment effectively separates the positive electrode material from the Al foil by decomposing the binder at high temperatures. Hanisch *et al*. [41] proposed a method called "adhesion neutralization via incineration and impact liberation" (Fig. 2(c)). First, the binder PVDF is decomposed by heat treatment. Subsequently, jet impact is used to keep the cathode material separate from the current collector, successfully achieving the separation of the cathode material from the Al foil. With a roasting time of 90 min and a 1-min jet impact, the recovery rate of the cathode material reached 97%, with only 0.1% Al content.

Based on the high-temperature decomposition of the binder, Zhao *et al*. [57] employed a pyrolysis-coupled mechanical milling method to recover electrode materials (Fig. 2(d)). The pyrolysis process effectively removed organic binders, and subsequent ball milling increased the overall recovery rate of electrode materials from 38.91% to 93.70%. Under the conditions of thermolysis at 650°C, a ball milling mass ratio of 2:3, and a ball milling time of 15 min, the recovery rate of the cathode material and graphite anode reached 97.89% and 86.90%, respectively. Moreover, the chemical valence of the cathode material was reduced in a reductive thermal decomposition atmosphere, which is advantageous for subsequent recovery processes.

Compared with the heat treatment method, the eutectic molten salt method requires lower temperatures and does not result in harmful gases, such as HF. This is achieved by adding substances, such as nitrates and acetates, during high-temperature heating, which eliminates HF and forms unsaturated double bonds, leading to the decomposition of PVDF. Ji *et al*. [42] proposed a method to eliminate PVDF by mixing and calcining it with a LiOAc–LiNO$_3$ molten salt system and cathode material (Fig. 2(e)). Under the reaction conditions of a LiOAc-to-LiNO$_3$ molar ratio of 3:2, molten salt-to-

cathode mass ratio of 10:1, reaction temperature of 300°C, and holding time of 30 min, the stripping rate of the binder PVDF reached 98.5%. The eutectic molten salt method requires a lower reaction temperature than the heat treatment method. However, the chemical reagents employed in the reaction process are relatively expensive, thereby increasing recycling costs to some extent.

In addition to the aforementioned methods, another frequently used laboratory-stage method is the alkali dissolution method. This method involves using sodium hydroxide to break up the current collector, thereby achieving the separation of the cathode material from the Al foil. The reaction process of NaOH dissolving the Al foil is illustrated in reaction formulas (6) and (7). However, the alkali dissolution method is associated with higher costs and tends to generate a significant amount of wastewater. Moreover, the obtained cathode material still requires subsequent calcination to remove the binder.

$$Al_2O_3 + 2NaOH + 3H_2O = 2Na[Al(OH)_4] \qquad (6)$$

$$2Al + 2NaOH + 6H_2O = 2Na[Al(OH)_4] + 3H_2 \qquad (7)$$
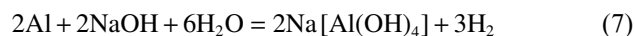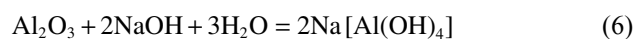
In summary, preprocessing of cathode materials can enhance recovery efficiency. However, the generation of toxic substances during preprocessing raises safety and pollution concerns, adding substantial costs to disposal. Therefore, the focus of future pretreatment technology should be on developing environmentally friendly pretreatment closed-loop recycling techniques, reducing equipment requirements to minimize costs while maximizing benefits.

4. Recovery technologies for valuable metals

After pretreating the cathode material, the recovery of valuable metals is an important aspect of the entire recycling process. The current recovery technologies for precious metals mainly include pyrometallurgy [13–14,58–59], hydrometallurgy [16–18,60–70], pyro-hydrometallurgy [21, 71–74], and direct recycling [22–23,75–78]. During the period from January 2020 to February 2024, a total of 8860 papers on the recycling of spent ternary LIBs were published worldwide. Among them were 941 papers (10.6%) on pyrometallurgical recycling methods, 1720 papers (19.4%) on hydrometallurgical recycling methods, 3850 papers (43.5%) on direct recycling methods, and 2349 papers (26.5%) on other recycling methods. Fig. 3 and Table 1 summarize the recovery technologies, principles, advantages, and disadvantages of various valuable metals in spent ternary LIBs.

4.1. Pyrometallurgy

The pyrometallurgical process entails the high-temperature decomposition of organic materials in spent ternary LIBs, with precious metals being enriched in the form of alloys after reduction at elevated temperatures [12]. The advantages of pyrometallurgical processes include relatively simple operations, a wide range of material processing capabilities, high processing volumes, and widespread industrial applica-
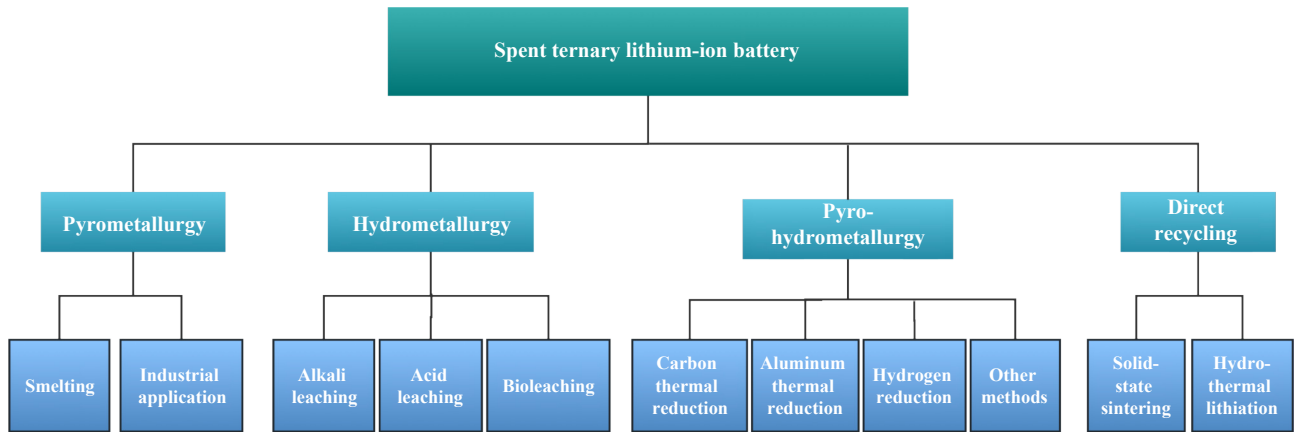
Fig. 3.   Recovery technologies for valuable metals.

Table 1.   Principles, advantages, and disadvantages of valuable metal recovery technology

Technologies	Principle of operation	Advantages	Disadvantages	Ref.
Pyrometallurgy	Removal of organic matter at high temperatures Enrichment of valuable metals in the form of alloys or metal compounds	No pretreatment simple process Large processing capacity Mature process Suitable for industrial applications	High energy consumption Toxic gas generation Large loss of lithium elements in the recovery process Poor safety	[13–14,58–59]
Hydrometallurgy	Chemical reaction between leaching agent and cathode material to separate and purify valuable metals in solution	Easy to control the recovery process Mild reaction conditions High product purity High recovery rate Less harmful gas emissions	Long process High cost of valuable metal separation Large amounts of waste residue Wastewater and waste gas generation	[16–18,37,60–70]
Pyro-hydrometallurgy	High-temperature pretreatment of cathode materials Wet leaching of valuable metals	Less expensive leaching process Suitable for large-scale production high-value-added products	More processes	[21,71–74]
Direct recycling	Lithium source was added to repair the cathode material	Avoid long purification steps Less pollution Low energy consumption	Less flexibility to handle different compositions, product quality easily affected	[22–23,75–78]

tions in factories. The main influencing factors of pyrometallurgy are heating temperature, heating time, additives, and types of purge gas [13].

4.1.1. Smelting

The smelting method involves heating spent ternary LIBs above their melting point using high temperatures to recover valuable metals from the batteries. Initially, at lower temperatures, the organic matter in the batteries decomposes, providing heat for the subsequent metal reduction process. Subsequently, at higher temperatures, new alloys are generated through thermal reduction.

In a pilot-scale recovery conducted by Hu *et al.* [14], valuable metals from cathode materials were recovered in an electric arc furnace (EAF, Fig. 4(a)). Lime was used as a slagging agent to form fluid slag at 1600°C, enabling the recovery of Ni, Co, and Mn in alloy form through smelting reduction. Li is concentrated and recovered in the form of Li_2CO_3 within the dust. First, waste steel and slagging agents are added to the valuable metals in the EAF, increasing the

carbon mass ratio of the steel melt to 4%. Then, spent batteries and slagging agent are uniformly mixed and added to the valuable metals in the EAF, and the thermal reduction reaction occurs at 1600°C. Finally, valuable metals in the spent batteries are recovered in alloy form. The ultimate recovery rates of Ni, Co, Mn, and Li were 97.7%, 97.9%, 85.3%, and 60.9%, respectively. The $CaO–Al_2O_3$ slag produced can be sold as a by-product. The method enables efficient recovery of Ni, Co, and Mn; however, the recovery rate of metallic Li remains less than satisfactory.

To address the challenge of low Li recovery rates in pyrometallurgical smelting, Xiao *et al.* [79] introduced a reduction smelting system based on $MnO–SiO_2–Al_2O_3$, utilizing carbon as a reducing agent (Fig. 4(b)). In the reduction smelting process conducted at 1550°C, Ni, Co, and Cu from spent ternary LIBs were concentrated into an alloy, whereas Mn and Li were enriched in the slag phase. Subsequently, Mn and Li in the slag phase were leached out using sulfuric acid (H_2SO_4). This approach led to the recovery of 79.86% of Mn
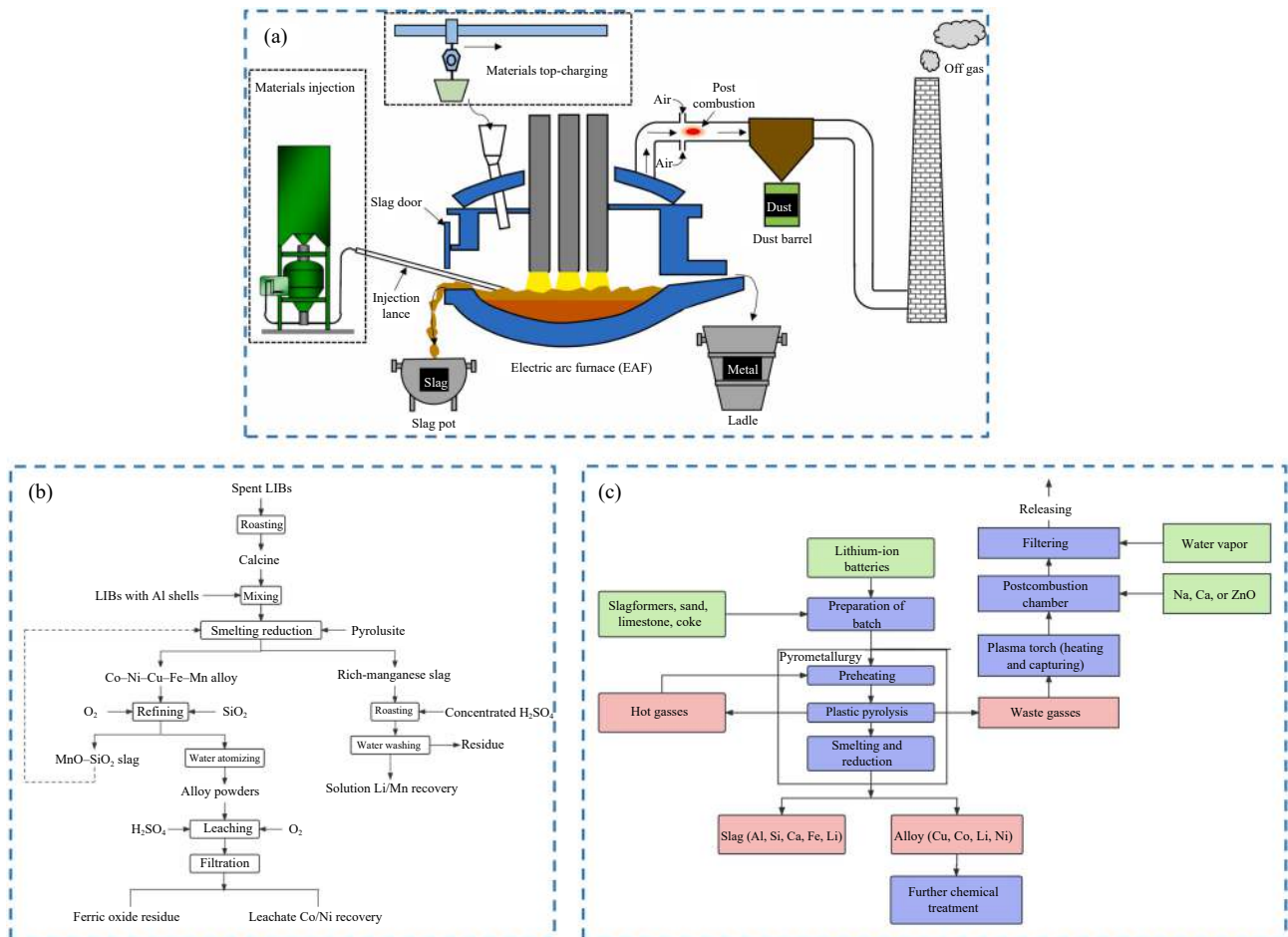
Fig. 4. (a) Flowchart of valuable metal recovery through the smelting method, (b) smelting reduction process based on the MnO–SiO$_2$–Al$_2$O$_3$ slag system, and (c) Umicore battery recycling flowchart. (a) Reprinted from *J. Power Sources*, 483, X.F. Hu, E. Mousa, and G.Z. Ye, Recovery of Co, Ni, Mn, and Li from Li-ion batteries by smelting reduction-Part II: A pilot-scale demonstration, 229089, Copyright 2021, with permission from Elsevier; (b) Reprinted by permission from Springer Nature: *J. Sustain. Metall.*, Recovery of valuable metals from spent lithium-ion batteries by smelting reduction process based on MnO–SiO$_2$–Al$_2$O$_3$ slag system, S.W. Xiao, G.X. Ren, M.Q. Xie, *et al.*, Copyright 2017; (c) Reprinted from *Lithium-ion Battery: Advances and Applications*, G. Pistoia, 23, 529–551, Copyright 2014, with permission from Elsevier.

and 94.85% of Li, effectively preventing the loss of metallic Li in the slag phase.

The smelting method is a simple process that requires no pretreatment and enables efficient recovery of Ni, Co, and Mn. Li is recovered through leaching with carbonated water instead of acid leaching, reducing pollutant emissions. Furthermore, the smelting method is readily scalable and suitable for industrial production.

4.1.2. Industrial applications

A large number of spent ternary LIBs have been generated in the current market, and the tremendous market resources have attracted numerous battery recycling companies. The pyrometallurgical recycling process of spent ternary LIBs is already highly mature in industrial production, with relatively simple operations and high recovery rates, and mainly involves pyrometallurgy and subsequent refining processes to improve product purity [15].

Umicore has developed a pyrometallurgical process (Fig. 4(c)) for disassembling waste batteries into individual cells and feeding them into a shaft furnace with three temperature zones, namely, the preheating, plastic pyrolysis, and high-

temperature melting zones [80]. In the preheating zone, waste batteries evaporate electrolytes at a temperature below 300°C. The plastic pyrolysis zone removes the separator and organic components at a temperature of 700°C. In the high-temperature melting zone, waste batteries are melted to obtain an alloy containing Cu, Ni, Co, and iron (Fe), with Li, Al, Si, Ca, and part of Fe entering the bottom slag of the furnace. Finally, the alloy obtained from pyrometallurgical recycling is leached out using hydrochloric acid (HCl). The metals in the leach solution are recovered through solvent extraction, yielding Cu, Fe, CoCl$_2$, and Ni(OH)$_2$ as the final products.

Pyrometallurgy currently dominates valuable metal recovery, offering simplicity, high capacity, mature technology, and easy industrial implementation. However, the process consumes a significant amount of energy, and the combustion of organic materials can generate harmful gases, necessitating the installation of gas recovery equipment, which adds to the overall costs. In addition, a substantial amount of Li is often trapped in slag, making recovery difficult and resulting in metal losses. Sole reliance on pyrometallurgy is insufficient for the complete recovery of precious metal from
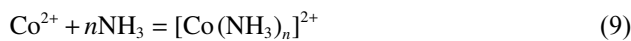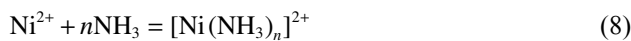
spent ternary LIBs [13]. The understanding of the thermodynamics, kinetics, and cathode material phase transformations of pyrometallurgy is limited. Thus, the creation of a comprehensive framework for pyrometallurgical recycling is urgently needed.

4.2. Hydrometallurgy

Compared with pyrometallurgy, the advantages of hydrometallurgy include relatively low cost, mild conditions, and high metal recovery, driving its development for the recovery of waste LIBs. Hydrometallurgy recovers valuable metals by utilizing leaching agents to chemically react with cathode materials. The addition of agents, such as hydrogen peroxide (H_2O_2), $NaHSO_3$, $NaNO_2$, and glucose, boosts the leaching efficiency. Further details on metal recovery via hydrometallurgical techniques are provided in subsequent sections.

4.2.1. Alkaline leaching

Alkaline leaching selectively extracts metals by leveraging the unique coordination chemistry of ammonium ions with various metal ions. Ammonia solution ($NH_3 \cdot H_2O$) serves as the leaching agent, while ammonium salts (i.e., $(NH_4)_2CO_3$, $(NH_4)_2SO_4$, and NH_4Cl) regulate the solution pH. Ammonium ions can form stable amino complexes with Ni, Co, Li, and Cu, as indicated in reaction formulas (8) to (10). Metals, such as Al, Fe, and Mn, have low complexation capability with ammonium salts, making it difficult to form stable complexes, thus achieving selective leaching of metal elements [16].

$$Ni^{2+} + nNH_3 = [Ni(NH_3)_n]^{2+} \tag{8}$$

$$Co^{2+} + nNH_3 = [Co(NH_3)_n]^{2+} \tag{9}$$

$$Li^+ + nNH_3 = [Li(NH_3)_n]^+ \tag{10}$$

Because of the alkalinity and chelating properties of ammonia, after ammonium and metal ions form stable amino complexes, the amino complexes can react with –OH to form precipitates, as shown in reaction formula (11) [60]:

$$[M(NH_3)_n]^{2+} + 2OH^- = M(OH)_2 \downarrow + nNH_3 \uparrow$$
$$(M^{2+} = Ni^{2+}, Co^{2+}, or\ Mn^{2+}, n = 1-6) \tag{11}$$
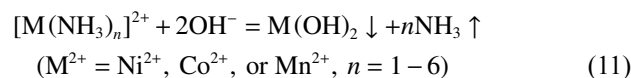
Wang *et al*. [17] devised a method for recovering valuable metals from spent ternary LIBs via ammonia leaching and subsequent adsorption separation (Fig. 5(a)). After carbon reduction heating pretreatment, the cathode material was leached with an $NH_3 \cdot H_2O$–NH_4HCO_3 solution using H_2O_2 as the reducing agent to form a solution system containing Co^{2+}–Ni^{2+}–Li^+–NH^{4+}. The Li-ion sieve was used to selectively separate Li^+ from the solution, and NH_4^+ was reused through ammonia distillation. Then, the Li^+-adsorbed Li-ion sieve was desorbed using HCl, neutralized with NaOH, and carbonized with Na_2CO_3 to obtain Li_2CO_3 products with purity greater than 99.5%. The final products are Li_2CO_3, $NiSO_4$, and $CoSO_4$, with direct recovery rates of Li, Ni, and Co reaching 76.19%, 96.23%, and 94.57%, respectively. Ammonia can be recycled in a closed loop.

Wang *et al*. [16] proposed a new ammonia leaching system and investigated effective Mn utilization in selective

leaching (Fig. 5(b)). Selective leaching of Li, Co, and Ni from spent ternary LIBs used NH_3–$(NH_4)_2CO_3$–Na_2SO_3, with the addition of $(NH_4)_2CO_3$ to form manganese carbonate ($MnCO_3$) precipitation. Multiple leaching cycles achieved high rates: 98.4% for Li, 99.4% for Co, and 97.3% for Ni. The residue produced high-purity $MnCO_3$ (>99%), reducing harmful emissions. This method is suitable for large-scale LIB recycling and high-purity $MnCO_3$ synthesis.

The advantages of alkaline leaching include low recycling costs, high selectivity of ammonia for valuable metals, such as Ni, Co, and Cu, and the formation of stable complexes. However, alkaline leaching generates a significant amount of alkaline wastewater, and the volatility of ammonia poses operational challenges in actual production, requiring substantial subsequent treatment.

4.2.2. Acid leaching

Compared with alkaline leaching, acid leaching generates fewer waste gases and exhibits higher leaching efficiency. Initial acid leaching employs strong acids, including H_2SO_4 [18,68–69,81–82], HCl [66,70], nitric acid, phosphoric acid (H_3PO_4), and other inorganic acids. The addition of specific reducing agents effectively dissolves valuable metals in the cathode materials. Organic acids, such as citric acid (H_3Cit) [63,67], tartaric acid, oxalic acid [83], and malic acid [84], have proven effective as leaching agents with the potential for enhancement through reducing agents or mechanochemical methods.

H_2SO_4 coupled with H_2O_2 as the reducing agent is the most common leaching combination because of its cost-effectiveness and high leaching efficiency. Yang *et al*. [18] developed a method for the stepwise recovery of valuable metals from $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$. The leaching process is expressed in reaction equation (12). The leaching rates of Ni, Co, Li, and Mn were 100%, 100%, 100%, and 94%, respectively. He *et al*. [68] further optimized the process parameters built on H_2SO_4 leaching (Fig. 5(c)). Under the optimal reaction conditions of H_2SO_4 concentration of 1 M, H_2O_2 concentration of 1vol%, solid–liquid ratio of 40 g/L, reaction temperature of 40°C, stirring speed of 400 r/min, and leaching time of 60 min, the leaching rate achieved for Li, Ni, Co, and Mn was 99.7%.

$$2LiMO_2 + 3H_2SO_4 + H_2O_2 = Li_2SO_4 + 2MSO_4 +$$
$$4H_2O + O_2 \ (M = Ni, Co, Mn) \tag{12}$$
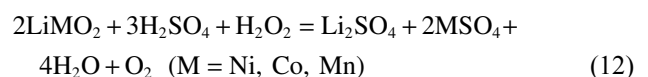
Given the presence of chloride ions in HCl, it can serve as a reducing agent, making it a favorable alternative to H_2SO_4 combined with H_2O_2. Wang *et al*. [66] achieved leaching rates of over 99% for Li, Ni, Co, and Mn after leaching for 1 h under the conditions of HCl concentration of 4 M, leaching temperature of 80°C, and solid–liquid ratio of 20 g/L. Wen *et al*. [70] further elucidated the leaching mechanism of HCl. Initially, Li is dissolved by the leaching agent, forming a transitional phase with low Li content. The second step is slower than the first step, mainly involving the dissolution of the transitional phase. The reaction equations are presented in (13) to (15). However, HCl is highly corrosive and produces chlorine gas during leaching, posing risks to human health and the environment. Economically and environmentally,
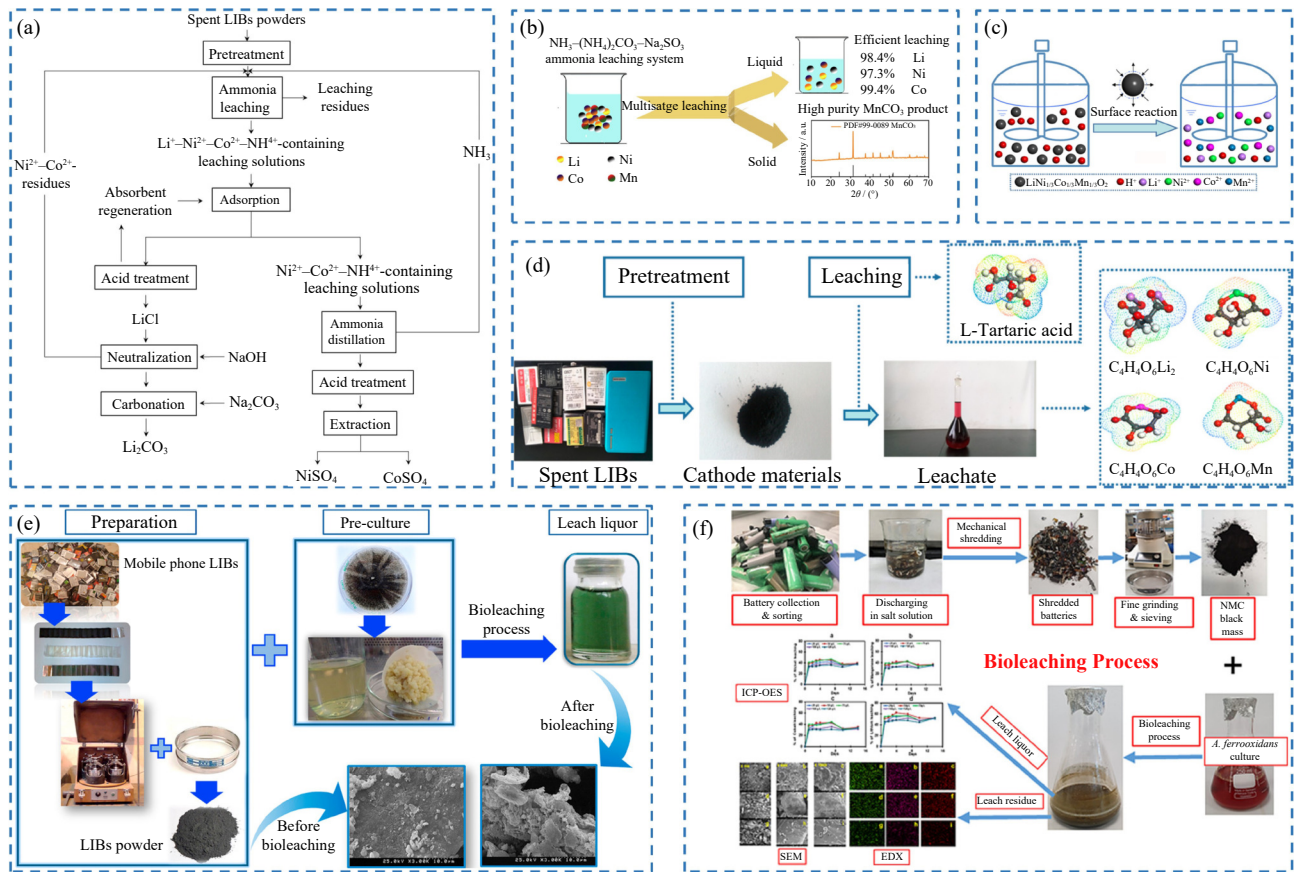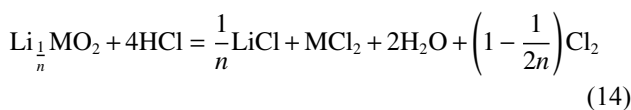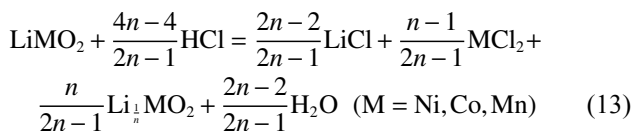
Fig. 5. **(a)** Recovery of Li, Co, and Ni from spent ternary LIBs by ammonia leaching, **(b)** selective ammonia leaching, **(c)** sulfuric acid leaching of cathode materials, **(d)** organic acid leaching of cathode materials, **(e)** *Aspergillus Niger* for bioleaching of cathode materials, and **(f)** autotrophic acidophilic iron-oxidizing bacteria for bioleaching of cathode materials. (a) Reprinted with permission from H.Y. Wang, K. Huang, Y. Zhang, *et al.*, *ACS Sustainable Chem. Eng.*, 5, 11489–11495 (2017) [17]. Copyright 2017 American Chemical Society; (b) Reprinted from *Waste Manage.*, 114, C Wang, S.B Wang, F Yan, Z. Zhang, X.H. Shen, and Z.T. Zhang, Recycling of spent lithium-ion batteries: Selective ammonia leaching of valuable metals and simultaneous synthesis of high-purity manganese carbonate, 253–262, Copyright 2020, with permission from Elsevier; (c) Reprinted from *Waste Manage.*, 64, L.P. He, S.Y. Sun, X.F. Song, and J.G. Yu, Leaching process for recovering valuable metals from the LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ cathode of lithium-ion batteries, 171–181, Copyright 2017, with permission from Elsevier; (d) Reprinted with permission from L.P. He, S.Y. Sun, Y.Y. Mu, X.F. Song, and J.G. Yu, *ACS Sustainable Chem. Eng.*, 5, 714–721 (2017) [37]. Copyright 2017 American Chemical Society; (e) Reprinted from *J. Power Sources*, 320, N.B. Horeh, S.M. Mousavi, and S.A. Shojaosadati, Bioleaching of valuable metals from spent lithium-ion mobile phone batteries using *Aspergillus Niger*, 257–266, Copyright 2016, with permission from Elsevier; (f) Reprinted with permission from J. Jegan Roy, M. Srinivasan, and B. Cao, *ACS Sustainable Chem. Eng.*, 9, 3060–3069 (2021) [86] Copyright 2021 American Chemical Society.

chlorine gas needs to be recovered for subsequent HCl production, reducing production costs.

$$LiMO_2 + \frac{4n-4}{2n-1}HCl = \frac{2n-2}{2n-1}LiCl + \frac{n-1}{2n-1}MCl_2 +$$
$$\frac{n}{2n-1}Li_{\frac{1}{n}}MO_2 + \frac{2n-2}{2n-1}H_2O \quad (M = Ni, Co, Mn) \quad (13)$$

$$Li_{\frac{1}{n}}MO_2 + 4HCl = \frac{1}{n}LiCl + MCl_2 + 2H_2O + \left(1-\frac{1}{2n}\right)Cl_2 \quad (14)$$

$$2LiMO_2 + 8HCl = 2LiCl + 2MCl_2 + 4H_2O + Cl_2 \quad (15)$$

H_3PO_4, with lower corrosiveness than H_2SO_4 and HCl, contributes to a smaller environmental impact during the leaching process. Zhuang *et al.* [85] utilized H_3PO_4 as the leaching agent and citric acid as the reducing agent. Under the conditions of a H_3PO_4 concentration of 0.2 M, citric acid concentration of 0.4 M, a solid–liquid ratio of 20 g/L, reaction temperature of 90°C, and reaction time of 30 min, the leaching rates of Li, Ni, Co, and Mn reached 100%, 93.38%, 91.63%, and 92.00%, respectively. Compared with single inorganic strong acid leaching, this method has the following advantages: lower acid consumption, shorter leaching time, and no need for additional reducing agents.

Compared with inorganic acids, organic acids pose less harm to the environment, making them a promising leaching agent. Chen *et al.* [63] used citric acid as the leaching agent and D-glucose ($C_6H_{12}O_6$) as the reducing agent. The concentration of citric acid was 1.5 mol/L, the solid–liquid ratio was 20 g/L, the reducing agent dosage was 0.5 g/g, the reaction temperature was 80°C, and the reaction time was 120 min. The leaching rates of Ni, Co, Mn, and Li were 91%, 92%, 94%, and 99%, respectively. After leaching, valuable metals were selectively precipitated and separated. The leaching

process is illustrated in reaction equation (16), where Cit represents citrate.

$$18LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2 + 18H_3Cit + C_6H_{12}O_6 =$$
$$6Li_3Cit + 2Ni_3(Cit)_2 + 2Co_3(Cit)_2 +$$
$$2Mn_3(Cit)_2 + 33H_2O + 6CO_2 \qquad (16)$$
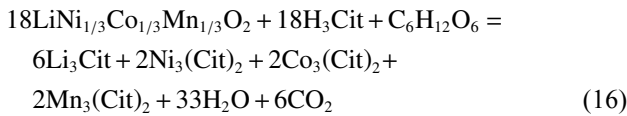
Tartaric acid has a lower cost and a higher acidity than typical organic acids. He *et al*. [37] achieved high leaching rates by utilizing tartaric acid as the leaching agent and H_2O_2 as the reducing agent (Fig. 5(d)). Under the optimal leaching conditions of tartaric acid concentration of 2 M, H_2O_2 concentration of 4vol%, solid–liquid ratio of 17 g/L, leaching temperature of 70°C, and leaching time of 30 min, the leaching rates of Li, Ni, Co, and Mn were 99.07%, 99.31%, 98.64%, and 99.31%, respectively. Furthermore, no toxic gases were generated during the reaction, and the residual tartaric acid after the reaction was biodegradable.

Hydrometallurgy works at lower temperatures, yielding high purity and effective recovery of most metals. However, hydrometallurgy requires component sorting before leaching, increasing storage space and costs. In addition, similar metal properties in the solution lead to high separation costs. Integration with pyrometallurgy should focus on selectively leaching valuable metals to reduce chemical use and environmental impact.
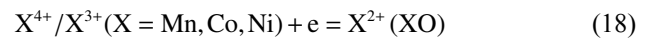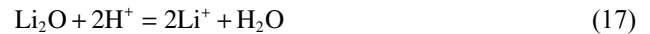
4.2.3. Bioleaching

In recent years, bioleaching has gained recognition as an eco-friendly leaching method, aligning with growing environmental awareness. In contrast to alkaline and acid leaching, bioleaching minimizes environmental impact by using acids produced by microbial metabolism to leach metals. Key microbial species involved include acidophilic sulfur-oxidizing bacteria, Fe-oxidizing bacteria, and fungi, such as *Aspergillus niger*.

Bahaloo *et al*. [19] employed *A. niger* for bioleaching valuable metals from spent ternary LIBs (Fig. 5(e)). After cultivating *A. niger* in a 100-mL sucrose medium for 14 d, the filtrate containing fungal metabolites, primarily citric acid, was obtained through filtration. Subsequently, the cathode material was immersed in the filtrate for 16 d, resulting in leaching rates of 100% for Cu, 95% for Li, 70% for Mn, 65% for Al, 45% for Co, and 38% for Ni.

To enhance the efficiency of bioleaching, Roy *et al*. [86] employed autotrophic acidophilic Fe-oxidizing bacteria to leach cathode materials under high solid–liquid ratios (Fig. 5(f)). Achieving a ratio of 100 g/L, they recovered 90% of Ni, 92% of Mn, 82% of Co, and 89% of Li within 72 h. The ratio resulted in reduced wastewater production, indicating scalability. Future endeavors should aim to minimize the bioleaching time and extend the application of the method to various battery types.

In another study, Xin *et al*. [87] developed a mixed energy source–mixed culture system for bioleaching spent ternary LIBs. Continuously generated H_2SO_4 leaches out Li, whereas Fe^{2+} in bacteria reduces insoluble high-valent nickel, cobalt, and manganese oxides into soluble forms. The reaction formulas are presented in (17) to (19). The recovery rates

of Li, Ni, Co, and Mn were all above 95% with the adjustment of the pH.

$$Li_2O + 2H^+ = 2Li^+ + H_2O \qquad (17)$$

$$X^{4+}/X^{3+}(X = Mn, Co, Ni) + e = X^{2+} (XO) \qquad (18)$$

$$XO + 2H^+ = X^{2+} + H_2O \qquad (19)$$

Bioleaching is used in detoxifying urban sludge, treating industrial wastewater, and restoring polluted soil. Compared with other methods, bioleaching has the following advantages: lower cost, environmental friendliness, and mild reaction conditions. However, industrial development has the following problems: microbial cultivation complexities, extended reaction times, intricate process control, and limited processing capacity. Future efforts should focus on cost reduction, shorter times, and higher efficiency [88].

4.3. Pyro-hydrometallurgy

To enhance revenue, companies often prefer the combined pyro-hydrometallurgical approach for recycling spent ternary LIBs. Pyro-hydrometallurgy involves reacting a reducing substance with the cathode material to disrupt the layered structure, converting it into low-valent metal oxides. Pyro-hydrometallurgical techniques include carbon, Al, and hydrogen reduction. Table 2 outlines the leaching rates of valuable metals in these processes.

4.3.1. Carbon thermal reduction

The carbon thermal reduction method blends cathode powder with graphite and subjects it to high-temperature roasting, which breaks down the cathode material, producing low-valence metal oxides. Hydrometallurgical processes follow at ambient temperature, minimizing the need for additional agents. This approach ensures efficient metal recovery. Fig. 6(a) shows the relationship between ΔG and metal oxide temperature.

Hu *et al*. [20] utilized carbon thermal reduction to destroy the layered structure of the cathode material (Fig. 6(b)). After calcination for 3 h at 650°C with a 19.9% carbon addition, the resulting product primarily comprised Li_2CO_3, Ni, Co, and MnO. Li_2CO_3 was recovered through the carbonate solution immersion method. Meanwhile, the remaining metals were reclaimed using H_2SO_4, yielding valuable products such as Li_2CO_3, $NiSO_4$, $CoSO_4$, and $MnSO_4$. Impressively, Li reached 84.7%, and Ni, Co, and Mn exceeded 99% through this method.

To further improve the recovery of valuable metals from spent ternary LIBs, Lei *et al*. [21] employed a combination of reduction heat treatment and electrochemical leaching (Fig. 6(c)). Under reduction heat treatment conditions, the cathode material was converted into Li_2CO_3, NiO, Co_3O_4, Mn_2O_3, and MnO_2. This process destroyed the layered structure, which eased the leaching of valuable metals, resulting in ultimate recoveries of 100% for Li, 90.59% for Ni, 90.53% for Co, and 66.40% for Mn.

In the carbon thermal reduction method, the graphite anode serves as the reducing agent, decreasing the need for additional reducing agents and acids. Traditional methods

Recovery method	Leaching rate / %				Ref.
	Li	Ni	Co	Mn	
Carbon thermal reduction, carbon water leaching, and sulfuric acid leaching	84.7	>99	>99	>99	[20]
Carbon thermal reduction and electrochemical leaching	100	90.59	90.53	66.4	[21]
Waste graphite thermal reduction and sulfuric acid leaching	>99	>99	>99	>97	[89]
Waste graphite thermal reduction and phosphoric acid selective leaching	99.1	1.2	4.5	96.3	[90]
Methane reduction roasting, carbon water leaching, and sulfuric acid leaching	88	98	98	98	[91]
Lignite reduction roasting, carbonation water leaching, and ammonia selective leaching	81	95	95	1.84	[92]
Starch reduction roasting, carbon water leaching, and ammonia selective leaching	82	98	98	<3	[93]
Catalytic carbothermic reduction	78.5	99.8	99.7	99.5	[94]
In situ aluminum–carbon reduction roasting, carbon water leaching, and alkaline leaching	>97	<0.5	<0.5	<0.5	[95]
In situ thermite reduction and sulfuric acid leaching	99	98	99	99	[96]
Selective hydrogen reduction roasting and water leaching	97	<0.1	<0.1	<0.1	[97]
Sulfation roasting, water leaching, and acid leaching	94	95	95	95	[98]
Sulfation roasting and selective lithium leaching	90.2	<0.001	<0.001	<0.001	[99]
Sulfuric acid leaching, sulfation roasting, and water leaching	96.92	<1	<1	<1	[100]
Nitration, selective roasting, and selective water leaching	93	<0.1	<0.1	<0.1	[101]
Chlorination roasting and selective water leaching	98	<1	<1	<0.1	[102]

struggle with depleted Li recovery rates, but carbon thermal reduction significantly improves them by selectively extracting Li. This method is effective, cost-effective, and environmentally friendly, showing promising prospects. Future efforts should focus on lowering temperatures, increasing Li extraction rates, and reducing carbon emissions.

4.3.2. Aluminum thermal reduction

Compared with carbon thermal reduction calcination, the Al thermal reduction method does not require separating positive electrode materials and current collectors. The Al thermal reduction method exhibits higher calcination efficiency and reduces the calcination temperature, thereby avoiding significant carbon dioxide (CO_2) emissions.

Ma *et al*. [95] conducted Al thermal reduction with 14.7% carbon and 7% Al at 650°C for 90 min. Post-reaction, Li in the cathode material was converted into Li_2CO_3, whereas Ni, Co, and Mn were transformed into insoluble elements or oxides, achieving selective metal leaching. Following carbonate solution immersion, the Li content of the solution exceeded 97%, with the leaching rates of Ni, Co, and Mn being lower than 0.5%, substantially improving Li recovery efficiency.

Because Al has a higher reactivity than carbon, it can reduce metals at lower temperatures, minimizing carbon emissions. Wang *et al*. [96] employed Al as *in situ* reducing agent in Al thermal reduction (Fig. 6(d)). After heating the powdered cathode at 520°C for 60 min, valuable metals were converted into $LiAlO_2$, Li_2O, NiO, CoO, and MnO. Acid leaching using H_2SO_4 resulted in elevated leaching efficiencies of 99.78%, 98.62%, 99.29%, and 99.91% for Li, Ni, Co, and Mn, respectively.

This method presents a novel possibility for recovering cathode materials without separating them from the Al foil, operating at lower temperatures. This method is more energy-efficient and environmentally friendly than traditional methods, making it suitable for industrial applications. Future efforts should focus on utilizing Al thermal reduction with current collector Al foil for resource recycling, cost reduction, and minimizing emissions.

4.3.3. Hydrogen reduction

To improve Li recovery and enhance product value, Shi *et al*. [103] employed a hydrogen reduction–water leaching method, followed by the recovery of Ni, Co, and Mn through a small amount of H_2SO_4 (Fig. 6(e)). Under the conditions of a reduction temperature of 450°C, reduction time of 150 min, solid–liquid ratio of 300 g/L, reaction temperature of 30°C, and leaching time of 10 min, the leaching rate of Li reached 99.6%. Subsequently, recycling of low-valent metal oxides of Ni, Co, and Mn was achieved using H_2SO_4. When acid leaching was replicated 5 times, the concentrations of Ni, Co, and Mn reached 144.79, 100.01, and 113.39 g/L, respectively. Then, the solution was regenerated through the coprecipitation method for commercial applications.

Liu *et al*. [97] produced battery-grade $LiOH·H_2O$ through hydrogen reduction calcination and subsequent water immersion and crystallization of the cathode material (Fig. 6(f)). In a hydrogen gas atmosphere, Li was converted into $LiOH·H_2O$ at a rate of 98% with 15 min of reduction calcination at 500°C, while Ni, Co, and Mn were transformed into metals or oxides. Subsequent selective leaching of Li through water immersion at room temperature resulted in high-purity $LiOH·H_2O$ (99.92%) through evaporation and crystallization, suitable for subsequent preparation of cathode materials. Compared with other calcination methods, this process avoids the generation of harmful gases and yields a high-purity LiOH solution without the need for additional separation and purification processes.

Hydrogen reduction is an efficient and clean method where the recovery process does not result in harmful gases and does not introduce impurities. Hydrogen reduction effectively avoids the separation process of various metals after
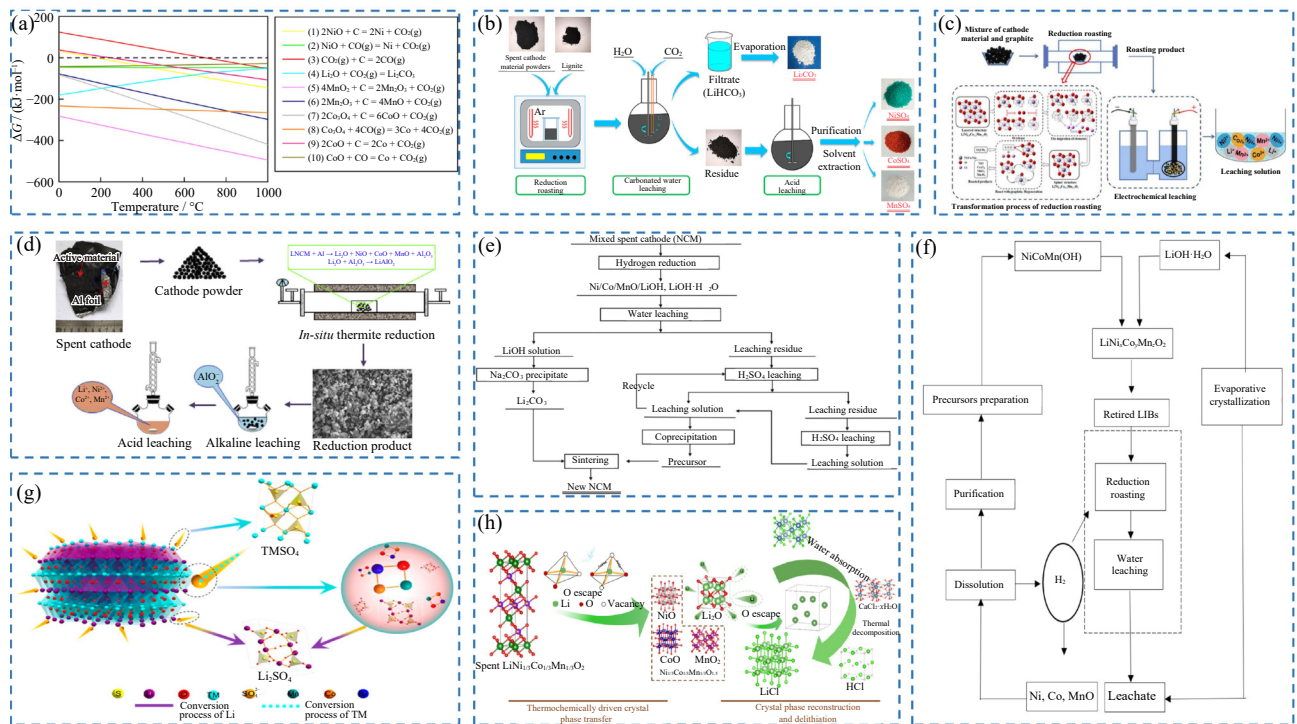
Fig. 6. (a) Relationship between ΔG during the thermal reduction process and the temperature of the metal oxide, (b) reduction roasting combined with multistage leaching for the recovery of cathode materials, (c) leaching valuable metals through reduction heat treatment and electrochemical methods, (d) aluminum thermal reduction for the recovery of cathode materials, (e) hydrogen reduction–water leaching method for the recovery of cathode materials, (f) hydrogen reduction roasting to recover cathode materials, (g) selective lithium extraction through sulfide roasting], and (h) selective lithium extraction through chloride roasting. (a, c) Reprinted with permission from S.Y. Lei, Y.T. Zhang, S.L. Song, *et al.*, *ACS Sustainable Chem. Eng.*, 9, 7053–7062 (2021) [21]. Copyright 2021 American Chemical Society; (b) Reprinted from *J. Power Sources*, 351, J.T. Hu, J.L. Zhang, H.X. Li, Y.Q. Chen, and C.Y. Wang, A promising approach for the recovery of high value-added metals from spent lithium-ion batteries, 192–199, Copyright 2017, with permission from Elsevier; (d) Reprinted from *J. Clean. Prod.*, 249, W.Q. Wang, Y.C. Zhang, L. Zhang, and S.M. Xu, Cleaner recycling of cathode material by *in-situ* thermite reduction, 119340, Copyright 2017, with permission from Elsevier; (e) Reprinted from *J. Environ. Chem. Eng.*, 11, G.C. Shi, N. Zhang, J. Cheng, *et al.*, Full closed-loop green regeneration and recycling technology for spent ternary lithium batteries: Hydrogen reduction with sulfuric acid cycle-leaching process, 111207, Copyright 2023, with permission from Elsevier; (f) Reprinted from *Sep. Purif. Technol.*, 259, F.P. Liu, C. Peng, Q.X. Ma, *et al.*, Selective lithium recovery and integrated preparation of high-purity lithium hydroxide products from spent lithium-ion batteries, 118181, Copyright 2021, with permission from Elsevier; (g) Reprinted with permission from J. Lin, L. Li, E.S. Fan, *et al.*, *ACS Appl. Mater. Interfaces*, 12, 18482–18489 (2020) [100]. Copyright 2020 American Chemical Society; (h) [101].

hydrometallurgical leaching, increasing the efficiency of metal recovery. This method has the potential to achieve closed-loop recycling in the field of battery recycling.

4.3.4. Other methods

In addition to the previously presented methods, H_2SO_4 roasting, nitric acid roasting, and chlorination are also utilized to recover valuable metals from waste cathode materials. Lin *et al.* [100] employed the sulfate calcination method for metal recovery (Fig. 6(g)). The process comprised two stages. Initially, the cathode material reacted with H_2SO_4, disrupting its structure and reducing Ni, Co, and Mn to divalent ions, forming sulfate. With the increase in temperature, Li^+ reacted with sulfate, producing water-soluble Li_2SO_4, while Ni, Co, and Mn transformed into insoluble metal oxides ($Ni_{0.5}Co_{0.2}Mn_{0.3}O_{1.4}$). Efficient separation of Li and other metals was achieved using only water, and sulfur existed in the form of sulfate, mitigating the emission of waste gases.

Peng *et al.* [101] uniformly mixed nitric acid with the cathode material and maintained it at 70°C for 5 h to form

metal nitrates (Fig. 6(h)). Selective calcination at 250°C for 1 h decomposed nitrates other than $LiNO_3$ into insoluble metal oxides and leached out using water. Huang *et al.* [102] mixed $CaCl_2$ with the cathode material at a mass ratio of 3:1 and subjected it to chlorination calcination at 800°C for 60 min. Li was converted into water-soluble LiCl, whereas the other metals were transformed into insoluble oxides ($Ni_{1/3}Co_{1/3}Mn_{1/3}O_{1.5}$). Li leaching efficiency reached 98% at room temperature, showing high selectivity for Li. Chlorination calcination minimizes the use of strong acids and reducing agents, reduces costs and pollution, and provides a promising path for metal recovery.

In summary, the pyro-hydrometallurgical recovery method enhances the leaching rate of valuable metals, especially Li, with minimal need for reducing agents. The pyro-hydrometallurgical recovery method also increases the added value of recovered products, making it suitable for large-scale industrial production. However, the process still generates waste gases, slag, and wastewater, posing risks to human

health and the environment. Future efforts should aim to reduce reaction temperatures, streamline processes, and minimize emissions while optimizing element recovery rates and achieving industrialization.

4.4. Direct regeneration

Traditional LIB recycling methods are complex, causing environmental pollution and high energy consumption. Researchers propose supplementing Li sources to restore cathode material performance without disrupting its structure. Direct regeneration establishes a closed-loop cycle for recovery, aiming to minimize costs and maximize economic value. Primary technologies include solid-state sintering, hydrothermal lithiation, and eutectic molten salt methods. Table 3 provides a summary of the direct recovery process.

4.4.1. Solid-state sintering

The solid-state sintering method entails uniformly mixing pretreated cathode materials with a Li source, adjusting the metal ratios, and subjecting them to high-temperature sintering. Through heat-driven processes, elements diffuse back to their original positions, restoring the composition and crystal structure of the cathode material and resulting in regenerated cathode material. Common Li sources used in solid-state sintering include LiOH, $LiNO_3$, and Li_2CO_3.

Jiang *et al.* [22] proposed regenerating cathode materials using $LiOH$–Li_2CO_3 eutectic molten salt (Fig. 7(a)). The molten salt provides metal ions while in a molten state, and Li^+ supplements the Li vacancy in the spent cathode materials. The cathode materials and the eutectic molten salt were combined with a mass ratio of 0.86:0.14 and sintered at 440°C for 5 h. Li^+ diffuses into the cathode materials from the molten salt. Then, an 8-h annealing process was conducted to transform the rock salt phase on the surface of the waste cathode material into the original layered phase, forming a uniform layered structure. The regenerated cathode material exhibits excellent electrochemical properties and is suitable for

industrial production, with a capacity retention rate of 89.06% after 200 cycles under 1 C conditions.

Mechanochemical activation before solid-state sintering can further enhance the chemical performance of the regenerated cathode material. Meng *et al.* [75] reported a method for mechanically and chemically activating and solid-state sintering the regenerated cathode material (Fig. 7(b)). First, Li_2CO_3 was added to the cathode material and subjected to ball milling (500 r/min, 4 h). Subsequently, the mixture was sintered at 800°C for 10 h to obtain the regenerated cathode material. Electrochemical performance testing showed that, at a discharge rate of 0.2 C, the first-cycle discharge capacity reached 165 mAh/g, and after 100 cycles, the capacity remained above 80%.

Current experiments show the successful regeneration of NCM111 and NCM523 LIBs. Sintering conditions vary with cathode composition and crystallinity. For NCM111 batteries, regardless of the sintering atmosphere (air or oxygen), the resulting samples exhibit similar electrochemical properties to the original. However, sintering NCM523 batteries in air yields poorer electrochemical performance than oxygen because of higher Ni content, leading to more rock salt phase formation and weakening material performance [105]. The optimal sintering temperature for polycrystalline NCM523 is 850–920°C, whereas for single-crystal NCM523, it should be maintained at 950°C. Pre-oxidation is necessary for NCM622 batteries with higher Ni content before sintering [106]. Solid-state sintering repairs cracks and enhances crystallinity in cathode materials during regeneration. However, uneven substance distribution in the regenerated cathode material leads to impurities, lowering the electrochemical performance of subsequent products.

4.4.2. Hydrothermal lithiation

The solid-state sintering method necessitates the calculation of Li deficiency in the cathode material and subsequent high-temperature restoration of its crystal structure.

Table 3. Direct recycling method for spent ternary lithium-ion batteries

| Methods	Cathode	Reaction conditions	Performance / (mAh·g^{-1})	Ref.
Solid-state sintering	NCM523	440°C, 5 h; 850°C, 12 h; mass ratio of $LiOH/Li_2CO_3$ = 0.84:0.16	First-cycle discharge capacity of 146.3 at 1 C, and 130.3 after 200 cycles	[22]
	NCM111	Mechanochemical activation, 800°C, 10 h, with Li_2CO_3	First-cycle discharge capacity of 165 at 0.2 C, and 132 after 100 cycles	[75]
	NCM523	300°C, 4 h, with $LiNO_3$ and LiOH; 850°C, 4 h, with Li_2CO_3	First-cycle discharge capacity of 143.9 at 0.1 C, and 134.6 after 100 cycles	[76]
	NCM111	450°C, 5 h; 900°C, 20 h, with Ni, Co, and Mn salts and Li_2CO_3	First-cycle discharge capacity of 155.4 at 0.1 C, and 129 after 30 cycles	[77]
Hydrothermal lithiation	NCM111	220°C, 4 h; 850°C, 4 h in O_2	First-cycle discharge capacity of 157.4 at 0.1 C, and 123.8 after 100 cycles	[23]
	NCM523	225°C, 8 h; 800°C, 3 h, with 4 M LiOH	Retaining >80% of capacity over 2000 cycles at 0.1 C	[78]
	NCM622	125°C, 30 min, with 4 M LiOH, H_2O_2	Retaining >80% of capacity over 1500 cycles at 0.5 C	[78]
	NCM523	150°C, 12 h; 850°C, 12 h, with saturated ethanol solution of $LiNO_3$	Retaining >90% of capacity over 560 cycles at 1 C	[104]
Eutectic molten salt	NCM523	300°C, 4 h; 800°C, 8 h	Retaining >89.6% of capacity over 200 cycles at 1 C	[24]
	NCM523	mass ratio of $LiNO_3/LiOH$ = 3:2, 300°C, 2 h; Li_2CO_3, 850°C, 4 h	Retaining 134.6 of capacity over 100 cycles at 1 C	[76]
	NCM523	mass ratio of $LiOH/LiNO_3/CH_3COOLi$) = 9:6:10, 400°C 4 h; Li_2CO_3, 850°C 6 h	Retaining >93.7% of capacity over 100 cycles at 0.5 C	[25]
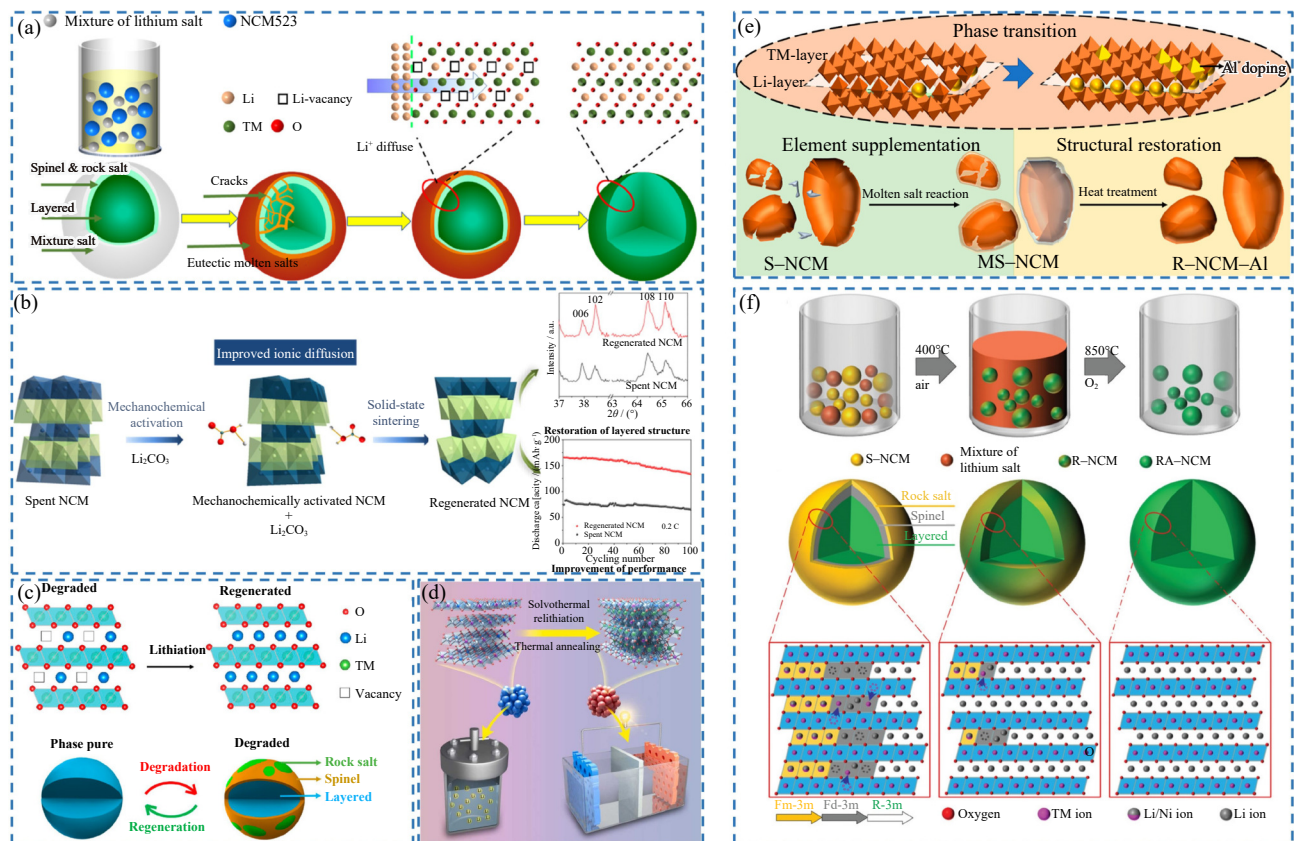
Fig. 7. (a) Regeneration of cathode materials through solid-state sintering, (b) mechanochemical activation and solid-state sintering, (c) hydrothermal lithiation for regenerating cathode materials, (d) regenerating cathode materials using a saturated ethanol–LiNO$_3$ solution, (e) two-step direct recycling method, and (f) regeneration of cathode materials using the ternary molten salt system. (a) Reprinted with permission from G.H. Jiang, Y.N. Zhang, Q. Meng, *et al.*, *ACS Sustainable Chem. Eng.*, 8, 18138–18147 (2020) [22]. Copyright 2020 American Chemical Society; (b) Reprinted from *Waste Manage.*, 84, X.Q. Meng, J. Hao, H.B. Cao, *et al.*, Recycling of LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ cathode materials from spent lithium-ion batteries using mechanochemical activation and solid-state sintering, 54–63, Copyright 2019, with permission from Elsevier; (c) Reprinted with permission from Y. Shi, G. Chen, F. Liu, X.J. Yue, and Z. Chen, *ACS Energy Lett.*, 3, 1683–1692 (2018) [23]. Copyright 2018 American Chemical Society; (d) Reprinted from *Nano Energy*, 120, J.H. Zhou, X. Zhou, W.H. Yu, Z. Shang, Y. Yang, and S.M. Xu, Solvothermal strategy for direct regeneration of high-performance cathode materials from spent lithium-ion battery, 109145, Copyright 2024, with permission from Elsevier; (e) Reprinted with permission from C.X. Xing, H.R. Da, P. Yang, *et al.*, *ACS Nano*, 17, 3194–3203 (2023) [24]. Copyright 2023 American Chemical Society; (f) Z.Y. Qin, Z.X. Wen, Y.F. Xu, *et al.*, *Small*, 18, 2106719 (2022) [25]. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

However, the diffusion of elements during this restoration process poses challenges, making it difficult to uniformly mix a small amount of Li with the cathode material for even supplementation. By contrast, the hydrothermal lithiation method offers a cathode material restoration process at relatively lower temperatures, eliminating the need for precise Li deficiency calculation.

The hydrothermal lithiation method involves reintroducing Li into spent ternary LIB cathodes by reacting them with a Li-containing solution. Shi *et al.* [23] mixed spent NCM111-type cathode material with a LiOH solution and conducted a reaction at 220°C for 4 h to inject Li into the cathode material (Fig. 7(c)). However, the performance of the cathode material after hydrothermal treatment was unsatisfactory, requiring a short, high-temperature sintering process to enhance its properties. After annealing at 850°C for 4 h, the regenerated cathode material exhibited excellent electrochemical performance. At a discharge rate of 0.1 C, the first-

cycle discharge capacity was 157.4 mAh/g, and after 100 discharge cycles, the capacity remained at 123.8 mAh/g. After hydrothermal sintering, the cathode material regained its original morphology, and its crystal structure was restored to the layered form, indicating significant improvement in electrochemical performance and structural characteristics.

Because of the high solubility of Li ions in water, when the hydrothermal reaction cools down, Li in the cathode material dissolves back into the water, leading to poor Li supplementation effects. Zhou *et al.* [104] proposed a new method for hydrothermal Li supplementation (Fig. 7(d)). They mixed spent cathode material with saturated ethanol–LiNO$_3$ solution, heat-reduced it at 150°C for 12 h, and annealed the heat-reduced cathode material at 850°C for 12 h to regain its layered structure. The regenerated cathode material exhibited excellent electrochemical performance, with an initial discharge capacity of 146.2 mAh/g at a current density of 0.1 C. At a current density of 1 C, the regenerated

cathode material showed outstanding cycling stability after 560 cycles, with a capacity retention of 90.23%, whereas the capacity retention of commercial material was only 71.93%. This method helps reduce energy consumption and environmental pollution compared with the solid-state sintering method and provides a feasible approach for cathode material recycling.

Compared with solid-state sintering, the hydrothermal lithiation method does not require precise calculation of the amount of Li source added. In addition, the hydrothermal lithiation method consumes relatively low energy, and the performance of the recycled batteries can reach their original level. The hydrothermal lithiation method is suitable for spent batteries at different recycling levels. Yu *et al.* [107] successfully regenerated NCM111 and NCM622 LIBs using the hydrothermal lithiation method, achieving excellent electrochemical performance. Subsequent annealing is needed to achieve the desired electrochemical performance, but this does not detract from the fact that the hydrothermal lithiation method is an efficient and cost-effective approach to recycle spent ternary LIBs.

4.4.3. Eutectic molten salt

Eutectic molten salt compounds, which can be melted at relatively low temperatures, offer a compelling solution. In contrast to the solid-state sintering method, the eutectic molten salt approach boasts a higher ion diffusion rate and more abundant Li sources. Importantly, this approach can be conducted at atmospheric pressure, thereby reducing costs and enhancing the safety of the reaction process.

Xing *et al.* [24] proposed an efficient two-step direct recycling method (Fig. 7(e)) utilizing Al elements from the cathode current collector to fill metal vacancies in the spent cathode material and restore its layered structure. Initially, a molten LiOH–LiNO$_3$ mixture reacted with Al impurities at 300°C for 4 h. During this process, Al impurities oxidized, forming free Al^{3+} ions introduced on the surface of the cathode material, creating an Al(OH)$_3$ coating. The cathode material underwent heat treatment, i.e., annealing at 800°C for 8 h, resulting in the generation of NCM–Al material with Al^{3+} ions filling atomic vacancies. The heat-treated cathode material exhibited a complete layered structure and excellent electrochemical performance, maintaining 89.6% of the initial capacity after 200 cycles at 1 C.

To prevent Li evaporation during cathode material regeneration, Shi *et al.* [76] proposed a method combining eutectic molten salt and annealing. Initially, the cathode material was mixed with a eutectic Li salt (LiNO$_3$–LiOH = 3:2) and heat-treated at 300°C for 2 h to permit sufficient time for Li ions to diffuse and eliminate Li deficiency. Then, excess Li$_2$CO$_3$ was added, followed by sintering in oxygen at 850°C for 4 h and annealing aimed at restoring crystal structure and electrochemical performance. Additional Li$_2$CO$_3$ compensated for Li evaporation. The regenerated cathode material exhibited complete restoration of electrochemical performance and cycling stability, with a capacity of 134.6 mAh/g after 100 cycles, even slightly outperforming the original NCM523 sample. For highly degraded NCM523 batteries, convention-

al solid-state sintering is insufficient for full restoration. The addition of Co$_2$O$_3$ and MnO$_2$ to molten salt compensates for metal losses in the cathode material [108]. Because of its capability to overcome proton-sensitive environments, solid-state sintering has promising prospects for regenerating high-Ni cathode materials, such as NCM622 and NCM811 [109].

Currently, many binary eutectic molten salt systems have been successfully implemented for the direct recovery of cathode materials. However, fully restoring the Li content of the crystal lattice and eliminating the cation mixing phenomenon remain unresolved challenges. Compared with binary molten salt systems, ternary molten salt systems have lower eutectic points and densities, requiring fewer molten salts. Qin *et al.* [25] proposed a method for regenerating cathode materials using a ternary eutectic salt system (LiOH–LiNO$_3$–CH$_3$COOLi = 9:6:10; Fig. 7(f)). The waste cathode material was initially thoroughly mixed with the ternary eutectic salt and then heat-treated at 400°C for 4 h. After thermal reduction, the cathode material was immersed in deionized water to dissolve the remaining Li salts on the surface. Subsequently, the cathode material was combined with excess Li$_2$CO$_3$ and sintered in oxygen at 850°C for 6 h to obtain the regenerated cathode material. The regenerated cathode material maintained 93.7% of its initial capacity after 100 cycles at 0.5 C, exhibiting excellent electrochemical performance. This method not only fully replenishes the missing Li in the cathode material but also enables the spinel phase in the cathode material to regain the original layered structure. The regenerated cathode material exhibits an electrochemical performance comparable to commercial cathode materials.

Compared with traditional methods, direct regeneration swiftly reintroduces valuable components to the market at lower costs. Recycled cathode materials match and even surpass the performance of commercial cathode materials because of their enhanced electrochemical properties. However, efficient and cost-effective recovery of residual Li salts is crucial for molten salt methods. Advancing this recovery is pivotal for the future of direct restoration and recycling. Currently, most direct restoration methods are in the laboratory stage. Future research should prioritize streamlined processes, reduce energy consumption, and minimize environmental impact to accelerate industrialization.

5. Separation and purification of valuable metals

After the leaching of cathode materials, metal ions, such as Li, Ni, Co, Mn, Al, and Fe, are added to the leaching solution to separate and purify the valuable metals in the solution. The main methods include solvent extraction, chemical precipitation, and electrochemical deposition. Table 4 summarizes the separation and purification technologies in the literature [18,110-119].

5.1. Solvent extraction

The acid leaching–solvent extraction method is currently

Table 4.   Summary of the separation and purification processes after hydrometallurgy

Recovery method	Sample	Additive	Ref.
Solvent extraction	Lithium nickel cobalt manganese oxide battery (LNCM)	Cyanex 272, dimethylglyoxime (DMG), P204, P507, PC-88A	[110,114–119]
Chemical precipitation	LNCM	$H_2C_2O_4$, NaOH, Na_2CO_3	[111]
Electrochemical method	Lithium nickel cobalt oxide battery (LNC)	Cyanex 272	[112]
Combined separation	LNCM	DMG, D2EHPA, $(NH_4)_2C_2O_4$, Na_2CO_3	[18,113]

the mainstream approach in the industry for recycling spent ternary LIBs. Solvent extraction is a liquid–liquid extraction process that separates metals based on the difference in dis-

tribution coefficients of different metal ions in two immiscible solvents in the leaching solution (Fig. 8(a)) [28]. Common organic extractants, such as P204, P507, Cyanex 272,
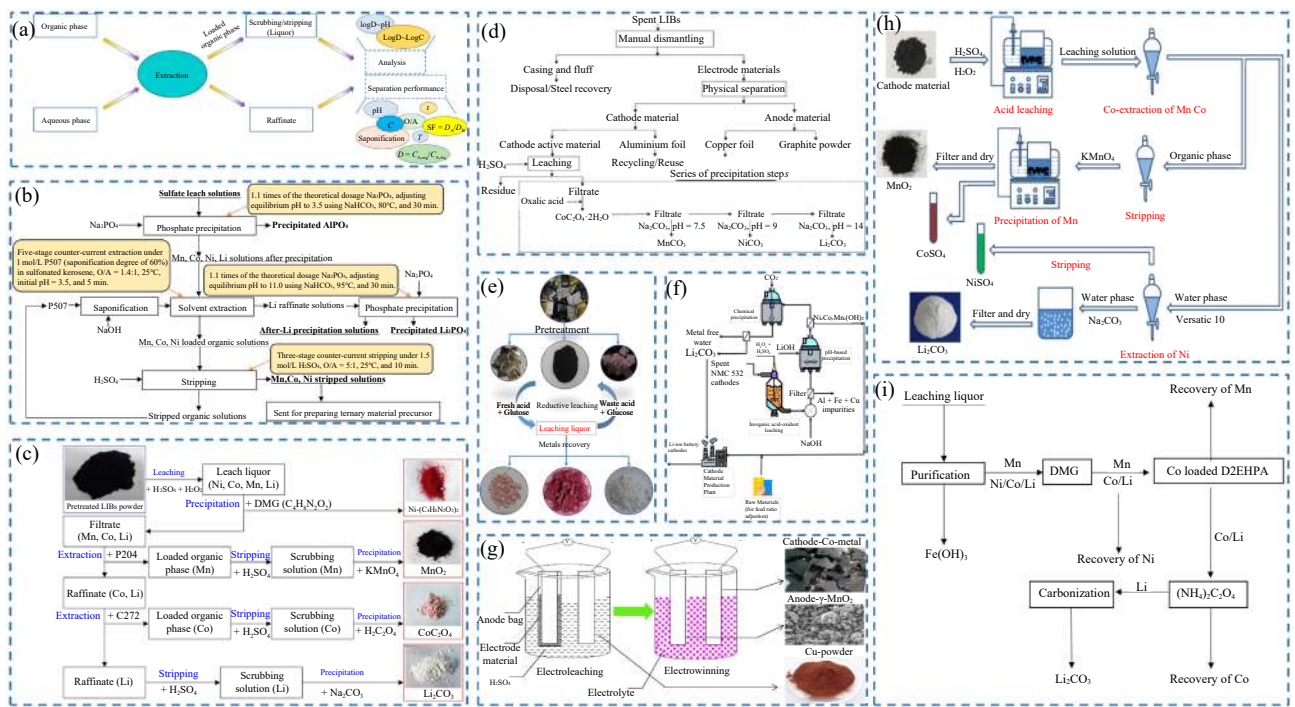

Fig. 8.   Principle and method of solvent extraction: (a) the solvent extraction mechanism, analysis, and separation performance; (b) valuable metals are separated through co-extraction; (c) organic solvent stepwise extraction of valuable metals; (d) chemical precipitation method for separating valuable metals; (e) organic acid leaching, followed by stepwise precipitation of valuable metals; (f) preparation of ternary precursor using sodium-free precipitant; (g) electrochemical deposition method for the recovery of valuable metals; (h) selective extraction combined with selective precipitation for the recovery of valuable metals; (i) combined separation method to recover valuable metals from leachate. (a) Reprinted with permission from F. Arshad, L. Li, K. Amin, *et al.*, *ACS Sustainable Chem. Eng.*, 8, 13527–13554 (2020) [28]. Copyright 2020 American Chemical Society; (b) Reprinted from *Hydrometallurgy*, 210, K.F. Zhang, H.L. Liang, X.C. Zhong, H.Y. Cao, R.X. Wang, and Z.Q. Liu, Recovery of metals from sulfate leach solutions of spent ternary lithium-ion batteries by precipitation with phosphate and solvent extraction with P507, 105861, Copyright 2022, with permission from Elsevier; (c) Reprinted from *Sep. Purif. Technol.*, 306, C.Y. Li, G.F. Dai, R.Y. Liu, *et al.*, Separation and recovery of nickel cobalt manganese lithium from waste ternary lithium-ion batteries, 122559, Copyright 2023, with permission from Elsevier; (d) Reprinted from *Chem. Eng. J.*, 281, P. Meshram, B.D. Pandey, and T.R. Mankhand, Hydrometallurgical processing of spent lithium ion batteries (LIBs) in the presence of a reducing agent with emphasis on kinetics of leaching, 418–427, Copyright 2015, with permission from Elsevier; (e) Reprinted from *J. Clean. Prod.*, 112, X.P. Chen, B.L. Fan, L.P. Xu. T. Zhou, and J.R. Kong, An atom-economic process for the recovery of high value-added metals from spent lithium-ion batteries, 3562–3570, Copyright 2016, with permission from Elsevier; (f) Reprinted from *Chem. Eng. J. Adv.*, 17, T. Tawonezvi, D. Zide, M. Nomnqa, M. Madondo, L. Petrik, and B.J. Bladergroen, Recovery of $Ni_xMn_yCo_z(OH)_2$ and Li_2CO_3 from spent Li-ionB cathode leachates using non-Na precipitant-based chemical precipitation for sustainable recycling, 100582, Copyright 2024, with permission from Elsevier; (g) Reprinted from *Waste Manage.*, 68, G. Prabaharan, S.P. Barik, N. Kumar, and L. Kumar, Electrochemical process for electrode material of spent lithium ion batteries, 527–533, Copyright 2017, with permission from Elsevier; (h) Reprinted from *Waste Manage.*, 102, Y. Yang, S.Y. Lei, S.L. Song, W. Sun, and L.S. Wang, Stepwise recycling of valuable metals from Ni-rich cathode material of spent lithium-ion batteries, 131–138, Copyright 2020, with permission from Elsevier; (i) Reprinted from *Waste Manage.*, 38, X.P. Chen, Y.B. Chen, T. Zhou, D.P. Liu, H. Hu, and S.Y. Fan, Hydrometallurgical recovery of metal values from sulfuric acid leaching liquor of spent lithium-ion batteries, 349–356, Copyright 2015, with permission from Elsevier.

and PC-88A, find widespread industrial use for the extraction and separation of metals from spent ternary LIBs.

Zhang *et al*. [116] initially employed sodium phosphate to separate Al from the leachate, followed by utilizing a 1 mol/L P507 solution (with 60% saponification degree) as the organic phase. Using a sulfonated kerosene solvent with an O/A ratio of 1.4:1, they performed co-extraction of Ni, Co, and Mn from the leachate. Li was concentrated in the extraction solution, and the recovery process is depicted in Fig. 8(b). Following five countercurrent extraction stages, Ni, Co, and Mn were extracted from the organic phase. Then, a 1.5 mol/L H_2SO_4 solution stripped the metals from the organic phase. This method achieved a recovery rate of over 98% for Ni, Co, and Mn, with only a 3.05% loss of Li. However, co-extraction did not achieve stepwise separation of valuable metals, leading to products with reduced economic value, necessitating subsequent steps for sequential separation.

To achieve stepwise separation, Li *et al*. [117] employed different extractants (Fig. 8(c)). Dimethylglyoxime (DMG) was used to preferentially separate Ni because of the high Ni content of the leachate, enabling the subsequent extraction of Mn. P204 was utilized for Mn extraction, and C272 was utilized for Co extraction. Li in the raffinate was precipitated as Li_2CO_3 using Na_2CO_3. This process achieved stepwise separation of valuable metals and reuse of the extractant, reducing production costs and facilitating industrial implementation.

Chen *et al*. [110] employed another extraction and separation process. Initially, they used 0.1 M Cyanex 272 as an extractant to efficiently separate Ni and Co from the leaching solution. Then, they adjusted the equilibrium pH to 2.95, used 0.2 M D2EHPA at an organic–water ratio of 1 to separate Co and Mn, and used DMG to separate Ni and Li. Finally, saturated solutions of NaOH and Na_2CO_3 were used for precipitation. The purity of the obtained Mn product reached 90%, and the purities of the Li, Co, and Ni products exceeded 99.5%.

In summary, solvent extraction has the following advantages: high purity of the recovered products, short extraction time, mild conditions, high selectivity, and good separation effects. However, the high cost of extractants and the complexity of the process limit the industrial applications of solvent extraction. Future research should focus on selecting cost-effective extractants and using inexpensive solvents to replace current expensive solvents. Further optimization of extraction conditions is necessary to achieve lower extraction costs and higher efficiency.

5.2. Chemical precipitation

Compared with solvent extraction, chemical precipitation is a more cost-effective and faster process without the need for expensive extractants. Stepwise separation of elements is achieved using various precipitants in the leaching solution. Common precipitants, such as oxalic acid, $(NH_4)_2CO_3$, $H_2C_2O_4$, Na_3PO_4, H_3PO_4, NaOH, and Na_2CO_3, can form precipitates with most of the valuable metal ions.

In a study conducted by Meshram *et al*. [111], oxalic acid

was added dropwise to the leaching solution to obtain cobalt oxalate precipitate (Fig. 8(d)). Under optimal conditions (i.e., oxalic acid concentration of 1 M, pH of 1.5, temperature of 50°C 323 K, and reaction time of 2 h), cobalt oxalate purity reached 95.91%, with 3.81% Ni and 0.28% Mn. Subsequent NaOH addition enabled selective Mn precipitation using Na_2CO_3. Approximately 92% of Mn was recovered as $MnCO_3$, and $NiCO_3$ precipitate was obtained by adjusting the pH and adding saturated Na_2CO_3 solution, resulting in 89% Ni recovery. By adjusting the metal proportions in the leaching solution, multiple metal elements could be coprecipitated, facilitating the regeneration of the cathode material.

In addition, Chen *et al*. [63] proposed an economically and environmentally friendly precipitation method for recovering various valuable metals with a rapid process (Fig. 8(e)). Using citric acid as the leaching agent and glucose as the reducing agent, selective precipitation of metal elements was achieved using different precipitants. The residual filtrate could be reused as a leaching agent. Under optimized conditions, the leaching rates of Li, Ni, Co, and Mn were 99%, 91%, 92%, and 94%, respectively. The use of DMG, oxalic acid, and H_3PO_4 for sequential precipitation without adjusting the solution pH simplified the operation process and reduced the costs. The entire recovery process achieved an atomic utilization efficiency of up to 98%, effectively realizing closed-loop recovery.

Traditional chemical precipitation methods often use sodium-based precipitants, leading to sodium in the wastewater that remains unrecoverable. Tawonezvi *et al*. [120] addressed this issue by using a sodium-free precipitant for the effective recovery of various valuable metals and the preparation of a ternary precursor (Fig. 8(f)). Finally, the recovery rates of Ni, Co, and Mn exceeded 98%, and the recovery rate of Li exceeded 91%. The process avoided the difficulty of separating Li and Na in the subsequent steps, achieving closed-loop recovery of valuable metals in cathode materials and exhibiting significant potential in the future recycling industry.

Although chemical precipitation has the advantages of simplicity, cost-effectiveness, and high recovery rates of valuable metals, challenges persist in impurity generation and complete separation of metals in multimetal solutions. Future research should focus on effectively removing impurities and obtaining high-purity products.

5.3. Electrodeposition

Electrodeposition can effectively overcome the issue of insufficient product purity. Its principle involves using the potential difference of different metal ions under an external electric field to electrolyze or extract the metal ions from the leaching solution, followed by electrodepositing the extracted metal ions.

Lupi *et al*. [112] first used Cyanex 272 to separate Co and Ni in the leaching solution and then electrodeposited Ni using a constant current density of 250 A/m², an electrolysis temperature of 50°C, and a pH of 3–3.2. The Ni content of

the solution was less than 100 mg/L. Shen *et al*. [121] extracted impurities from the leaching solution and directly electrodeposited the leaching solution using a Co starting electrode as the cathode and a titanium plate as the anode, with a current density of 235 A/m^2 and an electrolysis temperature of 55–60°C. The product quality can reach the 1A$^\#$ Co standard, and the current efficiency is 92.08%. The Co recovery rate is greater than 93%.

Prabaharan *et al*. [122] used H$_2$SO$_4$ to electrochemically leach the cathode material (Fig. 8(g)). Under the conditions of a current density of 400 A/m^2, H$_2$SO$_4$ concentration of 2 M, and reaction time of 3 h, the leaching rates of Co and Mn exceeded 99%. Then, under the conditions of pH of 2–2.5, reaction temperature of 90°C, and current density of 200 A/m^2, electrodeposition was conducted to recover Co, Cu, and Mn, with total recovery rates of more than 96%, 97%, and 99%, respectively.

Electrodeposition yields high metal purity and recovery rates without introducing additional impurities. The disadvantages are the increased cost and large energy consumption. In actual industrial production, several separation methods are often combined according to the actual situation to ensure that the metal recovery process is more economically efficient.

5.4. Combined separation

Given the similar chemical properties of transition metals, such as Ni, Co, and Mn, complete separation from a solution using a single method poses a challenge. The efficiency of metal recovery and reduction of metal losses can be enhanced by employing combined separation methods that leverage the strengths of each method. The key lies in the sequence of operations for each method and the consequent order of metal ion separations.

In a study conducted by Yang *et al*. [18], selective extraction was performed on cathode material leachate (Fig. 8(h)).

Mn and Co were selectively extracted using the extractant PC-88A. Under the extraction conditions of pH of 5, PC-88A concentration of 30vol%, and O/A ratio of 2:1, 98% of Mn and over 90% of Co were co-extracted. Versatic™ Acid 10 was employed to separate Ni and Li from the residue. Under the conditions of pH of 4, O/A ratio of 1:3, and Versatic™ Acid 10 concentration of 30vol%, approximately 100% of Ni was removed, and Li was precipitated with Na$_2$CO$_3$ to obtain Li$_2$CO$_3$. Finally, Mn and Co were separated using KMnO$_4$, achieving over 90% separation efficiency. This combined extraction and precipitation method efficiently separated various metals.

Chen *et al*. [113] investigated a comprehensive recovery process including chelation, precipitation, and solvent extraction (Fig. 8(i)). Ni was selectively precipitated using dimethylformamide chelation, whereas Mn and Co were separated using D2EHPA. Finally, CoC$_2$O$_4$ and Li$_2$CO$_3$ were sequentially precipitated using (NH$_4$)$_2$C$_2$O$_4$ and Na$_2$CO$_3$. The method achieved high recovery rates of Ni, Co, Mn, and Li at 98.7%, 98.2%, 97.1%, and 81%, respectively. This approach enables closed-loop recovery of multiple valuable metals from positive electrode material leachate.

The combination of chemical precipitation and solvent extraction effectively recovers valuable metals from spent ternary LIBs. Although widely used in industrial production, the process is complex. Future efforts should focus on recycling chemicals and developing simpler, cleaner methods.

6. Disposal of toxic components

People often focus on the recovery of valuable metals but always ignore toxic components. Improper handling may cause severe environmental pollution. Therefore, the recovery of toxic substances is critical. For example, potential sources of pollution during preprocessing are listed in Table 5.

Table 5. Potential pollution sources for each component

Pollution source	Main components	Chemical characteristics	Potential pollution
Cathode	LiCoO$_2$, LiFeO$_4$, LiMn$_2$O$_4$, LiNiO$_2$, and LiNi$_x$Co$_y$Mn$_z$O$_2$	Reacting with acids/reducing agents to form heavy metals	Heavy metals, such as Ni, Co, and Mn
Anode	Graphite	Dust exploding in open flame or at high temperatures	Dust pollution
Binder	PVDF and PTFE	Forming hydrogen fluoride and fluorinated organic compounds in the pyrolysis process	Organic and fluoride pollution
Solute salt	LiPF$_6$, LiClO$_4$, and LiBF$_4$	Strong corrosive, easy hydrolysis, and thermal decomposition	Fluoride and phosphorus
Solvent	DME, EC, EMC, DMC, PC, VC, and FEC	Easy hydrolysis, volatilization, and decomposition	Organic pollution
Separator	PP and PE	Release of carbon monoxide/aldehydes/organic acids on combustion	Organic and white pollution

6.1. Binders

The cathode material is bonded to Al foil using binders, such as PVDF or PTFE. In Section 2, methods for separating the cathode material from the Al foil, including solvent dissolution, alkali dissolution, and heat treatment, were discussed. Each method has its advantages and disadvantages. Importantly, none of the aforementioned methods effectively recovers the binders.

Wang *et al*. [123] proposed employing CaO to enhance

binder recovery by facilitating PVDF decomposition at a lower temperature (Fig. 9(a)). The optimal reaction conditions involve 300°C for 10 min, with a CaO/cathode material mass ratio of 8:1. Post-reaction, the cathode material achieves an effective separation rate of 97.1%. This method not only efficiently separates the cathode material from spent ternary LIBs but also proves applicable to other Li battery types, such as LiFePO$_4$ and LiCoO$_2$, offering a novel avenue for industrial PVDF recycling.

PVDF is widely used as a binder, but its chemical stability complicates recycling [124]. Aqueous binders with non-covalent bonds, such as water-soluble polymers and composite binders, are promising choices. Because of the characteristics of non-covalent bonds, these alternatives can achieve self-repair functionality with the potential for future materials to be more recyclable.

6.2. Electrolytes

The electrolyte in spent ternary LIBs is a highly polluting substance, often neglected in recycling processes. Its complex composition includes Li salts and volatile organic compounds, leading to environmental pollution and resource wastage. Current recovery methods mainly use supercritical or organic solvent extraction. Table 6 lists the details of these methods.

6.2.1. Supercritical CO$_2$ extraction

To address pollution concerns in electrolyte recovery, the use of supercritical CO$_2$ is promising because it is nontoxic, environmentally friendly, and highly stable. In its supercritical state, it combines gas-phase viscosity with liquid-phase density, aiding efficient electrolyte separation because of its favorable solubility for nonpolar substances.

Liu *et al.* [125] proposed an electrolyte recovery method composed of supercritical CO$_2$ extraction, resin, molecular sieve purification, and composition supplementation (Fig. 9(b)). Operating at 15 MPa and 40°C, the system achieved an 85% extraction rate, collecting electrolytes at low temperatures. A molecular sieve and resin removed water and impurities, with component supplementation synthesizing the electrolyte. A LIB cycled 100 times at 0.2 C using the regenerated electrolyte maintained 66% capacity.

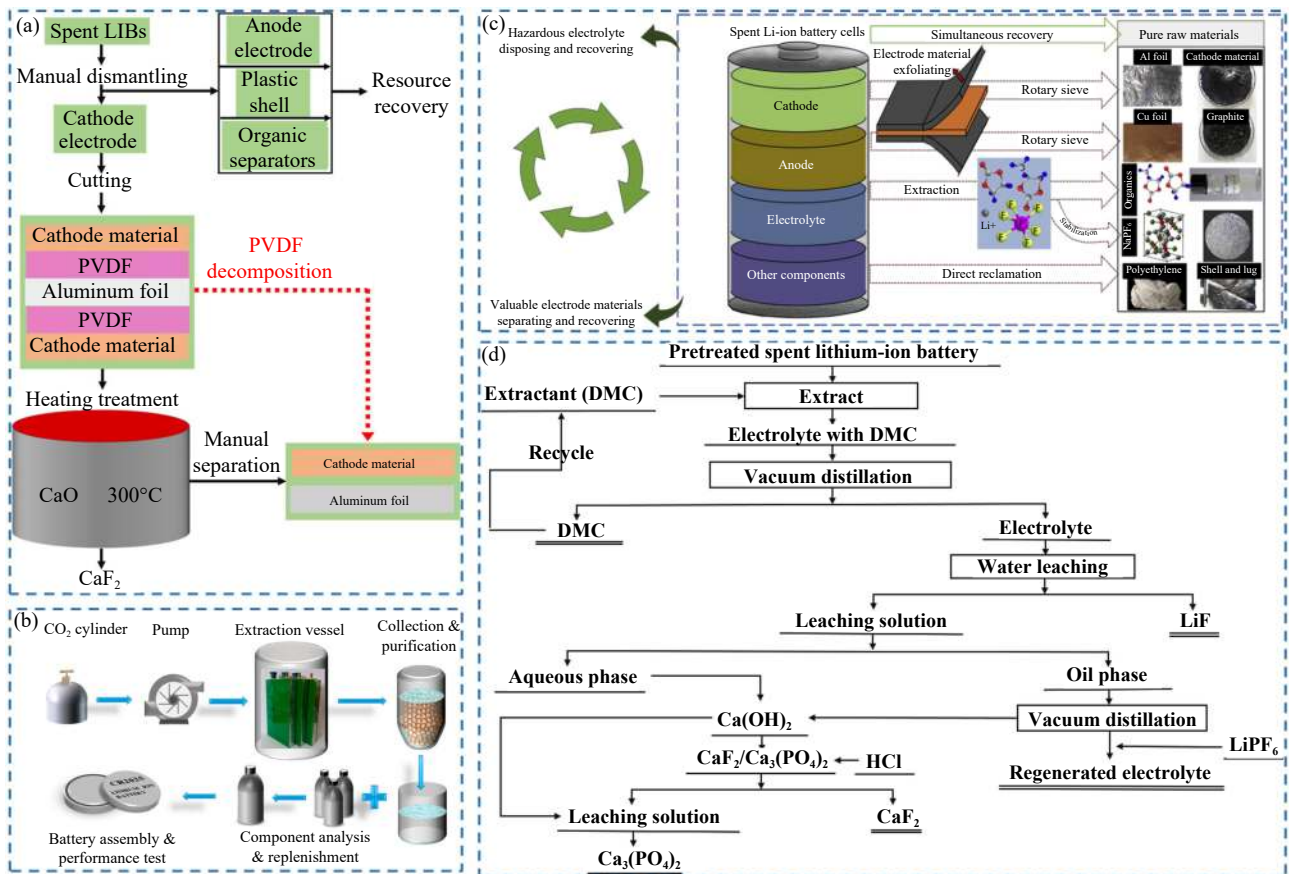Mu *et al.* [126] extracted electrolytes from spent ternary

Fig. 9. (a) Using CaO for the decomposition and absorption of PVDF, (b) supercritical CO$_2$ extraction method for electrolyte recovery, (c) organic solvent extraction method for electrolyte recovery, and (d) recovering and regenerating electrolytes. (a) Reprinted with permission from M.M. Wang, Q.Y. Tan, L.L. Liu, and J.H. Li, *ACS Sustainable Chem. Eng.*, **7**, 12799–12806 (2019) [123]. Copyright 2019 American Chemical Society; (b) Reprinted with permission from Y.L. Liu, D.Y. Mu, R.H. Li, Q.X. Ma, R.J. Zheng, and C.S. Dai, *J. Phys. Chem. C*, **121**, 4181–4187 (2017) [132]. Copyright 2017 American Chemical Society; (c) Reprinted from *J. Hazard. Mater.*, **375**, K. He, Z.Y. Zhang, L. Alai, and F.S. Zhang, A green process for exfoliating electrode materials and simultaneously extracting electrolyte from spent lithium-ion batteries, 43–51, Copyright 2017, with permission from Elsevier; (d) Reprinted from *Sep. Purif. Technol.*, **335**, G.C. Shi, J. Wang, S.H. Zhang, *et al.*, Green regeneration and high-value utilization technology of the electrolyte from spent lithium-ion batteries, 126144, Copyright 2024, with permission from Elsevier.

Table 6. Principles, advantages, and disadvantages of electrolyte recovery methods

Methods	Principle	Advantages	Disadvantages
Supercritical CO_2 extraction method	By changing the external pressure and temperature, the nature of the supercritical fluid is changed, and the substances in the supercritical fluid are separated according to their differences in solubility.	No need to use solvents No need for subsequent decontamination High recovery efficiency Environmentally friendly	High requirements for reaction equipment High production costs Unsuitable for industrial production
Organic solvent extraction method	Electrolytes are dissolved in an organic solvent based on their differences in boiling point, and the electrolytes and organic solvent are separated by distillation.	No need to use strong acids and alkalis in the recovery process Reusable extractant Suitable for industrial production	Low electrolyte recovery rate Organic solvent not widely used High cost of subsequent decontamination

LIBs by supercritical CO_2 extraction. During the extraction process, organic substances and binders were removed, and electrolyte extraction and cathode material separation were synchronously realized. The optimal conditions were 38°C, 15 min, and 10 MPa, achieving a stripping efficiency of 98.86wt% for Al foil and cathode material. Adding solvents, such as ACN/PC, at a ratio of 3:1 to supercritical CO_2 at 25°C and 6 MPa increased the electrolyte recovery rate to approximately (89.1 ± 3.4)wt%.

Supercritical CO_2 extraction eliminates solvent loss, ensuring high recovery efficiency and a pollution-free process. However, the high-pressure conditions of supercritical CO_2 extraction increase production costs, impeding industrial development. Future endeavors should prioritize enhancements in processes and equipment to mitigate production costs.

6.2.2. Organic solvent extraction

Because of the high costs, achieving industrialization with supercritical CO_2 extraction is challenging. Therefore, researchers are exploring more economical and environmentally friendly methods. Solvent extraction has become the mainstream electrolyte recovery method because of its low energy consumption, high recovery rates, and capability to reuse the extraction agent. Solvent extraction relies on the capability of the electrolyte to dissolve in a specific organic solvent. The cathode material is immersed in the solvent so that the electrolyte is dissolved, and distillation separates and recovers the electrolyte based on different boiling points.

He *et al.* [127] developed a green process for recovering electrode materials and electrolytes from spent ternary LIBs by immersing the cathode material in an aqueous exfoliating and extracting solution (AEES, Fig. 9(c)). The electrolyte dissolves and reacts with AEES, and $LiPF_6$ is converted into stable $NaPF_6$ and Li salt. These compounds precipitate when mixed with EC and PC, yielding high recovery rates of electrolyte, Al foil, Cu foil, and electrode materials. The process avoids strong chemicals, produces no waste gas or wastewater, and has the potential for industrial use.

Not only restricted to recovering the electrolyte, Shi *et al.* [128] achieved a complete closed-loop recycling of waste electrolytes, going beyond extraction (Fig. 9(d)). Initially, the electrolyte is extracted as a whole to remove impurities. Then, the regenerated electrolyte is prepared based on market needs by adding different components. DMC was used for extraction, with subsequent vacuum distillation separat-

ing DMC loaded with electrolytes for reuse. The electrolyte reacted with deionized water, precipitating Li salt, which was then washed and dried to obtain regenerated Li salt (LiF). By blending Li salt with an organic solvent, the regenerated electrolyte was prepared, exhibiting performance similar to commercial electrolytes.

This method eliminates organic phosphates and toxic gas generation from $LiPF_6$ hydrolysis, ensuring closed-loop electrolyte recycling. However, its lengthy and complex process hampers industrialization. Future research should simplify operations and explore cost-effective and eco-friendly recycling methods.

Organic solvent extraction boasts a high extraction rate, and the reusability of the extractant reduces recovery costs. However, this process requires a substantial amount of organic solvent, potentially leading to increased organic waste generation and subsequent impurity removal costs. Currently, organic solvent extraction remains in the laboratory stage and has not undergone industrialization. Future research should prioritize the development of green, environmentally friendly, and cost-effective extractants.

In addition to traditional electrolyte recovery, researchers have explored biopolymer-based electrolytes from materials such as lignin and cellulose. These electrolytes eliminate the need for battery separators, providing physical isolation between cathodes and anodes, safety, corrosion resistance, and easy recyclability.

6.3. Separators

Separators prevent direct contact between the cathode and anode of a battery, which is crucial for safety. However, their recycling is often overlooked. Disposal methods, such as incineration or landfilling, pose environmental risks. Therefore, the recycling of separators should not be underestimated.

Natarajan *et al.* [129] rinsed a separator with deionized water and utilized it in the production of new batteries. They assessed its mechanical properties, electrical conductivity, interfacial resistance, and electrochemical capacity and compared them with those of commercially available separators. Their findings indicated the outstanding performance of the recycled separator, affirming the viability of regenerating used battery separators. Nevertheless, obtaining fully intact separators in real recycling processes poses challenges, and achieving practical production still needs further development.

Biodegradable separators offer promising alternatives to traditional separators. Zhao *et al.* [130] developed a non-woven fabric separator (L-PAN) using lignin and polyacrylonitrile as raw materials. The separator exhibited a porosity of 74% and an electrolyte absorption rate of 790%. After high-temperature baking at 150°C for 15 min, its size did not significantly change. Batteries employing this separator underwent 50 cycles at 0.2 C, sustaining a discharge capacity of 148.9 mAh/g with a capacity retention of 95%, surpassing commercial PP separators in all aspects. L-PAN, characterized by low cost and a simple preparation process, has been proven suitable as a separator for LIBs.

In summary, recycling separators is vital for the economic benefits of battery recycling. However, current reports on separator recycling are limited. Future research on separator recycling should not only focus on more economical and feasible methods but also consider pathways, such as reconverting separators into hydrocarbon compounds, to achieve closed-loop recycling of all components of spent ternary LIBs.

7. Economic analysis of the recycling process

Economic analysis is crucial for assessing the viability and market application potential of recycling technologies. Wang *et al.* [131] conducted an economic analysis of the recycling process, highlighting that the profitability of battery recycling depends on the types and proportions of elements within the battery. $LiCoO_2$ exhibited the highest recycling profits because of the relatively high price of Co as opposed to other metals [132]. Ternary LIBs followed in profitability. Batteries with low Ni and Co contents exhibited either low or negative recycling values.

For pyrometallurgical methods, the profitability of the recycling process relies significantly on the Co and Ni contents of the batteries. Enhancing the profitability of pyrometallurgical recycling is closely tied to the efficient recovery of Li, a challenging aspect as a notable portion of Li is often unrecoverable and ends up in the slag during recycling. Although hydrometallurgy involves more steps than pyrometallurgy, it yields higher product purity. Opting for inorganic acids as leaching agents is advantageous because of their lower cost, and H_2O_2 as a reducing agent offers a notable price advantage over alternatives, such as $NaHSO_3$ and ascorbic acid [85]. Future efforts should aim for selective metal extraction to minimize chemical usage and boost metal recovery rates.

In the pyro-hydrometallurgical combined recovery method, carbon thermal reduction roasting, followed by the leaching of valuable metals [133], is widely used. This approach benefits from utilizing graphite from battery cathodes as a reducing agent, lowering reaction temperatures compared with traditional pyrometallurgical methods, reducing acid consumption in subsequent leaching processes, and yielding products of comparable purity to those obtained using hydrometallurgical methods. Hydrogen reduction roasting yields even higher purity products without emitting CO_2, thus gaining increasing attention. However, the use of high-temperature equipment in reduction roasting increases operational costs, necessitating the development of safer and more cost-effective equipment to improve the economic feasibility of the process. The economic benefits of other pyro-hydrometallurgical combined recovery methods remain unexplored because of the lack of industrial examples.

Compared with traditional pyrometallurgical and hydrometallurgical methods, direct recycling exhibits lower energy consumption and reduced greenhouse gas emissions because of its shorter recovery process that preserves crystal structures. Zhou *et al.* [104] based their analysis on the EverBatt 2020 model developed by the Argonne National Laboratory in the United States to measure energy consumption, CO_2 emissions, income, and costs of various recovery methods (Fig. 10(a)–(c)). The graphs show that pyrometallurgical recovery has the highest energy consumption and CO_2 emissions among pyrometallurgy, hydrometallurgy, and direct recovery methods, whereas direct recycling has lower energy consumption, less CO_2 emissions, and the highest profit compared with other methods. According to the analysis of Fig. 10(c) and (d), profits from the pyro-hydrometallurgical combined recovery method surpass those from traditional or even direct recovery methods. However, the pyro-hydrometallurgical approach entails a more intricate process than direct recovery, resulting in higher equipment and labor costs.

Yang *et al.* [134] compared the income generated by different recycling technologies in processing 10000 t of waste LIBs with similar chemical properties using the EverBatt 2020 model (Fig. 10(e)). Results show that the direct recovery method yields higher returns than both pyrometallurgy and hydrometallurgy. The income difference generated by direct recycling is particularly pronounced for batteries, such as $LiCoO_2$ (LCO), $LiNiCoAlO_2$ (NCA), $LiFePO_4$ (LFP), and $LiMn_2O_4$ (LMO) when compared with traditional hydrometallurgical and pyrometallurgical methods.

Utilizing the EverBatt 2020 model, Lander *et al.* [135] conducted a comprehensive comparison of battery recycling methods for different battery types across various countries. Their analysis provided crucial insights into the economic costs of global battery recycling (Fig. 10(f)). The cost model encompasses various stages, including battery collection, transportation, and income generation from battery materials. Because of China's efficient transportation network and well-regulated recycling systems, the costs of battery recycling in China are lower than those in other countries. Directly recycling NCA batteries in China yields the highest net profit, whereas employing pyrometallurgy for LMO battery recycling in Belgium generates the lowest profit. Profits from recycling vary based on the battery type, with higher Co content leading to increased profitability because of its superior value. Compared with manufacturing batteries from raw materials, direct recycling reduces costs by 30.19% for NCM111 batteries, 26.37% for NCM622 batteries, and 25.61% for NCM811 batteries [136].
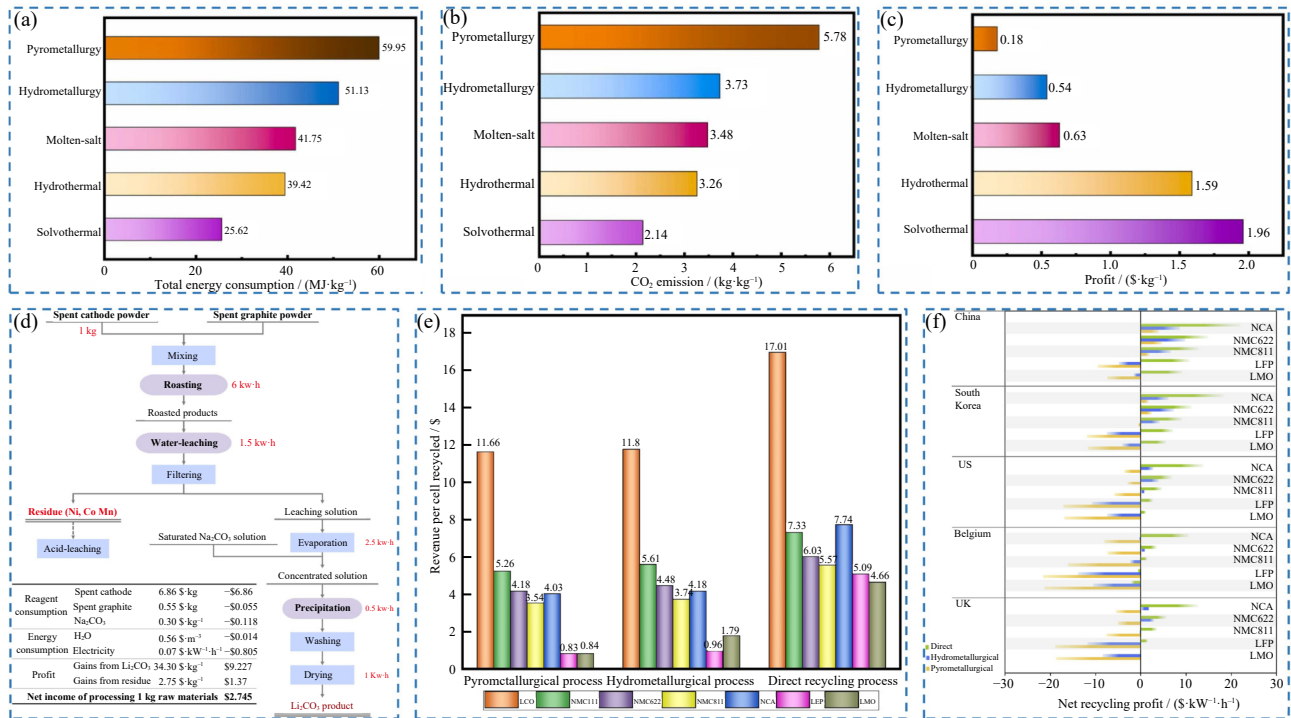
Fig. 10. (a) Energy consumption of various recovery methods, (b) CO$_2$ emissions of various recovery methods, (c) profit of pyrometallurgy, hydrometallurgy, and direct recovery methods, (d) profit of pyro-hydrometallurgy methods, (e) income generated per kilogram of battery recycling, and (f) net profits of various countries through different methods of battery recycling. (a–c) Reprinted from *Nano Energy*, 120, J.H. Zhou, X. Zhou, W.H. Yu, Z. Shang, Y. Yang, and S.M. Xu, Solvothermal strategy for direct regeneration of high-performance cathode materials from spent lithium-ion battery, 109145, Copyright 2024, with permission from Elsevier; (d) Reprinted from *J. Environ. Chem. Eng.*, 11, Q. Yuan, J. Zeng, Q.X. Sui, *et al.*, Thermodynamic and experimental analysis of lithium selectively recovery from spent lithium-ion batteries by in-situ carbothermal reduction, 111029, Copyright 2023, with permission from Elsevier; (e) Reprinted from *Energy Storage Mater.*, 36, Y. Yang, E.G. Okonkwo, G.Y. Huang, S.M. Xu, W. Sun, and Y.H. He, On the sustainability of lithium ion battery industry–A review and perspective, 186–212, Copyright 2021, with permission from Elsevier; (f) [135].

Indirect costs during battery recycling significantly impact environmental and economic benefits. Remanufacturing batteries reduces pollutant emissions compared with manufacturing from raw materials. On average, greenhouse gas emissions decline by approximately 2.85%, 10.24%, and 34.52% for pyrometallurgical, hydrometallurgical, and direct recycling methods, respectively. Direct recycling yields the highest reduction in greenhouse gas emissions, ranging from 29.27% to 38.15%, whereas pyrometallurgical recycling shows the smallest reduction, only 1% to 4.76%, because of its combustion processes [136].

To enhance future battery recycling benefits, the following points are considered: (1) Policy support across regions: Implement supportive policies for the recycling industry in various regions to stimulate growth. (2) Cost-effective labor in recycling locations: Employ cost-effective labor in recycling locations where the workforce is affordable and costs are relatively fixed. (3) Reduction of transportation costs: Minimize the transportation costs associated with collecting used batteries after recycling. (4) Scale of battery recycling: Promote the formation of a certain scale in battery recycling operations to enhance efficiency and benefits. (5) Differentiated recycling methods: Implement suitable recycling methods for different battery types to recycle high-value batteries whenever possible.

8. Summary and outlook

The recycling and utilization of spent ternary LIBs have garnered significant attention, with researchers worldwide achieving notable progress. Presently, three primary methods, namely, pyrometallurgy, hydrometallurgy, and direct recycling, are employed for waste LIB recycling. Despite some companies utilizing these methods, several challenges persist in the recycling process. To address these issues, the following recommendations are proposed:

As battery technology advances, countries must prioritize battery recycling and strengthen related legislation. Policies should set a legal framework for battery recycling across the entire lifecycle, from production to final disposal. Collaborative efforts between governments and businesses are critical to creating a comprehensive battery recycling network, ensuring proper channels for recycling batteries.

Pretreatment is essential to enhancing valuable metal recovery efficiency. However, the generation of toxic substances during this stage poses risks to human health and the environment. Future pretreatment efforts should prioritize the development of fully enclosed, near-zero emission processes to reduce pollutant emissions at the source. Furthermore, production equipment requirements need to be streamlined, and costs need to be reduced to maximize overall efficiency.

To address metal losses and pollution concerns in the pyrometallurgical smelting process, the development of a concise separation and purification technology is essential. This technology should encompass pyrometallurgical enrichment and co-electrodeposition of valuable metals to achieve the economically viable, environmentally friendly, and fully recyclable utilization of ternary LIBs.

To address the challenges of prolonged processes and excessive chemical reagent consumption in hydrometallurgy, methods that combine reduction roasting with selective leaching for valuable metal retrieval need to be explored. In contrast to complete metal leaching followed by separation, selective leaching consumes fewer reagents, exhibits higher selectivity, and boosts Li recovery rates. This approach streamlines the recovery timeline, reduces expenses, and lessens environmental footprints, aligning better with efficient and eco-conscious principles.

Compared with traditional pyrometallurgical and hydrometallurgical recycling methods, direct recycling has garnered significant attention because of its shorter recycling process, lower recycling costs, and reduced environmental impact. In articles related to the recycling of waste ternary LIBs over the past 5 years, the direct recycling method accounted for 43.5%. Researchers from various countries have conducted in-depth studies on the direct recycling of LIBs. However, most direct recycling methods are currently designed for specific materials. Spent cathode materials with different compositions and degradation levels may require different treatment methods. Therefore, a key focus of future research will be on adapting direct recycling for assorted materials.

Furthermore, artificial-intelligence-based machine learning has substantial value in battery recycling as it predicts Li battery lifespan and guides recycling processes. Training machine learning models with extensive historical data enhances accuracy. This approach minimizes ineffective experiments, reduces recycling costs and environmental impact, and improves metal recovery efficiency. Thus, investigating battery recycling through machine learning has promising potential.

In summary, future research should concentrate on developing fully enclosed, near-zero emission pretreatment technologies and short-process separation and purification technologies for Li–Ni–Co–Mn through pyrometallurgical enrichment, electrodeposition, and waste liquid recovery technologies. The aim is to ensure economical, green, and comprehensive resource utilization of ternary LIBs, reduce environmental pollution, and establish an efficient and complete spent ternary LIB recycling system.

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Conflict of Interest

The authors declare no conflict of interest.

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