

Review Article

Advances in lithium-ion battery recycling: Strategies, pathways, and technologies

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ABSTRACT

The use of lithium-ion batteries in portable electronic devices and electric vehicles has become well-established, and battery demand is rapidly increasing annually. While technological innovations in electrode materials and battery performance have been pursued, the environmental threats and resource wastage posed by the resulting surge in used batteries have been overlooked. Spent batteries are technically inoperable but contain excess metal inside the structure, making recycling essential for environmental protection and recovery of scarce resources. The battery recycling industry has gradually emerged under the influence of government implementation and ecological protection trends. However, the annual recycling volume is still insufficient compared to the output volume of used batteries. Therefore, more recycling plants and advanced technologies are imperative to improve recycling efficiency. This article summarizes pretreatment, pyrometallurgical, and hydrometallurgical processes and technologies in three major parts, analyzes their applicability and environmental friendliness using industrial examples, highlights their technical shortcomings and problems, and emphasizes the bright future of battery recycling.

1. Introduction

Lithium-ion batteries (LIB) are the mainstay of power supplies in various mobile electronic devices and energy storage systems because of their superior performance and long-term rechargeability [1]. In recent years, with growing concerns regarding fossil energy reserves and global warming, governments and companies have vigorously implemented replacing oil and natural gas with clean energy and conventional cars with electric vehicles (EVs). LIBs are currently the most suitable battery for EV applications. Consequently, the demand for LIBs has increased dramatically, which jumped from 185 GWh in 2020 to 685 GWh in 2024 and will exceed 2035 GWh by 2030, according to the statistical data from Statista shown in Fig. 1(a) [2]. The consumption of metals and organic materials to produce large quantities of LIBs is remarkable. A typical LIB module comprises active materials, such as LiCoO₂ (LCO), LiNiO₂ (LNO), LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ (NCA), LiMnO₂ (LMO), LiNi_xCo_yMn_zO₂ (NCM), LiFePO₄ (LFP) cathode and anode current collectors (Al and Cu foil), electrolytes, alloys, and a polyester plastic shell covering, along with graphite [3]. Fig. 1(d) depicts the percentage composition of each component within the battery, highlighting the presence of substantial quantities of valuable metals, indicating significant recycling potential.

Unprocessed electronic waste and the pollution from spent LIBs undermine the goal of using electricity to reduce environmental pollution. These problems include potential water source contamination by leaking electrolytes, land salinization by heavy metals, and toxic substances throughout the food chain that affect human health. Therefore, the development of a detailed battery recycling system is crucial. Moreover, amid the surging demand for batteries, the annual generation of spent LIBs is rapidly increasing, with the volume doubling from less than 170000 tons in 2019 to 360000 tons in 2023 and is expected to sharply increase to over 1.22 million tons by 2030, as demonstrated in Fig. 1(b) [4]. Owing to technological advancements, a positive market outlook, and an increasing number of discarded batteries, the battery recycling volume has increased annually, from 9 GWh in 2019 to 50 GWh in 2024, with projections estimating a surge of over 230 GWh by 2030, as shown in Fig. 1(c) [5]. Many battery recycling firms are established worldwide—such as the United States; Belgium and Germany in Europe; and China, Japan, and South Korea in Asia—which utilize various recycling processes that are mainly classified into three types: pretreatment, pyrometallurgical, and hydrometallurgical processes [6]. This review summarizes the classification of pretreatment (sorting, discharging, disassembly, and crushing); smelting and roasting processes in pyrometallurgy; and leaching and selective extraction processes in

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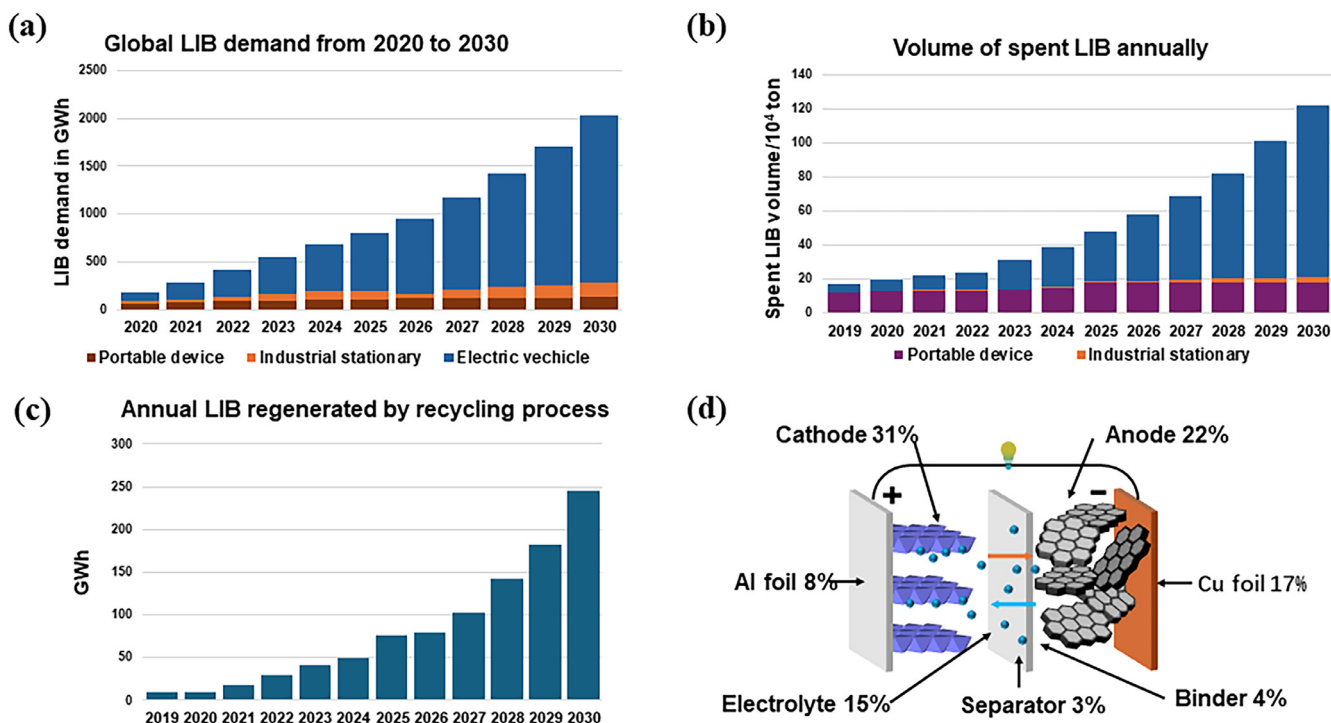


Fig. 1. (a) Worldwide LIB demand from 2020 to 2030 data from Statista [2]. (b) Worldwide volume of spent LIB generated annually [4]. (c) Worldwide volume of LIB regenerated by recycling process annually [5]. (d) Graphical representation of the percentage of each component in an LIB.

hydrometallurgy. Furthermore, the strengths and weaknesses of laboratory results and industrial cases are discussed.

2. Pretreatment process

Pretreatment is the initial and vital step in the battery recycling process, which converts batteries from compact, solid units into fractured parts and fine particles for subsequent refinement. Primary pretreatment processes include sorting, discharging, disassembly, and crushing.

2.1. Battery sorting

Batteries are highly commercialized and technology-intensive products with varying parameters such as type, size, and model. Battery recycling is a downstream process that deals with end-of-life batteries of different types and health conditions. Many established battery-recycling plants require a standardized presorting process to distinguish spent LIBs, as direct recycling reduces the efficiency of recovering valuable metals. The Umicore process does not include pretreatment steps such as sorting and smelting waste batteries directly, resulting in low metal recovery; however, rapid and straightforward pyrometallurgy leads to continued utilization [7]. Therefore, a meticulous sorting process is imperative for achieving a superior battery recycling industry. Fig. 2(a) shows a flowsheet for sorting spent LIBs [8]. Initially, the health of the batteries is evaluated, discerning those that retain a viable utility value. For instance, spent LIBs extracted from EV battery modules, which continue to exhibit enduring lifespans, can be repurposed as small-scale mobile electronic devices and auxiliary energy reservoirs. Subsequently, nonreusable batteries exhibiting deformities or structural impairments also undergo a selection process based on the congruity of size and shape [9]. This step can facilitate disassembly, crushing, and other processes and avoid operational difficulties caused by versatile shapes; fractured batteries can be directly smelted and recycled by pyrometallurgy. The screening based on the cathode material is then used to ensure the purity of the final product. Sony focuses on recycling NCM, NCA, and LCO batteries to refine Co; their final product, enriched with cobalt oxide, is

obtained through a meticulous sorting step to eliminate parts without Co maximally [10]. The study by Wang et al. [11], which compared mechanical pulverization outcomes strictly classified by the cathode material versus those broadly classified by battery type, confirmed that pulverizing old batteries with identical cathode materials mitigates overheating, sticking, and side reactions and enhances the uniformity of the pulverized particle size [12]. Manual sorting, as shown in Fig. 2(b) is still widely used in ongoing industrial recycling processes. This is because the complex conditions of the batteries require manual identification [13]. However, electrolyte leakage from the crushed LIBs and electricity risks pose safety and security concerns. To avoid these issues, some companies have already adopted machine-assisted and automated equipment, including robotic arms and standardized assembly lines, as shown in Fig. 2(c) [14]. With advances in technology such as X-ray scanning shown in Fig. 2(d), sorting has been used to accelerate the process [15].

2.2. Battery discharging

Although the waste battery may retain up to 20% of its electricity, which is insufficient for peak capacity, hasty dismantling poses a high risk of leakage accidents [16]. The electrolytes of LIBs are mostly corrosive; therefore, controlled discharge of batteries coupled with benign neutralization of electrolytes must be executed to prevent accidents [17]. A liquid medium is frequently used to short-circuit a battery and drain electricity during discharge, as shown in Fig. 3(a) [18]. Chloride salts such as NaCl and KCl are commonly used in aqueous solution discharge methods because of their cost-effectiveness and favorable conductivity. This method involves submerging used batteries in a salt solution, which is more accessible for discharging via a short circuit [19]. The leaked electrolyte is also diluted in the solution without a vigorous reaction. Sulfate solutions, such as (Na_2SO_4 , ZnSO_4 , and MnSO_4) are also used for discharging.

A paradox occurs when selecting the discharge medium: media with low discharge efficiency have a long discharge time; hence, the solution concentration must be elevated to increase efficiency. Media with high

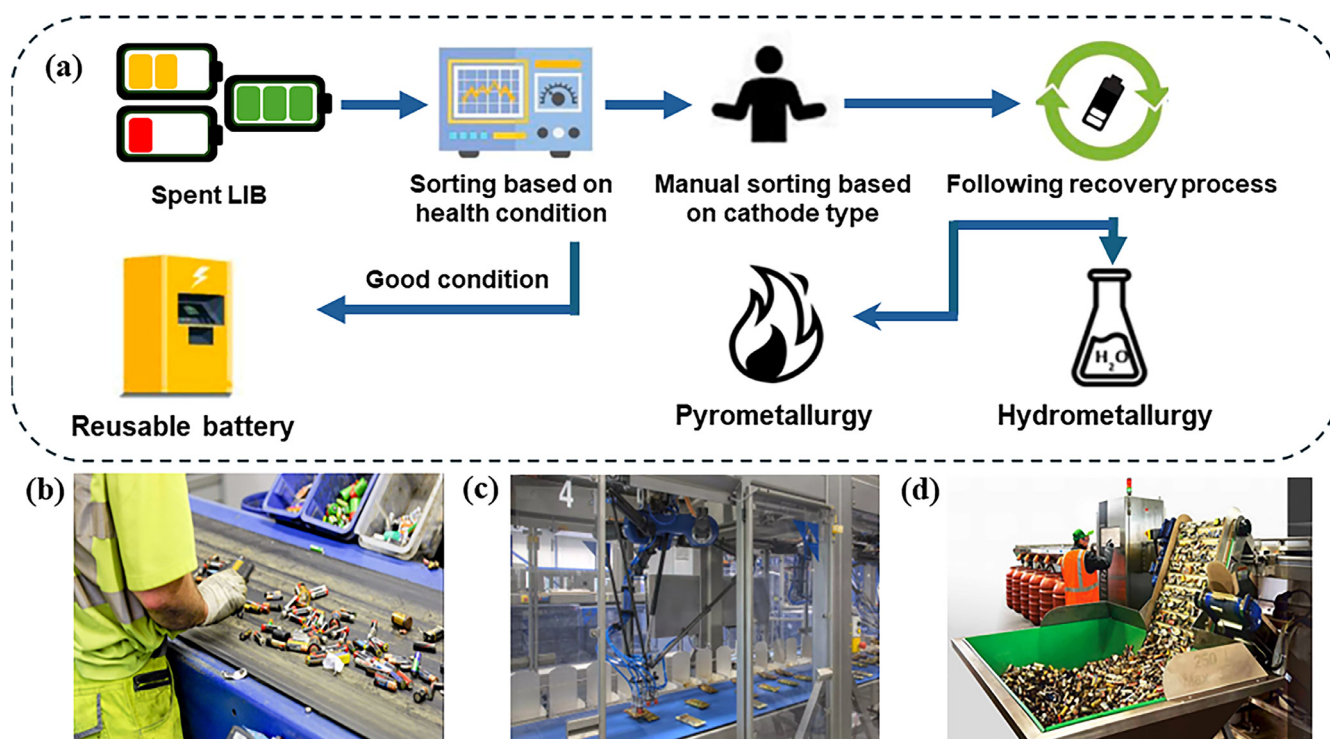


Fig. 2. (a) Flow chart presenting the sorting process in the recycling of LIBs. (b) Image of manual sorting of spent LIBs [12]. (c) Image of mechanical arm-assisted sorting of spent LIBs [14]. (d) Image of X-ray scanning that assisted in the sorting of spent LIBs [15].

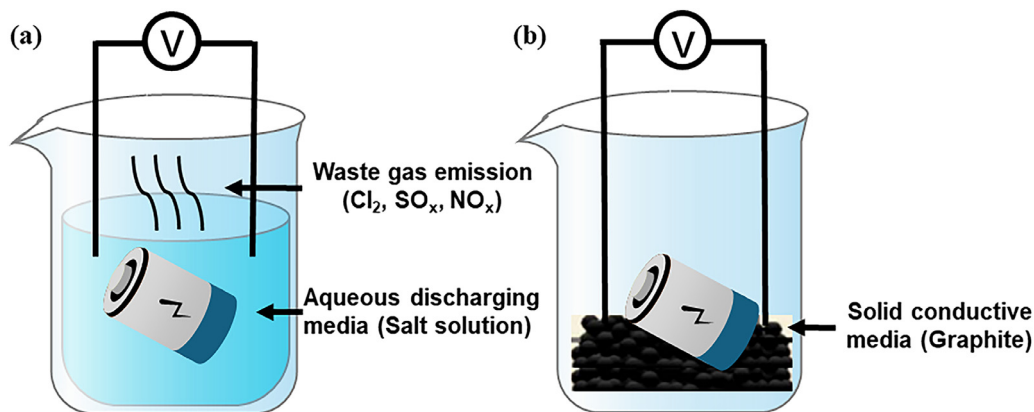


Fig. 3. (a) Schematic of an LIB discharging in a liquid medium. (b) Schematic of an LIB discharging in a solid medium.

discharge efficiencies face corrosivity, high costs, and safety problems. In a study by Li et al. [20], a standard cylindrical LIB (18 mm in diameter and 65 mm in length) consumed over 1460 min to exhaust electricity in the NaCl solution and required to increase the solution concentration to enhance the discharging ability. Solutions such as MnSO₄ and FeSO₄ significantly reduce the discharge time; however, their cost is substantially higher than that of NaCl. Thus, balancing cost-effectiveness and discharge efficiency is crucial for selecting the medium for the battery discharge process [21].

Solid conductive media are also employed to deactivate batteries; Fig. 3(b) shows the discharging process of an LIB in a solid medium. A typical example is graphite powder, which is an excellent conducting material. In a comparative test of the discharge performance of waste LIBs in different media conducted by Wang et al. [22], graphite powder was used in the discharging treatment of LCO with approximately 2600 mAh remaining and discharged to only 6.8% after 16 h, a speed equivalent to 1 mol/L NaCl, which only discharges to 13.5% remain-

ing. However, these methods are primarily applicable on a minor scale or laboratory stage; moreover, graphite is not only a good conductor of electricity but also has high thermal conductivity. Therefore, detecting the occurrence of dramatic thermal effects or other safety concerns is necessary in the industry [23].

Pyrolysis and incineration during the pretreatment step of pyrometallurgy can also have a discharging effect because the electrolyte can be decomposed directly at high temperatures, naturally excluding the risk of leakage [24]. Ultrasonic oscillation and inert gases are auxiliary methods for enhancing discharge efficiency. This is mainly attributed to the cavitation effect of ultrasound, which increases the movement of conductive ions, thereby facilitating the release of electrons [25]. Discharging in an inert gas-rich environment can reduce leakage accidents because electrolyte activity decreases in a relatively low-oxygen-content environment. Considering the industrial requirements and economic feasibility, discharging with liquid media coupled with enhancing technology is more efficient.

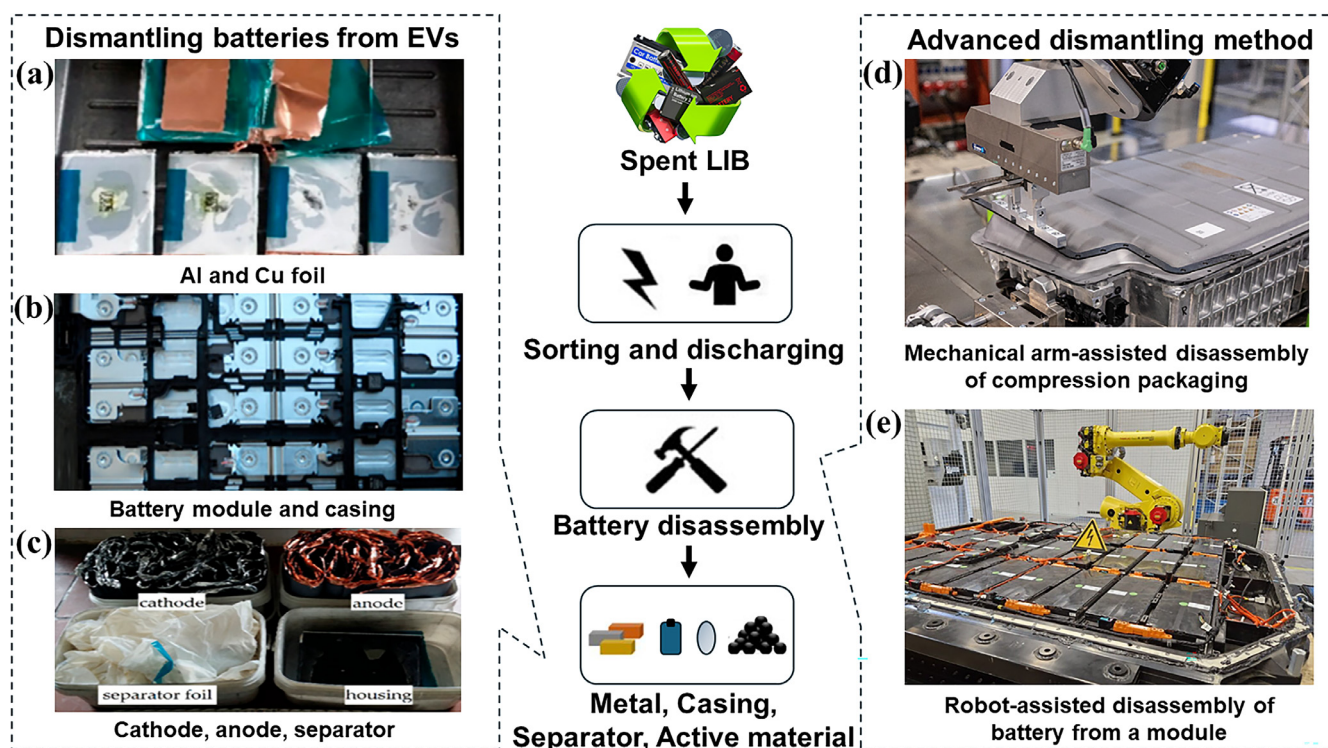


Fig. 4. Flowchart of the battery disassembly process. Dismantling battery part from an EV battery module. (a) Al and Cu foil, (b) casing, and (c) active material and separator; reprinted with permission from Ref. [27]. Copyright 2022 MDPI. (d) Image of mechanical arm-assisted disassembly of compression packaging [29]. (e) Image of robot-assisted sorting and disassembly of a battery [30].

2.3. Battery disassembly

Battery disassembly also prepares for subsequent recycling processes. In addition to the active material obtained via chemical processes for extraction, components such as the Al casing, Cu foil, separator, and current collector are also candidates for reuse via the disassembly process [26]. Fig. 4 shows the battery disassembly step, and Figs. 4(a)–(c) illustrate the components of the LIB module dismantled from EVs [27]. Because battery disassembly requires the identification of various parts, manual operation remains the safest and most productive approach, particularly in established large-scale battery recycling facilities [26]. The Umicore factory predominantly recycles EV batteries. For example, the maximum daily capacity of their workshop is approximately 10 tons of battery parts [28]. Every stage of disassembly requires manual involvement; however, this approach guarantees the precision of disassembly, and the high labor costs and limited operating speeds are inadequate to meet the rising recycling demand.

Lander et al. [31] evaluated the dismantling of waste batteries used by familiar automobile companies including BYD, Tesla, and Volkswagen. They found that manual disassembly of standard battery modules typically takes an average of 40–60 min and is associated with high labor costs. Consequently, a growing preference has been observed for more efficient mechanically assisted or automated disassembly. The electronic clamp introduced by Schmitt et al. [32] in 2011 and the robotic arm proposed by Wegner et al. [33] for production lines enabled the semiautomatic disassembly of batteries. These technologies are integrated with methodological strategies and camera recognition systems to facilitate the repetitive action of packaging and screws, followed by manual operations for complex tasks. Furthermore, the advent of collaborative robots has made it possible to automate disassembly. Hathaway et al. [34] demonstrated the efficacy of using robots for disassembling Nissan automobile battery modules, reducing the disassembly time by at least 50% compared with the manual method. Robotic operation is computer-regulated, allowing operators to monitor the distance

and intervene when necessary, thus replacing the physical presence at the disassembly site. The two methods of advanced battery disassembly are depicted in Figs. 4(d)(e). The robotic arm shown in Fig. 4(d) is applied to remove the sealed packaging of the battery module. In Fig. 4(e), the robot sorts used batteries, which did not require labor involvement.

2.4. Battery crushing and flotation

Battery crushing and flotation represent another widely utilized and effective pretreatment techniques that typically occur parallel to or after battery disassembly. While recyclers like Retrie Technologies [35], Recupyl Valibat [36], and Akkuser [37] choose direct shredding to enhance recycling speed and reduce costs, firms such as Accurec prefer detailed sorting, dismantling, and then shredding, which can eliminate the interference of impurities and plastics [38]. During a typical battery crushing procedure, spent LIBs can be comminuted into small particles for further metal extraction based on various mechanical disintegration techniques, such as direct shearing, rotary milling, cutting milling, hammer milling, and grinding. These mechanical methods can pulverize large, bulk, and inhomogeneous spent LIBs into small particles, including plastic particles and black mass-enriched active material [39]. The general crushing and flotation processes are illustrated in Fig. 5.

Crushing typically involves the use of a large industrial shredder operating in a chamber or a batch [41]. Currently, industrial crushing methods are categorized into two types: dry and wet crushing. Direct dry crushing offers a straightforward approach for crushing material without water or additives. In the Batrec process, spent LIBs are crushed into granules using a shredder and hammer mill, without pretreatment [42]. The advantage of direct dry crushing is its ease of handling; however, its drawbacks include the presence of chaotic particles and potentially unsatisfactory product purity. In addition, batteries may encounter issues such as overheating, explosions, strong oxidation when Li is exposed to

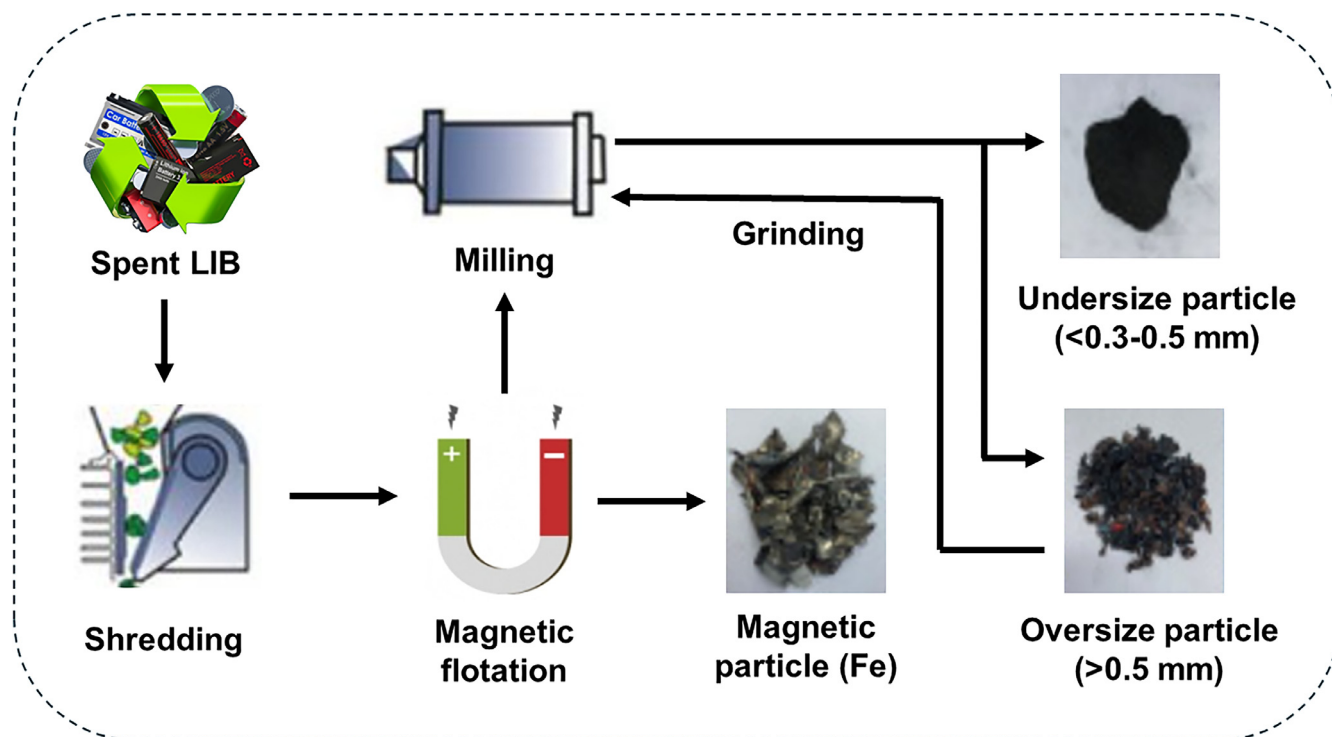


Fig. 5. Flowchart depicting a battery undergoing mechanical crushing, magnetic flotation, and separation processes. Image captured and reproduced from column-shaped waste LIBs; reprinted with permission from Ref. [40]. Copyright 2023 Elsevier.

air and dust, and gas generation during crushing, necessitating stringent pollution and safety controls.

Dry crushing in a cryogenic and inert atmosphere can mitigate these risks by operating at low temperatures, thus suppressing electrolyte activity and reducing the potential for violent reactions. Crushing in an oxygen-isolated chamber filled with inert gas can also prevent Li oxidation. These enhancements allow the processing of an insufficiently discharged spent battery, thereby reducing the stress on the battery-discharging step. In the Recupyl crushing process, Li stabilization was achieved by pumping CO₂ into the chamber [43]. Similarly, wet crushing is based on principles that suppress electrolyte activity and stabilize Li by employing water and other control reagents. In the Horiba process [44], a low-concentration halogen solution is sprayed into the batch during crushing to effectively control the process.

The size of the crushed battery particles is typically inhomogeneous owing to their differentiated ductility, and diverse crushing equipment and processes also influence the particle size. Thus, efficient separation of crushed particles is critical. The Fe components in the battery can be readily separated using a magnetic flotation machine, whereas the remaining materials require an additional sieving step. Based on the laboratory findings by Zhang et al. [45] and Prabakaran et al. [46], the particle size of crushed active material is typically less than 0.25 mm, while those of Al, Cu, and plastic particles mostly exceed 0.25 mm. In certain instances, the particle size of crushed Cu and Al foils ranges from 0.2 to 1.44 mm, attributed to toughness. Wang et al. [11] found that particles crushed under cryogenic and aqueous conditions yielded different results compared to dry crushing (<0.5 mm). Therefore, combining the actual procedure to design a particle screen with appropriate specifications is necessary to optimize separation. In industrial production, differences in equipment are particularly pronounced. Retrieval Technologies employs a 707 μm screen to segregate Al, Cu, and plastic, subsequently grinding the residual material and utilizing a 105 μm screen to isolate finely milled active materials [47]. Recupyl Valibat adopts a comparable approach but utilizes a 500 μm screen because it produces finer particles [48].

3. Metal extraction method

3.1. Pyrometallurgy

Pyrometallurgy, which is a prevalent industrial technology for recovering valuable metals from spent LIBs, relies on thermal treatments to trigger physical and chemical transformation [49]. Pyrometallurgy is crucial in industrial battery recycling because of its operational simplicity and scalability. Depending on the operating equipment and temperature, pyrometallurgical processes, including pyrometallurgical pretreatment (incineration and pyrolysis) and pyrometallurgical extractive processes (calcination and smelting), differ significantly. Pyrometallurgy can either independently recover valuable metals or be integrated with hydrometallurgy for further refined recovery. The pyrometallurgical process is illustrated in Fig. 6.

3.1.1. Preprocessing in pyrometallurgy

Pyrolysis and incineration are two promising pretreatment methods in pyrometallurgy and some hydrometallurgical processes, both of which separate active materials from organic materials and undesired substances such as plastic fragments, binders, and separator residues.

Pyrolysis, situated between the pretreatment and main pyrometallurgical processes, primarily utilizes the thermochemical degradation of organic components to separate active substances. Pyrolysis typically occurs at a temperature range of 600–800 °C in an oxygen-free environment [50]. Pyrolysis requires either a vacuum or an operating environment rich in inert gas to ensure the stability of the electrolyte vapor and toxic gas. The Accurec hydrometallurgical process in Germany has incorporated pyrolysis as a pretreatment method to remove electrolytes and solvents [51]. The spent LIBs are subjected to pyrolysis in a rotary roaster at 600 °C after the preceding pretreatment. This process ensures that the active material maintains its structural integrity and minimizes interference from the electrolyte and separator fragments. Additionally, pyrolysis renders the Al and Cu foils brittle, facilitating the grinding and milling of finer particles during mechanical crushing [52].

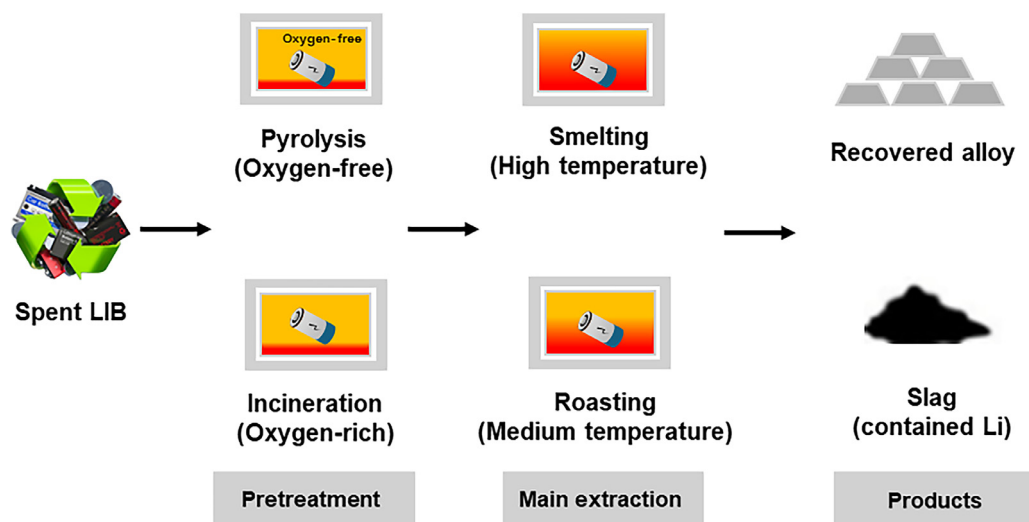


Fig. 6. Flowchart of the pyrometallurgical process.

Incineration is another thermal method that is employed for pyrometallurgical pretreatment. Incineration eliminates the organic component through direct combustion, preserving the active material for subsequent processing in the oxygen-rich environment at temperatures ranging from 700 to 800 °C [53]. In the German Nickelhütte–Aue process, incineration in a drum furnace effectively removes plastic packaging, graphite, separators, and electrolytes from spent batteries [54]. The post-incineration product consists of a black mass rich in metals and slag. Pyrolysis and incineration are both effective battery treatment methods [55]. Incineration is suitable for consecutive processes owing to its operational simplicity and adequate reaction without preprocessing; however, its drawbacks include significant energy consumption and substantial Li loss. Pyrolysis is a more delicate pretreatment process that preserves the material structure by relying solely on physical transformations to separate battery components. This makes pyrolysis particularly suitable for intricate multistep battery recycling procedures. Both methods require proper waste management to control the generation of hazardous gases such as fluoride, CO, electrolyte vapor, and high CO₂ emissions.

3.1.2. Primary extractive process in pyrometallurgy

The primary step in pyrometallurgy involves roasting spent batteries in a high-temperature calciner, triggering a reduction reaction coupled with Al and graphite within the battery or introducing additional reducing agents to convert metals from high- to low-valence states. Depending on the reaction temperature and additive type, they can be categorized into various processes.

Smelting, a typical high-temperature roasting method for pyrometallurgical recovery of LIBs, involves directly placing untreated waste battery materials into the roaster at medium temperatures (600–800 °C) to eliminate electrolyte interference and other substances as the pretreatment step, followed by continuous increase in temperature to complete the extraction process [56]. Subsequently, the battery material is heated to its melting point (over 1400 °C), where graphite and Al in the LIB act as reducing agents, forming an immiscible molten phase and slag. Upon cooling, the molten phase typically comprises an alloy rich in elements such as Ni, Fe, Co, and Cu, whereas the slag contains oxides or salts of Al, Mn, and Li [57]. The Umicore process employs a smelting method to recover LIBs, including medium-temperature pyrolysis for pretreatment, followed by upper-temperature smelting [58]. Moreover, Umicore addresses the technical limitations of pyrometallurgy such as the low recovery rate of Li, which is only found in slags. Metallurgical plants recycle slag to extract the remaining Li and then use it as a precursor for concrete in the construction industry. Umicore aims to maximize

eco-friendliness during recycling. It employs ultra-high-temperature (UHT) air purification technology to mitigate environmental impacts, which reduces the dust content in slag and diminishes toxic gas emissions.

Carbothermic reduction roasting is an exceptional method for refining metals and is more complex than smelting but conducted under medium-temperature condition (600–1000 °C). This process necessitates the pretreatment of the material by pyrolysis or incineration to eliminate organic material interference, thereby ensuring the purity of the recovered metals [59]. Carbothermic reduction roasting utilizes a reducing agent for carbon sources (such as charcoal, coke, or graphite) to convert low-solubility high-valent metal electrodes into high-solubility low-valent metal compounds. For example, LNO undergoes multistage reduction reactions and degrades into soluble Li₂CO₃ and Ni compounds [60]. Similarly, NCM composite metal oxides can be reduced to Li₂CO₃, CoO, NiO, and MnO₂ [61]. Combined with the subsequent leaching in hydrometallurgy, this technique significantly enhances the potential for recovering valuable metals. Contrary to smelting, carbothermic reduction roasting operates at relatively mild temperature (typically 600–1000 °C), thus conserving energy. Smelting is inefficient for Li recovery and often converts Li into slag. In contrast, carbothermic reduction roasting preserves Li as a metal oxide and salts [62]. Carbothermic reduction roasting has some disadvantages: the carbon introduced into the reaction system is often wasted owing to its low reactivity, and carbon consumption inevitably results in large amounts of greenhouse gas emissions.

Salt-assisted roasting is a progressive technique based on carbothermic reduction roasting. The solubility of Li₂CO₃ (13.282 g/L, 20 °C) in carbothermic reduction roasting is unsatisfactory, leading to additional energy and material consumption during subsequent hydrometallurgical leaching [63]. Salt-assisted roasting generates salts with high water solubility and low crystallinity, thus facilitating the following extractive processes. Typical salt-assisted roasting is classified into three categories based on salt additives: chlorination, sulfation, and nitration, with low reaction temperatures ranging from 400 to 1000 °C. Chlorination roasting predominantly utilizes salts such as NaCl and NH₄Cl to produce highly soluble LiCl (820 g/L, 20 °C) at 450 °C and final products containing (LiCl, LiOH, Co₃O₄, MnO_x, Ni–Co–Mn–O, 99.5% for Li, M < 1%, (M = Ni, Co, and Mn)) [64]. Sulfurization roasting requires sulfuric acid and salts such as H₂SO₄ and (NH₄)₂SO₄. Li et al. [64] confirmed the feasibility of this method through an LCO recovery experiment. They achieved a 99.3% Li recovery rate through salt-assisted roasting using H₂SO₄ and successfully obtained Li₂SO₄ (348 g/L, 20 °C) [65], Co₃O₄, and Co₂O as the final products. Similarly, nitric acid roasting

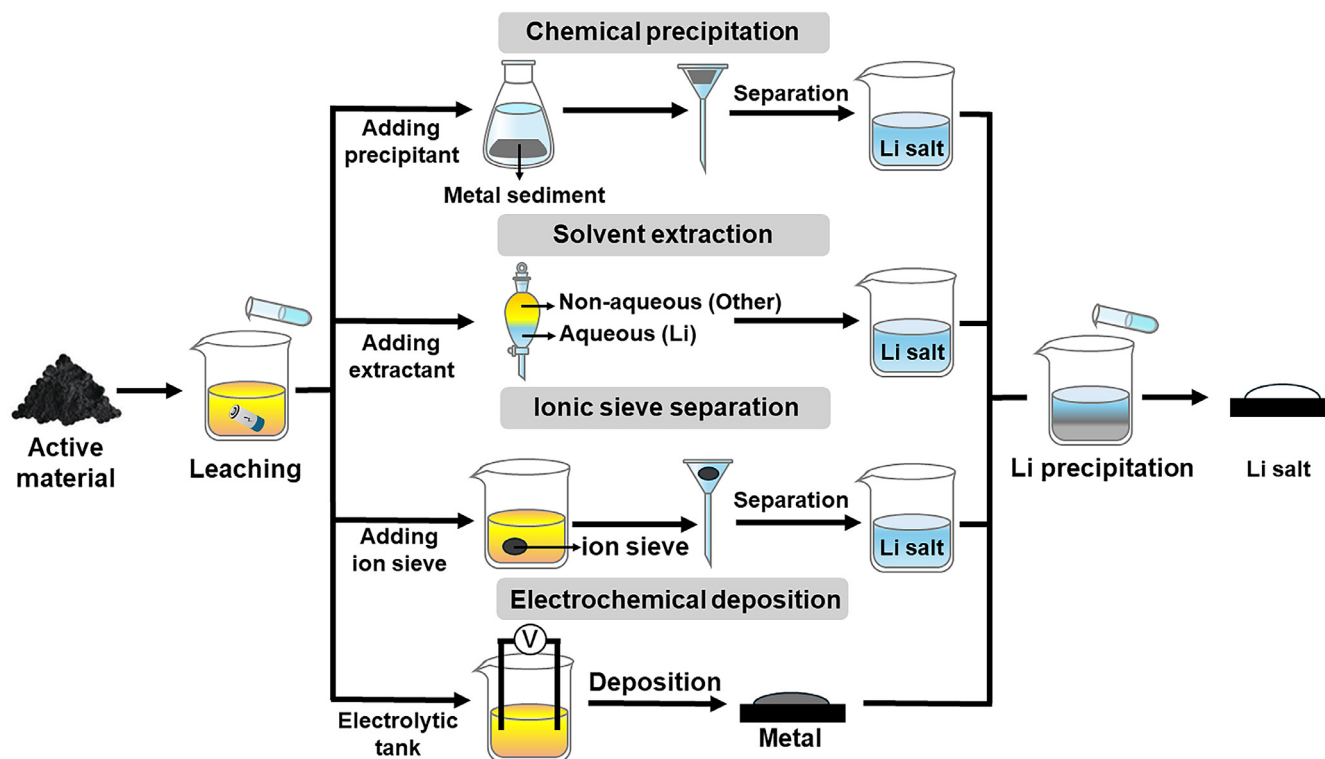


Fig. 7. Flowchart of the hydrometallurgical process.

ing uses HNO_3 to produce LiNO_3 (522 g/L, 20 °C) at significantly lower reaction temperature of 250 °C and final products containing (LiNO_3 , Co_3O_4 , 93% for Li, metal ion <0.1%) [66]. Salt-assisted roasting, whether by chlorination, sulfurization, or nitration, uses high temperatures to convert metals in the oxide state into metal salts, which are then separated according to the difference in the solubility of the salts. This method is identical to hydrometallurgy and demonstrates matching metal recovery during the experimental stage [67]. However, the main limitations of salt-assisted roasting are the high energy consumption associated with high-temperature roasting, the emission of secondary harmful gases (Cl_2 in chlorination, SO_x in sulfation, and NO_x in nitration), and product purity defects. Salt-assisted roasting has the advantage of a direct yield of valuable metal products compared to the current complex process. If the product quality is increased to a higher purity with superior separation, the method can be industrialized on a large scale in combination with appropriate contamination treatment, which could be a sustainable process for battery recycling in the future.

In addition, the traditional carbothermic reduction roasting process requires significant energy to increase the reaction temperature, which inevitably leads to high fuel consumption. Microwave-assisted carbothermic reduction roasting is an environment-friendly and energy-efficient method that uses microwaves instead of conventional heat sources. In non-contact heating, microwaves generate heat through electromagnetic radiation that induces resonance between particles, offering temperature levels compatible with traditional carbothermic reduction roasting [68]. According to Pindar et al. [69], the heating efficiency of microwave-assisted carbon-reduction roasting significantly, which surpasses that of the conventional heating method beyond 600 °C, thereby enhancing the reaction efficiency. However, microwave-assisted carbon-reduction roasting has several technical limitations. First, the size of the equipment limits its industrial applicability. Second, the reaction kinetics associated with the processing of large volumes of spent LIBs warrant further research.

3.2. Hydrometallurgy

Hydrometallurgy is another mainstream method for recycling spent LIBs. Battery recycling aims to realize a circular economy and the regeneration of valuable materials. However, pyrometallurgy is contrary to some of these desires, and applying the product in an alloy form and achieving low metal recovery encounter certain barriers. Hydrometallurgy addresses these limitations by primarily utilizing aqueous dissolution to ionize the active materials from spent LIBs, followed by the selective extraction of different metals. Hydrometallurgy also offers precise recovery, high product purity, and significantly lower energy consumption than pyrometallurgy [70].

In hydrometallurgical processes, leaching can be broadly classified into three types depending on the reagent used to ionize the active material: acid leaching, bioleaching, and alkaline leaching [71]. The selective extraction stage of hydrometallurgy is categorized based on the physical and chemical properties involved, specifically chemical deposition, solvent extraction, and physical adsorption. Hydrometallurgy generally requires comprehensive pretreatment to remove the separator and over-pack and reduce the particle size of the active material to ensure an effective reaction and exclude impurity interference [72]. Fig. 7 shows a flowchart of the hydrometallurgical process.

3.2.1. Leaching

The leaching step in hydrometallurgy involves converting metallic elements from a solid active material to an ionic state in an aqueous solution, following which the individual metals are recovered separately. Therefore, the leaching efficiency directly affects the metal recovery and product quality. The main factors affecting leaching are temperature, leaching agent type, and pH value [73].

3.2.1.1. Acid leaching

Inorganic acid leaching is extensively utilized and industrialized in hydrometallurgy. Typical acids include HCl , H_2SO_4 , HNO_3 , and H_3PO_4 .

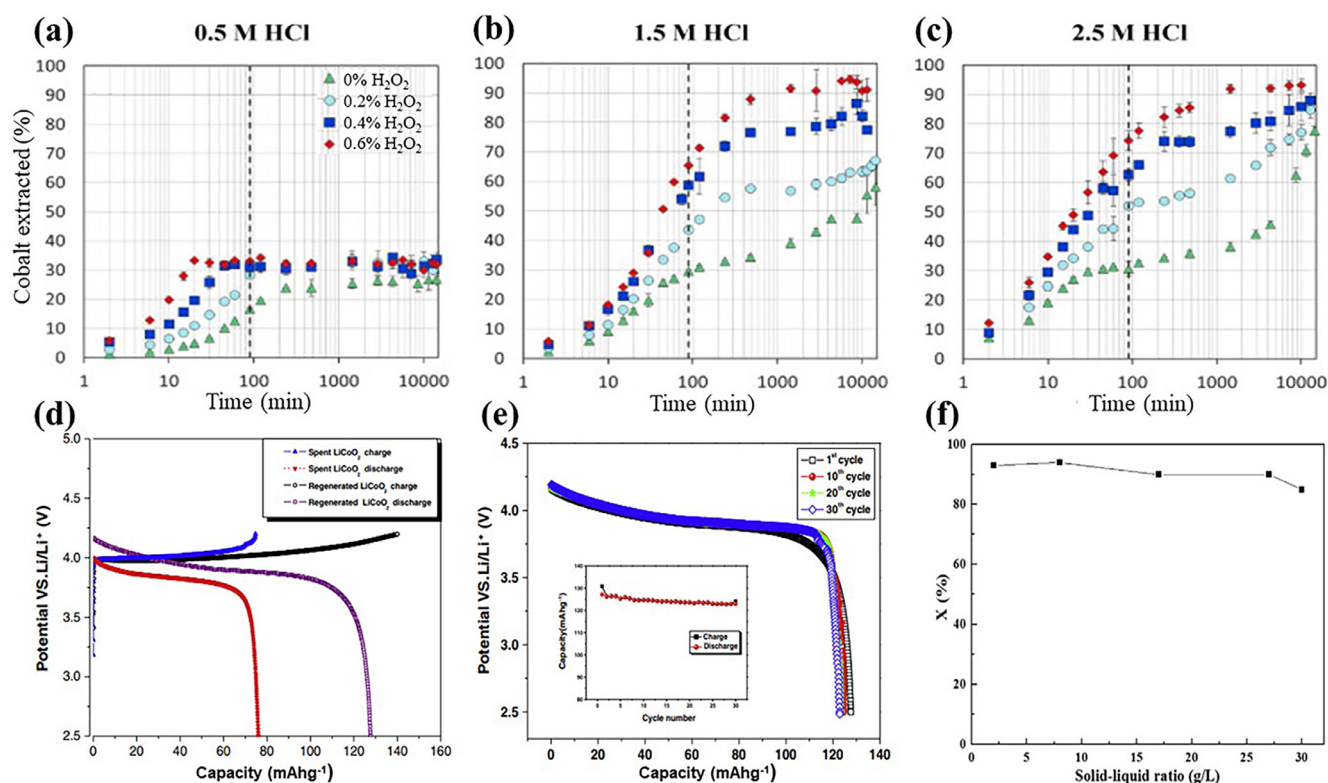


Fig. 8. (a)–(c) Effect of the H₂O₂ reducing agent on leaching efficiency during LCO leaching with different HCl concentrations; reprinted with permission from Ref. [79]. Copyright 2022 Elsevier. (d)(e) Electrochemical properties of LCO regenerated from HNO₃ leaching solution; reprinted with permission from Ref. [84]. Copyright 2011 Elsevier. (f) Effect of solid-liquid ratio on leaching efficiency in the leaching of LCO with H₃PO₄; reprinted with permission from Ref. [85]. Copyright 2017 Elsevier.

With its high acidity, HCl can dissolve most metals and their compounds because of its high dissociation constant in aqueous solution [74]. Li et al. [75] successfully recovered LCO using 4 mol/L HCl as leaching agent at 80 °C with a solid-liquid ratio of 50 g/L, achieving leaching efficiency of over 97% at Li and 99% at Co. This indicated that HCl is a highly effective leaching agent for metals and other compounds. LCO and HCl react vigorously to form soluble CoCl₂ and LiCl, accompanied by the release of Cl₂. Subsequently, Co and Li are recovered through selective extraction. The most significant issue with this process is safety concerns regarding strong acids and the release of toxic Cl₂, necessitating safety facilities and exhaust gas management in laboratory and industrial environments. In some tests, the leaching efficiency was unsatisfactory owing to the leaching agent ratio, reaction temperature, and other factors [74]. This was attributed to the incomplete reaction of stable high-valence metals in the active materials and the intense bonding energy. Reducing agents can convert high-valence metals into divalent soluble ionic states, such as Co³⁺ to Co²⁺ in LCO and Mn⁴⁺ to Mn²⁺ in NCM, thereby accelerating the leaching speed and efficiency; thus, they are frequently introduced in the leaching process. Typical reducing agents used in inorganic acid leaching are H₂O₂, NaHSO₃, and glucose [76]. Guimarães et al. [77] demonstrated that the NCM leaching method achieved a leaching efficiency of 88% with 1 mol/L H₂SO₄ at a solid-liquid ratio of more than 1:10 without the reducing agent. The leaching process reported by Meshram et al. [78], wherein 1 mol/L H₂SO₄ and 0.075 mol/L NaHSO₃ were used as reducing agents, resulted in a leaching rate of more than 90% for each metal at 20 g/L. Cerrillo-Gonzalez et al. [79] investigated the effect of reductant usage on the leaching efficiency at different HCl concentrations and reported that an elevated amount of reductant significantly increased the leaching efficiency of the metal (Figs. 8(a)–(c)). Li et al. [80] discovered that H₂O₂ as a reducing agent significantly reduced the amount of Cl₂ in the exhaust

gas during HCl leaching, suggesting that the reducing agent suppressed the generation of toxic gases. A similar phenomenon was observed in H₂SO₄ leaching experiments, where toxic SO_x gas emissions were curtailed [81]. Kang et al. [82] investigated the recycling process using H₂SO₄ as leaching agent and achieved a leaching rate of over 99% in LCO for Li and Co under optimized conditions (60 °C and 2 mol/L H₂SO₄ with 6% H₂O₂ as a reductant). Based on the above experimental examples can prove, the introduction of a reducing agent can efficiently increase the leaching rate and reduce the consumption of the leaching agents, then inhibit the generation of toxic gases.

HNO₃ is another commonly used acid in inorganic acid leaching, which requires an additional reducing agent to ensure efficient leaching. Yuliusman et al. [83] used 3 mol/L HNO₃ and H₂O₂ as reducing agents to leach Co from LCO and obtained a Co leaching efficiency of over 98%. In a study by Li et al. [84], an LCO leaching solution with HNO₃ was shown to be directly regenerable into high-purity LCO crystals, rather than lithiated salts, using an electrochemical precipitation technique at a constant current, offering a novel recycling pathway. According to the cycling performance of the regenerated LCO shown in Figs. 8(d)(e), the new electrode material had intact electrochemical properties. H₃PO₄ is also frequently used as a leaching agent because of its multiprotonic properties and suitable acidity, which allow it to ionize high quantities of H⁺ in aqueous solutions. During the leaching process of H₃PO₄, PO₄³⁻ forms precipitates with metal ions other than Li, such as Co, and selective extraction can be accomplished directly. This advantage is most obvious in the recovery process of LCO because only Li and Co are present, and Co can be separated with Co₃(PO₄)₂ precipitates. Pinna et al. [85] used a combination of 2 mol/L H₃PO₄ and 2% H₂O₂ to leach LCO and obtained a Li leaching efficiency of more than 99%. The data in Fig. 8(f) shows that the solid-liquid ratio has less effect on the leaching efficiency; therefore, H₃PO₄ can be used as a highly ef-

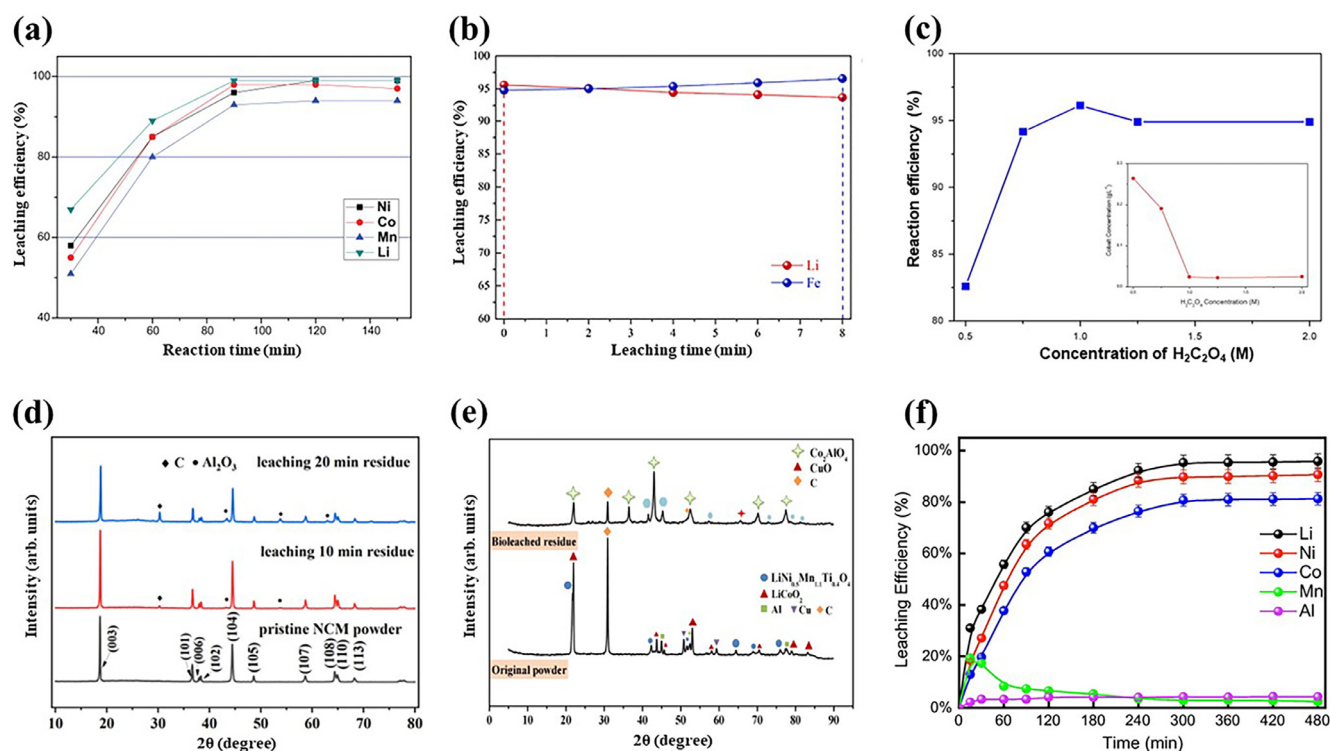


Fig. 9. (a) Diagram of reaction time and leaching efficiency during leaching of LCO with 1 mol/L citric acid; reprinted with permission from Ref. [89]. Copyright 2019 Elsevier. (b) Diagram of reaction time and leaching efficiency during leaching of LFP with 2 mol/L citric acid; reprinted with permission from Ref. [90]. Copyright 2019 Elsevier. (c) Diagram of the effect of concentration on leaching efficiency during oxalic acid leaching of LCO; reprinted with permission from Ref. [92]. Copyright 2012 Elsevier. (d) Comparison of XRD results between the original NCM electrode powder surface and the NCM powder surface after leaching using malic acid; reprinted with permission from Ref. [94]. Copyright 2022 Wiley-VCH. (e) Comparison of XRD results between the original electrode powder surface and the powder surface after leaching using *Aspergillus niger*; reprinted with permission from Ref. [100]. Copyright 2018 Elsevier. (f) Diagram of leaching efficiency corresponding to reaction time in the leaching of NCM by a mixed ammonia-based solution; reprinted with permission from Ref. [106]. Copyright 2017 Elsevier.

efficient and stable leaching agent and can reduce the consumption of the leaching agent. Several of the aforementioned inorganic acids are also used as leaching agents in established battery recycling plants because of their ultrahigh solubility, such as Accurec and Battery Resources using H_2SO_4 , Umicore using HCl, and Recupyl Valibat using a combination of H_2SO_4 and H_3PO_4 . Inorganic acid leaching is a potent and technologically efficient hydrometallurgical process. However, disadvantages stem from its strong acidity, which causes equipment corrosion, difficulties in treating waste liquids, and secondary atmospheric pollution. Therefore, future research on inorganic acid leaching may be directed toward realizing environmental-friendly routes.

Considering environmental concerns, substituting inorganic acids with organic acids as leaching agents in hydrometallurgy has attracted increasing attention. Organic acids generate less pollution than inorganic acids [86], and most organic acids are derived from plants and animals, which enhances their recyclability. Organic acids are weak electrolytes, and their acidity is determined by the number of functional groups and capacity to ionize H^+ in aqueous systems (indicated by their pK_a values) [87]. Typical organic acids include citric, oxalic, malic, ascorbic, and acetic acids.

Citric acid, a natural compound with the formula $\text{C}_6\text{H}_8\text{O}_7$, is abundant in citrus fruits. Three hydroxyl groups allow each mole of citric acid to dissociate three moles of H^+ in a solution, providing sufficient acid to act as a leaching agent. In a study by Li et al. [88], 1.25 mol/L citric acid combined with 1% H_2O_2 reductant at 90 °C and a solid-liquid ratio of 20 g/L were employed to leach LCO, acquiring Li and Co leaching efficiencies of 99% and 90%, respectively. Yu et al. [89] used 1 mol/L citric acid and H_2O_2 to treat LCO cathode materials under the conditions of 70 °C and a solid-liquid ratio of 40 g/L and achieved both Li and Co

leaching efficiencies of 99% in a simple and direct method with quick 90 min reaction time, as shown in Fig. 9(a). LFP is more difficult to recover than other materials because of its stable olivine crystal structure. Thus, the consumption of acid for dissolution increases during inorganic acid leaching. Li et al. [90] achieved a leaching efficiency of 99% for Li from LFP using 2 mol/L citric acid and a solid-liquid ratio of 20 g/L, with the addition of 1% H_2O_2 reductant, and the relatively high leaching efficiency is shown in Fig. 9(b). This indicates the adequate acidity of citric acid as an acid-leaching agent for electrode materials and its high selectivity for multiple metals. Oxalic acid is another notable organic acid leaching agent that is particularly effective for recovering LCO. It is a moderately acidic dicarboxylic acid commonly found in plants and has the chemical formula $\text{C}_2\text{H}_2\text{O}_4$ [91]. Oxalic acid is similar to H_3PO_4 in that oxalate ions can combine with Co^{2+} and Li^+ to form the insoluble precipitate CoC_2O_4 and soluble $\text{Li}_2\text{C}_2\text{O}_4$, respectively, allowing one-step Co separation and highly selective Li recovery. In addition, oxalic acid can be used as a substitute for reducing agents. This is supported by the findings of a study by Sun et al. [92], wherein the recovery of LCO in 1 mol/L oxalic acid without any reducing agent reached 95% and was higher with the addition of a small amount of reducing agent, as shown in Fig. 9(c).

Malic acid, a cost-effective and widely available diacid with the chemical formula $\text{C}_4\text{H}_6\text{O}_5$, offers superior biodegradability and reusability compared to inorganic acids, making it highly suitable for hydrometallurgical processing [93]. Malic acid exhibits asymmetric stretching vibrations in three isomers (D-malic acid, L-malic acid, and DL-malic acid). DL-malic acid is particularly effective in recovering LCO and NMC. Li et al. [87] used 1.5 mol/L DL-malic acid at 90 °C with a solid-liquid ratio of 20 g/L and 4% H_2O_2 and achieved over 99% leach-

ing of Li and 93% leaching of Co from LCO. Cheng et al. [94] reported that the leaching efficiencies of NCM of Li, Co, Ni, and Mn reached 98.1%, 97.1%, 96.2%, and 97.6%, respectively, with 2 mol/L DL-malic acid at 90 °C with a solid-liquid ratio of 30 g/L and 1.5% H₂O₂. The X-ray diffraction (XRD) graph in Fig. 9(d) demonstrates the ability of DL-malic acid to dissolve metal, showing that the spurious peaks which are corresponding to metals are significantly reduced after treatment with DL-malic. Ascorbic acid (Vitamin C) is a vital antioxidant in humans. Its polyhydroxy structure enables the dissociation of hydrogen ions in aqueous solutions, thereby serving as an effective leaching agent in hydrometallurgy [95]. Leaching efficiencies of 94.8% and 98.5% for Co and Li, respectively, were achieved using 1.25 mol/L ascorbic acid solution at a leaching temperature of 70 °C and solid-liquid ratio of 25 g/L [96]. Organic acids such as lactic, tartaric, aspartic, and formic acids have been investigated as leaching agents for LIB cathode materials [97]. The reducing properties of organic acids owing to their complex double-bond structure can cover off the reducing agent dosage; however, insufficient acidity compared to inorganic acids limits their ability to dissolve metals [98]. From an industrialization perspective, the plant requires a process with stable performance, while a wide variety of organic acids with fluctuating properties are available, and further research is required to achieve a leap from the laboratory to the plant. Thus, identifying the optimal leaching conditions for efficient and cost-effective processes is a key future direction for organic acids in hydrometallurgical research.

3.2.1.2. Bioleaching

Bioleaching is a hydrometallurgical leaching method that enhances the environmental recyclability of organic acids. Bioleaching mainly uses natural metabolites from microorganisms, such as fungi and bacteria. Microorganisms metabolize acidic secretions to dissolve metals and combine them with metal ions to form complexes that are dispersed in an aqueous solution to complete leaching [99]. In a study by Bahaloo et al. [100], bioleaching for the uniform grinding of electrode materials using gluconic acid produced by *Aspergillus niger* as the leaching agent yielded promising results. The optimized temperature and solid-liquid ratio led to leaching efficiencies of 100%, 94%, 72%, 62%, 45%, and 38% for Li, Cu, Mn, Al, Ni, and Co, respectively. The XRD results in Fig. 9(e) show that NCM peaks were evident in the non-bioleached material, whereas after leaching, the Li-, Ni-, and Mn-related peaks were no longer detected, indicating that NCM had been dissolved. *Acidithiobacillus ferrooxidans* [101], *Acidithiobacillus thiooxidans* [102], and *Leptospirillum ferriphilum*s [103] have also been used for bioleaching metabolites. Joseph et al. [104] successfully regenerated high-purity graphite (99.87%) with favorable electrochemical properties (400 mAh/g and a retention rate of 100% after 200 cycles) from effluent after bioleaching with *Acidithiobacillus ferrooxidans*. In conventional acid leaching, carbon is typically directly converted into carbonate and can only be recovered as a salt. Although the metal leaching rate of this microbial leaching method is relatively low, carbon recovery can be achieved, thus providing new ideas for bioleaching. However, another experiment using *Aspergillus niger* as the acid source yielded less satisfactory results; only 87% of Li, 13% of Ni, and 25% of Co were leached during the NCM recovery process. This fluctuation is attributed to the strong influence of temperature on the acid secreted during microbial cultivation. In other tests, microbial leaching was significantly affected by the interference of external factors, such as temperature, solid-liquid ratio, catalysts, and metal content of the solution [105]. In a study by Zeng et al. [103], the adoption of Ag⁺ as a catalyst for bioleaching with *Acidithiobacillus ferrooxidans* significantly increased Co leaching from 43% to 90% and reduced the leaching time by seven days. In summary, bioleaching has several limitations. First, time-consuming and continuous microbial cultivation is unfavorable for industrial applications. Second, the process is impeded by slow kinetics, with leaching times often spanning a few weeks. Third, the culture status of microorganisms profoundly affects the acidity and leaching efficiency. In addition, they are sensi-

tive to metals and struggle with the leaching of high-purity materials. Despite these obstacles, bioleaching has demonstrated potential for battery recycling. Its environmental friendliness and minimal consumption of natural resources warrant further investigation.

3.2.1.3. Alkaline leaching

In contrast to acid leaching, which predominantly utilizes acid to dissolve the active material, alkali leaching mainly relies on the interaction between hydroxides and metal ions to facilitate the leaching or separation process [107]. The primary approach to alkali leaching involves the use of strong alkali- and ammonia-based solutions as leaching agents. However, metal ions tend to combine with OH⁻ to produce hydroxide precipitates during alkali leaching, which directly completes the separation. Therefore, alkali leaching cannot be considered as the total meaning of the leaching process, but instead as a separation method between leaching and selective extraction.

Ammonia solution is suitable as leaching agents, including NH₃·H₂O, (NH₄)₂CO₃, NH₄HCO₃, NH₄Cl, and (NH₄)₂SO₄ [108]. The fundamental principle is the formation of complexes via the combination of NH₄⁺ and metal ions, and the creation of hydroxide precipitates at varying pH values, facilitating leaching and separation [109]. In ammonia-based systems, ions such as Li⁺, Ni²⁺, Co²⁺, and Cu²⁺ tend to form complexes with NH₄⁺, resulting in [M(NH₃)_n]²⁺ complexes that are selectively leached from solution. Conversely, Al³⁺, Fe³⁺, and Mn²⁺ react with OH⁻ to form hydroxide precipitates at specific pH value [110]. Qi et al. [111] introduced an effective ammonia leaching system using a mixed solution of 120 g/L NH₃·H₂O and 80 g/L NH₄HCO₃ to recover Co and Li from spent LIBs. This approach achieved leaching rates of 91.16% and 97.57% for Co and Li, respectively. Zheng et al. [106] proposed another ammonia-leaching hydrometallurgical process. In their study on NCM recovery, they use an optimized mixed ammonia-based solution (4 mol/L NH₃·H₂O and 1.5 mol/L (NH₄)₂SO₄) and 0.5 mol/L Na₂SO₃ as reductant. This combination achieved high leaching efficiencies of 95.3%, 80.7%, and 89.8% for Li, Co, and Ni but poor leachabilities for Mn and Al. Lower selectivity for Al and Mn can be clearly seen in Fig. 9(f). However, this also facilitates the subsequent separation process, as the addition of NaOH can easily separate Al by Al(OH)₃ precipitation, and Mn is precipitated by pH modulation and the formation of the (NH₄)₂Mn(SO₃)₂·H₂O precipitate. Notably, the dosage and concentration required for alkaline leaching are significantly higher than those required for acidic leaching, limiting the economic feasibility and processing time. Moreover, a strong alkali such as NaOH is particularly effective for recovering Al, an amphoteric metal soluble in both acids and alkalis and capable of forming NaOH precipitates under alkaline conditions [112]. Al deposits are typically processed industrially via alkaline washing during pretreatment. Alkaline leaching is a promising process that has been proven feasible at the laboratory stage. Although alkali cannot be used as a universal leaching agent, it can participate in detailed recovery by utilizing the selectivity for specific metals. Table 1 summarizes the aforementioned leaching agents and their optimal operating conditions.

3.2.2. Selective extraction

Leaching transforms the active material of spent LIBs into an ionic state in an aqueous solution. Subsequent selective extraction leverages the physicochemical properties of ions to isolate specific metals through methods such as chemical deposition, physical adsorption, and electroplating for the regeneration of the electrode materials [113]. Because of the diverse metal ions in solution, multiple extractions are usually necessary to complete the final recovery. Therefore, selecting suitable extraction processes and arranging optimized process combinations are critical for enhancing recovery efficiency.

3.2.2.1. Chemical precipitation

Chemical precipitation is the predominant selective extraction method in industry, utilizing the differential solubility of metal ions

Table 1
Summary of the optimal conditions of leaching agents.

| Leaching agent | Cathode type | Temp. (°C) | S/L (g/L) | Efficiency (%) | Ref. |
|---|--|------------|-----------|---|-------|
| Inorganic acid | | | | | |
| 4 mol/L HCl | LiCoO ₂ | 80 | 50 | Li: 97% Co: 99% | [75] |
| 1 mol/L H ₂ SO ₄ | LiNi _x Co _y Mn _z O ₂ | 90 | 0.1 | Li: 88% | [77] |
| 1 mol/L H ₂ SO ₄ + 0.075 mol/L NaHSO ₃ | LiNi _x Co _y Mn _z O ₂ | 95 | 20 | Li: 96.7% Co: 91.7% Ni: 96.4% Mn: 87.9% | [78] |
| 2 mol/L H ₂ SO ₄ + 6% H ₂ O ₂ | LiCoO ₂ | 60 | 100 | Li: 99% Co: 99% | [82] |
| 3 mol/L HNO ₃ + 3% H ₂ O ₂ | LiCoO ₂ | 90 | 60 | Li: 98% Co: 98% | [83] |
| 2 mol/L H ₃ PO ₄ + 2% H ₂ O ₂ | LiCoO ₂ | 90 | 8 | Li: 99% | [85] |
| Organic acid | | | | | |
| 1.25 mol/L Citric acid + 1% H ₂ O ₂ | LiCoO ₂ | 90 | 20 | Li: 99% Co: 90% | [88] |
| 1 mol/L Citric acid | LiCoO ₂ | 70 | 40 | Li: 99% Co: 99% | [89] |
| 2 mol/L Citric acid + 1% H ₂ O ₂ | LiFePO ₄ | 90 | 20 | Li: 99% | [90] |
| 1 mol/L Oxalic acid | LiCoO ₂ | 80 | 50 | Li: 99% Co: 99% | [92] |
| 1.5 mol/L Malic acid + 4% H ₂ O ₂ | LiCoO ₂ | 90 | 20 | Li: 99% Co: 93% | [87] |
| 2 mol/L DL-Malic acid + 1.5% H ₂ O ₂ | LiNi _x Co _y Mn _z O ₂ | 90 | 30 | Li: 98.1% Co: 97.1% Ni: 96.2% Mn: 97.6% | [94] |
| 1.25 mol/L Ascorbic acid | LiCoO ₂ | 70 | 25 | Li: 98.5% Co: 94.8% | [96] |
| Bioleaching | | | | | |
| <i>Aspergillus niger</i> | Mixture | / | / | Li: 94% Co: 38% Ni: 45% Mn: 72% | [100] |
| <i>Aspergillus niger</i> | LiNi _x Co _y Mn _z O ₂ | / | / | Co: 25.8% Ni: 13% | [105] |
| Alkaline leaching | | | | | |
| 120 g/L NH ₃ ·H ₂ O + 75 g/L NH ₄ HCO ₃ | LiCoO ₂ | 70 | / | Li: 91.2% Co: 97.6% | [111] |
| 4 mol/L NH ₃ ·H ₂ O + 1.5 mol/L (NH ₄) ₂ SO ₄ | LiNi _x Co _y Mn _z O ₂ | 70 | 10 | Li: 95.3% Co: 80.7% Ni: 89.8% | [106] |

at various pH values and temperatures. The addition of precipitating agents resulted in the formation of insoluble hydroxide precipitates and low-solubility metal salts, enabling metal recovery. This method exploits the unique properties of each metal ion for separation [114]. Common precipitants include NaOH, Na₂CO₃, Na₃PO₄, NH₃·H₂O, and (NH₄)₂C₂O₄. Co readily forms Co(OH)₂ and Co₂C₂O₄ precipitates in the presence of (NH₄)₂C₂O₄ at high pH. Ni typically precipitates as Ni(OH)₂ and Ni₂CO₃ in alkaline environments and Na₂CO₃. Mn forms Mn(OH)₂ precipitates that may decompose into MnO₂ under similar conditions. Al, Cu, and Fe typically precipitate as hydroxides [72]. This separation process frequently involves complex systems containing multiple metal ions. Therefore, the selection of an appropriate precipitant and application sequence are vital for achieving efficient metal recovery. Natarajan et al. [115] demonstrated a process for recovering NCM using 3 mol/L acetic optimized acid leaching system, coupled with 7.5% H₂O₂ under 70 °C and solid-liquid ratio at 20 g/L. The process involved detailed pretreatment to remove the Al and Cu foils. In the chemical precipitation process, the low solubility of CoS was exploited by adding (NH₄)₂S, which resulted in efficient Co precipitation under pH values of 6. Subsequently, the pH was increased using saturated Na₂CO₃, leading to the precipitation of Mn as MnCO₃. Finally, high-purity Li₂CO₃ was obtained through filtration and evaporation of the residual solution, achieving Li, Co, and Mn recoveries of 99.4%, 99.2%, and 98.3%, respectively. The process of separating the metal ions can be further visualized by the color change of the leachate at different pH values in Fig. 10(a). The variation in the remaining ratio of metals in the system with increasing pH is shown in the bar chart Fig. 10(b). Yang et al. [116] provided a pre-mechanochemical activation method to improve the efficiency of LFP battery recycling and reduce the size of the active material through mechanical shearing and efficient ball milling and then used H₃PO₄ as a leaching agent for selective recovery using chemical precipitation. Approximately 93.05% and 82.55% of Fe and Li could be recovered as FePO₄·2H₂O and Li₃PO₄. A comparison of the leaching efficiencies before and after the mechanochemical activation is shown in Fig. 10(c). Chemical precipitation is preferred for large-scale industrial metal recovery because of its simplicity, high metal selectivity, and low operational costs. The precipitants currently used in many plants are generally NaOH and Na₂CO₃, with NaOH being used to regulate the pH to form hydroxide precipitates for metals and Na₂CO₃ primarily to generate Li₂CO₃ as one of the best choices for the preparation of active materials.

3.2.2.2. Solvent extraction

Solvent extraction is also a powerful recovery technique that is similar to chemical precipitation and uses the solubility difference of metal ions in aqueous solutions. Li⁺ is more soluble than other metal ions. Solvent extraction allows the leaching solution to be divided into an aqueous phase containing Li⁺ and an oil phase with the remaining metal, and then specific metal ions are separately recovered in the oil phase [117]. Different extractants exhibit different metal preferences. Typical extractants used for solvent extraction include 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (PC-88A), diethylhexylphosphonic acid (DEHPA), di(2-ethylhexyl) phosphoric acid (D2EHPA), and bis(2,4,4-trimethylpentyl) phosphonic acid (Cyanex272) separated well from Co, Mn, and Ni, and some other extractants such as 5-nonylsalicylaldehyde Acorga (M5640), trioctylamine (TOA), and N-[N,N-di(2-ethylhexyl)aminocarbonylmethyl]glycine (D2EHAG) are used for Fe and Al [5]. The effectiveness of the extractants depends on various factors, such as the extractant concentration, extraction time, leaching solution pH, and organic/aqueous system ratio. Therefore, researchers have investigated the optimal combinations for efficient extraction. Wang et al. [118] explored the recovery of high-purity Co from an NCM leaching solution comprising of 7 g/mL H₂SO₄ and 1.5 g/mL H₂O₂. They employed a two-step extraction process using D2EHPA to remove Cu and Mn at pH = 2.7. Subsequently, 80.13% of Co was extracted using PC-88A at pH = 4.25, followed by the formation of CoC₂O₄ by adding oxalic acid. The trend of decreasing solubility of Co ions in the system with increasing pH is shown in Fig. 10(d), which proves that Co can be extracted highly selectively at pH = 4.25. The remaining aqueous-phase solution yields Li₂CO₃ by adding Na₂CO₃.

Wang et al. [119] reported specialized extraction of Co and Mn during the recovery of an NMC electrode material using Cyanex272. A leaching rate of over 94% was achieved for Li, Co, Ni, Mn, and Al by employing 2 mol/L acetic acid as the leaching agent and 4% H₂O₂ as the reducing agent with a solid/liquid ratio of 20 g/L. The extraction process utilized an extractant composed of 15% Cyanex272, 10% tributyl phosphate, and 75% sulfonated kerosene with an organic-aqueous phase ratio of 1:1. This method resulted in the extraction of over 90.13% of Al, 95.72% of Co, and 98.93% of Mn. This process was further enhanced by adding saturated Na₂SO₄ to precipitate the Li salts from the remaining liquid phase. Synergistic extraction utilizing mixtures of two or more extractants significantly enhances metal selectivity compared to the use of a single extractant. Pranolo et al. [120] demonstrated an approach

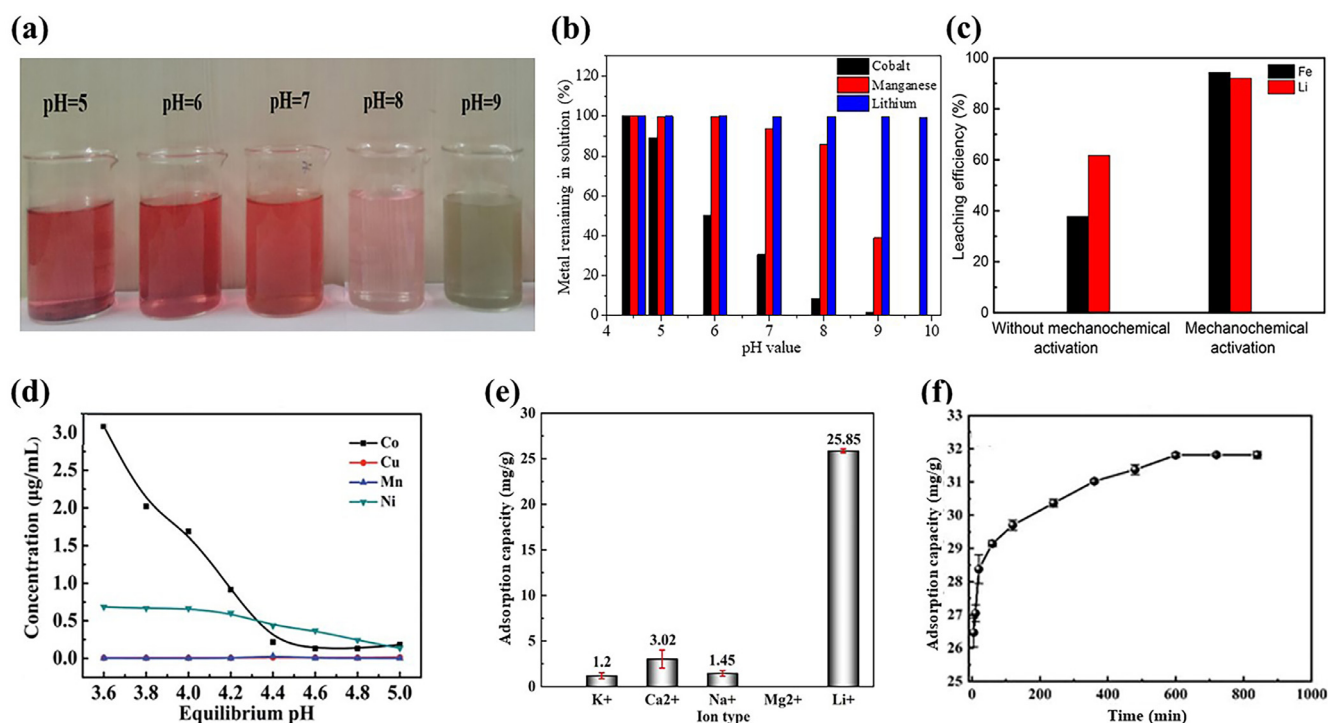


Fig. 10. (a) Images of solution color changes for the separation of metal ions by sulfide precipitation from an acetic acid leaching solution; reprinted with permission from Ref. [115]. Copyright 2018 Elsevier. (b) Bar chart of the influence of metal ions on pH in an acid leaching system; reprinted with permission from Ref. [115]. Copyright 2018 Elsevier. (c) Comparison of original and activated LFPs and in leaching efficiency; reprinted with permission from Ref. [116]. Copyright 2017 American Chemical Society. (d) Diagram showing ion concentration changes during the separation of Co from H₂SO₄ leachate of NCM using PC-88A; reprinted with permission from Ref. [118]. Copyright 2016 Royal Society of Chemistry. (e) Diagram of adsorption capacity versus time during Li-ion adsorption on Mn-Ti ion sieves; reprinted with permission from Ref. [121]. Copyright 2023 MDPI. (f) Li adsorption selectivity from the salt solution on the Mn-Ti ion sieve (pH = 12, T = 45 °C); reprinted with permission from Ref. [121]. Copyright 2023 MDPI.

using an adjusted extractant to separate dissolved materials from spent LIBs leached with H₂SO₄. This solution was treated with a mixture of 7% PC88A and 2% Acorga M5640 in kerosene, and Fe³⁺, Cu²⁺, and Al³⁺ were successfully isolated from Co²⁺, Ni²⁺, and Li⁺. Subsequently, Cu, Fe, and residual Al were extracted from the organic phase using 100 g/L H₂SO₄. Co was extracted from Ni and Li using 15% Cyanex 272 in kerosene at pH = 5.5–6.0. Finally, Li and Ni were separated using Dowex IX resin. From the experimental results described above, solvent extraction is a powerful extraction method, particularly because of its high selectivity for specific metals and the high purity of the metal salt products. However, extractants are generally expensive; therefore, the process is costly, as in the method of Pranolo et al., which employs various extractants. Thus, chemical precipitation to extract readily separable metals, combined with solvent extraction to separate the remaining metals and obtain high-purity Li, is an optimized process.

3.2.2.3. Other material extraction technologies

Ion sieving is a novel and promising method for metal recovery. This technique is based on the principle of preparing porous materials that are highly selective for single metal ions by using specific materials such as resin and manganese dioxide crystals and placing ion sieve in solution to adsorb metal ions for recovery. Ding et al. [121] presented a Mn-Ti hybrid ion sieve dedicated to recovering Li ions with a maximum Li-ion adsorption capacity of 32 mg/g. Fig. 10(e) shows that the peak adsorption capacity of 32 mg/g is reached after more than 600 min. Moreover, in the control test of the adsorption capacity of the different metal ions shown in Fig. 10(f), the data prove that the selectivity for Li is better than that of the others. Strauss et al. [122] described a resin for recovering NMC that was highly selective for Ni and Co, resulting in 99% Ni and 98.5% Co recoveries. However, while these novel materials indeed occupy a position of remarkable selectivity and recyclability for specific

metals, they are generally expensive and require subsequent processing. Therefore, its industrialization prospects depend on the specific process requirements.

Electrochemical deposition is a well-established metallurgical technique used in the steel industry. This principle mainly uses different redox potentials to realize deposition. Myoung et al. [123] demonstrated that the recovery of Co from HNO₃ resulted in an LCO leaching solution, using the reduction potential of divalent Co ions for constant current discharge. Although Co(OH)₂ can be deposited on a Ti substrate, the recovery is unsatisfactory due to low reaction kinetics. In addition, the recovery of specific metals through gel systems and polymer molecular sieves has been reported with the aim of increasing the metal recovery rate and compensating for environmental concerns in current technologies. The specific processes and recovery performances of the aforementioned selective extraction methods are summarized in Table 2.

4. Discussion

The aforementioned battery treatment methods have proven to be effective in the treatment of LIBs. However, the strengths and weaknesses determine their industrial feasibility. Table 3 lists the combinations of processes currently applied in major battery recycling plants.

The industrial combination of hydrometallurgy and pyrometallurgy depends on the process design and choice of target products. In the case of Pyro + Hydro process in Umicore, pyrometallurgical thermal roasting is used as pretreatment to eliminate impurity interferences, followed by inorganic acid leaching to ionize metal, and obtain metal salts. The LCO active materials are regenerated by pyrolysis via reoxidation between Co₃O₄ and the Li salt solution. In addition, Ni(OH)₂ can be produced from an acid leaching solution of Ni by pyrometallurgy and recrystallization from a separate production line. The Nickelhütte-

Table 2
Summary of selective extraction processes.

| Cathode type | Leaching agent | Extractive process | Recovery efficiency | Ref. |
|--|--|--|--------------------------------------|-------|
| Chemical precipitation | | | | |
| LiNi _x Co _y Mn _z O ₂ | 3 mol/L Acetic acid + 7.5% H ₂ O ₂ | 5% (NH ₄) ₂ S precipitates Co as CoS; Na ₂ CO ₃ precipitates Mn as MnCO ₃ ; continue adding Na ₂ CO ₃ and evaporate to precipitate Li ₂ CO ₃ | Li: 99.4%, Co: 99.2%, Mn: 98.3% | [115] |
| LiFePO ₄ | 0.6 mol/L H ₃ PO ₄ + 2% H ₂ O ₂ | LiFePO ₄ mechanochemical activation; leaching in H ₃ PO ₄ , recovered LFP as FePO ₄ ·2H ₂ O and Li ₃ PO ₄ | Li: 82.55%, Fe: 93.05% | [116] |
| Solvent extraction | | | | |
| LiNi _x Co _y Mn _z O ₂ | 7 g/mL H ₂ SO ₄ + 1.6 g/mL H ₂ O ₂ | D2EHPA extracts Cu and Mn at pH = 2.7; PC-88A extracts Co and Ni at pH = 4.25; Co precipitates as CoC ₂ O ₄ upon adding H ₂ C ₂ O ₄ | Co: 99.5% | [118] |
| LiNi _x Co _y Mn _z O ₂ | 2 mol/ L Acetic + 4% H ₂ O ₂ | 10% TBP, 15% Cyanex272, and 75% sulfonated kerosene as organic phase to extract Al, Co, and Mn; (NH ₄) ₂ S ₂ O ₈ precipitates Mn; NaOH precipitates Al and Co; adding Na ₂ CO ₃ to form Li ₂ CO ₃ | Al: 90.13%, Co: 95.72%, Mn: 98.93% | [119] |
| Mixture | 3 mol/L H ₂ SO ₄ + 2% H ₂ O ₂ | 7% PC88A and 2% Acorga M5640 extract Fe, Cu, and Al; 15% Cyanex 272 in kerosene at pH = 5.5–6.0 extracts Co; Dowex IX resin extracts Ni from Li | Al: 95%, Co: 96%, Mn: 97%, Li: 99.5% | [120] |
| Novel method | | | | |
| Mixture | 2 mol/L H ₂ SO ₄ + 2% H ₂ O ₂ | Mn-Ti hybrid ion sieve selectively adsorbs Li | Li: over 80% | [121] |
| LiNi _x Co _y Mn _z O ₂ | / | Resin selectively recovers Ni and Co | Ni: 99%, Co: 98.5% | [122] |
| LiCoO ₂ | / | Electrochemical deposition | / | [123] |

Table 3
Summary of industrial LIB recycling process.

| Company | Battery type | Pretreatment | Selective extraction |
|-----------------|----------------|----------------------|----------------------|
| Umicore | All | / | Pyro + Hydro |
| Accurec | All | Thermal + Mechanical | Pyro + Hydro |
| Nickelhütte Aue | All except LFP | Thermal | Pyro + Hydro |
| SNAM | Ni-Cd/NMC | Thermal | Pyro + Hydro |
| EDI | All | Mechanical | Hydro |
| AkkuSer | All | Mechanical | Hydro |
| Duesenfeld | All | Mechanical | Hydro |
| Promesa | NMC/LCO/LNO | Mechanical | Hydro |
| Redux | All | Thermal + Mechanical | Hydro |
| SungEel HiTech | All | Mechanical | Hydro |
| Kyoei Seiko | All | / | Pyro |
| Dowa | All | Thermal | Pyro + Hydro |
| Brump | Ni-Cd/NMC | Thermal + Mechanical | Hydro |
| GEM | NMC/LCO/LNO | Mechanical | Hydro |
| Retriev | All | Thermal + Mechanical | Pyro + Hydro |
| Onto | All | Mechanical | Hydro |

Aue process aims to achieve industrial recovery of massive quantities of mixed electrode materials by applying pyrometallurgical smelting instead of a refined pretreatment step, followed by the selective recovery of valuable metals by hydrometallurgy. Therefore, the process characteristics of different companies clarifies that the application of metallurgical methods is closely linked to actual production needs and operating costs.

From the processes used in the pretreatment stage of each company, the vast majority of companies applying hydrometallurgy will carry out exhaustive mechanical pretreatment and sorting-discharging-disassembly-crushing. Hydrometallurgy requires reactions to occur in an aqueous solution, and therefore involves the size reduction of the active material. However, its pretreatment process is labor-intensive, and workers will be in close contact with the spent LIBs, which inevitably raises safety concerns. This is not concerning for pyrometallurgical-only companies because the main reaction occurs in the furnace. Their processes should focus more on the operation and maintenance of large equipment, and attempt to compensate for metal losses at high temperatures.

The primary advantages of pyrometallurgical processes are their straightforwardness and the capacity to handle large volumes without intricate pretreatment. However, these characteristics are double-edged, including the need for a substantial heat source and a roaster operating at high temperatures, leading to considerable energy consumption. Moreover, the combustion of organics during processing emits hazardous gases, posing severe contamination risks, and necessitating sophisticated waste-treatment systems.

In the two-pretreatment method of pyrolysis and incineration, pyrolysis is more suitable to be combined with the subsequent process because it is less destructive to the material, whereas incineration is appropriate to be used alone for pyrometallurgy because of its high temperature, which undoubtedly wastes energy if cooled down to hydrometallurgy. Among the three main pyrometallurgical processes, smelting, carbothermal reduction roasting, and salt-assisted roasting are versatile because of the reduction reactions required to recover the active material and the presence of carbonate in the final products. However, smelting is suitable for pyrometallurgy because of the UHT and violent oxidation reaction, most typically in the pyrolysis-smelting process of Umicore. A comprehensive performance comparison of pyrometallurgy is shown in the radar chart in Fig. 11. Each parameter represents: scale-up, the applicability in mass production; damage, the thermodynamic variability of the material; simplicity, the simplicity of the process; eco-friendliness, the degree of harm to the environment; cost, the cost of the process and energy consumption; energy efficiency, temperature span, and heat utilization; waste gas, exhaust gas emissions; chemical additives, the use of additives in the reduction process; and product purity, the ratio of the target product to the design requirements.

As shown in Table 3, hydrometallurgy is the most widely used recovery process. This depends on the original intention of battery recycling process design, which is to utilize and resynthesize waste LIB materials to achieve a circular economy. This has led to the fact that although enterprises apply pyrometallurgy to thermally treat in-flow spent batteries for industrial-scale production, the vast majority use hydrometallurgy to recover each metal and the relevant metal salt as products rather than

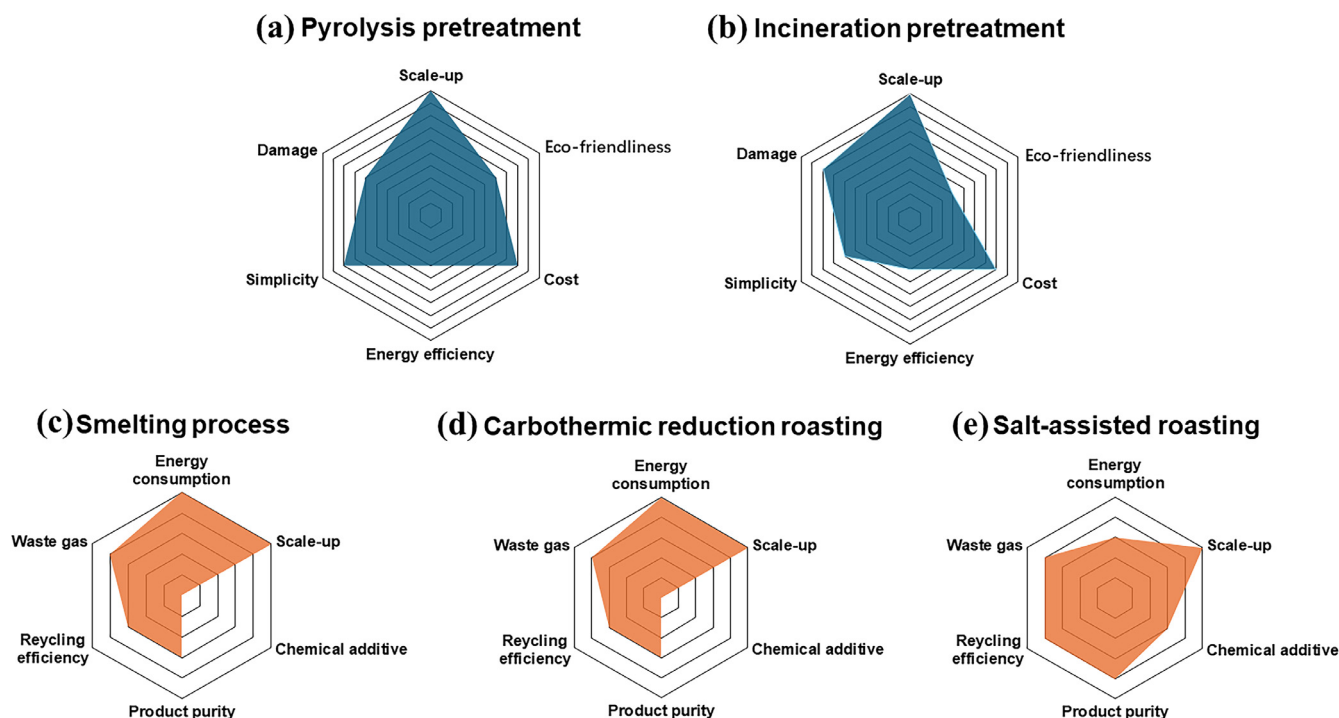


Fig. 11. Performance comparison of thermal pretreatment: (a) pyrolysis, (b) incineration; pyrometallurgical process, (c) smelting, (d) carbothermic reduction roasting, and (e) salt-assisted roasting.

slag and alloys in pyrometallurgy. Hydrometallurgy involves two major steps, namely leaching and selective extraction. The leaching process utilizes various reagents, and its performance can be measured using two major criteria: leaching efficiency and environmental friendliness. Inorganic acids are currently the most used in industry, with the highest efficiency among the leaching agents; the leaching speed is rapid, but they emit toxic gas pollution. Organic acids can solve the problem of exhaust gas pollution but are prevented from industrialization owing to insufficient acidity and leaching efficiency. Bioleaching aligns with circular economy standards; however, low acidity, high cultivation costs, and long reaction times prevent enterprises from doing so.

The most significant advantage of selective hydrometallurgical extraction over pyrometallurgy is its precise recovery. The two most powerful methods, chemical precipitation and solvent extraction, can efficiently recover metals, but their disadvantages include large volumes of chemical reagents and wastewater treatment at the end of the pipeline. The two newer extraction methods, electrochemical deposition and ion sieving, are restricted by their high costs and are difficult to industrialize. The radar chart in Fig. 12 provides a more detailed and intuitive view of the advantages and disadvantages of each extraction method. Each parameter represents the scale-up, the applicability to large-scale production; simplicity, the simplicity of the process; environment friendliness, the degree of harm to the environment; chemical cost, the consumption of leaching agents and recovery reagents; and recycling efficiency, the ability to recycle spent LIBs.

In addition to the evaluation of the metallurgical performance, byproducts are discussed to eliminate harm. Dust, heavy metal vapors, and particles are likely to appear in pyrometallurgy; therefore, efficient filtering equipment and adsorption devices must be installed to prevent overflow and leakage. Most LIB configurations contain sulfides that decompose to release toxic SO_x gas during pyrometallurgy and hydrometallurgy. Therefore, wet desulfurization and adsorption desulfurization technologies can be arranged at the end of the pipeline to neutralize the hazards. Conductive activated carbon widely exists in LIB [124]. The incomplete combustion of carbon during pyrometallurgical heating produces flammable and explosive CO. Efficient combustion tech-

nology should be considered in the process design to ensure full combustion. NO_x emissions in the air become precursors of acid rain and photochemical smog and are often present in nitrate-assisted roasting and nitric acid-related hydrometallurgy [125]. Therefore, selectively catalyzing the conversion of nitrogen oxides into harmless substances is crucial. The liquid electrolytes in LIB often contain fluorides. Under high-temperature pyrometallurgical treatment, toxic and highly corrosive HF gas is effused, which is extremely harmful to the environment and the human respiratory system. Therefore, a fluorine-free treatment can be performed via washing, precipitation, and membrane separation. The management of harmful gases is an indispensable link in industry and a crucial indicator for realizing a circular economy.

The comprehensive design of hydrometallurgical processes is based on laboratory results, where process design and optimization are carried out using small-scale experiments aimed at maximizing recovery efficiency and various process parameters such as leaching agent, reaction temperature and time, and leaching solution concentration [126]. Advanced testing modes and characterization were used to determine the structure of the target product and whether it was consistent with the desired results of the experimental scheme. After validating the hydrometallurgical process through experimental results, it becomes sufficiently stable and reproducible for industrialization. The costs of reagents, energy consumption, potential safety issues, and product profitability must be in line with the expectations of the enterprise. In the pilot stage, a small-scale production line will be designed based on the experimental results, which involve chemical engineering unit operations and fluid performance tests to verify the feasibility of the scaled-up process. Emergency measures and waste disposal devices must also be considered based on the satisfactory process performance. In the industrialization phase, the priority is plant location, local policies, raw material and water supply, and transportation. Subsequently, during the initial operation of the plant the process parameters must be adjusted based on the actual conditions to ensure stability during long-term operation. The transition from laboratory to industrial production is a multiple-step pathway that requires exhaustive consideration of technical, economic, environmental, and safety factors. Through systematic experimental re-

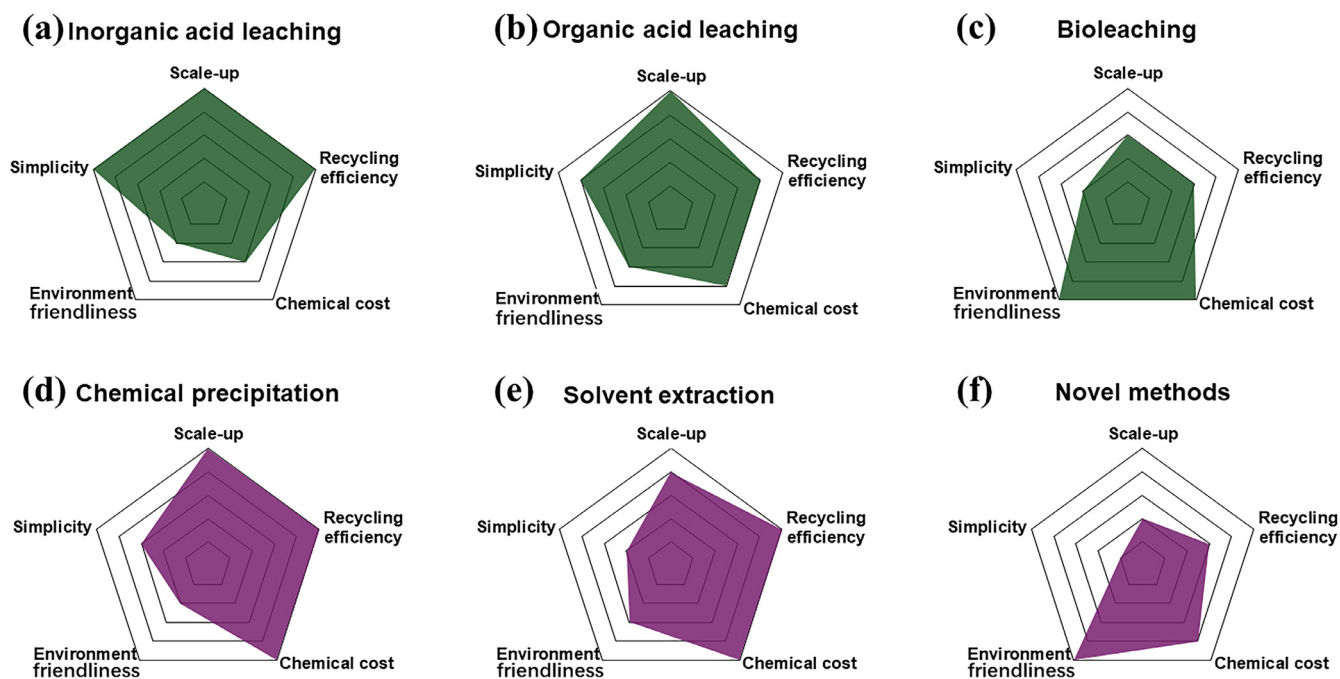


Fig. 12. Performance comparison of the leaching process in hydrometallurgy: (a) inorganic acid leaching, (b) organic acid leaching, (c) bioleaching; hydrometallurgical selective extraction, (d) chemical precipitation, (e) solvent extraction, and (f) novel extraction.

search, pilot scale-ups, plant design and construction, and continuous process optimization, the industrial production of battery-recycling hydrometallurgical processes can be successfully realized.

Solid-state batteries (SSBs) have been extensively studied and gradually commercialized because they can solve the problems of electrolyte leakage and the spontaneous combustion of traditional LIBs [127]. However, the exploration of recycling models remains in its infancy. The first issue to consider is the peculiar solid electrolyte of SSBs; therefore, mechanical crushing pretreatment is necessary, and direct pyrometallurgical smelting is abandoned because of insufficient kinetics and higher energy consumption. Secondly, many design configurations are available for SSB and a lack of sufficient experience in dismantling and recycling [128]. Sulfide and halogen SSBs undergo violent oxidation reactions and release toxic gases after being crushed and exposed to air. Oxidized SSBs cause mechanical passivation and unevenness during the crushing process owing to their hard ceramic textures. Structure-integrated SSBs are difficult to recycle during automated disassembly and require manual intervention. Therefore, the recycling process of SSB is different from the traditional LIB recycling process, which requires detailed classification according to the various configurations of SSB followed by mechanical crushing, and then further processing by pyrometallurgy or hydrometallurgy based on actual circumstances, which brings challenges to the established battery-recycling enterprise and limitations on flexibility.

5. Conclusion and outlook

Contemporary renewable energy applications are flourishing, paralleling the internal combustion engines in the industrial revolution. Although electricity has brought exponential growth in human productivity, the massive demand for batteries owing to the main energy storage devices for electricity, generates a large amount of waste. However, statistics show a massive gap between the volumes of used batteries produced and recycled each year, indicating that improving the recycling capacity of waste batteries is crucial. Battery recycling technology satisfies the needs of the recycling industry and the future development

direction toward establishing safer, greener, and more economical pathways.

- (1) From a technical perspective, safety issues are the most significant, and the safety hazards associated with extensive manual pretreatment intervention must be avoided by equipping workers with labor protection. Safety in metallurgical processes requires the rational design of process units and operating parameters.
- (2) From an environmental perspective, the significance of battery recycling lies in the circular economy and reduction in the ecological damage caused by industrial products. The challenges caused by metallurgical emissions and wastewater necessitate a comprehensive waste management system to maximize the benefits of battery recycling.
- (3) Various new types of batteries, such as potassium-ion batteries, sodium-ion batteries, and all-solid-state lithium batteries, are gradually being commercialized and are expected to produce waste batteries after large-scale application. Therefore, future technologies should focus on designing a recycling process based on the characteristics of new batteries.
- (4) Economically, profits are the most essential for the survival of an enterprise. Therefore, the government should provide subsidies and advocate technological development to continuously promote progress in the battery-recycling industry.

Declaration of Competing Interest

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

CRediT authorship contribution statement

Ziwei Tong: Writing – review & editing, Writing – original draft. **Mingyue Wang:** Writing – review & editing. **Zhongchao Bai:** Supervision. **Huijun Li:** Supervision. **Nana Wang:** Writing – review & editing, Supervision.

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References

- [1] J.T. Warner, *Lithium-Ion Battery Chemistries: A Primer*, first ed., Elsevier, Amsterdam, 2019.
- [2] M. Placek, Projected global battery demand from 2020 to 2030. <https://www.statista.com/statistics/1103218/global-battery-demand-forecast/>, 2022 (accessed 25 August 2022).
- [3] T. Kim, W. Song, D.-Y. Son, L.K. Ono, Y. Qi, Lithium-ion batteries: Outlook on present, future, and hybridized technologies, *J. Mater. Chem. A* 7 (2019) 2942–2964, doi:10.1039/c8ta10513h.
- [4] C. Jamasnie, Recycled lithium batteries market to hit \$6 billion by 2030. <https://www.mining.com/recycled-lithium-batteries-market-to-hit-6-billion-by-2030/>, 2021 (accessed 29 September 2021).
- [5] V. Agarwal, M.K. Khalid, A. Porvali, B.P. Wilson, M. Lundström, Recycling of spent NiMH batteries: Integration of battery leach solution into primary Ni production using solvent extraction, *Sustain. Mater. Technol.* 22 (2019) e00121, doi:10.1016/j.susmat.2019.e00121.
- [6] L. Brückner, J. Frank, T. Elwert, Industrial recycling of lithium-ion batteries-A critical review of metallurgical process routes, *Metals* 10 (2020) 1107, doi:10.3390/met10081107.
- [7] J. Yu, Q. Tan, J. Li, Exploring a green route for recycling spent lithium-ion batteries: Revealing and solving deep screening problem, *J. Clean. Prod.* 255 (2020) 120269, doi:10.1016/j.jclepro.2020.120269.
- [8] M. Kaya, State-of-the-art lithium-ion battery recycling technologies, *Circ. Econ.* 1 (2022) 100015, doi:10.1016/j.cec.2022.100015.
- [9] W. Yu, Y. Guo, S. Xu, Y. Yang, Y. Zhao, J. Zhang, Comprehensive recycling of lithium-ion batteries: Fundamentals, pretreatment, and perspectives, *Energy Storage Mater.* 54 (2023) 172–220, doi:10.1016/j.ensm.2022.10.033.
- [10] E. Fan, L. Li, Z. Wang, J. Lin, Y. Huang, Y. Yao, F. Wu, Sustainable recycling technology for Li-ion batteries and beyond: Challenges and future prospects, *Chem. Rev.* 120 (2020) 7020–7063, doi:10.1021/acs.chemrev.9b00535.
- [11] X. Wang, G. Gaustad, C.W. Babbitt, Targeting high value metals in lithium-ion battery recycling via shredding and size-based separation, *Waste Manag.* 51 (2016) 204–213, doi:10.1016/j.wasman.2015.10.026.
- [12] Bebat, Sorting batteries? This is how we do it. <https://www.bebat.be/en/blog/how-sorting-batteries>, 2024 (accessed 2024).
- [13] A.M. Bernardes, D.C.R. Espinosa, J.S. Tenório, Recycling of batteries: A review of current processes and technologies, *J. Power Sources* 130 (2004) 291–298, doi:10.1016/j.jpowsour.2003.12.026.
- [14] R. Recycling, Electronics processor begins recycling robotics. <https://resource-recycling.com/recycling/2024/03/05/electronics-processor-begins-recycling-robotics/>, 2024 (accessed 5 March 2024).
- [15] L. Systems, Pioneering X-ray NDT. <https://www.linevsystems.com/products/x-ray-ndt-imaging/>, 2024 (accessed 2024).
- [16] S. Saxena, C.Le Floch, J. MacDonald, S. Moura, Quantifying EV battery end-of-life through analysis of travel needs with vehicle powertrain models, *J. Power Sources* 282 (2015) 265–276, doi:10.1016/j.jpowsour.2015.01.072.
- [17] S. Ojanen, M. Lundström, A. Santasalo-Aarnio, R. Serna-Guerrero, Challenging the concept of electrochemical discharge using salt solutions for lithium-ion batteries recycling, *Waste Manag.* 76 (2018) 242–249, doi:10.1016/j.wasman.2018.03.045.
- [18] J. Xiao, J. Guo, L. Zhan, Z. Xu, A cleaner approach to the discharge process of spent lithium ion batteries in different solutions, *J. Clean. Prod.* 255 (2020) 120064, doi:10.1016/j.jclepro.2020.120064.
- [19] D. Gao, Y. Zhou, T. Wang, Y. Wang, A method for predicting the remaining useful life of lithium-ion batteries based on particle filter using kendall rank correlation coefficient, *Energies* 13 (2020) 4183, doi:10.3390/en13164183.
- [20] J. Li, G. Wang, Z. Xu, Generation and detection of metal ions and volatile organic compounds (VOCs) emissions from the pretreatment processes for recycling spent lithium-ion batteries, *Waste Manag.* 52 (2016) 221–227, doi:10.1016/j.wasman.2016.03.011.
- [21] T. Zhang, Y. He, F. Wang, L. Ge, X. Zhu, H. Li, Chemical and process mineralogical characterizations of spent lithium-ion batteries: an approach by multi-analytical techniques, *Waste Manag.* 34 (2014) 1051–1058, doi:10.1016/j.wasman.2014.01.002.
- [22] H. Wang, G. Qu, J. Yang, S. Zhou, B. Li, Y. Wei, An effective and cleaner discharge method of spent lithium batteries, *J. Energy Storage* 54 (2022) 105383, doi:10.1016/j.est.2022.105383.
- [23] S. Rothermel, M. Evertz, J. Kasnatschew, X. Qi, M. Grütze, M. Winter, S. Nowak, Graphite recycling from spent lithium-ion batteries, *ChemSusChem* 9 (2016) 3473–3484, doi:10.1002/cssc.201601062.
- [24] R. Sommerville, J. Shaw-Stewart, V. Goodship, N. Rowson, E. Kendrick, A review of physical processes used in the safe recycling of lithium ion batteries, *Sustain. Mater. Technol.* 25 (2020) e00197, doi:10.1016/j.susmat.2020.e00197.
- [25] C. Lei, I. Aldous, J.M. Hartley, D.L. Thompson, S. Scott, R. Hanson, P.A. Anderson, E. Kendrick, R. Sommerville, A.P. Abbott, Lithium ion battery recycling using high-intensity ultrasonication, *Green. Chem.* 23 (2021) 4710–4715, doi:10.1039/D1GC01623G.
- [26] H. Bae, Y. Kim, Technologies of lithium recycling from waste lithium ion batteries: A review, *Mater. Adv.* 2 (2021) 3234–3250, doi:10.1039/D1MA00216C.
- [27] D.M. Werner, T. Mütze, U.A. Peuker, Influence of cell opening methods on electrolyte removal during processing in lithium-ion battery recycling, *Metals* 12 (2022) 663, doi:10.3390/met12040663.
- [28] D.L. Thompson, J.M. Hartley, S.M. Lambert, M. Shiref, G.D.J. Harper, E. Kendrick, P. Anderson, K.S. Ryder, L. Gaines, A.P. Abbott, The importance of design in lithium ion battery recycling-a critical review, *Green. Chem.* 22 (2020) 7585–7603, doi:10.1039/D0GC02745F.
- [29] Fraunhofer, New technologies for the disassembly of electric vehicle batteries and motors. https://www.ipa.fraunhofer.de/en/press-media/press_releases/new-technologies-for-the-disassembly-of-electric-vehicle-batteries-and-motors.html, 2023 (accessed 22 May 2023).
- [30] Itoinsider, Robotic battery disassembly: A key to the UK's net zero future. <https://www.iotinsider.com/iot-insights/robotic-battery-disassembly-a-key-to-the-uks-net-zero-future/>, 2023 (accessed 19 May 2023).
- [31] L. Lander, C. Tagnon, V. Nguyen-Tien, E. Kendrick, R.J.R. Elliott, A.P. Abbott, J.S. Edge, G.J. Offer, Breaking it down: A techno-economic assessment of the impact of battery pack design on disassembly costs, *Appl. Energy* 331 (2023) 120437, doi:10.1016/j.apenergy.2022.120437.
- [32] J. Schmitt, H. Haupt, M. Kurrat, A. Raatz, Disassembly automation for lithium-ion battery systems using a flexible gripper, 2011 15th Int. Conf. Adv. Robot. (2011) 291–297, doi:10.1109/ICAR.2011.6088599.
- [33] K. Wegener, W. Chen, F. Dietrich, K. Dröder, S. Kara, Robot assisted disassembly for the recycling of electric vehicle batteries, *Procedia CIRP* 29 (2015) 716–721, doi:10.1016/j.procir.2015.02.051.
- [34] J. Hathaway, A. Shaarawy, C. Akdeniz, A. Afkian, R. Stolkin, A. Rastegarpanah, Towards reuse and recycling of lithium-ion batteries: Tele-robotics for disassembly of electric vehicle batteries, *Front. Robot. AI* 10 (2023) 1179296, doi:10.3389/frobt.2023.1179296.
- [35] H. Wang, B. Friedrich, Development of a highly efficient hydrometallurgical recycling process for automotive Li-Ion batteries, *J. Sustain. Metall.* 1 (2015) 168–178, doi:10.1007/s40831-015-0016-6.
- [36] M. Mohr, J.F. Peters, M. Baumann, M. Weil, Toward a cell-chemistry specific life cycle assessment of lithium-ion battery recycling processes, *J. Ind. Ecol.* 24 (2020) 1310–1322, doi:10.1111/jiec.13021.
- [37] J. Jung, P. Sui, J. Zhang, *Hydrometallurgical Recycling of Lithium-Ion Battery Materials*, first ed., CRC Press, Boca Raton, 2023.
- [38] D. Marinos, B. Mishra, *Processing of Lithium-Ion Batteries for Zero-Waste Materials Recovery*, first ed., CRC Press, Boca Raton, 2016.
- [39] G. Tian, G. Yuan, A. Aleksandrov, T. Zhang, Z. Li, A.M. Fathollahi-Fard, M. Ivanov, Recycling of spent lithium-ion batteries: A comprehensive review for identification of main challenges and future research trends, *Sustain. Energy Technol. Assess.* 53 (2022) 102447, doi:10.1016/j.seta.2022.102447.
- [40] B. Yan, E. Ma, J. Wang, Research on the high-efficiency crushing, sorting and recycling process of column-shaped waste lithium batteries, *Sci. Total Environ.* 864 (2023) 161081, doi:10.1016/j.scitotenv.2022.161081.
- [41] F. Treffer, *Lithium-ion Battery Recycling*, Springer, Berlin, 2018 (first ed.).
- [42] J. Li, X. He, X. Zeng, Designing and examining e-waste recycling process: Methodology and case studies, *Environ. Technol.* 38 (2017) 652–660, doi:10.1080/09593330.2016.1207711.
- [43] D. Latini, M. Vaccari, M. Lagnoni, M. Orefice, F. Mathieux, J. Huisman, L. Tognotti, A. Bertei, A comprehensive review and classification of unit operations with assessment of outputs quality in lithium-ion battery recycling, *J. Power Sources* 546 (2022) 231979, doi:10.1016/j.jpowsour.2022.231979.
- [44] L. Alcaraz, C. Diaz-Guerra, J. Calbet, M.L. Lopez, F.A. Lopez, Obtaining and characterization of highly crystalline recycled graphite from different types of spent batteries, *Materials* 15 (2022) 3246, doi:10.3390/ma15093246.
- [45] G. Zhang, Z. Du, Y. He, H. Wang, W. Xie, T. Zhang, A sustainable process for the recovery of anode and cathode materials derived from spent lithium-ion batteries, *Sustainability* 11 (2019) 2363, doi:10.3390/su11082363.
- [46] G. Prabaharan, S.P. Barik, N. Kumar, L. Kumar, Electrochemical process for electrode material of spent lithium ion batteries, *Waste Manag.* 68 (2017) 527–533, doi:10.1016/j.wasman.2017.07.007.
- [47] C.M. Costa, J.C. Barbosa, R. Gonçalves, H. Castro, F. Del Campo, S. Lancers-Méndez, Recycling and environmental issues of lithium-ion batteries: Advances, challenges and opportunities, *Energy Storage Mater.* 37 (2021) 433–465, doi:10.1016/j.ensm.2021.02.032.
- [48] D. Yu, Z. Huang, B. Makuza, X. Guo, Q. Tian, Pretreatment options for the recycling of spent lithium-ion batteries: A comprehensive review, *Miner. Eng.* 173 (2021) 107218, doi:10.1016/j.mineng.2021.107218.
- [49] K. Meng, G. Xu, X. Peng, K. Youcef-Toumi, J. Li, Intelligent disassembly of electric-vehicle batteries: A forward-looking overview, *Resour. Conserv. Recycl.* 182 (2022) 106207, doi:10.1016/j.resconrec.2022.106207.
- [50] C. Liu, J. Lin, H. Cao, Y. Zhang, Z. Sun, Recycling of spent lithium-ion batteries in view of lithium recovery: A critical review, *J. Clean. Prod.* 228 (2019) 801–813, doi:10.1016/j.jclepro.2019.04.304.
- [51] J. Klimko, D. Oráč, A. Miškuřová, C. Vonderstein, C. Dertmann, M. Sommerfeld, B. Friedrich, T. Havlík, A combined pyro- and hydrometallurgical approach to recycle pyrolyzed lithium-ion battery black mass part 2: Lithium recovery from Li enriched slag-thermodynamic study, kinetic study, and dry digestion, *Metals* 10 (2020) 1558, doi:10.3390/met10111558.
- [52] A. Kwade, M. Möller, J. Müller, J. Hesselbach, S. Zellmer, S. Doose, J. Mayer, P. Michalowski, M. Powell, S. Breitung-Faas, Comminution and classification as important process steps for the circular production of lithium batteries, *KONA Powder Part J.* 40 (2023) 50–73, doi:10.14356/kona.2023006.
- [53] G. Lombardo, B. Ebin, M.R.S.J. Foreman, B.-M. Steenari, M. Petranikova, Incineration of EV lithium-ion batteries as a pretreatment for recycling-determination of

- the potential formation of hazardous by-products and effects on metal compounds, *J. Hazard. Mater.* 393 (2020) 122372, doi:10.1016/j.jhazmat.2020.122372.
- [54] J. Neumann, M. Petranikova, M. Meeus, J.D. Gamarra, R. Younesi, M. Winter, S. Nowak, Recycling of lithium-ion batteries-current state of the art, circular economy, and next generation recycling, *Adv. Energy Mater.* 12 (2022) 2102917, doi:10.1002/aenm.202102917.
- [55] J. Yang, F. Firsbach, I. Sohn, Pyrometallurgical processing of ferrous slag “co-product” zero waste full utilization: A critical review, *Resour. Conserv. Recycl.* 178 (2022) 106021, doi:10.1016/j.resconrec.2021.106021.
- [56] X. Hu, E. Mousa, Y. Tian, G. Ye, Recovery of Co, Ni, Mn, and Li from Li-ion batteries by smelting reduction—Part I: a laboratory-scale study, *J. Power Sources* 483 (2021) 228936, doi:10.1016/j.jpowsour.2020.228936.
- [57] G. Ren, S. Xiao, M. Xie, B. Pan, J. Chen, F. Wang, X. Xia, Recovery of valuable metals from spent lithium ion batteries by smelting reduction process based on FeO-SiO₂-Al₂O₃ slag system, *Trans. Nonferrous Met. Soc. China* 27 (2017) 450–456, doi:10.1016/S1003-6326(17)60051-7.
- [58] A. Sonoc, J. Jesviet, V.K. Soo, Opportunities to improve recycling of automotive lithium ion batteries, *Procedia CIRP* 29 (2015) 752–757, doi:10.1016/j.procir.2015.02.039.
- [59] W. Yu, Y. Zhang, J. Hu, J. Zhou, Z. Shang, X. Zhou, S. Xu, Controlled carbothermic reduction for enhanced recovery of metals from spent lithium-ion batteries, *Resour. Conserv. Recycl.* 194 (2023) 107005, doi:10.1016/j.resconrec.2023.107005.
- [60] G. Lombardo, B. Ebin, M.R.S. Foreman, B.M. Steenari, M. Petranikova, Chemical transformations in Li-ion battery electrode materials by carbothermic reduction, *ACS Sustain. Chem. Eng.* 7 (2019) 13668–13679, doi:10.1021/acssuschemeng.8b06540.
- [61] J. Xiao, R. Gao, L. Zhan, Z. Xu, Unveiling the control mechanism of the carbothermal reduction reaction for waste Li-ion battery recovery: Providing instructions for its practical applications, *ACS Sustain. Chem. Eng.* 9 (2021) 9418–9425, doi:10.1021/acssuschemeng.1c02628.
- [62] S. Windisch-Kern, A. Holzer, L. Wiszniewski, H. Raupenstrauch, Investigation of potential recovery rates of nickel, manganese, cobalt, and particularly lithium from NMC-type cathode materials (LiNi_{1-x-y}Mn_xCo_yO₂) by carbo-thermal reduction in an inductively heated carbon bed reactor, *Metals* 11 (2021) 1844, doi:10.3390/met11111844.
- [63] W. Cheng, Z. Li, F. Cheng, Solubility of Li₂CO₃ in Na-K-Li-Cl brines from 20 to 90 °C, *J. Chem. Thermodyn.* 67 (2013) 74–82, doi:10.1016/j.jct.2013.07.024.
- [64] M. Li, D. Constantinescu, L. Wang, A. Mohs, J. Gmehling, Solubilities of NaCl, KCl, LiCl, and LiBr in methanol, ethanol, acetone, and mixed solvents and correlation using the LIQUAC model, *Ind. Eng. Chem. Res.* 49 (2010) 4981–4988, doi:10.1021/ie100027c.
- [65] X. Zhang, X. Zeng, Y. Shan, Z. Li, Y. Zeng, E. Asselin, Solubility and modeling of Li₂SO₄·H₂O in aqueous H₂SO₄-MgSO₄ solutions for lithium extraction from spodumene, *J. Chem. Eng. Data* 67 (2022) 919–931, doi:10.1021/acs.jced.2c00022.
- [66] M. Li, L. Wang, K. Wang, B. Jiang, J. Gmehling, Experimental measurement and modeling of solubility of LiBr and LiNO₃ in methanol, ethanol, 1-propanol, 2-propanol and 1-butanol, *Fluid Phase Equilib.* 307 (2011) 104–109, doi:10.1016/j.fluid.2011.03.017.
- [67] X. Qu, B. Zhang, J. Zhao, B. Qiu, X. Chen, F. Zhou, X. Li, S. Gao, D. Wang, H. Yin, Salt-thermal methods for recycling and regenerating spent lithium-ion batteries: A review, *Green Chem.* 25 (2023) 2992–3015, doi:10.1039/D2GC04620B.
- [68] J. You, Z. Qin, G. Wang, M. Rao, J. Luo, Z. Peng, S. Zou, G. Li, Recycling valuable metals from spent lithium-ion battery cathode materials based on microwave-assisted hydrogen reduction followed by grind-leaching and magnetic separation, *J. Clean. Prod.* 428 (2023) 139488, doi:10.1016/j.jclepro.2023.139488.
- [69] S. Pindar, N. Dhawan, Recycling of mixed discarded lithium-ion batteries via microwave processing route, *Sustain. Mater. Technol.* 25 (2020) e00157, doi:10.1016/j.susmat.2020.e00157.
- [70] S. Maroufi, M. Assefi, R.K. Nekouei, V. Sahajwalla, Recovery of lithium and cobalt from waste lithium-ion batteries through a selective isolation-suspension approach, *Sustain. Mater. Technol.* 23 (2019) e00139, doi:10.1016/j.susmat.2019.e00139.
- [71] H.J. Kim, T. Krishna, K. Zeb, V. Rajangam, C.V.V.M. Gopi, S. Sambasivam, K.V.G. Raghavendra, A comprehensive review of Li-ion battery materials and their recycling techniques, *Electronics* 9 (2020) 1161, doi:10.3390/electronics9071161.
- [72] Z. Liang, C. Cai, G. Peng, J. Hu, H. Hou, B. Liu, S. Liang, K. Xiao, S. Yuan, J. Yang, Hydrometallurgical recovery of spent lithium ion batteries: Environmental strategies and sustainability evaluation, *ACS Sustain. Chem. Eng.* 9 (2021) 5750–5767, doi:10.1021/acssuschemeng.1c00942.
- [73] N. Akhmetov, A. Manakhov, A.S. Al-Qasim, Li-ion battery cathode recycling: An emerging response to growing metal demand and accumulating battery waste, *Electronics* 12 (2023) 1152, doi:10.3390/electronics12051152.
- [74] W. Gao, C. Liu, H. Cao, X. Zheng, X. Lin, H. Wang, Y. Zhang, Z. Sun, Comprehensive evaluation on effective leaching of critical metals from spent lithium-ion batteries, *Waste Manag.* 75 (2018) 477–485, doi:10.1016/j.wasman.2018.02.023.
- [75] J. Li, P. Shi, Z. Wang, Y. Chen, C.C. Chang, A combined recovery process of metals in spent lithium-ion batteries, *Chemosphere* 77 (2009) 1132–1136, doi:10.1016/j.chemosphere.2009.08.040.
- [76] A. Chernyaev, Y. Zou, B.P. Wilson, M. Lundström, The interference of copper, iron and aluminum with hydrogen peroxide and its effects on reductive leaching of LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂, *Sep. Purif. Technol.* 281 (2022) 119903, doi:10.1016/j.seppur.2021.119903.
- [77] L.F. Guimarães, A.B. Junior, D.C.R. Espinosa, Sulfuric acid leaching of metals from waste Li-ion batteries without using reducing agent, *Miner. Eng.* 183 (2022) 107597, doi:10.1016/j.mineng.2022.107597.
- [78] P. Meshram, Abhilash, B.D. Pandey, T.R. Mankhand, H. Deveci, Acid baking of spent lithium ion batteries for selective recovery of major metals: A two-step process, *J. Ind. Eng. Chem.* 43 (2016) 117–126, doi:10.1016/j.jiec.2016.07.056.
- [79] M.M. Cerrillo-Gonzalez, M. Villen-Guzman, C. Vereda-Alonso, J.M. Rodríguez-Maroto, J.M. Paz-Garcia, Acid leaching of LiCoO₂ enhanced by reducing agent. Model formulation and validation, *Chemosphere* 287 (2022) 132020, doi:10.1016/j.chemosphere.2021.132020.
- [80] L. Li, Y. Bian, X. Zhang, Q. Xue, E. Fan, F. Wu, R. Chen, Economical recycling process for spent lithium-ion batteries and macro- and micro-scale mechanistic study, *J. Power Sources* 377 (2018) 70–79, doi:10.1016/j.jpowsour.2017.12.006.
- [81] C. Peng, F. Liu, A.T. Aji, B.P. Wilson, M. Lundström, Extraction of Li and Co from industrially produced Li-ion battery waste – Using the reductive power of waste itself, *Waste Manag.* 95 (2019) 604–611, doi:10.1016/j.wasman.2019.06.048.
- [82] J. Kang, G. Senanayake, J. Sohn, S.M. Shin, Recovery of cobalt sulfate from spent lithium ion batteries by reductive leaching and solvent extraction with Cyanex 272, *Hydrometallurgy* 100 (2010) 168–171, doi:10.1016/j.hydromet.2009.10.010.
- [83] Yuliusman, R. Fajaryanto, A. Nurqomariah, Silvia, Acid leaching and kinetics study of cobalt recovery from spent lithium-ion batteries with nitric acid, in: E3S Web Conf., 67, 2018, p. 03025, doi:10.1051/e3sconf/20186703025.
- [84] L. Li, R. Chen, F. Sun, F. Wu, J. Liu, Preparation of LiCoO₂ films from spent lithium-ion batteries by a combined recycling process, *Hydrometallurgy* 108 (2011) 220–225, doi:10.1016/j.hydromet.2011.04.013.
- [85] E.G. Pinna, M.C. Ruiz, M.W. Ojeda, M.H. Rodriguez, Cathodes of spent Li-ion batteries: Dissolution with phosphoric acid and recovery of lithium and cobalt from leach liquors, *Hydrometallurgy* 167 (2017) 66–71, doi:10.1016/j.hydromet.2016.10.024.
- [86] R. Golmohammadzadeh, F. Rashchi, E. Vahidi, Recovery of lithium and cobalt from spent lithium-ion batteries using organic acids: Process optimization and kinetic aspects, *Waste Manag.* 64 (2017) 244–254, doi:10.1016/j.wasman.2017.03.037.
- [87] L. Li, J.B. Dunn, X. Zhang, L. Gaines, R. Chen, F. Wu, K. Amine, Recovery of metals from spent lithium-ion batteries with organic acids as leaching reagents and environmental assessment, *J. Power Sources* 233 (2013) 180–189, doi:10.1016/j.jpowsour.2012.12.089.
- [88] L. Li, J. Ge, F. Wu, R. Chen, S. Chen, B. Wu, Recovery of cobalt and lithium from spent lithium ion batteries using organic citric acid as leachant, *J. Hazard. Mater.* 176 (2010) 288–293, doi:10.1016/j.jhazmat.2009.11.026.
- [89] M. Yu, Z. Zhang, F. Xue, B. Yang, G. Guo, J. Qiu, A more simple and efficient process for recovery of cobalt and lithium from spent lithium-ion batteries with citric acid, *Sep. Purif. Technol.* 215 (2019) 398–402, doi:10.1016/j.seppur.2019.01.027.
- [90] L. Li, Y. Bian, X. Zhang, Y. Yao, Q. Xue, E. Fan, F. Wu, R. Chen, A green and effective room-temperature recycling process of LiFePO₄ cathode materials for lithium-ion batteries, *Waste Manag.* 85 (2019) 437–444, doi:10.1016/j.wasman.2019.01.012.
- [91] A. Verma, R. Kore, D.R. Corbin, M.B. Shiflett, Metal recovery using oxalate chemistry: A technical review, *Ind. Eng. Chem. Res.* 58 (2019) 15381–15393, doi:10.1021/acs.iecr.9b02598.
- [92] L. Sun, K. Qiu, Organic oxalate as leachant and precipitant for the recovery of valuable metals from spent lithium-ion batteries, *Waste Manag.* 32 (2012) 1575–1582, doi:10.1016/j.wasman.2012.03.027.
- [93] L. Yao, H. Yao, G. Xi, Y. Feng, Recycling and synthesis of LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ from waste lithium ion batteries using d, l-malic acid, *RSC. Adv.* 6 (2016) 17947–17954, doi:10.1039/C5RA25079J.
- [94] X. Cheng, G. Guo, Y. Cheng, M. Liu, J. Ji, Effect of hydrogen peroxide on the recovery of valuable metals from spent LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂ batteries, *Energy Technol.* 10 (2022) 2200039, doi:10.1002/ente.202200039.
- [95] S. Refly, O. Floweri, T.R. Mayangarsi, A. Sumboja, S.P. Santosa, T. Ogi, F. Iskandar, Regeneration of LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ cathode active materials from end-of-life lithium-ion batteries through ascorbic acid leaching and oxalic acid coprecipitation processes, *ACS Sustain. Chem. Eng.* 8 (2020) 16104–16114, doi:10.1021/acssuschemeng.0c01006.
- [96] L. Li, J. Lu, Y. Ren, X. Zhang, R. Chen, F. Wu, K. Amine, Ascorbic-acid-assisted recovery of cobalt and lithium from spent Li-ion batteries, *J. Power Sources* 218 (2012) 21–27, doi:10.1016/j.jpowsour.2012.06.068.
- [97] E.A. Dalini, G. Karimi, S. Zandevakili, M. Goodarzi, A review on environmental, economic and hydrometallurgical processes of recycling spent lithium-ion batteries, *Miner. Process. Extr. Metall. Rev.* 42 (2021) 451–472, doi:10.1080/08827508.2020.1781628.
- [98] R. Sattar, S. Ilyas, H.N. Bhatti, A. Ghaffar, Resource recovery of critically-rare metals by hydrometallurgical recycling of spent lithium ion batteries, *Sep. Purif. Technol.* 209 (2019) 725–733, doi:10.1016/j.seppur.2018.09.019.
- [99] J.J. Roy, B. Cao, S. Madhavi, A review on the recycling of spent lithium-ion batteries (LIBs) by the bioleaching approach, *Chemosphere* 282 (2021) 130944, doi:10.1016/j.chemosphere.2021.130944.
- [100] N. Bahaloo-Horeh, S.M. Mousavi, M. Baniasadi, Use of adapted metal tolerant *Aspergillus niger* to enhance bioleaching efficiency of valuable metals from spent lithium-ion mobile phone batteries, *J. Clean. Prod.* 197 (2018) 1546–1557, doi:10.1016/j.jclepro.2018.06.299.
- [101] Z. Liu, X. Liao, Y. Zhang, S. Li, M. Ye, Q. Gan, X. Fang, Z. Mo, Y. Huang, Z. Liang, W. Dai, S. Sun, A highly efficient process to enhance the bioleaching of spent lithium-ion batteries by bifunctional pyrite combined with elemental sulfur, *J. Environ. Manag.* 351 (2024) 119954, doi:10.1016/j.jenvman.2023.119954.
- [102] N. Sadeghi, F. Vakilchah, Z. Ilkhani, S.M. Mousavi, Assessment of the visible light effect on one-step bacterial leaching of metals from spent lithium-ion batteries cathode pretreated by a bio-chemical lixiviant, *J. Clean. Prod.* 436 (2024) 140432, doi:10.1016/j.jclepro.2023.140432.
- [103] G. Zeng, S. Luo, X. Deng, L. Li, C. Au, Influence of silver ions on bioleaching of

- cobalt from spent lithium batteries, *Miner. Eng.* 49 (2013) 40–44, doi:10.1016/j.mineng.2013.04.021.
- [104] J.J. Roy, E.J.J. Tang, M.P. Do, B. Cao, M. Srinivasan, Closed-loop graphite recycling from spent lithium-ion batteries through bioleaching, *ACS Sustain. Chem. Eng.* 11 (2023) 6567–6577, doi:10.1021/acssuschemeng.2c07262.
- [105] E. Gerold, F. Kadisch, R. Lerchhammer, H. Antrekowitsch, Bio-metallurgical recovery of lithium, cobalt, and nickel from spent NMC lithium ion batteries: A comparative analysis of organic acid systems, *J. Hazard. Mater. Adv.* 13 (2024) 100397, doi:10.1016/j.hazadv.2023.100397.
- [106] X. Zheng, W. Gao, X. Zhang, M. He, X. Lin, H. Cao, Y. Zhang, Z. Sun, Spent lithium-ion battery recycling – Reductive ammonia leaching of metals from cathode scrap by sodium sulphite, *Waste Manag.* 60 (2017) 680–688, doi:10.1016/j.wasman.2016.12.007.
- [107] L. Chen, X. Tang, Y. Zhang, L. Li, Z. Zeng, Y. Zhang, Process for the recovery of cobalt oxalate from spent lithium-ion batteries, *Hydrometallurgy* 108 (2011) 80–86, doi:10.1016/j.hydromet.2011.02.010.
- [108] W. Lv, Z. Wang, H. Cao, X. Zheng, W. Jin, Y. Zhang, Z. Sun, A sustainable process for metal recycling from spent lithium-ion batteries using ammonium chloride, *Waste Manag.* 79 (2018) 545–553, doi:10.1016/j.wasman.2018.08.027.
- [109] S. Wang, C. Wang, F. Lai, F. Yan, Z. Zhang, Reduction-ammoniacal leaching to recycle lithium, cobalt, and nickel from spent lithium-ion batteries with a hydrothermal method: Effect of reductants and ammonium salts, *Waste Manag.* 102 (2020) 122–130, doi:10.1016/j.wasman.2019.10.017.
- [110] X. Meng, K.N. Han, The principles and applications of ammonia leaching of metals – A review, *Miner. Process. Extr. Metall. Rev.* 16 (1996) 23–61, doi:10.1080/08827509608914128.
- [111] Y. Qi, F. Meng, X. Yi, J. Shu, M. Chen, Z. Sun, S. Sun, F. Xiu, A novel and efficient ammonia leaching method for recycling waste lithium ion batteries, *J. Clean. Prod.* 251 (2020) 119665, doi:10.1016/j.jclepro.2019.119665.
- [112] W. Zhang, X. Li, Y. Jin, G. Chen, Y. Li, S. Zeng, Nano-Co₃O₄ anchored helical carbon nanofibers as an anode material for Li-ion batteries, *J. Electroanal. Chem.* 922 (2022) 116730, doi:10.1016/j.jelechem.2022.116730.
- [113] J. Qing, X. Wu, L. Zeng, W. Guan, Z. Cao, Q. Li, M. Wang, G. Zhang, S. Wu, A Novel approach to recycling of valuable metals from spent lithium-ion batteries using hydrometallurgy, focused on preferential extraction of lithium, *J. Clean. Prod.* 431 (2023) 139645, doi:10.1016/j.jclepro.2023.139645.
- [114] N. Vieceli, C.A. Nogueira, C. Guimaraes, M.F.C. Pereira, F.O. Durao, F. Margarido, Hydrometallurgical recycling of lithium-ion batteries by reductive leaching with sodium metabisulphite, *Waste Manag.* 71 (2018) 350–361, doi:10.1016/j.wasman.2017.09.032.
- [115] S. Natarajan, A.B. Boricha, H.C. Bajaj, Recovery of value-added products from cathode and anode material of spent lithium-ion batteries, *Waste Manag.* 77 (2018) 455–465, doi:10.1016/j.wasman.2018.04.032.
- [116] Y. Yang, X. Zheng, H. Cao, C. Zhao, X. Lin, P. Ning, Y. Zhang, W. Jin, Z. Sun, A closed-loop process for selective metal recovery from spent lithium iron phosphate batteries through mechanochemical activation, *ACS Sustain. Chem. Eng.* 5 (2017) 9972–9980, doi:10.1021/acssuschemeng.7b01914.
- [117] P. Zhang, T. Yokoyama, O. Itabashi, T.M. Suzuki, K. Inoue, Hydrometallurgical process for recovery of metal values from spent lithium-ion secondary batteries, *Hydrometallurgy* 47 (1998) 259–271, doi:10.1016/S0304-386X(97)00050-9.
- [118] F. Wang, R. Sun, J. Xu, Z. Chen, M. Kang, Recovery of cobalt from spent lithium ion batteries using sulphuric acid leaching followed by solid-liquid separation and solvent extraction, *RSC Adv.* 6 (2016) 85303–85311, doi:10.1039/C6RA16801A.
- [119] K. Wang, G. Zhang, M. Luo, M. Zeng, Separation of Co and Mn from acetic acid leaching solution of spent lithium-ion battery by Cyanex272, *J. Environ. Chem. Eng.* 10 (2022) 108250, doi:10.1016/j.jece.2022.108250.
- [120] Y. Pranolo, W. Zhang, C. Cheng, Recovery of metals from spent lithium-ion battery leach solutions with a mixed solvent extractant system, *Hydrometallurgy* 102 (2010) 37–42, doi:10.1016/j.hydromet.2010.01.007.
- [121] Y. Ding, N.T.H. Nhung, J. An, H. Chen, L. Liao, C. He, X. Wang, T. Fujita, Manganese-titanium mixed ion sieves for the selective adsorption of lithium ions from an artificial salt lake brine, *Materials* 16 (2023) 4190, doi:10.3390/ma16114190.
- [122] M.L. Strauss, L. Diaz, J. McNally, J. Klaehn, T.E. Lister, Separation of cobalt, nickel, and manganese in leach solutions of waste lithium-ion batteries using Dowex M4195 ion exchange resin, *Hydrometallurgy* 206 (2021) 105757, doi:10.1016/j.hydromet.2021.105757.
- [123] J. Myoung, Y. Jung, J. Lee, Y. Tak, Cobalt oxide preparation from waste LiCoO₂ by electrochemical-hydrothermal method, *J. Power Sources* 112 (2002) 639–642, doi:10.1016/S0378-7753(02)00459-7.
- [124] J. Ordoñez, E.J. Gago, A. Girard, Processes and technologies for the recycling and recovery of spent lithium-ion batteries, *Renew. Sustain. Energy Rev.* 60 (2016) 195–205, doi:10.1016/j.rser.2015.12.363.
- [125] S.O. Kilian, B. Wankmiller, A.M. Sybrecht, J. Twellmann, M.R. Hansen, H. Wiggers, Active buffer matrix in nanoparticle-based silicon-rich silicon nitride anodes enables high stability and fast charging of lithium-ion batteries, *Adv. Mater. Interfaces* 9 (2022) 2201389, doi:10.1002/admi.202201389.
- [126] L. Gaines, Lithium-ion battery recycling processes: Research towards a sustainable course, *Sustain. Mater. Technol.* 17 (2018) e00068, doi:10.1016/j.susmat.2018.e00068.
- [127] M. Ahuis, S. Doose, D. Vogt, P. Michalowski, S. Zellmer, A. Kwade, Recycling of solid-state batteries, *Nat. Energy* 9 (2024) 373–385, doi:10.1038/s41560-024-01463-4.
- [128] L.M. Riegger, R. Schlem, J. Sann, W.G. Zeier, J. Janek, Lithium-metal anode instability of the superionic halide solid electrolytes and the implications for solid-state batteries, *Angew. Chem. Int. Ed.* 60 (2021) 6718–6723, doi:10.1002/anie.202015238.