Energy Materials

Review

Electrochemical technology to drive spent lithium-ion batteries (LIBs) recycling: recent progress, and prospects

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Abstract

The widespread use of lithium-ion batteries (LIBs) in recent years has led to a marked increase in the quantity of spent batteries, resulting in critical global technical challenges in terms of resource scarcity and environmental impact. Therefore, efficient and eco-friendly recycling methods for these batteries are needed. The recycling methods for spent LIBs include hydrometallurgy, pyrometallurgy, solid-phase regeneration, and electrochemical methods. Compared to other recycling methods, electrochemical methods offer high ion selectivity and environmental friendliness. Assembling research on the recycling and reutilization of spent LIBs, with a focus on the various electrochemical techniques that can enhance these processes, is essential. A thorough analysis of the characteristics and evolution of these methods remains crucial to advancing the field of electrochemical technology in battery recycling. This review first discussed the necessity of recycling spent LIBs from multiple perspectives and briefly introduced the main pyrometallurgical and hydrometallurgical recycling technologies, analyzing their advantages and disadvantages. Moreover, we comprehensively summarized the current applications of electrochemical technology in the recycling of spent LIBs, including pretreatment, leaching, element separation, and regeneration. Then, we analyzed the characteristics and advantages of different electrochemical techniques in the LIB recycling process and discussed the obstacles encountered in the application of electrochemical technology

and their solutions. Finally, a comparison between electrochemical technology and traditional recycling processes was provided, highlighting the potential advantages of electrochemical technology in reducing recycling costs and minimizing waste emissions.

INTRODUCTION

The continuous growth of the global population and rapid economic development have increased the demand for energy, disturbing the equilibrium between supply and demand. This imbalance has resulted in an increase in energy prices, supply chain disruptions, and a resulting energy crisis[1]. As a result, the advancement of efficient energy storage technologies has emerged as a critical response to these crises internationally. Among these technologies, lithium-ion batteries (LIBs) serve as a preeminent choice for renewable energy storage, providing lightweight construction, eco-friendliness[2], high energy density, and superior specific energy and voltage properties[3]. LIBs also have good capacity retention[4], an extensive operating temperature range, and prolonged service life[5]. These attributes have pushed their widespread integration across various sectors, including portable electronics, aerospace, new energy vehicles, electric bicycles, and medical devices, allowing LIBs to achieve market dominance. According to recent data[6], in 2023, global LIB shipments increased to 1,202.6 GWh, a 25.6% increase from the previous year. Meanwhile, power batteries led with 865.2 GWh, representing 71.94% of the total, while energy storage batteries comprised 224.2 GWh or 18.64%, and small-sized batteries comprised 113.2 GWh or 9.41%. Power and energy storage batteries together accounted for over 80% of global shipments. Projections have indicated that by 2030, driven by commitments to carbon neutrality, emission peaks, and an expanding market for new energy vehicles, LIB shipments could exceed 6,080.4 GWh, with a compound annual growth rate of 22.80%[7].

The rapid expansion of LIB production has led to escalating demand for raw materials, predominantly sourced from non-renewable earth minerals. Concurrently, a surge in LIB shipments is expected to generate a significant volume of waste due to their limited lifespan. A report estimated that by 2030, the global volume of spent LIBs will reach 11 million metric tons[8]. Consequently, transitioning from mineral resources to recycled LIBs as the primary source of raw materials for LIB manufacturing offers multiple benefits. This shift not only diminishes reliance on finite mineral resources and prolongs their availability, but also reduces environmental pollution from battery waste. Additionally, this strategy supports the green and sustainable development of the LIB industry.

Due to the increasing significance of developing and applying recycling technologies for spent LIBs, countries worldwide have acknowledged the importance of recycling these batteries and have enacted various incentive policies. Notably, the United States, Germany, Japan, and China have instituted measures for the recycling of exhausted LIBs[9]. Moreover, the ReCell Center, headed by Argonne National Laboratory, has devised foundational principles for sustainable recycling. These principles encompass strategies for recyclability, direct recycling, repair, regeneration, and recovery of other high-value components[10].

LIBs are fundamentally composed of a cathode (positive electrode), an anode (negative electrode), an electrolyte, and a separator. Additional components include binders, conductive carbon black, current collectors, tabs, and packaging materials [Figure 1A and B][11-12]. The cathode materials comprise lithium
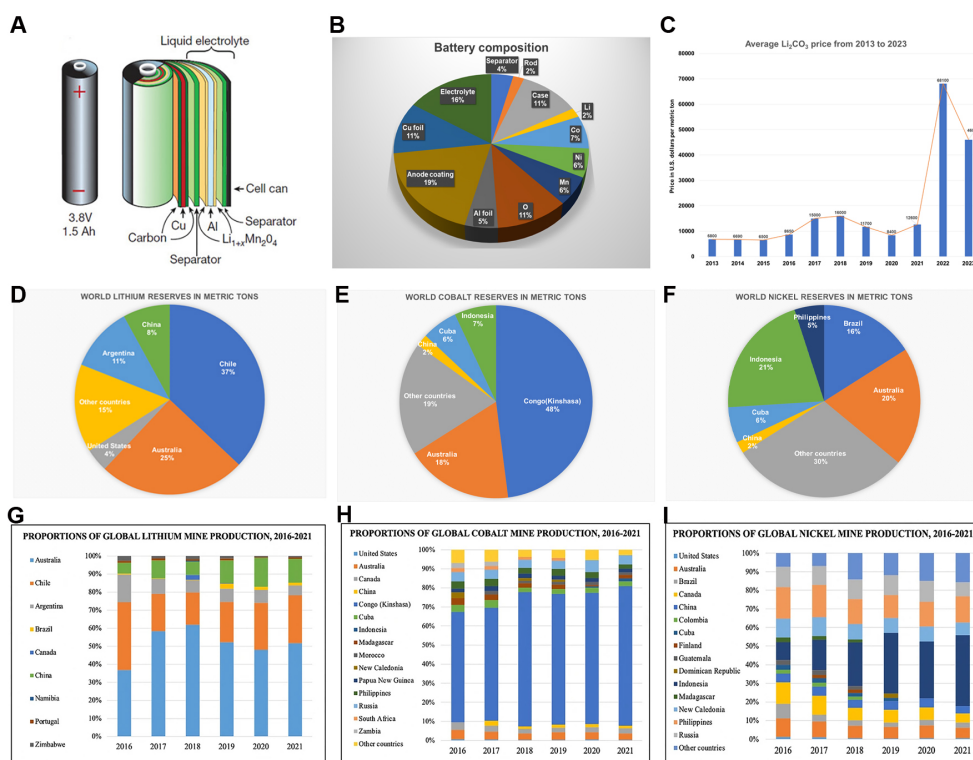
Figure 1. (A) Components of cylindrical LIBs[11]. Copyright 2020 Wiley[12]. (B) Composition of the conventional rechargeable battery[12]. Copyright 2020 American Chemical Society[12]. (C) Average Li_2CO_3 price from 2013 to 2023[24]. (D) Global lithium reserves according to USGS 2023 data. (E) Global cobalt reserves according to USGS 2023 data. (F) Global nickel reserves from USGS 2023 data. (G) Global lithium mine production proportions, 2016-2021. (H) Global cobalt mine production proportions, 2016-2021. (I) Global nickel mine production proportions, 2016-2021. (D-I) Figures reprinted with permission from Ref.[29]. Copyright 2023 Springer[29].

cobalt oxide (LCO), lithium manganese oxide (LMO), lithium nickel cobalt aluminum oxide (NCA), lithium iron phosphate (LFP), and lithium nickel manganese cobalt oxide (NCM). Graphite serves as the predominant material for the anode[13-18]. Owing to the critical metals such as lithium (Li), nickel (Ni), and cobalt (Co) present in cathode materials, recycling efforts of spent LIBs are chiefly directed toward reclaiming these cathode materials.

Current mainstream recycling processes for spent LIBs primarily include pyrometallurgy, hydrometallurgy, electrochemical methods, and cathode material regeneration. Another promising recycling method involves directly converting spent cathode materials into new materials with high-added value or specific functions, such as novel catalysts or adsorbents with excellent performance, commonly referred to as regenerated functional materials. This recycling technology can shorten the recovery process for spent cathode materials, broaden the application range of the regenerated materials, and provide significant environmental and economic benefits[19]. Compared to other recycling methods, electrochemical recycling technology has gained increasing attention, primarily because electrochemical recycling technology serves as a green and environmentally friendly method, using electrons as a green redox mediator to drive reactions without the need for large amounts of toxic chemicals, and also provides a mild, operationally feasible, and efficient approach that avoids complex, lengthy processes, and harsh reaction conditions. Specifically, electrochemical redox mediation can achieve metal dissolution, metal deposition, separation, and regeneration by adjusting anodic redox pairs (i.e., M/Mn^+, H_2O/OH, Cl^-/Cl_2, and Fe^{2+}/Fe^{3+}) and cathodic redox pairs (i.e., Mn^+/M, O_2/H_2O_2, H_2O_2/OH)[20]. Therefore, electrochemical recycling technology offers a

wider application range in the recycling process of spent LIBs. During the pretreatment process, by using the spent electrode as the working electrode, active material/graphite can be stripped from the current collector under the action of an applied current and generated bubbles. In the leaching process of spent cathode materials, using electrochemical technology instead of traditional chemical reagents can provide a reaction driving force to greatly reduce the consumption of chemical reagents and the generation of wastewater, and improve the efficiency of metal leaching. In the separation stage, the redox potentials of different metal ions in the leachate differ, and the separation of different metal ions can be achieved by adjusting the electrolysis conditions, thus avoiding the use of extractants in traditional extraction separation processes. In addition, electrochemical technology can achieve the regeneration of spent cathode materials. Adopting electrochemical recycling technology can enhance the integration, compatibility, operability, and controllability of the overall process, making it more conducive for practical industrial applications[21].

In this review, we discuss the imperative of recycling spent LIBs from economic, environmental, and sustainability standpoints. We then summarize existing recycling and utilization technologies for LIBs, encompassing pyrometallurgical, hydrometallurgical, and electrochemical methods. Particular emphasis was placed in this review on the pivotal role of electrochemical techniques in the recycling process, detailing stages such as preprocessing, leaching, separation of elements, and regeneration. We also highlighted the unique features and benefits of various electrochemical methods in recycling LIBs, and concluded by synthesizing these discussions and projecting future directions for the utilization of electrochemical methodologies in this domain.

THE NECESSITY OF RECYCLING SPENT LIBS

Resource properties of spent LIBs

As a highly recyclable secondary resource, spent LIBs contain substantial quantities of valuable metallic elements, including Co, Ni, and Li, with concentrations surpassing those in natural ores[22,23]. The manufacturing cost of LIBs also remains highly dependent on the fluctuation of raw material prices, such as lithium. As shown in Figure 1C, the price of lithium carbonate rapidly increased to $68,100 in 2022, a 440% increase compared to the previous year. However, by 2023, the price of lithium carbonate dropped back to $46,000, a significant decrease of 32.45% compared to 2022[24]. These substantial price fluctuations will inevitably affect the stability of supply and profitability for LIB manufacturers. Therefore, appropriate recycling technologies can not only promote the establishment of a closed-loop and stable supply chain for these materials, but also diminish the complexity of extraction from natural ores. Consequently, this approach may lead to a potential reduction in the cost of LIB materials, providing an economic advantage in the manufacturing of LIBs[25].

Environmental problems of spent LIBs

Increasing demand for LIBs has precipitated a marked increase in spent units. Currently, only a minor portion of these batteries is subjected to recycling and resource recovery, with the majority still relegated to landfills or disposed of illegally[26]. LIBs, which contain heavy metals such as Co, Ni, and manganese (Mn) (all recognized carcinogens), and toxic organic electrolytes, may emit harmful HF gas upon contact with water. As a result, these materials are considered hazardous waste. The improper disposal of these batteries can lead to substantial emissions of noxious substances into the environment, threatening ecological integrity and public health[27]. Consequently, recycling these batteries not only enhances resource efficiency, but also advances the development of a green and sustainable LIBs sector[28].

Uneven distribution of production resources

The essential raw materials used for LIB production are primarily found in a few countries. In terms of the distribution of natural resources, Chile, Australia, and Argentina hold over 70% of the world's lithium

resources, as shown in Figure 1D-F. The Democratic Republic of Congo and Australia account for 66% of global cobalt resources, while 41% of global nickel resources are concentrated in Australia and Indonesia. This uneven distribution of natural resources has led to disparities in the production output of Li, Co, and Ni worldwide[29]. As shown in Figure 1G-I, the production of lithium in Australia and nickel in Indonesia demonstrated a yearly increase from 2016 to 2023, with the Democratic Republic of Congo consistently remaining the top global producer of cobalt[29]. The centralization of these vital resources can significantly influence the raw material availability for LIBs, resulting in notable fluctuations in the cost and stability of the supply chain[30]. Recycling spent LIBs presents a valuable opportunity, as it can overcome the geographical constraints on resource availability, thus stabilizing the supply chain and reducing manufacturing costs[31-32].

TRADITIONAL RECYCLING STRATEGIES FOR SPENT LIBS

The recycling process for spent LIBs primarily consists of two key stages: pretreatment and the recovery of valuable metals[33-37]. Pretreatment involves steps such as battery discharge, disassembly, cell crushing, and sieving. Following pretreatment, the positive and negative electrode materials are converted into powder form, and traditional metallurgical techniques are then used to separate and recover valuable metals from the powder. The metals and their compounds retrieved can subsequently be employed in the manufacturing of new LIBs or for other purposes, facilitating resource reuse and the environmentally friendly treatment of pollutants.

Currently, conventional recycling processes for spent LIBs primarily consist of pyrometallurgy and hydrometallurgy[38], with the respective recycling flows depicted in Figure 2. Pyrometallurgy, a high-temperature metallurgical process, is extensively utilized in industrial production, especially in Europe and North America, owing to its simplicity, large processing capacity, and efficiency. Conversely, hydrometallurgy utilizes acid (or alkali) aqueous solutions to extract valuable metals from spent LIBs. This method is prevalent used in China, given its high recovery rates, low energy consumption, minimal toxic gas emissions, and high purity of the recovered metals.

Pyrometallurgical recovery technology

Pyrometallurgical technology encompasses a series of physical and chemical reactions at high temperatures, enabling the retention of metals in the positive electrode material in alloy form and facilitating their separation from impurities. Typically, a reducing agent is added during the reaction to collect different metals under a reducing atmosphere as either alloy or slag. Figure 3A and B illustrates the typical process flow. Pyrometallurgical processes consist of three main steps. The initial step involves crushing the entire battery and processing it in a rotary kiln for reduction roasting, segmented into low and medium-temperature phases. The aim of the low-temperature stage, at approximately 300 °C, involves evaporating the electrolyte and minimizing explosion risks. The medium-temperature phase is then increased to 700 °C, utilizing a negative electrode graphite, separator, and binder, which generates reducing gas upon heating, as reducing agents for preliminary reduction of Ni, Co, and Mn. The second step elevates the temperature above 1,200 °C for further reduction and smelting, allowing Ni, Co, and copper (Cu) to enter the alloy phase, which can be subsequently separated by magnetic separation[39]. The third step applies hydrometallurgical technology for alloy leaching and separation, facilitating the recycling of valuable metals from the positive electrode material. The primary pyrometallurgical recycling processes for LIBs include high-temperature smelting and calcination, with the latter subdivided into direct, atmosphere-assisted, and salt-assisted calcination. Compared to high-temperature smelting, calcination operates at lower temperatures, potentially improving metal recovery rates by producing water-soluble salts. This method can reduce acid consumption and the emission of toxic gases in subsequent stages.
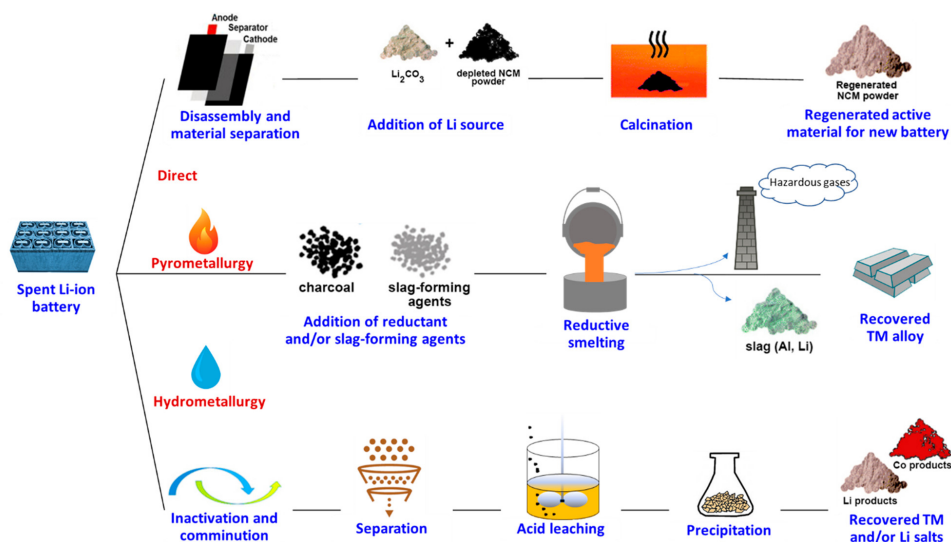
Figure 2. Typical direct, pyrometallurgical, and hydrometallurgical recycling methods for recovery of LIB active materials[38]. Copyright 2022 American Chemical Society[38].
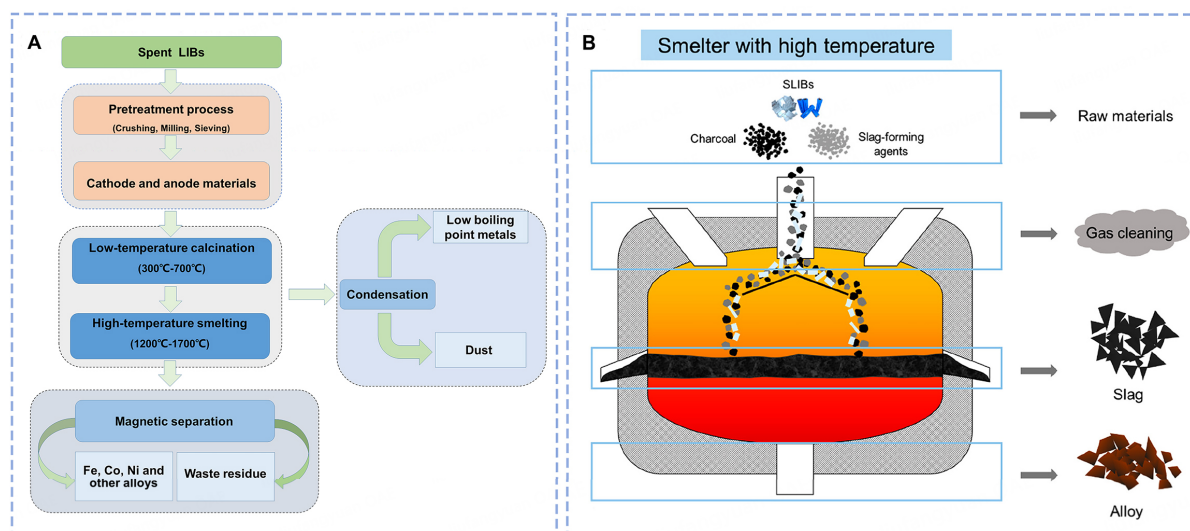

Figure 3. (A) Flowchart of the pyrometallurgical process for recycling spent LIBs. (B) A typical pyrometallurgical treatment process of spent LIBs[39]. Copyright 2021, the American Chemical Society[39].

High-temperature smelting technology for LIB recycling was first introduced in the Umicore battery recycling process[40]. Instead of mechanically preprocessing individual batteries, this process utilizes specialized ultra-high temperature (UHT) technology, incorporating slagging agents, to directly smelt spent batteries at elevated temperatures. This process can produce an alloy containing valuable metals (Co, Ni, Fe, and Cu), which can be subsequently separated through hydrometallurgical technology [Figure 4A][41]. Plastics, solvents, and graphite will be incinerated, exiting in gaseous form, while Li, aluminum (Al), and Mn will be lost to the slag and not recovered [Figure 4B][42]. UHT technology facilitates the safe processing of large volumes of complex metallic waste. The mixture, containing batteries, coke, and slagging agents (limestone, sand), is introduced into the furnace, with optimal feedstock comprising 30-50 wt% spent batteries to yield economically viable cobalt and nickel products. Preheated air at 500 °C is then injected at
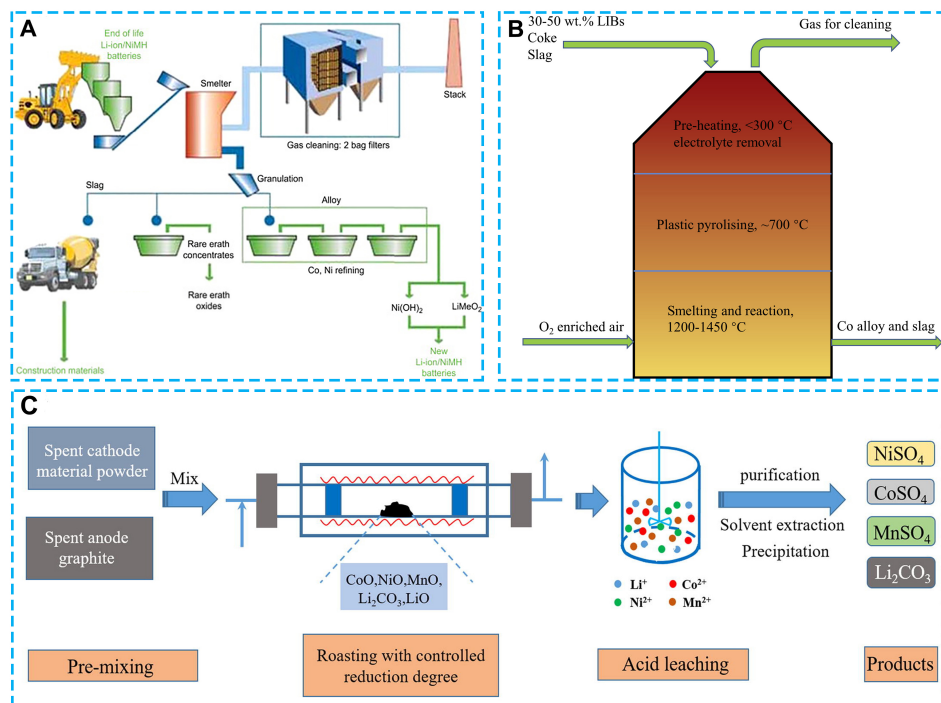
Figure 4. (A) Flowsheet showing the Umicore/Rhodia's VAL'EAS™ battery scrap recycling process[41]. Copyright 2014 Elsevier[41]. (B) Detailed illustration of the smelting process[42]. Copyright 2022 Elsevier[42]. (C) Recovery of spent LIBs through reduction roasting and facile acid leaching processes[43]. Copyright 2020 Elsevier[43].

the furnace base, which can be segmented into three temperature zones, namely, preheating, plastic pyrolysis, and smelting. The inaugural pilot plant was operational for several years in Hofors, Sweden. Drawing from this experience, a second-generation pilot plant was launched in Hoboken, Belgium, in 2011, with an annual capacity of 7,000 tons. The primary benefits of this process include the elimination of mechanical battery preprocessing and high recovery rates of Co, Ni, and Cu. However, this process necessitates extremely high temperatures, exceeding 1,500 °C, resulting in considerable lithium loss and leading to increased energy consumption and resource depletion.

Zhang *et al.* explored the recovery of valuable metals from spent LIB cathodes [Figure 4C] using a reduction roasting approach that capitalized on repurposed graphite from anode materials[43]. This two-step method consisted of a reduction roast at 600 °C for 3 h, followed by leaching with sulfuric acid (H_2SO_4), thus eliminating the need for additional reducing agents. The findings demonstrated that this process achieved leaching rates exceeding 99% for Ni, Co, and Li, and over 97% for Mn. This innovative method not only repurposed waste graphite, enhancing energy efficiency, but also precluded the substantial generation of hydrogen gas during metal recovery. Yan *et al.* also suggested an improved process of carbothermal reduction for the preferential extraction of lithium, which was combined with water leaching from spent $Li(Ni_xMn_yCo_{1-x-y})O_2$ (NMC) batteries[44]. When the roasting temperature was below 800 °C, Co and Ni were reduced to their elemental forms, while Mn remained in oxide form, and Li was converted to Li_2CO_3. When the roasting temperature exceeded 900 °C, Li was mainly converted to Li_2O. Lithium was extracted as lithium hydroxide and lithium carbonate with an efficiency of 93% following water leaching for 30 min using a 5 mL/g liquid-to-solid ratio. The researchers also investigated the effect of impurities on the recovery rate of Li, and determined that Cu had no significant effect. However, the lithium recovery rate decreased in the presence of Al due to the formation of lithium aluminate.

The pyrometallurgical process can facilitate the rapid conversion of valuable metals into alloys at elevated temperatures, predominantly using iron (Fe) ore-based techniques for cobalt and nickel extraction. This method has a straightforward operation and efficient elimination of organic materials, binders, plastics, and other components from spent LIBs, making it appropriate for industrial-scale production. Nevertheless, this process has considerable disadvantages, including excessive energy consumption, significant material loss yielding high input costs, inadequate purity of the recovered valuable metals, and the production of hazardous substances such as dioxins and furans. These issues result in substantial secondary pollution and pose challenges in complying with contemporary environmental protection standards.

Hydrometallurgical recovery technology
Hydrometallurgy serves as a well-established and widely used technology for recycling spent LIBs. This method mainly utilizes inorganic acids, organic acids, ammonia-based reagents, and similar chemicals to leach valuable metals from pre-treated cathode active materials into a solution. Subsequently, valuable metals can be separated from this solution through processes such as precipitation and extraction. The hydrometallurgical process flow is shown in Figure 5.

Hydrometallurgy involves two primary processes, namely, leaching and purification. The decision between common leaching methods, such as acid and alkali leaching, depends on the physical and chemical properties of the target metals. Acid leaching utilizes inorganic agents such as hydrochloric acid (HCl), H_2SO_4, nitric acid (HNO_3), and phosphoric acid (H_3PO_4), and organic agents such as citric acid, oxalic acid, and formic acid for extraction purposes, as shown in Table 1.

Leaching methods can be characterized by their high recovery efficiency, low energy consumption, and rapid reaction rates, making them highly suitable for recycling spent LIBs. However, the non-selective nature of acid leaching increases the complexity and expense of metal separation. Inorganic acid leaching typically requires high acid concentrations, resulting in significant corrosiveness and necessitating specialized equipment. Additionally, this process often mandates the extensive addition of water or alkalis for neutralization, complicating post-treatment procedures. The leaching process will emit hazardous gases, presenting risks to human health and the environment. When utilizing organic acids as leaching agents, the process remains limited to low solid-to-liquid ratios and suffers from slow leaching rates, making it impractical for large-scale industrial use. Furthermore, the prolonged degradation cycles of organic acids contribute to potential environmental pollution.

Ammonia leaching has recently attracted significant interest due to its selective extraction capabilities targeting metals such as Li, Ni, Co, Al, Fe, and Mn. Nevertheless, concerns regarding additional wastewater generation remain a challenge. The intricate binding mechanisms between the metals of value and ammonia-based leachates remain improperly understood and require more thorough investigation. Subsequent to hydrometallurgical leaching, the leachate contains valuable metal ions such as Li^+, Ni^{2+}, Co^{2+}, and Mn^{2+}, and impurity ions such as Fe^{2+}, Al^{3+}, and Cu^{2+}. Conventional separation techniques such as solvent extraction, chemical precipitation, and electrodeposition have been typically employed to isolate and concentrate these valuable metals from complex mixtures.

ELECTROCHEMICAL TECHNOLOGY TO DRIVE SPENT LIBS RECYCLING

Electrochemical technology has found extensive application in the extraction of precious metals such as gold and silver from industrial wastewater[64], valuable metals from tailings[65], trace metals from solid waste[66], and lithium from brine[67-70]. This popularity is due to the high selectivity of electrochemical methods for different metal ions, enabling the dissolution or deposition of specific metal elements by adjusting electrolysis conditions, thus facilitating the separation of various metal elements.

Table 1. Summary of some research results for leaching of spent LIBs in acid leaching

Acid	Cathode materials	Leaching agent	T (°C)	S/L ratio (g/L)	Time (min)	Leaching rate (%)	Ref.
Inorganic acids	LiFePO$_4$	2.5 M H$_2$SO$_4$	60	100	240	Li:97; Fe:98	[45]
		1.0 M HNO$_3$ + 1.7 vol% H$_2$O$_2$	70	10	30	Li: 99; Fe: 99	[46]
	Li$_2$CoO$_2$	4.0 M HCl	80	-	120	Li: 97; Co: 99%	[47]
		2.0 M H$_2$SO$_4$ + 2.0 vol% H$_2$O$_2$	60	33	120	Co: 96.3; Li: 87.5	[48]
		2.0 M H$_2$SO$_4$ + 5.0 vol% H$_2$O$_2$	80	50	60	Co: > 99; Li: > 99	[49]
		2.0 M H$_2$SO$_4$ + 8.0 vol% H$_2$O$_2$	75	50	60	Co: 98	[50]
		1.0 M HNO$_3$ + 1.7 vol% H$_2$O$_2$	75	10	30	Co: 99; Li: 99	[51]
		1.0 M H$_2$SO$_4$	95	50	240	Co: 66.2; Li: 93.4; Ni: 96.3; Mn: 50.2	[52]
	Mixture	1.0 M H$_2$SO$_4$ + 5.0 wt% H$_2$O$_2$	95	50	240	Co: 79.2; Li: 94.5; Ni: 96.4; Mn: 84.6	[53]
		1.0 M H$_2$SO$_4$ + 0.78 wt% NaHSO$_3$	95	20	240	Co: 91.6; Li: 96.7; Ni: 96.4; Mn: 87.9	[53]
		4.0 M HCl	80	20	60	Co: 99.5; Li: 99.9; Ni: 99.8; Mn: 99.8	[54]
Organic acids	Li$_2$CoO$_2$	1.5 M succinic acid + 4.0 vol% H$_2$O$_2$	70	15	40	Li: 96; Co: 100	[55]
		1.25 M ascorbic acid	70	25	20	Li: 98.5; Co: 94.8	[56]
		1.25 M citric acid + 1.0 vol% H$_2$O$_2$	90	20	30	Li: 91; Co: 91	[57]
		1.0 M H$_2$C$_2$O$_4$	80	50	120	Li: 98	[58]
		1.5 M malic acid + 2.0 vol% H$_2$O$_2$	90	20	40	Li: 94; Co: 93	[59]
	NCM	1.2 M DL-malic acid + 1.5 vol% H$_2$O$_2$	90	40	30	Co: 94.3; Li: 98.9; Ni: 95.1; Mn: 96.4	[60]
		1.0 M acetic acid + 6.0 vol% H$_2$O$_2$	70	20	60	Co: 97.7; Li: 98.4; Ni: 97.3; Mn: 97.1	[61]
		2.0 M maleic acid + 4 vol% H$_2$O$_2$	70	20	60	Co: 98.4; Li: 98.2; Ni: 98.1; Mn: 98.1	[61]
		1.0 M citric acid + 12 vol% H$_2$O$_2$	60	80	40	Total metals: > 98	[62]
		0.5 M citric acid + 1.5 vol% H$_2$O$_2$	90	20	60	Co: 99.8; Li: 99.1; Ni: 98.7; Mn: 95.2	[63]

Electrochemical pretreatment

Methods for separating current collectors from active materials include mechanical processing[71], thermal treatment[72], leaching[73], and solvent treatment[74]. Mechanical processing consists of crushing and sieving to isolate the cathode material powder, which unfortunately produces a powder material contaminated with impurities such as copper or aluminum from the current collector. Thermal treatment involves the decomposition of the binder [polyvinylidene fluoride (PVDF)] at elevated temperatures to segregate the cathode active powder, though at a significant energy cost. Leaching employs substantial quantities of acid to dissolve copper or aluminum foil, consequently producing harmful gases. Solvent treatment utilizes organic solvents to dissolve PVDF, facilitating the
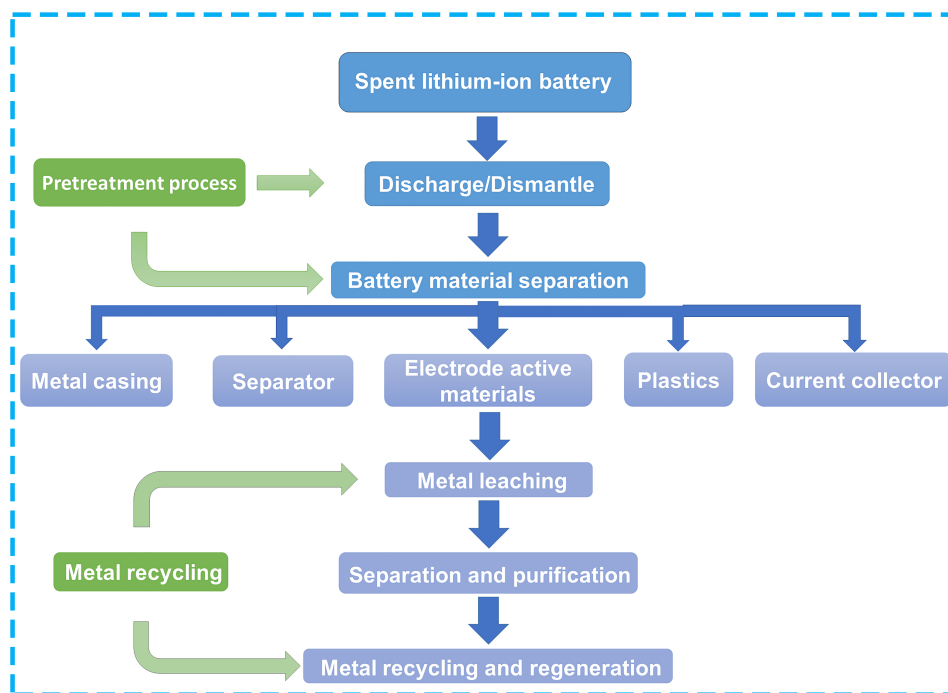
Figure 5. Hydrometallurgical process flowchart of spent LIBs.

separation of cathode powder. However, this method consumes considerable volumes of solvents, posing a risk to human health. To enhance separation efficiency between the current collector and cathode material, researchers have explored the electrochemical technique to separate the active material and current collector.

Cao *et al.* developed a method for separating copper foil from graphite in the anode by using the disassembled anode of LIBs as the cathode, graphite as the anode, and employing Na_2SO_4 (1.5 g/L) solution as the electrolyte, as shown in Figure 6A[75]. At 30 V, the complete separation of the current collector (copper foil) and graphite was achieved within 25 min. The generation of hydrogen gas on the surface of the copper foil during electrolysis created gaps, facilitating the detachment of graphite. Moreover, this method reduced the bonding force, increasing the separation efficiency. The resulting copper foil was recyclable without additional processing. Residual Li^+ from the spent graphite entered the solution during electrolysis, and dissolved copper could be reclaimed through precipitation to a lesser extent. The purity of the regenerated graphite was approximately 95%, with energy consumption of around 4.70 kWh/kg.

The previously mentioned electrochemical methods can also facilitate the separation of aluminum foil from active materials, though with changes in the electrode reactions. Chu *et al.* employed a neutral Na_2SO_4 solution as the electrolyte, positioning the dismantled cathode of NCM batteries as the electrolytic anode and utilizing either copper or aluminum as the electrolytic cathode, as shown in Figure 6B[76]. Oxygen gas was also produced between the aluminum foil and active materials during electrolysis. Similarly, echoing the charging dynamics of LIBs, Li^+ migrated from the cathode material into the solution, achieving the separation of lithium and transition metals. At an optimal electrolysis voltage of 30 V, the lithium dissolution efficiency reached 77%, with the separation of Ni, Co, and Mn in their solid forms [Figure 6C-F]. The anodic reactions are expressed as:
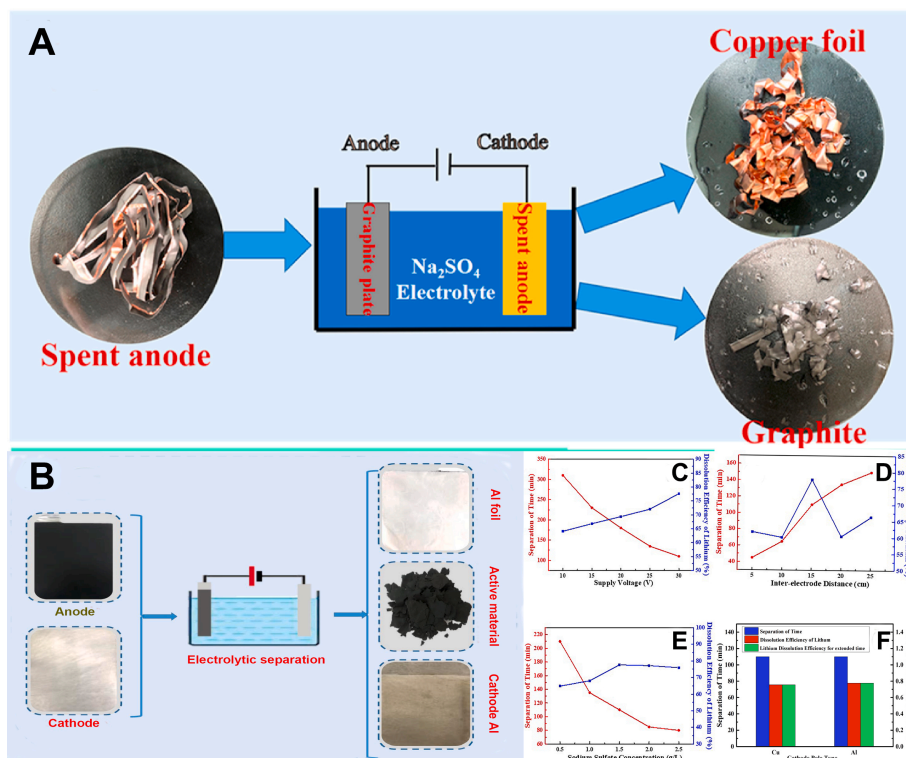
Figure 6. (A) Graphite anode prior to electrolysis, accompanied by the recovered copper foil and anode active materials post-electrolysis[75].Copyright 2021 Elsevier[73].(B) Schematic of electrolytic separation. (C) Influence of supplied voltage on lithium dissolution and separation duration. (D) Impact of inter-electrode spacing on lithium dissolution and separation duration. (E) Concentration effect of sodium sulfate on lithium dissolution and separation duration. (F) Consequences of electrolysis duration on lithium recovery and separation time. (B-F) Figures reprinted with permission from Ref.[74].Copyright 2021 Elsevier[75].

$$LiNi_xCo_yMn_zO_2 - ne^- \rightarrow Li_{1-n}Ni_xCo_yMn_zO_2 + nLi^+ \qquad (1)$$

$$4OH^- - 4e^- \rightarrow O_2 + 2H_2O \qquad (2)$$

Electrochemical leaching

Hydrometallurgical techniques for recycling LIBs present widespread applicability and yield high-purity products, making these techniques a favored method. These techniques encompass dissolving valuable metals from depleted batteries into acidic or alkaline solutions, followed by purification processes such as extraction and precipitation to eliminate any impurities, culminating in the production of high-purity products. The leaching step has shown to be especially pivotal, significantly influencing the recovery efficiency of valuable metals. However, to improve leaching efficiency, substantial amounts of leaching solution are typically used, leading to the production of large volumes of wastewater. By integrating electrochemical methods for leaching positive electrode materials, these challenges can be mitigated, with electrochemical reactions relying on an external electric current.

Lei *et al.* devised a pioneering process for recycling LIBs by integrating reduction roasting with electrochemical leaching, as shown in Figure 7A-D[77]. The process involved reduction roasting of the spent $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ material at 1,600 °C for 120 min, which released O_2 and disrupted its layered structure, resulting in a mixture of Li_2CO_3, NiO, Co_3O_4, MnO_2, and Mn_2O_3. This disruption of the layered structure enhanced valuable metal leaching. The roasted material was subsequently encased in polypropylene bags
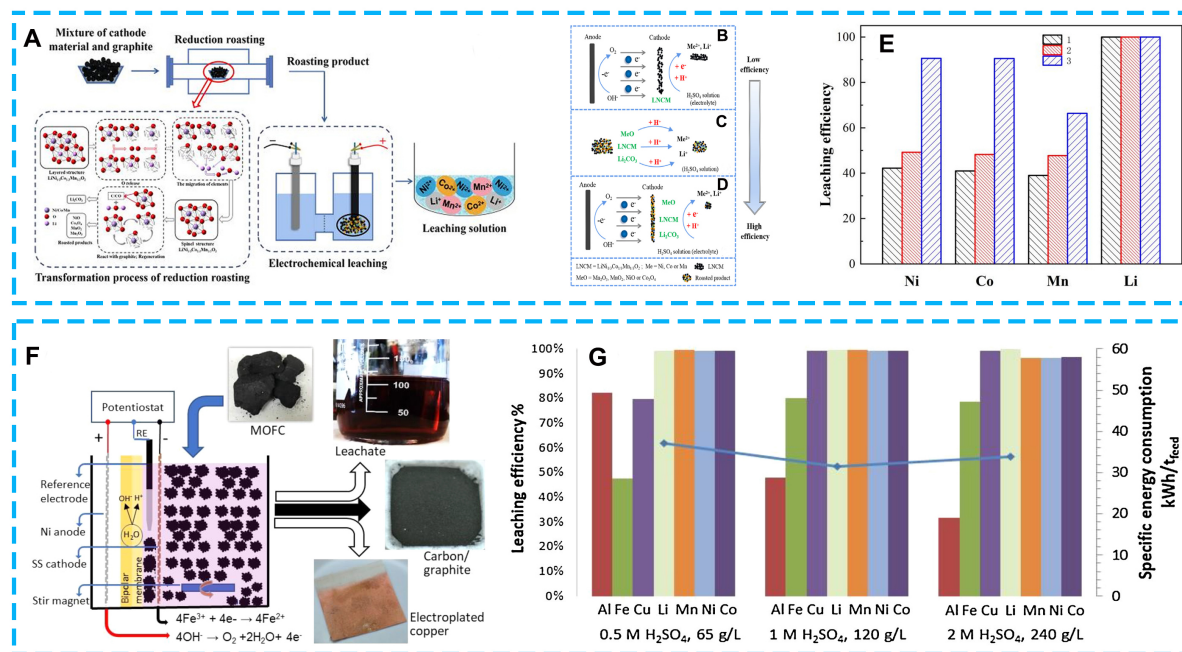
Figure 7. (A) Flowsheet illustrating the recovery of spent LIBs through thermal reduction and electrochemical leaching processes. (B) Mechanism of the reaction for the direct electrochemical leaching of cathode materials. (C) Mechanism of the reaction for thermal reduction process followed by acid leaching. (D) Mechanism of the reaction involving thermal reduction process followed by electrochemical leaching (green represents reactants, with red indicating substances introduced during the leaching processes). (E) Comparative evaluation of metal leaching effectiveness among the three methods: (1) direct electrochemical leaching; (2) thermal reduction process combined with acid leaching; (3) thermal reduction process coupled with electrochemical leaching. (A-E) Figures reprinted with permission from Ref.[77].Copyright 2021 American Chemical Society[77].(F) Schematic representation of the electrochemically assisted leaching of metals from MOFC, where the leachate, carbon/graphite materials, and electrowon copper can be separately recovered. (G) Leaching efficiency of metals and specific energy consumption at various tested pulp densities. (F-G) Figures reprinted with permission from Ref.[78].Copyright 2020 Elsevier[78].

and attached to a graphite cathode, with a titanium (Ti) anode. The setup utilized G1204 [an anion exchange membrane (AEM)] as the separator and 1.5 M H_2SO_4 as the electrolyte. Subsequently, the roasted product underwent further reduction through electrochemical methods at room temperature, with a current of 0.8 A applied for 150 min. The leaching rates of Li, Co, Ni, and Mn were recorded as 100, 90.53, 90.59, and 66.40%, respectively, as shown in Figure 7E. Compared to identical leaching conditions involving direct acid leaching and the electrochemical leaching of thermally treated roasted spent cathode materials, this method proved to substantially minimize the utilization of chemical reagents such as reducing agents and acid, while also achieving higher metal recovery rates and yielding greater economic benefits.

Electrochemical leaching can also be used to process mixtures of different spent LIB materials. Diaz *et al.* developed a method using electrochemical techniques to extract valuable metals from mixed crushed LIB metal oxide filter cakes (MOFC), composed of $LiCoO_2$, $LiMn_xCo_yO_2$, $LiNi_xMn_yCo_zO_2$, $LiCu_xMnO_2$, $LiNi_xCo_yAl_zO_2$, current collectors (aluminum and copper foil), and graphite[78]. The electrolytic cell comprised an anodic chamber and a cathodic chamber separated by a bipolar membrane (BPM), as depicted in Figure 7F. The anode comprised nickel foam, immersed in a 1 M KOH solution, while the cathode was constructed from stainless steel mesh, with the cathode chamber electrolyte ranging from 0.5-2 M H_2SO_4, enhanced by 10 mM $FeSO_4$ and the addition of MOFC. During the electrolysis process, Fe^{2+} served as the reducing agent, facilitating the reduction of Co^{3+} ions, and improving their leaching rate. With a slurry concentration of 65 g/L and a controlled low acid concentration, voltage, current, and electrolyte

pH, the leaching rates of Li, Ni, Co and Mn exceeded 96% within 8 h, as shown in Figure 7G. The process generated electrolytic copper and graphite carbon as by-products. Compared to conventional acid leaching, this methodology noticeably decreased acid consumption and produced a lower pH leaching solution, significantly reducing wastewater treatment costs.

Electrochemical separation

After leaching the positive electrode materials, the efficient separation of diverse valuable metal elements from the intricate leach solution serves as a vital process step in the recycling of spent LIBs. Due to the high ion selectivity of electrochemical techniques, multiple metal elements in the solution can be effectively separated, with the resulting metal products post-separation exhibiting greater purity, making them suitable for direct use in the regenerative synthesis of cathode materials.

Electrochemical deposition

Electrochemical deposition involves the process in which metal ions of value within the leaching solution obtain electrons under an applied electric field, subsequently depositing on the cathode to form a coating. The order in which electrochemical deposition of varied metal ions occurs will be dictated by the properties of the metal ions, electrolyte composition, pH, temperature, and current density. Consequently, by modifying these conditions, specific metal ions can be selectively reduced, facilitating the separation of valuable metals. Compared to alternative separation techniques, electrochemical deposition offers benefits such as straightforward raw materials, reduced costs, a concise process, high product purity, and excellent performance.

Prabaharan *et al.* employed electrochemical techniques to extract Co and Mn from spent LIBs [Figure 8A-C][79]. At a concentration of 2 M H_2SO_4, with a current density of 400 A/cm², and after an electrolysis period of 3 h, the leaching rate of Co and Mn reached close to 100%. Additionally, Cu from the batteries was concurrently deposited at the cathode during the leaching, removing the need for further Cu separation and recovery processes. Electrochemical deposition facilitated the recovery of Mn and Co from the leaching solution. In this process, Co was deposited at the cathode through electrochemical reduction, while Mn was oxidized to form MnO_2 at the anode. The respective reactions during electrochemical deposition are expressed as follows.

Cathode:

$$Co^{2+} + 2e^- \rightarrow Co \qquad\qquad (3)$$

$$2H^+ + 2e^- \rightarrow H_2 \qquad\qquad (4)$$

Anode:

$$2H_2O \rightarrow O_2 + 4H^+ + 2e^- \qquad\qquad (5)$$

$$Mn^{2+} + 2H_2O \rightarrow MnO_2 + 4H^+ + 2e^- \qquad\qquad (6)$$

The pH of the electrolyte was found to significantly influence the quality of deposited cobalt metal. As the pH increased from 1 to 4.5, the current efficiency of Co deposition improved from 33.2% to 97.1%, although the purity of the product declined to 85.3%. When the pH was maintained between 2 and 2.5, the deposited cobalt metal demonstrated enhanced brightness, and the impurity content remained below 0.8%. Optimal
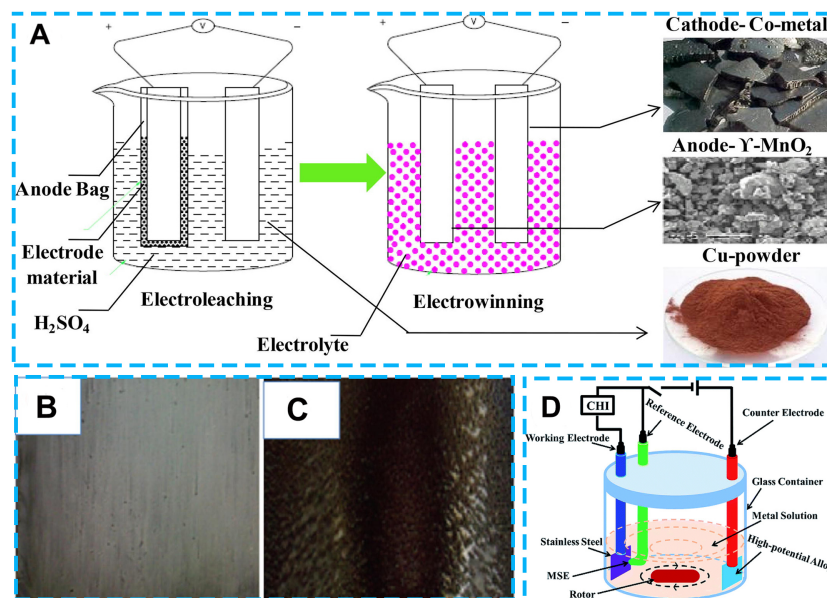
Figure 8. (A) The method of electrodeposition for the separation of cobalt from spent LIBs. Characteristics of cobalt metal deposition at (B) a pH of 2.5 and (C) a pH of 4.5. (A-C) Figures reprinted with permission from Ref.[79]. Copyright 2017 Elsevier[79] (D) Schematic illustration of the electrodeposition apparatus[83]. Copyright 2019 Royal Society of Chemistry[83].

conditions for complete deposition of Co and Mn included an electrolyte pH range of 2 to 2.5, a temperature of 90 °C, and a current density of 200 A/m^2, while the recovery rates for Co, Cu, and Mn exceeded 96%, 97%, and 99%, respectively, leading to product purities of 99.2% for cobalt metal, 99.5% for copper metal, and 96% for MnO$_2$.

Freitas *et al.* employed HCl and H$_2$O$_2$ to leach spent LiCoO$_2$ powder materials, and subsequently used the leaching solution as the electrolyte for cobalt recovery using the electrochemical method[80]. As the pH increased, the reductive potency of hydrogen ions diminished, enhancing the current efficiency of cobalt deposition. The maximum current efficiency, amounting to 96.90%, was achieved at a pH of 5.40, while cobalt deposition nucleation at the cathode was continuous. By contrast, at a pH of 2.70, the nucleation shift to an instantaneous mode affected the morphology of the cobalt deposits[81-82].

In addition to metals such as Ni, Co, Mn, and Li, the leachate from spent LIBs cathode materials contains impurities including Fe, Cu, and Al. Typically, Al can be precipitated by adjusting the pH of the leachate. However, due to the similar precipitation pH values of Cu^{2+}, Co^{2+}, and Ni^{2+}, pH adjustment alone remains insufficient for Cu removal. Freitas *et al.* explored the impact of Cu presence in the leachate on Co electrodeposition[80]. The leaching of spent cathode materials containing Co and Cu was conducted using H$_2$SO$_4$ and H$_2$O$_2$, with resultant leachate serving as the electrolyte for electrodeposition, utilizing Pt as the anode. Co and Cu were electrodeposited onto platinum, glassy carbon, or aluminum cathodes. At a pH of 5.4, the Co/Cu multilayers that formed on the cathodes showed increased porosity, primarily due to the continuous nucleation mechanism. At a pH of 2.7, the Co/Cu multilayers exhibited reduced porosity, reflecting a shift from continuous to instantaneous nucleation. Therefore, the separation of Cu and Co through electrodeposition demonstrated difficulties. Because Cu^{2+} has a higher standard electrode potential for reduction compared to hydrogen evolution potential, copper ions(II) can be selectively separated, unlike Ni^{2+}, Co^{2+}, and Mn^{2+}. Peng *et al.* successfully employed an electrochemical method to selectively remove copper ions (II) from the leachate, thus achieving the preparation of high-purity cobalt [Figure 8D][83].

If a notable difference in the reduction potentials of valuable metal ions in the leach solution is present, electrodeposition can separate and recover different valuable metals, achieving high metal purity. However, if the reduction potentials of valuable metal ions are similar (i.e., Co and Ni), electrodeposition will occur simultaneously for metals with close reduction potentials, leading to decreased metal purity. Therefore, in the recycling process of spent LIB cathode materials, Ni and Co will be initially separated from the leaching solution via extraction, followed by electrodeposition to independently prepare elemental Ni and Co on the cathode.
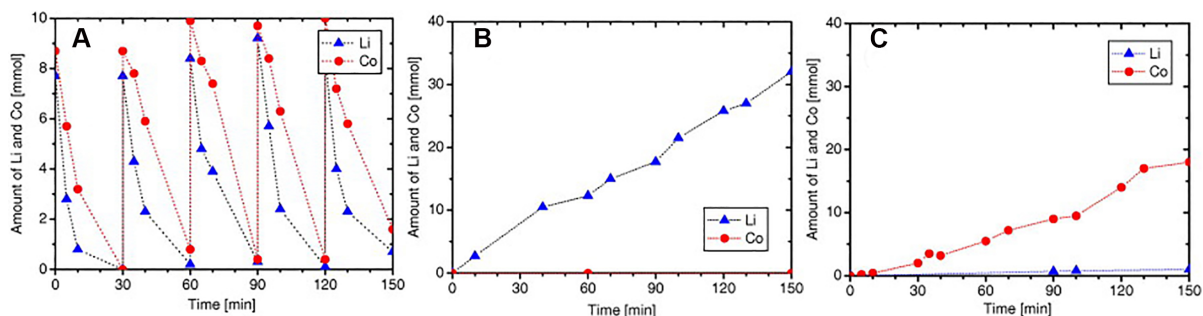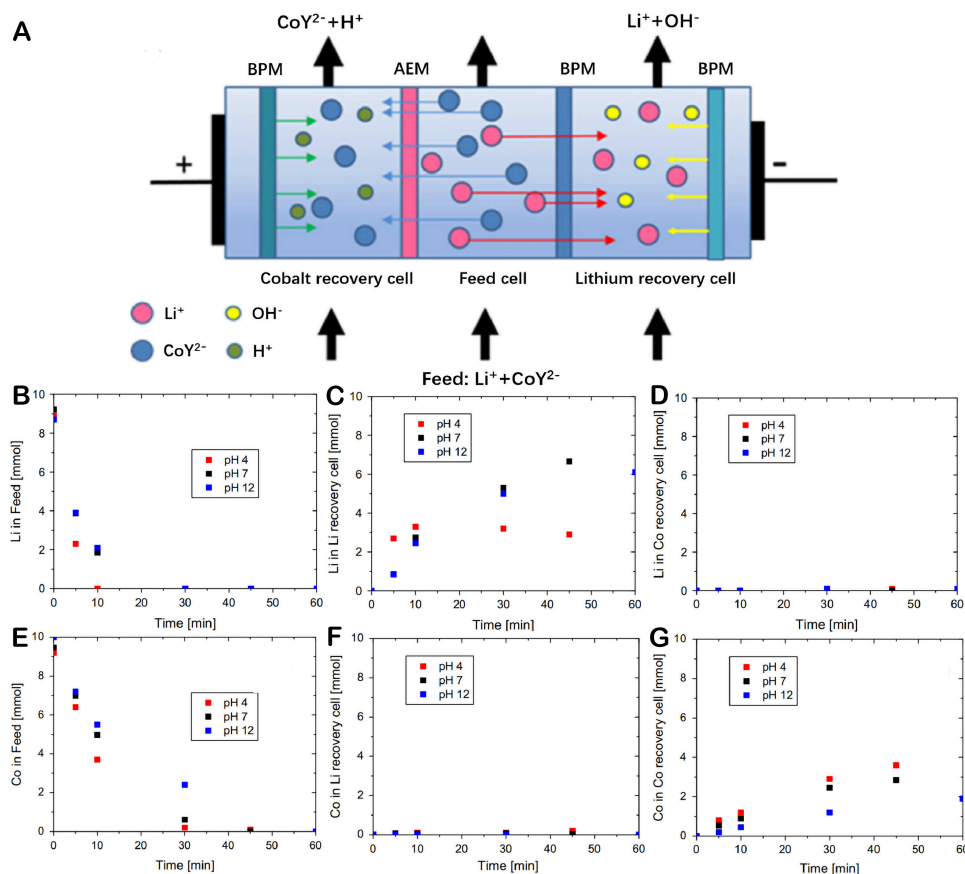
Electrodialysis

Electrodialysis involves the movement of various metal ions at distinct rates across a semi-permeable membrane, driven by an external electric field and influenced by their charge and size disparities. This method facilitates the selective migration of ions, enabling the efficient separation of valuable metals. In the recycling of spent LIBs cathode materials, electrodialysis has been extensively employed for the separation and recovery of critical metals such as Ni, Co, and Li, offering vital technical support for the recycling processes of LIBs.

In the leaching solution of spent LIB cathode materials, lithium ions coexist with other transition metal ions. To efficiently separate lithium from transition metal ions, Iizuka *et al.* introduced a method utilizing BPM electrodialysis in conjunction with metal ion complexation, which specifically enhanced the separation of Li^+ and Co^{2+} in the leaching solution, with ethylenediaminetetraacetic acid (EDTA) serving as the complexing agent[84,85]. At pH levels above 4, the formation of anionic groups CoY^{2-} resulted from the complexation of EDTA with Co^{2+}, leaving Li^+ as the cations in the solution. Thus, exploiting the charge disparity, Co^{2+} and Li^+ separation could be realized through electrodialysis. Figure 9A presents the configuration of the electrodialysis system, which included three electrolysis cells separated by BPMs, AEMs, and cation exchange membranes (CEMs). The cobalt recovery cell was linked to the anode (stainless steel), while the lithium recovery cell was connected to the cathode (Ti/Pt). The leaching solution and EDTA were introduced into the feed cell, where under the influence of an electric field, CoY^{2-} migrated to the cobalt recovery cell through the AEM, and Li^+ moved to the lithium recovery cell through the CEM, thus separating Li^+ from Co^{2+}. Figure 9B-G illustrates the variations in Li^+ and Co^{2+} concentrations across the three cells over time, demonstrating how the Li and Co concentrations progressively increased in their respective recovery cells. The selectivity of Li and Co achieved a notable value of 99%.

In the electrodialysis process, the ion exchange membrane could easily capture and stabilize cobalt and lithium ions, leading to lower recovery rates for these metals. To address this issue, a semi-batch experiment was conducted. Initially, the feed solution was added to the feed cell and operated for 30 min, after which it was replenished with a fresh solution. This replacement cycle was repeated every 30 min for a total duration of 150 min. After each 30 min of operation, the metal concentration in the feed cell significantly decreased, approaching zero over time [Figure 10A]. Despite the increase in cycles, the metal ion removal rate from the feed solution remained consistent. Conversely, the concentration of lithium ions in the lithium recovery cell and cobalt in the cobalt recovery cell linearly increased with operation time, as shown in Figure 10B and C. These findings suggested that this method not only effectively separated lithium and cobalt ions from the feed solution but also concentrated the metals through semi-batch operation.

Chan *et al.* pioneered a method employing electrodialysis technology for the separation of Li, Co, Mn, and Ni from the $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ (NMC111) cathode material of spent LIBs[86]. This process encompassed the EDTA-mediated complexation of Ni and Co, followed by three-stage electrodialysis for the separation of Li, Co, Mn, and Ni, the subsequent decomplexation of Ni and Co with EDTA, and a purification step to

Figure 9. (A) Method principle for Co and Li separation based on electrodialysis. Variations over time in Li quantities within the cells; impact of initial pH levels: (B) feed cell, (C) Li recovery cell, and (D) Co recovery cell. Variations over time in Co quantities within the cells; impact of initial pH levels: (E) feed cell, (F) Li recovery cell, and (G) Co recovery cell. (A-G) Figures reprinted with permission from Ref.[85]. Copyright 2023 Elsevier[85].

Figure 10. Changes with time in amounts of Li and Co in cells. (A) feed cell, (B) Li recovery cell, and (C) Co recovery cell[84]. Copyright 2013 Elsevier[84].

recover the final products. As shown in Figure 11A, the electrodialysis apparatus comprised Pt/Ti anodes, 316 stainless steel cathodes, and five chambers spatially arranged between two CEMs and two AEMs.

The separation of Li, Co, Mn, and Ni from NMC111 via electrodialysis consisted of a three-stage process: Ni in Stage 1; Co in Stage 2; and Li and Mn in Stage 3. During Stage 1, as shown in Figure 11B, the leachate comprised Li^+, Mn^{2+}, Co^{2+}, Ni^{2+}, and SO_4^{2-}. The introduction of EDTA selectively complexed with Ni to form
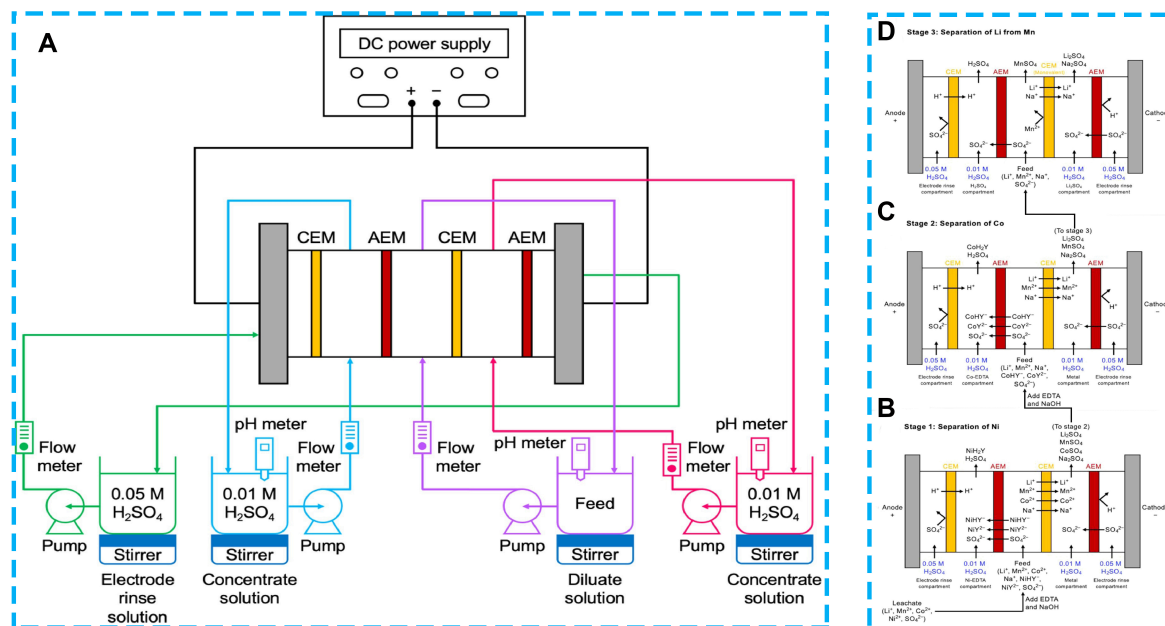
Figure 11. (A) Schematic diagram showing the electrodialysis experimental setup for the separation of Li, Ni, Mn, and Co from NMC111. Principles of the three-stage electrodialysis process for separating Li, Ni, Mn, and Co from NMC111: (B) separation of Ni in Stage 1; (C) Separation of Co in Stage 2; (D) separation of Li from Mn in Stage 3. (A-D) Figures reprinted with permission from Ref.[86]. Copyright 2012 Elsevier[86].

anionic Ni-EDTA species ($NiHY^-$ and NiY^{2-}). Driven by an electric field, $NiHY^-$, NiY^{2-}, and SO_4^{2-} ions traversed the AEM into the Ni-EDTA complex chamber, where they reacted with H^+ migrating from the electrode rinsing chamber to form NiH_2Y and H_2SO_4. Concurrently, Li^+, Mn^{2+}, Co^{2+}, and Na^+ ions migrated through the CEM to the metal chamber, reacting with SO_4^{2-} from the electrode rinsing chamber to form Li_2SO_4, $MnSO_4$, $CoSO_4$, and Na_2SO_4. These salts served as the input for Stage 2. As a result, Ni was effectively separated from Li, Mn, and Co in the first stage.

In Stage 2 [Figure 11C], the solution originating from the metal chamber of Stage 1 contained Li^+, Mn^{2+}, Co^{2+}, Na^+, and SO_4^{2-} ions. The addition of EDTA preferentially formed Co-EDTA complex anions ($CoHY^-$ and CoY^{2-}). Similar to Stage 1, $CoHY^-$, CoY^{2-}, and SO_4^{2-} ions were transported through the AEM to the Co-EDTA complex chamber, where they combined with H^+ ions migrating from the electrode rinsing chamber to form CoH_2Y and H_2SO_4. Concurrently, Li^+, Mn^{2+}, and Na^+ were transported through CEM to the metal chamber, and combined with SO_4^{2-} ions migrating from the electrode rinsing chamber to form Li_2SO_4, $MnSO_4$, and Na_2SO_4. These products served as the feed solution in Stage 3, achieving the separation of Co from Li and Mn in Stage 2.

In Stage 3 [Figure 11D], the solution from the metal chamber of Stage 2 contained Li^+, Mn^{2+}, Na^+, and SO_4^{2-}. Since Mn^{2+} ions did not completely form Mn-EDTA complex anions, changing the membrane configuration in the electrodialysis cell with monovalent CEMs enhanced selectivity for monovalent over divalent cations. Consequently, SO_4^{2-} ions passed through AEM to the H_2SO_4 compartment, joining H^+ ions migrating from the electrode rinse compartment to produce H_2SO_4. Simultaneously, Li^+ and Na^+ ions were transported through the monovalent CEM to the Li_2SO_4 compartment, where they merged with SO_4^{2-} ions migrating from the electrode rinsing compartment, forming Li_2SO_4 and Na_2SO_4. Mn^{2+} ions were hindered by monovalent CEM and retained in the feed compartment. Thus, Li was separated from Mn in Stage 3.

During the electrodialysis process, a 99.3% separation of Ni was achieved in the first stage when the molar ratio of EDTA to Ni was 1.1. In the second stage, with a molar ratio of EDTA to Co of 1.2, 87.3% of Co was separated. In the third stage, monovalent CEM facilitated the sequential separation of approximately 99% of Li and Mn. Post-experiment, Ni and Co were desorbed from EDTA at a pH below 0.5, allowing for the recovery of EDTA solids. Selective precipitation was then utilized to recover all four metals with purities exceeding 99%.

Due to the intricate composition of spent LIB cathode materials, which resulted in a diverse array of metal cations in the leachate, simple electrodialysis techniques were found to be inadequate for separation. The addition of chelating agents to form complexes with specific metal ions, converting them into anions for separation from other cations, offers a viable approach. Nevertheless, this method remains constrained by protracted separation times and the increased consumption of reagents.

Electrochemical lithium stripping
Electrochemical lithium stripping, grounded in the charge and discharge mechanisms of LIBs, employs electrical current instead of chemical reagents to drive reactions, thus facilitating selective lithium-ion removal from positive electrode materials. This approach can significantly diminish reagent consumption and circumvent lithium loss, thereby enhancing lithium recovery rates.

To recover the cathode material $LiMn_2O_4$, a slurry electrolysis method was proposed for the recuperation of Li and Mn [Figure 12A][87]. In the electrolytic cell, a filter cloth (< 50 μm) was employed to segregate the anode and cathode chamber. The electrolyte comprised a mixed solution of H_2SO_4 and $MnSO_4$, with graphite (cathode) and ruthenium-plated titanium electrode (anode), which was operated at 90 °C. Spent $LiMn_2O_4$ was introduced into the cathode chamber and dispersed. $LiMn_2O_4$ powder dissolved in the cathode chamber during electrolysis, releasing Mn^{2+} and Li^+ ions [Figure 12B]. The influence of H_2SO_4 and $MnSO_4$ concentrations, along with slurry and current densities, on the rates at which lithium and manganese leached is shown in Figure 12C-J. Optimal conditions included a slurry concentration of 75 g/L, a current density of 40 mA/cm², a reaction time of 20 h, and a 1 M solution of H_2SO_4 and $MnSO_4$. Under these conditions, the leaching rates of lithium and manganese reached 99% and 92%, respectively, with cathode and anode current efficiencies of 77% and 62%. After electrolysis, Mn^{2+} was oxidized to Mn^{4+} and precipitated as MnO_2 in the anode chamber, while Li^+ in the cathode reacted with Na_2CO_3 to produce Li_2CO_3 [Figure 12B]. The purities of the recovered MnO_2 and Li_2CO_3 were 92.33% and 99.59%, respectively, allowing for their direct reuse as raw materials to synthesize $LiMn_2O_4$ cathode materials. A preliminary economic analysis of recovering 1 ton of $LiMn_2O_4$ using this method was conducted on the recovery of lithium, indicating total revenue from the recovered products of \$2,353.59, with reagent and energy costs of \$442.43 and \$392.00, respectively, demonstrating the economic viability of this process.

Li *et al.*[88] introduced a method for recycling $LiFePO_4$ cathode materials that integrated the charging dynamics of $LiFePO_4$ batteries with a slurry electrolysis strategy, as illustrated in Figure 13A. This method employed an electrolytic cell divided into anode and cathode chambers by an AEM, with sodium chloride serving as the electrolyte, and Ru-coated Ti electrodes facilitating electrolysis. Within the anode chamber, used $LiFePO_4$ underwent oxidation under a positive potential to yield $FePO_4$, which liberated lithium ions into the electrolyte. Due to the insolubility of $FePO_4$ in water, it could be easily isolated through filtration. Concurrently, in the cathode chamber, a hydrogen evolution reaction produced sodium hydroxide as a secondary product. The impact of variables such as the leaching time, electric current density, sodium chloride concentration, and $LiFePO_4$ concentration on lithium extraction is detailed in Figure 13B-E. This method successfully extracted over 98% of lithium into the electrolyte and recovered more than 96% of iron
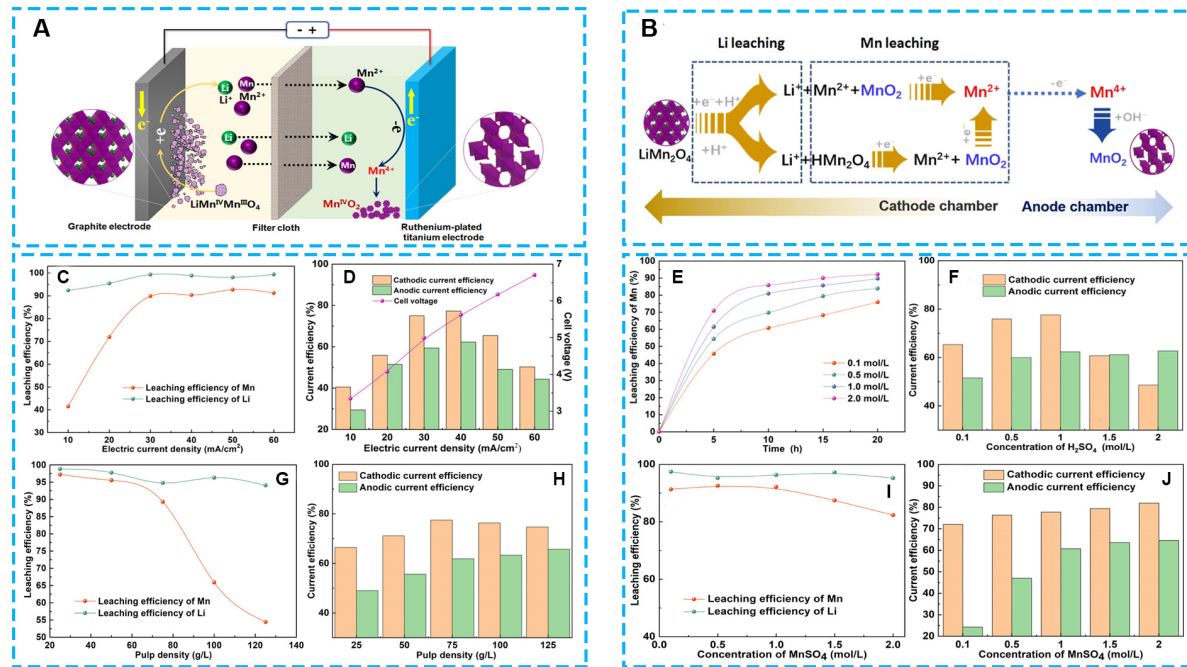
Figure 12. (A) Schematic representation of cathode material $LiMn_2O_4$ electrolysis. (B) Mechanism diagram of the cathode material $LiMn_2O_4$ electrolysis. Impact of electric current density on (C) the leaching efficiency, and (D) electrode current efficiency and cell voltage. Influence of H_2SO_4 concentration on (E) the leaching efficiency of Mn and (F) current efficiency. Impact of density on (G) leaching efficiency and (H) current efficiency. Influence of $MnSO_4$ concentration on the (I) leaching efficiency and (J) current efficiency. (A-J) Figures reprinted with permission from Ref.[87]. Copyright 2019 American Chemical Society[87].
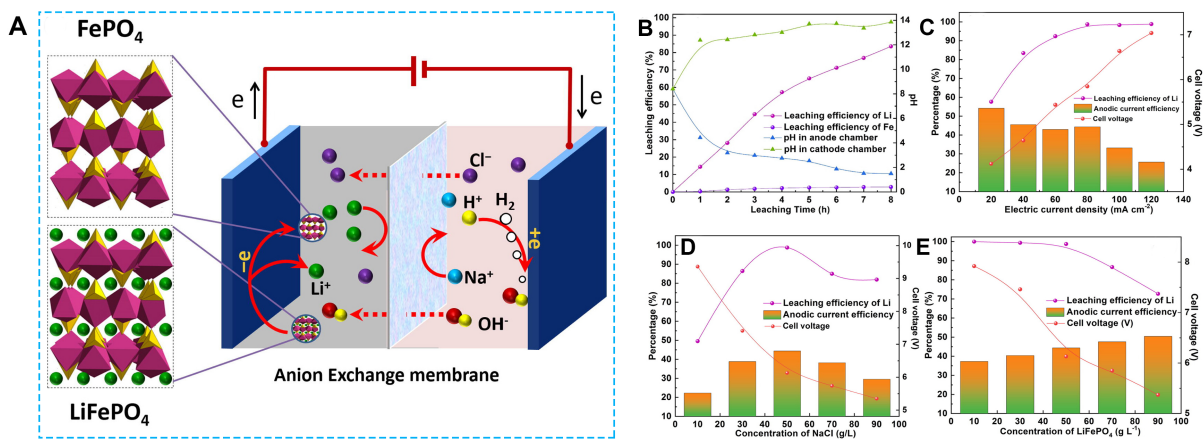

Figure 13. (A) Diagram illustrating the electrolysis process. Impact of (B) leaching duration, (C) electric current density, (D) sodium chloride concentration, and (E) $LiFePO_4$ concentration on the leaching efficiency of lithium[87]. (A-E) Figures reprinted with permission from Ref.[88]. Copyright 2019 Elsevier[88].

in the form of $FePO_4$, consuming 2,613.33 k/Wh of energy. Electron-driven reactions during slurry electrolysis negated the necessity for chemical reagents, such as oxidizing agents or acids. Filtration of the anode chamber yielded $FePO_4$, and the addition of sodium carbonate (Na_2CO_3) to the filtrate, thus, facilitated the recovery of lithium ions as $LiCO_3$.

Based on this method, a process route was proposed for the recycling of LiFePO$_4$ cathode materials through slurry electrolysis, as illustrated in Figure 14. The spent LiFePO$_4$ underwent oxidation and delithiation in the anode chamber due to electron activity. Concurrently, in the cathode chamber, the hydrogen evolution reaction occurred, producing NaOH. A minor amount of Cl$_2$ released during the slurry electrolysis process could be absorbed by the NaOH solution in the cathode chamber. More than 99% of Li could be leached into the electrolyte, resulting in an anolyte containing 7.55 g/L of Li. The high efficiency and selectivity of this process could enable the recovery of the most valuable elements without the need for prior separation and purification. The purity of the recovered FePO$_4$ reached 99.15%, allowing its use as a raw material for synthesizing LiFePO$_4$. The generated NaOH in the cathode electrolyte aided in removing Fe from the anode electrolyte. After filtration, Li$_2$CO$_3$ precipitated through evaporation and the addition of Na$_2$CO$_3$, reaching a purity of 99.69%. The resultant mother liquor, with a Li content of 2.53 g/L and Na content of 35.72 g/L, could be recycled as a cathode electrolyte. An economic analysis for recycling 1 ton of spent LiFePO$_4$ material was performed, and the costs for reagents and energy were identified as $71.45 and $395.15, respectively, while the revenue from the sale of Li$_2$CO$_3$, FePO$_4$, and NaOH products was approximately $2,846.01, demonstrating the economic viability of this recycling technology.

Employing NaCl as the electrolyte can decrease processing costs, while using lithium salts as electrolytes in both the anode and cathode can remove impurity elements and enhance conductivity. Li *et al.* utilized Li$_2$SO$_4$ and LiOH as the anode and cathode electrolytes, respectively, employing platinized titanium electrodes for electrolysis to achieve higher current efficiency[89]. The study added LiFePO$_4$ to the anode electrolyte, which underwent continuous leaching for Li$^+$ and FePO$_4$. Throughout the electrolysis process, Li$^+$ moved from the anode compartment to the cathode compartment through a CEM, driven by an electric field. Subsequent to electrolysis, LiOH·H$_2$O was produced through evaporation and crystallization. Under the optimal conditions of a current density of 60 mA/cm^2, an Li$_2$SO$_4$ concentration of 50 g/L, an LiOH concentration of 20 g/L, and an LiFePO$_4$ concentration of 100 g/L, the leaching rate of lithium surpassed 96%. The process achieved a current efficiency of 85.81%, with an energy consumption of 2,775.07 k/Wh.

Electrochemical regeneration

One of the primary failure mechanisms of LIB cathodes is the ongoing loss and consumption of Li$^+$ during cycling. Consequently, cathode material repair can be achieved by directly replenishing Li. Electrochemical regeneration processes often utilize conventional three-electrode or two-electrode systems, with the degraded cathode material acting as the working electrode for Li$^+$ insertion and structural restoration. The application of a cathodic potential to the depleted cathode serves as the principal driving force, effectively initiating the regeneration process and significantly reducing the activation energy required for Li$^+$ migration to lithium vacancies. This can lead to lithiation and structural repair of the material. After replenishing Li, the cathode material generally requires annealing in a specific atmosphere to completely restore its crystal structure, thus tightly organizing Li atoms within the structure.

Zhang *et al.* presented a technique for rejuvenating LiCoO$_2$ cathode materials by electrochemically driving Li$^+$ insertion into the depleted Li$_x$CoO$_2$[90]. As shown in Figure 15, the electrochemical apparatus included the cathode (spent Li$_x$CoO$_2$), anode (platinum foil), and reference electrode [Ag/AgCl saturated with KCl, 0.199 V *vs.* Normal Hydrogen Electrode (NHE)], with the electrolyte consisting of Li$_2$SO$_4$ solution at a specific concentration. The regeneration mechanism, as shown in Figure 15A, involved Li$^+$ migration toward vacancies within the Li$_x$CoO$_2$ structure, prompted by an electric current. Once a threshold voltage was achieved, Li$^+$ insertion concluded. Subsequent annealing at 700 °C expelled crystalline water, revitalizing the LiCoO$_2$ lattice structure. The completion time for full reduction decreased with increasing Li$^+$ concentration (0.1 to 1 M) and current density (0.12 to 0.42 mA/cm^2). The surface morphology and crystalline configuration of the regenerated material mirrored those of commercial LiCoO$_2$, achieving
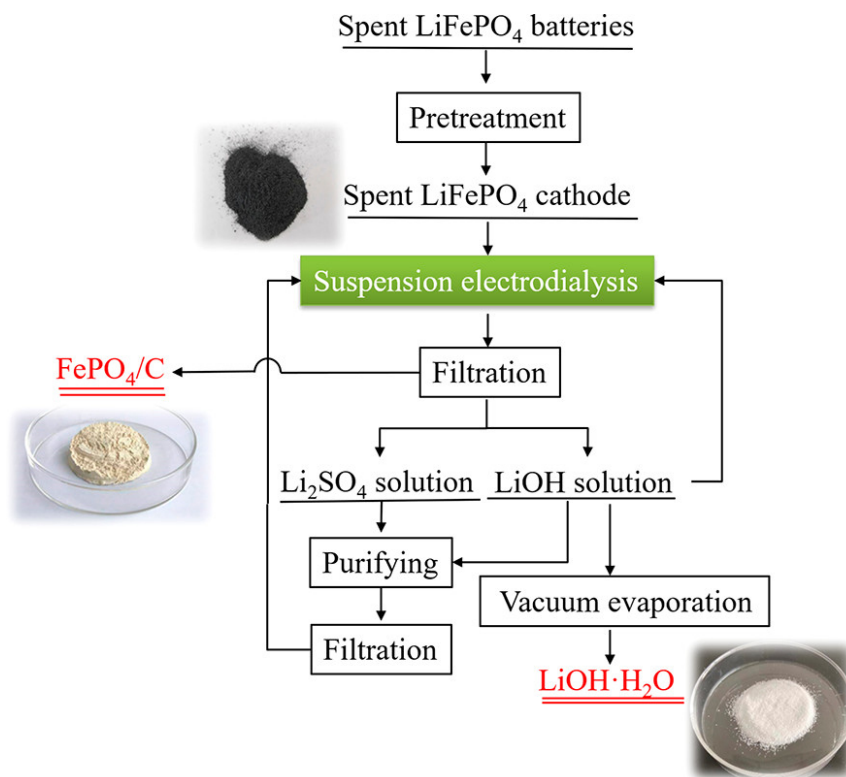
Figure 14. Flowsheet of the slurry electrolysis for recycling spent $LiFePO_4$[88]. Copyright 2019 Elsevier[88].

charge capacities of up to 136 mAh/g. Notably, the presence of impurities in the spent material significantly impaired the electrochemical properties of the regenerated $LiCoO_2$. Thus, purifying the regenerated cathode material of extraneous elements could pose a significant challenge for subsequent investigations.

Yang *et al.* recycled spent Li_xCoO_2 from dismantled LIBs, employing it as the cathode[91]. $LiCoO_2$ was used as the anode with the electrolyte of Li_2SO_4, facilitating the integration of Li^+ into Li_xCoO_2 through electrolysis, as shown in Figure 16A. After the working electrode voltage reached the cutoff point, Li_xCoO_2 fully transitioned to $LiCoO_2$. The reduced material underwent sintering at 700 °C for 6 h, yielding the regenerated product. The process then involved utilizing the $LiCoO_2$ electrode to replenish the depleted Li^+ in the electrolyte. As shown in Figure 16B, compared to conventional pyrometallurgy and hydrometallurgy, this method drastically reduced energy consumption to 6 mJ/kg and presented significant prospects for advancement.

In addition to directly replenishing the failed cathode material through electrochemical methods, another technique involves synthesizing the cathode material directly through electrochemical processes post-leaching, minimizing subsequent elemental separation steps and facilitating the direct reuse of the cathode material.

Wang *et al.* developed a method based on suspension electrolysis technology to directly leach $LiCoO_2$ in the anode region while re-synthesizing $LiCoO_2$ in the cathode region [Figure 17A][92]. This technique employed spent cathode material powders, derived from the crushed and mixed cathodes of various mobile phone batteries, containing elemental compositions of Co (46.50 wt%), Li (5.85 wt%), Mn (3.22 wt%), Ni (2.69 wt%), Cu (0.07 wt%), Al (11.35 wt%), and Fe (0.17 wt%). In the electrolytic apparatus, an acrylic
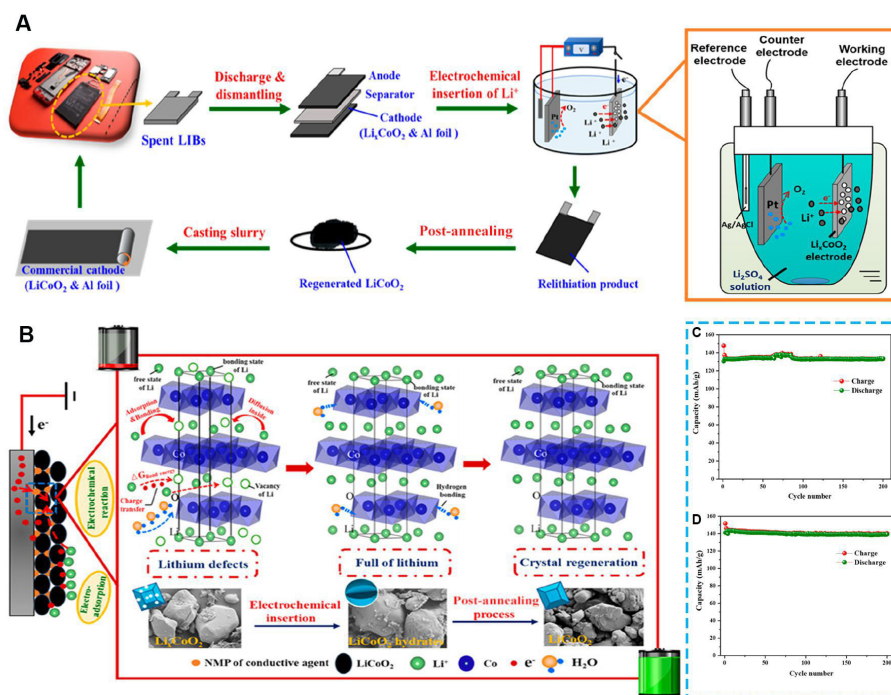
Figure 15. (A) Method for electrochemically inserting Li$^+$ into Li$_x$CoO$_2$ electrodes from the spent LIBs, thus generating new LiCoO$_2$ materials. (B) The proposed mechanism for directly regenerating LiCoO$_2$ materials through the electrochemical insertion of Li$^+$ ion into the Li$_x$CoO$_2$ electrode. Cycling performance of the Li/LiCoO$_2$ electrode from (C) the regenerated LiCoO$_2$ electrode and (D) commercial LiCoO$_2$ electrode at C/5 current rate. (A-D) Figures reprinted with permission from Ref.[89]. Copyright 2020 American Chemical Society[90].
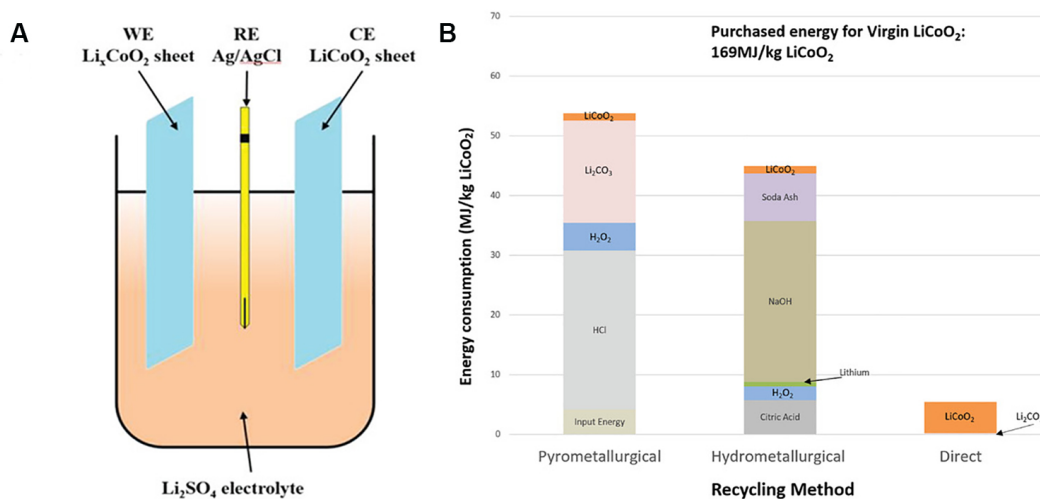

Figure 16. (A) The electrolytic cell used in the re-lithiation process under higher current density (0.4 mA/cm^2). (B) Comparative analysis of energy consumption between pyrometallurgy, hydrometallurgy, and direct recycling approaches for LiCoO$_2$. Figures reprinted with permission from Ref.[91]. Copyright 2020 Wiley[91].

fabric separated the cell into the anode and cathode compartments, utilizing platinum-coated titanium electrodes. The electrolyte was composed of NH$_4$HCO$_3$, (NH$_4$)$_2$SO$_3$, and NaF, where NH$_4$HCO$_3$ acted as a coordinating agent, (NH$_4$)$_2$SO$_3$ as a reducing agent, and NaF improved the conductivity of the electrolyte.
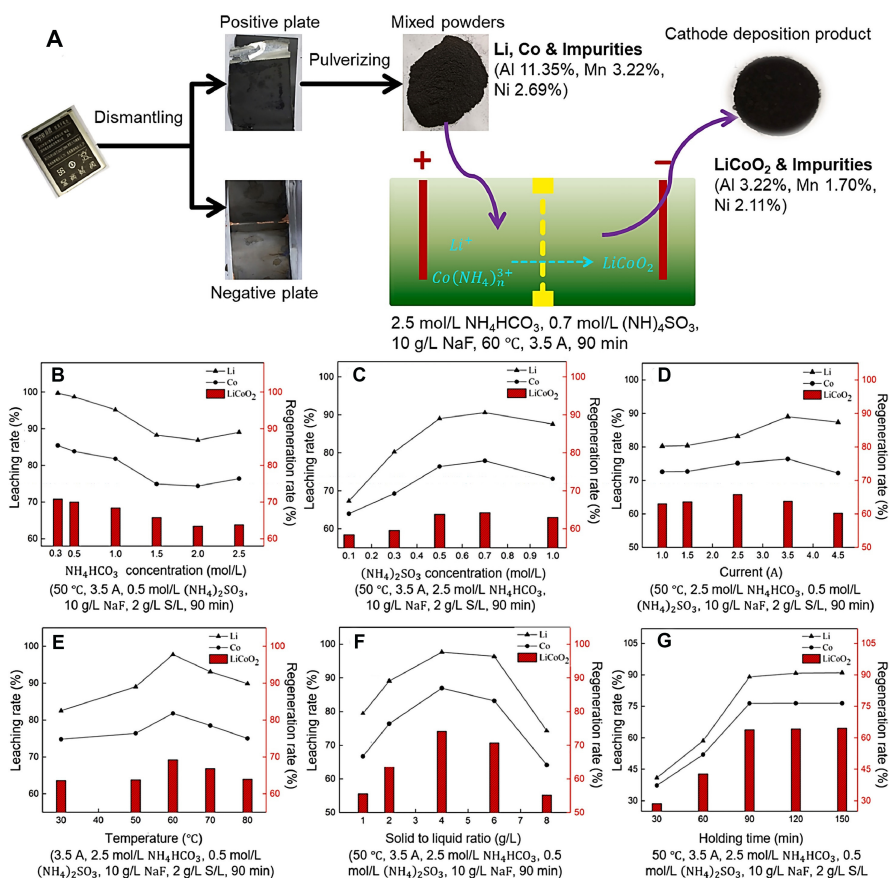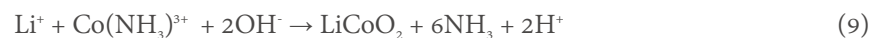
Figure 17. (A) Flow diagram depicting the recovery process of $LiCoO_2$ from discarded mobile phones. Impact of the (B) NH_4HCO_3 concentration, (C) $(NH_4)_2SO_3$ concentration, (D) current, (E) temperature, (F) solid-to-liquid ratio, and (G) holding time on the leaching rates of lithium and cobalt, and the regeneration rate of $LiCoO_2$. (A-G) Figures reprinted with permission from Ref.[84]. Copyright 2023 Elsevier[84].

The influence of NH_4HCO_3 and $(NH_4)_2SO_3$ concentrations, current, temperature, and holding time on the leaching rate and regeneration rate are shown in Figure 17B-G. The optimal conditions were 2.5 M NH_4HCO_3, 0.7 M/L $(NH_4)_2SO_3$, solid-to-liquid ratio of 4 g/L, temperature of 60 °C, current of 3.5 A, and holding time of 90 min. Under these conditions, Co and Li exhibited leaching rates of 55.4 and 71.8 wt%, respectively, with an $LiCoO_2$ recovery rate of 51.5 wt%. The primary reactions are detailed in:

$$Co^{3+} + 2NH_3 + 1/2SO_3^{2-} + OH^- \rightarrow Co(NH_3)^{2+} + 1/2SO_4^{2-} + 1/2H_2O \qquad (7)$$

$$Co(NH_3)_2^{2+} + 4NH_3 - e^- \rightarrow Co(NH_3)_6^{3+} \qquad (8)$$

$$Li^+ + Co(NH_3)^{3+} + 2OH^- \rightarrow LiCoO_2 + 6NH_3 + 2H^+ \qquad (9)$$

Based on the re-synthesis mechanism of $LiCoO_2$, Li *et al.* suggested regenerating $LiCoO_2$ through controlled electrochemical deposition reactions[93]. Following the leaching of spent $LiCoO_2$ with HNO_3, a solution of 4 M LiOH was introduced, and the pH of the leaching solution was adjusted to 11, to serve as the electrolyte for the electrolysis process. The electrolytic cell employed a Pt plate cathode and Ni plate anode, as shown in Figure 18. During electrolysis, a current density of 1.0 mA/cm^2 was applied at 100 °C for 20 h. Co $(OH)_2$ suspended in the 4 M LiOH solution was converted into $HCoO_2^-$ and migrated towards the anode due to the
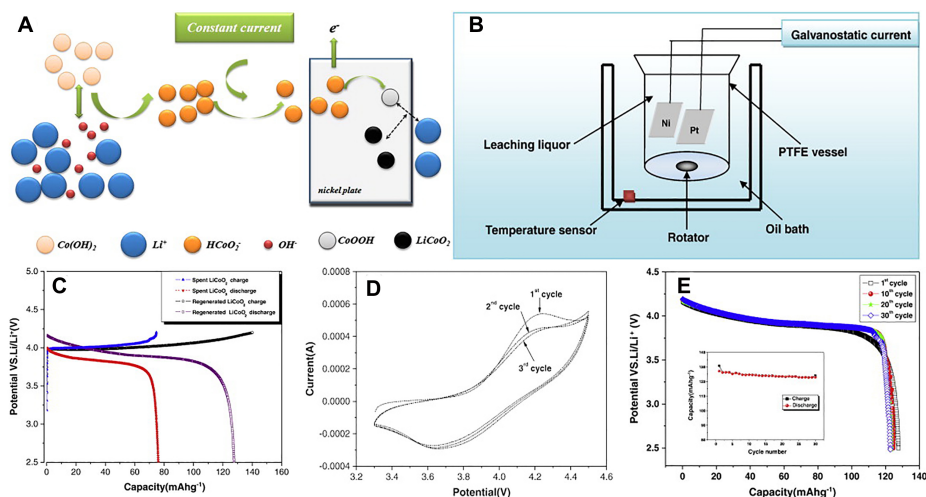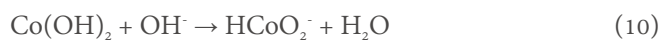
Figure 18. (A) Illustration of the re-synthesis mechanisms of $LiCoO_2$. (B) Schematic showing the recycling instrument using electrochemical deposition. (C) Charge-discharge characteristics of the spent and regenerated $LiCoO_2$ at a rate of 0.1 C. (D) Cyclic voltammogram of the $LiCoO_2$ material at a scan rate of 5 mV/s. (E) Cycling performance of regenerated $LiCoO_2$ at a rate of 0.1 C. (A-E) Figures reprinted with permission from Ref.[93]. Copyright 2011 Elsevier[93].

electric field. After reaching saturation near the anode, $HCoO_2^-$ ions deposited on the nickel plate as Co $(OH)_2$. Concurrently, electron transfer from Co $(OH)_2$ to the electrode occurred, changing the oxidation state of Co to +3 and forming a CoOOH film. In a highly concentrated LiOH solution, a Li^+/H^+ exchange occurred, leading to the formation of $LiCoO_2$. The primary reactions during electrolysis are expressed as:

$$Co(OH)_2 + OH^- \rightarrow HCoO_2^- + H_2O \qquad (10)$$

$$HCoO2^- \rightarrow CoOOH + e^- \qquad (11)$$

$$Li^+ + CoOOH \rightarrow LiCoO_2 + H^+ \qquad (12)$$

The initial capacities for charging and discharging of the regeneration $LiCoO_2$ were 130.8 and 127.2 mAh/g, respectively, in contrast to the capacity of commercial LCO of 140 mAh/g, as illustrated in Figure 18C. After 30 cycles, the capacity degradation remained below 4%, with a charging efficiency of 99.1%, as shown in Figure 18E. This method directly regenerated the positive electrode material from the filtrate of spent $LiCoO_2$. However, the electrochemical performance of the synthesized $LiCoO_2$ did not meet that of its commercial counterpart. The recycling process necessitated high temperatures and prolonged reaction times, leading to increased energy consumption. Moreover, the use of platinum electrodes may be impractical for large-scale applications.

Materials synthesized through electrochemical recycling can be applied in electrochemical sensors, supercapacitors, pseudocapacitors, and catalysts. Gonçalves *et al.* utilized AISI 430 stainless steel as the substrate and the leachate of spent LIB cathode materials as the electrolyte to prepare cobalt-containing materials through potentiostatic electrolysis[94]. These materials were used as non-enzymatic electrochemical sensors for glucose detection. The sensor demonstrated a sensitivity of 70.2 μA/(mmol·cm²) within a linear range of 1-10 mmol/L, providing a novel approach for developing sensors from recycled materials. Barbieri *et al.* investigated the recycling of cobalt from spent LIB cathodes[95]. The materials were recovered in the form of β-Co$(OH)_2$ and Co_3O_4 through thermal treatment, and both chemical and electrochemical

precipitation methods were employed to obtain the starting materials. The final products were used to fabricate electrodes comprising Co_3O_4, carbon black, and epoxy resin. These electrodes demonstrated high reversibility, charging efficiency, and specific capacitance (13.0 F/g at 1.0 mV/s), indicating their potential use as pseudocapacitors. Aboelazm *et al.* utilized electrodeposition under a magnetic field to form cobalt oxides from spent LIBs[96]. The resulting nanostructures exhibited a large electroactive surface area, which contributed to their excellent electrochemical performance and capacitive behavior. Electrochemical tests demonstrated a capacitive retention of 96% after 5,000 cycles and a charge storage capacity of 1,273 F/g at a current density of 1 A/g. Falqueto *et al.* utilized recycled cobalt from spent LIBs as a catalyst for azo dye degradation. Metallic cobalt was obtained through electrodeposition (-1.1 V, 15 C/cm², pH 2.7) from a solution leached from the spent LIB cathodes[97]. When combined with 0.27 mol/L H_2O_2, the material achieved a decolorization efficiency of 85% for azo dye after 210 min under UV radiation, indicating promising catalytic properties.

COMPARISON OF THE VARIOUS RECYCLING PROCESS FOR SPENT LIBS

Table 2 compares different recycling methods. Generally, pyrometallurgy operates at high temperatures (> 700 °C), resulting in high energy consumption and the emission of toxic and hazardous gases during the roasting process. However, it does not produce wastewater, with strong adaptability to raw materials, and involves simple process steps, making it widely used commercially with a profit margin of approximately -2.6 to 0.26 kg^{-1}. Compared to pyrometallurgy, hydrometallurgy has lower energy consumption, higher metal recovery rates, and produces higher-quality products. However, hydrometallurgy involves complex operational steps and requires large amounts of chemical reagents, leading to increased acidic waste, with a profit margin of approximately -1.4 to 0.225 $/kg.

By contrast, electrochemical techniques have broader applicability in the recycling of spent LIBs. These techniques utilize electron-mediated redox reactions instead of high-temperature roasting and chemical reagents as the reaction driving force, allowing reactions to proceed at lower temperatures and reagent concentrations. As a result, electrochemical methods offer advantages over traditional recycling methods in terms of process conditions and resource consumption. These methods also require relatively low electricity and reagent consumption, reducing costs, and generating non-toxic or -hazardous substances, leading to minimal waste and lower environmental costs. The metal recovery rate using electrochemical methods can exceed 99%, with high product quality, resulting in higher economic benefits. Although electrochemical regeneration methods offer low energy and reagent consumption, they cannot remove impurities from waste materials, leading to the inferior electrochemical performance of regenerated cathode materials compared to the original materials. Additionally, the regeneration method requires precise determination of lithium content in spent cathode materials to determine the necessary amount of lithium supplementation, making it less adaptable for raw materials and requiring stringent regeneration conditions, and hindering large-scale application.

CONCLUSION AND OUTLOOK

The growing global use of LIBs has led to a significant increase in their disposal, creating considerable environmental risks. As a result, the organic electrolytes and heavy metals contained in these materials will seep into the soil and water bodies, causing significant ecological damage. Additionally, these batteries serve as a source of valuable metals, such as Ni, Co, and Li, making their recycling a critical area of current research.

The advantages of pyrometallurgical recycling encompass its capability to process a broad spectrum of feedstocks, its high operational capacity, facile methodology, and the elimination of pre-treatment

Table 2. Comparison of the various recovery processes for spent LIBs[98]

Method	Advantages	Disadvantages
Pyrometallurgy	• No wastewater • Fewer processing steps • Direct melting allows recovery of metals as alloys	• Larger energy input required • Hazardous gases emissions • Li loss
Hydrometallurgy	• High sustainability • High extraction efficiency • Low energy consumption • Little hazardous gas emission • Low capital cost	• Complex operation steps • A large quantity of waste • Hazardous gases emissions • Additional expense for disposal of the hazardous gases, acidic leachates, and acid wastewater
Electrochemistry method	• Low operating cost • Minimal use of chemicals • Metal recovery rate is greater than 99% • No waste emissions	• The energy consumption in the process of separating the current collector and the cathode material is high (4.7 kwhkg^{-1}) • The potentials of cobalt ions and nickel ions in the leachate are similar and cannot be separated by electrodeposition The electrochemical delithiation process is prone to side reactions, resulting in reduced current density and current efficiency (< 86%) • The electrochemical performance of the recycled cathode material is worse than that of the original cathode material

prerequisites. In developed nations, pyrometallurgy has emerged as the predominant technology for recycling spent LIBs, primarily attributed to the fact that recycling firms often do not bear the feedstock expenses and can levy disposal charges. Nonetheless, pyrometallurgical recycling is not without its disadvantages, which include substantial energy requirements, low metal recovery rates, rigorous equipment demands, and the need for additional alloy separation post-processing. Moreover, conventional pyrometallurgical approaches fail to recuperate lithium, leading to a loss in valuable lithium resources. To enhance the extraction and purification of valuable metal from spent LIBs, pyrometallurgy must be integrated with hydrometallurgical processes, thus compounding the complexity of the overall recycling methodology.

Compared to pyrometallurgy, hydrometallurgical recycling offers benefits such as increased efficiency, lower emissions of toxic gases, enhanced purity of the recovered metals or metal salts, and more moderate reaction conditions. Consequently, in China, by leveraging well-established metallurgical technologies and a robust hydrometallurgical industry, hydrometallurgy has emerged as the predominant technology for recycling spent LIBs. However, hydrometallurgical recycling processes are characterized by longer durations, higher chemical usage, and increased wastewater discharge, leading to greater environmental pollution.

The utilization of electrochemical techniques in recycling spent LIBs significantly differs from traditional pyrometallurgy and hydrometallurgy. This technology dramatically reduces the utilization of chemical reagents while improving the efficiency of element separation and recovery rates, showcasing considerable industrial applicability. During the preprocessing stage, applying voltage aids in separating active substances from the current collector, enabling the detachment of positive electrode materials and the recovery of intact, reusable aluminum/copper foils. Additionally, electrochemical-assisted leaching, driven by external current, can facilitate the efficient leaching of positive electrode materials while minimizing the need for chemical reagents in hydrometallurgical processes. Electrochemical deposition, by applying specific potentials, utilizes the differences in deposition potentials among various metal ions in the leaching solution to facilitate the targeted separation and recovery of valuable metals. Electrodialysis, which involves the selective movement of ions through a semi-permeable membrane under an electric field, allows for the selective separation of metal ions in the leaching solution. Importantly, electrochemical techniques can also regenerate cathode materials from spent LIBs. By applying an external voltage, lithium ions can be reintroduced into the cathode materials, compensating for lithium ion loss and achieving the direct

regeneration of these materials.

In the process of recycling spent LIBs, electrochemical technology holds significant promise for future applications. Future research should mainly focus on the following aspects.

(1) Technical optimization and process improvement: Future development of electrochemical methods should prioritize optimizing process parameters to enhance recovery efficiency and metal purity. This includes improving electrode materials, optimizing electrolyte compositions, and fine-tuning operational conditions to achieve more efficient and stable metal recovery.

(2) Minimizing energy consumption and environmental impact: By utilizing clean energy sources (e.g., wind and solar power) to supply electricity, the carbon footprint of the electrochemical recovery process may be significantly reduced. Additionally, developing more efficient electrodes and electrochemical equipment to lower energy consumption and improve energy efficiency could serve as a key direction for future research.

(3) Multi-metal recovery and separation: Given the coexistence of multiple metals in spent LIBs, future development of electrochemical methods should focus on achieving the efficient separation and recovery of various metals. By adjusting electrochemical parameters, the selective separation of different metal ions may be realized, avoiding the use of complex chemical reagents and extractants and reducing environmental burden.

(4) Scale-up and industrial application: Currently, electrochemical recycling technology is primarily at the laboratory research stage. Future efforts should aim to scale these technologies for industrial application. This includes developing large-scale, efficient electrochemical recycling equipment and drawing on the successful experiences of other electrochemical industries, such as electroplating and electrodeposition, to drive the industrialization of this technology.

(5) Comprehensive utilization of waste and circular economy: Future electrochemical recycling methods should not only focus on metal recovery but also explore the comprehensive utilization of waste generated during the process. For example, by using by-products generated during recovery to produce new materials or directly applying recovered metals to manufacture new batteries or other functional materials, resource closed-loop recycling may be achieved, promoting the development of a circular economy.

(6) Interdisciplinary collaboration and innovation: The future development of electrochemical recycling technology should rely on collaborative innovation across disciplines such as chemistry, materials science, environmental science, and engineering. Through interdisciplinary cooperation, new electrode materials may be developed, innovative electrochemical reaction systems may be explored, and new recovery pathways can be identified, driving breakthrough advancements in the application of electrochemical methods in LIB recycling.

DECLARATIONS

Visualization, validation: Xiao C

Conflicts of interest
All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate
Not applicable.

Consent for publication
Not applicable.

REFERENCES

1. Hantanasirisakul K, Sawangphruk M. Sustainable reuse and recycling of spent Li-ion batteries from electric vehicles: chemical, environmental, and economical perspectives. *Glob Chall* 2023;7:2200212. DOI PubMed PMC
2. Fu Y, He Y, Qu L, et al. Enhancement in leaching process of lithium and cobalt from spent lithium-ion batteries using benzenesulfonic acid system. *Waste Manag* 2019;88:191-9. DOI
3. Zhang X, Xie Y, Lin X, Li H, Cao H. An overview on the processes and technologies for recycling cathodic active materials from spent lithium-ion batteries. *J Mater Cycles Waste Manag* 2013;15:420-30. DOI
4. Ordoñez J, Gago E, Girard A. Processes and technologies for the recycling and recovery of spent lithium-ion batteries. *Renew Sustain Energy Rev* 2016;60:195-205. DOI
5. Zhou L, Zhang K, Hu Z, et al. Recent developments on and prospects for electrode materials with hierarchical structures for lithium-ion batteries. *Adv Energy Mater* 2018;8:1701415. DOI
6. evtank.cn. Beijing: China YiWei institute of economics; c2024. Available from: http://www.evtank.cn/DownloadDetail.aspx?ID=547 [Last accessed on 18 Jul 2024].
7. itdcw.com. Beijing: battery network; c2023. Available from: https://www.itdcw.com/news/hangyebaogao/011G332922023.html [Last accessed on 18 Jul 2024].
8. Natarajan S, Aravindan V. Burgeoning prospects of spent lithium-ion batteries in multifarious applications. *Adv Energy Mater* 2018;8:1802303. DOI
9. Fan E, Li L, Wang Z, et al. Sustainable recycling technology for Li-ion batteries and beyond: challenges and future prospects. *Chem Rev* 2020;120:7020-63. DOI
10. recellcenter.org. Chicago: U.S. Department of energy office of science, UChicago Argonne LLC. Available from: https://recellcenter.org/research [Last accessed on 18 Jul 2024].
11. Hou J, Yang M, Wang D, Zhang J. Fundamentals and challenges of lithium ion batteries at temperatures between -40 and 60 °C. *Adv Energy Mater* 2020;10:1904152. DOI
12. Arshad F, Li L, Amin K, et al. A comprehensive review of the advancement in recycling the anode and electrolyte from spent lithium ion batteries. *ACS Sustain Chem Eng* 2020;8:13527-54. DOI
13. Liu W, Li X, Xiong D, et al. Significantly improving cycling performance of cathodes in lithium ion batteries: the effect of Al_2O_3 and $LiAlO_2$ coatings on $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$. *Nano Energy* 2018;44:111-20. DOI
14. Kretschmer K, Sun B, Su D, Zhao Y, Wang G. Scalable preparation of $LiFePO_4$/C nanocomposites with sp^2-coordinated carbon coating as high-performance cathode materials for lithium-ion batteries. *ChemElectroChem* 2015;2:2096-103. DOI
15. Yuan L, Wang Z, Zhang W, et al. Development and challenges of $LiFePO_4$ cathode material for lithium-ion batteries. *Energy Environ Sci* 2011;4:269-84. DOI
16. Okubo M, Hosono E, Kim J, et al. Nanosize effect on high-rate Li-ion intercalation in $LiCoO_2$ electrode. *J Am Chem Soc*

    2007;129:7444-52. DOI

17. Luo F, Wei C, Zhang C, et al. Operando X-ray diffraction analysis of the degradation mechanisms of a spinel $LiMn_2O_4$ cathode in different voltage windows. *J Energy Chem* 2020;44:138-46. DOI

18. Xia S, Huang W, Shen X, et al. Rearrangement on surface structures by boride to enhanced cycle stability for $LiNi_{0.80}Co_{0.15}Al_{0.05}O_2$ cathode in lithium ion batteries. *J Energy Chem* 2020;45:110-8. DOI

19. Li P, Luo S, Zhang L, et al. Progress, challenges, and prospects of spent lithium-ion batteries recycling: a review. *J Energy Chem* 2024;89:144-71. DOI

20. Xue Y, Wang Y. Green electrochemical redox mediation for valuable metal extraction and recycling from industrial waste. *Green Chem* 2020;22:6288-309. DOI

21. Kim K, Candeago R, Rim G, Raymond D, Park AA, Su X. Electrochemical approaches for selective recovery of critical elements in hydrometallurgical processes of complex feedstocks. *iScience* 2021;24:102374. DOI PubMed PMC

22. Du K, Ang EH, Wu X, Liu Y. Progresses in sustainable recycling technology of spent lithium-ion batteries. *Energy Environ Mater* 2022;5:1012-36. DOI

23. Chen M, Ma X, Chen B, et al. Recycling end-of-life electric vehicle lithium-ion batteries. *Joule* 2019;3:2622-46. DOI

24. tatista.com. Average lithium carbonate price from 2010 to 2023, Available from: https://www.statista.com/statistics/606350/battery-grade-lithium-carbonate-price/ [Last accessed on 18 Jul 2024].

25. Ma X, Azhari L, Wang Y. Li-ion battery recycling challenges. *Chem* 2021;7:2843-7. DOI

26. Mrozik W, Rajaeifar MA, Heidrich O, Christensen P. Environmental impacts, pollution sources and pathways of spent lithium-ion batteries. *Energy Environ Sci* 2021;14:6099-121. DOI

27. Chan KH, Anawati J, Malik M, Azimi G. Closed-loop recycling of lithium, cobalt, nickel, and manganese from waste lithium-ion batteries of electric vehicles. *ACS Sustain Chem Eng* 2021;9:4398-410. DOI

28. Lisbona D, Snee T. A review of hazards associated with primary lithium and lithium-ion batteries. *Process Saf Environ* 2011;89:434-42. DOI

29. Miao Y, Liu L, Xu K, Li J. High concentration from resources to market heightens risk for power lithium-ion battery supply chains globally. *Environ Sci Pollut Res Int* 2023;30:65558-71. DOI

30. Harper G, Sommerville R, Kendrick E, et al. Recycling lithium-ion batteries from electric vehicles. *Nature* 2019;575:75-86. DOI

31. Larcher D, Tarascon JM. Towards greener and more sustainable batteries for electrical energy storage. *Nat Chem* 2015;7:19-29. DOI PubMed

32. Meshram P, Pandey B, Mankhand T. Extraction of lithium from primary and secondary sources by pre-treatment, leaching and separation: a comprehensive review. *Hydrometallurgy* 2014;150:192-208. DOI

33. Wang Y, An N, Wen L, et al. Recent progress on the recycling technology of Li-ion batteries. *J Energy Chem* 2021;55:391-419. DOI

34. Li L, Zhang X, Li M, et al. The recycling of spent lithium-ion batteries: a review of current processes and technologies. *Electrochem Energ Rev* 2018;1:461-82. DOI

35. Shi Y, Zhang M, Meng YS, Chen Z. Ambient-pressure relithiation of degraded $Li_xNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ ($0 < x < 1$) via eutectic solutions for direct regeneration of lithium-ion battery cathodes. *Adv Energy Mater* 2019;9:1900454. DOI

36. Lai Y, Zhu X, Li J, et al. Efficient recovery of valuable metals from cathode materials of spent $LiCoO_2$ batteries via co-pyrolysis with cheap carbonaceous materials. *Waste Manag* 2022;148:12-21. DOI

37. Li J, Lai Y, Zhu X, et al. Pyrolysis kinetics and reaction mechanism of the electrode materials during the spent $LiCoO_2$ batteries recovery process. *J Hazard Mater* 2020;398:122955. DOI

38. Baum ZJ, Bird RE, Yu X, Ma J. Lithium-ion battery recycling - overview of techniques and trends. *ACS Energy Lett* 2022;7:712-9. DOI

39. Zhou M, Li B, Li J, Xu Z. Pyrometallurgical technology in the recycling of a spent lithium ion battery: evolution and the challenge. *ACS EST Eng* 2021;1:1369-82. DOI

40. Makuza B, Tian Q, Guo X, Chattopadhyay K, Yu D. Pyrometallurgical options for recycling spent lithium-ion batteries: a comprehensive review. *J Power Sources* 2021;491:229622. DOI

41. Rombach E, Friedrich B. Chapter 10 - recycling of rare metals. In: Worrell E, Reuter MA, editors. Handbook of recycling. Amsterdam: Elsevier; 2014. pp. 125-50. DOI

42. Xu P, Tan DH, Gao H, Rose S, Chen Z. Recycling of Li-ion batteries for electric vehicles. In: Cabeza LF, editor. Encyclopedia of energy storage. Amsterdam: Elsevier; 2022. pp. 98-107. DOI

43. Zhang Y, Wang W, Fang Q, Xu S. Improved recovery of valuable metals from spent lithium-ion batteries by efficient reduction roasting and facile acid leaching. *Waste Manag* 2020;102:847-55. DOI

44. Yan Z, Sattar A, Li Z. Priority lithium recovery from spent Li-ion batteries via carbothermal reduction with water leaching. *Resour Conserv Recy* 2023;192:106937. DOI

45. Zheng R, Zhao L, Wang W, et al. Optimized Li and Fe recovery from spent lithium-ion batteries via a solution-precipitation method. *RSC Adv* 2016;6:43613-25. DOI

46. Chen X, Ma H, Luo C, Zhou T. Recovery of valuable metals from waste cathode materials of spent lithium-ion batteries using mild phosphoric acid. *J Hazard Mater* 2017;326:77-86. DOI PubMed

47. Li J, Shi P, Wang Z, Chen Y, Chang CC. A combined recovery process of metals in spent lithium-ion batteries. *Chemosphere* 2009;77:1132-6. DOI

48. Zhu S, He W, Li G, Zhou X, Zhang X, Huang J. Recovery of Co and Li from spent lithium-ion batteries by combination method of acid leaching and chemical precipitation. *T Nonferr Metal Soc* 2012;22:2274-81. DOI

49. Jha MK, Kumari A, Jha AK, Kumar V, Hait J, Pandey BD. Recovery of lithium and cobalt from waste lithium ion batteries of mobile phone. *Waste Manag* 2013;33:1890-7. DOI PubMed

50. Bertuol DA, Machado CM, Silva ML, Calgaro CO, Dotto GL, Tanabe EH. Recovery of cobalt from spent lithium-ion batteries using supercritical carbon dioxide extraction. *Waste Manag* 2016;51:245-51. DOI PubMed

51. Lee CK, Rhee K. Reductive leaching of cathodic active materials from lithium ion battery wastes. *Hydrometallurgy* 2003;68:5-10. DOI

52. Meshram P, Pandey BD, Mankhand TR. Recovery of valuable metals from cathodic active material of spent lithium ion batteries: leaching and kinetic aspects. *Waste Manag* 2015;45:306-13. DOI PubMed

53. Meshram P, Abhilash, Pandey BD, Mankhand TR, Deveci H. Comparison of different reductants in leaching of spent lithium ion batteries. *JOM* 2016; 68:2613-2623. DOI

54. Wang R, Lin Y, Wu S. A novel recovery process of metal values from the cathode active materials of the lithium-ion secondary batteries. *Hydrometallurgy* 2009;99:194-201. DOI

55. Li L, Qu W, Zhang X, et al. Succinic acid-based leaching system: a sustainable process for recovery of valuable metals from spent Li-ion batteries. *J Power Sources* 2015;282:544-51. DOI

56. Li L, Lu J, Ren Y, et al. Ascorbic-acid-assisted recovery of cobalt and lithium from spent Li-ion batteries. *J Power Sources* 2012;218:21-7. DOI

57. Li L, Ge J, Wu F, Chen R, Chen S, Wu B. Recovery of cobalt and lithium from spent lithium ion batteries using organic citric acid as leachant. *J Hazard Mater* 2010;176:288-93. DOI

58. Sun L, Qiu K. Organic oxalate as leachant and precipitant for the recovery of valuable metals from spent lithium-ion batteries. *Waste Manag* 2012;32:1575-82. DOI

59. Li L, Dunn JB, Zhang XX, et al. Recovery of metals from spent lithium-ion batteries with organic acids as leaching reagents and environmental assessment. *J Power Sources* 2013;233:180-9. DOI

60. Sun C, Xu L, Chen X, Qiu T, Zhou T. Sustainable recovery of valuable metals from spent lithium-ion batteries using DL-malic acid: Leaching and kinetics aspect. *Waste Manag Res* 2018;36:113-20. DOI PubMed

61. Li L, Bian Y, Zhang X, et al. Economical recycling process for spent lithium-ion batteries and macro- and micro-scale mechanistic study. *J Power Sources* 2018;377:70-9. DOI

62. Yao L, Feng Y, Xi G. A new method for the synthesis of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ from waste lithium ion batteries. *RSC Adv* 2015;5:44107-14. DOI

63. Li L, Bian Y, Zhang X, et al. Process for recycling mixed-cathode materials from spent lithium-ion batteries and kinetics of leaching. *Waste Manag* 2018;71:362-71. DOI

64. Feng Y, Yang L, Liu J, Logan BE. Electrochemical technologies for wastewater treatment and resource reclamation. *Environ Sci Wat Res* 2016;2:800-31. DOI

65. Wang M, Tan Q, Chiang JF, Li J. Recovery of rare and precious metals from urban mines - a review. *Front Environ Sci Eng* 2017;11:1-17. DOI

66. Ambaye TG, Vaccari M, Castro FD, Prasad S, Rtimi S. Emerging technologies for the recovery of rare earth elements (REEs) from the end-of-life electronic wastes: a review on progress, challenges, and perspectives. *Environ Sci Pollut Res Int* 2020;27:36052-74. DOI PubMed

67. Kim S, Lee J, Kim S, Kim S, Yoon J. Electrochemical lithium recovery with a $LiMn_2O_4$-zinc battery system using zinc as a negative electrode. *Energy Tech* 2018;6:340-4. DOI

68. Calvo EJ. Electrochemical methods for sustainable recovery of lithium from natural brines and battery recycling. *Curr Opin Electroche* 2019;15:102-8. DOI

69. Zhou G, Chen L, Chao Y, Li X, Luo G, Zhu W. Progress in electrochemical lithium ion pumping for lithium recovery. *J Energy Chem* 2021;59:431-45. DOI

70. Petersen HA, Myren THT, O'sullivan SJ, Luca OR. Electrochemical methods for materials recycling. *Mater Adv* 2021;2:1113-38. DOI

71. Bi H, Zhu H, Zu L, Bai Y, Gao S, Gao Y. A new model of trajectory in eddy current separation for recovering spent lithium iron phosphate batteries. *Waste Manag* 2019;100:1-9. DOI

72. Wang F, Zhang T, He Y, et al. Recovery of valuable materials from spent lithium-ion batteries by mechanical separation and thermal treatment. *J Clean Prod* 2018;185:646-52. DOI

73. Guo Y, Li F, Zhu H, Li G, Huang J, He W. Leaching lithium from the anode electrode materials of spent lithium-ion batteries by hydrochloric acid (HCl). *Waste Manag* 2016;51:227-33. DOI

74. Contestabile M, Panero S, Scrosati B. A laboratory-scale lithium-ion battery recycling process. *J Power Sources* 2001;92:65-9. DOI

75. Cao N, Zhang Y, Chen L, et al. An innovative approach to recover anode from spent lithium-ion battery. *J Power Sources* 2021;483:229163. DOI

76. Chu W, Zhang Y, Chen L, Wu K, Huang Y, Jia Y. Comprehensive recycling of Al foil and active materials from the spent lithium-ion battery. *Sep Purif Technol* 2021;269:118704. DOI

77. Lei S, Zhang Y, Song S, et al. Strengthening valuable metal recovery from spent lithium-ion batteries by environmentally friendly

reductive thermal treatment and electrochemical leaching. *ACS Sustain Chem Eng* 2021;9:7053-62. DOI

78. Diaz LA, Strauss ML, Adhikari B, Klaehn JR, Mcnally JS, Lister TE. Electrochemical-assisted leaching of active materials from lithium ion batteries. *Resour Conserv Recy* 2020;161:104900. DOI

79. Prabaharan G, Barik SP, Kumar N, Kumar L. Electrochemical process for electrode material of spent lithium ion batteries. *Waste Manag* 2017;68:527-33. DOI PubMed

80. Freitas M, Celante V, Pietre M. Electrochemical recovery of cobalt and copper from spent Li-ion batteries as multilayer deposits. *J Power Sources* 2010;195:3309-15. DOI

81. Freitas M, Garcia E. Electrochemical recycling of cobalt from cathodes of spent lithium-ion batteries. *J Power Sources* 2007;171:953-9. DOI

82. Freitas MBJG, Garcia EM, Celante VG. Electrochemical and structural characterization of cobalt recycled from cathodes of spent Li-ion batteries. *J Appl Electrochem* 2009;39:601-7. DOI

83. Peng F, Mu D, Li R, et al. Impurity removal with highly selective and efficient methods and the recycling of transition metals from spent lithium-ion batteries. *RSC Adv* 2019;9:21922-30. DOI PubMed PMC

84. Iizuka A, Yamashita Y, Nagasawa H, Yamasaki A, Yanagisawa Y. Separation of lithium and cobalt from waste lithium-ion batteries via bipolar membrane electrodialysis coupled with chelation. *Sep Purif Technol* 2013;113:33-41. DOI

85. Li X, Liu S, Yang J, He Z, Zheng J, Li Y. Electrochemical methods contribute to the recycling and regeneration path of lithium-ion batteries. *Energy Stor Mater* 2023;55:606-30. DOI

86. Chan KH, Malik M, Azimi G. Separation of lithium, nickel, manganese, and cobalt from waste lithium-ion batteries using electrodialysis. *Resour Conserv Recy* 2022;178:106076. DOI

87. Li Z, He L, Zhao ZW, Wang D, Xu W. Recovery of lithium and manganese from scrap $LiMn_2O_4$ by slurry electrolysis. *ACS Sustain Chem Eng* 2019;7:16738-46. DOI

88. Li Z, Liu D, Xiong J, He L, Zhao Z, Wang D. Selective recovery of lithium and iron phosphate/carbon from spent lithium iron phosphate cathode material by anionic membrane slurry electrolysis. *Waste Manag* 2020;107:1-8. DOI

89. Li Z, He L, Zhu Y, Yang C. A green and cost-effective method for production of LiOH from spent $LiFePO_4$. *ACS Sustain Chem Eng* 2020;8:15915-26. DOI

90. Zhang L, Xu Z, He Z. Electrochemical relithiation for direct regeneration of $LiCoO_2$ materials from spent lithium-ion battery electrodes. *ACS Sustain Chem Eng* 2020;8:11596-605. DOI

91. Yang T, Lu Y, Li L, et al. An effective relithiation process for recycling lithium-ion battery cathode materials. *Adv Sustain Syst* 2020;4:1900088. DOI

92. Wang J, Lv J, Zhang M, et al. Recycling lithium cobalt oxide from its spent batteries: an electrochemical approach combining extraction and synthesis. *J Hazard Mater* 2021;405:124211. DOI

93. Li L, Chen R, Sun F, Wu F, Liu J. Preparation of $LiCoO_2$ films from spent lithium-ion batteries by a combined recycling process. *Hydrometallurgy* 2011;108:220-5. DOI

94. Gonçalves SA, Garcia EM, Taroco HA, et al. Development of non-enzymatic glucose sensor using recycled cobalt from cell phone Li-ion batteries. *Waste Manag* 2015;46:497-502. DOI

95. Barbieri EMS, Lima EPC, Lelis MFF, Freitas MBJG. Recycling of cobalt from spent Li-ion batteries as β-Co $(OH)_2$ and the application of Co_3O_4 as a pseudocapacitor. *J Power Sources* 2014;270:158-65. DOI

96. Aboelazm EAA, Ali GAM, Algarni H, Yin H, Zhong YL, Chong FK. Magnetic electrodeposition of the hierarchical cobalt oxide nanostructure from spent lithium-ion batteries: its application as a supercapacitor electrode. *J Phys Chem C* 2018;122:12200-206. DOI

97. Falqueto JB, Magnago LB, Rocha AKS, et al. Photocatalytic properties of Co/Co_3O_4 films recycled from spent Li-ion batteries. *Ionics* 2018;24:2167-73. DOI

98. Roy JJ, Cao B, Madhavi S. A review on the recycling of spent lithium-ion batteries (LIBs) by the bioleaching approach. *Chemosphere* 2021;282:130944. DOI PubMed