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Review

Recycling of Lithium Batteries—A Review

Xiaowei Duan [1], Wenkun Zhu [2,*], Zhongkui Ruan [1], Min Xie [3,*], Juan Chen [4] and Xiaohan Ren [1,*]

[1] Institute of Thermal Science and Technology, Shandong University, Jinan 250061, China; duanxiaowei@mail.sdu.edu.cn (X.D.); rzk@mail.sdu.edu.cn (Z.R.)
[2] School of Energy Science and Engineering, Harbin Institute of Technology, Harbin 150001, China
[3] HE National Engineering Research Center-Power Equipment Company Ltd., Harbin 150028, China
[4] School of Energy and Power Engineering, Shandong University, Jinan 250061, China; juanchen@sdu.edu.cn
* Correspondence: 19b302003@stu.hit.edu.cn (W.Z.); alice.m.xie@icloud.com (M.X.); renxh@sdu.edu.cn (X.R.)

Abstract: With the rapid development of the electric vehicle industry in recent years, the use of lithium batteries is growing rapidly. From 2015 to 2040, the production of lithium-ion batteries for electric vehicles could reach 0.33 to 4 million tons. It is predicted that a total of 21 million end-of-life lithium battery packs will be generated between 2015 and 2040. Spent lithium batteries can cause pollution to the soil and seriously threaten the safety and property of people. They contain valuable metals, such as cobalt and lithium, which are nonrenewable resources, and their recycling and treatment have important economic, strategic, and environmental benefits. Estimations show that the weight of spent electric vehicle lithium-ion batteries will reach 500,000 tons in 2020. Methods for safely and effectively recycling lithium batteries to ensure they provide a boost to economic development have been widely investigated. This paper summarizes the recycling technologies for lithium batteries discussed in recent years, such as pyrometallurgy, acid leaching, solvent extraction, electrochemical methods, chlorination technology, ammoniation technology, and combined recycling, and presents some views on the future research direction of lithium batteries.

Keywords: spent cathode material; lithium-ion battery; recycling; pyrometallurgy; hydrometallurgy; biohydrometallurgy

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Citation: Duan, X.; Zhu, W.; Ruan, Z.; Xie, M.; Chen, J.; Ren, X. Recycling of Lithium Batteries—A Review. *Energies* **2022**, *15*, 1611. https://doi.org/10.3390/en15051611

Academic Editors: Salvador Rodríguez-Bolívar and Juan A. López-Villanueva

Received: 30 November 2021
Accepted: 18 February 2022
Published: 22 February 2022

1. Introduction

Since the first industrial revolution, the use of fossil fuels has emitted a large number of pollutants, causing the greenhouse effect and climate change, which has become a great challenge for mankind. Against this backdrop, the zero-emission and non-polluting nature of electric vehicles has made them the primary choice for all countries. Global electric vehicle sales have grown exponentially over the past decade, with around 5.1 million electric vehicles on the road worldwide in 2018. China, the USA, and Europe are currently the world's largest consumers of powered vehicles. The International Energy Agency estimates that the global sales of electric vehicles will reach 4 million in 2020 and 245 million in 2030 on the basis of current and expected policies, with corresponding annual sales growth of approximately 41% and a stock value of US$13 billion and US$130 billion [1].

The rapid development of powered vehicles has led to a rapid increase in the consumption of batteries. As one of the typical representatives of new energy power batteries, lithium-ion batteries (LIBs) are widely used in energy storage and electric vehicles due to their long cycle life, high specific energy, small self-discharge effect, small size, high working voltage, no memory effect, wide applicable temperature range, and green environmental protection. Several common LIBs (according to cathode material) are $LiCoO_2$ (LCO), $LiMnO_2$ (LMO), $LiNi_xCo_yMn_zO_2$ (NCM), and $LiFePO_4$ (LFP), and their composition and structure are shown in Figure 1 (% in the figure refers to wt%).

From 2015 to 2040, the production of LIBs for electric vehicles could reach 0.33 to 4 million tons [1], which would raise concerns for the resource supply chain. It is predicted that a total of 21 million end-of-life LIB packs will be generated between 2015 and 2040 [2]. Therefore, in order to relieve the pressure on the supply chain, protect the environment, and achieve sustainable development of the industry, it is necessary to develop efficient recycling processes as early as possible.

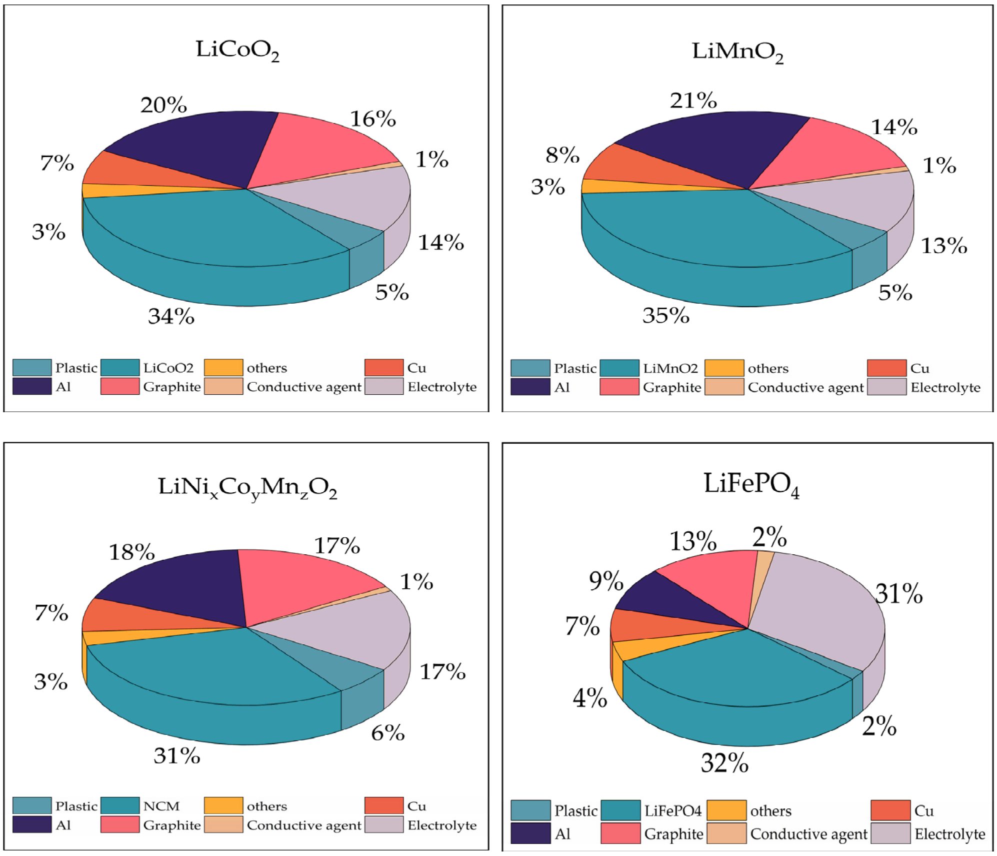


Figure 1. Structure and composition of several common types of lithium batteries.

The total global lithium (Li) demand forecast for 2016–2030 is expected to reach 1.79 million tons of lithium carbonate equivalent by 2030, as shown in Figure 2 [3,4]. With a predicted future increase in Li consumption, there may be issues regarding Li extraction, possibly leading to a rapid rise in Li price. Cobalt (Co) and nickel (Ni) face the same scenario. However, according to the mineral commodity summary data published by the USGS in 2020, the reserves and distribution of Li, Ni, and Co are shown in Figure 3 [5,6].

The average life cycle of a cell phone or laptop is 1–3 years, and that of EVs is 8–10 years [2]. In the future, a large number of LIBs will be retired and scrapped, and the recycling of spent LIBs is imminent. Fluorine-containing substances in them, such as hexafluorophosphates in batteries and the binder polyvinylidene fluoride (PVDF), may cause fluorine pollution and damage the ozone layer in the atmosphere [7]. The valuable metals in spent LIBs can enter the food chain by various methods, accumulating toxins and posing a serious risk to people's lives and property [8]. Studies have shown that spent LIBs contain many valuable metals in higher concentrations than those found in industrial ores, typically containing 5–20% cobalt, 5–10% nickel, 5–7% lithium, 5–10% copper, aluminum, and iron [9], and are valued at US$7708 per ton [10]. The lithium content of spent LIBs is approximately 10 times that of primary lithium ore (lithium pyroxene) and 30 times that of lithium chloride salts found in brine pools [11]. The metals therein will bring substantial economic benefits and mitigate the challenges posed by the scarcity of mineral resources if they can be effectively recovered. Therefore, proper and effective recycling of spent LIBs is of great importance, from the perspectives of environmental protection and resource recovery and economic development.

Today, commercial recycling processes rely on the profitability of recovering valuable cathode material from lithium-ion batteries. However, the most valuable element in the cathode, Co, has been intentionally reduced in new cathode material chemistry, making traditional LIB recycling more economically challenging. Therefore, optimizing or starting with existing recycling technologies to increase profits and maintain economic viability is necessary and urgent, which opens up numerous research opportunities to investigate cost reduction and the enrichment of business models, such as better disassembly techniques, sorting and separation methods, processes for universal recycling of batteries, recycling design, and standardization [12].

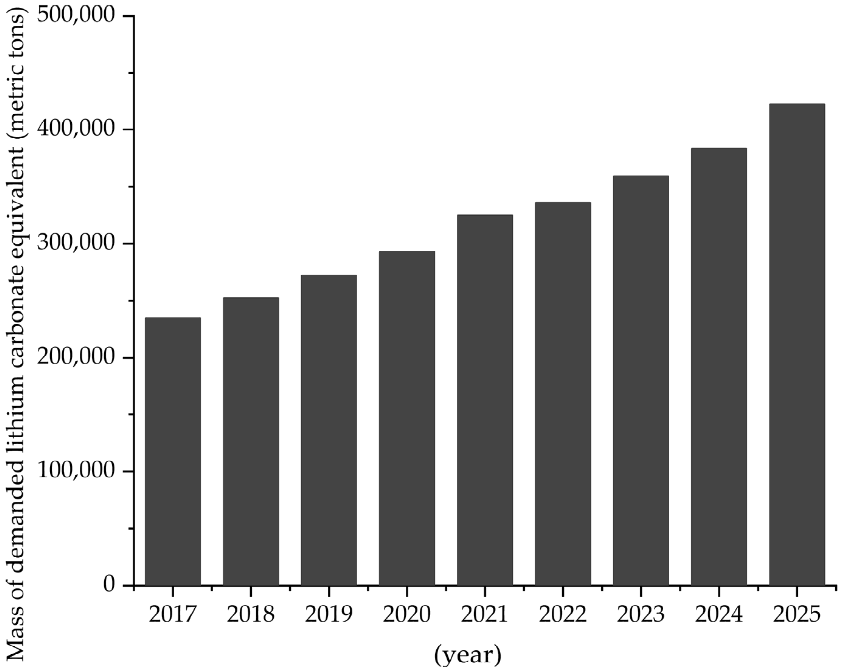
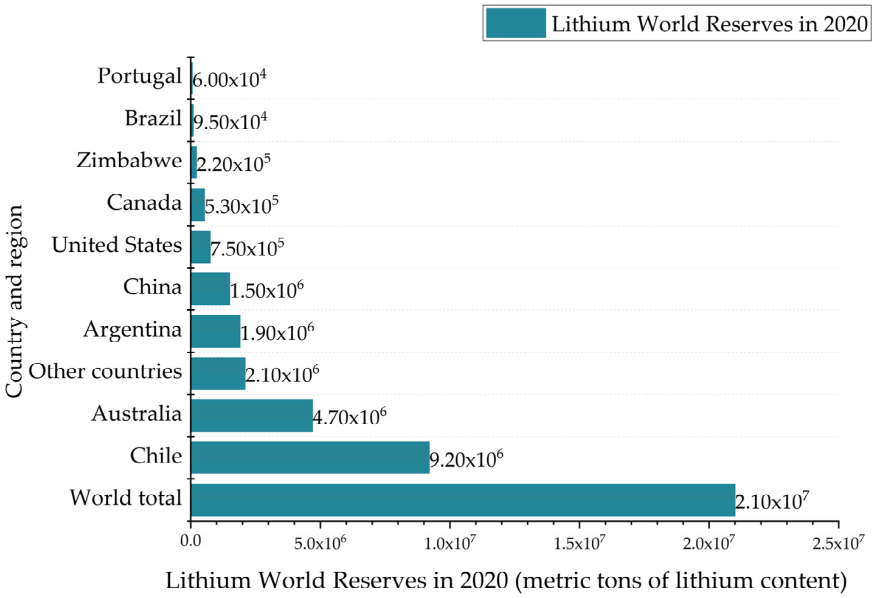


Figure 2. Projection of total worldwide lithium demand (in metric tons of lithium carbonate equivalent) from 2017 to 2025 [3,4].



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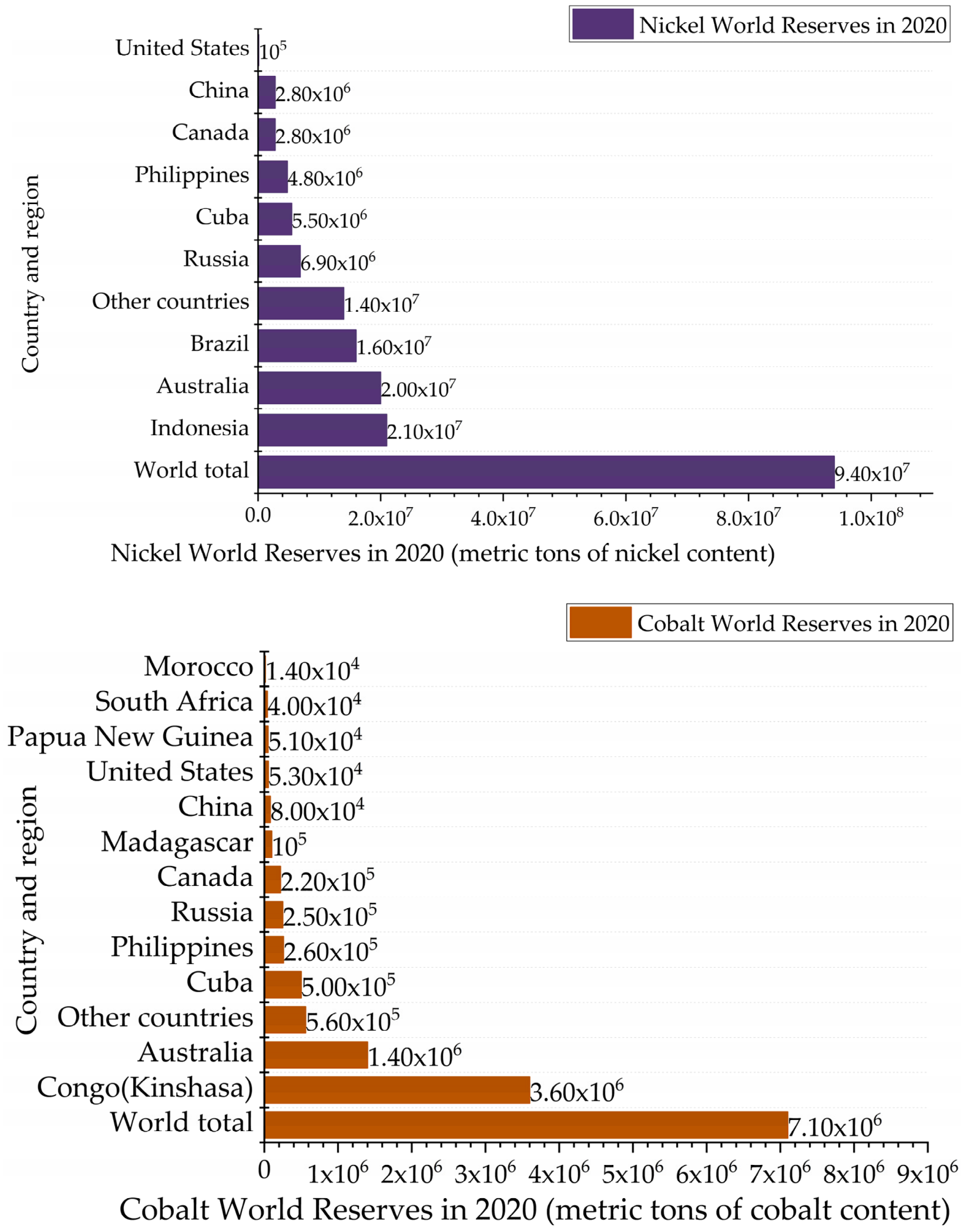

Figure 3. World reserves and proportions of lithium, nickel, and cobalt in 2020 (data from U.S. Geological Survey, Mineral Commodity Summaries, January 2021) [5,6].

Spent LIB's recycling processes usually first involve sorting the batteries by battery chemistries followed by deep discharge to avoid a violent reaction from the charged electrode materials exposed to the air. During discharge, positively charged lithium ions move from the anode through the electrolyte and separator to the cathode, causing spent cathode material to be enriched with lithium. The discharged batteries then go through physical disassembly, before undergoing electrolyte extraction, high-temperature melting and extraction, smelting, direct recycling, or hydrometallurgy extraction. In this article, we will summarize the pyrometallurgy process, the hydrometallurgy process, and the biohydrometallurgy process, as well as their advantages and disadvantages (Table 1).

The purpose of this article is to provide a comprehensive vision of the global recycling of power lithium-ion batteries and related key metals, using an environmentally sustainable development approach, through a comprehensive literature review, followed by an exploration of the major discoveries of mechanisms influencing the development of the

LIBs industry. The publication of this review article on power lithium-ion battery recycling is urgent, novel, and necessary.

Table 1. Comparisons of advantages and disadvantages for different methods.

Methodology	Advantage	Disadvantage
Pyrometallurgy	• Simplified recycling process • High processing capacity • High applicability	• Extensive energy consumption • Significant loss of Li • Severe secondary contamination
Hydrometallurgy	• High efficiency • High purified products • Low energy consumption • Low secondary pollution	• Extended recycling process • High chemicals consumption • Effluent discharging
Biohydrometallurgy	• Less pollution and consumption • Environmentally friendly • Microorganisms can be reused	• Difficult to cultivate efficient microbial bacteria • Long treatment cycle • Control of leaching conditions

2. Pre-Treatments

LIBs are composed of cathode material, anode material, a diaphragm, an electrolyte, and a binder, with different components bonded together. Some materials are flammable and toxic, meaning they cannot be handled together. Mechanical crushing can destroy the metal shell. Afterward, the organic membrane, spent anode, spent cathode, metal shell, and some electrode material particles can be released from each other, and they can then be separated according to physical differences [13].

The current recycling of LIBs focuses on the leaching, enrichment, and recovery of valuable metals from their cathode materials. It is necessary to obtain cathode materials with higher purity by certain pretreatment techniques before recycling. As shown in Figure 4, common pretreatment methods include "Discharging–Dismantling–Crushing–Sieving–Separation".

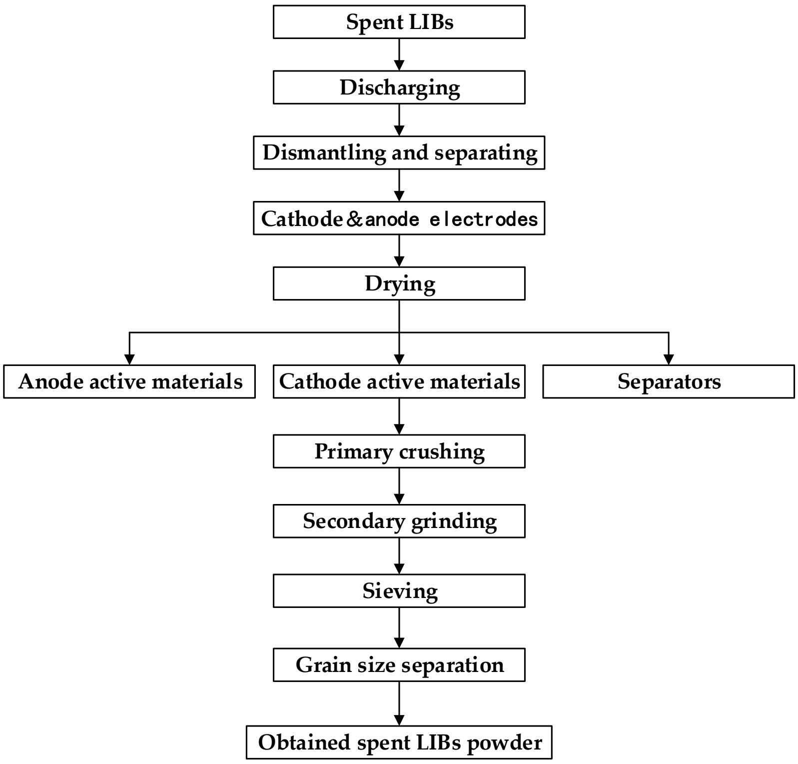

Figure 4. Process flow for pretreatment of recycled spent LIBs [14].

2.1. Discharging Process

Spent LIBs may contain a large amount of charge, and when the anode is in direct contact with the cathode, it will explode due to short circuit and spontaneous combustion and release a great deal of heat in a short period of time, while direct disassembly and shredding may trigger an explosive hazard.

NaCl solution is often used as the medium for discharging spent LIBs. Zhu et al. [15] used a 5 wt% NaCl solution to completely discharge the spent LIBs for 24 h and then dried them naturally. The voltage is ensured by a voltmeter and is below 2.0 V. Yao et al. [16] used NaCl, $FeSO_4$, and $MnSO_4$ solutions for discharging spent LIBs, and the related results are shown in Figure 5. To compare the discharge efficiency of spent LIBs more intuitively, the concept of active discharge time (ADT) was introduced in the discharge system. Higher values of ADT correspond to lower efficiencies. It is found that 0.8 mol/L of NaCl solution and 0.8 mol/L of $FeSO_4$ solution are the best discharge solutions for chemical discharge, and the $FeSO_4$ solution is more environmentally friendly than the NaCl solution.

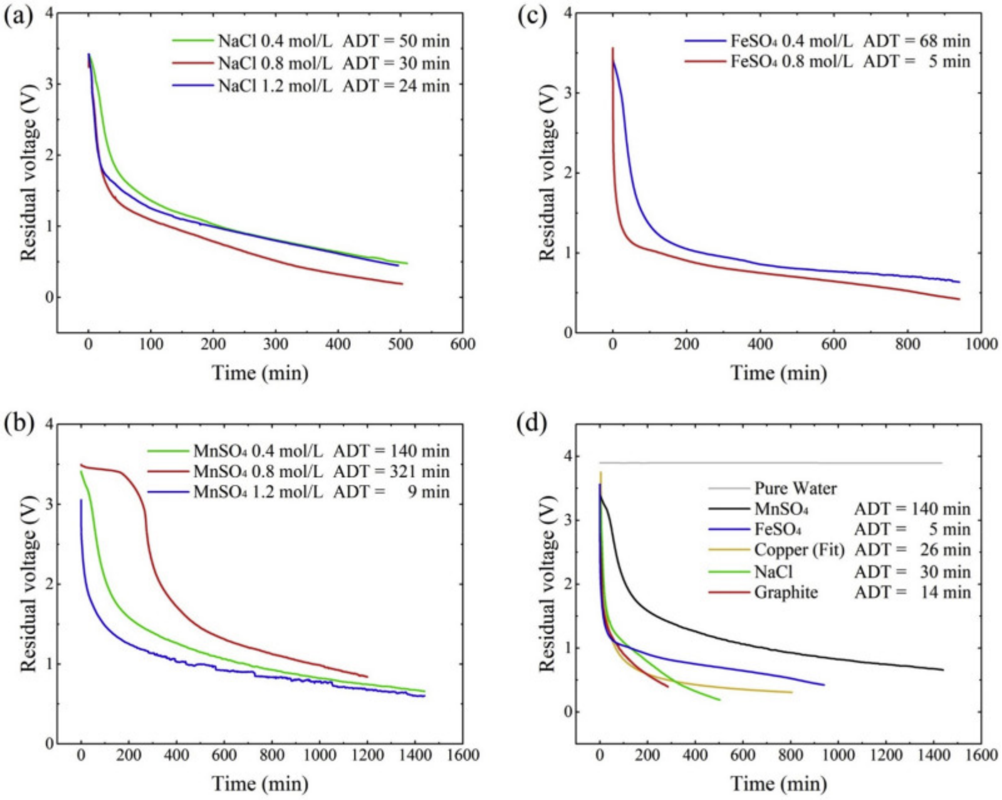

Figure 5. (**a**) Discharge curves of NaCl solutions, (**b**) $MnSO_4$ solutions, (**c**) $FeSO_4$ solutions, (**d**) both chemical and physical methods.

2.2. Mechanical Process

The discharged spent LIBs are disassembled and separated to obtain battery components such as electrode active material, collector fluid, and the battery shell. Then they are crushed, screened, magnetically separated, finely crushed, and sorted to obtain high-value materials.

Wang et al. [17] investigated the effect of crushing size on the recovery rate by separating the different components of LIBs in accordance with their crushing characteristics and found that the smaller the crushing size, the higher the metal recovery rate, with the cobalt content increasing from 68% (0.5–1 mm) to 82% (<0.5 mm). Wuschke et al. [18] used a gap rotary shear to crush LIBs, combining the processes of screening and sorting to separate the components of spent LIBs. Liu et al. [19] used a novel, highly selective, low-temperature grinding method to treat spent ternary LIBs. Compared with the conventional method, the cathode material is more abrasive, the 0.15 mm particle size is greatly increased, and the recovery of lithium, nickel, cobalt, and manganese is increased from 16% to 84%.

Mechanochemical methods are often used in the pretreating treatment phase for the recovery of spent LIBs. Wang et al. [20] used dry ice as a co-polishing agent to destroy the crystal structure of lithium cobalt oxide (LCO) in the discharged spent LiBs cathode material under the action of mechanical force and convert it into lithium carbonate (Li_2CO_3) and lithium-free residue (C/Co_3O_4). The optimal conditions for the recovery of Li_2CO_3 are determined as follows: The mass ratio of dry ice to LCO is 20:1, the rotational speed is 700 rpm, and the reaction time is 1.5 h. Under these conditions, the recovery of Li_2CO_3 can be up to 95.04 wt%. Xie et al. [21] found that Zn powder is an effective co-grinding agent for improving the recovery of valuable metals from cathode materials. The leaching rates of Li, Ni, Co, and Mn are increased from 72.0%, 42.5%, 31.2%, and 15.2% to 99.9%, 96.2%, 94.3%, and 91%, respectively, after mechanical chemical ball milling treatment using Zn and cathode materials. The above studies show that mechanical crushing helps to leach valuable metals from spent LIBs. Most current engineering practices use mechanical crushing combined with a hydrometallurgical process to recover spent LIBs.

In addition to the traditional shredding process, some researchers have proposed a more economical pretreatment process. Thompson et al. [22] suggest disassembling spent LIBs and then layering them to retain product value and simplify downstream chemicals. The shredded material can be recycled into new cathode material with cost savings of up to 20%. A similar process using disassembled batteries could save up to 80% (not considering the actual steps of disassembling the battery). As battery design progresses, separation and layering dominate because they allow for higher yields of purer products at a lower cost. It is a great method for optimizing the entire supply chain of LIBs.

3. Pyrometallurgy Treatments

Pyrometallurgy is the process of separating the constituent materials of spent LIBs, which have been initially separated by physical crushing, and then subjecting them to high-temperature pyrolysis to remove the organic binder. It also allows the oxidation reduction and decomposition of the metals and their compounds in the LIBs, and then the products are recovered by different means. As shown in Figure 6, a common pyrometallurgy treatment process is summarized in this article.

The valuable metals, mainly lithium, cobalt, manganese, and nickel, are extracted from the spent LIB cathode material by pyrometallurgy treatments, as concluded in Table 2.

Xin et al. [23] cut the spent LIB cathode material into 2 × 2 cm pieces and roasted them in a muffle furnace at 600 °C to remove PVDF. The calcined cathode pieces are crushed and sieved to obtain cathode active powder. Zhang et al. [24] first used reduction roasting to directly treat the whole spent LIB and dissociate and convert the cathode material into simple substances. The hazardous electrolytes, binders, and membranes are broken down into gases and can be treated by using well-established and widely used techniques. Over 81% of the lithium can be preferentially extracted from the roasted product by aqueous carbonate leaching. Additional oxidative ammonia leaching can leach over 95% of Ni, Co, and Cu, while Mn in the ammonia leach residue can be recovered by a beneficiation process. The researchers studied the recovery characteristics of pyrolysis of used LIBs under different atmospheres. Tao et al. [25] cut the cathode material into small 5×5 cm pieces, placed the full component pieces in a tube furnace, and pyrolyzed them under a nitrogen atmosphere. The pyrolysis slag is ground and sieved to obtain a mixed powder of cathode and anode materials, which is dissolved in deionized water, and the lithium is leached using carbonic acid to obtain a lithium carbonate precipitate. The cobalt in the filtrate is leached using sulfuric acid and evaporated and crystallized to give cobalt sulfate, resulting in a final leaching filtration of 99.1% and 87.9% for cobalt and lithium, respectively. Wang et al. [26] roasted the cathode material NCM in a nitrogen (oxygen-free) atmosphere for 1.5 h at 350 °C and leached it with sulfuric acid, with >99% leaching of lithium, nickel, cobalt, and manganese. Yang et al. [27] roasted the cathode powder under a methane atmosphere and used carbonic acid for the selective leaching of lithium. The leaching of the filtrate with sulfuric acid results in a leaching rate of 88% for Li and over 98% for Mn, Ni, and Co. Some researchers have added a number of other chemicals to the pyrolysis process to improve recovery efficiency. Xu et al. [28] mixed dried LCO, deionized water, a certain amount of carbon, and concentrated sulfuric acid and subjected it to selective roasting (400–800 °C) in a muffle furnace. Li is recovered as Li_2SO_4 and Co as CoO and Co_3O_4 with a recovery of 92% for Li and 100% for Co. The reactions involved are as follows:

$$4LiCoO_2 + 6H_2SO_4 + 22H_2O \rightarrow 2Li_2SO_4 + 4CoSO_4 \cdot 7H_2O + O_2(g) \tag{1}$$

$$8Li_2SO_4 + 16.5C + 9CoO(g) \rightarrow 8Li_2CO_3 + Co_9S_8 + 8.5CO_2(g) \tag{2}$$

Ammoniation is often used in the high-temperature pyrolysis of LIBs. Xiao et al. [29] mixed the cathode material of a ternary lithium battery with NH_4Cl in a 1:3 ratio and roasted it in a tube furnace at a heating rate of 10 K/min, a roasting time of 20 min, and a temperature of 589.94 K. The leaching rate of the metal is close to 100%. His team [30] also mixed the cathode material with urea and added it to the reactor at a certain filling ratio. The thermal reduction reaction is conducted in a tube furnace at a 10 K/min ramp rate under an argon (Ar) atmosphere. At the end of the reaction, the roasted product is subjected to water leaching to provide water-soluble lithium carbonate and insoluble cobalt metal, with a lithium leaching rate of 99.96% and 100% selectivity. The reactions involved are as follows:

$$2LiCoO_2(s) + 2NH_3(g) \rightarrow 2Co(s) + 3H_2O(g) + Li_2O(s) + N_2(g) \tag{3}$$

$$\begin{gathered}6LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2(s) + 2NH_3(g) + 18HCl(g) = 6LiCl(s) + 2NH_4NiCl_3(s) + \\ 2NH_4CoCl_3(s) + 2NH_4MnCl_3(s) + N_2(g) + 12H_2O(g)\end{gathered} \tag{4}$$

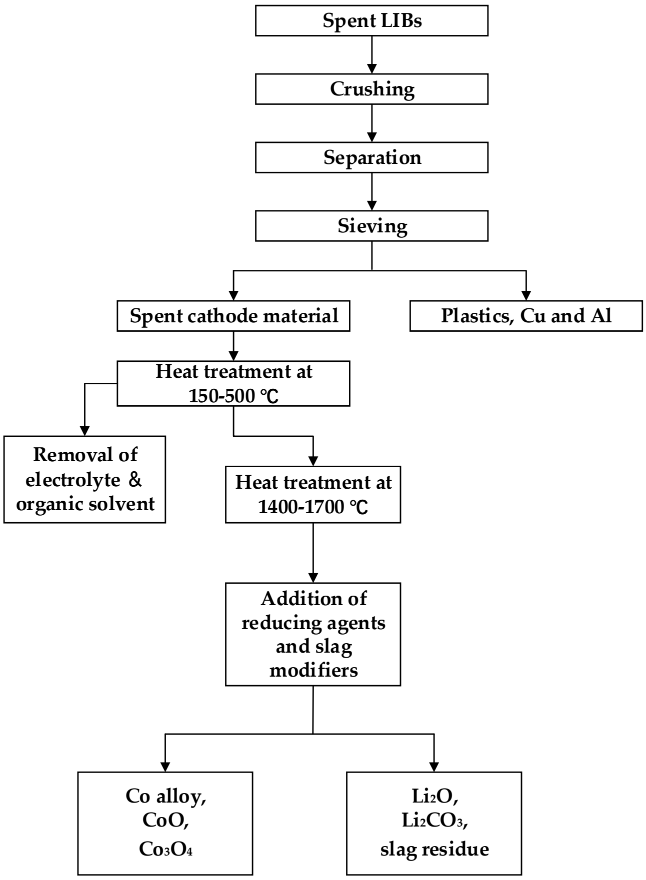

Figure 6. Flow chart of pyrometallurgy treatment process for recovering cathode material.

Table 2. Several main pyrometallurgy processes.

Active Ingredients	Recycling and Disposal Methods	Parameter Conditions	Leach Efficiency (%)				Ref.
			Li	Co	Mn	Ni	
LCO	pyrometallurgy	LCO to H_2SO_4 ratio 2:1, 20% carbon content, heating temperature of 873 K, holding time 120 min	92	100			[28]
NCM	pyrometallurgy	NCM mixed with NH_4Cl in a ratio of 1:3, roast at 623 K for 20 min	100	100	100		[29]
LCO	pyrometallurgy	LCO to urea ratio of 1:2, temperature 823 K, holding time 20 min	99.9				[30]
LCO LMO LNO	pyrometallurgy, ultrasound assist	heating temperature of 873 K, holding time 30 min, 4 mol/L H_2SO_4 leaching	99	99	99	99	[31]
NCM	pyrometallurgy	1:1 mix of cathode and anode materials, heating temperature of 573 K, holding time 10 min		99.2		97.9	[32]
LCO	thermal disengagement, thermal transformation	5:1 mix of cathode and anode materials, heating temperature of 1673 K, holding time 20 min		96			[33]
NCM		19:1 mix of cathode and anode materials, heating temperature of 923 K, holding time 60 min	82.2	99.1		97.1	[34]
LCO	vacuum pyrolysis	heating temperature of 973 K, holding time 30 min	99	99			[35]

Some researchers used spent materials as additives to co-pyrolyze and recycle spent LIBs. Makuza et al. [31] mixed various cathode materials (LMO, $LiNiO_2$, LCO) and graphite and reduction roasted them at 500 °C–1000 °C for 15–120 min. The roasted products are then dry ground at 3000 r for 1–10 min, and the lithium is leached out of them using ultrasound-assisted carbonic acid and evaporated and crystallized to obtain $LiCO_2$ (purity greater than 99.5%). Ni, Mn, and Co in the filter residue are leached out using H_2SO_4, whereby the leaching rate is greater than 99% and the filter residue is graphite. Qiu et al. [32] mixed the dismantled spent LIB cathode material and anode material 1:1 and heated them in a heating furnace under vacuum to 1450 °C. Nickel and cobalt are obtained after vacuum reduction and separated by magnetic separation with a recovery of 97.91% for nickel and 99.21% for cobalt. Hossain et al. [33] heat-treated the cathode and anode foils in an argon atmosphere at 650 °C with a holding time of 5–30 min. The treated cathode and anode materials were ground into a fine powder, the cathode active material and anode powder are mixed in a 5:1 ratio, heat-treated at 1400 °C, and heat-treated in a tube furnace in an argon atmosphere for 20 min to recover cobalt with a purity of 96%. Ma et al. [34] used anode powder as a reducing agent with ternary lithium battery cathode material in an Ar gas atmosphere for reduction roasting, water leaching its product to recover lithium, and evaporation crystallization to obtain $LiCO_3$. Ammonia leaching is used for the effective separation of Ni and Co, and the recoveries of Li, Ni, and Co are 82.2%, 97.1%, and 99.1%, respectively. The reactions involved are as follows:

$$Co^{2+} + nNH_3^{2+} \rightarrow Co(NH_3)_n^{2+} \tag{5}$$

$$Ni^{2+} + nNH_3^{2+} \rightarrow Ni(NH_3)_n^{2+} \tag{6}$$

In recent years, some researchers have used vacuum pyrolysis to treat spent LIBs. Sun et al. [35] found that the cathode material is completely stripped from the aluminum foil by cathode powder consisting of LCO and CoO at a temperature of 600 °C, a vacuum evaporation time of 30 min, and a residual gas pressure of 1.0 kPa. The recovery rate of lithium cobalt is more than 99%.

4. Hydrometallurgy

The hydrometallurgy process uses reagents such as hydrochloric acid (HCl), nitric acid (HNO_3), sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4), organic acids, and hydrogen peroxide (H_2O_2) to extract and separate the cathode metals, usually operating below 100 °C, and can recover lithium in addition to the other transition metals [36].

This paper reviewed various hydrometallurgy methods developed in the last decade for the recovery of cathode materials for lithium-ion batteries from various battery chemicals, such as LCO, LMO, NCM, and LFP, for the recovery of cobalt, nickel, manganese, and lithium.

As shown in Figure 7, hydrometallurgy works to crush and dissolve spent batteries, and then uses suitable chemical reagents to selectively separate the metal elements in the leaching solution, yielding high-grade cobalt metal or lithium carbonate. Hydrometallurgy is more suitable for recycling spent LIBs with single chemical composition, and its equipment investment cost is low, suitable for the recycling of small- and medium-scale spent lithium batteries. Therefore, this method is widely used at present.

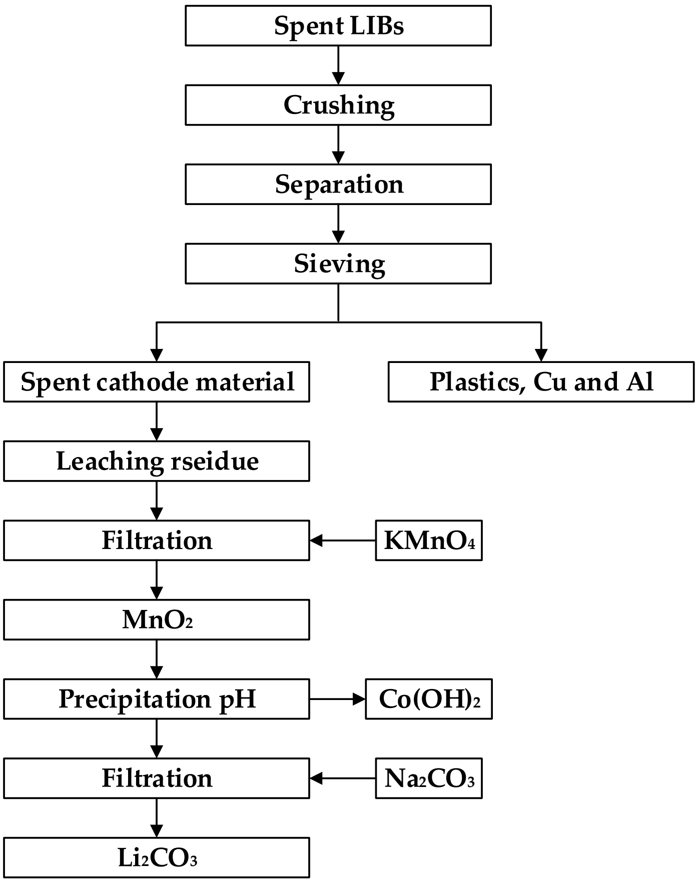

Figure 7. Flow chart of the hydrometallurgical process for recovering battery cathode material.

The valuable metals, mainly lithium, cobalt, and manganese, are extracted from the spent LIB cathode material by the acid leaching process, as concluded in Table 3.

Table 3. Several major acid leach recovery processes.

Leaching Treatment		Auxiliary Means	Leach Temp	Leach Efficiency (%)			Reference
Inorganic Leaching Agent	Reducing Agent			Li	Co	Mn	
4 mol/L HCl			80 °C	99	99		[37]
4 mol/L HCl			80 °C	99	99	99	[38]
2 mol/L H_2SO_4				76	76		[35]
2 mol/L H_2SO_4	H_2O_2		80 °C	99	99		[35]
2 mol/L H_2SO_4	H_2O_2				99.9		[39]
4 mol/L H_2SO_4	H_2O_2		70 °C	99	99	100	[23]

Table 3. *Cont.*

Leaching Treatment		Auxiliary Means	Leach Temp	Leach Efficiency (%)			Reference
2 mol/L H_2SO_4	H_2O_2	ultrasound	30 °C	98.6	94.6		[40]
1 mol/L HNO_3			75 °C	75	40		[41]
1 mol/L HNO_3			75 °C	75	40		[42]
1 mol/L HNO_3	H_2O_2		75 °C	95	95		[43]
1.5 mol/L H_3PO_4	$C_6H_{12}O_6$		80 °C	98	100		[44]
1.5 mol/L malic acid	grape seed		80 °C	99	92		[45]
10 mol/L HCOOH	H_2O_2		80 °C	99.5			[46]
0.5 mol/L ascorbic acid		microwave	125 °C	100	100	100	[47]
57.8% (*v*/*v*) lemon juice	H_2O_2	ultrasound	40 °C	100	96	96	[48]
citric acid		microwave				94	[49]
$H_2C_2O_4$-H_3PO_4				100	98.2	100	[50]
H_2SO_4-$FePO_4 \cdot 2H_2O$			80 °C	96	96	96	[51]
0.5 mol/L HCl-0.5 mol/L ascorbic acid			90 °C	97.72	97.25		[52]
0.5 mol/L CH_3COOH-0.2 mol/L ascorbic acid	bagasse pith	ultrasound	50 °C	98	98	98	[53]

Once the valuable metal has been leached, the metal can be recovered through a series of processes including precipitation and solvent extraction. After the leaching process, the recovered material can be reformulated to regenerate the lithium cathode material.

4.1. Acid Leaching

Most of the active cathode materials in LIBs can be dissolved in acid. Thus, the pretreated electrode material can be leached with an acid solution to achieve separation of the active material from the collector fluid, and then combined with the principle of a neutralization reaction to precipitate and purify the target metal, thereby achieving recovery of high-purity components. Acid solutions utilized by the acid leaching method are conventional inorganic acids, including hydrochloric acid, sulfuric acid, and nitric acid.

Zhang et al. [37] and Wang et al. [38] used HCl solutions to leach spent LIB cathode materials. Zhang et al. [37] used a 4 M HCl solution to leach spent LIBs, achieving leaching efficiencies of over 99% for Co and Li. The optimum working conditions are 80 °C with a reaction time of 1 h. Wang et al. [38] leached spent LIBs in 4 M HCl solution with leaching efficiencies of over 99% for Co, Mn, Ni, and Li. The optimum working conditions are an 80 °C leaching temperature, 1 h leaching time, and a 0.02 g/mL solid-to-liquid (S/L) ratio. The reactions involved are as follows:

$$2LiCoO_2 + 8HCl \rightarrow 2LiCl + 2CoCl_2 + 4H_2O + Cl_2 \quad (7)$$

$$2LiMn_2O_4 + 16HCl \rightarrow 2LiCl + 4MnCl_2 + 8H_2O + 3Cl_2 \quad (8)$$

The selective recovery of the metal from the leachate is carried out in multiple steps. First, the Mn in the leachate reacts selectively with the $KMnO_4$ reagent and nears completion, and the Mn is recovered as MnO_2 and manganese hydroxide. Second, nickel in the leachate is selectively extracted by dimethylglyoxime near completion. Third, the pH is adjusted by using a sodium hydroxide solution to selectively precipitate cobalt hydroxide. The addition of a saturated Na_2CO_3 solution precipitated Li_2CO_3. The purity of lithium, manganese, cobalt, and nickel is 96.97 wt%, 98.23 wt%, 96.94 wt%, and 97.43 wt%, respectively [38]. The reactions involved are as follows:

$$3Mn^{2+} + 2MnO_4^- + 2H_2O \rightarrow 5MnO_2 + 4H^+ \quad (9)$$

Sun et al. [35], Cheng et al. [39], Xin et al. [23], and Jiang et al. [40] used H_2SO_4 solution as the leaching agent, and a reducing agent needs to be introduced to improve its efficiency due to the low efficiency of sulfuric acid leaching. Sun et al. [35] achieved a leaching rate of

76% with 2 M sulfuric acid. Introducing hydrogen peroxide as a reducing agent, leaching at 80 °C and a 50 g/L S/L ratio for 60 min can recover more than 99% of cobalt and lithium. Cheng et al. [39] used sulfuric acid as a leaching agent and hydrogen peroxide as a reducing agent to leach the cathode material powder and extracted Co^{2+} using Cyanex272 with a 99% extraction rate. Xin et al. [23] leached the treated active cathode material in a hydrogen peroxide sulfate system and prepared transition metal-doped α-MnO_2 and β-MnO_2 by deep oxidation with potassium permanganate and ozone, respectively, with the recovery of manganese up to 100%. Jiang et al. [40] used an ultrasonic-assisted sulfuric acid–hydrogen peroxide system to leach valuable metals from used lithium batteries with 94.63% for cobalt and 98.62% for lithium. The reactions involved are as follows:

$$2LiCoO_2 + 3H_2SO_4 + H_2O_2 \rightarrow Li_2SO_4 + 2CoSO_4 + 4H_2O + O_2 \quad (10)$$

$$2LiMnO_2 + 3H_2SO_4 + H_2O_2 \rightarrow Li_2SO_4 + 2MnSO_4 + 4H_2O + O_2 \quad (11)$$

Castillo et al. [41] and Lee et al. [42,43] used HNO_3 for the leaching of LMO. Castillo et al. [41] used 2 mol/L of nitric acid to leach LIBs, separating all the lithium and manganese from the other metals, allowing 100% of the lithium to be leached. The addition of NaOH solution to reach pH 10 selectively precipitates manganese hydroxide. Lee et al. [42,43] used HNO_3 alone for the leaching of $LiCoO_2$ with 40% leaching of Co and 75% of Li. The addition of 1.7 vol.% H_2O_2 as a reducing agent and leaching at 75 °C for 1 h increases the leaching of Co and Li to 95%. Because Co^{3+} is re-reduced to Co^{2+}, it is easier to dissolve. The reactions involved are as follows:

$$LiMn_2O_4 + 10HNO_3 \rightarrow 2Mn(NO_3)_2 + LiNO_3 + 5NO_2 + 5H_2O + 2O_2 \quad (12)$$

Meng et al. [44] used glucose as the reducing agent and phosphoric acid as the leaching agent to recover Co and Li from the LCO collected from spent LIBs, with leaching rates of approximately 98% and 100% for Co and Li. During the leaching process, glucose is sequentially oxidized and decomposed to form monocarboxylic acids, including gluconic acid, tartaric acid, oxalic acid, and formic acid.

The leaching of spent LIBs using inorganic strong acids generates large amounts of spent liquids, as well as some harmful gases such as chlorine gas (Cl_2) and sulfur trioxide (SO_3), which can pollute the environment. These spent liquids are difficult in terms of being treated harmlessly. Researchers have tried to treat spent LIBs using organic acids, such as malic acid, citric acid, oxalic acid, malic acid, and ascorbic acid. Zhang et al. [45] used grape seeds as a reducing agent for the leaching of spent LCO materials. Under the optimized conditions of 0.6 g/g grape seeds, 1.5 mol/L malic acid, 180 min, 80 °C, and a slurry density of 20 g/L, approximately 92% Co and 99% Li can be leached. Zeba et al. [46] used formic acid to recover manganese, nickel, and lithium from spent LIBs by using it as a leaching and reducing agent for nickel and manganese. The addition of H_2O_2 in the leaching solution rapidly dissolves insoluble cobalt. Manganese, nickel, and cobalt are recovered by extraction. Lithium (99.5 wt%) is recovered as formate, a high-value-added by-product, by careful evaporation of the final aqueous solution, thereby reducing the final spent generation. Lei et al. [47] used 0.5 M ascorbic acid at 125 °C with an S/L ratio of 10 g/L. The closed-vessel microwave system can leach 100% of Li, Co, and Mn from the spent cathode material. Oxalic acid is used to recover Co and Mn, generating oxalate precipitates. Esmaeili et al. [48] investigated the leaching of valuable metals from spent LIBs using ultrasound-assisted bioacid. Organic acids from lemon juice and hydrogen peroxide are used as leaching agents. The three influencing factors of the S/L ratio, lemon juice content, and H_2O_2 volume fraction are optimized through response surface analysis. The recoveries of Li, Co, and Ni are 100%, 96%, and 96%, respectively, when the S/L in the leachate was 0.98% (*w*/*v*), the lemon juice was 57.8% (*v*/*v*), and the H_2O_2 was 8.07% (*v*/*v*). Pindar et al. [49] used citric acid to leach the spent LIB cathode material with microwave assistance, greatly improving the dissolution rate of manganese in citric acid (from 9% to 94%), and lithium is recovered as Li_2CO_3. Tao et al. [50] first used 0.5–2 mol/L oxalic acid solution to leach lithium from the spent cathode material for approximately 2–4 h, used phosphoric acid solution to leach nickel and cobalt, and utilized sulfuric acid to leach manganese for 1–3 h. The recoveries of Li, Ni, Co, and Mn are close to 100%, 99.5%, 98.2%, and 100%, respectively. Compared with the traditional "one leaching, multi-step separation" process, this "multiple leaching, multistep separation" process can improve the leaching rate by selectively leaching the metals from spent LIBs.

Almost all leaching processes require large amounts of acid and the reducer/oxidizer to achieve the desired leaching results, with acid concentrations ranging from 1.0 M to 3.0 M and high consumption of the reducer/oxidizer (e.g., 2–6 vol% hydrogen peroxide). Furthermore, large amounts of acid or the reductant/oxidizer are practically ineffective for accurate recovery of the target metal, and any unreacted acid or reductant/oxidizer ends up in the effluent and causes secondary contamination. It can be observed that different additives are used to reduce or oxidize the corresponding spent cathode materials (e.g., reductants for LCO and oxidizers for LFP), resulting in a single batch of different types of cathode materials that cannot be recovered synergistically. Therefore, the balance between simplifying the recycling process and saving chemical/energy consumption should be fully considered in order to pursue the efficient and green recycling of different metals from spent LIBs. Unlike conventional leaching processes that require reducing or oxidizing agents, the different redox properties of LCO and LFP are fully utilized to avoid the use of additional reducing or oxidizing agents. Moreover, due to the intrinsic motivation of the redox reactions of LCO and LFP and the transformation of transition metals, especially Fe, the amount of acid is presumed to be significantly reduced. The dissolved metals in the leachate can then be recovered efficiently and selectively as different products depending on the differences in solubility. Liu et al. [51] mixed the cathode material NCM with LFP in a certain ratio, added 100 mL of the sulfuric acid solution and heated it in a water bath, and added $FePO_4 \cdot 2H_2O$ after 0.5 h. The reductant-free recycling of spent ternary LIBs is achieved via the introduction of $FePO_4 \cdot 2H_2O$ crystals and spent LFP. Jiang et al. [52] prepared diluted H_2SO_4 in a 250 mL conical flask reactor, and then added a fixed molar ratio of LCO and LFP mixed cathode materials for leaching experiments. During the leaching process, the reactor was kept in a water bath with magnetic stirring equipment to control the reaction temperature at 50 °C and the stirring speed at 500 rpm. A reducing environment can be provided for the leaching of LCO from rapidly dissolved Fe(II) in LFP, and the leaching of Co can be improved by reducing Co(III) to Co(II). Under the optimized leaching conditions of sulfuric acid (0.5 M), leaching time (20 min), S/L ratio (30 g/L), and LCO/LFP (1 molar ratio), more than 99% of Li, Fe, and P and 92.4% of Co:1 can be extracted.

Mixed acid systems are often used to leach spent LIBs. Chan et al. [53] recovered lithium, cobalt, nickel, and manganese from $LiNi_{0.15}Mn_{0.15}Co_{0.70}O_2$, the cathode material of used LIBs for electric vehicles. A systematic experimental and theoretical approach based on experimental design and response surface methodology is used to determine the optimum leaching agent and optimal operating conditions for HCl with $H_2SO_4 + H_2O_2$. The recovery of all four metals is 100% using a mixture of 1.0 M H_2SO_4 and 0.62 wt% H_2O_2 with an L/S ratio of 25.8 mL/g, a leaching temperature of 51 °C, and a leaching time of 60 min. At pH above 11, cobalt, nickel, and manganese are coprecipitated as $Ni_{0.15}Mn_{0.15}Co_{0.70}(OH)_2$, and lithium is precipitated as lithium carbonate. These precipitates are mixed and sintered to form a new cathode material for the manufacturing of batteries with high electrochemical performance. Xing et al. [54] achieved ultrafast leaching of spent cathode materials (97.72% leaching of lithium and 97.25% leaching of cobalt in 10 min at an S/L ratio of 10 g/L and a temperature of 363 K) in a 0.5 M hydrochloric acid and 0.5 M L-ascorbic acid system. Yan et al. [55] proposed a hybrid organic acid (acetic acid and ascorbic acid) and sugarcane bagasse pith as leaching and reducing agents for the recovery of valuable metals (Li, Ni, Co, Mn) from ternary LIB cathode materials using a comprehensive hydrometallurgy system with the assistance of ultrasonic waves. More than 98% of the valuable metals can be leached at a temperature of 50 °C, a time of 40 min, an S/L ratio of 20 g/L, a bagasse pith dosage of 0.3 g, an acetic acid dosage of 0.5 M, an ascorbic acid dosage of 0.2 M, and an ultrasonic power of 450 W. Nayaka et al. [56] used organic acids iminodiacetic acid and maleic acid to dissolve used LIB cathode materials, allowing the recovery of 100% Li and 97% Co.

4.2. Chlorination Technology Process

To reduce the use of inorganic acid and reduce environmental pressure. Liu et al. [57] and Nshizirungu et al. [58,59] proposed the use of chlorination technology to recycle spent LIBs without additional inorganic acid. Liu et al. [57] used an autoclave to treat used polyvinyl chloride (PVC) and spent LIBs. The PVC is dechlorinated and substituted to produce hydrochloric acid, which was used to leach the spent LIB cathode material. Under optimal conditions, Co recovery exceeds 95% and Li recovery is close to 98%. The whole process has no release of any toxic chlorine-containing organic compounds and recycles spent LIBs and PVC, which has good environmental benefits. Nshizirungu et al. [58] investigated the leaching efficiency of spent chlorinated polyvinyl chloride (CPVC) under subcritical hydrothermal conditions for lithium and cobalt from spent LIBs. The leaching efficiency is improved by using spent CPVC as a source of hydrochloric acid. His team compared the leaching of valuable metals from PVC and CPVC from ternary lithium battery cathode materials in closed containers. They found that CPVC outperforms PVC in the extraction of valuable metals from NCM cathode materials due to the higher Cl content in CPVC [59].

4.3. Ammoniation Technology Process

Some researchers have used an ammonia leaching process to recover spent LIBs. Liu et al. [60] used a solution consisting of ammonia sulfite, ammonia, ammonia carbonate, and deionized water to leach the cathode active material of used ion batteries. Co and Ni are converted into complexes $[Ni(NH_3)_n]^{2+}$, $[Co(NH_3)_m]^{2+}$, Mn is converted into $(NH_4)_2Mn(SO_3)_2 \cdot H_2O$ and $(NH_4)_2Mn(SO_4)_3$ precipitates, and Li is leached as metal ions. The leaching rates of Co, Li, Ni, and Mn were 84.56%, 90.31%, 64.13%, and 4.53%, respectively. Li et al. [61] used an ammonia-sodium sulfite-ammonium chloride system to leach LCO. After 5 h of ball milling, the leaching time of LCO is shortened from 48 h to 4 h. The Li and Co leaching rates are increased from 69.86% and 70.80% to 88.86% and 98.22%, respectively. Chen et al. [62] proposed a heat treatment–ammonia leaching process for the recovery of valuable metals from cathodically active powder. A new Co_3O_4 phase appears in the cathodically active powder roasted at 550 °C, indicating the collapse of the layered structure of LCO. In the spinel structure of $LiMn_2O_4$, the valence of manganese increases to form $Li_4Mn_5O_{12}$. Ammonia leaching is conducted in a $(NH_4)_2SO_4$-$(NH_4)_2SO_3$ solution using calcined cathode powder as the raw material. Under optimum conditions, the leaching rates of 98%, 81%, 92%, and 98% are obtained for nickel, cobalt, manganese, and lithium, respectively. The ammonia solution can be reused after the recovery of the valuable metals. Overall, this new recovery method has the advantages of high metal recovery efficiency, availability of equipment, and environmental friendliness, which can meet the requirements of green chemistry and has great potential for industrial production.

4.4. Solvent Extraction

Keller et al. [63] used an ion exchange agent (di(2-ethylhexyl)phosphoric acid to selectively extract manganese from the leachate, with up to 94% extraction under optimum conditions. Vakylabad et al. [64] selectively extracted cobalt and nickel ions with xanthate complexes at room temperature and then washed with ammonia to obtain pure cobalt complexes. The complexes are converted to pure Co_3S_4 nanospheres by mild treatment (250 °C, 1 h) with 98% extraction of Co. Choubey et al. [65] used a sulfuric acid–hydrogen peroxide system to leach spent LIBs, adding NaOH, and precipitation to remove impurities, such as aluminum, iron, and copper. The filtered liquid is further diluted prior to solvent extraction. Versatic acid is added to LIX84-I to synergistically extract nickel from the leachate with an extraction rate of 99.1%. Liu et al. [66] separated lithium (Li)-nickel (Ni)-cobalt (Co)-manganese (Mn) by tandem extraction with P227 (di(2-ethylhexyl)phosphonic acid) and P204 (di(2-ethylhexyl)phosphoric acid) extractants, respectively. At the same time, high-purity solid products, such as MnO_2, Li_2CO_3, NiO, and Co_3O_4, are prepared through precipitation. The recoveries and purity of lithium, nickel, cobalt, and manganese in the final products are 96.15%/100%, 91.54%/98%, 91.15%/93%, and 91.56%/100%, respectively. Nguyen et al. [67,68] found that Cyanex 301 (bis(2,4,4-trimethylpentyl) dithiophosphonic acid) extracts copper better than other metal ions compared with Aiquat 336 (*N*-methyl-*N*,*N*,*N*-trioctylammonium chloride). Ion exchange with Teva-SCN resin allows the complete separation of Co from Mn. Mn is quantitatively extracted using a two-stage staggered flow extraction method with a mixture of propylamine 336 (trioctyl/decylamine mixture) and PC 88A (2-ethylhexyl hydrogen-2ethylhexyl phosphonate), adjusting the pH of the Co-free extract solution to 3. The synthetic ionic liquid (ALI-CY) is used for the complete extraction of Ni, and Li remains in the final extract solution. The metal ions in the loaded organic phase are completely reverse extracted with suitable reagents (5% aqua regia for Cu, 5% NH_3 for Co, weak H_2SO_4 solution for Mn, and weak H_2SO_4 solution for Ni).

5. Biohydrometallurgy

Biohydrometallurgy involves the use of microbial leaching to convert useful components of the system into soluble compounds and selectively dissolve them, enabling the separation of target and magazine components, and the recovery of valuable metals, such as lithium, nickel, and cobalt.

Bahaloo-Horeh et al. [69], Mishra et al. [70], Zeng et al. [71], Roy et al. [72], Sadeghabad et al. [73], Cai et al. [74], and Heydarian et al. [75] used biohydrometallurgy to leach valuable metals from spent LIBs. *Aspergillus niger* is an effective fungus in the bioleaching process because of its ability to produce organic acids and chelating agents during its growth phase. It can solubilize metals based on three main mechanisms: Acidolysis, complexolysis, and redoxolysis. In acidolysis, biogenic acids leach metals by protonating oxygen atoms that cover the surface of metallic compounds. The association of protons and oxygen with water causes the metal to detach from the surface. The acidolysis mechanism is quite similar to the conventional acid-leaching mechanism [68]. Bahaloo-Horeh et al. [69] studied the use of a modified *Aspergillus niger fungus* to recover lithium, manganese, copper, aluminum, cobalt, and nickel from spent lithium-ion mobile phone batteries, developing a green, efficient, and simple process. The advantage of the adapted *Aspergillus niger fungus* is found to be its adaptation to heavy metals, producing more gluconic acid and increasing the leaching rate of metals. At a slurry concentration of 1% (w/v), the leaching rates of lithium, copper, manganese, aluminum, nickel, and cobalt by Aspergillus niger are 100%, 94%, 72%, 62%, 45%, and 38%, respectively. Mishra et al. [70] cultured *Acidithiobacillus ferrooxidans* with elemental sulfur and ferrous ions as an energy source, and metabolites, such as sulfuric acid and ferric ions, are produced in the leaching medium. These metabolites help to dissolve metals in spent batteries, with cobalt biodissolving faster than lithium and Co leaching rates increasing from 41% to 65%. Zeng et al. [71] investigated the effect of copper ions on the leaching of LCO by *Thiobacillus* ferrous oxide (A.F). The results show that in the presence of 0.75 g/L copper ions, all of the cobalt (99.9%) enters the solution after 6 d of bacterial leaching, whereas in the absence of copper ions, the dissolution rate of cobalt is only 43.1% after 10 d. Roy et al. [72] increased the sulfuric acid content in the medium at high slurry densities using *Thiobacillus* ferrous oxide, and three cycles of incubation for 72 h resulted in the recovery of 94% cobalt and 60% lithium. Sadeghabad et al. [73] used *Thiobacillus* ferrous oxide acidophilus culture supernatants to extract zinc and manganese from spent button batteries. Manganese and zinc recoveries of 99% and 53%, respectively, are achieved by leaching with 10 g/L of spent button battery powder for 21 d at an initial pH of 2 and a temperature of 30 °C. Cai et al. [74] obtained ferrous oxide-based bacterial populations from neutral sludge in culture enrichment. They have a short leaching cycle and strong organic tolerance and have greater potential for application in the recycling of spent metal lithium batteries, showing a higher leaching curve for the cathode materials $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ (NCM523) and $LiMn_2O_4$. Heydarian et al. [75] performed bioleaching of spent LIBs for laptop computers under two-step conditions on the basis of the bacterial activity of a mixture of *Thiobacillus* ferrous oxide and *Thiobacillus* sulfate oxide strains. Maximum metal recoveries of 99.2%, 50.4%, and 89.4% for lithium, cobalt, and nickel, respectively, are achieved at an optimum inoculum level of 3/2, optimal conditions of 36.7 g/L iron sulfate, 5.0 g/L sulfur, and an initial pH of 1.5.

Dolker et al. [76] used a combination of *Bacillus* lysine-citric acid for the recovery of spent LIBs. The citric acid method is used to separate copper and aluminum foils from the black powder. It leaves lithium and cobalt in a synthetic extractant, and the lithium is further separated by leaching and the cobalt is further separated by biosorption with the proposed hybrid combination. A 25% increase in lithium leaching and a 98% increase in cobalt biosorption can be achieved using this hybrid treatment. The reactions involved are as follows:

$$C_2H_4O_4 \rightarrow C_2HO_4^- + H^+ \tag{13}$$

$$C_2HO_4^- \rightarrow C_2HO_4^{2-} + H^+ \tag{14}$$

Xin et al. [77] first explored the release of valuable Li, Co, Mn, and Ni from three typical spent electric LIB cathodes, LFP, $LiMn_2O_4$, and NCM, by bioleaching at a slurry concentration of 1%. The cultures are inoculated with pure A.T (oxysulfate bacilli), pure L.F (iron screw bacilli), or mixed (A.T and L.F). Accordingly, three bioleaching systems, the sulfur–A.T system, the pyrite–L.F system, and the mixed energy–mixed culture system (MS-MC), are established. The results show that the highest extraction efficiency of Li is achieved by the sulfide–A.T system, indicating that the release of Li is due to the acid solubilization of bio-H_2SO_4. The mixed energy–mixed culture system shows the highest solubilization of Co, Ni, and Mn, indicating that the activation of these metals is the result of the combined effect of Fe^{2+} reduction and acid solubilization. Lithium extraction occurs because of a noncontact mechanism, which is necessary for the activation of Co, Ni, and Mn between the cathode and the cell. pH adjustment greatly improves the leaching performance of the bacteria due to the promotion of bacterial growth, with Li and Mn extractions reaching 95% and Co and Ni release rates increasing from 43.5% and 38.3% to 96% and 97%, respectively.

6. Other Recycling Treatments

6.1. Closed-Loop LIBs Recycling Process

Strategies for the direct recovery of the cathode by the process exist and have attracted increasing interest in recent years. Many researchers have aimed to recycle spent LIBs by directly generating electrode materials to build a closed-loop industrial chain and reduce the pressure of spent liquid disposal. Zhao et al. [78] used ultrasonic cavitation to fully separate lithium cobalt oxide (LCO) and aluminum foil. The lithium in the negative electrode material is directly used as a lithium-leaching solution and applied to the ultrasonic repair of spent LCO. Peng et al. [79] effectively separated aluminum foil, lithium-containing compounds, and high-purity $FePO_4$ using a one-step oxidative leaching reaction at room temperature. LFP with good chemical properties is successfully synthesized by using the resulting $FePO_4$ and $LiCO_3$ precipitated in the leachate, with a lithium leaching rate of up to 98%. Ribeiro et al. [80] used citric acid and nitric acid as leaching agents for the cathode and anode materials, respectively. Graphene oxide (GO) is prepared from the recovered graphite using a modified Hummers method. The GO and recovered CoO are mixed and heat-treated at 450 °C for 2 h using the sol-gel method, and the resulting hybrid material is used as the electrode material. Fan et al. [81] used DMC to clean the obtained ternary LIB cathode material to remove the electrolyte. It is then calcined at 600 °C for 2 h to remove PVDF and carbon black, with the HF and CO_2 generated during the process being absorbed by the NaOH solution. The cathode material is separated from the aluminum foil to obtain the failed NCM523, which was dissolved in deionized water with LiOH, NiO, MnO_2, and $NH_4H_2PO_4$ and stirred vigorously. The NCM523 is directly regenerated by ion replenishment and ion-doping heat treatment. Xing et al. [82] used sulfuric acid as the leaching agent and 30% H_2O_2 as the reducing agent, with magnetic stirring at 400 r/min and an S/L ratio of 10 g/L for 2 h at 90 °C. The leachate is concentrated using a rotary evaporator and used as a precursor for the preparation of $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$. It is prepared through calcination using a coprecipitation method with the addition of the appropriate sulfate. The lithium recovery is 81.2% in the closed-loop circuit process. Chu et al. [83] used sulfuric acid and H_2O_2 to leach mixed cathode powders with over 99% leaching of each metal. Li_2CO_3 is recovered from the residual solution by adding saturated Na_2CO_3. Ternary cathode precursors are prepared directly from the leach solution. The precursors were mixed with Li_2CO_3 and roasted to resynthesize the ternary cathode material $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$. Fan et al. [84] NCM523 was cut into 2 × 2 cm squares. Then, these pieces were stirred in water for 15 min. In this way, the cathode material and the aluminum foil are separated by the shear force of the water flow. Since the aluminum foil remains intact, it can be removed from the water by clamping or filtering. Afterward, the cathode material is filtered and dried at 80 °C for 12 h. Finally, the degraded NCM523 (denoted as D-NCM523) is regenerated by quantitative mixing with LiOH, after which it is directly subjected to a solid-state sintering process (800 °C, 8 h). The powder obtained was regenerated NCM523. The electrochemical performance showed that the regenerated material was comparable to the original material in terms of cycling and multiplicative performance, maintaining capacity retention of 94.5% after 100 cycles and good capacity recovery after 1C cycles. Sa et al. [85] synthesized high-performance $Ni_{1/3}Mn_{1/3}Co_{1/3}(OH)_2$ precursors and NCM cathode materials. Ma et al. [86] cut, shredded, and sieved the discharged batteries. Steel cases, collectors (aluminum and copper), electronic circuits, plastic, and bag materials are removed and recycled. The remaining black material consists of graphite, carbon, cathode material, and some residues of Al, Cu, and Fe. Afterward, a hydrometallurgy process is implemented to dissolve the different anode materials and metals in the leach solution. At the same time, graphite, carbon, and undissolved materials are filtered out. First, impurities in the leachate, including copper, iron, and aluminum, are removed through a series of pH adjustments, leaving behind nickel, manganese, and cobalt ions. The leach solution contained some impurities, including Cu, Fe, and Al. The impurities were significantly removed after the impurity removal step. In addition, the concentration of Na increased due to the addition of NaOH to control the pH to remove the impurities. Furthermore, the concentration of Ni, Mn, Co, and Li decreased due to the volume change after the impurity removal step. The recoveries of Ni, Mn, and Co were above 90%. Next, various NMC were fabricated by adjusting the ratio of Ni, Mn, and Co to the desired ratio by adding pristine metal sulfates as needed. The recycled NCM was demonstrated to have excellent multiplicity and cycling performance, which was verified by various industry-grade tests.

In addition to the preparation of electrode materials, they are recycled as energy storage materials, adsorbent materials, and supercapacitors. Ji et al. [87] used formic acid and hydrogen peroxide for the leaching of LFP and achieved a leaching rate of 98.84% for Li and less than 1% for Al and Fe, allowing the collection of a high-purity Li_3PO_4 product. The leached residue synthesizes $Fe_2P_2O_7/C$. The simultaneous separation of Li, Fe, and Al is achieved, and the leached residue is converted into a new LIB energy storage material. Schiavi et al. [88] leached the spent cathode material. The dissolved metal is precipitated in the form of carbonate. The obtained precipitated carbonate is then dissolved to prepare an electrolyte and electrodeposited into nanoporous alumina templates to prepare nanowire battery cathodes for use as supercapacitors. Zou et al. [89] used the spent LFP battery cathode material as a raw material to generate mesoporous core–shell adsorbents using a simple alkali-leaching process. It has a good adsorption function for removing heavy metal ions from water. Suarez et al. [90] synthesized LiF using hydrofluoric acid to dissolve the spent LIB cathode material (LCO).

Although the direct regeneration process is relatively simple, impurities and damaged structures in the spent cathode material can affect the electrochemical performance of the resynthesized material [91].

6.2. Electrochemical Methods

Electrochemical methods are often used in the recycling of spent LIBs. Chu et al. [92] used aluminum foil and electrode active material obtained from spent LIBs as the anode and sulfuric acid solution as the electrolyte, and electrolysis resulted in complete separation of the aluminum foil and electrode active material. Copper enters the electrolyte as an impurity and is electrodeposited on the cathode, Ni, Co, and Mn remain undissolved in the active material, and Al is insoluble in the solution, where $LiCO_3$ can be collected at high purity and enriched to a certain extent to be recycled. Meng et al. [93] investigated the leaching of LCO generated from spent LIBs by electrochemical cathodic reduction. A possible control mechanism for the leaching of cobalt from spent LCO is determined through thermodynamic, kinetic, and electrochemical impedance spectroscopy. When the malic acid concentration was 1.25 mol/L, the working voltage was 8 V, the temperature was 70 °C, and the time was 180 min, the leaching rate of cobalt is approximately 90%, and the leaching rate of lithium is approximately 94%. To save energy, some researchers have used a two-chamber electrolysis system. Lv et al. [94] used a hydrogen peroxide sulfate system to leach spent LIBs. Using 304 stainless-steel plates as cathodes and platinum or lead plates as anodes, the two chambers are separated by an anion exchange membrane, with the leaching solution as the cathode solution and $(NH_4)_2SO_4$ as the anode solution. Electrolysis in a constructed two-chamber electrochemical reactor yields cobalt metal (>99% purity) and Li_2CO_3, with the simultaneous synthesis of sulfate.

7. Conclusions: Future Perspective of the Research

As the mineral resources on earth are limited, the demand for mineral resources is growing rapidly with economic development, which will lead to a shortage of mineral resources and soaring prices. The valuable metal content in spent LIBs is higher than the concentration in natural ores, and it is a good choice to replace natural ores as a high-concentration mineral source. At the same time, spent LIBs that are not treated and discarded can cause serious environmental safety problems. Thus, the recycling of used LIBs is imperative whether from the perspective of resource recovery or environmental protection.

Among the existing methods to recover valuable metals from lithium batteries, pyrometallurgy is highly energy-intensive, generates large amounts of spent gas and slag, and can only produce alloy intermediate products with low recovery efficiency. Hydrometallurgy requires large amounts of acids, such as hydrochloric acid (HCl), sulfuric acid (H_2SO_4), nitric acid (HNO_3), phosphoric acid (H_3PO_4), formic acid (HCOOH), malic acid, ascorbic acid, lemon juice, citric acid, and iminodiacetic acid. Leaching with HCl may produce chlorine gas and leaching with HNO_3 may produce NO_x. Moreover, the separation and purification steps of the resulting solution are tedious, and the solvent extraction method is mostly used in production practice. The current recovery of valuable metals focuses on Ni, Co, and Mn, and the resulting lithium-containing spent solution is under great pressure for treatment and has a great impact on the environment. Ammonia leaching enrichment can achieve preferential extraction of individual metals, but the metal leaching rate is inferior to that of acid-leaching enrichment. Biometallurgy has certain difficulties in the recovery of valuable metals from spent lithium batteries, specifically because spent lithium batteries contain large amounts of valuable metals and toxic electrolytes, which have a certain impact on microbial activity. The combined method of pyro roasting and hydrometallurgy can destroy the structure of the positive active material at low temperatures and transform the valuable metals into a form that can be easily leached. In the subsequent water/acid leaching stage, the extraction of individual metals (e.g., Li) can be prioritized and the efficient leaching of valuable metals can be achieved without the use of reducing agents, which has good prospects for future applications.

Methods to achieve more efficient, more environmentally friendly, and safer recycling must be the research hotspot in the coming years and beyond. The following research directions can be proposed to achieve these goals:

1. Understand the upstream and downstream materials of lithium battery production and clarify the target products of spent battery recycling.
2. Build a closed-loop industrial chain, reuse reagents, minimize the use of chemical reagents and emissions, and reduce the pressure of spent liquid treatment.
3. Understand the impurities that enter the recycling process, seek means to reduce the content of impurities, produce purer products, and improve the economic value and practicality of products.
4. Develop the products of all by-products in the actual industrial chain to improve the economy of the whole chain.
5. Research new processes that are more economical and environmentally friendly.

Many researchers have explored new recovery techniques. Water leaching is a new method proposed in recent years. Li et al. [95] used water leaching to separate graphite, copper, and lithium using the water solubility of the binder. Lithium (92.82%) is leached at 80 °C, and graphite (100%) is shed. The spent cathode material obtained completely dissociated properties, and the efficiency of leaching lithium is comparable to that of acid due to the complete removal of the binder. Yao et al. [96] proposed a novel recovery technique for manganese from spent LIB cathode materials, including a vacuum reduction process and a gasification–condensation process. The manganese in the cathode material (NCM) is first decomposed to manganese oxide and then reduced to zero-valent manganese by using aluminum. The zero-valent manganese is separated from the rest of the material by gasification in the heating zone and condensation in the condensation zone. Some nanoflakes of zero-valent Mn (100 nm thickness) are found, indicating the potential of this process to produce nanoflake materials. No difficult spent water, toxic gases, or spent hazardous solids are found in the recovery process. Chlorination technology is a better idea to recover spent lithium batteries while solving the environmental problem concerning the difficulty of recycling and disposing of spent PVC and has high research value. However, the high pressure required in the process and the corrosion problems caused by the presence of chloride ions have high requirements for the equipment and are still in the laboratory stage. This technology needs to be further explored before it can be applied in production practice.

Author Contributions: Writing original draft preparation, X.D.; supervision, W.Z. and M.X.; investigation and data curation, Z.R.; funding acquisition, J.C.; supervision and writing-review and editing, X.R. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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