Recycling of Spent Li-Ion Batteries

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Lithium-ion batteries (LIBs) are a widely used energy storage technology as they possess high energy density and are characterized by the reversible intercalation/deintercalation of Li ions between electrodes. The rapid development of LIBs has led to increased production efficiency and lower costs for manufacturers, resulting in a growing demand for batteries and their application across various industries, particularly in different types of vehicles. In order to meet the demand for LIBs while minimizing climate-impacting emissions, the reuse, recycling, and repurposing of LIBs is a critical step toward achieving a sustainable battery economy.

Keywords: battery recycling ; hydrometallurgy ; pyrometallurgy ; waste battery management ; lithium-ion battery

1. Pretreatments

The initial stage of the recycling process involves pretreatment, where the battery casing is separated from the valuable components [1][2][3][4][5][6][7]. Spent LIBs often retain a residual voltage, which, if left unaddressed, can pose a safety risk due to the potential for combustion or explosion. Discharge, battery disassembly, and sorting are typically involved in the pretreatment of waste LIBs. Following pretreatment, the waste batteries can be broken down into various components such as aluminum and copper foils, separators, plastic, and others. Manual disassembly involves carefully removing the battery shell with specialized tools while taking safety precautions to obtain the battery core coil, which can then be manually separated into its constituent parts, including the cathode, anode, and organic diaphragm. In contrast, mechanical processing can be performed on a larger scale and is more cost-effective, making it a more economically viable option. The most valuable component of a battery cell is black mass, and mechanical pre-treatment is primarily designed to achieve its optimal recovery and separation. To accomplish this, a sequence of mechanical processes, including crushing, sieving, magnetic separation, fine crushing, and classification, is typically performed in a specific order.

Widijatmoko proposed a flowchart for the recovery of black mass [8]. The cells underwent shredding and subsequent sieving to partition the components into various size fractions. The fine black mass was extracted from the coarse foils using an attrition scrubbing technique. Among the different size fractions, the 850 µm fraction was found to yield the most desirable black mass recovery composition with minimal copper and aluminum content during milling. However, a significant portion of the black mass remained bound together by the polyvinylidene fluoride (PVDF) binder [9].

2. Pyrometallurgy

Pyrometallurgy is a widely used recycling method that focuses on recovering valuable metal elements from spent LIBs, such as metals, metal oxides, or alloys [10][11]. The technology involves a metallurgical process that separates and extracts valuable metals from solid resources at high temperatures based on their melting and boiling points. The process is physical and chemical and comprises three stages: pyrolysis, metal reduction, and gas incineration. During the pyrometallurgical process, the organic components of LIBs are first thermally degraded, followed by the production of metal alloys using reducing agents at around 1500 °C. Finally, the gas is pyrolyzed and quenched at around 1000 °C to prevent the formation and release of toxic gas [12]. The pyrometallurgical process offers several advantages, such as a short process flow, low equipment requirements, and strong operability. It is also a mature technology and is currently the most diffused way to recycle LIBs in the available plants. However, the process also has some disadvantages. High energy consumption is one of the primary concerns associated with pyrometallurgy, as well as significant environmental pollution due to the release of pollutants during the process. The process also results in low product purity, and metals cannot be often recovered as single metals or single oxides, but as metal alloys [13].

One of the most significant challenges associated with pyrometallurgy is the difficulty in recovering lithium and aluminum during the reduction smelting process due to their vigorous reducing activity. The slag-forming agent also enters the slag phase, requiring further treatment. Overall, despite the challenges, pyrometallurgy remains a widely used recycling method due to its efficiency and effectiveness in recovering valuable metals from spent LIBs.

The carbothermic reduction can also be applied to recover metals from spent LIBs. Carbothermic reduction is a process in which a metal oxide is reduced to a metal using carbon as the reducing agent [14]. In the case of spent LIBs, the metal oxides that are present in the cathode material can be reduced to their respective metals using this process. The process involves mixing the spent battery material with carbon, typically in the form of coke, and heating the mixture in a furnace to high temperatures (usually around 1000–1200 °C). The carbon reacts with the oxygen in the metal oxide, forming carbon dioxide, and the metal is left behind. The metal can then be recovered and reused [15]. This step is generally followed by solvent extraction and chemical precipitation. In particular, combining pyrometallurgical technologies with hydrometallurgical processes is a common approach to recovering valuable metals from spent LIBs. Umicore, for instance, uses this method to first obtain Co-Ni-Cu-Fe alloy through the reduction and smelting of spent LIBs, and then utilizes hydrometallurgy to obtain high-purity single metals and compounds [16].

Several studies suggest that microwave irradiation can lower the temperature required for reactions, even in non-catalytic reaction systems, by several hundred degrees when compared to conventional heating systems [17].

Recently, microwave radiation has been proposed as a sustainable alternative to conventional pyrometallurgical processes for recovering Li, Co, Mn, and Ni from spent LIBs. This approach utilizes a hybrid heating mechanism obtained by combining microwave radiation with other heating methods [18]. The black mass obtained from spent LIBs contains graphite, which can cause heating due to the interfacial polarization of carbon atoms. Hybrid heating technology utilizes an external susceptor to achieve carbothermic reduction conditions in just a few minutes. A significant advantage of this method is that it does not require the separation of anode and cathode materials during the pretreatment process. It can also process a mixture of various discarded LIB materials, which is typical in industrial recycling plants that do not segregate spent battery types. Consequently, primary waste sorting before treatment is unnecessary, which is not feasible in hydrometallurgical processes intended for specific waste recovery.

3. Hydrometallurgy

Hydrometallurgy is a promising recycling method due to its low energy consumption and ability to recover a wide range of valuable metals. One of the main advantages of the hydrometallurgical process is the ability to recover metals individually, as opposed to the pyrometallurgical process, where metals are recovered as alloys. This allows for greater control over the purity of the final products, as well as the potential for greater economic value.

In the leaching process, various chemical reagents, such as acids or alkalis, are used to dissolve the metal ions from the battery waste. Acid leaching is a commonly used method for recovering valuable metals from spent LIBs, where sulfuric or hydrochloric acid is used to dissolve the metal ions [19]. Alkali leaching, on the other hand, uses a basic solution, typically sodium hydroxide or potassium hydroxide, to extract the metal ions [20][21][22][23]. Biological leaching involves the use of microorganisms to dissolve metals, while special solvent leaching utilizes specific solvents to selectively extract certain metals [24].

After leaching, separation and purification techniques are used to remove impurities and isolate the metal ions for further processing.

Solvent extraction is a process that separates metal ions from impurities in a two-phase system by using solubility differences between the metal ions and the solvent. This technique is used after metal leaching and helps to remove impurities like aluminum, copper, and iron to achieve the desired metal purity. Chemical precipitation is another method used for metal separation and impurity removal. The process involves adjusting the pH of the solution to precipitate different metals.

In the hydrometallurgy process, inorganic acids like nitric acid (HNO_3), phosphoric acid (H_3PO_4), hydrochloric acid (HCl), and sulfuric acid (H_2SO_4) are commonly used as leaching agents [25]. However, these acids can release toxic gases such as Cl_2, SO_3, and NO_x during the leaching process, and the waste acid solution requires neutralization with a strong base to prevent water pollution [26].

On the other hand, the use of organic acids (either alone or in combination) like malic acid ($C_4H_6O_5$) [27], oxalic acid ($C_2H_2O_4$) [28], citric acid ($C_6H_8O_7$) [29], and formic acid (CH_2O_2) is considered more environmentally friendly. Organic acids can act as chelating agents, precipitants, and even reducing agents during the leaching process [30].

The efficiency of leaching Li, Mn, Co, and Ni from various cathode materials of waste LIBs, including NMC, LCO, and LMO, is influenced by both the process temperature and time. As the temperature increases, the efficiencies also tend to increase due to the endothermic nature of cathode material dissolution. The effect of time on the leaching efficiency depends on factors such as the type of leaching agent, leaching temperature, and the type of cathode material. In general, longer leaching times tend to improve the leaching efficiency, up to a certain point where further increases in time do not significantly improve the efficiency [31].

One potential disadvantage of hydrometallurgy is the generation of large amounts of wastewater containing chemical reagents and impurities, which require treatment and disposal. Additionally, the recovery of certain metals, such as lithium, can be challenging due to their high solubility and reactivity. Overall, however, hydrometallurgy offers a promising approach to the sustainable recycling of spent LIBs.

4. Biometallurgy

Bioleaching is a bio-hydrometallurgy method that employs microorganisms such as fungi, chemolithotrophic bacteria, and acidophilic bacteria as leaching agents to extract valuable metals from a substrate. These microorganisms use ferrous ions and sulfur as energy sources to produce metabolites in the leaching medium that facilitate the recovery of metals [32].

Selective microbial bacteria can be employed to facilitate the leaching of valuable elements through specialized metabolic processes [33]. One example of a microorganism that can be used for bioleaching is *Aspergillus niger*, a haploid filamentous fungus. *A. niger* facilitates bioleaching by secreting low molecular weight metabolites, such as organic acids, that dissolve metals from batteries. To extract Co and Li from spent LIBs, the spent medium bioleaching method was employed using the organic acids produced by *A. niger* [34].

Compared to traditional metal recovery methods, bioleaching presents several benefits, including complete metal recovery, simplicity, cost-effectiveness, and lower energy consumption. One of the significant advantages of bioleaching is that it does not require harsh conditions or specialized industrial equipment, making it an attractive technology for metal recovery. However, the slow kinetics of the process are a potential limitation. Although bioleaching is a promising technique, it takes longer to recover metals than other methods, which can be a disadvantage in terms of processing time and efficiency. Nevertheless, ongoing research in this field is focused on improving the kinetics of bioleaching and making it more efficient for industrial applications [35]. Due to the requirement for microorganisms to adapt and undergo genetic modification to withstand the toxicity of the leachate media from spent LIBs, as well as the relatively slow kinetics of the process, bioleaching is not currently well-suited for large-scale applications [32].

5. Solvometallurgy

Solvometallurgy is an extremely recent approach developed for the recycling of waste-LIBs as an alternative to the hydrometallurgical processes and to overcome their main limitations. Indeed, as discussed in the previous paragraphs, hydrometallurgy exploits water-based solutions of leaching agents with inorganic and organic acids as the most reported for industrial and laboratory scale research, respectively [36][37][38]. This leads to the creation of large volumes of wastewater as, typically, the solubility of the leached metals is low in this water-based solution. Moreover, in the case of inorganic acid leaching, the formation of hazardous gas species such as NO_x, SO_x, and HCl need to be accounted for as a source of secondary pollution [36][38][39]. Solvometallurgy is based on the use of alternative leaching systems such as ionic liquids and deep eutectic solvents (DESs); particularly, this last class of compounds has led to appealing results since the first report of their exploitation for cathode recycling [40][41][42][43].

Generally, DESs are based on biodegradable and inexpensive components; from a structural and functional point of view, they present medium-high viscosity, low volatility, non-flammability, extremally low toxicity, and high thermal stability, thus presenting a desirable combination of favorable characteristics as possible leaching systems for w-LIBs. Indeed, due to their peculiar composition, the solubility of metals in the DES is generally high and, thus, the production of wastewater is reduced or eliminated [41][44][45][46][47][48].

DESs formally can be classified as a class of ionic liquids, and they are made of two or more components forming a eutectic mixture at room temperature. The condition to obtain a eutectic mixture is to combine a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA) [49]. Recently, the general formula has been proposed as Cat+ X- zY with Cat+ as the cation, X- as the Lewis base, and Y as a Broensted acid; concerning this, a classification of DESs to rationalize the variety of compositions has been proposed [37][49][50]. Almost all the DES compositions that appeared in the literature for applications in the recycling of cathodes from waste-LIBs contain choline chloride as HBA and belong to Type III according to the classification reported above [49]. Several reports have appeared in the literature exploring several HBDs, reporting high efficiency for the leaching of LCO, NMC, and LMO materials [40][48][49][50][51][52][53][54][55][56]. In minor extension, DES has also been used for the detachment of electrodes from the current collector and anode recycling [57] [58]; today, most studies are focused on the degradation of cathode components.

The range of explored conditions is wide, with the main parameters affecting the leaching process being the time (60 min–48 h), temperature (80–240 °C), and the liquid–solid ratio [37][40][42][49][50][51][52][53][54][55][56]. The mechanism driving the leaching is still not completely clear; the presence of a reducing agent seems to be necessary to force the Co^{3+}/Co^{2+} reduction and favor the degradation of the LCO materials [49][50][51][59]. The reducing ability of the HBD has been assessed through density functional theory (DFT) analysis and Capacitance-voltage (CV) measurements, but this kind of study on the leaching mechanism is still in its infancy. Several studies report the possibility of recovering the DES systems after the leaching process and propose its reuse for several leaching cycles; this aspect must be further investigated and combined with the determination of the leaching mechanism. Indeed, if the leaching reaction is driven by a reductive decomposition of the cathode material, the oxidation of the DES must be inferred. Thus, for a full recovery of the DES and its reuse, this oxidation must be reversed or compensated with a change in the DES composition. As a perspective, beyond the promising results obtained up to now in the high-yield degradation of cathode components, some efforts are needed to understand and rationalize the effect of the DES composition on the leaching process and to obtain insight into the leaching mechanism. This can lead to a further optimization of compositions and conditions for a more effective leaching process. As already stated, only small efforts have been made in the field of exploitation of DES for the detachment of electrodes from the current collectors and for the recycling of the anodes; also, these topics can be of high relevance in the future.

Overall, the different developed technologies here described present both advantages and weak points. Indeed, pyrometallurgy is the mainstream method at the industrial scale, and is the most diffuse and mature, with high recycling volume capacities and extremely simple operations. At the same time, it suffers from some severe limitations, the main one being the possibility to recover only a fraction of elements of interest. Indeed, with the technologies implemented today, it is not possible to recover lithium, considered one of the most critical and strategic elements, while also considering the new regulation proposal from the EU that makes Li recycling and reuse mandatory [60]. Hydrometallurgy can encompass this limitation if not associated with preliminary pyrometallurgical steps (as often implemented) but as an alternative independent strategy. Although still limited, it is already industrially exploited and is expected to grow rapidly thanks to this particularly appealing factor. The main drawback of such an approach is the creation of large amounts of wastewater due to the limited solubility of the relevant metals in water-based solutions [61]. Solvometallurgy represents, in this sense, a possible and appealing alternative as it allows for low-temperature operation (80–250° typically), complete dissolution of the cathode materials, and high yields of recovery of different elemental species.

6. Direct Lithium Supplementation

Direct lithium supplementation is a method of recycling the cathode of LIBs that involves replenishing the lithium content in the cathode material to restore its capacity and cycling performance [62]. This method aims to address the issue of lithium deficiency in spent LIBs, which can lead to a decrease in the overall performance of the battery. Direct cathode regeneration methods have been proposed as a means of closed-loop recycling, which can mitigate raw material shortages and supply chain risks [63]. The regeneration process involved supplementing metal ions, granulation, ion doping, and heat treatment, generally resulting in excellent electrochemical performance. One study proposed the use of an eutectic LiI-LiOH salt with a low eutectic point to create a Li-rich molten environment, which offers excess lithium and benefits ion diffusion compared to a solid environment [62]. This eutectic salt, combined with additives, simplifies the recycling process and endows the cathode materials with lithium supplementation and structural ordering, leading to the restoration of capacity and stable cycling performance. Another study developed a green, efficient, closed-loop direct regeneration technology for reconstructing the $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ cathode material from spent LIBs [64].

Nevertheless, the applicability of the approach is constrained when faced with diverse cathode chemistries and degradation scenarios observed in different spent LIBs. Nearly all documented direct recycling techniques prove effective solely for one or two categories of spent cathodes characterized by a limited degree of degradation [62]. Specifically, these are instances where the cathode materials exhibit a high residual capacity and minimal structural damage. Existing direct recycling methods, however, largely neglect highly degraded cathodes marked by low residual capacity and significant structural defects, primarily due to the challenges associated with their repair.

7. Anode and Electrolyte Recovery

In recent years, there has been increasing attention given to anode recycling, although it has not yet been established to the same extent as cathode recycling. Anode recycling is becoming an increasingly important aspect of LIB recycling. At present, anodes for LIBs can be manufactured using a variety of materials, such as natural or artificial graphite, carbonaceous materials, or even silicon. Among these options, graphite is the most widely used material in commercial applications due to its excellent conductivity, stability, and low cost. In fact, graphite is the most applied material in commercial anode production processes [65]. Several approaches have been reported in the literature, including pre-treatment, pyrolysis, hydrometallurgy, supercritical, and water treatment. Recycling anodes involves removing the active material (e.g., graphite) from the copper or aluminum foil substrate. One common method is to use pyrometallurgical processes to treat the anode material at high temperatures, which oxidizes the carbonaceous material and leaves behind a mixture of metal oxides. This mixture can be further processed using hydrometallurgical techniques to extract valuable metals such as lithium and cobalt. Another method involves the use of mechanical processes, such as grinding and sieving to separate the anode material from the substrate, followed by further processing using hydrometallurgical techniques [66].

Anode recycling has the potential to reduce the demand for virgin graphite and other raw materials, as well as decrease the environmental impact of producing new anodes. However, the challenge with anode recycling is that the graphite particles can become contaminated with metals and other impurities during the cycling process, which can affect the performance of the recycled anode material.

Like anodes, the recycling of electrolytes has gained attention in recent years. Typically, electrolytes are evaporated or burned during thermal processes, but various methods have been proposed to recover lithium from this component [67]. The initial technique involved in the recovery of the electrolyte was liquid extraction. Subsequently, a method utilizing sub- and supercritical media was proposed, which exhibited relatively high recovery rates. This method was also utilized for the retrieval of binders [68]. However, alternative methods for valorization have also been reported [69].

8. Current Collector Recycling

Current collectors, such as Al and Cu foils, are irreplaceable components of LIBs and have a significant impact on their performance. The recycling and reusing of these current collectors can contribute to reducing total global emissions and the demand for new materials [70]. Several strategies have been proposed for the separation and recovery of current collectors from spent LIBs. Pyrolysis and physical separation have been studied as effective methods for the recovery of valuable materials, including current collectors [71]. Another study developed a physical separation process using thermal and mechanical treatments to recover active cathode materials from current collectors [72]. The ultrasound-assisted Fenton reaction has also been explored for the selective removal of binders to recover cathode materials from current collectors [73]. Additionally, a solvent-based recovery process has been developed for the low-temperature and efficient separation of electrode materials from current collectors without damaging the active materials or corroding the metal foils [74]. These studies demonstrate various approaches to recycling and reusing current collectors in LIBs, contributing to the sustainable development of LIBs and the electric vehicle industry.

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