

Review

An Overview of the Sustainable Recycling Processes Used for Lithium-Ion Batteries

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Abstract: Lithium-ion batteries (LIBs) can play a crucial role in the decarbonization process that is being tackled worldwide; millions of electric vehicles are already provided with or are directly powered by LIBs, and a large number of them will flood the markets within the next 8–10 years. Proper disposal strategies are required, and sustainable and environmental impacts need to be considered. Despite still finding little applicability in the industrial field, recycling could become one of the most sustainable options to handle the end of life of LIBs. This review reports on the most recent advances in sustainable processing for spent LIB recycling that is needed to improve the LIB value chain, with a special focus on green leaching technologies for Co-based cathodes. Specifically, we provide the main state of the art for sustainable LIB recycling processes, focusing on the pretreatment of spent LIBs; we report on Life Cycle Assessment (LCA) studies on the usage of acids, including mineral as well as organic ones; and summarize the recent innovation for the green recovery of valuable metals from spent LIBs, including electrochemical methods. The advantage of using green leaching agents, such as organic acids, which represent a valuable option towards more sustainable recycling processes, is also discussed. Organic acids can, indeed, reduce the economic, chemical, and environmental impacts of LIBs since post-treatments are avoided. Furthermore, existing challenges are identified herein, and suggestions for improving the effectiveness of recycling are defined.

Keywords: spent LIBs; recycling; environmental impact; pretreatment; green hydrometallurgy



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1. Introduction

Lithium-ion batteries (LIBs) have conquered portable device and electrical automotive markets since their first commercialization in the early 1990s by SONY [1]. Thanks to their unique characteristics, such as high energy and power density, high reaction reversibility, and long storage life, LIBs have been employed in a wide variety of applications, from large industrial storage to individual purposes, such as domestic applications. Thus, in the past 10 years, the production of LIBs has exponentially grown along with the global energy demand. Therefore, efficient and sustainable recycling processes must be developed to face the huge number of spent LIBs that will flood the world in the next decade [2]. Indeed, according to the US Department of Energy, global stationary and transportation,

combined with the annual energy storage market, are projected to increase fourfold by 2030 to more than 2500 GWh from the 2018 baseline [3]. The prediction of the increasing trend is shown in Figure 1, where the global EV vehicle production [4] and the projected energy until 2030, divided by market application, transportation, stationary source, and PSH (pumped-storage-hydropower), are presented.

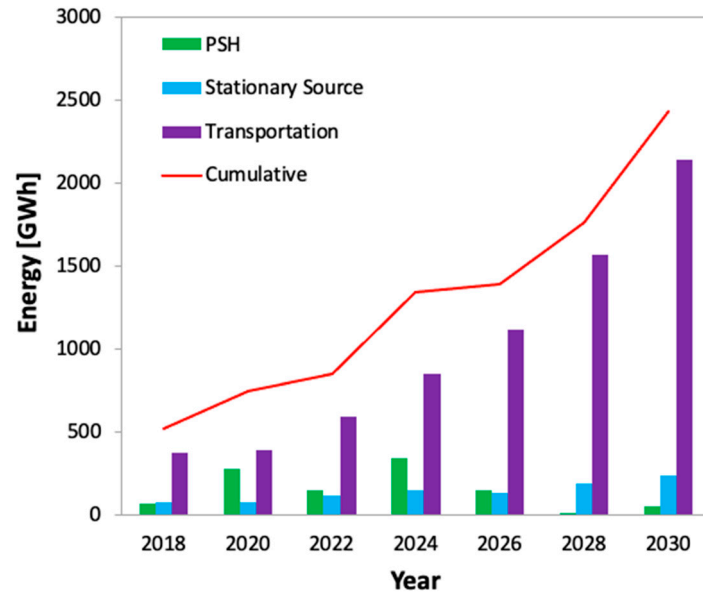


Figure 1. Increase prediction in energy demand until 2030 divided by sector. Data available in [3]; figure obtained from data elaboration.

The New Energy Outlook of BloombergNEF [5] reports a detailed long-term scenario analysis on the future of the energy economy until 2050, as summarized in Figure 2. The zero-emission scenario for 2050 forces a rapid and great deployment of renewable, nuclear, and other low-carbon technologies. Renewable energies require electrical energy storage, such as lithium-ion batteries, in order to deliver energy when required.

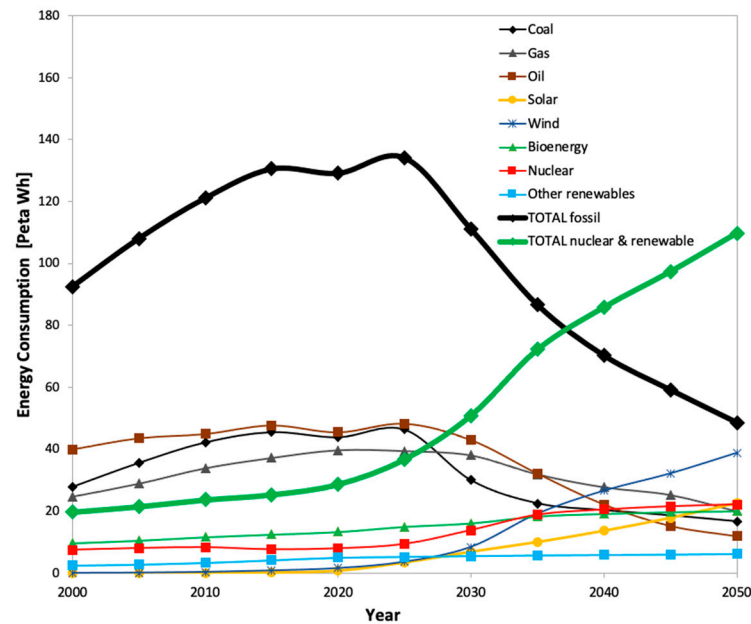


Figure 2. Trend of the energy composition to achieve net-zero emission in 2050. Data elaborated from [5]; figure obtained from data elaboration.

As the production of LIBs for EV is going to dramatically increase, several threats will come to light, such as the unavoidable forthcoming lack of raw materials and disposal issues. Most of the elements used in batteries (e.g., Co, Mn, Al, and Li, and Cu and Ni, which were just recently added as strategic raw materials) have already been enlisted in the EU critical raw materials (CRMs) directory [6,7]. Hence, promoting a more rational use of CRMs, their substitution and/or reuse in a secondary application is becoming mandatory. The second use of aged EV-LIBs has already become a hot spot in the energy storage landscape [8] despite the meagre numbers of EV on the market today. Hence, developing sustainable and economic methods to reintegrate spent LIBs at an industrial scale represents an urgent need.

Despite many economic and environmental advantages, the recycling of LIBs is still in its early stages because of many hindrances, including science and technology gaps, economic impediments, collection, logistics, sorting barriers, and regulatory lacks [9]. Many factors act as obstacles in recycling processes development. The large fluctuation of raw materials' prices and availability, together with decreasing battery production costs, heavily contribute to the economics of recycling, effectively discouraging the shift to far-reaching policies that could impose strict regulations to the recycling of spent LIBs.

Additionally, technological advances in LIB development comprise several cathode chemistries, such as LiCoO_2 (LCO), $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ (NMC), LiFePO_4 (LFP), $\text{LiNi}_x\text{Co}_y\text{Al}_{1-x-y}\text{O}_2$ (NCA), and LiMn_2O_4 (LMO), adding another layer of complexity to spent LIB recycling. Furthermore, different materials involve different recycling processes, hence implementing that global battery flow management could reduce the collection, sorting, and recovery efficiencies of spent LIBs [10]. In this regard, a recent report from the World Economic Forum and the Global Battery Alliance argues that a battery passport should be established in order to label diagnostics and shared data, especially for EV batteries [11].

Today, a typical LIB cell is composed of a cathode, an anode (generally based on graphite composites or lithium titanate), two current collectors (Cu and Al foils for anodes and cathodes, respectively), a separator, an electrolyte, an outer case, and sealing parts. Solvents and salts compose the electrolytes; the most used salt is LiPF_6 [12].

Natural graphite is the most used anode material in recent batteries. However, it is also listed as a CRM in the European Union [6,7]; thus, several studies have been proposed to guarantee the recycling of this component. Furthermore, the weight percentage of graphite in a common battery can be between 10 and 15%, making it 10% of the cost of the device [13]. In addition, in the past few years, the global graphite industry recorded a steady growth of the demand and a tight supply chain due to an increased demand for EVs [14]. Several techniques have been investigated for the recovery and reuse of spent anodes, such as reintegration into the battery supply chain of regenerated [15] and remanufactured [16] materials. Graphite is usually recovered in the filtrate after the leaching of black mass. Before reusing it in fresh LIB cells, the recovered graphite must undergo a purification step to achieve battery-grade parameters. A common technique for its regeneration involves acid leaching [17] to remove metal impurities, such as Cu and Li, and thermal treatment [18] for the removal of organic components of the solid electrolyte interphase. More sustainable processes have been reported in the literature, such as bioleaching [19]. However, diving deeper on this topic is behind the purpose of this review article.

Organic compounds, such as dimethyl carbonate (DMC) and ethyl carbonate (EC) [20], are commonly employed as solvents. Separators, which prevent a short circuit from undergoing direct contact between the cathode and anode, are usually made of single or multi-layers of polyethylene or polypropylene [21]. The most used materials in commercial LIBs and their hazardous threats are summarized in Table 1. Many efforts have been focused on recovering valuable metals from active cathode materials in an economically viable way, especially for cobalt and nickel. However, recycling other materials, such as graphite, metal foils, and electrolytes, could enhance recycling revenues and maximize profitability.

Table 1. Overview on the most used materials in LIBs and their environmental risks.

Components	Materials	Hazardous	GHS Hazard Statements
Cathodes	LiCoO ₂ , LiNiO ₂ , LiNi _x Co _y Mn _{1-x-y} O ₂ , LiFePO ₄	Heavy metals (particularly Ni and Co) need special treatments to avoid causing environmental and human threats.	H317 may cause an allergic skin reaction (LiCoO ₂ , LiNiO ₂ , LiNi _x Co _y Mn _{1-x-y} O ₂). H351 is suspected of causing cancer (LiCoO ₂ , LiNiO ₂ , LiNi _x Co _y Mn _{1-x-y} O ₂).
Electrolyte salts	LiPF ₆ , LiBF ₄	Fluorine-based materials which can produce corrosive gas: hydrogen fluoride (HF).	H301 is toxic if swallowed (LiPF ₆ , LiBF ₄). H311 is toxic when in contact with skin (LiPF ₆ , LiBF ₄). H314 causes severe skin burns and eye damage (LiPF ₆ , LiBF ₄). H341 causes germ cell mutagenicity (LiBF ₄). H372 causes damage to organs through prolonged or repeated exposure if inhaled (LiPF ₆).
Electrolyte solvents	EC, DMC, EMC, DEC	Flammable volatile compounds. Low flash points.	H225 is highly flammable liquid and vapor (DMC, DEC, EMC). H302 is harmful if swallowed (EC). H319 causes serious eye irritation (EC). H373 may cause damage to organs (Kidney) through prolonged or repeated exposure if swallowed (EC).
Binders	Polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE)	Can generate HF and organofluorine compounds when burnt.	
Separators	Polyethylene (PE), polypropylene (PP), and their combinations	Carbon oxides can be generated when PE and PP are heated.	

Three different recycling routes are mainly employed to recycle spent LIBs: pyrometallurgical, hydrometallurgical, and direct recycling processes [22]. The first two are designed to recover materials and salts, while the latter directly reuses and reconditions electrode materials with which new batteries are made on a lab scale. Each of these processes needs the cell to be discharged before the treatment. Moreover, the discharged cell needs to be pretreated at different levels depending on the recycling technology [23].

1.1. Pyrometallurgical Process

The pyrometallurgical process extracts valuable metals through the thermal treatment of spent batteries in high-temperature furnaces (ca. 900–1400 °C). Generally, spent batteries are fed into the heat chamber to separate elements: target metals turn into alloys thanks to a carbothermal reduction (commonly Co, Cu, Ni, and Fe), while scrap metals form a slag (commonly Li, Al, and Mn). Eventually, the two resulting feeds can be treated with a hydrometallurgical process and/or sold to other industries as secondary raw materials. This process is the natural progression of already existing plants used for the recycling of other types of batteries [24]. G. Ren et al., in [25], proposed a new slag system to reach high yields in recovering Co (99.03%), Cu (99.30%), Ni (99.30%), and enriched slag with MnO (47.03%) and Li₂O (2.63%). In a typical pyrometallurgical process, Li will end up in the slag phase from which it can be reextracted. The major drawbacks in pyrometallurgical technology are mainly represented by (i) rigorous requirements regarding gaseous phases post-treatment, (ii) high energy consumption, and (iii) the fact that most of the Li, Al, and Mn end up in the slag, which is usually not recovered or downcycled to the production of cement [24]. Furthermore, components such as electrolytes and/or plastics are burnt and lost during this process [25]. However, it has recently been demonstrated that Li can be recovered as Li₂CO₃ using a low-temperature treatment (900–1000 °C) due to

the reductants forming (CO, H₂, and CH₄) from organic material inside the battery (e.g., separator, electrolyte, and graphite). The efficient recovery of Li and Co as Li₂CO₃ and CoO can also be carried out by employing carbon black as a reducing agent, as proposed in [26], in which high yields were achieved, even at 600 °C, thus highly reducing the energy costs of the entire process.

1.2. Hydrometallurgical Process

Through the hydrometallurgical process, valuable metals can be recovered using leaching agents combined with reductants [27]. Figure 3 schematically describes the main process steps in pyrometallurgical and hydrometallurgical technologies.

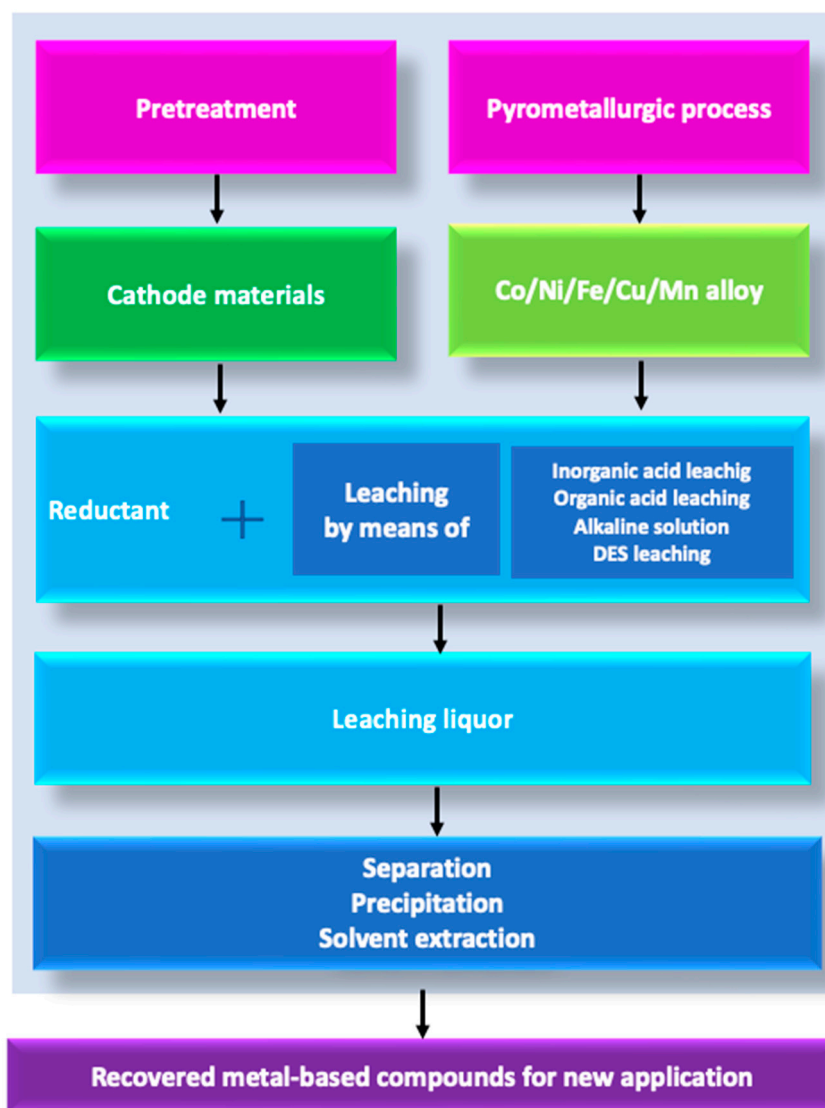


Figure 3. Flow chart of the main steps of hydrometallurgical and pyrometallurgical recycling processes for lithium-ion cells [27].

In hydrometallurgical processes, mineral acids have been largely employed [28–30], reporting high recovery yields of Co, Ni, and Li using HCl, HNO₃, or H₂SO₄ [28–33].

However, the use of highly concentrated mineral acids leads to many drawbacks, such as high costs of reactants and of the wastewater stream treatment, and an overall high environmental impact related to the disposal of the spent acids [34]. Hence, to overcome these obstacles, many researchers have focused on shifting to organic acids, such as citric

acid ($C_6H_8O_7$) [35,36], oxalic acid ($H_2C_2O_4$) [37], malic acid ($C_4H_5O_6$) [38,39], and L-tartaric acid ($C_4H_6O_4$) [40,41].

1.3. Direct Recycling Process

The term direct recycling refers to all the processes which do not involve the destruction of the crystalline structure of cathode materials. Specifically, cathode materials are commonly regenerated or repaired and ready to be used in fresh batteries, rather than dissolved in acidic media. The regeneration/repairing step generally involves a stoichiometric adjustment of the cathode material, commonly given by a reductant coupled to a Li salt, which may be followed by a sintering step. For instance, in [42], B. Gangaja et al. proposed a method to regenerate spent LFP cathodes ($Li_{1-x}FePO_4$ with $x < 1$) by using LiI, which can act as both a reducing agent and a Li source. By performing the reaction at $80\text{ }^\circ\text{C}$ in acetonitrile, they were able to restore the original stoichiometry and performances of LFP. In ref. [43], P. Xu et al. proposed a method for the regeneration of the layered NMC cathode. The regeneration consisted of two steps, i.e., (i) hydrothermal treatment in the presence of LiOH, and (ii) short annealing in the presence of Li_2CO_3 to reconstitute the crystalline structure. The authors also demonstrated the possibility of regenerating and remanufacturing cathodic materials from NMC from mixed batteries that were originally used in cell phones and laptops [44].

As demonstrated by the ReCell consortium [45], direct recycling can be more efficient in terms of cost and GHG emissions compared to the other recycling routes and mining. However, each direct recycling process must be tailored to a specific cathode chemistry. Furthermore, the risk of regenerating an obsolete cathode chemistry for the preparation of new cells has to be considered. For these reasons, even if direct recycling is a promising route for the green and efficient recycling of LIBs, its use is still hindered, and research must tackle these issues.

1.4. Scope of the Review

This review summarizes the most recent lab-scale processes in organic hydrometallurgical leaching and electrochemical processes as efficient technologies to recover valuable components from LIBs. Specifically, economic and environmental evaluations of different approaches are reported. Different leaching agents are compared using Life Cycle Assessment (LCA) methodologies proposed by the different authors. We then provide an insight into the most utilized pretreatment processes on both the industrial and laboratory scales. Furthermore, several sustainable processes for the recycling of spent LIBs are evaluated and discussed. In particular, green hydrometallurgical technologies employing organic acids and sustainable recovery processes for dissolved metals, such as precipitation and electrochemical methods, are reported. Challenges and perspectives are also highlighted to direct future work on battery recycling.

2. Economic and Environmental Aspects

The Life Cycle Assessment (LCA) approach is frequently used to evaluate the environmental impact of a recycling process and the reuse of materials. Several authors highlighted the absence of a viable technology for recycling LIBs, suggesting the implementation of a robust infrastructure for the recovery of battery materials by promoting policies and incentives [46,47]. The increment in the LIB waste stream has also been detected by many researchers and industries that are implementing innovative and sustainable systems (such as the above-cited Battery Identity Global passport) for the recycling of lithium-ion batteries [10,48,49].

Both economic and environmental advantages come from spent LIB recycling since the end-products would be reintroduced into the value chain [50]. In this perspective, the primary production can be integrated with an urban mining strategy [51]. In particular, J. Dewulf showed that if the LIB cathode materials came from recycling process instead of virgin materials, more than 50% of resources would be saved [52]. Yoo and co-authors

demonstrated, through an LCA analysis, that the life cycles of greenhouse gas emissions of recycled LiOH are up to 72% lower than those of virgin LiOH production originally extracted from Australian brine [53].

GaBi software was recently employed to compare the impacts, in terms of the LCA, of two different extraction processes for cobalt oxalate from cathode materials, employing acidic or basic routes. This work highlights that the acidic process is cheaper compared to alkaline leaching routes. Furthermore, from the analysis of greenhouse gas emissions, it was found that a lower quantity of CO₂ equivalents (4.38 kg) could be produced by using acid leaching instead of the alkaline ones (6.37 kg of CO₂ equivalents) [54], thus producing a lower environmental impact.

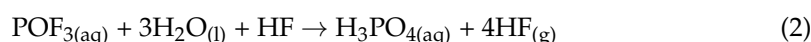
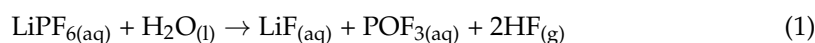
As mentioned above, the usage of organic acids in hydrometallurgical processes is more sustainable than the use of mineral ones [55]. In ref. [56], S. Anwani et al. recently proposed a comparison between different acidic compounds by evaluating the greenhouse gas emissions in terms of the kg CO₂ equivalents of each compound. It was found that the use of oxalic acid would lead to a lower environmental impact than the use of other mineral acids, with an emission of 4.02 kg CO₂ equivalents.

In addition, Li and co-authors [57] studied the influence of organic acids, such as citric acid, malic acid, and aspartic acid, on the environmental impact and efficiency of the cobalt leaching process from LIB cathodes. Moreover, variables such as the reaction time, temperature, reductant concentrations, and energy consumption needed to produce each acid were optimized according to the yield of Co extraction. Finally, they found that citric acid is the most economical and environmental valuable compound considering the Full Fuel Cycle (FFC) value (Argonne National Laboratory's Greenhouse Gases, Regulated Emissions and Energy use in Transportation, GREET) of 33 MJ kg⁻¹ (the recovery efficiency of Co was considered as 90% for the calculation).

The beneficial and rational use of the recovered resource can be obtained with a proper disposal of LIBs, while also considering the efficiency of the different recycling techniques [58]. The most sustainable processes proposed from the literature review are described below.

3. Hydrometallurgical Recycling of Spent LIBs

A summary of the currently available treatment approaches is shown in Figure 4, where a simplified scheme summarizing the main steps of the hydrometallurgical recovery of LIBs is shown. Prior to processing, the spent LIBs should be fully discharged to minimize the involved workers' risk of electrocution, short-circuit, and then undergo thermal runaway. A commonly proposed route to safely discharge LIBs is by immersing spent batteries in a NaCl-saturated solution [59]. Thanks to the conductivity of the solution, a current between the positive and negative terminals will flow and safely discharge the device. However, if the produced current is too high and/or the solution is corrosive (e.g., NaCl), the internal components of the battery can be exposed [60]. When the electrolyte LiPF₆ is exposed to water, a series of chain reactions occurs, leading to the formation of HF (Equations (1) and (2)).



Other stabilization routes, not involving the discharge of the spent devices, have been proposed in the literature, such as heating at $T < 300$ °C and cryogenic grinding with liquid N₂, in which the cryogenic temperature can temporarily mitigate any possible side reaction and thermal runaway.

In addition, a series of physical separations needs to be performed to collect the cathode material. The main pretreatment processes are described below.

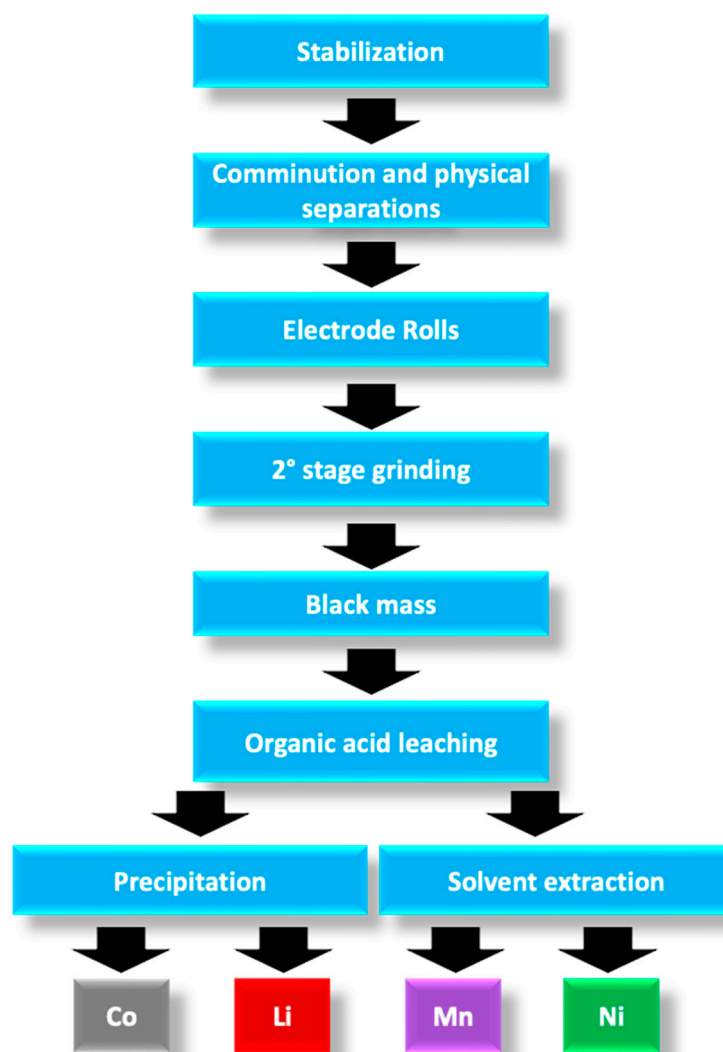


Figure 4. Simplified scheme of the basic steps of hydrometallurgical recycling process of spent battery.

3.1. Pretreatments

The initial stabilization of the spent battery is necessary to prevent potential danger to users and materials. There are several main possibilities [61]: the discharge, which is necessary before the dismantling of the battery housing to avoid self-ignition, short-circuit, or, in other cases, thermal deactivation by means of cryogenic deactivation, which is often used for primary lithium metal batteries used in small electronics, and heat deactivation. Inert atmosphere protections, where spent batteries are opened in a N_2 - or CO_2 -saturated atmosphere, and the absence of oxygen can reduce the reactivity of the cells [62,63]. After the discharge, the internal components of the spent LIBs must be extracted to begin the recycling process. The extraction is commonly achieved by comminution since it is the fastest and more autonomous route [64–69]. In this case, toxic gasses from degraded electrolytes and fine particles ($<200\ \mu m$), mainly composed of electrode materials, are released during the shredding process. In particular, by using commercial batteries, more than 46 species of released gasses have been detected, such as from electrolyte-component species (EC, DMC), hydrocarbons (C_6H_6 and C_2H_4), oxygenated hydrocarbons (CH_2O), and other species, including acids (HF) and fluorine-containing gasses (CH_3F , POF_3) [70]. Furthermore, even though the cells are discharged, there is still the risk of thermal runaway when performing the comminution step due to short-circuits. For this reason, comminution is commonly carried out in an inert atmosphere or in a media to avoid this kind of event. For instance, inert gases, such as Ar and N_2 , or even a vacuum, can be used during comminution

(for example, in the patent DE102018102026A1). Even CO₂ can be used, which is able to convert the Li-compounds that are present in the electrolyte in Li₂CO₃ [71], or as shown in the patent US7820317B2. Grinding in the presence of a water spray has also been proposed [72], in which the sprayed H₂O acts as a heatsink and mitigates the temperature rise due to the short-circuit occurring during the comminution. Also, immersion in water can mitigate the risk of thermal runaway, with the issue of having, in turn, to treat the water used in the process [73].

In some cases, extraction by manually opening and dismantling the cell has been proposed. Eventually, a series of physical separation [74] such as density separation [64,75], magnetic separation [76,77], froth flotation [78–80], and sieving must be used to separate and collect the cathode active material.

Generally, anode and cathode materials are adhered, respectively, to Cu and Al current collectors by using the fluorine-based polymer binder as polyvinylidene fluoride (PVDF) [23], which hinders their separation from the Al/Cu foils. Thus, several routes have been explored for the detachment of active materials from their respective foils, such as the dissolution of PVDF [81–84], the dissolution of the Al current collector [85,86], and the thermal decomposition of PVDF [87,88]. These methods will be briefly discussed in the following Sections 3.1.1–3.1.3.

3.1.1. Solvent Dissolution of PVDF

Organic solvents are, in general, used in a solvent-assisted scrap process. A good organic solvent must have a high affinity to the binder to also weaken the adhesion between the current collector foils and active material. In the late 1980s and early 1990s, early studies were conducted on the affinity and solubility of PVDF [89] and PTFE [90] in several solvents. However, the most used solvent today is N-methylpyrrolidone (NMP), which can dissolve PVDF and PTFE [91]. NMP is a good solvent for PVDF (solubility ca. 200 g kg⁻¹ of solvent). The recovery of the cathode materials can then be achieved by simply filtering the NMP solution. However, it is well known that NMP is highly toxic both for the environment and human health [92] (GHS hazard statements 360d–319–335–315), obviously hindering its industrial application [93].

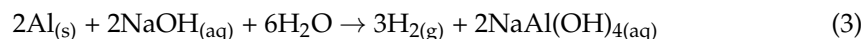
Only a handful of solvents are able to dissolve PVDF, i.e., dipolar aprotic molecules such as N,N-dimethylacetamide (DMAC), N,N-Dimethylformamide (DMF), dimethylsulfoxide (DMSO), Dihydrolevoglucosenone (Cyrene), and triethylphosphate (TEP) [94]. N,N-dimethylacetamide (DMAC) was used as a solvent for the separation of the LCO cathode material from Al foil due to its economic edge over NMP [95], despite the 10% (in weight) PVDF solubility. Due to the lower boiling point of DMAC (165 °C) with respect to NMP, it can be easily evaporated by heating the solution at 120 °C for 12 h [96]. He et al. studied DMAC, DMF, DMSO, and ethanol under ultrasonic treatments as alternative solvents to NMP. The key parameters that affect the peel-off efficiency were identified in the solvent nature, the temperature, the power, and the time of ultrasonication step. Also, Ren et al. compared mechanical stirring and ultrasonic treatment used to separate graphite electrode materials from copper foils, with efficiencies from 84% to 91 for each treatment, respectively [97].

In recent works from Belharouak's research group [82,98], the solvents triethylphosphate (TEP) and dihydrolevoglucosenone (Cyrene) have been proposed as possible green solvents for the dissolution and separation of PVDF from black mass. In both cases, dissolution occurs at $T \geq 100$ °C, with short dissolution times of 1 h and 30 min for Cyrene and TEP, respectively. The PVDF was then recovered by temperature-induced phase separation (TIPS) and non-solvent-induced phase separation (NIPS) when Cyrene and TEP were used, respectively. Water-processable binders have attracted keen interest in recent years thanks to the possibility of reducing the environmental and energy impacts of the production of LIBs. Furthermore, when recycling electrodes with water-processable binders, such as sodium carboxymethylcellulose (NaCMC) or polyacrylic acid (PAA), H₂O can be used as a

solvent for the dissolution of the binder and the detachment of the black mass from the current collector, leading to a greener binder removal step [99,100].

3.1.2. Al Current Collector Dissolution by NaOH

In many recycling processes, the active cathode materials are separated from Al foils using NaOH solutions. This method has high efficiency yields for the treatment of LCO-based LIBs, as reported in [101], where 2M of alkaline NaOH solution was used to detach Al foil from different spent LIBs (LiCoO₂, LiMn₂O₄, and LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂). The cathode materials were immersed in the alkaline solution for 2 h, and the Al foil was dissolved in NaOH according to the following reaction (Equation (3)):



After filtration, the residue was dried at 80 °C and then calcined at 700 °C for 5 h to remove the acetylene black, binder, and other organic components. However, small amounts of Co and Cu were detected in the alkali leaching solution, but they were considered acceptable in comparison to the total of LCO and Cu foil [50]. This method has the advantage of a high efficiency detachment of an Al current collector while avoiding the previous manual treatment. However, the recovery of Al from a solution of NaAlO₂ is hard due to the stability of the solution itself. Moreover, wastewater from this process poses environmental hazards, so it needs to be treated.

3.1.3. Thermal Decomposition of the PVDF Binder

The thermal treatment method is based on heating cathode materials at 250–350 °C. At these temperatures, PVDF decomposes, leading to an easier separation of cathode-active material from Al foils. This is a safe method to remove an organic binder, while other components undergo degradation at 600 °C. Cathode materials can be easily separated by sieving and grinding in ball milling. Refs. [102,103] after discharging and dismantling LIBs from laptops and heating cathode active materials at 250–300 °C for 30 min, facilitating the detachment of the valued powder. The authors of [104] proposed a novel method to separate the cathode material by imposing vacuum pyrolysis on the disassembled cell materials. The electrolyte and binder are decomposed and evaporated by heating at 450 °C. When the temperature reaches 550 °C, the adhesion between the cathode material and current collector is hardly reduced, making the detachment simpler. The main advantage of using a thermal treatment lies in its simple functionality. Nevertheless, it releases poisonous gases from the degradation of fluorine compounds, which introduces new threats, and the emissions should be controlled [105].

Off-gas treatments are not often discussed in the literature; however, as reported in [106], the major products formed during the thermal degradation of the binder are CO, CO₂, H₂O, and HF. Thus, a CO₂ capture system, as well as an alkaline scrubber, are suggested to treat the gaseous product of the binder pyrolysis.

3.2. Sustainable Recycling Technologies of Spent LIBs

Conventional hydrometallurgical methods mainly involve the use of a mixture of strong inorganic acids (e.g., H₂SO₄, HCl, and HNO₃) and reductants (e.g., H₂O₂) as leaching agents, which generate high amounts of secondary polluting gases, such as SO₃, Cl₂, and NO_x [30,107]. Obviously, employing these compounds on an industrial scale could imply serious danger to workers and the environment. Organic acids combined with bio-based reductants have been largely studied as alternative green leaching agents that promise to address the concern of environmental safety by using non-hazardous materials. For example, bio-based compounds, such as tea waste [108] or fruit peel waste [109], have been used as reductants with citric acid as a leaching agent, yielding high recovery efficiencies from many LIB chemistries, including Co (91.3%), Li (80.5%), Ni (90.1%), and Mn (92.2%). Table 2 summarizes the most used green compounds in the recycling processes of LIBs. Alongside organic acids, Deep Eutectic Solvents (DESS) are worth mentioning as a different class of

sustainable compounds that recently emerged as potential leaching agents that can dissolve metals from electrode materials [110–112]. These solvents are eutectic mixtures of hydrogen bond donors and acceptors that are often cheaply obtained, easily prepared, and composed of relatively nontoxic and biodegradable compounds. Additionally, there are no requirements of reductants when DESs are used, which contribute to lower the overall costs of the recycling process [113]. Typical compounds utilized as hydrogen bond donors are thiourea ($\text{CH}_4\text{N}_2\text{S}$), urea ($\text{CH}_4\text{N}_2\text{O}$), malonic acid ($\text{CH}_2(\text{COOH})_2$), glucose ($\text{C}_6\text{H}_{12}\text{O}_6$), imidazole ($\text{C}_3\text{H}_4\text{N}_2$), and ethylene glycole ($\text{HOCH}_2\text{CH}_2\text{OH}$). The hydrogen bond acceptors that are generally employed are choline chloride ($\text{HOC}_2\text{H}_4\text{N}[\text{CH}_3]_3\text{Cl}$), tetramethylammonium chloride ($(\text{CH}_3)_4\text{NCl}$), and tetrabutylammonium chloride ($[\text{CH}_3(\text{CH}_2)_3]_4\text{NCl}$) [114].

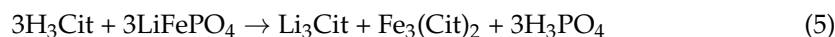
Table 2. Summary of main leaching agents, reductants, and their significance.

Type of Battery	Leaching Agents	Reductants	Conditions (T, t, S/L Ratio)	Leaching Efficiency	Relevance	Ref.
Spent mobile phone	HCl	-	95 °C, 70 min, 10 g L ⁻¹	Li 97.59% Co 99.74%	No H ₂ O ₂ was used. High HCl concentration and high-temperature process.	[30]
NMC	Citric acid	Biomass reductants (Phylotacca Americana, tea waste)	120 °C, 90 min, 30 g L ⁻¹	Li 98.0% Co 96.0%	High temperature used but mild acid concentrations. Investigation of leaching mechanism by IR. Closing loop of the process by recycling of leaching agent.	[108]
LCO POWDER	DES (ChCl:EG)		220 °C, 24 h, 0.02 g g ⁻¹	Co 94.14%	Environmentally friendly process used to leach Co with high efficiency. High temperature and time involved.	[115]
LiFePO ₄	Citric acid, acetic acid, chloride acid, nitric acid, sulfuric acid	H ₂ O ₂	50 °C, 30 min, 120 g L ⁻¹	Li 94.08%	High Li recovery efficiencies and economic assessment of 1 ton of LFP recycling process.	[116]
LiFePO ₄	Citric acid	H ₂ O ₂		Li 97.82% Fe 95.62%	Extracted materials used for a resynthesized material.	[117]
Mixed LIBs	Succinic acid	H ₂ O ₂	90 °C, 60 min, 20 g L ⁻¹	Li 96% Co 100%	Innovative and green method for the recovery of Co with high yields.	[118]
NMC	Citric fruit juice	-	90 °C, 20 min, 50 g L ⁻¹	Li about 100% Mn 99% Ni 98% Co 94%	Total green process in which mixture of acid and flavonoids inside citric fruit juice work as leaching agent and reductant.	[34]
LCO	Citric acid	Orange peel fruit	100 °C, 4 h, 25 g L ⁻¹	Li 100% Co 100%	Co-tackling the twin challenges of resource depletion and waste accumulation: fruit peel waste used as reducing agent for the recycling of end-of-life LIB waste.	[109]
LCO	Oxalic acid	-	95 °C, 150 min, 15 g L ⁻¹	Li 98.0% Co 97.0%	The usage of reductants is totally avoided since oxalic acid has great affinity for Li and Co. Simple and shortcut method for the high recovery of valuable Li and Co.	[37]
LCO, NMC	Tartaric acid	H ₂ O ₂	70 °C, 30 min, 17 g L ⁻¹	Li 99.1% Mn 99.3% Ni 99.3% Co 98.6%	Highly efficient process to recover metals from mixed electrode materials under relatively low temperature and low leaching time.	[40]
LCO	Maleic acid	Ascorbic acid	80 °C, 25 min, 2 g L ⁻¹	Li 94% Co 91%	Novel process introducing microwave irradiation to reduce leaching time.	[119]

Green Hydrometallurgy

Li et al., in [120], proposed a method for the recycling of LiFePO₄ from spent batteries using citric acid as leaching agent and H₂O₂ as a reductant at room temperature. The novelty of this process consists of the addition of citric acid powder and H₂O₂ directly

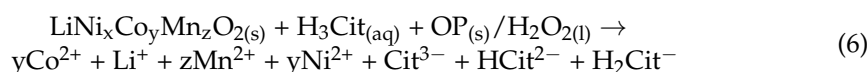
during the mechanical pretreatment (a grinding process), so that the leaching process starts at the very early stage. The leaching reaction using the two different reducing agents can be described as follows (Equations (4) and (5)):



It has been highlighted that when H_2O_2 is used alone, it is not able to efficiently leach Fe (approximately 3% of recovery yield) since it is oxidized to form FePO_4 . On the other side, the Li leaching efficiency is around 100%. As a comparison, when LFP is co-grinded with H_2O , Li and Fe are both efficiently extracted from the cathode material into the solution because of different mechanochemical reactions, achieving high yields under optimized conditions, namely 97.82% and 95.62% for Li and Fe, respectively.

A total green method to recycle LCO spent batteries was developed, up-cycling organic waste residues to be employed as reductants. The reducing capacity of orange peel waste has been attributed to two different mechanisms. The first is associated with the “reducing sugar theory”, which has been postulated in previous works [121,122]. Heating sugars up to 100 °C under acidic conditions could degrade 30% of the cellulose that is contained in organic waste residue into glucose, and up to 70% of the hemicellulose could be rapidly converted into aldehyde-containing reducing sugars such as xylose, arabinose, and mannose [123]. Furthermore, the oxidation of glucose can produce polyhydroxyacids (gluconic and aldonic) and aldaric acids (aldoses and CO_2), which contribute to the acidic reaction environment. Several peel fruit wastes were also used in [124], where they were processed to obtain a lixiviant waste-based material.

The latter mechanism of action implies another possible source of reducing components thanks to the presence of antioxidants, such as phenolic acid and flavonoids, which can be hydrolyzed into reducing substances [125]. The obtained reduced sugars were added directly into a H_3Cit 1.5 M leaching solution. Under optimized conditions, the leaching efficiencies of valuable metals were Co: 91.3%, Li: 80.5%, Ni: 90.1%, and Mn: 92.2%, which were recovered from a black mass lixiviant using the following (Equation (6)) reactions [109]:

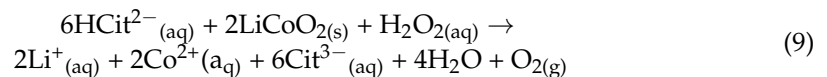
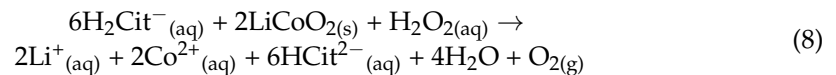
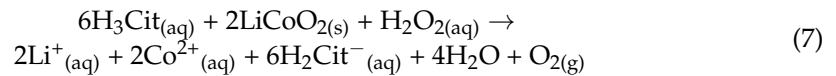


A further toxicity evaluation of the byproducts from this leaching process outlined that the solid waste, containing mostly C (64.2%) and O (33.3%), does not represent possible hazardous threats for human health or the environment. Hence, the application of fruit peel waste can embody one of the most sustainable and valuable baselines for future scale-up and optimization in battery recycling technology.

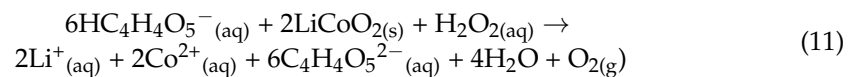
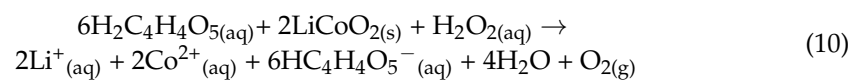
The capability of citric acid as a leaching agent has also been investigated on NMC cathodes from spent EV batteries [126]. In addition, sucrose has been used as a reductant in order to replace H_2O_2 , which is easily decomposed in the presence of light and air [127]. After the leaching step, the recovery yields of the dissolved metal ions depend on the precipitation process: in this study, it was used a co-precipitation method that can also be carried out in separate stages using different agents for different metal ions, hence resulting in a non-economic suitable process [128]. Oxalic acid can be used to overcome this issue since it forms stable compounds with metal ions (Li, Co, Ni, and Mn). Furthermore, the use of oxalic acid reduces the co-precipitation times by about 30 min. In fact, it was reported that hydroxides and carbonates, the most commonly used compounds, co-precipitate metal ions from spent LIBs during a contact time from 12 to 24 h [129].

Alternatively, other organic acids retrieved from fruit wastes can be employed as lixiviant in metal recycling hydrometallurgy [130], eventually extracted from lemon juice, which is rich in citric, ascorbic, and malic acids as lixiviant [131]. The LIB wastes were selected from mobile phone batteries, composed mainly of LCO cathodes. The leaching

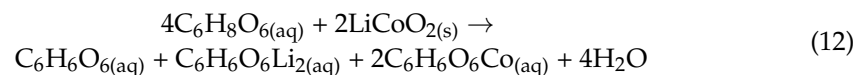
moisture was composed of lemon juice and H_2O_2 as a reducing agent. Citric acid has three carboxylic groups that can release 3 H^+ equivalents. The leaching of LiCoO_2 by citric acid can be described as the following three-step reactions (Equations (7)–(9)):



Malic acid undergoes an analogous mechanism in which the leaching of Li^+ and Co^{2+} occurs with the three-step reductions of the malic acid (Equations (10) and (11)):



Ascorbic acid is also involved in the reduction of Co^{3+} to Co^{2+} , and it generates dehydroascorbic acid (Equation (12)):



The reaction chamber was ultrasonicated to enhance the leaching time and yields in the following optimal conditions: 90 mg g^{-1} of citric acid, 0.86 mg g^{-1} of malic acid, and 1.24 mg g^{-1} of ascorbic acid with ultrasonication at a 37 kHz frequency and at 40 °C for 45 min, giving 100% recovery yields of Li, Co, and Ni. In addition to the high leaching yields reached through this process, further consequent wastewater treatments were avoided [130]. The authors realized a novel process in which an LIB-ternary feed, composed of $\text{LiCoO}_2/\text{LiNiO}_2/\text{LiMn}_2\text{O}_4$, was leached with hydrothermal water at 60–90 °C by adding 0.4 mol L^{-1} of H_3Cit . The solid-to-liquid ratio (S/L) was 6.0 g L^{-1} of each oxide material. High yielding was reached in the recovery of Li, Ni, and Co (81%, 73%, and 100%, respectively) at 90 °C for 20 min. The Mn in LMO cathodes was completely leached, even at 60 °C, due to the Jahn–Teller effect, which can induce a phase transformation in the LiMn_2O_4 spinel structure. The leaching of Ni could be improved by employing a binary LIB cathode system ($\text{LiCoO}_2/\text{LiNiO}_2$) at 100 °C for 20 min, but at the expense of recovering Co, which resulted in an efficiency of less than 16% [132].

It has been established that nearly 100% of Li, Mn, Ni, and Co, can be recovered in the presence of citric acid, malic acid, and ascorbic acid from lemon juice. Moreover, the presence of flavonoids in the leaching solution actively contributes to the mixture-reducing environment. In fact, it has been reported that the flavonoids contained in lemon juice behave as reducing agents [133]. Furthermore, the presence of various cations, like Ca^{2+} , Na^+ , and K^+ , improves the complexation efficiency since they can be easily replaced in citrate and malate anion structures by valuable metal ions, Li^+ , Mn^{2+} , Ni^{2+} , and Co^{2+} . The complexation mechanism is described in Figure 5 [34].

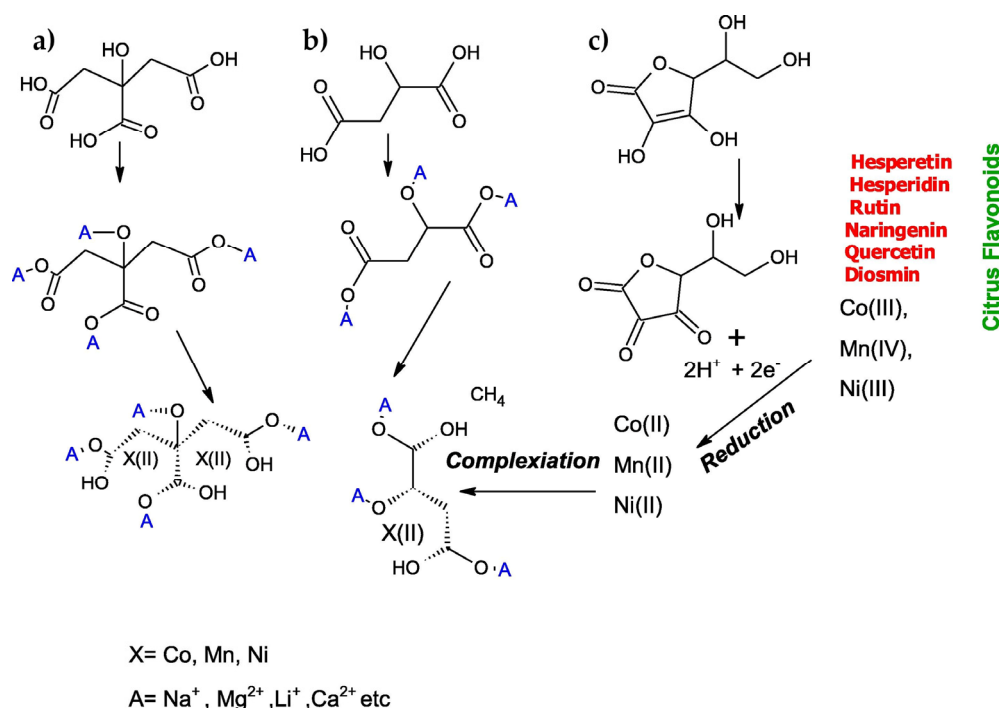


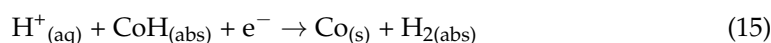
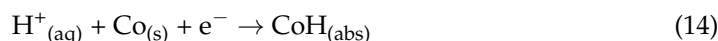
Figure 5. Complexation mechanism of metals during the leaching reaction, where the following steps are described: (a) formation of metal complexes with citric acid, (b) formation of metal complexes with malic acid, (c) reduction of Co(III), Mn(IV), and Ni(III) to Co(II), Mn(II), and Ni(II) in the presence of ascorbic acid and citrus flavonoids [34]. Copyright Elsevier/© 2016 Elsevier Ltd. <http://dx.doi.org/10.1016/j.wasman.2016.09.039>, accessed on 24 November 2023.

The role of counterions can be explained by the correlation between the pH and the electrochemical behavior of citrate and malate complexes compared to the unbounded species. It was found that the pH of the leaching solution was 5.9 instead of 2.4, and it was 1.9 in the case of individual citric and malic acid, indicating the larger presence of complexed citrate and malate with Co²⁺, Mn²⁺, and Ni²⁺. This phenomenon was also confirmed by ref. [134], where the presence of sodium citrate in the leaching solution containing Co²⁺, Fe²⁺, Ni²⁺, and Cu²⁺ promoted the formation of dissolved complexes, forming pseudo-stable structures at a higher pH than in acidic conditions. Hence, this process enhances the complete dissolution of valuable metals while avoiding parasitic precipitations. The metal complexes dissolved in the leachate solution are then recovered using Na₂CO₃ and oxalic acid.

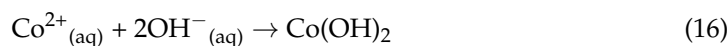
3.3. Electrochemical Methods

Electrochemical processes can play key roles in metal extraction and recovery, both for solid wastes and dissolved species. By selecting appropriate electrode and cell designs, electrochemical methods can bring three main significant advantages to modern recycling technologies, including (i) the simplification of the process given by a lower number of steps; (ii) lower energy involved and higher selectivity using molecular-designed Faradaic processes [135]; and (iii) the integration of multiple processes, such as the multicomponent purification of metals from complex matrices and metal recovery in tandem with organic compound degradation [136]. For solid wastes, once metals are leached as solvated ions, trace metals can be plated on an electrode surface by Faradaic reactions while avoiding bulky steps. Interfacial selectivity can play a central role in improving the purity of the recovered material, lowering energy costs, and maximizing recovery efficiencies. Recycling critical elements contained in LIB cathodes using electrochemical processes can represent one of the valid alternatives to the disadvantages brought out by pyrometallurgical and hydrometallurgical technologies.

As ions in solution, valuable metals can be separated by chemical precipitation, extraction, or electrodeposition. First, due to its ready redox potential for deposition, cobalt electroreduction can be an efficient method to directly produce alloys with controlled morphologies [137,138]. The solution composition, pH, and applied potential directly influence the electrodeposition mechanisms and the deposit morphology depending on the nucleation pathways. Indeed, at a pH < 4.00, cobalt electrodeposition occurs through the unstable hydride intermediate, CoH, to be reduced to a metallic form as a result of the absorption of hydrogen on the electrode following the reactions [139] (Equations (13)–(15)):

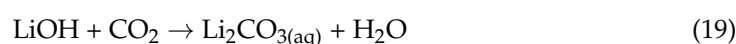
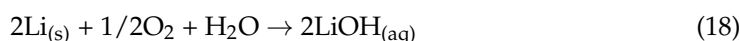


At a pH above 4.00, the reaction proceeds with the initial formation of $\text{Co}(\text{OH})_2$, which is subsequently reduced to Co metal (Equations (16) and (17)).



In [138], an electrodeposition process to recover Co from LIB wastes after acidic leaching from an LCO cathode material was reported. Thus, by applying a current density of 10.0 A cm^{-2} and a static potential of -1.00 V (vs. H^{+}/H_2), the electrodeposition of cobalt starts at -0.80 V , reaching the highest yield of 96.90% in an acidic condition at pH 5.40.

Lithium can be selectively recovered using electrochemical processes as lithium carbonate or hydroxide. In [140], an innovative and environmentally friendly recycling system was proposed. Figure 6 schematically describes the waste-to-lithium (WTL) process. Lithium from battery wastes from LiFePO_4 and $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ are directly collected in a cathode waste chamber. Li^{+} ions are electrochemically plated to metallic lithium onto a Ni mesh. Once collected, it can be reconverted in chemical precursors such as lithium carbonate and hydroxides via the subsequent reactions (Equations (18) and (19)):



Electrosorption has also been intensively explored as a technique that is able to capture metals from solutions. Due to their intrinsic lithium intercalation properties, battery electrodes can be employed as capturing matrices to recover valuable metals from batteries. Lithium manganese oxide (LMO) has been extensively used to selectively extract lithium from wastewater by LIB recycling plants. To decompose organic pollutants that are eventually present in wastewater, a boron-doped diamond electrode has been used. During cathode regeneration, the dissolved lithium can then be concentrated [141]. LiFePO_4 has also been studied as a selective absorbent of lithium from a liquid phase in a dual system with silver as a counter-electrode [142], and $\lambda\text{-MnO}_2$ electrodes have been employed for lithium recovery from brine [143].

In [144], a selective electrodeposition of Co over Ni was demonstrated via the control of the electrolyte and the electrode interfaces. By tuning the concentration of chloride ions in the electrolyte solution, the authors observed the distinct formation of the anionic complex $[\text{CoCl}_4]^{-}$ and the cationic complex $[\text{Ni}(\text{H}_2\text{O})_5\text{Cl}]^{+}$. Furthermore, thanks to the functionalization of the electrode surface with a positive polyelectrolyte, the authors were able to selectively electro-extract Co while Ni remained in the solution.

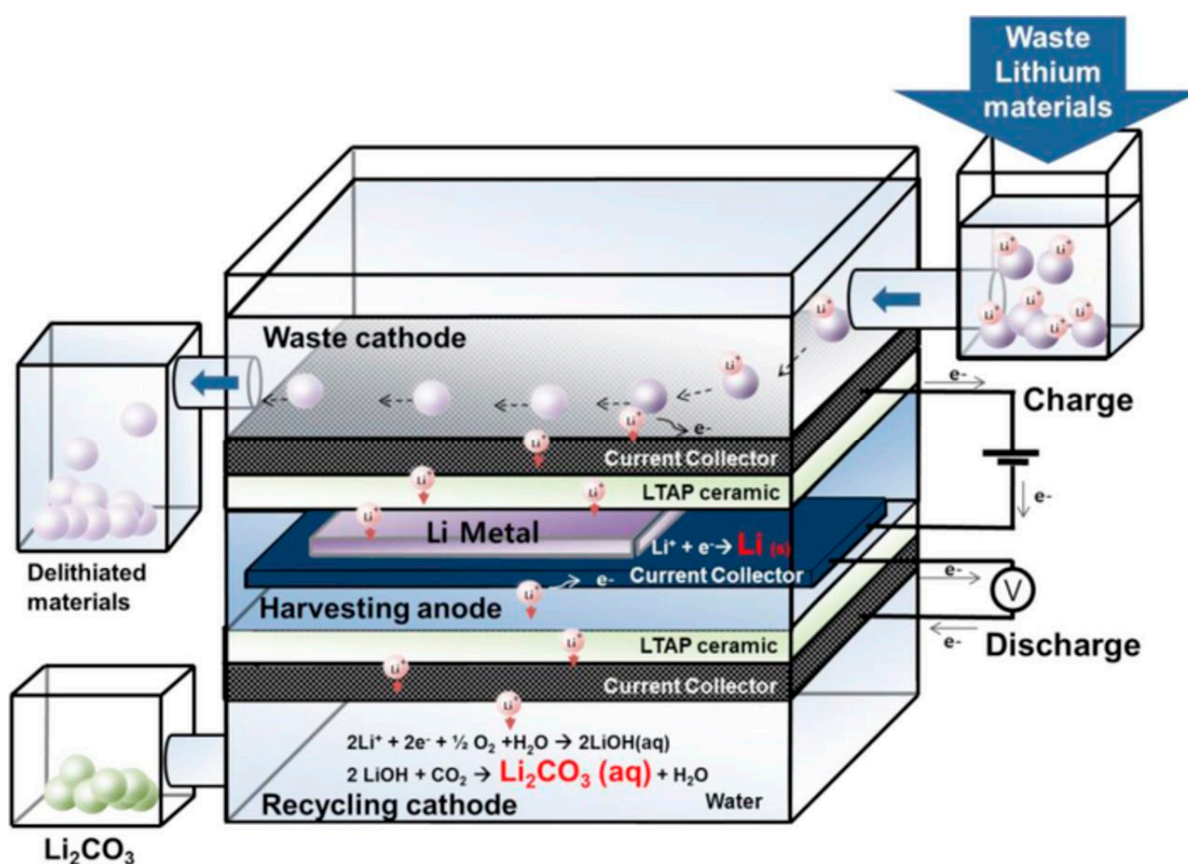


Figure 6. Schematic diagram of WTL process. Li ions in the waste cathode compartment move to the harvesting anode chamber and form Li metal when the system is charged. During the discharging of the system, Li_2CO_3 or LiOH can be produced in the recycling cathode compartment by reacting with H_2O , O_2 , and CO_2 (© The Electrochemical Society, reproduced by permission from IOP Publishing; all rights reserved) [140].

4. Separation of the Leached Metals

The separation of valuable components from the post leaching solution also represents a major challenge in the recycling process of spent LIBs. The decision for the most effective process is, of course, related to the type of LIBs treated. However, the most proposed and employed method for the separation of metals from the leaching liquor is solvent extraction [145]. Solvent extraction is commonly achieved with the use of a chelating agent and a nonpolar solvent. The chelating agent will form a complex with the target metal, which will be soluble only in the nonpolar solvent, or it will show a greater affinity to water, achieving high degrees of separation from the other metals. Chelating agents such as Cyanex 301, Cyanex 272, and D2EHPA have been largely used for the separation of the target metals, Co, Ni, Mn, and Li, from the leaching liquor of NMC-based cathodes. The most used nonpolar solvent in this kind of operation is kerosene. This process was not only reported on the laboratory scale, but also on the industrial scale, such as, for instance, in the Duesenfeld Patent, DE102018102026A1.

A further separation method consists of the use of ion exchange resins, such as Dowex M4195 [146] or the K350 resin from DuPont [147]. Other separation methods may involve selective precipitation, such as, for instance, in the case of Ni, which can be selectively precipitated with the formation of the complex with dimethylglyoxime [148].

5. Conclusions and Perspectives

As the markets for electronic devices and electric vehicles grow, the number of spent LIBs will soon become a critical threat that must be addressed to face future challenges in terms of sustainability for human health and environmental risks.

Despite the many benefits of recycling LIBs that exist, technical, logistic, economic, and legislative barriers must be solved. A complete waste battery collection management system must be pursued as a fundamental goal to tackle the uncontrolled waste battery streams. Furthermore, political and economic incentives and initiatives need to be undertaken to encourage consumers to submit spent LIBs to assigned collection points.

As aforementioned, the recycling processes for spent LIBs cannot always be considered in terms of hazardous issues. In fact, if properly handled and processed, safe battery recycling is not a hard task to accomplish. The available literature related to battery recycling highlights that mechanical treatment, pyrometallurgy, hydrometallurgy, or their combination represent the main routes for the recovery of valuable components from spent LIBs. Hydrometallurgical processes have been demonstrated to be one of the most viable and sustainable technologies in the extraction of lithium, nickel, cobalt, and manganese from spent LIB cathodes. In recent years, many papers have been published focusing on hydrometallurgical greener processes to recycle spent LIBs by employing organic acids, such as citric acid, oxalic acid, maleic acid, or their mixtures. The use of organic acids has been demonstrated to be both environmentally and economically viable as an alternative to traditional metal extraction processes, since the resulting wastewater does not need to be further treated in high-cost post processes. Meanwhile, implementing organic-based leaching processes on an industrial scale is far from being achieved by recycling companies. Moreover, besides lowering the complexity of managing the leaching liquor, most of the research papers report that using organic acids diminishes the energy loss and the quantity of CO₂ produced. However, some critical aspects still need to be addressed: (1) Leaching mechanisms still need to be further investigated in view of possible industrial applications. For example, the change in the crystal structure during leaching could bring a deeper insight into the reaction mechanisms. More studies focused on the selection of leaching reagents and operation conditions are needed. (2) Step-by-step processes to shift from lab-scale to industrial pilot plants still need to be designed and remain of crucial priority. (3) Most of the scientific papers on this topic are focused only on the critical factors affecting yielding efficiencies, while more efforts could be employed to include cost efficiencies and energy consumption to bring a more holistic view to the total process. (4) Additionally, enhancing the collection of spent LIBs will become a hotspot in the next years. Efforts need to be made to optimize this crucial step within the lifetime of an LIB in order to avoid uncontrollable landfill disposals. (5) Lastly, a standardized mechanism in manufacturing, classification, collection, and recycling processes will considerably minimize the differences in raw materials, reducing, at the same time, the energy consumption of every step in the life cycles of future LIBs.

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MUR-MAECI (Ministero degli Affari Esteri e della Cooperazione Internazionale); and “Production processes of LIB cathodes designed for direct recycling”, ENEA-MASE (Ministero dell’Ambiente e della Sicurezza Energetica), Piano Triennale di Realizzazione (2022–2024). F.S. and A.S. acknowledge the MOST—Sustainable Mobility Center project, funded by the European Union Next-Generation EU (PIANO NAZIONALE DI RIPRESA E RESILIENZA (PNRR) e MISSIONE 4 COMPONENTE 2, INVESTIMENTO 1.4 e D.D. 1033 17/06/2022, CN00000023). This manuscript reflects only the authors’ views and opinions; neither the European Union nor the European Commission can be considered responsible for them. P.S. acknowledges the MOST—Sustainable Mobility Center project, funded by the European Union Next-Generation EU—CN00000023.

Data Availability Statement: The data presented in this study are openly available in all cited references as reported in the References section.

Conflicts of Interest: Author Daniele Marchese and Matteo Cavalletti are employed by the MI-DAC S.p.A. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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