

Review

Recovery and Recycling of Valuable Metals from Spent Lithium-Ion Batteries: A Comprehensive Review and Analysis

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Abstract: The recycling of spent lithium-ion batteries (Li-ion Batteries) has drawn a lot of interest in recent years in response to the rising demand for the corresponding high-value metals and materials and the mounting concern emanating from the detrimental environmental effects imposed by the conventional disposal of solid battery waste. Numerous studies have been conducted on the topic of recycling used Li-ion batteries to produce either battery materials or specific chemical, metal or metal-based compounds. Physical pre-treatment is typically used to separate waste materials into various streams, facilitating the effective recovery of components in subsequent processing. In order to further prepare the recovered materials or compounds by applying the principles of materials chemistry and engineering, a metallurgical process is then utilized to extract and isolate pure metals or separate contaminants from a particular waste stream. In this review, the current state of spent Li-ion battery recycling is outlined, reviewed, and analyzed in the context of the entire recycling process, with a particular emphasis on hydrometallurgy; however, electrometallurgy and pyrometallurgy are also comprehensively reviewed. In addition to the comprehensive review of various hydrometallurgical processes, including alkaline leaching, acidic leaching, solvent (liquid-liquid) extraction, and chemical precipitation, a critical analysis of the current obstacles to process optimization during Li-ion battery recycling is also conducted. Moreover, the energy-intensive nature of discussed recycling process routes is also assessed and addressed. This study is anticipated to offer recommendations for enhancing wasted Li-ion battery recycling, and the field can be further explored for commercialization.

Keywords: lithium-ion batteries; cathodes; recycling; recovery; valuable metals; cobalt; nickel; lithium



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1. Introduction

In the last decade, the world has launched a global trend targeting environmental conservation in order to achieve environmental, economic and even social sustainability. Attributed to their non-renewable nature, fossil fuels, which have long met our society's energy needs, are gradually exhibiting a variety of detrimental effects on the environment and energy security. In order to replace traditional internal combustion engines with electric cars and equipment powered by renewable energy storage sources, many organizations and countries are actively devoting resources to this effort. Ultimately, they will be able to circumvent the hurdles accrued from fossil fuel utilization. As anticipated, the demand for portable electronic devices, such as smartphones, tablets, notebooks, radios, laptops, and other devices, that are likewise powered by electric storage systems (i.e., batteries), has dramatically increased in recent years.

These aforementioned factors triggered the development and widespread application of a variety of energy storage technologies, including nickel-metal hydride batteries (NiMH), lithium-ion batteries (Li-ion Battery), conventional lead-acid batteries (Pb-acid),

and nickel-cadmium batteries (NiCd) [1]. If the target of the global Paris Climate Accords is to be met, batteries must undoubtedly be a crucial part of climate action. The adoption of new cutting-edge technologies has played a significant role in the steady rise in the use of batteries as power sources for portable electronics and electric vehicles over the past few decades. The rising demand is largely due to portable electronics like mobile phones and microcomputers. Due to their superior electrochemical performance in terms of power density, energy density, and long-lasting stability, Li-ion batteries are currently the most extensively deployed and consumed battery technology. It is anticipated that their use in the automotive industry will further increase demand for Li-ion batteries. This trend is depicted in Figure 1.

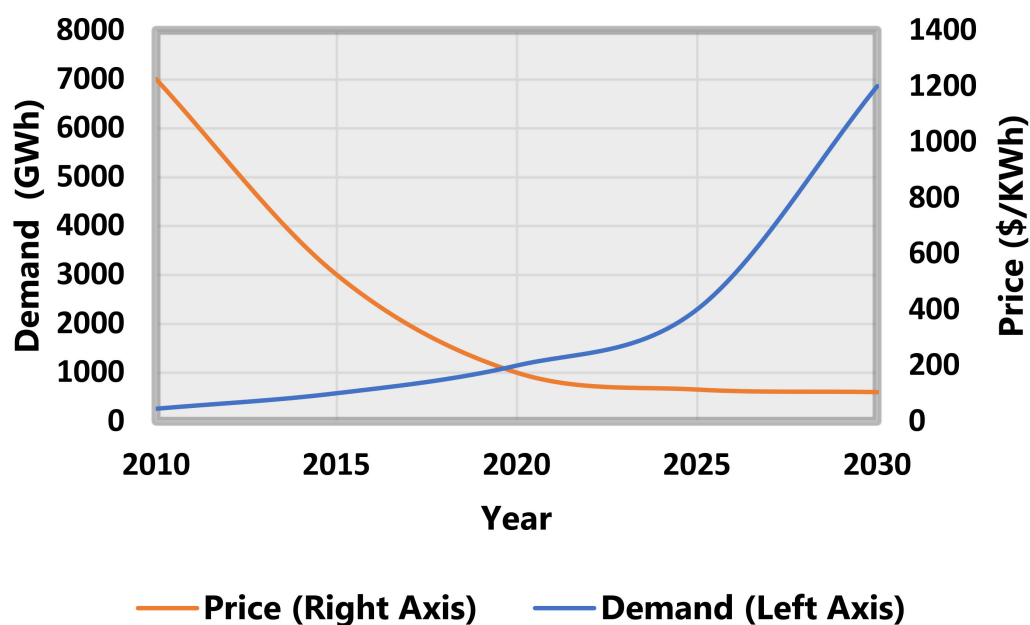


Figure 1. The demand-led market growth of Li-ion batteries (data derived from [2]).

The Energy Sector Management Assistance Program (ESMAP) [2] reported that the Li-ion battery market grew from 5 billion US\$ in 2005 to approximately US\$18 billion in 2015, with a significant proportion of applications in electronic devices. The Li-ion battery market is extrapolated to reach over 75 billion US dollars in 2025, accounting for 70% of the market for rechargeable batteries, as indicated in Figure 2.

The upsurge of Li-ion batteries is currently hampered by a lack of sufficient raw materials as well as environmental pollution accrued from spent Li-ion batteries. Landfilling is the traditional method of disposing of spent Li-ion batteries; however, the heavy metals and organic electrolytes present in spent Li-ion batteries will possibly leak and spill into the surrounding environment, ultimately posing a heavy threat to both the environment and human health. When the amount of Li-ion batteries being consumed increases significantly to meet demand in the coming years, these issues will become noteworthy and remediation essential due to the corresponding large quantity of spent Li-ion batteries accumulated in landfills.

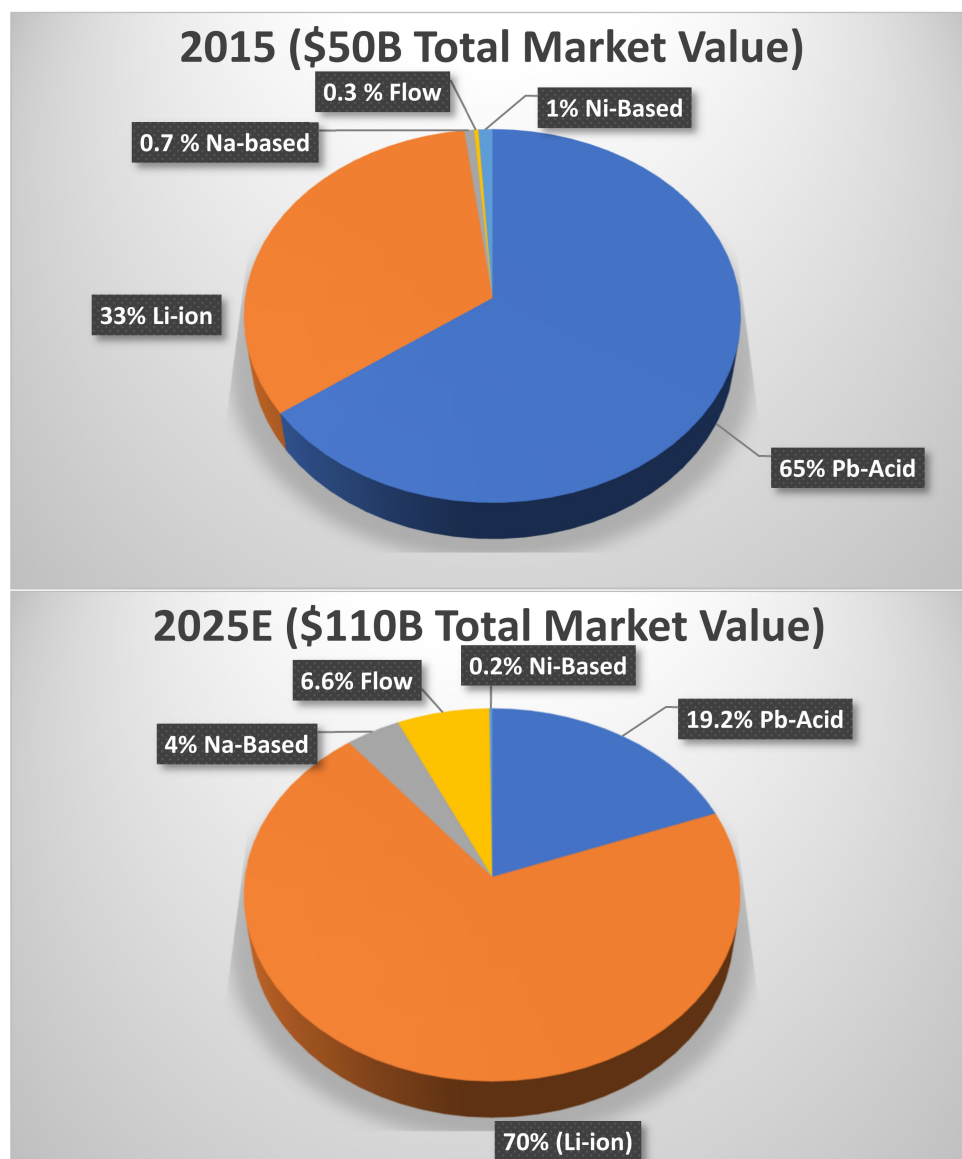


Figure 2. Rechargeable Li-ion battery market size (data derived from ref. [3]).

In an attempt to avoid the apparent inevitable consequences of disposing of batteries in landfills, countries and economic unions are introducing bills and laws to reduce e-waste in landfills. In particular, the EU introduced Directive 2006/66/Ec of the European Parliament to address the waste of old electric and electronic devices and batteries. The measures aim to curb the presence of spent batteries in landfill sites [4]. This means that end-user consumers and companies will have to submit e-waste for recycling by taking it to a licensed recycler of electric and electronic waste equipment.

The widespread and continuously escalating levels of consumption of Li-ion batteries generate large amounts of spent Li-ion batteries, which must be recycled using eco-friendly and economically viable process routes. Closed-loop recycling process routes should ideally provide sufficient materials for the manufacture of new Li-ion batteries. It is evident that recycling, recovering, and reusing Li-ion batteries will be a key initiative in assisting countries (both developed and developing) to make a rapid and sustainable transition to clean energy generation. If recycling and reuse practices are implemented effectively on a large scale, greenhouse gas (i.e., CO₂, CH₄, and NO_x) emissions and environmental damage should be curtailed.

Li-ion batteries constitute significant amounts of valuable metals such as Copper (Cu), aluminum (Al), lithium (Li), cobalt (Co), manganese (Mn), and nickel (Ni), with Co being the most valuable [5]. Assuming that the valuable metal content in Li-ion battery cathodes can be effectively recovered in its pure metallic form, approximately US\$10,000 monetary value of Co is present in 1 metric ton of spent Li-ion batteries [6,7]. The market value of Li is significantly lower, on average US\$6500 per ton, but has increased steadily since 2010, reaching US\$40,000 a ton in Jan 2022 [8]. As a result, the recovery of these valuable metals provides an economic incentive for the development of the Li-ion battery recycling processes [6]. Furthermore, the unsustainable use of valuable materials through irresponsible disposal of spent Li-ion batteries contributes largely to environmental pollution and degradation [5].

Currently, the two processes most frequently used to recover valuable metals (Ni, Co and Li) from spent Li-ion batteries are pyrometallurgy and hydrometallurgy [6,9,10]. However, pyrometallurgical processes entail several drawbacks, such as the by-production of hazardous gases and excessive energy consumption. In order to refine the waste and derive purer forms, such as salts, hydroxides, and metals, a hydrometallurgical process is often necessary [10]. As a result, numerous studies have suggested that the utilization of the leaching process to recover valuable metals from used Li-ion batteries can be beneficial [5,11,12]. However, it is essential to employ processes that don't create novel environmental hazards. Organic acids, which are less corrosive and more environmentally friendly than conventional leaching/electrolyte agents (i.e., inorganic acids), offers an ideal alternative [13].

In order to recover valuable metals (Co, Ni, and Li) from spent Li-ion battery waste, the process often starts with acid leaching. The leaching solution typically constitutes an acid plus added reducing agent additive. This process oxidizes the metals to more soluble states (ions) [9,14]. More than 99% (by mass) of Co, Ni and Li metals can be leached when a sufficiently strong acidic solution is utilized. However, this process releases toxic gases (i.e., Cl_2 , NO_x , and SO_3) and acid residue that poses a severe threat to both the environment and human health [6]. The effective recovery of metals from spent Li-ion batteries is imperative due to the growing interest in sustainable management of natural resources and the reduction of environmental pollution. Recycling and recovering valuable metals can lessen, in an attempt to eliminate, environmental pollution and solve the crisis of Co, Ni, and Li scarcity and circulability [5,14,15].

In light of the environmental and economic concerns, it is necessary and imperative to separate, reuse and recycle all components of Li-ion batteries in order to circumvent problems accrued from spent Li-ion battery disposal [5,16]. Considering the complexity of the raw materials, it is difficult to design and successfully run a single-stage recycling process that is both economical and environmentally friendly. Therefore, it is a common practice to recycle spent Li-ion batteries using a multistage combination of physical and chemical methods. Physical dismantling, crushing, sieving, heating, and mechanochemical treatment are common physical techniques used to enhance recycling efficiency [17,18]. Pyrometallurgy and hydrometallurgy are two major subsets of the chemical recycling process routes. Hydrometallurgical processes edge pyrometallurgical processes, which are often carried out at high temperatures due to more environmentally friendly process pathways, milder reaction conditions and higher valuable metals recovery efficiency, especially Li [5,9,18]. These advantages mark hydrometallurgical processes as a more preferable and ideally promising process for processing and recycling spent Li-ion batteries.

In this review, the up-to-date status of Li-ion battery technology and recently developed recycling processes, together with conventional recycling processes, are systematically discussed, focusing mostly on the hydro, pyro and electro-metallurgical processes. Furthermore, the challenges and drawbacks of each recycling process route are analysed and discussed. The regional and international regulations, treaties and agreements and legislations concerning spent Li-ion battery waste management are also highlighted and briefly

reviewed. The primary aim of this review is to provide comprehensive present and future guidelines for the processing of spent Li-ion batteries.

2. Lithium-Ion Development Batteries over the Years

The first commercial rechargeable Li-ion batteries were prototyped by SONY in the early 1990s and consisted of a LiCoO_2 (LCO) cathode and a carbonaceous anode [19,20]. Since its commercial inception, Li-ion batteries have been viewed as the most promising “green battery” due to their high energy and power density, exceptional design flexibility, and prolonged lifespan when compared to other battery technologies [21]. Lithium manganese oxide (LMO), LMO-based rich, layered materials (LMR, NMC), Lithium cobalt oxide (LCO), lithium nitrate oxide (LNO), lithium iron phosphate (LFP), lithium nickel manganese cobalt oxide (NMC), and lithium nickel cobalt aluminum (NCA) are some of the novel types of Li-ion batteries that have been intensively researched in recent years to meet the exponentially growing need for creating battery-powered gadgets [17].

The market value, circulability (cm) and supply risk of several Li-ion active cathode materials are quantified and evaluated using correlations from Bloomberg Precious and Industrial Markets, as guided by Lv et al. [22]. The data correlations demonstrate that recycling LCO and NCM is slightly more imperative, feasible, and profitable than recycling other active cathode material formulations due to the high Co content nature of their respective formulations. In the last decade, low-circulability and high-cost metals (in active cathode materials) with high supply risks have been gradually replaced by high-circulability and low-cost metals with lower supply risks. It is consequently necessary to improve Co circulability and research new active cathode materials in order to alleviate supply risk pressure.

The McKensie battery manufacturing model (2020) predicts that the production of Li-ion batteries will continue to grow rapidly between 2010 and 2030. The model extrapolated the production to reach 7500 GWh in 2030 [1,2,23]. One driving factor is the rapid development and production of electric vehicles, whose sales have boomed vastly in recent years. As NCM, NCA, and LiFePO_4 become more crucial active cathode materials for power batteries, the amount of valuable metals like Li, Ni, and Co that must be recycled through the recycling streams will increase proportionately [17,18,21]. The spent Li-ion battery waste stream will become significantly complex if processed without effective classification and management [17,18,21]. Nevertheless, data from ESMAP [2] indicated that less than 25% of the spent batteries available for recycling were recycled in 2020. Meanwhile, CSIRO [23] reported that less than 2% of Li from spent Li-ion batteries was recycled in the world in the same year despite the amount of spent Li-ion batteries surging from 180,000 metric tonnes in 2014 to 600,000 metric tonnes in 2020. Contrasting this trend to Figure 3, which depicts the global growth in the amount of spent Li-ion batteries and the market size of Li-ion batteries in the global market from 2008 to 2030, it is evident that there is a positive correlation between the amount of spent Li-ion batteries and the market size of Li-ion batteries. Therefore, from the market revenue of Li-ion batteries, the consumption and demand trends of spent Li-ion batteries could be extrapolated [22,24]. The recycling processes of spent Li-ion batteries need to be studied and developed further urgently to establish industrial process routes that are more cost-effective and environmentally friendly than current processes.

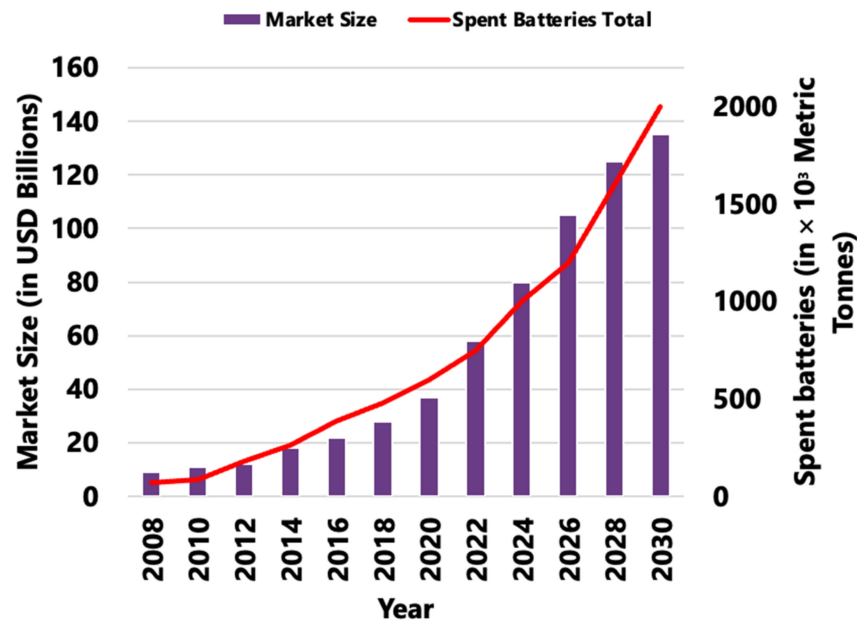


Figure 3. Global market size and total battery spent estimation of Li-ion batteries over the years (Data derived from refs. [1,2,23]).

3. Why Recycle Lithium-Ion Batteries?

Figure 4 depicts the surge in global demand for rechargeable batteries by battery application over the years [24]. Up to date, portable electronics like cell phones and notebooks or personal computers (PCs) have accounted for the majority of the Li-ion battery demand. It is anticipated that demand for such tiny gadgets will exponentially rise over time. After a succession of advancements, the market for Li-ion batteries will prosper with the aid of various Li-ion battery applications, including solar panel systems, electrical power tools, smart grids, and especially electric automobiles. According to extrapolations (Figure 4), the market for rechargeable batteries for electric vehicles will surpass 7000 GWh in 2030, while the overall market for batteries will top 10,000 GWh.

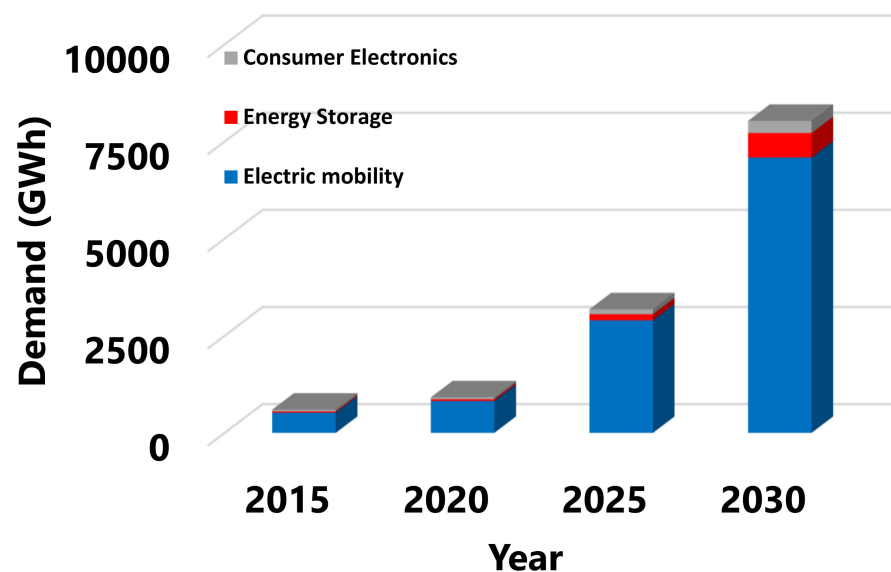


Figure 4. Global demand for battery technologies by application from 2015 to 2030 (Data derived from ref. [25]).

The typical lifespan of Li-ion batteries is 3–4 years. As deposits in the electrolyte created during charging hinder ion transit over time, the capacity of the cell declines. Age and cycling both result in an increase in internal resistance, which lowers the cell's capacity to conduct current. Additionally, as internal resistance increases, the terminal voltage decreases. Older batteries, therefore, do not charge as quickly as new ones (the charging time required decreases proportionally). Li-ion batteries will inevitably contribute significantly to solid waste, which must not be disregarded [24].

Since Li-ion batteries do not contain any substances that are hazardous to the environment on their own, they are harmless and deemed suitable for landfill disposal. However, if Li-ion battery materials in a landfill leak and eventually come into contact with water, hazardous materials will be produced that will seep into the groundwater, making the landfill hazardous to the environment. Poisonous HF can be emitted when LiPF_6 in the electrolyte decomposes and reacts with water: $\text{LiPF}_6 + \text{H}_2\text{O} \rightarrow \text{POF}_3 + 2\text{HF} + \text{LiF}$ [17,24]. Additionally, internal short-circuits during decomposition may occur and release a lot of heat and oxygen, leading to an explosion. Li-ion batteries constitute cobalt, copper, nickel, and iron, which, upon leaking to the ecosystem, are toxic to living organisms and could cause considerable injury and probably result in death. The same is true for humans. Additionally, discarding the spent batteries as waste necessitates the extraction of more metals, which has a considerably greater negative impact on the environment than simple recycling. Even though Li-ion batteries can be recycled completely, millions of tons of them are nonetheless disposed of in landfills every year, taking up space that could be spared.

While Li-ion batteries are NOT extensively and effectively recycled, Pb-acid batteries are recycled to a degree of 97%, and more than 50% of the lead supply originates from recycled batteries [25]. Despite the enormous increase in Li demand, the study of the geological resource base for Li reveals that not enough Li is present in the Earth's crust to support the production of electric vehicles in the requisite quantities using only Li-ion batteries [23]. Recycling can significantly lower the amount of Li needed. Having a recycling system in place will allay worries that the adoption of Li-ion battery-powered vehicles will result in a shortage of lithium carbonate and a overreliance on nations like China, Russia, and Bolivia, who hold the majority of the world's Li reserves [2].

Conventional electrochemical Li-ion batteries constitute valuable metallic elements such as Co, Mn, Fe, and Ni.

Figure 5 depicts a typical composition of a Li-ion battery. Table 1 shows the approximate value per metric ton (in the year 2022) for the key valuable components in a standard Li-ion battery technology [7]. Large-scale economic and non-complex Li-ion battery recycling will undoubtedly benefit the environment and the economy as more and more Li-ion batteries are produced and consumed [26]. As noted, active cathode materials contribute the largest share of the overall cost of the battery; hence, the emphasis on recycling should be primarily focused on the cathode component.

Table 1. Approximate value for main components in a typical Li-ion cell (April 2022) (data derived from ref. [7]).

Component	Approximate Value
	US\$/Ton
Cobalt	87,633
Aluminium	2753
Nickel	28,370
Manganese	2000
Iron	300
Electrolyte	1500
Copper	9219
Lithium	59,720

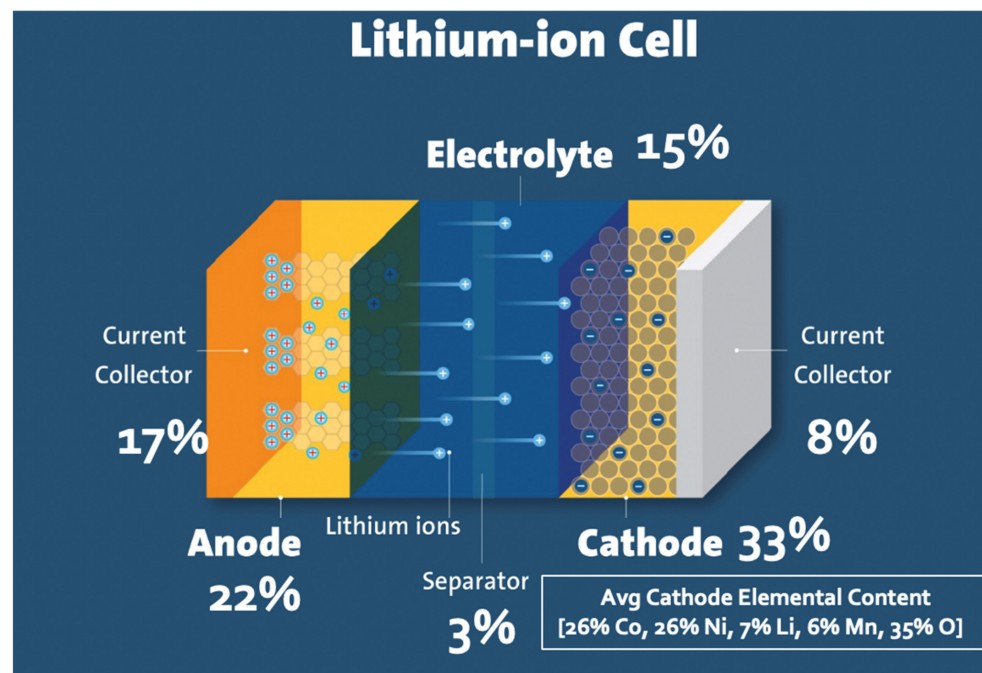


Figure 5. Typical Li-ion battery composition (data derived from [17,18,21]).

4. Conventional Recycling Methodologies

4.1. Overview

Spent Li-ion batteries constitute mainly valuable metallic components such as Ni, Co, and Li and less valuable elemental components such as P, Al and Fe [5,27]. The recovery of highly valuable metals like Li, Ni, and Co from active cathode materials is the primary objective of recycling spent Li-ion batteries, an initiative largely driven by environmental and economic concerns, as highlighted in prior sections.

Spent Li-ion batteries are conventionally recycled by employing hydrometallurgy, pyrometallurgy, bio metallurgy or electrometallurgy or a combination of all or some of them at the industrial and pilot scale [28,29]. Figure 6 depicts a schematic representation of a typical recycling scheme, which typically entails four primary steps: pre-treatment, metal extraction, product and component refining, and battery production.

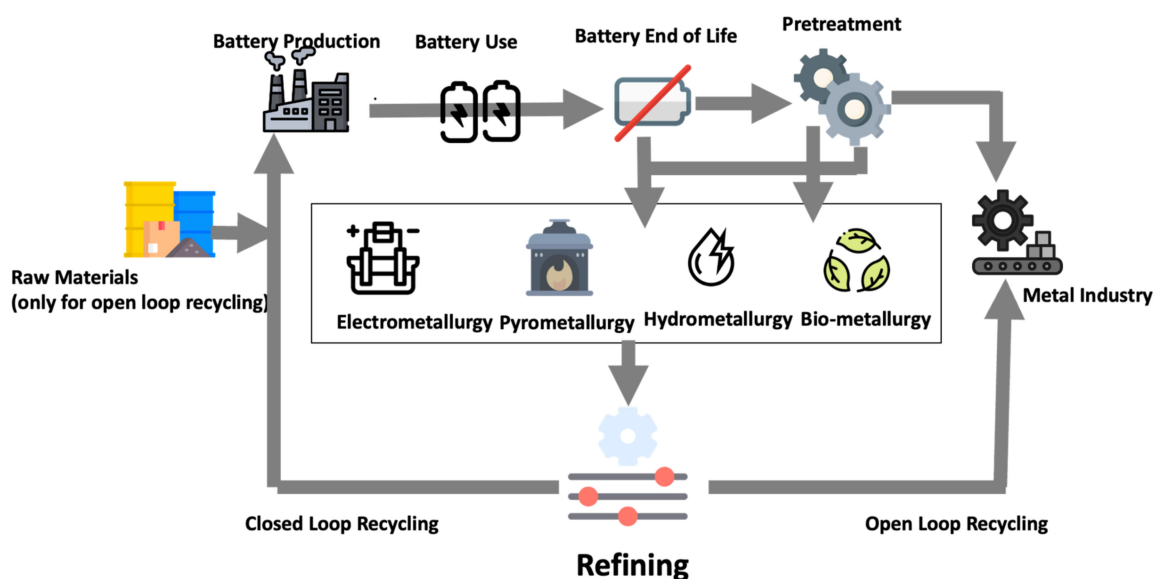


Figure 6. Conventional recycling stages for spent Li-ion batteries.

To avoid runaway spontaneous combustion of battery elements or short-circuiting during the subsequent disassembling or dismantling step, spent Li-ion batteries are typically first fully discharged to empty all the remaining power. To discharge spent Li-ion batteries, they are usually immersed in a salt solution [3,5,9]. Following the discharging step, the fully discharged spent Li-ion batteries are processed through mechanical separation and automated or manual dismantling. The goal of this step is to remove the plastic or metal casings and separate the internal components of spent Li-ion batteries (i.e., anode, cathode and separator) for further recycling processing. Following the disassembling step, the active cathode material is separated from the current collector through chemical, thermal or physical treatment processes (e.g., thermal treatment method, manual scraping method, NaOH dissolution method, solvent dissolution method, ultrasonic-assisted separation method, or mechanical methods) [9]. The recovered active cathode material is then channelled to the next stage for further processing. The conventional recycling mythologies for spent Li-ion batteries are depicted in Figure 7.

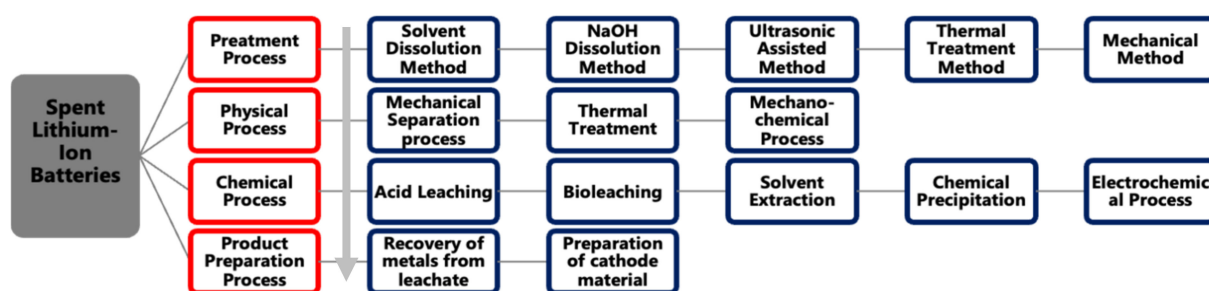


Figure 7. Recycling mythologies for spent Li-ion batteries.

4.2. Pre-Treatment Process

The various waste battery streams are often subjected to either a mechanical or chemical pre-treatment procedure in order to prepare them for later processing. Pre-treatment also increases the efficiency of the overall battery recycling process. The subsequent processes will be more fluid if thorough pre-treatment is administered. Dismantling, crushing, screening, heat treatment, mechanochemical technique, dissolving, and other pre-treatment procedures are the primary pre-treatment processes. Due to their vastly differing physical qualities, several valuable metals, components or materials, such as Cu, Al, and carbonaceous anode, are simple to recover and recycle through pre-treatment. Pre-treatment processing plays a significant role in separating and recovering active cathode materials and organic binders from the current collector as they make subsequent process execution much less energy and time intensive [30].

Shin et al. [31] described a single-stage pre-treatment process in which the spent Li-ion batteries were directly crushed to an appropriate size, followed by fine crushing and sieving to remove aluminum foil which would affect the leaching process. At the conclusion of the process, metallic material was collected using magnetic separation. The pre-treatment technique requires the removal of the organic binder, which is crucial. Thermal treatment, ultrasonic cleaning, and dissolution in an organic reagent are the ideal processes for undertaking such a task [31–34].

To separate different materials, Granata et al. [32] used a splitter and a two-rotor crusher. Thermal processing at 300 °C for two hours removed the organic binder. However, the breakdown of organic materials like PVDF resulted in the production of harmful and poisonous fumes such as HF and exhaust gases that has been contaminated with heavy metals. As a result, it seems necessary to use a system that includes a cooler, a condensation chamber, bag filters and carbon filters as tail gas processes to dispose of harmful gases. Researchers experimented with organic dissolution reagents to dissolve the organic binder in light of the drawbacks entailed by the heat treatment. For instance, the dissolution reagent used to dissolve PVDF is a mixture of N, N-dimethylformamide (DMF) and N-methyl pyrrolidone (NMP) or ethanol, although the dissolution reagent (solvent) itself is

typically referred to as a toxicant [34]. Citrus fruit juice (CFJ) was described by Pant and Dolker [35] as a green, non-toxic, and eco-friendly solvent to make up for the drawback of utilizing a hazardous solvent as a dissolution reagent. To accomplish successful dissolution, the CFJ procedure is often carried out under extreme temperature conditions (typically over 90 °C) [22,35].

The mechanochemical process, in addition to mechanical processing methods, is an imperative process that alters raw materials mechanically to affect their physicochemical properties through the utilization of high-energy ball milling [36–39]. The grinding and rubbing of particles could also unintentionally activate various chemical reactions. The activity of the materials will subsequently be improved following the mechanochemical conversion. In light of this, mechanochemical technology is frequently utilized in pre-treatment operations of spent Li-ion battery active cathode particles to alter, modify or disrupt their respective crystal structure in order to enhance the leaching efficiency [36]. Even though pre-treatment processes have been the subject of a lot of research, there are still certain practical challenges that must still be overcome, as summarized in Table 2. Furthermore, the adoption of various pre-treatment techniques is still hampered by the disorganized and less effective classification of Li-ion spent batteries, complex disassembly and dismantling processes, and inefficient valuable metal extraction (i.e., Co, Ni and Li) [14,40]. Pre-treatment processes must therefore be utilized in conjunction with other physicochemical procedures to achieve the goal of efficiently recycling all valuable materials or metals in spent Li-ion batteries.

Table 2. Advantages and disadvantages of conventional pre-treatment methods (Data gathered from refs. [14,40]).

Method	Advantages	Disadvantages
Solvent Dissolution method	High separation efficiency	The costlier the solution, the high degree of toxicity
NaOH method	Simple operation with high separation efficiency	Alkali wastewater is harmful to the ecosystem, and Al extraction is challenging since it is in an ionic state
Ultrasonic assisted separation	The operation method is simple, with no hazardous or toxic traits	High capital cost, noise pollution
Thermal treatment	Simple operation, high-efficiency process	Capital cost is the high, high toxic gas emission
Mechanical methods	Operation method that is simple to employ	High levels of hazardous gas emissions and incomplete metal removal from spent Li-ion batteries

Effective separation of the active cathode material from the foil is achieved via solvent dissolution, ultrasonic-assisted separation, sodium hydroxide (NaOH) dissolution, thermal treatment and mechanical separation methods [22]. The methods are discussed in detail in the following sections.

4.3. Solvent Dissolution Method

The solvent dissolution process weakens the bond between the substrate and active cathode material by dissolving the binder material. Selection of the most effective organic solvent to dissolve and weaken the binder is a key step in the solvent dissolution process. The organic solvent N-methyl pyrrolidone has been widely utilized to extensively dissolve the PVDF binder [22]. Zhou et al. [41] proposed utilizing dimethylformamide (DMF) to dissolve the binder PVDF. The solubility of PVDF in DMF was found to be 175 g·L⁻¹ at 60 °C. The active material in the PVDF-based cathode was compatible with DMF solvent.

However, the PTFE-based active cathode material was not appropriately suitable for dissolution in DMF [22,40].

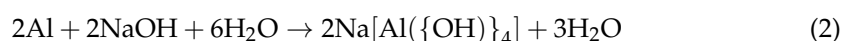
Zhang et al. [42] effectively extracted the Li-ion battery active cathode material from the Al foil current collector using the trifluoroacetate (TFA) solvent. The active cathode material from the Al foil current collector can be successfully extracted using the solvent dissolution process, according to numerous research. For PVDF-based active cathode material, the majority of studies had achieved success, but for PTFE-based active cathode material [40], it had been very challenging to remove the active cathode material from the Al substrate. The solution used in this procedure is often costly and hazardous to human and environmental health [22,40].

The latest developments in Li-ion pre-treatment processes were discussed by Zhang et al. [40]. The substrate (aluminum foil) dissolution method was employed to dissolve the foil from the electrode-substrate matrix by employing alkaline solutions. The method entails the selective dissolution of the foil without dissolving the active cathode materials [22,40]. In addition to the aforementioned methodologies, a high-temperature process is also utilized, but because it disintegrates the electrode materials and ultimately dissolves them, the method is not ideally feasible. The electrode materials that were recovered after removing the battery casing were heated with an N-methyl pyrrolidone (NMP) solution at approximately 100 °C in the pilot process for recycling Li-ion batteries that Zhou et al. [41] described. Graphite and LiCoO₂ were successfully extracted from the collector using this process while Al and Cu were still in their metallic state.

Triethyl phosphate was utilized by Bai et al. [43] to extract Li-ion battery active cathode material (e.g., NMC, LCO, etc.) by dissolving the PVDF binder. Through a solvent-based separation process, electrochemically active components were removed from cathode scraps gathered during the manufacturing process of electrodes without altering their physicochemical properties, electrochemical characteristics, and crystallography. The aluminum foils that were recovered were spotless and exhibited no signs of corrosion after PVDF dissolution. The polymer-based binder can also be recovered using wet phase inversion (a non-solvent-induced phase separation technique) [43].

4.4. NaOH Dissolution Method

Numerous proposed methods for separating or isolating the Li-ion active cathode materials from the aluminum foil substrate included leaching the cathode using a NaOH solution. Ideally, the components can be separated using the amphoteric properties of aluminum [44]. The separation of active cathode material from aluminum foil substrate was accomplished by utilizing a 10 wt% NaOH solution for 300 min at ambient temperature [45]. The process effectively dissolved over 97% of the aluminum foil substrate. The aluminum oxide protective layer covering the substrate surface dissolves (Equation (1)) along with the aluminum foil (Equation (2)) when a NaOH solution solvent targeting substrate is used [22,44].



Advantages of this technology include high separation efficiency, ease of operation and effective separation. However, the effective recovery of Al is hampered due to its existence in ionic form. Furthermore, the NaOH alkali wastewater (is hazardous to environmental and human health).

4.5. Ultrasonic-Assisted Separation

Since the polymeric binders have high adhesive strength, it is relatively challenging to remove active cathode material from the aluminium foil current. The ultrasonic treatment process is regarded to be an ideal practical process for eliminating active cathode material from the Al foil substrate due to the cavitation effect generated by ultrasonic sound waves. Li et al. [46] put forth the ground-breaking idea of recycling used Li-ion batteries by

integrating crushing and ultrasonic washing to recover the Co compound. The alternate approach enhances the Co recovery efficiency while lowering energy consumption and environmental pollution. In order to separate the electrode materials from their support substrate, Li-ion batteries were crushed through a 12 mm aperture screen before being processed into an ultrasonic washing vessel. A 2 mm aperture screen was utilized to filter the cleaned materials in order to obtain the underflow items, specifically the recovered electrode material. The active cathode material remains adhered to the substrate surface when utilizing solely the mechanical approach, and only the components phase matrixes (not elemental or chemical components) are separated when employing the ultrasonic washing method [22].

Li et al. [46] investigated how the cavitation effect (from ultrasonic treatment) and agitation affected the separation of active cathode materials. The study established that when mechanical agitation alone was applied, the majority of the active cathode materials remained adherent to the surface of the Al substrate. Only a portion of the active cathode materials was separated when the ultrasonic-assisted separation method was utilized independently. However, practically all of the active cathode materials could be effectively removed from the Al substrates when both techniques were applied concurrently. This effect is attributed to the cavitation effect generated during ultrasonic treatment, which can produce more pressure to liquefy and scatter insoluble contaminants. The mechanical agitation's washing effect further enhances the separation of active cathode materials from the substrate [47].

He et al. [48] iterated that the separation of active cathode materials from Al foil substrate by ultrasonic treatment is a functional result of the binder dissolution and the cavitation effect induced by the ultrasonic waves. Based on this mechanism, when NMP was employed as the cleaning solution, the stripping efficiency of the active cathode material was over 99% at a temperature of 70 °C and ultrasonic power of 240 W for 90 min of continuous ultrasonic treatment. The active cathode material exhibited low aggregation after being removed from the Al foil substrate by ultrasonic treatment, which facilitated the subsequent active cathode material dissolution process (leaching process) [22,48].

4.6. Thermal Treatment Method

Vacuum pyrolysis is a straightforward method for extracting active cathode material. The pyrolysis process evaporates or breaks down the electrolyte and binder, which in turn weakens the active cathode material matrix-substrate bond [49–51]. The thermal treatment approach employs high temperatures to break down the binder, weakening the foil substrate-active cathode material bond. The active cathode materials can subsequently be effectively removed via physical separation processes (such as sieving, magnetic separation, crushing, etc.) [50].

Although some materials, such as acetylene black, conductive carbon, etc., oxidize beyond 350 °C and generally decompose above 600 °C, PVDF binder is typically reported to decompose above 350 °C [46,50]. Vacuum pyrolysis has been proposed by Sun and Qiu [49] as a novel process for effectively separating active cathode material from the current collector (Al foil). Pyrolysis weakens the adhesion between the active cathode material and the current collector by evaporating or decomposing the electrolyte and binder. The active cathode materials only disintegrated from the collectors when the pyrolysis temperature was more than 450 °C. When the pyrolysis temperature was below 450 °C, the active cathode materials remained bonded to the current collectors. The extent and effectiveness of separation improved with temperature nominally between 500 and 600 °C. Since the aluminium foil remained brittle at temperatures above 600 °C, it was difficult to remove the active cathode material from the collector. The active cathode materials from the Al collectors are separated by employing heat treatment in a reducing atmosphere [51]. It was demonstrated that it is feasible to effectively separate the active cathode materials from the current collectors by adjusting the temperature of the reducing atmosphere [50]. Additionally, the molecular structure of the active cathode materials is altered during this process, which makes it easier

to leach cathode metals during the leaching phases. Thermal treatment has several benefits, including ease of use and high separation efficiency. The binder and additives are thermally treated; however, this process by-produces hazardous gases.

4.7. Mechanical Method

Mechanical pre-treatment processes, such as sieving, crushing, magnetic separation, and other similar processes, are widely recognized as useful in the context of recycling spent Li-ion batteries. Zhang et al. [42] investigated the process, mechanical and chemical mineralogical characterizations of spent Li-ion battery waste by integrating several analytical methods in order to give fundamental information pertaining to mechanical separation processes. It was discovered that used Li-ion batteries exhibited good selective crushing characteristics during processing. Three components make up the crushing by-products of wasted Li-ion batteries: an Al-enriched fraction (>2 mm), an Al- and Cu [1,2,23]-enriched fraction (0.25–2 mm), and a Co- and a graphite-enriched fraction (0.25 mm). The active cathode materials derived from a fraction of less than 0.25 mm in terms of mineral phase and chemical state were found to have kept their original crystalline structure and chemical state in Li-ion batteries. However, these powders included a coating of hydrocarbons on their surface that made flotation operations problematic.

Shin et al. [31] developed a combination process that used mechanical separation to gather the active cathode materials and a hydrometallurgical procedure to recover valuable metals from the wasted Li-ion batteries. After a variety of mechanical processes, including crushing, sieving, and magnetic separation, enriched LiCoO_2 particles were produced. These particles were then finely ground to separate the LiCoO_2 from tiny fragments of aluminium foil. Prior to the metal-leaching process, mechanical separation can increase the efficiency of the targeted metal recovery. The main drawback of mechanical procedures is that the components of used Li-ion batteries cannot be entirely separated from one another. In addition, the environment is put in danger because of the disintegration of LiPF_6 , DEC, and PC during mechanical processes [52]. The process flow chart of the conventional mechanical treatment methodologies is depicted in Figure 8.

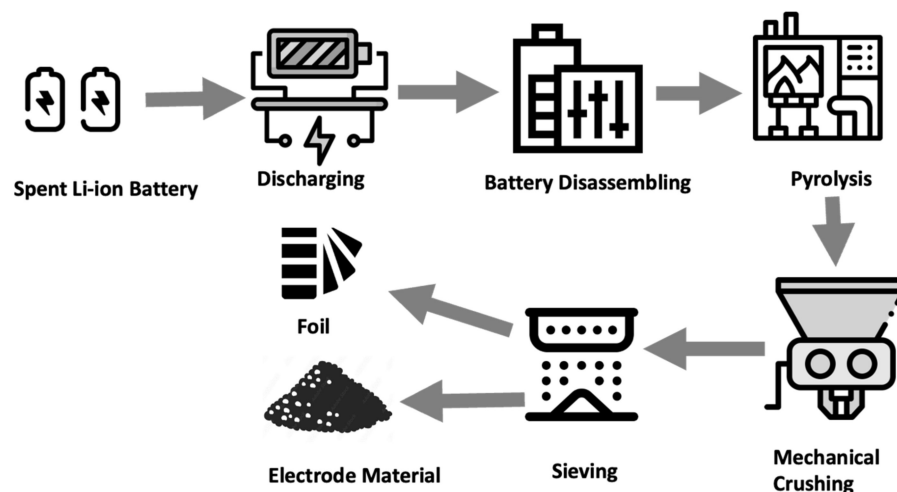


Figure 8. Process flow chart of conventional mechanical pre-treatment process route.

There are still existing challenges with the pre-treatment processing of spent Li-ion batteries despite the fact that numerous pre-treatment technologies have been established by researchers. A summary of the benefits and drawbacks of various pre-treatment techniques is summated in Table 2.

4.8. Physical Processes

4.8.1. Pyrometallurgical Process

A subset of extractive metallurgy, pyrometallurgy employs heat to physically and chemically modify ore and concentrates in order to recover valuable metals [29,53]. In order to recover heavy metals (such as Cd, Pb, Cu, Zn, etc.) from depleted Ni-Cd batteries, Ni-Fe or Zn-Mn dry batteries, pyrometallurgical methods have been extensively researched [22,54]. In pyrometallurgical operations, smelt slags are frequently utilized to segregate metals, with certain metals going to the slag and the target metals becoming alloys. Most pyrometallurgical processes, with the exception of the Umicore technology, require pre-treatment processing [49,53,55,56]. By incorporating CaO + SiO₂, pyrolusite, and minute amounts of Al shells into the processing of spent Li-ion batteries, Ren et al. [57] presented a novel slag system of MnO-SiO₂-Al₂O₃. The mixture was then heated for 30 min at 1475 °C. This innovative technique produced a high-purity metallic alloy with Ni (99%), Co (99%), and Cu (99%), as well as enhanced slag with MnO (46%) and Li₂O (2.5%) [22,57].

Li ions are usually trapped in the slag phase in a standard pyrometallurgical process, which has to be further processed to be extracted in the pure metallic form [58]. Recently, attention has been directed to the carbothermal reduction process as a low-cost, non-complex, and consistently repeatable pyrometallurgical route to recycle Li, Co and other valuable metals [53]. The mixed spent Li-ion batteries can be converted into lithium carbonate, metal oxide, or pure metal through this carbothermal reduction process. Water leaches lithium carbonate in one step, whereas the carbon (from graphite) in the leachate slag burns to by-produce carbon dioxide, leaving metal oxide as the remaining residue [53,59]. The following stage involves wet magnetic separation to further separate lithium carbonate, graphite, and pure metal [60]. The pyrometallurgical technologies, however, now confront challenges in lowering energy consumption and meeting the stern and rigorous specified requirements for modern treatment processes. The pyrometallurgical process, which primarily entails pyrolysis, is comprehensively summarized in Figure 9.

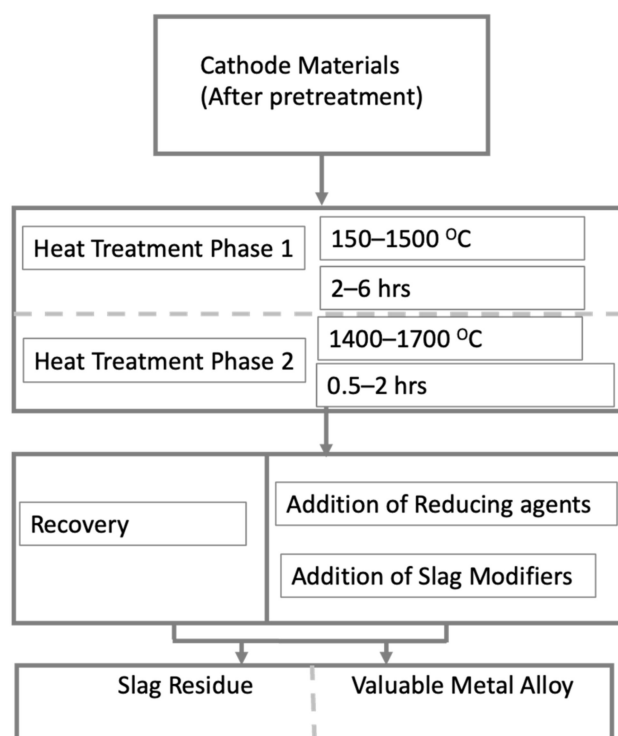


Figure 9. Conventional pyrometallurgical processes for spent Li-ion batteries (Data gathered from refs. [53,58,59]).

4.8.2. Hydrometallurgical Process

Leaching and extraction constitute most of a typical hydrometallurgical process. In comparison to the pyrometallurgical process, it entails numerous added advantages, including high valuable metal extraction efficiency, low energy intensity, less harmful gas emission, and low capital and production costs. Commercialization of hydrometallurgy has enormous possibilities. However, when it comes to disposing of waste materials, the process entails considerable challenges. The hydrometallurgical process, which primarily entails leaching, solvent (liquid-liquid) extraction, chemical precipitation, and electroreduction process, is comprehensively summarized in Figure 10. Among these, a relatively small portion of the research is reported on the recovery and recycling of spent Li-ion batteries by the electrochemical process because of its high energy-intensive nature, even though past research does imply its viability for recovering Co-based compounds and pure Co metal [18,61–63].

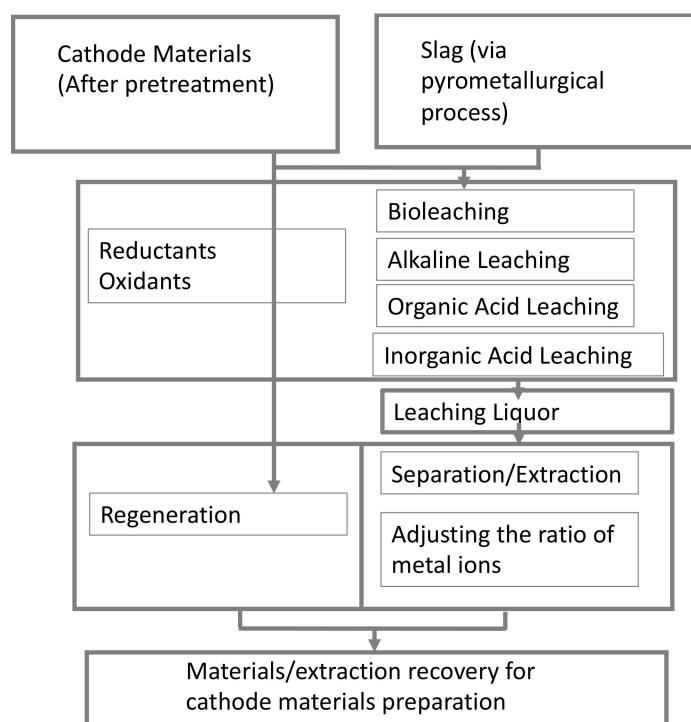
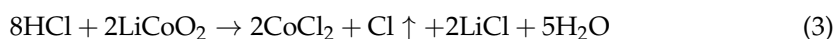


Figure 10. Conventional hydrometallurgical recycling and recovering processes for spent Li-ion batteries (Data gathered from ref. [18]).

4.9. Chemical Processes

4.9.1. Conventional Leaching

The primary phases of the recycling of spent Li-ion batteries, akin to most metallurgical processes, include the dissolution of the active cathode materials in the leachants (leaching reagents), followed by reduction, separation, and extraction. In earlier research studies, in-organic acid reagents, such as nitric acid (HNO₃), hydrochloric acid (HCl), and sulphuric acid (H₂SO₄), were conventionally utilized as leaching agents and proved to be practically successful and effective, but drawbacks, such as the by-production of secondary pollutants and the complexity of extractive separation and purification processes, also surfaced [32,49,64]. The chemical reaction of the leaching process using HCl as the leaching agent can be annotated as:



Similar reactions occur when different monoatomic or polyatomic acids are used for leaching. In the absence of reductants, the leaching efficiency of Co proceeds in the

following order: $\text{HCl} > \text{HNO}_3 \approx \text{H}_2\text{SO}_4$. The relatively higher leaching efficiency of HCl is mostly effectuated by the reducibility nature of HCl [65]. Therefore, unless H_2O_2 or other reductants are added, the leaching efficiency of the majority of reagents would be limited. The leaching + reduction reaction mechanism can be annotated (using LiCoO_2 as an example):

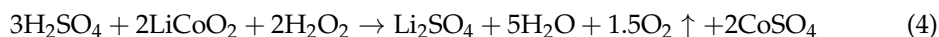


Figure 11a annotates how reductants like H_2O_2 or ascorbic acid can enhance the leaching properties of leaching reagents. At normal temperatures, Co^{2+} is much more easily dissolved than Co^{3+} , yet Co^{3+} is primarily substantial in spent Li-ion active cathode materials. Therefore, the leaching efficiency and reaction kinetics will undoubtedly be enhanced when the Co^{3+} is transformed into Co^{2+} . Moreover, because Co^{3+} has a significantly different solubility constant from Mn^{2+} , Cu^{2+} and other metal ions, the shadow in

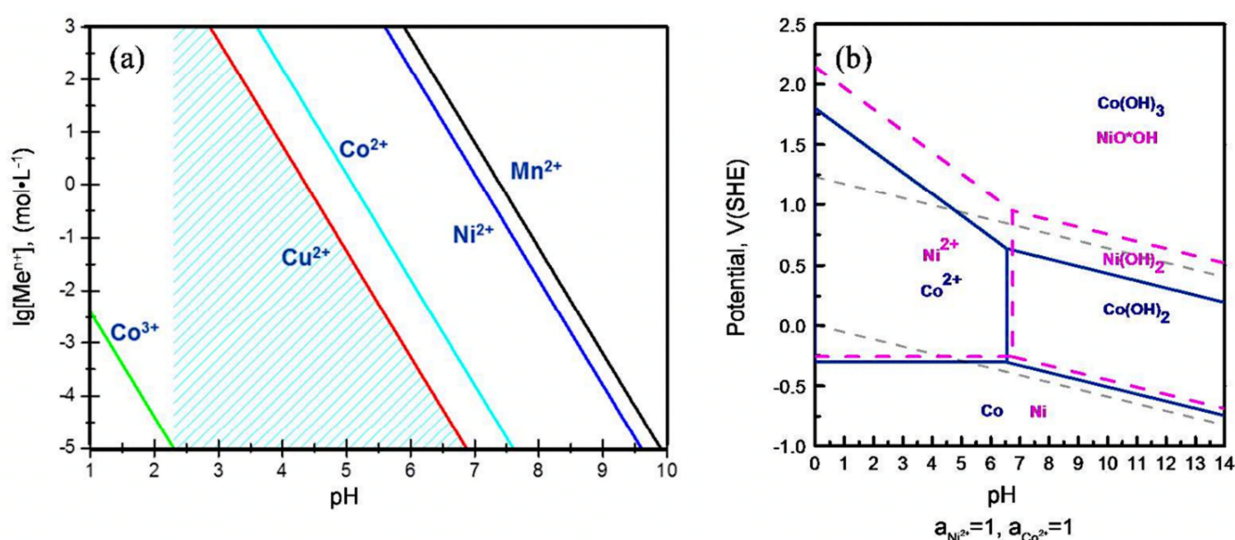


Figure 11. (a) Correlation between equilibrium aqueous metal ion concentration (at 25 °C) and pH; (b) Potential (E vs. SHE) and pH diagram for the Ni-H₂O and Co-H₂O systems (at 25 °C, Co = Ni = 0.2 mol L⁻¹) (Figure adapted from ref. [22]).

Figure 11a would be an ideal region to isolate Co^{3+} from these metal ions and other metal ions. Leaching efficiency and reaction rate would initially rise in line with an increase in reductant concentrations, and then they would reach a plateau, where they would not fluctuate noticeably [13].

Numerous organic leaching reagents, such as oxalic acid, citric acid, malic acid, ascorbic acid, aspartic acid, and glycine, are intensively explored to address the issues that arise when employing the inorganic leaching reagents [12,13,66,67].

Li et al. [46] iterated that while the leaching efficiency of Li is consistently steady throughout those various leaching media, the leaching efficiency of Co is higher when employing citric acid compared to HCl or H_2SO_4 . Most organic acids have a similar reaction mechanism to citric acid, with a few exceptions like oxalic acid [12,13,46,68]. Oxalic acid may serve as both a reductant and a leachant; consequently, Co and Li leaching could attain leaching efficiencies of more than 97% [12,13].

An alkaline-based leaching system, like NH_3 , has also been researched in addition to the acid-based leaching system. An NH_3 - $(\text{NH}_4)_2\text{SO}_4$ system with high metal selectivity during leaching was demonstrated by Zheng et al. [69]. A similar leaching system containing NH_3 , $(\text{NH}_4)_2\text{SO}_4$, and $(\text{NH}_4)_2\text{CO}_3$ was employed by Ku et al. [70]. In spent Li-ion batteries, Co and Ni have a high valence state which makes them difficult to dissolve, whereas Cu was easily separated from Co and Ni in the NH_3 -based system [69,70]. $(\text{NH}_4)_2\text{CO}_3$ served

as a pH buffer to maintain a stable leaching solution's pH, while $(\text{NH}_4)_2\text{SO}_4$ was added as a reductant to upsurge the leaching efficiencies of Ni and Co.

Additionally, the supercritical fluid used in metal extraction processes offers an ideal leachant alternative. Bertuol et al. [11] effectively leached cobalt from spent Li-ion battery active cathode material using supercritical CO_2 extraction using H_2SO_4 (as cosolvent) and H_2O_2 (as reductant additive). The results indicated that 95% leaching efficiency could be attained by reducing the reduction process duration and H_2O_2 consumption from 60 min to 5 min and 8 vol% to 4 vol%, respectively [11,22]. Liu and Zhang [71] synthesized the acid leachant for the leaching process through the dichlorination of PVC using subcritical water as the catalyst. At 350 °C temperature, PVC/LCO ratio of 3:1 and 16:1 S/L ratio, approximately 96% of Co and nearly 99% of Li were leached from the base active cathode material. However, the operation is complex and entails high capital costs due to the rigorous equipment requirements, high-pressure and high-temperature environment. All of the economic and technical challenges highlighted above have dampened interest in utilizing supercritical fluid in battery recycling [22,71].

Table 3 provides a summated overview of the Li-ion battery active cathode material leaching processes over the years. Though there are numerous reports on Li-ion battery active cathode material leaching processes, only a small proportion focus on detailing the leaching process mechanism at the molecular or atomic level based on the crystallographic method. Takacova et al. [72] explored the change of spent Li-ion battery active cathode sub-particles in the HCl and H_2SO_4 leaching mediums. The work also detailed the influence of temperature on Li and Co extraction from active cathode mass, a case for both leaching reagents through kinetics (activation energy) and thermodynamics studies. Such studies foster further investigations on the active cathode material leaching process in the future. The more the leaching process mechanisms are understood, the more opportunities arise for enhancing the efficiency of the leaching process [72,73].

Table 3. Summative review of leaching spent Li-ion batteries using different leaching reagents.

Leaching Process and Active Cathode Material Leached	Reagent	Temp	Time	Leaching Efficiency (%)		Refs.
		(°C)	(min)	Co	Li	
Inorganic Acid Leaching						
Spent Li-ion batteries (LCO)	0.7 M H_3PO_4 + 4 vol % H_2O_2	40	60	98	96	[74]
Spent Li-ion batteries (LCO + NMC)	1 M H_2SO_4 + 0.075 M NaHSO_3	95	240	92	97	[55]
Spent Li-ion batteries (LCO)	1 M HNO_3 + 1.7 vol % H_2O_2	75	60	96	96	[75]
LCO	1.75 M HCl	50	90	98	97	[76]
Spent Li-ion batteries (LCO) (from e-gadgets)	2 M H_2SO_4 + 5 vol % H_2O_2	75	60	71	98	[77]
LCO	2 M H_2SO_4 + 5 vol % H_2O_2	75	30	94	96	[78]
LCO	2 M H_2SO_4 + 2 vol % H_2O_2	60	120	97	87	[79]
LCO	2 M H_2SO_4 + 0.4 g/g Sucrose	95	120	96	99	[80]
Spent Li-ion batteries (LCO) (from cell phones)	2% vol % H_3PO_4 + 2 vol % H_2O_2	90	60	98	89	[81]
LiNixMnyCozO (NMC) compounds	4 M H_2SO_4 + 5 vol % H_2O_2	65–70	120	97		[82]
LCO	4 M HCl	80	30	91	94	[83]
LFP and LMO	6.5 M HCl + 5 vol % H_2O_2	30	60		76	[84]

Table 3. Cont.

Leaching Process and Active Cathode Material Leached	Reagent	Temp (°C)	Time (min)	Leaching Efficiency (%)		Refs.
				Co	Li	
Alkaline Leaching						
Spent Li-ion batteries (Li(Ni _{1/3} Co _{1/3} Mn _{1/3})O ₂)	4 M NH ₃ -1.5 mol/L (NH ₄) ₂ SO ₄ + 0.5 M Na ₂ SO ₄	80	300	81	96	[69]
Organic Acid Leaching						
Spent Li-ion batteries (LCO)	1.5 M citric acid + 0.2 M salicylic acid (15 g L ⁻¹), 6 vol % H ₂ O ₂	90	90	99	97	
Spent Li-ion batteries (LCO)	0.4 M tartaric acid + 0.02 M ascorbic acid	80	60	94	96	[13]
Spent Li-ion batteries (LCO)	1.5 M Citric Acid + 0.2 M Salicylic Acid + 6 vol % H ₂ O ₂	90	90	99	97	[85]
Spent Li-ion batteries (LCO)	0.5 M glycine + 0.02 M ascorbic acid	80	120	92		[13]
Spent Li-ion batteries (LCO)	1 M iminodiacetic acid + 0.02 M ascorbic acid	80	120	98	90	[12]
Spent Li-ion batteries (LCO)	1 M maleic acid + 0.02 M ascorbic acid	80	120	98	96	[12]
LCO	1 M oxalate + 5 vol % H ₂ O ₂	80	120	97		[85]
Spent Li-ion batteries (LCO)	1 M oxalic acid	95	150	97	98	[67]
Spent Li-ion batteries (LCO)	1.5 M succinic acid + 4 vol % H ₂ O ₂	70	40	98	95	[86]
Spent Li-ion batteries (LCO)	2 M citric acid + 0.6 g/g H ₂ O ₂ (H ₂ O ₂ /spent Li-ion batteries)	70	80	96	98	[87]
Spent Li-ion batteries, (LCO & LiNi _{0.5} Co _{0.2} Mn _{0.3} O ₂ (NMC))	2 M L-tartaric acid + 4 vol % H ₂ O ₂	70	30	97	99	[88,89]

In this section, quantitative methods for leaching rates of Li and Co are proposed for gaining a magnified visualization of the advantages and disadvantages entailed by using various leaching reagents. The metal leaching rate is annotated as:

$$r_M = W_M \times a \times R/t \quad (5)$$

where r_M denotes the metal leaching rate, W_M (w/w %) denotes the weight or mass percentage of metal in spent Li-ion batteries active cathode materials, a (%) denotes the metal leaching efficiency, R (g/L) denotes the solids to liquid ratio, and t denotes the leaching time. This equation quantifies leaching efficiencies for different leaching reagents for comparison. The leaching efficiency of valuable metals typically exceeds 90%. However, to reach high leaching efficiencies, some of the processes utilize a low R or long leaching time. To analyse recycling, greenhouse gas (GHG) emissions, energy consumption, and operational costs were quantified using stoichiometric consumption of materials under the assumption 1 kg of Co is leached from spent Li-ion battery active cathode material by various leaching processes [22].

Lv et al. [22] further stated that additional relative evaluation index data was acquired from the GREET (Greenhouse gases, Regulated Emissions, and Energy use in Transportation) model developed by Argonne National Laboratory. The energy consumption, GHG emission, and cost of organic chemicals are significantly higher than those of inorganic reagents, as indicated in Figure 12. However, considering the biodegradability nature of organic leaching reagents and reduced flue gas emission from the processing, the advantages accrued from util $r_M = W_M \times a \times R/t$ zing organic reagents in leaching processes are quite apparent [22,66]. Moreover, the relevant data for H₂SO₄ about GHG emissions and energy consumption was not presented. H₂SO₄ has a substantially higher rate of valuable metal

leaching than other reagents for a high S/L and short leaching reaction time. However, H_2SO_4 is usually produced as a by-product of other chemical processes in many chemical plants, i.e., copper smelting. Consequently, information on GHG emissions and energy use in the manufacturing of H_2SO_4 is lacking [22].

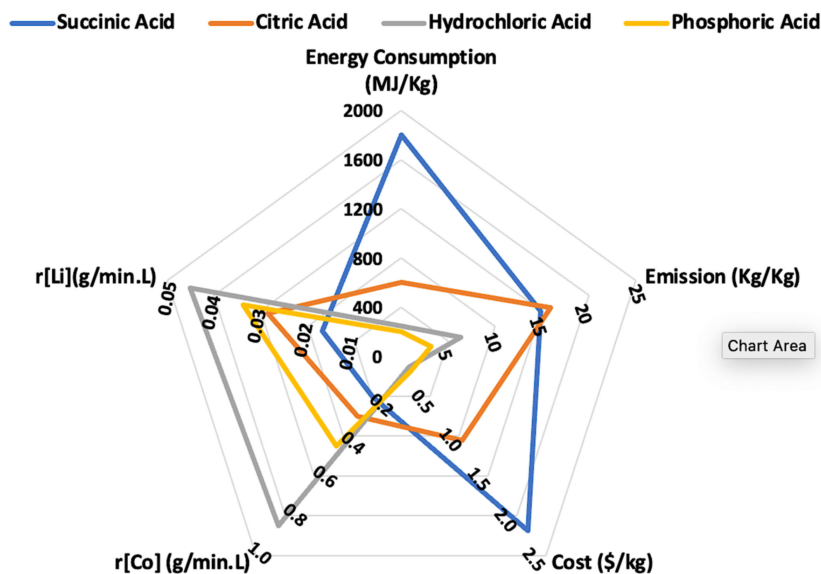


Figure 12. Spider chart for a relative evaluation index of leaching spent Li-ion batteries with various conventional leaching reagents (Data derived from refs. [6,22,66,81,87]).

In summation, the leaching performance was shown to be primarily influenced by the temperature, leaching time, solid-to-liquid ratio (S/L), agitation speed, and leachant as well as the reductant concentration. The leaching rate and efficiency both decrease as the solid-liquid ratio (S/L) increases. However, the leaching rate and efficiency would be increased by increasing leaching time, temperature, agitation speed and concentrations of leachant and reductant [73]. It should be noted that the leaching rate and efficiency would stagnate when a certain maximum quantity value of these factors is reached. These figures will guide future development efforts in the leaching process optimization upon processing different chemistries of Li-ion batteries using different leachants.

4.9.2. Bio-Metallurgical Process

The bio-metallurgy process utilizes microorganisms (bacteria) to treat and recover metals. The ability of microorganisms (or microbes) to transform insoluble solid materials into soluble and extractable forms is the driving factor influencing the effectiveness of a typical bio-metallurgical process [90,91]. (*Acidithiobacillus ferrooxidans*, a chemolithotrophic and acidophilic bacteria, was employed by Mishra et al. [92] as a leaching bacterium. The reaction operates optimally at 30 °C and a pH level of 2.5; however, even with a long leaching duration with added Fe^{2+} acting as a catalyst, the leaching efficiencies of Co and Li both were rather low [90,92,93]. The Co leaching efficiency could, however, reach more than 98% in just 7 days in an *Acidithiobacillus ferrooxidans* leaching system with 0.02 g/L of Ag^+ as a catalyst, according to data by [94] and Chen et al. [95]. Cu^{2+} can be employed similarly as the catalyst for the *Acidithiobacillus ferrooxidans* leaching systems. Combining diverse bacteria cultures in one system was trialled, such as acidophilic sulphate-oxidizing bacteria and iron-oxidizing bacteria systems [96,97]. Fungal leaching has numerous advantages over bacterial leaching, including the ability to thrive across a wide pH range, tolerance for hazardous and toxic chemicals, and the ability to conduct at a high leaching rate [93,98,99]. To accomplish the leaching process, various organic acids found in fungus metabolites have been employed [93,98,99].

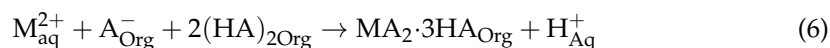
Bio-metallurgical processes utilize less energy consumption routes under mild conditions compared to conventional processes, making them ideal environmentally friendly processes [99]. The bio-metallurgical process, however, has fatal flaws when applied in industrial production; this is due to its slow kinetics and poor pulp density. In one investigation, the pulp density went up from 1–4%, which resulted in a drastic fall in bioleaching efficiency for Co and Li of 52–10% and 80–37%, respectively [100]. The bio-metallurgical processes are still very time-intensive even though high pulp concentration can be utilized to obtain high Co and Li leaching efficiencies by regulating leaching reaction temperature, upping the dose of mixed energy substrates, and altering the pH [100]. The bio-metallurgical processes for recycling spent Li-ion batteries are thus still a long way from being applied in industry, despite the fact that they entail significant energy-saving processing routes.

4.9.3. Solvent Extraction

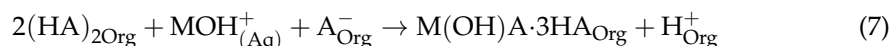
The primary objective of the battery recycling process is the extraction of pure metal or metal-based compounds. The recycling of pure metal or metal complexes will be necessarily hampered by the coexistence of different metal ions in the leachate. Additionally, the attempt at single-step precipitation is ineffective for producing pure metals due to the overlap of the precipitation pH range of several metals. Therefore, in order to attain acceptable levels of purity, the leaching solution must go through several separations and extraction stages, such as selective precipitation, solvent extraction and electrochemical processes.

The solvent extraction process, also known as the liquid-liquid extraction process, leverages the disparity in relative solubilities of compounds in two immiscible liquids, usually polar and non-polar solvents, to separate the compounds from one another [22]. Despite the challenges encountered in the separation of substances exhibiting similar functional groups, the process has proven to be reliable and robust; consequently, it is widely utilized in the extraction metallurgy sector (e.g., Co, Ni, Cu, molybdenum, and tungsten extraction and purification) and refining processes (e.g., nuclear processing, organic compound synthesis) [101,102].

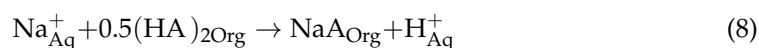
In solvent extraction, the equilibrium pH has a considerable effect on the selective extraction of specific metals. The di(2-Ethylhexyl)phosphoric acid (D2EHPA), for instance, is effective in extracting Cu and Mn ions but has poor selectivity for Co extraction at a pH range of 2.2–3.0 [37]. The extraction of Co with the cationic extractant D2EHPA is more effective at high pH (the higher the PH, the higher the extraction efficiency) [103]. The metal extraction reaction imitates the below-highlighted mechanism [32,104]:



or



where $2(HA)_{2Org} + A_{Org}^{-}$ represents the saponification reaction as:



At pH 4.5, the extractant PC-88A can effectively extract Ni and Co ions from a pool of numerous metal ions; however, at pH levels lower than 3, it is ineffective according to Wang et al. [37]. Due to its remarkable selectivity, Cyanex 272 has received much research attention as an extractant. Swain et al. [78] extracted 85.42% Co from the leachate at pH 5 using Cyanex 272, 5 vol% tributyl phosphate (TBP) as a phase modifier, and paraffin (kerosene) as diluents. A similar system was designed by Jha et al. [77], although isodecanol was utilized as a phase modifier. At pH 5.0, the Co extraction efficiency was 99.9% [77,78,105].

The optimal pH scales of numerous extraction reagents are summarized in Figure 13 [83,106–109]. It is evident that some reagents effectively extract Ni and Co in the pH range of 3–5; however, the reactor must be corrosion-resistant to withstand such conditions. Cy-

naex 272 and P507 may be an ideal additive as it possesses the ability to alter the optimal pH for solvent extraction. For example, in Figure 13, the ideal pH, when the PC-88A is utilized solely to selectively extract Co, the ideal pH falls between 3.2 and 4.2. However, Ni extraction efficiency is low in this pH range. The addition of trioctylamine (TOA) as a phase modifier will shift and expand the ideal pH range from 3–4 to 3.5–5, which provides more room for adjustment of operational parameters since its greater than the previous range.

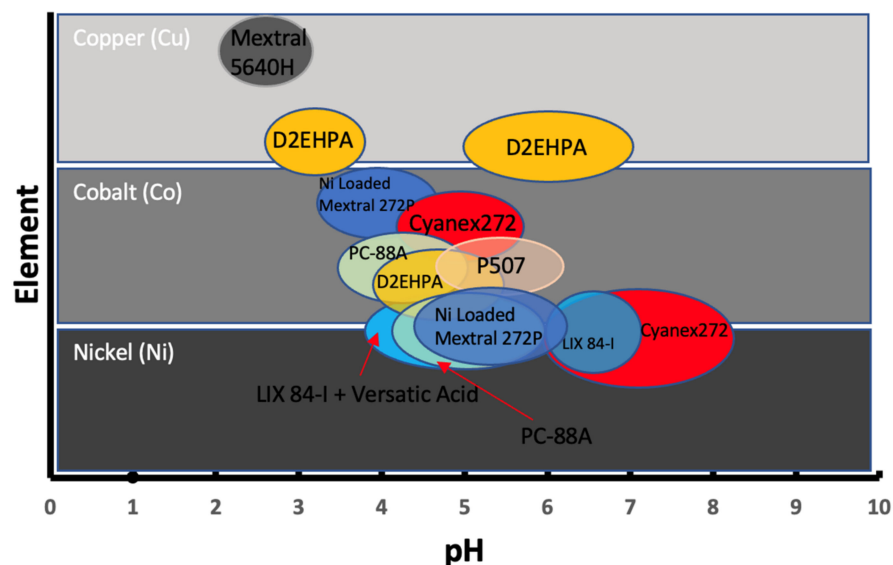
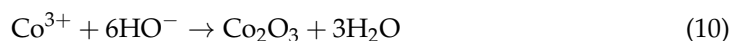
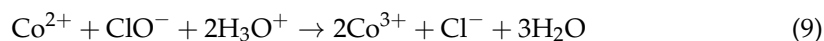


Figure 13. Effect of pH on the solvent extraction of Cu, Ni and Co using different extraction reagents (at 25 °C and A:O = 1, except for Mextral 5640H (A:O = 2)) (Data derived from refs. [22,83,106,109]).

4.9.4. Chemical Precipitation

In order to effectively recover specific metals from complex multi-metal solutions through selective precipitation, a single-stage chemical method has been extensively studied and employed. However, often, it is challenging to precipitate only one ion selectively from a multi-metallic ion solution.

As indicated in the E-pH diagram depicted in Figure 11 (band Co^{2+}), Co^{2+} and Ni^{2+} are prone to coprecipitating via a neutralizing reaction because the stable regions of $\text{Co}(\text{OH})_2$ and $\text{Ni}(\text{OH})_2$ overlap vastly. However, Figure 11b also demonstrates a minor overlap between the stable regions of Ni^{2+} and $\text{Co}(\text{OH})_3$. Therefore, one feasible route is to convert Co^{2+} to Co^{3+} in order to accomplish selective precipitation of Co^{3+} in this small region. Joulié et al. [65] demonstrated the viability and efficacy of this process route. The Ni and Co recovery efficiencies both exceeded 99% when sodium hypochlorite (NaClO) was used as an oxidant [65]. The reaction mechanism can be annotated as:



It should be highlighted that no Mn is present in the oxidation-precipitation process system, as outlined by Joulié et al. [65]. If Mn is present, at pH 2 the Mn^{2+} is oxidized to Mn^{4+} yielding MnO_2 or $\text{Mn}(\text{OH})_4$ hydroxide according to the reaction:



In order to chemically precipitate Ni^{2+} as a nickel dimethylglyoxime chelating precipitate from mixed multi-metal solutions of Mn, Ni and Co, the dimethylglyoxime reagent (DMG, $\text{C}_4\text{H}_8\text{N}_2\text{O}_2$) is extensively employed. When DMG reagent is utilized, nearly over 95% of Ni^{2+} may precipitate at ambient temperature within 20 min, as re-

ported by Chen et al. [87]. The pK_{sp} values for Li^+ , Ni^{2+} and Co^{2+} are on the order of $NiC_2O_4 \approx CoC_2O_4 \gg Li_2C_2O_4$ [35]. The predominant metal ion in the leachate after Co^{2+} and Ni^{2+} are precipitated is Li^+ , which can precipitate effectively as Li_3PO_4 or Li_2CO_3 [110].

4.9.5. Active Cathode Material Resynthesis

Solvent extraction (liquid-liquid extraction), chemical precipitation, and ion exchange, the conventional extraction and separation processes, are frequently not economically viable to use in industrial production due to their significant drawbacks, such as convoluted recycling routes and high waste production and high chemical reagent consumption. Therefore, it is necessary and imperative to conduct research into less time-consuming and more effective processes for recycling spent Li-ion batteries. Recent research has focused on material synthesis technologies that achieve one-step recovery of metals from leachate to regenerate materials, such as the leaching-resynthesis process or direct physical process, in order to shorten the route, avoid the challenges accrued from separating metal ions from one another, reduce secondary pollution, and improve the recycling efficiencies of valuable metals [50,111,112]. The leaching-resynthesis process, which is a subset of regeneration processes, resynthesizes the electrode materials in fewer steps through sol-gel or coprecipitation process routes.

In one study, Sa et al. [112] employed leachate solution as raw liquor and a conventional coprecipitation process to regenerate NMC ($LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$) in an N_2 atmosphere at ambient temperature. The specific capacity of the regenerated active cathode material falls to 80% (120 mA h g^{-1}) after 50 cycles. Lu et al. [113] used ascorbic acid for leaching and adjusted the pH and metal ion ratio of the leachate to produce regenerated active cathode material $LiCo_{0.33}Ni_{0.33}Mn_{0.33}O_2$ through a sol-gel process. A similar method was employed by Zou et al. [114] to recover and recycle spent active cathode materials and produce high electrochemical performance regenerated active cathode materials. The regenerated active cathode materials exhibited electrochemical similarities to those of commercial batteries in terms of rate capacity and cycle life, which should be underlined [114,115]. Among these, the regenerated active cathode materials recovered through ascorbic acid leaching processing exhibit much better electrochemical characteristics than their respective counterparts synthesized from other processes [22,115]. Other than that, the research data indicates that active cathode material from various leachates exhibits few differences in electrochemical properties [22].

An alternative ideal process route that has been extensively developed by numerous researchers is the synthesis of various reactive materials from the Li-ion battery waste in addition to regenerated active cathode materials. To synthesize sintered or hydrothermal cobalt ferrite ($CoFe_2O_4$) precursor, Yao et al. [115] demonstrated a straightforward process route that comprised pre-treatment, H_2SO_4 leaching, filtering, sol-gel, and calcination methods (S- $CoFe_2O_4$ or H- $CoFe_2O_4$). The reactive materials produced exhibited superior physicochemical properties in terms of train derivative coefficient ($1.69 \times 10^{-9} \cdot A^{-1}$) and magnetostriction coefficient (158.5 ppm) [116].

Direct recovery is the process of recovering valuable components from spent Li-ion batteries without using complex chemical processes [117,118]. Prior to processing spent Li-ion batteries, they were disassembled into multiple individual cells. After that, supercritical CO_2 was used to treat the individual cells, and the electrolytes were drained and stored. It is possible to extract CO_2 from the electrolyte by reducing the pressure and temperature, thereby regenerating the electrolyte. The cells were then broken apart, sorted, and disassembled. In the end, the active cathode material was gathered, cleaned and repurposed [119–121].

Chen J et al. [122] reported a process route to directly regenerate LFP from spent soft-pack Li-ion batteries. In the case of no recovery of electrolyte, the spent Li-ion batteries were disassembled, crushed and cleaned in the sealed box. The residual PVDF binder and material decomposition after thousands of charge and discharge cycles lower the energy density of recovered LFP material and its electrochemical performance. The electrochemical

performance of the regenerated electrode was enhanced after heat treatment at 650 °C, discharging nearly the same nominal capacity and energy density as the starting novel active cathode material.

Song et al. [123] sintered the spent active cathode materials with fresh active cathode materials to regenerate LFP electrode materials from spent Li-ion batteries. The electrochemical performance of the regenerated LFP battery active cathode material is nearly equal to that of a fresh LFP active cathode material. Zhang et al. [120] recorded a recovery efficiency of active cathode materials of 98.2% when recovery was executed through direct pyrolysis and physical recovery. The advantages of a direct physical recovery process are primarily minimal energy use, quick recovery pathways, environmental friendliness, and a high recovery rate. However, it is unclear whether the recovered active cathode material will match the long-term properties of a typical fresh active cathode material.

4.10. Electrochemical Process

Myoung et al. [124] potentiostatically reduced Co ions from waste LCO by using an HNO₃ leachant solution into Co(OH)₂ on a titanium cathode in an electrochemical set-up. CoO was subsequently precipitated via a dehydration process. When subjected to ideal pH circumstances and precise CoO heat treatment, island-shaped Co(OH)₂ particles were produced on a titanium (Ti) material [18,51]. Swain et al. [78] recovered cobalt from spent Li-ion batteries by employing H₂SO₄ leaching and electroreduction [78]. Over 98% of Cobalt was dissolved in an acid leachant with a concentration of 10 M at 70 °C for 60 min. The leachate liquor was purified by the hydrolysed deposition processed at the interval between pH 2.0 and 3.0 at 90 °C.

Lowering the dissolved oxygen and nitrate ions could raise the local electrode pH. Therefore, with the optimum pH circumstances, Co(OH)₂ material can precipitate. Hence, this process provides an ideal route to improve LiCoO₂ production from cobalt oxide. Co-remediation by electro-winning and sulfuric acid leaching was studied and demonstrated by Sharma et al. [125]. Approximately 99% of the cobalt in the spent Li-ion batteries was dissolved at a temperature of 70 °C for 60 min with a 10 mol L⁻¹ H₂SO₄ concentration. In the pH range of 2.0–3.0 and at 90 °C, hydrolysed deposition cleans the leachant. Cobalt cathode was effectively deposited on the cathode plate at a current density of 235 Am⁻² [126–128].

This electrochemical methodological approach is deemed feasible and viable for the industry scale-up. The electroreduction mechanism is worthy of exploring due to the relatively high recovery of pure cobalt from spent Li-ion batteries. It does not add specific stimulants, and it removes impurities in comparison to several hydrometallurgical processes for metal recovery from spent Li-ion batteries [127,129]. Nevertheless, this approach has the drawback of being extremely energy intensive.

5. Valuable Metal Recovery and Preparation

5.1. Metal Recovery

The final product stream, after the metal dissolution process, constitutes metal ions (i.e., Co²⁺, Li⁺, Ni²⁺, and Mn²⁺). The successful recovery and separation of these valuable metals, therefore, require a product recovery phase. Chemical precipitation, also known as selective precipitation, and solvent extraction (liquid-liquid extraction), are two often widely separation and recovery processes [3,5,130]. Notably, the by-products of the hydro or bio-metallurgical processes are essentially leachate, whereas the by-products of the pyrometallurgical process are subjected to acidic dissolution so as to be converted to leachate.

Liquid-Liquid extraction, also known as solvent extraction, is a methodology that separates metallic compounds based on the difference of their relative solubilities in two immiscible liquids, while chemical or selective precipitation employs a specific reagent that can precipitate specific metallic ions while leaving impurities or undesirable compounds in the aqueous solution [6,10,131]. In order to effectively recover Ni, Co, and Li, there have been numerous studies and reports targeting the recycling of spent Li-ion batteries. To effectively recover metals from leachate solution after metal dissolution, regulation of the

pH of the leachate and employing various precipitants (e.g., NH_4OH , NaOH , and Na_2CO_3) is necessary for optimizing selective precipitation. NaOH is still the widely utilized precipitant, though several organic solvent systems are being used to study solvent extraction (e.g., Cyanex 272, PC-88A, saponified P507, etc.). The target metals were recovered with an overall recovery efficiency of 85% and a minimum leaching efficiency of 90% [10].

5.2. Metal Preparation

Purification and preparation of recovered products for subsequent steps are the main goals of preparation step (e.g., commercial sales as construction materials, synthesis of new active cathode materials etc.). Purification, crystallization, dewatering, and oxidation stages are then employed to formulate a stable solid state from the products obtained through the product recovery steps [5,9,130]. Following the recovery and preparation processes, they are categorized for various reasons. Valuable components can be used for the synthesis of new active cathode materials (e.g., NMC, LFP, LCO, etc.) or commercial sales for other applications (e.g., pure Li, pure Ni, pure Co, etc.). The recovered materials can also be used in the steel industry or building materials [58,129].

6. Industrial Developed Processes

6.1. Umicore Process

One of the most widely applied industrial recycling techniques for spent Li-ion batteries and NiMH batteries is the Umicore battery recycling process. The process doesn't entail any pre-treatment for spent batteries. The Umicore process combines hydrometallurgical and pyrometallurgical unit activities [2,132]. The primary goal of this recycling process is to recover alloys of Co, Ni, and Cu. The slag portion of the process is used to recycle Li and rare earth elements. The simplified flow chart below (Figure 14) illustrates the Umicore recycling process.

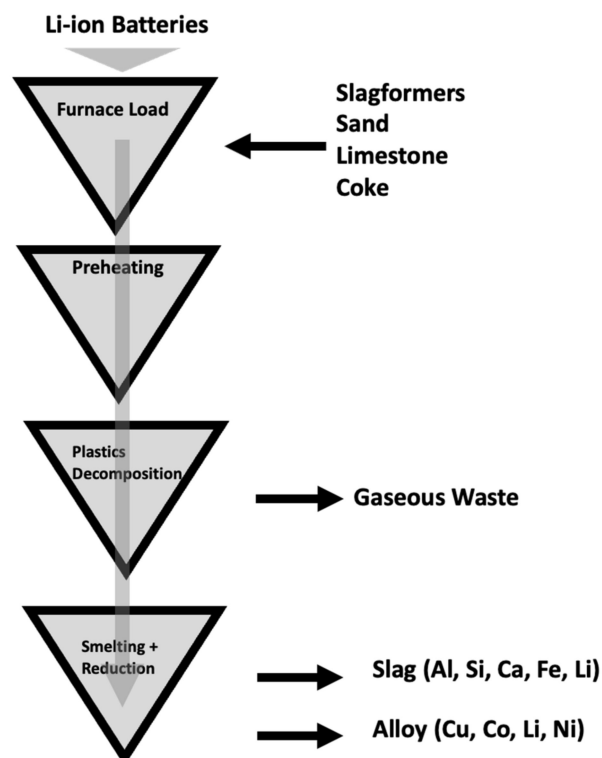


Figure 14. Process flow diagram for the Umicore process (Data derived from refs. [2,132]).

The Isa Smelt furnace technology is used in this process route to lessen the need for mechanical pre-treatment of spent batteries. There are three distinct temperature zones in the furnace when it is in use:

The top pre-heating zone: In order to evaporate battery electrolytes, the temperature in this zone must be kept below 300 °C. Explosion risks from dangerous compounds in electrolytes are reduced by gradual heating to the desired temperature.

The middle pyrolyzing zone: A temperature of roughly 700 °C is maintained in this zone to remove plastic from spent batteries. This exothermic removal process also supplies heat energy to the top zone.

The bottom smelting zone: The purpose of this zone, which has a temperature range of 1200–1450 °C, is to separate the remaining battery components through the alloy and slag phases. The alloy phase is made up of cobalt, copper, nickel, and iron, whereas the slag also contains various metal oxides, including Li oxides.

The alloy goes through several hydrometallurgical operations, and the removed slag is sold for use in construction. Ni, Co, Zn, Cu, and Fe are then dissolved and precipitated to help the material transition out of the alloy phase. Ni and Co are recovered as nickel hydroxide (Ni(OH)₂) and cobalt chloride (CoCl₂), respectively. The fresh LiCoO₃ active cathode material can then be made by oxidizing CoCl₂ and burning it with LiCoO₃ (LCO). The absence of mechanical battery pre-treatments and the high rate of valuable metal components (such as nickel and cobalt) recovery are the key advantages of this process.

6.2. Toxco Process

The Toxco process for recycling spent Li-ion batteries is based on hydrometallurgy. This process involves pre-treating the battery, separating the components, leaching, purifying the solution, and precipitating the Li [2,132]. The Toxco battery recycling process flow sheet is depicted in Figure 15.

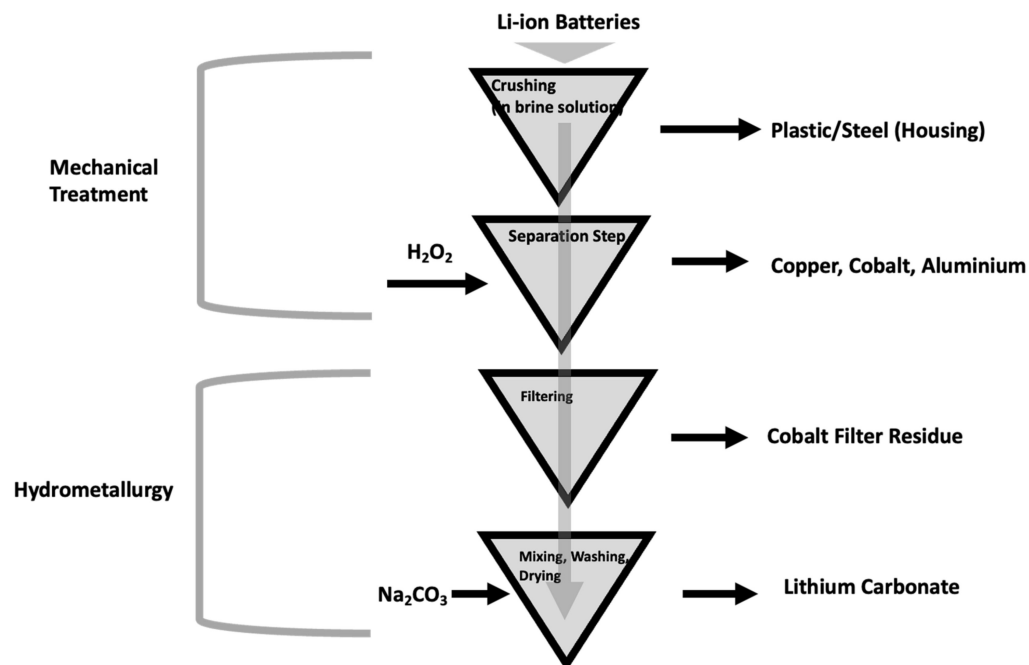


Figure 15. Toxco process flow diagram (Data derived from refs. [132]).

Spent batteries are chilled down to approximately 175–195 °C by liquid nitrogen in proprietary pre-treatment with cryogenic cooling [1,2]. This temperature range effectively brings the reactivity of Li-ion battery components below the threshold for an explosion. Additionally, at this cryogenic temperature, the plastic case of spent Li-ion batteries becomes brittle, making them susceptible to breakage. The batteries are then crushed in a Li brine

after being torn and put through a hammer mill. During hammer milling, the Li component dissolves to produce a solution of LiCl, LiSO₃, and Li₂CO₃.

The screw press integrated inside the hammer mill separates the Li solution and undissolved products. The so-called fluff and the Li solution's undissolved components, such as fine carbon and metal oxide, necessitate additional treatments. After that, the fluff is sent through a shaking table to separate the high-density Co-Cu mixture from the low-density stainless steel and plastic mixture. All of these products are packaged and available for purchase. Before filtration, the Li solution is kept in a holding tank. In order to prevent contamination of the Li product with Na, Li(OH)₂ is used to modify the pH of the solution rather than sodium hydroxide. To produce the finished product, Li₂CO₃, the solution in the holding tank is dewatered, compressed with filters, and purified.

6.3. INMETCO Process

The International Metals Reclamation Company (INMETCO) battery recycling process applies a pyrometallurgical process for recovering valuable metallic material from spent batteries [1,2,132]. The process entails three stages: (1) feedstock preparation, mixing, and pelletizing, (2) component reduction; and (3) melting and alloy casting.

The spent Li-ion batteries are first discharged, dismantled, stripped of their plastic casing, drained of their electrolytes, and the remaining components shredded. The remaining solid waste is assorted with a carbonaceous reductant. The liquid wastes of Ni and Cd are added to the solid waste mixture as it is pelletized. These pellets are then combined with shredded spent battery components before being channelled into the reduction stage. The reduction stage is carried out at 1260 °C for approximately 0.5 h to reduce metal oxides to their pure metallic state. The gas emitted from this reduction phase is scrubbed, and the outlet scrubbing liquid is then fed to the wastewater treatment facility. The treated water from the wastewater treatment facility is circulated back to the scrubbing process for reuse. The reduced solid mixture is smelted to produce an alloy containing Ni, Fe, Cr, and Mn. The alloy is cast to make pig alloy, which is then further processed to make stainless steel in the stainless-steel industry.

Overall, these hybrid processes plant setups, recycling research, and strict recycling laws (e.g., in China and Europe) show major efforts to recycle spent batteries. The current recycling rate for spent Li-ion batteries is just about 5%, as was previously stated [2,23]; this means current battery recycling processes for recycling are incapacitated to handle disposed Li-ion batteries amount, especially in the coming years when the battery waste is expected to reach enormous figures as projected by multiple algorithms [133–135].

Furthermore, the amount of alloy metals that can be recovered using the above-stipulated process routes from spent Li-ion batteries is relatively minimal (e.g., Ni, Co, Cu). The resultant slag still has a significant proportion of unrecovered valuable components and is sold at low costs as construction materials. Attributable to their high energy requirements, as well as their high costs for collection and transportation, INMETCO recycling processes are less economically attractive [5,6,23]. In order to upsurge revenue and draw additional investment for the recycling of the spent Li-ion battery waste, it is important to improve the quality of recovered products from the recycling process (i.e., recycling spent Li-ion batteries into pure, effective, and valuable components). Because of the enormous amount of spent Li-ion batteries projected in the coming years, more capacitated recycling facilities will be required. As a result, developing a comprehensive and efficient recycling system for extracting and recovering valuable metals from spent Li-ion batteries is critical to achieving global sustainability.

7. Summary of Recycling Spent Li-Ion Batteries

The Li-ion battery hydrometallurgical recycling process, as stipulated above, is preferred out of the various available processes because it entails low energy consumption, minimal gas emissions, and, most significantly, high product purity and recovery rate [6]. These advantages, consequently, outweigh the high chemical usage disadvantage. In addi-

tion, the recycling process can also guarantee a good economic return when implemented at the plant level.

A variety of metallic ions are also present in leachate after the acid-leaching process. In order to recover and produce regenerated active cathode materials for commercial sales, it is necessary to separate or isolate these metallic ions. Henceforth, liquid-liquid extraction (solvent extraction) and/or chemical precipitation are employed for that purpose, as previously indicated. They both deliver high metal separation efficiency and material purity [3,6,131]. These findings are identified as the starting foundations for the development of spent battery recycling processes based on the context of research outcomes.

The variation of leachant concentration, pulp density (S/L ratio), reductants and their concentration, reaction time, and especially reaction temperature can directly influence the leaching efficiency of valuable metals from spent Li-ion battery cathodic materials [6,16]. As a result, efforts to optimize the leaching stage are required to achieve optimal extractive leaching efficiency for cathodic metals entailing low energy, chemical and time consumption.

Solvent extraction and selective chemical-based precipitation are both employed in the product recovery stage [136]. Solvent extraction utilizes toxic chemicals and complex process routes; thus, selective precipitation requires further investigative exploration, as a possible alternative to solvent extraction, in order to assess the viability and effectiveness of the selective precipitation process route for metal recovery, as well as to further pursue and develop a recycling process that could easily be scaled up from laboratory scale to pilot scale and ultimately industrial scale [18,24,134,136]. Solvent extraction, however, requires the use of toxic organic chemicals as well as complicated experiment sub-process routes [21,82,134,137].

Hydrometallurgical, pyrometallurgical, bio-metallurgical, electrometallurgy, or mechanical unit operations are frequently combined or integrated together in industrial processes to recycle spent batteries [6,22,131]. In Section 6, well-developed hydrometallurgical and pyrometallurgical recycling processes are briefly discussed, namely the Umicore process, INMETCO and Toxco Process.

8. Conclusions and Outlook

Currently, the profitability of Li-ion batteries recycling is marginal in developed economies and not economically feasible in regions with low Li-ion battery feedstocks. Although Li-ion contribute to large amount of battery sales in recent years coupled with their longer life span, the volume of Li-ion batteries in the battery end of life (spent) waste stream is still limited in some regions. For the emerging Li-ion recycling industry, a lack of consistent supply of spent batteries is a significant economic barrier. This issue is further complicated in many jurisdictions, where spent batteries are exported to Asian countries.

In recent years, the main waste stream of Li-ion batteries is from portable electronics which are normally small in device size. It is expected that with the high-volume inception of Li-ion batteries into EVs in the near future, the recycling of Li-ion batteries will experience a dramatic increase globally as several supply chain gaps will be resolved. SNAM (France), Toxco (Canada), AEA Technology (UK), and Umicore (Belgium) are just a few of the global businesses that have set up whole production lines to recover and recycle valuable metals from spent Li-ion battery waste. They are primarily concentrating on using hydrometallurgical, pyrometallurgical, or an integration of both processes.

Traditional metallurgical procedures, which are lengthy and involve pre-treatment, leaching, and purification, are less competitive in terms of economic value than more recent, quicker methods, including selective extraction, regeneration, and repair operations. Despite the fact that numerous publications have examined metal recycling processes for used Li-ion batteries, only a few of them have shown to be economically viable on an industrial scale. There is currently no commercially available technique for recycling garbage mixed with various cathode-active materials. It is necessary to thoroughly investigate numerous mechanisms of physicochemical changes in the recycling process. Discussion and establishment of a comprehensive Li-ion battery recycling scheme are required. We

think that future research on the recycling of used Li-ion batteries should concentrate on the following areas:

- The key issues are whether the lab-scale innovations have the potential for industrial applications and how to scale them incrementally.
- The subprocesses underlying the leaching process are yet unclear. To help in choosing the ideal leaching reagent and operation circumstances, a lot of work still has to be done. A deep investigation is required, for instance, on changes in the crystallography induced by the leaching process. Insight into the response mechanism during leaching will be made possible by this, and it will be very beneficial.
- The majority of the valuable metals in the spent Li-ion batteries have not yet been selectively leached. Future comparative research investigations ought to be improved.
- The majority of investigative research and studies on the recycling of spent Li-ion batteries have only considered the kinetics and the impact of operational parameters on the leaching process; however, more work needs to be put into developing a comprehensive evaluation system so that more important factors, like the overall process energy consumption, can be taken into account.
- Additionally, since spent Li-ion batteries are harmful to the environment, efforts also need to be focused on improving collection efficiency and minimizing landfilling.
- There should be no restrictions on how spent Li-ion batteries are recycled, and designing, producing, and recycling Li-ion batteries need to take a complete, all-encompassing life cycle approach.

Last but not the least, the complexity of raw materials will be greatly reduced by a global homogenized manufacturing, categorization, collecting, and recycling system, which will consequently reduce the overall recycling process energy consumption.

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