Recycling and environmental issues of lithium-ion batteries: advances, challenges and opportunities

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Abstract

Lithium-ion batteries, LIBs, are an essential part of our daily lives. They may seem unnoticed, but they are ubiquitous through mobile phones, tablets, laptop computers and many other consumer electronic devices. Their demand has strongly increased in recent years, and it is expected to further grow, driven by the increase of electric vehicles. This increase in the demand for LIBs also brings environmental issues related to the mining, extraction and purification of scarce materials such as cobalt, nickel and lithium.

This work provides an overview on the relevance of recycling LIBs and their environmental impact. It also analyses the components of LIBs and evaluates their value in the world market. Although there is a strong focus on lithium, other critical metals, such as cobalt and nickel, are also addressed.

Different recycling methods for the different battery components are reported together with the main achievements. The advantages and disadvantages of the different used methods are discussed, and their environmental issues are considered. Finally, the main environmental issues associated with the production, use and end of life of LIBs for electric vehicles are described.

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1. Introduction

The demand for lithium-ion batteries, LIBs, has grown very significantly over the last ten years, driven by consumer electronics. Today there are 7.19 billion active mobile phones [1], close to 1 billion laptop computers, and another billion tablets worldwide [2]. This demand for LIBs from the consumer electronics sector not only will remain high, but it will increase even more due to the increasingly relevant concept of energetic transition, that will lead to the shift from fossil fuels based mobility towards the electric vehicle, EV, in the automotive industry [3].

In order to get a better understanding of the dynamics of this demand, regarding both the producers and the consumers, a couple of studies were carried out recently. A trade-linked material flow analysis framework was developed to study the lithium flow over its life cycle, both at a national and international levels [4]. China, Chile and Australia are the leaders in lithium extraction, which is mainly used in the production of batteries for consumer electronics. China is also the main importer of lithium materials, that are mostly traded in the form of ores, carbonates and concentrates [4]. The Chinese lithium industry has contributed significantly to the recent increase in LIB production. It relies on the imports of lithium minerals that are processed and transformed into final products, essentially batteries for a large variety of devices, such as smartphones, laptops and electric vehicles, and which are then exported across the world [5]. It was estimated [6] that 0.5 million tonnes of lithium-based materials have been produced in China during 2020.

This situation calls for adequate lithium re-use and recovery strategies to be implemented soon, or lithium and cobalt reserves, to name perhaps the scarcest of the metals involved in the production of LIBs, will be significantly reduced [7, 8]. Meanwhile, important environmental damage will occur as a result of LIB production and disposal. In these damages are included ecosystems destruction during mining, and highly polluting activities related to metal extraction and LIB production [9]. Later, LIB disposal, which often occurs together with the electronic devices that they have powered, is not only polluting, due to the heavy metals present, but also economically wasteful, as most of those highly valuable materials could be recovered and reused [10]. For example, mobile phones have a replacement rate between 12 and 18 months, regardless of their actual condition. Less than four years ago, the recycling rate for LIBs from mobile phones was

below 5% [10]. This figure may have gone up a bit today, but it likely remains below 10% [11, 12].

Lithium-battery recycling can help to preserve the environment, save resources, reduce the volume of waste, and also bring economic benefits [13]. Lithium, cobalt and nickel are critical to the operation of LIBs, but they are also relatively scarce. Thus, it is necessary to develop practices and governance strategies that allow sustainable exploitation of their natural resources, as well as efficient recycling processes that will allow the reduction of the pressure on the natural resources. Despite this urgent need and its benefits, recycling effectively is a very challenging task. Interventions for more sustainable exploitation in the context of suppliers and consumers are possible. Producers should focus on the development of mechanisms for the long-term production and materials efficiency of these metals. At the same time, consumers should be educated to support the circular economy concept, seeking high recycling rates [14].

LIB recycling presents large advantages in natural resources savings. It is estimated that recycling can save up to 51% of the extracted natural resources, including the reduction in the use of fossil fuels and nuclear energy necessary in the extraction and production processes [15]. However, achieving full independence from virgin resources seems impossible, because in a constantly growing market, the available recycled resources are always less than the demand [15].

LIB recycling will not be a reality unless it is economically viable. Most of the valuable materials in a LIB are in the cathode, which is the last component to be removed in the disassembly process [16], increasing the cost of its recovery, due to the different disassembling process steps that must be taken to recover it. However, each manufacturer produces different types of devices, using different materials, shapes, morphologies and proportions, leading to the necessity of a vast recovery infrastructure, capable of responding to these differences [17, 18]. There are also limitations in the recycling processes because of the lack of implementation of good environmental practices. For example, many people do not remove the batteries from spent devices when it is time to discard them, preventing any chance of recovery [19].

This review focuses on LIB materials all along the different stages of their lifecycle. The scarcity of materials and their prices with a particular focus on lithium are discussed. A comprehensive review of the current state-of-the-art in the recycling processes of LIBs is thus presented. The latest developments and the proposed processes are reported, as well as the main advantages and disadvantages of each one. The processes' efficiencies are

also presented, together with an analysis of the current situation of lithium resources as well as information on other materials relevant in battery manufacturing.

This paper addresses in a clear and objective way the economic and environmental benefits that can be brought by the recycling of LIBs. This question gains even more relevance in relation to the area of electric mobility, where it will have significantly large impact. The main focus on cathode materials is due to their high relevance and value, and also because of the difficulty to effectively recycle their components, making it the most widely studied battery component. The necessity of standardizing battery materials and their conformation, as well as the need to apply legislation to incentive the battery recycling are also approached.

2. Lithium-ion batteries (LIB)

Secondary batteries can be defined as reversible systems that turn their stored chemical energy into electricity to power an external circuit during their discharge phase. During the charge phase, the cell is connected to an external energy source, and the electrode processes are reversed [20]. In particular, LIBs rely in lithium ions during the charge/discharge processes. Each cell has four main components: anode, cathode, separator and electrolyte. This section reports on lithium and other important battery materials in the world market and describes the construction and working principles of a LIB cell, focusing on its evolution from a materials perspective.

Lithium was first discovered in the minerals petalite ($LiAlSi_4O_{10}$) and spodumene ($LiAlSi_2O_6$) around 1817 by Swedish chemist Johan Arfwedson, and Berzelius named it after *lithos*, the Greek word for stone. Pure metallic lithium was first obtained in 1821 by the English chemist William Thomas Brande, by electrolysis of lithium oxide. Metallic lithium was eventually (1923) industrially produced (Metallgesellschaft AG) by electrolysis from a mix of lithium chloride (55%) and potassium chloride (45%), using a method discovered by Robert Bunsen and Augustus Matthiessen in 1855.

Lithium metal possesses a characteristic silver-white colour that tarnishes when exposed to the air, due to its high reactivity with oxygen. Metallic lithium should be stored under anhydrous atmosphere, mineral oil or vacuum-sealed. Due to this high reactivity, the natural forms of lithium are brines, rock minerals and salts. Lithium can also be found in river waters, surface waters, groundwaters and lakes where, depending on local geology and topography, its concentration is between 0.070 and 40 $\mu g.L^{-1}$ at the surface and between 170 and 190 $\mu g.L^{-1}$ in seawater, being the fourteenth most abundant element in the seawater. In soils, this element is also found in trace amounts with an average of 3-350 $mg.kg^{-1}$, also depending on local geology and topography [21].

Lithium is the most electropositive metal, with a potential of 3.045 V (vs the standard hydrogen electrode, SHE), it has an energy density of 3860 $mAh.g^{-1}$, and is the least dense (ρ = 0.534 $g.cm^3$) and lightest (A_r = 6.94 $g.mol^{-1}$) metal [22]. Its melting temperature is 180.5 °C, and has a specific heat capacity of 3.56 $J.g^{-1}.K^{-1}$ at 25 °C. When compared with other metals, all these properties make lithium the most characteristic and important element for energy storage today, as it is proven by its wide use in batteries [23].

Lithium is also important in other applications, including medicine and metallurgy. For instance, the chemical industry uses it to decrease the viscosity of glass and ceramic [24],

as desiccants for gas streams [25], to strength alloys [26], as base and nucleophile (organolithium) [27] and as a lubricant in automotive applications [28]. In medicine, lithium is used in the treatment of bipolar disorder [29], depression [30], dental [31] and headaches [32].

Regarding LIBs, they were first commercialised by Sony and Asahi Kasei in 1991, once the dendrite formation (lithium formations that grow in anode electrode interface during the charge/discharge process) problems had been solved [33]. Nowadays, most portable electronic devices, such as laptops, smartphones and pacemakers, and devices such as electric vehicles and power walls use LIBs to store and supply energy.

2.1. LIB materials and components

As stated before, a LIB is composed by two electrodes, a separator and an electrolyte system. The electrodes (anode and cathode) typically consist of a mixture of three components in contact with a current collector foil. These three components are a conductive material (CM), an active material (AM) and a binder solution (BS). These three components are mixed into a paste that coats the electrode side of the current collector. While anode and cathode use different active materials, the binder solution system is usually shared. The separator is a porous membrane, typically soaked in an ionic conductive electrolyte solution, that avoids physical contact between the electrodes.

2.1.1. Current collectors

Current collectors support the electrode materials and guarantee the passage of electrons through the external circuit. The current collector should provide high mechanical stability, high electron conductivity, high chemical stability (excellent corrosion resistance) and low weight and thickness [34]. Copper and aluminium are typical anode and cathode current collector materials, respectively, due to their electronic conductivity and stability [35]. Different surface treatments such as plasma treatment [36], and coatings as carbon [37], vanadium oxide [38], among others, can be applied to further enhance the current collector properties (such as electric conductivity and surface chemistry).

2.1.2. Electrodes

With respect to the electrode composition, the AM:CM:BS ratio and materials affects cell performance. The proportion between these components directly affects ionic

conductivity, porosity and conductivity, among other properties [39]. Different ratios between the AM:CM:BS have been reported [40]. Higher BS/CM ratios increase the interfacial resistance [41]. Higher AM proportions at the cathode lead to higher battery capacities, while at the anode ensure the lithium-ion storage capacity [42]. Thus, typical cathode compositions contain AM proportions in the range between 60 and 95%, CM around 2 to 25% and BS around 3 to 30% [42].

In a cathode with poly(vinylidene fluoride), PVDF, as a binder, a ratio of PVDF:CM of 5:4 allows to increase the rate capability of the electrode, decreasing the AM content down to around 80%. The ion-blocking effect of PVDF and the electronic conductivity of the CM (being carbon-black the most used) compete with the AM for the battery capacity [43].

The active material in LIBs is thus responsible for lithium intercalation and reservoir. Table 1 summarises the most common active materials used in LIBs, which are mainly lithium metal oxides and phosphates such as lithium cobalt oxide ($LiCoO_2$ - LCO), lithium iron phosphate ($LiFePO_4$ - LFP), lithium manganese oxide ($LiMn_2O_4$ - LMO), lithium nickel manganese cobalt oxide ($LiNiMnCoO_2$ - NMC) and lithium nickel cobalt aluminium oxide ($LiNiCoAlO_2$ - NCA). The most common active anode materials are graphite and silicon. The final application dictates the necessary voltage and charge capacity, which determines the selection of active material for each electrode.

Table 1 - Anode and cathode active materials with theoretical voltage and specific capacity, lithium precursor and synthesis method.

	Active material	Theoretical voltage (V)	Theoretical specific capacity $(mAh.g^{-1})$	Lithium precursor	Synthesis method	Ref
Cathode	$LiCoO_2$	3.8	274	$LiOH.H_2O$	solid-state	[44]
	$LiFePO_4$	3.4	170	Li_2CO_3	solid-state	[45]
	$LiMnO_2$	3.3	285	LiBr	solid-state	[46]
	$LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$	3.7	280	$LiOH.H_2O$	Co-precipitation	[47]
	$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$	3.7	279	$LiOH.H_2O$	Co-precipitation and solid-state	[48]
Anode	Graphite	0.2	372	-	Natural	[49]

| Silicon nanowire | 0.5 | 4200 | - | Vapor–liquid–solid method | [50] |

Carbon black is the most common conductive material used in LIBs [51]. It keeps the electrical contact between the active material particles and the current collector. Also, thanks to its high electrical conductivity and large surface area, it decreases the electrode polarisation potential and improves the cycle life of the battery [52].

Finally, the binder material provides mechanical support to the electrode structure through the bonding of the AM and CM and the adhesion to the current collectors. However, it should be also electrochemically inert and allow ionic conduction [53]. Despite its low content in the electrode (between 2 and 5%), and its chemical inertness, the binder plays an essential role with respect to electrode performance. The binder must also ensure easy processability during electrode manufacture, display low electrolyte swelling, and should be economic and environmentally friendly.

PVDF and copolymers, [54] and polypropylene (PP) [55] are the most common binders used in LIB production. The binder system also includes solvents that facilitate mixing of the binder resin together with the AM and CM. However, the solvents commonly used due to their good solubility properties [37], such as N-methyl-2-pyrrolidone (NMP) or N N-Dimethylformamide (DMF), tend to be toxic and teratogenic. Greener alternatives (such as water) should be explored to improve processing and reduce the environmental footprint of the production process. As shown in Figure 1, the use of water instead of NMP, for example, brings important benefits (less energy consumption and equipment, reduction of the industrial wastes) by also modifying the manufacturing processes during the electrode production. The exclusion of some steps, such as ventilation, controlled environment and solvent recovery systems, are some examples of the positive effect in this change [53]. Processability, safety, and availability in nature are some of the selection criteria for alternative new green solvents. In this scope, water-based electrode manufacturing routes could provide both improved safety and more sustainable and environmentally friendly electrochemical energy storage devices [56].
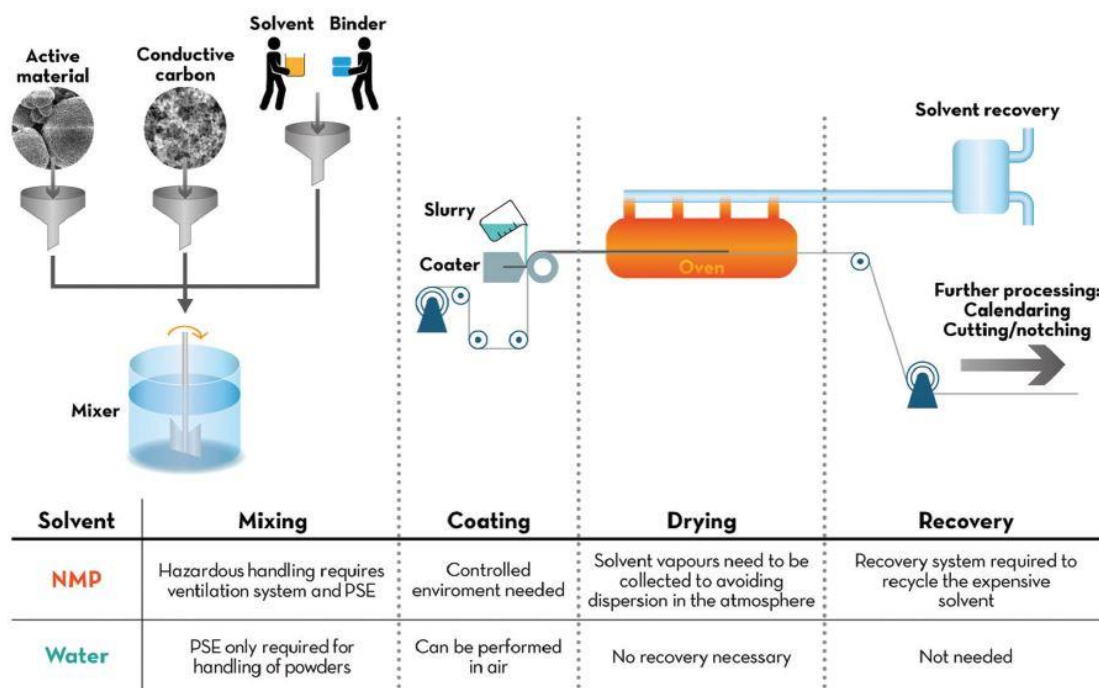
Figure 1 – Schematic representation of the battery electrode manufacturing process showing the advantages of using water vs NMP as the primary solvent for each step. PSE means pressurized solvent extraction [56].

2.1.3. Separator and electrolyte

The purpose of the separator is to increase cell safety by preventing short circuits between anode and cathode. The main requirements of the separator are: a) high ionic conductivity, b) uniform porous structure, c) good wettability, c) excellent chemical stability (between the separator and the electrolyte at working voltage and temperature), d) low thickness e) limited shrinkage and f) low electric conductivity [57].

Each separator/electrolyte system has different compositions and properties, depending on the application. The most common systems involve porous membranes, typically based on non-woven materials soaked in a liquid electrolyte. However, due to the difficulty to fabricate nonwoven fabrics thinner than 25 μm, other polymeric separator types have also been widely studied [58].

Commercial separators are based on microporous polyolefin membranes, such as polypropylene (PP) [59] and polyethylene (PE) [55], and in fluorinated polymers, as PVDF and its copolymers [60]. Studies in this field are focussing on improving porosity [61], wettability [62], thermal stability [63] and ionic conductivity; sometimes by using ionic liquids [64], polymers [63] and particles addition [65], among others. More

environmentally benign separators, that avoid the use of synthetic polymers, are being investigated based on natural polymers and materials such as cellulose [66] or silk [67], among others, or even recycled polymers. These polymers have the advantage of reducing the produced residues [68]. Another subject of increasing interest is the use of solid-state electrolytes to avoid the use of liquid electrolytes [69]. Solid state electrolytes include solid polymer electrolytes and inorganic solid electrolytes, the main difference being the use of a polymer or an inorganic material as matrix. Gel polymer electrolytes combine both the characteristics of the solid and the conventional electrolytes (Figure 2) [70]. These materials could avoid safety and performance problems related to thermal shrinkage and low ionic conductivity (five orders of magnitude lower) of the conventional separators without electrolyte [71].
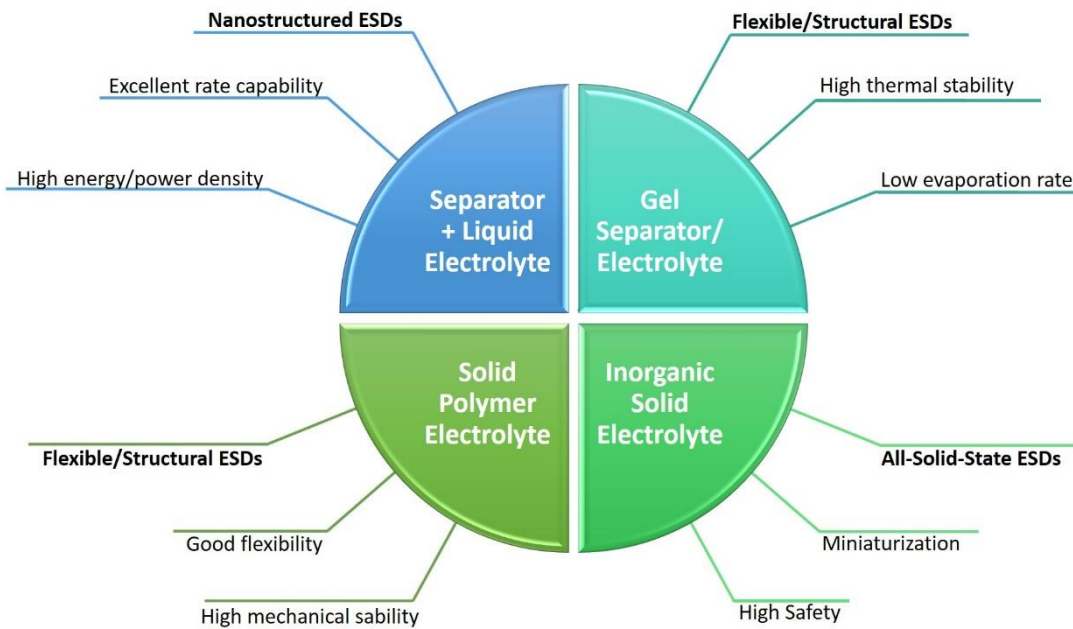
Figure 2 - Different separator/electrolyte in future ESDs. Based on [70].

The selection of the electrolyte is essential because the reactions that occur at the electrode/electrolyte interface are determinant in battery performance. The ideal electrolyte should be environmentally friendly and easy to process, but also cost-effective and must enable excellent battery performance. Thus, the ideal electrolyte must possess wide electrochemical window, low viscosity, good wettability towards separator and electrode, high flash point and, more importantly, high ionic conductivity [72]. The selection of a particular electrolyte system also depends on the final application [70], but it also needs to be compatible with the electrode materials and the fabrication process.

The electrolyte is typically a high-grade lithium salt, such as lithium hexafluorophosphate (LiPF$_6$), lithium tetrafluoroborate (LiBF$_4$), lithium bis(trifluoromethanesulfonyl)imide) (LiTFSI), or others, dissolved in dipolar aprotic organic alkyl carbonate solvents, such as ethylene carbonate / dimethyl carbonate (EC/DMC). The reactions of the electrolyte during battery operation can lead to the undesirable formation of a layer (solid electrolyte interface - SEI) that can decompose the electrode. The addition of fluoroethylene carbonate [73] and other additives [74] have been proposed to prevent this degradation.

2.2. Operation of Li-ion batteries

Figure 3 shows a schematic representation of a LIB cell and its operation principle. Inside the cell, during the spontaneous redox reaction (discharge), lithium-ions move from the anode (negative electrode), across the electrolyte, towards the cathode (positive electrode), which is reduced [75]. Lithium-ion transport is reversed during the charge process, and ions travel from the cathode to the anode. Note that electrons travel through the external circuit in the same direction as lithium-ions do inside the cell to maintain the charge balance. Electrons leave the electrode active material through the current collector (highly conducting metal) to reach the external circuit [35].

To ensure that electrons exit the cell, the separator, a microporous membrane sandwiched between anode and cathode, prevents short-circuiting of the electrodes. The separator also allows the exchange of lithium-ions through it. The electrolyte, which fills the separator and comes in touch with the electrodes, ensures the ionic conductivity and mobility not only between the electrodes but also inside the electrodes [76].
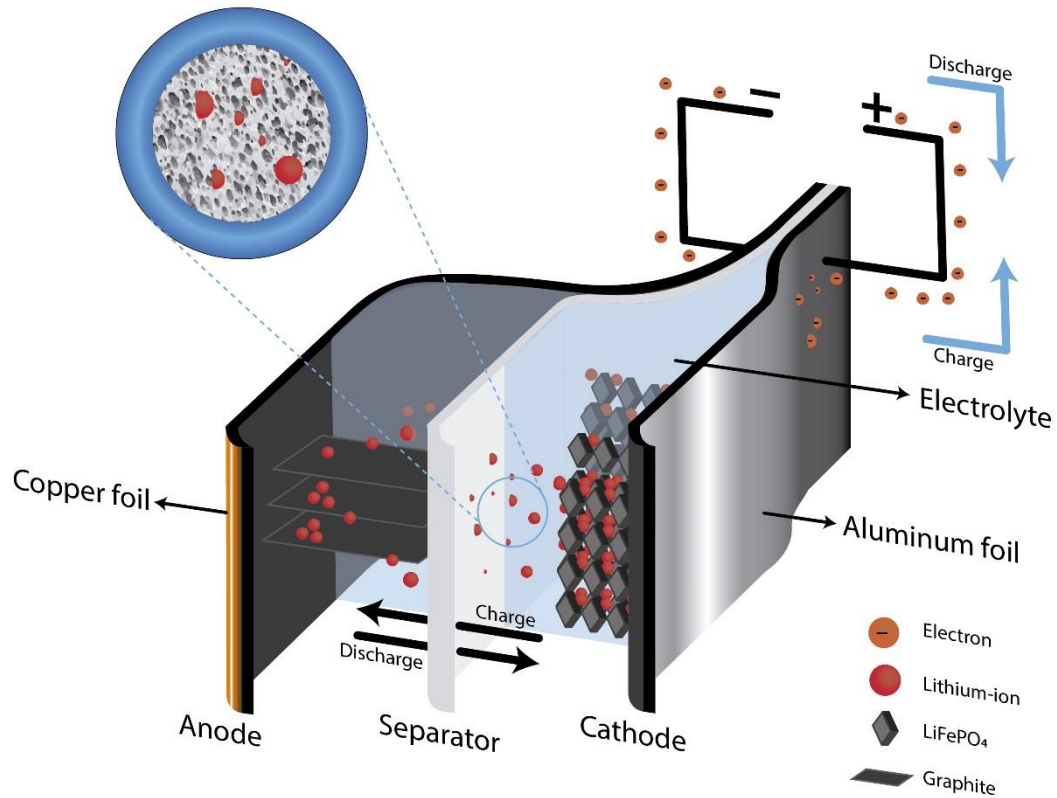
Figure 3 - LIBs components, charge and discharge process and lithium-ion movement in LIBs.

2.3.   Market demand, natural resources, and LIB production costs

Nowadays lithium is more than just another metal used in different markets. Lithium is considered a key material to replace fossil fuels and hence as part of the solution to the important issue of climate change. The application of LIBs in electric vehicles and other renewable energy storage systems will lower the consumption of fossil fuels [77]. Lithium end-use consumption has strongly increased over the last years. In 2015 the two main end-use markets of lithium were batteries (35%) and glass and ceramics (32%) [78]. As Figure 4 shows, the worldwide lithium battery market rose to 65%, while that for ceramics and glass decreased to 18% [79].

Figure 4 - Global lithium end-use market shares. Source: US Geological Survey 2019.

To framework this increase in the use of lithium in energy applications, note that the global energy market is estimated to be worth 250 billion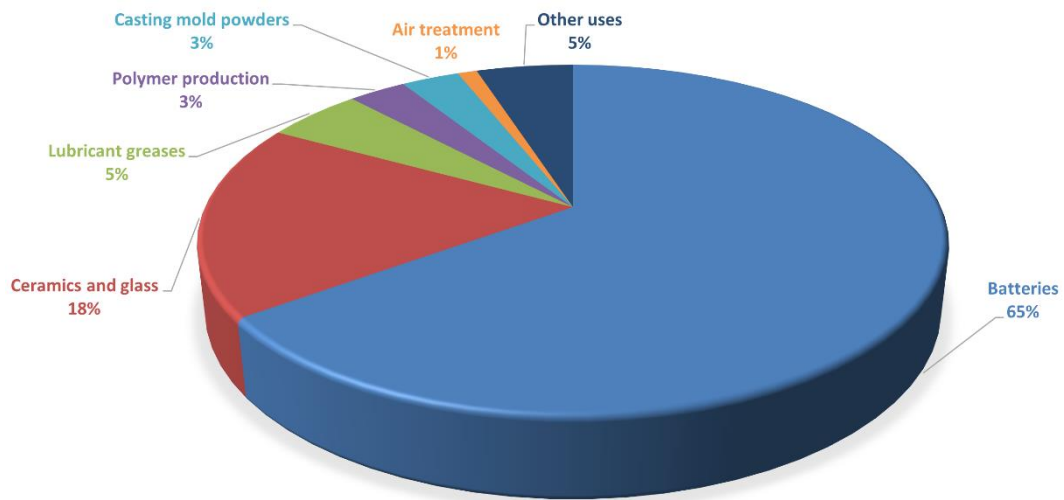 € by 2025. As previously mentioned, the surge in consumer electronics and the Internet of Things (IoT) are driving an increasing demand for lithium in the form of LIBs. Figure 5 forecasts that both supply and demand will continue to grow in the near future. This increase in demand resulted in a 61% price rise for battery-grade carbonate, only in 2016-2017 [80]. However, if the forecast is correct, the price of lithium carbonate and lithium hydroxide may decrease slightly between 2019 and 2021, holding a price of around 12.000 US$ t^{-1}, and then rising again until 2025. According to the Benchmark Mineral Intelligence Agency, the peak in the lithium price observed in 2018 was due to the approaching end of Chinese subsidies to the EV. Those subsidies resulted in higher lithium demand and production. The following price relaxation is due to the de-stocking of excess supply, also resulting from the end of subsidies. Beyond that, it will increase recoverable lithium resources [81].
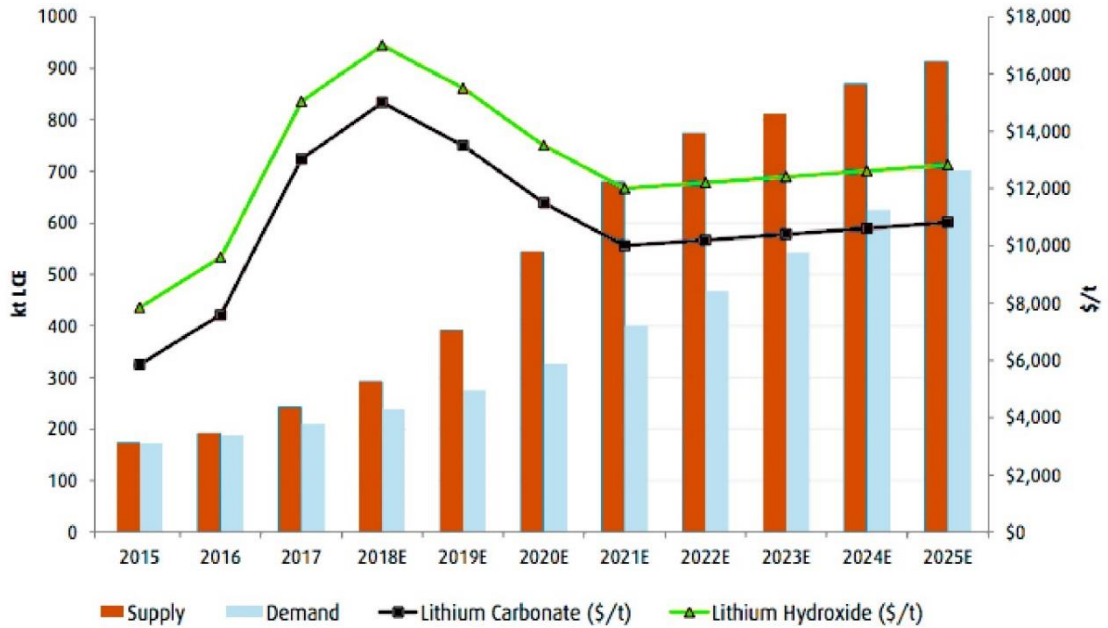
Figure 5 - Estimated world lithium consumption and production (excluding U.S. production)[80].

2.3.1. Lithium sources

As stated before, lithium can be found in brines and hard rock, complex aluminium silicate deposits - pegmatites. Pegmatites are intrusive igneous rocks that contain lithium. Typical examples are spodumene, petalite, amblygonite, lepidolite, eucryptite, triphylite and zinnwaldite. Lithium is also present in quartz, mica and feldspar [23]. From an economic viewpoint, spodumene is the most important pegmatite due to its high lithium content (8%, Li_2O) and its relative abundance in extensive deposits (spodumene is found in more than 8 countries). Table 2 summarises the total world lithium reserves (brines and ores) by country. All these countries have increased the mine production of lithium since 2017, but Australia is the leading overall producer, with 42.000 tons of lithium in 2019. This is roughly 55% of the world output.

On the other hand, Chile holds the largest lithium reserves, containing roughly 8.6M tons. Other countries, such as Bolivia, Canada and Namibia, also possess a large amount of lithium resources, however they are not being explored nowadays, despite the fact that there are projects to develop mining operations there [82]. Looking at the total world reserves and considering the present production and expected demand growth, there

seems to be plenty of lithium for the next hundred years. However, it has been forecast that lithium demand may soon exceed its supply in a scenario in which not even recycling processes will stop this trend [83]. Other studies conclude that, by 2050, the cumulative demand for lithium will range between 74 and 248% of the reserves, while the cobalt cumulative demand will be 50% of its reserves [83]. The variability in these predictions probably originates in the uncertainties underpinning the assumptions made to venture them.

Moreover, cobalt and nickel will present supply problems well ahead of lithium. It is also reasonable to believe that, by then, alternative, cleaner, and more efficient energy sources will have been developed [84]. However, if dependence on LIBs lasts very long, the environmental damage derived from extraction and processing of lithium and other (rarer) metals can be so extensive that environment protection reasons should be enough to encourage recycling policies and measures worldwide.

Figure 6 shows the worldwide distribution of lithium reserves and mining explorations, as well as the primary trade flux between the producer and consumer countries. This trade flux is the main driver of the worldwide lithium prices, which are dependent of various factors, such as the location of the lithium source (that affects the labour costs for example), and the type of mining operation (hard rocks are usually more expensive than brines).

Table 2 – Lithium reserves and production. Australia is the leading producer, but Chile has the largest reserves [82]. [a] Estimated; [b] For Australia Joint Ore Reserves Committee-compliant reserves were about 1.7 million tons.

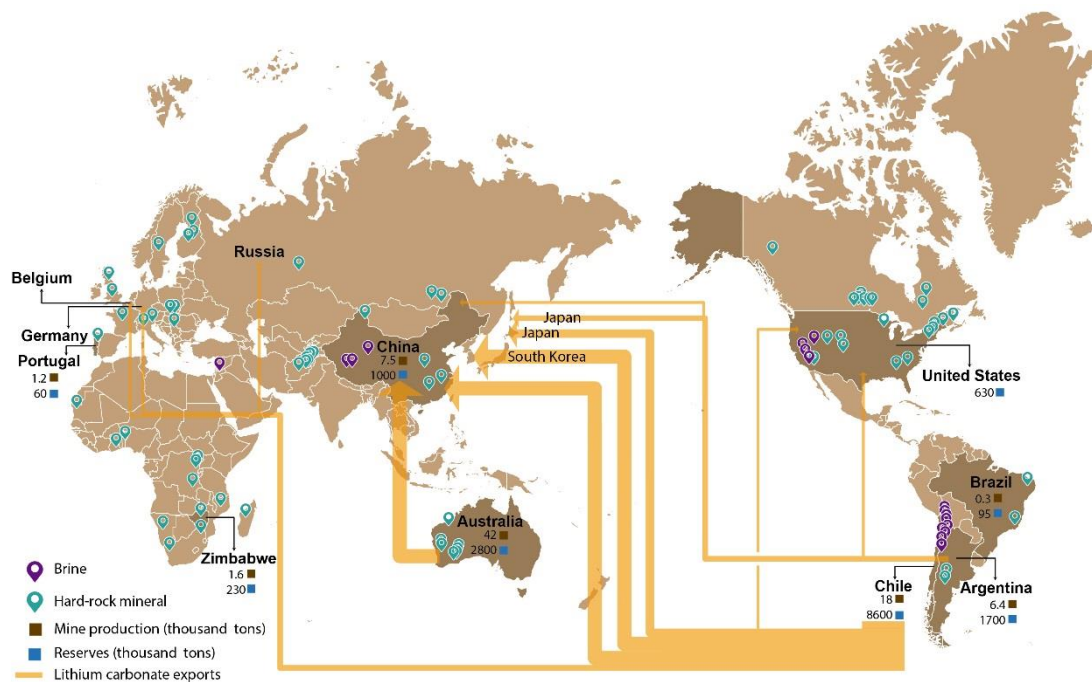| Country	Mine production (tons)		Reserves (tons)
	2018	**2019**[a]	
Chile	17.000	18.000	8.600.000
Australia	58.800	42.000	2.800.000[b]
Argentina	6.400	6.400	1.700.000
China	7.100	7.500	1.000.000
United States	-	-	630.000
Zimbabwe	1.600	1.600	230.000
Brazil	300	300	95.000
Portugal	800	1.200	60.000
World total (rounded)	92.000	77.000	15.115.000

Figure 6 - World lithium reserves and exploits, and lithium trade.

2.3.2. Lithium prices

Lithium prices are affected by supply and demand, but three key drivers have a strong influence on them: (i) the Chinese market monopoly, (ii) the control of natural lithium reserves across the globe and, (iii) South American politic instability and social unrest. China is the leading manufacturer of consumer electronics and LIBs, but its market is heavily dependent on Australian spodumene ore imports as shown in Figure 6. Chile has the largest reserves, but Australia is the most productive country today. Second, three companies control 90% of the world lithium: SQM, American FMC Lithium and Albemarle Corporation. Last, the fast production volumes that are polluting groundwater heavily, and which will reach the regulated lithium extraction limits for 2030 near to 2023, [78] are stirring political and ecological turmoil in South America, particularly in Chile.

2.3.3. The cost of LIB manufacturing

The fabrication of LIBs involves different materials beyond the previously mentioned. From packaging to the active material, LIBs are composed of different metals and plastics, all of which have an impact on LIB price and the environment. Figure 7a shows the mass content contribution of the different materials involved in the fabrication of a battery pack for the automotive industry and Figure 7b the cost of the larger contributors

of these materials. It is observed that, despite the fact that some materials are used in very small amounts, their contribution to the final price of the LIB is much more significative, due to their high prices, such as cobalt and nickel, for example.
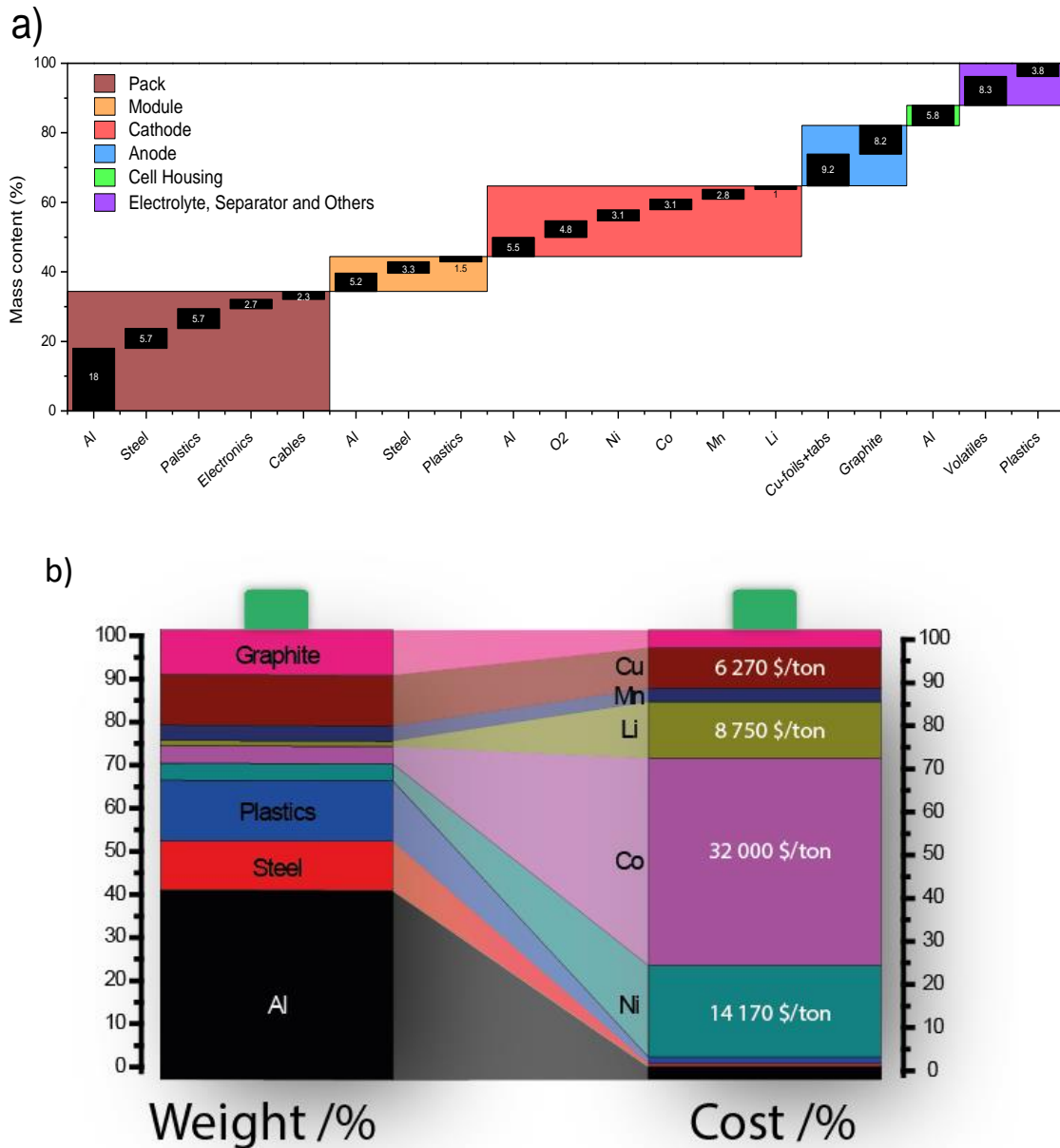
Figure 7 - a) Components of a LIB automotive pack and their mass content, based on [85] and b) manufacturing materials weight and cost percentage of a LIB.

Figure 8a also shows that materials cost represents 74.9% of the production of an automotive battery pack (graphite anode and NMC cathode). The primary strategies to reduce this figure are to find new materials with lower costs, or to improve the manufacturing process yield and productivity. Figure 8b shows that the cathode accounts

for ca. 49.5% of the total material costs. The metals, lithium, cobalt and manganese, and their scarce and expensive cost presented in Figure 7b, increase the manufacturing value of this component. Figure 8c shows how costs build up during LIB manufacturing. An undesirable effect of multi-step processes like this is that yield decreases as the likelihood of defects and production errors possibly increases. One way to reduce the number of process steps is to form strategic partnerships with material manufacturers, that can work together to find best battery conformation to later facilitate the recycling process [85].
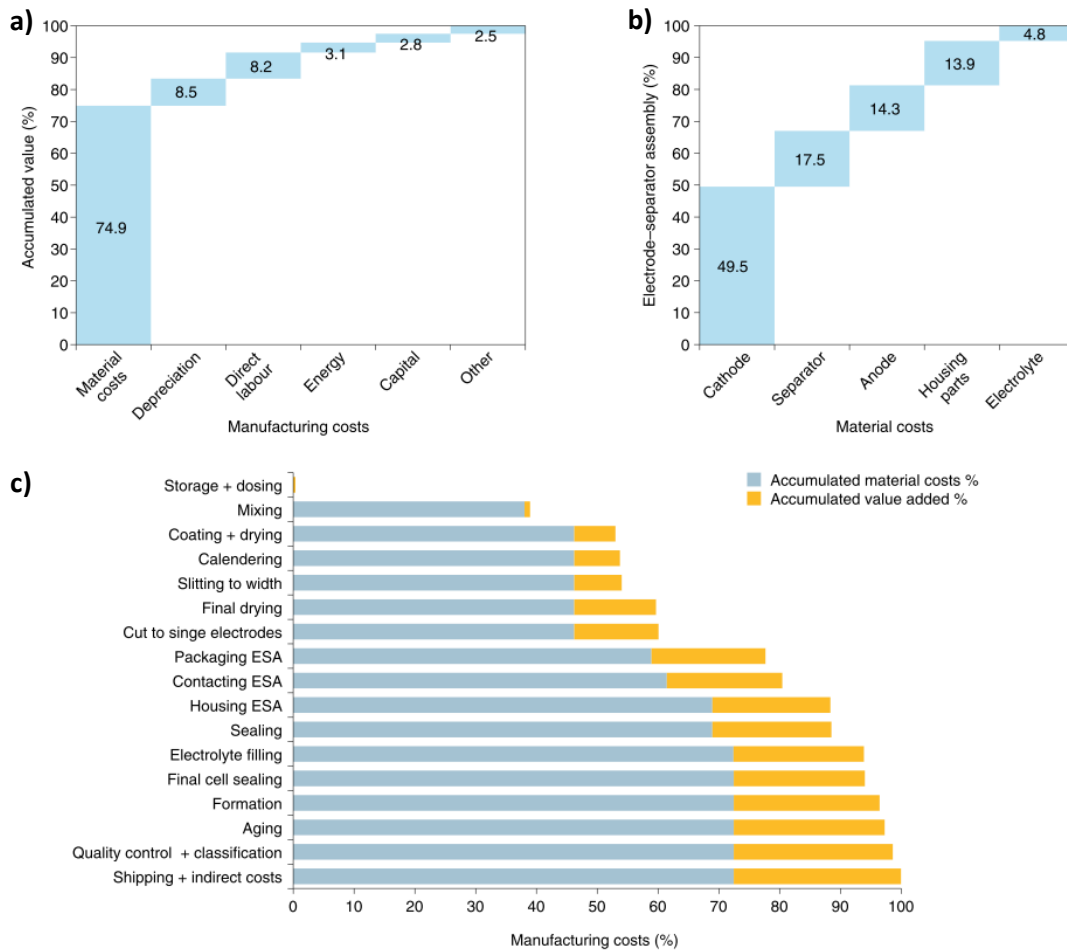
Figure 8 - Manufacturing cost of a) all LIB processes, b) material cost process and c) for main productions steps [85].

The cost of lithium metal foils used in coin cells can change significantly from 250-1000 US\$ kg-[1] to 100-300 US\$ kg-[1] only by the changing of the foil thickness from 20 μm to 200 μm, respectively. These costs strongly depend on the processing technique used, such as extrusion, rolling or vapour deposition [86]. New concepts are emerging at laboratory and pilot-scale that reduce the production cost and improve cell performance.

Besides lithium, LIBs cost also depends on elements such as cobalt, graphite, nickel and manganese. Lithium battery cathodes, such as LCO and $LiNiO_2$, contain 6-12 % of cobalt and 36-45 % of nickel. Consequently, the increasing battery demand will also increase the price of these other metals in addition to lithium [87]. The price of cobalt has increased from 22 to 81 US\$ kg^{-1} between 2012 and 2018. Cobalt is expensive because it is comparatively rare and very sought after. Cobalt is usually a sub-product of copper and nickel mining, but it is uneconomical in that form, as most of those deposits contain only 0.003% of cobalt, whereas to achieve prices of 100 to 150 US\$ kg^{-1}, deposit concentrations above 0.1% are needed. As a result, roughly just 10^7 tons of the 10^{15} tons available in Earth's crust are profitable to extract. In addition to cobalt, nickel is also rare, and only 10^8 tons of the 10^{15} tons available are profitable to explore. Figure 9 shows the top country reserves and prices for lithium, nickel, cobalt and graphite [78]. Similarly, to lithium, the cost of nickel and cobalt also varies according to its availability in different locations with distinct socio-economical situations. On the other hand, the cost of graphite remains nearly constant due to its high availability worldwide.
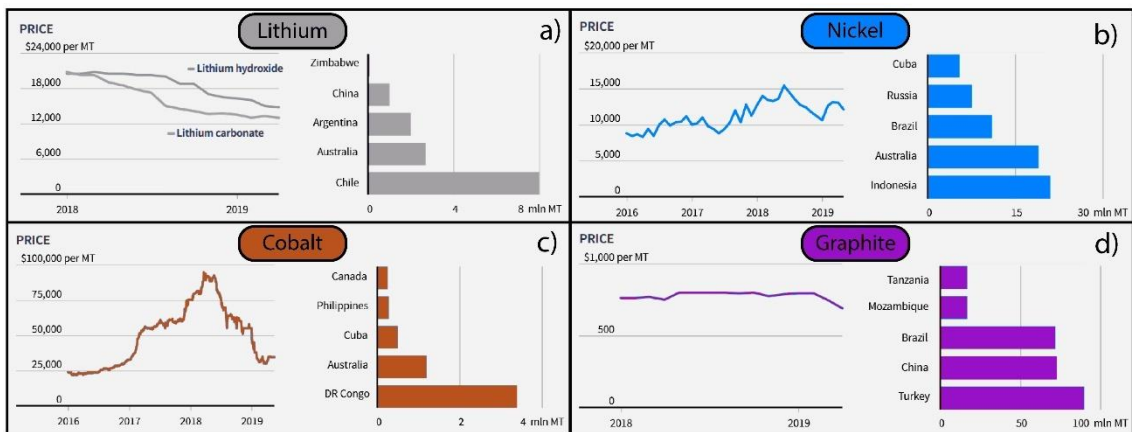
Figure 9 – Main country reserves and price trends for a) lithium, b) nickel, c) cobalt and d) graphite. Based on United States Geological Survey; Benchmark Mineral Intelligence; Refinitiv Datastream. Reuters graphics.

Next to lithium, cobalt is a key component in the fabrication of LIBs, in particular with respect to the future of the electric vehicle. The cobalt demand is expected to grow by 70% until 2020. An amount far higher than that of nickel (4%) and manganese (2%). As the LIB technology interconnects these elements, the impact of the increasing quantity of elements such as cobalt will also affect lithium demand. China, the first consumer of cobalt, commits 75% of it to battery production. The high demand of cobalt is one of the

reasons for the scepticism surrounding LIBs for electrical mobility, as a demand of 190 kilotons per year is estimated by 2050 (around 70-kilo tons in 2019) [88]. That is why recycling assumes a critical importance in this field, in order to reduce the demand for pristine resources.

3. Lithium-ion batteries: Environmental issues and recycling strategies

The relevant economic and environmental problems stemming from how lithium batteries are used today are strongly intertwined. Some problems, as natural resource pressure and pollution resulting from exploration and processing of metals, are originated from the massive current and expected increasing future demand for lithium and heavy metals such as cobalt and nickel for energy storage. At the current pace of demand, the readily available lithium may run out soon, and its price will rise [89]. The situation is similar for cobalt and nickel, which are even scarcer than lithium. These and other environmental issues caused by the exploration, use and disposal of LIBs are approached in the following sections. Furthermore, recycling strategies will be discussed showing different ways to solve the mentioned economic and environmental issues from LIBs. The recycling processes that have already been studied are reported for each main LIB components, analysing their advantages as disadvantages.

3.1. Environmental impact of LIBs

Environmental issues are related to the extraction and processing of lithium sources but, more importantly, to the pollution resulting from the careless disposal of lithium batteries, which contain toxic materials, including heavy metals such as nickel and cobalt [90].

Focusing back on lithium, this metal is a scarce resource with very high demand. Exhausting lithium resources will worsen the above mentioned economic and environmental problems. Higher lithium prices will eventually turn the exploitation of low-concentration resources more attractive. This may still prove more accessible and more profitable than recycling, but it may well lead to additional/extensive environmental damage due to mining, extraction, and purification processes, that rely on energy consumption and production of industrial wastes. Despite the pressing need to use lithium and other metals required by LIBs more efficiently, the recycling of this type of materials and equipment is still about only 10% in global terms, implying that the remaining 90% ends up in landfills, making valuable materials unrecoverable [11, 12].

This situation needs to be changed because natural lithium reserves alone cannot support the foreseeable future demand. This demand will be driven mainly by the transition to the electric mobility concept, that intends to replace the conventional internal combustion engine vehicles (ICEV) with the more environmentally friendly EVs. It has been proven that the emissions of an EV are significantly lower than the ICEV, particularly when the charge of the EV is made relying on renewable energy sources, according to an European Commission study (Figure 10) [91]. These results include the environmental cost of the production and disposal of batteries in the EVs and are caused by the significantly lower number of parts of an EV when compared with an ICEV.
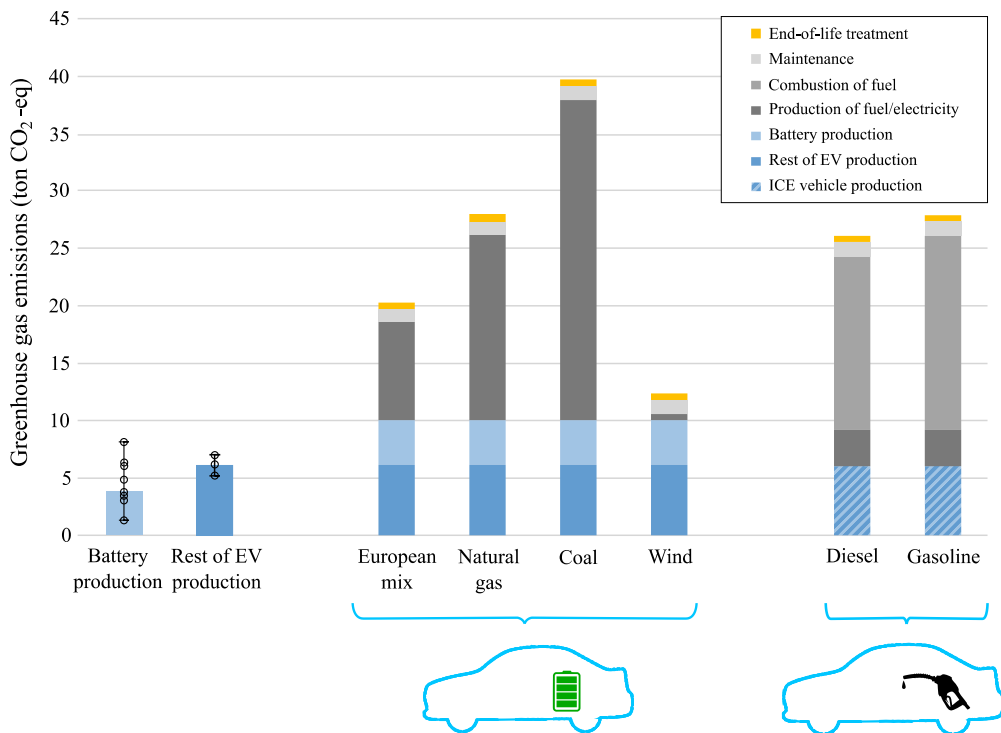
Figure 10 - Lifecycle GHG emissions of mid-sized 24 kWh battery EV and ICE vehicles [91]. The vehicle's operational lifetime is assumed to be 150 000 km.

Although EV production stage is more carbon-intensive than ICE vehicles once battery production is considered, EVs can compensate this in the use stage, and become eco-friendlier with the use of an electricity mix that is based more on the renewable sources. With the expected growth of the EV market, due to the reasons stated above, it is also expected a huge demand on the LIB demand for the automotive industry, which will urge even more the necessity of recycling the spent batteries, to respond to the needs of the production chains, and simultaneously reduce the disposal of spent batteries.

Despite their advantages, LIBs present different environmental impacts, in particular during the production process and at the end of their life cycle. Recycling, in combination

with renewable energy sources, can reduce the environmental footprint of the LIB industry. Recycling mainly protects the environment in two ways through the recovery of scarce and valuable materials. First, metal recovery reduces the dependence on mining and refining. Second, recycling minimises the amount of waste which, in many cases, also happen to be toxic (due to the use of toxic elements and some acids) or non-biodegradable [92].

LIBs are better than primary batteries in terms of natural resource conservation because they can be used multiple times, avoiding the extraction of more resources to fabricate new devices. However, to fabricate truly environmentally friendly LIBs, the energy stored in batteries should be also mainly from renewable sources.

Clean and efficient energy sources are essential to decarbonising the economy and hence reducing greenhouse gas emissions. Such systems would allow to charge batteries during high production hours that would be discharged later, during periods of higher demand.

This section covers some of the most critical environmental effects associated with LIB production, operation, dismantling and disposal.

Life Cycle Assessment (LCA) of LIBs is a powerful tool in the product development phase to identify potential hazards, environmental impacts and relevant stages in the product life cycle [93], so that the right measures can be adopted at each stage [4, 9, 15]. It allows the modulation of different theoretical situations, introducing different relevant variables and comparing the results that can potentially be applied in practice. LCA also allows comparing the impacts of different production chains and can make predictions of the future industry impacts in different scenarios [94]. LCA shows the contribution of different steps and components in the environmental impact of each device, which allows the possibility to replace them with more sustainable ones, reducing the global impact of the battery [95]. Last, it can help assess human health impacts in the different life stages of a battery [96]. However, it is difficult to have access to all needed data, and some critical assumptions have to be made, which can sometimes lead to inaccurate predictions [97].

For instance, the life-cycle of lithium-air batteries has been analysed from raw materials production to recycling process in order to evaluate the main environmental impacts when compared to those of other types of battery and to study their potential for a sustainable wide range application [98]. The study shows that the production phase generates the most impacts. However, the increase in cell efficiency results in the production of fewer cells [98]. The new main impact in this new scenario is caused by energy losses in the

form of heat during the battery charge/discharge process. Compared to the best battery technologies today, the environmental impact of lithium-air batteries is 4 to 9 times lower. Recycling can prevent 10 to 30% of the production-related environmental impact. However, no large-scale recycling methods are currently in use, once lithium-air batteries are not widely used nowadays [98].

Regarding the benefits of recycling versus mining and refining lithium and rare metals, the increased demand will lead to higher lithium prices, making the exploitation of less accessible reserves profitable. However, exploiting those lower-quality reserves will have negative impacts on the explored areas. It is therefore essential to find alternatives to diversify the energy storage systems and to prevent the intensive exploitation of natural resources alone [99]. Estimations of future battery recycling claim a reduction of the dependence on natural resources by up to 50%. Because not all materials are recyclable, natural resources will also continue to be necessary [15].

When applied to a circular economy scenario, the waste management of spent LIBs shows excellent potential to reduce the use of energy in the production of new devices. The application of the spent LIBs in stationary energy storage systems can increase even more this effect [100]. However, the recycling and reuse of materials from spent LIBs is not always cost-effective. Depending on the type of battery and the materials involved, the cost of the recovery can be higher than the extraction cost of new materials [101].

Like every other industrial process, the production of LIBs presents hazards and environmental risks associated with the synthesis of materials, fabrication processes and waste management. Cathode scraps from the industrial production of LIBs can be treated to recover pure metals such as Co, Ni and Li using a sulphate leach mixture in a selective extraction process. This strategy significantly reduces the environmental impact associated with the industrial production of batteries and optimises the use of mineral resources [102]. An interesting and eco-friendly approach consists in the use of biodegradable and low-cost materials, such as chitin and rice husks, as adsorbents for recovery of cobalt from leaching steps of recycling of used LIBs. It was concluded that pH 6 is the best for adsorption of the metals, which presents a pseudo-second order model curve. Cobalt recovery rates up to 95% were achieved using chitin (50 mg.g^{-1}), which makes it an ecological and low-cost adsorbent to recover valuable materials from used LIBs [103].

LIBs also present issues related to ecotoxicity and human health. In faulty or incorrectly used LIBS, short-circuits, overcharging or overheating can lead to fires and explosions.

Safety tests have been developed to avoid these incidents throughout battery life. However, the large variety of devices with different compositions and characteristics results in different performance during these tests. As a result, despite these safety checks, incidents still happen occasionally [104].

Moreover, a significant number of battery models show higher levels of cobalt, copper and nickel than recommended [105]. Some even contain lead and thallium, which significantly increase the ecotoxicity of LIBs (Figure 11) [105]. Lithium manganese oxide and lithium cobalt oxide are other materials used in LIBs with proved long-term chronical effects on some crustacean populations [106].
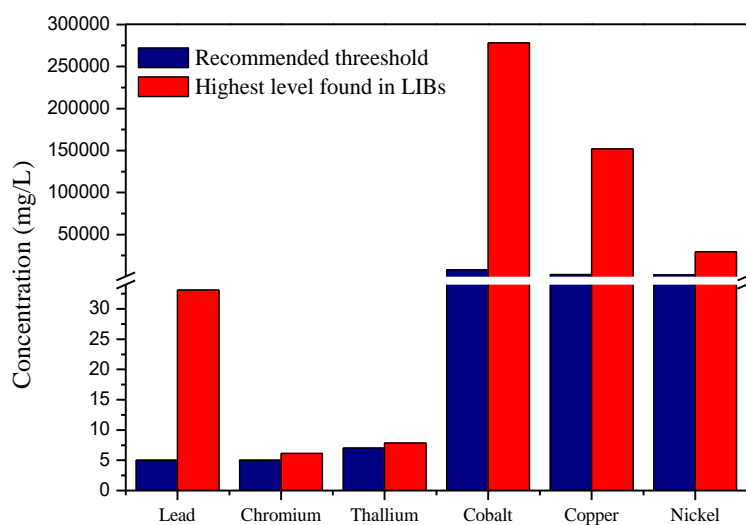
Figure 11 - Comparison between the component levels measured in LIBs and the recommended threshold. Based on [105].

Replacing the most hazardous components in a battery with safer materials is a valid approach to reduce the negative impacts of LIBs. An interesting work focusing on organic LIBs based on dilithium benzenediacrylate electrodes, presented an environmentally friendly recycling process Water is used for solubilisation of the organic electrode material, which is much less harmful than the conventionally used DMF or NMP solvents, but there are some concerns on the effect and stability of water in the battery [107].

The recycling potential of LIBs has been compared to present recycling systems of lead-acid and nickel-metal-hydride batteries. Despite their environmental and operational advantages compared to secondary batteries, the latter are more easily recovered because they have similar composition and construction, and this allows the recovery of high-

quality materials using nearly the same processes. On the other hand, there are many different types of LIBs, and the range of materials involved is too wide to enable the development of "universal" recycling systems. Different processes have been proposed addressing the recovery of specific materials from different battery types [108].

An enhanced method for improved separation of copper, cobalt and lithium was developed [109]. The proposed method uses self-driven microbial fuel cell (MFCs) and microbial electrolysis cells (MECs), which are considered as promising technologies, due to less energy consumption associated. Consequently, this leads to an environmentally friendly global process of batteries recycling [109]. The use of DL-malic acid ($C_4H_5O_6$), as leaching agent, is reported as an innovative way to fulfil an environmentally friendly leaching method, to recover cobalt (90 wt.%) and lithium (nearly 100 wt.%) metals from cathode active materials. The combination of hydrogen peroxide in a DL-malic acid solution can effectively step up the leaching efficiency [110]. Also, the utilisation of DL-malic acid can contribute to a final regenerated cathode active material, which presents high specific discharge capacity of 147.2 mAh.g^{-1}, and favourable electrochemical cycling performance [111]. The literature reports on a new strategy to recycle materials from spent LIBs, based on the use of organic linkers as leaching agents, which in turn can precipitate the valuable metals as polymers from a NiMnCo solution [112].

Finally, some battery components can be put to other uses before recycling them at the end of their life. Spent cathodes from LIBs can be used as catalysts in the degradation of organic dyes, solving the problem of the spent LIBs disposal and the textile industry effluents treatment simultaneously. $LiCoO_2$ was shown to degrade methylene blue 200 times faster than pure H_2O_2, because of the reduction of this process' activation energy [113]. Anode materials can also be reused successfully. Zhao et al. prepared an adsorbent for treatment of heavy metals in waters using MnO_2 modified graphite sorbents, with high removal rate for Pb(II) Cd(II) and Ag(I) [114].

3.2. Recycling strategies: direct recycling, pyro- and hydrometallurgical processes

The question about recycling is not whether to recycle or not, but how to do it most effectively. Market forces and regulation will determine whether and when used batteries undergo remanufacturing, refurbishing or recycling, and what are the most effective processes to achieve those objectives.

The adoption of recycling techniques and processes, framed in a closed loop (circular economy), is considered as the fundamental way for a more sustainable use of materials and resources when compared with the way they are used nowadays, while also avoiding the real risks of environmental pollution and public health issues related to toxicity. This circular economy concept will lead to more cost-effective devices, creating a more competitive and greener economy, and reducing the need to extract and process natural resources continuously. Additionally, the reduction in the production of new materials and the use of less energy demanding processes will further promote environmental sustainability by lowering the current dependence on the carbon fossil fuels [115].

Different tools and models exist to quantify both the economic and environmental implications of the LIB supply chain. Thus, material flow analysis quantifies the flow and stocks of materials [116]. On the other hand, the life cycle cost indicator can determine the expenses throughout the full cycle life of a battery [116]. Using more specific perspectives, cost-benefit analysis is a decision tool to assess the best approach in terms of economic advantages and, last, eco-efficiency can be defined as the ratio between the economic benefit and the environmental gain or the material recycling rate, performing the calculation of the overall performance of a determined recycling process or facility [116].

The material and energy flow analysis (MEFA) is a method to interpret the complete or partial processes to determine the possible sources and consumers of the materials, substances, pollutants and their corresponding energy flows of the processes. A newsworthy MEFA study was conducted on the production step of the LIBS, considering the materials included in the batteries, such as electrodes, electrolytes, metal-salts, plastics and other metals, like the casing and current collectors [117]. The analysis results prove that recycling based in thermal processes like smelting is recommended, using 80% less energy than the process of production of new original materials. According to the authors, considering the share of energy consumption of new materials and component productions in the overall energy necessary for a battery pack production, the recycling

of a cathode electrode material can achieve a reduction of 21.6% to 15.9%, resulting in a whole energy demand reduction of the recycling process estimated in 5.7% [117].

As alternative to the recycling of the battery components, the reuse of spent batteries in applications that require less energy consumption is also a valid option. Data show that most discarded batteries can still work at acceptable performance levels for many charge-discharge cycles [118]. However, if material recycling is a more profitable option, then remanufacturers may prefer to recover and recycle the materials instead of reuse the complete devices [118]. Possible reuse of laptop LIBS through the evaluation of the number of charge and discharge cycles can be used to check the most cost-effective recycling plan for these batteries. The study demonstrates that reusability information can help defining the most effective pricing policies in order to address whether the most successful path is to reuse the battery or to recycle its components [77].

A study has been presented considering the scenario of the reuse of LIBS from mobile applications, such as smartphones, in remote areas of developing countries. The idea is the collecting of the batteries from end-of-life smartphones and keeping them for a second life as to store solar energy. Many areas in developing countries are remote and isolate, and require the use of off-grid electricity systems. This limited electric supply makes even lighting difficult [119]. Second-life batteries can be connected to solar panels for charging, and then be used to power LED-based systems. This represents a safe, sustainable, reliable and low-cost light source, that can replace candles and kerosene lamps. For example, a 2-year-old standard LIB (2000 cycles of charge/discharge) that was used with a rate of one cycle per day, will have 1250 cycles left at the end of the average smartphone life. A 12 V 3.1 Ah battery will have the energy to powering a 5 W LED lamp for 4 hours at the cost of $35 per unit and will last for three years. This compares well with the typical annual cost of candles and kerosene lamps, established as $54 [120].

Higher lithium prices will encourage the thorough use of lithium batteries in "second-life" applications and their recycling at their end of life. As an example, Busch et al. report on a scenario where LIBS from electric vehicles are reused in grid-attached energy storage [116]. Therefore, the reuse of the batteries can offer an outstanding resource economy and significantly reduce the demand for new cobalt and lithium. In terms of demand indicators, the reuse of batteries from vehicles to grid-attached storage can contribute to a notable reduction of primary lithium demand by up to 30,000 kg per year

after 2030, and a worldwide reduction in the cobalt demand, which can be decreased by around 30% in 2033 [116].

Attending to the previously discussed topics, government incentives to battery re-use and recycling through legislation, education and tax policies are highly recommendable to accelerate the transition to a more sustainable economy. For example, considering subsidies and tax breaks for industrial companies is a way to generate profit for the recycling industry, and to make this process more economically appealing [11]. However, tax relief alone does not work, and other measures are simultaneously needed too. A recent study conducted in China showed that even if people know that batteries can be recycled and want to recycle, a majority does not know where to return their spent batteries [12]. Thus, country-wide recycling systems also need a collection infrastructure that is widely known to the population. Some of the proposed solutions include that the government may partially support this infrastructure, i.e., creating state-owned collection stations. The implementation of the recycling concept in public education at an early stage is another recommendation, ensuring that environmental concerns are respected and considered early on. The academic community can also contribute by developing more and better recycling strategies and techniques, fully taking into account that these approaches need to be transferred, implemented and scaled up at the industrial level, thus allowing the effective massive recycling of the materials of the LIBS [12].

From a business perspective, recycling is a source of new opportunities, particularly in countries with little or no natural lithium resources. In Europe, EC Directive 2006/66/EC states a clear objective to minimise the adverse effects and impact of batteries on the environment. The shift towards the electric vehicle can put the European combustion automotive industry at risk, if it is not prepared for the needed changes. Car manufacturers are now acting on the realisation of the strategic importance of batteries to their future business model. While many are investing heavily on battery manufacture, few are known to be investing in battery re-use and recycling.

Meanwhile, the recycling assessment is based on a metric named recycling efficiency, defined as the ratio between the recycling output fraction and weight of recycling input fraction, and a target of 50% is set. In the specific case of the Umicore industrial battery recycling process flow, which includes the recycling of used batteries from hybrid and electric vehicles, the effective recycling efficiency (60% for steel casing batteries) is better than the target set by the EC directive [121]. Different companies have their own recycling chain processes, that combine various methods to recover the different materials

at distinct efficiencies. However, There is still a gap between the environmental concerns and the technological developments, that needs to be close, by improving the recycling efficiencies and the sustainability of LIBs [122].

The German government, in turn, has established a strategic plan to promote sustainable growth of electric mobility [123] and gain industrial leadership in this emerging area. The growing use of electric vehicles has led to the necessity to organise a recycling plan for the creation of economic value from spent batteries. For this, investment plans for the implementation of recycling industries with economic profit available for potential investors, have been studied. Likewise, these recycling industries will severely reduce the waste material volume from spent LIBS, and consequently increase valorisation. The study results show that, due to the expected future growth of the utilisation of electric vehicles, the estimated annual amount of waste will reach 340,000 metric tones by 2040 in Germany [123]. There are ongoing plans to select strategic locations for collection and treatment industries, involving several partners in the supply chain: electric vehicle dealers, vehicle treatment operators, battery and material manufacturers and the recycling agents. This industrial strategy requires the creation of a joint consortium network where all the partners share costs and the business risks associated with the collection and recycling processes in order to lower the risks in the long term [123]. The aim is to make the battery recycling market more attractive for incoming investors. This means that batteries from electric vehicles need to be correctly electrical and thermal managed by an end-of-life strategy, which requires to be framed within the vehicle life cycle and supply chain.

The chemical analysis of used batteries provides insights and valuable information for the proposal and execution of recovery methods and recycling plans. 1 kg of sieved (<1 and 1-3 mm) and magnetically separated lithium battery ($LiCoO_2$), waste materials with less than 3 mm particle size contains about 250 g of cobalt, 120 g of copper, 110 g of nickel and 31 g of lithium that can be recovered. Also, a low metal release to aqueous solutions was verified [124].

As stated before, sometimes a spent battery is reused in a second use approach, in applications that do not require its full original capacity (Figure 12). Afterwards, once LIBS reach their end of life, different recycling strategies may be followed. The main approaches to recycling are "direct recycling" methods and "pyro- and hydrometallurgical" methods.

Direct recycling approaches aim to recover and refurbish the cathode material (active material mainly) to produce new batteries with it. Herein, methods are presented that apply a re-functionalisation of the active material and others that directly precipitate the desired active material, from spent LIBs cathode powders. Pyro- and hydrometallurgical methods, on the other hand, focus on recycling the metals and components of the battery. Their goal is to recover valuable components/elements from the end-of-life LIBs for later use as raw materials to be used directly in the production of new batteries.

Each of these approaches has its advantages and disadvantages. Pyro- and hydrometallurgical methods are unspecific and yield high recycling rates on the elements. However, several different steps may be needed to recover all the metals and materials of interest, which may involve toxic solvents and concentrated acids for the recovery, possibly leading to health problems and safety hazards, associated to the dangerous materials handled during the manufacturing process. In contrast, the main advantage of direct recycling methods is their high specificity, as they seem to address only one active material at a time. Akin to direct recycling methods, some direct recycling methods also use toxic solvents and acids in the process. However, these are a minority. This is because most methods focusing on the re-functionalisation of the active material are based on high-temperature processes. Although thermal processes may be considered more green, due to the fact that they are acid and solvent free, they can be disadvantageous, as their high energy consumption may deem them unattractive.

A negative point of both approaches is that very few authors mention what is done to recover the other parts of the battery, for example, anode material, current collectors, electrolyte, separator, and plastics.

As a final note, an essential difference between these two approaches is that while pyro- and hydrometallurgical methods are measured in terms of recovery rates, direct recycling methods are measured in terms of battery performance. The latter does not provide information on recovery rate, which makes it more challenging to evaluate the efficiency of the process. Instead, the electrochemical performance of the new battery is compared to that of the "original" one. Although almost always the performance is excellent, in the new battery, there are always performance losses, and very few [125] information is found on the number of times that a given battery/active material can be recycled before the electrochemical performance becomes unacceptable.
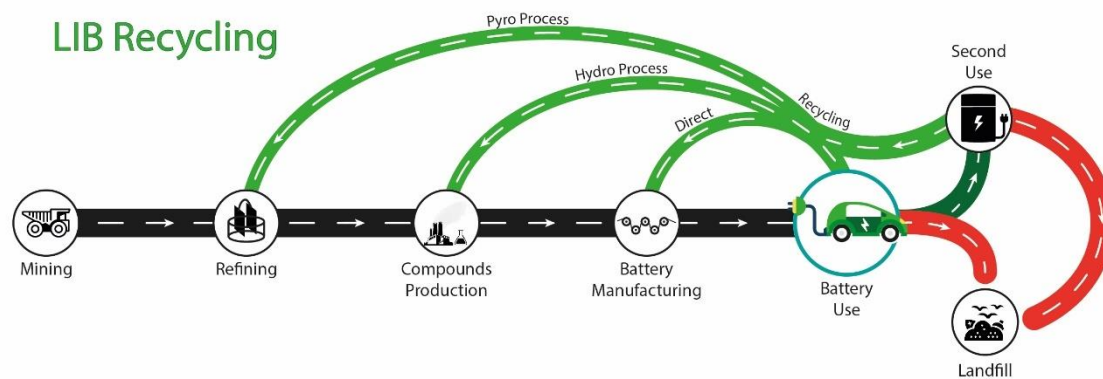
Figure 12 - Lithium-ion battery recycling routes.

3.3. Recycling of lithium-ion batteries

After battery use, different approaches can be followed (Figure 12). The first relevant decision is whether to dispose the spent battery in landfills, which should be avoided, or to reuse/recycle it. As stated before, the battery can be reused in other applications, and for that, battery health must be considered. When the battery materials are too degraded to use, whether they come from first or second use, different recycling paths can be followed. Each recycling process will lead to the different stages of the battery production chain. Direct recycling methods lead to the battery manufacturing, hydrometallurgical processes lead to the compounds' production and with pyrometallurgical processes it is possible to obtain the raw materials [126].

Different types of batteries, including nickel-metal hydride, rechargeable LIBs and primary LIBs may be recycled in a unique mechanical route process, avoiding the necessity to separate the spent devices into parts. The powder obtained from the mechanical pretreatment, which includes a two blade rotors crusher and a hammer crusher with a 5 mm sieve, can be further subject to chemical leaching, allowing the extraction of cobalt, nickel and manganese [127]. A process to recover most of the battery compounds, using simple, cost-effective, and environmentally friendly methods was developed. This process is based on selective dissolution in dilute acid, which precipitates the metal part of the battery. After that, chemical and thermal treatments allow the recovery of almost all battery components, including insoluble plastics, transition metals and alkaline ions [128]. In another approach, the use of water and the contents of waste Li-ion batteries for the electrodes in a Li–liquid battery system has been demonstrated in which electricity was produced [129].

Most recycling methods, on the other hand, require the separation of the battery into parts, as they specialise in the recovery of materials from specific components.

Regarding the selection of the best recycling processes and methods, the combination of several criteria supports decision models for the selection of the optimal recycling solution. Among these criteria, environmental impact, energy consumption, health and safety factors, recovery of materials, process time, labour cost, initial facility investment and flexibility rate are the most common. Depending on how they are combined, a fuzzy multi-criteria decision logic model (analytical hierarchical process) can provide several combinations and results. Despite the criteria specified, some authors support that the best operational recycling combination results from the aggregation of hydrometallurgy and pyrometallurgy processes [130]

Pyrometallurgical processes operate at high temperatures and are usually associated with high atmospheric emissions. Hydrometallurgical processes, on the other hand, consist of leaching steps in acid or alkaline medium and purification processes to dissolve the metallic fraction [131]. The main final products obtained from pyrometallurgy and hydrometallurgy are alloys/metal compounds, and solutions containing metal ions, respectively [131].

3.4. Recycling processes for batteries

The first approach to consider involves processing the whole battery rather than the separate components. Toxco and Sony processes are two commercial LIB recycling processes already in use. In the Toxco process, the material is cooled in liquid nitrogen and then shredded. After that, the lithium is set in contact with water, where it reacts to produce hydrogen, and allows the recovery of metallic cobalt and lithium hydroxide. In contrast, the Sony process involves heating the battery materials. Then, the lithium, plastics and hydrogenated compounds are caught by mean of a proprietary gas treatment system, while cobalt is subject to a hydrometallurgical process [131]. The use of microwaves to promote the carbothermal reduction of the cathode materials, using the graphite from the anode under ambient condition proved to achieve better recycling rates than recycling the electrodes separately [132].

The hydrometallurgical recycling process consists of several intermediate steps to achieve the recovery of valuable metals and materials. Broadly, the batteries are classified by type, dismantled and completely discharged trough a deep discharge step to avoid safety risks

of possible reactions with air. Batteries may be dismantled by crushing, sieving, milling, froth flotation, pneumatic, magnetic and densimetric split process [2].

The final particle size of wet and dry crushed materials of wasted LIBS was studied to assess the differences. Wet crushing uses a blade crusher equipment with water medium, in which the particles fed to the crusher at high speed, are fractured when they encounter to the stationary elements of the crusher. In the dry crushing method, batteries are chopped into pieces with a shear crusher, followed by crushing by impact. XRD, SEM and EDX analysis results showed that the dry technique led to a more selective crushing of the components, as well as to the obtention of purer electrode materials [133].

Hyuntae Bae et al. have developed an innovative waste-to-lithium (WTL) recycling system. The system, represented in Figure 13, consists of a delithiation electrochemical reaction in which the lithium metal is harvested from lithium-containing waste materials through a charge step. Moreover, by a discharging process, the harvested lithium metal is recycled into air-stable LiOH by reaction with water, and then, by reaction between the obtained LiOH and CO_2, Li_2CO_3, is produced. The authors claim that with this method, the recycling of spent LIBS can be boosted up, by a cost-effective and manageable scaling approach because the system is designed to work at room temperature, avoiding the use of heat and elevated temperatures, or even hazardous acid chemicals [134]. A method to reactivation of the active materials was developed, based on ultrasonic hydrothermal renovation. In this process, the spent $LiCoO_2$ is removed from the collector, separated from the organic compounds and reactivated with H_2O_2 and argon at 90 °C. The recovered active materials can be applied in new batteries with discharge capacities of around 130 mAh.g^{-1} [135]. $LiCoO_2$ can also be recovered by calcination at high temperatures and addition of Li_2CO_3, allowing for regeneration of the cathode materials with similar properties to those of the commercial materials [136]. This Li_2CO_3 can be obtained by the recycling of $LiCoO_2$ by the addition of NaCl and SiO_2 as mechanochemical reaction agents and Na_2CO_3 as precipitation reagent, via a sustainable recycling process [137]. The application of DC electric fields in spent LIBs is also a versatile and green strategy to extract lithium ions from the cathode structure, and dissolve them in aqueous solution [138]. Other cathode materials, as $Li(Ni_{0.6}Co_{0.2}Mn_{0.2})O_2$ can be regenerated by roasting at 350°C, followed by the addition of $(NH_4)_2SO_4$, in an acid free process, without any reduction agent [139]. $LiMnO_2$ was reportedly regenerated using a pyrometallurgical process, by application of high temperatures, and addition of manganese acetate. The recovered cathode presented acceptable battery performance [140].
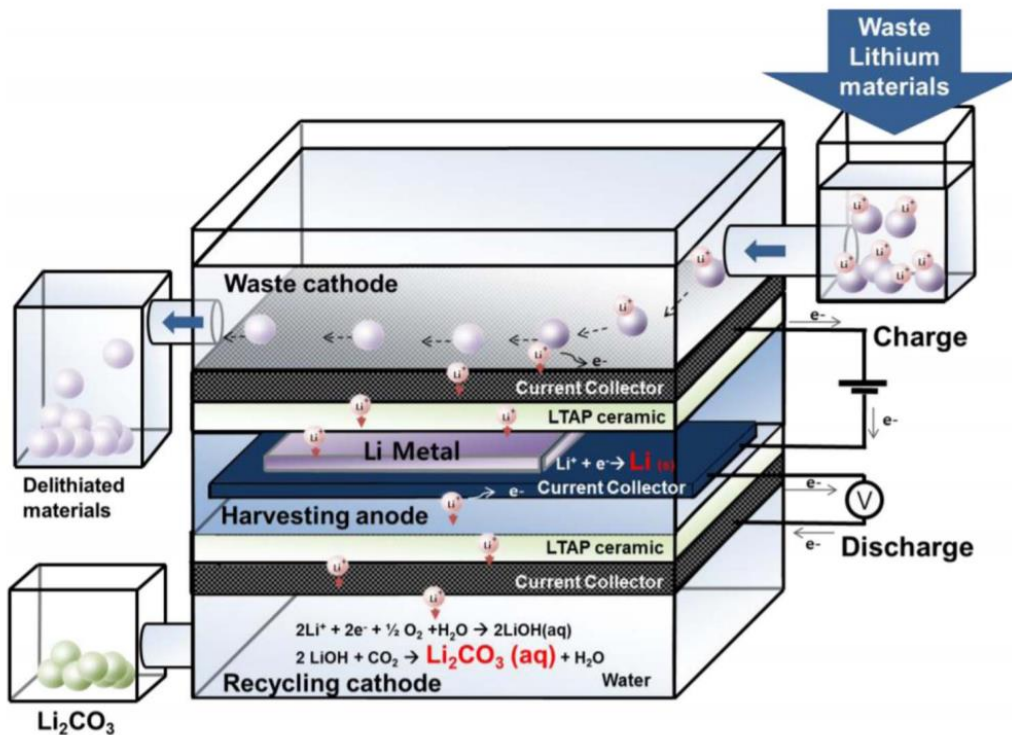
Figure 13 - Schematic representation of the waste-to-lithium system [134].

Chemical precipitation can be considered as an alternative way to process the recycling of spent batteries, allowing the recovery of pure metal salts from $LiFePO_4$ active material. This strategy was designed with a base in the called solid-liquid equilibrium phase behaviour, leading up to optimal operating conditions, namely, NaOH amount to be added to recover the most of $FePO_4$ (7.5 ml of NaOH for a full removal of Fe^{3+}) [141].

Then, electrolyte and salts are removed by vacuum distillation, and solvents and heat dissolve the binder. This enables the separation of the current collector foils from the electrode materials. After grinding, a leaching step follows to purify further the electrode materials and metals, which are extracted by precipitation or solvent extraction [92].

Christian Hanisch et al. proposed a novel strategy for the recycling used batteries, using thermal decomposition of PVDF binder, causing a weakening in the adhesion between the active materials in the electrode coating ink, and the current collector thin film. Then, the active materials in the coating ink are entirely separated from the current collector, by the technique created by the authors, called adhesion neutralisation via incineration and impact liberation (ANVIIL), which uses an air-jet-separator (Figure 14a). The most significant advantage of this method is the regaining of highly pure materials with a

consistent and very similar size distribution [142]. In this process, it is possible to regain 97.1% of the coating (0.1% of Al impurities). It is claimed that the regained materials are 30 times purer than state-of-the-art ones [142].

A novel process based on the bipolar membrane electrodialysis and the metal-ion chelation has been reported. The effect of the initial ethylenediaminetetraacetic acid (EDTA) concentration (0.01-0.03 M) as chelating agent, at initial pH 7.0 of Na^+ ion feed solution was studied. The pH of the feed solution slightly decreased for all EDTA concentrations. The addition of the EDTA to a combined solution of lithium and cobalt from spent LIBS, can lead up to very high selectiveness ratios 99% [143].

The industry of solar cells manufacturing generates waste from silicon debris particles, produced during the cutting of silicon ingots, as thin wafers, for the construction of the photovoltaic cells, which are estimated in 40% of the mass of the ingots, that are not reused. Additionally, a silicon sludge waste is generated and needs to be recycled. These two waste materials can be reused, extracting the present silicon nanoparticles in the materials, by the aerosol assisted technique, and then recovered by ultrasonic spray drying (Figure 14b). This low-cost approach can positively value the waste materials by producing regenerated silicon anodes for LIBS [101, 103, 143].
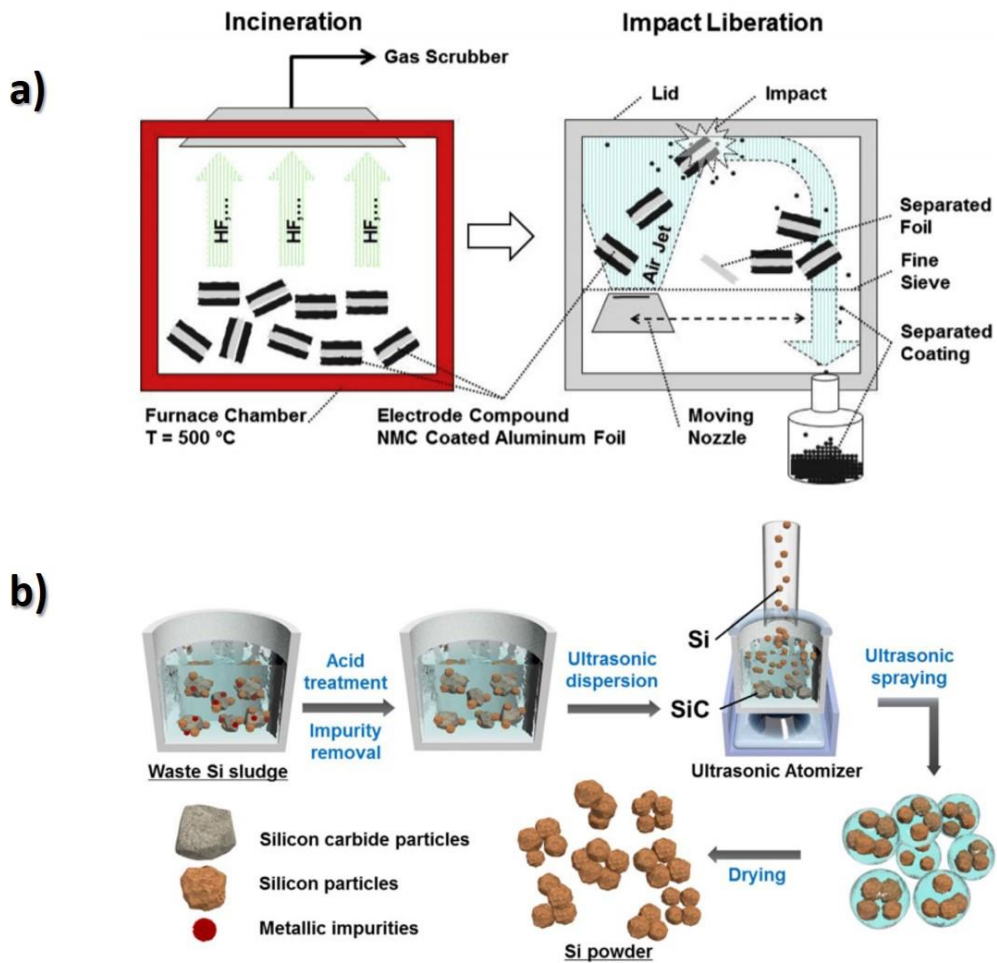
Figure 14 – a) Representation of the experimental process of adhesion neutralisation via incineration and impact liberation [142] and b) schematic representation of the proposed ultrasonic aerosol assisted silicon extraction method [144].

Cobalt from wasted LIBS can be recovered by solvent extraction and leaching, being recovered almost 99.9% of cobalt, from the solution of Cyanex 272 as extractant, isodecanol as phase modification and kerosene as diluent. One final product is a hydrated cobalt salt, prepared several evaporation steps, crystallisation, precipitation and cementation methods (**¡Error! No se encuentra el origen de la referencia.**15).
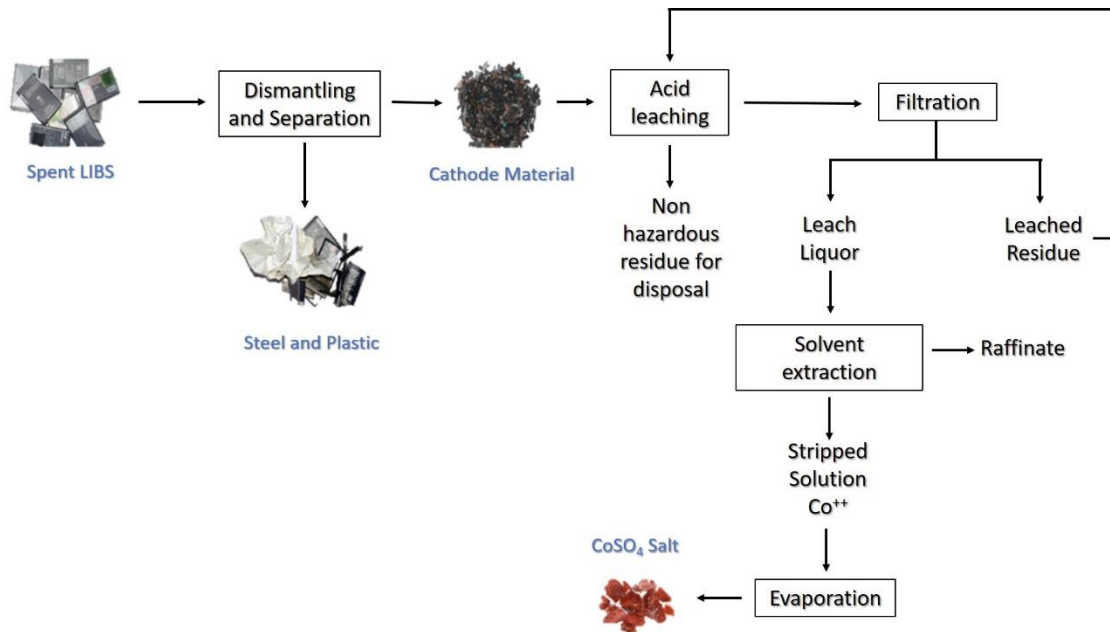
Figure 15 - Schematic representation of the several steps to recover cobalt from spent LIBS. Based on [145].

Considering the safety risks associated with the possibility of battery explosion during the recycling processes, some authors have proposed a method that prevents explosion during thermal treatments. This technique needs the use of a electric furnace with SiC heater in a temperature range of 300-600 °C for 2 hours, where it is possible to treat the wasted batteries under an inert argon atmosphere, leading to the safe recovery of electrode powders (32-35 wt.% for Co and 3-5 wt.% for Li) by further chemical leaching [146].

An interesting magnetic electrode was developed for LIBS to overcome the challenge of battery recycling. The magnetic properties can be achieved using magnetic Fe_3O_4 particles (dispersed and uniform size of 100 nm) as an electrode. The magnetic susceptibilities of a mixed powder of Fe_3O_4, $LiFePO_4$ and conductive agent (1:1:1) was evaluated with an external field between -1 and 1 T, presenting a super-paramagnetic behaviour without remanence or coercivity. It is claimed that the produced batteries are easier to recycle and have a lower manufacturing cost. Also, the batteries exhibit some advantageous properties, as anti-vibration and non-fatigue behaviour, with excellent results even up to 1000 working cycles, perfect for hard conditions (anti-vibration and non-fatigue) engineering machines [147].

An experiment carried out with a multi-step process, done with several types of used and crushed LIBS, led to considerable recovery rates for aluminium, manganese, nickel, cobalt and lithium (97%) [148]. The process consists of an alkali decomposition, followed

by acid leaching. Then, the metals are precipitated individually, from the leach mixture, according to various pH levels. Initially, Al is recovered in a filtration process, with a 4.0 M NH_4OH solution. Mn is precipitated at pH 7.5, Ni is obtained at pH 9 and at pH 11-12 Co is precipitated. Finally, Li is obtained as Li_2CO_3 using a solution of Na_2CO_3 [148].

The scientific area of thermodynamics can serve as study base for the development of a novel strategy to optimise the recycling of LIBS. A study reports that, the high-temperature metal recovery process, which involves several steps, as material size reduction, chemical and thermal reduction, smelting and casting, needs to be improved, because it is associated with losses of energy (primarily in the smelting step). These losses are related to the conversion of electricity into heat, being considered energy dissipated and not used yet [149].

Mechanochemistry is a scientific discipline aiming to help in the progress of recycling LIBS. The mechanochemical process is a method were a chemical reaction is induced by direct adsorption of mechanical energy. That enables the recycling of some value metals (lead, gold, copper, lithium, cobalt, molybdenum and nickel), from various electronic devices including cathode ray tube funnel glass, fluorescent lamps, LCD screens, and also LIBS, with the advantage of avoiding the use of strong acids. However, despite the potential of this kind of process, its energy consumption and productivity need to be improved to make the process scalable [150].

Selective separation and recovery of some precious metals, like copper, cobalt and lithium, from the leachate of wasted LIB in acid chloride media with solvent impregnated resins, is reported as an effective method. The selectivity of the process is advantageous as it avoids the necessity to treat each electrode separately from its current collector (Al and Cu), by remove the metals of both of them in the same process [151].

Yang Guo et al. proved that the hydrochloric acid (HCl) leaching is an effective method to separate lithium and graphite from anodes. That work noted that leaching at 3 M HCl concentration for 80 °C for 90 minutes at a S/L ratio of 1:50 $g.ml^{-1}$ could lead to a maximum leaching efficiency of 99.4%. Figure 16a shows the disassembly steps for the recycle of the lithium-ion anodes [152].

As part of an experiment, some $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ LIBS scraps were recycled by hydrogen and carbon reductive treatment and sulfur acid leaching, and then subject to solvent extraction, to recover Co, Ni and Mn metals. For example, the use of oxidants such as potassium permanganate and chlorine dioxide can effectively remove Mn, from the NCM solution [153].

In the recovery process of used LIBS from smartphones, it is necessary to dismantle and separate the electrodes from the steel casing and plastic. Then the electrodes are crushed, and the metals are recovered by leaching and solvent extraction steps (Figure 16b) [154]. Graphite recovery from wasted LIBS is possible due to a method, involving electrolyte extraction subcritical carbon dioxide, which is considered very promising because it leads to almost complete and efficient utilisation of all the entire components of the LIB. With this method, electrolyte can be recovered at an efficiency of 90%, including the conductive salt [155]. Also, was demonstrated the ability to regain the capacity of a lithium iron phosphate (LiFePO$_4$) cathode using a functionalisation treatment based on re-lithiation techniques [156].

A new thermal treatment technique was investigated, to reuse the materials, giving the addition of avoiding the explosion behaviour (thermal runaway) and risks, during the recycling process, contributing to better sustainability. **¡Error! No se encuentra el origen de la referencia.**16c represents the steps of the proposed recycling process, including the studied thermal treatment (300-600 °C for 2 hours), the crushing and sieving processes (<105 µm), the hydrometallurgical process and magnetic separation. Cobalt and lithium were recovered at 49 wt.% and 4 wt.%, respectively [157].
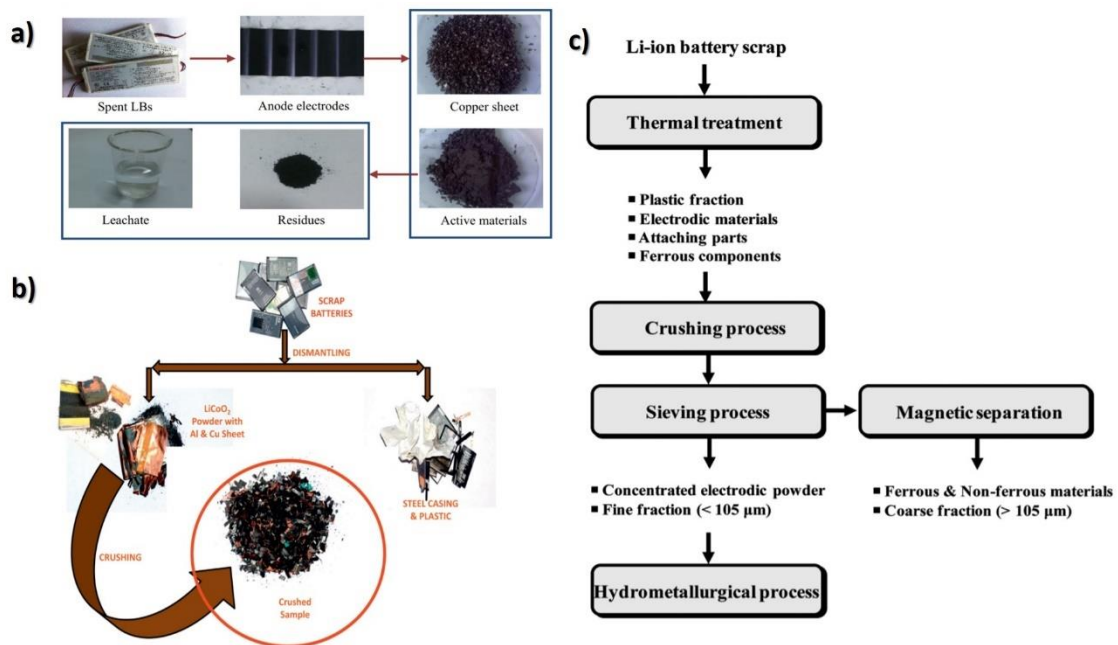

Figure 16 – a) Disassembly and recycling process of the active material from the anode of a wasted LIB [152]; b) process of sample recycling preparation from spent smartphones

LIBS [154] and c) process flow of the thermal treatment method for recycling of spent LIBS [157].

An experiment carried out with an off-gas producing process, with extraction, drying and condensation was successfully reported, to study the influence on the exhaust gas flow, as well, as the composition, derivative of the drying and condensation variables. The higher performance proposed recycling process involves and combines several steps, such as the discharge, dismantling, shredding, extraction, drying and separation [158]. Future trend include the possibility to inject the electrode materials in the battery structure, which allow the reuse of the battery cell, leading to a significant reduction of recycling steps, necessary products, spent energy, and consequently the costs. The proof of concept for the envisioned strategy is shown for injectable batteries [159].

3.5. Component-based recycling

Alternatively, to whole-battery-based methods, most works reported to date focus on the development of highly specific processes addressing the recovery of material from a particular LIB component.

3.5.1. Current collectors

For any recycling process to work correctly, the active materials need to be separated from the metallic current collectors first. This can be achieved in acid baths. The acids react with the copper and aluminium thin films, weakening the adhesion of the active material to the current collector, and facilitating the separation [147]. Vacuum pyrolysis is an efficient separation technique that allows the reuse of the aluminium foils, by peeling the cathode materials from the current collector at efficiencies near 100% and without damaging it [160]. Heated ionic liquids have also been used to dissolve the binder from the cathode materials, which separates them from the current collector, allowing an efficient recover the aluminium foils [161]. The metallic portion of spent LIBs can be recycled using mechanical pre-treatments as mechanical shredding and size-based sorting steps. Each metal type can be segregated in different size fractions, facilitating the recycling process, and allowing a more efficient separation [162]. Effective pre-treatments, such as crushing and sieving, proved to enhance the subsequent leaching treatments, with higher recovery efficiencies for the electrode powders [163]. Ultrasonic washing, with an ultrasonic frequency of 40 Hz and electric power of 100 W, has been demonstrated to separate electrode materials, particularly $LiCoO_2$ cathodes, from their

support substrate, increasing the recover efficiency of Co and Li to 99% and 97%, respectively, and reduced the overall energy needs and pollution of the process [164]. Ethylene glycol is an effective compound to delaminate electrode materials at low temperatures and separate them from the current collectors without damaging them [165].

3.5.2. Recovery of cathode materials

Most of the recycling efforts to date have focused on the cathode due to its higher content in lithium and other valuable metals. Five types of cathodes were studied by quantifying the natural resource output needed in the production of each one in a closed-loop scenario. The impact of composition, properties and production techniques of the different cathodes was also analysed. It was concluded that the main impact related to natural resources used were metal supply and energy used in the production of the cathodes. This study also showed the importance to evaluate every type of device individually, by taking into account the objectives and targets for each one of them [166].

The cathode is also the most challenging component to recycle, because of its structural complexity and the variety of active materials present. However, it is also the most studied component, with a growing number of studies made every year, through the publication of about 143 articles in 2019, which target recovery of lithium compounds but also other rare metal elements, such as cobalt, iron, manganese or nickel. The choice of the recycling method to use is dependent on the target metal to recover, because each method has different recovery efficiencies, usually making them more suitable for one type of material. Furthermore, attention is needed to properties of some metals, that can affect the efficiency of the process, leaving impurities in the structure of the recovered materials. For example, Cu Ni, Co and Mn metal ions, have similar solubilities which can leave some impurities in NCM batteries when chemical precipitation processes are used. These impurities can affect the efficiency of the recycled battery, more specifically Cu metal that can short circuit the cell, or Cu ions that can improve the discharge capacity [167].

Some procedures can be optimised to obtain high recovery efficiencies for several metals regardless of the active materials. A new low-temperature methodology with high efficiency has been proposed to recycle Li-ion batteries economically for mixed cathode materials, including $LiCoO_2$, $LiMn_2O_4$, $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$, and $LiFePO_4$ were employed in the recovery process [168]. The process, schematised in Figure 17a, used 4M sulfuric acid and 30wt% hydrogen peroxide (2-3 hours at 70-80ºC) for leaching.

Residual $LiFeO_4$ was filtrated out at this step. Next, pH was adjusted to precipitate $Fe(OH)_3$ while Mn^{2+}, Co^{2+} and Ni^{2+} remain in solution. The concentrations of Mn^{2+}, Co^{2+} and Ni^{2+}, were determined, and their ratios adjusted to 1:1:1 with the addition of $CoSO_4$, $NiSO_4$, and $MnSO_4$ (stirring for 2h). pH was increased to 11 (addition of NaOH) and the mixture of $Co(OH)_2$, $Ni(OH)_2$ and $Mn(OH)_2$ was co-precipitated. The solid mixture was then washed with distilled water. Na_2CO_3 was added to the solution (40ºC) and then proceeded to filtrate it and recover Li_2CO_3. The recovered materials were then used in the production of new cathode material ($LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$). This process recovers almost 100% of Ni, Mn, Co, and experiments demonstrate that about 80% of Li is recycled in the form of Li_2CO_3 [168].

Figure 17b summarises a closed-loop process reported to recover lithium carbonate from cathode scrap of LIB.
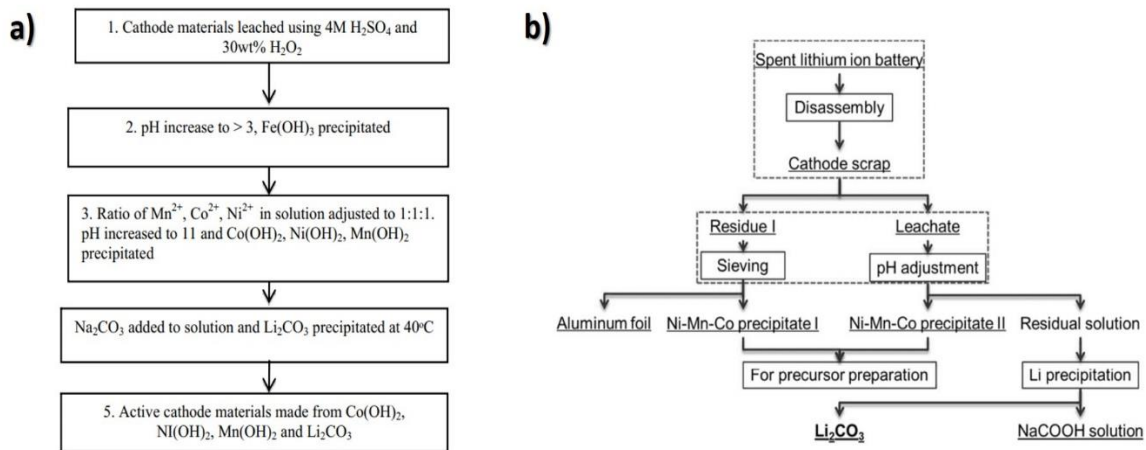
Figure 17 - a) Flow chart for separation and synthesis process for mixed cathode material [168] and b) simplified flow-sheet of the recovery process based on formic acid [169].

Lithium could be selectively leached into solution using formic acid while aluminium remained as metallic form, and most of the other metals from the cathode scrap could be precipitated out [169]. The separation of the remaining Ni, Co and Mn from the leachate, Li_2CO_3 with a purity of 99.90% could be obtained. The final solution after lithium carbonate extraction can be further processed for sodium formate preparation and Ni, Co and Mn precipitates are ready for precursor preparation for cathode materials. As a result, the global recovery rates of Al, Li, Ni, Co and Mn reported were 95.46%, 98.22%,

99.96%, 99.96% and 99.95% respectively, achieving the effective recycling of materials from cathode scrap of spent LIBs [169].

Other authors created a closed-loop recycling process where new cathode materials can be made from spent LIBS. They used spent LIBs primarily composed of $LiCoO_2$ and, in a second experiment, cathode materials with $LiMn_2O_4$, $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ and $LiFePO_4$ powders added to the shredded used batteries. In both cases the batteries are discharged, then shredded. The steel casing is removed from the shredded material by magnetic separation. Cathode materials are separated from the aluminium current collectors by dissolving the aluminium in NaOH. Next, the remaining cathode powders were then separated by sieving. Last, copper current collectors were separated from the remaining material, mainly plastic, by density separation. The recovery efficiencies of this process are reportedly close to 90% [170]. Acid leaching processes were optimized to effectively recover Ni, Li, Mn and Co materials. The combination of different acetic and ascorbic acid concentrations leads to different leaching efficiencies. Under optimal conditions over 95% of the total leached metals can be recovered [171].

Table 3 presents a comprehensive list of the different methods used to recycle and recover cathode materials, highlighting their main advantages and disadvantages

Table 3 – Summary of cathode recycling processes reported in the literature.

Initial material	Process	Conditions	Obtained Material	Efficiency (%)	Advantages	Disadvantages	Ref
$LiCoO_2$	Acid leaching	Addition of HCl	Co, Li	~100	High recovery efficiencies	Use of toxic reagents	[172]
$LiCoO_2$	Acid leaching	Addition of HCl and NaOH	Li, Co	-	Environmentally friendly	High temperatures needed	[173]
$LiCoO_2$	Acid leaching	Addition of H_3PO_4	$Co_3(PO_4)_2$	99	High purity of recovered materials	Use of toxic reagents	[174]
			Li	99			
$LiCoO_2$	Acid leaching	Addition of H_3PO_4	Co	98	High recovery rates	High temperatures needed	[175]
			Li	97			
$LiCoO_2$	Acid leaching	Addition of glucose and H_3PO_4	Co	98	Environmentally friendly process	Requires high temperatures	[176]
			Li	~100			
$LiCoO_2$	Acid leaching	reaction time 2.5 h, H_2O_2 dosage 1.6 $mL.g^{-1}$, H_2SO_4 concentration 3.0 $mol.L^{-1}$, reaction temperature 70 °C, and the dosage of H_2SO_4 7.0 mL g-1.	Co	99.5	High purity of cobalt	Acid use and high temperatures	[177]
$LiCoO_2$	Acid leaching	Addition of H_2SO_4 and H_2O_2	$CoOH_2$	-	Good electrochemical performance	Requires high temperatures	[178]
$LiCoO_2$	Acid leaching	Addition of H_2SO_4 and Cyanex 272	Co	93	High purity cobalt obtained	Use of toxic reagents	[179]
			Li	94			
$LiCoO_2$	Acid leaching	Addition of H_2SO_4, Acorga M5640 and Cyanex 272	Cu	98	High recovery rates	Use of toxic reagents	[180]
			Co	97			
$LiCoO_2$	Acid leaching	1.5 M DL-malic acid, 2.0 vol.% hydrogen peroxide, a leaching	Co	96	High metal recovery rate	Toxic materials, high temperatures	[110]

		temperature of 90 ºC, an S:L ratio of 20 g.L^{-1} and a time interval of 40 min					
LiCoO$_2$	Acid leaching	Addition of malic acid and oxalic acid	CoC$_2$O$_4$	99	Simple process	High temperatures needed	[181]
LiCoO$_2$	Acid leaching	Addition of Cyanex 272	Co	~100	Almost full recovery of Co	Cyanex 272 requires much care	[182]
LiCoO$_2$	Acid leaching	Addition of D2HEPA and Cyanex 272	Co, Cu, Mn, Al	~100	Easily adaptable to different LIB technologies	Many steped process	[183]
LiCoO$_2$	Acid leaching	Addition of nitric acid	LiCoO$_2$	-	Good Cycling performance	Use of toxic reagents	[184]
LiCoO$_2$	Acid leaching	Addition of citric acid and H$_2$O$_2$	Co	90	High recovery rate for Li	Low recovery rate for Co	[185]
			Li	~100			
LiCoO$_2$	Acid leaching	Addition of citric acid; ultrasonic agitation	Co	96	Environmentally friendly	Few metals recovered	[170]
			Li	~100			
LiCoO$_2$	Acid leaching	Addition of citric acid (from citrus juice);	Li	~100	Environmentally friendly	Complex process	[186]
			Mn	99			
			Ni	98			
			Co	94			
LiCoO$_2$	Acid leaching	Addition of mild organic acids (iminodiacetic and maleic)	Li	99	Environmentally friendly	Low Cobalt recovery rate	[187]
			Co	91			
LiCoO$_2$	Acid leaching	Addition of HNO$_3$	Li	85	Good electrochemical performance of the recovered material	Low recovery efficiencies	[58]
			Co	85			
LiCoO$_2$	Mechanochemical pretreatment/l	Magnetic stirring; constant	Li	77	Low energy consumption	Low efficiency for lithium recovery	[188]
			Co	91			
			Mn	100			
			Ni	99			

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	eaching with HNO_3	temperature (25°C)					
$LiCoO_2$	Ultrasonic treatment; acid dissolution; precipitation	Use of H_2SO_4	Li	95	High recovery efficiency	High temperatures needed	[189]
			Co	99			
$LiCoO_2$	Re-synthesis by acid leaching and calcination	Addition of citric acid; calcination at 450°C	$LiCoO_2$	-	Almost the same performance when compared with the original materials	High temperatures needed	[190]
$LiCoO_2$	Re-synthesis by vacuum-assisted heat-treating and solid-state reaction	Heat treatment in vacuum at 600°C;	$LiCoO_2$	-	Simple process	Low discharge capacity of synthesised materials	[191]
$LiCoO_2$	Hydrothermal reaction	Immersion in LiOH solution, at 200°C	$LiCoO_2$	-	Allows separation and renovation in one step	Full separation is not achieved	[192]
$LiCoO_2$	Grinding; water leaching	Addition of waste PVC	$LiCl$, $CoFe_4O_6$	-	Low cost	Low Co recovery efficiency	[193]
$LiCoO_2$	Ultrasonic radiation	Addition of LiOH; ultrasonic power=800 W	$LiCoO_2$	-	Simple method	High energy consumption	[194]
$LiCoO_2$	Thermal decomposition; solid-state reaction	Decomposition at 700°C	$LiCoO_2$	-	Effective recovery of nonstoichiometric, disordered and deformed materials	Requires high temperatures	[126]
$LiCoO_2$	Supercritical fluid extraction	Addition of supercritical CO_2	Co	95	Reduces the amount of H_2O_2 needed	Energy demanding	[195]
$LiCoO_2$	Electrodeposition	pH=5.4; potential of -1V	Co	96	Simple method	Energy demanding	[196]

LiCoO$_2$	Smelting reduction	1550°C in Ar atmosphere, Addition of CaF$_2$ and CaCl$_2$	Co	99	High recovery efficiency	High temperatures needed	[197]
			Ni	99			
			Mn	99			
			Li	99			
LiCoO$_2$	Solvent method	Addition of DMF; thermal treatment at 300°C	LiCoO$_2$	-	Low cost	High temperatures needed	[198]
LiCoO$_2$	Spouted bed elutriation	Air velocity from 1 to 21 m/s	LiCoO$_2$	-	Inexpensive	Low recovery efficiency	[199]
LiCoO$_2$	Mineral processing	Crushing; sieving	Cu	90	No need for chemical solutions	Energy demanding	[200]
			Co	94			
			Al	94			
LiCoO$_2$, CoO	Vacuum pyrolysis; Oxalate leaching	High temperatures; Addition of Oxalate and H$_2$O$_2$;	CoC$_2$O$_4$.2H$_2$O	98	Environmentally compatible	High energy consumption	[201]
LiCoO$_2$, graphite	Assisted flotation	Addition of Fenton reagent	Co	99	Allows simultaneous recovery of anode and cathode materials	The separation process is not very effective	[202]
			Mn	89			
			Cu	95			
			Al	88			
LiFePO$_4$	Acid leaching	Addition of H$_3$PO$_4$	FePO$_4$.2H$_2$O	75	Recovered materials with good electrochemical performance	Low recovery efficiency	[203]
LiFePO$_4$	Acid leaching	Addition of citric and malic acid	Li	95	Environmentally friendly	Multistep process	[204]
			Cu	97			
			Al	47			
			Fe	4			
			P	1			
LiFePO$_4$	Acid leaching		Li	95			[205]

		Addition of methyl sulfonic and p-toluene sulfonic acids	Fe	95	Use of weak acids	Low battery efficiency	
$LiFePO_4$	Thermal treatment	Heating at high temperatures (400-600°C)	$LiFePO_4$	97	Environmentally friendly	High Energy demand	[206]
$LiFePO_4$	Thermal treatment and acid dissolution	Annealing at 700°C; Addition of HCl	$FePO_4.2H_2O$	-	Green process	High temperatures needed	[207]
$LiFePO_4$	Solution-precipitation	Addition of H_2SO_4	$FePO_4$	98	Good electrochemical performance	Use of toxic reagents	[208]
		Addition of Na_2CO_3	Li_2CO_3	97			
$LiFePO_4$; $LiMnO_2$	Leaching-flotation-precipitation	Addition of HCl; Addition of $[Hbet][Tf_2N]$, n-butyl xanthate and a-Terpineol; Addition of $KMnO_4$	Li	81	High purity recovered metals	Low recovery efficiencies	[209]
			Fe	85			
			Mn	81			
$Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$	Acid leaching	Addition of lactic acid	Li	98	Environmentally friendly	Complex process	[210]
			Ni	98			
			Co	99			
			Mn	98			
$Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$	Acid leaching	Addition of $(NH_4)_2SO_3$	Ni	95	Selective leaching of different metals	Low Mn leaching efficiency	[211]
			Co	88			
			Li	97			
$Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$	Acid leaching	Addition of trichloroacetic acid	Ni	93	High selectivity	Low Al leaching efficiency	[212]
			Co	91			
			Mn	89			
			Li	99			
$Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$	Acid leaching	2 M H2SO4, 5 vol% H2O2, 60 C, 300 rpm, 50 g/500 mL, and 2 h.	Li	98	High recovery percentage	acid use and long time	[213]
			Co	98			
			Mn	98			
			Ni	98			
$Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$	Acid leaching	Addition of H_2SO_4	$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$	-	Good electrochemical	Complex process	[214]

					performance of the recovered material		
Li(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)O$_2$	Acid leaching	Addition of nitric acid	LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$	-	Simple and cheap method	Low performance of the recovered materials	[215]
Li(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)O$_2$	Microwave carbothermic reduction, acid leaching	Microwave power of 100-700W for 30 min; addition of fumaric acid	Co	98	High efficiency	High energy consumption	[216]
			Ni	98			
			Mn	96			
LiCo$_{0.415}$Mn$_{0.435}$Ni$_{0.15}$O$_2$	Acid leaching	3 mL 30% H$_2$O$_2$ in 100 ml of 2 M HNO$_3$ heated at 70 °C	-	-	synthesise cathode material	Very specific and complicated	[13]
LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$	Acid leaching	Addition of HCl	Co	~100	High recovery rates	Low purities on the obtained metals	[217]
			Ni	99			
Li(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)O$_2$; LiCoO$_2$; LiMnO$_2$	Selective precipitation	Addition of DMG reagent	Ni	98.7	High selectivity	Use of toxic reagents	[218]
		Addition of Co-D2EHPA	Mn	97.1			
		Addition of [(NH$_4$)$_2$C$_2$O$_4$]	CoC$_2$O$_4$.2H$_2$O	98.2			
		Addition of Na$_2$CO$_3$ at 95°C	Li$_2$CO$_3$	81.0			
Li(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)O$_2$	Hydrometallurgical leaching	Addition of citric acid	Li	93	Environmentally friendly	Lower electrochemical performance	[219]
			Co	99			
Li(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)O$_2$	Solvent dissolution; heat treatment	Addition of NMP; calcination at 800°C	LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$	-	High discharge capacities	High temperatures needed	[220]
Li(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)O$_2$	Solvent extraction	Addition of DH2EHPA and kerosene	Mn	~100	Low temperatures required	Complex process	[221]
			Co	99			
			Ni	85			
Li(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)O$_2$	Reduction roasting	Roasting at 650°C for 3h; Leaching with H$_2$SO$_4$	Ni	99	High recovery efficiencies	Requires high temperatures	[222]
			Co	99			
			Mn	99			
			Li	85			

α-MnO$_2$	Thermal regeneration	Addition of dimethyl carbonate, heating at 300°C	α-MnO$_2$	-	Allows several regenerations	High temperatures needed	[125]
Mixed cathode materials	Acid leaching	4M sulfuric acid and 30wt% hydrogen peroxide (2-3 hours at 70-80ºC)	Ni	100	unspecified cathode material, low temperature	just focus on recycling the active material, acid use	[168]
			Mn	100			
			Co	100			
			Li	80			
Mixed cathode materials	Acid leaching	Addition of (NH$_4$)$_2$SO$_3$, (NH$_4$)$_2$CO$_3$	Ni	25	High Cu leaching efficiency	Low efficiency for other metals	[223]
			Co	80			
			Cu	100			
Mixed electrode materials	Acid leaching	Addition of acids produced by *Aspergillus niger*	Li	~100	Environmentally friendly	Low leaching efficiencies for some metals	[224]
			Mn	77			
			Ni	54			
			Co	64			
			Al	75			
			Cu	~100			
Mixed electrode materials	Leaching/ precipitation with HCl	Addition of hypochlorite	Mn	>99	High selectivity	Different optimal conditions for each metal	[225]
		Addition of NaOH at pH 4.5	Al(OH)$_3$	<1			
		Addition of NaOH at pH 5.5	Cu(OH)$_3$	<1			
		Addition of Na$_2$CO$_3$	CoCO$_3$	>99			
		Addition of Na$_2$CO$_3$	Li$_2$CO$_3$	>99			
Mixed electrode materials	Hydrometallurgical	Leaching with NaOH and H$_2$SO$_4$; Precipitation with (NH$_4$)$_2$C$_2$O$_4$ solution	CoC$_2$O$_4$	-	Simple process	Energy demanding	[226]
Mixed electrode materials	Grinding flotation	Using of Hardgrove and flotation apparatus	LiCoO$_2$	49	No use of toxic reagents	Low recovery efficiencies	[227]
			Graphite	74			
Mixed electrode materials	Oxygen-free roasting, wet magnetic separation	30 minutes at 1000°C	Co	95	No need for chemical solutions	High temperatures needed	[208]
			Li	98			
			Graphite	91			

Mixed spent batteries	Acid leaching	Addition of H_2SO_4	Mn	65	Separation of various metals with one process	Low recovery efficiencies for Mn and Ni	[228]
			Cd	99			
			Zn	100			
			Co	74			
			Ni	68			

3.5.2.1.   Chemical methods: leaching

Hydrometallurgical processes are and have been intensely investigated. Ni, Co, Li and Mn can be recovered from disposed of LIBs in a sulfuric acid leach mixture [229]. The selective precipitation of the metals using different agents, dimethylglyoxime reagent for Ni, di-(2-ethylhexly) phosphoric acid (D2EHPA) for Mn, ammonium oxalate solution for Co and saturated sodium carbonate solution for Li. This allowed high recovery efficiencies (98.7% for Ni, 98.2% for Co, 97.1% for Mn and 81% for Li) [218].

Hydrometallurgy is also reported in the recovery of cobalt in spent LIBS (LIBs) through sulphuric acid-hydrogen peroxide system, producing cobalt up with purity up to 99.50%, determined by 0.5 mol.L^{-1} oxalic acid solution [177]. The addition of a microwave irradiation step to the process proved to increase the recovery efficiency [216].

An efficient hydrometallurgical recycling process including pre-treatment has been developed attending to the used electrodes, showing the possibility to recover, in a single process, high-grade graphite, cathode metals and lithium carbonate. The leaching efficiencies for metals (Co, Ni, Cu and Li) are in the range of 98.6–99.9 % under the reported optimum conditions: 80 ℃, 50 g.L^{-1} of hydrogen peroxide, 2 mol.L^{-1} of sulphuric acid or 4 mol.L^{-1} of hydrochloric acid in 2 h [230]. The introduction of a mechanochemical pretreatment before the leaching steps can increase these efficiencies further, to near 100% [188].

A study of the optimal conditions in Li and Co recovery from cathode active materials was performed. The use of oxalate as a leaching agent and precipitant element proved to be effective, especially at high concentrations and higher temperatures [201]. Hydrochloric acid [172, 173, 217, 225], lactic acid [210], citric acid (Figure 18) [170, 185, 186, 219], nitric acid [58, 184], sulfuric acid [178-180, 189, 228], oxalic acid [175] and Cyanex 272 [182, 183, 231] are some of the acids that can be used effectively to extract Li, Co or Mn at high efficiency and low energy consumption, due to the absence of thermal processes. Mild organic acids, such as iminodiacetic and maleic acid, are also environmentally friendly alternatives, although their efficiencies are lower than the stronger acids reported before [187].

The acids used in the leaching process can also be produced biological activity with satisfactory results [224]. Combining oxalic acid and malic acid allows the production of cobalt oxalate, which can be used as a precursor for the synthesis of $LiCoO_2$, without the need to use Hydrogen peroxide as reducing agent [181]. The association of glucose with phosphoric acid to reduce cobalt (III) into cobalt (II) was reported. At the end of the

leaching process oxalic acid was added, in order to precipitate the Co with an efficiency of 98%, as Co-oxalate [176].

Fenton reagent can be successfully applied in the separation of $LiCoO_2$ and graphite using assisted flotation methods [202] The ratios of Fe^{2+}/H_2O_2 and that of liquid/solids at room temperature have investigated. The optimum conditions are such that the Fe^{2+}/H_2O_2 ratio is 1:120, and the liquid-solid ratio is 75:1 so that most of the layer coating electrode materials surface based on organic materials can be removed [202].

A hydrothermal method with immersion in LiOH aqueous solution allows the simultaneous regeneration and partial separation of $LiCoO_2$ from spent electrodes [192]. The use of supercritical fluids proved to significantly reduce the leaching time and the amount of H_2O_2 needed for the effective recovery of Cobalt [195]. Just like $LiCoO_2$, $LiFePO_4$ can also be successfully leached using different agents such as phosphoric acid [203]. The leaching methods for the recovery of $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ active material involve the use of nitric acid [215]. Work on this active material showed that the optimum conditions by leaching methods are treatment with 2 M H_2SO_4, 5 vol % H_2O_2, 60 °C, 300 rpm, 50 g/500 mL, reaching leaching efficiencies of valuable metals (Co, Li, Ni, Mn) over 98 %, with concentrations of Co 10.4 $g.L^{-1}$, Li 12.3 $g.L^{-1}$, Ni 16.1 $g.L^{-1}$, Mn 14.5 $g.L^{-1}$, and Al 0.3 $g.L^{-1}$, respectively [213]. Also, for this active material, a new process for the synthesis of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ from valuable recycled metals of waste LIBS by citric acid as both a leaching and chelating agent was developed. NMP was used to separate the active material from the aluminium foil. Then the leaching process was carried out with 0.5-2.0 $mol.L^{-1}$ concentrations of citric acid, also varying the H_2O_2 concentration (0-25 Vol.%). Some parameters, including time and temperature, were variated to optimize the process [232].

Electrodeposition with 99% Al working electrodes and an area of 0.40 cm^2 shows promising results under specific conditions (pH=5.4 and voltage applied of -1 V), with efficiencies up to 96% for metals [196]. Methods of oxygen-free roasting and wet magnetic separation were developed to recycle Li, Co and graphite. The main advantage of these methods is that they prevent the addition of chemical solutions to the process, which means that there are fewer costs in the treatment of waste solutions, making these techniques more environmentally friendly alternatives [208].

Xu et al. developed a method to recover $LiCoO_2$ from spent LIBs using DMF and a thermal treatment. This method has a low cost, and the recycled $LiCoO_2$ can be

successfully used in Ni/Co batteries as negative materials (cathode electrode) with high efficiencies [198].

Another approach was developed for spent $LiCoO_2$ batteries which were dismantled, separated and recycled without secondary pollution, avoiding the production of residues as acids or other subproducts from recovery processes [233]. The electrochemical process of Etoile-Rebatt aqueous solution technology enabled the recovery and renovation of $LiCoO_2$ exhibiting an initial discharge capacity of 134.8 mAh.g^{-1}, and a discharge capacity retention of 95.9% after 50 cycles [234]. Wet and dry crushing methods have been adopted to experiments on recycling of $LiCoO_2$ material [133]. It was demonstrated that the recycling of $LiCoO_2$ cathode material can yield $Co(OH)_2$ and Co_3O_4 films for supercapacitors applications [235] where 10.0 g of the cathode material were dissolved in 1.0 L of HNO_3 3.0 mol.L^{-1} and stirred for 2 h at 80 ℃ [236] and alkaline medium (KOH 6 mol.L^{-1}) [237].
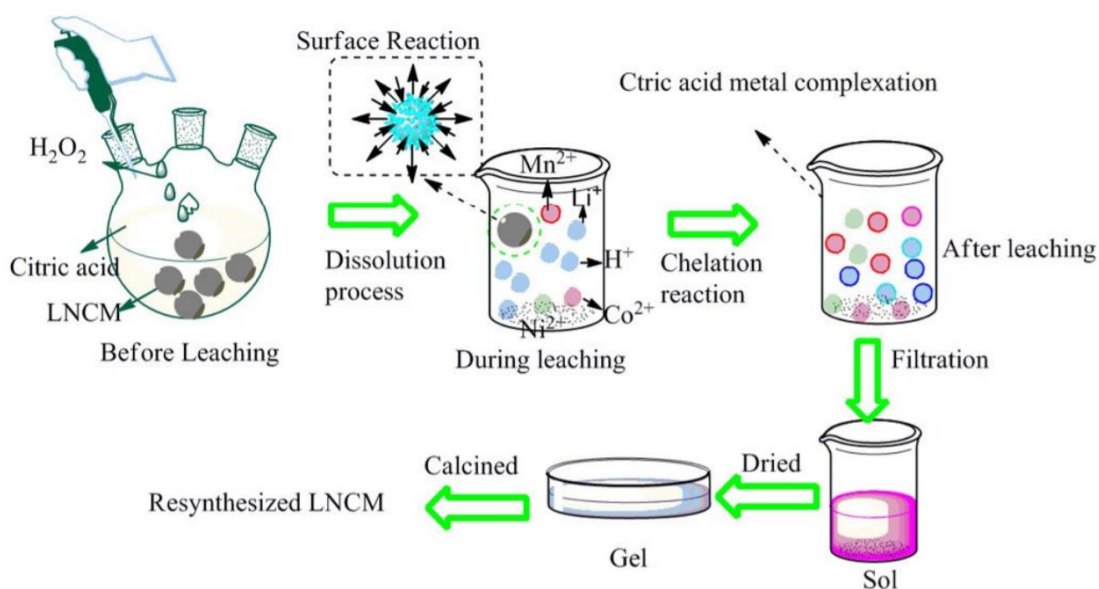

Figure 18 - Schematic diagram of the proposed process of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ active material resynthesis [232].

The preparation of a crystalline $FePO_4 \cdot 2H_2O$ phase with lithium sources from spent batteries can be used for the optimised synthesis (heat treatment with best results at 700 °C) of carbon-coated $LiFePO_4$ regenerated active materials. It was found that the prepared powder presents satisfactory electrochemical performances, highlighting the discharge capacity of 140 mAh·g^{-1} at 1C, and high capacity retention (99%) [207]. Simple thermal processes with high-efficiency rates can recover LiFePO4 cathode materials. However, the high temperatures needed to decompose the binders make this process energy costly

[206]. An optimised and simple technique involving dissolution and precipitation with PEG-6000 surfactant at pH 2, for recovery and regeneration of LiFePO$_4$ cathodes was studied, with a focus on the reducing of the cost and lowering the resulting material waste. The regenerated carbon-coated LiFePO$_4$ active material was then synthesised by carbon thermal reduction, ultimately leading to an excellent electrochemical performance on battery tests, very similar to the conventional ones (120.4 mAh.g^{-1} for the recovered cathodes and 121.5 mAh.g^{-1} for a commercial one, at 1C rate) [208]. Weak acids can be used as a greener alternative to the leaching process, despite the lower efficiencies achieved [205].

Different separation and heat treatment methods for the recovery and regeneration of Li(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)O$_2$ active material from electrode scraps were investigated, showing potential for satisfactory electrochemical battery performance. Some authors [238] re-synthesized Li(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)O$_2$ after recovering the materials. High recovery efficiency (>99% for all the metals) was achieved, showing that their recycling process is practical and commercially viable [238]. The solvent dissolution in NMP and calcination at 800°C presented the highest reversible discharge capacity, while the direct calcination at 600°C showed the best cycling performance [220]. Solvent extraction methods using D2EHPA and kerosene [221] are effective processes to recover metals from battery scraps. Weng et al. developed a method to regenerate Li(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)O$_2$ with pretreatment, leaching, purification and controlled crystallization-solid state synthesis. This process allows the efficient removal of manganese, maintaining only a small amount in the structure of the produced Li(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)O$_2$. The traces of manganese proved to be beneficial to the cycling performance of recycled cathodes [214]. A three-step process was developed to recover Li, Fe and Mn at high efficiencies, from spent mixed LiFePO$_4$ and LiMnO$_2$ cathodes. The steps included leaching with HCl and H$_2$O$_2$, flotation with the addition of betainium bis(trifluoromethylsulfonyl) imide ([Hbet][Tf$_2$N]) ionic liquid, n-butyl xanthate and α-Terpineol, and finally precipitation with KMnO$_4$ and Na$_3$PO$_4$. This process presents both economic and environmental benefits due to its high efficiency (80.93% for Li, 85.40% for Fe and 81.02% for Mn), and capability to extract several metals at the same time [209]. A combined process with several steps was also studied. The steps included alkali leaching, reduction roasting, carbonated water leaching and sulfuric acid leaching. This method can recover more than 99% of the Co, Ni and Mn content, and also 85.7% of the lithium from the spent LIB [222].

The use of ammonia-based compounds, such as ammonium carbonate and ammonium sulphite as leaching agents instead of acid proved to be effective, with good efficiencies for Ni, Co and Li, of more than 98% [211, 223]. The effect of high temperatures under Argon atmosphere was studied, and proved to significantly increase the recovery efficiency of the metals [197].

Biodegradable trichloroacetic acid was used to dissolve LIB scraps with high leaching rates for Ni, Co, Mn and Li, and low Al leaching (7%) [212]. Bertuol et al. studied the efficiency of the spouted bed elutriation technique, in the separation of the spent LIB materials, were particles of different sizes, shapes and densities are separated by a stream of a fluid in a given direction. By variating the airflow velocity in the equipment, the separation of different types of material (metals, polymers and active electrode materials) was achieved easily and inexpensively [199].

A method of recycling metals from a synthetic LIB waste aqueous solution using phosphonate organic linkers was studied. The linkers act as precipitating agents that react with metals, forming materials with potential application as coordinated polymers. Efficient selective precipitation of Manganese and Cobalt was achieved [239]. The use of Na_2CO_3 as precipitating agent at the first step to obtain Li_2CO_3, followed by a second precipitation with Na_3PO_4 proved to be effective in the recovery of Li_3PO_4, with an efficiency rate of 92% [240].

A green process with prospective environmental and economic significance has been experimentally and theoretically established for the sustainable recovery of metals from spent LIBs. Three leaching systems were explored for the application of different biomass as reducing agents. The powders of waste cathode materials were obtained from a pre-treatment operation. Then, waste cathode materials were dissolved in citric acid ($C_6H_8O_7$, H_3Cit) together with different reducing agents (Tea Waste, Phytolacca Americana branches and hydrogen peroxide). Finally, Co and Li-ions dissolved in the lixivium were treated with oxalic and phosphoric acid solutions to recover Co and Li. H_3Cit (citric acid) & tea waste and H_3Cit & H_2O_2 systems revealed similar leaching abilities (96% Co and 98% Li; 98% Co and 99% Li, respectively), and the recycled citric acid, which is recovered using stronger acids ($H_2C_2O_4$ and H_3PO_4), demonstrates similar leaching capability as fresh acid according to circulatory leaching experiments [241]. Citric fruit wastes can be used to recover spent LIBs with high recovery efficiencies in a green process that involves drying, milling, acid leaching and filtration [204].

$LiCoO_2$ from spent LIB cathodes can also be recovered and successfully used as anode material for Ni/Co power batteries. These batteries use $Ni(OH)_2$ as cathode material and Co-based materials as anode, with KOH aqueous solution as electrolyte [242].

Recently, an innovative approach to recover $LiFePO_4$ batteries was reported. 0.20 M $[Fe(CN)_6]^{3-}$ solution enabled the selective removal of lithium with efficiencies up to 99.8% at room temperature [243].

3.5.2.2.   Physical methods

Physical methods avoid the use of harmful reagents, including concentrated acids and bases. Grinding flotation is a separation process based on wettability differences between the electrode materials, such as $LiCoO_2$ and graphite, which makes some materials to float while others sink. However, the efficiency of this method is somewhat low (49% for $LiCoO_2$ and 74% for graphite) , and it needs further improvement [227]. Zhang et al. studied the use of crushing and separating methods in LIB recycling process. They found that spent LIBs display excellent selective crushing properties, which allowed them to separate different materials based on particle size. By using mineral processing techniques, it was possible to create a systematic procedure for recycling these materials [200].

Figure 19 represents a novel mechanochemical technique based on co-grinding and water leaching to yield LiCl and $CoFe_4O_6$. This method, which can simultaneously recycle battery $LiCoO_2$ and PVC, is very interesting for the industry because it can be scaled up, with good economic feasibility and financial profit (estimated as \$1.07 of profit from the recycling of 1kg of wasted LIBS), derived from the recycling and recovery of lithium. [193]. $LiCoO_2$ electrodes from wasted LIBS can be regenerated, using ultrasonic irradiation for 6, 9 and 12 hours. The authors claim that the renovated batteries can offer excellent charge and discharge performance, with an associated value of 99% of charge efficiency, comparable to the commercial batteries [194]. Vacuum-assisted heat-treating followed by a solid-state reaction at high temperatures also showed some potential, despite the lower discharge capacities obtained [191].

Cathode materials from spent $LiFePO_4$ batteries have also been directly regenerated by a green method at high temperatures. This method avoids the use of acid leaching, using Li_2CO_3 in the regeneration process. A temperature range from 600 to 800 °C was studied. Cathodes recovered at 650 °C presented the best physical, chemical and electrochemical performance [244]. Also for this active material, a green recycling process and a small

scale model line was developed to recycle cathode powders after heat-treatment at high temperatures, especially at 650 °C, cathode powders are effectively repaired and could be reused in Li-ion batteries [245].
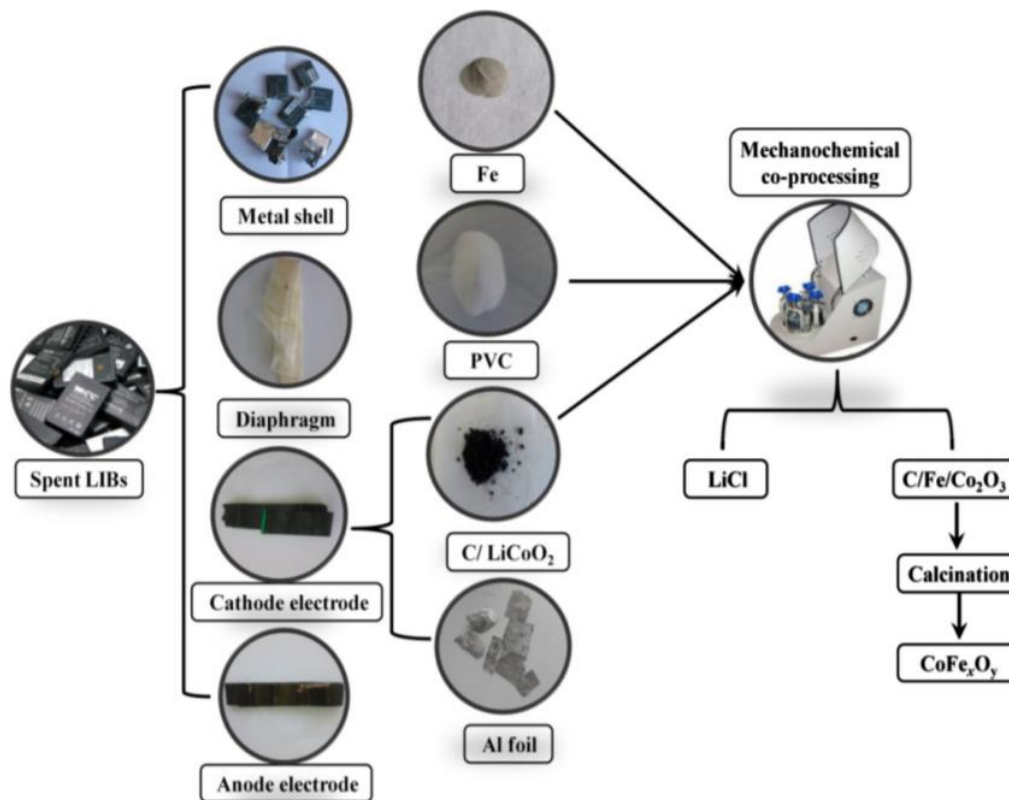

Figure 19 - Process flow of the mechanochemical method for recycling of used LIBS [193].

The production of Manganese oxide cathodes is an interesting approach, as it presents some advantages for the recycling process. These electrodes are binder-free, which means that there is one less component to recover. Also, when thermal treatment is applied, the material recovers nearly its original properties. With an initial discharge capacity of 115 mAh.g^{-1}, and a loss of 72 mAh.g^{-1} after 50 cycles, the regeneration process allowed a recovery for the 101 mAh.g^{-1}. The process can be repeated several times without efficiency loss, making manganese oxide cathodes a promising candidate for green and easily recyclable batteries in the future [125].

A new method, named direct recovery, was developed to overcome the challenges of the cost of recycling processes, that demand high energy consumption and expensive reagents. Direct recovery is a simple technique, consisting in the bathing of the cathode in a chemical solution to regenerate it by changing its chemical composition. This

technique is very appealing, as it has the advantages of being a low-temperature process that uses less energy and has lower emissions and less waste associated compared with hydrometallurgical and pyrometallurgical processes. Direct recovery is a low-cost technique, which contributes to several money savings [246]. The re-synthesis of spent $LiCoO_2$ with a process of leaching followed up by sol-gel method, with calcination at high temperatures, is found to produce excellent cycle life performance in regenerated batteries [190].

3.5.2.3. Second life beyond batteries

Sometimes, there is no need to reuse the battery spent materials in the same application. Some applications require a simpler reconversion of the materials, making them more attractive for the recycling of spent materials. The active material lithium cobalt oxide can be recycled from wasted LIBs and transformed into an electrocatalyst for oxygen evolution reaction with improved properties, such as higher current density (after 500 cycles of charge and discharge) in comparison with pristine active materials [247]. Decomposition of methylene blue dye can be effectively achieved by photo Fenton [248] reaction, using re-synthesised $CoFe_2O_4$ from spent LIBs [248]. Citric acid is also effective in the recovery of compounds with good photocatalytic properties [249].

Recovered cobalt from the acid dissolution of $LiCoO_2$ can be used for electrodeposition in solid oxide fuel cells, enhancing their electrical and morphological properties [250]. Spent cathodes were used to develop a new anode for oxygen evolution reaction. After thermal treatment, graphite was added to the remaining $LiCoO_2$ and Co_3O_4 from the cathode to produce the new electrode [251]. Spent $LiCoO_2$ cathode powders can be used to treat waste waters, particularly to remove sulphur pollutants [252]. These powders are also effective in the removal of levofloxacin hydrochloride in waste waters [253]. Heavy metals in polluted waters can be also removed with powders from spent $LiFePO_4$ cathodes by alkaline leaching process [254]. The application of spent cathode materials in the removal of oxygenated VOCs was studied and proved successfully, by the synthesis of manganese and cobalt based metal oxides catalysts [255].

Another example is the preparation of magnetic NiCo ferrite nanocrystalline particles, manufactured by sol-gel combustion, from wasted LIBs. It is interesting to note that, the variation of the temperature of the calcination process can lead up to controlled changes in the magnetic properties of these ferrites, which can be integrated as high-quality

materials for high-density recording devices, high frequencies devices and magnetic refrigerators [241].

3.5.3. Recovery of anode materials

Typically, the recycling of the anode is based on the recovery of carbonaceous materials, with different methods, such as hydrometallurgical and thermal, as presented in Table 4. Cobalt can be recycled with a hydrometallurgical method, consisting of alkali leaching, reductive acid leaching and chemical deposition of cobalt oxalate. Next, cobalt oxalate can be used for the synthesis of nano-Co_3O_4 as active anode material [226].

The recycling of single-wall carbon nanotubes using acid and thermal treatments has proven economically viable, with the costs of the recovery being significantly lower (50-75%) than the costs of the synthesis of new nanotubes from raw sources [256].

Some materials from other applications can be successfully recycled and reused in LIBs. Slurry wastes from photovoltaics solar cells are good candidates to produce silica-based active materials for anodes [257-259]. This silica can also be obtained in rice husks, that possess large amounts of nanoporous silica layers in their constitution, which allied to the massive rice production worldwide, presents a significant source of silica for application in anodes [260]. Carbon-based active materials can be recycled from various sources, such as tier-rubber- derived materials [261], bioalgal biomass residues [262], pyrolysed fly ash [263], windshield glass of vehicles [264] and spent lead-acid batteries, for being used as anode material [218]. The study of recycled CuCl powders proved that the reuse of this material as the active anode material is viable, with a discharge capacity of 171.8 mAh.g^{-1} at 2C rate [265]. CuCl can also be recycled from spent printed circuit boards, using liquid-phase chemical reduction, and then used as anode material in LIBs with satisfactory performance [266].

Table 4 - Advantages and disadvantages of each reported recycling process for anode materials.

Initial material	Process	Conditions	Obtained Material	Efficiency (%)	Advantages	Disadvantages	Ref
Single-wall carbon nanotubes	Acid reflux/HCl acid	Addition of HCl and HNO_3; vacuum filtration	Single-wall carbon nanotubes	-	Low cost	Loss of charge/discharge efficiency	[256]
Graphite	Acid leaching	filtration	Graphite	>99.5	High recovery rates	High temperatures	[230]
Graphite	Fenton reagent assisted flotation process	Fe^{2+}/H_2O_2 ratio is 1:120,	Graphite	-	Room temperature	Toxic solvents	[202]
Graphite	Ultrasonic vibration and sieving	Nitrogen atmosphere at 1673k for 4h	Graphite	99.5	High recovery rates	High temperatures	[267]
Graphite	Electrolysis/ Precipitation	Addition of Na_2SO_4	Graphite	-	High purity materials	High voltages needed	[268]
Graphite	Sonication/ acid leaching	Thermal treatment at 500°C Addition of H_2SO_4	Graphite	99	High purity	High temperatures	[269]

Graphite is widely used as the anode on LIBs. Recovering battery-grade graphite from used LIB anodes is difficult due to the physicochemical changes occurring to graphite during battery operation. These changes include surface modification of graphite electrodes, graphite oxidation, formation of a solid electrolyte interface (SEI) and co-intercalation of solvent molecules into the structure of graphite [270]. One solution to this problem is the recovery of graphite from other applications outside LIBs. Alternatively, graphite material may be recycled as graphene by a facile treatment of electrolysis. This treatment included a charge to 2.3V in a 120 cycled cell and the electrolysation of the cell during 10 hours using aluminium anode and molybdenum cathode. Finally a last step of ultrasonic cleaning was applied in the cathode material during one hour [271]. Ultrasonic recovery of graphite is achieved by simple ultrasonic vibration in nitrogen atmosphere at high temperatures. This process allows not only the recovery or the graphite but also the

separation of the copper [267]. Anode recycling can include electrolysis processes to remove the Cu foil, and precipitation with Na_2SO_4 to recover the graphite that can be used in new batteries with excellent cycling stability and high coulombic efficiency [268]. The spent graphite can also be reconverted in 2D graphene oxide that can be used for other applications, using a modified Hummers method [272]. Similarly to cathode materials, acid leaching with H_2SO_4 can also be used to recover the graphite, for posterior uses [269].

3.5.4. Separator/electrolyte

Recycling the electrolyte of LIBs is a critical concern. Liu et al. [273] reported a method based in a supercritical CO_2 extraction, resin, and molecular sieve purification, can contribute to producing a regenerated high ionic conductivity electrolyte, almost close to the commercial ones. Figure 20 represents the steps involved in this proposed method, which are supercritical CO_2 extraction to separate the electrolyte, followed by its collection and purification in a glovebox under argon atmosphere. Then the collected electrolytes were electrochemically evaluated, and finally, batteries were assembled and tested. This process leads up to the production of new batteries with satisfactory electrochemical performance [273].
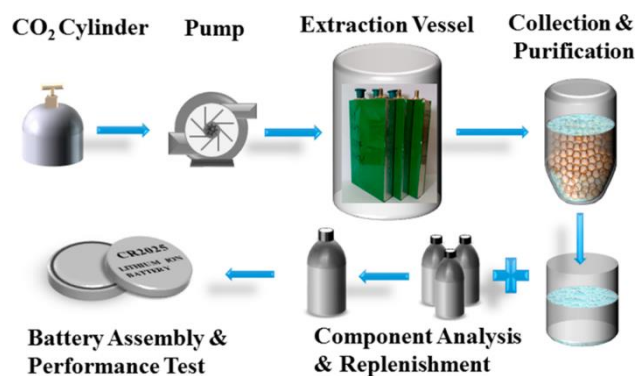

Figure 20 - Schematic representation of reclaimed electrolytes produced from spent LIBs [273].

Electrolytes are a vital component in LIBs. However, their toxic and harmful nature makes the recovery of electrolytes an important environmental issue. An environmentally friendly process to recover electrolyte solutions using extraction with transcritical CO_2 was proposed by Mu *et. al*. This method uses free solvent residues and allows the recovery of organic carbonate solvents from the electrolytes. Pressure plays a crucial role in the

efficiency of the process during extraction, yielding higher efficiencies at higher pressures. On the other hand, lower temperatures increase extraction rates [274].

Electrolyte recovery by cell immersion in a suitable solvent for a few hours has been demonstrated [275]. Different solvents can be used, as long as their boiling point at reduced pressure is below the lithium salt decomposition temperature (~80ºC), so that anhydrous electrolyte may be recovered.

Separators can be recovered using a pneumatic separation method, with an efficiency of about 98%, that avoids the disposal of plastic pollutants. The optimization of the conditions, with flow velocities between 3 cm/s and 7.8 m/s, leads to better recovery efficiency rates [276].

4. Electric vehicle: a case study

Fully battery-powered electric vehicles, which have been considered a promising alternative to internal combustion engine (ICE) vehicles, are finally gaining broad consumer interest thanks to the fast-paced progress in battery technology over the recent years.

It is expected that most of the expected LIB capacity over the next years will be applied to electric vehicles (EV) [99]. As such, it is of great importance to analyse the environmental impact of LIB when used in this application. A more realistic view of the EV environmental impact needs to consider both the impacts throughout the EV life, including during driving. LCA analysis can aid in making informed decisions and recommendations that ensure a sustainable transport sector with a focus on greenhouse gas emissions and energy use.

Electrified transportation offers significantly better energy efficiency over older technologies, namely ICE vehicles. Thus, although highly dependent on the driving style, the energy efficiency of electric vehicles ranges between 75-82%, compared to the meagre 16-25% efficiency of ICEs [277-279]. On top of this, EV drivetrains are much simpler in design and have significantly fewer moving parts compared to ICE drivetrains, which brings additional economical (lower maintenance) and environmental gains [280]. Results from different studies [281, 282] differ on the question of greenhouse gas emissions from electric cars, generally focusing on the use phase and how EVs contribute to the emissions when driving.

Figure 21 summarises the different stages considered in a LIB life cycle assessment. Interactions are shown between the different phases, considering their normal lifespan

flow (production, to use and then end-of-life), as well as new relations that recycling and second-life utilisation brings to the life cycle assessment.
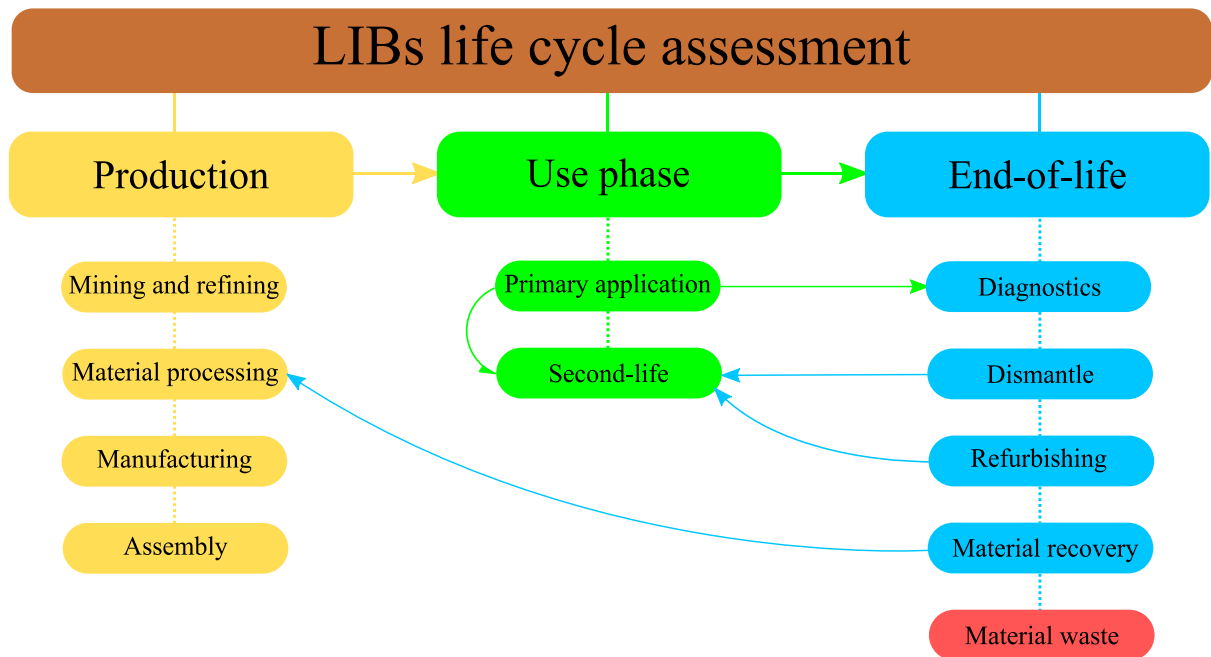

Figure 21. LIB life cycle assessment diagram and the relations between the different stages.

4.1. Battery production

Several works [283-287] have studied greenhouse gas emission during the LIB production stage with substantially different results, mainly due to uncertainty of production as a result of sparse data and pilot-scale methods, differences in material data modelling and approximation of materials to similar ones, and electricity mix.

The electricity mix is a critical factor for greenhouse gas emissions at the production stage. According to Romare *et al.* [288], manufacturing contributes significantly (45-60%) to the total emissions in the production stage, mainly by electricity use, indicating that production site electricity mix is one of the main factors affecting the overall environmental impact of the EV. Assuming a fossil fuel share in manufacturing in the range of 50-70%, it turns out that the contribution of mining and refining to the carbon footprint of LIBs is relatively small (despite the significant environmental impact of fossil fuels). Thus, as the impact of the electricity mix in the production stage depends on the location of the production plants, the emissions from the electricity can vary significantly between countries. The study concludes that greenhouse gas emissions of 150-200 kg CO_2-eq/kWh battery correspond to the greenhouse gas burden of current battery

production, and that it is nearly independent of the cell chemistry (NMC, LFP or LMO) [288].

4.2. Use phase

EV powertrains LIBs do not produce direct emissions in the use phase, which is why they are considered an eco-friendly alternative to internal combustion engine (ICE) vehicles. Furthermore, typical battery-powered EV drivetrains have 90% fewer moving parts [289], require no maintenance such as oil changes or timing belts, and their ability to use regenerative braking saves energy and makes their brake pads last longer, further lowering the usage emissions when compared with ICE vehicles.

However, EVs produce emissions indirectly through the energy sources used to recharge the batteries. Again, the local energetic mix source and their associated emissions are essential to estimate if the environmental impact from use phase emissions footprint may be as bad as that of ICEs.

4.3. Second-life

The continuous growth in EV sales brings about a new question: what do we do with those LIBs that are unsuitable for EV powertrains? Batteries are removed from service due to the capacity loss produced by continuous cycling. It is estimated that after 8 to 10 years of service in EV, batteries no longer to meet the power range required by their users. At that point, however, used EV powertrain batteries still retain about 70-80% of their original capacity. This allows prolonging the life of the batteries by reusing them in less demanding applications – giving them a second-life. Applications such as residential and industrial energy storage, grid stabilisation and storage, mobile energy storage, powertrains for low-speed electric vehicles and forklifts and utility-scale battery storage are the primary examples of potential second-lives for retired LIBs.

Some reports [290] estimate that second-life battery capacity will reach 275 GWh per year by 2030 due to the mass adoption of the EV as eco-friendlier transportation. As the adoption of the EVs started to get noticeable sales to the public in 2010 going forward, the first batch of EV LIBs is reaching their end-of-life status, contributing to a foreseeable increase in the volume of retired batteries.

Currently, several pilot initiatives bring new applications for retired LIBs, away from their primary application. Table 5 summarises some of the second-life initiatives presented by EV manufacturers.

Table 5 –Second-life initiatives proposed by EV manufacturers for retired EV LIBs.

Designation	Promoters	Application segment	Ref.
xStorage	Nissan, Eaton	Residential and buildings energy storage, grid	[291]
4R Energy	Nissan, 4R Energy	Residential and buildings energy storage	[236]
ELSA	The ELSA Consortium (Nissan, Renault, AÜW, European Union's Horizon 2020)	Residential, buildings and energy industrial storage, grid	[237]
The Light Reborn	Nissan	Lighting	[238]
Nissan-FreeWire	Nissan, FreeWire	Mobile energy storage	[239]
Commercial energy storage powered by second-life batteries	Nissan, Green Storage	Grid	[240]
Second-life battery storage for fast-charging stations	Renault, Connected Energy	Utility-scale battery storage	[241]
Second-life smart home battery	Renault, Powervault	Residential energy storage	[242]
Daimler-BAIC	Daimler, BAIC	Grid	[243]
BMW's second-life battery farm in Leipzig	BMW	Grid	[244]
Second-life BMW batteries connected to UC San Diego's grid	BMW, EVgo	Residential energy storage, grid	[245]
Second-Life 2.8 MWh Energy Storage Solution in Hamburg	BMW, Bosch	Grid, fast-chargers energy storage	[246]
Hybrid Car Batteries in Yellowstone	Toyota	Lighting, residential energy storage	[247]
Electrified Vehicle Battery Reuse and Recycling Verification Project	Toyota, Chubu Electric Power	Grid	[248]
Wärtsilä and Hyundai energy storage partnership	Hyundai, Wärtsilä	Utility-stage and commercial energy storage	[249]
360-kWh Mobile Charging Station	Volkswagen	Mobile energy storage	[250]

The LIBs second-life environmental impact is difficult to quantify but extending the useful life of LIBs beyond their original application can reduce the overall impact. The value of second-life batteries is determined by several factors, namely battery design, their condition after their first life, the intended use for the battery in its second-life and the cost/value of recycling. Additionally, there are economic, technical and regulatory factors that impact the difficulty for companies to profit from second-life batteries. However, given that batteries are the most expensive component of an EV, the potential value for retired LIBs remains high as their reuse becomes economically appealing. However, the difficulties in the quality assurance of retired batteries lead to business concerns about the possibility of ending up with lower quality products in second-life applications for other applications, such as mobile phones, computers, and sensors.

4.4. End-of-life

According to a study on the economic feasibility of end of life vehicle LIBs [292], there are three ways to create value from used batteries at the end of their life in electric vehicles because the battery may still be able to store a significant energy level. These options are remanufacturing, repurposing and recycling.

Remanufacturing processes consist in repairing the battery by the replacement of damaged cells and keeping it in use for continuous integration in electric vehicles.

Repurposing by reengineering is a process in which the battery is repaired and then put to a different use than the original one. This includes, for example, integration in stationary systems of renewable energy storage. Last, recycling involves the disassembly of all the components of the battery, safely recovering them, and thus reusing the valuable metals for the synthesis of regenerated materials and batteries.

4.4.1. Remanufacturing

Remanufacturing of spent LIBs to recover their charge/discharge capacity is an important step to reduce the need for new materials extraction and processing. A cost-benefit analysis showed that remanufacturing a battery could save about 60% of the total cost of production of a new battery [293]. Moreover, it is estimated that a remanufacturing rate of 55% can lead to a reduction of the new batteries production needs in 10% [294].

4.4.2. Repurposing

As shown in Figure 21, to use the LIBs in second-life applications, it is essential to diagnose the batteries on removal from the vehicle at the end of their primary application, particularly in terms of their capacity, safety and structural condition. Afterwards, dismantling and refurbishing may be needed depending on the LIBs design and the second-life application at hand. Nonetheless, some initiatives already project the LIBs considering their subsequent second-life application [252]. In this case, a packed module and battery management system was designed to seamlessly transition from vehicle energy storage to stationary energy storage at the end of their vehicle life. Thus, battery design can be optimised not only for their primary application but also for their intended second-life application, minimising or even excluding adaptation work between applications.

4.4.3. Recycling

End-of-life treatment can provide the recycling of materials and can be advantageous from both the environmental and resource conservation perspectives. During this phase, recycled materials can replace primary materials, supporting the preservation of natural resources and lowering environmental impact than virgin materials [295].

Recycling of LIB is currently low, mainly driven by legislation. European Union directives regulate environmental regulations, such as end-of-life directives, that require automobile manufacturers to extend the responsibility of their vehicles and products beyond the use phase (directive 2000/53/EC). Car manufacturers are responsible for taking back their products with the end goal of reusing or recycling. Furthermore, Directive 2006/66/EC stipulates minimum recycling rates to minimise the negative impact of batteries and waste batteries on the environment. Specifically, 45% of spent LIBs must be collected, and at least 50% of the average weight of LIBs should be recycled, excluding energy recovery. This way, the current battery recycling market is driven by legislation and metal value.

There are several technologies and combinations of technologies in use or being developed. First, the EV battery packs are disassembled, due to safety reasons, also facilitating the recycling of battery materials. Individual cells are handled next. Although several technologies could be used to recycling LIB cells, pyro-metallurgical recycling is one of the most used at near commercial scale, while hydrometallurgical methods (tables

3 and 4) are still in prototype stages in Europe, while one plant in North America that takes larger volumes [296].

The downside of the pyrometallurgical method, however, is the elevated temperatures required (about 1400 °C), due to the two options of the pyrometallurgical method: direct vacuum evaporation of lithium, or selective entraining gas evaporation of lithium. Lithium is subsequently recovered either via recovery of lithium metal by distillation in vacuum for 120 minutes at 1400°C or in the form of lithium oxide, in the case of the second option of the method [297].

Nowadays, the LIBs used in the automotive industry are not being recycled. One reason could be the relatively low penetration of EVs in the global market, together with the fact that electric vehicles are also made to last the same time of the vehicle itself, so it is expected a lifetime of about 8-10 years for those LIBs, which means that there are not many devices to recycle nowadays. However, soon the situation will change, mainly because of the increase in the electric vehicles market share in recent years.

Batteries used in electric vehicles are considered at the end cycle life when they keep approximately 80% of their original performance. Packs of these batteries can be reconverted and applied in energy storage systems. This application can duplicate the life cycle of these devices. However, the batteries need to undergo a reconversion process to change their purpose from transportation to stationary use [298].

5. Final remarks

The increasing relevance of LIBs is strongly related to interconnectivity and mobility, being present in many daily used electronic mobile devices. With the current development of the electric mobility the demand for more efficient and sustainable LIBs will rise in the coming years. This increase in demand boosts the prices of scarce materials such as cobalt, nickel and lithium, to name the most critical ones. Mining, extraction and purification of these metals to battery-grade quality are highly damaging from an environmental viewpoint. Despite all the effort required to produce those LIBs, the valuable materials involved are landfilled and become irrecoverable only a couple of years later. To make matters worse, the environment is damaged further as electronic waste, which includes LIBs, is one of the most polluting on earth.

Battery recycling is, therefore, an urgent financial and environmental obligation. Recycling begins with the consideration of giving batteries a second life before dismantling. Most cells still hold over 80% of their original capacity at the time of their disposal. They are, by no means, useless. Some examples of second-life applications are powertrains for low-speed vehicles or residential and industrial energy storage. It is at their end of life that they can be taken apart to recover their highly valuable components and materials. At this stage, battery condition is newly assessed to decide the most suitable recycling approach. The main options are so-called pyro- and hydrometallurgical methods and direct recycling. Pyro- and hydrometallurgical processes aim to recover the raw materials used in the batteries, particularly the metals, so that they can be used again in the production of new cells, or even in other applications that require the same metals. This path allows for high metal recovery rates (above 90%), but it requires high energy and hazardous materials consumption. In contrast, the latter view is about refurbishing some of the battery components, such as the cathode, to be assembled in new batteries. In this case, there is no need to produce a new battery component, reducing the overall energy and hazardous materials consumption, when compared with direct recycling. However, this approach results in lower battery performance. Therefore, pyro- and hydrometallurgical methods are measured in terms of recovery rates, and direct recycling methods are assessed in terms of battery performance. In an environmental context, the main objective must be the reduction of landfill disposal, by incentive the second use of batteries, and adopting recycling strategies after reaching the battery end of life. In the latter, it is relevant to place the recycled materials in advanced stages of the value chain. This means that the early stages of the chain value (mining, refining, production) can be

reduced both at the energetic and material consumption levels, leading to a more sustainable and circular economy model.

However, the production of new batteries is not always the goal. Some parts may find applications outside energy storage field. For example, cathodes may work as catalysts for the degradation of organic material, or as absorbents for heavy metal contaminants.

This work has reported on the most common recycling methods for all battery components, with a focus on cathode active materials. The most studied recycling method is hydrometallurgical, in particular with acid leaching processes. While they lead to high recovery rates, they can be environmentally harmful due to the chemicals involved in the process. In contrast, pyrometallurgical processes operate at high temperatures and are usually associated with high atmospheric emissions.

One of the issues facing the recycling of LIBs is the wide variety of cell designs in terms of materials and construction. This diversity makes it very hard to come up with a valid "universal" recycling process. Perhaps, this is one of the areas where legislation can act to support and encourage the adequate disposal and recycling of LIBs. For instance, directives and national acts regulate the recycling of lead-acid batteries. The reason may be that these devices have been in the market for a long time, but the use of LIBs will continue to grow. Because legislation alone does not work, consumers need to be aware of the importance of recycling, both in economic and environmental terms. Also, business actors need to be able to find the right incentives to re-design or reengineer the battery supply chain into a closed loop. More environmentally friendly materials and processes can be used to create value. In this sense, life cycle assessment, LCA, methods, can be a great assessment tool. The emerging industry of the electric vehicle, EV, represents a huge opportunity to do the right things from the early stages. The rapid shift from petrol to batteries will make it a necessity in the immediate future. Ideally, this should be an international effort addressing the complete LIB supply chain because the environmental and economic implications are global. Mining and purifying scarce metals such as cobalt, nickel and lithium will continue to be necessary. However, recycling can protect the environment by acting as a buffer for the demand of raw materials of natural origin. Thus, recycling LIBs will take a critical role by satisfying a significant part of the lithium demand in future years.

Acknowledgements

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