

Fredrik Nævisdal

# Lithium Recovery from Lithium-Ion EV Battery Waste: A Review of Current Methods and Challenges

Bacheloroppgave i Lektorutdanningen i realfag for trinn 8 - 13  
(kjemi og matematikk)

Veileder: Sulalit Bandyopadhyay

Medveileder: Erik Prasetyo

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Norges teknisk-naturvitenskapelige universitet

Fakultet for naturvitenskap

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Kunnskap for en bedre verden



## Abstract

The burgeoning electric vehicle (EV) industry and the consequent surge in demand for lithium-ion batteries (LIBs) have resulted in a substantial increase in battery waste. Current recycling capacity struggles to keep pace with this mounting waste, and effective lithium recovery remains a challenge in commercial plants. This bachelor thesis provides a comprehensive overview and analysis of existing methods and obstacles associated with lithium recovery from lithium-ion EV battery waste. The primary objectives are to assess the efficiency, environmental impact, and economic feasibility of various recovery methods, as well as to pinpoint key challenges and opportunities for enhancement. The review focuses on three principal lithium recovery techniques: pyrometallurgical, hydrometallurgical, and direct recycling processes. The findings indicate that while pyrometallurgical processes are widely employed, they exhibit high energy consumption and significant environmental concerns. In contrast, hydrometallurgical processes demonstrate greater lithium recovery rates and reduced environmental impact but necessitate extensive pre-treatment procedures. Direct recycling methods, still in developmental stages, hold the potential to address drawbacks of the other techniques but grapple with challenges concerning battery design and low-grade product. This review underscores the imperative for more sustainable and efficient lithium recovery processes and stresses the need to tackle technological and regulatory hurdles to foster a circular economy in the EV battery sector.

## Sammendrag

Den voksende elbilsindustrien og den tilknyttede økningen i etterspørselen etter litium-ion-batterier (LIB) har resultert i en betydelig økning i batteriavfall. Nåværende resirkuleringskapasitet strever med å holde tritt med dette økende avfallet, og effektiv litiumgjenvinning forblir en utfordring i kommersielle gjenvinningsanlegg. Denne bacheloroppgaven gir en omfattende oversikt og analyse av eksisterende metoder og hindringer knyttet til litiumgjenvinning fra litium-ion-batteriavfall fra elbiler. Hovedmålene er å vurdere effektiviteten, miljøpåvirkningen og økonomisk gjennomførbarhet av ulike gjenvinningsmetoder, samt å identifisere nøkkelutfordringer og muligheter for forbedring. Gjennomgangen fokuserer på tre hovedteknikker for litiumgjenvinning: pyrometallurgiske, hydrometallurgiske og direkte gjenvinningsprosesser. Funnene indikerer at selv om

pyrometallurgiske prosesser er mye brukt, har de høyt energiforbruk og betydelige miljømessige bekymringer. I motsetning til dette viser hydrometallurgiske prosesser større litiumgjenvinningsrater og redusert miljøpåvirkning, men krever omfattende forbehandlingsprosedyrer. Direkte gjenvinningsmetoder, som fortsatt er i utviklingsstadiene, har potensiale til å håndtere ulempene med de andre teknikkene, men sliter med utfordringer knyttet til batteridesign og lavverdig produkt. Denne gjennomgangen understreker behovet for mer bærekraftige og effektive litiumgjenvinningsprosesser og understreker behovet for å takle teknologiske og regulatoriske hindringer for å fremme en sirkulær økonomi i EV-batterisektoren.

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# 1 Introduction

The rapid transition towards electric vehicles (EVs) is driven by the goal of reducing greenhouse gas emissions and foster a more sustainable transportation sector. Lithium-ion batteries (LIBs) has become the only viable energy storage solution for EVs, because of their high energy density, extended cycle life, and impressive power capabilities. This has led to the production and use of LIBs experiencing an accelerating increase in recent years. Even the possibility of lithium scarcity is becoming a relevant issue. The International Energy Agency's (IEA) net-zero emission scenario stipulates that all passenger car sales must transition to electric vehicles by 2050.<sup>1</sup>

In principle, extracting the metal from battery waste offers a sustainable alternative to obtaining it from primary reserves. While significant advancements have been made in lithium recovery research, the extraction process is still intricate and associated with considerable environmental impact.<sup>2</sup> End-of-life (EOL) EV LIB is currently recycled by mainly two methods, pyrometallurgy and hydrometallurgy. Pyrometallurgical methods are usually energy intensive, release carbon dioxide from burning graphite and other organic feed and lose valuable material in slag contributing to resource depletion. Hydrometallurgical methods on the other hand, can produce large amounts of chemical waste that have to be treated or recycled. Although less energy-intensive, hydrometallurgy usually also require some form of pyrolysis, often resulting in the formation of dangerous gases.<sup>3</sup>

Lithium recovery from EOL LIBs not only addresses the environmental concerns associated with waste accumulation, but also mitigates the risk of lithium supply shortages and price fluctuations. By efficiently recovering high quality lithium from battery waste, countries can reduce their reliance on imported lithium resources, foster a circular economy, and promote the development of sustainable supply chains.<sup>4,5</sup> To kickstart this, various countries and regions have implemented regulations and set material recovery targets.<sup>6,7</sup>

The primary objective of this thesis is to provide a review of current methods and challenges related specifically to lithium recovery from EV LIB waste. By evaluating each step in several



LIB recycling methods based on their effect on lithium recoverability, this thesis aims to inform and give an introductory overview to fellow students, researchers and interested parties, on how to effectively approach lithium recoverability.

The review comprises five main sections. The initial section presents an overview of LIBs, delving into their composition and various types. Following this, the lifecycle and path of lithium, from its source to the recycling plant, are examined. Subsequently, a technical analysis of both commercially operational and developing recycling methods is provided. Finally, the methods that have been presented are reviewed and discussed to find areas of improvement and challenges in regard to their recovery of lithium.

## 2 The physical configuration of the electric vehicle lithium-ion batteries

### 2.1 Battery Cell

A lithium-ion battery can be broken down into individual cells, which are the basic building blocks of the battery. Each cell consists of several key components that work together to store and release electrical energy. The primary components are the two electrodes: a cathode made of a lithium metal oxide, and an anode made from natural graphite or other carbon-based materials that contain high-energy sites for the lithium-ions. When the batteries go from a charged to a discharged state, the lithium-ions travel from their high-energy sites in the graphite layers through the separator and back to their positions in the lithium metal oxide cathode.<sup>8</sup> Schematically illustrated in figure 1.

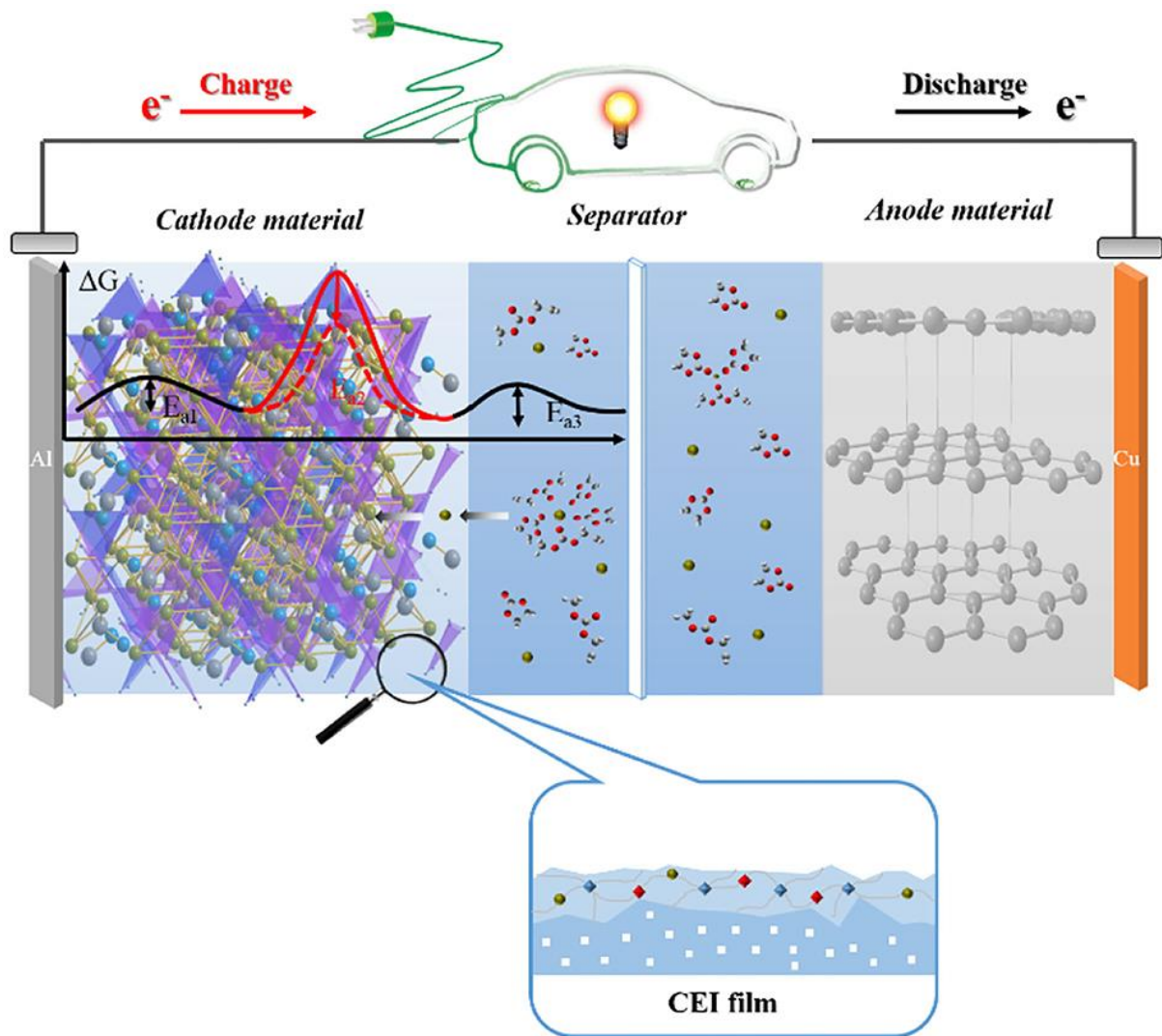


Figure 1: A diagram of a lithium-ion battery. The lithium-ion batteries travel from the cathode material through the separator to the graphite anode during charging, and back during discharge. The CEI film is the Cathode Electrolyte Interface film.<sup>9</sup>

## 2.2 Battery Components

During the manufacturing process, the electrode materials are mixed with a binder, a usually organic compound like polyvinylidene fluoride (PVDF) that makes the electrode material adhere to the current collector. The current collector ensures the flow of electrons from each electrode through the external circuit to the other electrode. The cathode-binder slurry is applied to a current collector made of aluminium, while the anode-binder slurry is applied to a current collector made of copper.<sup>3</sup>

In addition to the electrodes, binder, and current collectors, a LIB cell also contains an electrolyte and a separator. The electrolyte is a liquid, gel-like, or ceramic substance containing lithium salts dissolved in an organic solvent, which is imbedded in the separator to enable the flow of lithium ions between the cathode and anode during charging and discharging. The separator is a thin, porous membrane made of polymer materials, such as polyethylene (PE) or polypropylene (PP), that physically separates the cathode and anode to prevent electrical short circuits while still allowing the passage of lithium ions.<sup>3</sup>

The battery cell is encased in a protective outer layer, which provides structural support, protects the cell from external factors, and helps contain the electrolyte. The casing can be made of steel (for prismatic and cylindrical cells) or a multi-layered laminate material (for pouch cells). See figure 3.<sup>2</sup> Prismatic and pouch cells are called stack cells and have similar cell configuration and differ mostly on the module level. The stack and cylindrical cell configurations are shown in Figure 2.<sup>10</sup>

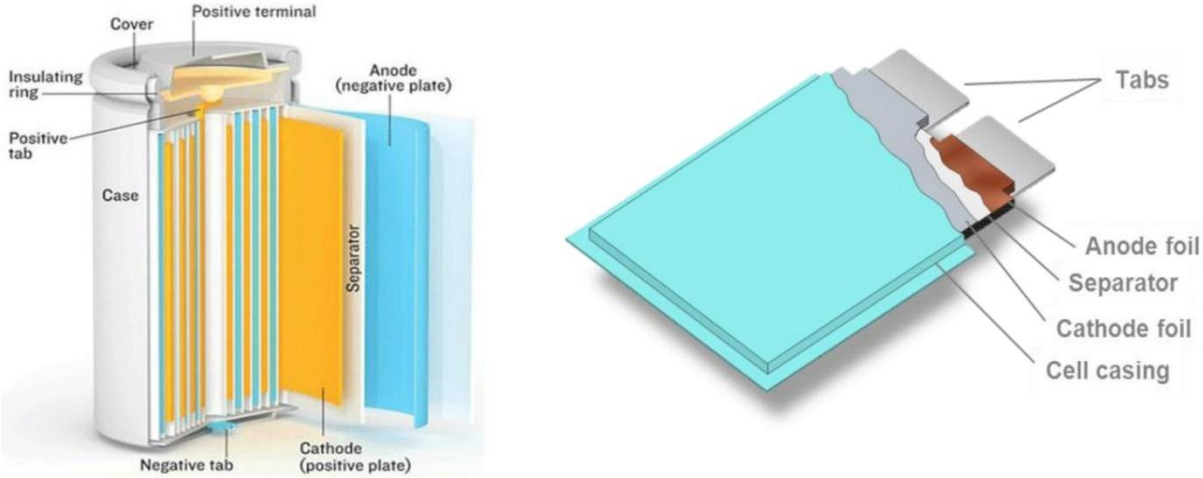


Figure 2: LIB cylindrical and stack cell configuration.<sup>10</sup>

2.3 Battery pack assembly

Individual cells are grouped into modules, with cells connected in series or parallel configurations to achieve the desired voltage and capacity. Modules, consisting of several to hundreds of cells, are then combined and connected electrically to form the battery pack, as shown in figure 3.<sup>2</sup> The assembled battery pack is enclosed in a protective casing made of

materials like plastics, steel, aluminum, or plastic-metal composites, providing structural support and protection.<sup>2</sup>

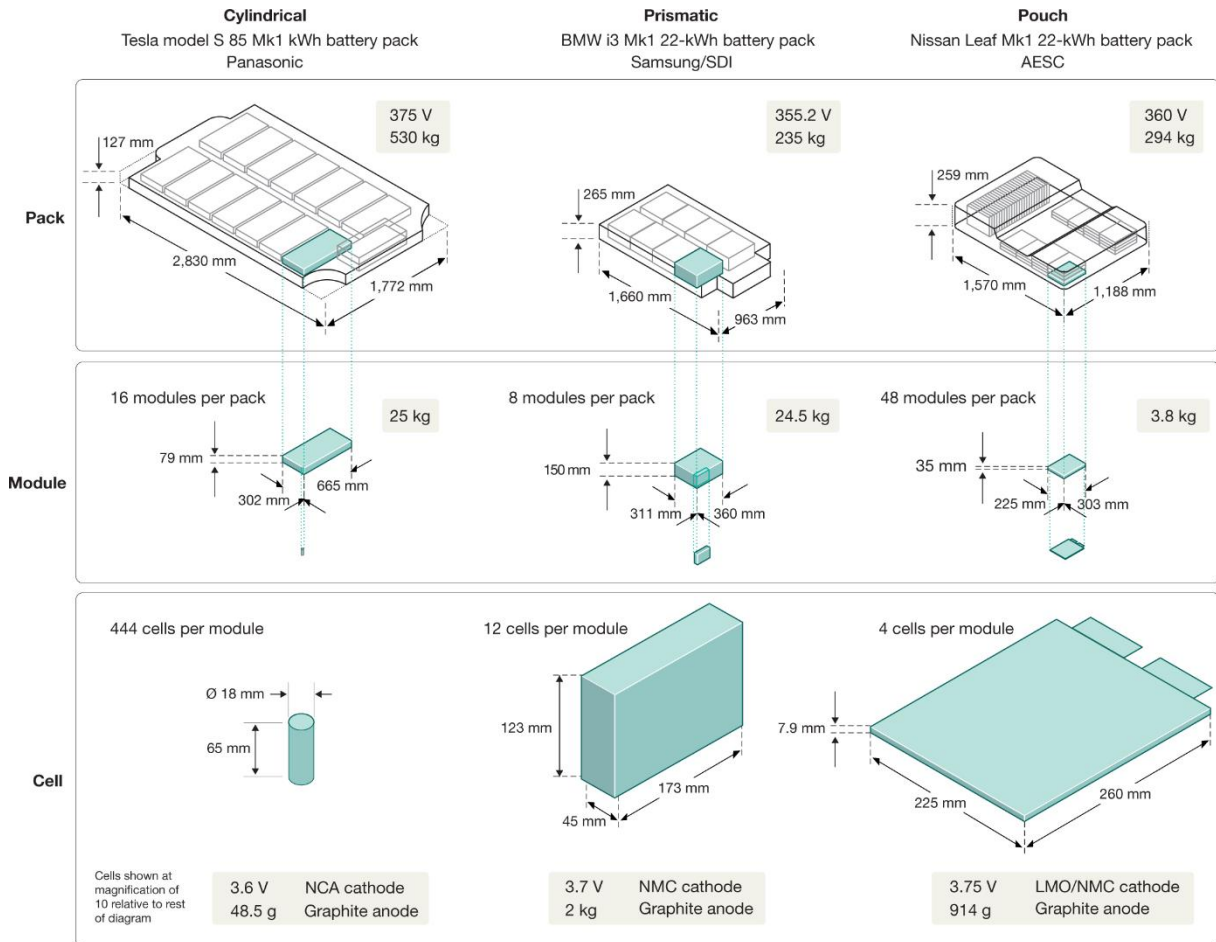


Figure 3: Examples of three different battery packs and modules (cylindrical, prismatic and pouch cells) in use in three popular electric car models.<sup>2</sup>

## 2.4 Cathode Chemistries

Lithium-ion batteries encompass various cathode chemistries and physical configurations, with each LIB type named according to its cathode composition. For the purposes of this thesis, the most significant and relevant chemistries include LiNiMnCoO<sub>2</sub> (NMC), LiNiCoAlO<sub>2</sub> (NCA), LiMn<sub>2</sub>O<sub>4</sub> (LMO), and LiFePO<sub>4</sub> (LFP), see figure 4. Each of these types possesses several variations, with NMC being particularly diverse, including NMC111, NMC532, NMC622, and NMC811. The numbers denote the mole number and relative proportions of each element; for instance, NMC111 contains equal parts of nickel, manganese, and cobalt, while NMC532 comprises five parts nickel, three parts manganese, and two parts

cobalt.<sup>2</sup> The transition from NMC111 to NMC811 reflects the ongoing trend to reduce cobalt usage, primarily due to its high cost and classification as a conflict mineral, predominantly sourced from areas with political risk.<sup>3</sup>

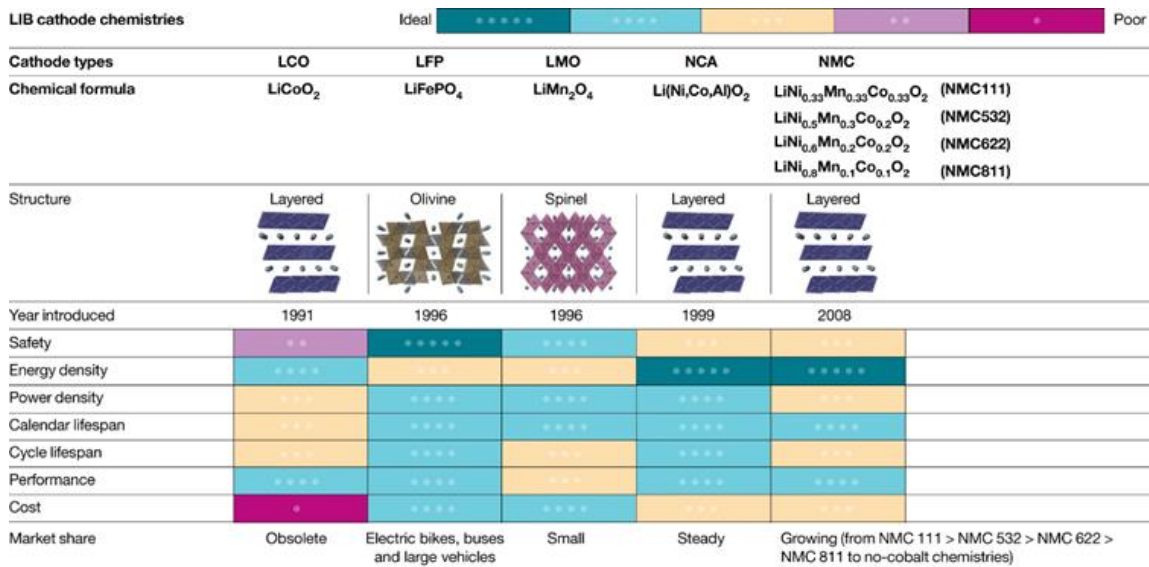


Figure 4: LIB cathode chemistries, their properties and market share.<sup>2</sup>

### 3 Lithium lifecycle: following lithium from source to recycling

#### 3.1 Lithium

Lithium is widely used in batteries to enhance their electric performance, particularly in weight sensitive applications. Owing to it having the lowest standard reduction potential among all elements, lithium enables the maximization of cell potential. Additionally, as the lightest metal and possessing one of the smallest ionic radii among cations, lithium imparts high energy-to-weight ratios to lithium-based electrode materials. Moreover, its small size enables lithium to occupy a greater number of sites, facilitating a diverse range of material structures.<sup>3</sup>

#### 3.2 Raw production

Lithium is primarily extracted from various lithium-bearing minerals. Spodumene is the most common source, but other notable minerals containing lithium include petalite, amblygonite, lepidolite, and eucryptite (refer to table 1 for their respective lithium content). As of 2019,

Australia stands as the world's largest lithium producer, accounting for approximately 43.5% of the global lithium production. The country's substantial output is attributed to several large-scale mining operations, which predominantly extract lithium from spodumene deposits.<sup>11</sup>

Table 1. Various lithium minerals and their lithium content.<sup>11</sup>

Mineral	Chemical formula	Lithium (wt%)
Spodumene	$\text{LiAlSi}_2\text{O}_6$	3.73
Petalite	$\text{LiAlSi}_4\text{O}_{10}$	2.09
Amblygonite	$(\text{LiNa})\text{AlPO}_4(\text{F, OH})$	3.44
Lepidolite	$\text{K}(\text{Li, Al})_3(\text{Si, Al})_4\text{O}_{10}(\text{F, OH})_2$	3.58
Eucryptite	$\text{LiAlSiO}_4$	5.51

The ore is first crushed to liberate lithium-containing minerals and separated using beneficiation techniques. The resulting spodumene concentrate undergoes calcination and is treated with either sulfuric acid or a chlorine-containing reagent. This yields lithium sulfate ( $\text{Li}_2\text{SO}_4$ ) or lithium chloride ( $\text{LiCl}$ ), which is then leached, purified, and precipitated into either lithium carbonate ( $\text{Li}_2\text{CO}_3$ ) or lithium hydroxide ( $\text{LiOH}$ ) depending on the desired product.<sup>12,13</sup>

Chile, the world's second-largest lithium producer, accounts for 32.8% of global production, primarily exploiting brine deposits found in salt flats or salars, see figure 5. As shown in table 1, lithium-containing minerals have a lithium content ranging from 2% to 5.5%, while table 2 indicates that the lithium content in brine varies between 0.023% and 0.15%.<sup>11</sup>

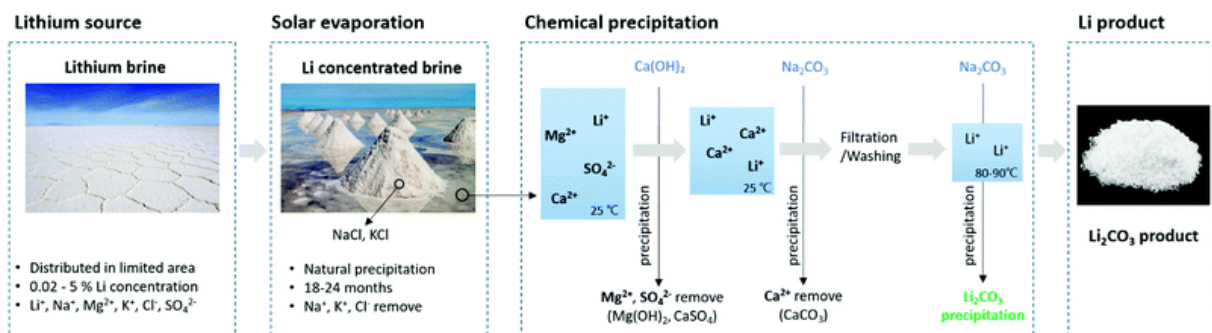


Figure 5: Lithium production from brine and salars.<sup>11</sup>

To extract lithium, brine is pumped from underground reservoirs to shallow surface ponds. The process typically takes place in hot desert areas like the Atacama Desert, where high solar radiation rapidly evaporates water from the ponds, increasing the lithium concentration. Heavy use of sparse water resources can lead to adverse environmental effects.<sup>2</sup> However, the process is still slow, taking from 18 to 24 months. As the evaporation process progresses, impurities such as magnesium, calcium, sodium, and potassium precipitate out before lithium, enabling selective removal. Once the lithium concentration reaches a suitable level, sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) is added to precipitate lithium carbonate ( $\text{Li}_2\text{CO}_3$ ), which is then collected, washed, filtered, and dried.<sup>11</sup>

Table 2. Lithium content of lithium salt lakes<sup>11</sup>

Salt lake	Country	Li (wt%)
Atacama	Chile	0.15
Hombre muerto	Argentina	0.062-0.065
Rincon	Argentina	0.033
Uyuni	Bolivia	0.035
Silver peak	USA	0.023
Zhabuye lake	China	0.12
DXC salt lake	China	0.04

### 3.3 Use and reuse

Effective use and reuse strategies of LIBs play a critical role in promoting a circular economy, conserving resources, and reducing environmental impacts.<sup>5</sup> Even after their primary use in EVs, LIBs can retain a substantial portion of their capacity, making them well-suited for second-life applications.<sup>3</sup> Such applications encompass stationary energy storage systems, backup power supplies, and grid support services, which facilitate the integration of intermittent renewable energy sources and ensure energy resilience during peak electricity consumption hours.<sup>14</sup>

### 3.4 EU regulatory mandates on lithium-ion battery recycling

Starting in 2016 EU member countries had to collect at least 45wt% of LIBs and recover at least 50wt%.<sup>3</sup> However, now the EU is experiencing significant shifts in its lithium policy. In March 2023, Politico<sup>15</sup> reported that the European Commission aims to ease regulatory barriers for lithium mining projects by designating them as "projects of overriding public interest." As early as 2020, the EU included lithium in its list of critical raw materials and implemented regulations prohibiting the export of lithium-ion battery (LIB) waste. These regulations also mandated the recovery of 35% of lithium from collected LIB waste by 2025 and 70% by 2030.<sup>6</sup> These legislative measures are ambitious, with there being no lithium recovered from LIB recycling as of 2020.<sup>4</sup> Reaching the targets poses a considerable challenge. Existing recycling facilities will need to implement lithium recovery technology and new recycling capacity will need to be built to accommodate the increasing supply of EOL LIBs, as well as closing the existing gap in capacity.<sup>3</sup>

## 4 The approaches to lithium recovery and their effects on yield

LIB recycling can be broadly classified into three categories: direct, pyrometallurgical, and hydrometallurgical methods, as illustrated in figure 6. These categories encompass various approaches to treating end-of-life (EOL) LIBs for the recovery of valuable materials. This section provides a general overview of these primary recycling categories. The commercial plants in operation and planned as of November 2021, can be seen in figure 7.<sup>16</sup>



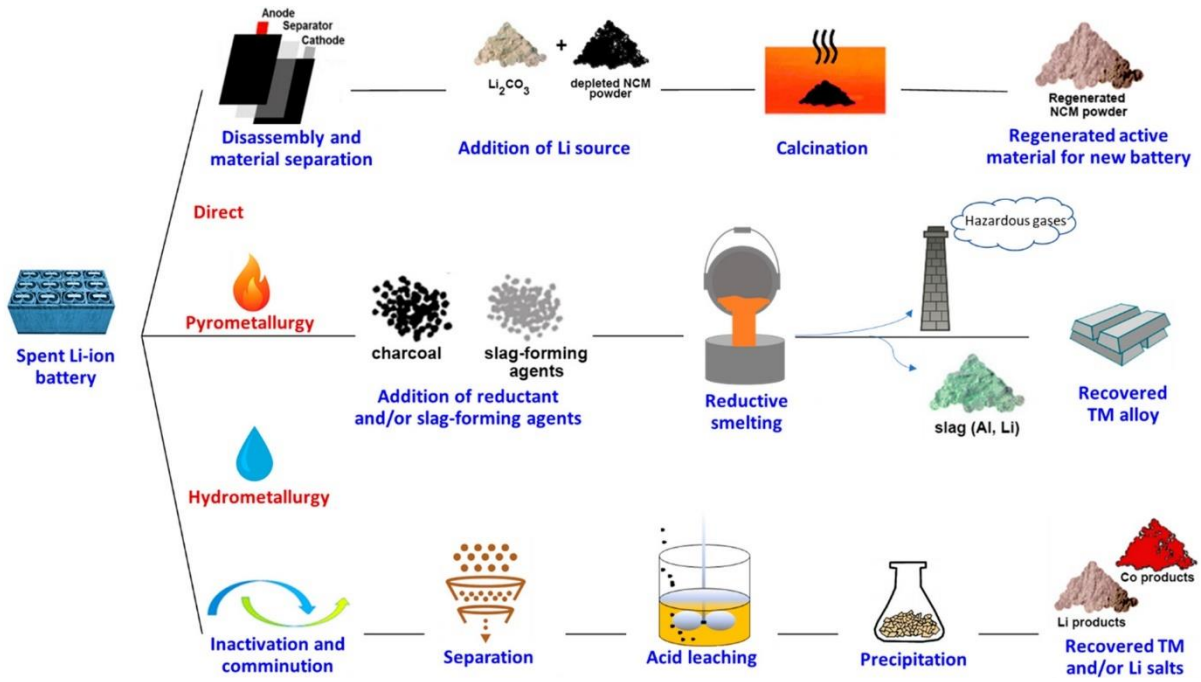


Figure 6: Illustration of prominent direct, pyrometallurgical and hydrometallurgical recycling methods.<sup>16</sup>

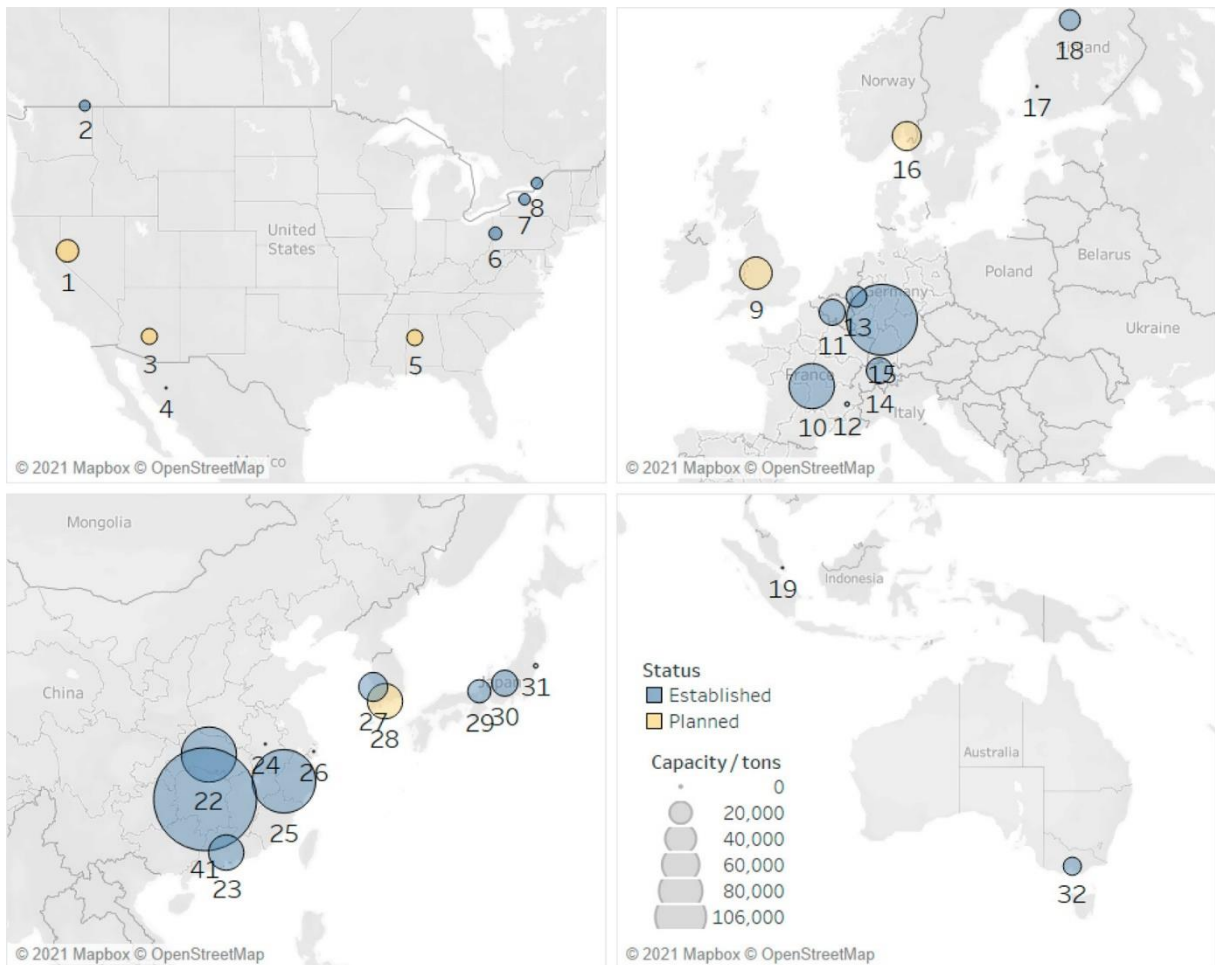


Figure 7: 32 recycling facilities planned or established with capacity if known.<sup>16</sup>

#### 4.1 Deactivation and mechanical treatment

Upon arrival at the recycling facility, EOL batteries may still retain some residual charge. The presence of lithium in the anode graphite layers can be reactive, and many LIBs contain flammable organic compounds and plastics, as well as additives that can generate hydrogen fluoride (HF) gas in the event of runaway temperatures.<sup>20</sup> Processing without addressing these risks can lead to short-circuiting, subsequent fires or explosions, and the release of hazardous emissions. Because of diverse configurations of battery packs any dismantling is carried out manually by trained personnel, exacerbating these safety concerns.<sup>2</sup>

To mitigate these risks, recyclers employ various methods for deactivating the batteries before dismantling or processing. Several approaches exist and are proposed, such as immersing the batteries in a sodium chloride (NaCl) solution<sup>20</sup>, extracting the electrical energy for grid usage or connecting the batteries to a resistive load that converts the electrical energy into.<sup>10</sup> An alternative approach, employed by Retrie Technologies (now part of Cirba Solutions), involves cryogenically cooling the batteries to approximately -200°C using a continuous flow of liquid nitrogen. This method is energy intensive, but significantly reduces the reactivity of lithium by several orders of magnitude. Another approach entails gradually heating the batteries to evaporate the electrolyte in an inert atmosphere. The batteries bloat until holes are created and gasses including the electrolyte escape.<sup>3</sup>

Mechanical treatment serves as the next crucial step in the recycling process. This method focuses on the physical separation of battery components using various mechanical techniques, such as crushing, shredding, sieving and magnetic separation. When the deactivated batteries are crushed and shredded, they are divided roughly into larger and smaller pieces. The larger pieces are mostly fragments of the current collectors made from copper and aluminium as well as the steel casings and plastic bits. While the smaller pieces are the active electrode materials. Then the pieces are sieved to separate them by size. Some processes also separate and sort by density and magnetism to separate the specific materials more efficiently. Most promisingly is the use of advanced AI algorithms that can separate the materials with the use of a camera. Unfortunately, this technology is limited by the varying physical configurations of the various LIBs.<sup>2</sup>

## 4.2 Black mass and pre-treatment on lithium recoverability

The residual mass that is left after separating out the larger fragments of copper, aluminium, steel and plastics, is colloquially known as black mass (BM), after its soft and powdery black texture.<sup>18</sup>

Mousa et al.<sup>18</sup> and Dadé et al.<sup>19</sup> investigated the chemical composition of BM before treatment, presented in table 3 compared to theoretical composition in table 4. Black mass sample 1 (BM1) and BM2 are each sourced from two different types of NMC-cathode batteries at the same recycling facility and was only mechanically treated with fragments up to 4mm in size. BM3, BM4 and BM5 were sourced from different recyclers and in addition to mechanical treatment were subjected to pyrolysis, heat treatment in absence of oxygen, with particles up to 0.4mm. The chemical composition of BM1 through BM5 was analysed with Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). ICP-OES is an analytical technique that utilizes high-temperature plasma to atomize and excite sample elements, causing them to emit light at characteristic wavelengths. By measuring the emitted light's intensity and comparing it to known standards, ICP-OES enables rapid, sensitive, and accurate multi-element analysis across a wide range of sample types.<sup>18,19</sup>

Table 3. Chemical composition of Black mass samples analyzed with ICP-OES.<sup>18,19</sup>

	Element	Ni	Co	Mn	Li	Al	Cu	C
Sample	Cathode	wt%						
BM1 <sup>18</sup>	NMC	5.1	17.5	3.0	3.9	1.6	3.9	36.0
BM2	NMC	12.5	5.4	10.9	2.6	4.8	3.1	42.1
BM3 <sup>19</sup>	Mix	4.70	18.00	5.50	3.40	5.40	4.00	54.30
BM4	Mainly NMC811	21.40	7.27	7.50	9.78	7.98	1.98	40.80
BM5	Mainly NMC532	16.40	8.33	9.32	4.25	1.11	2.15	35.38
Average	-	12.0	11.3	7.2	4.8	4.2	3.0	41.7

Table 4. Theoretical Chemical Composition (wt.%)<sup>19</sup>

	Formula	Theoretical Chemical Composition (wt.%)								
		Li	Ni	Mn	Co	Al	Ti	Fe	P	O
LCO	LiCoO <sub>2</sub>	7.09	-	-	60.21	-	-	-	-	32.69
NMC111	LiNi <sub>0.33</sub> Mn <sub>0.33</sub> Co <sub>0.33</sub> O <sub>2</sub>	7.24	20.20	18.91	20.28	-	-	-	-	33.37
NMC442	LiNi <sub>0.4</sub> Mn <sub>0.4</sub> Co <sub>0.2</sub> O <sub>2</sub>	7.22	24.41	22.85	12.25	-	-	-	-	33.14
NMC532	LiNi <sub>0.5</sub> Mn <sub>0.3</sub> Co <sub>0.2</sub> O <sub>2</sub>	7.19	30.39	17.07	12.21	-	-	-	-	33.14
NMC622	LiNi <sub>0.6</sub> Mn <sub>0.2</sub> Co <sub>0.2</sub> O <sub>2</sub>	7.17	36.33	11.34	12.16	-	-	-	-	33.01
NMC811	LiNi <sub>0.8</sub> Mn <sub>0.1</sub> Co <sub>0.1</sub> O <sub>2</sub>	7.13	48.27	5.65	6.06	-	-	-	-	32.89
NCA	LiNi <sub>0.8</sub> Co <sub>0.15</sub> Al <sub>0.05</sub> O <sub>2</sub>	7.22	48.87	9.20	-	1.40	-	-	-	33.30
LNO	LiNiO <sub>2</sub>	7.11	60.12	-	-	-	-	-	-	32.77
LMO	LiMnO <sub>2</sub>	7.39	-	58.52	-	-	-	-	-	34.09
LFP	LiFePO <sub>4</sub>	4.40	-	-	-	-	-	35.40	19.63	40.57
LTO	LiTiO <sub>2</sub>	8.00	-	-	-	-	55.14	-	-	36.86

Mousa et al.<sup>18</sup> also analyzed the chemical composition of BM1 and BM2 after heat treatment in air with an X-ray Diffraction (XRD) analysis when a Thermogravimetric analysis (TGA) test had determined that all graphite had disappeared. The XRD analysis showed that the heat treatment had decomposed most of the lithium metal oxide cathode material into their respective metal oxide, NiO, MnO, CoO). They propose that the decomposition of the cathode material is due to the elevated temperature and decomposition of PVDF binder.<sup>18</sup>

An analysis of the morphological structure of BM1 and BM2 was also carried out with Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS), and it was shown that the larger pieces constituted a larger fraction of the aluminium and copper in the sample, while the graphite was mostly distributed in the smaller fractions. This is explained by crushed aluminium and copper foil not as easily breaking into smaller fractions due to being more ductile than graphite and lithium metal oxide cathode. The SEM-EDS analysis also showed that some binder remained even after the heat treatment in both BM1 and BM2, as well as fluoride cuboids and carbonaceous residue imbedded in the lithium metal oxide surfaces. More research on the morphology of heat-treated black mass could help recyclers

prevent the formation of these compounds which present a challenge for lithium and other valuable material recovery.<sup>18</sup>

### 4.3 Direct recycling

In direct recycling, the objective is to recover components from end-of-life (EOL) lithium-ion batteries (LIBs) using minimal processing steps and chemical treatments. Common for direct recycling methods is that the batteries are disassembled, the active material is separated out and purified before the recycled material is treated to reach battery grade – usually by calcinating it with virgin material.<sup>16</sup>

One method involves manual disassembly, followed by the purification of anode and cathode materials using supercritical carbon dioxide (CO<sub>2</sub>). Supercritical CO<sub>2</sub> refers to a state in which CO<sub>2</sub> exhibits properties of both liquid and gas at pressures and temperatures above its critical point. The supercritical CO<sub>2</sub> permeates the battery cell, dissolving and extracting the electrolyte and its additives. The purified cells and recovered electrolyte can then be recycled.<sup>20</sup>

The battery cell undergoes mechanical treatment, and its components are separated. Cathode materials are collected and directly incorporated into new battery manufacturing, while the other components are recycled through standard processes. Although some experimental results indicate lower electrochemical performance and density, these properties can be enhanced to meet basic requirements by sintering with fresh cathode powder or applying heat treatment. Direct recycling offers several advantages, including a shortened recycling pathway, reduced energy consumption, and a high recovery rate.<sup>20</sup>

### 4.4 Pyrometallurgy

Pyrometallurgy is a high-temperature process that involves the smelting and refining of metals from ores, concentrates, or recycled materials. However, lithium is rarely recovered, as it frequently ends up in the slag used for making concrete or is otherwise lost during the process. Still, extracting lithium from the slag is possible. The slag is grinded into small

particles that are leached and precipitate out lithium carbonate ( $\text{Li}_2\text{CO}_3$ ), but the process is neither efficient nor economical. Despite this, pyrometallurgy remains the primary recycling approach for LIBs in commercial operations. It is important to note that many of these facilities do not focus exclusively on LIB recycling, instead using them as a secondary feedstock alongside other materials. One such example is the Inmetco’s pyrometallurgy-based plant, where EOL LIBs are one of several input materials and lithium is not recovered. See figure 8.<sup>3</sup>

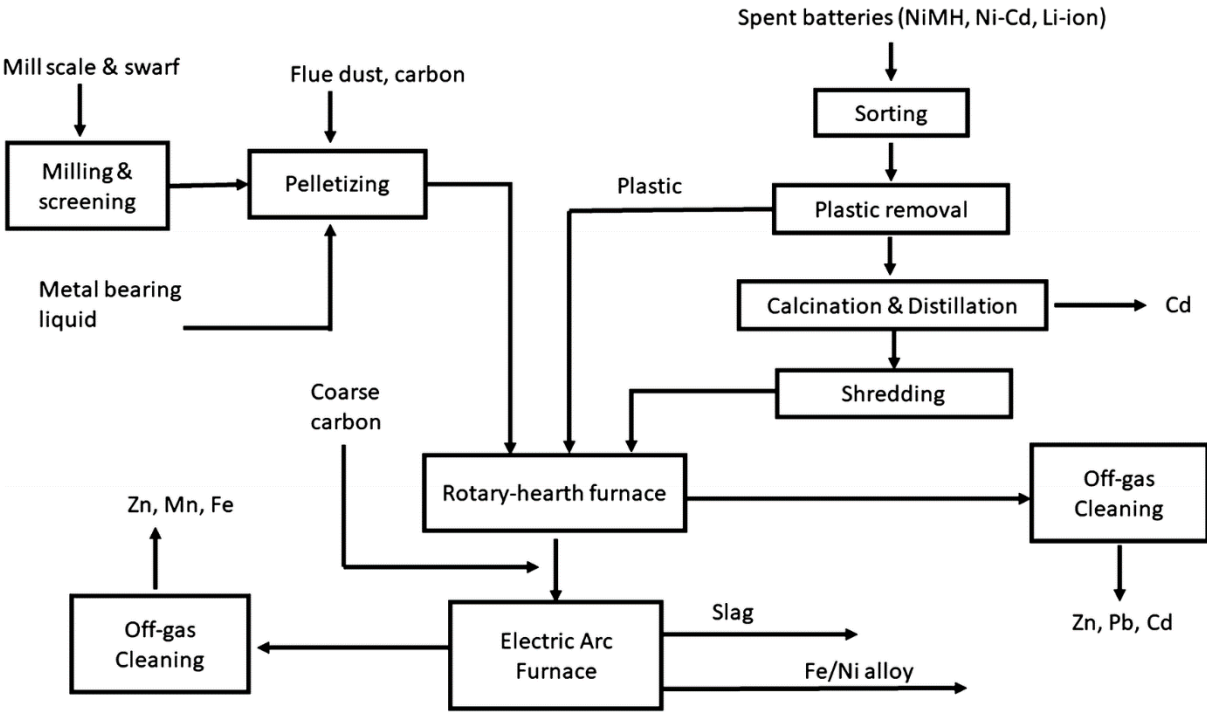


Figure 8: Schematic diagram of the Inmetco process<sup>3</sup>

The pyrometallurgical process generally encompasses several stages, including pre-treatment, smelting, converting, and refining. Initially, EOL LIBs often undergo pre-treatment to eliminate hazardous materials and ready the battery waste for smelting. This step may involve mechanical processes such as shredding or crushing to decrease particle size.<sup>20</sup> During smelting, battery waste is exposed to extremely high temperatures, causing the targeted metals to melt and separate from other components. A combination of reducing agents and fluxes, are often introduced to improve the separation and recovery of valuable metals. The molten metal mixture is subsequently transferred to a converting stage, where it undergoes further processing to eliminate impurities and enhance metal purity. Finally, the refined metals

undergo electrolytic refining or chemical treatment to attain the desired level of purity. These recovered metals can then be repurposed in the production of new LIBs or other applications.<sup>3</sup>

## 4.5 Hydrometallurgy

Hydrometallurgical methods recover metals with the use of aqueous solutions to leach and precipitate, or electrochemically extract, out the targeted metal(s). In the context of recovering lithium during LIB recycling, hydrometallurgical methods offer clear advantages compared to pyrometallurgical methods. This includes a higher recovery rate for lithium, purer lithium product and a lower energy requirement. In this section the different hydrometallurgical methods for recovering lithium will be presented. A schematic of three hydrometallurgical processes for recovering lithium first presented in this section is provided in figure 9.

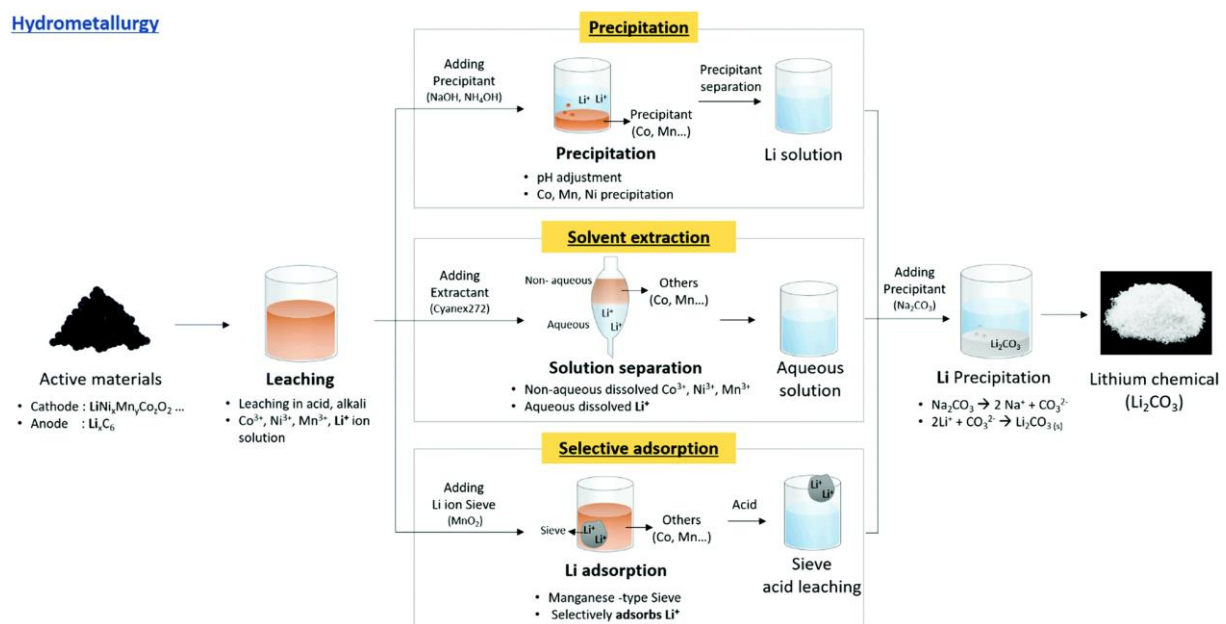


Figure 9: Schematic of processing leachate into lithium carbonate through precipitation, solvent extraction or selective adsorption.<sup>11</sup>

### 4.5.1 Leaching

Leaching is submerging metal containing compounds in an aqueous solution and dissolving the metals using a leaching agent if necessary. The step is potentially the most important for the yield of a hydrometallurgical recovery method, as anything that is not leached out into solution will not be recovered. Before leaching begins, the black mass might receive

additional pre-treatment. These pre-treatments include heat treatment and milling. By milling the particles, the particle sizes are decreased, which leads to a larger surface area which can increase the reactivity with the leaching agent in the aqueous solution. By heat-treating the black mass, binder and other organic material that traps and shields the lithium from the leaching agent can be removed.<sup>3,11</sup>

The leaching agent can be an acid or alkali, but the most widely used leaching agent is sulphuric acid ( $\text{H}_2\text{SO}_4$ ). It is inexpensive, readily available in large quantities and capable of breaking up the crystal lattice of the lithium containing compounds.<sup>11</sup> Despite these advantages a lot of work has gone into finding other potential leaching agents, because waste sulphuric acid solution is generated. Other leaching agents include hydrochloric acid (HCl) and nitric acid ( $\text{HNO}_3$ ). However, they have their own downsides including respectively producing chlorine gas ( $\text{Cl}_2$ ) and nitrogen oxide ( $\text{NO}_x$ ). In many cases alkaline leaching agents like sodium hydroxide (NaOH) or potassium hydroxide (KOH) can not be used either, as they are less efficient especially for leaching the economically significant cobalt and nickel. In addition, both the strong acids and alkalines have adverse effects on the equipment through corrosion. A lot of research has therefore taken place to find replacements like the organic acids oxalic acid and citric acid and determine if they can replace  $\text{H}_2\text{SO}_4$  as the leaching agent.<sup>17</sup>

#### 4.5.2 Precipitation

Precipitation involves converting the dissolved lithium ions into solid precipitates by introducing a precipitating agent or altering the solution's physical or chemical conditions, such as pH, temperature, or concentration. Since lithium can be selectively precipitated out, it is possible to obtain high-purity lithium compounds.<sup>11</sup>

Lithium can be precipitated as  $\text{Li}_2\text{CO}_3$  by introducing a sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) solution to the leachate, or as LiOH, by adding a calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) solution. Nevertheless, precipitating lithium as  $\text{Li}_2\text{CO}_3$  is generally more straightforward since increasing the leachate's pH enhances the availability of carbonate ions ( $\text{CO}_3^{2-}$ ) in the solution, thereby further reducing its already lower solubility, as depicted in table 5. Control of parameters such



as pH, temperature, and the concentration of the precipitating agent is crucial for minimizing the solubility of the target compound, ensuring efficient and selective lithium recovery.<sup>11</sup>

Table 5: Solubility of different lithium compounds<sup>11</sup>

Compound\condition	g/L, 25°C	g/L, 40°C
Li <sub>2</sub> CO <sub>3</sub>	12.9	10.8
LiOH	129	-
LiCl	815	-

Once the precipitation process is complete, the solid lithium precipitates are separated from the liquid phase through filtration or sedimentation. The separated precipitates then undergo further processing, such as washing, drying, or calcination, to yield the final battery-grade lithium compound.<sup>11</sup>

#### 4.5.3 Solvent Extraction and Selective Adsorption

Solvent extraction and selective adsorption are techniques for selectively recovering and purifying the targeted metals. Solvent extraction is based on the preferential partitioning of metal ions between two immiscible phases: an aqueous phase (leachate) and an organic phase containing a selective extractant. By carefully choosing the extractant and controlling process conditions, selective separation and efficient recovery of target metals can be achieved. After extraction, the metal ions are stripped from the organic phase using a fresh aqueous solution, often an acid or complexing agent.<sup>11</sup>

Selective adsorption, on the other hand, involves the preferential binding of lithium ions to solid adsorbents, enabling their extraction from complex mixtures without requiring multiple separation steps. Various materials, such as ion-exchange resins, inorganic materials, and functionalized polymers, have been employed as adsorbents due to their high affinity for lithium ions. These materials can exhibit high selectivity for lithium ions, because of lithium's small size, as it is the only metal that will fit in their specific crystal structures and surface chemistries.<sup>11</sup>

#### 4.5.4 Electrochemical extraction

Electrochemical extraction is an emerging hydrometallurgical method for lithium recovery, offering high selectivity, efficiency, and environmental sustainability. This technique involves processes such as electrowinning, electrodeposition, or electro-dialysis, which apply an electric potential to separate and recover lithium ions selectively in an aqueous solution.<sup>11</sup>

Electrowinning involves reducing metal ions at the cathode in an electrolytic cell, selectively depositing lithium metal on the cathode surface. Electrodeposition selectively deposits lithium ions onto a suitable substrate under controlled conditions, achieving high selectivity and purity. Electro-dialysis uses ion-exchange membranes to transport lithium ions selectively across an electric potential gradient, making it suitable for low-concentration solutions and continuous operation. In the electrochemical extraction process, the solution containing lithium ions is prepared, the electrolytic cell is assembled, and an electric potential is applied to drive selective transport or deposition of lithium ions, see figure 10. Recovered lithium may undergo further processing, such as purification or conversion to lithium compounds, depending on the intended application.<sup>11</sup>

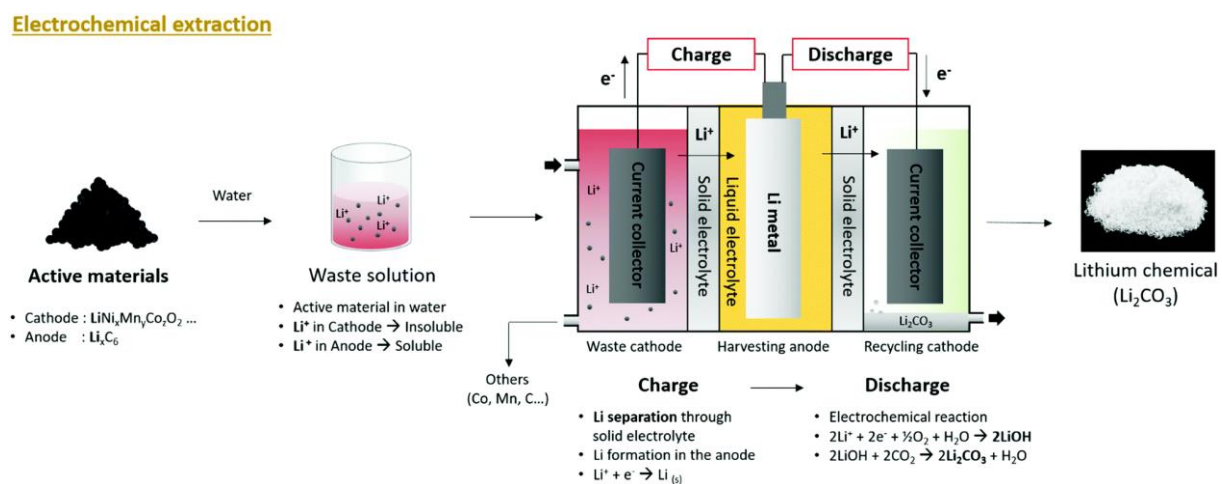


Figure 10: Schematic of electrochemical extraction from black mass to lithium carbonate<sup>11</sup>

#### 4.5.6 Novel methods

In addition to the conventional hydrometallurgical methods for lithium recovery, ongoing research and development efforts have led to the emergence of novel techniques that aim to improve the efficiency, selectivity, and sustainability of lithium extraction. These innovative

methods often combine or adapt existing technologies and materials to address specific challenges in lithium recovery.<sup>3,11</sup> Some notable examples of novel methods for lithium recovery include membrane processes, ionic liquids, and bioleaching.<sup>17</sup>

Membrane processes, such as nanofiltration, ultrafiltration, and reverse osmosis could potentially be used in lithium recovery. These processes employ specialized membranes with specific pore sizes or surface chemistries that enable the selective separation of lithium ions from other metal ions and impurities. Membrane processes offer advantages such as low energy consumption, continuous operation, and minimal waste generation.<sup>17</sup>

Ionic liquids are a class of non-aqueous, low-melting-point salts that have attracted interest for their unique properties, such as negligible vapor pressure, non-flammability, and high thermal stability. These properties make ionic liquids suitable for applications in lithium recovery, such as solvent extraction, electrodeposition, or selective adsorption. Researchers are exploring the potential of ionic liquids to improve the selectivity and efficiency of lithium extraction, as well as to minimize the environmental impact of the process.<sup>17</sup>

Bioleaching is a biotechnology-based method for lithium recovery that use bacteria to selectively extract lithium ions from ores or waste materials. The bacteria eat metal oxides, produce organic acids or enzymes that solubilize and complex lithium ions, enabling their separation and recovery. Bioleaching offers advantages such as low energy consumption and reduced use of chemicals. However, the process is typically slower than conventional hydrometallurgical methods and may require further optimization to achieve efficient lithium extraction.<sup>17</sup>

## 5 Discussion and summary of strategies for high lithium recoverability and their challenges

### 5.1 Trade-offs in high lithium recovery methods

The challenge of high lithium recovery from EOL EV LIBs, is not the absence of methods with high lithium recovery rates. Instead, the challenge lies in the fact that these methods often involve trade-offs, sacrificing other valuable aspects in exchange for high recovery rates. High recovery methods has some negative side like high operating or capital costs, utilize significant amounts of toxic or harmful chemicals, generate greenhouse gas emissions, exhibit inflexibility to input variations, yield low-grade output, encounter difficulties in scaling, or prove to be too time-consuming to be used. Many of these challenges can and probably will be combated with further research and development, however, there is an urgent need to deploy these methods immediately or in the near future. This is because recycling capacity is currently trailing, and not set to meet, the volume of waste generated. Additionally, the importance of preventing waste accumulation of EOL LIBs becomes apparent, when considering the risks associated with fires and leakage of hazardous materials if it ends up in unsuited landfills.

The question therefore becomes what trade-offs are acceptable and not, to regulatory authorities and recycling companies. The EU gives an example of the priorities on the regulatory side, with their concerns for environmental impacts and on efficiency with recent new regulations setting material targets on lithium recovery of 35 % within 2025 and 70 % within 2030. The recycling companies on the other hand are private enterprises, which means they are mostly concerned with the economic aspects of the operation. Such as the capital investment requirement, costs of operation and economic value of the recovered materials. A viable recycling method will therefore have to recover lithium at least somewhat efficiently, have low environmental impacts and be profitable.

### 5.2 Pyrometallurgical methods

Because pyrometallurgical methods are energy-intensive, with usually low rates of recovery for lithium, and emissions of both greenhouse gases and toxic gasses, it might not be a promising solution to EV LIB recycling. However, with flexibility in input material, lower

complexity and existing recycling capacity, it could play a key role in initially processing supply of EOL LIB. Arguably better to treat EOL LIBs than let it end up in landfills.

### 5.3 Direct recycling

Direct recycling offers a more promising approach to EV LIB recycling. By minimizing processing and chemical treatments, this method effectively reduces energy consumption, associated costs, and waste generation. Moreover, direct recycling typically yields high recovery rates. However, its limitations include a narrow focus on specific cathode chemistries, resulting in reduced flexibility. Additionally, the manual disassembly of battery cells poses safety concerns and necessitates trained personnel. Automation could alleviate these concerns, but steps might first need to come from manufacturers to make computer systems able to identify the different components. This could for example be achieved by marking the components with a QR-kode or other identifying insignia. Furthermore, to guarantee battery-grade quality from direct recycling, it may be necessary to blend the recycled product with virgin material. Consequently, complementary recycling methods or raw production processes may be required, particularly for addressing damaged end-of-life lithium-ion batteries that direct recycling cannot adequately process.

### 5.4 Hydrometallurgical methods

Hydrometallurgical methods present a viable alternative for EV LIB recycling, as they typically exhibit lower energy consumption and higher lithium recovery rates compared to pyrometallurgical methods. Utilizing a combination of leaching, solvent extraction, and precipitation techniques, hydrometallurgy can effectively recover lithium. Although these processes do often involve the use of large amounts of chemicals, which may raise environmental concerns, recent advancements have focused on minimizing chemical usage and exchanging toxic compounds with more environmentally friendly alternatives. Despite the potential for longer processing times and increased complexity, hydrometallurgical methods offer a potential solution. Questions around the profitability of hydrometallurgical methods are relevant, as the complexity of the process can lead to high capital requirements. Additionally, the large volume of the chemicals needed in the process might not yet be commercially available and potentially add to operative costs.

## 5.5 Emerging lab-based methods

Emerging lab-based methods represent an important frontier in EV LIB recycling, focusing on developing innovative and efficient techniques that address many of the challenges with current methods for lithium recovery. They mostly address specific steps of hydrometallurgical methods. For example, bioleaching could replace consumption of large amounts of heated H<sub>2</sub>SO<sub>4</sub> or other toxic leaching agents, with microorganisms that can achieve the same at room temperature. Electrochemical processing, membrane processes and the use of ionic liquids for dissolution and separation if incorporated, could increase selectivity, lower energy requirements and be more environmentally friendly. While these techniques show promise, their current lab-scale status presents challenges for immediate industrial-scale implementation. Key considerations for scaling up include capital investment, process optimization and commercial availability of materials. As research progresses, these cutting-edge technologies may eventually improve commercial lithium recovery methods. However, practical deployment will require further development, validation, and a concerted effort to address the technical and economic challenges associated with transitioning from lab-scale to industrial-scale operations.

## 6 Conclusion

The adoption of lithium-ion batteries (LIBs) as the energy storage solution for electric vehicles (EV) has allowed the world to realistically pursue dramatic reductions in the emissions of the transport sector. However, recovery of lithium from the EV LIBs that have reached their end-of-life (EOL) is still lacking or completely absent. This alone makes the pyrometallurgical methods that dominate the recycling facilities of today, not the future of EV LIB recycling. Large-scale building of recycling facilities employing efficient and cost-effective hydrometallurgical methods is needed to recover the valuable resource lithium is. Which will at the same time, prevent the accompanying negative environmental effects of raw resource extraction. Further development and research on pre-treatment of black mass and novel lab-based methods like bioleaching, electrochemical processing, use of ionic liquids and membrane processing is needed to improve the economics and environmental friendliness of hydrometallurgical methods. In addition, studies around the economics and scalability of direct recycling and novel lab-based methods, could help uncover obstacles on the path to commercial adoption. Finally, the urgency of the situation has been highlighted by recent regulatory changes that have set ambitious targets for lithium recovery.

## 7 References

- (1) International Energy Agency. Global EV Outlook 2022: Securing Supplies for an Electric Future; OECD, 2022.
- (2) Harper, G.; Sommerville, R.; Kendrick, E.; Driscoll, L.; Slater, P.; Stolkin, R.; Walton, A.; Christensen, P.; Heidrich, O.; Lambert, S.; Abbott, A.; Ryder, K.; Gaines, L.; Anderson, P. Recycling Lithium-Ion Batteries from Electric Vehicles. *Nature* 2019, 575 (7781), 75–86. <https://doi.org/10.1038/s41586-019-1682-5>.
- (3) Pinegar, H.; Smith, Y. R. Recycling of End-of-Life Lithium Ion Batteries, Part I: Commercial Processes. *J. Sustain. Met.* 2019, 5 (3), 402–416. <https://doi.org/10.1007/s40831-019-00235-9>.
- (4) Blengini, G. A.; El Latunussa, C.; Eynard, U.; de Matos, C. T.; Wittmer, D. M. A.; Georgitzikis, K.; Pavel, C. C.; Carrara, S.; Mancini, L.; Unguru, M.; Blagoeva, D.; Mathieux, F.; Pennington, D. W. Study on the EU’s List of Critical Raw Materials (2020): Final Report; Publications Office of the European Union, 2020.
- (5) Ziemann, S.; Müller, D. B.; Schebek, L.; Weil, M. Modeling the Potential Impact of Lithium Recycling from EV Batteries on Lithium Demand: A Dynamic MFA Approach. *Resour. Conserv. Recycl.* 2018, 133, 76–85. <https://doi.org/10.1016/j.resconrec.2018.01.031>.
- (6) European Parliament Research Service. New EU Regulatory Framework for Batteries: Setting Sustainability Requirements; 2021. [https://www.europarl.europa.eu/RegData/etudes/BRIE/2021/689337/EPRS\\_BRI\(2021\)689337\\_EN.pdf](https://www.europarl.europa.eu/RegData/etudes/BRIE/2021/689337/EPRS_BRI(2021)689337_EN.pdf).
- (7) Ackermann, T.; Polly, S.; Zeiler, F. New EU Battery Regulation – Additional challenges for companies. *JD Supra*. <https://www.jdsupra.com/legalnews/new-eu-battery-regulation-additional-1970453/> (accessed 2023-04-18).
- (8) Li, L.; Zhang, X.; Li, M.; Chen, R.; Wu, F.; Amine, K.; Lu, J. The Recycling of Spent Lithium-Ion Batteries: A Review of Current Processes and Technologies. *Electrochem. Energy Rev.* 2018, 1 (4), 461–482. <https://doi.org/10.1007/s41918-018-0012-1>.
- (9) Zhao, D.; Li, S. Regulating the Performance of Lithium-Ion Battery Focus on the Electrode-Electrolyte Interface. *Front. Chem.* 2020, 8, 821. <https://doi.org/10.3389/fchem.2020.00821>.

- (10) Zubi, G.; Dufo-López, R.; Carvalho, M.; Pasaoglu, G. The Lithium-Ion Battery: State of the Art and Future Perspectives. *Renew. Sustain. Energy Rev.* 2018, 89, 292–308. <https://doi.org/10.1016/j.rser.2018.03.002>.
- (11) Bae, H.; Kim, Y. Technologies of Lithium Recycling from Waste Lithium Ion Batteries: A Review. *Mater. Adv.* 2021, 2 (10), 3234–3250. <https://doi.org/10.1039/d1ma00216c>.
- (12) Swain, B. Recovery and Recycling of Lithium: A Review. *Sep. Purif. Technol.* 2017, 172, 388–403. <https://doi.org/10.1016/j.seppur.2016.08.031>.
- (13) Barbosa, L. I.; Valente, G.; Orosco, R. P.; González, J. A. Lithium Extraction from  $\beta$ -Spodumene through Chlorination with Chlorine Gas. *Miner. Eng.* 2014, 56, 29–34. <https://doi.org/10.1016/j.mineng.2013.10.026>.
- (14) Heelan, J.; Gratz, E.; Zheng, Z.; Wang, Q.; Chen, M.; Apelian, D.; Wang, Y. Current and Prospective Li-Ion Battery Recycling and Recovery Processes. *JOM (1989)* 2016, 68 (10), 2632–2638. <https://doi.org/10.1007/s11837-016-1994-y>.
- (15) Zimmermann, A. Europe’s green dilemma: Mining key minerals without destroying nature. *POLITICO*. <https://www.politico.eu/article/europes-green-dilemma-mining-key-minerals-without-destroying-nature/> (accessed 2023-04-18).
- (16) Baum, Z. J.; Bird, R. E.; Yu, X.; Ma, J. Lithium-Ion Battery Recycling—Overview of Techniques and Trends. *ACS Energy Lett.* 2022, 7 (2), 712–719. <https://doi.org/10.1021/acsenergylett.1c02602>.
- (17) Pinegar, H.; Smith, Y. R. Recycling of End-of-Life Lithium-Ion Batteries, Part II: Laboratory-Scale Research Developments in Mechanical, Thermal, and Leaching Treatments. *J. Sustain. Met.* 2020, 6 (1), 142–160. <https://doi.org/10.1007/s40831-020-00265-8>.
- (18) Mousa, E.; Hu, X.; Ánnhagen, L.; Ye, G.; Cornelio, A.; Fahimi, A.; Bontempi, E.; Frontera, P.; Badenhurst, C.; Santos, A. C.; Moreira, K.; Guedes, A.; Valentim, B. Characterization and Thermal Treatment of the Black Mass from Spent Lithium-Ion Batteries. *Sustainability* 2022, 15 (1), 15. <https://doi.org/10.3390/su15010015>.
- (19) Dadé, M.; Wallmach, T.; Laugier, O. Detailed Microparticle Analyses Providing Process Relevant Chemical and Microtextural Insights into the Black Mass. *Minerals (Basel)* 2022, 12 (2), 119. <https://doi.org/10.3390/min12020119>.



(20) Huang, B.; Pan, Z.; Su, X.; An, L. Recycling of Lithium-Ion Batteries: Recent Advances and Perspectives. *J. Power Sources* 2018, 399, 274–286.  
<https://doi.org/10.1016/j.jpowsour.2018.07.116>.

