MCCXXII

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Topic: Recycling of Lithium-ion Batteries

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ABSTRACT

Due to the rise in popularity of portable electronics, electric vehicles, and renewable energy storage systems, there has been a considerable growth in the demand for lithium-ion batteries. However, development has also resulted in environmental issues due to the mining of lithium from natural resources and the depletion of materials based on lithium. However, due to limited lithium supplies and an increase in lithium use of 18% from 2018 to 2019, lithium depletion is anticipated to occur soon. The creation of novel technologies for recycling lithium-ion batteries has therefore become crucial.

Technology to recycle lithium-ion batteries has been developed because of this. In accordance with each stage and technique, this thesis focuses on the technologies that can recycle lithium compounds from EoL lithium-ion batteries. Pre-treatment and lithium extraction are the two processes, and lithium extraction is split into three methods: pyrometallurgy, hydrometallurgy, and electrochemical extraction. The three methods will be compared to investigate benefits, drawbacks, lithium extraction effectiveness, cost, environmental impact, and level of commercialization. It will be also outlined upcoming requirements for enhancing recycling technologies.

1.INTRODUCTION

The use of lithium-ion batteries (LIBs) has grown tremendously between their initial discovery in the 1970s and the awarding of the Nobel Prize in 2019 [1-4]. As people have come to adore and rely on power and the comfort that LIBs, their production, and disposal are more frequently being discussed in political environment-related issues.

Inventories of lithium, cobalt, and other metals are scarce and dispersed unevenly, while Its mining uses a lot of work and energy and produces significant pollution [5,6]. [7,8] More than 70% of the cobalt in the world comes from Congo, [9] and no other nation produces more than that than 5%. 70% of the world's production comes from China and Mozambique. Natural graphite, a crucial component of anodes. [10] As a natural disasters, conflict, or decisions about how to allocate resources could also alter this materials' accessibility.

Resource availability and scarcity are crucial issues because due to the limited device lifespan, whether because of design obsolescence, updates to more recent smartphone models, or, quite frequently, the LIB is getting close to the end of its life. Most Discarded LIBs are eventually stacked or dumped, waste energy and non-renewable natural resources while contaminating the land [18].

As of February 2019, the number of electric cars (EVs) worldwide has increased by 64% to over 5.6 million, greater than in 2018. [11] 58% of all automobiles sold globally in 2040 to be electric vehicles (EVs). [12] With the rapid expansion of EV number and the enormous size of their batteries (The battery in the Tesla Model 3 Long Range has 4416 cells is 480 kg.

[13] There will continue to be a lot of LIB waste produced which, if not recycled and utilised, will put enormous pressure environmental effects and faster mineral depletion reserves. LIBs are a challenge for recycling because they are complex structures, one of the five common electrolytes, a separator, an anode, cathodes, and current collectors as well as packaging elements for instance, the International Energy Agency provides estimates that the sales of electric vehicles in 2019 alone generated the total amount of garbage is 500,000 tons of LIB waste created, by the year 2040 may reach 8 million tons [14].

2.Lithium-ion battery

Many factors contribute to the popularity of lithium-ion batteries. Lithium is first and foremost a highly light metal, which makes it perfect for use in batteries. Due to their high energy density, lithium-ion batteries can store a lot of energy in a small amount of space.

In applications where space is a critical consideration, such as with aircraft, this characteristic is particularly helpful. The very high discharge rate of lithium-ion batteries is especially useful in applications where speed is crucial. When compared to other battery types, they also have a relatively low self-discharge rate. Lithium-ion batteries can therefore be utilized in circumstances where the battery must always be inside the gadget.
Finally, compared to other types of rechargeable batteries, lithium-ion batteries have a very long lifespan [19].

Li-ion batteries made it feasible for cordless vacuums to be created, in major part. Electric vehicles, power equipment, energy storage systems, and small appliances all use lightweight, high energy density Li-ion batteries, which have higher capacity and efficiency than other batteries. Today, let's examine Li-ion batteries from top to bottom [15].

Fig. 1 Battery from Samsung SDI Batteries

Cathode, anode, electrolyte, and separator are the four parts of a lithium-ion battery?

Cathode, anode, electrolyte, and separator are the four essential components of a lithium-ion battery. A Li-ion battery needs every component since it cannot operate if one of them is missing [15].

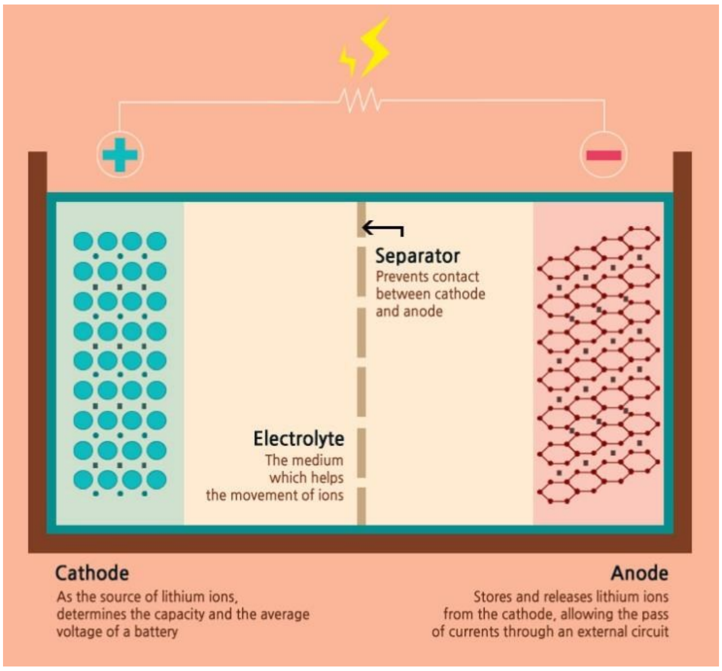


Fig. 2_The Li-ion Battery's Four Parts

I.A Li-ion battery's voltage and capacity are determined by its "cathode."

The lithium in a lithium-ion battery undergoes chemical processes to produce electricity. For this reason, lithium is naturally introduced into the battery, and the area where the lithium is located is known as the "cathode." Lithium oxide is utilized for cathodes because lithium in its elemental form, which consists of lithium and oxygen, is unstable. The term "active material" refers to a substance like lithium oxide that blocks the electrode reaction of the actual battery. In other words, lithium oxide serves as the active component in the cathode of a Li-ion battery [15].

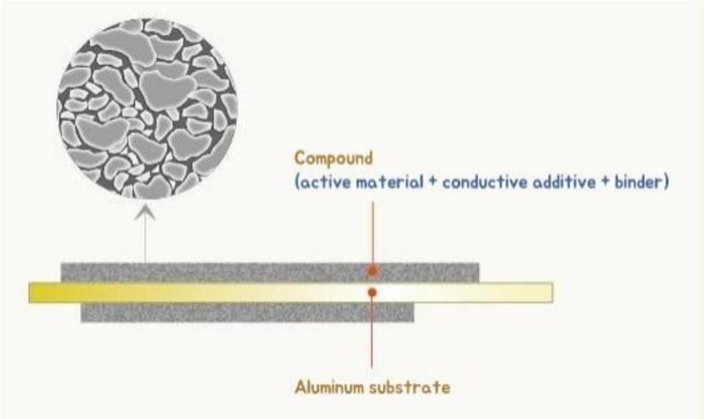


Fig. 3 Cathode

If you examine the cathode closely, you will notice that the thin aluminium foil used to support the cathode's frame has been coated with a mixture of active material, conductive additive, and binder. Lithium ions are included in the active material, which also has a conductive additive to improve conductivity. The binder serves as an adhesive, assisting the conductive additive and active material in adhering firmly to the aluminium substrate.

Because the sort of active material used for the cathode determines the battery's capacity and voltage, the cathode is crucial in establishing the characteristics of the battery.

The capacity increases with the amount of lithium present, and the voltage rises with the magnitude of the potential difference between the cathode and the anode.

Depending on the kind, the potential difference between anodes and cathodes is typically minor for anodes and somewhat significant for cathodes.

As a result, the cathode is crucial in determining the battery's voltage [15].

II. Electrons are sent across a wire by "anode."

The anode substrate is coated with active material, just like the cathode.

The function of the anode's active material is to allow reversible absorption and emission of lithium ions produced by the cathode while permitting electric current to flow through the external circuit. Lithium ions are kept in the anode, not the cathode, when the battery is being charged.

Lithium ions now naturally flow back to the cathode through the electrolyte, and the electrons (e-) separated from lithium ions move along the wire creating electricity at the point where the conducting wire joins the cathode to the anode (discharge state).

The anode substrate is coated with active material, a conductive additive, and a binder. Graphite with a stable structure is employed for the anode.

Graphite is ideal for use as an anode because of its structural stability, low electrochemical reactivity, capacity to store large amounts of lithium ions, and affordability [15].

III. The term "electrolyte" only permits ion mobility.

Lithium ions pass through the electrolyte and electrons move through the wire, it was explained when discussing cathode and anode.

This is essential for allowing a battery to use electricity.

We won't be able to use electricity if ions pass through the electrolyte, and safety will also be at risk.

The element that fulfils this crucial function is the electrolyte.

It acts as the conduit that allows only lithium ions to travel back and forth between the cathode and the anode.

High ionic conductivity materials are primarily used for the electrolyte so that lithium ions can travel back and forth readily [15].

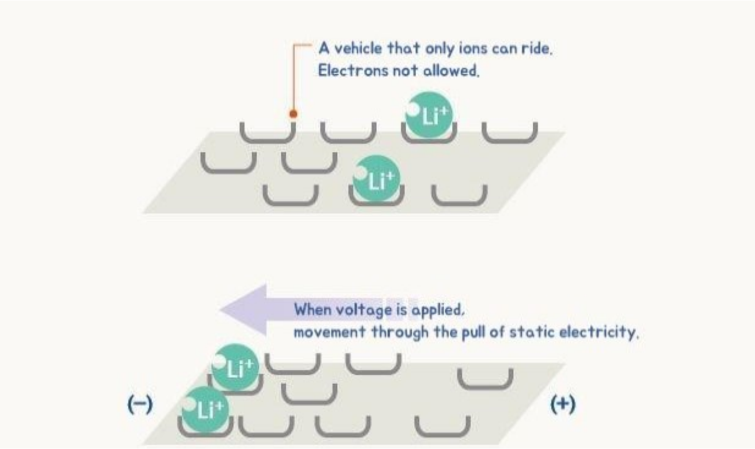


Fig. 4 Electrolyte

There are salts, solvents, and additives in the electrolyte.

Lithium ions travel via salts, which are organic liquids used to dissolve the salts. Small amounts of additives are added for various applications. This method of making electrolyte prevents electrons from passing through and only permits ions to flow to the electrodes.

Additionally, the type of electrolyte affects how quickly lithium ions migrate. Therefore, only electrolytes that adhere to strict requirements can be used.

IV.” Separator”, the impermeable wall separating the cathode and the anode.

The electrolyte and separator determine a battery's safety, while the cathode and anode determine a battery's fundamental performance.

Separator keeps cathode and anode apart by acting as a physical barrier.

It carefully allows only the ions to pass through the interior tiny hole while obstructing the direct flow of electrons.

It must therefore meet all the physical and electrochemical requirements.

Currently available synthetic resin separators include polyethylene (PE) and polypropylene (PP).

We have examined the four key factors that affect how well Li-ion batteries function thus far.

Currently, Samsung SDI is stepping up research and development of novel materials for improving battery performance.

while steadfastly carrying on its efforts to enhance the functionality of current materials and key technologies.

Through the development of high-capacity, high-efficiency Li-ion batteries,

Samsung SDI wants to lead the way in the development of batteries that will improve the quality of life for people all over the world [15].

Different Types of Lithium-Ion Batteries

Lithium-ion batteries come in a wide variety of designs, each with unique features. Each version has a somewhat different manufacturing procedure.

Here are the several kinds of lithium-ion batteries and how they differ from one another.

I) Lithium Cobalt Oxide Batteries – The most typical kind of lithium-ion battery is this one. They are found in a wide range of gadgets, including electric cars, computers, and telephones.

II) Lithium Manganese Oxide Batteries –Compared to lithium cobalt oxide batteries, these are less expensive and less potent. When large discharge rates are not necessary, they are employed.

III) Phosphate Batteries – Of all lithium-ion batteries, these ones have the maximum energy density. They are utilized in electric vehicles and other high-power gadgets as a result.

IV) Cobalt Batteries –Compared to lithium-ion and lithium-cobalt oxide batteries, these batteries last longer. They are utilized in drones, electric vehicles, and other gadgets where a longer lifespan is desired.

Manufacturing Process of Lithium-Ion Batteries: Step by Step

Depending on the type of battery being produced, the lithium-ion battery manufacturing process can change. But certain actions are the same across all variants. Look at how lithium-ion batteries are made below. Lithium-ion battery components must first be extracted.

Although additional elements are occasionally extracted as well, graphite and lithium are the two main ingredients. To extract the lithium ions, the minerals are treated after mining. Then, carbon (graphite) and lithium metal are used to make the electrodes. The cathode and electrolyte are produced after the electrodes and electrolytes have been mixed. Lithium metal is used to make the anode once more.

Between the anode and electrolyte, a separator is inserted, and the cell is then sealed. After that, the battery is packaged and tested [19].

Step 1: Lithium Extraction

Extraction of the lithium is the initial stage of the manufacture of lithium-ion batteries. Depending on the type of lithium-ion battery, this can be accomplished in a few different ways.

Lithium can be extracted using either carbonate conversion or a solvent extraction.

I) Solvent Extraction - To extract lithium from its ore, this process uses an aqueous solution. A hydrochloric acid treatment and an organic solvent are used to dissolve the ore. The lithium in the solvent is then ionized using an ion exchange technique.

II) Carbonate Conversion- Lithium is dissolved in water with this process using a solution of sodium carbonate and carbon dioxide. After that, the mixture is separated and filtered to get rid of contaminants and get lithium carbonate.

Step 2: Anodization and Coating

The anode and cathode are then produced by manufacturers. The electrodes are made of a lithium metal and graphite combination. After that, the electrodes are coated and anodized.

I) Anodization- The electrodes are subjected to a chemical solution that causes the electrodes' surface to oxidize. After that, the anode is submerged in an electrolytic solution to create a porous layer on the electrodes' surface. To create a non-porous layer, the cathode is treated with a separate chemical mixture.

II) Coating- A solid polymer electrolyte is next applied to the electrodes as a coating. Graphite or a polymer electrolyte is used to coat the anode, while a lithium-containing electrolyte is used to coat the cathode.

Step 3: Battery Formation and Assembly

Electrolytes and electrodes are joined to form the cathode and electrolyte after the electrodes are made. The cell is then sealed after the anode has been put into the cathode.

I) Cathode and Electrolyte Combination– A vacuum chamber is filled with the cathode and electrolyte, and pressure is then applied to compel the two components to come together. The electrodes are given a substance to give them stiffness while keeping their flexibility.

II) Anode Insertion – Anodes are forced into cathodes by placing them in graphite dies and applying pressure. Next, a vacuum chamber is used to heat the entire cell to 180 degrees Celsius. The vacuum chamber's pressure pushes the two electrodes together.

III) Cell Sealing – When the cell cools to ambient temperature, the chamber is once more put under a vacuum, which makes the electrodes and electrolytes fit very tightly.

Step 4: Storage and Testing

The battery is put through a series of tests after it is created to make sure it satisfies quality requirements. To measure the cells' discharge rate, they are charged and discharged. To confirm that the cell voltage and energy are accurate, additional tests are conducted. Following storage, the batteries are prepared for packaging and delivery to clients.

Lithium-ion batteries need to be stored properly to maintain their lifespan. Between -20 degrees Celsius and 25 degrees Celsius, the batteries should be kept cool and dry. Additionally, they need to be kept at a low humidity level of under 50%.

Finally, it's important to keep lithium-ion batteries away from sources of intense heat, sparks, or fires.

Summing up

Depending on the type of battery being produced, the manufacturing process may vary slightly. However, there are a few procedures that apply to all varieties of lithium-ion batteries. The first step is the mining of the raw ingredients for lithium-ion batteries. They are then treated to remove the lithium ions [19].

2.1 Market trend of Lithium –ion batteries

Since the 1990s, when the Sony Corporation made LIBs available for purchase, they have been widely used in electric equipment and cars, energy systems, and portable electronic gadgets [20]. From only 9 billion dollars in 2005 to almost 45 billion dollars in 2016, the LIB market increased, with a large percentage of its applications being in electrical devices [21]. This potential market is anticipated to reach roughly 80 billion US dollars in 2025, accounting for 70% of the market for rechargeable batteries.

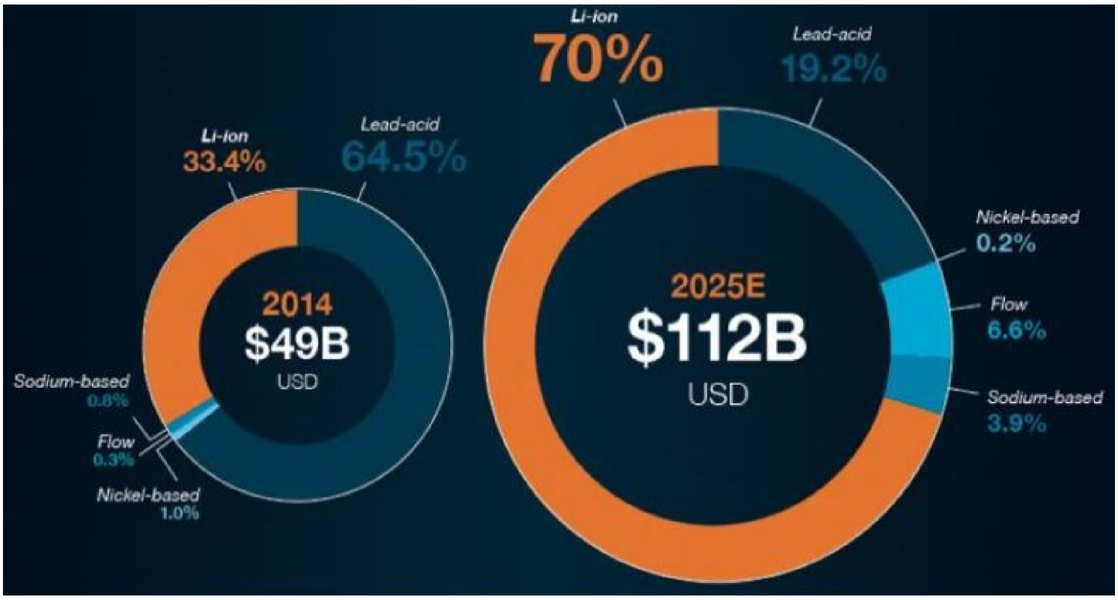


Fig. 5. Rechargeble battery market size

The LIB market is booming because of its widespread application. Since electric vehicles and power storage systems are used widely in the coming decade, the market for LIBs is expected to grow significantly. It is anticipated that in 2025, the market will be worth about 80 billion US dollars, and that in 2030, there will be a total demand for 390 GWh of electricity. According to the table 1, when EVs, HEVs, and PHEVs advance and become more common, the road transportation sector will overtake the portable electronics sector and become the largest sector of the LIB market within the next ten years. The necessity to store energy from renewable energy sources or in an off-grid energy system would also significantly increase the need for LIBs [22].

Table 1. Market Growth for LIBs

	2010	2015	2020	2025	2030
Cell phones	6	11	17	28	44
Tablets	1	7	12	17	25
Pc	12	9	9	9	11
Portable electronics, other	3	4	7	12	20
Portable electronics, total	21	31	45	66	100
Electric vehicles	0	11	65	115	200
Plug-in hybrid electric vehicles	0	2	8	13	25
Hybrid electric vehicles	0	0	2	7	15
Road transport, other	0	0	1	2	5
Road transport total	0	13	76	137	245
Storage in power supply	0	0	2	10	30
Other applications	1	1	2	7	15
Total	22	45	125	220	390

The amount of lithium consumed increased by 18% from 49000 tons in 2018 to 57700 tons in 2019. [23] The estimated amount of lithium deposits worldwide is 17 billion tons. The world's lithium reserves will run out if consumption continues to rise by 18% annually. About 63 million tons of lithium will be required in 30 years, which is 40 million tons higher than the available reserves (FIG 6). The market for lithium-ion batteries is expected to grow rapidly, notwithstanding the possibility that greater lithium sources will eventually be found. Lithium shortages are predicted by an increasing number of organizations worldwide, and in recent years, these projections have drawn significant scientific attention [24,25].

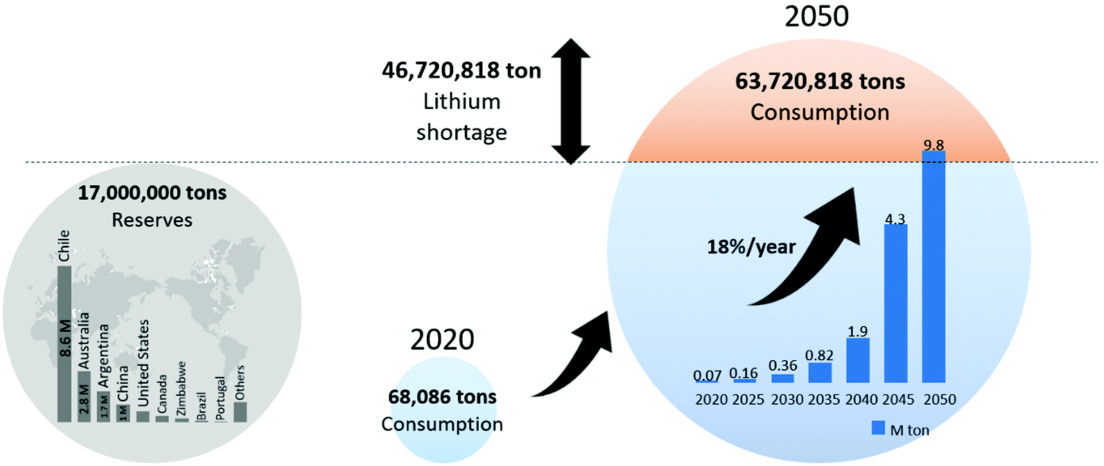


Fig. 6. After 30 years, assuming an 18% annual increase in lithium usage, the world's lithium supplies will be exhausted.

2.2 Waste Generated Annually

Most of the lithium-ion battery waste has been the subject of research on lithium recycling. Anode, cathode, electrolyte, and separator are the components of lithium-ion batteries. Lithium-ion batteries work through the flow of Li+ ions and electrons. Depending on its capacity and use, the cathode is made of lithium-containing substances such $LiFePO_4$ and $LiNi_{0.3}Mn_{0.3}Co_{0.3}O_2$. Graphite and other carbon-based materials that can receive lithium ions make up the anode. For electrical conduction and durability, a polymer binder such as polyvinylidene fluoride (PVDF) connects the cathode and the anode to aluminium or copper foil. Typically liquid, electrolytes transport lithium ions between the cathode and anode. Typically, they are lithium salts (such LiPF6) that have been dissolved in ethylene carbonate (EC) or dimethyl carbonate (DMC). the polymers

In comparison to other batteries, a lithium-ion battery has a lifespan of up to three years in small electronic devices and five to 10 years in bigger ones. However, lead-acid batteries and Ni-Cd batteries have lifespans of fifteen to twenty years and five to ten years, respectively. [26-30] Currently, small electronics represent for 80% of lithium-ion battery utilization, with EV and ESS applications making up less than 20%. [31] In 2012, the amount of lithium-ion battery disposal was predicted to be 10700 tons. [32] This amount has risen steadily each year, and in 2020 it may reach up to 250000 tons. [31] It is anticipated that there will be more lithium-ion batteries in use as EVs and ESSs are widely adopted. Government agencies or businesses approved by the manufacturer collect used lithium-ion batteries. Lithium-ion batteries are typically disposed of by consumers in a location authorized by the government or they are voluntarily collected by the appropriate agency. However, Australia, the EU, and the US only collect 2-5% of lithium-ion batteries (Fig-7) [33]. Consumer ignorance and the propensity to sell gadgets rather than recycle them are to blame for the poor collection rate. Although it may differ by nation, there isn't enough physical and legal infrastructure to ensure widespread collecting of discarded lithium-ion batteries and their efficient, secure, and cost-effective transportation. To considerably raise the collection rate, significant improvements are needed [34].

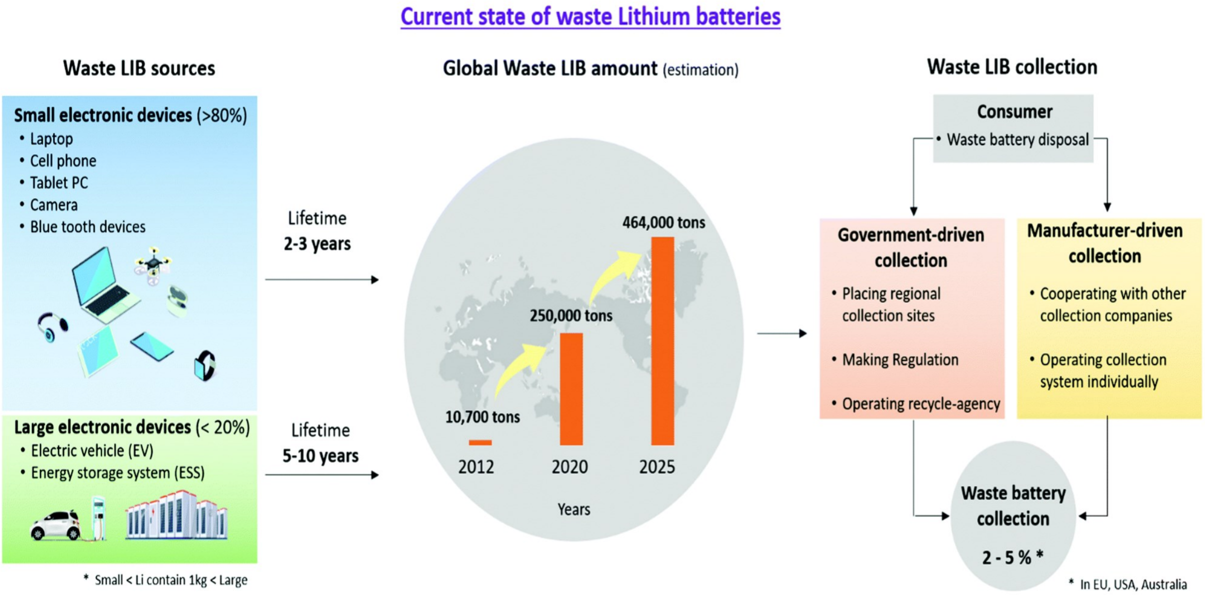


Fig. 7. Sources, quantity, and collection of discarded lithium-ion batteries.

3. Lithium and Cobalt

Lithium

A chemical element with the atomic number 3 and the symbol Li is lithium. It is a delicate, white-silver alkali metal. It is the least dense metal and the least dense solid element under typical conditions. As with all alkali metals, lithium must be stored under vacuum, in an inert atmosphere, or in an inert liquid such as mineral oil or pure kerosene. It has a shiny sheen when cut, but damp air quickly corrodes it to a dull silvery Gray, then a black patina. Only in (often ionic) compounds, such pegmatitic minerals, which were previously the principal source of lithium, can it ever occur freely in nature. It is prevalent in ocean water and is frequently recovered from brines because of its solubility as an ion. Electrolysis is used to separate lithium metal from a solution of lithium chloride and potassium chloride.

Heat-resistant glass and ceramics, lithium grease lubricants, flux additives for the manufacturing of iron, steel, and aluminium, lithium metal batteries, and lithium-ion batteries are only a few of the industrial uses for lithium and its compounds. More than 75 percent of the production of lithium is used for these purposes.

Although its activities are unknown, trace levels of lithium are found in biological systems. Lithium salts have shown promise in the treatment of mental illnesses including bipolar disorder as an antidepressant and mood stabilizer [35].

Cobalt

A chemical element with the atomic number 27 and the symbol Co is cobalt. Apart from minor concentrations found in alloys of naturally occurring meteoric iron, cobalt is only ever found in the Earth's crust in a chemically mixed state. The free element created by reductive smelting is a hard, shiny metal that is silver-Gray in colour.

Cobalt-based blue pigments have been used for jewellery, paint, and to give glass a characteristic blue tinge since the dawn of time, but for a very long time, it was believed that the colour came from the well-known metal bismuth. Some of the minerals that produce blue pigments were long known as "kobold ore" (German for "goblin ore"). This was because they were deficient in recognized metals and gave off toxic fumes that contained arsenic when melted. [36] Such ores were revealed to be reducible in 1735 to a new metal, the first discovered since antiquity, which was subsequently given the kobold moniker.

Lithium-ion batteries and the creation of magnetic, wear-resistant, and high-strength alloys require cobalt predominantly. Glass, ceramics, inks, paints, and varnishes all have a distinctive deep blue hue because to the compounds cobalt silicate and cobalt (II) aluminate ($CoAl2O4$, cobalt blue). Only cobalt-59, a single stable isotope of cobalt, is found in nature. A crucial radioisotope for industry is cobalt-60, which is utilized to create high-energy gamma rays as well as a radioactive tracer [37].

3.1 History of Lithium and Cobalt

a) lithium

Brazilian Jozé Bonifácio de Andralda e Silva made the first lithium mineral discovery, LiAlSi4O10, on the Swedish island of Utö in the 1790s. When tossed onto a fire, it was noted to produce a bright scarlet blaze. Johan August Arfvedson of Stockholm examined it in 1817 and concluded it contained lithium, a then-unknown metal. He understood that this was a new alkali metal that was lighter than sodium. He was unable to electrolyze it to separate it from sodium, though. William Brande managed to get a modest amount in 1821 using this method, but not enough to do measurements. It wasn't until 1855 that the British chemist Augustus Matthiessen and the German chemist Robert Bunsen were able to electrolyze molten lithium chloride to produce it in large quantities [38].

b) cobalt

A tiny glass piece that was bright blue with cobalt was found in the tomb of Pharaoh Tutankhamen, who ruled Egypt from 1361 to 1352 BC. In China, cobalt blue was employed in pottery glazes and was known there even earlier.

A dark blue ore from some nearby copper mines caught the attention of Stockholm chemist Georg Brandt in 1730. After establishing that it included a hitherto unknown metal, he gave it the name by which its ore was derided by German workers, where it was occasionally mistaken for a silver ore. In 1739, he published the findings. Other scientists questioned his claim that he had discovered a new metal for a long time, claiming that his new element was a mix of iron and arsenic. Eventually, though, it came to be accepted as an element in its own right [39].

3.2 Importance

a) lithium

Rechargeable batteries for cell phones, computers, digital cameras, and electric vehicles are lithium's most significant application. Some non-rechargeable batteries for devices like heart pacemakers, toys, and clocks also include lithium.

Aluminium and magnesium are combined with lithium metal to create alloys that are stronger and lighter. Armor plating is made from a magnesium-lithium alloy. High-speed trains, bicycle frames, and aircraft all make use of aluminium-lithium alloys.

Lithium oxide is utilized in specialty glassware and glass ceramics. One of the most hygroscopic substances known is lithium chloride, which is employed in industrial drying systems and air conditioning systems (as is lithium bromide). A general-purpose and high-temperature lubricant is lithium stearate. Although the exact mechanism by which lithium carbonate acts on the brain is still unclear, it is utilized in medications to treat manic depression. Hydrogen is stored in lithium hydride to be utilized as a fuel [38].

b) cobalt

Cobalt can be magnetized like iron, which is why magnets are made from it. To create exceptionally potent magnets, it is alloyed with nickel and aluminum.

In gas turbine generators and jet turbines, where high-temperature strength is crucial, other cobalt alloys are utilized.

Cobalt metal is occasionally used in electroplating due to its appealing look, hardness, and corrosion resistance.

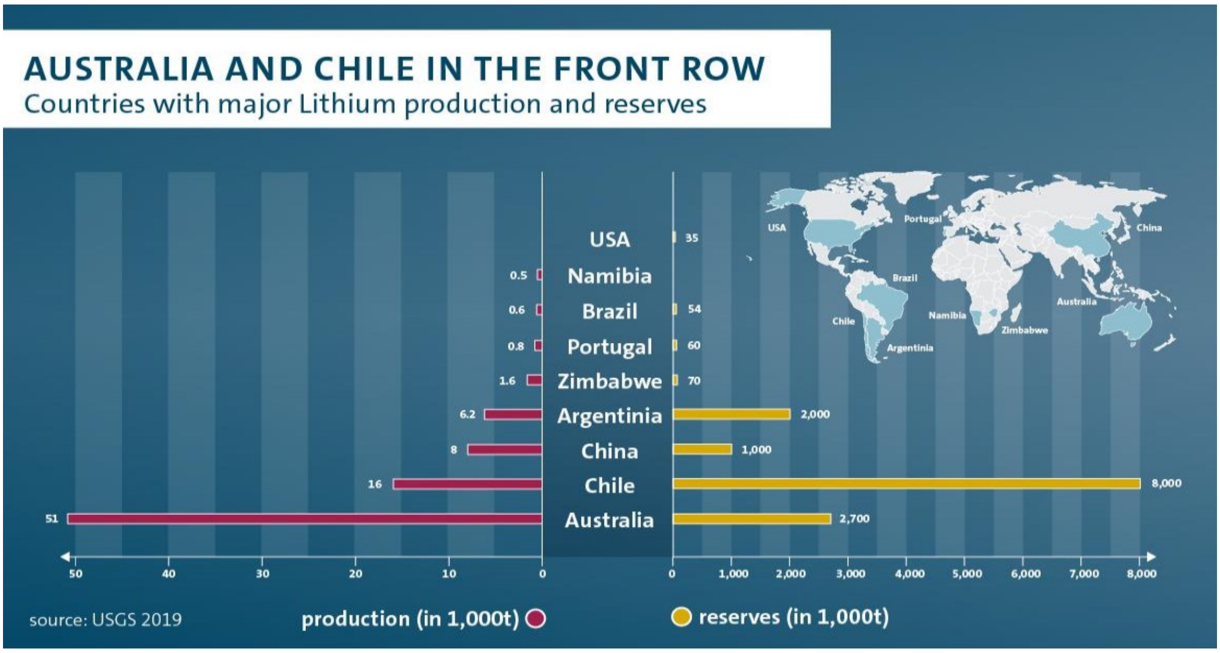
Since ancient times, cobalt salts have been utilized to create vivid blue hues in paint, porcelain, glass, pottery, and enamels.

Cancer is treated with radioactive cobalt-60, which is also utilized in some nations to preserve food [39].

3.3 Place of Extraction

LITHIUM

Chile has the greatest known lithium deposits in the world, at 8 million tons. This places in the South American nation ahead of Australia (2.7 million tons), Argentina (2 million tons), and China (1 million tons). Portugal has fewer of the valuable raw materials in Europe. The estimated 14 million tons of total reserves worldwide. This is equivalent to 165 times the output volume in 2018.


AUSTRALIA AND CHILE IN THE FRONT ROW
Countries with major Lithium production and reserves

source: USGS 2019

Fig. 8. Countries with major lithium production and reserves

Australia was by far the largest provider of lithium in 2018 with 51,000 tons, followed by Chile (16,000 tons), China (8,000 tons), and Argentina (6,200 tons). This is demonstrated by data from the USGS (United States Geological Survey). The top four nations have long dominated the scene, with Australia only recently pulling away from Chile in the standings.

Simply said, lithium from Australia comes from mining ore, whereas lithium from Chile and Argentina comes from salt deserts, or salars. The following describes how raw elements are extracted from salars: large basins are used to catch the evaporating saltwater that contains lithium that is brought to the surface from underground lakes. Up until the lithium is acceptable for use in batteries, the leftover saline solution is further treated via several processes [40].

COBALT:

Cobalt is a by-product of copper and nickel production, hence nations that generate large amounts of those two metals also produce large amounts of cobalt. The US Geological Survey selected the top 10 cobalt producers in the world in 2017, and they are shown below [43].
[43] In 2016, the DRC produced 66,000 metric tons of cobalt, a 3,000 metric ton increase from 2015. However, this number dropped to 64,000 in 2017. 60% of the cobalt in the world is made there. Cobalt production in China remained constant between 2015 and 2016. The biggest producer of refined cobalt in the world and the biggest exporter of cobalt to the US is China. Cobalt is mostly a by-product of nickel and copper mining in Canada. Russia was the fourth-largest cobalt producer in the world in 2016. Russia, which was the second-largest producer of cobalt in 2017, intended to raise its output. Cobalt output fell in Australia throughout 2015, 2016, and 2017. Like Russia, most of Australia's cobalt production results from the mining of copper and nickel. The Philippines government made the decision to reduce cobalt production, which may continue in the future, to maintain environmental sustainability [41,42].

<u>Global producers of cobalt [41]</u>

Figure - Reserves

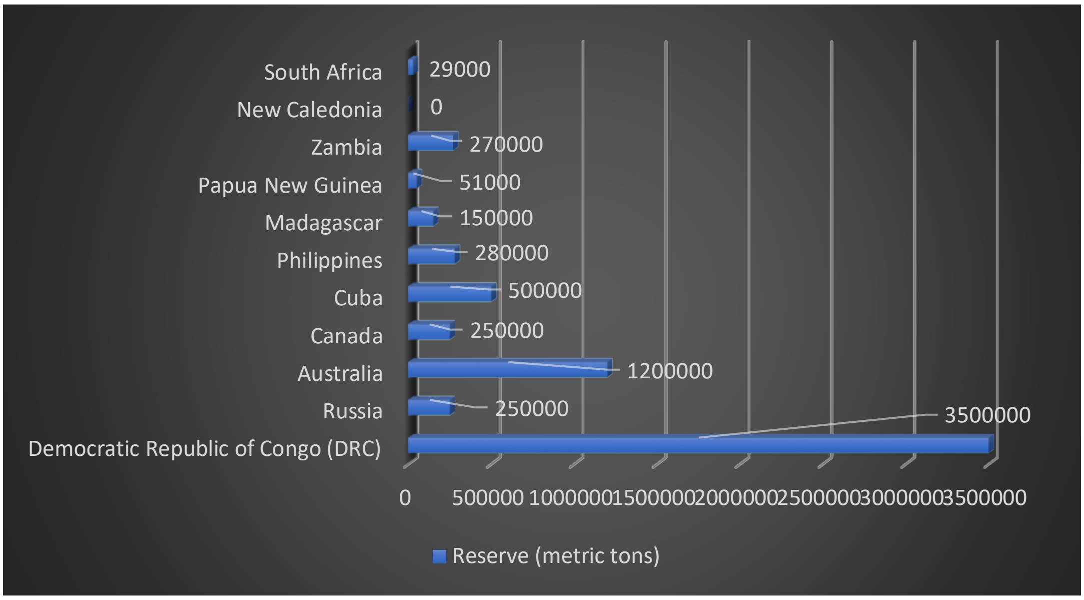


Fig. 9. Reserves

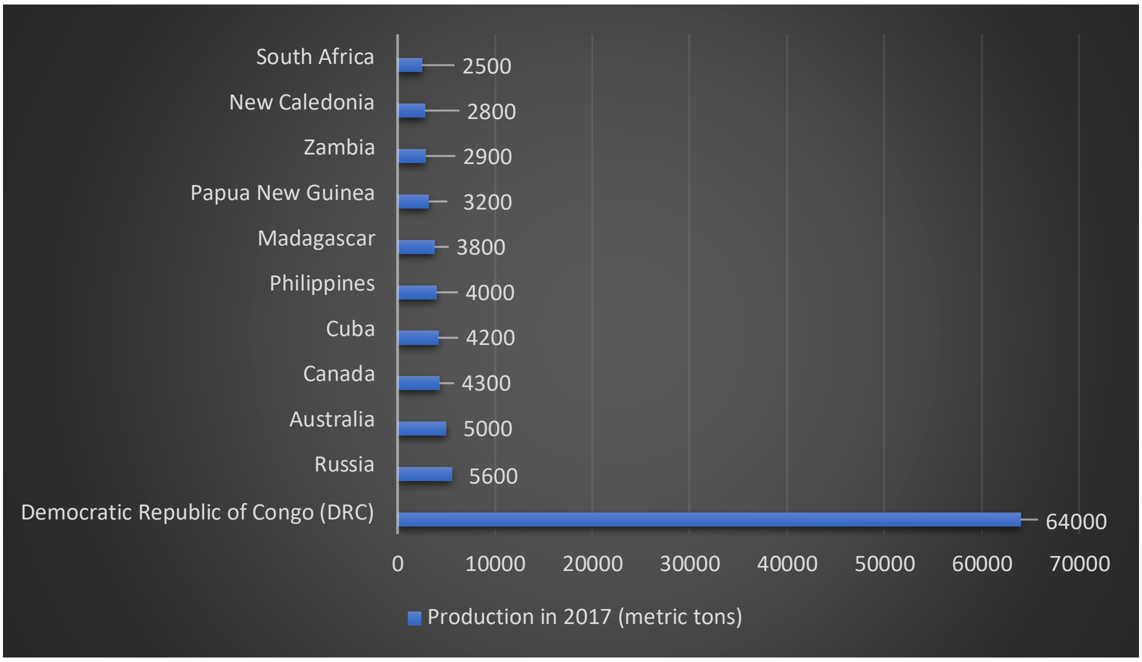


Fig. 10. Production

3.4 Extraction Process

Lithium

Underground brine deposits and mineral ore deposits are the two principal sources of commercial lithium. Depending on the raw material, many techniques are used to extract and treat lithium, some of which are as follows:

A) Conventional lithium brine extraction

Liquid brine pools beneath salt flats, known as salars, the majority of which are found in southwestern South America and China, are where the vast majority of today's lithium is recovered. Geothermal brines and oil field brines are two more sources of lithium-rich brine, and they are discussed below.

Lithium brine recovery is normally a simple but time-consuming process that can take several months to several years to finish. The subsurface salar brine resources must be accessed by drilling, after which the brine is pumped to the surface and distributed to evaporation ponds. The brine is left in the evaporation pond for several months or years, or until sun evaporation has removed the majority of the liquid water content. Salar brines are highly concentrated and frequently include sodium and potassium in addition to lithium. Typical facilities run a number of sizable evaporation ponds of varying ages, and while they wait for the lithium content to reach a concentration that is ideal for further processing, they may collect other metals (such as potassium) from the younger ponds. Reverse osmosis (RO) is sometimes used to concentrate lithium brine in order to hasten the evaporation process.

When an evaporation pond's brine reaches the ideal lithium concentration, it is pumped to a plant for lithium extraction. Depending on the makeup of the brine field, this procedure may vary, but typically includes the following steps:

- Pre-treatment- Filtration and/or ion exchange (IX) purification are typically used in this step to remove any impurities or undesirable components from the brine.
- Chemical treatment- Then, by precipitation, a variety of chemical solvents and reagents may be used to separate the desired products and by-products.
- Filtration- The brine is subsequently filtered to remove precipitated solids.
- Saleable lithium production- The product is then filtered and dried for sale after the brine has been treated with a reagent, such as sodium carbonate to create lithium carbonate. Other commonly available forms of lithium, such as lithium hydroxide, lithium chloride, lithium bromide, and butyl lithium, can be made using a variety of reagents, depending on the final product that is needed.
- The residual brine solution is sent back into the underground reservoir after the lithium extraction procedure is finished [44].

B) Hard rock / spodumene lithium extraction

Mineral ore resources produce almost 20 tons of lithium yearly, yet they only contribute a minor portion of the world's lithium production. Only five minerals are actively mined for lithium production, even though well over 100 distinct minerals contain some quantity of lithium. The most prevalent of them is spodumene, followed by lepidolite, petalite, amblygonite, and eucryptite.

Mineral ore deposits frequently contain more lithium than salar brines, but they are more expensive to reach since they need to be mined from hard rock formations. Lithium extraction from mineral ore can be twice as expensive as brine recovery because of the additional energy, chemicals, and materials needed for the process, which has decreased its market share.

The method used to extract lithium from ore can change depending on the particular mineral deposit in question. Typically, the procedure involves taking the mineral stuff out of the earth, heating it, and then crushing it. The powdered mineral is crushed and mixed with chemical reactants, such as sulfuric acid. The resulting slurry is then heated, filtered, and concentrated through an evaporation process to produce marketable lithium carbonate, while the wastewater produced is treated for reuse or disposal [44].

C) Other lithium extraction processes

Lithium can be generated from a few different sources outside salar brine and mineral ore, though such production is not yet common. These additional lithium sources consist of:

- Hectorite clay- The development of efficient clay processing methods has involved a significant investment in research and development. These methods include water disaggregation, hydrothermal treatment, acid, alkaline, chloride, and sulphate leaching. None of these approaches has, to this point, shown to be commercially feasible for lithium extraction from clay.

- Seawater- Our oceans are thought to contain hundreds of billions of tons of lithium, making them a desirable source for supplying future lithium demand. While current methods, such as co-precipitation extraction and hybrid IX-sorption, have been successful in removing lithium from seawater, newer membrane technologies hold greater potential for reducing the price of saltwater extraction.
- Recycled brines from energy plants- As the demand for lithium rises globally and new technologies are developed, efforts to extract lithium from geothermal brines are becoming more and more popular. Although they may be modified depending on the brine stream's composition, the procedures used adhere to standard brine extraction.
- Recovered oil field brine- Technically, the extraction of lithium from oil field brines is no different from ordinary brine extraction; the only distinction is the brine's origin.
- Recycled electronics- Although lithium-ion battery recycling doesn't really fit the definition of extraction, it will become a more important supply of the metal as demand rises.

Although each of them is a potential supply of lithium, the technology to extract brine from them are not yet sufficiently developed to make them a viable or cost-effective alternative to mining mineral ore or salar brine [44].

Cobalt

Depending on the ore grade, size, and surface type, cobalt can be extracted through open-pit mining, underground mining, or a mix of open-pit and underground mining. Depending on the body or deposit type, which may include considerable amounts of cobalt, these two mining techniques can be used singly or in combination. Pyrometallurgy, hydrometallurgy, and vapor-metallurgy are the three fundamental processes used in the cobalt extraction process [45]. The cobalt extraction method is briefly explained by a flowchart in Fig 11.

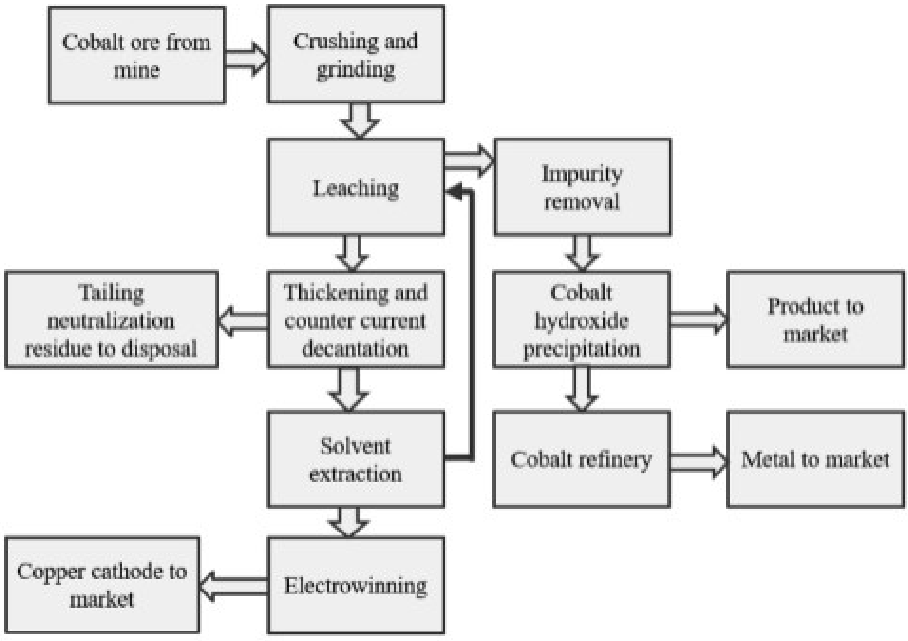


Fig. 11. Cobalt extraction method

- Open-pit mining - This technique, which is believed to be the most cost-effective for extracting minerals, can be employed if the ore is close to the surface. Using trucks or other conveying equipment, overburdens are removed in this sort of mining in order to extract the needed metals [46].
- Underground mining- When the ore body is more than 100 meters below the surface, typical mining systems are used in underground mining.
- Hydrometallurgy- The most prevalent method of hydrometallurgical processing is pressure acid leaching. In pressure acid leaching, iron ore is heated to a high temperature and pressure for 90 minutes while being combined with a sulfuric acid solution. Primary and secondary metals are then changed into sulfate salts after this point. Then, using a counter-current decantation circuit (CCD), these sulfate salts are cleaned, yielding a clear nickel and cobalt solution as well as residue. This mixed metal solution is given to a high-pressure oxygen re-leaching process. The cobalt and nickel are then separated using an oxide reagent. For ores where there should be less acid use, the pressure acid leaching method is appropriate [46].
- Electro-winning- In copper belt mining, these procedures are employed to filter the metal-rich solution. Heating and electrolyting are done after filtering. Cobalt precipitates during electrolyting onto stainless steel, forming high purity cathodes, and then the acid is recycled [47].
- Vapometallurgy- At typical atmospheric pressure, these procedures are employed to extract cobalt from laterite ores. Ore, matte, and concentrate can all be used to extract and purify cobalt. By passing carbon monoxide and other gases through the recovered

metal-containing ore, cobalt is then deposited in a separate chamber by the evaporated gases [48].

- Pyrometallurgy- As a result, the ore is heated in order to separate the metals according to their distinctive qualities and traits, such as melting point and density. In sulfide ores where smelting-based recovery is feasible, this technique is used. Smelting produces cobalt products with carbonates and oxides [49, 46].

4. Recycling Plants

Consumer electronics, stationary energy storage, and the electric vehicle (EV) industry are all dominated by lithium-ion batteries. But the sustainability of Li-ion batteries depends on their entire lifecycle, including end-of-life management. Concerns over the availability of raw materials like cobalt are also growing. Recycling can bring back the embedded value of battery metals, generating additional revenue and a circular supply chain that is protected against changes in the price of battery components. The Li-ion battery recycling industry is anticipated to grow significantly over the next two decades as stakeholders throughout the supply chain for these batteries recognize the possibilities of recycling. Nearly 12 million tonnes of Li-ion batteries will be recycled in 2042, yielding valuable metals worth $49 billion USD [50].

As businesses get ready for the widespread availability of used Li-ion batteries, interest in and investments in the Li-ion battery recycling market have increased over the past year. Currently, the bulk of consumer gadgets never go through recycling (e.g., laptops and mobile phones). Because EV batteries must be handled by experts when they can no longer be used in vehicles, it is simpler to create a collection network for them. The extended producer responsibility (EPR) mandates that original equipment manufacturers (OEMs) handle retired batteries in various nations. In the coming decades, as EV batteries start to approach their end-of-life, we will see an exponential expansion in the number of retired EV batteries accessible for recycling, which will cause them to dominate the market and create enormous value potential [50].

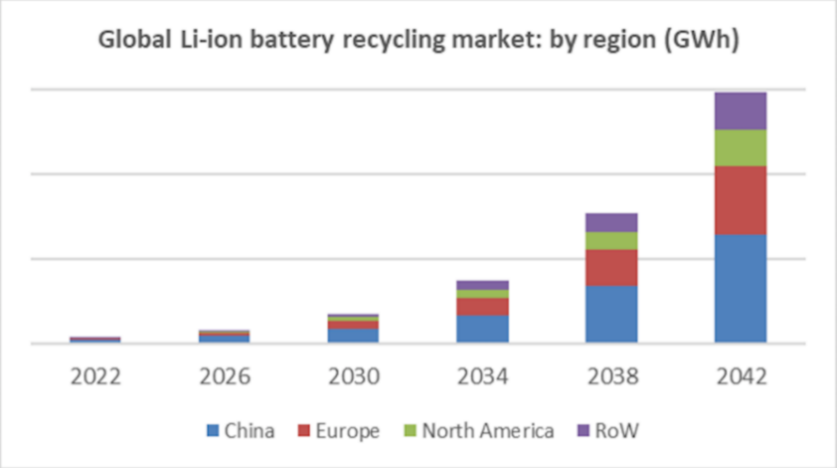


Fig. 12. Global li-ion battery recycling market: by region (GWh)

The research offers a thorough analysis of the Li-ion battery recycling market's current situation, including a global technical and policy deep-dive. Due to the early adoption of Li-ion battery management policies, China clearly dominates, although Europe and North America are starting to catch up. Following the examination of data from more than 85 Li-ion battery recyclers globally, IDTechEx published a report on numerous commercial-scale recycling facilities slated to open in these locations in 2022 or 2023. The research analyses developments in direct recycling in addition to current descriptions of mechanical, hydro, and pyrometallurgical processes. Direct recycling, though still in the pre-commercial stage, presents a promising method that can revitalize used cathodes and perhaps recover other battery parts like the anode and foils with significant environmental advantages. Direct recycling might become economically viable as the market ages and economies strive for advanced circularity [50].

We discovered that to effectively recycle Li-ion batteries, a number of important concerns must be resolved. One of the most crucial conditions for effective Li-ion battery recycling is battery collecting. The low volume of batteries that need to be recycled or the high cost of collection might hurt the economics of recycling if there was no effective network for collecting batteries. Another issue is the insufficient recycling design, which makes battery disassembly and sorting expensive and time-consuming. While EV batteries' sheer size and ease of collection present a tremendous opportunity, they also present several technological and financial difficulties. Because of the EV battery packs' varied designs and high voltage, safe disassembly will always be a difficult and time-consuming process. In addition, EV batteries' $/kWh value will be lower than that of consumer electronics batteries, requiring recyclers to extract more material at greater purity levels and efficiency levels to break even on their recycling process [50].

Another hot question surrounding EV batteries at the end of their useful lives is whether they should be recycled to recover the raw materials or given a second chance in alternate uses like stationary energy storage. Whether or not used EV batteries are recycled in the end, they will still need to be disposed of. Recycling should be the final resort when the batteries can no longer be used because it is the least sustainable action in a circular economy. Though, a lot more variables are considered. Technically, giving old EV batteries a second life shouldn't have any impact on their ability to be recycled; but, doing so will prolong the recycling process, which will affect the logistics and economics of recycling. In this, we go through the economics of recycling Li-ion batteries as well as the major variables that could affect its value [50].

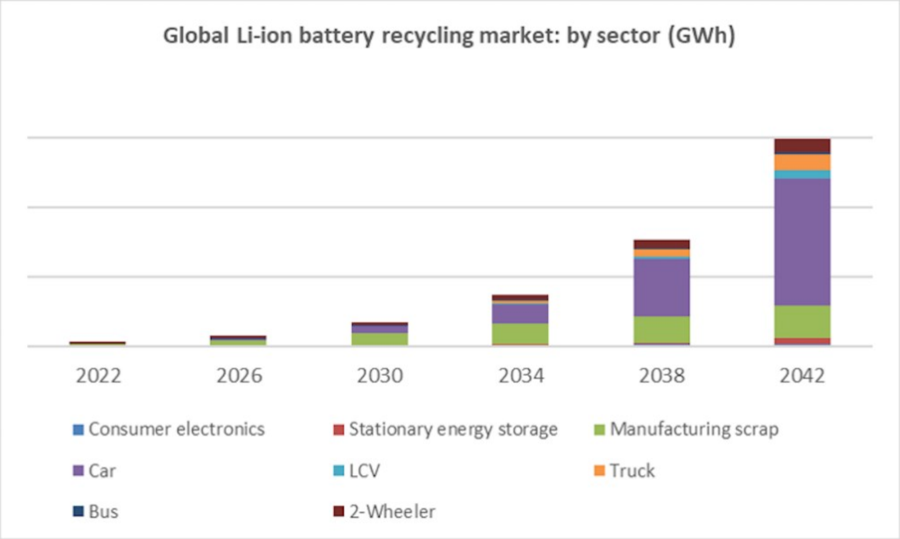


Fig. 13. Global li-ion battery recycling market: by sector (GWh)

The Li-ion battery recycling market is forecasted for the years 2020 through 2042 in this IDTechEx analysis, both in terms of market value and volume. The forecasts are segmented by geography, cathode chemistry, the lithium-ion battery industry (consumer electronics, stationary energy storage, manufacturing scrap, and electric vehicles), and the important metals recovered (lithium, cobalt, nickel, manganese, copper, and aluminium). Electric automobiles, light-commercial vehicles, medium- and heavy-duty trucks, buses, and two-wheelers are the different categories of EVs (scooters and motorcycles). GWh, Ktonne, and $billions of data are provided together with a bottom-up examination of recycling rates [50].

The market for recycling lithium batteries is expected to increase from USD 4.6 billion in 2021 to USD 22.8 billion in 2030 [51].

This suggests that from 2021 to 2030, CAGR will be 19.6%. Some of the significant prospects for the lithium-ion battery recycling market are rising investments in EVs and incentives to promote battery recycling [51].

The lithium-ion battery has a short lifespan and is constructed of rare elements like lithium, cobalt, and nickel. It is challenging to disassemble it and recover all its parts. Hazardous compounds found in used batteries include acids and heavy metals like mercury and lead. This creates a significant issue for the electric vehicle (EV) market. Its storage and recycling capabilities hold the key to the problem.

In the foreseeable future, it appears that the number of EVs on the roads will continue to grow exponentially. The industry has already predicted 6.6 million global sales in 2021, up from 3 million in 2018. As a result, there will be more used batteries in the environment. the environment. If not addressed, these could have an adverse effect on health and pose environmental risks. Consequently, controlling them is an urgent necessity.

Several start-ups and some established companies are up for the challenge of recycling lithium-ion batteries [51].

The top five battery recycling companies on the planet are listed below.

I) Inc. Lith ion Recycling (Canada)

Canada-based the company Lith ion Recycling (https://www.lithionrecycling.com/) enables the management of lithium-ion batteries in an efficient and profitable manner. Direct recycling offers a less expensive option to battery makers and makes it simple to retrieve valuable cathode materials. With an annual processing capacity of 7,500 metric tonnes, the company has one of the greatest recycling capacities in the entire globe. This is the same as 20,000 electric automobiles, to put it simply.

Then what? The company is proud to have a 95 percent recovery rate. The use of technology completes the cycle of battery regeneration. By making essential components easy to reach, it will reduce the cost of automobiles over the long term [51].

II) Li-Cycle Inc (Canada)

For recycling lithium-ion batteries, the Canadian start-up Li-Cycle (https://li-cycle.com) combines mechanical size reduction and hydrometallurgical resource recovery methods. The recycling is provided by the business.

technique for processing lithium-ion batteries securely while emitting little greenhouse gas. As a result, it makes it possible for all lithium-ion batteries to have a sustainable end-of-life pathway. Their recycling method's main advantage is the creation of a non-hazardous product, which reduces transportation liability and sharply reduces expenses.

The Canadian company's overall recycling capacity increased to a massive 20,000 tonnes per year with the addition of Spoke 3 facility in the previous year [51].

III) Firma Duesenfeld (Germany)

German Duesenfeld develops an electrolyte recovery technique (https://www.duesenfeld.com/). This method combines mechanical and thermodynamic procedures to recover more raw materials while reducing the energy needed for recycling. Low (/www.saurenergy.com) due to energy-efficient methods and the capacity to recover a significant amount of material.

11/28/22, 8:47 PM Saur Energy International lists its top picks for lithium battery recycling companies for the new EV era at this link: https://www.saurenergy.com/opinion/5-best-lithium-battery-recycling-firms-for-the-new-ev-era 2/8 carbon footprint when recycling processes are finished. By 2020, the company had built a cutting-edge facility processing more than 3000 tonnes of recycled Li-ion batteries annually.

The issue of a battery's core being irreparably damaged is solved by the electrolyte recovery technique. It's interesting to note that the technology uses subfreezing temperatures to reverse the negative effects of the electrolytes. This process doesn't generate harmful fluorine compounds. Reduced energy consumption is also possible, particularly following the stages of washing and combustion [51].

IV) Fortum (Finland) (Finland)

In order to recycle the battery materials, Fortum (https://www.fortum.com) also combines mechanical and hydrometallurgical processes. With the construction of a new plant last year, the company's capacity for recycling reached 3000 tonnes annually. Lithium, cobalt, manganese, and nickel from the battery can be recovered using low-CO2 techniques and used to make new batteries. The methods used to treat batteries are reliable, efficient, and sustainable. They assert that the combination of mechanical and hydrometallurgical recycling techniques can recycle 80% of a battery. It's interesting to note that the dark mass of the battery contains 95% recoverable precious metals [51].

V) Envirostream (Australia) (Australia)

The only significant onshore mixed-battery recycling company in Australia is Envirostream (https://envirostream.com.au/). With collecting units, multiple drop-off locations, and full battery processing, it provides a variety of battery collection and disposal services. Its claimed spent battery sorting capacities increased to 4,000 kg per day with the installation of its second battery recycling operation in Laverton, Victoria, last year. It has a lot of room to grow over the next few decades. Australia produces up to 3,000 tonnes of lithium-ion battery trash annually, according to the CSIRO. It was interesting to see that it said the garbage amount would reach 100,000 tonnes by 2036! [51].

Asia's Competition for Lithium Battery Recycling

The market for electric vehicles is expected to grow significantly in Asia's two most populous economies, China and India. Battery recycling facilities now have the difficulty of meeting the demands of a large consumer base.

In the battle to recycle lithium, India is trailing. According to projections, India will require extra recycling capacity of 60,000 tonnes over the following five years. Currently, Lohum, Attero, Recykal, and Karo Sambhav are the leading companies in this field in India.

Currently, Lohum states that it recycles 6000 tons of lithium-ion batteries (1GWh) or 0.5 million electric 2W annually.

Others, like Attero, can recycle 1,000 metric tons of lithium-ion batteries annually. In contrast, India already produces more than 50,000 tonnes of lithium-ion battery trash annually. India's capacity is therefore far smaller, necessitating an increase in recycling capacity.

On the other side, 77% of Asia's capacity for recycling EV batteries is found in China. China, one of the biggest EV marketplaces in recent years, has around 200,000 tons of decommissioned power batteries by 2020. By 2025, the amount is predicted to increase to around 780,000 tons. China's top recycling companies include GEM, Quzhou Huayou Cobalt New Material, and Hunan Brunp Recycling Technology (formerly a scrap company) [51].

5. Materials and Methods

5.1 Types of Recycling Techniques

Since the 1990s, recycling of lithium-ion batteries has been actively explored and lately acquired popularity. However, more expensive materials like cobalt are the subject of most research, rather than lithium. As a result, little attention has been paid to recovering lithium from old batteries. Since cobalt is the most expensive component of a lithium-ion battery, there has been a lot of study into ways to lower its concentration or replace it with LiFePO4 or LiNi0.3Mn0.3Co0.3O2 [52]. But lithium, which is utilized in the cathode, electrolyte, and anode of lithium-ion batteries, is a crucial element that cannot be replaced. Therefore, a thorough analysis of lithium recycling from lithium-ion battery recycling is required.

There are two main ways to extract lithium from a lithium-ion battery. The discarded battery is put through a pre-treatment procedure to separate the lithium-containing active material (cathode, anode) from the peripheral pieces because it is difficult to extract lithium from the packed battery (plastic, polymer). Following that, lithium is extracted chemically from the active components using pyrometallurgy, hydrometallurgy, and electrochemical techniques (Fig 14). The pre-treatment and lithium extraction techniques are described.

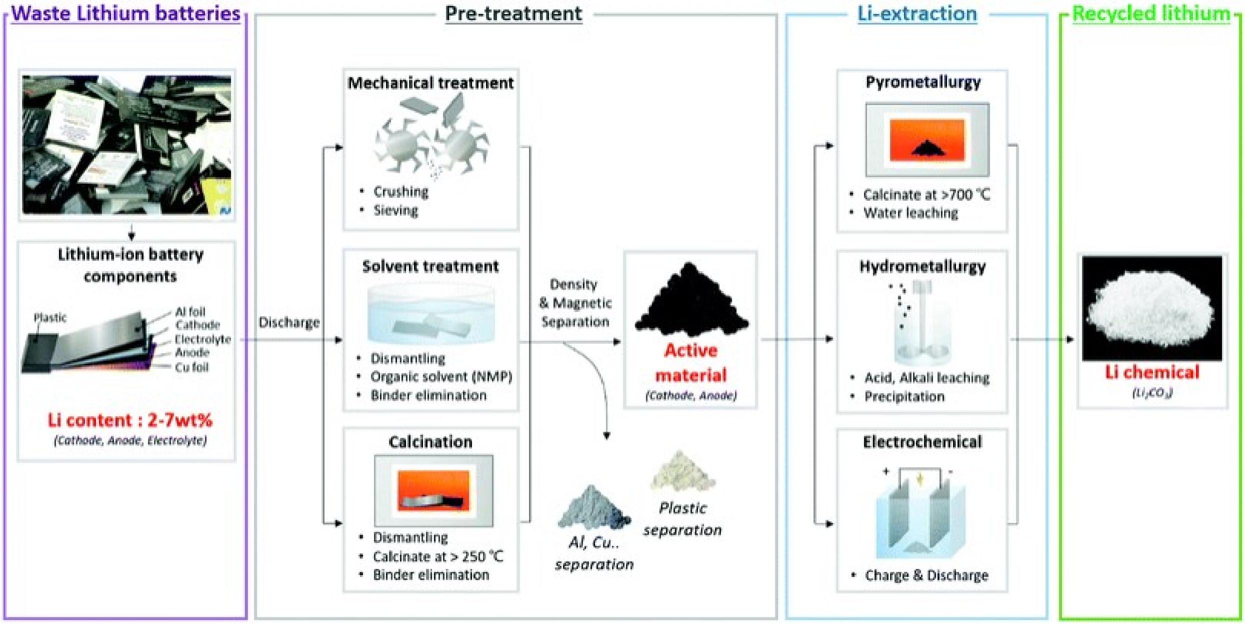


Fig. 14. Schematic diagram of the overall lithium recycling stages and methods from discarded lithium-ion batteries.

- Pre-treatment methods for waste lithium-ion battery

It is challenging to determine how much power is still in a used lithium-ion battery. There may still be some power in the battery even after it has lost all of its charge. Furthermore, treating the batteries directly is ineffective since lithium-ion batteries include a variety of elements. A pre-treatment procedure is therefore crucial. Only when used lithium-ion batteries are completely exhausted can they be securely pre-treated and separated. If not, a local short-circuiting risk exists that the battery will blow up or release hazardous fumes. Using electronic technology and conductive liquids, Hauck and Kurrat explored several battery discharge procedures [53].

The most popular technique involves immersing the battery in a conductive liquid, like a NaCl solution. Even though NaCl is the most often used conductive solution, research on the corrosion and discharge rates of other conductive liquids is still ongoing [54,55]. Mechanical separation, solution treatment separation, and calcination treatment separation are three main categories of techniques for separating the active material from the discarded battery.

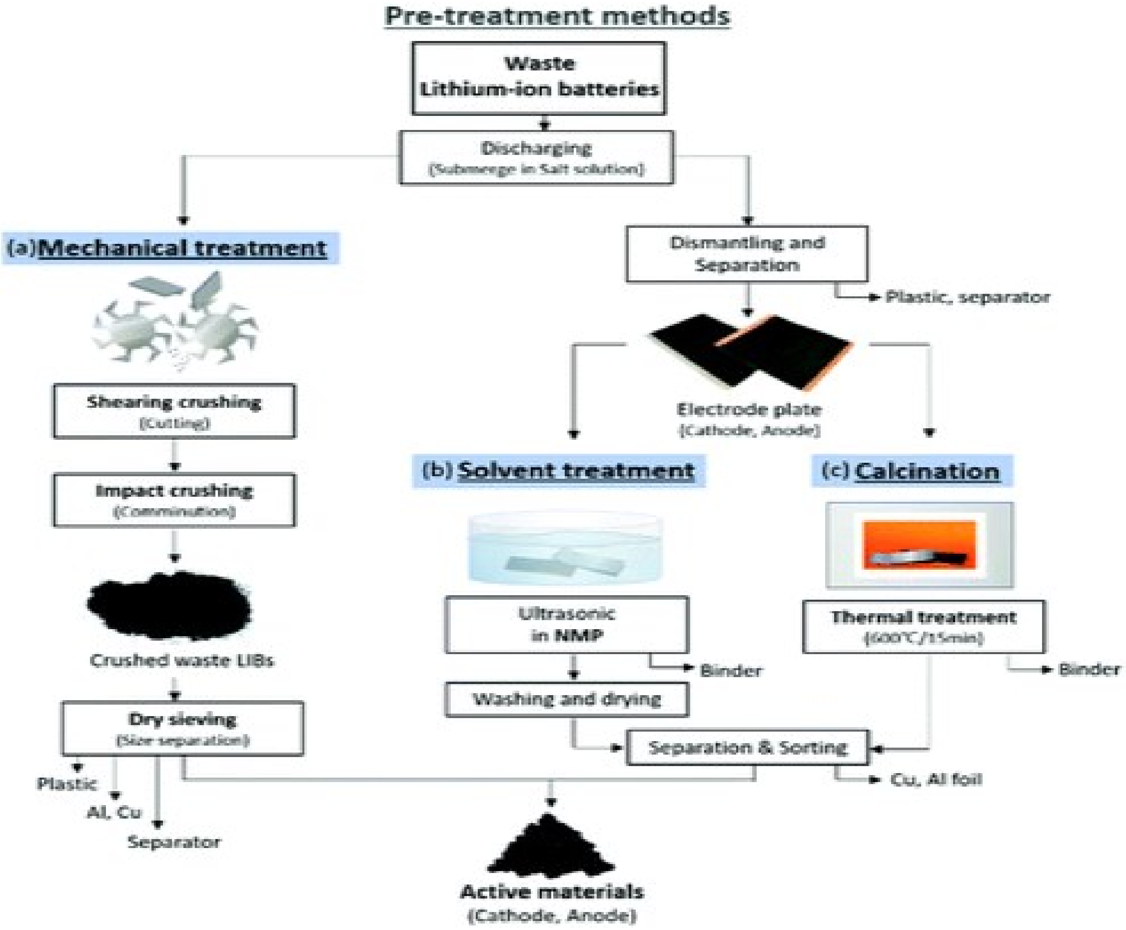


Fig. 15. Example of pre-treatment technology and processes of waste LIBs; (a) mechanical (b) solvent treat and (c) calcination.

- Mechanical pre-treatment-

The process of mechanical pre-treatment entails physically grinding the depleted lithium-ion batteries [56-59]. Because the mechanical characteristics of the battery's many compartments vary, a grinder that can grind every compartment equally is required. Usually, air is excluded to produce a grinding chamber. There are many tools utilized, including hammer mills, granulators, and blade crushers. After grinding, the active material (cathode, anode) and other material (Al, Cu) are separated using the difference in density and magnetic characteristics. By shear crushing a spent battery that had been drained via immersion in a NaCl solution, Zhang et al. formed battery bits [60].

They ground the batteries for 20 seconds at 3000 rpm using impact crushing equipment with blade crushers. By use of dry sifting, the crushed bits were divided into four size groups. The 0.075 mm cathode and anode components were isolated from the bigger plastic fragments, Al, Cu, and polymers. LiCoO2 and graphite were separated using flotation after the hydrocarbon material on the surface was eliminated (Fig 15a). Due to its ease of use and adaptability, mechanical pre-treatment is the most popular method of lithium-ion battery separation. The process can generate noise, dust, and hazardous gases, so it's important to put up a reliable separation system. Additionally, utilizing this procedure makes it challenging to guarantee the proper separation of all elements.

- Solvent pre-treatment

In the lithium-ion battery, the active components are separated from the Al and Cu foils via a process called solvent pre-treatment [61-64]. This procedure separates the active components by removing the additional binder material that strengthens the foil contact with it. On Al and Cu foil, the cathode and anode were joined with a binder. The active substance and metal foil can be separated by removing the binder. The electrode plate can be submerged at 100 °C in N-methyl-2-pyrrolidine (NMP) to dissolve the binder and separate the Al and Cu foils, which is a well-known technique. He and his colleagues drained the lithium-ion battery by soaking it in a NaCl solution, and they then manually detached the battery using needle-nose pliers [63]. The cathode was divided into small pieces after the electrode plate, separator, metal case, and plastic had been removed. The cathode pieces were submerged in NMP for two hours at 80 °C, which caused the binder to dissolve and the Al foil and cathode material to separate (Fig 15b). The active components are often attached to batteries using a PVDF binder, while some batteries utilize PTFE binders, which necessitate the use of an appropriate organic solvent. Additionally, this process calls for the use of organic solvents heated to about 100 °C, which raises the cost and results in hazardous waste products.

- Calcination pre-treatment

The abandoned lithium-ion battery is subjected to calcination per-treatment at temperatures between 150 and 500 °C to remove carbon and organic impurities [64-68]. Additionally, the PVDF binder (which joins the active materials and metal foil) can be eliminated by calcinating at 250 °C to 350 °C, which lessens the adherence of the active materials on the Al and Cu foils. Yang and colleagues divided the cathode components into small pieces and heated the tube furnace to 550–650 °C in a nitrogen environment [68]. Then, utilizing gravity separation, the cathode material, and the current collector (Al foil) were quickly separated (Fig 15c). However, calcination treatment can produce harmful gases, necessitates costly calcination equipment, and is energy intensive.

Lithium extraction technologies from pre-treated waste lithium-ion battery

Lithium is extracted using a variety of techniques from the pre-treated active material. This study concentrated on the extraction of lithium while other approaches concentrate on the extraction of Co, Ni, or Mn. Additionally, this analysis does not include processes that result in useful lithium compounds such Li2CO3 and Li3PO4 and instead concentrates on those that do. The three processes for extracting lithium—pyrometallurgy, hydrometallurgy, and electrochemical extraction—are depicted in Fig. 7.

➢ Pyrometallurgy

By evaporating organic material at high temperatures and creating reactions in the cathode and anode, pyrometallurgy makes lithium soluble in water [69-79]. Then, lithium was reused in the aqueous solution. The pre-treated active ingredients were ground into a powder and then calcined. Lithium metal oxides from the cathode and anode react at temperatures above 700 °C to produce Li2CO3 and metal oxides. The reactions are depicted in eqn (1)- (5)

$$C + 12LiMO_2 \rightarrow 6Li_2O + 4M_3O_4 + CO_2 \qquad (1)$$

$$C + 4LiMO_2 \rightarrow 2Li_2O + 4MO + CO_2 \qquad (2)$$

$$2M_3O_4 + C \rightarrow 6MO + CO_2 \qquad (3)$$

$$Li_2O + CO_2 \rightarrow Li_2CO_3 \qquad (4)$$

$$2MO + C \rightarrow 2M + CO_2 \qquad (5)$$

To dissolve the lithium (Li2CO3) in the water, the calcinated powder is next subjected to water leaching. The water doesn't allow the metal oxide to dissolve. The process involved water leaching through filtration, separating the aqueous solution's undissolved metal oxide to create a Li2CO3 solution, and then evaporating the remaining water to create Li2CO3 (Fig. 16). The procedure for using this technology is straightforward and can handle a lot of discarded lithium-ion batteries. Using LiCoO2 and graphite from a lithium-ion battery that had already been handled, Li et al. recycled lithium using pyrometallurgy [71]. To produce Co, /Li2CO3, and graphite compounds, the separated active components were calcined in nitrogen at 1000 °C for 30 min. Wet magnetic separation was used to remove the lithium from this compound while it was submerged in water. In order to produce a powder containing lithium, Pindar et al. separated lithium-ion batteries and calcined them at 800 °C for 45 min. The powder was then dissolved in a mass of water that was 50 times more than the mass of the powder [75].

As a consequence, 90% of the lithium was recovered using a mixture of Li2CO3 and LiF. Lithium was separated from LiMn2O4, LiCoO2, and LiMnxCoyNizO2 mixed with graphite by Xiao et al. using pyrometallurgy. After being taken out of the battery, the cathode material was calcined for 30 minutes at 700 °C in a vacuum. Li2CO3, a metal oxide that had been calcinated, was then treated with water (25 g L1) for separation.

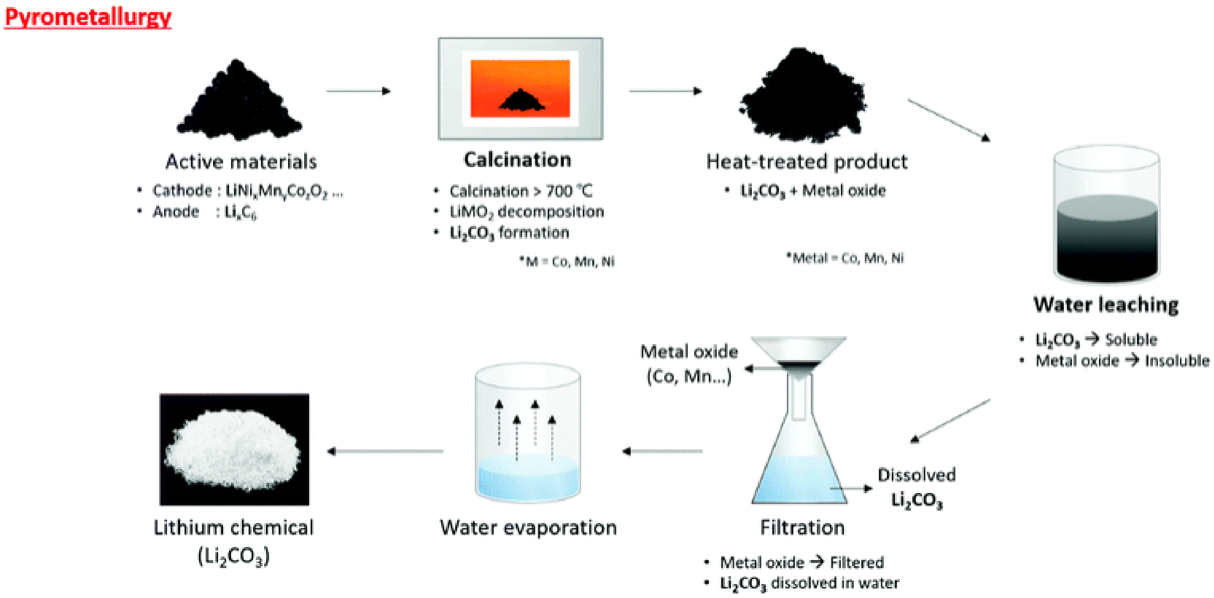


Fig.16. Overall schematic of lithium recycling from pre-treated waste LIB components by pyrometallurgy process (71).

To increase the effectiveness of the lithium extraction during roasting, several pyrometallurgy techniques employ additional acids. Liu et al. nitrated the lithium-ion battery wastes with nitric acid before roasting them for 60 minutes at 250 °C. After roasting, lithium solution was created by leaching with water, and Li2CO3 was created by carbonation after low-temperature roasting [76]. Li et al. recycled Li2SO4 from NCM523 material by sulfation roasting, using H2SO4 along with the roasting and water leaching processes [79]. Pyrometallurgy also employs chlorination roasting, which transforms sintered lithium slag ($xLi_2OyCaOzAl_2O_3nSiO_2$) into LiCl during the roasting process. Chang et al. employed $CaCl_2$ and $LiAl(SiO_3)_2$ to roast it at 1000 °C for 90 minutes to produce LiCl (eqn (6)).

$$CaCl_2 + Li_2O \rightarrow CaO + 2LiCl \qquad (6)$$

The need for additional stages after calcination is the main disadvantage of the pyrometallurgy approach for recycling lithium. The product is typically separated after being dissolved in water or another solvent during this additional step.

However, a lot of solvent is needed because Li2CO3 only dissolves in 13 g L-1 of solution. In addition, the pyrometallurgy process necessitates complex calcination machinery and may result in the release of hazardous gases. The information on the pyrometallurgy research is summarized in Table 2.

Table 2 Summary of condition and residue parameters of pyrometallurgy processes of waste LIBs investigated in the literature.

Spent materials	Residue	Efficiency	Purity	Condition
Electrode materials	Li concentrate	>90%	>99%	• 1700 °C–1750 °C
$LiCoO_2$ + C	Co + Li_2CO_3 + C	98.93%	—	• 1000 °C/30 min in O_2 free
C + $LiMn_2O_4$, $LiCoO_2$, $LiMn_xCo_yNi_zO_2$	Li_2CO_3 + metal oxide	81.90%	99.7%	• 700 °C/30 min
$LiMn_2O_4$ + C	Li_2CO_3 + MnO	91.3%	99.7%	• 800 °C/45 min
Cathode materials	Li_2CO_3	84.7%	—	• 650 °C/3 h • Water leaching [100 °C/0.5 h]
LIB lithium slag	LiCl	Evaporate 97.45%	—	• 1200 °C/1 h • 1000 °C/90 min with $CaCl_2$
Cathode materials	Li_2CO_3 solution	>90%	—	• 800 °C/45 min
LIB scraps	Li_2CO_3	90%	99.95%	• 70 °C/5 h HNO_3 • Roasting 100–300 °C
$LiCoO_2$	Li_2CO_3 solution	36%	—	• 700 °C with carbon
Electrode materials	Li_2CO_3	80%	98%	• Carbothermal 850 °C/45 min

➢ Hydrometallurgy

The most widely used technique for extracting lithium is hydrometallurgy. Lithium in the pre-treated active materials is ionized using acids and bases, followed by leaching to produce Li+ solutions, which can then be used to extract lithium. Nitric acid, hydrochloric acid, and other inorganic acids were employed. To boost the leaching efficiency, heat or redox processes employing H2SO3, NH2OH, and H2O2 were used. H2O2 is the most used reductant among redox agents due to its low cost and lack of toxicity. H2O2's great reducibility allows it to speed up the leaching reaction. However, utilizing an acid with a low pH might cause the emission of dangerous gases like Cl2 and NOx, which has a negative impact on the environment. So, the use of weak acids like citric acid and oxalic acid is being investigated. Acids or bases can be used to leach lithium compounds, which can then be produced through precipitation, solvent extraction, or selective adsorption [80-106].

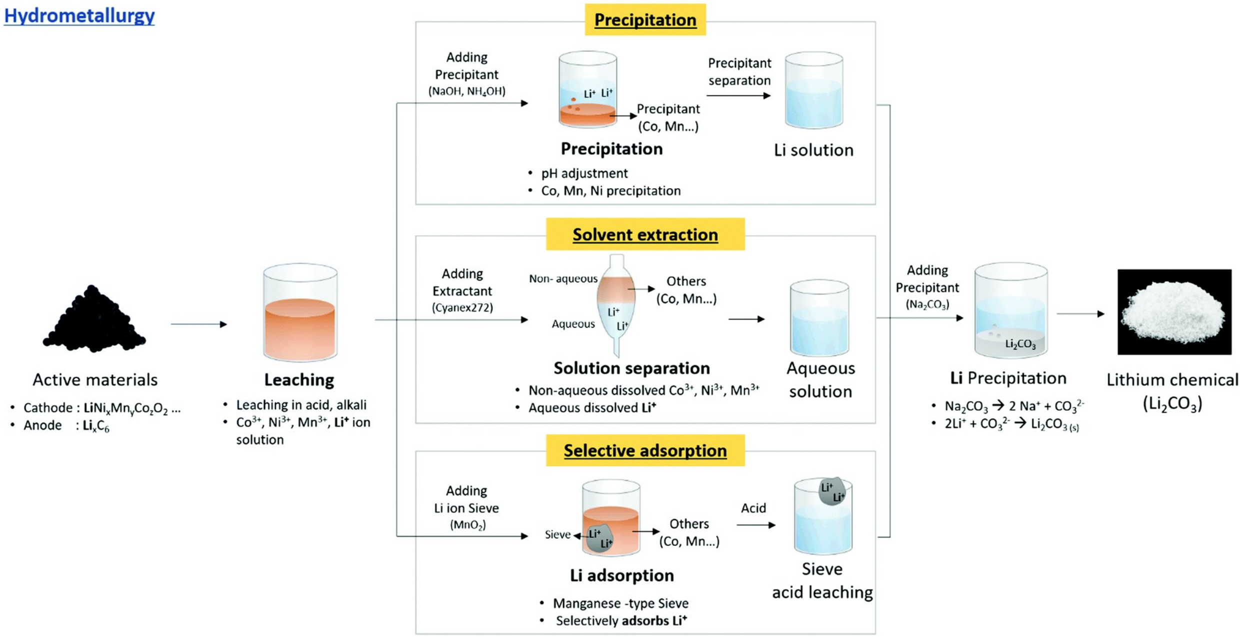


Fig. 17. Overall schematic of lithium recycling from pre-treated waste LIB components by hydrometallurgy process.

i) Precipitation. The most used technique for removing lithium from leached solutions is precipitation. The different solubilities of metal compounds, which vary depending on the pH and temperature, are used in this approach [80-100]. Precipitated substances include oxalates and transition metal hydroxides, which have limited solubility. In order to precipitate other dissolved metals, precipitants like NaOH, Na3PO4, and Na2CO3 are typically utilized. Lithium is then extracted as Li2CO3 or Li3PO4 by reacting Li+ and precipitants. For instance, due to the creation of CO32 ions, Li2CO3 has a higher propensity to create low-solubility Li2CO3 under high pH circumstances. Furthermore, precipitation is facilitated by the solubility decreasing at higher temperatures (12.9 g L-1 at 25 °C, 10.8 g L-1 at 40 °C). Li2CO3 has a significantly lower solubility compared to other chemicals (LiOH - 129 g L1, LiCl - 815 g L1 at 25 °C), which makes it easier to precipitate. Among hydrometallurgy processes, this one is the safest, most cost-effective, and most effective (in terms of retrieval efficiency). From separated LiNi0.3Mn0.3Co0.3O2 electrode material, Gao et al. precipitated Li2CO3 [87]. Using 2M formic acid at 70 °C and H2O2 as a reductant, LiNi0.3Mn0.3Co0.3O2 was leached. The pH was then raised by adding solutions of NaOH and NH4OH. Co, Mn, and Ni precipitate as hydroxides and segregate when the pH rises. To produce Li2CO3, a saturated Na2CO3 solution was added to the original mixture. 98.22% of the lithium was purportedly recovered using this method. Precipitation was employed by Yang et al. to isolate lithium from LiFePO4, the cathode of a lithium-ion battery [88]. Because LiFePO4 cathodes are challenging to leach, the crystal structure must first be broken down through calcination or another chemical process. LiFePO4 was ball-milled with DEDTA-2Na to break up the crystal structure, and mechanochemical activation sped up the leaching process. 0.6 M H3PO4 (50 g L1) was used for leaching for 20 min, and then stirring for 9 h at 90 °C to separate FePO4 and 5 M of NaOH to precipitate lithium as Li3PO4 was added. Li2CO3 was produced by Natarajan et al. from a cathode containing Co and Mn. The anode material was leached using 3 M acetic acid and H2O2, and then (NH4)2S was used to precipitate Co as CoS and Na2CO3 to precipitate Mn as MnCO3 [89]. Na2CO3 was added to the solution to precipitate Li2CO3 after Co and Mn had been taken out. Yang et al. look on recycling lithium from the anode material (graphite). They used a two-stage calcination technique to gather the graphite. Lithium was afterwards almost completely leached into a liquor using 1.5 M of HCl. Li2CO3 was precipitated by changing pH and adding sodium carbonate to the solution.

Although these precipitation techniques have received the most investigation, producing the desired property profile requires precise control of the operating parameters (pH, Li concentration, and temperature).

ii) Solvent extraction- Lithium and the leached cathode material are separated using a two-phase system in solvent extraction [101–105]. Ions from polar and nonpolar liquids are separated using relative solubility. Lithium is separated from the stratified solution and precious metals (Co, Ni, and Mn) are primarily extracted using nonpolar extractants. Co, Ni, and Mn were divided using Cyanex272, PC-88a, and D2EHPA. Lithium and LiCoO2 were separated by solvent extraction by Zhang et al. 98 HCl was used to leach the cathode material, and PC-88A was employed to separate the Co and Li ions [100]. pH elevation improved PC-88A's ability to extract cobalt. This feature allowed lithium to be separated as an aqueous solution at pH 6.7, while cobalt was separated using an organic solvent. Following cobalt extraction, lithium aqueous solution from the separated raffinate was mixed with Na2CO3 to precipitate Li2CO3. Lithium was recovered from LiNi0.3Mn0.3Co2.100 by Chen et al. They used 2 M H2SO4 at 70 °C for 90 minutes to leach the LiNi0.3Mn0.3Co0.3O2 powder, then 0.1 M Na-Cyanex272 at pH 6 to separate cobalt and manganese (using an organic solvent), as well as lithium and nickel (as an aqueous solution) [103]. Using 0.2 M Na-D2EHPA at pH 2.95, cobalt and manganese were extracted from the organic solvent. Dimethylglyoxime (DMG), which is reactive to nickel at pH 9 but not to lithium, is used to separate lithium and nickel from the aqueous solution. When the nickel is removed as a solid, only lithium remains in the solution. Li2CO3 was produced by adding Na2CO3 to the solution. A substance called Cyanex936P was very recently created, and it can separate lithium from other alkaline metals. This could be a fantastic extractant for recycling lithium-ion batteries. Although solvent extraction takes less time than precipitation, it also requires more expensive solvents and additional extractant chemicals like cyanex272 and PC-88A. The extraction efficiency is highly impacted, therefore precise control of the parameters, such as pH and solvent concentration, is also required.

iii) Selective adsorption- Utilizing a lithium-ion sieve to absorb the dissolved lithium, selective adsorption separates lithium. The method used to extract lithium from solutions like lithium brines gave rise to the development of lithium-ion sieves, which are inorganic adsorbents that are very selective for lithium in a lithium-containing solution. Lithium-ion sieves use a vacancy to only let lithium ions pass because lithium is the smallest metal ion. Among the inorganic solvents, lithium manganese oxide offers the highest selectivity, capacity, and stability. Its low toxicity makes it the most often used material, in addition to its other benefits. Wang et al. used an $NH_3-H_2O-NH_4HCO_3$ solution with H_2O_2 [106]. to leach lithium from lithium-ion batteries. The leached Li, Co, and Ni solutions were used to selectively adsorb lithium using a manganese-type lithium-ion sieve. After being separated, the lithium-adsorbed lithium-ion sieve was dissolved in HCl. After that, Li_2CO_3 was separated using NaOH and Na_2CO_3. Low contamination is possible with this straightforward technique utilizing lithium-ion selective sieves; however, spinel-structured manganese-type lithium-ion sieves are highly expensive and call for an extra leaching procedure to separate the lithium mixed with MnO_2.

The hydrometallurgy approach is typically the most popular in the laboratory and the one that is closest to commercialization because it ensures good recovery rates and doesn't call for additional equipment. However, this process can result in additional chemical costs due to the high amount of acid and base needed for leaching (in relation to the lithium-ion battery). In addition, the costs associated with discarding the used products can be significant. Table 3 displays various lithium extraction procedures, conditions, and outcomes, with an emphasis on studies that produced the final compound after leaching.

Table 3 Summary of condition and residue parameters of hydrometallurgy processes of waste LIBs investigated in the literature

Spent materials	Method	Residue	Efficiency	Purity	Condition	Ref.
$LiCoO_2$	Precipitation	Li_2SO_4	90%	—	• 4 M H_2SO_4, H_2O_2 [80 °C/4 h] • Ethanol, LiOH	
LIB scraps	Precipitation	LiF	50%	>99 wt%	• 500 °C/5 h, $KHSO_4$	

					• 9 M H_2SO_4, 30 wt% H_2O_2 (3 mL g^{-1}) [90–100 °C] • 6 M NaOH
Cathode materials	Precipitation	Li_2CO_3	80 ± 1%	96.97%	• 4 M HCl, [80 °C] (20 g L^{-1}) • Na_2CO_3 [100 °C]
Cathode materials	Precipitation	Li_2CO_3	71%	—	• 2 M H_2SO_4, 2% H_2O_2 (33g L^{-1}) [60 °C] • Na_2CO_3 [50 °C]
Mixed cathode materials	Precipitation	Li_2CO_3	80%	—	• 4 M H_2SO_4, 30 wt% H_2O_2 (50 g L^{-1}) [70–80 °C] • NaOH, Na_2CO_3 [40 °C]
$LiNi_{0.3}Mn_{0.3}Co_{0.3}O_2$	Precipitation	Li_2CO_3	Leaching 99.7%	—	• 3.0 M trichloroacetic acid, 4.0 vol% H_2O (50 g L^{-1}) [70–80 °C] • Saturated Na_2CO_3 solution
Cathode materials	Precipitation	Li_3PO_4	89%	—	• Citric acid + H_2O_2 • $C_4H_8N_2O_2$, $(NH_4)_2C_2O_4$, D2EHPA [55 °C] • 0.5 M Na_2PO_4
$LiNi_{0.3}Mn_{0.3}Co_{0.3}O_2$	Precipitation	Li_2CO_3	98.22%	99.9%	• 2 M formic acid, 2 vol%

				H_2O_2 (50 g L^{-1}) [70 °C] • Saturated Na_2CO_3 [20–60 °C]
$LiFePO_4$	Precipitation Li_3PO_4	82.55%	96.5%	• Ball mill with EDTA–2Na, 0.6 M H_3PO_4 (50 g L^{-1})
Cathode material + graphite	Precipitation Li_2CO_3	Leaching 99.9%	99.4%	• 3 M acetic acid, 7.5%vol H_2O_2 (20 g L^{-1}) [70 °C/40 min] • Saturated Na_2CO_3
$LiFePO_4$	Precipitation Li_2CO_3	95.05%	99.95 wt%	• 0.8 M CH_3COOH, 6 vol% H_2O_2 (120 g L^{-1}) [50 °C/30 min] • Saturated Na_2CO_3 [95 °C]
Cathode materials	Precipitation Li_2CO_3	>90%	99.93%	• 3.5 M acetic acid (40 g L^{-1}), H_2O_2 4vol% [60 °C] • Saturated Na_2CO_3 [20–60 °C]
Cathode materials	Precipitation Li_3PO_4	85.56%	—	• Oxidation at 600 °C, 0.28 M H_2SO_4 + H_2O_2 (16 g L^{-1}) [85 °C/2 h] • NaOH, Na_3PO_4

Anode	Precipitation Li_2CO_3	Leaching ≈ 100%	>99%	• 1.5 M HCl (100 g L^{-1}) • CO_2
$LiNi_{0.3}Mn_{0.3}Co_{0.3}O_2$	Precipitation Li_2CO_3	Leaching 99%	—	• 2 M H_2SO_4 + 4 vol% H_2O_2 (50g L^{-1}) [50 °C/2 h] • $KMnO_4$, $C_4H_8N_2O_2$ • Na_2CO_3 [90 °C]
$LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$	Precipitation Li_2CO_3	76%	>99.5%	• 1 M of oxalic acid (10g L^{-1}) [95 °C/12 h] • 5 M K_2CO_3 [80 °C/4 h]
$LiFePO_4$	Precipitation Li_2CO_3	99.35%	—	• Ball mill with citric acid, H_2O_2 (20 g g^{-1}) • Saturated Na_2CO_3 [95 °C]
Cathode	Precipitation Li_2CO_3	38%	99.48%	• 1 M H_2SO_4, 5 vol% H_2O_2 [60 °C/1 h], sonication • 2 M NaOH
$LiFePO_4$	Precipitation Li_2CO_3	80%	—	• 4 M MSA acid (80 g L^{-1}) 18%, H_2O_2 • 5% NaOH solution, 30% Na_2CO_3 [96 °C/30 min]

$LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$	Precipitation	Li_2CO_3	91.23%	99%	• Sodium persulfate (400 g L^{-1}) [85 °C] • Na_2CO_3
$LiNi_xMn_yCo_{1-x-y}O_2$	Precipitation	Li_3PO_4	Leaching 99.1%	—	• 750 °C/3 h, 2.75 M H_3PO_4 [40 °C/10 min] • 10 M NaOH
LIB scraps	Solvent extraction	Li_2CO_3	80%	>98%	• 4 M H_2SO_4 (100 g L^{-1}) glucose [90 °C] • D2HEPA, CYANEX 272, saturated Na_2CO_3
$LiCoO_2$	Solvent extraction	Li_2SO_4 Solution	Leaching 100%	>99.5%	• 600 °C/2 h, 2.25 M H_2SO_4 [80 °C/30 min] • PC88A
$LiNi_{0.3}Mn_{0.3}Co_{0.3}O_2$	Solvent extraction	Li_2CO_3	Leaching 94%	—	• 2 M H_2SO_4 H_2O_2 (33 g L^{-1}) [70 °C] • Cyanex 272 • Saturated Na_2CO_3
LIB scraps	Solvent extraction	Li_2CO_3	72%	99.7%	• H_2SO_4–H_2O_2 mixture • NaOH, D2EHPA, Cyanex 272,

					kerosene, Na_2CO_3 [95 °C]
$LiCoO_2$	Solvent extraction	Li_2CO_3	86.2%	74.2%	• 0.5 M HCl [60 °C] • Cyphos IL-101, saturated Na_2CO_3 [60 °C]
$LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$	Selective adsorption	Li_2CO_3	Leaching 81.2%	>99.5%	• $NH_3{\cdot}H_2O$ (367.5 g L^{-1}) + NH_4HCO_3 (140 g L^{-1}) + H_2O_2 (63.24 g L^{-1}) [manganese type lithium ion-sieves • 0.5 M HCl leaching (10 g L^{-1}) • NaOH, Na_2CO_3

Electrochemical extraction

Using a lithium-selective transmissive membrane, electrochemical extraction processes remove lithium from previously treated active substances. Using a Li-ion conductive ceramic solid electrolyte, the active material powder from the pre-treated waste lithium-ion battery is dissolved in water to extract lithium from the powder state. In contrast to the anode, which dissolves in water to generate LiOH, the powdered cathode of the pre-treated active material does not dissolve when submerged in water (aq). Lithium metal can be created during charging by separating the dissolved and undissolved lithium using the solid ceramic electrolyte. The oxygen evolution reaction (OER) (eqn (7)) can be used to separate the Li+ dissolved in water when charging occurs.

$$2LiOH \rightarrow 2Li^{+} + 2e^{-} + 1/2O_2 + H_2O \tag{7}$$

The undissolved Li^{+} in the cathode powder can be separated by the same reaction as that of DE lithiation in the cathode material Equ (8) and (9).

$LiMO_2 \rightarrow Li^+ + e^- + MO_2$ (M = Co, Mn, Ni) (8)

$LiFePO_4 \rightarrow Li^+ + e^- + FePO_4$ (9)

Depending on the kind of cathode material in the waste, the charging potential varies. Due to the action of LiOH, the aqueous solution changes when the active substance is added to water to form a strong base. Depending on the pH, the OER reaction during charging has a different operating voltage, and in strongly basic conditions ($pH > 11$), the OER reaction takes place below 3.6 V (107). Li^+ is removed immediately from the cathode powder in the case of the LiFePO4 cathode powder because the delithiation reaction potential is 3.5 V, which is lower than the voltage of the OER reaction in the strong base. However, as the delithiation potential is larger than that of the strong base OER reaction, Li+ extraction from the solution rather than the cathode powder happens first for LiCoO2 (3.9 V), LiMn2O4 (4.0 V), and LiNi0.3Mn0.3Co0.3O2 (3.7 V). However, due of the features of the OER reaction, the pH of the aqueous solution falls during charging as the OER reaction's operating voltage gradually rises. Li+ extraction from the powder is made possible when the OER reaction's potential exceeds that of the cathode powder material. Li+ can be removed and separated from both solution and powder by this OER reaction and the reaction for each cathode material, and when Li+ can no longer be extracted, the charging of the system is automatically finished.

Following charging, the isolated Li+ is released into water, travels through another ceramic solid electrolyte, and then performs an oxygen reduction reaction (ORR) with water and electrons to create an aqueous LiOH solution. LiOH is a powerful base that is used to capture CO2 because it reacts with CO2 quickly to generate Li2CO3 (Fig. 18). These equations (eqns (10) and (11)) can be used to express how Li2CO3 is formed.

$2Li^+ + 2e^- + 1/2O_2 + H_2O \rightarrow 2LiOH$ (10)

$2LiOH + 2CO_2 \rightarrow 2Li_2CO_3 + H_2O$ (11)

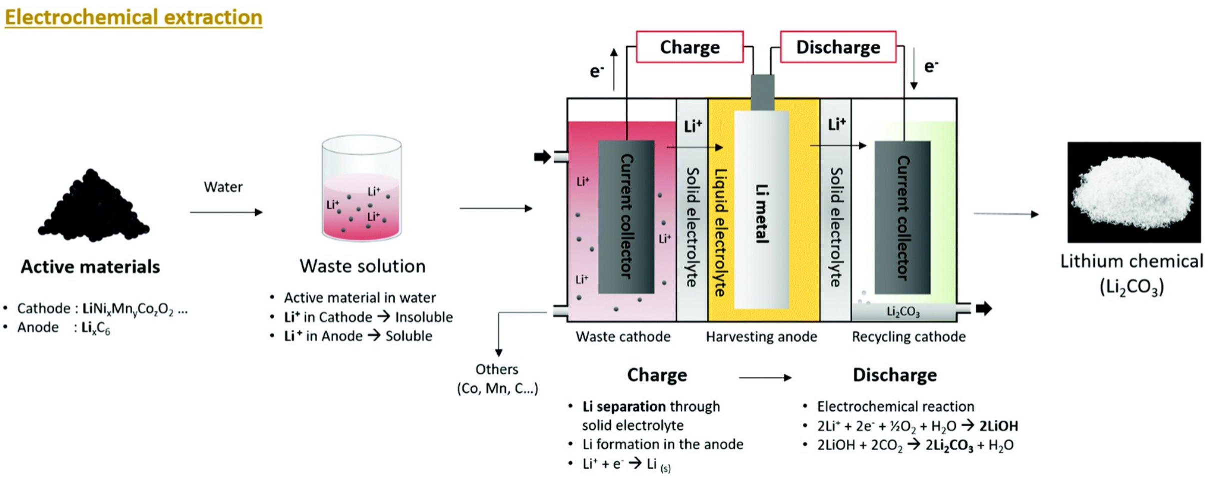


Fig. 18. Overall schematic of lithium recycling from pre-treated waste LIB components by electrochemical extraction process.

Li2CO3 powder can be produced by electrochemical extraction without the need for drying or precipitation. When the system is discharged continually, Li2CO3 powder spontaneously precipitates. When discharge occurs, the water's Li+ concentration progressively rises, followed by a rise in the Li2CO3 concentration. Additionally, due to the ORR, H2O is used up and the concentration of Li2CO3 rises in comparison to the drop in solvent supply. Li2CO3 naturally precipitates because of this.

An electrochemical method was created to remove lithium from a used lithium-ion battery's cathode, anode, and electrolyte [108]. The Li1+x+yTi2xAlxP3ySiyO12 solid electrolyte used in this device has physically separated liquid cathode and anode components and transmits lithium in a selective manner. The liquid cathode contains 1 M LiPF6-EC: DMC, LiFePO4, LixC6, and LiFePO4. Lithium is extracted from the anode and then transferred through a solid electrolyte through electrochemical charging. In later research, a sophisticated technique was created to isolate lithium from the cathode powders LiFePO4, LiMn2O4, and LiNi0.3Mn0.3Co0.3O2. Each compartment in this system—a trash cathode, a harvesting anode, and a recycling cathode—is physically isolated from the others by a solid electrolyte. In the real electrochemical system, solid electrolytes were bonded to both sides of a polymer film that served as the system's body. An anode was then positioned in the centre to create a harvesting anode. To divide the battery into three compartments, a harvesting anode was added between the waste cathode and recycling cathode (Fig. 15a). As depicted in Fig. 15b, the constructed electrochemical lithium extraction system can extract lithium through electrochemical charging and discharging. The lithium-ion battery's cathode powder contacted the waste cathode's current collector. Li+ is extracted from the cathode powder during electrochemical charging, passes through the solid electrolyte, and then undergoes an electrochemical reaction at the harvesting anode to produce metallic lithium (Fig. 19c). Li2CO3 can be created by releasing the separated lithium from the harvesting anode into the distilled water and causing a reaction with the elements water, oxygen, and CO2. Using this system, it was demonstrated that Li2CO3 can be recycled using tests on actual discarded lithium-ion batteries.

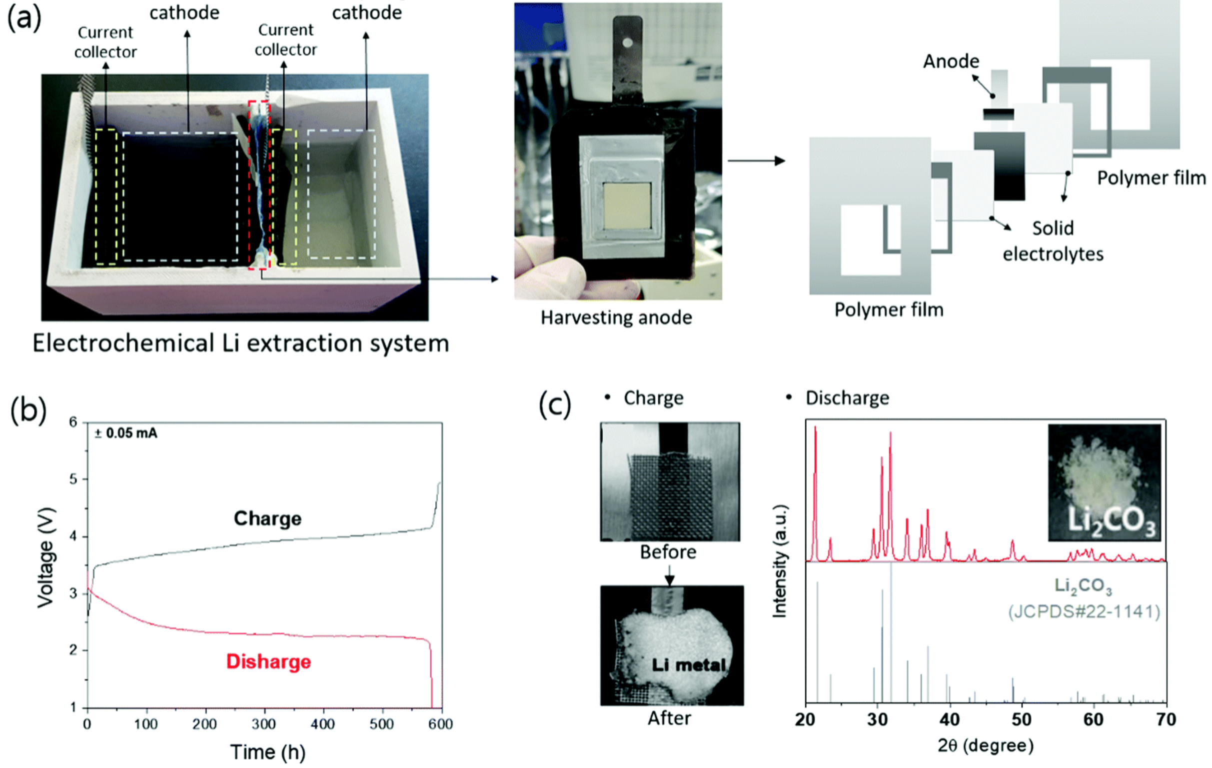


Fig.19.Prismatic design of electrochemical Li-extraction process. (b) Charge and discharge voltage profile during Li-extraction. (c) Li metal formation after charging and Li_2CO_3 formation after discharging.

When recycling active material powder, the electrochemical extraction process can extract 75–95% of the lithium from it. If necessary, it can also extract lithium metal in addition to Li2CO3 molecules. Inductively coupled plasma analysis was used to analyse the recycled lithium metal, and the results revealed 99% purity. In a separate experiment, the finished compound, Li2CO3, had a purity of 99.6% when it was tested using the Standardization Administration of the People's Republic of China (SAC) method of acid-base titration.

This process merely needs to be charged and discharged; it doesn't call for any additional chemical substances or a rise in temperature. This method makes it possible to recycle lithium-ion batteries in an eco-friendly way while simply utilizing water. High-purity lithium can also be separated and employed as an energy storage device by employing a unique solid electrolyte that only permits lithium to pass through. This technique, however, has only been tested on a small scale in the laboratory and needs the setup of an electrochemical system and solid electrolyte; more study is needed before it can be scaled up for commercial use. The research techniques utilizing electrochemical extraction are listed in Table 4. By designing a cell structure, increasing the area of the solid electrolyte, and stacking the system, research is being done to scale up the system and increase the efficiency and speed of Li extraction. In addition, research is being done on Li-ion batteries as well as glasses that contain lithium because this electrochemical method of lithium extraction can extract lithium from LiOH as well as other lithium solutions in any form.

Table 4 Summary of condition and residue parameters of electrochemical recycling processes of waste LIBs investigated in the literature

Spent materials	Residue	Efficiency	Purity	Condition
$LiFePO_4$, C_6, $LiPF_6$	Li metal	—	—	Current 0.1 mA cm^{-2}
Cathode powders, LIB scraps	Li metal, Li_2CO_3	75–92%	99% (metal)	Current 0.05 mA

Pyrometallurgy, hydrometallurgy, and electrochemical extraction have all been suggested as ways to recover lithium compounds from a lithium-ion battery that has already been handled. These strategies are currently being studied, and it is possible to combine them to overcome their individual shortcomings.

Quantitative metrics for the lithium recycling processes using electrochemistry, hydrometallurgy, and pyrometallurgy are shown in Table 5. The effectiveness of recycling, additional chemical costs, operating temperature, complexity, pollutant output, and commercialization level are a few examples of these indicators. Since the pre-treatment procedures can change depending on the kind and quantity of lithium-ion batteries, the approaches only take the lithium extraction process into consideration after that. The literature that is now accessible on the techniques yields the lithium recycling efficiency and purity. After considering the necessary quantity and price, the price was normalized per kilogram of discarded active material powder [109-111]. Operating temperature takes into account the range of temperatures required for lithium extraction. The crucial steps for each approach are looked at for complexity. Each recycling process has the potential to produce a variety of pollutants, and the degree of commercialization distinguishes between systems that have already achieved widespread use and those that are still in the laboratory.

Table 5 Quantitative calculation table for each factor of lithium recycling technologies from waste LIBs

Li recycling method	Recycle efficiency (%)	Purity (%)	Additional chemical cost ($ kg^{-1})	Temperature (°C)	Complexity	Potential pollutions	Commercial readiness
Pyrometallurgy	80–98.9	98–99.95	1.894 m^{-3} (flowing gas (N_2), depends on furnace size)	650–1700	2 Steps • Oxygen free roasting • Wet magnetic separation	Volatile organic compounds	Commercialized [Accurec GmbH]
Hydrometallurgy [precipitation]	76–98.2	96.5–99.97	3.18 (CH_2O_2, H_2O_2*etc.*)	50–100	3 Steps • Leaching • Other metal precipitation (pH adjustment) • Li precipitation	Inorganic waste Acidic waste	Commercialized [TOXCO (Retriev)]
Hydrometallurgy [solvent extraction]	72–86.2	74.2–99.7	73.3 (H_2SO_4, PC88A *etc* .)	60–90	4 Steps • Leaching • Solvent extraction • Solution separation • Precipitation	Inorganic waste Organic waste Acidic waste	On research
Hydrometallurgy [selective adsorption	Leaching 81.2	>99.5	14.9 (NH_3, HCl *etc.*	30	4 Steps • Leaching • Sieve adsorption • Sieve leaching	Acidic waste	On research

Electrochemical extraction	75–92	>99 (metal)	—	Room temp.	• Precipitation 2 Steps • Charging • Discharging	–	On research

Based on Table 5, Fig 20. uses a spider plot to describe the traits of each approach. The graphic displays the relative sizes of the various measures used in lithium extraction.

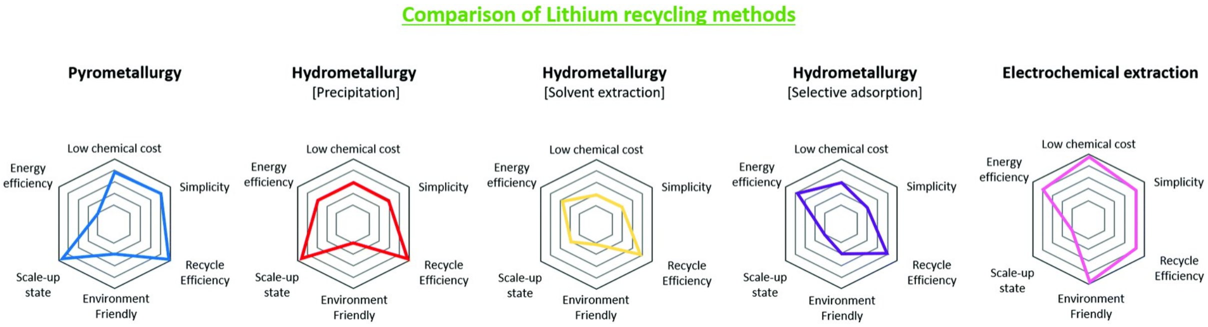


Fig.20. Performance and industrial comparisons of lithium recycling technologies from waste LIBs, pyrometallurgy, hydrometallurgy and electrochemical extraction.

6. Legislation in India and Europe

EU

Regulation of the recycling of any waste item is heavily influenced by legislation. Government agencies can help create a successful circular economy by defining goals for collection rates, recycling efficiency, and disposal obligations as well as by enforcing safety standards. The extended producer responsibility (EPR), which places the producer in charge of handling (End of life) EOL products, is a key idea in this regard. Physical and financial duties are typically distinguished from one another. [112, 113] Physical accountability involves making sure that trash is properly handled, which includes collection, transportation, sorting, reuse, recycling, and disposal. [112] Most of the time, these tasks can be assigned to other parties. [112-114] The financial accountability pertains to funding the operations and enables manufacturers to absorb and include the costs of waste treatment in their prices. [112, 113] Regulations governing the handling of obsolete batteries differ per nation. The following presents the regulations of the EU, one of the world's largest battery markets (Table)

2006	Battery Directive (Directive 2006/66/EC)
2012	Waste Electrical and Electronic Equipment (WEEE) Directive (Directive 2012/19/EU)
2020	Proposal for a regulation of the European Parliament and of the Council concerning batteries and waste batteries, repealing Directive 2006/66/EC and amending Regulation (EU) No 2019/1020

The Battery Directive [Directive 2006/66/EC] and the Waste Electrical and Electronic Equipment (WEEE) Directive [Directive 2012/19/EU] are two current legislations in the EU. These regulations include an actual and monetary EPR. Member nations are obligated to set up collection programs for used portable batteries in the form of drop-off locations close to consumers. Battery manufacturers must cover the costs of collection, treatment, recycling, and disposal. Producers and distributors must also offer free battery returns for industrial, automotive, and portable batteries, including those used in electric vehicles (EVs). Before residual compounds can be dumped or burned, industrial, automobile, and collected portable waste batteries must first be treated and recycled using the best practices available to safeguard public health and the environment. The directives establish minimum collection goals and recycling efficiency for member states to maximize the separate collection of used batteries from mixed municipal garbage. The average yearly mass of portable batteries introduced to the market over the preceding three years is divided by the mass of portable trash batteries recovered in one year to determine the collection rate. By 2012 and 2016, the minimum collection rates were established at 25% and 45%, respectively. The directive establishes recycling efficiency targets of 65%, 75%, and 50% by average weight for Pb-acid, Ni-Cd, and other battery types, respectively. [114,115]

The effectiveness of the 2006 Battery Directive was assessed by the European Commission in a revised report dated 2019. The majority of nations met the 25% collecting objective by 2012, the report claims. The subsequent goal of 45% by 2016 has, however, only been attained by 14 member states. A total of 35 000 tons of waste portable batteries, or 56.7% of the total, are dumped in municipal trash streams each year. According to the report's findings, further collection targets should be established for the future as the current ones are insufficient. Another issue is that automotive and industrial batteries' collection targets have not yet been established, just those for waste portable batteries (including EV batteries). [115] The collection rate computation is deemed improper by the European Association of National Collection Systems for Batteries (Eucobat), according to another statement. As a result, the figure is unrealistic because it does not account for the various lives of various battery types or potential battery exports. It is suggested as a solution to calculate collection rates depending on the battery cells that are accessible for collection. [116]

The European Commission filed a legislative proposal in 2020 to replace the 2006 Battery Directive as part of the European Green Deal. The new regulations greatly outpace existing law in many ways and are designed to aid the EU's transition to a contemporary, resource-efficient, and competitive economy. As a result, new collection goals for used portable batteries (apart from those for e-bikes and other light-duty vehicles) are 45% by 2023, 65% by 2025, and 70% by 2030. The proposal establishes a legislative framework for the creation of suitable collection schemes for industrial, automotive, and EV batteries but does not specify collection targets for these battery types. The plan also calls for a revision of the collection goals for 2030, including considering changing the formula used to determine collection rates so that it takes into account the quantity of waste batteries that are already accessible for collection. By 2025, new recycling efficiency targets for LIBs and Pb-acid batteries are 65% and 75%, respectively. Furthermore, by 2030, it has been determined that the goal material recovery rates should be 95% for cobalt, 95% for copper, 95% for lead, 95% for nickel, and 70% for lithium. Additional regulations include minimum performance and durability standards, extended battery labeling, a battery passport for batteries with capacities exceeding 2 kWh, minimum recycled material contents in new industrial and automotive batteries, and more. [114] [117]

INDIA

The Need for Recycling

Recycling is crucial right now to help India move toward self-sufficiency and allay concerns about expanding battery demand, restricted access to raw materials in the nation, and expected price increases for batteries. Recycling can replenish raw materials used in battery production, promoting a circular economy for batteries.

In his speech at a post-budget webinar on March 4, 2022, Honorable Prime Minister Shri Narendra Modi emphasized the nation's emphasis on the circular economy. The Battery Waste Management Rules, 2022 (BWMR, or "Rules") were introduced by the Ministry of Environment, Forest, and Climate Change (MOEFCC) on August 24, 2022, in accordance with these principles. The Extended Producer Responsibility (EPR) requirements of the regulations are focused on promoting the recycling of used batteries.

The History of Battery Waste Management

Rules-The Central Pollution Control Board (CPCB) issued the notice Batteries (Management and Handling) 2001 to address the collecting and recycling of spent lead acid batteries. In 2010, it was revised to become Battery (Management and Handling) Rules.

The Battery Waste Management Rules, 2022, which were announced by the MOEFCC on August 24, 2022, include the following significant improvements over their forerunners:

- The Rules apply to all other battery types as well, including lithium-ion and redox flow batteries.
- To meet the demand for battery recycling across the portable, automotive, industrial, and electric vehicle battery industries, Extended Producer Responsibility (EPR) was introduced to the draft guidelines.
- Manufacturers and producers are required by EPR to take responsibility for the collecting, storage, transport, recycling, and disposal of used batteries.

Impact of BWMR on Recycling

- establishes minimum annual recovery targets for EPR: 70% in 2024–2025; 80% in 2025–2026; and 90% starting in 2026–2027.
- prohibits the manufacturer from disposing of batteries in landfills or burning them; only recycling and refurbishing is permitted.
- Ensures recycling by all the target stakeholders, including manufacturers, producers, collection centres, importers, re-conditioners, re-furbishers, dismantlers, assemblers, dealers, recyclers, auctioneers, vehicle service centres, consumers, and bulk consumers.
- reinforces the stance of numerous state EV policies that emphasize battery recycling and "urban mining" by setting up working committees, providing incentives, or providing subsidies. Tamil Nadu, Madhya Pradesh, Uttar Pradesh, Delhi, Punjab, Maharashtra, and Telangana are a few of these states. [118]

7. discussions

7.1 Best Technique among them-

There is a greater need to scale novel battery recycling techniques to meet the necessary circular economy goals as EV and portable battery output rises globally. The supply channels that sustain artisanal mining, however, can be unstable and unethical, and precious metals mining for LIB is frequently not environmentally viable. This raises the question of what procedure should be followed for battery recycling to save money and protect the environment.

According to numerous research, hydrometallurgy is a more resource- and environmentally friendly recycling technique than pyrometallurgy. It enables more element recovery while using less energy, producing much less greenhouse gas emissions, little to no air emissions, and purification. Our battery recycling process doesn't produce any wastewater, which helps to lessen its negative environmental effects. It can also frequently be powered by solar energy, making it a self-sufficient solution.

kinder to the environment

The burning of graphite, solvents, and separators resulted in 361 tons of direct CO2 emissions per kg/t of metal, according to the study of cobalt recycling.

When tested under identical conditions, hydrometallurgy, in contrast, had no effect at all, making it the more environmentally friendly choice.

It has been established that hydrometallurgy, as opposed to pyrometallurgy, has a less harmful impact on the environment when used for LIB recycling. These are some effects of this approach:

- Lithium, aluminium, and manganese recovery
- reduced emissions.
- None were released (wastewater treatment)
- lower prices

Other troublesome emissions from lithium hexafluorophosphate and polyvinylidene fluoride, such as hydrogen fluoride, fluorine, phosphorus pentafluoride, and phosphoryl fluoride, can be emitted during battery processing employing pyrometallurgy processes. [119]

CONCLUSION

In conclusion, recycling lithium-ion batteries is crucial for lowering their negative environmental effects and recovering precious minerals and metals. There are several recycling processes, such as pyrometallurgy, hydrometallurgy, and electrochemical methods.

The hydrometallurgical process is regarded as the most environmentally benign of these processes since it uses recyclable and non-toxic solvents, emits fewer greenhouse gases, and uses little energy. In this process, metals from the battery parts are dissolved in a liquid solution, then the metals are separated and purified.

Overall, recycling lithium-ion batteries through environmentally friendly methods is crucial for sustainable development and the conservation of natural resources. It is important for stakeholders to prioritize the adoption of such methods to ensure the responsible disposal of batteries and mitigate their impact on the environment.

By establishing a more organic recycling cycle that is comparable to that of other elements, these upcoming efforts will make lithium an eco-friendly and cost-effective driving force for future technology. In addition to the advancement of lithium recycling technology, it is critical to raise public awareness of the limited supply of lithium and to enhance the perspectives of sellers, developers, and recycling professionals in this area. Furthermore, for a more sustainable lithium economy, government-level policy interests and support are essential.

Future Requirements for Recycling Techniques

To produce a better and more sustainable lithium cycle, each technique of recycling lithium needs to be developed for commercialization. The following directions for research and development in this area are necessary for a more active lithium recycling market.

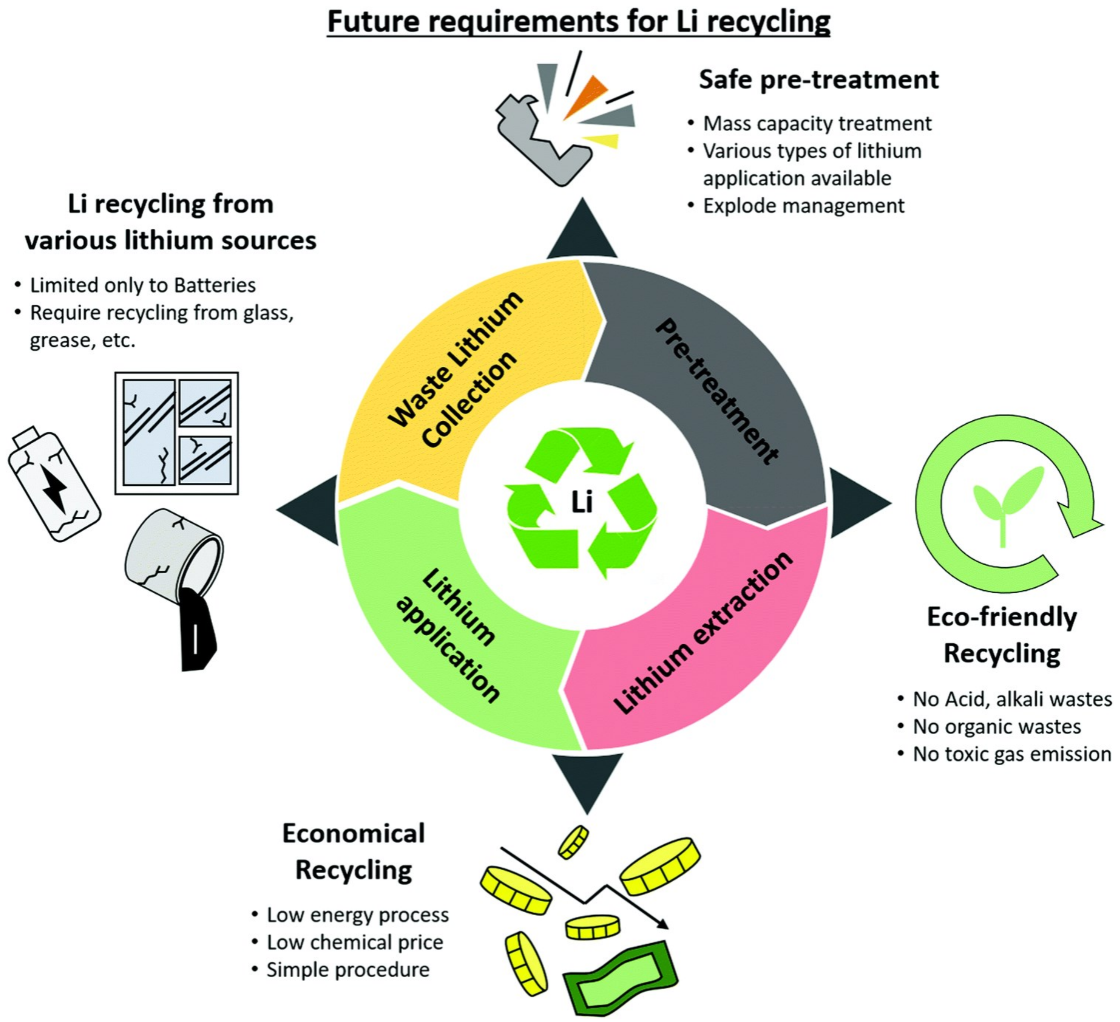


Fig. 21. Future requirements for Li recycling

- Although lithium-ion batteries are the primary cause of the rise in lithium demand, new technological advancements are required to extract lithium from other items. Research on the extraction of lithium from non-batteries is scarce. As of 2019, 35% of the lithium is utilized in casting, grease, and glass, therefore greater consideration needs to be given to recycling the lithium from these items. The greatest alternative might be to use the machinery created for recycling lithium-ion batteries to remove lithium from other sources of used lithium. This has a good overall impact on the entire lithium cycle.
- It is challenging to process lithium materials concurrently, even when they are sorted and collected for recycling. The cathode, anode, and electrolyte materials used in batteries, as well as the battery sizes, vary greatly. The possibility of issues like explosions exists while processing them simultaneously. To automatically sort or categorize the discharged lithium material, a policy is required. To improve the effectiveness of recycling lithium, it is also crucial to pre-treat items that contain the metal. It is possible to process sizable amounts of lithium materials to greatly

speed up the lithium cycle using a safe and ecologically friendly pre-treatment technique.

- The methods currently being actively investigated or marketed also have a negative impact on the environment. Technology for recycling lithium should not only lessen the shortage of lithium but also reduce waste to avoid polluting the environment. Most recycling techniques in use today, however, result in pollution. This includes the toxic gases produced when lithium waste is heated, as well as the leaching agents such acids, bases, and organic solvents. Additionally, this results in higher costs. The process' commercialisation may be hampered by the added expenses and steps. As a result, much thought should be given to simplifying the procedure to reduce waste products or figuring out how to reuse the waste products from these procedures.
- Economics cannot be disregarded in such a process. Recycling would not be suitable or practicable from an economic standpoint if the cost of purchasing is less than the cost of recycling. Current techniques that operate at high temperatures, with acids or bases, or both are typically expensive and energy intensive. More chemicals used during the procedure will make it more expensive. Lithium recycling is economically unfavourable because the quantities of acids and bases needed are much higher than those of the recycled product. Therefore, techniques for recycling acids and bases or reducing operating temperature must be developed to reduce the cost and energy needed for lithium recycling. The development of lithium recycling technologies will gain more attention if an economically feasible approach is discovered. [34]

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