MASTER OF SCIENCE IN PETROLEUM AND MINING ENGINEERING

MASTER’s DEGREE THESIS

Title

Environmental impact analysis of Lithium extraction activity and Li-Ion batteries recycling

Candidate

Bilal Ahmed

S264612

AcademicSupervisor(s)

Prof. Glenda Taddia

Academic Co-supervisor(s)

Dott.ssa Martina Gizzi

Dott. Mondani Michele

Academic year: 2021/2022

Contents

1. Introduction

The Kyoto Protocol, the Paris Agreement, and the UN Sustainable Development Goals (SDGs) have been signed by most UN member countries, resulting in a drive for strict CO_2 emission limits to limit climate change by integrating more green and renewable energy technology systems in the transportation, electric power, and manufacturing sectors. The global effort to decarbonize modern civilization has sparked increased interest in lithium (Li), a fundamental component of lithium-ion batteries (LIBs) used in green technologies such as electric vehicles (EVs) and renewable energy storage systems [1]. Because of their high energy density, low weight, and extended lifespan, lithium-ion batteries (LIBs) have been widely pushed as a possible power source for electric vehicles (EVs) to mitigate climate change [2].

Lithium demand in the battery sector has almost doubled in the last five years and is expected to continue to rise in the near future, owing to three factors:

(1) To attain a low-carbon/carbon-neutral society, governments will continue to promote clean,green, and renewable energy technology.

(2) An alternative battery storage system on equivalent or better than LIBs is still far from being realized.

(3) The distinct physical and chemical characteristics of lithium make it essential in manyapplications aside from energy storage devices [3].

In the proposed work it is discussed the extraction of Lithium through different processes and also its production through Recycling and their Environmental impact regarding extraction and also recycling. Lithium is a critical component of the rechargeable battery industry. According to the United States Geological Survey (USGS), batteries account for 65 percent of the lithium end-use market. From personal devices to grid storage systems and autos, batteries are a driving force in the modern economy. Lithium is a plentiful resource in the lithosphere, and it can be found in brines and hard rock deposits [4].

Primary lithium resources can be broken down into ores and brines, while secondary resources include spent lithium-ion batteries and electronic wastes. Brines such as those found at the Salar de Atacama, one of the world's most important lithium production sites, account for around a quarter of the world's lithium supply today. The brine is pumped from underground into shallow man-made ponds where the water evaporates, containing roughly 25% salt and 75% water by mass. The evaporative process takes 9 to 14 months, during which time different forms of saltcan be harvested at different phases of evaporation. The lithium chloride concentrate is then delivered to a chemical facility, where unwanted components are eliminated in small amounts. Finally, purified lithium chloride is used to make lithium carbonate and lithium hydroxidemonohydrate. These are the lithium compounds that are sold to producers of battery cathodes nowadays [5].

However, recycling of lithium-ion batteries (LIBs) is still in its early stage. Many technologies have been developed that include a combination of mechanical processing followed by hydrometallurgical or pyrometallurgical processing, generally after thermal pre-treatment. All of these approaches have advantages and disadvantages in terms of applicability, safety, environmental impact, component recovery efficiency, and cost. Lithium-ion batteries (LIBs) now outperform other batteries when it comes to providing primary power for electric vehicles and portable electronic devices [6]. The anode is usually formed of graphite or lithium-titanate oxide, and the cathode is usually made of Li metal oxide. Li-salts, organic solvents (such as diethyl carbonate and ethylene carbonate), and additives are routinely used in the electrolyte. A plastic microporous membrane is used to make the separator, which prevents direct contact between the anode and the cathode. Metals like as Al and Cu are commonly employed as current collectors, with Al also serving as the primary material for battery containers [7].

The aim is to describe the importance of Lithium extraction for the purpose of Automotive industry. So than it is explained primary supply process of lithium and its path along the supply chain ending up with the recycling process. Moreover, it is discussed the environmental impact of lithium extraction on water and also analyzed the impacts of recycling by comparing it with different studies. Recycling, on the other hand, has an environmental impact due to the consumption of energy and materials during the recovery process. By doing this comparison for the reliability and robustness of the results, we can observe large quantitive change in the GHG emission (kg CO_2/kg) and Energy Consumption (MJ/KG) due to using a recycled materials under a closed-loop scenario and comparing with those of using a virgin materials for the manufacturing of Traction batteries.

As a result, recycling methods should be designed to have the least amount of environmental impact possible. This might be interpreted as a desire to recover high-quality valuable materials while reducing energy and resource usage throughout the recycling process. It is important to comprehend the mass flux of these wastes in this competition. The global weight of retired LIBs is expected to exceed 500,000 tons in 2021, rising to 1,700,000 tons by 2035, with a global projected business of $3 billion [8]. Then, in the next decades, due to the expected increase of LIBs production to billions of devices per year, recycling will undeniably be more urgent and strategic than ever.

1.1 Operation of Li-ion batteries

A schematic depiction of a LIB cell and its working principle is shown in Figure 1. During the spontaneous redox process (discharge) inside the cell, lithium-ions migrate from the anode (negative electrode), via the electrolyte, to the reduced cathode (positive electrode). During the charge process, lithium-ion transport is reversed, and ions go from the cathode to the anode. To maintain charge balance, electrons pass via the external circuit in the same direction as lithium- ions do inside the cell. Electrons travel from the electrode active material to the external circuit via the current collector (a highly conducting metal) [8].

The separator, a microporous membrane positioned between the anode and cathode, prevents short-circuiting of the electrodes, ensuring that electrons escape the cell. The separator also permits lithium ions to pass through it. The electrolyte that fills the separator and encounters the electrodes enables ionic conductivity and mobility both between and within the electrodes [9].

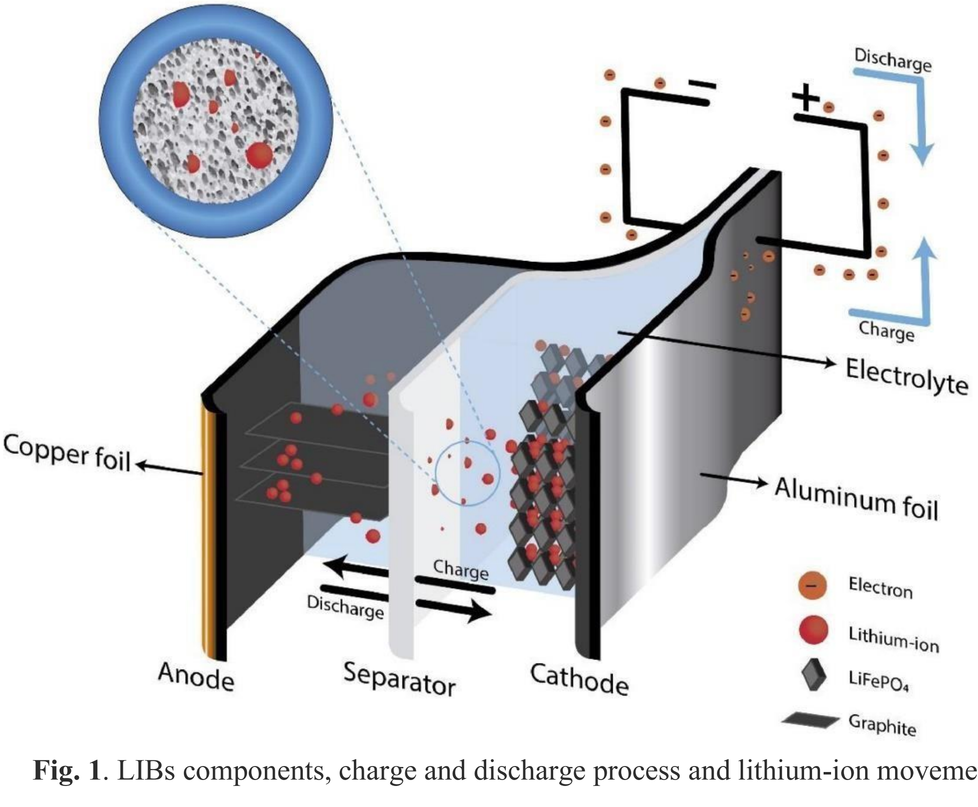


Fig. 1. LIBs components, charge and discharge process and lithium-ion movement in LIBs.

2. Extraction of Lithium

Mineral deposits can be divided into two types: resources, which are "geologically assured quantities that are available for exploitation," and reserves, which are "quantities that can be exploited under existing technical and socioeconomic conditions". While resources have limited real-world value, their conversion into economically recoverable reserves makes them appropriate for production and societal usage. However, only a small percentage of resources may be classified as recoverable reserves, adding to their economic scarcity [10]. It is important to note that actual reserves are dynamic, and change based on a variety of factors such as available technology, economic demand, political concerns, and social factors.

Technological advancements may boost reserves by allowing for the exploration of new deposit types or cutting production costs. Due to difficulty determining the ore grade and tonnage in advance, deposits that have been exploited for some time can grow or reduce their reserves. Depletion and decreasing concentrations may increase recovery costs, thus lowering reserves. Declining demand and prices may also reduce reserves, while rising prices or demand may increase them. Political decisions, legal issues or environmental policies may prohibit exploitation of certain deposits, despite the fact significant resources may be available.

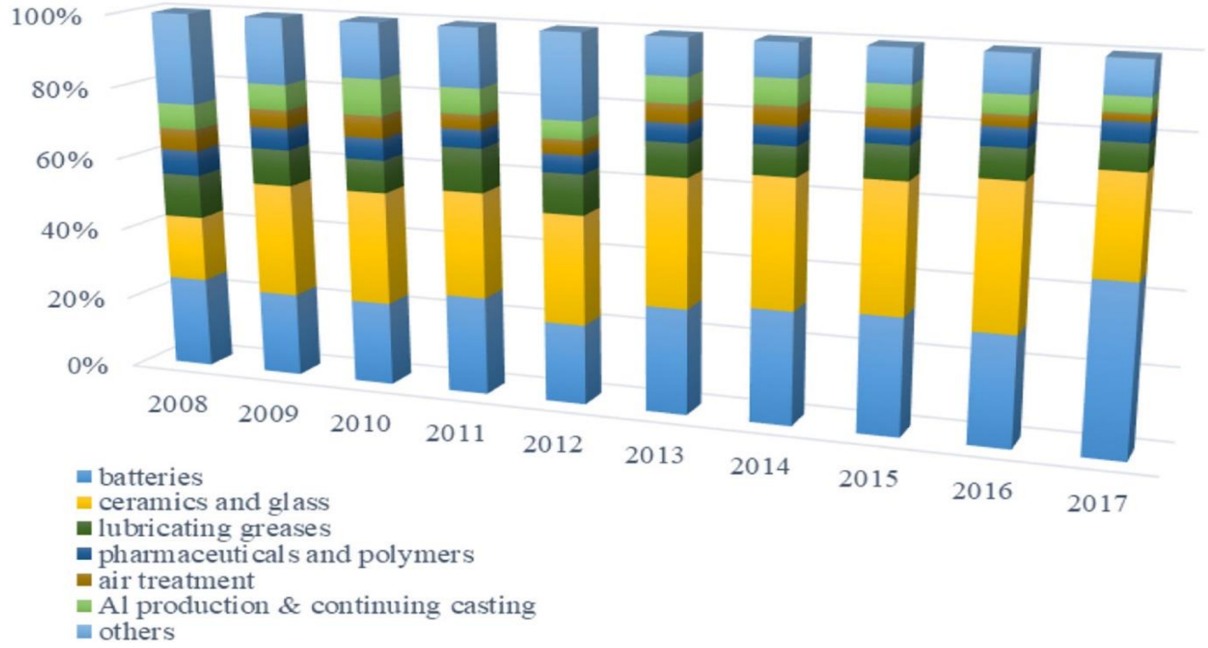


Fig. 2. The distribution of global end-use lithium markets in the last decade. Data obtained from the U. S. GeologicalSurvey.

Lithium (Li), as the lightest metal and 25th most abundant element on earth, has found various important applications in many fields such as ceramics, greases, aerospace, polymers, metal additives, and particularly in the Li-ion batteries (Fig.2.) [11].

In 2019 the nine countries with the biggest reserves were (in descending order) Chile, Australia, Argentina, China, the U.S.A, Canada, Zimbabwe, Brazil and Portugal. In terms of production, the pictures lightly vary with Australia, Chile, China, Argentina, the U.S.A, Zimbabwe, Portugal, Brazil and Canada being them a in producers, listed in decreasing order of importance [12] Lithium is found naturally in minerals, clays, brines, and seawater, with brines and a few ores being particularly valuable for exploitation due to the high economic concentration of lithium. According to the United States Geological Survey (USGS), lithium resources have expanded significantly as a result of ongoing investigation, with more than 53 million tons discovered as of2018, while lithium output climbed by 13% to 43,000 tons in 2017. Australia (spodumene activities), Chile, and Argentina (brine operations) account for almost 80% of global Li production (Fig. 3) (USGS, 2018).

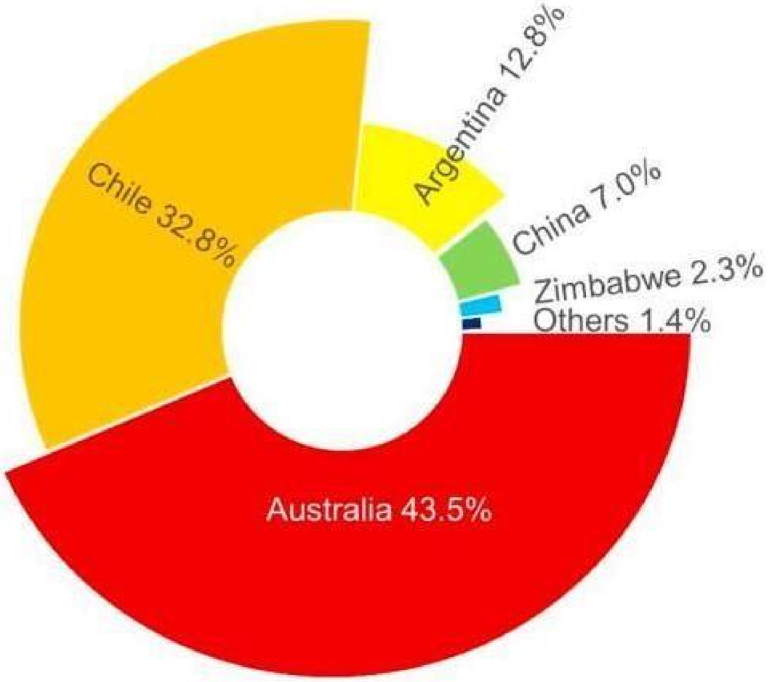


Fig. 3. Global lithium production by country (Excludes U. S. production). Data obtained from the U.S.Geological Survey

Commonly, extracting lithium from these stores includes two methods. One is building a mine, extracting the clay or ore, and isolating the metal through a complex process. The second is to pump underground water stores to the surface. The resulting pools of briny fluid are cleared out to evaporate, and lithium is expelled from the dried salts that remain.

The first process frequently entailed displacing thousands of acres of dirt and rock (known as overburden material), causing disruption to nearby land, and eradicating plant life. The second process may require huge amounts of fresh water, which is quite often sourced from wells, streams, or aquifers that are also used for farming or drinking water, making fresh water a valuable resource in the dry regions where lithium deposits are found.

2.1 Extraction from Brine

Salt-lake brine is one of the most substantial and potential lithium resources. As shown in (Fig. 4.), approximately 70% of global lithium reserves exist in salt lake brines, where continental brines account for the largest proportion (59%). Brine is a significant potential resource for lithium recovery. From an economic and scientific standpoint, the following factors must be considered when recovering lithium from brine: I the availability of the pond ground and the suitability of the location for solar evaporation, (ii) the concentration of lithium in brine, (iii) the ratio of alkaline earth and alkali metals to lithium, and (iv) the complexity of phase chemistry. Lithium brine resources are classified into three types: I evaporative, (ii) geothermal, and (iii) oil field brines. Approximately 50% of the initial natural brine remains in the residual brine after brine evaporation. This phenomenon has been attributed to the precipitated salts' retention of lithium. Because the residual brine contains a higher concentration of Mg2+ than Na+ and K+, lithium recovery from it is more difficult.

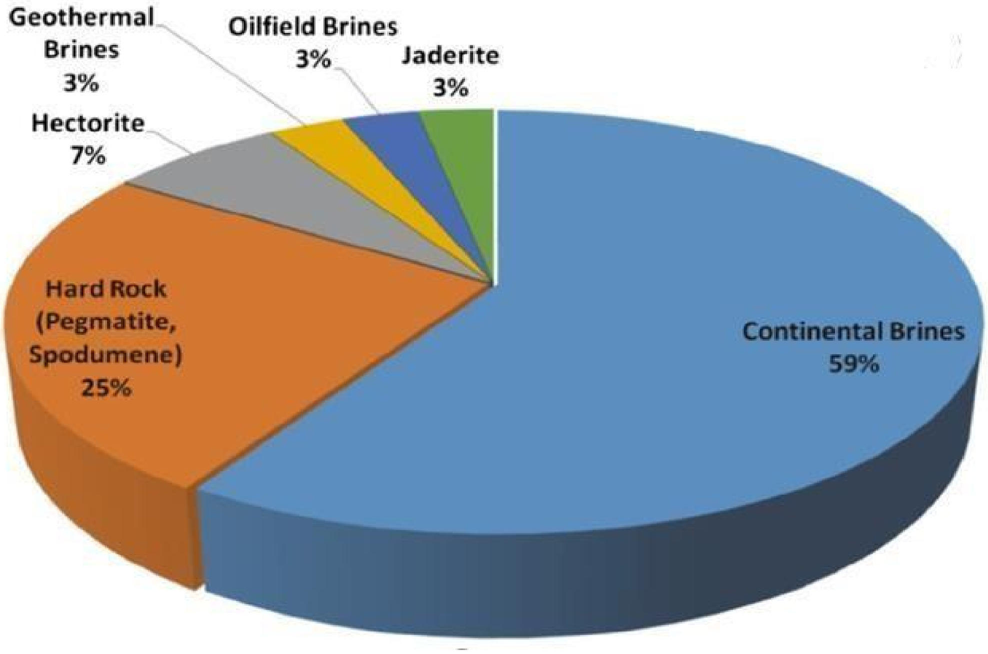


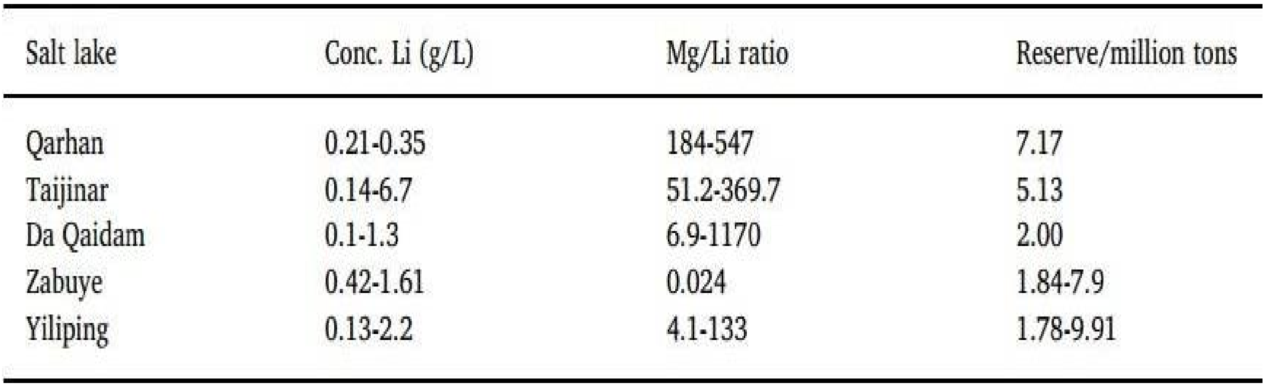
Fig.4. Distribution of Potential of lithium resources

Lithium recovery from brine does not follow a set of rules because each procedure is unique to the brine field's composition. For lithium production from brines, the solar evaporation-precipitation process has long been the industry standard commercial procedure. Lithium is mined in large quantities from liquid brine pools beneath salt flats known as Salars, the majority of which are found in southwestern South America and China. Lithium produced from brines presently has the largest share of the world lithium carbonate production particularly because the Li extraction from brines with the conventional solar evaporation and precipitation process is still the most cost- effective Li production method [13].

Lithium brine recovery is usually a simple but time-consuming process that can take anywhere from a few months to a few years. The subsurface Salar brine resources must be accessed through drilling, and the brine must then be pumped to the surface and dispersed to evaporation ponds. The brine is left in the evaporation pond for months or years until solar evaporation has removed most of the liquid water content. Salar brines are highly concentrated and often contain potassium and sodium in addition to lithium. While waiting for the lithium content to reach a concentration that is suitable for further processing, facilities often operate many large evaporation ponds of varying ages, and may extract additional metals (e.g., potassium) from younger ponds.

As brine lakes are found at high altitudes and in low-rainfall zones, solar evaporation is an excellent method for lithium extraction. The crystalline species and the order of sedimentation in brines are determined by their initial chemical composition, therefore the recovery procedures and operations of different brine lakes are usually distinct. On the saline systems, owing to varying amounts of cations and anions, a large range of ionic salts can be formed, such as chloride, sulfate, and carbonate. The brine composition determines the processes selected and operation difficulty. In particular, the critical factor Mg/Li ratio increases the complicity, which can be attributed to the nearly identical properties between Mg2+ and Li+ [13]. Brine with a low Mg content (Mg/Li mass ratio 6) is typically injected into a series of ponds (thousands of acres) for solar evaporation.

Table 1. The properties of some salt lakes in China

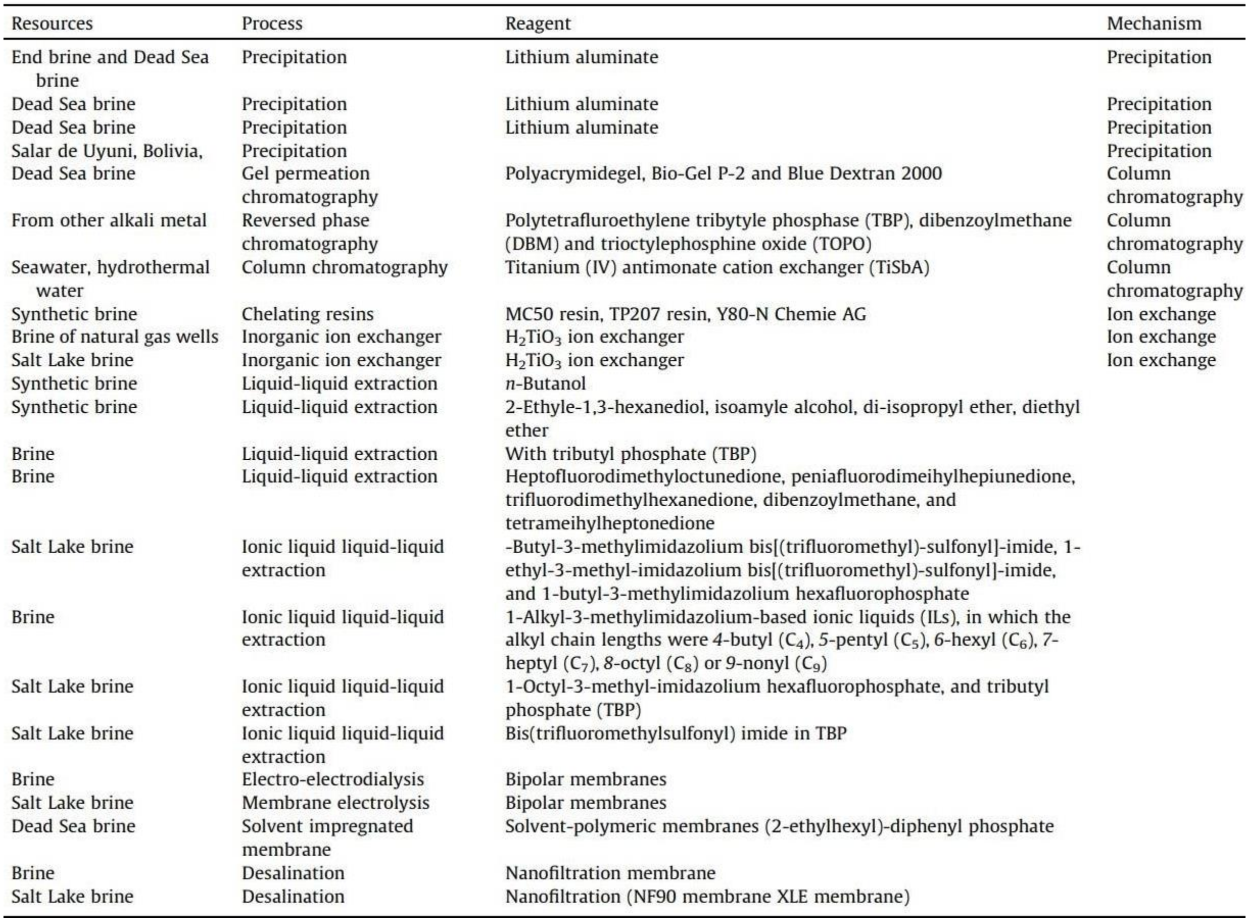


Salt lake	Conc. Li (g/L)	Mg/Li ratio	Reserve/million tons
Qarhan	0.21-0.35	184-547	7.17
Taijinar	0.14-6.7	51.2-369.7	5.13
Da Qaidam	0.1-1.3	6.9-1170	2.00
Zabuye	0.42-1.61	0.024	1.84-7.9
Yiliping	0.13-2.2	4.1-133	1.78-9.91

Unfortunately, most known brines around the globe have high Mg/Li ratio. In China, over 80% lithium exist in brines and often have higher Mg/Li ratio (the highest reaching up to 1837:1) compared to those in South America (Table. 1). Hence, a significant number of studies have been carried out to investigate the separation of Mg and Li and the recovery of Li from the brines with high Mg/Li ratios [14].

In literature various technique has been reported for separation and purification of lithium are reviewed below. Recently, [15] have proposed general flow sheet for production of lithium from brine and seawater. In the proposed process ion-exchange, liquid-liquid extraction, adsorption, and electrodialysis are the important hydrometallurgy process needed for concentrating the lithium prior to production has been proposed [16]. Recovery of lithium from both brine and synthetic brine through the various process has been reviewed bellow and summarized in Table.2.

Table. 2 The following are the main processes from extracting lithium from brine.



Resources	Process	Reagent	Mechanism
End brine and Dead Sea brine	Precipitation	Lithium aluminate	Precipitation
Dead Sea brine	Precipitation	Lithium aluminate	Precipitation
Dead Sea brine	Precipitation	Lithium aluminate	Precipitation
Salar de Uyuni, Bolivia,	Precipitation		Precipitation
Dead Sea brine	Gel permeation chromatography	Polyacrymidegel, Bio-Gel P-2 and Blue Dextran 2000	Column chromatography
From other alkali metal	Reversed phase chromatography	Polytetrafluroethylene tributyle phosphase (TBP), dibenzoylmethane (DBM) and trioctylephosphine oxide (TOPO)	Column chromatography
Seawater, hydrothermal water	Column chromatography	Titanium (IV) antimonate cation exchanger (TiSbA)	Column chromatography
Synthetic brine	Chelating resins	MC50 resin, TP207 resin, Y80-N Chemie AG	Ion exchange
Brine of natural gas wells	Inorganic ion exchanger	H_2TiO_3 ion exchanger	Ion exchange
Salt Lake brine	Inorganic ion exchanger	H_2TiO_3 ion exchanger	Ion exchange
Synthetic brine	Liquid-liquid extraction	*n*-Butanol	
Synthetic brine	Liquid-liquid extraction	2-Ethyle-1,3-hexanediol, isoamyle alcohol, di-isopropyl ether, diethyl ether	
Brine	Liquid-liquid extraction	With tributyl phosphate (TBP)	
Brine	Liquid-liquid extraction	Heptofluorodimethyloctunedione, peniafluorodimeihylhepiunedione, trifluorodimethylhexanedione, dibenzoylmethane, and tetrameihylheptonedione	
Salt Lake brine	Ionic liquid liquid-liquid extraction	-Butyl-3-methylimidazolium bis[(trifluoromethyl)-sulfonyl]-imide, 1-ethyl-3-methyl-imidazolium bis[(trifluoromethyl)-sulfonyl]-imide, and 1-butyl-3-methylimidazolium hexafluorophosphate	
Brine	Ionic liquid liquid-liquid extraction	1-Alkyl-3-methylimidazolium-based ionic liquids (ILs), in which the alkyl chain lengths were *4*-butyl (C_4), *5*-pentyl (C_5), *6*-hexyl (C_6), *7*-heptyl (C_7), *8*-octyl (C_8) or *9*-nonyl (C_9)	
Salt Lake brine	Ionic liquid liquid-liquid extraction	1-Octyl-3-methyl-imidazolium hexafluorophosphate, and tributyl phosphate (TBP)	
Salt Lake brine	Ionic liquid liquid-liquid extraction	Bis(trifluoromethylsulfonyl) imide in TBP	
Brine	Electro-electrodialysis	Bipolar membranes	
Salt Lake brine	Membrane electrolysis	Bipolar membranes	
Dead Sea brine	Solvent impregnated membrane	Solvent-polymeric membranes (2-ethylhexyl)-diphenyl phosphate	
Brine	Desalination	Nanofiltration membrane	
Salt Lake brine	Desalination	Nanofiltration (NF90 membrane XLE membrane)	

2.1.1 Conventional precipitation processes

This procedure can be used in arid climates to allow for significant evaporation of brine water in large-scale ponds. Because brine lakes are found at high altitudes and in locations with little rainfall, solar evaporation is an excellent method for extracting lithium. The crystalline species and the order of sedimentation in brines are determined by their initial chemical composition, therefore the recovery procedures and operations of different brine lakes are usually distinct. Typically, the brines that ideally contain a low Mg (Mg/Li mass ratio < 6) are pumped into a series of ponds (thousands of acres) for solar evaporation. It generally takes several months (between 1.5 to 2 years for SQM operation in Atacama, Chile) to obtain the end lithium production. NEO Lithium company has completed a bench-scale evaporation cycle without the need of additives, concentrating brine up to 3.8% Li [17].

Reacting lithium with aluminum and precipitating lithium- aluminate is an alternative method for lithium precipitation. This methodhas received a lot of attention as a green alternative to the evaporation-precipitation method. The process has shown excellent performance for lithium-precipitation and Li/Mg separation.

As an improvement to this process. It has been shown that magnesium could be removed from the brines in an initial MgAlCO3-layered double hydroxide material (MgAlCO3-LDHs) precipitation step, effectively removing Mg from 117 g/L to 0.02 g/L. The conventional evaporation-precipitation method can have a significant impact on ecosystems, particularly evaporating water from locations with dry climate. The process presents poor recovery and expensive capital investment [18]. A general illustration of lithium extraction process is given in Fig.5.

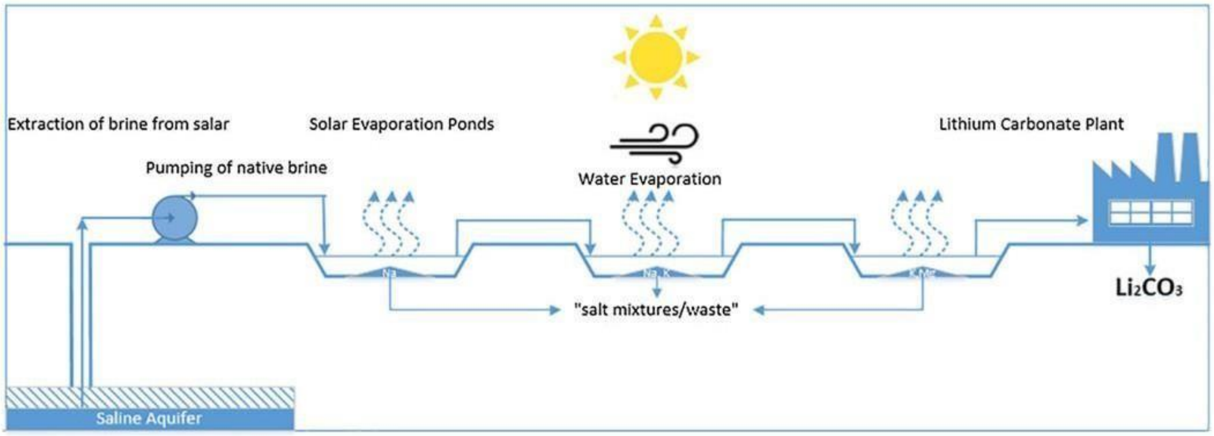


Fig.5. General flowsheet of evaporation and crystallization [19]

2.1.2 Lithium Recovery via Solvent Extraction

Lithium solvent extraction is essentially a stand-alone process, whereas adsorption and ion exchange typically require an additional concentration step, either through smaller solar evaporation ponds, forced (artificial) evaporation, or solvent extraction, before the purified solution can be converted to the final product. Solvent extraction is perhaps the most widely used technique for the separation and purification of metals ions and it is promising for selective removal of residual Mg from Li-rich brine. solvent extraction has the advantages of low chemical and energy consumption, low waste generation, recyclable extractants, and simple equipment requirements, and it has been tested on the pilot scale in China for the lithium recovery. The method is developed based on the TBP/FeCl3 system patented in 1970 by Nelli and Arthur, which has a high selectivity of Li+ over Mg2+ in chloride media. Using a specific chelating agent such as trioctylphosphine oxide or tributyl phosphate, the solvent extraction method can selectively extract lithium in the presence of other metal ions. This approach uses as extractants, large quantities of organic solvents, which not only corrodes process equipment, but also pollutes the environment. Therefore, developing sustainable lithium extraction technology from water resources is becoming a crucial issue [20]. Several studies have brought to light more sustainable extraction and separation of Li from brines using innovative organic systems, these methods are mentioned below.

- Neutral extraction systems.
- Synergistic solvent extraction systems.
- Room temperature ionic liquid systems.
- Crown ether systems.

2.1.3 Lithium Recovery via Electrochemical processes

An electrochemical method for lithium extraction was firstly proposed by [21]. They conducted preliminary research on a system in which -MnO2 was used as the working electrode in various metal chloride solutions. The electrochemical ion pump refers to the working electrode, which has specific characteristics such as ion-sieves (EIP). Taking advantage of the electrochemical insertion, the system demonstrated excellent performance and considerable feasibility in Li extraction from brines. The basic idea behind selective EIP is to capture Li+ from brine and release it into a recovery solution. This electrochemical Li extraction is a promising technique that requires the most critical factor: highly effective electrodes with excellent selectivity, competitive Li capacity, long-term stability, and minimal energy consumption.

The principle of rocking-chair LIBs is used to create electrochemical battery technology. It's thought to be a promising method for recovering lithium from salt-lake brines and seawater. It is made up of a variety of lithium selective and counter electrodes with unique structures capable of separating Li+ from other ions (Na+, K+, $Ca_{2+,}$ Mg2+, and so on). Because positive electrodes of batteries have a high lithium selectivity, a recovery solution with a high Li purity can be easily obtained. This method outperforms other methods such as precipitation and ion sieve in terms of Li separation efficiency [22]. It has several advantages, including low energy consumption and initial investment, high lithium insertion capacity, high reversibility, a green lithium intercalation/deintercalation process, and the absence of chemical reagents and purification in industrial operations. Due to the limited stability of electrodes and the concentration of the aqueous solution, the growth of industrial applications has been modest in recent years. Practical uses are further limited by the substantial initial investment required by electrode materials. Many tests have been carried out utilizing a variety of electrode materials and aqueous solutions with diverse properties. In future large-scale practical applications, the electrochemical-battery technique shows tremendous importance and enormous potential for lithium extraction [23].

Many researchers are investigating the improvement of the electrochemical Li extraction systems, and the recent developments are presented as follow:

- Salt-capturing battery system
- Selective-exchange battery system
- Rocking-chair battery system.

2.1.4 Lithium Recovery via Adsorption

Adsorption approach has now developed into an excellent candidate method for extracting Li from brines. Adsorbents, such as ion-sieve oxides, present an efficient ion recognition and screening performance for specific metal ions extraction. Lithium can be easily selected over alkaline and alkaline-earth metal ions from brines by using lithium-ion sieves (LIS). The LIS can be mainly divided into two types of adsorbents:

The spinel lithium manganese oxide (LMO) type with high adsorption rate and superior lithium selectivity, and the lithium titanium oxide (LTO) type with low dissolution loss and long recyclability [23]. Other inorganic hydrous oxide ion-sieves have also been proposed, including LiSbO3, LiNbO3, LiMg0.5Mn1.5O4, LiAlMnO4, and LiFeMnO4. Typically, the corresponding precursors present a stable framework and transfer to adsorbents by striping the target ions from crystal sites. Recently, the synthesis processes and Li extraction performances of ion-sieves have been extensively studied [24]. A variety of modifications and innovative structures of ion-sieves have also been proposed. Fig.6 demonstrates the comparison of several ion-sieves on Li adsorption capacities.

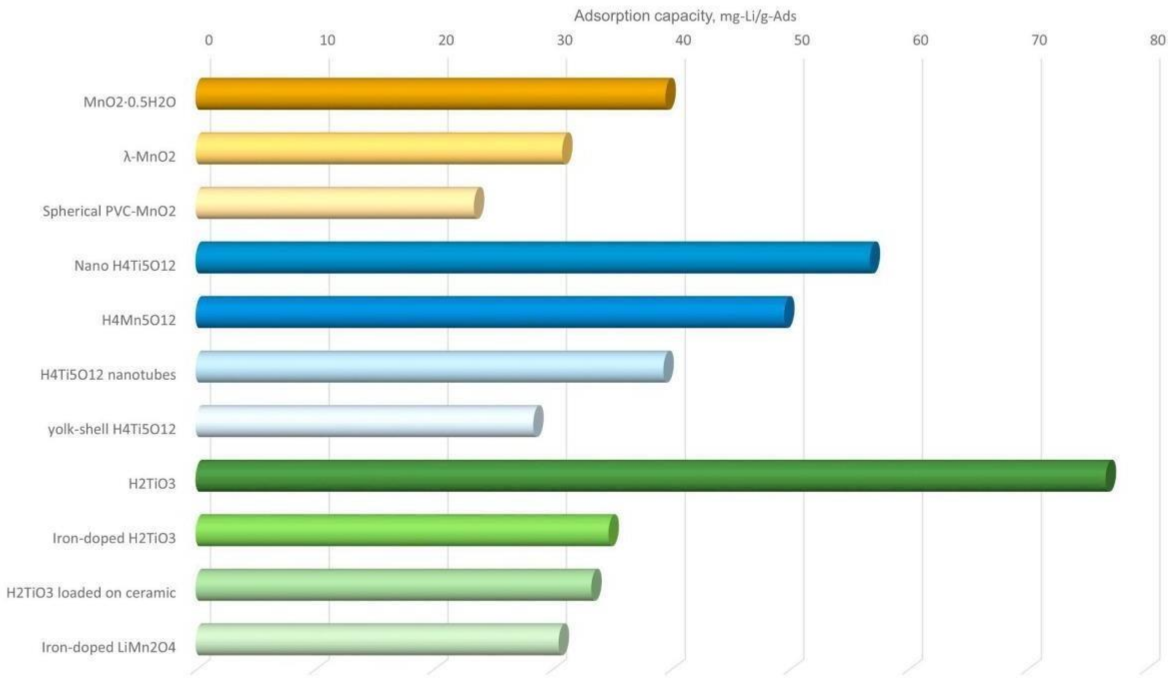


Fig.6. The comparison of lithium adsorption capacities by different ion-sieves.

Adsorption can be carried by two different processes, such as:

- Lithium manganese oxide (LMO)
- Lithium titanium oxide (LTO)

2.1.5 Lithium Recovery Using Membrane Technologies

Membrane technology has been used in industrial applications for several decades as a viable solution for value extraction and separation [25]. Because of its advantages of great energy efficiency and ease of operation in a continuous process, membrane-based separation technology is seen as a potential and ecologically friendly alternative for lithium recovery. With the techniques of Donnan exclusion, dielectric exclusion, and steric hindrance, a nanofiltration membrane may collect monovalent ions without the need of chemicals. Using low-grade heat, membrane distillation crystallization can produce fresh water while also recovering minerals from high- concentration brine. Ionic liquids, ion-imprinted polymers, and ion sieves are all highly selective adsorbents for Li+ that are immobilized onto the membrane carriers by the supported liquid membrane, ion-imprinted membrane, and ion-sieve membrane, respectively.

These adsorption membrane-based technologies can boost adsorption capacity, reduce energy consumption, and allow for continuous operation when compared to traditional solvent extraction methods (easy regeneration). Furthermore, monovalent selective ion-exchange membranes are used as the separation media in electricity-driven membrane-based technologies such as selective electrodialysis and capacitive deionization of permselective exchange membranes to efficiently separate monovalent cations/anions under the electric field [26].

Membrane technology as a novel method for lithium extraction from brines has been reported recently, which are reviewed as follows:

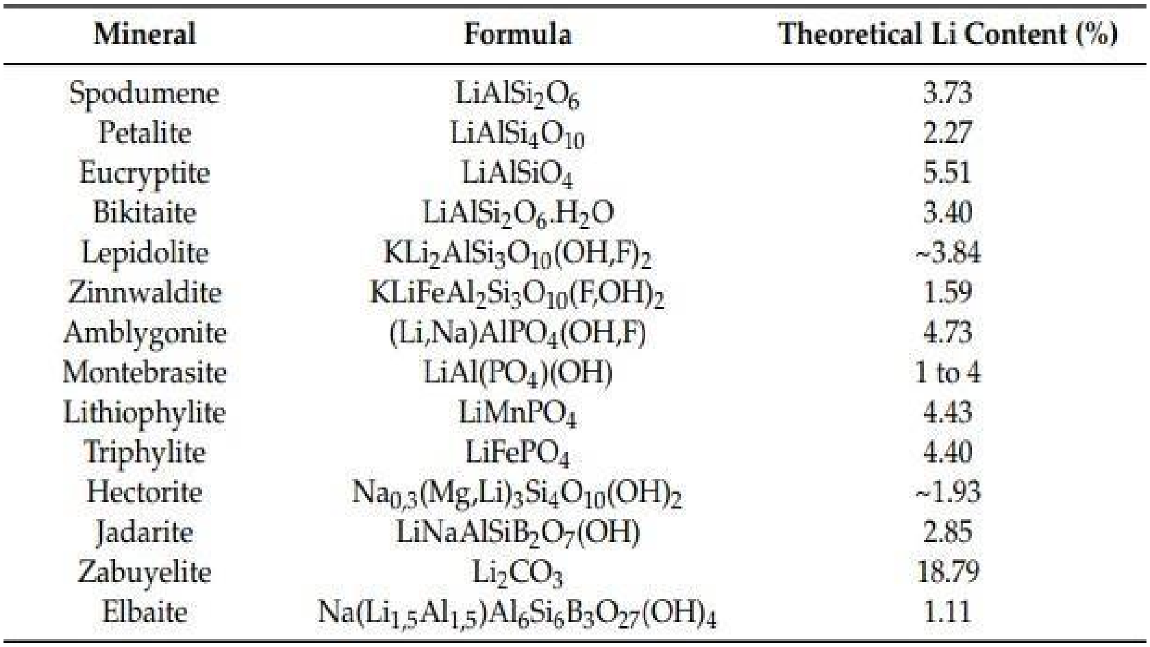
- Nanofiltration (NF)
- Electrodialysis (ED)
- Liquid membrane electrodialysis

2.2 Minerals Ore

Lithium extraction from minerals is primarily done with minerals occurring in pegmatite formations. However, pegmatite is rather challenging to exploit due to its hardness in conjunction with generally problematic access to the belt-like deposits they usually occur in. Recent estimations evaluate pegmatites as 23% to 30% of the lithium identified reserves. Extracting lithium from ores has higher operating costs than conventional extraction from brine, however, the theory of supply and demand makes the processing economically prudent because of the increasing price of lithium. Lithium-rich pegmatites, despite being one of the main sources of lithium worldwide, are very rare in comparison to pegmatites, forming less than 0.1% of the family. The lithium minerals containing lithium inside those pegmatites are numerous and their lithium content great varies [27]. Recovery rates for mining typically range from 60 to 70%, although significant treatment is required for transforming the produced Li into a marketable form.

Some of the Li containing minerals are listed below in the Table 3.

Table 3. Principal lithium-bearing



Mineral	Formula	Theoretical Li Content (%)
Spodumene	$LiAlSi_2O_6$	3.73
Petalite	$LiAlSi_4O_{10}$	2.27
Eucryptite	$LiAlSiO_4$	5.51
Bikitaite	$LiAlSi_2O_6.H_2O$	3.40
Lepidolite	$KLi_2AlSi_3O_{10}(OH,F)_2$	~3.84
Zinnwaldite	$KLiFeAl_2Si_3O_{10}(F,OH)_2$	1.59
Amblygonite	$(Li,Na)AlPO_4(OH,F)$	4.73
Montebrasite	$LiAl(PO_4)(OH)$	1 to 4
Lithiophylite	$LiMnPO_4$	4.43
Triphylite	$LiFePO_4$	4.40
Hectorite	$Na_{0,3}(Mg,Li)_3Si_4O_{10}(OH)_2$	~1.93
Jadarite	$LiNaAlSiB_2O_7(OH)$	2.85
Zabuyelite	Li_2CO_3	18.79
Elbaite	$Na(Li_{1,5}Al_{1,5})Al_6Si_6B_3O_{27}(OH)_4$	1.11

2.2.1. Spodumene

Spodumene is the most important lithium mineral in pegmatites, amblygonite ($LiAlPO4(F,OH)$) is widespread but rarely of economic importance, and petalite, eucryptite ($LiAlSiO4$) and lepidolite ($KLi2AlSi4O10F2$) are less common. Pegmatite is the name of a vast family that comprises, among other things, lithium aluminosilicates. Pegmatites are classified as either granitic or non-granitic. Spodumene is a pegmatitic granitic granitic granitic granitic granitic granitic granitic gran Pegmatites that form a pluton are referred to as a group due to their distinct nature. Pegmatite groups share a granitic source but differ owing to the type of the source, depth, and so on [28]. In the case of spodumene, a relation between its phases and other lithium aluminosilicates, such as eucryptite or petalite, exists in a quartz-saturated environment (Fig 7). This relationship between α- spodumene, β-spodumene and γ-spodumene, which is named virgilite, shows that the crystallization of the minerals must have occurred under about 700 °C since β-spodumene does not occur naturally and virgilite is very rare and mostly found as inclusions.

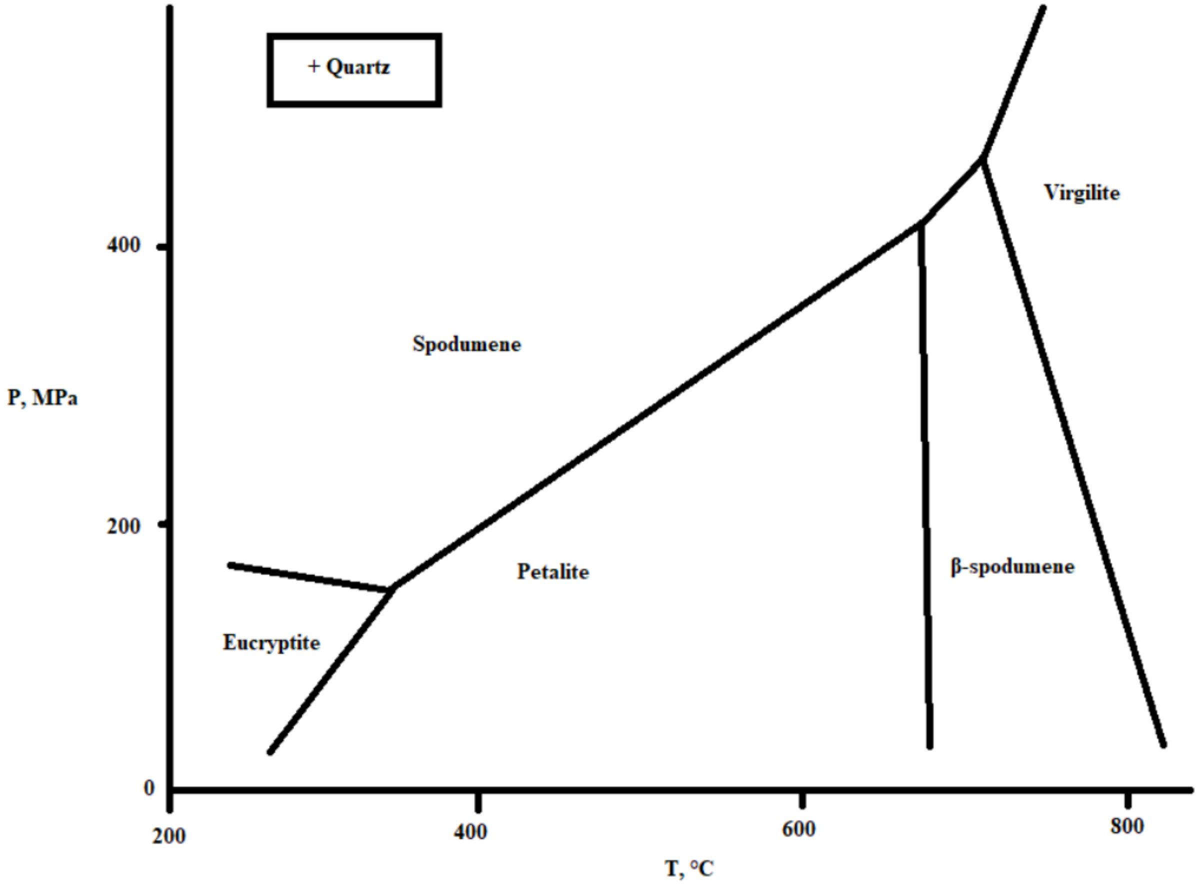


Fig 7, Stability relations among eucryptite (LiAlSiO4), α-spodumene (LiAlSi2O6), petalite (LiAlSi4O10), β-spodumene (LiAlSi5O12) and virgilite (LiAlSi5O12).

The α, β, γ System

Spodumene is an aluminosilicate of lithium. It has been described for the first time in 1800 for an occurrence in Üto, Sweden [29]. Its name is derived from ancient Greek spodumenos, which means “burnt to ashes”, due to its grey ash-like color when grinded. Its color ranges from green to purple. Spodumene can produce two kinds of gems, hiddenite (green), and kunzite (purple). The mineral is mostly associated with quartz and albite, with sometimes traces of beryl. Geologists only call it spodumene. However, in the lithium industry, the mined natural material is referred to as α-spodumene. Its chemical formula is LiAlSi2O6 and it has a monoclinic structure and a density of 3.184 g/cm3.

The second phase is called β-spodumene or spodumene-II. It is the most known phase of the system, due to its reactivity towards extraction. It is obtained after high temperature treatment of α-spodumene and is the base mineral of almost every lithium extraction processes. It has a tetragonal structure and a density of 2.374 g/cm3. It has the particularity to be present in the Li2O–Al2O3–SiO2 ternary equilibrium system. Therefore, it is possible to synthesize it directly into this form following, for example, the LiAlO2 + Al6Si2O13 = 3Al2O3 + β-LiAlSi2O6 reaction [30]. The third phase is less known and has several different names. It is referred to as virgilite, γ- spodumene or spodumene-III. It has a hexagonal structure and a density of 2.399 g/cm3. The formation of a pure γ-spodumene sample has not been reported yet. Moreover, γ-spodumene’s peaks are fewer in number and lower in intensity, making it difficult to identify γ-spodumene in a sample. The phase transitions occur during the thermal treatment via a phenomenon called decrepitation. The latter is an expansion of the crystal lattice of the compound after reaching a determined temperature.

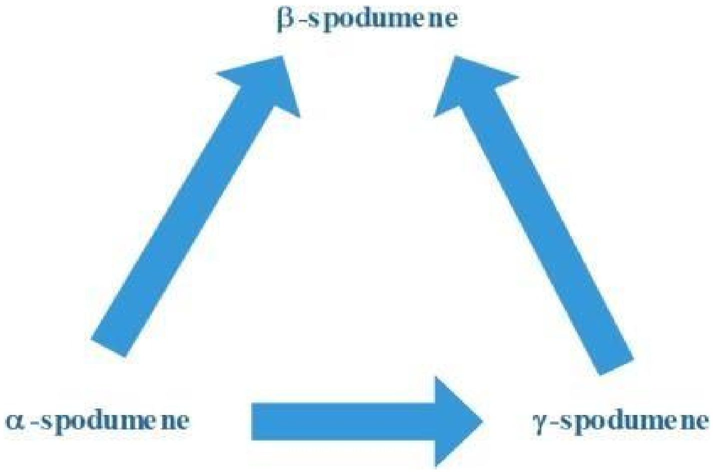


Fig.8. Transitions occurring at high temperature (above 900 ◦C) in the spodumene system.

The α-spodumene to β-spodumene transition occurs above 950 °C and is endothermic. The crystal lattice expands massively (27%) during the phase transition. The γ-spodumene is known to appear before the β-spodumene [31] but is metastable and transitions to β-spodumene at higher temperatures. The transitions existing within the spodumene system can be summarized as follows (Fig.8). Every single transition is irreversible.

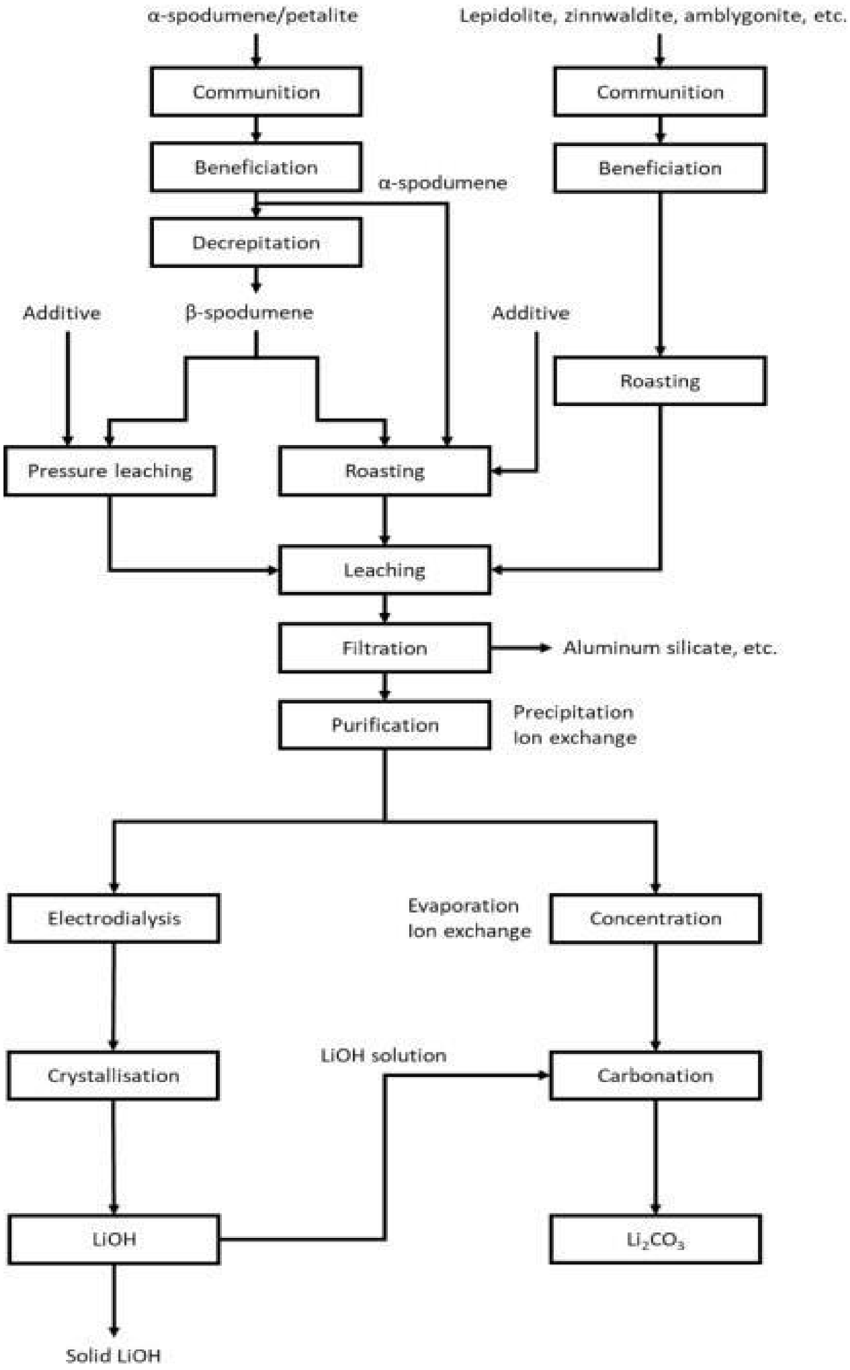


Fig. 9. Flow sheets to produce lithium compounds from mineral sources. Few steps, such as electrodialysis, have only been tested in feasibility studies [32]

The lithium compounds production from minerals follows a simple succession of steps. Every raw mineral must be grinded before being cleaned. A heat treatment is then applied before roasting. The process allows the recovery of lithium but not the production of technical lithium hydroxide of lithium carbonate. Another step, such as carbonation or electrodialysis is needed (Fig.9).

The Traditional Process

When it comes to the actual phase conversion of spodumene, the process has been known since the 1950s. The process has been patented [33] and, still nowadays, heavily dominates the lithium production industry. This process starts with the crushing of spodumene ore. The cause behind the grinding of the spodumene is an acceleration of the heat transfer between the surrounding atmosphere and the mineral. The crushed mineral is then heated in a furnace at, at least, 1000 °C for 30 minutes. The thermal treatment will allow the α-spodumene to decrepitate into β-spodumene. This process is stated to be exclusive to spodumene. The other lithium-bearing minerals being impossible to decrepitate using this method. It was the first process to efficiently extract lithium from spodumene (85% to 90% lithium yield at the time) and was scaled up shortly after [34]. The lithium extraction went from total digestion of minerals such as lepidolite (K(Li,Al)3(Si,Al)4O10(F,OH)2) or amblygonite ((Li,Na)AlPO4(F,OH)) followed by complex purification to selective extraction of lithium.The process is based on the higher reactivity of β-spodumene towards sulphuric acid. The acid is brought into contact with the β-spodumene and heated at about 250 °C. It is reported that the temperature can go as low as 200 °C but cannot reach higher than 300 °C, temperature at which the sulphuric acid starts to decompose. The acid excess must be at least 30% to ensure the availability of the protons after reactions with impurities such as potassium or sodium. Dependingon the grade of the ore, acid excess can go up to 140%. The reaction between the sulphuric acid and the spodumene is presented below:

$$2\ \mathrm{LiAlSi_2O_6}\ (\mathrm{s}) + \mathrm{H_2SO_4}\ (l) \rightarrow 2\mathrm{HAlSi_2O_6}\ (\mathrm{s}) + \mathrm{Li_2SO_4}(\mathrm{s})$$

After the reaction between the acid and the concentrate, the lithium sulfate is leached by water in which it is dissolved while leaving the least concentrate in its solid state. The lithium sulfate can thereafter be precipitated as is or transformed into lithium chloride or lithium carbonate.

Hence, β-spodumene has a more open structure. This structure would allow the diffusion of ions through its matrix via a pseudo-Brownian movement. This statement was later confirmed by crystallographic studies [35] which confirmed that the structure of β-spodumene presents pseudo-zeolithic channels in which protons and lithium cations are free to move. The aluminosilicate portion of β-spodumene is in fact isostructural to keatite, which presents those channels. An important heat production is observed during the acid roasting around 175 °C. This exothermic reaction is linked to the formation of liquid lithium bisulfate (LiHSO4) as a reaction intermediate. since it has a melting point of around 170 °C. This process was so efficient and easy to implement that it has been considered the one and only method of extracting lithium from spodumene in the lithium industry.
From there, two major steps can be pointed out:

- Extraction from β-spodumene
- Decrepitation of α-spodumene

3. Recycling of Li-ion Batteries

With the rapid development of lithium-ion batteries and electric vehicles in recent years, lithium battery recovery has emerged as a hot research topic [36]. More than 3000 research papers have been published on this topic between 2008 and 2018. Basically, there are two steps combined in the recycling process of LIBs (Fig. 10). In the beginning, the mechanical recycling process (also known as the physical recycling process) entails crushing, screening, and separation, which are all steps in the disassembly process. The goal of this is to returning lithium-ion batteries from electric vehiclesby means of a process separation of the cell into particles that can be retrieved by the environment chemical reprocessing.

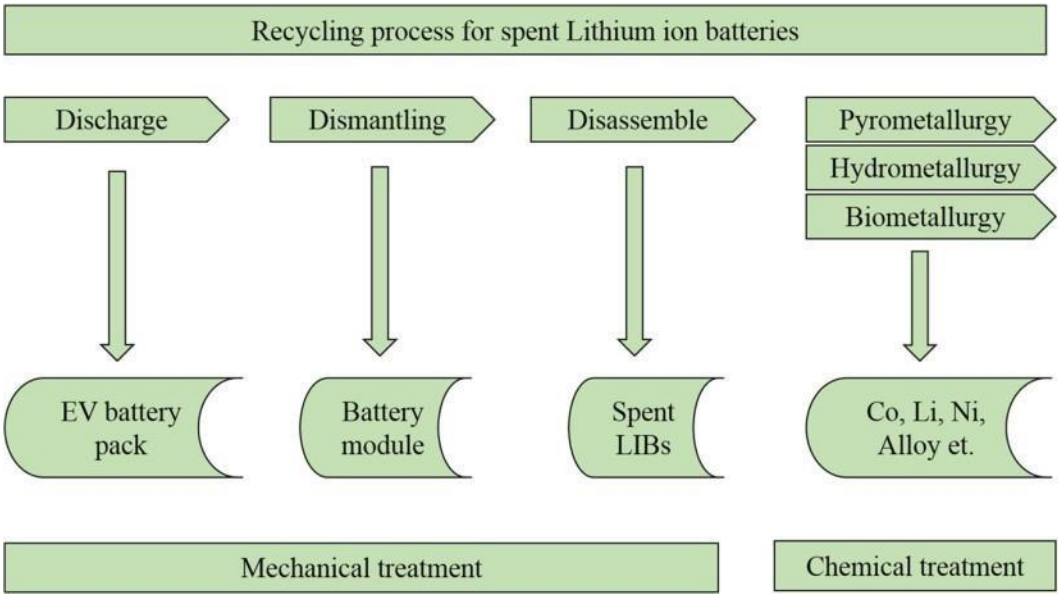


Fig. 10. A comprehensive process of recycling of lithium-ion batteryfrom EVs.

The following are the primary challenges in the physical process:

a) In EVs, the battery pack container has a different design and connection.

b) Variations in battery module size and design, as well as variable battery management systems.

c) During the disassembly procedure, the lithium-ion battery may explode.

d) Harmful gases and hazardous compounds may be formed during the dissolving and dissolution of the battery, polluting the environment.

e) Automation of the disassembly process [37].

Chemical recycling (metallurgy procedures include pyro-, hydro-, bio-metallurgy, and combination approaches) is carried out based on the work of the first stage. The goal of the second stage is to recycle precious metals and raw materials, particularly cobalt and lithium, from wasted batteries [38].

The following are the primary obstacles at this stage:

a) Energy usage.

b) The breadth and diversity of recovery methods.

c) Pollution-related environmental consequences.

d) Investments and expenditures determined by economies of scale.

e) Recycling efficiency

Furthermore, before recycling lithium-ion batteries from electric vehicles (EVs) there is the opportunity of a second use of lithium-ion batteries. According to study by [39], batteries with a residual capacity of 70–80 % cannot be employed in electric vehicles but they can be exploited for domestic uses.

3.1 Mechanical recycling process

3.1.1 Process of returning spent lithium-ion batteries out of EVs

The battery pack enclosure, which comprises battery modules and a battery management system, is normally found at the bottom of an electric vehicle (BMS). To ensure high voltage and capacity, the battery module is coupled in series and parallel with a lithium battery. In most cases, a module contains more than one hundred cells. As a result, an electric car's overall battery count may reach 1000. (Tesla electric car has more than 7000 batteries). The battery pack is dismantled into a battery module, and the battery module is dismantled into a single cell in the mechanical recycling process. It is then crushed into granules and screened for further recycling. With the rise of electric vehicles, a vast number of battery packs containing millions of wasted lithium-ion batteries, will be a major concern for humans in the not too distant future [15].

Disassembly planning and assessment of automation potentials forspent lithium-ion batteries.

With the impact on the environment and resources in mind, finding efficient and safe techniques to extract the lithium battery from the battery pack during the recovery process has become a major research topic. As a result, researchers proposed several ideas to attain this goal. Some authors [40] demonstrated how the disassembly process can be automated using a flexible gripper technology (Fig. 11) [41].

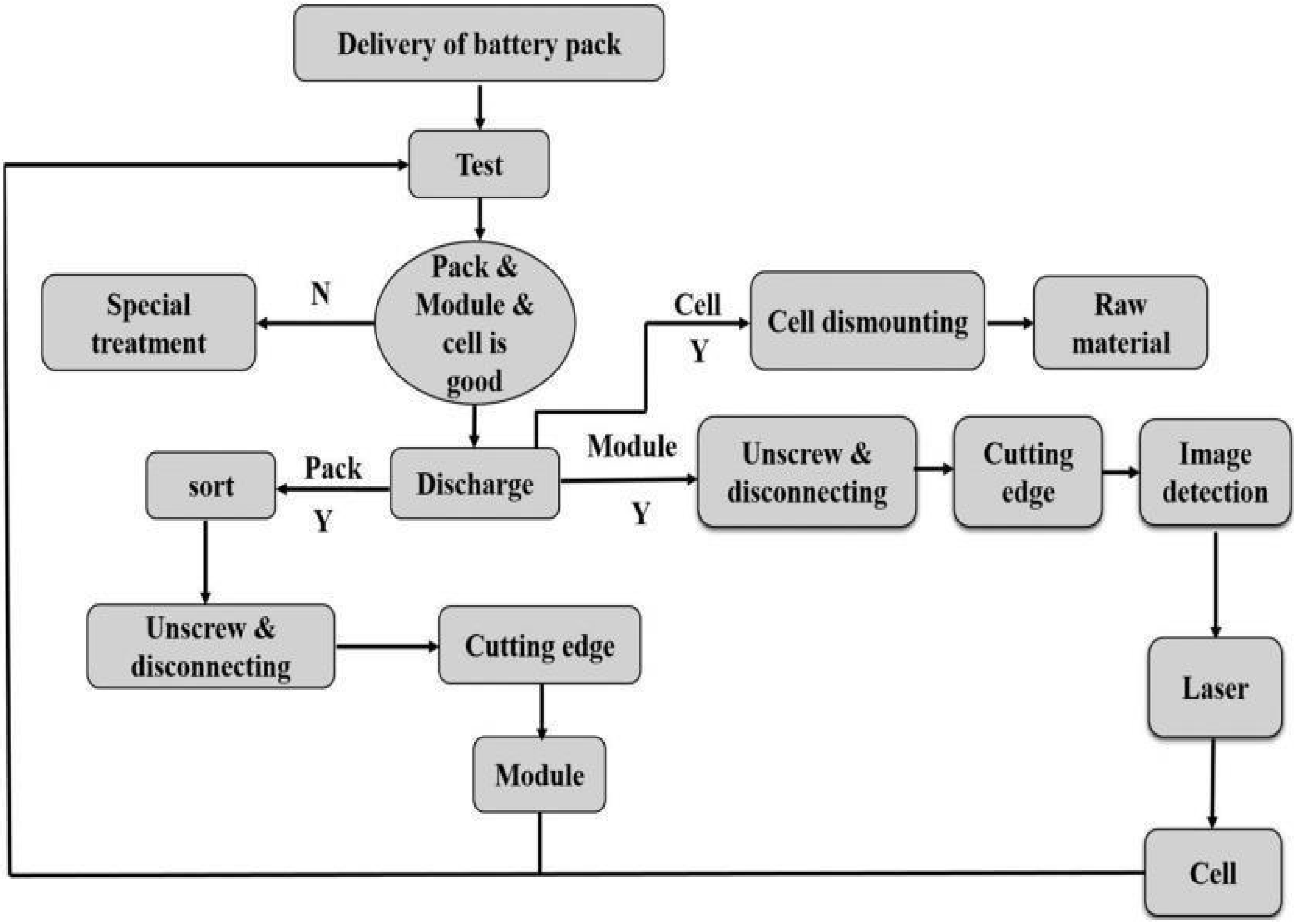


Fig. 11. Semi-automated disassembly concepts for recycling of Batterypack.

[42] Depicted a more tangible notion of semi-automated disassembly processes on the autonomously recycling lithium-ion battery recycling process. The main point was that before disassembling a spent battery, each component (including the battery pack, module, and cell) should be tested for performance. A modular method with separation, detection, control and sub modules is used to evaluate several sensors for intelligent pack disassembly.

Intelligent integration of disassembly system

A properly disassemble sequence is required to improve the efficiency of the recycling process. The methodical assessment approach was used to solve the complexity challenge in dismounting the EV battery pack, as shown in Fig. 12.

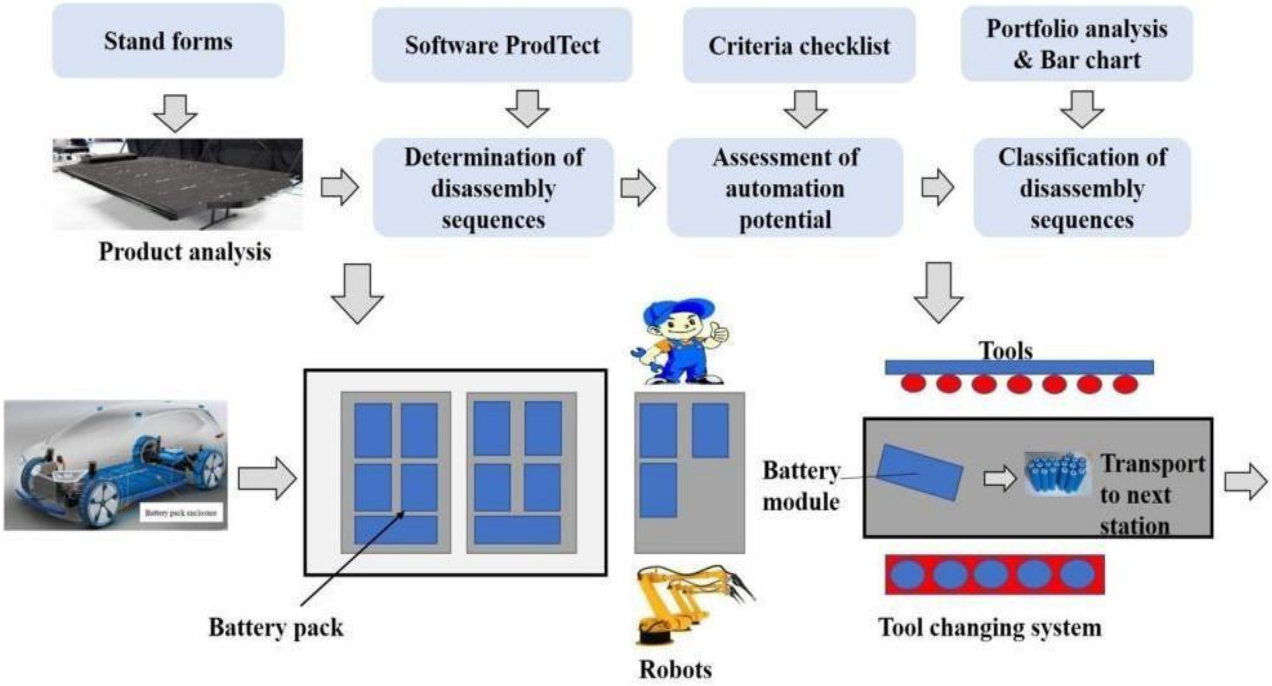


Fig. 12. Intelligent and Integrated disassembly system of Batterypacks.

First, a product study was performed to determine the specifications of the battery pack.

Second, a special software program was used to determine the disassembly sequences. The possibility for automation was then assessed using a criteria checklist, and the final disassembly sequences were established using a bar chart. This method has the advantages of being intuitive, simple to envision, and having the ability to visualize complex product structures. Furthermore, this integrated method can depict disassembly objects while also displaying joining processes and disassembly timeframes [43]. Even though various concepts for solving the automation problem have been developed, the integrated system and intelligent workstation continue to play a significant part in the recycling process.

[44] Implement a new disassembly system and workstation based on the Audi Hybrid battery system to improve the efficiency of automation mechanical treatment. To ensure a possible disassembly order, a disassembly matrix and disassembly priority graphs were created. According to their findings, the efficiency of workstations will improve when workers and intelligent robots collaborate. Meanwhile, based on the results of the big data analysis, the location of the lithium battery recycling factory should include transportation costs.

3.1.2 Further treatment of recovery processes

The focus lays on removing hazardous sources and separating the components of wasted LIBs to recover the raw material more efficiently. Crashing, screening, and separation are all common steps in the process. Mechanical crushing and separation are common technologies used in the secondary recycling process [45]. After the suitable mechanical conditioning treatment, materials such as anode, cathode, electrolyte, and separator can be obtained. Mechanical conditioning separates cell materials using various combination, size, and concentration methods.

[46] Proposed a novel approach for separating the coating and foil of used lithium-ion battery electrodes. Thermogravimetric analysis, tape adhesion tests, atomic absorption spectroscopy, particle size analysis, and gravimetric sieve analysis were used to characterize the process. It can be found that 97.1% w/w of the electrode coating can be regained with aluminum impurities of only 0.1% w/ w, which is 30 times purer than the comparison process. The

details about crushing step process and closed-loop Li-ion battery is analyzed by [47].

3.2 Metallurgy processes

The recovery methods of components on LIB cells, particularly cathode materials, can be separated into hydrometallurgy, pyrometallurgy, bio metallurgy and also a combination of these methods, after mechanical processes. Fig 13 illustrates a flow diagram of a typical recycling process [41].

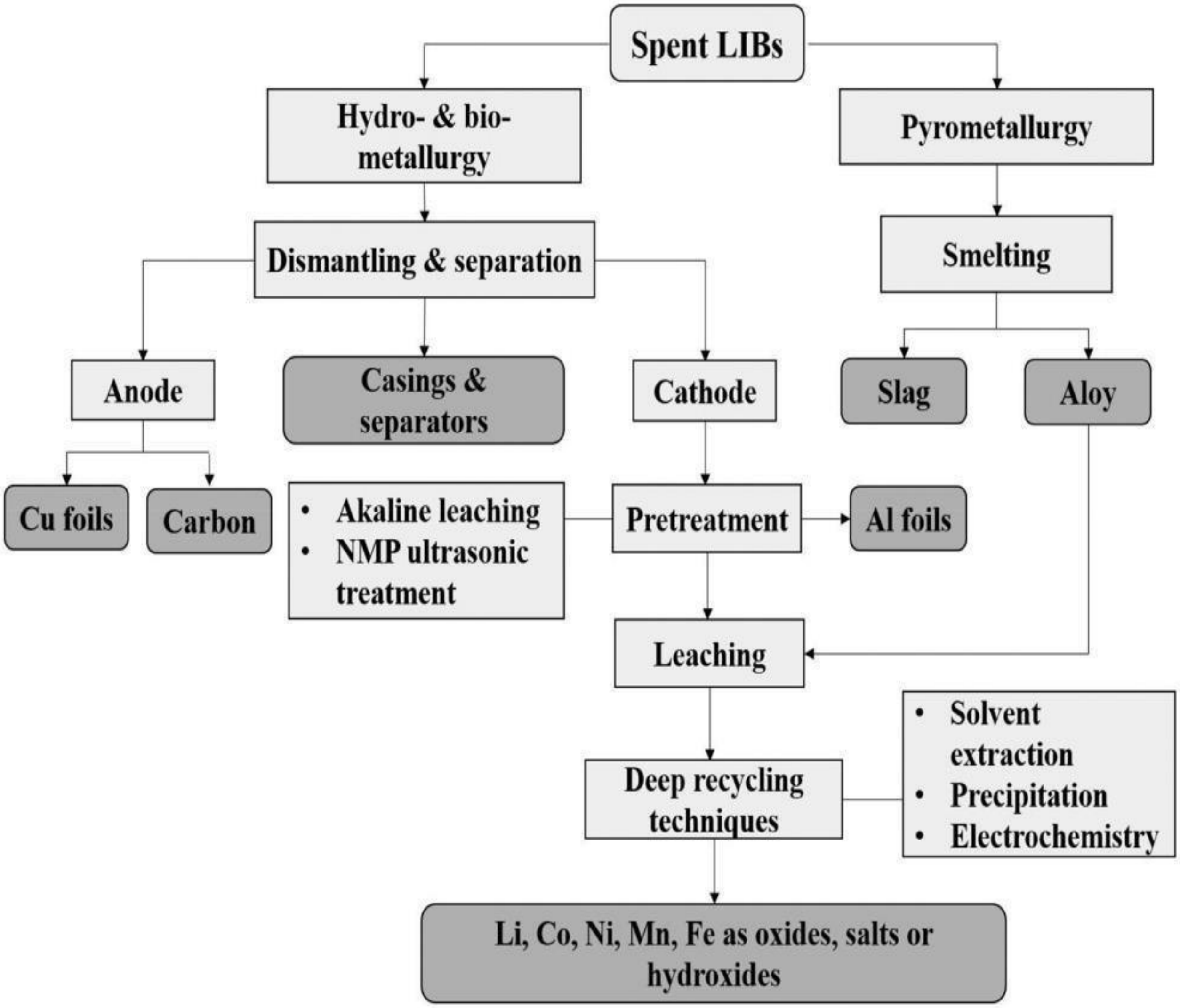


Fig. 13. Flow chart showing typical recycling processes.

3.2.1 Pyrometallurgy

Thermal treatment is used in pyrometallurgy to breakdown the components of wasted LIBs. There are usually two steps in this procedure. To begin, wasted LIBs are heated to a low temperature in a furnace to limit the risk of bursting and evaporation of the electrolyte. Second, all plastics and solvents are burned at a higher temperature, causing slag and alloy formation. The alloy, which is made up of cobalt, nickel, copper, and iron, is frequently subjected to hydrometallurgical and bio metallurgical processing. Some companies, such as Umicore, Accurec, Sony, Onto, and Inmetco, have successfully yoked pyrometallurgical technologies to aqueous processes [48].

Copper, nickel, and cobalt could be effectively recycled using this procedure, resulting in refined and collected alloys. Other dangerous compounds, such as solvents and polymers, are burned, which give a significant amount of process energy while also removing their toxicity. Furthermore, several spent LIBs can be handled at the same time, lowering production costs, and simplifying operations on a wide scale. Pyrometallurgy is frequently used in the manufacturing industry. For batteries that do not contain Ni or Co metals, the economics are not favorable, leaving the future recycling of LIBs as an unresolved problem.

3.2.2 Hydrometallurgy and bio metallurgy

All spent LIBs are initially discharged, deconstructed, and split into outer casing, cathode, anode, and separator. The primary goal of these methods is to recover valuable metals from cathode; they include pre-treatment, leaching, and deep recycling techniques. To remove active material from Al foil, pre- treatment includes N-Methyl pyrrolidone (NMP) dissolving, ultrasonic treatment, and alkaline leaching. Then, to put precious metals into solution, leaching treatments such as acid-leaching and bioleaching are performed. Finally, deep recycling procedures like solvent extraction, precipitation, or electrochemistry make it easier to separate metals in solution [49].

Pre-treatment

The cathodes are submerged in Sodium Hydroxide (NaOH) solution to dissolve Al foils into solution in the alkaline leaching processes. Al foils and active compounds are effectively separated after washing with water and filtering [50]. The following is the reaction of Al foils in NaOH:

$$2AL + 2NaOH + 2H_20 \rightarrow 2NaAlO_2 + 3H_2$$

NMP ultrasonic treatment is currently being widely used to benefit from both NMP dissolving and ultrasonic treatment. [49] Used an ultrasonic apparatus with NMP as the ultrasonic solvent to conduct an experiment at ambient temperature. According to the findings of the experiments, this strategy not only reduces separation time but also has a positive impact on environmental health because the evaporation of NMP at 100 °C is exceedingly poisonous and unhealthy for humans.

Acid-leaching

Acid leaching has become the most extensively used approach in both academic and industrial research in recent years. To isolate and recover a marketable product, this method takes advantage of the chemical characteristics of metals in aqueous solution. In one of the most used method [51], valuable metals from cathode materials are leached out using either inorganic acids, such as H2SO4, HNO3, HCl, or various organic acids, such as succinic, ascorbic, aspartic, malic, oxalic, and citric, as well as reducing agents (e.g., H2O2, NaHSO3, Na2SO3), which make the various metal-forms easily dissolve in the acid solutions through oxidizing them to higher oxidation states. Other authors [52] investigated the sulfuric, nitric, and hydrochloric acid leaching of LiNi0.8Co0.15Al0.05O2 cathode. The leaching efficiency in HCl solution is maximum because the presence of chloride ions reduces the stability of surface-layer formation, resulting in the dissolution process. The best conditions for leaching out all valuable metals, according to tests, were a 4 M HCl solution at 90 °C and an 18-hour leaching interval.

Then, it has been also studied [53] the leaching of LiCoO2, Li2CoMn3O8, and (Li0.85Ni0.05)(NiO2) cathodes with H2SO4 and a reducing agent (NaHSO3). This experiment found that cathodes could gain 87.9 % of Mn, 96.4 % of Ni, 91.6 % of Co, and 96.7 % of Li under ideal circumstances of 0.075 M NaHSO3 and 1 M H2SO4 at 95 °C with a 4 h leaching time.

Bioleaching

Because of its ecologically friendly, low-cost approach and improved efficiency, bioleaching has been regarded a promising technique to replace traditional acid-leaching. To convert insoluble metals into solution, this method takes advantage of interactions between low-grade trash or ores and living microorganisms (fungi and bacteria). Autotrophic-cells involving iron (II)-oxidizing bacteria and sulfur compound oxidation are frequently used in bacterial bioleaching to generate a variety of metabolites such as ferric ions and acid sulfuric. For the first time, [54] Investigated this approach to recover several valuable metals from LIB cathode materials (such as LiFePO4, LiMn2O4, and LiNi xCoyMn1-x-yO2). 98 % of Li from LiFePO4, 96 %of Mn and 95 % of Li from LiMnO2, and roughly 95 % of four metals from LiNixCoyMn1-x-yO2 were recovered in the experiment.

Fungal leaching is more capable of tolerating harmful chemicals than bacterial leaching. To date, fungi such as Penicillium chrysogenum, Aspergillus niger, and Penicillium simplicissimum have been used to excrete metabolites in the form of organic acids that act as dissolving and chelating agents with metals from a variety of waste materials and ores. Some studies [55] investigated the fungal bioleaching of spent LIBs using Aspergillus niger in the wide-ranging conditions to recycle Ni, Co,Al, Mn, Li, and Cu metals. The experimental results indicated that 38% of Ni, 45% of Co, 65% of Al, 70% of Mn, 95% of Li and 100% of Cu were recovered.

Deep recycling techniques.

The important metals could be selectively separated from mixtures of leach fluid using a variety of methods (e.g., solvent extraction, precipitation, electrochemistry, and combination methods) after several pre-treatment and leaching procedures. Using a variety of extractants, the solvent extraction method is commonly used to extract and separate various metals from filtrate. Precious metals are also precipitated using the chemical precipitation process. Lithium can be precipitated by adding oxalic acid (H2C2O4), sodium carbonate (Na2CO3), or phosphoric acid to the leaching solution (H3PO4). NaOH, ammonium hydroxide (NH4OH), dimethylglyoxime, and potassium permanganate are commonly used to precipitate other metals including Co, Ni, and Mn (KMnO4) [56]. In fact, both methods are usually combined to gain highly effective separation.

Another method is to use hydrometallurgy to recover several precious metals from the sulfuric acid leaching liquid of used LIB cathodes [57]. First, after purification, nickel ions were selectively precipitated and recovered using dimethylglyoxime. Second, using Co-loaded D2EHPA and a solvent-extraction technique, Mn and Co were separated. Finally, sodium carbonate and ammonium oxalate were used to precipitate Li and Co in the forms of Li2CO3 and CoC2O4.2H2O, respectively, to recover Li and Co. The proportion of recycling efficiency under optimum conditions gained as following: 81% of Li, 98% of Co, 99%, of Ni and 97% of Mn.

4. Environmental Impacts

4.1 Impacts of extraction of Li Brine

A mineral resource differs from a mineral reserve since it is a concentration of minerals at a known location with known size and character, whereas a mineral reserve is an estimate of the tonnage and mineral content within a mineral deposit that can be extracted from a technical-economical point of view. Annual sales of electric vehicles (EVs) are predicted to exceed 40 million by 2028, demanding a $10 billion– $12 billion investment in the worldwide lithium industry over the next decade to meet global demand [58].

However, the anticipated increase in the production of lithium-ion batteries, as well as the associated extraction and processing of lithium, has prompted major worries about the potential implications and impacts. The currently prevalent method of extracting lithium from natural brines, for instance, results in the loss of approximately 95% of the brine-extracted water, significantly depleting natural aquifers on which residents rely [59].

The brine is first pumped from the subsurface space, where it exists as enormous, underground saline lakes (or salars), into a succession of large, shallow open-air evaporation ponds. The goal is to raise the concentration of brine via natural evaporation driven by the sun and wind. Given that salar brines are found at high elevations and in arid places, evaporation using sun and wind energy is very cost effective. Using this evaporative method, a series of ponds can be created and built in such a way that salts of various ions can be harvested progressively, until the concentration of lithium in the form of lithium chloride reaches roughly 6,000 parts per million. Undesirable chemical components must be removed from the mixture before the lithium chloride can be pumped out and delivered to a treatment plant for further processing. Borates, for example, are removed using solvent extraction procedures, while magnesium is removed by precipitating magnesium cations with lime. Soda ash is added to the brine concentrate to precipitate lithium carbonate.

In some circumstances, the solid lithium carbonate is dissolved and re-precipitated several times until it reaches the requisite battery-grade purity. In general, it can take anywhere from one to two years from the time the brine is pumped from the ground to the time the finished lithium product is processed [60].

Furthermore, evaporation technology provides toxicity concerns to flora and fauna (i.e., plant and animal life) through unintentional leaks or spills, and might potentially impact communities, ecosystems, and agricultural activities. The Lithium Triangle has had an arid climate for a long time. Volcanic and hydrothermal activity that leach lithium from volcanic rocks and drain it underground to the aquifer produce concentrated brines in a confined evaporitic basin with a salt flat and salty lagoons or brines [61]. The separation of lithium from brines (very saline solutions with salt concentrations more than that of ordinary saltwater) differs dramatically from that of solid rock. Additional natural elements, like as sodium chloride, are usually present in the brine mixture; the real lithium level ranges between 0.01 and 0.2 percent. The cations contained in the brine combination in total are Na+, Li+, K+, Mg2+, and Ca [62].

Significant quantities of lithium can be found in waste storage ponds, tailings piles, processed waters, evaporate basins, and transported products, in addition to the toxic chemicals used in lithium processing; these have biophysical consequences that could negatively impact human metabolism, neuronal communication, soil ecology, and aquatic life. Furthermore, evaporation ponds are generally lined with polyvinyl chloride (PVC) as a protective barrier, which may fail and allow pollutants into the environment [63]. Environmental effect evaluation tools, such as life-cycle assessment, which are used in other engineering disciplines, are considerably constrained in mining due to a lack of well-defined measurable impact categories (e.g., water toxicity, eutrophication) and functional units. In many life-cycle assessment studies, functional units are employed to quantify production. For example, brine evaporitic technology can have negative effects on water usage, flora and fauna, waste generation and disposal, and land subsidence, although there have been few studies that link the amount of lithium generated to the intensity of these environmental problems. According to some estimates, evaporative technique consumes around 500,000 gallons of water each ton of lithium extracted [18].

According to the Chilean government's Committee of Non-Metallic Mining, the amount of water pumped out of Salar de Atacama grew by 21% between 2000 and 2015. As a result, local groundwater levels in certain areas have dropped by up to one meter per year. In arid locations like the lithium triangle, groundwater is critical for human consumption, livestock, crop irrigation, and local plant species, therefore contamination is a legitimate concern [64].

It is critical to distinguish between the two forms of water that are extensively used in lithium mining from brines. The first form of water is brine, which has a high ionic strength of at least 170 g/ L total dissolved solids (TDS), with TDS values typically exceeding 300 g/L. The second type of water is fresh water, with a salinity of less than 10 g/L TDS. Brine water is found within the salar's boundaries. Fresh water can be found at the salar basin's edge in free aquifers, alluvial fans, and fluvial system deposits. Water for industrial usage is obtained through wells drilled and collected from freshwater reservoirs, however this water is frequently unfit for human use without further treatment [65]. The volume of evaporated water is enormous, and it should be kept far away from human or animal use. Except for small-scale sodium chloride makers, who also evaporate brine, no one was using brine water before lithium mining corporations began extraction. Because the total salts concentration in brine is 9 times higher than in sea water, it is not appropriate for drinking and has no use for irrigation. Brine water is frequently thought to be a static deposit. Even in the absence of any exploitation, brine water is in dynamic equilibrium with the environment, with a gradual turnover controlled by evaporation and recharging from the rare rains.

The second point of contention is fresh water. Separate wells are utilized by mining corporations for their own supply of fresh water, which is utilized in various stages of the extraction/purification process. Deionization will be used to purify some of the fresh water. The creation of the concentrated lime solution and the purification of lithium carbonate will need the most fresh/deionized water (washing, re-dissolution, and re-precipitation of primary lithium carbonate). According to data published by Argentina's Provincial and National Mining Offices, 5 to 50 m3 of fresh water are required per ton of final battery grade Li2CO3 produced. This may not appear to be a large volume, but it is being pumped out of parched country [18].

It's easy to see why both residents and environmentalists are keeping a close eye on how mining corporations use fresh water. However, there is concern regarding possible interactions between the different aquifers, such as brine water and fresh water.

The most significant impact is on the availability of fresh water. Because water is the key limiting ecological component in such an arid environment, if lithium mining disrupts the region's hydric balance, it will have an impact on local flora and fauna. Microbial activity in the surroundings of salars and in the salars themselves has a less obvious potential impact. Stromatolites have recently been discovered in great numbers in many areas throughout the Lithium Triangle. This location is one of the few places on the planet where both fossil and living stromatolites can be found. Furthermore, due to the harsh climatic and geographic conditions, such as extremely high salinity and solar irradiation, as well as extreme pH values and high arsenic content, these stromatolites (blue-green algae) are particularly interesting, as their study could shed a lot of light on the origins and early stages of life on Earth [68].

4.2 Impacts of Recycling

Due to the chemical and energy-intensive nature of the recycling processes, there is still debate on whether battery recycling can achieve a net reduction in environmental effect. As a result, scientific understanding regarding the effects of traction battery recycling has sparked a lot of interest, and it can help government agencies enhance present battery regulations. Using theoretical calculation data, researchers calculated the environmental impacts of traction recycling batteries, but came up with various answers. The former concluded that both hydrometallurgical and direct recycling of lithium manganese oxide (LMO) LIB can significantly reduce life cycle greenhouse gas (GHG) emissions (up to 54 % compared to no recycling), whereas they latter concluded that only direct recycling of nickel manganese cobalt oxide (NMC) LIB and nickel cobalt oxide (NCA) LIB can achieve a visible reduction of GHG emission, which cannot be significantly reduced by hydrometallurgical and pyrometallurgical technology. Based on European industry data, it was claimed that by optimizing the recycling process, pyrometallurgical recycling technology might provide large net environmental benefits [69].

Although the environmental impacts of traction battery recycling have been quantified in recent life cycle assessment (LCA) studies, there are still substantial uncertainties. Furthermore, China, which is one of the world's major producers and customers of electric vehicles, has received little attention. The benefits of traction battery recycling were researched in China, although the statistics utilized were estimates. Furthermore, these studies gave less attention to other environmental aspects such as resource depletion and toxicity substance emissions, which are both key requirements in determining environmental impact. Furthermore, these studies do not take into consideration future recycling technology situations, making them unable to provide prospective knowledge to stakeholders [70][71].

For battery recycling companies around the world, two mature methods (pyrometallurgical and hydrometallurgical recycling) are currently available. Because it is simple to operate and has a high productivity, pyrometallurgical recycling is frequently used in companies like Umicore, Inmetco, Accurec, and Glencore. Hydrometallurgical recycling is commonly utilized in China because it has a high recovery efficiency and requires a low-temperature operating environment (Brunp, Huayou Cobalt, GEM, and GHTECH) [72].

We are discussing about the environmental consequences of recycling traction LIBs and making batteries out of recycled materials. The essential procedures, materials, and other aspects that have a significant impact on the overall impacts of traction LIB recycling have been discovered. The analysis will provide scientific knowledge to stakeholders such as EV recyclers and manufacturers, policymakers, environmental researchers, and non-governmental organizations (NGOs), and will aid in the management of EOL traction LIBs. Iron phosphate (LFP) LIB and nickel manganese cobalt oxide (NMC) LIB are two extensively produced and used traction LIBs in China [73].

Because the design of the battery pack is exceptionally complicated and diverse, there is a lack of data on its mass and composition, the effects of LIB recycling and manufacture are studied at the cell level. Hydrometallurgical recycling technology, which is a commercially available process, and direct recycling technology. From the study of [2], they described the system boundary of the life cycle of traction LIB, and four stages are included: manufacturing, use, collection, and recycling. While, considering the use phase was the same for virgin or second LIB, which was not considered in their study. The LIBs recycling and manufacturing LCIs in their study were primarily derived from relevant firms and expert estimates in China. Ecoinvent 3.7 was used to model upstream processes such were resource extraction, raw material production, energy generation, transportation, and infrastructure [74].

4.2.1 Traction Battery Recycling

All the processes were modeled in openLCA 1.10. and considered Two recycling firms, one in Hunan province with an NMC recycling capacity of 100 kt/year and the other in Jiangxi province with an LFP recycling capacity of 25 kt/year, provided the principal LCIs for hydrometallurgical recycling technology. As indicated in Fig. 14, hydrometallurgical technology involves two basic processes: mechanical and chemical.

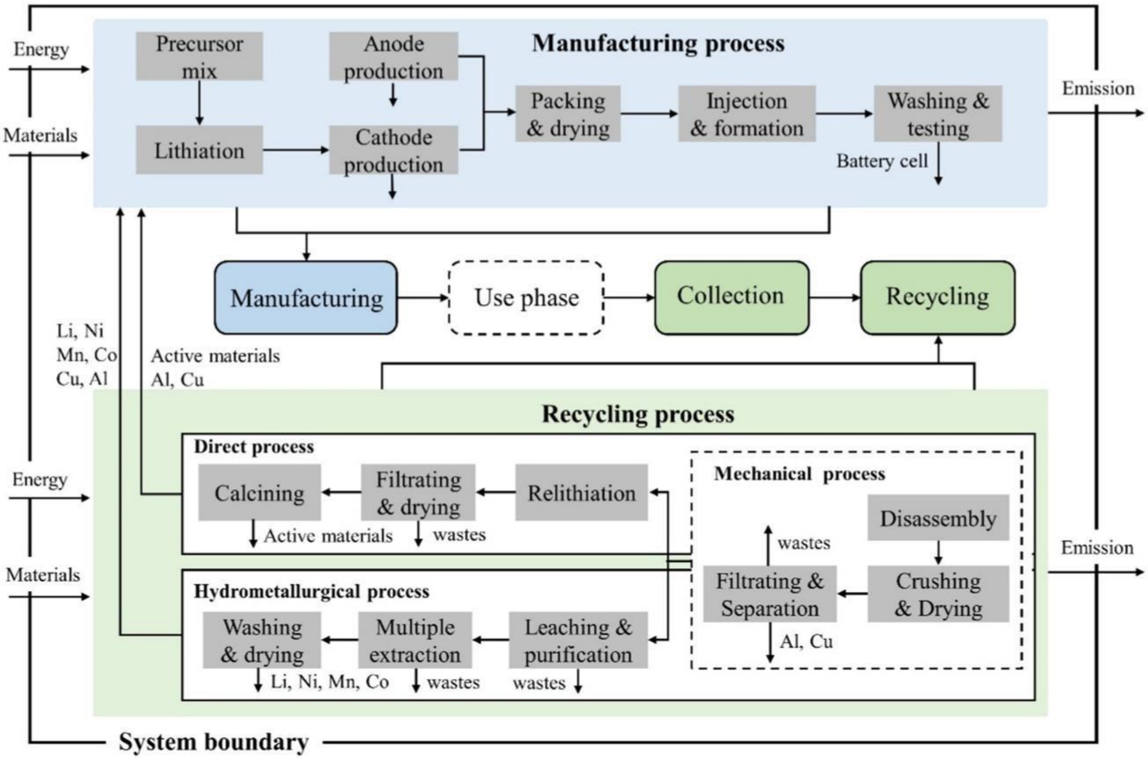


Fig. 14. The system boundary of the life cycle of lithium-ion traction battery manufacturingand recycling.

The mechanical method for NMC and LFP is similar in that traction batteries are dismantled manually to obtain battery cells. The battery cells are then automatically crushed into tiny bits, which are then dried using natural gas to breakdown and evaporate the electrolyte. The pieces are then sorted into several components using the air classification method, including black powder for the next chemical step, metal scraps such as aluminum (Al) and copper (Cu) for reuse, and non-recyclable solids (separator and other general wastes) for disposal. For the two types of batteries, the chemical process is different. For NMC, the leaching process involves mixing black powder with H2SO4 in an aqueous solution at a specific temperature, then separating the leaching residues. The recovering efficiency of lithium is estimated to be 82% for LFP and 80% for NMC. The recovering efficiency of Al and Cu is estimated to be 90% for LFP and NMC, while it is also 90% for Mn, Co, and Ni [2]. Because direct recycling is laboratory-scale method, the LCI is derived from published literature and scaled into the functional unit. Direct recycling also necessitates the dismantling of the battery, crushing of the cell, and separation of the deteriorated active powder. The relithiation technique is subsequently applied to the deteriorated active powder. The powder is first relithiated with LiOH before being combined with Li2CO3 solution for LFP. To make recycled cathode materials, the relithiated powder is dried and calcined. For NMC, the powder is relithiated with LiOH and then washed with water to remove any remaining LiOH. The dried and calcined relithiated powder is then used to make recycled cathode materials. For cathode materials, such as LiFePO4 for LFP and LiNi1/3Co1/3Mn1/3O2 for NCM, the recovery efficiency is anticipated to reach 90% [75].

4.2.2 Traction Battery Manufacturing

The primary LCIs for battery manufacturing were obtained by consulting employees at two manufacturing companies in Anhui for NMC and Shandong for LFP, respectively, with manufacturing capacities of 2.7 and 1.6 GWh/year [2]. Cathode, anode, separator, electrolyte, and cell container are the five components of a battery cell. The cathode is made up of an Al foil positive collector and a layer of positive electrode paste, which is made up of positive active material, a small quantity of binder, and black carbon. LiFePO4 for LFP and LiNi1/3Co1/3Mn1/3O2 for NMC are the positive materials. A Cu foil collector is covered with a negative electrode paste comprised of graphite, black carbon, and a little quantity of binder on the anode. To prepare the electrode paste, combine the solvents N-methyl-2-pyrrolidone for the positive electrode and deionized water for the negative electrode to make a slurry that is then applied to the collectors and evaporated. The cathode and anode electrodes are reduced to size and winded with the separator to produce the cell stacks after manufacture. The tabs are welded, and the stacks are put into the -based cell container. After washing, the cell is finally filled with electrolyte and sealed.

4.2.3 Material reuse scenario

Recent studies [2] established a closed-loop recycling scenario, in which recovered material was used as a substitute for raw resources to avoid the negative effects of the main production route. Assuming all metal compounds for battery manufacture came entirely from recycled retired batteries in this scenario. As a result, the number of retired batteries needed to recover appropriate metal compounds was calculated using eq:

$$Q = 1/\beta$$

where Q (dimensionless) is the required quantity of retired LIBs, and β is the materials' recovery efficiency. The hydrometallurgical recovered metal compounds (NiSO4, CoSO4, MnSO4, and Li2CO3) would go into the precursor mix phase in this scenario, while the direct recovered active materials would go into the cathode production step Fig14. Before being reused, reclaimed aluminum and copper wastes need be purified and treated.

4.2.4 Transport

Raw materials and retired batteries are transported to manufacturers and recyclers as part of the transportation process. Because China has the most established traction LIB supply chain, from resource extraction to battery manufacture and recycling, it has been assumed that all transportations (except for ores mining) occurred within China [76]. Because the types of transportation and distances are still unknown due to the various suppliers, the approach used by [2] is to propose a baseline transportation scenario in which the retired batteries and required materials are first transported by freight rail and then by a freight lorry with a 32-ton load capacity. The transport distance was calculated using China's average transport distance, whichis 688 km for rail freight and 174 km for road freight, respectively [77].

5. Methodology

Life Cycle Assessment (LCA) is a quantitative and qualitative analysis tool for determining the environmental impact of products, processes, and activities across their entire life cycle. The most important thing is to examine the situation. Energy usage and its potential environmental impact acquisition of raw resources, manufacture, and use of products to resource recycling, and explain the evaluation's findings, as well as make recommendations for energy savings and emission reduction reductions and environmental improvements.

LCA is based on well-established processes that follow worldwide best practices. The approach is then highly strict and difficult, as it requires knowledge of various characteristics and considers the full-chain process from raw material extraction to device production, usage, consumption, and disposal. For this reason, precise information (such as market development) and possible envisioned scenarios are required to simulate the environmental impacts of materials in terms of energy flows, emissions, and waste streams over the course of a product's whole life cycle. Indeed, there are few research on LCA of technologies for LIBs recovery in the literature, and most of them are focused to a single procedure [94].

According to ISO 14040 Life cycle assessment – Principles and framework (1998), LCA consists of four stages:

1. Goal and scope definition

Describe the system to be studied such as the product, process or activity, determine the goal of the study, and describe the scope including impact assessment methodology and system boundaries.

2. Life cycle inventory analysis (LCI)

Identify and quantify relevant inputs and outputs to the system. These may include the use of resources and releases to air, water and land associated with the system.

3. Life cycle impact assessment (LCIA)

Associate inventory data with specific environmental impacts. Evaluate the significance of potential environmental impacts using the results of the LCI.

4. Life cycle interpretation

Interpret the results of the inventory analysis and impact assessment phases in relation to the objectives of the study. Provide conclusions and recommendations.

A life cycle assessment (LCA) is a method for determining a product's environmental impact throughout its life cycle activities. By identifying the process with the greatest impact, LCA can assist in improving the product's sustainable design. As a result, it has become a key tool for establishing a foundation for policy decisions [95]. While the quality of an LCA is largely determined by the data upon which it is based, primary data are necessary to eliminate uncertainty caused by a lack of knowledge about the products under consideration. Currently, LCAs focus on gathering primary data for onsite production processes, which is how it is usually done. However, LCAs typically gather data for upstream processes from sources including as models, LCA databases, and published literature [96].

5.1 Impact assessment methodology

The results of the life cycle inventory are transformed into mid-point level indicators to characterize the impacts of resource consumption and pollutant discharge to assess the environmental profile [2]. Four indicators have been used in their study:

- **Global warming potential (GWP):** It is a measure of how much energy a ton of a gas will absorb over a specific length of time in comparison to a ton of carbon dioxide emissions (CO2). The greater the GWP, the more a given gas heats the Earth in comparison to CO2 during that time period. The time period usually used for GWPs is 100 years.
- **Cumulative Energy Demand (CED) :** To analyze the environmental performance of a unit manufacturing process, the concept of cumulative energy demand may be used, which includes not only the direct energy usage during the process, but also the indirect energy (i.e., embodied energy) owing to material consumption. It may also provide a complete evaluation technique for process strategy.
- **Mineral Depletion Potential (MDP):** Mineral depletion potential is one of the factors considered in LCAs. It refers to the amount of energy produced via nonrenewable resources. It is also an indicator of the effects on mineral resources, which play a significant role in limiting the expansion of the battery sector.
- **Human Toxicity potential (HTP):** The Human Toxicity Potential (HTP) is a quantitative toxic equivalency potential (TEP) that was originally created to express

the potential harm of a unit of chemical released into the environment. HTP considers both inherent toxicity and general source-to-dose relationships for pollutant emissions.

The GWP and CED were used because of their connection to climate change, which has sparked widespread controversy among scientists and the public. MDP is an indicator that shows the effects on mineral resources, which are also a major impediment to the growth of the battery sector. Furthermore, the implications of harmful material emissions are examined in HTP [79]. The GWP is based on the IPCC report (IPCC, 2014), while the last three indicators are from the IMPACT World+ database [78].

By understanding the importance of the above mentioned indexes, we compared the result of the [2] with different studies results. The main purpose of comparing it with other studies results are to identified the reduction in the GWP and energy consumptions, used for recycling process. As some authors used only virgin materials, while some authors used Hydrometallurgical recycling technology and some used Direct recycling technology .We can see the difference clearly by comparing the result of GWP and energy consumptions to others studies. As main aim of [2] is on using Direct recycling method which causes a large reduction in the energy consumption with respect to others and it is also known that the recovered materials required more material inputs and more energy during their virgin production.

6. Results and discussion

6.1 Environmental impacts of traction LIB recycling

From the studies taken as a reference [2], the traction battery cells under consideration (Fig. 14) described the process impacts (positive value) and avoided impacts (negative value) of the two recycling processes. The material and energy inputs, which are heavily influenced by the chemical process, are the principal sources of process impacts. In the case of LFP, there is no noticeable difference between hydrometallurgical and direct technology in terms of process impacts. In the case of NMC, the hydrometallurgical technology has bigger process impacts than the direct technology in all impact categories, with ratios of 1.9, 2.4, 1.4, and 1.5 for GWP, CED, MDP, and HTP, respectively. The main reason was that the hydrometallurgical approach required additional resources (such as sodium hydroxide and sulfuric acid) and energies in the chemical process to remove metal components from the NMC cathode. In comparison, there was no statistically significant difference between the two methods when it came to the process consequences of LFP recycling.

The avoided impacts, which relate to the recycling benefits derived from recovered materials, are heavily reliant on the impacts experienced during their primary manufacture. It has been discovered that the direct technology's evaluated consequences are much more than those of the hydrometallurgical technology for a certain battery cell (Fig. 15). This is because the active materials recovered by the former are byproducts of the metal compounds (e.g., lithium, cobalt, nickel, and manganese) recovered by the latter, which necessitate extra inputs and hence have greater impacts during the manufacturing process.

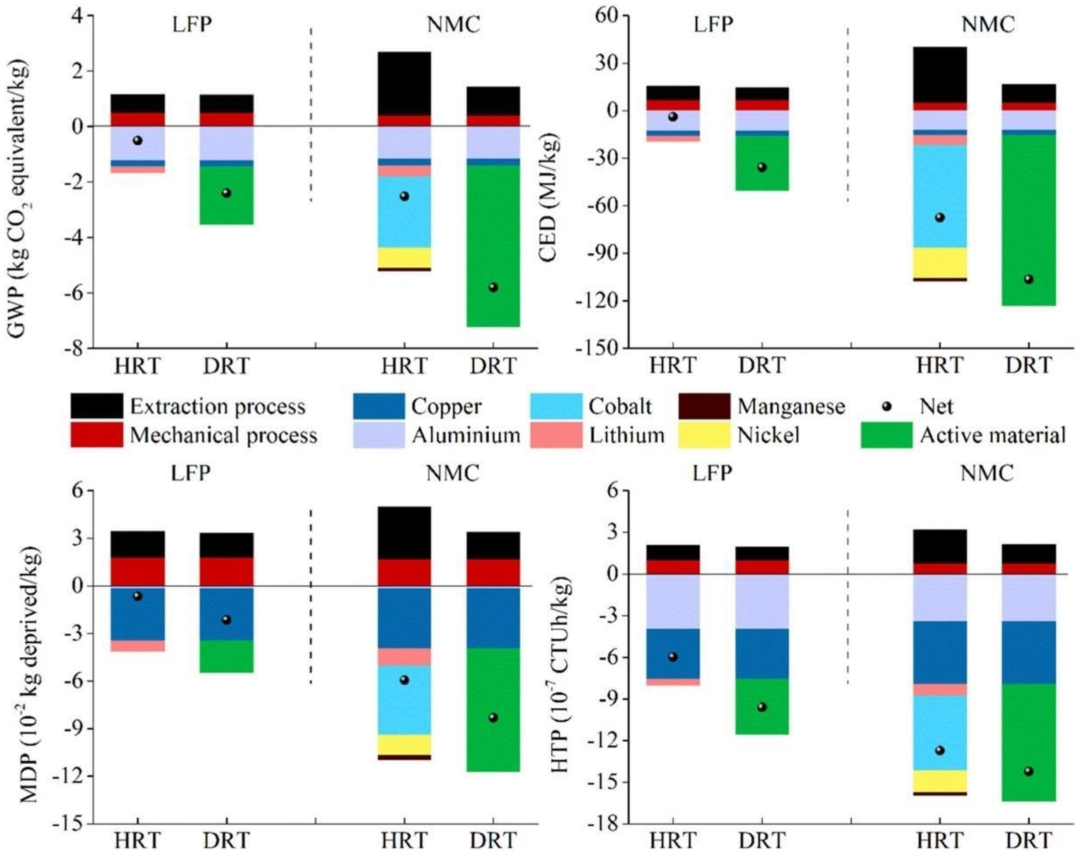


Fig. 15. Environmental impacts of two analyzed recycling technologies for the two lithium-ion traction batteries: (a) global warming potential, (b) cumulative energy demand, (c) abiotic resource depletion, and (d) human toxicity potential. HRT: hydrometallurgical recycling technology. DRT: direct recycling technology. Here, lithium, nickel, manganese, and cobalt refer to the corresponding metal compounds.

The net impact of LIB recycling is calculated by subtracting the process impacts from the recycling benefits. Negative net impacts can be achieved for the four impact categories of the examined battery cells, as shown in Fig. 15. It shows that LIB recycling, using any of the two technologies, offers net environmental advantages in terms of carbon emissions, resource usage, and toxic chemical emissions. Direct technology provides bigger net benefits than hydrometallurgical technology for a given cell type, especially for NMC, with the biggest net recycling benefits of the investigated impact categories, due to comparatively low process inputs and high avoided impacts. However, in comparison to hydrometallurgical technology, direct technology is an unproven method that has only been tested in the lab and may not be suitable for changing cathode materials [2].

6.2 Environmental impacts of material reusing

The environmental consequences per kg of traction LIB generation were determined by the [2], utilizing virgin and recycled materials, as shown in Fig, 16 for the primary production. LFP cell manufacturing generally causes smaller environmental impacts per kg, which is 36%, 45%, 50%, and 28% lower than NMC cell for GWP, CED, MDP, and HTP, respectively. The differences stem from the cathode material, which accounts for over 37%–43% and 50% of themanufacturing impacts for LFP and NMC cells, respectively. Metal compounds (such as nickel, manganese, and cobalt) are present in the precursor of NMC cathode, which need more material and energy to process than the iron phosphate precursor used in LFP cathode, resulting in greater environmental implications during manufacture. N-methyl-2-pyrrolidone (NMP), the solvent used in cathode manufacture, is another significant contributor, accounting for 13–16 % of GWP and 16–20 % of energy requirement, depending on battery cells.

The energy used in manufacturing is another significant contributor to GWP and CED for the LIB cells under consideration, particularly for LFP, where the shares are projected to be 41% and 34%, respectively. As for MDP and HTP, the anode material is the second-largest contributor, sharing 46% and 33% for LFP and 36% and 30% for NMC, respectively. The reason for this is the widespread use of copper as an anode electrode substrate, which has a significant influence on toxicity and resource depletion. Only a small percentage of all effect categories are caused by transportation (Fig. 15). Transportation accounts for less than 0.5% of GWP, CED, and MDP cell types, and 1.2–1.6 % of HTP cell types.

For both the recycling technologies and the two battery chemistries, there are decreases in manufacturing impacts in all impact categories when recycled materials are used as inputs instead of virgin materials (Fig. 15.). GWP and CED reduction potentials for LFP are projected to be 7–13 % and 4–10 %, respectively, depending on recycling methods, but MDP and HTP have much lower reduction potentials (17–30 % and 42–58 %, respectively). Similarly, reusing materials in NMC manufacturing has lower GWP and CED reduction potentials (14–27 cent and 20–34 %, respectively) than MDP and HTP (39–54 % and 56–64 %). The fundamental reason for this is that, as a significant contributor to GWP and CED, manufacturing energy cannot be reduced through recycling. MDP and HTP, on the other hand, may be greatly decreased by reusing copper in anode material, which accounts for a significant percentage of both effect categories (Fig. 16c-16d).

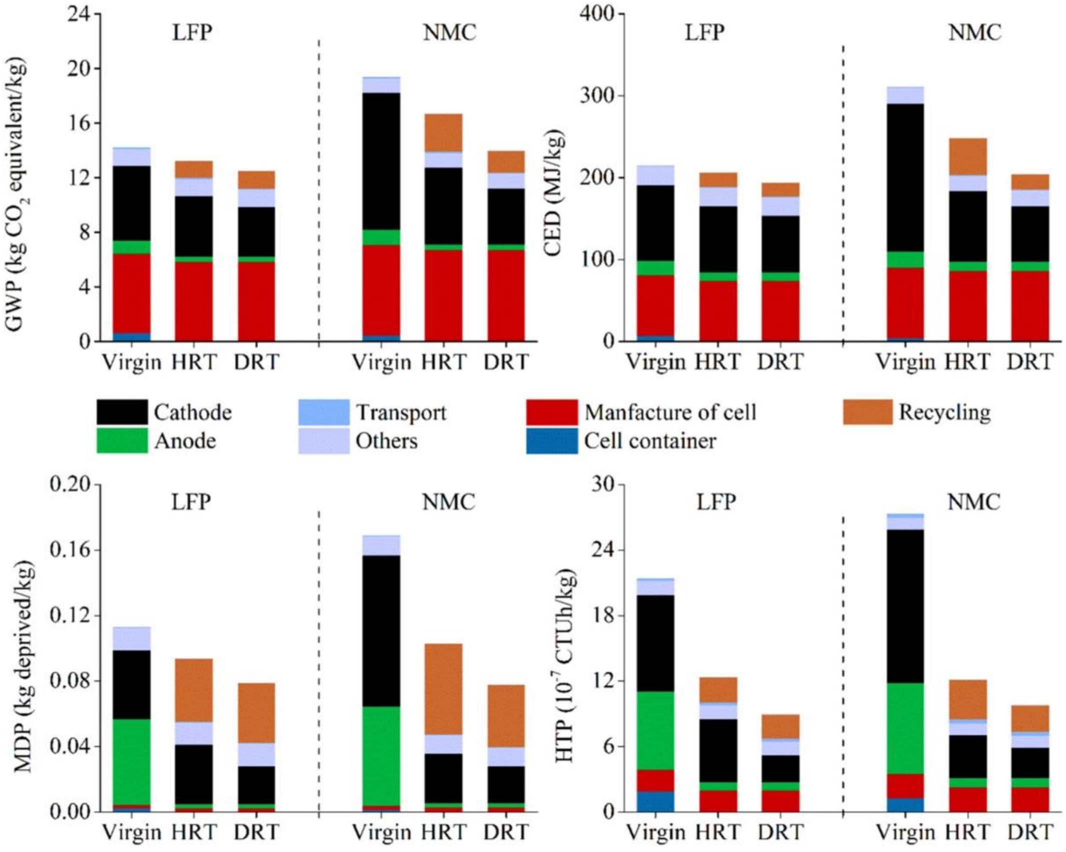


Fig.16 . Environmental impacts of the production of lithium-ion traction batteries using virgin and recycled materials: (a) global warming potential, (b) cumulative energy demand, (c) abiotic resource depletion, and (d) human toxicity potential. HRT: Using recycled materials by hydrometallurgical technology. DRT: Using recycled materials by direct technology.

In compared to hydrometallurgical recycling, adopting direct recycling materials in cell manufacture might provide a higher reduction potential of impacts in all circumstances, as shown in Fig. 16. The additional benefits gained by direct recycling are especially substantial for LFP. Using GWP and CED as an example, hydrometallurgical recycling can reduce emissions by 7% and 4%, respectively, while direct recycling can cut emissions by 12% and

10%. Correspondingly, for NMC, the differences of reduction potential among hydrometallurgical and direct recycling are also substantial, particularly for MDP (39% versus 54%) and HTP (55% versus 64%).

6.2.1 Comparison with previous studies

By comparing the reference study with the different studies, the results of existing LIBs LCA studies are reviewed, including energy density, GHG emissions, and cumulative energy demand of manufacturing and recycling for LFP and NMC. [80][81][82][83][84][85][86][87][88][89][70][90][91][71][92].

As Table 4 shows, the result of [2], GHG emission for LFP and NMC manufacturing (14.2 and 19.4 kg CO2 eq/kg) are in the midrange of literature estimates (7.3–24.0 and 8.9–30.5 kg CO2 eq/kg), while [2], estimates of energy requirements (214.8 and 310.7 MJ/kg) are in the upper end of the range of the existing results for LFP and NMC (64.4–222.6 and 70.4–314.9 MJ/kg). The large range of the existing results can be attributed to the differences in battery design, data source of the supply-chain process (i.e. material production and cell manufacturing), and assumption scopes. For examples [87], provides the lowest estimates of GHG emissions Using a top-down technique that combines modeling battery design and literature information, , which may overlook some facts that would have a significant impact on the results. For example, their study avoids the use of 1-Methyl-2-pyrrolidinone (NMP) as a solvent in the manufacturing of positive electrode paste, which is projected to emit 2.2 and 2.6 kg CO2 eq/kg for LFP and NMC, respectively.

Table 4. Comparison of GWP and CED results between reference case and previous studies.

Study	Process considered^d	Specific energy (kWh/kg)	GHG emission (kg CO_2/kg)			Energy consumption (MJ/kg)		
			Virgin	HRT^a	DRT^b	Virgin	HRT^a	DRT^b
LFP								
[80]	M	0.100	17.0					
[81]	M	0.088	22.0			205.0		
[83]	M					80.0		

[84]	M+T+R					64.4	-6.5	
[87]	M+T+R	0.100	7.3	0.9	1.7	98.0	5.0	17.0
[89]	M+T+R	0.065	24.0			222.6		
[90]	M+R	0.108	10.9	-0.4				
[2]	M+T+R	0.120	14.2	-1.0	-1.7	214.8	-8.4	-21.4
NMC								
[81]	M	0.112	22.0			209.0		
[82]	M	0.174	30.5			103.9		
[83]	M					110.0		
[84]	M+T+R					70.4	-12.2	
[85]	M+T+R	0.080	11.1			120.0		
[88]	M+T+R	0.065	20.4	-1.6		314.9	-24	
[87]	M+T+R	0.210	8.9	-0.9	-0.6	120.0	-17	-13
[90]	M+R	0.170	12.8	-2.8				
[71]	M+R	0.164	11.3	-0.8		163.8	-14.0	
[91]	M+T+R	0.120	12.1	-3.6		126.3	-18.0	
[92]	R			-2.1			-33.5	
[2]	M+T+R	0.150	19.4	-2.7	-5.4	310.7	-62.7	-106.6

([a] HRT = Hydrometallurgical recycling technology ;[b] DRT = Direct recycling technology; [c] Cylindrical cell with US average electricity grid data. ; [d] M = Manufacturing; T = Technology; R = Recycling)

Some researches have looked into the impact of recycling on the battery production process (Table 4). [87] calculated both hydrometallurgical and direct technology for LFP and concluded that recycling would not provide benefits but would increase the burden in terms of GHG emissions and energy demand. This is owing to the absence of a mechanical recycling process, in which electrode materials (Al and Cu foil) can be recovered and significant environmental implications avoided. Hydrometallurgical recycling would be estimated to enhance impacts for both the reference study [2] and [90] if this proportion was excluded. As a result, existing study revealed that LFP recycling will not considerably lower GHG emissions or energy demand, particularly in the chemical recycling of lithium compounds.

In comparison, existing studies provide larger estimates of the reduction potential of NMC recycling than those of LFP, that is, −0.8 to −3.6 kg CO2 eq/kg versus −1.7 to 1.7 kg CO2 eq/kg for GHG emission and − 12.2 to −106.6 MJ/kg versus −21.4 to 17.0 MJ/kg for energy demand. It's not surprising, because, as previously said, NMC reusing recovered material needs greater energy and materials inputs during virgin manufacture, resulting in significant recycling benefits. The benefits of NMC recycling, according to the [2], are substantially greater than in earlier research, particularly in terms of energy demand. The main reason is the differences in upstream LCI data sources used [87] the GREET model to calculate the energy demand factor of Co compound, which is substantially lower than the figure used in the study (121 MJ/kg against 753 MJ/kg) derived from the Ecoinvent 3.6 database. The two figures correspond to the lower and top limits of a range (216-399 MJ/kg) described in a recent LCA focusing on Co production in China [93]. Furthermore, [87] utilized a factor of US mix electricity that is substantially lower than the Chinese mix employed in the [2] analysis (6.83 versus 9.75 MJ/kg). As a result, more efforts should be made to increase the quality of battery recycling LCA by increasing the LCI's reliability for upstream inputs.

7. Conclusion

LIBs are becoming increasingly important because to their interconnection and mobility. The demand for more efficient and sustainable LIBs will increase in the future years as electric mobility develops. The price of scarce elements like as cobalt, nickel, and lithium, to mentiona few, rises because of this increase in demand. From an environmental standpoint, mining, extraction, and purifying of these metals to battery-grade quality are extremely harmful.Despite the considerable work necessary to manufacture those LIBs, the valuable materials involved are landfilled and become irrecoverable after only a few years. To make this situation worse, the ecosystem is further harmed because electronic garbage, which includes LIBs, being one of the most damaging on the planet.

As the demand of lithium in automotive industry is increasing over the past years, so the extraction of lithium will simultaneously be increasing as well. So, as predicted the increase in the production of Li-ion batteries as well as their impact on the environment, has given rise to major worries about the potential implications and impacts. One of the major contributors of lithium is extraction from brine, which required a lot of fresh water for obtaining some quantity of lithium, resulting major loss in the depleting of the natural aquifers on which the residents rely. Extraction through brines also causing toxicity to plants and animal life.

As a result, battery recycling is critical economically and environmentally obligation. Before removing batteries, recyclers suggest providing them a second life. Just at time of disposal, most cells retained more than half of their initial capacity. They are far from worthless. Powertrains for low-speed vehicles, as well as home and industrial energy storage, are examples of second life uses. When they reach the end of their useful life, they can be disassembled to retrieve their pretty useful components and materials. At this point, the battery state is being evaluated to choose the best recycling method. However, the overall benefits of direct technology exceed those from hydrometallurgical technology due to fewer chemical requirements and less influence from recovered materials in the earlier.

The results indicate that traction LIB recycling can have significant net environmental benefits for both LFP and NMC in terms of lowering carbon emissions and human hazards, as well as mitigating resource depletion, indicating a promising future for EOL traction battery management. As a result, creating chemical-free recycling technology is essential to maximizing the sustainability of battery recycling.

The direct reuse of recycled products in traction LIB production would result in a reduction in all the environmental concerns examined. However, the potential for reduction varies depending on the impact category. Manufacturing with recovered materials would have a substantially lower reduction potential for GWP and energy demand than it would for mineral depletion and toxic substance emissions because of unavoidable metal compounds and energy demand in primary manufacture. A full supply chain management strategy, in addition to recycling, is needed to increase the sustainability of traction LIBs, including use of cleaner electricity, the development of metal-free battery types, and the incorporation of directly recovered material in battery manufacture. The comparison research reveals that there is significant variety among the available literature results given by differences in traction LIB design, LCI sources of supply-chain process, and assumption scopes.

8. References

[1] Liu, G., Zhao, Z. and He, L., 2020. Highly selective lithium recovery from high Mg/Li ratio brines. Desalination, 474, p.114185.

[2] Jiang, S., Hua, H., Zhang, L., Liu, X., Wu, H. and Yuan, Z., 2022. Environmental impacts of hydrometallurgical recycling and reusing for manufacturing of lithium-ion traction batteries in China. Science of The Total Environment, 811, p.152224.

[3] Kavanagh, L., Keohane, J., Garcia Cabellos, G., Lloyd, A. and Cleary, J., 2018. Global lithium sources—industrial use and future in the electric vehicle industry: a review. Resources, 7(3), p.57

[4] Jaskula, B.W., 2008. US Geological Survey Minerals Yearbook. US Geological Survey, Reston, VA, USA.

[5] Ejeian, M., Grant, A., Shon, H.K. and Razmjou, A., 2021. Is lithium brine water?. Desalination, 518, p.115169.

[6] Hua, Y., Zhou, S., Huang, Y., Liu, X., Ling, H., Zhou, X., Zhang, C. and Yang, S., 2020. Sustainable value chain of retired lithium-ion batteries for electric vehicles. Journal of Power Sources, 478, p.228753.

[7] Fahimi, A., Ducoli, S., Federici, S., Ye, G., Mousa, E., Frontera, P. and Bontempi, E., 2022. Evaluation of the sustainability of technologies to recycle spent lithium-ion batteries, based on embodied energy and carbon footprint. Journal of Cleaner Production, p.130493.

[8] Myung, S.T., Hitoshi, Y. and Sun, Y.K., 2011. Electrochemical behavior and passivation of current collectors in lithium-ion batteries. Journal of Materials Chemistry, 21(27), pp.9891-9911.

[9] Arora, P. and Zhang, Z., 2004. Battery separators. Chemical reviews, 104(10), pp.4419-4462.

[10] Vikström, H., Davidsson, S. and Höök, M., 2013. Lithium availability and future production outlooks. Applied Energy, 110, pp.252-266.

[11] Liu, G., Zhao, Z. and Ghahreman, A., 2019. Novel approaches for lithium extraction from salt-lake brines: a review. Hydrometallurgy, 187, pp.81-100

[12] U.S. Geological Survey 2020).

[13] Li, L., Deshmane, V.G., Paranthaman, M.P., Bhave, R.R., Moyer, B.A. and Harrison, S., 2018. Lithium recovery from aqueous resources and batteries: A brief review. Johnson Matthey Technology Review, 62(2).

[14] Gao, D., Guo, Y., Yu, X., Wang, S. and Deng, T., 2018. Extracting lithium from the high concentration ratio of magnesium and lithium brine using imidazolium-based ionic liquids with varying alkyl chain lengths. Journal of Chemical Engineering of Japan, 49(2), pp.104-110

[15] Swain, B., 2017. Recovery and recycling of lithium: A review. Separation and Purification Technology, 172, pp.388-403.

[16] NEO Lithium, 2019. http: //www.neolithium.ca/. New Tech Lithium Corp, 2019. http://americanpotashcorp.com.

[17] Tadesse, B., Makuei, F., Albijanic, B., Dyer, L., 2019. The beneficiation of lithium minerals from hard rock ores : A review. Miner. Eng. 131, 170–184

[18] Flexer, V., Baspineiro, C.F. and Galli, C.I., 2018. Lithium recovery from brines: A vital raw material for green energies with a potential environmental impact in its mining and processing. Science of the Total Environment, 639, pp.1188-1204.

[19] Onishi, K., Nakamura, T., Nishihama, S. and Yoshizuka, K., 2010. Synergistic solvent impregnated resin for adsorptive separation of lithium ion. Industrial & engineering chemistry research, 49(14), pp.6554-6558.

[20] Kanoh, H., Ooi, K., Miyai, Y. and Katoh, S., 1993. Electrochemical recovery of lithium ions in the aqueous phase. Separation science and technology, 28(1-3), pp.643-651.

[21] Liu, X., Chen, X., He, L. and Zhao, Z., 2015. Study on extraction of lithium from salt lake brine by membrane electrolysis. Desalination, 376, pp.35-40.

[22] Lawagon, C.P., Nisola, G.M., Cuevas, R.A.I., Torrejos, R.E.C., Kim, H., Lee, S.P. and Chung, W.J., 2019. Li1− xNi0. 5Mn1. 5O4/Ag for electrochemical lithium recovery from brine and its optimized performance via response surface methodology. Separation and Purification Technology, 212, pp.416-426.

[23] Wang, S., Li, P., Zhang, X., Zheng, S., Zhang, Y., 2017. Selective adsorption of lithium from high Mg-containing brines using HxTiO3 ion sieve. Hydrometallurgy 174, 21–28.

[24] Timmer, J.M.K., 2001. Properties of nanofiltration membranes ; model

development and industrial application door.

[25] Quist-Jensen, C.A., Ali, A., Drioli, E. and Macedonio, F., 2019. Perspectives on mining from sea and other alternative strategies for minerals and water recovery–The development of novel membrane operations. Journal of the Taiwan Institute of Chemical Engineers, 94, pp.129-134.

[26] mineralsLabbé, J.F.; Daw, G. Panorama 2011 du marché du lithium; Rapport public 2012,

[27] BRGM/RP-61340-FR; BRGM: Orléans, France, 2012; p. 94

[28] Jahns, R.H. and Tuttle, O.F., 1963. Layered pegmatite-aplite intrusives. *Mineralogical Society of America Special Paper*, *1*, pp.78-92.

[29] d'Andrada, J.B. Der eigenschaften und kennzeichen einiger neuen fossilien aus Schweden und Norwegen nebst einigen chemischen bemerkungen ueber dieselben. Allgemeines J. Chem. 1800, 4, 28–39]

[30] Lu, H. Formation of β-Eucryptite and β-spodumene from Topaz Mixture. Ph.D Thesis, University of NewSouth Wales, Sydney, Australia, 2005.

[31] Peltosaari, O.; Tanskanen, P.A.; Heikkinen, E.P.; Fabritius, T. α!γ!β-phase transformation of spodumene with hybrid microwave and conventional furnaces. Miner. Eng. 2015, 82, 54–60.

[32] Tran, T.; Luong, V.T. Lithium production processes. In Lithium Process Chemistry; Elsevier: Amsterdam, The Netherlands, 2015; pp. 81–124.

[33] Ellestad, R.B.; Leute, K.M. Method of extracting lithium values from spodumene ores. U.S. Patent 2,516,109, 25 July 1950.

[34] Hader, R.N.; Nielsen, R.L.; Herre, M.G. Lithium and its compounds. Ind. Eng. Chem. 1951,43, 2636–2646.

[35] Skinner, B.J.; Evans, H.T. β-spodumene solid solutions and the join Li2O–Al2O3–SiO2. Am.J. Sci. 1960, 258-A, 312–324.

[36] Dessemond, C., Lajoie-Leroux, F., Soucy, G., Laroche, N. and Magnan, J.F., 2019. Spodumene: The lithium market, resources and processes. Minerals, 9(6), p.334.

[37] Liao, Q., Mu, M., Zhao, S., Zhang, L., Jiang, T., Ye, J., Shen, X. and Zhou, G., 2017. Performance assessment and classification of retired lithium ion battery from electric vehicles for energy storage. International Journal of Hydrogen Energy, 42(30), pp.18817-18823.

[38] Zeng, X., Song, Q., Li, J., Yuan, W., Duan, H. and Liu, L., 2015. Solving e-waste problem using an integrated mobile recycling plant. Journal of cleaner production, 90, pp.55-59.

[39] Wang, W. and Wu, Y., 2017. An overview of recycling and treatment of spent LiFePO4 batteries in China. Resources, Conservation and Recycling, 127, pp.233-243.

[40] Natkunarajah, N., Scharf, M., Scharf, P., 2015. Scenarios for the return of lithium-ion batteries out of electric cars for recycling. Procedia CIRP 29, 740–745.

[41] Schmitt, J., Haupt, H., Kurrat, M., Raatz, A., 2011. Disassembly automation for lithiumion battery systems using a flexible gripper. 2011 15th Int. Conf. Adv. Robot. pp.291–297.

[42] Yun, L., Linh, D., Shui, L., Peng, X., Garg, A., Le, M.L.P., Asghari, S. and Sandoval, J., 2018. Metallurgical and mechanical methods for recycling of lithium-ion battery pack for electric vehicles. Resources, Conservation and Recycling, 136, pp.198-208.

[43] Weyrich, P.M., Natkunarajah, N., Sc, M., 2013. Conception of an Automated Plant for the. pp. 1–4.

[44] Herrmann, C., Raatz, A., Mennenga, M., Schmitt, J., Andrew, S., 2012b. Assessment of automation potentials for the disassembly of automotive lithium ion battery systems. Leveraging Technol. Sustain. World 149–154.

[45] Song, B., Yeo, Z., Kohls, P., Herrmann, C., 2017. Industrial symbiosis: exploring big-data approach for waste stream discovery. Procedia CIRP 61, 353–358.

[46] He, Y., Zhang, T., Wang, F., Zhang, G., Zhang, W., Wang, J., 2017a. Recovery of LiCoO2and graphite from spent lithium-ion batteries by fenton reagent-assisted flotation. J. Clean. Prod. 143, 319–325.

[47] Hanisch, C., Loellhoeffel, T., Diekmann, J., Markley, K.J., Haselrieder, W., Kwade, A., 2015. Recycling of lithium-ion batteries: a novel method to separate coating and foil of electrodes. J. Clean. Prod. 108, 1–11.

[48] Diekmann, J., et al., 2017. Ecological recycling of lithium-ion batteries from electric vehicles with focus on mechanical processes. J. Electrochem. Soc. 164 (1), A6184–A6191.

[49] Meshram, P., Pandey, B.D., Mankhand, T.R., 2015a. Recovery of valuable metals from cathodic active material of spent lithium ion batteries: leaching and kinetic

aspects. Waste Manage. 45, 306–313.

[50] Yang, L., Xi, G., Xi, Y., 2015. Recovery of Co, Mn, Ni, and Li from spent lithium ion batteries for the preparation of LiNixCoyMnzO2 cathode materials. Ceram. Int. 41 (9), 11498–11503.

[51] Li, L., et al., 2017. Sustainable recovery of cathode materials from spent lithium-ion batteries using lactic acid leaching system. ACS Sustain. Chem. Eng. 5 (6), 5224–5233.

[52] Hu, J., Zhang, J., Li, H., Chen, Y., Wang, C., 2017. A promising approach for the recovery of high value-added metals from spent lithium-ion batteries. J. Power Sources 351, 192–199.

[53] Joulié, M., Laucournet, R., Billy, E., 2014. Hydrometallurgical process for the recovery of high value metals from spent lithium nickel cobalt aluminum oxide based lithium-ion batteries. J. Power Sources 247, 551–555.

[54] Meshram, P., Pandey, B.D., Mankhand, T.R., 2015b. Hydrometallurgical processing of spent lithium ion batteries (LIBs) in the presence of a reducing agent with emphasis on kinetics of leaching. Chem. Eng. J. 281, 418–427.

[55] Xin, Y., Guo, X., Chen, S., Wang, J., Wu, F., Xin, B., 2015. Bioleaching of valuable metals Li, Co, Ni and Mn from spent electric vehicle Li-ion batteries for the purpose of recovery. J. Clean. Prod. 116, 249–258.

[56] Horeh, N.B., Mousavi, S.M., Shojaosadati, S.A., 2016. Bioleaching of valuable metals from spent lithium-ion mobile phone batteries using aspergillus Niger. J. Power Sources 320, 257–266.

[57] He, L.P., Sun, S.Y., Song, X.F., Yu, J.G., 2017b. Leaching process for recovering valuable metals from the LiNi1/3Co1/3Mn1/3O2 cathode of lithium-ion batteries. Wast Manag. 64, 171–181.

[58] Chen, X., Chen, Y., Zhou, T., Liu, D., Hu, H., Fan, S., 2015a. Hydrometallurgical recovery of metal values from sulfuric acid leaching liquor of spent lithium-ion batteries. Waste Manag. 38 (1), 349–356).

[59] www.mining.com/web/sqm-lithium-mining-needs-least-10b-investment-10-years accessed January 2020

[60] https://eandt.theiet.org/content/articles/2019/08/lithium-firmsare-depleting-vital-water-supplies-in-chile-according-to-et-analysis.

[61] Kaunda, R.B., 2020. Potential environmental impacts of lithium mining. Journal of Energy & Natural Resources Law, 38(3), pp.237-244.

[62] Stamp, A., Lang, D.J., Vadenbo, C. and Wäger, P.A., 2009. Primary and secondary supply options for lithium and their contribution to the environmental impact of a lithium-ion battery. In World Resources Forum, 16th September.

[63] Kesler, S.E., Gruber, P.W., Medina, P.A., Keoleian, G.A., Everson, M.P. and Wallington, T.J., 2012. Global lithium resources: Relative importance of pegmatite, brine and other deposits. Ore geology reviews, 48, pp.55-69.

[64] Wanger, T.C., 2011. The Lithium future—resources, recycling, and the environment. Conservation Letters, 4(3), pp.202-206.

[65] www.bloomberg.com/news/features/2019-06-11/saving-the-planet-with-electric-carsmeans-strangling-this-desert.

[66] Concha, G., Broberg, K., Grandér, M., Cardozo, A., Palm, B. and Vahter, M., 2010. High-level exposure to lithium, boron, cesium, and arsenic via drinking water in the Andes of northern Argentina. Environmental science & technology, 44(17), pp.6875-6880.

[67] Haynes, W.M. ed., 2014. CRC handbook of chemistry and physics. CRC press.

[68] Izquierdo, A.E., Grau, H.R., Carilla, J. and Casagranda, E., 2015. Side effects of green technologies: the potential environmental costs of Lithium mining on high elevation Andean wetlands in the context of climate change.

[69] Albarracín, V.H., Kurth, D., Ordoñez, O.F., Belfiore, C., Luccini, E., Salum, G.M., Piacentini, R.D. and Farías, M.E., 2015. High-up: a remote reservoir of microbial extremophiles in central Andean wetlands. Frontiers in microbiology, 6, p.1404.

[70] Melin, H.E., Rajaeifar, M.A., Ku, A.Y., Kendall, A., Harper, G. and Heidrich, O., 2021. Global implications of the EU battery regulation. Science, 373(6553), pp.384-387.

[71] Qiao, Q., Zhao, F., Liu, Z. and Hao, H., 2019. Electric vehicle recycling in China: Economic and environmental benefits. Resources, Conservation and Recycling, 140, pp.45-53.

[72] Xiong, S., Ji, J. and Ma, X., 2020. Environmental and economic evaluation of remanufacturing lithium-ion batteries from electric vehicles. Waste Management, 102, pp.579-586.

[73] Chen, M., Ma, X., Chen, B., Arsenault, R., Karlson, P., Simon, N. and Wang, Y., 2019. Recycling end-of-life electric vehicle lithium-ion batteries. Joule, 3(11), pp.2622-2646.

[74] Jiang, S., Zhang, L., Hua, H., Liu, X., Wu, H. and Yuan, Z., 2021. Assessment of end-of-life electric vehicle batteries in China: Future scenarios and economic benefits. Waste Management, 135, pp.70-78.

[75] https://www.ecoinvent.org/database/database.html.

[76] Xu, P., Yang, Z., Yu, X., Holoubek, J., Gao, H., Li, M., Cai, G., Bloom, I., Liu, H., Chen, Y. and An, K., 2021. Design and optimization of the direct recycling of spent Li-ion battery cathode materials. ACS Sustainable Chemistry & Engineering, 9(12), pp.4543-4553.

[77] China relies on ores imports, such as cobalt ore and spodumene. Olivetti, E.A., Ceder, G., Gaustad, G.G. and Fu, X., 2017. Lithium-ion battery supply chain considerations: analysis of potential bottlenecks in critical metals. Joule, 1(2), pp.229-243.

[78] NBSC, N., 2008. China statistical yearbook 2008.

[79] Bulle, C., Margni, M., Patouillard, L., Boulay, A.M., Bourgault, G., De Bruille, V., Cao, V., Hauschild, M., Henderson, A., Humbert, S. and Kashef-Haghighi, S., 2019. IMPACT World+: a globally regionalized life cycle impact assessment method. The International Journal of Life Cycle Assessment, 24(9), pp.1653-1674

[80] Sun, X., Hao, H., Hartmann, P., Liu, Z. and Zhao, F., 2019. Supply risks of lithium-ion battery materials: An entire supply chain estimation. Materials Today Energy, 14, p.100347.

[81] Zackrisson, M., Avellán, L. and Orlenius, J., 2010. Life cycle assessment of lithium-ion batteries for plug-in hybrid electric vehicles–Critical issues. Journal of Cleaner Production, 18(15), pp.1519-1529.

[82] Majeau-Bettez, G., Hawkins, T.R. and Strømman, A.H., 2011. Life cycle environmental assessment of lithium-ion and nickel metal hydride batteries for plug-in hybrid and battery electric vehicles. Environmental science & technology, 45(10), pp.4548-4554

[83] Ellingsen, L.A.W., Majeau-Bettez, G., Singh, B., Srivastava, A.K., Valøen, L.O. and Strømman, A.H., 2014. Life cycle assessment of a lithium-ion battery vehicle pack. Journal of Industrial Ecology, 18(1), pp.113-124.

[84] Dunn, J.B., Gaines, L., Kelly, J.C., James, C. and Gallagher, K.G., 2015. The significance of Li-ion batteries in electric vehicle life-cycle energy and emissions and recycling's role in its reduction. Energy & Environmental Science, 8(1), pp.158-168.

[85] Hendrickson, T.P., Kavvada, O., Shah, N., Sathre, R. and Scown, C.D., 2015. Life-cycle implications and supply chain logistics of electric vehicle battery recycling in California. Environmental Research Letters, 10(1), p.014011.

[86] Kim, H.C., Wallington, T.J., Arsenault, R., Bae, C., Ahn, S. and Lee, J., 2016. Cradle-to-gate emissions from a commercial electric vehicle Li-ion battery: a comparative analysis. Environmental science & technology, 50(14), pp.7715-7722.

[87] Qiao, Q., Zhao, F., Liu, Z., Jiang, S. and Hao, H., 2017. Cradle-to-gate greenhouse gas emissions of battery electric and internal combustion engine vehicles in China. Applied energy, 204, pp.1399-1411.

[88] Ciez, R.E. and Whitacre, J.F., 2019. Examining different recycling processes for lithium-ion batteries. Nature Sustainability, 2(2), pp.148-156.

[89] Cusenza, M.A., Bobba, S., Ardente, F., Cellura, M. and Di Persio, F., 2019. Energy and environmental assessment of a traction lithium-ion battery pack for plug-in hybrid electric vehicles. Journal of cleaner production, 215, pp.634-649.

[90] Marques, P., Garcia, R., Kulay, L. and Freire, F., 2019. Comparative life cycle assessment of lithium-ion batteries for electric vehicles addressing capacity fade. Journal of Cleaner Production, 229, pp.787-794.

[91] Mohr, M., Peters, J.F., Baumann, M. and Weil, M., 2020. Toward a cell-chemistry specific life cycle assessment of lithium-ion battery recycling processes. Journal of Industrial Ecology, 24(6), pp.1310-1322.

[92] Sun, X., Luo, X., Zhang, Z., Meng, F. and Yang, J., 2020. Life cycle assessment of lithium nickel cobalt manganese oxide (NCM) batteries for electric passenger vehicles. Journal of Cleaner Production, 273, p.123006.

[93] Rajaeifar, M.A., Raugei, M., Steubing, B., Hartwell, A., Anderson, P.A. and Heidrich, O., 2021. Life cycle assessment of lithium-ion battery recycling using pyrometallurgical technologies. Journal of Industrial Ecology, 25(6), pp.1560-1571.

[94] Zhang, T., Bai, Y., Shen, X., Zhai, Y., Ji, C., Ma, X. and Hong, J., 2021. Cradle-to-gate life cycle assessment of cobalt sulfate production derived from a nickel–copper–cobalt mine in China. The International Journal of Life Cycle Assessment, 26(6), pp.1198-1210.

[95] Liang, Y., Su, J., Xi, B., Yu, Y., Ji, D., Sun, Y., Cui, C. and Zhu, J., 2017. Life cycle assessment of lithium-ion batteries for greenhouse gas emissions. Resources, conservation and recycling, 117, pp.285-293.

[96] Guinee, J.B., Heijungs, R., Huppes, G., Zamagni, A., Masoni, P., Buonamici, R., Ekvall, T. and Rydberg, T., 2011. Life cycle assessment: past, present, and future.

[97] Yuan, Z., Pan, X., Chen, T., Liu, X., Zhang, Y., Jiang, S., Sheng, H. and Zhang, L., 2018. Evaluating environmental impacts of pig slurry treatment technologies with a life-cycle perspective. Journal of Cleaner Production, 188, pp.840-850.