

An Exhaustive Review on Recycling Trends of Spent Lithium ion Batteries: Current Scenario, Key Process, Challenges in India

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Abstract— The rapid transition to create and use of sustainable energy to replace fossil fuels has raised demand for batteries. Therefore the Lithium-ion batteries have become an essential component in energy storage applications due to their increased use in electric vehicles, consumer gadgets, and grid-scale storage. It comprise with lithium (2-3%), cobalt (15-25%), manganese (7-12%), copper (10%), aluminum (15%), and nickel (3-8%), which are regarded as a ready secondary supply. The huge consumption of Lithium ion batteries would generate a significant quantity of end-of-life batteries in coming years. The use of these wastes is critical, as it provides environmental and economic benefits while also conserving natural resources. Due to high environmental impact by these waste LIBs and also due to the increasing demand for corresponding critical metals, the recycling of spent lithium ion batteries has attracted significant attention in recent years. In this Paper, complete recycling process is summarized including Pyro metallurgy, Hydrometallurgy, and physical pretreatment techniques, either separately or in combination; especially focusing on hydrometallurgy due to its more advantage as compared to other process/technology. Hydrometallurgical techniques includes leaching with inorganic substances like H_2SO_4 , HCl , and HNO_3 or organic acids. Followed by solution purification, precipitation, and solvent extraction techniques. The present review focus on current situation of LIB recycling in India and also focuses on the current scenario, challenges and the available technology for recovering metals from spent LIBs and provides a critical analysis of related research.

Keywords: Black mass; Critical metals; Hydrometallurgy; Leaching.

I. INTRODUCTION

With the introduction of the first commercial lithium-ion battery (LIB) in 1991 by Sony, which consisted of a non-graphitic carbon anode and a $LiCoO_2$ (LCO) cathode, LIBs have become widely employed [1]. Presently, Lithium-ion batteries (LIBs) rank among the most significant energy storage devices. They power cell phones, laptops, video cameras, and electric vehicles (EVs) [2]. In instance, demand for electric vehicles (EVs), which include hybrid and plug-in hybrid vehicles, has been rising quickly, and future significant increase is anticipated [3]. Due to the rising demand for LIBs around the world, there is now a possible risk to human health and the environment from the waste from wasted LIBs [4]. By 2030, it is predicted that batteries with a capacity of almost 1000 GWh will be made accessible for a second life, encompassing stationary energy storage and backup power. But after their second usage, these massive volumes of dead batteries will eventually be discarded, which will encourage LIB recycling [5]. Recycling can generally be viewed as beneficial if the environmental benefits from the recovered materials surpass any negative effects on the environment generated by the recycling procedures [6]. Because of their high energy density, low self-discharge, quick charging, and long lifespan, lithium-ion batteries (LIBs) have become the most widely used power source for

consumer electronics. Due to their role in decreasing greenhouse gas emissions, lithium ion batteries (LIBs) have become increasingly in demand over the past 30 years, notably in electric vehicles (EVs) [7], [8]. As a result, several nations have banned the sale of new gasoline and diesel vehicles starting in 2030. There were 3 million electric vehicles in the world's inventory as of 2017, and if all EV targets are reached, the number of electric vehicles on the road is expected to reach 230 million by 2030 [9]. Some of the novel types of Li-ion batteries that have been thoroughly researched recently to meet the rapidly increasing demand for battery-powered devices are lithium manganese oxide (LMO), lithium cobalt oxide (LCO), lithium nitrate oxide (LNO), lithium iron phosphate (LFP), lithium nickel manganese cobalt oxide (NMC), and lithium nickel cobalt aluminium (NCA). These batteries are based on LMO-based rich, layered materials (LMR) [10]. The hazardous compounds found in LIBs that usually end their economic life include organic solvents and heavy metals, which are harmful to human health and the environment [11]. However, they do have significant concentrations of deposits of valuable metals, such as manganese (Mn), cobalt (Co), nickel (Ni), and lithium (Li). Lithium (2-3%), cobalt (15-25%), manganese (7-12%), copper (10%), aluminum (15%), and nickel (3-8%) among other elements, are found in LIBs and are regarded as ready secondary sources [12]. Figure 1 below

illustrates the percentage composition of these metals.

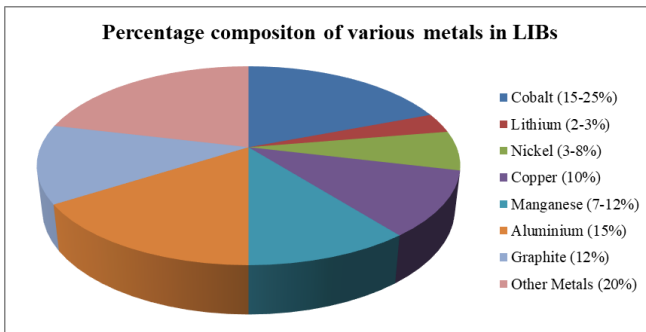


Figure 1:- Percentage composition of various metals in LIBs.

For this reason, it is crucial to manage and recycle LIBs properly in order to preserve the environment and maximize its economic value. The wet-thermal combination process, pyrometallurgy, hydrometallurgy, and mechano-physical approach are the most often used recycling methods for wasted LIBs. Aerobic roasting and pyrolysis are two typical classifications for pyrometallurgy, which is the use of high-temperature treatment for metal enrichment and impurity separation in used LIBs [13], [14]. In order to recover precious metals like Ni, Co, Mn, Cu, and others in the form of metal alloys, which can subsequently be processed further to generate LiCoO_2 , discarded LIBs are now recycled industrially via pyrometallurgy. However, Li cannot be recycled because it enters the slag here [15], [16]. In addition, the recycling process will release a large number of fumes, CO, HF and volatile organic compounds, all of which are bad for the environment [17]. Hydrometallurgy technology is very useful for recovering metal. When compared to pyrometallurgy, the economical, ecologically benign, and successful hydrometallurgical recovery of leftover LIBs has attracted a lot of attention [18], [19]. Different battery chemistries and cell types can be easily processed using pyrometallurgy, however because manganese, aluminum, and lithium are downcycled, its recycling efficiency is lower than hydrometallurgical techniques. Although hydrometallurgical techniques are renowned for their exceptional metal-specific selectivity, they may entail intricate, multi-step recovery processes [20]. Numerous reviews have been conducted on the leaching of metals from spent LIBs, and a number of semi-commercial systems (1000–5000 t/a) have been implemented. Strong acids like HCl, HNO_3 , and H_2SO_4 are the most often used leaching agents, and H_2O_2 is frequently added as a reducing agent [21]. Because copper is already present in battery waste, it has also been employed as a reducing agent of lithium cobalt oxide (LCO) in H_2SO_4 leaching. To increase the purity of the finished goods, the aluminum current collector is further dissolved using alkaline solutions of NaOH or LiOH before acidic leaching [22], [23]. Ultrasonic delamination of the

active elements from the current collectors, which keeps the current collectors in their metallic (and easier to recycle) condition, is an alternate technique to enhance the quality of the waste stream [24]. Although it is costly and hazardous, binder dissolving employing solvents like N-methyl pyrrolidone (NMP) has also been used to separate current collectors and active materials. Due to their less hazardous nature, other solvents including dimethyl isosorbide (DMI) have been studied more recently. In addition to being more selective in their metal leaching, organic acids like citric, maleic, ascorbic, L-tartaric, and oxalic acids have also shown promise in the extraction of metals from wasted LIBs [25], [26]. LIB leaching has also made use of bioleaching techniques, in which fungi like *Aspergillus Niger* and *Penicillin simplicissimum* generate these organic acids. However, their uses are limited by prolonged leaching durations and sterilization requirements [27]. An overview of the several ways that LIBs are treated is provided in this article. A thorough review is conducted of the handling of LIBs in order to recover the contained metal values. The global status of LIB recycling is also represented in this report.

II. INTERNATIONAL & NATIONAL SCENARIO OF LIBS RECYCLING

A. International LIBs Recycling Scenario

The majority of recycling techniques used are hydrometallurgical. At the moment, the majority of LIB recyclers are located in China, South Korea, Japan, Europe, the US, and Canada. In contrast, in 2018 an estimated 97,000 tons of batteries reached recyclers, of which 67,000 were processed in China and 18,000 in South Korea. These two nations were and continue to be the leaders in the production of cells and battery components. Sixty-one percent of the major international enterprises engaged in lithium recycling are based outside the European Union (EU), while the remaining 39 percent are based within the EU [28], [29]. The exact global Scenario of the leading LIB recycling across several nations are displayed in Figure 2.

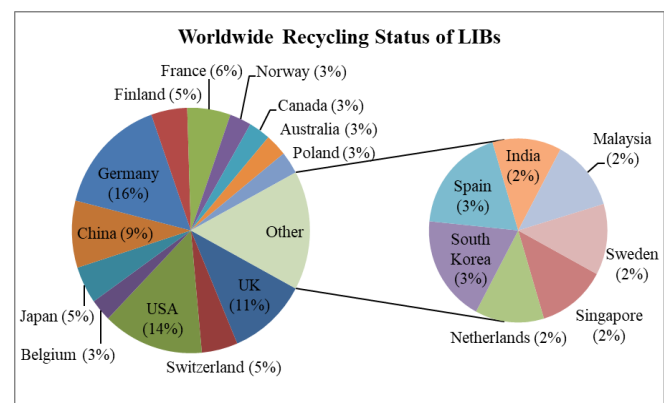


Figure 2:- Worldwide Recycling Status of LIBs. India LIBs Recycling Scenario

There are around 472 dismantlers and recyclers registered in India, with an installed capacity of approximately 14,26,685 metric tonnes annually, according to a report by NITI Aayog, the Central Pollution Control Board’s (CPCB) authorization granted under the E-Waste (Management) Rules 2016 and Battery Waste Management Rules 2022. The two main methods used in India for recycling lithium-ion batteries are mechanical extraction of black mass and end-to-end recycling to extract metals. Mainly in India 90% recycler doing only Black mass extraction and only 10% recycler showing interest in metal extraction from waste lithium ion battery. End-to-end recycling is a comprehensive recycling process in which the firm focused on every aspect of the recycled product’s operations, from collecting used/spent batteries from collection centers to extracting black mass and segregating vital minerals to creating the recycled batteries or extract metals like lithium, cobalt, Manganese and Nickel for other uses. Due to challenges with demand, legislation, and technology, this concept has not yet been broadly embraced in India. Yet, it is anticipated that the situation will alter when major firms enter the market. In India, another method of recycling lithium-ion batteries involves extracting black matter through a mechanical process called disassembly. Utilizing a mechanical procedure, the businesses in this process take spent batteries from both organized and unorganized sectors and separate the aluminum, cobalt, and plastic components from the remaining elements to create a black mass. They then transmit it to other sizable businesses who have the technological means to either transport it to their centralized hub abroad or extract minerals from the black mass. Several domestic firms, including Attero, Exigo, Lohum and others, have an established recycling plant in India, according to a report released from NITI Aayog. Eco Tantra and E-waste recyclers India are currently getting ready to construct their lithium-ion battery recycling plant in India. For example, businesses like Exigo, Tata Chemicals, and Attero have already developed their own lithium-ion battery recycling facilities across the nation, positioning themselves as major participants in the nation’s battery recycling ecosystem. As the only business that can now recycle LFP batteries profitably, Attero aims to invest over 300 crores (INR) to acquire 22% of the potential battery recycling market in

India. To extend the life and track the performance of the battery, Ziptrax uses cutting-edge technology at their recycling facility, such as artificial intelligence and patent-pending technology for the recovery and rejuvenation of cathode and essential battery materials. Furthermore, companies such as Batx, Li-Circle, and E-Waste recyclers India, ReCy Energy intend to establish lithium-ion battery recycling facilities throughout the nation, with the goal of increasing the plant’s capacity by 2025. ReCy Energy Private Limited, LOHUM, and Deshwal Waste Management are a few other Indian plants that are engaged in LIB recycling. Figure 3 below shows the distribution of household recyclers together with their locations. Table I lists the domestic recyclers together with their output (black mass & critical metals), locations, and technologies [30].

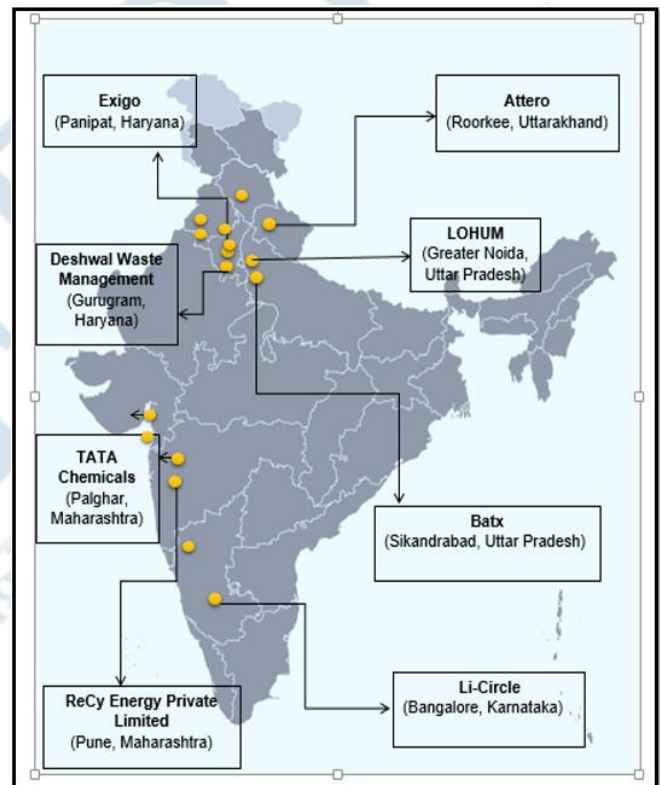


Figure 3: Distribution of domestic recyclers with their locations.

Table I: List of domestic recyclers with their locations, technology, and output (black mass & critical metals).

S.No.	Recyclers	Location	Technology	Output (Black mass, critical metals, etc.)
1.	TATA Chemicals	Palghar, Maharashtra	Hydrometallurgy	Lithium, Cobalt Sulphate
2.	Exigo	Panipat, Haryana	Mechanical + Hydrometallurgy	Black mass , Li, Co, Mn & Ni Salts
3.	Attero	Roorkee, Uttarakhand	Mechanical + Hydrometallurgy	Li, Co, Mn & Ni Salts
4.	Batx	Sikandrabad, Uttar Pradesh	Mechanical + Hydrometallurgy	Black mass , Li, Ni, Mn & Co salts

S.No.	Recyclers	Location	Technology	Output (Black mass, critical metals, etc.)
5.	LOHUM	Greater Noida, Uttar Pradesh	Mechanical + Hydrometallurgy	Black mass; Li, Co, Mn & Ni Salts
6.	Li-Circle	Bangalore, Karnataka	Hydrometallurgy	Li, Co & Ni Salts
7.	ReCy Energy Private Limited	Pune, Maharashtra	Hydrometallurgy	Li, Co, Mn, Ni Salts, Graphite
8.	Deshwal Waste Management	Gurugram, Haryana	Hydrometallurgy	Li, Co, Mn and Ni Salts

III. STRUCTURE & COMPONENTS OF LIBS

LIBs are made up of several components, including a positive electrode (cathode), a negative electrode (anode), an electrolyte, and a separator, as well as current collectors made of iron, copper, or aluminium [31]. Figures 4 and 5 show various components and percentage compositions of LIB.

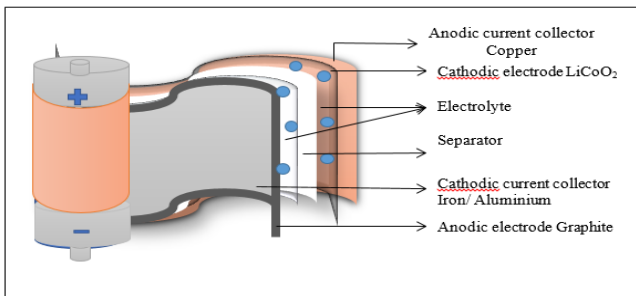


Figure 4:- Various Components if Lithium Ion Battery (LIB).

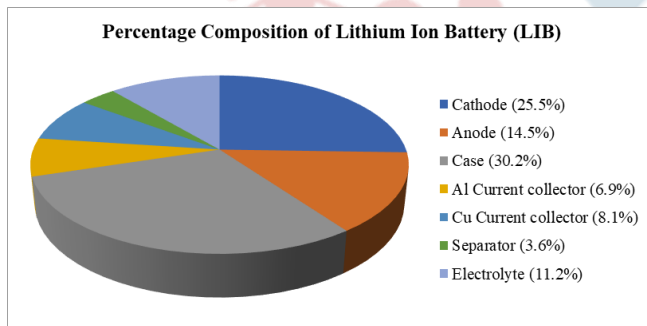


Figure 5:- Percentage Composition if Lithium Ion Battery (LIB).

Goodenough’s group began exploring oxide cathodes in the 1980s with the goal of increasing cell voltage and producing lithium-containing cathodes. The cell voltage is determined by the difference in redox energy between the anode and cathode. This implies that in order for the cathode to function, greater oxidation states with a lower lying energy band must be stabilized, whereas the anode must stabilize lower oxidation levels with a higher lying energy band [32], [33]. In other words, the cathode should seek for the lowest possible energy, whereas the anode should aim for the

highest possible energy. These core notions enable the identification of three types of oxide cathodes: polyanion oxides ($Ln_2(MoO_4)_3$), spinel oxides ($Li_{1-x}Mn_2O_4$), and layered oxides ($Li_{1-x}CoO_2$). When it comes to electronic conductivity, the layered and spinel oxide classes are highly dense and have good values, while the polyanion oxide class has lower values and poor conductivity [34], [35].

Parts	Composition
Outer Casing	Stainless steel, aluminum, Plastic and polymers
Cathode	Al coated with $LiCoO_2$; $LiMn_2O_4$; etc.
Anode	Cu Coated with Graphite
Insulating Separator	Polyethylene or Polypropylene films
Electrolyte	$LiPF_6$; $LiBF_4$

Figure 6 : Different Foils Present in Lithium ion Battery

Lithium iron oxide ($Li_xM_yO_z$) coated on aluminum foil (in Figure 6) serves as the cathode material for lithium-ion batteries. Anode: The negative active material in lithium-ion batteries is coated on copper foil with active material (tin, graphite, etc.). It was the lithium metal anode that produced dendrite formation and short circuit problems. Among the substances that comprise the first generation anode are graphite and other carbon-based cocaines. After then, scientists have focused on the second generation, which includes alloys made of silicon, tin (Sn), and lithium titanate (LTO) [36]. In contrast, the separator- which is mostly composed of a porous membrane material plays a critical and indispensable role in LIBs. An integral part of LIB separators for the absorption of electrolytes is the porous membrane positioned between the cathode and anode electrodes of the battery. During the charging and discharging cycles of LIBs, a separator facilitates the movement of lithium ions (Li^+), which are electrically conductive, between the cathode and anode electrodes [37]. Presently, the most commonly used polymeric materials for creating porous membranes in rechargeable batteries, especially LIBs, are polyethylene (PE), polypropylene (PP), poly(tetrafluoroethylene) (PTFE), poly(vinylidene fluoride) (PVDF), poly(methyl methacrylate) (PMMA), polyimide (PI), polyesters, poly(vinyl chloride) (PVC), poly(ethylene oxide) (PEO), polyacrylonitrile (PAN), poly(ethylene terephthalate) (PET),

and cellulose and its derivatives. Lithium-ion batteries employ four different types of electrolytes: liquid, polymer, ceramic, and composite (polymer-ceramic). Lithium salts that dissolve in organic or ionic liquids are the basis of non-aqueous electrolytes, which are present in liquid electrolytes [37], [38]. The polymer matrix dissolves the lithium salt directly in organic solvents, maintaining the mechanical properties of polymer electrolytes. Among the often used lithium salts are LiClO_4 , LiPF_6 , LiBF_4 , LiAsF_6 , LiCF_3SO_3 , and $\text{LiN}(\text{CF}_3\text{SO}_2)_2$. Composite electrolyte systems employ fillers of different kinds, sizes, and concentrations of ceramic fillers [39], [40].

IV. WORKING OF LIBS

LIBs are electrochemical cells that have the ability to reversibly transform chemical energy into electrical energy

and works on the principle of redox reaction. In essence, they are energy storage devices designed to have the best energy density possible in rechargeable batteries. Electrons flow between the anode and the cathode as a result of the oxidation (electrode to electrolyte) and reduction (electrolyte to electrode) reactions. In a rechargeable LIB, lithium ions travel between the anode and the cathode.

The battery is charged when lithium ions migrate from the cathode, which is often made of lithium metal oxide, to the anode, which is primarily graphite. In the opposite scenario, the battery is discharged. Lithium ions (Li^+) flow from the negative electrode to the positive electrode when the battery is being used, while current flows in the reverse way [41]-[43]. Figure 7 below shows how a lithium-ion battery (LIB) operates. Table II lists the oxidation-reduction processes occurring at the anode and cathode.

Table II:- The oxidation-reduction reactions taking place at the anode and cathode of LIBs.

	Anode (Oxidation)	Cathode (Reduction)
Charge =	$\text{LiMO}_2 \longrightarrow \text{Li}_{1-x}\text{MO}_2 + x\text{Li}^+ + xe^-$	$y\text{C} + x\text{Li}^+ + xe^- \longrightarrow \text{Li}_x\text{C}_y$
Discharge =	$\text{Li}_x\text{C}_y \longrightarrow y\text{C} + x\text{Li}^+ + xe^-$	$\text{Li}_{1-x}\text{MO}_2 + x\text{Li}^+ + xe^- \longrightarrow \text{LiMO}_2$
Total =	$\text{LiMO}_2 + y\text{C} \longleftrightarrow \text{Li}_{1-x}\text{MO}_2 + \text{Li}_x\text{C}_y$ (M=Co, Ni, Mn)	

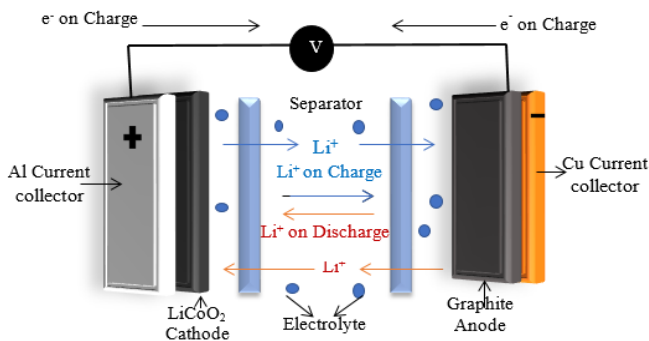


Figure 7:- Working of Lithium Ion Battery (LIB).

V. RECOVERY OF CRITICAL METALS FROM LIBS

The procedures covered in this section are standard methods of recycling the majority of battery types. The preparation and pretreatment process, which eliminates contaminants, is the initial stage of recycling. The concentrate is then moved on to the pyrometallurgy stage. The result of pyrometallurgy is transported to hydrometallurgy for certain applications where refined materials are required. Hydrometallurgy is being attempted to replace pyrometallurgy in the industry due to inefficiencies and environmental concerns [44], [45]. The ensuing subsections provide an explanation of each of these procedures. A flow chart for the extraction of essential metals from LIBs is shown in Figure 8.

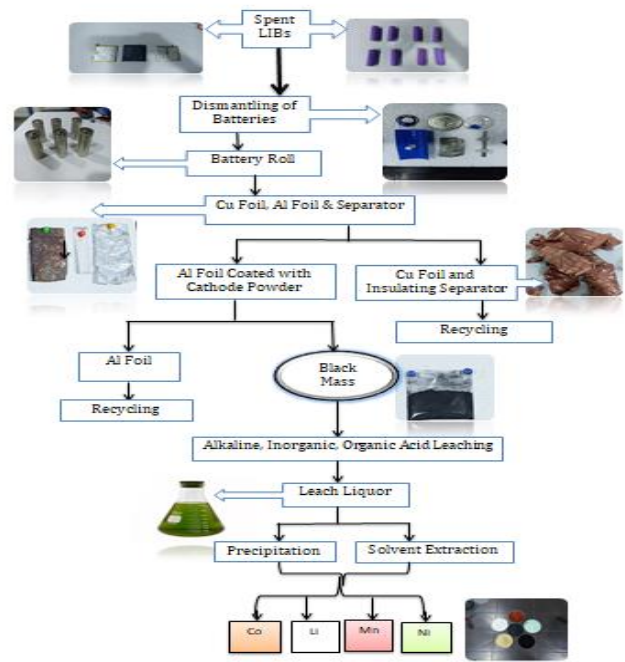


Figure 8:- Flow chart represents recovery of critical metals from LIBs.

A. Preparation and Pretreatment Process:

The pretreatment process involves breaking down the batteries from a large battery pack into smaller cells or modules, separating the plastic casing, and discharging the

cells. This can be done mechanically, thermally, or a combination of both [46]. Pretreatment includes actions including hand separation and material crushing, as well as pyrolysis and/or mechanical processing [47]. This phase involves crushing the cells in a CO₂ gas atmosphere, which causes the volatile organic electrolyte to evaporate and gather as non-useful condensate [48]. The target materials (Black mass) are then separated from the other materials as represented in figure 9.

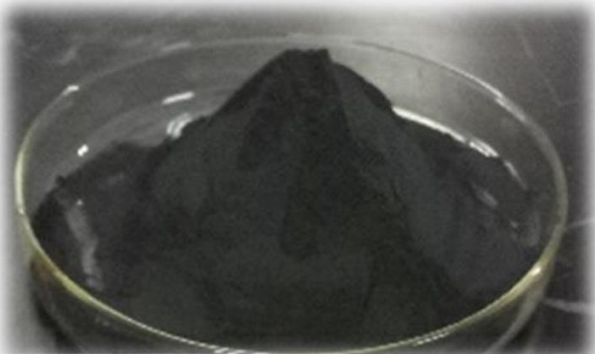


Figure 9: Black mass extracted through pretreatment method

B. Pyrometallurgical Recovery:

In the pyrometallurgical step, the residue is extracted and purified after the pretreatment procedure. In a standard pyrometallurgical process, Li ends up in the slag phase for Li-ion batteries, which needs to be refined and removed [49]. As a result, it must be purified in order to provide feed for the hydrometallurgical stage of the final refining process [50]. The pyrometallurgy process itself uses materials that are removed from the residual that are undesirable in hydrometallurgy, such as fluorine, chlorine, graphite, and phosphorus. In this method, the component metal oxides are reduced to an alloy consisting of Co, Cu, Fe, and Ni using a high-temperature furnace [51]-[53]. It should be mentioned that while it is not feasible commercially, lithium can potentially be recovered using pyrometallurgy. This method is approved for use in the consumer Li-ion and LA battery markets. The main disadvantages of this approach are the quantity of materials that can be recovered, the high energy expenditures, and the creation of harmful gasses [57].

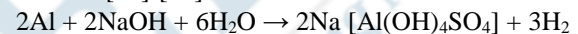
C. Recovery of metal by hydrometallurgical methods:

Alkaline (NaOH) reagents, organic acids like oxalic acid, formic acid, and malic acid, and inorganic acids like H₂SO₄, HCl, and HNO₃ are used in the development of leaching processes to recover metals from the material obtained after mechanical pretreatment and physical separation processes. Moreover, the amino acid glycine is proposed to be leached with ascorbic acid as a reducing agent. After leaching, hydrometallurgical techniques such as ion exchange, solvent extraction, precipitation, and solution purification can be applied. Due to their relative affordability, inorganic acids

have greater benefits than organic acids. Other reducing agents that have been investigated recently include D-glucose, cellulose, *Phytolacca Americana*, grape seeds, orange peels, and waste tea. Metal recovery and purification procedures are applied to leaching solutions that contain metals including Li, Co, Mn, and Ni [58], [59].

a. Alkaline leach:

To extract the active material from the Al and Cu foils and dissolve the binder, the electrodes are first treated with N-methyl-2-pyrrolidone (NPM). Following this phase, metals like copper and aluminum are extracted before lithium and cobalt are leached. Aluminum can be recovered from cathode material selectively by using alkaline (NaOH) leaching [60]. After that, the dissolved aluminum is recovered using NH₄OH precipitation (pH: 5). With ammonia (NH₄OH) solution (4 M NH₄OH, 80 °C, 66.6 g/L, 60 min.), some studies yielded 98% Al and 65% Cu recovery, with Co and Li still present in the solids. The particles are subsequently leached using different acids to recover Li, Co, and other present metal values after the selective leaching of Cu and Al [61]-[64].

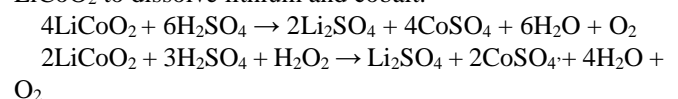


b. Inorganic acids for leaching:

For the purpose of recovering metals from lithium-ion batteries, inorganic acids like phosphoric acid (H₃PO₄), hydrochloric acid (HCl), nitric acid (HNO₃), and sulfuric acid (H₂SO₄) have been thoroughly researched. This is explained by their comparatively low cost, efficiency as leaching reagents, well-understood reaction chemistry, and easy access to downstream treatments for metal recovery and solution purification procedures [65], [66].

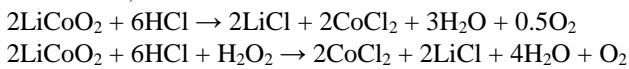
1) Sulfuric acid leaching:

Sulfuric acid (H₂SO₄), the least expensive inorganic acid, is frequently employed in the leaching of metals from primary or secondary sources, including copper, cobalt, and nickel. Additionally, it is the most researched reagent for the leaching of metals from lithium-ion battery cathode material [67]. In order to attain high metal extractions, high acid concentrations (2-4 M H₂SO₄) are frequently needed. As a result, the resulting pregnant leach solutions have high sulfate contents. Furthermore, because of the high acidity, a large quantity of neutralizing reagent is frequently needed to neutralize the leach solution before the metals are recovered downstream [68]-[70]. In order to attain a high rate and extent of metal (e.g., cobalt) extractions in sulfuric acid leaching, inorganic reducing reagents such as H₂O₂ (1-15%), NaHSO₃, and Na₂S₂O₅ are used as reductants [71], [72]. Below are the processes that occur when sulfuric acid is leached from LiCoO₂ to dissolve lithium and cobalt.



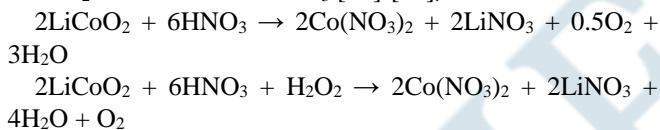
2) Hydrochloric acid leaching:

Hydrochloric acid (HCl) is another frequently utilized leaching reagent in the metal extraction process from LIBs. The main drawbacks of this reagent system are that it releases harmful Cl_2 gas during leaching and is extremely corrosive, necessitating the use of equipment that is resistant to corrosion, which raises operational and capital expenses. Despite the fact that the sulphuric acid system is usually preferred, hydrochloric acid is more potent than sulphuric acid because it contains chloride, which gives hydrogen ions a far higher activity [73]-[78]. Below is a representation of the lithium and cobalt dissolution reactions from LiCoO_2 in HCl solutions;



3) Nitric acid leaching:

Nitric acid (HNO_3) can be used as an oxidizing lixiviant due to its high oxidizing potential ($E_0 = +0.96 \text{ V}$). However, the cost is higher than that of other mineral acids. In the leaching of sulfuric acid, it can also be utilized as an oxidant. The reaction below illustrates how Li and Co dissolve when LiCoO_2 is leached with HNO_3 [79]-[85].



c. Organic acid leaching:

Many organic acids (malic acid, $\text{C}_4\text{H}_6\text{O}_5$, tartaric acid, $\text{C}_6\text{H}_8\text{O}_7$, citric acid, $\text{C}_6\text{H}_8\text{O}_7$, oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$, succinic acid, $\text{C}_4\text{H}_6\text{O}_4$, etc.) have been tested for the treatment of lithium-ion batteries due to the hazardous nature of inorganic acids [86]-[89]. H_2O_2 is frequently employed in organic acid leaching as a reductant to change Co^{3+} into Co^{2+} [90]-[92]. Ascorbic acid was claimed to offer advantages over citric and malic acid, including low temperature and quick leaching duration under the same leaching circumstances. Because cobalt precipitates as oxalate salt (CoC_2O_4), oxalic acid leaching is more beneficial than other organic acid leaching. High acid concentrations are frequently needed to achieve high metal extractions because organic acids have comparatively slow leaching kinetics [93]-[95]. It has also been suggested that organic acids like p-toluenesulfonic acid (TSA) and methanesulfonic acid (MSA; $\text{CH}_3\text{SO}_3\text{H}$) can be used to leach Li and Co from lithium-ion batteries [96]. Compared with most organic acids, tartaric acid ($\text{C}_4\text{H}_6\text{O}_6$) is more acidic and less expensive. It was employed in the selective recovery and separation of Co as a precipitating and leaching reagent. 99.07% Li, 98.64% Co, 99.31% Ni, and 99.31% Mn extractions were recorded in a 2 M tartaric acid solution (4% H_2O_2 , 17 g/L solids ratio, 70 °C, 30 min.) [97]-[99]. Widely employed as an organic lixiviant, citric acid ($\text{C}_6\text{H}_8\text{O}_7\text{-H}_3\text{Cit}$) ionizes to H^+ , H_2Cit^- , HCit^{2-} , and Cit^{3-} in leaching solutions, forming complexes like Li_3Cit and

$\text{Co}_3(\text{Cit})_2$ [100]-[102]. The production of hazardous gases, dust, and high energy costs are common problems with pyrometallurgical processes. Hydrometallurgical processes are suitable for small-scale applications and have certain advantages, including reduced emissions of harmful gases and relatively low investment costs. Pyrometallurgical procedures may have poorer metal recovery efficiency than hydrometallurgical ones. However, in pyrometallurgical operations, batteries do not need to be separated. The majority of industrial recycling processes are pyrometallurgical in nature, despite the fact that hydrometallurgical methods are the focus of intensive research and development studies [103]-[104].

VI. SOLUTION PURIFICATION AND METAL RECOVERY

Solution purification and metal recovery phases may need complicated procedures for the selective recovery of metals of interest because lithium-ion battery leaching solutions are extremely acidic and include a variety of metals [105]. The cathode material comprises different quantities of foil-derived Fe, Cu, and Al depending on the mechanical pretreatment that was used. Efficient and selective recovery of metals can be achieved by avoiding Cu and Al leaching, which will facilitate downstream processing. Li, Co, and Ni are typically extracted to extract metals like Cu, Fe, Mn, and Al [106]-[107]. Solvent extraction techniques or precipitation can then be used to recover these from pure solutions.

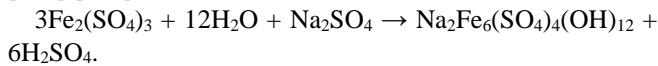
A. Solvent extraction:

A liquid organic reagent is bonded to the metal in the solution to facilitate solvent extraction (SE), which is the process of removing the metal from the inorganic (aqueous) phase into the organic phase. From the leaching solutions of lithium-ion batteries, it is used to extract metals and eliminate contaminants [113]. With the widespread usage of hydroxy-oxime derivatives (Acorga M5640) and bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272), di-(2-ethylhexyl) phosphoric acid (D2EHPA), and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A) in SE applications, there is no shortage of SE reagents. High reagent requirements for concentrated solutions, difficulties with Co/Ni/Mn separation, and expensive capital and operational expenses are the primary obstacles to solvent extraction [114]-[115]. While lithium is still in solution, metals including Cu, Al, Co, Ni, Fe, and Mn can be extracted selectively at pH (6.5) by employing an appropriate SE procedure. Pregnant leach solutions of waste LIBs appear to be treated with SE reagents such as PC-88A, Acorga 5640, and Cyanex 272 [116].

B. Precipitation:

Using NaOH or CaCO_3 , pregnant leach solutions are treated to precipitate contaminants including Cu, Fe, Al, and Mn. The technique of precipitating metals from leaching

solutions is rather straightforward and easy. One of the key factors influencing the precipitation of metals is pH, which, in the right circumstances, enables their selective recovery or elimination. In this way, Co and Li salt can be recovered as shown in figure 10 specifically from pregnant leach solutions by precipitation, taking advantage of the pH difference that allows for the creation of their respective hydroxides. Iron is extracted as jarosite (pH 3-3.5; 95 °C) from the leach solution [108]-[109].



In order to recover manganese as MnO_2 or Mn_2O_3 , potassium permanganate (0.5 M KMnO_4) was added to the solution [112]. Similarly Nickel in the form of Nickel Hydroxide can be recovered by adding NaOH to the pregnant leach solution to increase the pH up to 11.

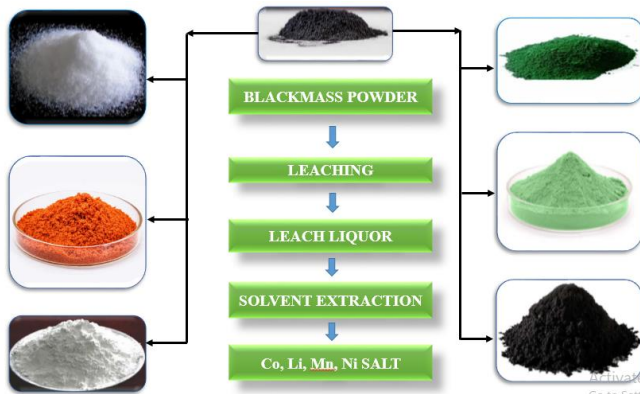
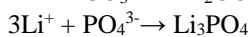
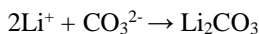


Figure 10: Metals Extracted from Waste LIBs

Oxalic acid recovers cobalt as $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (99.3% purity), while phosphoric acid (H_3PO_4 , 0.5 M) (60 °C, 30 min. 300 rpm) recovers lithium as Li_3PO_4 (98.5% purity). There have been claims that the citric acid that is left over after the metal recovery phase can be used again. At a pH of 11, nickel hydroxide then precipitates. Ammonium oxalate precipitation from purified leaching solutions is used to recover cobalt [110]-[111]. The usual methods for removing lithium from a solution are Na_2CO_3 or H_3PO_4 .



VII. CHALLENGES AND TRENDS FOR RECYCLING

Despite being supported by governments worldwide, LIBs' reputation as a green countermeasure to global warming has come under scrutiny in both technical and popular media. Unquestionably, a large number of publications- some of dubious quality- described LIBs as a major source of pollution and a worldwide environmental problem with detrimental effects on the ecosystem. Although there is a noticeable environmental impact associated with the manufacturing of LIBs, numerous scientific studies have shown the advantages of LIBs. Furthermore, recycling used

LIBs is a fundamental and essential way to lessen this environmental impact. Governments and the lithium battery industry have worked hard over the last ten years to establish and expand recycling programs. The circular economy is currently the focus of many publications and activities [117]. Nevertheless, a number of obstacles prevent LIB recycling from growing quickly and scaling up.

A. To begin with, it is expensive to collect wasted LIBs and necessitates the participation of every stakeholder in the consumption chain, including producers, sellers, governments, waste management companies, and consumers. For example, despite well-established rules and a thriving recycling business, less than 20% of spent LIBs in the European Union were collected in 2016, according to Eucobat (European Compliance Organizations for Batteries) [118]-[119], [123]. Recovery rates in North America are estimated to be about 5%. Shipment of spent LIBs, especially big lithium-ion battery packs, presents challenges in addition to collection. This crucial element is one of the most talked-about subjects at workshops and conferences, as demonstrated by the NaatBat 2019 Battery Conference in Buffalo. The United Nations Committee of Experts on the Transport of Dangerous Goods also studies it, and multiple sessions are devoted to this area [120]-[123].

B. Secondly, planning the variation of material Inflow is challenging due to the diversity of LIB materials and the quick advancement of technology. Cathode composition has undergone a significant evolution in the last ten years, moving from the early stages of LCD to novel compositions like NMC, LFP, NCA, and LMO. Furthermore, several items with cathode additives, like yttrium, are already on the market and will eventually go through the recycling process. Furthermore, anode material modification is currently occurring, moving from graphite to LTD and silicon-based materials. Furthermore, the field of electrolyte additives for lithium-ion batteries is one that is constantly evolving; in just 24 months, 312 patents on different additives were filed. In conclusion, the present research endeavour aimed at developing solid-state Li batteries is confronting novel obstacles that demand prompt contemplation of the post-consumption destiny of these innovative gadgets to streamline the recycling process. Battery recycling plants will continue to face challenges in managing waste, maintaining mass balance, and mitigating health and safety issues. One such example is propane sulfone, which must be accurately managed as a safety issue because it is adopted in certain compositions [119]-[121], [123].

C. Ultimately, the industry's viability is weakened by the fierce competition among battery recyclers and the price instability of commodities. These factors limit recycling profit margins. In order to address this issue, producer

responsibility must be strengthened. For example, producers of LFP and LMO systems must be held accountable for their waste and must participate in recycling costs when recovered materials cannot cover processing costs. In Europe, where the producer and importer split the recycling cost of alkaline batteries, this idea is already widely embraced [120]-[123].

In order to promote a circular economy strategy through the improvement of closed-loop processes leading to the regeneration of battery grade precursors or compounds with little environmental impact, all battery producers, as well as makers of mobile phones, laptops, and EVs, as well as end users, must collaborate globally. Closing the loop with respect to several materials is best achieved using procedures that combine chemical and mechanical approaches.

VIII. CONCLUSION

The increasing use of electric cars (EV & HEV) and portable electrical and electronic devices (mobile phones, laptops, video cameras, etc.) has led to a rise in the significance of lithium-ion batteries (LIBs) in recent years. As a result, there has been a recent trend of rising lithium and cobalt prices and demand. By the end of year 2050, there will be shortage of 46,720,818 tons lithium hence recycling of waste LIBs is the only option to meet the demand. While recycling, LIBs need to be handled carefully because they include electrolytes and heavy metals (Cu, Pb, Cd, and Zn) that are hazardous for the environment and Human health. The recycling of LIBs involves the use of mechanical, hydrometallurgical, and pyrometallurgical treatment procedures. Nonetheless, it appears that the majority of research has focused on hydrometallurgical processes, which frequently entail the leaching of metals and the recovery of metals following the removal of contaminants from leaching solutions. In order to leach lithium-ion batteries (LIBs), sulfuric acid is frequently combined with different reducing agents. As eco-friendly substitutes, biodegradable organic acids are also heavily advertised. Leach solutions are treated using chemical precipitation and/or solvent extraction techniques to recover metals in a variety of forms. Research and development efforts appear to be ongoing in order to create sustainable technologies and procedures that may efficiently recover metals from spent LIBs, with a focus on lowering expenses, streamlining recycling procedures, and minimizing environmental damage.

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