Green recycling methods to treat lithium-ion batteries e-waste: A circular approach to sustainability

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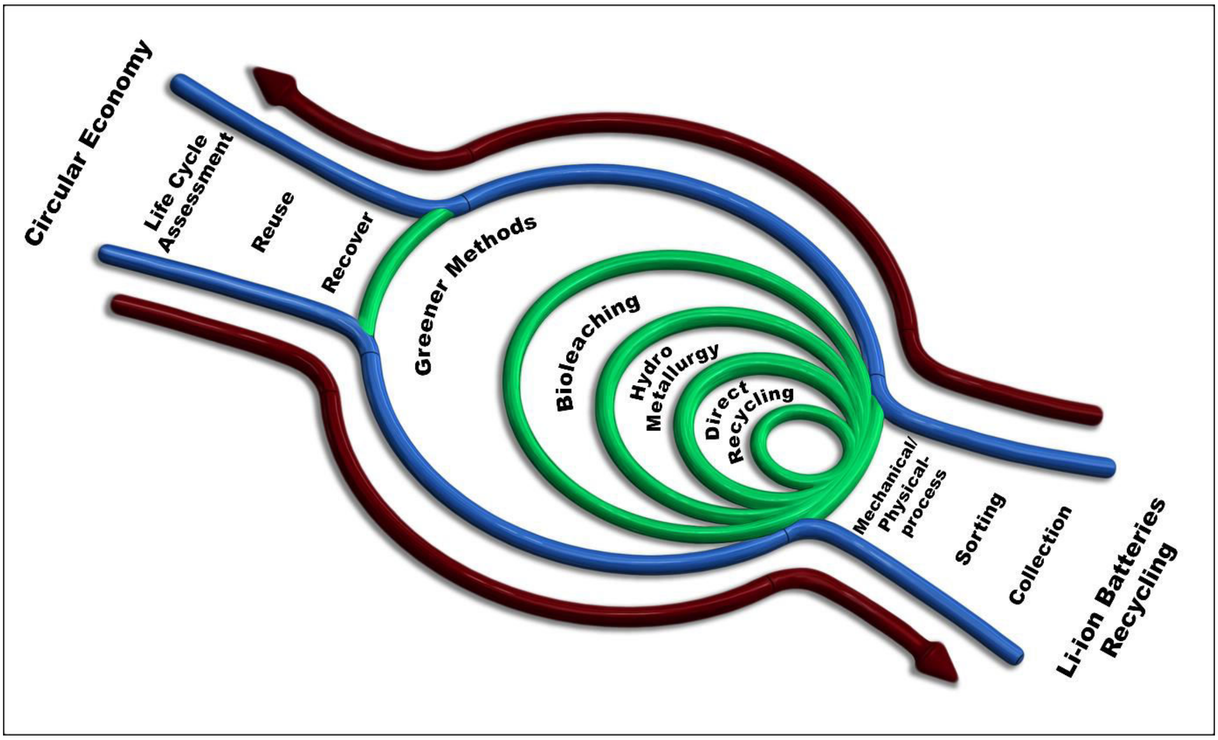
Abstract:

E-waste generated from end-of-life spent lithium-ion batteries (LIBs) is increasing at a rapid rate owing to the increasing consumption of these batteries in portable electronics, electric vehicles, and renewable energy storage worldwide. On the one hand, landfilling and incinerating LIBs e-waste poses environmental and safety concerns owing to their constituent materials. On the other hand, scarcity of metal resources used in manufacturing LIBs and potential value creation through the recovery of these metal resources from spent LIBs has triggered increased interest in recycling spent LIBs from e-waste. State of the art recycling of spent LIBs involving pyrometallurgy and hydrometallurgy processes generates considerable unwanted environmental concerns. Hence, alternative innovative approaches towards the green recycling process of spent LIBs are essential to tackle large volumes of spent LIBs in an environmentally friendly way. This review focuses on such evolving techniques for spent LIBs recycling based on green approaches, including bioleaching, waste for waste approach, and electrodeposition. Furthermore, we discuss ways to regenerate strategic metals post-leaching, efficiently re-process extracted high-value materials, and reuse them in applications including electrode materials for new LIBs. This review highlights the concept of "circular economy" through closed-loop recycling of spent LIBs achieved through green-sustainable approaches.

Keywords: Battery e-waste, recycling, electrodeposition, bioleaching, Circular economy, Metal-organic framework (MOF)

Abstract Graphics



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Abbreviations:

SS	Stainless steel
Pb-8 Sb	Impure Sb, containing up to 8% Pb
SCE	Saturated calomel electrode
RT	Room temperature
RE	Reference electrode
CE	Counter electrode
WE	Working electrode
SOFC	Solid oxide fuel cells
CAM	Cathode active material
ILs	Ionic liquids

W4W	Waste for Waste
EVs	Electric vehicles
LIBs	Lithium-ion batteries
FVW	Fruit and Vegetable Waste
LCO	Lithium cobalt oxide
LMO	Lithium Manganese oxide
NMC	Lithium Nickel manganese cobalt oxide
OP	Orange peel
E-waste	Electronic waste
ORP	Oxidation-reduction potential

1. Introduction

Advances in electric vehicles (EVs), portable electronic devices, and renewable grid energy storage systems have increased the demand for lithium-ion batteries (LIBs) with higher energy storage capacities, faster charging capabilities, and increased cycle life. [1-4] Global lithium-ion battery market is estimated to reach $95 billion by 2025, with an expected compound annual growth rate (CAGR) of around 16% that is forecasted to lead to around 11 million metric tons of spent LIBs waste generated by 2030. [5] The volume of discarded/spent LIBs is predicted to rise by 59 % from 10,700 tons in 2012 to 464,000 tons in 2025. [6] Presently, less than 6% of spent LIBs waste are recycled worldwide, while most of them end up in landfills posing environmental concerns as these spent LIBs consist of toxic metals (Co, Mn, Ni) and flammable electrolytes that may react with water releasing harmful gases. [7-9] These piles of spent LIBs also represent valuable secondary resources of critical elements (such as lithium, manganese, cobalt, nickel, etc) that are of geopolitical supply risk fuelled by their growing demand in new LIBs production. Interestingly, the constituents elements employed in LIB manufacturing are only abundant and mined in selected geographical locations worldwide. For instance, the Republic of Congo produces about 60% of the world's cobalt, Australia and Chile produce 80% of lithium, and China produces 70% of graphite.[10] However, these critical elements can potentially be recovered from spent LIBs, thus avoiding the depletion of finite resources and reducing over-reliance on classical mining to maintain the supply chain.[6-9] Recycling of spent LIBs waste, on the one hand, would reduce and/or eliminate potential environmental impacts and, on the other hand, would recover and reuse valuable metal recycling of resources, thus promoting a circular economy approach based on sustainable LIBs development industries.

State-of art industrial processes for spent LIBs recycling are mainly based on (i) pyro-metallurgy and/or (ii) hydrometallurgy approaches. Pyrometallurgy involves melting spent LIBs at very high temperatures (>1000 degC) and recovering metal resources from the remaining slag.[11] Pyrometallurgy is (i) energy/cost-intensive, (ii) leads to loss of metals in slag, and (iii) involves hazardous gaseous emissions, thus not environmentally friendly. Hydrometallurgy involves treating spent LIBs in concentrated corrosive acids to dissolve and extracts metals. Hydrometallurgy operates at lower temperatures and offers higher metal recovery efficiency than pyrometallurgy (Table 1). However, multiple complex treatment steps and selectivity of strong acid reagents that lead to gaseous emissions and wastewater production poses environmental concerns of hydrometallurgy. [12-17] In an effort to lower the energy and environmental footprints, novel green recycling approaches towards spent LIBs have been investigated to achieve higher recycling efficiency and reuse of critical elements. This review presents a summary of greener and environmentally friendly recycling approaches of spent LIB. We address the detailed assessment of battery recycling process starting from pre-treatment, such as sorting, dismantling, and shredding of LIBs followed by metal extraction processes from black mass and their regeneration and reusability.

2. Lithium-ion batteries types and pre-treatment

Primary non-rechargeable lithium batteries consist of lithium metal anode and metal oxide cathode in which the following chemical reactions occur at the anode (Equation 1) and MnO_2 cathode (Equation 2)

$$\mathrm{Li} \rightarrow \mathrm{Li}^{+} + \mathrm{e}^{-} (\text{anode}) \text{ ....}(1)$$
$$\mathrm{Li}^{+} + \mathrm{e}^{-} + \mathrm{MnO_2} \rightarrow \mathrm{LiMnO_2}\left(\text{cathode}\right) \text{ ....}(2)$$

Secondary rechargeable lithium-ion batteries consist of lithium containing oxide as a cathode, graphite anode, and lithium salt in an organic solvent as electrolyte. During charging of these batteries, lithium is removed (deintercalated) from the cathode ($LiCoO_2$) and inserted (intercalated) into graphite anode. While discharging, the reverse reaction process takes place reversibly, as shown in Equation 3, 4. [18-19] The lithium-ion moves in the electrolyte within the cell, and the electron moves in the external circuit, providing current.

$$\mathrm{LiC_x} \longleftrightarrow \mathrm{C_x} + \mathrm{Li}^{+} + \mathrm{e}^{-} \text{ ....}(3)$$

$$\mathrm{LiCoO_2} \leftrightarrow \mathrm{Li_{1-x}CoO_2} + \mathrm{xLi}^{+} + \mathrm{xe}^{-} \text{ ....}(4)$$

There are different types of lithium-ion batteries based on the constituent cathode, anode, and electrolyte materials. The most commercially used anode is graphite and lithium titanate. The electrolyte typically is a mixture of lithium containing salts (such as lithium hexafluoro phosphate, $LiPF_6$) dissolved in organic carbonates (such as ethylene carbonate or diethyl carbonate) as solvent. The cathode is generally made up of three classes of materials: a layered oxide (e.g., $LiCoO_2$, $LiNi_{0.3}Mn_{0.3}Co_{0.3}O_2$), a polyanion (e.g., $LiFePO_4$), or a spinel (e.g., $LiMn_2O_4$). The physio-electro properties of different LIB types are described in Table 2**.** [22-25] Depending on the applications, there are different form factors of LIBs such as cylindrical, prismatic, and pouch configurations that employ various packaging materials.

Efficient recycling processes should address the recovery, recycling, and reuse of these packaging materials. Some parameters that should be considered when employing LIBs for various applications include capacity, power, voltage, charging and discharging rates, cost, life span, safety, and environmental impact. Currently, LIBs have capacities ranging from 550 mAh to 2.5 Ah for portable and stationary applications and up to 45 Ah or higher for high power and energy applications. [18-22] With the advancements in LIBs, numerous innovative approaches have been developed for newer positive (cathode) and negative (anode) electrode and electrolyte materials. Hence, recycling processes that are being developed should be able to accommodate these variations in the LIBs constituent chemistry to be able to recover materials efficiently.

Recycling of LIBs consists of several pre-treatment steps such as sorting, discharging, dismantling, shredding, mechanical-physical process of separation followed by metal extraction, metal recovery, metal reuse. The waste LIBs collected are manually sorted, and fully discharged to <0.5V using a salt solution in the preliminary pre- treatment step to prevent any fire or explosion risk during the shredding process. Mechanical shredding of spent LIBs consists of crushing and shredding LIBs using duo-directional shredder blades in an inert atmosphere purged with argon or nitrogen to break apart and shred the batteries with the casing/packaging materials. The mechanical shredding process occurs in an inert atmosphere to prevent the presence of oxygen during shredding, which might lead to lithium reacting violently with oxygen leading to fire risk. The detailed pre-treatment process used in our facility is shown in **Figure 1**. The shredded materials should be stored in a fume cupboard or under exhaust suction to remove any toxic electrolyte and volatile organic compounds (VOCs) after being collected from the drum at the bottom of the mechanical shredder. After the drying process under exhaust, subsequent pre-treatment processes would include milling, sieving, magnetic separation, froth flotation, or a combination of these processes would lead to black mass powder. It is necessary to do fine grinding to reduce shredded battery materials to near micron-sized particles to form black mass powder. Various green recycling approaches are described in the following sections that are employed on extracted black mass powder after pre-treatment steps to extract and leach out elements. Pre-treatment steps affect the quality and constituent of the black mass powder and can affect the metal recovery efficiencies in the following green recycling approaches.

3. Greener Recycling Approaches

3.1. Bioleaching

Bio-hydrometallurgy, as a green technology, is a promising method for metal extraction from spent LIBs, printed circuit boards (PCBs), and other e-wastes. [26-28] The bio-hydrometallurgical process has attracted great attention recently because it is a cost-efficient and eco-friendly alternative to conventional processes such as pyrometallurgy and hydrometallurgy.[29, 30] The extraction of metals from secondary sources such as ores, concentrates and recycled or waste materials using microbes, such as bacteria, fungi, and archaea, is called "bioleaching or bio-hydrometallurgy." Chemistry, biology, and metallurgical phenomenon are all involved in this interdisciplinary extraction process.[31- 33] Bioleaching is used to extract and treat metals from ores and wastes, as well as for reducing pollution and greenhouse gas emissions.[31-35] In the bioleaching process, microbes act as a biocatalyst by producing lixiviants (leaching agents) such as H_2SO_4 or organic acids through their metabolism, which can dissolve the metals from their ores and secondary resources such as LIBs, PCBs, and other e-wastes.[30] The bioleaching process comprises of various groups of microbes, such as chemolithotrophic prokaryotes, heterotrophic bacteria, and fungi. For many years, these microbes have been widely used to extract valuable metals (e.g., cobalt, nickel, manganese, and copper) from ores and other secondary sources.[34, 36-40] In the bioleaching process (explained in **Figure 2),** valuable metals are extracted from waste LIBs by naturally existing biological microorganisms using their metabolic products. Microorganism assisted dissolution and recovery of elements from spent LIBs has immense potential as a green recycling technology because it is safe for the environment, has no harmful gases emitted, has low operational costs and energy requirements. The aim of spent LIB recycling employing a green bioleaching process is to extract the metal constituents from them and reuse them in new LIBs, thus reducing battery waste and in that process reducing exposure of LIB toxic constituents in the environment.

3.1.1 Microbes used in Bioleaching Process

Earlier, bioleaching systems were developed towards the recovery of metals from ores. In the 1980s, the first commercial bioleaching facility was created to recover copper utilizing acid-producing acidophilic bacteria such as A. ferrooxidans and A. Thiooxidans. [41] Later, when the metal was covered with an intractable covering of metal sulfides, making cyanide extraction difficult, bioleaching technology was used for gold mining. [42] Metal extraction from spent batteries has been done using a bioleaching process since the late 1990s. Many research publications on metal extraction from LIBs using a bioleaching technique have been published since 2000 and reviewed in detail. [33,34,37,43] The microbes used in the bioleaching process have evolved over the years and have been categorized into mesophiles (below 40 °C), moderate thermophiles (45 °C – 70 °C), and thermophiles (70 °C or above) and fungi (below 35 °C). [37] Bioleaching of spent LIBs can be performed either using single or multiple microorganisms in combination (consortia) to experiment with the synergistic effects.

3.1.1.1 Bacteria for LIBs bioleaching

The most extensively studied mesophilic bacteria in LIBs bioleaching are *Acidithiobacillus ferrooxidans, Acidithiobacillus thiooxidans,* and *Leptospirillum* *ferrooxidans*; moderate thermophilic microbes are sulfur-oxidizing *Acidithiobacillus caldus,* and iron-oxidizing *Leptospirillum ferriphilum*. [30, 34, 44- 46] The bioleaching studies of LIBs reported using single and mixed bacteria are shown in **Table 3**. The bioleaching process, aided by the bacteria, converts the metal complex from an insoluble form into water-soluble metals by bio-oxidation. During this process, the microbes gain energy by rupturing and breaking LIBs wastes into their constituent metallic complexes. [47] Bioleaching of LIBs using mesophilic bacteria is usually performed in acidic pH between 1 and 3, at almost room temperatures of around 30-32 °C, where most of the metal ions are soluble in solution. One of the critical parameters and challenges in the bioleaching process is the pulp density (w/v) or referred as solid to liquid ratio (S/L ratio), which controls the viability of microbes in liquid solution vs the amount of solid black mass from spent LIB. The bioleaching efficiency decreases considerably with increasing solid content (S/L ratio) because of the alkaline nature of the spent LIBs and toxic compounds, including electrolytes and binders. [31,32] As seen in **Table 3**, varying the bacterial pulp density,0.25-10%, results in different leaching efficiencies of individual elements such as Li, Co, Ni, Mn.

3.1.1.2. Fungi for LIBs bioleaching

Aspergillus niger, Penicillium simplicissimum, and Penicillium chrysogenum are the most studied fungi for bioleaching of LIBs (**Table 3**). [44, 48-59] Fungi-mediated bioleaching of LIBs usually takes place at a near-neutral pH or alkaline, and the dissolution of the LIB components increases the pH of the solution.[56] The fungi-mediated bioleaching is performed by acidolysis, complexolysis (generation of organic acids), redoxolysis, and metal dissolution occurs at near-neutral or alkaline conditions. The metabolites of organic acid form a complex with metallic components, and the resulting complex has low toxicity.[49,50] Fungi-based bioleaching requires carbon-based primary nutrients such as glucose and sucrose into the leaching solution. Alternatives carbon-based sources such as food-processing wastes, potato processing waste, and sugarcane bagasse have been supplemented as primary nutrients and studied. [51,54] Bacteria-based bioleaching has been successfully demonstrated at higher pulp density (10%) as compared to fungi-based (2%) bioleaching Table 3.

3.1.2 Factors affecting the bioleaching process

The potential of microorganisms and chemical composition of spent LIBs waste determines the bioleaching process' leaching efficiency. The kinetics of the bioleaching process can be improved by optimizing the microbe's growth conditions, including temperature, pH, redox potential, $O_{2,}$ and CO_2 supply, growth nutrients, metal toxicity, and pulp density. [34]

The microbial growth depends on the specific nutrient and their dosages. Concentration and dose of nutrients and microbes are essential to produce metabolites, which are associated with the metal solubilization of LIBs. *A. ferrooxidans* utilize ferrous salts as their major nutrition for the production of biogenic sulphuric acid and Fe^{3+} ions, and *A. thiooxidan* needs elemental sulfur. Fungi, on the other hand, require sucrose or glucose as a carbon source, which can be replaced with cost-effective alternatives such as food processing wastes, potato processing waste, and sugarcane bagasse.[48, 55, 56] An adequate amount of oxygen supply (1%-10%) is also required for the optimal growth and function of the microorganism, which can be attained by various methods, including aeration, stirring, or shaking.[57,58] However, at high pulp densities, the aeration may be less due to limited air penetration caused by the high viscosity of the solution, thus decreasing the leaching efficiency. Microbes are well grown in an optimum pH condition to produce their metabolites. The *Acidiophilic* bacteria's optimal pH is in the range of 1.5 – 2.5.[34, 45-46, 55] The ideal pH for *A. niger* mediated bioleaching is around 5.0 [49,54]. The oxidation/reduction potential (ORP) is also an important and crucial factor in ferric sulfate-mediated bioleaching, mainly determined by the Fe^{3+}/Fe^{2+} redox couple. Here, high concentrations of Fe^{3+} indicate high potentials.[59,60] The ORP during the bioleaching process can be controlled by using chemical reductants or controlling the oxygen supply. When ferrous ions oxidize into ferric ions during bacterial growth, the redox potential rises; however, it drops dramatically in the first few days of LIB bioleaching and decreases even more at high pulp densities (S/L). [60-64] So far, there is no study on the optimal ORP range for increasing metal leaching efficiency in LIB bioleaching. The bioleaching efficiency can also be enhanced by carrying out the process at the microorganism's optimal temperature. The optimal temperature range for the acidophilic bacteria is between 28 and 30 °C. The majority of the fungi-mediated bioleaching has been carried out at 30 °C. Although higher temperatures help to improve the kinetics of the bioleaching process, they can also decrease microbial viability. To enhance the leaching efficiency, moderately thermophilic and thermophilic bacteria can be utilized at their optimal temperature.[50, 57,58, 65,66] Different microbes have different sensitivity to metal tolerance; however, at high pulp densities (S/L ratio), the metal toxicity is high; thus, the metal dissolution is slower due to reduced microbial activity. When LIB bioleaching is performed at high pulp densities, the viscosity of the leaching media increases, thus, decreasing dissolved oxygen and air supply to the microbe. The diffusion of oxygen into the bottom of the leaching medium is reduced when the viscosity is high; this influences the metabolism of the microorganisms, thus, reducing metal leaching efficiency. [34, 57,58]

The recovery of metals from LIB by the bioleaching process happens only through the metabolites produced by the microorganism. The ability of acidophilic bacteria to produce sulphuric acid and sustain the cyclic regeneration of Fe(III) ions, which can leach out various metals from complex battery matrices and promote acidophile growth by stabilizing the pH of the leaching medium, demonstrates the efficacy of bacterial bioleaching. On the other hand, fungal bioleaching efficiency is entirely dependent on excreted organic acids, which utilize the O_2/ H_2O redox pair to oxidize LIB metals by complexing with protonated metals. The efficacy of various bioleaching systems by single bacteria, mixed bacteria, and fungi was evaluated using the leaching percentage of different metals. Generally, the metals leaching efficiency (amount of extracted metals) after the bioleaching process would be determined by comparing the amount of metal leached from the black mass using aqua regia [62-64] solution that is assumed to leach out and dissolve all the elements from spent LIB. The detailed leaching efficiency of bacteria and fungi for various metals using the bioleaching process is given in Table 3.

3.1.3 Enhancing leaching efficiency in bioleaching process

There are different ways to enhance the kinetics of the bioleaching process. The addition of metal ions such as Ag^+ (0.02 g/L) and Cu^{2+} (0.75 g/L) can enhance the leaching efficiency by accelerating the electron transfer through the oxidation process and increasing metal solubility by forming intermediate metal complexes that can be very soluble in water.[67,68] The inhibitory as well as toxic effects of these metal ions on microorganisms are challenging when using them in the bioleaching process. Thus, engineering the microorganism to tolerate higher concentrations of metallic ions like Ag^+ and Cu^{2+} is necessary. Another approach is to employ ultrasound bioleaching or sono-bioleaching, which improves the metal solubility by increasing the stirring at both macroscopic and microscopic stages, therefore increasing the metabolic activities of microbes.[69] The microbial tolerance against the metal toxicity at high pulp densities can be increased through the serial adaptation of bacteria or fungi over a long period by increasing the pulp densities gradually. [49,70] The adaptive microorganism is resistant to the toxic LIB components and can continue its growth and activity during the bioleaching process. The microorganism can be used as a combination of two or more species in the bioleaching process to increase the tolerance against high metal toxicity to improve the leaching efficiency.[71-73] In the bioleaching of LIBs, a mixed culture of iron-oxidizing-bacteria *A. ferrooxidans* and *L.ferriphilum* and sulfur-oxidizing bacteria such as *A. thiooxidans, Alicyclobacillus* sp, and *Sulfobacillus* sp. have been employed.[64,70] In our studies, increasing the production of bacterial metabolites such as biogenic sulphuric acid and ferric ions in the culture medium could increase the leaching efficiency at high pulp densities.[62-64] By genetically engineering microbe's, heavy metal resistance, acid endurance, and Rubisco-free carbon fixation pathways, the tolerance against metal toxicity, the fluctuating and challenging process conditions, and reduction in the time for metal extraction can be improved.[74-76]

3.2 Food waste-enabled waste for waste (W4W) leaching approaches

Traditional hydrometallurgical methods heavily involve strong acids such as HCl, HNO_3, and H_2SO_4, producing gaseous products that are ecologically detrimental. [77-79] Therefore, the primary research focus over the past decade has been finding suitable alternatives to replace the strong acids in the metal leaching process. Bioleaching described in the previous section is one such alternative. Several other studies have employed weak organic acids such as citric acid, malic acid, succinic acid, and tartaric acids to replace strong acids in the metal leaching process. Such weak organic acids have been proven successful with a competitive leaching performance (**Table 4**). Notably, with the assistance of 0.5-15 vol% H_2O_2, which serves as a reductant, the resulting H_2O_2-weak organic acid combination can extract up to >95% of metals from spent LIBs waste. One of the drawbacks of weak acids is the need to add H_2O_2 that has a concern owing to its explosive chemical status and chemically unstable nature that has set the quest for greener alternatives to replace H_2O_2 in this hydrometallurgy-based process. Trials on applying sodium thiosulfate ($Na_2S_2O_3$) and sodium bisulfite ($NaHSO_3$) as a reducing agent in the LIB waste recycling process instead of H_2O_2 have shown promises, in which ~ 50-90% of the Li, Co, Mn, Ni were retrieved from the LIBs waste. [80,81] Nevertheless, the introduction of Na^+ into the metals-containing leaching lixiviant produces undesirable adverse effects on the final recovered metals and incur additional operating steps and costs for the final product purification. Thus, searching for a green reductant such as from food waste will have a far-reaching impact on the development of sustainable close-looped recycling of spent LIBs.

Like LIBs waste, food waste has also increased exponentially on a global scale over the last two decades. The EU's annual food waste production is estimated to be 123 kg per person, and fruit and vegetable waste (FVW) accounts for ~ 60% of the total food waste. [82] Unfortunately, the majority of the FVW ends up in landfills or incinerated. FVW contains a wide range of reactive molecules, including dietary fibers, catechins, phenolic acids, and flavonoids, and the current handling of FVW results in a significant waste of valuable resources. [79] Recently, researchers have started investigating the possibility of using these "unnoticed and under-utilized" food waste materials as a low-cost and sustainable green way to recycle LIBs e-waste. Recent successes in using tea and plant wastes [79], grape seeds [83], discarded orange peel [84], food waste-derived products like glucose [85] and ethanol [86] as green reductants to effectively recover precious metals from LIBs waste have validated the concept of waste for waste (W4W). **Figure 3** shows various types of food waste employed in the recent progress on the food-waste enabled W4W approaches for recycling spent LIBs. The lignocellulosic content, including cellulose and hemicellulose content, have been reported to be critical for the efficient removal of metals using these various food waste types. [87,88] The traditional H_2O_2-based reductive leaching process (**Equation 5**) of extracting metals from spent LIBs is likely to cause occupational hazards and increase operational costs. In contrast, the incorporation of food waste-based natural reductants into the metal leaching process provides a safer and more cost-effective solution for recovering valuable metals sustainably from the spent LIBs.

$$\mathrm{Li_aCo_bMn_cNi_dO_e + H_2O_2 + H^+ \rightarrow Li^+ + Co^{2+} + Mn^{2+} + Ni^{2+} + O_{2(g)} \uparrow + H_2O} \quad \text{….}(\mathbf{5})$$

Where a, b, c, d, e, refer to the number of respective atoms present in the molecular formula of the cathode in the spent LIBs. Note that the reaction is not balanced, and the value of a-d is subject to change due to different types of cathode materials.

3.2.1. Pre-treatment of food waste

Pre-treatment of food waste is shown to be necessary to enable the breakdown of the lignocellulosic structure and the release of reductants, including reducing sugars to use food waste as a reductant in the LIBs recycling. There are three types of existing technologies for pre-treating food waste: physical, chemical, and biological. [89] Physical pre-treatments are commonly employed to reduce the size of food waste to enhance its reaction surface area and reactivity. Ultrasonication, grinding, extrusion, and ball-milling are commonly employed physical pre-treatments methods. In terms of industrial scale-up and applicability, grinding and extrusion are highly recommended due to their ease of scale-up operation and efficiency. Food waste is also reported to have been treated chemically or biologically after physical pre-treatments for depolymerization, crystallinity reduction, and the production of reducing agents.

Chemicals such as acids (e.g., sulfuric acid, citric acid, etc.) and alkalis (e.g., potassium permanganate) have been used for cleaning, pre-treatment, and activation of food waste. These involve higher temperature and pressure pre-treatment. Alternatively, ionic liquids have also been employed that produce reducing molecules from food waste under milder conditions as compared to acids and alkalis, albeit at a higher chemical cost. Biological pre-treatments involve enzymatic reactions of food waste to convert them to reducing molecules. Even though this approach is attractive in terms of low operation temperature, the efficiency of this process is the least among the other above pre-treatment processes and hence not widely used.

3.2.2 Different food wastes employed for spent LIBs recycling

3.2.2.1 Tea and plant waste

A sustainable hydrometallurgical process for effective metal leaching from spent lithium cobalt oxide (LCO) batteries employed tea and plant waste as reductants by Chen et al. [79] In this work, the collected LCO battery waste was subjected to multiple pre-treatment steps to separate the cathodes from anodes, separators, metallic current collectors (i.e., Cu and Al), preceding to the subsequent metal leaching experiments (**Figure 4**). After drying the tea and plant (Phytolacca Americana branch) waste that was mineralized and used for the leaching without any prior chemical modifications. [79] When the leaching efficiency of metals (such as Li and Co) in the presence of tea/plant waste or H_2O_2 as a reducing agent was compared, the leaching performance of tea/plant waste was found to be comparable to that of H_2O_2. This is because the mass of reducing molecules was comparable, indicating that these two waste materials could be used as a replacement for H_2O_2. After careful analysis of the impact of multiple parameters such as time, temperature, reductant amount, acidity, pulp density on the leaching performance of tea/ plant waste; 80%-99% of the metals could be leached out at the optimal working conditions: 80 min, 70 °C, 2.0 M citric acid, reductant dosage 0.6 g/g, and pulp density 50 g/L). Around 93% of Li and 98% of Co were precipitated by adding phosphoric acid and oxalic acid after the leaching process. The recovered Li_3PO_4 and CoC_2O_4 after precipitation had a purity of > 98%. Another study confirmed the concept of using tea waste as a green reductant to extract valuable metals from spent LIBs, where 2 M H_2SO_4 aided with tea waste powder was effectively leached out 100% of Li, Ni, Mn, and 90% of Co from the mixed spent LIBs.[90] The optimal condition for the above leaching process was found to be: 120 min, 90 °C, tea waste dosage 0.3 g/g, at a pulp density of 50 g/L. Further analysis by XRD, SEM, and FTIR confirmed and demonstrated the successful dissolution of the cathode materials.

A possible working mechanism for tea/ plant waste was proposed. Tea/plant waste is considered a rich source of lignocellulose and polyphenols (e.g., catechins), and these saccharides and polyphenols can be used as potential reducing agents to accelerate metal dissolution. It is known that cellulose and hemicellulose can be degraded into glucose and other mono/oligosaccharides under acidified conditions [91,92]. The obtained glucose and other sugars are effective reductants because of the presence of aldehyde groups. As a result, the conceived idea was that the lignocellulose component of tea/ plant waste would be decomposed into reducing sugars such as d-glucose, fructose, arabinose, etc., which would then serve as a reductant in the redox-based metal dissolution process. On the other hand, the reducing potential of polyphenols has been well documented and used in many other applications such as nanomaterials synthesis and medical use. [93-95] Chen *et al.* have tentatively demonstrated the oxidation of polyphenols including epigallocatechin gallate (EGCG), epigallocatechin (EGC), and theaflavin-3,3digallate during the leaching process. [79] FTIR analysis of the molecular structure of tea waste before and after the leaching indicated a decrease in the intensity of the -OH peak. At the same time, an increase in the intensity of the C=C peak confirms the conversion of polyhydric groups to the oxidized product, i.e., aldehyde/carboxylic group.

3.2.2.2 Grapeseed waste

Aside from tea waste and plant waste, the discarded grape seeds, which contain various polyphenols such as catechins, EGCG, and EGC, can be used as a green reductant for metal extraction from spent LIBs. Zhang *et al.* recently investigated and validated the use of grape seeds for reductive metal leaching. Around 92% of Co and 99 % Li could be leached out at the optimal conditions, i.e., 0.5 g spent cathode materials, 1.5 M malic acid, 0.3 g grape seeds at 80 ˚C for 180 min [83]. However, pre-treatment steps such as manual dismantling were performed before the leaching experiments to separate the cathode materials from other parts. Cathode current collector (Al foil) was removed by pre-leaching the spent cathode materials using 6 % NaOH solution. **Equation 6 and 7** describes how NaOH removes Al from the cathode materials.

$$2Al + 2NaOH + 2H_2O = 2NaAlO_2 + 3H_2 \quad \text{.......} \textbf{(6)}$$

$$Al_2O_3 + 2NaOH = 2NaAlO_2 + H_2O \quad \text{..............} \textbf{.(7)}$$

Interestingly, the authors revealed that the grape seed-enabled reductive leaching consists of two steps, i.e. surface chemical reaction and reactive ions diffusion, as evidenced by SEM, TEM, XPS, and UV-Vis spectroscopy, as well as analysis of the physicochemical properties of cathode materials such as surface morphology, metal valency, etc. at different time intervals of leaching.[83] Notably, only Co^{3+} was formed during the first 40 minutes of the leaching experiment, whereas Co^{2+} predominated after 180 minutes. As a result, the authors proposed that the reduction of Co by grape seeds lags for 40 minutes to allow the H^+ provided by the malic acid to attack the surface of cathode materials, forming $Co(OH)_3$; which flocs on the surface and etches the surface to improve the diffusion of the reactive reducing molecules into the materials, as well as the subsequent redox reaction initiated by grape seeds.

3.2.2.3 Orange peel waste

Waste from fruits and vegetables is known to be rich in numerous kinds of reducing molecules, such as dietary fibers, phenolic acids, and flavonoids; yet these vital naturally derived reducing substances are mostly turned into waste and dumped into landfills. Because of this, our group conceptualized that it is possible to utilize fruit waste as a reductant in leaching valuable metals from LIBs waste. Specifically, we investigated the possibility of using orange fruit peel waste as a green reductant to recover valuable metals from spent LIBs. Orange peel has an acidic nature and an abundance of dietary fibers such as cellulose and hemicellulose, as well as antioxidants such as phenolic acids and flavonoids. Recently, we have reported a green reductive leaching process using discarded orange peel (OP) to effectively solubilize Li and Co from the spent LCO battery powder in a citric acid-based leaching solution. [84] The detailed workflow of our study is shown in **Figure 5**. [84]. Our study gave an in-depth understanding of how individual factors (i.e., size of OP, amount of OP, leaching temperature, acidity, slurry density) modulate the metal leaching efficiency in the OP leaching system of LCO batteries. Optimal leaching conditions of 100°C for leaching temperature, 200mg OP, 1.5M citric acid, 4 hours for leaching time, and 25g/L for slurry density provided the highest leaching efficiency of >80% of metals such as Li, Co, Mn, and Ni from black mass obtained from spent LCO batteries. We investigated the underlying mechanism of operation and found that according to the reducing sugars and antioxidants theory, our ABTS and DNS analysis revealed a significant increase and abundance of reducing sugars (0 to 2.8 g/L) as well as antioxidants (0 to 0.1 mM) in the OP containing leaching liquor compared to the control, which contained only citric acids. More importantly, OP has comparable reducing power to H_2O_2 at equal mass, implying that it has the potential to replace H_2O_2 as a future green reductant for the rapid extraction of valuable metals from spent LIBs. In addition to that, the environmental impact of the post-leaching solid waste was carefully evaluated for its cytotoxicity to several human cell lines. Finally, to develop a closed-loop process, the recovered metals were used to synthesize an LCO cathode and then produce a brand-new recycled LCO battery [84].

3.2.3 Food waste-derived reducing agents

3.2.3.1 Glucose

As previously stated, one of the proposed working principles for food waste is to use it as a reductant due to its abundance in cellulose and hemicellulose, which can be converted into reducing sugars such as glucose, xylose, arabinose, and others in an acidified solution at elevated temperatures.[91,92] Thus, it is conceivable for the direct application of food waste-derived reducing sugars for hydrometallurgical green recycling of spent LIBs. Indeed, Meng *et al.* reported using glucose as a reductant to facilitate metal extraction from mix-type spent

LIBs containing phosphoric acids.[85] They successfully recovered > 98% Co and ~ 100% Li using 1.5 M phosphoric acid, 0.02 M glucose at 80 ˚C for 2 h. Chen *et al.* [90] has also reported the optimal conditions for recovering 98% Co and 96% Li at glucose 0.4 g/g, 3 M sulfuric acids at 95 ˚C for 2 h, with a slurry density of 25 g/L. The presence of hydroxyl and aldehyde groups in the glucose molecule exerts the reducing power and partakes in the redox reaction with the Co^{3+} in the spent cathode materials. As a result, Co^{3+} is reduced to Co^{2+} and readily soluble in the leaching solution, while glucose is oxidized into various carboxylic acids. **Figure 6** shows a diagram of the possible oxidized products of metal leaching by glucose and phosphoric acid.[86]

3.2.3.2 Ethanol

Ethanol has been well researched over the years as an alternative transportation fuel for various vehicles. However, its ability to act as a reducing agent to facilitate metal extraction from spent LIBs has only been revealed recently. [96,97] Food waste, such as corn cobs, corn stalks, sugar cane waste, and rice straw, can be easily converted into ethanol via yeast-assisted fermentation and enzymatic reaction. [98] Various approaches for converting food waste into ethanol have been extensively reviewed elsewhere. [99] Recently, Zhao *et al.* reported a green hydrometallurgical process using ethanol as a reductant to extract nearly 100% of the Co and Li from spent LIBs employing 6 M H_2SO_4, 5 vol% ethanol, 90 ˚C, 80 min. [86] The author attributed the reducing power of ethanol to its hydroxyl groups, which were oxidized to carboxylic acid groups during the dissolution process of the spent LIBs. The redox reaction involved in this work can be expressed as follows (**Equation 8**)

$$4LiCoO_2 + 6H_2SO_4 + CH_3CH_2OH \rightarrow 2Li_2SO_4 + 4CoSO_4 + CH_3COOH + 7H_2O \quad \ldots.. (8)$$

In addition to the mechanistic understanding of the oxidation of ethanol, the authors further reported the best-fit kinetic model to explain the ethanol-enabled metal dissolution process.

The kinetic model, known as the residual layer diffusion control model, is expressed in (**Equation 9**).

$$1 - 3(1 - x)^{\frac{2}{3}} + 2(1 - x) = kt \quad .... \textbf{(9)}$$

Where x is the leaching efficiency, k is the slope of the fitted trendline, and t is the reaction time (min).

Using **Equation 9**, along with the Arrhenius law and the optimal leaching condition, the activation energy of Co and Li in the ethanol-containing leaching liquor was obtained and compared with the control where only H_2SO_4 was used. The author noted a significant decrease in activation energy for Co (54.22 to 37.60 kJ/mol) and Li (52.04 to 37.03 kJ/mol) by using ethanol as the reductant. The lower activation energy metal readily undergoes a redox reaction, where the marked decline in the activation energy for both metals further emphasizes the strong reducibility of ethanol. Although the complete extraction of Co and Li via the ethanol-based leaching method is remarkable, the potential environmental impacts incurred by the acetic acid waste (equation 8) generated during the leaching reaction have also been discussed. Thus, proper handling of the leaching-derived acid waste is entailed without causing environmental pollution.

3.3 Electrochemical approaches

Electrochemical methods are well-developed, cost-efficient, environment-friendly, and easy to scale-up, and have widespread applications in sensing, energy, mining, etc., including metal extraction/recovery from different sources by electrochemical means.[110-113] Electrochemical methods for metal recovery were first applied in the mining industry to selectively electrodeposit pure metals from their natural ores. [114] This technology soon attracted researchers who were developing sustainable methods to recycle spent waste to adopt this method for recycling spent LIB. [113] Specifically, electrochemical approaches have been employed in different hydrometallurgical recycling stages, such as leaching [115] and recovery [116] of valuable metals from spent LIB waste **(Figure 7).** In an electrochemically-assisted leaching process, the applied electric current acts as a "reducing agent" to improve the metal extraction (dissolution) from their insoluble form in spent LIB waste into a soluble ionic form in the acidic leaching solution. [115] Therefore, it replaces explosive and expensive chemical reducing agents such as hydrogen peroxide (H_2O_2), enabling the leaching process to be safer and more cost-efficient.

Moreover, applying an electrolysis process, mildly acidic solutions are prepared in a sustainable approach from broadly available sources, e.g., seawater. [117,118] A wide range of electrochemical methods have been exploited for metal recovery from leaching solutions or directly from a cathode active material (CAM). [119, 120] Metal electrodeposition offers quick, simple, selective, and efficient recovery of metals (or their compounds in their pure state) in a highly controllable approach. Moreover, by adjusting the electrodeposition parameters, electrodeposited metal properties such as thickness, morphology, and crystal structure can be easily controlled. [120] Therefore, due to their varying physical and chemical properties, electrochemically extracted metals/metal compounds or their mixtures may not only be used as precursors to regenerate LIBs [121] but to generate materials that have a variety of other applications such as electrochemical supercapacitors [122,123], superhydrophobic coatings [124], electrochromic compounds [125], magnetic alloys [120], etc. (**Figure 7**). Hence the materials from spent LIB e-waste can potentially be applied in various applications enhancing the sustainability of the LIB industry.

3.3.1 Electrochemically-assisted hydrometallurgical processes

In a typical LIB, the negative electrode (anode) and positive electrode (cathode) constitute more than half of the LIB composition (**Figure 8A**). [128] The majority of recyclable metals are present in the CAM. Depending on the LIB type, the constitution and variety of metals present in LIBs may vary among the following ones: Li, Co, Ni, Mn, Al, and

Fe (**Figure 8B**). Additional amounts of Al (from the cathode collector), Cu (from the anode collector), and Fe (from the casing material) could be found in spent LIB residue if the case material and current collectors were not separated during a pre-treatment stage (**Figure 8C**). After the pretreatment process of spent LIBs described in Section 2, the metal-containing black mass is subjected to an acidic solution to dissolve the metals in their ionic form in a standard hydrometallurgical process. The dissolved ions are then recovered either by precipitation in alkaline media [129] or separated by solvent extraction. [130] As the most efficient acids cannot fully leach metals, chemical reducing agents such as H_2O_2 are usually added into an acidic leaching solution to improve the metal leaching efficiency. [131] During a recovery stage, metal ions present in the leaching solution are separated by adding chemicals, namely either strong bases to raise the pH of the leaching solution for metal precipitation [129] or organic extractants in a solvent extraction method. [130] Even though chemical-based hydrometallurgy approaches can enable selective and effective metal recovery, they suffer from drawbacks such as large chemical consumption, tedious and complicated handling protocols, secondary pollution generation, and the high cost of recycling. The low-recycling profit accordingly impedes the development and scaling-up of a chemical-based hydrometallurgical method in the recycling industry. Electrochemical methods have recently attracted considerable attention for recycling metals from spent LIBs because of their environmental compatibility, high efficiency and adoptability, operation viability, and cost-effectiveness when electrons are employed as “green redox reagents“ instead of hazardous chemicals. The standard reduction potentials of metals (**Figure 8D**) [127] are critical for selective metal electrodeposition, as explained in Section 3.3.1.2.1.

3.3.1.1 Electrochemically-assisted leaching/leaching solution generation

Electrochemically-assisted redox reactions have been exploited to facilitate the metal leaching process without the addition of chemical reductants **(Table 5).** [115, 132] Specifically, during sulfuric acid (H_2SO_4) leaching, Prabaharan *et al.* applied a direct current of 400 A/m^2 between the Pb anode and the stainless-steel (SS) cathode and achieved 99 % leaching rates for Co and Mn from the mixed spent LIBs, as compared to the H_2SO_4 leaching without a reducing agent (between 50 % and 80 %). [115] The electrochemically-assisted leaching showed no improvement when compared to a chemical reducing agent such as H_2O_2 (close to 99 %) [133]. However, this approach allowed for the re-use of the leaching solution, significantly reducing the amount of chemicals used and secondary waste generated. [126] A few years later, Li *et al.* successfully employed slurry electrolysis to both leach and electrochemically recover Li and Mn from LMO batteries **(Table 5).** [115,132,] Furthermore, the electrolysis process has been employed as an alternative sustainable approach to generate acidic leaching solutions from low-cost resources such as NaCl, seawater, or weak brine solutions for leaching complex spent LIBs waste **(Table 5).** [117] Even though electrochemically-generated leaching solutions were used, metal leaching efficiency was significantly lower than using strong inorganic acids with chemical reductants, and the preliminary studies indicated the process to be economically feasible. It was primarily based on the value of recoverable Co and Li if the existing challenges are addressed accordingly. For instance, different spent LIBs pretreatment protocols could be applied to separate highly acid-consuming elements such as Al, thus sustaining stable acidic pH during the leaching procedure.

3.3.1.2 Metal recovery by electrochemical approaches

Selective metal recovery in their pure state is achieved by electrochemical methods, such as classical electrodeposition, electrolysis, electrodialysis, when potential or current (electrons) is applied to initiate non-spontaneous electrochemical reactions. [113] The most common electrochemical recovery method is metal electrodeposition (electrowinning) from their leaching solution *via* a reduction reaction where the dissolved metal ions are precipitated into their solid metallic form on a cathodic electrode. The electron supply through the circuit from the anode to a cathode is driven by an external electric source, and its magnitude is selected based on the standard reduction potentials of metals recovered **(Figure 8D).**

3.3.1.2.1 Metal compatibility in electrochemical recovery

It is important to emphasize that electrodeposition is not a straightforward recovery method for each metal. In particular, easier electrodeposition is achieved with metals of higher standard reduction potentials. From all the metals found in spent LIB waste (**Figure 8D**), only Li (E^0 = -3.05 V *vs* NHS) cannot simply be electrochemically deposited from aqueous solutions due to its strong negative potential. Therefore, Li is often either discarded as a waste [125, 134-136] or recovered last as Li_2CO_3 by chemical precipitation after other metals have been recovered electrochemically. [132, 121, 137] To recycle LIBs without any wastage of Li, Ra *et al.*[138] developed an electrochemical relithiation process *via* the combined electrochemical and hydrothermal reactions where LCO is regenerated in one step. Using this methodology, CAM can be regenerated either directly from the LCO slurry without leaching [138] or from a leaching solution **(Figure 7)**. [139] It can also be used to regenerate precursors for other types of LIBs, such as LFP [140] or LMO. [141] However, the above research shows that the regenerated CAM demonstrates significantly lower energy capacity than the initial cathode capacity.

Another important consideration in the electrochemical recovery of metal is the metal co-precipitation due to their similar standard reduction potentials, which results in impurities of the deposited metal layer. By considering the adequate difference among the standard reduction potentials of Cu (E^0 = + 0.34 V *vs* NHS), Co (E^0 = -0.28 V *vs* NHS), Fe (E^0 = -0.44 V *vs* NHS), Mn (E^0 = -1.18 V *vs* NHS) and Li (E^0 = -3.05 V *vs* NHS) (**Figure 8D**) [127], i.e. the metals found in LCO, LMO, LFP batteries or their mixtures, separation of the individual metals by electrodeposition is feasible without additional chemicals for removal/recovery for these types of LIBs. [115] However, a great challenge in the recovery of pure metals is encountered when NMC, NCA or mixed spent LIBs from various sources are being recycled. A CAM obtained from NMC, NCA, or their mixture contains Co (E^0 = -0.28 V *vs* NHS) and Ni (E^0 = -0.26 V *vs* NHS), which are not compatible with electrochemical recycling because of their similar standard reduction potentials. Different approaches have been utilized to recycle NMC and NCA batteries or LIBs mixtures. For instance, before electrodeposition, Lupi *et al.* [134, 135] recovered pure Co and Ni from mixed LIBs when the two metals were first separated by solvent extraction. Dutta *et al.* [133] carried out a much more delicate recycling approach where the leachate containing Co, Li, Mn, Cu, and Fe ions was subjected to chemical precipitation/solvent extraction to obtain a pure solution of Co for its electrodeposition. The combined separation methodology is pretty complicated as well as results in high consumption of chemicals and disposal of incompletely recycled (metal-containing) waste. Therefore, instead of recycling each metal separately, Mesbah *et al.* [122] exploited an alternative, a one-step electrodeposition approach of Li-Ni-Mn-Co hydroxide film for supercapacitor device applications.

3.3.1.2.2 Critical factors for metal electrodeposition

The most extensive fundamental and practical research in electrochemical recycling has been done using LCO type of LIBs **(Table 6)** [116, 119-122, 139-145] because it is the most common type of LIBs. It has the highest content of Co, which is the most valuable metal found in LIBs due to its global scarcity. [146] Among several research groups working on LIB recycling, the most considerable work on metal electrochemical recycling from spent LIBs has been done by Garcia's group. [116, 119-122, 139-145] Through fundamental studies on metal electrodeposition from different leaching solutions (**Table 6**), different research groups have proven that the metal electrodeposition efficiency and deposited metal/metal product physicochemical properties highly depend on different parameters, e.g. electrode materials [134,135,142], electrochemical method [116,119,134,135,143], electrolyte conditions (pH)/composition [115, 119, 120, 143,144], current density [119, 120], mass transfer. Therefore, it is essential to select suitable technical components and parameters as well as electrolyte properties to improve the deposition yield and properties of the deposited metal(s). Specifically, the key factors for selecting electrodes for metal recovery are electrode stability, current efficiency, and inertness towards side reactions on a cathodic electrode, such as a hydrogen evolution reaction. Prabaharan *et al.* [115] and Lupi *et al.* [135] have used SS and Al, respectively, as cathode materials, which provide a relatively high hydrogen overpotential, are made of low-cost material, and enable easy recovery of metallic Co deposit.

On the other hand, since an anode is electrochemically inert, electrodes such as Pb alloys and Ti/IrO_2 are widely used. [115, 135] Moreover, electrodeposition behavior is highly affected by technical parameters of the process, such as current density. For instance, higher microporosity of the Co layer was observed with an increase in current density. [120] The higher current density also results in slightly lower current efficiency since the current is partly involved in hydrogen evolution reaction instead of direct deposition reaction of a metal. Mass transfer is also known to have a significant impact on metal electrodeposition behavior, as proven previously. [147]

Besides the impact of technical components and parameters, electrolyte properties such as pH are critical for metal recovery. The electrodeposition studies of Co from different sources, e.g. LCO [120, 142] or mixed LIBs [115], clearly demonstrated that the Co deposition yield, deposition morphology, and crystalline structure are pH-dependent. The highest yield of the deposited Co, most intense 3D crystal growth, and largest grain size within the layer were observed at pH 5.4 in the investigated pH range of 2.7-5.4. Freitas *et al.* performed simultaneous electrochemical-quartz crystal microbalance (E-QCM) studies to elucidate the Co electrodeposition mechanism as a function of pH. [142-143] It was revealed that electrodeposition of Co at pH 5.4 occurred *via* a direct reduction mechanism (**Equation 10**). Whereas at pH 2.7, electrodeposition occurred *via* a mechanism of Co^{2+} reduction with the formation of adsorbed hydrogen (**Equation 11**):

$$Co^{2+} + 2e^{-} \rightarrow Co(s) \quad \ldots\ldots\ldots\ldots \textbf{(10)}$$

$$Co^{2+} + 2H_2O + 4e^{-} \rightarrow Co(s) + 2OH^{-} + H_2 \ldots\ldots\ldots \textbf{(11)}$$

The combined approach of E-QCM measurements was later employed to investigate Cu deposition mechanism from spent LIB anodes. [116]

3.3.2 Alternative applications of electrochemically recovered metal compounds

The ultimate purpose of a closed-loop recycling approach of spent LIBs is to recycle and directly reuse valuable metals for LIB regeneration (Section 5.1). [137-139] However, electrochemically-recovered metal compounds also have a great prospect to be exploited for different alternative applications. In 2012, Garcia's group pioneered the research on the possibility of using recycled metallic Co as a supercapacitor [144]. The specific capacitance determined from cyclic voltammetry and electrochemical impedance spectroscopy measurements showed a good agreement, yielding the value of 625 F/g. This shows that Co recycling from spent LIBs is economically and environmentally viable for application in supercapacitor devices. As mentioned in Section 3.3.1.2.1, a mixed hydroxide supercapacitor was electrochemically deposited from NMC batteries, in which the recycling procedure is, otherwise, complicated if the goal is to recover each metal individually. [122] Later, Garcia *et al.* proposed the application of recycled Co in interconnects for solid oxide fuel cells (SOFC). [145] Rafsanjani-Abbasi *et al.* [124] developed a new electrochemical Co recycling process fabricating low resistivity superhydrophobic Co coating on a carbon steel surface when using ascorbic acid-assisted H_2SO_4 leaching system.

Moreover, it was demonstrated that a Cu layer could be formed electrochemically on an electrodeposited Co layer, thus forming the Co-Cu bilayer. [119] Thin Co-Cu multilayers are of great interest due to their giant magnetoresistance that can be exploited in magnetic field sensors. [148] Mei *et al.* electrochemically recycled the spent LPO and LCO batteries to obtain high-performance hematite/CoPi photoanodes for water splitting application. [149] The possibility to recover a variety of metal products with well-controlled physicochemical properties for different applications is a crucial advantage of electrodeposition.

3.4 Ionic Liquids and Deep Eutectic Solvents

Ionic Liquids (ILs) are organic salts that consist of organic or inorganic cations and anions, usually in a liquid state below 100°C. They have been seen as replacement options for sustainable and environmentally friendly solvents because of their low volatility, vapor pressure, and flammability. [150] Moreover, ILs allow structural metal coordination like a potential template or a structure-directing agent in the formation of materials, thus enabling metal removal from spent LIBs. [151] For example, high-quality Cu-BTC (HKUST-1) synthesis was reported, using cholinium ionic liquids (ILs) in water at room temperature. [152] Guillaume *et al.* reported that lithium, cobalt, and nickel could be extracted from leaching solutions using imidazolium-based ionic liquids [C_4mim][NTf_2] as diluents and tri-n-butyl phosphate TBP as a specific ligand with a low pH ($pH < 3$). [153] Selective extraction of Mn, Co, Ni, and Li have been explored using ionic liquids by the same group. In the first step, more than 90% of Mn was selectively extracted from the leaching solution using N,N,N',N'-Tetra-n-octyldiglycolamide (TODGA) extractant diluted in an ionic liquid, followed by 90% cobalt extracted using an ionic liquid tri-hexyltetradecylphosphonium chloride in the second step. Nickel was removed by deep eutectic solvents (DESs) based on lidocaine and carboxylic acids, leaving Li in the solution to be recovered by precipitation. [154] Another study investigated the extraction of metals from spent LIBs using deep eutectic solvents and achieved a leaching efficiency of more than 90% of Co and Li from LCO and

NMC-based LIBs. [155] Another type of Ionic liquids, such as trihexyl(tetradecyl)phosphonium chloride (Cyphos IL 101) or tricaprylmethylammonium chloride (Aliquat 336), has been investigated to extract Ni specifically from nickel-metal hydride batteries. [156]

4. Regeneration of materials from spent LIBs

Spent LIBs consist of several components from packaging materials, current collectors (Al, Cu), electrolyte containing lithium salt and organic solvent, cathode containing various metals, anode (primarily carbon/graphite based), polymeric fluorinated and non-fluorinated binders, conductive carbon additives, polymeric separator sheets, external tabs (Ni/Fe), etc. It is generally accepted that among these various components, cathode material possesses a higher economic recovery value as compared to others. Hence presently, less attention is paid to the regeneration of other components of the spent LIBs except for cathode. However, the electrolytes‘ toxicity, fluorinated binders, limited Lithium metal reserves, and the extensive use of carbon-based materials would stimulate proactive, innovative thoughts on the proper recycling of other components of spent LIBs, including anodes and electrolytes from spent LIBs. [13] Other challenges are posed in extracting these components from spent LIBs; for example, recycling of LIB electrolytes reports are rare because the majority of the electrolyte is bound on the separator and active materials, making extraction and collection difficult. Moreover, the electrolyte components are volatile, flammable, and toxic that would require recycling and recovery to be performed in a confined, safe environment. Finally, the electrolyte components exist as complex, which include lithium salts, organic solvents, and additives, making their separation and purification challenging. Hence, current regeneration approaches are focused mainly on cathode materials from spent LIBs.

There have been strategies reported on selective metal recovery from green leaching processes, which we highlight in section 4.1. However, in current industrial recycling processes, selective separation of the associated individual components from the leach liquor is still a significant problem for cost-saving, technology innovation, and process enhancement. Regeneration technologies of battery materials could be one way to potentially address this problem wherein it regenerates battery materials by utilizing the co-existence and collaborative extraction characteristics of valuable metal ions in a complex system, resulting in a closed-loop therapy with significant development potential. Researchers have developed several high-value regeneration ways of valuable components, including technologies such as coprecipitation-calcination regeneration, sol-gel-calcination regeneration, hydrothermal-calcination regeneration, electrodeposition regeneration, solvent extraction regeneration, etc. [157-159] Among which the coprecipitation approach is widely employed in regenerating valuable components synergistically into a precipitate from the leachate liquor. However, there are challenges associated with regeneration technologies that still need to be researched and addressed, including the addition of an excess of complexing/precipitating agent and their further removal, unwanted ion adsorption, agglomeration, side reactions leading to loss of extracted elements.

4.1 Metal recovery from green leaching process

After the green leaching processes, the leach liquor consists of elements mainly from the cathode and current collector, including Li, Mn, Ni, Co, Al, Fe, Cu etc. Solvent extraction and chemical precipitation are commonly reported to recover specific metal ions or to eliminate other impurities from the aqueous leaching solution. Cyanex 272 (Bis-(2,4,4-trimethylpentyl) phosphinic acid) and PC-88A (2-ethylhexyl phosphoric acid mono-2-ethylhexyl ester) are widely used solvents to separate cobalt from the leach liquor solution, and D2EHPA (di-(2-ethylhexyl) phosphoric acid) can selectively extract Mn from the leaching liquor. Lithium (Li), on the other hand, is difficult to efficiently remove using solvents from a mixed-metal leaching solution [13]. Transition metal ions such as Ni, Co, Mn are also precipitated using the solubilities of metal compounds at different pH levels. The most common precipitating agents used are sodium hydroxide (NaOH), oxalic acid ($H_2C_2O_4$), ammonium oxalate [$(NH_4)_2C_2O_4$], sodium carbonate (Na_2CO_3), and sodium phosphate (Na_3PO_4). In most cases, they form insoluble transition metal precipitates such as hydroxides, carbonates, or oxalates, as well as lithium carbonate or phosphate. [13,157]

Generally, solvent extraction is employed in separating both nickel and cobalt ions because of their similar properties [160]. Other approaches such as electrodeposition have been reported to recover pure nickel from spent LIBs [161]. In this study, CYANEX 272 was used to separate nickel and cobalt via solvent extraction, while nickel was later recovered by electrodeposition. Nan *et al.* (2005) have reported the precipitation of cobalt as oxalate and lithium as carbonate, respectively, finally regenerating $LiCoO_2$ cathode material from the recovered cobalt and lithium [162]. Chen *et al.* (2011), has recovered cobalt using an oxalate precipitation agent [158]. Iron, manganese, and copper from the leached solution were separated by selective precipitation as follows : (i) iron removal by precipitation with sodium hydroxide (NaOH), (ii) manganese removal by ammonium persulfate $(NH_4)_2S_2O_8$, and iii) copper removal by NaOH. Using solvent extractant P507, cobalt, nickel, and lithium were separated from the leached solution, and cobalt was finally precipitated using ammonium oxalate. The interesting aspect of recycling LIBs is the regeneration of electrode materials for new LIBs. Sol−gel or coprecipitation technologies can be used in the leaching-resynthesis process for synthesizing the regenerated cathode materials in short steps. [162,163]. Lee & Rhee (2002) regenerated the $LiCoO_2$ cathode material through the sol-gel method using citric acid and lithium nitrate from spent LIBs. [163]

4.2 Regeneration of battery cathode materials

In the final loop of the regeneration and recovery process, cathode materials are re-synthesized from individual salts recovered from leachates or leaching solutions through green recycling and assembled into new LIBs. Various synthesis methods [164] of regeneration have been applied depending on the type of battery materials, as described in the section below.

4.2.1. Regeneration of NMC

Solid-state synthesis is the primary reported method for cathode material synthesis, with many optimization procedures in terms of stoichiometry, synthesis temperature to improve the performance of the cathode materials formed. As $LiNi_xMn_yCo_zO_2$ (NMC) has multiple formulas depending on the composition intended, there is no single optimized synthesis procedure capable of producing all NMC materials. In the NMC111 ($LiNi_{0.3}Mn_{0.3}Co_{0.3}O_2$) context, a stoichiometric ratio of metals (Ni:Mn:Co: Li = 1:1:1:3) was added/topped up in the leaching solution using their acetate salts of the three transition metals (Ni, Co, Mn) and Li_2CO_3. [165]. This process includes a pre-heating step at 350°C for 4 hours in air, followed by further heating at 500°C to 900°C for 12 hours in an ambient atmosphere to obtain phase pure NMC111 cathode material. Li-rich NMC materials have also been experimented and optimized, with synthesis methods ranging from solid-state to solution synthesis [166]. In a hydrothermal synthesis, the leaching solution from the green recycling process is mixed with 4 M LiOH solution and heated at (120 °C- 200 °C) in a reactor followed by sintered with 5% Li_2CO_3 in an oxygen environment at 850 °C for 4 hours. [166] The sol-gel method can also be employed to synthesis Li-NMC cathode material by using citric acid as a chelating agent. However, when compared to solid-state and hydrothermal procedures, the operating process of this approach is more complex, and the preparation time is longer.[167] Different compositions of NMC have been synthesized when a different synthesis method is explored. Thus, for NMC materials, the selection and control of the composition of NMC ratio are critical for choosing the synthesis methods.

4.2.2. Regeneration of $LiCoO_2$

In the bid to re-synthesize LCO cathode materials from leached elements, the most common methods are via solid-state synthesis or hydrothermal synthesis. Solid-state synthesis of LCO cathode involves mixing the leach solution, which contains Li_2CO_3 and $CoCO_3$, and heating in a furnace in ambient atmosphere at 600ºC for 3 hours, followed by calcination at 900°C for 1 hour [168,169]. This process is suitable for recovering Li_2CO_3 and $CoCO_3$ from the leachates without the addition of the respective salts. Alternatively, hydrothermal synthesis has also been shown to be feasible for synthesizing pure $LiCoO_2$ material with a high success rate. Pure $LiCoO_2$ material can be synthesized by adding $Co(OH)_2$ and LiOH in the stoichiometric amount in deionized water and heating at 220°C in a hydrothermal autoclave [170]. Some of the less-explored synthesis methods reported for LCO include (1) the addition of $Co\ (NO_3)_2$, $LiNO_3$ in polyacrylic acid (PAA) and spin coating in a sol-gel synthesis process, (2) microwave synthesis of Co- and Li-methyl carboxylate salts and (3) molten salt synthesis of $Co(NO_3)_2$ and $LiNO_3$ with KOH and calcination in 650ºC for 8 hours in air were also explored in the synthesis of LCO cathode [171, 172,173].

4.2.3. Regeneration of $LiFePO_4$

Synthesizing $LiFePO_4$ using solid-state reaction is feasible, with a strict requirement of an inert synthesis atmosphere. The rationale is to prevent the oxidation and formation of Fe_2O_3, which is inevitable if calcination is conducted in the presence of O_2 gas in the air. By introducing an inert gas such as Ar, the calcination of $FePO_4$, Li_2CO_3 with a reducing agent (sugar) is feasible for the formation of $LiFePO_4$ materials [174]. In this same atmosphere, FeC_2O_4 as the iron source could also be utilized for the solid-state synthesis of $LiFePO_4$, with a prior step involving ball-milling of FeC_2O_4 and Li_2CO_3, calcination at 350°C for 10 hours, and then at 600°C for 10 hours [175]. The alternative method for synthesizing $LiFePO_4$ includes hydrothermal process using $FeSO_4$, LiOH, and H_3PO_4 in deionized water, where the solution needs to be heated in an autoclave at T=150°C = ~ 220°C (optimum temperature at 180°C) for 5 hours [176]. Carbon-thermal reduction process can also be used to regenerate $LiFePO_4$. In this method, a $FePO_4 . 2H_2O$ precursor was produced from the leaching solution by heat treatment, which was then calcined with Li_2CO_3 and glucose in N_2 environment to produce $LiFePO_4$/C. Overall, LiFePO4 regenerated via carbon-thermal reduction has superior electrochemical performances than regenerated via solid-state reaction. [164,177]

5. Reusability

The construction of new batteries from the regenerated electrode materials is the final step in the LIB recycling process. Commonly, coin cells or cylindrical cells are made from regenerated electrode material, and electrochemical performance such as charging, discharging capacity, and cycling stability tests are used to be performed. This section has discussed the reusability of leached and regenerated using various green recycling processes as potential cathode and anode materials in new LIBs constructed.

5.1 Reusability of cathode materials from green recycling process

Jai Kumar et al. recovered lithium as $LiCO_3$, and $FePO_4$ from $LiFePO_4$-based spent LIBs using citrus juices from lemon, orange, and apple, that contained organic acid. The recovered materials were then used to regenerate $LiFePO_4$ cathode, yielding a discharged capacity of 155.3 mAh/g and a capacity retention of 98.30 % over 100 cycles at 1C. [178] In another study, NMC cathode material was resynthesized from ascorbic acid leaching solution using oxalic acid co-precipitation method, followed by a hydrothermal and calcination process. The resynthesized sample had a charge capacity of 345.8 mAh/g and a discharge capacity of

258.8 mAh/g at 0.1C, and the capacity retention was 87% after 50 cycles. [179] Oxalic acid was used as leaching as well as a co-precipitation agent in another research to regenerate NCM cathode material through the calcination process. At 0.2C, the highest discharge capacity was 168 mAh/g, with a 91.5% capacity retention after 150 cycles. [180] Wu et al. extracted $LiCoO_2$ from LIB scraps using citric acid as a lixiviant and orange peel as a reductant to regenerate new cathode material. The regenerated cathode material's initial charge and discharge capacities were 120 and 103 mAh/g, respectively. [84] Ra et al. developed an electrochemical relithiation process in which LCO was produced in one step directly from slurry using a combination of electrochemical and hydrothermal reactions, allowing them to recycle and regenerate LCO without losing Lithium. The regenerated cathode active material (CAM) LCO battery had an initial discharge capacity of 134.8 mAh/g, with 95.9% retention after 50 cycles. [138] A CAM of LCO battery was regenerated from a leaching solution following the above methodology, and the regenerated LIB had a discharge capacity of 127 mAh/g and retained 96 % of its capacity after 30 cycles. [139] Another study found that refunctionalization of the $LiFePO_4$ cathode using electrochemical lithiation restored its original capacity of 150–155 mAh/g. [140]

5.2 Reusability of graphite from green recycling process

Graphite is used as an anode material in most commercial LIBs due to its long-term cycle stability, high capacity, better electrical conductivity, and superior thermal and mechanical stability. [181] Recycling graphite from LIB leaching residue is an exciting idea towards a cost-effective closed-cycle circular economy approach. Generally, residual cathode materials, and elemental Cu, Fe, Al, and other contaminants, can be found in the leaching residue. [182] Commonly, oxidative lixiviation using acids and other solvents can be used to remove impurities including Al, Cu, and Fe, whereas reductive lixiviation can be used to remove remaining cathode metals from the recycled graphite powders. [183]

Recently organic acid such as citric acid has been used to regenerate graphite from the spent anode. The optimal condition for impurity elimination from spent graphite was found to be 0.2 M citric acid at a pulp density of 20 g/L at 90 °C for 50 minutes. Spent graphite regenerated using citric acid had a discharge cell capacity of 330 mAh/g after 80 cycles. [184] Boric acid pre-treatment followed by a short annealing process has also been used to regenerate graphite from spent LIBs. The capacity of graphite pre-treated with boric acid and sintered at 1050 °C was 332 mAh/g, which remained unchanged after 100 cycles. [185] Our group has recycled graphite from bioleaching residue using citric acid. The recycled graphite had a discharging capacity of 320 mAh/g and is stable for more than 100 cycles. [186]. Such approaches are promising towards the direction of reuse of recycled graphite as a LIB anode.

5.3 Reusability as Metal-Organic Frameworks (MOFs)

The precipitation of leached metals recovered from spent LIBs into highly valuable Metal-Organic Frameworks (MOFs) opens up a new application possibility for these recovered, recycled metals.[187,188] Metal-Organic Frameworks (MOFs) are porous materials constructed from metals and organic linkers.[189] They are characterized by their high porosity, high thermal and chemical stability, which allows them to succeed in diverse applications such as gas separation, gas storage, or catalysis. [190] Moreover, MOFs have raised researchers' interest in their usage in electrochemical energy storage systems such as batteries. [191, 192] Developing MOF-based batteries through the recycling of LIBs will lead to a close-loop and reduce the environmental and ecological impact. Instead of separating individual metals to create a valuable, cost-effective method for making LIBs, it is also advantageous to develop an alternative route for higher-value products such as MOFs that could be produced from waste LIBs in a few steps.

One of the most significant concerns about MOFs in practical applications is the difficulty in obtaining such materials in large quantities. Spent LIBs provide an alternative source. To optimize the synthesis of MOFs for a greener approach, it is advisable to identify the key parameters that can influence material production, such as reagents, solvents, and synthesis methods. During the formation of MOFs, transition metals (such as nickel, manganese, and cobalt) extracted through the recycling of LIBs must form strong bonds with carboxylic acid ligands such as trimesic acid (BTC) or terephthalic acid (BDC). The solvent can be replaced with a greener one in the MOFs synthesis with similar properties of dissolving metals and organic ligands, while the temperature and reaction time are two critical factors affecting the MOF synthesis process from spent LIBs.

MOFs are synthesized from metal ions and organic linkers using conventional methods such as hydrothermal or solvothermal processes.[193] MOF with NMC (111) can be synthesized from a battery waste leaching solution [194] by solvothermal process and used as electrode materials. [195,196] The electrochemical properties of this MOF, as well as the corresponding reduced and oxidized materials, have revealed that they have exciting properties for use in battery materials. Recently, a novel method for producing MOFs from a real waste stream was reported. [197] Typically, a hydrothermal method was used to fabricate MOFs on a large scale in the regeneration process. [193] Initially, the spent LIBs were crushed into powder, while the metals were extracted in acidic solution, followed by the addition of an organic ligand and solvent into the metal leaching solution at a low thermal process. Using this procedure, a different form of MOFs can be synthesized by changing the experimental conditions. The presence of metals such as Al and Cu in the leached solution produced MOF (MIL-96, HKUST-1) with these metals as the centres. By fine-tuning the procedure, it was possible to selectively precipitate all Al and Cu in solution, producing a hybrid material with high porosity (around 700 m2.g-1 for MOF MIL-96). Moreover, it has been demonstrated that another Al-MOF known as MIL-53 can be obtained by using a different precipitating agent (BDC ligand), where these porous materials can be useful for other applications such as gas storage or separation. In order to accelerate the crystallization process and fabricate uniform crystals of MOFs, many alternative synthesis routes such as microwave-assisted, electrochemical, mechanochemical, Sonochemical, and spray drying have been reported in the literature. [198-200] For example, microwave-assisted synthesis is comparable to hydrothermal or solvothermal synthesis and can achieve similar materials and yields in different batches. Microwave-assisted MOF synthesis can be an alternative green approach that controls reaction temperature and time. Indeed, this waste-to-MOFs approach for greener MOFs synthesis is of interest for obtaining high value-added products on a large scale and potentially achieving an economically viable LIB recycling process through an open-loop cycle.

MOFs made up of metals from connectors are unsuitable for use as electrode materials. Other battery wastes where Al and Cu have been removed (mechanically) can be of interest for forming MOFs that can be reused as new electrode materials based on Co, Ni, and/or Mn. This should be investigated in the near future to validate such a process and create a closed-loop cycle with electroactive MOF precipitation. Upscaling of MOF synthesis usually encounters difficulties due to the longer reaction times, a large amount of solvents used, the low quality of obtained materials, the difficulty in ensuring reproducibility between batches, and the cost.

5.4 Waste combination

Green approaches in the synthetic route for MOFs are essential for using these materials in industrial applications. [201] Recently, a synthetic process has been developed for both the organic linker and metal centers based on only waste sources. [202] The process utilized Polyethylene terephthalate (PET) waste bottles as a source for organic ligand and LIB waste for metal source. The release of BDC ligand in solution is caused by the depolymerization of PET waste under alkaline conditions. Combining the two waste stream flows made it possible to obtain MOF MIL-53 in large quantities from waste materials with properties similar to the MOF synthesized from commercial chemicals. The above research work paves the way for an integrated solution for solid waste utilization concerning efficient process design, low-cost materials, and highly pure and porous synthesized materials. It demonstrates how different waste streams can be combined to lay the foundation for an integrated circular economy through various waste recycling processes (for batteries and plastics).

6. Conclusion and prospects

6.1 Bioleaching for battery recycling

The factors affecting the bioleaching process of LIBs are slow kinetics, microbial tolerance against metal toxicity, acidic environment, and low solid-liquid ratio (pulp density). [64] The limitations of the bioleaching process in large-scale industrial applications are the poor adaptability of microbes and rigorous leaching conditions. However, spent LIBs are the secondary source of metals, and their content is higher than the natural ores; for example, in order to extract one ton of lithium, around 750 tons of brine salts are needed, but only 28 tons of spent LIBs are sufficient. The difficulties in the bioleaching process can be accomplished by adapting the microbes to the toxic environment using microbial consortia and the addition of metal ions such as Ag^+ and Cu^{2+} to increase the kinetics using the omics approaches to modify the microorganisms. The microbial competencies, such as tolerance against metal toxicity and acidic environment, as well as increasing the metabolites production, can be achieved by genetically modifying the organism. [70, 76] The success of LIB bioleaching in a large-scale recycling process depends on the ability of microbes to tolerate toxic metals, cultivate microbes using low-cost nutrients, and optimize process kinetics. At a high solid content of 100 g/L (S/L), a leaching efficiency of 80–90% was obtained using the bioleaching process recently, which is an excellent indicator for the applicability of bioleaching for commercial recycling of spent LIBs in the coming years. [62-64] It is feasible to optimize all conceivable parameters which affect leaching efficiency in lab-scale bioleaching experiments. However, environmental factors such as humidity and outdoor temperature (sunlight) may play a crucial role when scaling up the bioleaching process at an industrial scale. Optimal humidity conditions favor and grow bacteria and transport nutrients, so it is necessary to evaluate humidity over time vs microbial growth vs bioleaching efficiency. [203] Temperature is another critical factor influencing microbial activity and, accordingly, metal bioleaching. The ideal temperature for bioleaching is the one that favors metal dissolving the most, which is also linked to bacterial activity throughout the metal extraction process. [204] A temperature control system is necessary when performing the LIB bioleaching at the factory scale. Conducting a life-cycle assessment is the best way for LIB bioleaching when scaling up the process. This method compiles and assesses the inputs, outputs, and potential environmental implications of a commercial production system. [205] By overcoming the challenges such as slow kinetics, microbial tolerance against metal toxicity, and high solid-liquid ratio (pulp density) in the bioleaching process, valuable metals can be recovered from the spent LIBs in an eco-friendly and energy-efficient way.

6.2 Food waste enabled battery recycling

Recent discoveries on food waste-based hydrometallurgical approaches have greatly expanded the list of available green reductants to recycle spent LIBs. Compared to the traditional hydrometallurgical methods whose success hinges on synthetic reductants such as H_2O_2, $NaHSO_3$ and NaS_2O_3, the use of food waste confers a safer and low-cost route to efficiently recover the precious metals like Co, Li, Mn, and Ni from the discarded cathodes. More importantly, the leaching efficiency for different metals is shown to reach an appreciable range (80-100%) using these green reductants, indicating their feasibility for replacing the conventional reducing chemicals. The mechanism of action for different kinds of food waste and its derivatives has been extensively studied. The consensus seems to be reached according to the data from different articles, and the theory of conversion of cellulose and hemicellulose, two significant parts of food waste, to reducing sugars has been proposed and tentatively verified. In addition, it is also believed that antioxidants like polyphenols also assist with the metal extraction process.

Treatment of post-processing of food waste-derived residues after metal leaching is an open technical issue that needs to be addressed in the coming years. These residues are rich in carbon and other valuable nutrients, such as nitrogen-containing organic molecules, which can be recovered and efficiently used again. However, the most common procedure for post-treatment of food waste residues is dewatering, which eliminates the moisture content, followed by disposal in landfills, which results in significant loss of valuable ingredients. [206] To reuse nitrogen-containing substances, scientists have begun to use microbes to stabilize the N-based nutrients, which are then used for soil enrichment and crop growth enhancement. The utilization of carbon compounds in food waste-derived residues, on the other hand, has received far less attention.

Future research is required in the era of the circular economy to develop a sustainable approach to commodify these carbon-rich waste products. Turning them into high-performance carbonic anodes is one strategy to upcycle them. [207] After all, using food waste as a next-generation green reductant will indeed surpass currently used chemical reductants. As the world's food waste and battery waste stockpiles are rising, an intelligent method that can examine both forms of trash in one place is essential. Considering the real-life LIBs recycling business dealing with ton-scale battery waste, it is necessary to find a way to translate the current findings in the laboratories to a realistic industrial recycling viable process. Fortunately, the recent works provide detailed experimental data on the laboratory scale and an in-depth mechanistic understanding of the food waste-based reductants approach, which is believed to lay a solid foundation for future attempts to upscale this green process.

6.3 Electrochemical battery recycling

Metal recovery by electrochemical technology is selective, efficient, and eco-friendly in nature and becoming an attractive alternative approach in developing sustainable recycling of LIBs. Due to its ability to improve processes in different stages of hydrometallurgy, i.e. leaching and recovery, in terms of time, product yield without adding additional chemicals, as well as using straightforward equipment, facilitates the metal recovery towards a faster and more efficient process while reducing the amount of secondary waste. Moreover, electrodeposition enables the possibility to tune physicochemical properties of recovered metal products during a deposition process, thus widening possibilities for their different applications. However, to advance the technology towards a more practical and scalable direction, the recovery procedures must be further improved to regenerate LIBs from the spent mixed batteries for their second life in a straightforward approach. Among the directions to improve are: (i) improvement of an electrochemical cell design and electrode material, development protocols for low-cost electrolytes, (iii) improvement of an operational process such as rotation for better ion transport.

6.4 Reusability of battery waste

Several pre-treatment and synthetic processes can be used to regenerate cathode materials such as $LiNi_xCo_yMn_zO_2$ (NMC), $LiCoO_2$ (LCO), and $LiFePO_4$ (LFP) from spent LIBs. As compared to commercial electrodes with exact stoichiometry, the regenerated cathode materials show similar initial cell performance. Long-term performance is a deeper, in-depth studies on the electrochemical behaviour of these regenerated electrodes in new LIBs that need to be studied. The cost of regenerating these cathode materials from spent batteries is significantly lower than the cost of preparing them from primary resources. Though the approach is promising, it still has some drawbacks and challenges that make it challenging to implement regeneration strategies in practice. During the regeneration process, the impurities Al, Cu, and Fe should be tightly controlled under the threshold level. As a result, additional treatment is often needed to eliminate impurity elements to enhance the performance of cathode materials. The regeneration of graphite from spent LIBs has been offered as a viable solution for meeting the anticipated demand for battery-grade graphite. However, a number of challenges and issues must be addressed based on available information and projected future growth in recovering battery-grade graphite. There should be a strategy for increasing the capacity of the graphite electrode while limiting irreversible capacity and graphite deterioration.

Although MOFs synthesis has been scaled up for industrialization, further research needs to be done on optimizing the synthesis parameters to control MOFs' properties to obtain a viable and marketable material. Indeed, the water-stability, quality, functionality, financial viability, and environmental-friendly production are essential for MOF synthesis. Therefore, the further development of the green synthesis method of MOFs is necessary for a future sustainable environment, and the focus is on recovering metals as MOFs and their reuse in a closed loop. This review highlights the need for a sustainable, cost-effective, and large-scale production of MOFs. In this perspective, the new approach for MOF synthesis can be from waste linker sources (e.g., plastic wastes) using greener solvents (e.g., water, bio-derived compounds) under milder ambient conditions. The main challenge is to create the best system that works in all conditions and allows metals and ligand solubility in a scalable manner.

Green Recycling methods of lithium-ion batteries is a step forward in a sustainable direction towards the circular economy, but this area is still in its infancy. Studies, as reviewed in this report, suggest promising results employing green recycling methods for spent LIBs; however, at this point, based on the studies performed, it is difficult to conclude which among the green recycling process is ideal for the future. Every recycling technique has its own set of benefits and drawbacks, as discussed and highlighted. Moving forward, detailed economic, cost-benefit analysis studies on the green recycling process needs to be conducted to provide the economic benefits of these processes at an industrial scale. When it comes to the sustainability of recyclable materials, lifecycle assessment (LCA) is the framework for examining, identifying, and evaluating the energy, material, and environmental implications of these green recycling processes, products and/or systems across its lifespan from the cradle to the grave. This method compiles and evaluates a commercial production system's inputs, outputs, and potential environmental consequences. The variables of efficiency, economy, and environment should all be examined and balanced while systematically analysing a particular green recycling technique with LCA. A reinterpretation of the ‘‘reduce, reuse, refurbish, and recycle" strategy as ‘‘redesign, reuse, recycle" for battery recycling is recommended based on current practice and projected future progress in this field. [3,13]

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Notes

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Figures

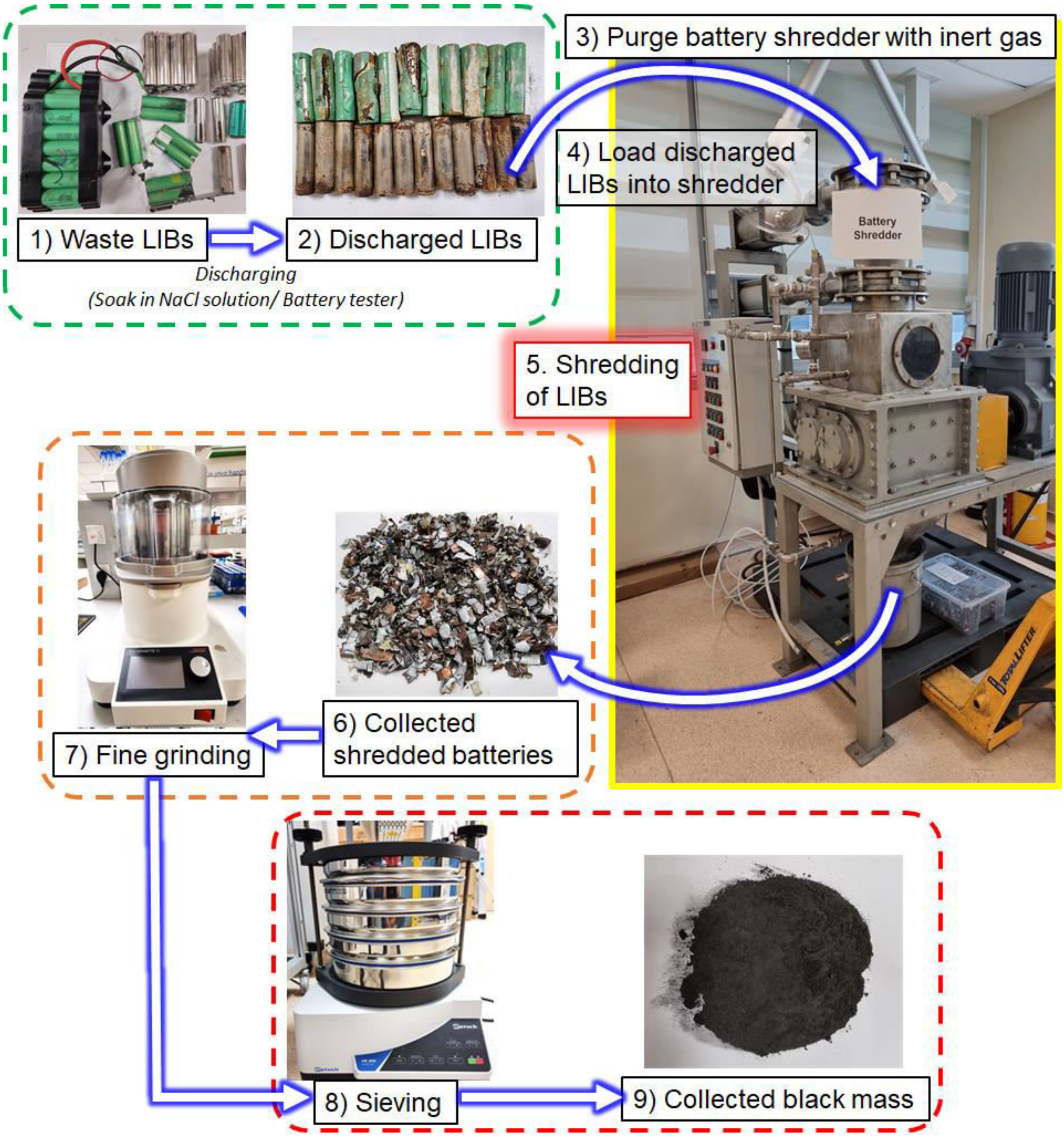

Figure 1: Process flow diagram of pre-treatment.

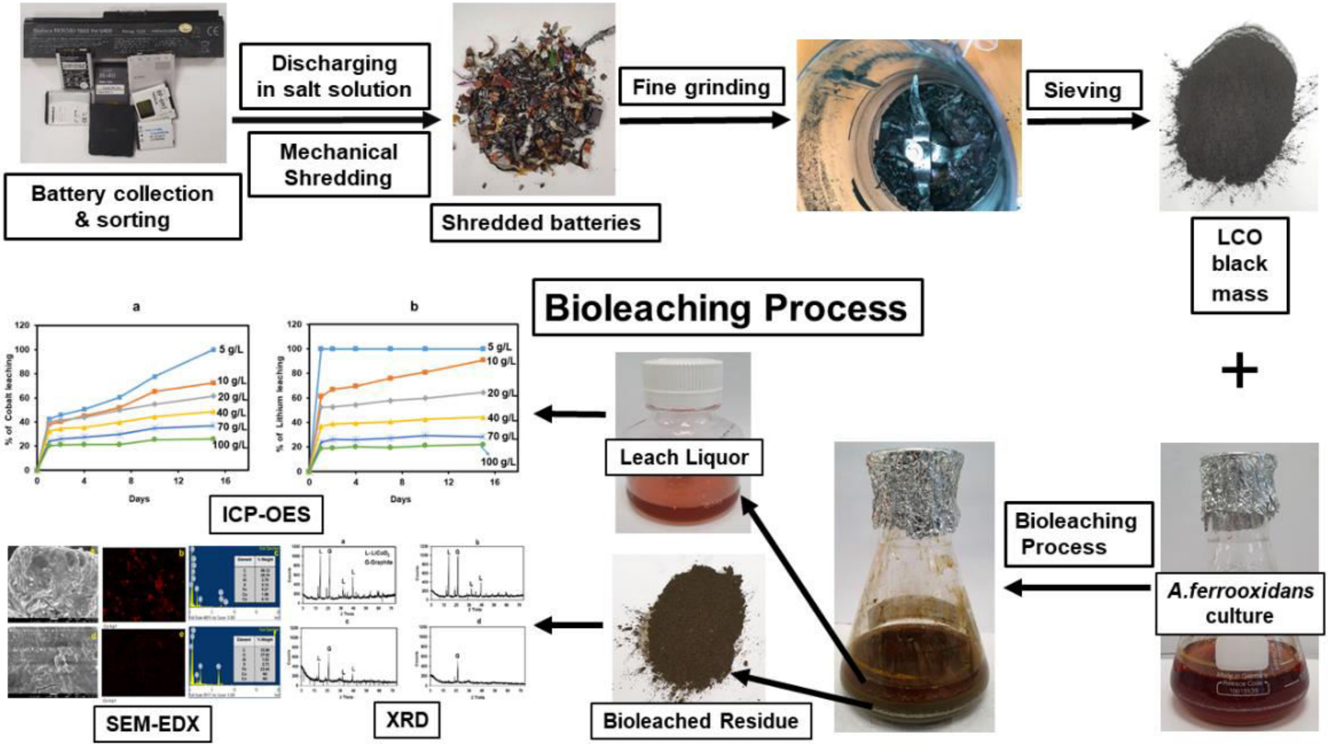

Figure 2: Typical bioleaching process , Reproduced with permission [62] Copyright 2021, Elsevier

Figure 3: An illustration representing various food waste employed in the recent progress on the food-waste enabled waste for waste (W4W) approaches for recycling spent LIBs. A) Tea Leaf B) Orange peel c) Grape seed D) Macadamia shell E) Corn cop

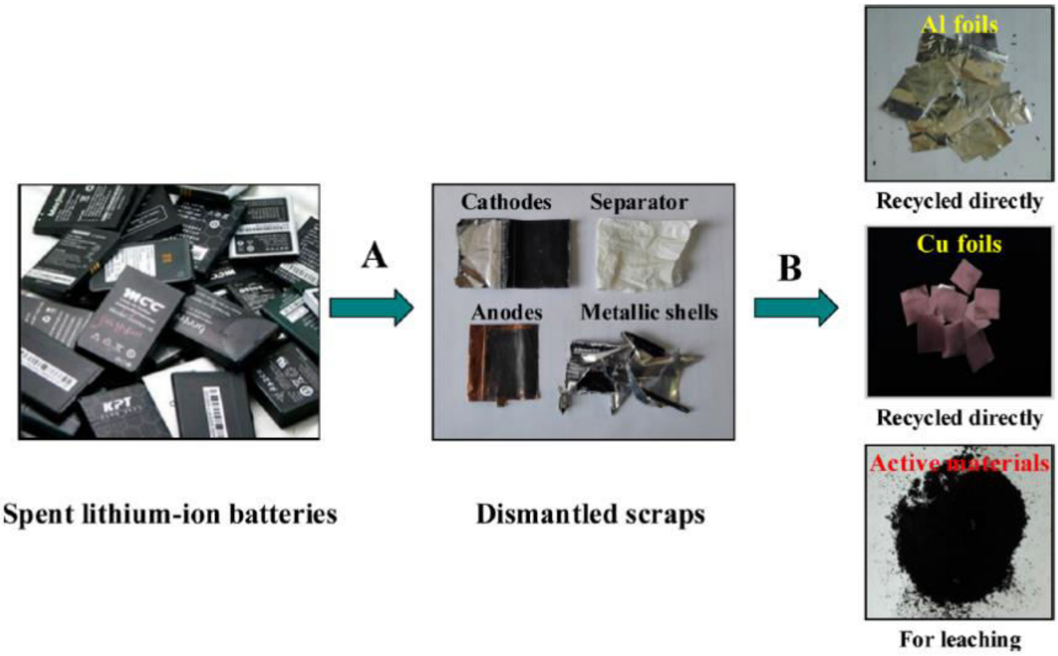

Figure 4: Mechanical processing of spent LIBs prior to leaching experiments.

A. Manual dismantling B. Peeling of Al/Cu foils for their direct recycling

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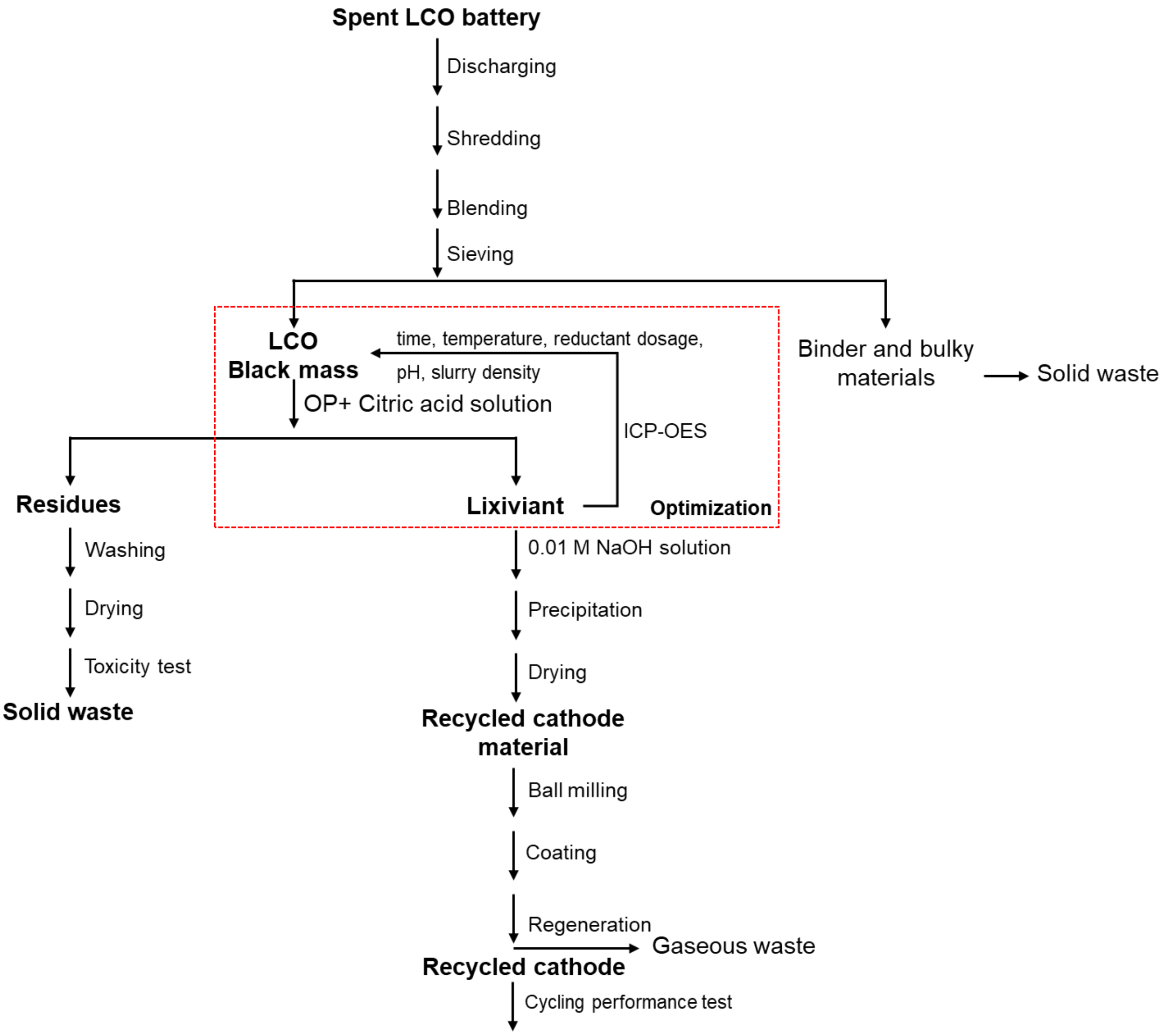


Figure 5: **An overview of the orange peel (OP)-based green hydrometallurgical process for the recycling of spent LIBs.** Reproduced with permission [84] . Copyright (2020), American Chemical Society

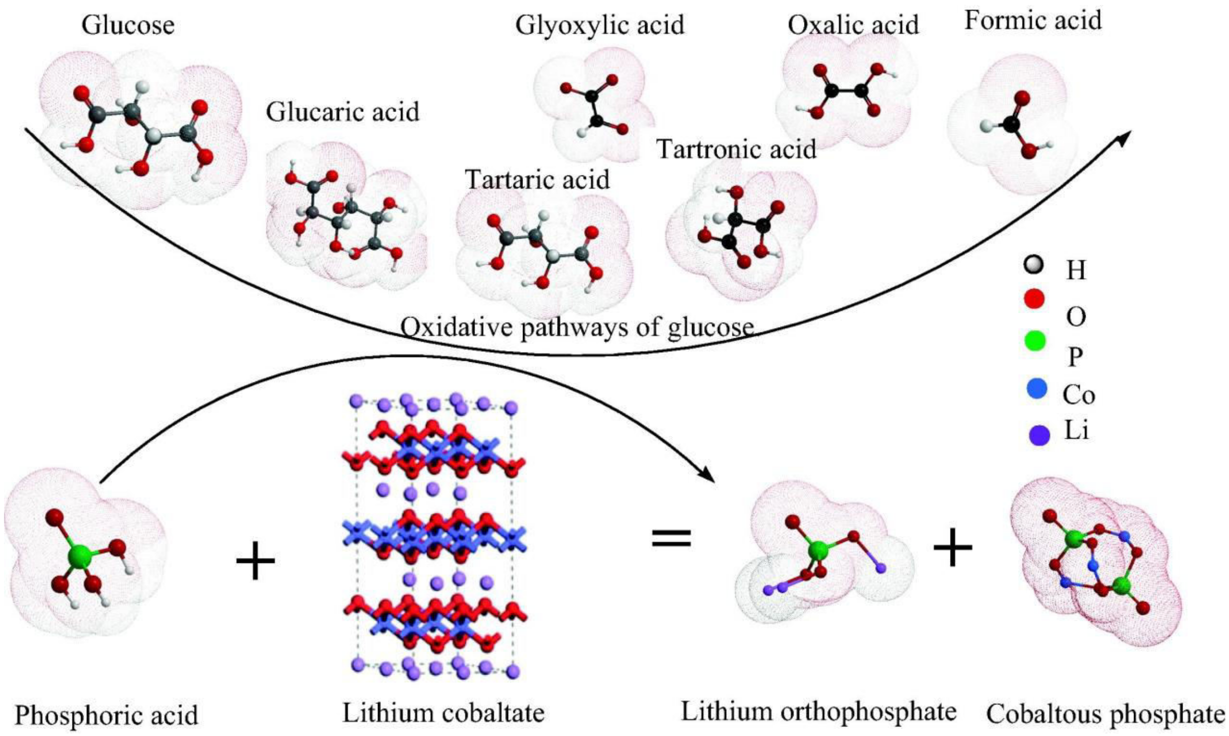


Figure 6: A possible leaching process of $LiCoO_2$ material in the glucose and phosphoric acid solution. Reproduced with permission [85] Copyright (2017), Elsevier.

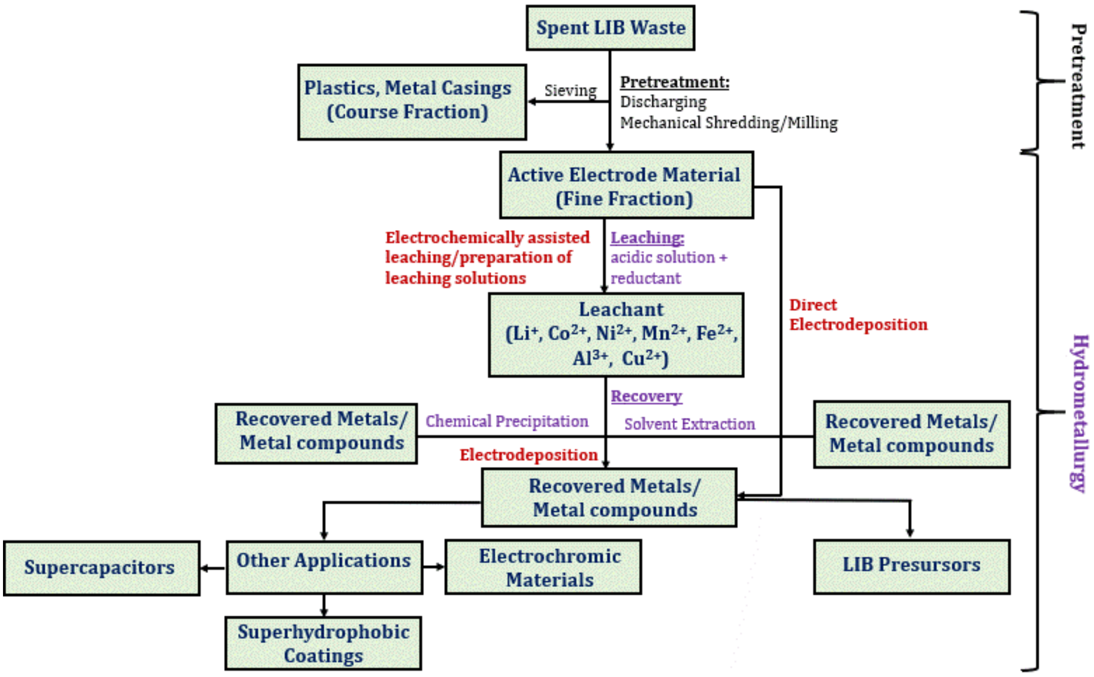
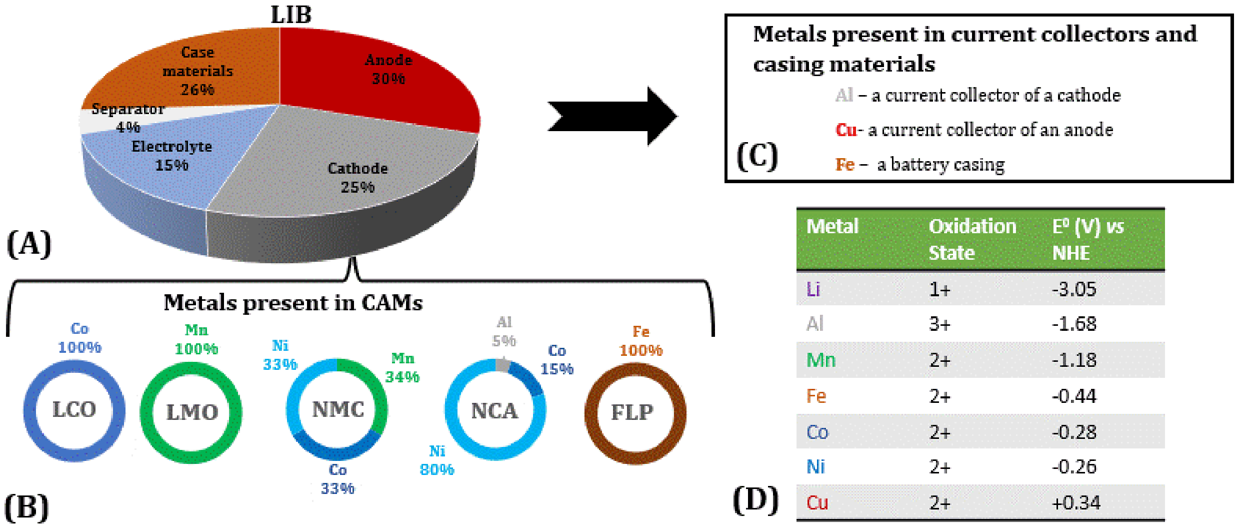


Figure 7: Flowchart of a hydrometallurgy recycling process of spent LIB waste, where the purple colour marks the commonly used processes, whereas the red colour indicates electrochemically assisted approaches.



Metals present in current collectors and casing materials

Al – a current collector of a cathode

Cu- a current collector of an anode

Fe – a battery casing

Metal	Oxidation State	E⁰ (V) vs NHE
Li	1+	-3.05
Al	3+	-1.68
Mn	2+	-1.18
Fe	2+	-0.44
Co	2+	-0.28
Ni	2+	-0.26
Cu	2+	+0.34

Figure 8: (A) Composition of a typical LIB; (B) Metals present in different types of CAMs (Li is not shown); (C) Metals present in current collectors and casing materials; (D) Standard reduction potentials of metals present in spent LIB waste.

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Tables

Table 1: Battery Recycling methods' advantages and disadvantages.

Recycling Method	Advantages	Disadvantages	References
Pyrometallurgy	Applicable to all battery types and configuration After sorting no other mechanical pre-treatment necessary High recovery of metals (e.g., Co, Ni, and Cu)	Cannot recycle/ treat Li, Al, and LFP batteries Gas clean-up is required to avoid toxic air emissions Energy and Capital intensive	15
Hydrometallurgy	Applicable to any battery chemistry Flexible in recovery processes to target specific metals High recovery rates and High purity can be achieved Energy and capital efficient Retains valuable cathode structure	Battery cells must be crushed (causing safety concerns) Cathode structure defects because of Acid treatment High volume of process efficient to be treated and recycled or disposed Not economical for lithium iron phosphate (LFP) batteries	16
Direct recycling	Practically all battery materials can be recovered, including anode, electrolyte, and foils Suitable for LFP batteries Energy efficient Convenient for recycling manufacturing scraps	Complex mechanical pre-treatment and separations are required Recovered material may not perform as well as virgin material or becomes obsolete by the time it is introduced to market Mixing cathode materials could reduce the value of recycled product Regeneration processes yet to be developed Not scaled up to industrial level	17

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Table 2: Physio-electro properties of lithium-ion batteries and types

Types of Li-ion batteries	Cathode	Anode	Nominal Voltages	Typical operating range	Specific energy (capacity)	Charge (C-rate)	Discharge (C-rate)	Cycle life	References
Lithium Cobalt Oxide (LCo)	$LiCoO_2$ (~60% Co	graphite	3.60V	3.0–4.2V/cell	150–200Wh/kg	0.7–1C, charges to 4.20V (most cells); 3h charge typical. Charge current above 1C shortens battery life.	1C; 2.50V cut off. Discharge current above 1C shortens battery life	500–1000, related to depth of discharge, load, temperature	22,25
Lithium Manganese Oxide (LMO)	$LiMn_2O_4$	graphite	3.70V-3.80V	3.0–4.2V/cell	100–150Wh/kg	0.7–1C typical, 3C maximum, charges to 4.20V (most cells)	1C; 10C possible with some cells, 30C pulse (5s), 2.50V cut-off	300–700 (related to depth of discharge, temperature)	22,25
Lithium Nickel Manganese Cobalt Oxide (NMC)	$LiNiMnCoO_2$	graphite	3.60V-3.70V	3.0–4.2V/cell, or higher	150–220Wh/kg	0.7–1C, charges to 4.20V, some go to 4.30V; 3h charge typical. Charge current above 1C shortens battery life.	1C; 2C possible on some cells; 2.50V cut-off	1000–2000 (related to depth of discharge, temperature)	22,55
Lithium Iron Phosphate (LFP)	$LiFePO_4$	graphite	3.20-3.30V	2.5–3.65V/cell	90–120Wh/kg	1C typical, charges to 3.65V; 3h charge time typical	1C, 25C on some cells; 40A pulse (2s); 2.50V cut-off (lower that 2V causes damage)	2000 and higher (related to depth of discharge, temperature)	22,25
Lithium Nickel Cobalt Aluminum Oxide (NCA)	$LiNiCoAlO_2$ (~9% Co),	graphite	3.60V	3.0–4.2V/cell	200-260Wh/kg 300Wh/kg predictable	0.7C, charges to 4.20V (most cells), 3h charge typical, fast charge possible with some cells	1C typical; 3.00V cut-off; high discharge rate shortens battery life	500 (related to depth of discharge, temp.)	22,55
Lithium Titanate (LTO)	lithium manganese oxide	Li_2TiO_3 (titanate)	2.40V	1.8–2.85V/cell	50–80Wh/kg	1C typical; 5C maximum, charges to 2.85V	10C possible, 30C 5s pulse; 1.80V cut-off on LCO/LTO	3,000–7,000	22,55

Table 3: Microorganisms used in the bioleaching of LIBs.

S. No	Organism Name	Single/ consortia	Nutrient Media	Temp & pH	Pulp Density w/v	Bioleaching Efficiency %	Reference
Bacteria used in the bioleaching of LIBs							
1.	*Acidithiobacillus Thiooxidans (80191)*	Single	Basel 317 + S power 1%	30°C / pH 3.3 & pH 2.4	0.25%	Li 22, Co 66	[44]
2.	Acidithiobacillus ferrooxidans (ATCC19859)	Single	9k medium+ S power + Fe(II) ion 3 g/L	30°C / pH 2.5	0.5%	Li 9, Co 65	[54]
3.	Acidithiobacillus thiooxidans(isolated)	Single	Basic medium + S powder 16 g/L + pyrite 16g/L	30°C / pH 1.0	1.0%	Li 85, Mn 19 Co 10, Ni 10	[73]
4.	Leptospirillium ferriphilum (isolated)	Single	Basic medium +S powder 16g/L + pyrite 16g/L	30°C / pH 1.0	1.0%	Li 31, Mn 42 Co 23, Ni 23	[73]
5.	Acidithiobacillus thiooxidans(isolated) and Leptospirillium ferriphilum(isolated)	Consortia	Basic medium + S powder 16g/L + pyrite 16g/L (1: 1 ratio)	30°C / pH 1.0	1.0%	Li 90, Mn 90 Co 96, Ni 97	[73]
6.	Acidithiobacillus ferrooxidans (PTCC1647) and Acidithiobacillus Thiooxidans(PTCC 1717)	Adapted mixed culture	Modified 9k medium + S powder 5 g/L+ FeSO4 36.7 g/L	32°C / pH 1.5	4.0%	Li 99.2, Co 50.4 Ni 89.4	[69]
7.	Acidithiobacillus Thiooxidans(PTCC 1717)	Single	9k Medium + S powder 5 g/L	30°C / pH 2.0	1.0 - 5.0%	Li 99, Co 60 Ni 20 (3% w/v)	[61]
8.	Acidithiobacillus ferrooxidans (PTCC 1647)	Single	9K medium + FeSO4.7H20 44.22 g/L	30°C / pH 2.0	1.0 -10%	Li 100, Co 88, Mn 20 (4% S/L)	[56]
9.	Acidithiobacillus ferrooxidans DSMZ 1927)	Single	Modified 9K medium + FeSO4.7H20 150 g/L	30°C / pH 2.0	10%	Co 94,Li 60	[62]
10.	Acidithiobacillus ferrooxidans DSMZ 1927)	Single	Modified 9K medium + FeSO4.7H20 150 g/L	30°C / pH 2.0	10%	Ni 90, Mn 92, Co 82, Li 89	[63]
Fungi used in the bioleaching of LIBs							
11.	*Aspergillus Niger (Isolated)*	Single	Sucrose medium	30°C / 2.4	0.25	Li 100, Co 82	[44]
12.	Aspergillus Niger (PTCC 5010)	Single/ adapted	Sucrose medium	30°C / 2.5	1.0	Li 100, Co 38 Cu 94, Mn 72 Ni 45	[48]
13.	Aspergillus Niger (PTCC 5210	Single	Sucrose medium	30°C / 3.0	2.0	Li 100, Co 55, Cu 100, Mn 77, Ni 37	[47]
14.	Aspergillus Niger (PTCC 5210)	Single	Sucrose medium	30°C / 1.0	1.0	Li 95, Co 45 Cu 100, Mn 70, Ni 38	[49]

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Table 4: A summary of several recent publications on the development of green hydrometallurgical processes

Acid	Reductant	Reaction steps	Results	Reference
Succinic acid	H_2O_2	1.5 M succinic acid; 4 vol% H_2O_2; 15 g/L S/L ratio; 70 ˚C; 40 min	100% Co and 96% Li were leached out	[99]
Malic acid	H_2O_2	1.5 M malic acid; 2 vol% H_2O_2; 20 g/L LCO; 90 ˚C; 40 min	90% Co and 100% Li were leached out	[100]
Citric acid	H_2O_2	2M citric acid; 2 vol% H_2O_2; 33g/L S/L ratio; 80 ˚C; 90 min	97% Ni, 95% Co, 94% Mn, and 99% Li were leached out	[101]
Tartaric acid	H_2O_2	2 M tartaric acid; 4 vol% H_2O_2; 17 g/L pulp density; 70 ˚C; 30 min	99.31% Mn, 99.07% Li, 98.64% Co, and 99.31% Ni were leached out	[102]
Formic acid	H_2O_2	10:1 molar ratio of formic acid and LCO; 6 vol% H_2O_2 20 g/L S/L ratio; 60 ˚C; 20 min	~ 99% Co and Li were leached out	[103]
Acetic acid	H_2O_2	2M acetic acid; 2.5 vol% H_2O_2 30g/L S/L ratio; 25 ˚C	~ 70% Co and Li were leached out	[104]
Ascorbic acid	-	1.25 M ascorbic acid; 25 g/L S/L ratio; 70 ˚C, 20 min	94.8% Co and 98.5% Li were leached out	[105]
Lactic acid	H_2O_2	1.5 M lactic acid; 0.5 vol% H_2O_2; 20 g/L S/L ratio; 70 ˚C; 20 min	97.7 Li, 98.2 Ni, 98.9 Co, and 98.4 Mn were leached out	[106]
Oxalic acid	H_2O_2	1 M oxalic acid; 15 vol% H_2O_2; 50 g/L S/L ratio; 80 ˚C; 60 min	~ 96% Co and Li were leached out	[107]
Aspartic acid	H_2O_2	1.5 M aspartic acid; 4 vol% H_2O_2; 10 g/L S/L ratio; 90 ˚C; 120 min;	60% Co and Li were leached out	[108]
Sulfuric acid	$NaHSO_3$	1 M H_2SO_4; 0.075 M $NaHSO_3$; 50 g/L S/L ratio; 95 ˚C; 240 min	93.4% Li, 66.2% Co, 96.3% Ni and 50.2% Mn were leached out	[81-82]
Sulfuric acid	$Na_2S_2O_3$	3 M H_2SO_4; 0.25 M $Na_2S_2O_3$; 1/15 S/L ratio; 90 ˚C; 180 min	99.95% Co, 99.71% Li were leached out	[109]

Table 5: Electrochemically-assisted leaching studies of metals from spent LIB waste.

Year	LIB Type	Leaching Procedure	Leaching Rate	Reference
		Electrochemically-assisted leaching		
2010	Mixed LIBs	Galvanostatic leaching at 400 A/m^2 in 2 M H_2SO_4 for 3h. Pb anode and SS cathode.	99 % of Co and Mn	[116]
2019	LMO	Galvanostatic leaching (at 400 A/m^2) of 75 g/l of CAM in the mixture of 1 M H_2SO_4 and 1M $MnSO_4$ (90 °C for 20 h). Ru-plated Ti anode and graphite cathode.	99 % of Li and 92 % of Mn	[132]
		Leaching in electrochemically generated leaching solution		
2018	Mixed LIBs	Leaching solution generation: graphite rod or Ti mesh electrodes. Electrolysation of 0.5 M NaCl at 4 and 8 V for 24 h. A single stage leaching: pulp density of 10 % (w/v) at 80 °C and room temperature with 200 rpm shaking for 2 h. Multistage leaching: 10 % (w/v) at 80 °C and room temperature with 200 rpm shaking for 1 h. Leaching again with a fresh anolyte solution after centrifugation.	Multistage leaching : <10 % for Co and Cu, 31 % Li, 59 % Ni, 28 % Mn	[117]
2020	LCO	0.1 M HCl anolyte and 0.1 M HNO_3 catholyte separated by a cation exchange membrane. Ru-plated Ti anode and SS cathode. Electrodialysis at 10 A/m^2 for 70 h at 25 °C.	56 % of Li and 25 % of Co	[118]

Table 6: Summary of research on metal recovery from spent LIBs by electrochemical methods.

LIB Type	Electrochemical Recovery Procedure	Products/ Recovery Rate	Research Scope/ Application	Reference.
	Recovery from H_2SO_4 Leachate			
NCA	Galvanostatic Ni deposition (Al cathode, Pb-8 Sb anode): 250 A/m^2, pH 3-3.2 at 50 °C; Potentiostatic Ni deposition (Al cathode, Ti anode): -1.2 to -1.5 *vs* SCE at RT.	Ni=87 % Co and Li not recovered.	N/A	[134]
Mixed LIBs	Galvanostatic Co deposition (Al cathode, Pb-8 Sb anode): 250 A/m^2, pH 4–6 at 25-50 °C; Galvanostatic Ni deposition (SS cathode, Pb-8 Sb anode): 250 A/m^2, pH 3.2 at 25-50 °C; Potentiostatic Co deposition (Al cathode, SS anode): -0.9 V *vs* SCE, pH 4-6, 30 °C; Potentiostatic Ni deposition (Al cathode, Ti anode): -1.5 *vs* SCE at RT.	Co=100 % Ni=87 % Li discarded as Li_2SO_4 solution	N/A	[135]
LCO	$Ag/AgCl_{sat}$ RE, Pt CE and Pt WE electrodes. Potentiostatic deposition: at -0.2, -0.3, and -0.4 V for 30 s. Potentiodynamic deposition: +0.1 ÷ +0.8 V, 20 mV/s. Electrolyte: pH adjustment to 2.0 or 4.5 by using KOH, then buffering with 0.10 M H_3BO_3 and 0.5 M K_2SO_4. Co^{2+} conc. 0.001 M.	Cu	Evaluation of Cu electrodeposition mechanism by QCM and electrochemical methods.	[119]
LCO	$Ag/AgCl_{sat}$ RE, Pt CE, Al, Pt and vitreous carbon WE electrodes. Potentiostatic deposition: Co at -1 V and Cu at -0.3 V for 50 and 100 s. Electrolyte: pH adjustment to 2.7 or 5.4 by using NaOH, then buffering with 0.10 M H_3BO_3. Co^{2+} and Cu^{2+} conc. equal to 0.001 M and 0.1 M.	Co and Cu multilayers	Evaluation of pH effect on metal layer growth, morphology, and crystalline structure. Co-Cu multilayers exhibit giant magnetoresistance.	[119]
LCO	$Ag/AgCl_{sat}$ RE, Pt CE, ferritic SS 430 WE electrodes. Potentiodynamic deposition: -0.5 ÷ -1 V, 20 mV/s. Potentiostatic deposition: -0.8, -0.9, -1.2, -1.5, -2 V. Electrolyte: pH adjustment to 3, Co^{2+} conc. 3.1 M.	Co=96 %	Coating on SOFC interconnects.	[145]
Mixed LIBs	Galvanostatic deposition at 200 A/m^2 in the leaching solution. Pb anode and SS cathode.	Co=96 % Cu=97 % Mn=99 %	Combined electro-leaching and electrodeposition system functioning at a zero liquid discharge tested at pilot scale.	[115]
Mixed LIBs	Galvanostatic deposition of Co was carried out at 200 A/m^2, pH 4, 60 °C for 4 h.	Co= 92 % Other metals discarded as waste.	N/A	[133]
LCO	Pt ring anode and St-12 plain carbon steel plate cathode. Electrodeposition: Current control mode at 200 A/m^2 for 600 s; Pulsed current mode (1500 cycles) consisting of 400 ms deposition time at 200 A/m^2 and 400 ms with no current. Electrolyte: leachate with or without 0.5 M boric acid.	$LiCo(CO)_4$	Corrosion resistive superhydrophobic coating.	[124]
LCO	Precipitation of $Co(OH)_2$ at pH 6.5 and calcination at 500 °C for 10 h to obtain Co_3O_4. Potentiostatic electroreduction (2.2 V for 3h) of Co_3O_4 to Co using Ni10Cu11Fe alloy as an anode, and the Co_3O_4 as a cathode. Electrolyte: molten Na_2CO_3-K_2CO_3. Precipitation of $LiCO_3$ at pH 10.3 (with addition of Na_2CO_3) when increasing pH with NaOH.	Co (99 %) and Li_2CO_3 (99 %)	Combined hydrometallurgical and pyro-electrochemical approach for a high recovery yield of Li and Co.	[137]

LCO	Co precipitation by liquid-liquid extraction, stripping, and galvanostatic deposition using Pb anode and SS cathode from Co solution (9 g/l) at 50-300 A/m^2.	Co=80 % Li not recovered.	N/A	[136]
LMO	MnO_2 electrodeposition during electrochemical leaching (Table 5). $LiCO_3$ chemical extraction by Na_2CO_3.	MnO_2 and Li_2CO_3	MnO_2 for synthesis of catalyst, ionic sieve, or a CAM for LMO regeneration.	[132]
	Recovery from HCl Leachate			
LCO	$Ag/AgCl_{sat}$ RE, Pt CE and Al WE electrodes. Potentiodynamic deposition: -0.7÷-1.5 V *vs* $Ag/AgCl_{sat}$, 10 mV/s. Potentiostatic deposition: at -0.8, -0.9, -1.0, -1.1, and -1.2 V. Electrolyte: leaching solution with pH adjustment.	Co=96.9 % at pH 5.4.	Evaluation of electrodeposition dependence on pH.	[142]
LCO	$Ag/AgCl_{sat}$ RE, Pt CE and Pt WE electrodes. Potentiodynamic deposition: 0÷-1.0 V *vs* $Ag/AgCl_{sat}$, 20 mV/s. Potentiostatic deposition: at -0.9 or -1.0 V. Electrolyte: leaching solution with pH adjusted to 2.7 or 5.4, respectively.	Co=100% at pH 5.4	Investigation of Co electrodeposition mechanism in different pH solutions by simultaniuos electrochemical-QCM technique.	[143]
LCO	$Ag/AgCl_{sat}$ RE, Pt CE and Al WE electrodes. Potentiostatic deposition was performed at -1.0 V, applying charge density (*via* adjusting the deposition duration) of 10, 50 and 100 C/cm^2. Electrolyte: leaching solution with pH adjusted to 2.7 or 5.4, respectively,	Co=100% at pH 5.4	Evaluation of charge density and solution pH impact on the electrodeposition efficiency as well as morphology, and crystalline structure of the Co electrodeposits.	[120]
LCO	$Ag/AgCl_{sat}$ RE, Pt CE and Pt WE electrodes. Potentiostatic deposition: at -1.0 V, applying charge density of 5 C/cm^2.	Co	Studies of super-capacitive behaviour of the recovered Co.	[144]
NMC	SCE RE, Pt sheet CE and Ni foam WE. Potentiodynamic deposition: -1.2÷-0.2 V *vs* SCE, 5 mV/s, 5 cycles. Electrolyte: leaching solution with pH adjusted to 6-7.	Li-Ni-Mn-Co hydroxides	Supercapacitor	[122]
	Recovery from HNO3 Leachate			
LCO	Electroreduction of Co^{2+} ions forming $Co(OH)_2$ (s) layer on Ti electrode by applying linear sweep voltammetry (LSV, 0÷-1.5V *vs* Ag/AgCl at 10 mV/s). Thermal dehydration at 400 °C converting $Co(OH)_2$ to Co_3O_4.	Co_3O_4 (Li not recycled)	Electrochromic compound	[125]
LCO	The pH 11 adjusted by adding fresh 4 M LiOH solution. Electrodeposition parameters: 10 A/m2; Ni anode; Pt cathode; T = 100 °C; time 20 h.	LCO	Refurbished LCO	[139]
	Recovery from Organic Acid Leachate			
LCO and LPF	F-doped tin oxide used as WE and CE, SCE RE. Potentiodynamic deposition of Fe film from the spent LPF cathode: -1.1 ÷ -0.5 V *vs* the SCE, 100 mV/s. Fe film convertion to hematite (Fe_2O_3) in air at 770 °C. Further, the Co phosphate (CoPi)-based catalyst photoelectrochemical deposition on the Fe_2O_3 films by using CAM from the spent LCO.	Fe_2O_3/CoPi	Fe_2O_3/CoPi photoanodes for water oxidation	[149]
	Direct Recovery			
LCO	Galvanostatic electrodeposition on Pt at 0.001÷10 A/m^2 (40-100 °C). Electrolyte: CAM dispersed in 4 M KOH and NaOH mixture.	LCO	Refurbished LCO	[138]

LCO	CAM pellet as a cathode and graphite rod anode. Potentiostatic electrodeposition at 1.0, 1.2, 1.5, and 1.8 V. Electrolyte: molten salt Na_2CO_3-K_2CO_3.	CoO or Co (99 %), Li_2CO_3 (85 %)	CoO and Li_2CO_3 used as precursors to resynthesize LCO	[121]