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POLITECNICO DI TORINO

Master's Programme in Energy Storage

METHOD OF SEPARATION OF ACTIVE MATERIAL FROM CURRENT COLLECTORS USING ULTRASONICATION

Making recycling more sustainable and economical using ultrasonication

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Abstract

The increasing demand for lithium-ion batteries has strained the supply chain and highlighted the need for efficient recycling methods to recover valuable materials. This thesis explores the application of ultrasonication as a promising preprocessing technique for material removal in battery recycling. Ultrasonication utilises waves to generate microbubbles that induce cavitation near the electrode surface, resulting in shear forces that facilitate material removal. The study investigates various parameters to optimise the efficiency of ultrasonication. Furthermore, the method demonstrates its potential to produce higher-purity materials compared to conventional shredding processes, thereby enhancing the value of recovered materials.

Keywords Battery Recycling, Ultrasonication, Green Chemistry, Lithium-ion Batteries, Pre- processing

Contents

Preface

I want to thank Professor Santasalo-Aarnio Annukka and Professor Silvia bodoardo , and my instructors Dr Neha Garg and Ms Martina Bruno for their guidance.

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Aravindda Swamy

Abbreviations

Abbreviations

ADR	Agreement concerning the International Carriage of Dangerous Goods by Road
CT	computed tomography
EOL	End Of Life
ESW	Electrochemical Stability Window
EU	European Union
EV	Electric Vehicle
GWh	Giga Watt Hour
LMNO	Lithium manganese nickel oxide
NASICON	sodium (Na) Super Ionic CONductor
OEM	Original Equipment Manufacturers
QR	Quick Response
RFID	Radio Frequency Identification

1 Introduction

The world is transitioning towards more intermittent renewable energy sources, and hence they require an energy storage option to provide consistent power. The most common source of electrochemical energy storage that is being used is batteries [1]. Lithium-ion batteries are the prevailing choice due to their extensive energy capacity and extended lifespan, making them highly popular for various applications such as portable electronic devices and electric mobility. [2]. It's been estimated that the global Lithium-ion battery demand is expected to rise from 300 GWh to 2000 GWh per year over the next decade, with a significant contribution from electric passenger vehicles [3]. The increasing demand for lithium-ion batteries necessitates the increased use of various battery materials such as copper, aluminium, lithium, manganese, cobalt, and nickel. These materials are projected to experience a significant surge of over five times in demand, while phosphorus is expected to grow by more than six times, along with iron, throughout the current decade [4]. The recent battery directives from the EU (2006/66/EC; 2008/98/EC) also emphasise that batteries shouldn't be sent to landfills due to their high levels of high metal content that could pollute and damage both groundwater and land [5].

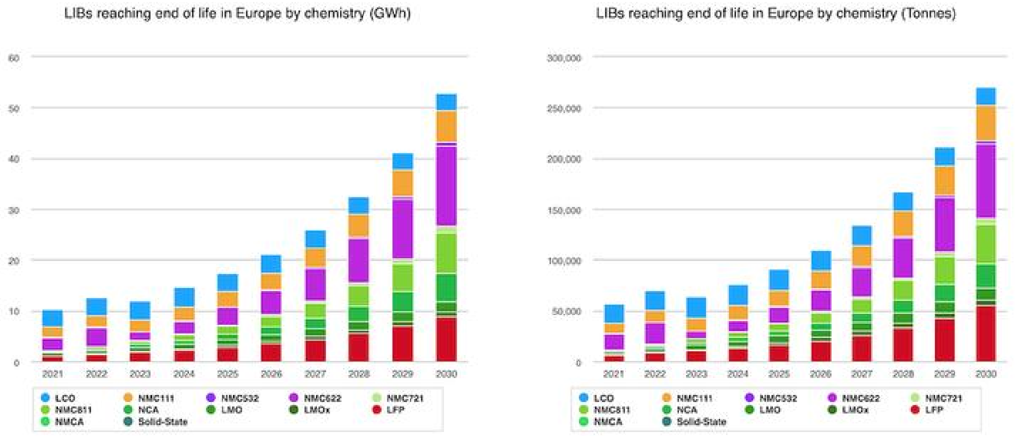

Figure 1 Batteries by chemistry reaching the end of life in Europe[6]

1.1 Recycling as a Secondary Source of raw material

To address the increasing demand, recycling has become a valuable source of secondary raw materials. By 2030, over 250 million tonnes of Li-ion batteries are expected to reach their end of life [5]. Different effective recycling technologies have been developed for spent lithium-ion batteries (LIBs), including hydrometallurgy, pyrometallurgy, and direct recycling. The pre-process involves battery pack collection, discharging, dismantling, and shredding.

The shredded material is then classified or sieved to separate materials based on their size [7]. This separation eliminates the larger components consisting of plastic, steel, aluminium, and copper.

Conversely, the combination of smaller components results in the formation of a mixture called the "black mass," which holds substantial quantities of lithium, manganese, cobalt, and nickel metals. These metals can be extracted from the black mass and recycled for the manufacturing of fresh batteries [8]. By extracting metals from the black mass, the dependence on new materials is diminished, thereby reducing the carbon footprint linked to additional mining operations. A critical stage in acquiring pure metal salts essential to produce cathode active materials is the purification of the leachate derived from the black mass, which involves the removal of impurities[9]. However, conventional methods like chemical addition or ion exchange have proven ineffective in meeting the required purity standards due to the complex composition of the water matrix, which contains high levels of interfering metals [10]. Therefore, it is crucial to identify a process that efficiently reduce impurities during the pre-processing or refining stages to achieve a profitable and scalable outcome in electric vehicle (EV) battery recycling.

This research explores the potential of Ultrasonication to separate Active material from Electrode sheets obtained for battery recycling. This method could provide an efficient and sustainable solution for metal reclamation from battery waste at a higher purity, with significant environmental and economic benefits. Utilizing ultrasonic waves with frequencies exceeding 20 kHz enables the agitation of a liquid sample. As these sound waves propagate through the liquid, they generate alternating cycles of high pressure (compression) and low pressure (rarefaction)[11]. During the low-pressure phase, intense sonic waves generate small vacuum bubbles or voids within the liquid. These bubbles collapse forcefully during the high-pressure phase, a phenomenon known as cavitation, resulting in the generation of extremely high local temperatures[12]. The thesis focuses on three primary objectives. Firstly, it aims to utilize ultrasonication to effectively remove the active materials from the electrode sheets. Secondly, it aims to identify and optimize the key parameters involved in the process, determining their ideal values for maximum efficiency. Lastly, the thesis aims to identify any potential challenges or bottlenecks that may hinder the implementation and scalability of the process.

1.2 Research Questions

Some of the potential research questions for this project, ultrasonication for active material removal from electrode sheets include:

1. **Whether Ultrasonication can be used as a potential preprocessing step in Battery recycling?**
2. **What would be the optimised parameters and efficiency of ultrasonication in removing the active material from the electrode sheets?**
3. **Identification of various hindrances and potential bottlenecks in the implementation methods and scalability of the process.**

Answering these research questions could help to provide insights into the potential use of Ultrasonication in the black mass separation process from electrode and the proposed method's economic, environmental, and social implications. The positive results could provide a sustainable and energy-efficient solution in the lithium-ion batteries recycling and help in the effective recovery of critical materials from recycling and reduce environmental pollution, thereby providing a path for a circular economy.

2 Literature review

2.1 Lithium-Ion Batteries

Batteries have played a crucial role in portable energy storage devices since the introduction of the first commercial primary battery in the 1800s [13]. With advancements, primary batteries were replaced by rechargeable or secondary batteries, with the lead-acid battery being the first successful example. However, the emergence of lithium-ion battery (LIB) technology in the 1980s revolutionized portable energy storage[14]. LIBs are rechargeable batteries that employ a specialized lithium-ion insertion material in both the positive and negative electrodes. This arrangement enables the exchange of lightweight Li-ions between the electrodes during cycling. This distinctive attribute allows LIBs to attain superior energy density and extended cycle life in comparison to other battery types, making them well-suited for portable electronic devices [14]. The first commercial implementation of lithium-ion batteries occurred in 1991 when Sony incorporated them into their mobile telephones, the predecessors of modern smartphones[15]. Today, LIBs dominate the battery market, with a global market value estimated at approximately 45 billion USD [16].

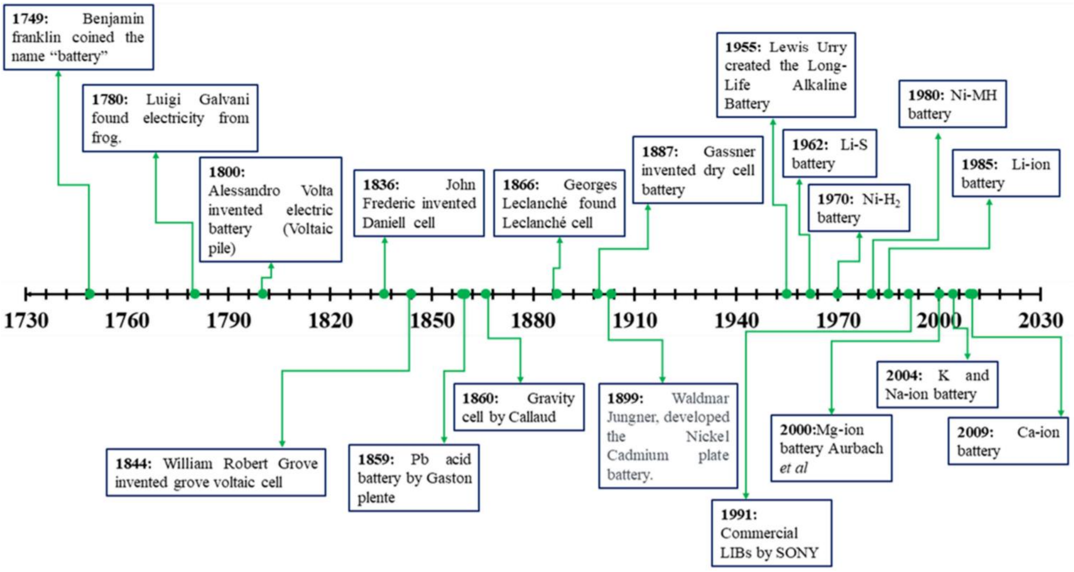

Figure 2 A brief history of the batteries[17]

2.1.1 Basic working and Intercalation

Battery systems consist of several essential components: anode, cathode, separator, electrolyte, and two current collectors (positive and negative). The anode and cathode serve as reservoirs for lithium, while the electrolyte facilitates the movement of positively charged lithium ions between the terminals by means of the separator. This ion migration generates free electrons within the anode, leading to a positive charge at the positive current collector.

Subsequently, the electric charge flows through the powered device, such as a cell phone or computer, and reaches the negative current collector. The separator acts as a barrier to prevent electron flow within the battery [15]. In conventional electrochemical cells, the charging and discharging process involves a redox reaction, which requires significant energy for charging and can lead to heat dissipation. Whittingham, at Exxon Corporation in the US, showcased the initial rechargeable lithium battery. This battery featured a cathode composed of TiS2, a lithium-metal anode, and a liquid electrolyte that included a dissolved lithium salt within an organic solvent. However, safety concerns arose due to limited cell voltage (<2.5 V) and during cycling, dendrites grew on lithium-metal anodes which posed a significant obstacle to the widespread adoption of cells utilizing sulphide cathodes and lithium-metal anodes. [18]. However, lithium-ion (Li-Ion) batteries employed today uses an intercalation mechanism rather than a redox reaction to address these challenges.

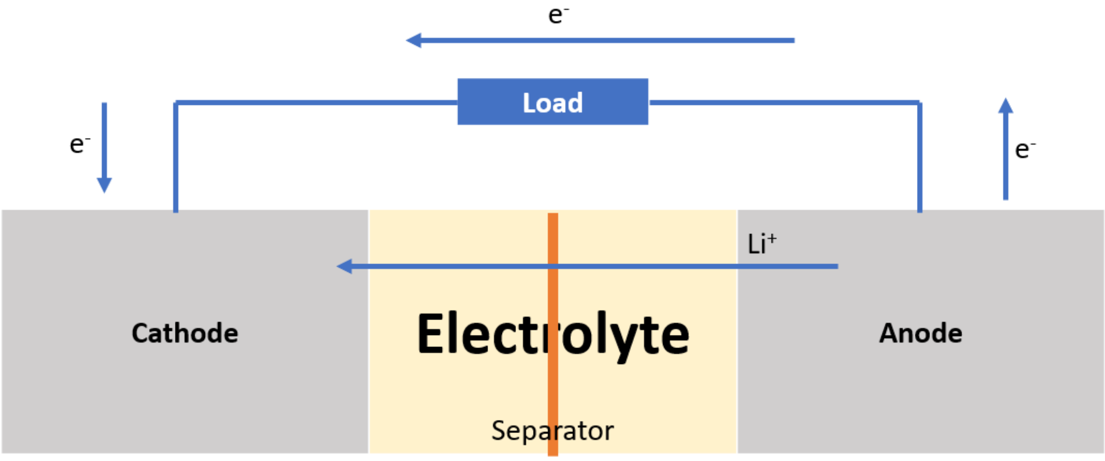

Figure 3 The basic components of a Li-ion battery cell during discharge [19]

Intercalation chemistry has been known for nearly two centuries and involves the interaction between guest molecules or ions and solid hosts. Intercalation is a fundamental process in which a mobile ion or molecule is inserted into available spaces within a crystal lattice and can be reversibly extracted. While it may have limited capacity, intercalation offers advantages such as minimizing volume changes and mechanical strain during the repeated insertion and extraction of alkali ions. Irrespective of the specific chemistry employed, this mechanism plays a vital role in determining the cycling performance of modern Li-ion battery electrodes. [20]. Understanding the intercalation process is essential for optimizing battery performance and exploring new electrode materials.

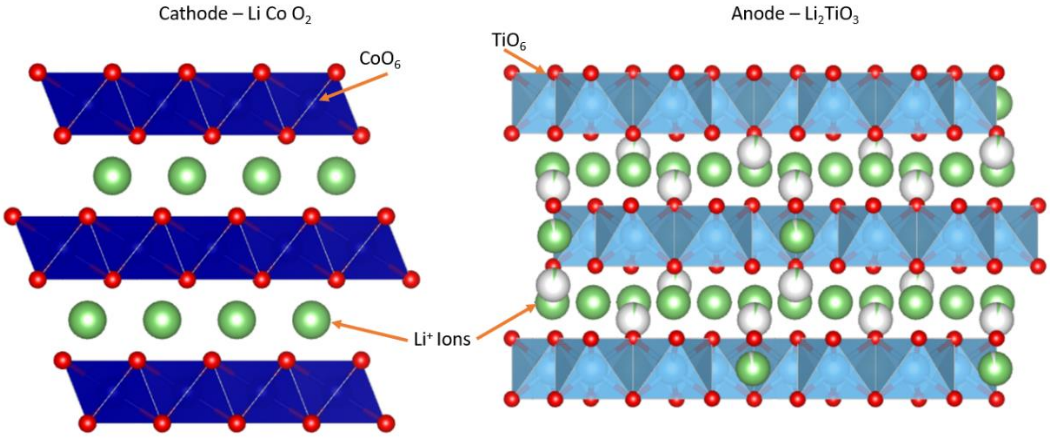

Figure 4 Layered cathode material $LiCoO_2$ and layered anode material Li_2TiO_3 [19]

The reversible insertion and extraction of lithium ions during charging and discharging are facilitated by the structures of the anode and cathode, enabling the intercalation mechanism. The energy density of a Li-Ion battery relies on the storage capacity and potential, which are influenced by the space available for the anode and cathode to accommodate lithium ions and the extent to which the intercalation reaction can be reversed.

2.1.2 Materials of the Li-ion batteries

Lithium-ion batteries (LIBs) comprise four crucial components: anode, cathode, separator, and electrolyte, enabling the movement of lithium ions during charging and discharging. Recent advancements have explored various materials for anode fabrication, including metallic lithium, graphitic carbon, synthetic graphite, lithium titanate, tin-based alloys, and silicon-based materials [21]. Similarly, commonly employed cathode materials encompass lithium nickel cobalt aluminium oxide (NCA), lithium cobalt oxide (LCO), Lithium Manganese Nickel Oxide (LMNO), lithium nickel manganese cobalt oxide (NMC), and lithium iron phosphate (LFP) [18], [22].

To facilitate ion movement, different electrolytes like LiPF6, LiClO4, LiAsF6, and LiCF3SO3, combined with binders, flame retardants, and electrolyte solvents, are utilized [23]. Ongoing research efforts are dedicated to enhancing the electrochemical performance of electrode materials. Challenges persist in the advancement of both cathode and anode materials, as well as electrolyte solutions. [24], [25].

The future of LIBs lies in advanced energy storage technology, with efforts directed towards addressing limitations associated with nanomaterials. Organic electrode materials have been explored, considering parameters such as energy and power density, cycle life, gravimetric density, electronic conductivity, energy efficiency, cost, and resource availability. Additionally, researchers have explored the modification and synthesis of graphene-based materials derived from diverse carbon sources for the purpose of energy storage applications in lithium-ion battery (LIB) electrodes [23].

A comprehensive examination has been conducted on the progress made in electrode materials and their characterisation methods, with a particular focus on lithium-ion batteries (LIBs) used in smart grids at large scale and EVs. The primary objective is to identify materials with superior attributes such as lower cost, cycle life, higher energy density, and enhanced safety, surpassing conventional LIBs that employ intercalation electrodes.[26].

Table 1: An Li-Ion battery Component, their weightage and commonly used materials [27]

Component	Wt(%)	Most Commonly Used Material
Casing	25	Steel/plastics
Cathode	27	$LiCoO_2$, $LiNi_xMn_yCo_zO_2$, $LiMn_2O_4$, $LiNiO_2$, $LiFePO_4$
Anode	17	Graphite/$Li_4Ti_5O_{12}$
Copper & Al current collectors	13	Cu/Al
Electrolyte	10	Electrolytic solutions such as $LiPF_6$ $LiClO_4$ and $LiSO_2$ dissolved in propylene carbonate, ethylene carbonate, or dimethyl sulfoxide
Separator	4	Polypropylene (Microporous)
Binder	4	Polivinylidene Difluoride (PVDF)

2.1.2.1 Cathode materials

The global lithium-ion battery market is experiencing growth propelled by the advancement of novel materials targeting the reduction of production costs. A crucial factor in enhancing safety, performance, and cost-effectiveness is the customisation of cathode materials, primarily by adjusting cobalt levels.[25]. Cathodes, the positive electrodes in lithium-ion batteries, have a crucial impact on voltage and overall battery performance. Currently, various cathode materials are being utilised in different applications, which include LCO for EVs, NMC for smartphones, and LFP for power tools[19], [21], [26]. NMC cathodes are particularly advantageous for large-size batteries as they reduce cobalt usage while maintaining higher safety and output [19]. On the other hand, LFP offers increased power and packing density without relying on rare metals like cobalt[27]. Additionally, high nickel-layered oxide cathodes like NCM are expected to gain popularity, enabling longer-range electric vehicles at more affordable prices [19].

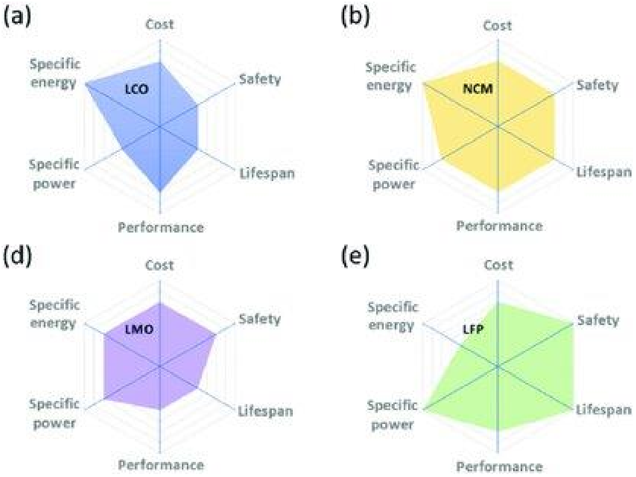

Figure 5 Radar plots were used to compare the qualities of various cathode materials, including $LiCoO_2$ (LCO), Li [Ni, Co, Mn]O_2 (NMC), Li[Ni, Co, Al]O_2 (NCA), $LiMn_2O_4$ (LMO), and $LiFePO_4$ (LFP) [28]

Since 1980, lithium cobalt oxide (LCO) has been utilised as a cathode material in lithium-ion batteries (LIBs). It provides consistent capacity and thermal stability, although it carries the risk of thermal runaway when exposed to high temperatures or overcharging. At elevated temperatures, LCO decomposition produces oxygen, presenting a potential combustion hazard.[29]. To improve the stability of cycles, lithium cobalt oxide (LCO) is commonly charged in a delithiated state at approximately 4.2 V vs Li+/Li. However, operating within the range of 3-4.5 V leads to a reduction in capacity due to irreversible structural modifications or fluctuations in volume.[30]. The presence of higher voltages above 4.5 V leads to an increase in impedance, negatively impacting the cycle performance of LCO. To enhance the stability of LCO cycles at higher voltages, methods such as applying metal oxide coatings or employing surface cleaning techniques have been explored. The utilisation of LiBOB electrolyte instead of LiPF6 allows for the development of high-voltage LCO cells with a capacity of 180 mA h g−1, but it comes at the cost of compromising thermal stability.[31]–[34].

The high capacity of around 200 mAh/g exhibited by lithium nickel oxide (LiNiO2) and its derivatives makes them highly promising as positive cathode materials for lithium-ion batteries. However, synthesising stoichiometric $LiNiO_2$ is challenging due to lithium vaporisation at high temperatures, leading to lithium loss. $LiNiO_2$ also experiences capacity fading when charged to high voltages, impacting its cycling stability. Despite the difficulties, $LiNiO_2$ was extensively studied as a potential alternative to LCO in the 1990s due to the abundance and lower cost of nickel [35]–[37]. The synthesis of LiNiO2 depends on various parameters and cation mixing, where nickel can occupy vacant lithium sites, leading to capacity loss[38] and structural changes during charge and discharge cycles contribute to capacity loss. Doping techniques involving Mg, Al, Co, and Ga have been explored to improve $LiNiO_2$ properties [29].

NCM (lithium, nickel, cobalt, and manganese) cathode materials offer higher power ratings and energy density compared to conventional batteries. They provide structural stability without directly participating in the charge and discharge process. Pristine $LiMnO_2$ (LMO) has garnered interest as an economical and eco-friendly substitute for LCO and LNO. Nevertheless, achieving the desired orthorhombic phase of LMO directly during synthesis poses challenges, leading to unstable voltage plateaus in the resulting material. Combining LMO and LNO has resulted in viable solid solutions, but maintaining stable capacity remains a challenge. Lithium iron phosphate ($LiFePO_4$) was the first phosphate cathode material introduced in 1997. Research in phosphate materials and polyanionic chemistry has focused on intrinsic and extrinsic properties, transportation control, electrode synthesis, and structural behaviour. The capacity loss can be linked to the development of distorted Li-deficient phases, which disrupt the process of Li-ion insertion and extraction. The discharge process has revealed the occurrence of two-phase reactions that influence the electrochemical stability of phosphate materials. Studies have also explored fluorinated cyclic phosphate solvents to enhance stability and prevent combustion [23].

2.1.2.2 Anode Materials

The selection of anode materials is a critical factor in the advancement of high-performance LIBs. Currently, graphite is extensively utilized as the primary anode material due to its low operating potential, practical capacity, and dependable discharge performance [39]. However, there is ongoing research on alternative anode candidates to overcome the limitations of graphite's energy density. Lithium metal is highly regarded as an excellent choice for anode material due to its impressive theoretical capacity and low redox potential [40]. As alternative anodes for LIBs, transition-metal compounds, including phosphides, oxides, and sulphides, with conversion-type reaction mechanisms, have demonstrated considerable potential. Transition-metal phosphides, in particular, exhibit reduced polarisation, enhanced lithium storage capabilities, and higher specific capacity [41]. Zinc anodes are frequently employed as sacrificial anodes for cathodic protection purposes; however, they suffer from stability issues. To address this, a synergistic approach has been developed, which involves a Cu-Zn solid solution interface along with a copper mesh skeleton. This innovative approach enables dendrite-free plating even across a broad range of current densities [42].

Micro-sized particles of silicon, aluminium, or bismuth offer high capacity and cost-effectiveness, but their rapid degradation and poor Coulombic efficiency are concerns [43]. Silicon has been extensively studied for its high capacity, but its substantial volume change during lithium insertion and extraction hinders its practical implementation. Graphite continues to be the primary anode material in commercial lithium-ion batteries (LIBs). However, incorporating high-capacity compounds like silicon-metal alloys, sub-stoichiometric silicon oxide, or elemental silicon with graphite can substantially enhance energy density and tackle volume change concerns [44], [45].

Table 2 Different Anode materials in Lithium-ion batteries[29]

Anode Materials	**Capacity ($mAhg^{-1}$)**	**Merits**	**Remarks**
Hard carbon	200–600	Excellent working potential	Less columbic efficiency
Carbon Nanotubes	1115	Cost-effective	Greater hysteresis voltage
Graphene	770/1115	Safe to operate	More irreversible capacity
LiTi4O5	176	Safer, Low cost	Lower capacities
TiO2	320	Greater power capability, good lifecycle	Lower energy densities
Germanium	1623	Greater Specific Capacities, Greater Energy densities, Excellent safety	Lower irreversible capacity, more fading capacity, less life cycle
Silicon	4213		
Silicon oxide	1562		
Antimony	661		
Tin	992		
Tin oxide	793		
Metal Oxides (Co_3O_4 ,CoO, MoO_2 /O_3 ,NiO, RuO_2 ,Cr_2O_3)	500–1200	Large capacity, energy, Minimal cost, eco-friendly	Lower Columbic efficiency, Unstable SEI formation, not good lifecycle, more hysteresis potential.
Metal phosphides/nitrides and sulphides	500–1800	Greater capacities, lower potential, the lower polarisation	Weak rate capability, short lifespan, and high production cost

Lithium metal anodes, renowned for their elevated gravimetric and volumetric energy densities, are considered the optimal option for high-energy batteries [46]. Layered black phosphorus offers desirable properties such as high theoretical capacity, inherent layered structure, and excellent electrical conductivity, making it suitable for high rate, capacity and storage [47]. A disordered rock salt $Li_3V_2O_5$ anode has been found to yield higher cell voltage compared to batteries with commercially available alternatives [48]. Additionally, Porous carbon-based anode materials, when coated with MoO_2 nanoparticles, have shown impressive cycling performance even under high current densities. These materials have demonstrated the ability to retain their reversible capacity after undergoing numerous cycles, indicating significant potential for future applications in lithium-ion batteries [49].

When considering specific capacity rankings, it is evident that alloys, transition metal oxides, and silicon-based materials possess the highest values. In contrast, carbon or graphene-based materials demonstrate comparatively lower capacities. While silicon and graphene may be more cost-effective based on weight, their drawback lies in experiencing substantial volume changes during cycling. Anode materials based on alloys are recognized for their enhanced safety, while transition metal oxides exhibit superior stability. While graphene has been widely studied as an anode material, silicon holds promise as a future candidate. Ongoing research focuses on novel approaches to enhance anode material performance, including the utilization of nitrogen-doped graphene matrices or porous carbon coated with MoO_2 nanoparticles, yielding promising results [49], [50].

2.1.2.3 Electrolytes

Lithium-ion batteries (LIBs) rely on electrolytes that contain liquid organic solvents, which must fulfil multiple criteria such as high dielectric constants, low viscosity, wide electrochemical stability windows (ESW), chemical inertness, thermal stability, suitable interfacial properties, and environmental safety. In advanced LIBs, cyclic and linear carbonates, including Ethylene carbonate, propylene carbonate (PC), DMC, DEC, and EMC, are widely utilized as the most commonly employed electrolyte solvents. However, research is focused on developing alternative solvents with improved thermal stability and safety features by incorporating electronegative substituents. $LiPF_6$ is the typical lithium salt used, but alternative salts like LiFAP and $LiBF_4$ are being explored due to limitations associated with $LiPF_6$ [51].

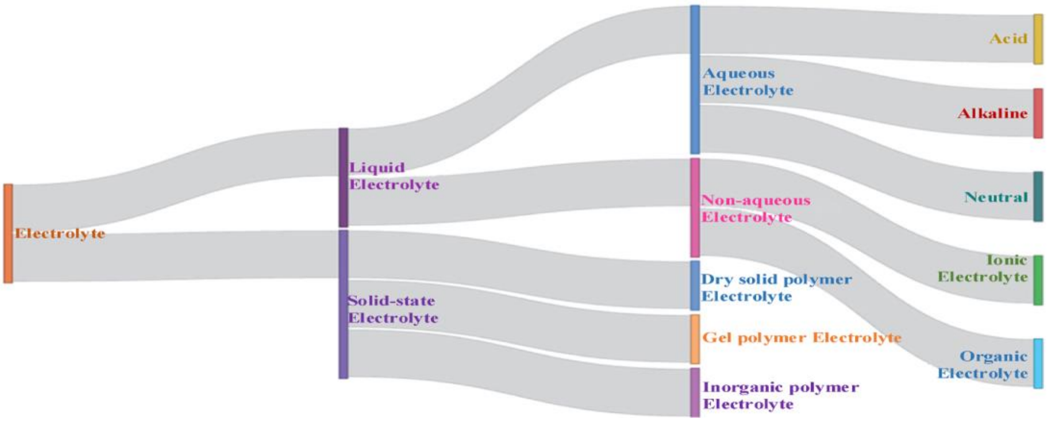

Figure 6 Types of electrolyte materials.[23]

Within the category of solid-to-liquid electrolytes, a diverse range of electrolyte types can be found, including aqueous and non-aqueous electrolytes, dry solid and gel polymers, ionic liquids, as well as organic and inorganic electrolytes. Solid-state electrolytes are being developed as high-performance materials due to their safety, energy density, and reversible electrochemical energy storage [52]. Different types of solid electrolytes, such as fluorinated orthoformate solvent-based electrolytes [53], garnet-type solid-state electrolytes [54], and LiF-rich solid electrolytes, show promise in improving battery capacity [43].

Polymer electrolytes have garnered significant interest in the realm of next-generation LIBs due to their remarkable energy density and enhanced safety features. To improve the stability of zinc deposition, techniques such as the utilization of Cu-Zn solid solution interfaces and the incorporation of polyacrylamide electrolyte additives have been employed in the modification of zinc anodes [42], [55]. Stability-wise, garnet and NASICON are considered the most stable electrolyte materials, with NASICON being chemically stable but less stable compared to lithium. Despite their lower physical stability, garnet and NASICON demonstrate superior electrochemical stability. Liquid electrolytes exhibit the highest ionic conductivity [23].

In the pursuit of high safety, energy density, and environmental friendliness, researchers are actively investigating diverse avenues to enhance lithium-ion battery (LIB) electrolytes and develop novel materials. Solid-state electrolytes and polymer electrolytes are emerging as particularly promising areas of research for the next generation of LIBs.

2.1.2.4 Binders

The main function of binders in battery electrodes is to establish a connection between the active material and conductive additives, while also securing the electrode materials to current collectors. This crucial role prevents the active material from disintegrating when subjected to the chemical and mechanical stresses encountered during its cycles of charging and discharging. Binders accomplish this binding function through either direct or indirect methods[56]

Direct binding involves the strong adsorption of binder materials onto active materials, creating bridges between them. For the polymeric binder to fulfill this requirement, it needs to possess reactive functional groups, such as carboxylic acid and alcoholic groups, capable of forming bonds with the surface of the active materials. Examples of binders that enable direct binding are gelatin, polyacrylic acid, and carboxymethyl cellulose [57].

Conversely, indirect binding takes place when non-fluorinated polymers such as polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF) adhere mechanically or physically to the active material’s surface. This process forms a network structure, where the particles of the active material are effectively captured[56].

The selection of binder material can have a significant impact on fabrication requirements and costs. There is ongoing research and development focused on innovative binder materials that offer improved cost-effectiveness and environmental friendliness compared to traditional PVDF binders.

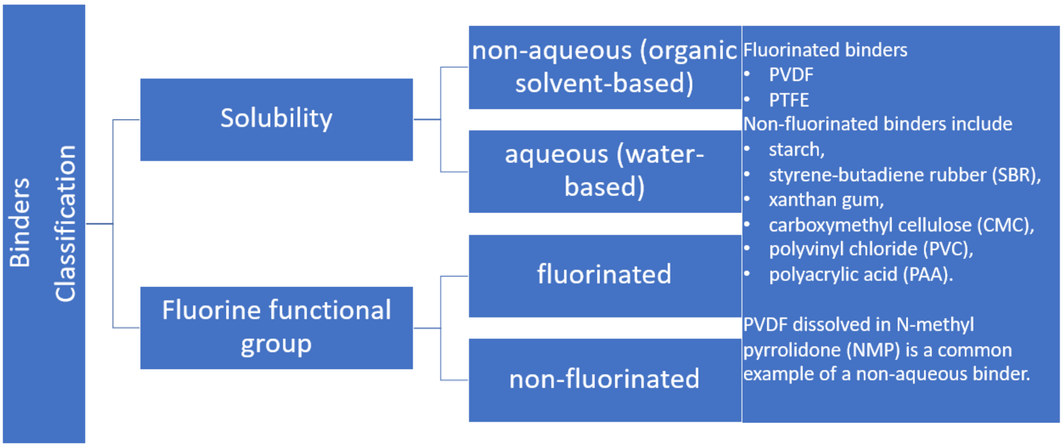

Figure 7 Binder classification based on Solubility and fluorine functional group[57]

The progress made in polymer technology has resulted in the identification of environmentally friendly and economically viable binders that can effectively accommodate diverse electrode materials. Aqueous-based binders present numerous advantages in terms of cost-effectiveness, environmental impact, and processing requirements related to air and humidity. Additionally, they facilitate rapid solvent evaporation. When compared to conventional PVDF-based binders, aqueous binders require a lower quantity (approximately 5%) while simultaneously enhancing the energy density of the cell [57].

Aqueous binders offer a significant advantage over PVDF binders as they exhibit reduced swelling tendencies in carbonate-based electrolytes. Moreover, they prove to be a more cost-effective option during the fabrication process. These aqueous binders have been employed since the 1990s, with gelatin between the electrode and current collector, playing a dual role as both a passivating layer and a binder for graphite particles[58]. Over the past few years, extensive research has been conducted on various polymers, hydrocolloids, and copolymers as potential aqueous binders for anodes containing graphite and Silicon and Li-rich metal oxide cathodes. Prominent battery companies, including Apple, Everyday Battery, and General Motors, have successfully showcased the electrochemical performance achieved using these aqueous binders. Well-known aqueous binders include the sodium salt of CMC, SBR, PAA, chitosan, and alginates [57].

2.2 Recycling of Li-ion batteries

A European study has identified lithium, cobalt, and natural graphite as potential critical materials for batteries due to limited supply and risks in the supply chain [59]. Chinese companies dominate the supply of anode and cathode materials, while Japanese companies supply a specific cathode material such as the nickel-cobalt aluminum oxide cathode material[59]. The majority of processed materials and components utilized in lithium-ion batteries are sourced from Asia, with China serving as the largest producer [60]. Among the key players in primary lithium production, three countries stand out: Australia, Chile, and China. Additionally, the Republic of Congo holds a significant position as the primary source of cobalt about 73% [61]. Accurately predicting future demand for these raw materials is crucial to avoid supply risks. Accurately anticipating the future demand for these raw materials is of utmost importance to mitigate potential supply risks. Furthermore, the imperative to recover materials from batteries has gained prominence, particularly due to the classification of lithium, cobalt, and phosphorus as critical raw materials by the European Union [62]. Presently, the recycling rate of lithium-ion batteries remains relatively low, underscoring the untapped potential of recycling as a valuable source for battery manufacturing materials [27]. To comply with EU regulations, the recycling efficiency needs to improve, aiming for a target of 65% by 2025 and 70% by 2030 [63]. The important aspects of the Proposed amendments for the Directive 2006/66/EC – Battery Directive can be found in Table 3

Table 3 Proposed amendments for the Directive 2006/66/EC – Battery Directive latest draft[64].

Time period	Actions to be followed	Article
January 2023	Rolling out of the battery directive and Additional marking for cadmium (>0.002%) and lead (>0.004%)	13
July 2024	Carbon footprint declaration for batteries	7
January 2026	Battery passport for batteries with a capacity greater than 2 kWh and an electronic exchange system that holds the online battery database, which links to the battery passport, has to be rolled out	64,65
	Performance classes set for portable and rechargeable batteries	7,9,10
Jan 2027	Percentage of recycled Li, Co, Pb and Ni in active material to be displayed in the industrial and electric-vehicle batteries with internal storage	8
Jan 2027	Detailed labelling of the battery is made necessary for the identification of batteries and their main characteristics	13
Jan 2030	minimum recycled active material: 12% cobalt; 85% lead, 4% lithium and 4% nickel	8
Jan 2035	minimum recycled active material: 20% cobalt, 10% lithium and 12% nickel and lead, 85%	8

Without pre-treatment, metal recovery leads to non-functional recycling, where the extracted alloys are not used for battery production. On the other hand, pre-treatment followed by metallurgical processes enables functional recycling, where the recovered metals can be reintroduced into battery manufacturing as shown in Figure 8. The technology of biometallurgy, depicted in grey, is currently not implemented on an industrial scale.

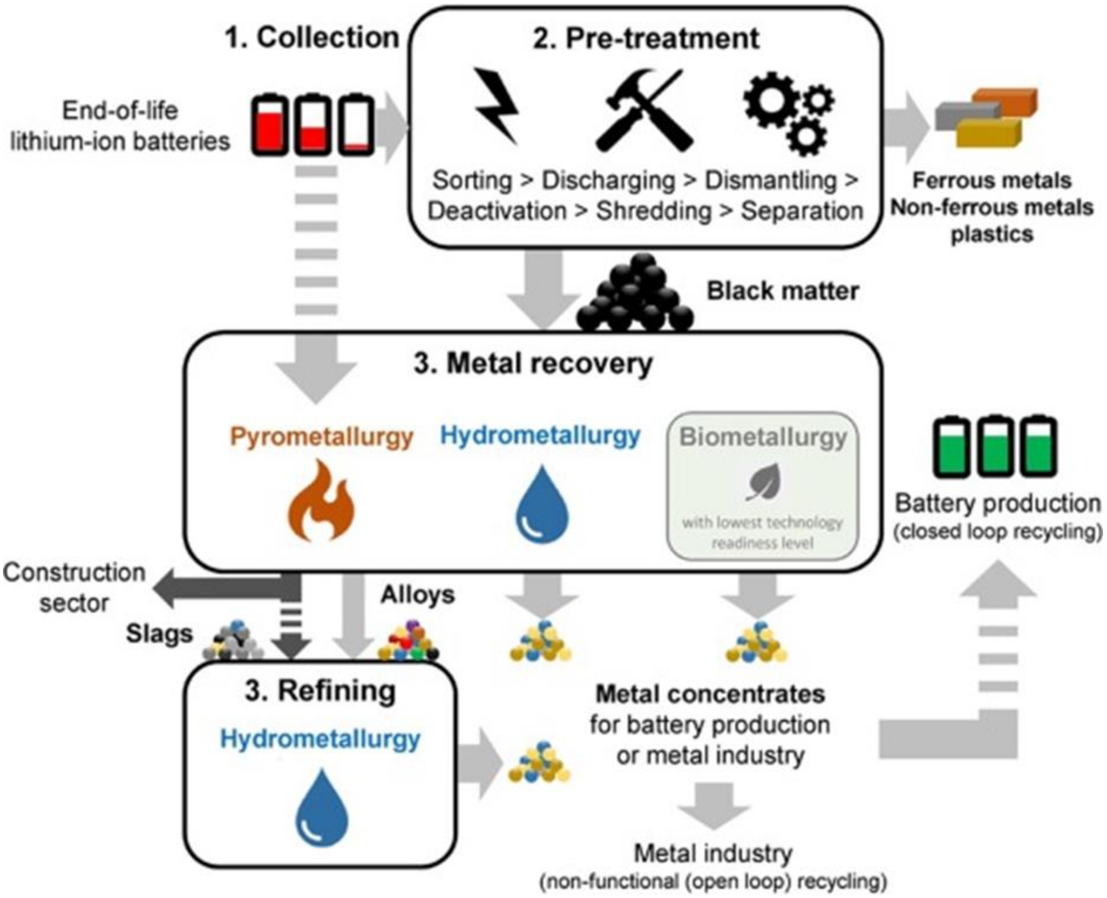

Figure 8 The diagram illustrates different recycling pathways for lithium-ion batteries [23].

The recycling of lithium-ion batteries (LIBs) presents both challenges and opportunities. Recycling methods for lithium-ion batteries can be broadly classified into three main categories: pyrometallurgical, hydrometallurgical, and physical processes. Among these, pyrometallurgy, followed by hydrometallurgical recovery, is often preferred due to its straightforward implementation and the capability to handle diverse feedstocks with limited pre-processing requirements. However, this method results in the consumption of several components, and only certain metals can be recovered as alloys, requiring additional separation steps [65]. Hydrometallurgical processes, on the other hand, allow for greater recovery of materials in terms of quantity and value. These processes offer the advantage of extracting metals in the initial phase and the potential to recover materials as precursors for LIB production [66]. Despite its potential, the full effectiveness of hydrometallurgical recycling methods for lithium-ion batteries has not been fully realized. To optimize recovery rates, further advancements in pre-treatment and disassembly techniques are necessary. This is particularly crucial in light of the decreasing prices of lithium-ion batteries and the growing efficiency of primary supply chains. By implementing improved hydrometallurgical processes, the establishment of a circular supply chain for lithium-ion batteries (LIBs) can be achieved. This approach not only preserves valuable materials but also reduces the energy and resources needed for their production. As a result, the overall sustainability of LIB manufacturing is enhanced[67].

2.2.1 Waste Collection and Transportation

The European Union (EU) has implemented regulatory measures to ensure the responsible management and recycling of lithium-ion batteries (LIBs) at the end of their life cycle. In accordance with the EU Battery Directive, manufacturers are obligated to provide a cost-free collection system for industrial and automotive batteries. Concerning electric vehicle (EV) LIBs, the End-of-Life Vehicle Directive stipulates that original equipment manufacturers (OEMs) are responsible for the retrieval of EVs, including their batteries. OEMs have the option to collaborate with third-party recycling firms or car workshops to facilitate the recycling procedures.

Safety is a critical aspect in dealing with end-of-life LIBs, as improper handling or storage conditions can result in leakage, outgassing, or thermal runaway, leading to significant damage and the release of hazardous substances. The International Carriage of Dangerous Goods by Road (ADR) agreement establishes comprehensive safety guidelines for the international transportation, storage, and packaging of goods. When it comes to lithium-ion batteries (LIBs), it is crucial to safeguard them against adverse weather conditions, mechanical impacts, and short circuits. Therefore, LIBs should be appropriately packaged in approved containers to ensure their secure transportation and storage [68].

For high-performance traction lithium-ion batteries (LIBs) extracted from electric vehicles (EVs), it is necessary to have a separate collection system in place to ensure their proper handling. It is of utmost importance to enforce stringent safety measures not only during the collection and storage of these batteries but also throughout the pre-treatment and recycling processes. By doing so, potential financial and health risks can be effectively minimized and mitigated [69].

2.2.2 The Need for Preprocessing

In the recycling of lithium-ion batteries (LIBs), preprocessing is a vital stage encompassing sorting, stabilisation, disassembly, and separation. Research has demonstrated that the integration of preprocessing techniques can result in improved material recovery efficiency and reduced energy consumption, outweighing the initial investment costs. Notably, studies have indicated that the implementation of a recycling process incorporating preprocessing is the most efficient approach to minimize GHG emissions and overall energy usage in LIB recycling[70].

The selection of preprocessing techniques significantly influences the life cycle assessment of lithium-ion batteries (LIBs). Multiple research studies have provided evidence that preprocessing, particularly methods such as disassembly and separation, has a beneficial impact in terms of reducing environmental footprints and minimizing overall environmental impacts. Safety is another important consideration, as LIBs can pose hazards such as electrical, chemical, thermal, and explosive risks. Thermal runaway, in particular, is a significant safety concern that can result from external mistreatment or internal malfunctioning of the batteries. Discharging LIBs during disassembly is recommended to reduce the risk of thermal runaways and potential fires[71].

However, there is no one-size-fits-all preprocessing method due to the diverse chemistries and non-standardised packaging of LIBs. Researchers have extensively investigated various strategies to enhance material recovery efficiency in the preprocessing stage of lithium-ion battery (LIB) recycling. These approaches encompass a wide range of techniques, including sorting methods[72], novel stabilisation methodologies[73], [74], and automated dismantling processes[75]. Each of these preprocessing techniques offers distinct technological, economic, and environmental advantages, alongside their inherent limitations.

The existing research on preprocessing focuses on specific aspects but lacks comprehensive consideration of commercial perspectives and standardization. Recycling companies use various methods based on material interests and regional laws, resulting in a lack of global standards[67].

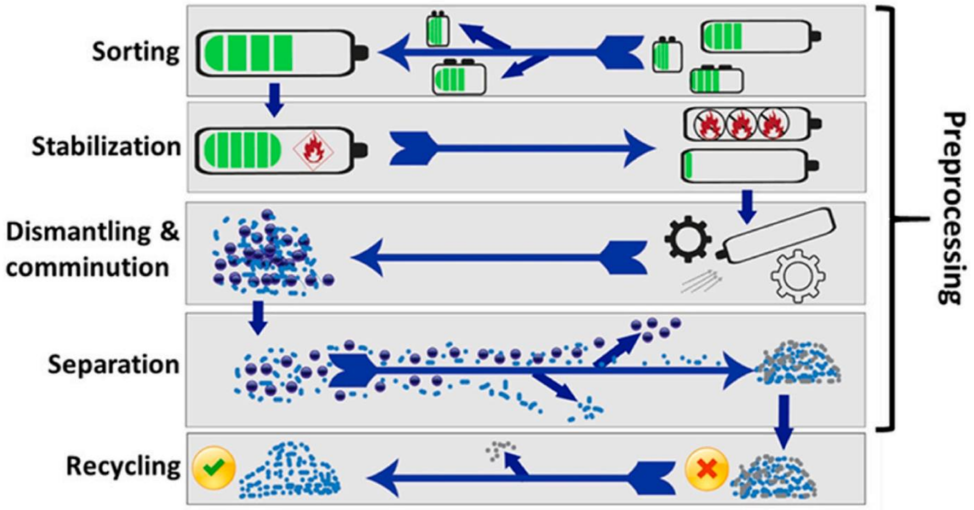

Figure 9 Different stages of most widely used preprocessing techniques[67]

2.2.3 Battery sorting

Sorting plays a vital role in the recycling of lithium-ion batteries (LIBs) by separating non-battery waste and categorizing batteries based on their chemistries, shapes, sizes, and condition. Both manual and automated sorting methods are employed, and multistage sorting approaches have been proposed to maximize efficiency[76], [77].

The sorting process typically involves a series of steps. Initially, a crane dumps battery barrels into large containers, and then manual pre-sorting takes place on a conveyor belt. Workers manually remove larger non-battery items, such as batteries from various electronic devices. Magnetic sorting is employed to capture any remaining batteries on the belt, followed by mechanical sorting using a shaker screen to further separate batteries based on size and shape. While manual sorting is commonly used in recycling companies, research suggests the use of machine learning and X-ray techniques for improved sorting accuracy, each with their own advantages and disadvantages[78]–[80].

Direct parameter measurement is a straightforward sorting method used in the recycling process of lithium-ion batteries (LIBs). It involves measuring various static and dynamic parameters of the batteries, including voltage, internal resistance, discharge capacity, and self-discharge rate. These measurements provide valuable information about the condition and performance of the batteries. However, some dynamic parameters are difficult to measure accurately. To overcome this challenge, alternative techniques such as computed tomography (CT), X-ray, or ultrasound scanning are being explored. These non-destructive imaging methods allow for the assessment of battery characteristics without causing damage. Although these techniques are still under development, they hold potential for enhancing the sorting process in LIB recycling[76].

Chemistry-based sorting is another approach used by many recycling firms to enhance the efficiency of hydrometallurgical processes. It involves identifying the battery's chemistry or cathode material type based on its operating principle and electrochemical parameters. Obtaining comprehensive information about the internal processes of a battery without causing any damage presents challenges, particularly when quantifying electrochemical characteristics. While basic estimation methods based on the battery's size, weight, and magnetic properties can provide some insights, accurately determining electrochemical parameters remains challenging. Recent advancements in research have focused on leveraging machine learning and deep learning algorithms to predict and analyse these parameters. However, further investigations are required to assess the accuracy and efficiency of the overall procedure[67].

2.2.4 Stabilization

To ensure safety and reduce the risk of fires, stabilisation techniques are implemented before opening a lithium-ion battery (LIB). These techniques aim to prevent thermal runaway, which is a highly undesirable event that can result in the generation of excessive heat, the loss of valuable components like electrolytes, polymers, separators due to combustion, and the release of toxic and corrosive substances[71]. By employing effective stabilisation methods, the potential hazards associated with LIBs can be mitigated, safeguarding both personnel and the environment.

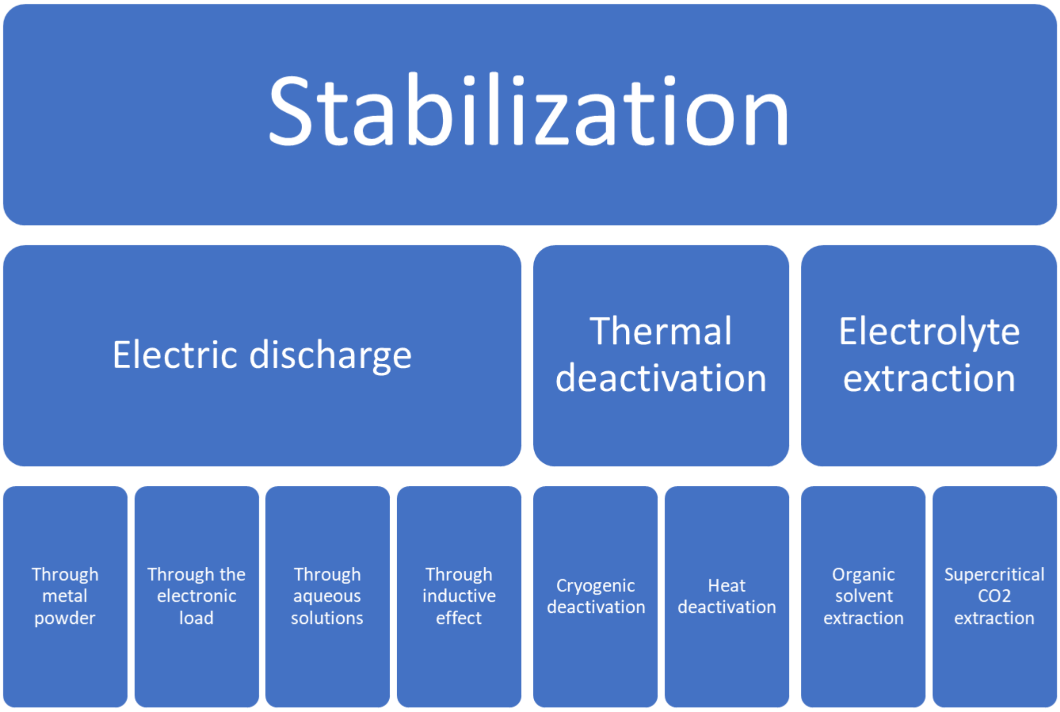

Figure 10 Stablisation classification and common methods[67]

2.2.4.1 Electric discharge

When disassembling spent lithium-ion batteries (LIBs), there is a potential danger of a short-circuit occurring between the anodes and cathodes. This short-circuit can result in the flow of a high-current current, which generates heat and can ignite the volatile electrolyte solvent, leading to a battery fire. To mitigate this risk, it is crucial to discharge the LIB before initiating the disassembly process. Discharging the battery is a standard procedure in LIB recycling as it stabilizes the battery and reduces the likelihood of self-ignition or a short circuit. By discharging the battery prior to disassembly, the potential hazards associated with short-circuits and thermal runaway can be minimized, ensuring the safety of personnel and the recycling facility[81]–[83]. Common methods of electric discharge are achieved by:

- Metal powder

- Electronic Load
- Electrochemical/ aqueous Solutions
- Inductive effect

2.2.4.2 Thermal Deactivation

Thermal deactivation is an essential process in the recycling of lithium-ion batteries (LIBs) to ensure their safe handling and deactivation. It involves carefully removing the chemical and energy rich components present in spent batteries to prevent any potential thermal events or hazards. Cryogenic freezing and heat deactivation are two commonly employed methods for achieving this objective[67].

Cryogenic freezing involves freezing and crystallising the electrolyte of spent LIBs at extremely low temperatures using liquid nitrogen, rendering the batteries nonconductive and reducing the risk of fire. While cryogenic freezing allows for processing large quantities of batteries simultaneously, it has limited adoption due to high capital and equipment costs[67].

Another method involves heating discharged LIBs prior to shredding and disassembling them, effectively removing the electrolyte and preventing thermal runaway. This controlled heating process ensures the safe elimination of combustible organic material and prevents the release of hazardous gases or metals during mechanical processing. These techniques contribute to the safe and regulated deactivation of LIBs during the recycling process[67].

2.2.4.3 Electrolyte Extraction

Extracting electrolytes from LIBs poses challenges because of the reactivity of lithium salts and the generation of toxic compounds when in contact with air or water. Aged LIBs complicate the process further as the electrolyte diffuses into the electrodes. The confidentiality of materials used in LIBs and complex pre-treatment processes also increase recycling costs. Traditional methods like calcination and evaporation release toxic gases, while a combined pyrometallurgical and hydrometallurgical process has limitations. Solvent extraction methods offer a more environmentally friendly approach. Developing effective recycling methods for aged electrolytes is crucial to minimise waste and environmental risks. The major technologies in Electrolyte extraction are Organic solvent extraction and Supercritical CO2 extraction[84]–[87].

2.2.5 Comminution

Comminution is a mechanical process used to break down battery packs into smaller pieces, resulting in a black material enriched in metals. It involves various methods such as ripping, shredding, crushing, and milling[88], [89]. Comminution can occur before or after manual disassembly of the batteries. There are three main processes of comminution: shredding, hammer milling, and granulating, each producing materials of different sizes and shapes. The size and morphology of the materials resulting from comminution have a substantial impact on the effectiveness of subsequent separation methods. To concentrate the valuable elements, the fragmented battery components undergo sorting using different separation methods. Comminution technologies, particularly mechanical crushing, offer higher processing efficiency and capacity compared to manual disassembly. The classification of comminution is typically done in stages to ensure a homogeneous size distribution and content of the battery fragments. Multiple stage crushing helps in the optimal segregation of battery elements, preventing entanglement of current collector particles in the black mass[88]–[90].

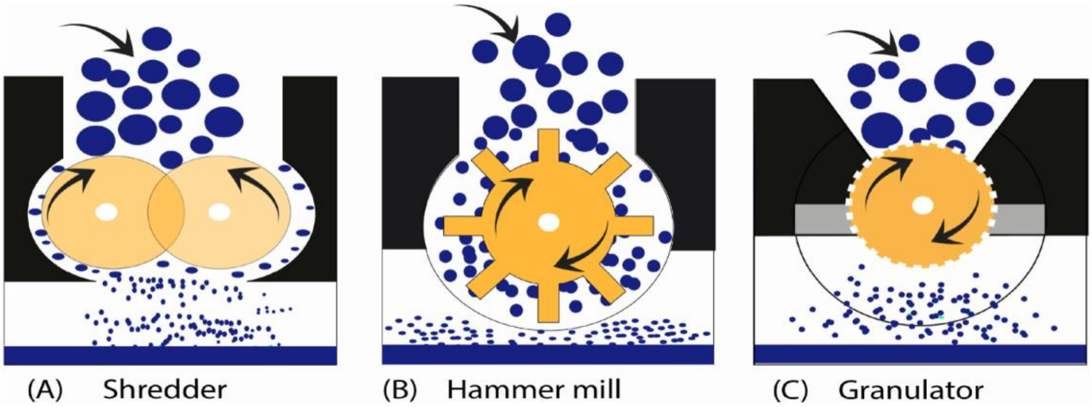

Figure 11 Comminution sequences of shredding followed by Hammer mill and lastly by granulating[67]

2.2.6 Dismantling

Manual dismantling of individual used batteries is a common practice, often done without proper safety precautions. Studies have shown that organic material leakage occurs during the dismantling process, with dimethyl carbonate (DMC) and tert-amylbenzene being the major organic vapor components. Specialized approaches, such as Z-folded separators, are required to validate acceptable levels of dimethyl carbonate. The concept of the Battery Identity Global Passport promotes the adoption of Z-folded approaches and dismantling methods that are automated, which utilize RFID tags and QR codes for battery identification. However, the diverse range of LIBs currently available poses challenges for achieving fully automated disassembly. Furthermore, during the end-of-life (EOL) stage, the degradation of bolts and screws in LIBs adds further complexities to automated disassembly processes[91]–[94].

Dismantling process progresses in the following way:

I. Removal of module and cells

II. Removal of casing
III. Removal of wire
IV. Removal of glue

Both Comminution and Dismantling has their own advantages and disadvantages, so which should be preferred? To shred the battery or not to Shred the battery ?

2.2.7 To Shred or Not to Shred

The decision between shredding and disassembly when recycling lithium-ion batteries (LIBs) involves trade-offs. The process of shredding provides the advantage of simplicity and the capability to handle various products without the requirement of opening them. However, it leads to a more intricate separation process and produces product streams that have low purity in the downstream stage. In contrast, disassembly offers the benefit of facilitating simpler separation processes and yielding purer products. However, it entails a more intricate and potentially hazardous procedure, particularly when it comes to opening battery cells. The complexity of disassembly is further compounded by the design of battery packs and modules, necessitating multiple steps and labour-intensive manual work, which can be time-consuming[93].

While shredding is commonly used in LIB recycling processes, it often focuses on recovering high-value materials such as cobalt while losing or not recovering other materials. Molten alloys are utilized to collect valuable metals, while the slag contains lithium, along with other oxides and gases, resulting in its loss. The advent of new cathode cells employing mixed metal cathodes highlights the importance of establishing efficient recycling methods for all types of lithium-ion batteries[93].

The primary objective of disassembly is to extract valuable materials and components for reuse or recycling, leading to the generation of material streams with high levels of purity. However, the process needs to be well-understood, safe, and potentially automated to reduce operational costs and time. Ensuring a secure and efficient dismantling process for lithium-ion batteries (LIBs) is crucial in the pursuit of a circular economy, where materials are recovered in waste streams of high purity for subsequent reuse and recycling. Disassembly presents notable advantages over shredding, particularly in terms of product purity, yield, and process simplicity, resulting in significant cost savings[93].

Fast delamination is important in disassembly to enable continuous flow processing and the recycling of lixiviant. Implementing measures to prevent the dissolution of the current collector in the recycling process brings about several benefits, including improved purity of the resulting products, increased reusability of the lixiviant, and enhanced process kinetics. In contrast, shredding the battery pack results in a blend of all the materials contained within it, necessitating additional steps to separate the various components[93].

Innovative recycling processes such as the Lithorec process employ a range of techniques, including electrical, mechanical, mild thermal, and hydrometallurgical methods, to extract valuable materials from lithium-ion batteries (LIBs). However, the intricate compositions and configurations of anode and cathode materials present inherent difficulties, leading to the contamination of material reservoirs and the depletion of resources such as plastics and lithium in mixed waste streams. Consequently, supplementary recovery approaches are necessary to address these challenges and enhance the overall efficiency of material retrieval[93].

In summary, the choice between shredding and disassembly for LIB recycling involves considering factors such as simplicity, purity of products, process complexity, and material recovery. Disassembly offers advantages in terms of product purity and value retention, but it requires careful optimization and automation to achieve economic feasibility.

2.2.8 Material Separation

After dismantling or comminution, further processing is carried out to obtain higher-quality materials. Physical separation techniques are employed to separate different components for subsequent reclamation processes. In the seperation process, various components are segregated, resulting in separate material streams such as plastic, separator and pouch material, metals (including steel casing, Ni and Al tabs), as well as Al and Cu current collectors. Additionally, there is a mixture of miscellaneous materials, encompassing components from both the negative and positive electrodes. This composite material plays a vital role in subsequent processing stages, such as metal dissolution and deposition. To ensure efficiency and cost-effectiveness, it is imperative to achieve effective physical separation, thereby minimizing the presence of contaminants and reducing the requirement for additional purification steps[95]–[98].

The general methods that are commonly used are[67]:

- Sieving/particle size separation
- Electrostatic separation
- Eddy current separation
- Magnetic separation
- Froth flotation
- Gravity/density separation

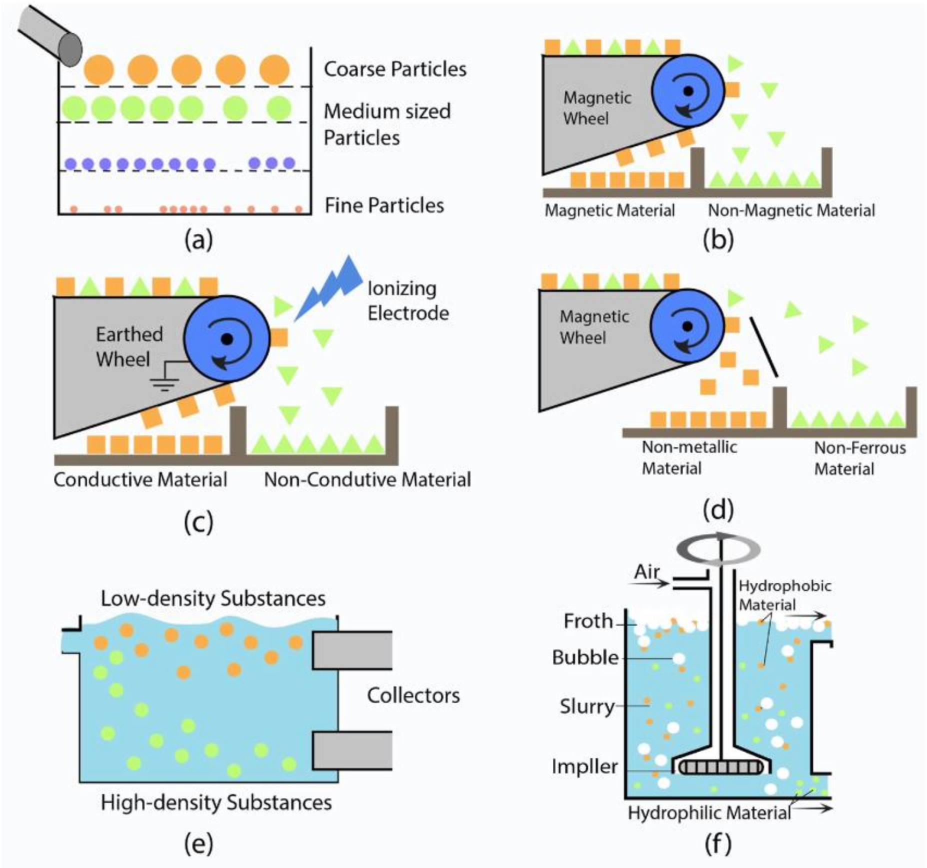

Figure 12 Separation techniques (a) Sieving/particle size separation, (b) Magnetic separation, (c) Electrostatic separation, (d) Eddy current separation, (e) Gravity/ density separation, and (f) Froth flotation.[67]

2.2.9 Material Refining Process

In the recycling of EoL LIBs, pre-treatment is an important step, where the black matter generated is used as the starting material for metal recovery. Metals like lithium, nickel, cobalt, and manganese present in the cathode materials are economically valuable but can have harmful environmental effects if released during recycling. The most common recycling routes involve pyrometallurgical methods followed by hydrometallurgical separation and refining processes. These methods aim to recover a Ni-Co alloy but often require further hydrometallurgical steps for purification. Hydrometallurgical processes achieve high recycling rates exceeding 90% and enable direct lithium recovery. In order to attain high selectivity and efficiency, chemical processes like leaching, extraction, precipitation, and crystallization are utilized. Although there is ongoing research on upstream lithium recovery, its commercial implementation is yet to be realized[99].

2.2.9.1 Hydrometallurgy

In the hydrometallurgical recovery of lithium-ion batteries (LIBs), post pretreatment, separate treatment of battery cases, electrodes, and membranes is commonly employed to enhance safety and recovery rates while reducing energy consumption. Acid and biological leaching are the two main methods used in hydrometallurgy. Acid leaching involves the use of inorganic and organic acids such as hydrochloric acid, sulfuric acid, nitric acid, and phosphoric acid. Factors like acid type, temperature, pH, reaction time, and additives influence the leaching performance. Hydrochloric acid is effective for leaching cobalt (Co) but produces toxic chlorine gas. Nitric acid is useful for hydrolyzing cathode materials and recovering Li and manganese (Mn). Sulfuric acid with hydrogen peroxide (H_2O_2) reduces Co^{3+} to Co^{2+} for efficient recovery. Phosphoric acid has also shown promising results. Mild organic acids like oxalic acid, acetic acid, citric acid, and tartaric acid have gained attention. Oxalic acid facilitates simultaneous leaching and precipitation, resulting in the direct separation of CoC_2O_4 without additional treatment. Acetic acid, citric acid, and tartaric acid have demonstrated high recovery rates for Li, Co, Ni, and Mn through leaching studies. Ultrasonic and microwave techniques have been explored to enhance the leaching process [99].

Bioleaching is a hydrometallurgical process that utilizes microorganisms like bacteria and fungi to dissolve spent electrode materials. In one study, chemotrophic and acidophilic bacteria were used to treat $LiCoO_2$, while another study explored the leaching performance of Alicyclobacillus SP for Li and Co at different concentrations. The recovery rates for Li and Co decreased as the ore slurry concentration increased. The survival of Aspergillus Niger fungi/bacteria was considered in another study, which also highlighted the impact of slurry concentration on bioleaching. The effects of electrolytes in the slurry on biological activity were investigated in a separate study involving Aspergillus Niger[100]–[102].

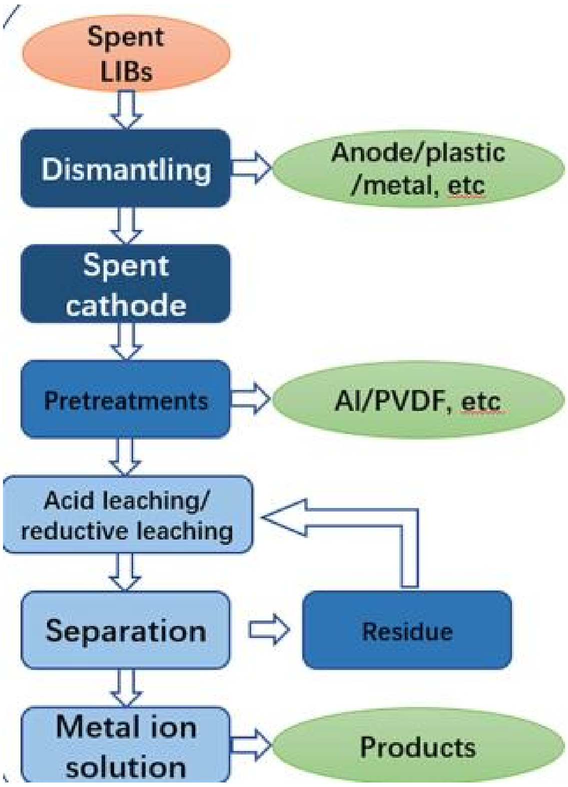

Figure 13 Draft sequence of hydrometallurgy [99].

2.2.9.2 Pyrometallurgy

Pyrometallurgical techniques are commonly employed for metal extraction in various industries, including the recycling of LIBs. Calcination, a process involving high temperatures in oxygen-poor environment, is used to decompose lithium metal oxides found in LIBs, such as LiCoO2. This leads to the release of oxygen and the formation of metal oxide and lithium carbonate. In contrast, the process of roasting takes place in an environment with an abundance of oxygen and is commonly employed in the treatment of sulfide minerals. Reduction processes, such as carbo-thermal reduction, aim to recover metals from metal oxides by converting them into metal alloys using a reducing agent like carbon. The effectiveness of reduction processes is determined by the oxygen level present in the metal oxide. The Umicore, Inmetco, Glencore, and Accurec processes are examples of pyrometallurgical methods used in LIB recycling. These processes involve a combination of steps such as pre-treatment, smelting, reducing, and leaching to separate and recover components like metals and lithium carbonate. Each process has its specific advantages and requirements, such as the utilization of C-rich compounds, pre-treatment steps, or the generation of slag for alternative applications in construction materials [99].

2.3 Ultrasonication as Preprocessing method

2.3.1 Ultrasonication – overview

Ultrasonication is a widely adopted mechanical method employed to disintegrate sludge. It utilizes the transmission of ultrasound waves through a medium, leading to compression and rarefaction of the medium. This process leads to the formation of microbubbles that violently collapse when they reach a critical size, resulting in cavitation. As the bubbles collapse, they generate intense conditions characterized by high temperatures and pressures of the range of 5000K and 500 bars. These conditions are accompanied by strong hydro-mechanical shear forces and reactive radicals. The hydro-mechanical shear forces and radicals play a significant role in breaking up clusters within the sludge and releasing material trapped between cells. It is worth noting that hydro-mechanical shear forces are more efficient in causing sludge rupture compared to radicals[11], [12].

2.3.2 Types of ultrasonication

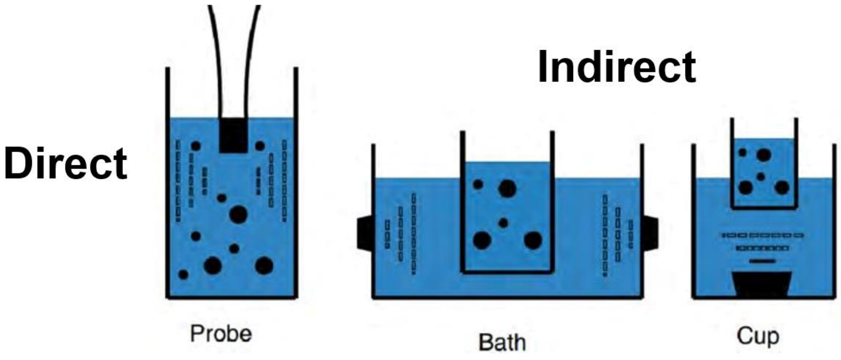

Figure 14 Types of Ultrasonication methods - Direct (left) and Indirect (middle and right) [103]

During indirect sonication, such as with a sonication bath or cup horn sonicator, the ultrasound waves before reaching the suspension (particle under ultrasonication), must pass through both the liquid in the bath and the wall of the sample container. Using an indirect sonication method, such as a sonication bath or cup horn sonicator, results in reduced energy being transferred to the suspension compared to direct sonication, where the probe directly contacts the suspension. Sonication baths usually operate at lower energy levels because the transducer is attached to the exterior of a metal tank. The ultrasonic waves are then transmitted to the tank surface and subsequently into the bath liquid[103].

Sonication, particularly at ultrasound frequencies, induces the formation, growth, and subsequent collapse of bubbles, leading to the generation of shock waves and extreme conditions. These conditions occur at the interface of the collapsing bubbles and include localized temperatures reaching up to 10,000 K, rapid temperature changes, pressure bursts of several MPa, and high-speed liquid jet streams. These effects, known as cavitation, are inherent to sonication and are independent of factors such as container cooling or the type of sonicator utilized[103].

2.3.3 Ultrasonication in battery recycling:

The study done by Lei et al demonstrates the effectiveness of high-powered ultrasound in rapidly delaminating the active material from the current collector in LIB. Through investigation, it was discovered that cavitation was responsible for the rapid breakage of the adhesive bond between the active layer and current collector within a mere 0.5 seconds upon entering the high-power ultrasound region. The efficiency of this delamination process relies on the type of polymer binder used, as water-soluable binders like SBR/CMC exhibit faster stripping tendencies. The delamination process can be further optimized by incorporating wetting agents and adjusting the pH. Simplifying the recycling of production scrap involves saturating the mixture of active material and binder with an organic solvent. This approach offers several advantages, including achieving high material recovery rates, enhancing throughput, and ensuring scalability of the process. As a result, high-powered ultrasonic delamination emerges as a noteworthy advancement in the field of battery recycling[104].

In a separate investigation[105], the utilization of sonication proved to be pivotal in the extraction of the black mass from lithium-ion batteries. The black mass, which encompasses active materials, a conductive additive, and binder, underwent sonication within an oxalic acid solution. Sonication proved to be a highly effective method, as it enabled the rapid and efficient delamination of the black mass from the current collectors. The cavitation induced by the sonication process disrupted the adhesive bond between the black mass and the metal foils, allowing for easy separation. Within a relatively short duration of 30 minutes for the anodic black mass and 5 minutes for the cathodic black mass, the sonication process successfully released the black mass components. Throughout the entire black mass extraction process, sonication played a crucial role in achieving efficient delamination of the black mass from the current collectors. The application of high-frequency sound waves during sonication facilitated the breakdown of the adhesive bond, enabling the successful separation of the black mass components for further recycling or reclamation purposes[104], [105].

3 Research material and methods

In this study, the focus was on the preparation and handling of the cathode and anode sheets, as well as the experimental setup for ultrasonication bath and the generation of black mass. The effects of ultrasonication on the cathode and anode sheets were analysed. The experimental setup involved the preparation of cathode and anode sheets from lithium-ion batteries. The sheets were then subjected to ultrasonication in a bath to generate the black mass. The ultrasonication process utilized high-frequency sound waves to disrupt the adhesive bond between the black mass and the sheets, facilitating its separation. The study examined the effects of ultrasonication on the cathode and anode sheets.

However, certain aspects were outside the scope of this study. These included battery dismantling and discharge, safe removal of the electrode sheets, electrolyte recovery, black mass purification, hydro metallurgical processes, and the recovery of battery materials from the black mass. Additionally, the specific effects of ultrasonication on the binder molecules were not analyzed in this study.

3.1 Electrode Composition

The electrode preparation process involves three key components: the active material, a conductive additive, and a binder. These components are applied onto a current collector, dried, and calendared. For the anode, a battery-grade copper current collector is used, while for the cathode, a battery-grade aluminium current collector is used.

In this study, various components and binder additives were used for both the anode and cathode electrodes. The specific details of these components and additives can be found in the provided table.

Table 4 Anode and cathode Material composition and their weightage

Material	Anode	Weightage (%)	Cathode	Weightage (%)
Active material	Graphite	95%	Lithium manganese nickel oxide (LMNO)	90%
Conductive additive	Carbon Black	0.5-1 %	Carbon black	5%
Binder + solvent	CMC/SBR + Water	3-4 %	PVDF + NMP	5%

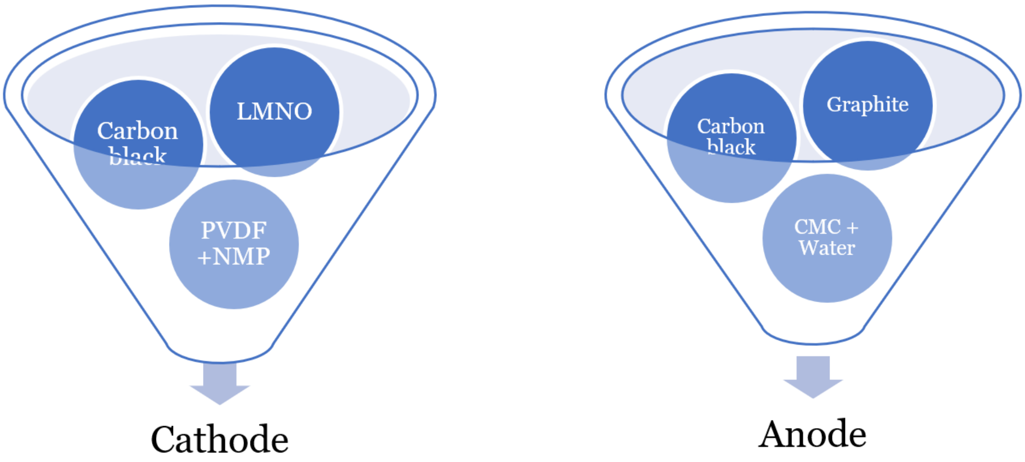

Figure 15 Anode and cathode components under the study and their major components

3.1.1 Electrode Preparation

The production of batteries begins with the crucial step of electrode fabrication, encompassing the creation of both the anode and cathode. The cathode material selected for this study is Lithium manganese nickel oxide (LMNO) (NANOMYTE SP-10), characterized by its chemical formula $LiMn_{1.5}Ni_{0.5}O_4$. To ensure efficient electron conduction within the cathode, carbon black (CB) (Sigma Aldrich) is blended with the LMNO powder. However, since LMNO and CB are in powder form, a binder is necessary to bind them together in a gel-like consistency. In this particular study, polyvinylidene fluoride (PVDF) (HSV 900 +ADX 160 Arkema) is employed as the binder for the cathode.

To prepare the cathode, a precise weight percentage of LMNO nanopowder and CB powder (90% and 5% respectively) is meticulously mixed using a mortar and pestle. The remaining 5% by weight, comprising PVDF, is added to a sealed Eppendorf vial. The exact compositions of the slurry are documented and can be referred to in Table 4 of this thesis.

In order to create a homogeneous slurry, the LMNO/CB mixture within the Eppendorf vial is combined with 200µL of N-methyl-2-pyrrolidone (NMP), a solvent chosen for its compatibility with PVDF. To achieve thorough mixing, a zirconium ball is added to the vial, which is then placed in a mechanical mixer. The vibrating motion of the mixer, maintained at a frequency of 150 Hz for a duration of 30 minutes, ensures that the slurry attains uniformity in composition and consistency.

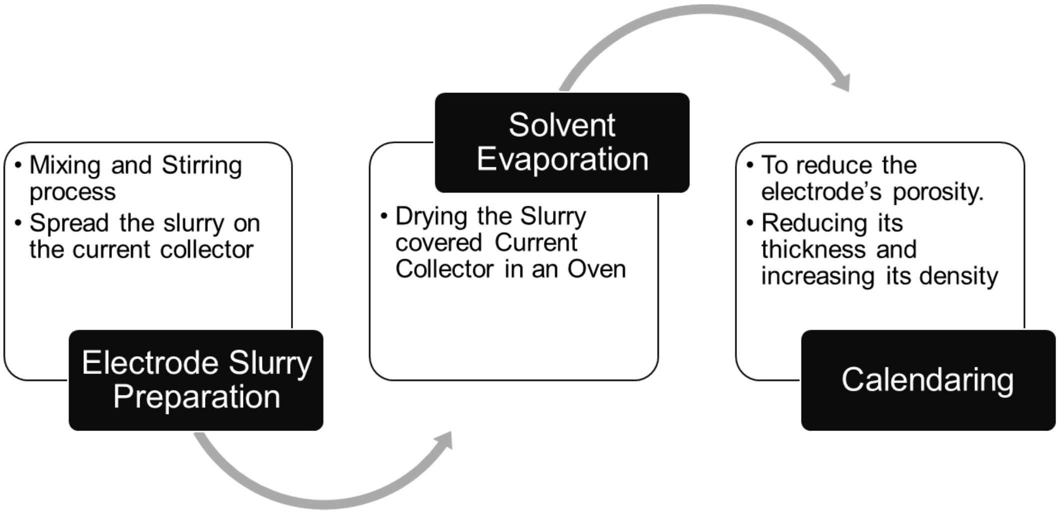

Figure 16 Electrode Preparation Process[106]

Subsequently, the cathodic slurry is carefully applied onto a meticulously cleaned Aluminium foil, which serves as the current collector for the cathode. To facilitate smooth spreading of the slurry, the Aluminium foil is first cleaned with ethanol and then pre-wetted with NMP. Using an Automatic Film Applicator equipped with a doctor blade, the slurry is evenly spread over the surface of the foil.

To complete the electrode fabrication process, the coated Aluminium foil is subjected to a drying stage. This entails placing the foil in an oven set at a temperature of 50°C for a duration of one hour. This drying step ensures that the solvent evaporates, leaving behind a solidified cathode layer adhering to the Aluminium foil.

For the anode preparation, a similar procedure is followed, albeit with some variations. The anode material used is graphite, combined with carbon black to enable electron conduction. However, instead of PVDF, a water-soluble SBR/CMC binder is utilized in this case. As a result, the solvent employed is water instead of NMP. The specific compositions of the anodic slurry can be found in the accompanying Table 4.

Cathode

Anode

Figure 17 The cathode and the anode made for the study with cathode produced in the form of coin cell and the anode in the form of a pouch cell

Once the drying process is completed, the resulting electrodes undergo calendaring. This step involves applying pressure to the electrodes to enhance their density and mechanical properties. For coin cell-sized electrodes, a hydraulic press is utilized, while mechanized techniques are employed for pouch cell-sized electrodes. These calendaring processes aid in achieving electrodes with the desired characteristics for subsequent battery assembly. These meticulous steps in electrode preparation are essential in ensuring the quality and performance of the resulting batteries.

3.2 Experimental setup:

The experimental setup for ultrasonication involved the utilization of an Elmasonic P 180H ultrasonicator. This particular model is equipped with two frequencies, namely 37kHz and 80kHz, providing flexibility in ultrasonic wave generation. The ultrasonicator has a generous operating volume capacity of 12.9 liters, allowing for the treatment of sizable samples. Notably, it incorporates a heating system to facilitate temperature control during the experiments.

In terms of power consumption, the total power draw of the Elmasonic P 180H can reach up to 1330 W. The ultrasonic power consumption, specifically at its maximum working capacity, is approximately 330 W, with a peak power output of around 1000 W. The integrated heater operates at 1000 W and offers a temperature range spanning from 30°C to 80°C. Additionally, the ultrasonicator possesses an IP rating of 20, indicating its degree of protection against solid objects, and generates an ultrasonic noise level of 105 dB.

The Elmasonic P 180H ultrasonicator was chosen for its capabilities to deliver efficient and controlled ultrasonic energy for the experimental procedures conducted. Its combination of power, frequency options, volume capacity, and temperature control features makes it well-suited for the required applications and contributes to the overall success of the research.

Figure 18 experimental procedure and setup

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In order to conduct the experiment, the electrode sheets were meticulously cut into appropriate sizes that could fit inside a 50ml beaker. Prior to placing the samples in the beaker, their weights were accurately measured to establish the initial mass. Subsequently, the beaker setup was carefully covered with a layer of parafilm to ensure the prevention of dust contamination. To release any pressure that might build up during the sonication process, a few small holes were made in the film.

To proceed with the experimental setup, the beaker containing the electrode samples, mounted on a fixture, was submerged into an ultrasonicator bath. It is important to note that the water level in the bath was maintained higher than the water level inside the beaker to facilitate efficient sonication. The ultrasonicator was equipped with various adjustable parameters such as frequency, temperature, time, and power, which were set according to the experimental requirements.

Once all the necessary parameters were configured, the experiment was initiated and carried out for the designated duration as per the experimental plan. After the specified duration, the electrode samples were carefully removed from the beaker. Visual examination was performed to detect any signs of damage or observable changes in the samples. Additionally, the samples were weighed again to determine their post-sonication mass. Throughout the experiment, all relevant experimental conditions, including the parameter settings, duration, and any additional observations, were diligently recorded for future analysis and reference.

This comprehensive experimental setup and procedure were employed in order to investigate and analyse the effects of ultrasonication on the electrode samples, providing valuable insights for the Thesis research.

3.3 Parameters

The experimental setup included several key parameters or variables that were carefully controlled and manipulated to investigate the effects of ultrasonication on the electrode samples. These variables consisted of frequency, power, temperature, liquid medium, liquid quantity, and time duration.

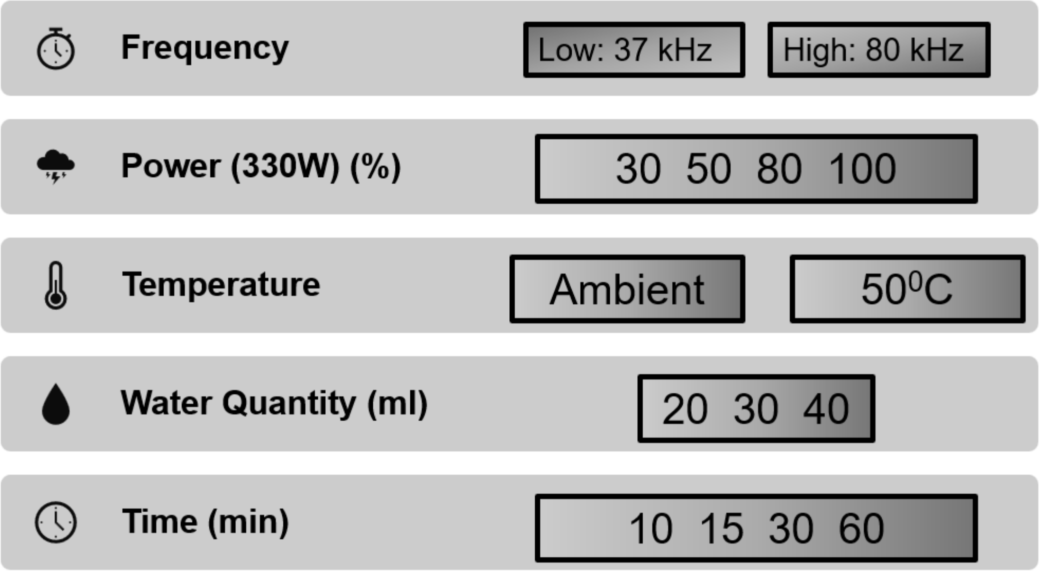


Figure 19 Parameters for the experiment and their value limits

The frequency parameter was determined by the ultrasonicator device used in the experiment, which offered two available frequencies of 37kHz and 80kHz. While the literature commonly reported the use of frequencies around 40kHz and 20kHz, our experimental setup allowed for comparing a slightly lower frequency of 37kHz and a higher frequency of 80kHz. This allowed us to explore the effects of ultrasonication within this range and assess any potential variations in outcomes.

Regarding power, the ultrasonicator device provided a wide range of power options, expressed as a percentage, ranging from a minimum of 30% to a maximum of 100%. The maximum power setting corresponded to a power output of 330W. By adjusting the power setting, we could control the intensity of the ultrasonic energy applied during the experiment and examine its influence on the electrode samples.

Temperature is an important parameter to consider, as it can impact the delamination process. While adhering to the principles of green chemistry that advocate for ambient temperature usage, we also aimed to investigate the effects of increased temperature. Based on our literature review, a higher temperature of 50°C was chosen to study the potential effects of elevated temperatures on the electrode samples.

In terms of the liquid medium used during ultrasonication, previous studies have utilized various solutions such as oxalic acid, sodium hydroxide, citric acid, and N-methyl-2-pyrrolidone (NMP). However, to align with the principles of green chemistry, our experiment employed deionized water as the liquid medium. This choice adheres to the principles of reducing derivatives and employing safer solvents and auxiliaries.

The quantity of the liquid medium used was dependent on the beaker setup and was sufficient to cover the electrode samples adequately. By using a standardized quantity of deionized water, we ensured consistent experimental conditions throughout the study.

The time duration for ultrasonication varied in the literature, ranging from 5 minutes to 60 minutes. To assess the effect of different exposure times, we selected specific time intervals of 10, 15, 30, and 60 minutes. This allowed us to investigate the impact of ultrasonic treatment duration on the electrode samples and assess the efficiency of material removal.

Based on these variables, a total of 32 experiments were conducted, systematically varying the frequency, power, temperature, liquid medium, and time duration. After the ultrasonication process, the electrode samples were evaluated for changes in their state, such as delamination or damage, and the removal efficiency of the materials of interest was analyzed.

The meticulous consideration and systematic variation of these experimental parameters contribute to the robustness and reliability of the research conducted for this thesis.

4 Results

4.1 Effect of frequency

The given box plot in the Figure 20 illustrates the impact of frequency on the cathode and anode sheets. It focuses on the percentage of mass loss, which is depicted on the y-axis, and various frequencies, which are represented on the x-axis. Additionally, the color shading within the plot signifies the density of points within specific regions. Darker shades indicate higher point densities, while lighter shades indicate lower densities.

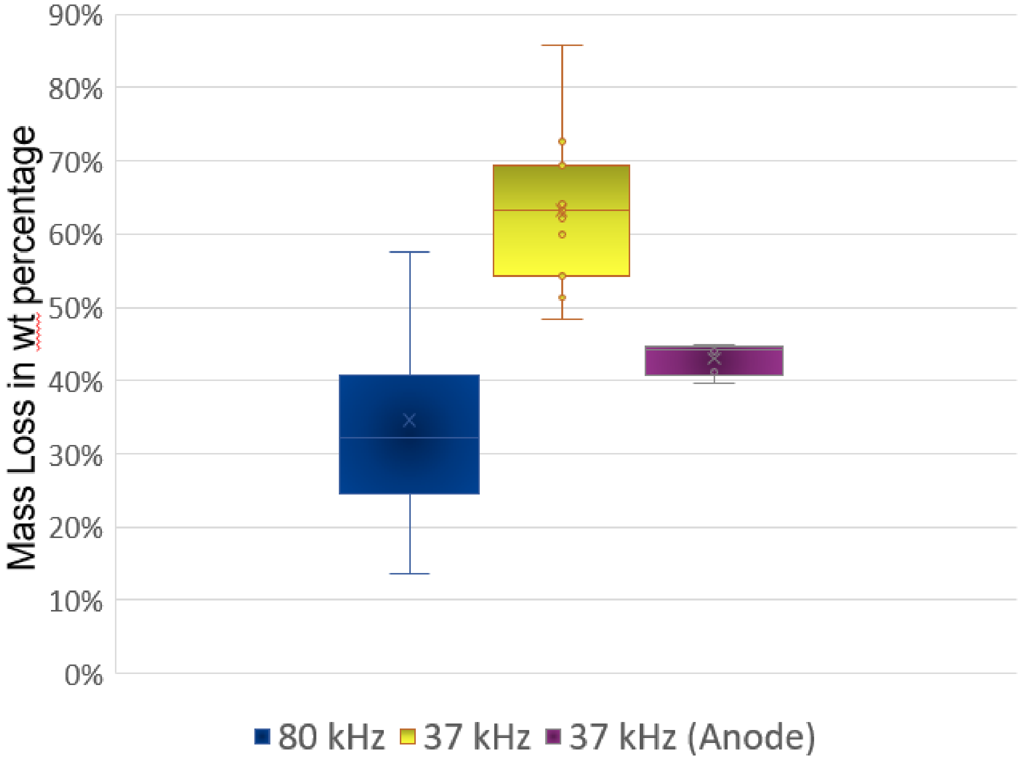


Figure 20 Mass Loss V/s Frequency

It was observed that increasing the frequency of ultrasonication to 80kHz had a noticeable effect on the cathode samples. Interestingly, this higher frequency appeared to reduce the overall impact of ultrasonication while simultaneously protecting the integrity of the aluminium current collector leading to a lower mass loss percentage as shown in Figure 20. This finding suggests that the use of a higher frequency may be advantageous in terms of minimizing potential damage to the current collector while still achieving the desired effects of ultrasonication on the cathode material.

On the other hand, when a lower frequency (37kHz) was employed, a more significant rate of material removal was observed. However, it was also observed that the lower frequency led to the generation of particulate contamination from broken aluminium particles, which had an adverse effect on the cathode material mixture. This contamination is likely a result of the more intense mechanical forces induced by the lower frequency ultrasonication, leading to a higher likelihood of damage to the aluminium current collector and subsequent release of aluminium particles into the mixture. Consequently, caution must be exercised when selecting the frequency parameter to ensure the preservation of the cathode material's quality and purity.

Interestingly, the anode current collector did not exhibit significant damage when subjected to ultrasonication at a frequency of 37kHz. It is speculated that this resistance to damage may be attributed to the anode current collector's double-coated structure, which provides a higher density and enhanced structural integrity. The dual coating likely contributes to maintaining the shape and integrity of the anode current collector under the pressure generated during ultrasonication, preventing significant damage and preserving its functionality.

These observations highlight the importance of selecting an appropriate frequency parameter for ultrasonication, taking into consideration both the desired material removal rate and the potential risks of damage or contamination.

4.2 Power Significance

The impact of altering the power percentage applied to the cathode can be examined using a box plot, accompanied by visual representations of before and aftereffects as shown in Figure 21. The box plot graphically displays the mass loss on the y-axis, while the x-axis represents various power levels measured in percentages. The maximum power level of 100% corresponds to 330W. The graph specifically showcases the power levels of 100%, 80%, and 30%, providing a clear comparison of their effects.

In addition other plots are available to visually represent the impact of power changes on the cathode at 80kHz (Figure 22) and anode at 37 kHz (Figure 23). These plots follow a similar format, with the y-axis representing the percentage of mass loss, and the x-axis displaying different power levels expressed in percentages. The figures demonstrate the effects of power changes at different frequencies.

For instance, there is Figure 22 illustrating the before and after effect of power changes on the cathode at a frequency of 80kHz. This figure provides a visual representation of the mass loss percentages associated with various power levels. Similarly, Figure 23 focuses on the impact of power variations on the anode, displaying the corresponding mass loss percentages.

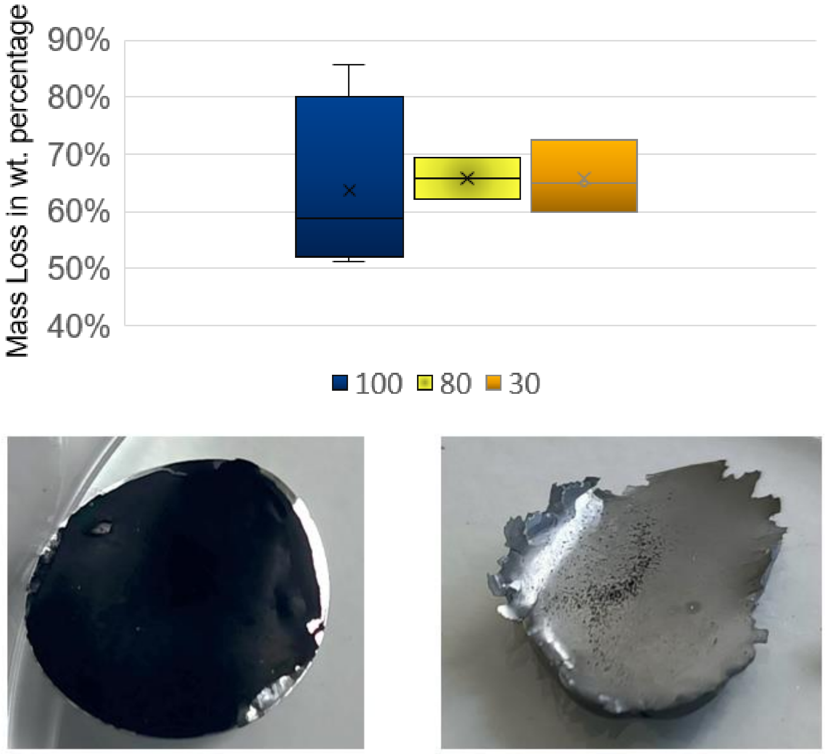


Figure 21 Effect of Power on Cathode at 37kHz and the damagind effect of higher power at a lower frequency

During the experimental investigation, it was observed that increasing the power at a frequency of 37kHz had a notable effect on the material loss of the cathode. Specifically, higher power levels resulted in a greater amount of material being removed. This observation can be attributed to the formation of an increased number of sonication bubbles in the water medium, leading to more frequent bursts of high-temperature and pressure microbubbles within the mixture. Consequently, this intense microbubble activity caused greater damage to the aluminium sheet, resulting in higher material loss.

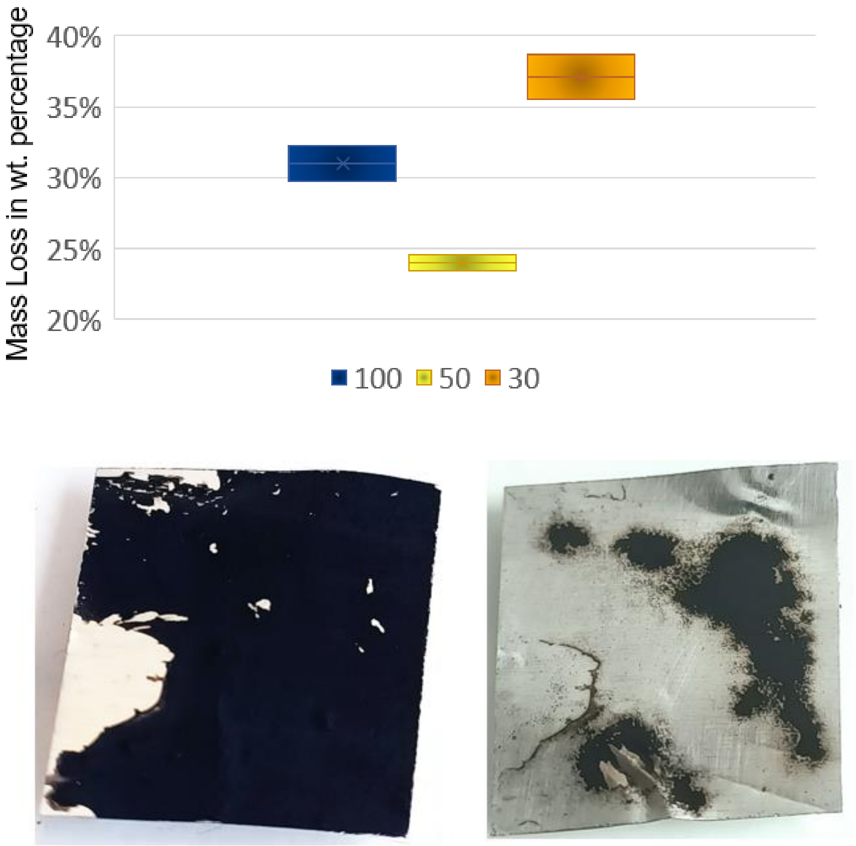


Figure 22 Effect of Power on Cathode at 80kHz and minimised material loss at higher frequency even at a higher power .

On the other hand, when the higher frequency of 80kHz was utilized, increasing the power did not exhibit a significant impact on the material loss. This phenomenon can be explained by the fact that the microbursts generated in the higher frequency range do not significantly affect the aluminium material. The observed variations in material loss at this frequency were primarily influenced by the thickness of the coating applied to the aluminium sheet. Thicker coatings offered better protection and reduced the susceptibility of the aluminium sheet to damage during ultrasonication.

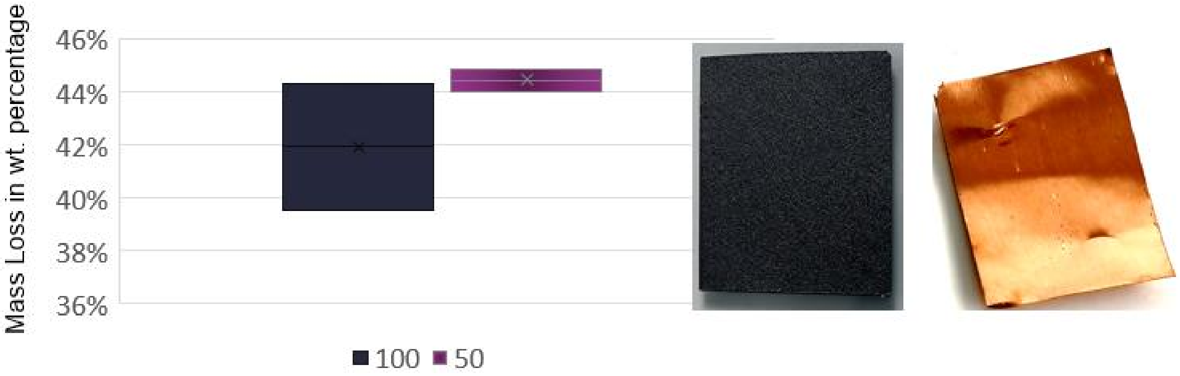


Figure 23 Effect of Power on anode at 37kHz and the optimal removal rate observed at a lower frequency

In contrast to aluminium, copper demonstrated a higher density and inherent resilience, making it more resistant to damage. Additionally, the copper current collector was double coated, further enhancing its ability to withstand the effects of ultrasonication. Consequently, the same impact observed in the aluminium sheet, where an increase in power led to higher material loss, was not observed in the case of copper. The unique properties of copper, including its density and double-coated structure, contributed to its greater resistance to damage and material loss during the ultrasonication process.
These findings underscore the importance of considering the interplay between frequency, power, and material properties when utilizing ultrasonication in electrode preparation. Further investigation and characterization of the effects of power and frequency on different materials used in electrode manufacturing would provide valuable insights for refining and optimizing the ultrasonication technique in battery production and recycling applications.

4.3 Effect of water quantity

The effect of water quantity on the material removal capability was studying at a single frequency of 37 kHz, which has the most material removal effect. The water quantity studied were 20, 30 and 40 ml. Their impacts were summarized in the form of box plot as shown in Figure 24, where the mass loss in weight percentage is tabulated in the y axis and the quantity of water is tabulated in a descending manner in the x-axis.

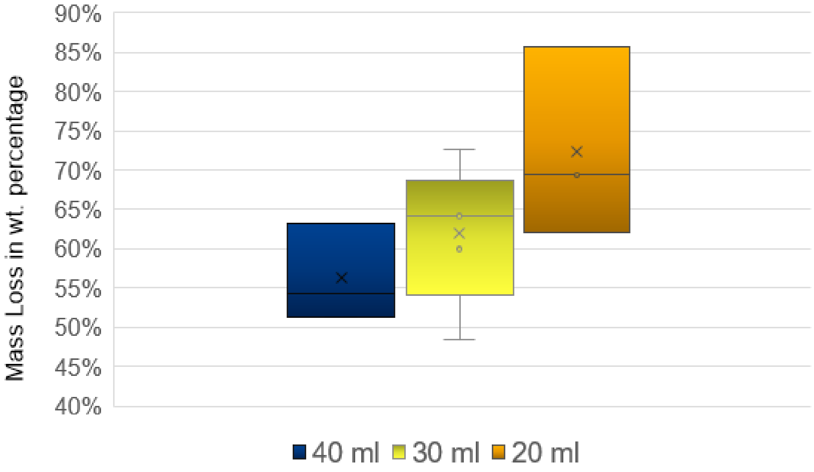


Figure 24 Effect of water quantity on Cathode at 37kHz

The experiment revealed that reducing the water volume led to a noticeable intensification of the sonication process. This intensified sonication resulted in higher levels of damage to the aluminium foil and increased mass loss in the electrode sheet. The higher mechanical stress caused by the intensified sonication led to the formation of microbubbles and subsequent bursts within the mixture, causing damage to the aluminium foil. Additionally, the increased intensity of the sonication process resulted in more vigorous agitation and erosion of the electrode material, leading to higher mass loss. However, to strike a balance between efficiency and minimizing the impact, subsequent experiments were conducted using a reduced volume of 30 ml.

4.4 Effect of temperature

To better understand how temperature affects a scenario, it's been found that a visual representation of the data is more effective than a chart. This is especially true when comparing the operating conditions of 80 kHz and 30 ml of water for 30 minutes, while changing the temperature between 50°C and room temperature as shown in Figure 25 and Figure 26.

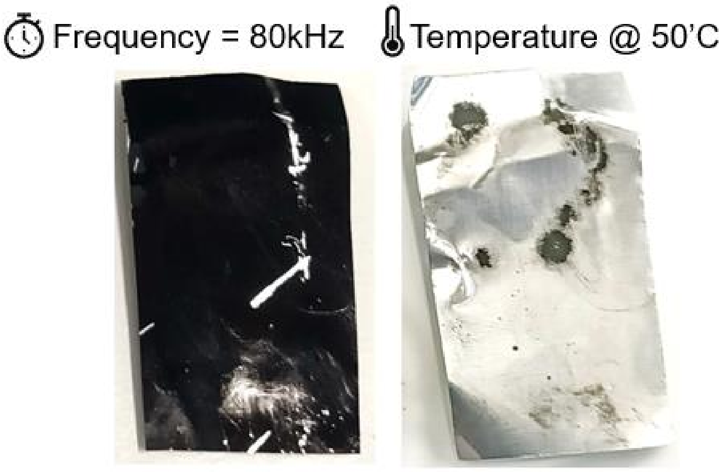


Figure 25 Improved removal rate visually observed at an elevated temperature of 50 C

The results indicate that an increase in temperature has a significant impact on the efficiency of material removal during ultrasonication. Specifically, higher temperatures were found to enhance the material removal efficiency when using the 80kHz frequency. This observation can be attributed to the beneficial effects of increased temperature on molecular diffusion.

The higher temperatures facilitate the mobility of molecules within the system, enabling them to diffuse more rapidly. This enhanced molecular diffusion plays a crucial role in the removal of materials from the electrode surface. As the molecules move more freely, they can effectively interact with the electrode material, leading to a more efficient removal process.

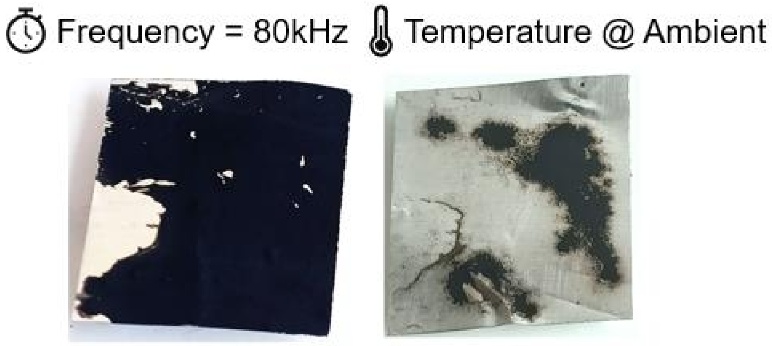


Figure 26 Presence of active material visually observed at ambient temperature

The improved material removal efficiency associated with higher temperatures is particularly pronounced when utilizing the 80kHz frequency. This finding suggests that the combination of a higher frequency and elevated temperature creates favorable conditions for enhanced molecular diffusion and subsequent material removal.
Overall, the results highlight the importance of considering temperature as a crucial parameter in ultrasonication processes. By optimizing the temperature in conjunction with the appropriate frequency, researchers can effectively enhance the material removal efficiency and promote the overall effectiveness of ultrasonication in electrode preparation.

4.5 Time effect

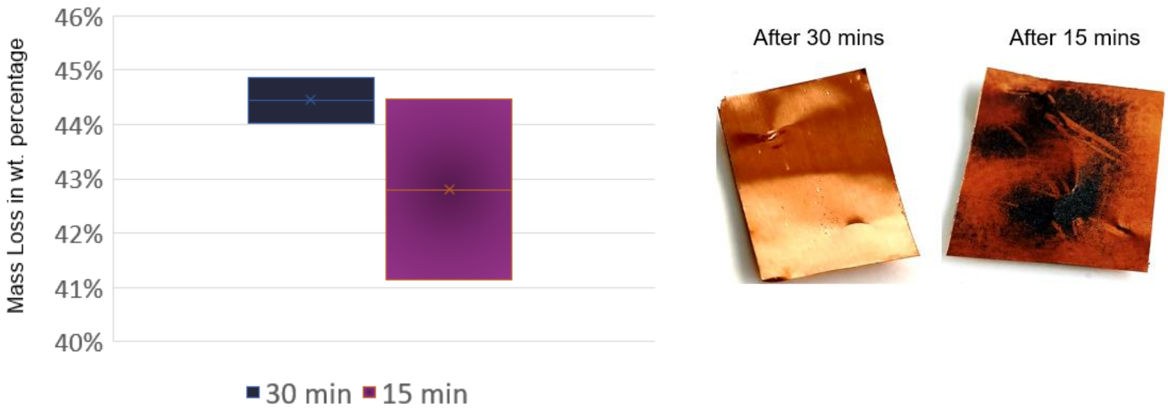


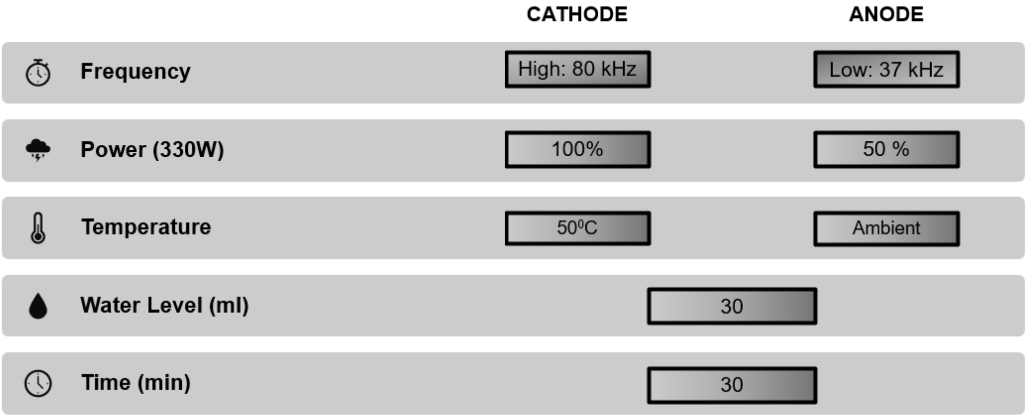
Figure 27 Effect of time on copper anodes (Left) , the visual effect of time in the anodes (Right) for the varing time of 30 and 15 mins

The impact of timing on the ultrasonication process was investigated by keeping the frequency and power constant. Interestingly, altering the timing had limited effects on the aluminium current collector. It was observed that either the collector remained intact without significant damage or the material removal reached a saturation point within a certain time limit. The time

duration for these experiments ranged from 5 minutes as the minimum to 60 minutes as the maximum.
In contrast, the effect of timing on the anode material was more pronounced. Increasing the time duration at the same power and frequency resulted in enhanced material removal from the anode. This suggests that longer exposure to ultrasonication positively influenced the removal efficiency. However, it is worth noting that as the timing increased, visible damage started to appear at the edges of the anode, indicating that extended sonication periods may have adverse effects on the structural integrity of the anode material.
These findings highlight the delicate balance that needs to be maintained when determining the optimal timing for ultrasonication. While longer durations can improve material removal, there is a risk of compromising the integrity of the electrode material. Therefore, careful consideration of the desired level of material removal and the potential damage to the electrode structure is crucial in determining the appropriate timing for ultrasonication.

4.6 Optimised parameters and further explorations

The experimental results reveal that optimizing different parameters is crucial for achieving minimal damage to the current collectors and optimal material removal rates. In the case of the cathode, a high frequency of 80kHz, a maximum power of 330 watts, and an elevated temperature of 50C are required to attain the desired material removal rate. These parameters provide the necessary energy and agitation to effectively remove the cathode material. Conversely, for the anode, a lower frequency of 37kHz, a power of 115W, and ambient temperature are sufficient to achieve optimal material removal. The use of a water-soluble binder in the anode formulation facilitates its efficient removal.



	CATHODE	ANODE
Frequency	High: 80 kHz	Low: 37 kHz
Power (330W)	100%	50 %
Temperature	50^0C	Ambient
Water Level (ml)	30	
Time (min)	30	

Figure 28 Optimised parameters for minimised damage to the current collector

In the optimized conditions, the water level and timing remain constant for both the anode and cathode. However, it is worth noting that further exploration is needed to study the effects of frequencies within the intermediate range. This would enable the identification of a single optimum frequency that can be applied to both the anode and cathode, thereby streamlining the process. The experimental results suggest that increasing the frequency reduces damage to the cathode current collector. Additionally, the double coating on the anode contributes to reduced damage, further enhancing its durability.

To gain a deeper understanding of the effects of ultrasonication at a molecular level, it is essential to conduct further studies. Quantifying these effects would be instrumental in reducing or eliminating additional purification steps and improving the efficiency and sustainability of the recycling process. Such investigations would provide valuable insights into the mechanisms underlying material removal and pave the way for enhancing the recycling process for batteries.

Overall, the findings from this study underscore the importance of optimizing various parameters for different electrode materials, highlighting the need for tailored approaches to achieve minimal damage and optimal material removal rates. These insights contribute to the advancement of battery recycling techniques, ultimately promoting a more sustainable and efficient circular economy for battery materials.

4.7 Industrial approach and bottle necks in Ultrasonication

The increasing demand for lithium-ion battery components has created a need for viable recycling options. However, Europe's current recycling capacity falls short, as it can only recycle 22% of the batteries produced or sold in 2020[107]. The existing recycling infrastructure in Europe is primarily focused on pyrometallurgical processes, which involve high-temperature operations such as smelting. While this method can recover some valuable materials, it has limitations in terms of recovery efficiency. Specifically, the infrastructural recovery efficiency for lithium in Europe is approximately 42% [107]. To address these challenges and improve recycling efficiency, there is a need to invest in the development of hydrometallurgical process plants. Hydrometallurgy involves the use of aqueous solutions to extract metals from their ores or recycled materials. However, to achieve higher purity levels, a pre-processing step is often necessary. This has led to the exploration of ultrasonication as a potential solution.

Ultrasonication offers several advantages that align with the requirements of sustainability, efficiency, and cost-effectiveness. By using water as the base liquid, ultrasonication adheres to the principles of green chemistry, minimising environmental impact. Additionally, the energy efficiency of ultrasonication is notable, with a wattage requirement of only 115W for a duration of

30 minutes to achieve anode removal. This energy efficiency is in contrast to traditional methods like shredding, which often incur recycling cost savings of approximately 20-50% less than disassembly[93].
The integration of ultrasonication into the pre-processing stage, specifically after the disassembly of lithium-ion batteries, holds the potential for enhancing recovery efficiency. Experimental findings from a master thesis suggest two approaches for incorporating ultrasonication: the single-frequency approach (SFA) and the dual-frequency approach (DFA).

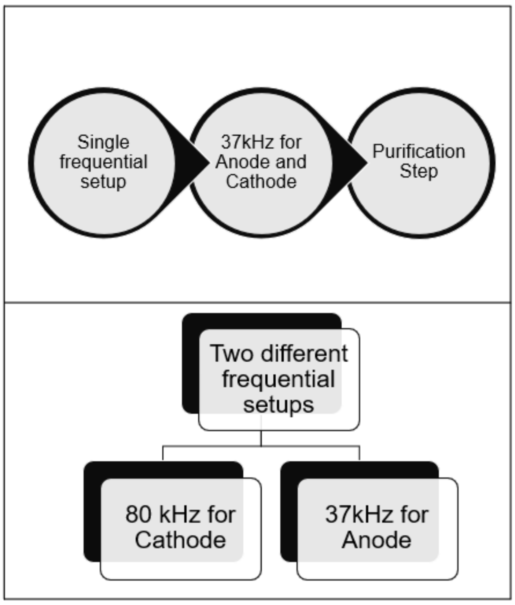


Figure 29 Single Freqiency Approach (top) and Dural Frequency Approach (bottom)

In the single frequency approach (SFA) of ultrasonication for the recycling of lithium-ion batteries, a single ultrasonic frequency is employed for both the anode and cathode in the ultrasonication bath setup. Experimental findings have shown that utilizing a frequency of 37kHz is effective in removing materials from dismantled electrode sheets.
However, it is crucial to exercise caution when including the anodes and cathodes in the same ultrasonication bath simultaneously. This precaution is necessary to prevent the potential electrolysis of water, which could lead to unwanted reactions and compromises in the recycling process.
To address the issue of aluminum contamination in the Blackmass and minimize the need for additional purification steps for the cathode, it is advisable to explore separate frequency setups for the anode and cathode during ultrasonication. The experiment conducted suggests that using a frequency of 80kHz for the cathode and 37kHz for the anode could yield favorable results.

Implementing different frequency setups for the anode and cathode helps reduce damage to the electrodes and minimize the introduction of aluminum contaminants. This reduction in aluminum contamination can potentially lessen the extent of purification steps required specifically for the cathode material, streamlining the recycling process.

By carefully selecting and applying the appropriate frequency setups for ultrasonication, focusing on separate frequencies for the anode and cathode, the efficiency of material removal can be enhanced. Furthermore, this approach helps mitigate contamination concerns, particularly aluminum contamination, and potentially reduces the need for additional purification steps, making the recycling process more efficient and cost-effective.

When evaluating the industrial adaptability of both the single frequency approach (SFA) and the dual frequency approach (DFA) for ultrasonication in battery recycling, it is important to consider potential bottlenecks and constraints.

The implementation of the dual frequency approach (DFA) may require significant capital investment to set up a two-frequency ultrasonication bath. Moreover, the need to adjust frequencies for each operation could pose practical challenges, as industries generally prefer single-purpose machines (SPMs) for streamlined processes. It is crucial to carefully assess the potential obstacles that incorporating a DFA system might present in existing production setups.

Preserving the integrity of electrodes is a critical consideration. Understanding the specific roles and requirements of the electrodes, as well as estimating the costs associated with purification methods, is essential to determine the feasibility of each ultrasonication approach.

Conducting a thorough cost-benefit analysis is crucial for both the single frequency approach (SFA) and the dual frequency approach (DFA). Factors such as volume, setup conditions, and scalability should be carefully evaluated to determine their impact on overall efficiency and economic viability. Optimisation of the process based on these considerations is key.

It is also important to acknowledge that there can be variations between laboratory-scale experiments and large-scale industrial implementations. Therefore, a systematic evaluation of proposed conditions is necessary. By addressing these considerations in a structured manner, the implementation of ultrasonication as a preprocessing step in battery recycling has the potential to be a valuable, beneficial, and sustainable addition to the overall process.

A comprehensive analysis of operational constraints, capital costs, electrode preservation, purification requirements, scalability, and cost-benefit considerations is essential to determine the suitability and industrial adaptability of ultrasonication approaches for battery recycling. By carefully assessing these factors, informed decisions can be made to ensure the effective and successful integration of ultrasonication into the recycling process.

5 Conclusions

This thesis delves into the potential of utilizing ultrasonication as a preliminary step in battery recycling and aims to identify the most effective parameters for its use. Our research also tackles the challenges surrounding its adoption in the industry. Our experimental findings indicate that ultrasonication holds great promise as a preprocessing technique.

Our research primarily focuses on assessing the efficiency of material removal through ultrasonication, as well as identifying the key factors that influence this process. These factors include frequency, power, temperature, water quantity, and time. By systematically varying these parameters, we were able to observe their distinct effects on both the anode and cathode electrodes. We found that optimal conditions varied for each electrode type and that different factors played a significant role in their damage or removal.

To ensure industrial scalability, we proposed the use of indirect ultrasonication, which improves operational efficiency and mitigates potential challenges associated with large-scale implementation. We also put forth two distinct approaches for industrial integration: the single-frequency approach (SFA) and the dual-frequency approach (DFA). We discussed the implementation issues and the necessity of cost analysis for both approaches.

In conclusion, our study highlights the importance of parameter optimisation in ultrasonication for efficient and damage-free material removal in battery recycling. Our proposed optimisation strategies and industrial implementation approaches, along with the utilisation of ultrasonication as a sustainable separation technique, contribute to the advancement of battery recycling practices. By addressing the pressing need for environmentally friendly and resource-efficient methodologies in this field, our research contributes to the development of a more sustainable future.

References

[1] K. Mensah-Darkwa, D. N. Ampong, E. Agyekum, F. M. de Souza, and R. K. Gupta, “Recent Advancements in Chalcogenides for Electrochemical Energy Storage Applications,” *Energies 2022, Vol. 15, Page 4052*, vol. 15, no. 11, p. 4052, May 2022, doi: 10.3390/EN15114052.

[2] T. B. Reddy, *Linden’s Handbook of Batteries, Fourth Edition*. McGraw-Hill Education, 2011. Accessed: Jul. 28, 2022. [Online]. Available: https://www.accessengineeringlibrary.com/content/book/9780071624213

[3] D. L. Thompson *et al.*, “The importance of design in lithium ion battery recycling – a critical review,” *Green Chemistry*, vol. 22, no. 22, pp. 7585–7603, Nov. 2020, doi: 10.1039/D0GC02745F.

[4] “BloombergNEF: battery metals rebounding; by 2030, annual Li-ion battery demand to pass 2TWh - Green Car Congress.” https://www.greencarcongress.com/2021/07/20210701-bnef.html (accessed Jul. 28, 2022).

[5] A. Vanderbruggen, A. Salces, A. Ferreira, M. Rudolph, and R. Serna-Guerrero, “Improving Separation Efficiency in End-of-Life Lithium-Ion Batteries Flotation Using Attrition Pre-Treatment,” *Minerals 2022, Vol. 12, Page 72*, vol. 12, no. 1, p. 72, Jan. 2022, doi: 10.3390/MIN12010072.

[6] “CES Online — Circular Energy Storage.” https://circularenergystorage.com/ces-online (accessed Apr. 12, 2023).

[7] S. Kim *et al.*, “A comprehensive review on the pretreatment process in lithium-ion battery recycling,” *J Clean Prod*, vol. 294, p. 126329, Apr. 2021, doi: 10.1016/J.JCLEPRO.2021.126329.

[8] “Let’s Talk Recycling: What is ‘Black Mass’? | BASF Catalysts.” https://catalysts.basf.com/blog/lets-talk-recycling-what-is-black-mass (accessed Apr. 12, 2023).

[9] D. Latini *et al.*, “A comprehensive review and classification of unit operations with assessment of outputs quality in lithium-ion battery recycling,” *J Power Sources*, vol. 546, p. 231979, Oct. 2022, doi: 10.1016/J.JPOWSOUR.2022.231979.

[10] “Situation Industry: Lithium-ion (Li-ion) Battery Recyling Process: Hydrometallurgical Black Mass Refining”, Accessed: Apr. 12, 2023. [Online]. Available: www.electramet.com

[11] “Ultrasonic Cleaning: What Is It? How Does It Work? Types Of.” https://www.iqsdirectory.com/articles/ultrasonic-cleaners/ultrasonic-cleaning.html (accessed Jun. 21, 2023).

[12] “Ultrasonication.” https://www.rsc.org/publishing/journals/prospect/ontology.asp?id=cmo:0001708 (accessed Jun. 24, 2023).

[13] G. Eichinger and J. O. Besenhard, “High energy density lithium cells: Part II. Cathodes and complete cells,” *J Electroanal Chem Interfacial Electrochem*, vol. 72, no. 1, pp. 1–31, Aug. 1976, doi: 10.1016/S0022-0728(76)80072-1.

[14] T. Maiyalagan and P. Elumalai, “Rechargeable lithium-ion batteries : trends and progress in electric vehicles,” p. 370.

[15] “How Lithium-ion Batteries Work | Department of Energy.” https://www.energy.gov/energysaver/articles/how-lithium-ion-batteries-work (accessed May 07, 2023).

[16] “Lithium-ion Battery Market Share, Size, Growth 2023-2028.” https://www.imarcgroup.com/lithium-ion-battery-market (accessed May 07, 2023).

[17] B. Ramasubramanian, M. V. Reddy, K. Zaghib, M. Armand, and S. Ramakrishna, “Growth mechanism of micro/nano metal dendrites and cumulative strategies for countering its impacts in metal ion batteries: A review†,” *Nanomaterials*, vol. 11, no. 10, Oct. 2021, doi: 10.3390/NANO11102476.

[18] A. Manthiram, “A reflection on lithium-ion battery cathode chemistry,” *Nature Communications 2020 11:1*, vol. 11, no. 1, pp. 1–9, Mar. 2020, doi: 10.1038/s41467-020-15355-0.

[19] “Intercalation - Solid State Chemistry @Aalto - Aalto University Wiki.” https://wiki.aalto.fi/display/SSC/Intercalation (accessed May 07, 2023).

[20] R. C. Massé, C. Liu, Y. Li, L. Mai, and G. Cao, “Energy storage through intercalation reactions: electrodes for rechargeable batteries,” *Natl Sci Rev*, vol. 4, no. 1, pp. 26–53, Jan. 2017, doi: 10.1093/NSR/NWW093.

[21] X. Fan *et al.*, “All-temperature batteries enabled by fluorinated electrolytes with non-polar solvents,” *Nature Energy 2019 4:10*, vol. 4, no. 10, pp. 882–890, Oct. 2019, doi: 10.1038/s41560-019-0474-3.

[22] W. Li, E. M. Erickson, and A. Manthiram, “High-nickel layered oxide cathodes for lithium-based automotive batteries,” *Nature Energy 2020 5:1*, vol. 5, no. 1, pp. 26–34, Jan. 2020, doi: 10.1038/s41560-019-0513-0.

[23] S. M. Abu *et al.*, “State of the art of lithium-ion battery material potentials: An analytical evaluations, issues and future research directions,” *J Clean Prod*, vol. 394, p. 136246, Mar. 2023, doi: 10.1016/J.JCLEPRO.2023.136246.

[24] F. Wu, J. Maier, and Y. Yu, “Guidelines and trends for next-generation rechargeable lithium and lithium-ion batteries,” *Chem Soc Rev*, vol. 49, no. 5, pp. 1569–1614, Mar. 2020, doi: 10.1039/C7CS00863E.

[25] B. Tang, L. Shan, S. Liang, and J. Zhou, “Issues and opportunities facing aqueous zinc-ion batteries,” *Energy Environ Sci*, vol. 12, no. 11, pp. 3288–3304, Nov. 2019, doi: 10.1039/C9EE02526J.

[26] J. P. Pender *et al.*, “Electrode Degradation in Lithium-Ion Batteries,” *ACS Nano*, vol. 14, no. 2, pp. 1243–1295, Feb. 2020, doi: 10.1021/ACSNANO.9B04365/ASSET/IMAGES/LARGE/NN9B04365_0028.JPEG.

[27] O. Velázquez-Martínez, J. Valio, A. Santasalo-Aarnio, M. Reuter, and R. Serna-Guerrero, “A Critical Review of Lithium-Ion Battery Recycling Processes from a Circular Economy Perspective,” *Batteries 2019, Vol. 5, Page 68*, vol. 5, no. 4, p. 68, Nov. 2019, doi: 10.3390/BATTERIES5040068.

[28] A. Hebert and E. McCalla, “The role of metal substitutions in the development of Li batteries, part I: cathodes,” *Mater Adv*, vol. 2, no. 11, pp. 3474–3518, Jun. 2021, doi: 10.1039/D1MA00081K.

[29] H. J. Kim *et al.*, “A Comprehensive Review of Li-Ion Battery Materials and Their Recycling Techniques,” *Electronics 2020, Vol. 9, Page 1161*, vol. 9, no. 7, p. 1161, Jul. 2020, doi: 10.3390/ELECTRONICS9071161.

[30] W. Yan *et al.*, “Review—Recent Advances and Remaining Challenges for Lithium Ion Battery Cathodes,” *J Electrochem Soc*, vol. 164, no. 1, p. A6220, Dec. 2016, doi: 10.1149/2.0351701JES.

[31] Z. Chen and J. R. Dahn, “Methods to obtain excellent capacity retention in LiCoO2 cycled to 4.5 V,” *Electrochim Acta*, vol. 49, no. 7, pp. 1079–1090, Mar. 2004, doi: 10.1016/J.ELECTACTA.2003.10.019.

[32] K. Wang *et al.*, “Recent advances and historical developments of high voltage lithium cobalt oxide materials for rechargeable Li-ion batteries,” *J Power Sources*, vol. 460, p. 228062, Jun. 2020, doi: 10.1016/J.JPOWSOUR.2020.228062.

[33] J. Cho, Y. J. Kim, and B. Park, “Novel LiCoO2 Cathode Material with Al2O3 Coating for a Li Ion Cell,” *Chemistry of Materials*, vol. 12, no. 12, pp. 3788–3791, 2000, doi: 10.1021/CM000511K.

[34] D. D. MacNeil and J. R. Dahn, “The Reaction of Charged Cathodes with Nonaqueous Solvents and Electrolytes: I. Li[sub 0.5]CoO[sub 2],” *J Electrochem Soc*, vol. 148, no. 11, p. A1205, Sep. 2001, doi: 10.1149/1.1407245/XML.

[35] T. Ohzuku, A. Ueda, and M. Nagayama, “Electrochemistry and Structural Chemistry of LiNiO2 (R3m) for 4 Volt Secondary Lithium Cells,” *J Electrochem Soc*, vol. 140, no. 7, pp. 1862–1870, Jul. 1993, doi: 10.1149/1.2220730/XML.

[36] L. D. Dyer, B. S. Borie, and G. P. Smith, “Alkali Metal-Nickel Oxides of the Type MNiO2,” *J Am Chem Soc*, vol. 76, no. 6, pp. 1499–1503, 1954, doi: 10.1021/JA01635A012/ASSET/JA01635A012.FP.PNG_V03.

[37] J. R. Dahn, U. von Sacken, and C. A. Michal, “Structure and electrochemistry of Li1±yNiO2 and a new Li2NiO2 phase with the Ni (OH)2 structure,” *Solid State Ion*, vol. 44, no. 1–2, pp. 87–97, Dec. 1990, doi: 10.1016/0167-2738(90)90049-W.

[38] B. Wu *et al.*, “In situ mitigating cation mixing of Ni-rich cathode at high voltage via Li2MnO3 injection,” *Energy Storage Mater*, vol. 53, pp. 212–221, Dec. 2022, doi: 10.1016/J.ENSM.2022.09.008.

[39] Y. Li, Y. Lu, P. Adelhelm, M. M. Titirici, and Y. S. Hu, “Intercalation chemistry of graphite: alkali metal ions and beyond,” *Chem Soc Rev*, vol. 48, no. 17, pp. 4655–4687, Aug. 2019, doi: 10.1039/C9CS00162J.

[40] Y. Zhang *et al.*, “Towards better Li metal anodes: Challenges and strategies,” *Materials Today*, vol. 33, pp. 56–74, Mar. 2020, doi: 10.1016/J.MATTOD.2019.09.018.

[41] Z. Zheng *et al.*, “Achieving Fast and Durable Lithium Storage through Amorphous FeP Nanoparticles Encapsulated in Ultrathin 3D P-Doped Porous Carbon Nanosheets,” *ACS Nano*, vol. 14, no. 8, pp. 9545–9561, Aug. 2020, doi: 10.1021/ACSNANO.9B08575/SUPPL_FILE/NN9B08575_SI_005.MP4.

[42] Q. Zhang *et al.*, “The Three-Dimensional Dendrite-Free Zinc Anode on a Copper Mesh with a Zinc-Oriented Polyacrylamide Electrolyte Additive,” *Angewandte Chemie International Edition*, vol. 58, no. 44, pp. 15841–15847, Oct. 2019, doi: 10.1002/ANIE.201907830.

[43] J. Chen *et al.*, “Electrolyte design for LiF-rich solid–electrolyte interfaces to enable high-performance microsized alloy anodes for batteries,” *Nature Energy 2020 5:5*, vol. 5, no. 5, pp. 386–397, Apr. 2020, doi: 10.1038/s41560-020-0601-1.

[44] S. Chae, S. H. Choi, N. Kim, J. Sung, and J. Cho, “Integration of Graphite and Silicon Anodes for the Commercialization of High-Energy Lithium-Ion Batteries,” *Angewandte Chemie International Edition*, vol. 59, no. 1, pp. 110–135, Jan. 2020, doi: 10.1002/ANIE.201902085.

[45] J. Asenbauer, T. Eisenmann, M. Kuenzel, A. Kazzazi, Z. Chen, and D. Bresser, “The success story of graphite as a lithium-ion anode material – fundamentals, remaining challenges, and recent developments including silicon (oxide) composites,” *Sustain Energy Fuels*, vol. 4, no. 11, pp. 5387–5416, Oct. 2020, doi: 10.1039/D0SE00175A.

[46] T. Krauskopf, F. H. Richter, W. G. Zeier, and J. Janek, “Physicochemical Concepts of the Lithium Metal Anode in Solid-State Batteries,” *Chem Rev*, vol. 120, no. 15, pp. 7745–7794, Aug. 2020, doi: 10.1021/ACS.CHEMREV.0C00431/SUPPL_FILE/CR0C00431_SI_001.PDF.

[47] H. Jin *et al.*, “Black phosphorus composites with engineered interfaces for high-rate high-capacity lithium storage,” *Science (1979)*, vol. 370, no. 6513, Oct. 2020, doi: 10.1126/SCIENCE.AAV5842/SUPPL_FILE/AAV5842_JIN_SM.PDF.

[48] H. Liu *et al.*, "A disordered rock salt anode for fast-charging lithium-ion batteries," *Nature 2020 585:7823*, vol. 585, no. 7823, pp. 63–67, Sep. 2020, doi: 10.1038/s41586-020-2637-6.

[49] C. Hou *et al.*, "Agaric-like anodes of porous carbon decorated with MoO2 nanoparticles for stable ultralong cycling lifespan and high-rate lithium/sodium storage," *J Colloid Interface Sci*, vol. 596, pp. 396–407, Aug. 2021, doi: 10.1016/J.JCIS.2021.03.149.

[50] R. Kumar *et al.*, "Recent progress in the synthesis of graphene and derived materials for next generation electrodes of high performance lithium ion batteries," *Prog Energy Combust Sci*, vol. 75, p. 100786, Nov. 2019, doi: 10.1016/J.PECS.2019.100786.

[51] J. Kalhoff, G. G. Eshetu, D. Bresser, and S. Passerini, "Safer Electrolytes for Lithium-Ion Batteries: State of the Art and Perspectives," *ChemSusChem*, vol. 8, no. 13, pp. 2154–2175, Jul. 2015, doi: 10.1002/CSSC.201500284.

[52] Q. Zhao, S. Stalin, C. Z. Zhao, and L. A. Archer, "Designing solid-state electrolytes for safe, energy-dense batteries," *Nature Reviews Materials 2020 5:3*, vol. 5, no. 3, pp. 229–252, Feb. 2020, doi: 10.1038/s41578-019-0165-5.

[53] X. Cao *et al.*, "Monolithic solid–electrolyte interphases formed in fluorinated orthoformate-based electrolytes minimize Li depletion and pulverization," *Nature Energy 2019 4:9*, vol. 4, no. 9, pp. 796–805, Sep. 2019, doi: 10.1038/s41560-019-0464-5.

[54] C. Wang *et al.*, "Garnet-Type Solid-State Electrolytes: Materials, Interfaces, and Batteries," *Chem Rev*, vol. 120, no. 10, pp. 4257–4300, May 2020, doi: 10.1021/ACS.CHEMREV.9B00427/ASSET/IMAGES/MEDIUM/CR9B00427_0044.GIF.

[55] D. Zhou, D. Shanmukaraj, A. Tkacheva, M. Armand, and G. Wang, "Polymer Electrolytes for Lithium-Based Batteries: Advances and Prospects," *Chem*, vol. 5, no. 9, pp. 2326–2352, Sep. 2019, doi: 10.1016/J.CHEMPR.2019.05.009.

[56] S. Pejovnik, R. Dominko, M. Bele, M. Gaberscek, and J. Jamnik, "Electrochemical binding and wiring in battery materials," *J Power Sources*, vol. 184, no. 2, pp. 593–597, Oct. 2008, doi: 10.1016/J.JPOWSOUR.2008.02.046.

[57] N. Lingappan, L. Kong, and M. Pecht, "The significance of aqueous binders in lithium-ion batteries," *Renewable and Sustainable Energy Reviews*, vol. 147, p. 111227, Sep. 2021, doi: 10.1016/J.RSER.2021.111227.

[58] M. Gaberscek, M. Bele, J. Drofenik, R. Dominko, and S. Pejovnik, "Improved carbon anode for lithium batteries. Pretreatment of carbon particles in a polyelectrolyte solution," *Electrochemical and Solid-State Letters*, vol. 3, no. 4, pp. 171–173, Apr. 2000, doi: 10.1149/1.1390992/XML.

[59] S. Bobba, S. Carrara, J. Huisman, F. Mathieux, and C. Pavel, “Critical Raw Materials for Strategic Technologies and Sectors in the EU - a Foresight Study,” *European Commission*, p. 100, 2020, doi: 10.2873/58081.

[60] “Mineral Commodity Summaries 2022 - Lithium”.

[61] “Mineral Commodity Summaries 2022 - Cobalt”.

[62] G. A. Blengini *et al.*, “Study on the EU’s list of Critical Raw Materials (2020) Final Report,” 2020, doi: 10.2873/904613.

[63] Eprs, “A new EU regulatory framework for batteries”, Accessed: Jul. 28, 2022. [Online]. Available: http://www.eprs.ep.parl.union.eu

[64] “EUR-Lex - 52020PC0798 - EN - EUR-Lex.” https://eur-lex.europa.eu/legal-content/EN/ALL/?uri=COM:2020:798:FIN (accessed May 10, 2023).

[65] B. Moradi and G. G. Botte, “Recycling of graphite anodes for the next generation of lithium ion batteries,” *Journal of Applied Electrochemistry 2015 46:2*, vol. 46, no. 2, pp. 123–148, Dec. 2015, doi: 10.1007/S10800-015-0914-0.

[66] A. Porvali *et al.*, “Mechanical and hydrometallurgical processes in HCl media for the recycling of valuable metals from Li-ion battery waste,” *Resour Conserv Recycl*, vol. 142, pp. 257–266, Mar. 2019, doi: 10.1016/J.RESCONREC.2018.11.023.

[67] H. Ali, H. A. Khan, and M. Pecht, “Preprocessing of spent lithium-ion batteries for recycling: Need, methods, and trends,” *Renewable and Sustainable Energy Reviews*, vol. 168, p. 112809, Oct. 2022, doi: 10.1016/J.RSER.2022.112809.

[68] “ADR 2021 - Agreement concerning the International Carriage of Dangerous Goods by Road | UNECE.” https://unece.org/adr-2021-files (accessed May 10, 2023).

[69] T. Nigl, M. Baldauf, M. Hohenberger, and R. Pomberger, “Lithium-Ion Batteries as Ignition Sources in Waste Treatment Processes—A Semi-Quantitate Risk Analysis and Assessment of Battery-Caused Waste Fires,” *Processes 2021, Vol. 9, Page 49*, vol. 9, no. 1, p. 49, Dec. 2020, doi: 10.3390/PR9010049.

[70] R. E. Ciez and J. F. Whitacre, “Examining different recycling processes for lithium-ion batteries,” *Nature Sustainability 2019 2:2*, vol. 2, no. 2, pp. 148–156, Feb. 2019, doi: 10.1038/s41893-019-0222-5.

[71] X. Feng, D. Ren, X. He, and M. Ouyang, “Mitigating Thermal Runaway of Lithium-Ion Batteries,” *Joule*, vol. 4, no. 4, pp. 743–770, Apr. 2020, doi: 10.1016/J.JOULE.2020.02.010.

[72] X. Lai *et al.*, “Sorting, regrouping, and echelon utilization of the large-scale retired lithium batteries: A critical review,” *Renewable and Sustainable Energy Reviews*, vol. 146, p. 111162, Aug. 2021, doi: 10.1016/J.RSER.2021.111162.

[73] L. P. Yao, Q. Zeng, T. Qi, and J. Li, "An environmentally friendly discharge technology to pretreat spent lithium-ion batteries," *J Clean Prod*, vol. 245, p. 118820, Feb. 2020, doi: 10.1016/J.JCLEPRO.2019.118820.

[74] J. Xiao, J. Guo, L. Zhan, and Z. Xu, "A cleaner approach to the discharge process of spent lithium ion batteries in different solutions," *J Clean Prod*, vol. 255, p. 120064, May 2020, doi: 10.1016/J.JCLEPRO.2020.120064.

[75] J. Schäfer, R. Singer, J. Hofmann, and J. Fleischer, "Challenges and Solutions of Automated Disassembly and Condition-Based Remanufacturing of Lithium-Ion Battery Modules for a Circular Economy," *Procedia Manuf*, vol. 43, pp. 614–619, Jan. 2020, doi: 10.1016/J.PROMFG.2020.02.145.

[76] C. Lyu, Y. Song, L. Wang, J. Li, B. Zhang, and E. Liu, "A new method for lithium-ion battery uniformity sorting based on internal criteria," *J Energy Storage*, vol. 25, p. 100885, Oct. 2019, doi: 10.1016/J.EST.2019.100885.

[77] G. Q. Zhang, L. M. Li, and S. Choi, "Robotic automated battery sorting system," *2012 IEEE Conference on Technologies for Practical Robot Applications, TePRA 2012*, pp. 117–120, 2012, doi: 10.1109/TEPRA.2012.6215664.

[78] W. Sterkens, D. Diaz-Romero, T. Goedemé, W. Dewulf, and J. R. Peeters, "Detection and recognition of batteries on X-Ray images of waste electrical and electronic equipment using deep learning," *Resour Conserv Recycl*, vol. 168, p. 105246, May 2021, doi: 10.1016/J.RESCONREC.2020.105246.

[79] H. Karbasi, A. Sanderson, A. Sharifi, and C. Pop, "Robotic Sorting of Used Button Cell Batteries: Utilizing Deep Learning," *2018 IEEE Conference on Technologies for Sustainability, SusTech 2018*, Mar. 2019, doi: 10.1109/SUSTECH.2018.8671351.

[80] B. Xia *et al.*, "Using Self Organizing Maps to Achieve Lithium-Ion Battery Cells Multi-Parameter Sorting Based on Principle Components Analysis," *Energies 2019, Vol. 12, Page 2980*, vol. 12, no. 15, p. 2980, Aug. 2019, doi: 10.3390/EN12152980.

[81] L. Gaines, K. Richa, and J. Spangenberger, "Key issues for Li-ion battery recycling," *MRS Energy & Sustainability*, vol. 5, no. 1, p. E14, Dec. 2018, doi: 10.1557/MRE.2018.13.

[82] Z. Wang, H. Yang, Y. Li, G. Wang, and J. Wang, "Thermal runaway and fire behaviors of large-scale lithium ion batteries with different heating methods," *J Hazard Mater*, vol. 379, p. 120730, Nov. 2019, doi: 10.1016/J.JHAZMAT.2019.06.007.

[83] H. Rouhi, E. Karola, R. Serna-Guerrero, and A. Santasalo-Aarnio, "Voltage behavior in lithium-ion batteries after electrochemical discharge and its implications on the safety of recycling processes," *J Energy Storage*, vol. 35, p. 102323, Mar. 2021, doi: 10.1016/J.EST.2021.102323.

[84] M. Grützke, X. Mönnighoff, F. Horsthemke, V. Kraft, M. Winter, and S. Nowak, "Extraction of lithium-ion battery electrolytes with liquid and

supercritical carbon dioxide and additional solvents," *RSC Adv*, vol. 5, no. 54, pp. 43209–43217, May 2015, doi: 10.1039/C5RA04451K.

[85] Y. Liu, D. Mu, R. Zheng, and C. Dai, "Supercritical CO2 extraction of organic carbonate-based electrolytes of lithium-ion batteries," *RSC Adv*, vol. 4, no. 97, pp. 54525–54531, Oct. 2014, doi: 10.1039/C4RA10530C.

[86] W. E. Org *et al.*, "ELECTROCHEMICAL SCIENCE Analysis on Extraction Behaviour of Lithium-ion Battery Electrolyte Solvents in Supercritical CO 2 by Gas Chromatography," *Int. J. Electrochem. Sci*, vol. 11, pp. 7594–7604, 2016, doi: 10.20964/2016.09.03.

[87] X. Mönnighoff *et al.*, "Supercritical carbon dioxide extraction of electrolyte from spent lithium ion batteries and its characterization by gas chromatography with chemical ionization," *J Power Sources*, vol. 352, pp. 56–63, Jun. 2017, doi: 10.1016/J.JPOWSOUR.2017.03.114.

[88] R. Sommerville, J. Shaw-Stewart, V. Goodship, N. Rowson, and E. Kendrick, "A review of physical processes used in the safe recycling of lithium ion batteries," *Sustainable Materials and Technologies*, vol. 25, p. e00197, Sep. 2020, doi: 10.1016/J.SUSMAT.2020.E00197.

[89] F. Maisel, P. Chancerel, G. Dimitrova, J. Emmerich, N. F. Nissen, and M. Schneider-Ramelow, "Preparing WEEE plastics for recycling – How optimal particle sizes in pre-processing can improve the separation efficiency of high quality plastics," *Resour Conserv Recycl*, vol. 154, p. 104619, Mar. 2020, doi: 10.1016/J.RESCONREC.2019.104619.

[90] X. Wang, G. Gaustad, and C. W. Babbitt, "Targeting high value metals in lithium-ion battery recycling via shredding and size-based separation," *Waste Management*, vol. 51, pp. 204–213, May 2016, doi: 10.1016/J.WASMAN.2015.10.026.

[91] D. L. Thompson *et al.*, "The importance of design in lithium ion battery recycling – a critical review," *Green Chemistry*, vol. 22, no. 22, pp. 7585–7603, Nov. 2020, doi: 10.1039/D0GC02745F.

[92] K. Wegener, W. H. Chen, F. Dietrich, K. Dröder, and S. Kara, "Robot Assisted Disassembly for the Recycling of Electric Vehicle Batteries," *Procedia CIRP*, vol. 29, pp. 716–721, Jan. 2015, doi: 10.1016/J.PROCIR.2015.02.051.

[93] D. Thompson, C. Hyde, J. M. Hartley, A. P. Abbott, P. A. Anderson, and G. D. J. Harper, "To shred or not to shred: A comparative techno-economic assessment of lithium ion battery hydrometallurgical recycling retaining value and improving circularity in LIB supply chains," *Resour Conserv Recycl*, vol. 175, p. 105741, Dec. 2021, doi: 10.1016/J.RESCONREC.2021.105741.

[94] G. Harper *et al.*, "Recycling lithium-ion batteries from electric vehicles," *Nature 2019 575:7781*, vol. 575, no. 7781, pp. 75–86, Nov. 2019, doi: 10.1038/s41586-019-1682-5.

[95] X. Zeng, J. Li, and N. Singh, “Recycling of Spent Lithium-Ion Battery: A Critical Review,” *http://dx.doi.org/10.1080/10643389.2013.763578*, vol. 44, no. 10, pp. 1129–1165, May 2014, doi: 10.1080/10643389.2013.763578.

[96] R. Sommerville, P. Zhu, M. A. Rajaeifar, O. Heidrich, V. Goodship, and E. Kendrick, “A qualitative assessment of lithium ion battery recycling processes,” *Resour Conserv Recycl*, vol. 165, p. 105219, Feb. 2021, doi: 10.1016/J.RESCONREC.2020.105219.

[97] B. Swain, “Recovery and recycling of lithium: A review,” *Sep Purif Technol*, vol. 172, pp. 388–403, Jan. 2017, doi: 10.1016/J.SEPPUR.2016.08.031.

[98] W. Zhang, C. Xu, W. He, G. Li, and J. Huang, “A review on management of spent lithium ion batteries and strategy for resource recycling of all components from them,” *Waste Management and Research*, vol. 36, no. 2, pp. 99–112, Feb. 2018, doi: 10.1177/0734242X17744655/ASSET/IMAGES/LARGE/10.1177_0734242X17744655-FIG2.JPEG.

[99] L. F. Zhou, D. Yang, T. Du, H. Gong, and W. Bin Luo, “The Current Process for the Recycling of Spent Lithium Ion Batteries,” *Front Chem*, vol. 8, p. 1027, Dec. 2020, doi: 10.3389/FCHEM.2020.578044/BIBTEX.

[100] D. Mishra, D. J. Kim, D. E. Ralph, J. G. Ahn, and Y. H. Rhee, “Bioleaching of metals from spent lithium ion secondary batteries using Acidithiobacillus ferrooxidans,” *Waste Management*, vol. 28, no. 2, pp. 333–338, Jan. 2008, doi: 10.1016/J.WASMAN.2007.01.010.

[101] Z. Niu, Y. Zou, B. Xin, S. Chen, C. Liu, and Y. Li, “Process controls for improving bioleaching performance of both Li and Co from spent lithium ion batteries at high pulp density and its thermodynamics and kinetics exploration,” *Chemosphere*, vol. 109, pp. 92–98, Aug. 2014, doi: 10.1016/J.CHEMOSPHERE.2014.02.059.

[102] N. Bahaloo-Horeh and S. M. Mousavi, “Enhanced recovery of valuable metals from spent lithium-ion batteries through optimization of organic acids produced by Aspergillus niger,” *Waste Management*, vol. 60, pp. 666–679, Feb. 2017, doi: 10.1016/J.WASMAN.2016.10.034.

[103] J. S. Taurozzi, V. A. Hackley, and M. R. Wiesner, “Ultrasonic dispersion of nanoparticles for environmental, health and safety assessment – issues and recommendations,” *http://dx.doi.org/10.3109/17435390.2010.528846*, vol. 5, no. 4, pp. 711–729, Dec. 2011, doi: 10.3109/17435390.2010.528846.

[104] C. Lei *et al.*, “Lithium ion battery recycling using high-intensity ultrasonication,” *Green Chemistry*, vol. 23, no. 13, pp. 4710–4715, Jul. 2021, doi: 10.1039/D1GC01623G.

[105] J. Marshall, D. Gastol, R. Sommerville, B. Middleton, V. Goodship, and E. Kendrick, “Disassembly of Li Ion Cells—Characterization and Safety Considerations of a Recycling Scheme,” *Metals 2020, Vol. 10, Page 773*, vol. 10, no. 6, p. 773, Jun. 2020, doi: 10.3390/MET10060773.

[106] R. Gonçalves, S. Lanceros-Méndez, and C. M. Costa, “Electrode fabrication process and its influence in lithium-ion battery performance: State of the art and future trends,” *Electrochem commun*, vol. 135, p. 107210, Feb. 2022, doi: 10.1016/J.ELECOM.2022.107210.

[107] M. Bruno and S. Fiore, “Material Flow Analysis of Lithium-Ion Battery Recycling in Europe: Environmental and Economic Implications,” *Batteries 2023, Vol. 9, Page 231*, vol. 9, no. 4, p. 231, Apr. 2023, doi: 10.3390/BATTERIES9040231.