A review of physical processes used in the safe recycling of lithium ion batteries

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Abstract

A review of separating methods used in domestic and electric vehicle lithium ion battery recycling is presented, focusing on physical processes which are commonly utilised prior to further chemical processing and purification steps. The four processes of stabilisation, disassembly, separation and binder negation are reviewed and the strengths and weaknesses in current research identified. The main limitation with current recycling methods is the comminution step, which mixes, sometimes intimately, the materials from different cell components. This mixed waste stream requires further physical separation, and produces cross contamination in the different material streams. Effective separation of battery components, which produces enhanced purity of waste streams is essential to providing a cost-effective recycling process for direct or "closed loop" recycling. Improvements in the separation process are possible if the materials are separated prior to comminution, to prevent contamination of the different materials streams. In addition to purity of waste streams, one area mostly neglected in the literature is the health and safety implications and hazards associated with the chemicals contained within the cells. Little information is known about the chemical reactions which may occur during the physical separation processes

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and this has been identified as an area which needs substantially more investigation.

1. Introduction

Lithium ion battery recycling is still in its infancy, but will become essential. Heelan et al. [1] reported that in 2016 approximately 95 % of Li-ion batteries ended up in landfill sites rather than being recycled, and in 2019 still only 5% of

5 LIB's are recycled in the European Union [2]. Recycling can provide a variety of benefits, such as; decreased pollution, avoidance of toxic byproducts, reduced land demand in the case of landfills, lessening demand on finite resources and decreasing the environmental costs associated with mining virgin resources [3, 4].

10 **Critical materials**: One key future consideration is around the ethical sourcing of some of the battery components. Several of the materials and elements associated with LIBs such as graphite, Li, Co, and Ni, have been designated as strategic elements and critical materials by the UK, EU and US [5, 6, 7, 8], partly due to the overall global scarcity of these elements, but mainly

15 due to the resource security from geographical and geopolitical factors.

Recycling Processes: Typically, energy intensive hydrometallurgical and pyrometallurgical processes are used for element extraction [9], the physical separation processes required prior to these extraction processes are often overlooked [10]. These processes are an extremely important part of the recycling

20 loop and offer further improvements on the recovery rates and costs [11, 12]. The main motivation for highly efficient physical processing is to ensure a concentrated feedstock for further chemical processing and metal recovery. Physical processes are differentiated here from chemical and thermal processes in that there is no significant chemical change in the materials. These processes are

25 generally used in early stages of the recycling loop. Effective separation pre-

cludes the need for repetitive separation techniques, and minimises the loss of valuable resources to waste streams. **Metals reclamation** focuses on the most valuable parts of a battery. Copper is reclaimed from the anode current collector, and cobalt and nickel from the cathode. These transition metals are typically recovered from the cathode using hydrometallurgical processes which are cost-intensive: the electrode materials are concentrated in the "black mass" which is dissolved in acid, after which solvent extraction is used to recover each metal separately. Materials other than the metal oxides are not recovered in the process, leading to a high volume of waste. In order to improve recycling efficiency, reduce the cost of consumable reagents, and reduce the volume and cost of waste requiring disposal, it is necessary to minimise the amount of superfluous material subjected to hydrometallurgical recovery.

Reuse or remanufacture: Recycling purely by physical means, such that the crystal structure or composition of the active material is not modified is termed "direct recycling" or "short loop recycling" in current literature [13, 14, 15, 16, 4, 17, 18, 19, 20, 21]. Development of new battery chemistries may mean that LIBs with obsolete battery chemistries cannot be short loop recycled but must be chemically processed into a more relevant cell chemistry. i.e: a nickel manganese cobalt (NMC) cell cannot be recycled to produce a nickel cobalt aluminium (NCA) cell without utilising hydrometallurgical processing [22, 12]. This is further complicated with differing chemistries which may benefit from different recycling methods, depending on the value and composition of the battery components. For example, pyrometallurgical recycling is only economical for batteries with a high cobalt or nickel content, due to the energy requirements of the process and the value of cobalt and copper [4], whereas cells with a manganese or iron rich content make this process economically unviable. Whilst few studies have been published which include cycling data for recycled graphite [13, 23, 24], all include some form of treatment in order to remove electrolyte, SEI, or binder, and thus improve performance. Moradi and Botte [25] emphasised the need to match the 99.9 % purity of new battery grade graphite in a recycled graphite product. In order to adequately assess the most

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economic methods of recycling, with least environmental impact, Life Cycle Analysis (LCA) is used to quantify the benefits of different recycling processes and has been reviewed extensively elsewhere, [26, 27, 28], therefore is not the topic of this review.

Safety is of particular importance for recycling of lithium ion batteries due to their hazardous nature. The four main hazards are electrical, chemical, thermal and explosive hazards [29]. During the disassembly of groups of connected lithium-ion batteries, appropriate tools and training must be used to minimise the risk of electric shock or causing a short circuit. Short circuiting or otherwise rapidly discharging a lithium-ion cell risks the cell self-heating to the point of thermal runaway. During thermal runaway lithium-ion cells self-heat to the point at which they catch fire, and burn under their own fuel, without need for an external supply of oxygen, releasing toxic gasses [30, 31, 32]. Nedjalkov et al. [33] identify eleven crucial gas mixture hazards from damaged LIBs, including styrene, biphenyl, acrolein, carbon monoxide (CO), carbonyl sulfide (COS), and hydrofluoric acid (HF). Cells with a gas-tight outer case may contain the gases evolved during thermal runaway to the point at which the cell casing fails, causing the cell to "pop" or explode. Alternatively, gasses given off during a thermal event may form an explosive mixture with air [29]. In addition the materials from the inside of a lithium-ion cell pose chemical hazards on their own. Nickel and cobalt powders are carcinogenic, electrolyte is flammable, electrolyte additives can be toxic as well as flammable, and lithium (in the case of lithium plating during cycling) will burn in air [32]. Taking all into consideration, the chemicals that are contained and produced during a "lithium ion event" are numerous, likely hazardous and to be avoided if at all possible. Therefore consideration must be taken when developing recycling procedures to protect the work force from these risks and hazards. Currently limited information is known about the specifics of chemical and safety hazards which may occur during the physical processes and further information is required.

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Efficient physical separation benefits are; low operating costs, and when optimised, more concentrated and "higher purity" feedstocks which allows for more expensive downstream processes. A clean separation of materials results in fewer steps being required to recover low concentrations of the desired components which are mixed in with waste materials. Avoiding these additional steps can save energy, the need for additional equipment, and thus CO_2 emissions. Higher purity waste streams also makes the low value materials more flexible in terms of potential applications for these waste products. Currently, methods focus upon initial grinding or shredding to produce a free flowing material. This can intimately mix the battery components, before materials sorting attempts to separate and purify these components into separate streams.

This study presents a review of primarily physical processes used in the safe recycling and disposal of lithium-ion batteries (LIB) and the separation of their constituent materials, ideally with an intent to re-use or recycle them. A schematic of the process flow is shown in figure 1. The cells are first stabilised to make safe, then disassembled or milled. The constituents are then separated into their relative waste streams, and the black mass is further purified to recover the cathode and anode critical material value. We discuss and identify strengths, weaknesses and improvements in physical sorting processes that are utilised to separate out the waste streams.

2. Stabilisation

Stabilising cells before opening them is performed in order to prevent thermal runway and product loss through fires. Thermal runaway is undesired due to the synthesis and release of hot, toxic and corrosive chemicals, and the loss of potentially retrievable components such as electrolyte and plastics to combustion [32, 31, 33]. An overview of stabilisation methods is shown in figure 2.
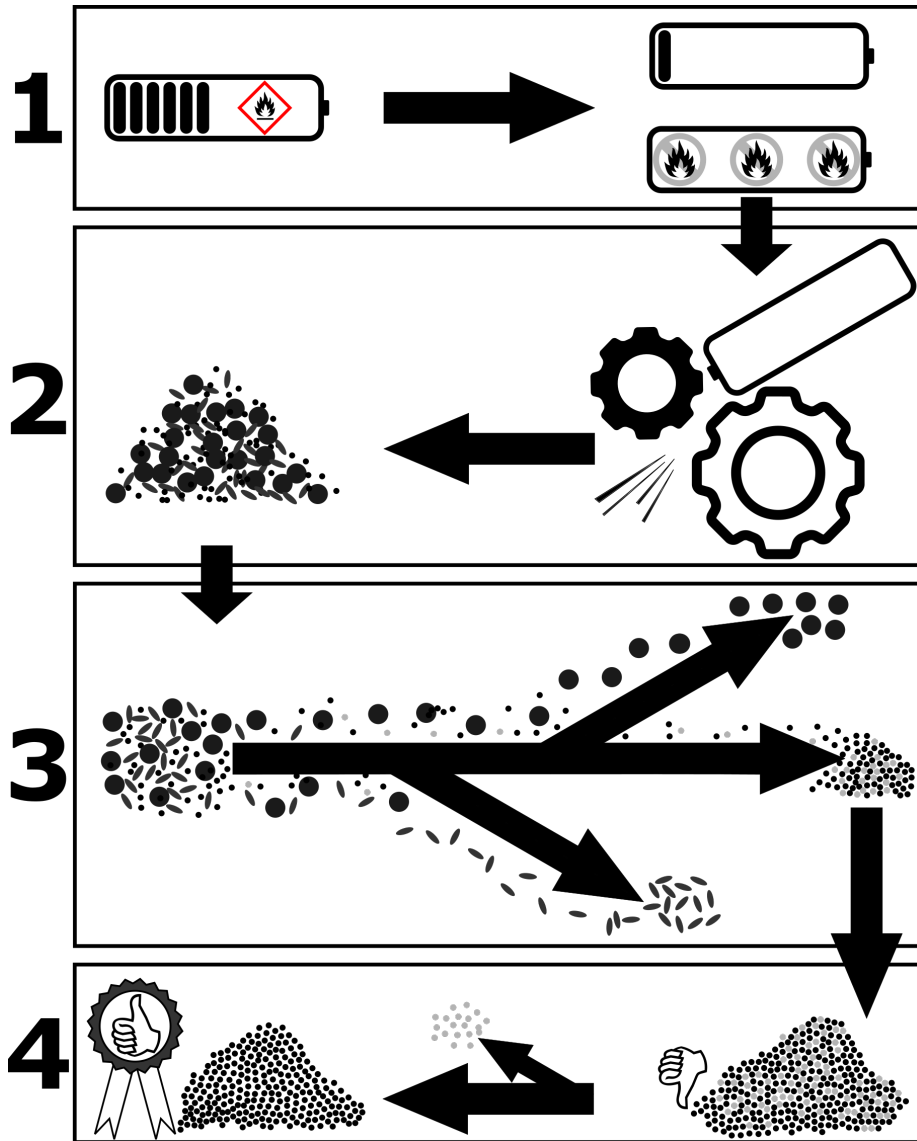
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Figure 1: Schematic diagrams of the process flow for lithium ion battery recycling and disposal: 1. Stabilisation, 2. Comminution, 3. Physical separation, 4. Black mass purification.
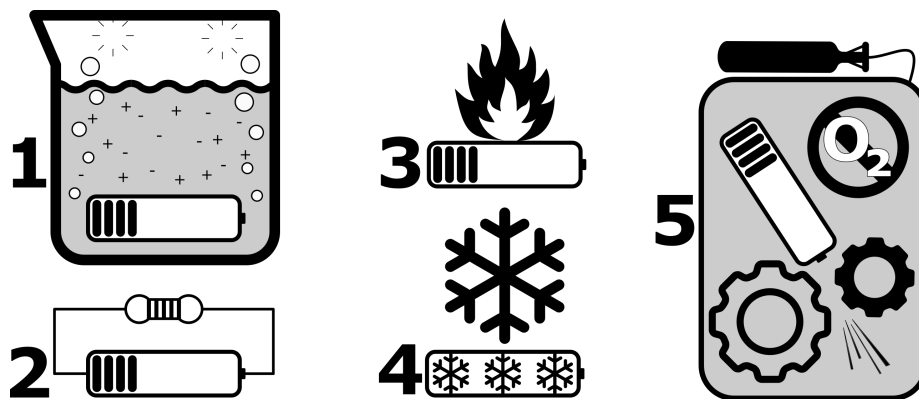
Figure 2: Summary of the stabilisation processes: 1. Ionic self-discharge, 2. Electrical discharge, 3, Thermal treatment, 4. Cryogenic treatment, 5. In process control.

2.1. Discharge

Literature describing commercial active discharge processes prior to recycling is limited, however the concept of prior-discharge for stabilisation is a very common physical process in LIB recycling research literature.

2.1.1. Electrical Discharge

In an ideal process, residual charge would be recovered, rather than dissipated and wasted. However, such retrieval is hard to achieve as it requires removal of battery protection circuitry, bypassing of any broken fuses, and the creation electrical connection to recover the stored energy. Papers which manually disassemble cells commonly discharge them first via connection to a resistor [34, 35], or immersion in a salt solution [36, 37, 10, 38, 39]. Other studies have explored discharge via conductive particles such as metal chips or powders and graphite [40, 41, 42, 43]. Sonoc et al. [35] investigated the energy that could be gained from electrical discharge from full discharge (around 3 V) to complete over-discharge (0 V). They concluded that less than 1 % of the nominal capacity could be obtained from complete over-discharging of 3V LIBs, but they did also show that disassembled cells at a voltage of 0.5 V could still spontaneously combust, this contradicts the work performed in our group where we

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have shown air stability of the cells and electrodes at end of life (70 % State of Health (SOH)) at 0 % SOC and 2.5 V cell voltage with a large format LMO-NMC // Graphite cell. The state of charge and state of health of the battery are difficult to determine without an electrochemical charge and discharge. Discharge prior to disassembly is common in literature, and it is generally assumed that this is accomplished via a resistor, but the precise details are often unclear [44, 45, 46, 47, 48, 49, 50, 51]. In addition, the terms *fully* or *completely* discharged, may indicate an open circuit voltage (OCV) anywhere between 3 V (i.e. the highest possible value for 0 % state of charge in a LIB) and 0 V. Discharging cells to 0 V results in the dissolution of Cu into the electrolyte. When subsequently left to rest after discharge the voltage increases and copper precipitates out and causes the distribution of Cu throughout the entire cell, contaminating downstream products (such as the cathode) unnecessarily [52, 53, 54].

2.1.2. Solution Discharge

Discharge via brine presents a challenge in the case of highly charged or damaged cells. The lithiated anode of charged cells has the potential to react violently with water if the cell casing is compromised. The cell casing can become compromised as corrosion can occur at the anode due to the reaction with the chloride ion [36]. Brine discharge electrolyses the water, producing hydrogen and chlorine gasses, which are flammable and toxic respectively, although evolved chlorine will chlorinate the water it is in. Cell-level water or brine immersion for discharge has not been studied in detail, with the majority of literature covering pack-level immersion, which can produce more more violent reactions [55, 56].

2.2. Thermal Pre-treatment

2.2.1. Cryogenic

Dorella and Mansur [57], Wang et al. [49] used liquid nitrogen to cool cells prior to disassembly. This solidifies the electrolyte, and metallic lithium is

significantly less reactive at such low temperatures. This method provides a safe manner in which to disassemble or comminute cells. Liu et al. [58] cooled electrodes with liquid nitrogen *during* comminution. As comminution was performed at a temperature below the glass transition temperature of the PVDF binder, it became brittle and liable to shattering, which improved the downstream froth flotation separation technique (see section 4.4).

2.2.2. Heat

Lee and Rhee [59] heated discharged LIBs at 100-150 °C for 1h prior to shredding to liberate the cells from their packaging. This is also likely to have caused the cells to rupture, and removed the electrolyte. This presents a potential hazard, as it could cause thermal runaway if the cells are not discharged [32, 60]. A similar approach was described by Granata et al. [61] for a mixed stream of primary lithium cells and other cells. The lithium primary cell recycling procedure was similar to other proposed procedures for recycling of NiMH and LIB, and thus adapted by to process a stream comprising lithium primary cells, NiMH and LIB. This procedure utilised a nitrogen atmosphere to mitigate some of the reactivity of lithium primary cells, however it was deemed necessary to use a 0.1 m^3 steel container to contain explosions as the mixed cells were heated to 300 °C for 2 hours. The ratio of cells in the feedstock was 2:2:1 NiMH : Lithium primary : LIB. Pyrolysis at higher temperatures of 400-600 °C to remove the electrolyte, binder, and separator has been utilised by a variety of authors [62, 63, 64, 65]. The evolved organic materials form a complex mixture, which has been analysed by Zhong et al. [64]. Whilst pyrolysis prior to comminution does cause challenges with gas handling and disposal of the evolved organics, comminution and separation of electrode coatings from foils is faster, according to Zhang et al. [62].

2.3. Electrolyte Extraction

Extraction of the electrolyte through use of supercritical or subcritical CO_2 has been demonstrated by a variety of authors [14, 13, 24]. Such techniques

offer the advantage of recovering the electrolyte solvent for purification and reuse rather than thermal recovery, and whilst some $LiPF_6$ recovery can be achieved with CO_2 alone, the addition of cosolvents has been shown to improve extraction [66].

2.4. Summary of stabilisation techniques

The stabilisation processes for the lithium ion cells discussed are; discharge (electrical and solution) cryogenic, thermal and in-process stabilisation. From a safety perspective, stabilisation to 2.5 V OCV or lower in an LCO or NMC - graphite cell, leaves minimal energy in the cell (< 2 %) and therefore the risk of thermal runaway is minimised [67]. Different cell chemistries will have different safe states of discharge or discharge voltages. In some cases, even when the cell is discharged, some areas of isolated highly lithiated active materials may occur which will catch fire upon opening. These stabilisation techniques are summarised in Table 1. The economic costs of different techniques will vary enormously depending on scale, regulatory regimes, and the markets for the products. Cryogenic cooling has been considered the most expensive based on the lack of scalability, and the costs involved in cooling processes. Inert processing is considered similarly, although inert environments are generally cheaper to create than cryogenic environments. Brine, or salt solution discharging is low cost in terms of materials. Discharge by energy recovery will depend on the battery size, and time restraints for both connecting devices up and waiting until they are safely discharged. It should be noted in this section that we are discussing the disassembling of cells rather than modules and packs.

The discharge process utilised can be either via a standard resistor where the energy is dissipated as heat, or discharged in brine solutions with subsequent electrolytic reactions. With **electrical discharge** methods the energy can also be reclaimed and repurposed, if it is economic to do so. The other stabilisation methods; cryogenic, thermal and in-process, are typically used before comminution processes and do not involve the assessment of state of charge of the cells, or the discharge of energy prior to processing. These processes merely utilise

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Stabilisation Technique	Advantages	Disadvantages
Electrical Discharging	Potential for energy recovery	Difficult to scale energy recovery
Brine or Salt Solution	Low cost	No energy recovery, Waste effluent may require cleaning
Cryogenic Processing	Safe, even in cases of metallic Li or Li plating	Energy intensive, high cost, poor scalability
Thermal Processing	Degrades binders and removes volatile components simultaneously	Electrolyte cannot be recovered, produces HF
Inert Gas Comminution	Avoids wetting materials	Will not stop a fire once started, requires gas handling and supply
Wet Comminution	Very cheap	Waste effluent may require cleaning

Table 1: Comparison of stabilisation techniques for the recycling of lithium-ion batteries, describing advantages and disadvantages.

the cells as they are received and rely upon engineering controls to minimise the effects of any hazardous reactions. With the electrical discharge processes, the materials streams may be able to be sorted at an earlier stage reducing the cross contamination of the different materials streams; cathode, anode, plastics. Due to the cost of stabilisation, the hazardousness of the materials involved, and the complexity of different battery architectures; opening and presorting is considered more expensive than the prevalent recycling approach of comminution and physical separation, despite being more effective in materials separation. **Solution discharge** can lead to corrosion at the terminals and subsequent water penetration into the cell. The water reacts with the cell components and renders it "safe", however the water completely destroys any potential reuse case for the cells or the materials. Non-halide salts discharge the cell effectively with less corrosion. In the salt discharge cases the energy cannot be reused or reclaimed, unlike in the energy recovery discharge process. Recovering energy from cells requires a higher capital cost, and is either a labour-intensive process, or will require advanced automation. Such automation would need to identify cell dimensions, cell format, and cell orientation, as well as have the means by which to form an electrical connection to each cell to recover the energy. Advantageously, such an energy recovery process would not need to dispose of any gases evolved from the electrolysis of salt solutions, and would be able to discharge to a 0 % state of charge, without overdischarging, dissolving the Cu current collector, and contaminating the waste streams. **Cryogenic pre-treatment** is where the cells are immersed in liquid nitrogen and frozen before any subsequent processing is performed. This is typically not done on a large scale, however it may offer a method of stabilising the cell for transport, and for subsequent shredding processes. However the cost of this process is likely a deterrent compared to the other passivation methods. **Thermal pre-treatment** or processing is described by its proponents as capable of handling a feed of mixed battery chemistries, allowing separation downstream. However, this technique does lose some material to difficult byproducts such as HF. For a mixed stream of cell chemistries, it seems apt, but ideally larger scale processes

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would separate other batteries from LIBs, and sort LIBs by chemistry, treating each separately, recovering a higher proportion of materials, and avoiding the evolution of HF. This presents it's own challenges and therefore opportunities in cell identification (especially damaged or worn cells), scalability, and the cost-effectiveness of treating small batches of material of disparate chemistries.

In-process stabilisation: Stabilisation during comminution does not remove hazards, but utilises engineering controls to limit risks, such as comminution under a spray of water, or under an inert gas blanket. The aqueous spray (water, or LiOH solution) acts as a heatsink, and hydrolyses any exposed lithium, whereas CO_2 forms a lithium carbonate layer on any exposed lithium metal. These precautions improve safety by inhibiting thermal runaway and prevent loss of material to gaseous byproducts of combustion caused by thermal runaway. It is noted that use of a water spray is much less energy intensive than using liquid nitrogen or liquid argon, described in the cryogenic stabilisation. As with cryogenic processing and brine discharge, this treats the cells as a bulk material, and does not require information on cell health, state of charge, format, or orientation.

3. Disassembly and Comminution

3.1. Dissassembly

Disassembly refers to the processes involved in removing cell packaging and accessing the active materials, this can be manual or automated. This method is currently used extensively for research purposes but not in any commercial process routes. The cell disassembly is mostly manual and the cells are opened using cutting tools to liberate the internal cell components, which are subsequently sorted by hand into the components; anode, cathode, separator. This method is often used to open cell for tear down analysis and determination of failure mechanisms [68].
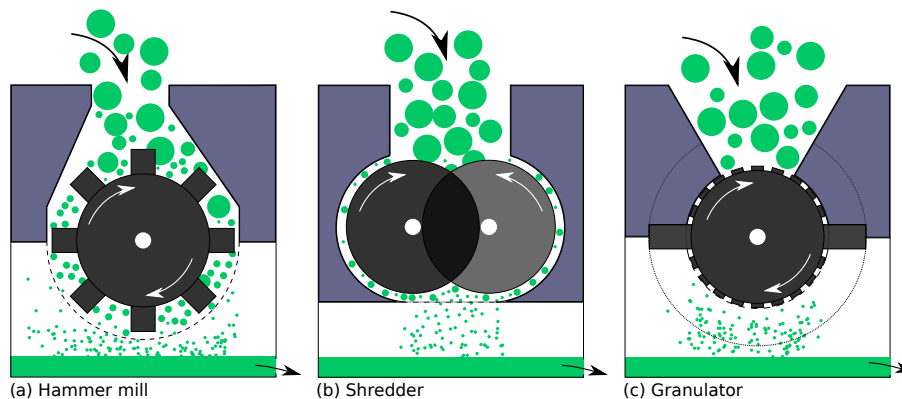
Figure 3: Schematic diagrams of three commonly used rotating comminution processes.

3.2. Comminution

₂₈₀ When discussing automated cell comminution processes, there are relatively clear distinctions between continuous and batch processes. Most cell-breaking techniques seem to be continuous, and generally involve rotating crushing devices. A variety of terminology is used to describe these approaches, including "hammer crushing" [61], "wet crushing" [37, 69, 70], "shear crushing" [37, 71], ₂₈₅ "impact crushing" [72, 71], and "cutting milling" [73]. All of these appear to be rotational processes, and therefore overlap considerably with the three classes of rotating crushing outlined in Figure 3: hammer milling (a), shredding (b), and granulating (c). Different comminution processes will produce materials with differing sizes and shapes, heavily influencing downstream separation tech- ₂₉₀ niques. Therefore, there is a need to distinguish key parameters in comminution before attempting to directly compare separation techniques in literature.

3.2.1. Shredding

Shredding is a common form of automatic cell disassembly, and is widely used in waste electrical and electronic equipment (WEEE) disposal. The definition ₂₉₅ of a shredder is not always consistent as the distinction between a granulator and a shredder can be based on the materials being shredded, or on a difference in the process. Shredding commonly refers to high torque, low speed rotation

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of interdigitated blades or knifes, whereas granulating is usually a higher-speed process where there may, or may not be interdigitated blades which serve to pull material between the fast-rotating axle(s), exploiting the brittleness of the feed to cause shattering.

3.2.2. Milling

Various studies have used hammer mills, particularly publications focused on industry [74, 75, 70, 4], but there are significantly fewer laboratory-scale studies that use a hammer mill for the initial breaking and crushing of the cells [41, 76]. Xiao et al. [77] used pilot scale equipment they termed a hammer crusher rather than a hammer mill. Zhang et al. [71] used a shear crusher to cut and an "impact crusher" to comminute batteries. The shear crusher opened and coarsely cut the cells such that some of the casing and separator could be removed, prior to liberation of coating from foils via impact crushing.

The influence of water on the comminution process was investigated by Zhang et al. [37]. Wet comminution prevented over-crushing and resulted in caking of fine materials, whilst dry comminution was slower to achieve the same level of liberation between foils and coatings, but resulted in fewer copper, aluminium and polymer materials in the fine fractions Zhang et al. [37]. These fine fractions are referred to as the "black mass", which is a free flowing material, mostly comprising electrode coatings.

3.3. High shear Mixing

A few recent publications have utilised a laboratory-scale high shear mixer, or blender in order to separate electrode coatings from electrodes [20, 15]. High shear mixing provides a simple laboratory-scale approach to separating electrodes from coatings

3.4. Disassembly and Comminution Summary

There is no standard process for comminution, however the output required comprises free flowing, consistently sized pieces that can be further separated

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by other physical processes. This can be obtained by automated rotary comminution techniques such as shredding and milling, which achieve similar mixed waste material outputs. These techniques will often give a variable outputs depending upon the environment and the feedstocks. The output of the disassembly will greatly influence downstream separation processes. Disassembly in lieu of commminution could help to avoid intimate mixing of different battery components, and provide recycled material of greater purity.

The disassembly processes are currently limited, they are mostly performed manually and used in forensic analysis of cells and extraction of components. Automated disassembly processes are highlighted here as a research gap in recycling of batteries, and the economic assessment of which needs studying and comparing with comminution.

In both automated and manual disassembly processes, first the cell is opened using tools such as; saws, sharp blades or lasers, then the components are sorted into packaging, electrolyte, separator, and electrode, prior to other materials separation stages. Ideally these manual processes would be fully automated, however due to variations in cell structures it is difficult. In order to automate the processes it will be first necessary to determine the cell type, and what materials are contained within the cell for sorting purposes. This can be done by automatic bar code readers or by reading the cell type text. However this does not fully distinguish between the different NMC types, electrolytes, separators and conductive additives in the cell.

In terms of chemical hazards; manual techniques are inherently more dangerous for the dissemblers. Even if automated, the complexity of the component sorting may make it harder to use the same gas blankets or passivating fluids used in established shredding or milling processes.

4. Separation

The feed stocks from the disassembly and comminution processes are further treated to produce higher purity materials streams. Physical separation is used

so that high concentration material feed stocks can be provided into later reclamation processing stages. The products of separation are the plastics; separator and pouch material, metal; steel casing, nickel and aluminium tabs, aluminium and copper current collector, and a "black mass". The black mass typically contains the materials from the negative and positive electrodes; graphite, PVDF, carbon black, metal oxides, with some aluminium and copper current collectors. This black mass is reclaimed for further processing such as metal dissolution and precipitation. The black mass separation processes (Section 5) are more complicated and hence more expensive with greater quantities of contaminants [78]. Excess aluminium in the cathode material has been shown to negatively influence battery performance [34], thus a good separation between foil and cathode powder in the physical separation step is required to avoid necessitating further purification.

4.1. Size separation

Size separation is a process common to all large scale LIB recycling techniques, mostly achieved through sieving both in the laboratory and at scale [71, 76, 51]. The black mass which is separated via this process is comprised mostly of the materials from the electrode coatings, graphite and metal oxides such as nickel, manganese and cobalt. The current collectors; copper and aluminium, can also be found within this mass, and their concentration will vary depending on comminution conditions. Laboratory scale experiments often generate black mass through comminution and sieving, relying on preferential comminution of electrode coatings to keep the Al and Cu content of the black mass low [79, 15, 71, 80]. Current collectors need to be removed from the black mass prior to hydrometallurgical extraction, in order to maximise cost-effectiveness [81, 82, 83]. As mentioned in section 3.2.2, water aids the milling process, and in this case a greater separation between fine and coarse materials is also observed [37]. A vibrating screen is shown in figure 4. Table 2 compares the recovery percentages which some authors have achieved through sieving, and describes the comminution and separation techniques applied to achieve separation, and
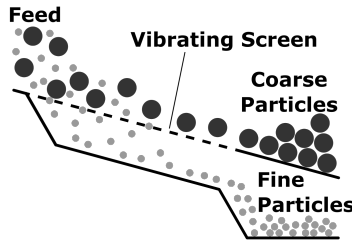
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Feed
Vibrating Screen
Coarse Particles
Fine Particles

Figure 4: Diagram of a vibrating screen, separating particles based on size.

in what order these processes were performed.

		Order of Processes					Recovery (%)		
Discharge	Disassembly	Comminution	Sieving	Other	Product	Paramter Optimisation	Before	After	Source
1	2	3^b	4	5^a	BM	High shear mixing		85.0	[15]
1		2*	5	3^c	LCO	500°C Pyrolysis 15 mins, 10°C/min Comminution time	90.7	98.2	[80]
					C		90.3	98.7	
					Cu		99.4	99.2	
					Al		99.3	98.8	
1		2,3	4		Cu			90.4	[71]
					Co			94.4	

Table 2: Comparison of recoveries by percentage mass achieved through sieving, and the order of processes applied beforehand. * Denotes parameters which were varied. [a] Washing, [b] Wet comminution, [c] Density, magnetic, and eddy current separation, BM Black Mass

4.2. Magnetic separation

Magnetic separation is used extensively to remove steel casings, as shown in Figure 5 [40, 84, 82, 85, 41, 86]. At scale, Recupyl [87], AkkuSer [88], and S.E.Val. s.r.l., (an electronics recycling company based in northern Italy [89]) use magnetic separation for this purpose. It has also been proposed as a sepa-
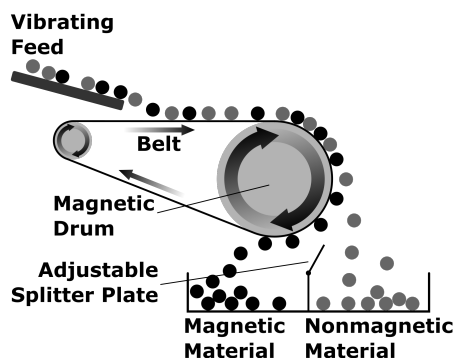
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Figure 5: A schematic demonstrating one method of magnetic separation, including a rotating magnetic drum, magnetic material such as casings, and non-magnetic material such as electrodes and plastics.

ration step in LIB or mixed LIB and NiMH waste streams by Barik et al. [90] and Al-Thyabat et al. [78]. Further separation of the contents of the cells are possible with this method and are currently being investigated. Wang et al. [91] separated cobalt by mechanochemically processing $LiCoO_2$ with Fe to form

395 $CoFe_xO_y$ and then magnetically separating the ensuing material.

When the black mass is formed into a slurry and subjected to wet magnetic separation steps of various intensities, several active material streams can be produced depending on the differing magnetic susceptibilities of the component active materials, and differing solvents in the slurry [25, 92]. Li et al. [93]

400 reported a Cobalt recovery of 96 % by applying magnetic separation on pyrolised electrode coatings. As the active material does not change from the oxide form, this is considered direct recycling. The cost-effectiveness of such a magnetic separation process for direct recycling of cathode materials is questionable, as differing NMC ratios will not separate easily. However it has applications in

405 recycling processes with a mixed feed of cells for extraction of cathodes [16]. The ReCell project has investigated the use of wet magnetic separation on mixtures of virgin cathode materials: lithium manganese oxide (LMO), nickel manganese cobalt oxide (NMC) and lithium cobalt oxide (LCO). Preliminary results appear promising, with recoveries of 94 %, 92% and 92% respectively [94].
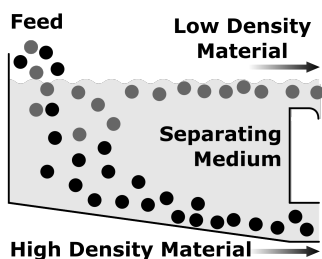
Figure 6: A schematic diagram showing simple density separation using a fluid of intermediate density. Low density material such as separator, can be removed from the remaining battery components by flotation on a fluid of intermediate density, such as water.

4.3. Density Separation

Density separation is used to separate out the low density plastics and papers, from the mixed cell waste. This can be achieved using shaker tables, vibrating screens, a fluid of intermediate density, or air separation [88, 87].

The use of a carrying fluid of intermediate density such as water [90, 78] or diiodomethane [41] as depicted in figure 6 can be used alone, or with a hydrocyclone to separate lighter components from heavier components. This is successful for the removal of plastics from the electrode materials and has also been reported for the separation of the copper and aluminium current collectors [76, 82, 88]. Density separation in the form of air classification has been described as a method to separate anodes and cathodes, as well as Al and Cu foils [83, 95]

4.4. Froth Flotation

Froth flotation operates by exploiting the difference in hydrophobicity between two materials. Fine bubbles are introduced to a vessel containing material to be separated. Frothing agents can be utilised to stabilise the foam. Common frothing agents include pine oil, alcohols and cyclical carbonates. Hydrophobic materials are collected by bubbles, transported to the surface, and remain within the stable froth on the surface. The froth laden with the desired hydrophobic fraction of material is then recovered, as shown in figure 7. In cases where the desired fraction is retained in the slurry, and the undesired fraction is floated in the

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froth, this is described as reverse flotation. In early froth flotation experiments [73] on the black mass recovered from milled LIBs, poor selectivity between cathode and anode powders was observed. This was due to the hydrophobic PVDF binder which was still stuck to the $LiCoO_2$ and graphite powders. If heat treated to 500 °C to decompose and remove the PVDF, froth flotation can separate carbons from the cathode materials successfully [75, 70, 96, 79, 80, 65, 64, 97]. The heat treatment decomposes the binder (producing HF [98, 64]) and may modify the carbon present in the sample. However it is also possible that this decomposition influences the surface of the metal oxide, either fluorinating the surface or by removing an organic layer on the MMO. The presence of an organic layer on the coating of electrode particles before heat treatment is confirmed through surface analysis techniques, and is shown to promote hydrophobicity of the cathode particles [99]. In lieu of heat treatment, cryomilling has been used by Liu et al. [58] to render the PVDF binder brittle, and prone to shattering during the comminution step, giving improved separation between active material and the binder. To maximise the separation using froth flotation, the difference in the hydrophobicity of the materials is exploited, and surface modification through binder decomposition, or surface treatment is essential to improve the selectivity of froth flotation [98, 73]. Fine grinding, comminution, or attrition can also maximise the hydrophobic graphite surfaces to enhance graphite and MO separation [19, 100, 15, 101, 20]. To prevent the release of toxic HF and P_2O_5 during the removal of the organic layer through heat treatment, Fenton's reagent (Fe^{2+} + H_2O_2) can instead be utilised to oxidise and remove the layer, however further work is required to remove the iron containing impurities from the products [102, 98]. A comparison of recent froth flotation separation results has made in table 3. This table compares the order of stabilisation and separation techniques used prior to froth flotation, and the improvements made through optimisation of parameters to grade and recovery by percentage mass.

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Order of Processes						Product	Parameter Optimisation	Grade (%)		Recovery (%)		Source
Discharge	Disassembly	Pyrolysis	Comminution	Sieving	Other			Before	After	Before	After	
1	2		3	4		LCO	Fenton's Reagent	55.6	75.0			[98]
		1	2	3		C	Attritioning	64.5	74.0		98.0	[100]
1	2		3*	4		LCO			97.2		49.3	[101]
1	2		3*	4		C			82.6		73.6	[101]
1	2		4*	5	3^a	LCO		69.9	88.2	70.9	74.3	[19]
1	2	*	3	4		LCO	Ultrasonication	67.3	93.9	74.6	96.9	[79]
1	2	*	3	4		C	Ultrasonication	51.1	93.6	42.2	87.8	[79]
1		3	2,4	5		LFP			88.7		49.7	[64]
		1	2	3		LFP		89.4	88.2	63.6	70.7	[65]
1	2		3^b	4	5^a	LCO	De-agglomeration	95.8	98.3	87.8	94.5	[15]
1		4	2*	5	3^c	LCO		94.7	95.0	83.8	91.4	[62]
1	2		*3^d	4		LCO		55.4	91.8	72.8	89.8	[58]
1			3	5	2^e, 4^f	LCO			100.0			[13]

Table 3: Comparison of grades and recoveries by percentage weight, achieved through froth flotation, and the order of separation techniques used beforehand. * Denotes parameters which were varied. ^{a} Washing, ^{b} Wet comminution, ^{c} Density, magnetic, and eddy current separation, ^{d} Cryomilling, ^{e} CO_2 extraction of electrolyte, ^{f} Density separation and Hydrothermal Treatment. LCO Lithium Cobalt Oxide, LFP Lithium Iron Phosphate.
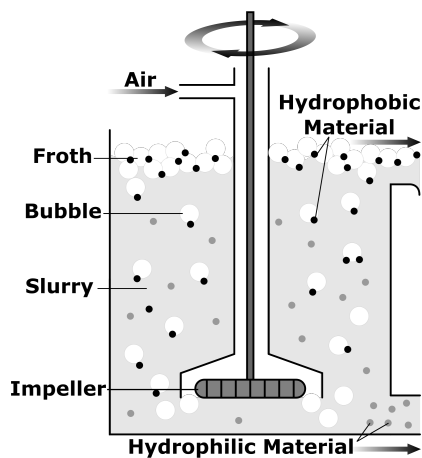
Figure 7: A schematic demonstrating one method of froth flotation, including an air dispersal system and air bubbles, hydrophilic material sinking to the bottom, and hydrophobic material in the froth.

4.5. Other Processes

460   Electrostatic separation was proposed by Zhang et al. [71] to isolate polymer separators from aluminium and copper, and is shown in Figure 8. Silveira et al. [103] applied electrostatic separation on three battery samples, and was able to separate a conductive (Electrode and coating) fraction with a 98.98 % grade, and a nonconductive (polymer) fraction with a 99.6 % grade. Eddy current

465   separators can be utilised to separate ferrous metals, non-ferrous metals, and non-metals [61, 104], and also aluminium from copper foils [105]. However to date there is nothing to indicate that these processes are utilised at scale for separation of lithium ion battery components.

4.6. Summary of Material Separation

470   Once the cells have been broken down, typically by milling or shredding, the materials are then separated primarily by size. Steel casings and ferromagnetic material can be removed through magnetic separation. The separator and packaging can be recovered through sieving, density separation, or electrostatic separation. Further separation of the plastics is achieved through density sep-
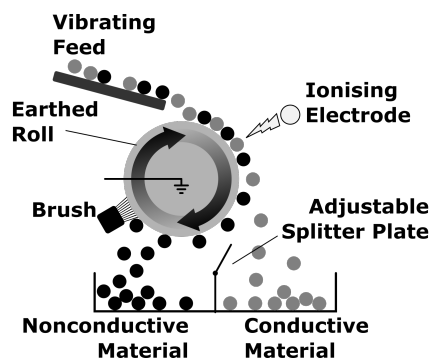
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Figure 8: A schematic demonstrating one method of electrostatic separation, including a rotating drum, positive electrode, and static brush. Non conductive material develops a static charge and is attracted to the drum, conductive material does not retain a charge and falls under gravity.

aration of the coarse fraction. The remaining material mainly consists of the black mass with the aluminium and copper current collector, which can be sieved into various "coarse" and "fine" fractions. The fine fraction typically consists of mainly the cathode and anode electrode composite materials. One disadvantage of this approach is that there is always a high level of contamination of aluminium in the fine black mass which needs to be further refined, although wet sieving results in a better separation of the finer components of the black mass from Al and Cu current collectors. It is possible to use froth flotation to separate carbon from mixed metal oxides. This requires thermal or chemical treatment to remove organic groups from the surface of mixed metal oxide particles and restore their hydrophilicity. These separation methods provide a partially contaminated waste stream, due to the intimate mixing of the materials during comminution. Further work is required to control both the particle size and the material properties for use in these separation methodologies.

5. Black mass separation

Binders such as polyvinylidene fluoride (PVDF) are used to stick the cathode and anode powders to each other, the conductive additive and the current

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collectors. Other binder systems such as Styrene Butadiene Rubber (SBR) and Carboxymethyl Cellulose (CMC) are also used. CMC is soluble in water, allowing for a much easier separation of electrode coatings and foils, however the SBR is utilised in the manufacturing process as an emulsion and still requires removing from the black mass after CMC removal [53, 1].

In order to adequately liberate the electrode active materials for recovery, it is necessary to break down the binder or otherwise separate or extract the cathode coatings (binder negation). Such a liberation is mainly achieved by thermal or chemical processing.

5.1. Thermal and chemical treatments

With **thermal liberation** treatments Hanisch et al. [82] showed that PVDF adhesion strength in LIB electrodes increases between 200-400 °C, but drops off after 15 minutes at 500 °C. Their "ANVIIL" process (Adhesion Neutralisation Via Incineration and Impact Liberation) involves pyrolising cathodes at 500 °C for 90 minutes, then using an air jet impact process for 1 minute to get a 97.1 % recovery of coating powders low in Al. Similar investigations into temperature and duration of heat treatment processes were conducted by other authors [97, 64, 96, 80]. As discussed in section 4.4, heat treatment is used extensively by authors in order to remove or degrade the binder on electrode coatings, and restore hydrophobicity or hydrophilicity prior to froth flotation [96, 79, 80, 65, 64, 97]. Dissolution of PVDF can be achieved by using hot solvents such as N-Methyl-2-pyrrolidone (NMP), N-N-dimethylacetamide (DMAC), N,N-Dimethylformamide (DMF), Dimethyl sulfoxide (DMSO), and Ethanol [106, 10, 21]. He et al. [38] investigated the effects of the aforementioned 5 solvents and the effect of adding ultrasonic agitation to the binder removal process, establishing that ultrasound-assisted NMP was the most effective binder removal process [50]. Disadvantages of NMP include cost and toxicity, hence why alternative solvents such as 1-Butyl-3-methyl-imidazolium-tetrafluoroborate ([BMIm][BF$_4$]) have been investigated [107]. Several **chemical processes** [50] use organic acids to separate Al and Cu current collec-

tors from the powder coatings. The cathodes can also be dissolved from the current collector with acids, a process which can be intensified by utilising reductive leaching by adding hydrogen peroxide to the acid leaching process. [108, 9, 109, 110, 111, 112, 113]. The Al current collectors can also be removed using NaOH, with some Li dissolution and minimal Co dissolution [111, 41, 86].

5.2. Mechanochemical treatments

An alternative binder negation method to thermal processing is mechanochemical processing. Mechanochemical processing involves mixing electrode materials with a reagent and some grinding media, grinding for extended periods to produce water or acid soluble metal complexes, and then dissolving the cathode coatings. Dissolution can be performed via acidic leaching [114], or using water. It is noted that mechanochemical processing does not evolve the toxic byproducts associated with thermal treatment of battery materials. Soluble chlorides of the metals can be synthesised from the metal oxides. Saeki et al. [115] used PVC (polyvinyl chloride) and Wang et al. [48] used PVC, NaCl, NH_4Cl, Zn_2Cl and $FeCl_3$ as chlorine donors to form soluble CoCl and LiCl, which was then dissolved with water, negating the need for hot acidic conditions, and the disposal of said acids. The observations of the metals reclaimed by each group were quite different due to the level of PVC utilised in the work, with 90 % of the cobalt being reclaimed when excess chloride was utilised. Wang et al. [48] also investigated EDTA as complexing agent for Co and Li removal. Recoveries of 98 % Co and 99 % Li were achieved by co-grinding with $LiCoO_2$:EDTA powders, then dissolving with water and recovering cobalt oxide and lithium carbonate via precipitation.

5.3. Summary of Black Mass Separation

The successful separation of the black mass is heavily reliant upon the removal of the polymer binder components. PVDF and analogues are notoriously difficult to remove and therefore harsh and environmentally detrimental methods such as thermal decomposition (which produces HF) or harmful organic

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solvents are generally used. The binder chemicals can reduce the effectiveness of the subsequent leaching processes and therefore it is essential to remove them. Metal extraction is typically performed by leaching with acids, or the cathode may be reclaimed by removal of the aluminum with alkali. The mechanochem-ical processes being investigated have only been investigated at a low level and requires significantly more research to understand their value. In these processes typically additional chemicals are utilised in a milling process to extract the metals without using acids or alkali saving additional expense. This black mass separation is the last step before the metal oxides are fully returned to their metals or remade into the precursor salts for re-manufacturing of cathodes. Interestingly very little has been reported about graphite extraction. Graphite is a very stable material, and it is assumed that the extraction will be via a physical process rather than a chemical process, however removal of organic species and functional groups from the surface of the graphite may be necessary if the graphite is to be re-used in a LIB.

Once the binder is removed froth flotation can be utilised to remove any additives. In all cases the contamination of the black mass from the initial shredding and milling processes causes additional work and expense to purify the cathode and anode materials. If the components were first separated that would reduce the level of contamination and has to date not been the subject of many investigations.

6. Summary and Outlook

The main physical processes involved in LIB recycling consist of stabilisation, opening, and separation and black mass collection. **Stabilisation** of the LIB prior to recycling can be achieved through brine or ohmic discharge, although there is confusion in literature as to whether the cell should be reduced to a 0 % state of charge, or to 0 V open circuit voltage. In-process stabilisation during shredding or milling is the current route preferred in industry, and the main process utilised for **opening** of the cells. The shredded or ground

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battery components are **separated** using sieves, filters, magnets, air separators and shaker tables to separate a lithium rich solution, low density plastics and papers, magnetic casings, coated electrodes and fine electrode powders. To liberate the **black mass** the coated electrodes and electrode powders are typically heated or milled to break down the PVDF binder, and allow for liberation of the coatings and modification of the surface of the carbon components. These powders can then be separated using froth flotation. The black mass separation for short loop recycling and materials reclamation has focused upon cathode and mixed metal oxides with little reported about graphite. There are many future opportunities for alternative reclamation methodologies, such as; electrostatic and eddy current separation processes, which to date has been limited in their usage. Further optimisation of chemical, thermal and mechanochemical methods is required to separate the electrode coatings from the current collectors in low cost and environmentally friendly processes. In particular novel mechanochemical processes can dissolve the relevant metals from the electrode coatings using water based solvents, precluding the use of expensive, toxic, and environmentally harmful solvents such as NMP, or the evolution of corrosive gasses such as HF during thermal treatment.

Materials purity is of importance for re-manufacturing in particular. Direct loop recycling can be employed which rather than complete conversion back to the component metals and metal oxides; utilises materials directly after separation. Here a route which separates out the components, with less materials mixing or contamination is preferred. This highlights a research gap for cell disassembly and component sorting for low contamination concentrated waste streams rather than shredding and subsequent sorting. Cell disassembly may lead to higher materials reclamation yields, higher purity waste streams and more complete liberation and reclamation of the black mass from the current collectors. This however requires more work prior to disassembly, where the chemistry, state of charge (SOC) and state of health (SOH) analysis is known before separation. **Safety:** The mechanical, chemical and process safety of recycling has not been considered extensively to date but is of great importance.

Several toxic chemicals are contained within the cell and can also be produced during the recycling processes. The chemical reactions and products that form upon comminution, thermal runaway, or by any of the above processes are not understood and the risks are difficult to assess. The potential exposure to harmful chemicals must be mitigated during the handling and transfer of the materials during these physical processes. If a closed process is used, then the chemicals are contained, however if the materials are moved from one process to another, the potential exposure to carcinogens and toxic chemicals is greater. The understanding of these chemical processes presents a research opportunity and challenge in itself. In terms of **disassembly** vs shredding, the cell chemistry, SOC and SOH will have a big impact upon safe dismantling of cells. Currently, cell disassembly has been performed manually only at a laboratory scale. However future research into greater automation and robotic disassembly techniques may offer alternative solutions to shredding and be able to overcome some of the hurdles in the dismantling process scale-up.

Design for disassembly of cells and electrode components for future for recycling of lithium ion batteries is also important for recycling. Issues regarding the binder negation still need resolving. Thermal treatment of PVDF produces HF, which is toxic. Manufacturing with alternative fluorine free and water soluble binders will be beneficial for binder removal through subsequent heat or solvent treatments.

If full (100 %) recyclability of lithium ion batteries is to be achieved then alternative methodologies to the current commercial processes are required. Current physical processes utilised in battery recycling are typically based around semi-automated discreet techniques, which need to be combined to be effective for materials separation. Other more automated, or robotic disassembly methods which separate out the cell components first, may offer opportunities for greater purity waste streams. This offers opportunities for future research into the health and safety, cell and component identification, and process control. A major opportunity highlighted here is in the separation of the black masses post cell disassembly or comminution. With purer black mass streams short or

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direct loop recycling is enabled without the requirement for further purification or chemical processes. In addition many of the reclaimed materials may have alternative use cases in other industries where small impurity levels can be tolerated. This should the the topic of future investigations for the facilitation of a 100 % recycled lithium ion battery.

Conflicts of interest

The authors declare no conflict of interest. The funders had no role in the writing of the manuscript, or in the decision to publish the results.

Nomenclature

LIB   Lithium-ion batteries

NMP   N-Methyl-2-pyrrolidone

OCV   Open Circuit Voltage

PVDF   Polyvinylidene fluoride

WEEE   Waste Electrical and Electronic Equipment

CMC   Carboxymethyl Cellulose

SBR   Styrene Butadiene Rubber

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