



## HEALTH AND SAFETY

# Considerations in Lithium-ion Battery Recycling



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# Abstract

As the transition from internal combustion engine vehicles (ICEV) to purely electric vehicles (EV) gathers pace, an increasing number of production facilities are being commissioned to meet the demand for millions of tonnes of lithium ion batteries.

At the same time, companies are investing in, and developing battery recycling technologies allowing for the recovery of the valuable materials and components that are found within the batteries. Generally speaking, lithium ion battery recycling/material recovery is a three stage process;

**1. Processing** the batteries to separate the components

**2. Refining** of the battery metals (and non-metals)

**3. (Re)synthesis** of battery components using the recycled material or in combination with virgin material

This document focuses only on stage one of the recycling process, in particular the shredding and material separation, as this is the most common method being installed in the UK and around the world. As global recycling capacity ramps up, mechanical shredding of batteries will generate tens of thousands of tonnes of shredded material to produce a product known as a 'black mass'. The recycling process needs to be designed in such a way as to minimise the risks posed by the hazardous chemicals within the batteries. Many companies are either entering the recycling sector for the first time or moving into the production and handling of hazardous chemicals for the first time. Such companies may not necessarily comprehend the severity of the risks associated with battery chemicals. Information pertaining to the hazards is widely available but scattered throughout the published literature which may not be accessible to some companies. There is currently no existing document that links the hazards specifically found on a battery shredding and material separation plant and describes how a normal situation found on such a plant could lead to elevated risk levels.

It is also important for recyclers to consider the hazards and risks of storage, handling and processing batteries prior to shredding. These hazards include electrical and fire hazards associated with the handling and storage of the batteries. There are also several hazards associated with the shredding itself such as the risk of fires and explosions. This document will not cover such hazards as the processes and procedures required for the safe handling and storage of batteries are developing to keep pace with battery technical innovations and are subject to on-going standards development. The document will also not consider the safe shredding of the batteries since this is relatively well developed and many companies offer "off the shelf" solutions. Recyclers should ensure that their shredders have at least some of the following safety features; inert atmosphere, fire detection system, fire extinguishing system and an explosion relief valve. This document focuses on the risks and hazards that arise once the batteries have been shredded as these risks are new to the recycling industry and are not yet well defined nor fully understood.

## DISCLAIMER

The document should not be used as a comprehensive list of hazards associated with battery recycling but rather as a starting point to understanding some of the known and unknown hazards that a recycler is likely to face. It is the legal responsibility of all operators to ensure their processes are safe and comply with the relevant health and safety regulations. Operators are encouraged to assess and manage risks by undertaking a hazard and operability analysis (HAZOP), a hazard analysis (HAZAN) as well as a dangerous substance and explosive atmosphere (DSEAR) assessment.

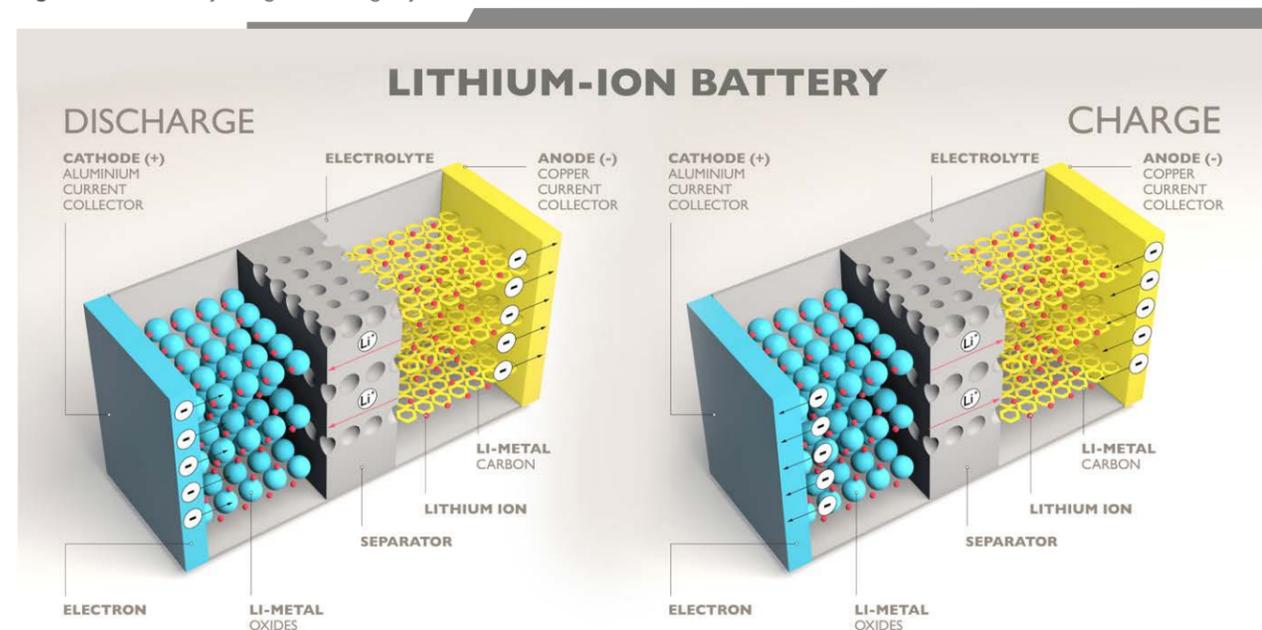
# 1. Working Principles of Lithium-ion Batteries

A lithium-ion battery is an electrochemical device that converts chemical energy into electrical energy and vice versa.

A battery pack may consist of hundreds or thousands of cells grouped into modules and connected together to achieve the power and energy requirements of the application. The cell, which is the building block of the pack, is composed of four main components: two electrodes (a cathode, and an anode), a separator and an electrolyte.

During normal use, energy is stored and released through the transfer of Lithium ions between the two electrodes via the separator and the electrolyte. The cathode is attached to the positive terminal of the cell, and the anode is attached to the negative terminal. There are several different lithium-based compounds that are used as cathode materials, but graphite is primarily used for the anode. During charging, lithium ions are transferred from the cathode to the anode, this transfer is facilitated by the electrolyte containing dissolved lithium ions (Li+), which improves diffusion speeds. To maintain balanced charge within the cell, electrons flow through an external circuit in the same direction to the lithium transfer. A separator facilitates the selective transfer of Li+ whilst maintaining electrical isolation between the positive and negative terminals to prevent unwanted discharging and short circuit. To safely discharge the cell, the cathode and the anode must be connected by the way of a load bank. The load bank regulates the flow of electrons and reduces their energy state, allowing for the safe transfer between the two electrodes.

Figure 1 Li-ion battery charge - discharge cycle



# 2. Battery components

A generic lithium-ion cell contains several different components. Table 1 shows these components and their compositions. Please note that the materials going into a battery are well known and defined but the material coming out once the battery has been shredded is not yet fully understood. Generally speaking, most of the components coming out after the shredding will be the same or very similar to those that went in, but there may be other chemicals present, resulting from the various reactions that occur throughout the lifetime of the battery. This is an important consideration that the operator need to be aware of, and they are encouraged to continually chemically analyse the material coming out of their shredders to build up a database, enabling them to install appropriate countermeasures should they find anything of concern. Operators, particularly those that are processing manufacturing scrap and/or prototype cells and modules have to be prepared for rapid changes in battery chemistry, components and their compositions. Newer chemistries may use chemicals that had not been considered when the recycling plant was designed and built.

Post shredding, the components need to be separated into concentrated individual streams before they can be refined and recycled. Table 1 shows a typical composition of the materials found in an 18650 lithium-ion cell. As can be seen, most of the mass is accounted for by the cathode and the anode active material powders. The cathode active powder may contain valuable metals such as nickel and cobalt alongside lithium. Together with the copper current collector, these four metals make up more than 90% of the value in an end-of-life cell (based on the current state of the art recycling technology). Generally, recycling processes are set up to recover the cathode and anode powders to form a product that is referred to as black mass. There is no strict definition of what constitutes black mass, but it is a ubiquitous term used throughout the battery recycling industry to refer to shredded battery components which appear as a black powder due to the presence of graphite. In an ideal process, the cathode and anode powders will be further separated out to produce two high purity streams but this is not possible or uneconomic given the current technology and so recyclers instead recover the powders together as a mixture.

Table 1 Typical composition of materials found in a Lithium-ion cell

Component	Material	Typical Mass %
Cathode active powder	Lithium-transition metal-oxide	30-40%
Anode active powder	Graphite mostly	15-25%
Separator	Plastic (such poly ethylene, poly propylene etc)	3%
Binder	Polyvinylidene fluoride (PVDF)	0.6-1.5%
Negative current collector	Copper	15%
Positive current collector	Aluminium	10%
Casing	Aluminium, steel	5-15%
Electrolyte components	<b>Various including (but not limited to)</b> <ul style="list-style-type: none"> <li>▶ Ethylene carbonate</li> <li>▶ Diethyl carbonate</li> <li>▶ Dimethyl carbonate</li> <li>▶ Ethyl methyl carbonate</li> <li>▶ Propylene carbonate</li> </ul>	12-15%
	<b>Electrolyte Salt</b> <ul style="list-style-type: none"> <li>▶ Lithium hexafluorophosphate</li> </ul>	1.5 - 2%
Electrolyte additives (including but not limited to)	<ul style="list-style-type: none"> <li>▶ Vinyl Carbonate</li> <li>▶ Lithium difluorophosphate</li> <li>▶ Fluoroethylene carbonate</li> </ul>	Unknown

### 3. Battery Recycling Process: A Brief Description

A typical battery recycling process based on shredding and material separation may be configured along the lines of the diagram shown in Figure 2.

Ideally, packs should first be discharged, but in some cases this will not be possible so the packs are dismantled into modules which are then discharged. When the cell is charged, lithium is stored at the negative electrode (anode), forming a highly unstable compound called graphite-lithium ( $C_6Li$ ). The lithium in  $C_6Li$  is in an elemental form and therefore highly reactive, particularly towards moisture, with which it reacts violently, generating heat and hydrogen. Discharging the cell forces most of the elemental lithium in the anode to travel to the cathode where it forms a stable compound. During the shredding process, the cells are cut open and the separator is damaged, providing a direct pathway between the anode and cathode thus enabling short circuits to occur. If the cells contain charge, it will flow uncontrollably from the anode to the cathode, generating large quantities of heat, leading to sparks, which could initiate thermal runaway or directly ignite the electrolyte causing a fire within the shredder. The heat can also destabilise the cathode oxide powders, generating oxygen which may allow the batteries/shred to burn even in anoxic atmospheres.

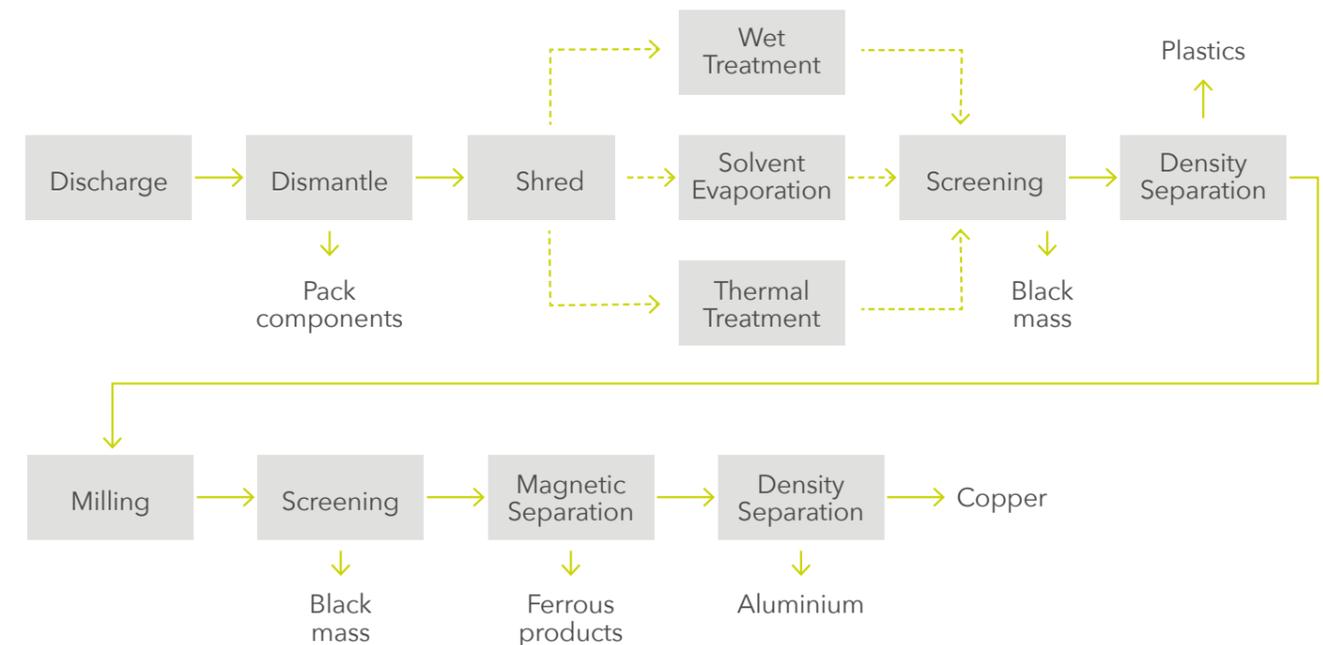
Discharging the cells prior to shredding decreases the quantity and the intensity of internal short circuits that will inevitably occur during the shredding process, preventing the temperature of the shred from reaching a point where sparking and combustion can occur.

The batteries are shredded using mechanical means, normally under an anoxic atmosphere, generated using an inert gas such as nitrogen, carbon dioxide or in a vacuum or under an aqueous/liquid solution. Recyclers need to be aware that the normal charge/discharge band for a lithium ion cell is 20-80%, therefore, even when discharged, there will be some elemental lithium present at the anode. This lithium will still be present when the battery is shredded, and the material is separated out.

Once shredded, the resulting shred must be quickly treated to remove or treat the organic solvents present in the electrolyte before any further processing can occur. The most common methods of electrolyte treatment are; chemical treatment (wet treatment), evaporation (drying) or pyrolysis (thermal treatment). Each method has hazards and risks associated with it and these will be discussed further on in the document. After the electrolyte treatment, there is normally a screening step that separates the initial black mass from the other components. This is followed by a density separation step to remove the lighter components such as the plastics. Next, the material is milled to exfoliate the remaining cathode and anode active powders from the foils and then screened to collect the rest of the black mass. The remaining material is passed through more separation steps such as magnetic separation to extract the magnetic metals and some recyclers even separate out the copper from the aluminium.



Figure 2 Schematic of a typical lithium ion battery shredding and material process



### 4. Regulatory Framework for Health and Safety Within Battery Recycling

Lithium ion battery recyclers operating in the UK or the EU need to be aware of the regulatory framework that their processes may fall under.

In addition to obtaining the necessary local and national environmental permits required to function as a licenced battery recycler, operators are reminded that, as with every industry, they need to carefully consider how the processes they propose to undertake may fit within the existing Health, Safety and Environmental legislative frameworks. This will involve (but not necessarily be restricted to) assessing and managing all the risks presented, and, wherever possible, reducing these risks as far as is reasonably practicable.

It is likely that operators will need to give specific additional consideration to the management of packs which may arrive with dangerous voltages, and the variety of hazards involved with creating and handling the 'black mass'.

It should be noted that the EU Batteries Directive has recently (2022) been significantly overhauled and extended, and that a UK consultation exercise on potential changes to the mirrored legislation within the UK is expected during 2023. The regulations in this area are, therefore, under review, and operators are encouraged to be vigilant of the regulatory changes and clarifications that are currently in the works at both the UK and European level, in addition to any recently generated information put into the public domain. These may clarify how existing Regulations relate to the production, storage, handling and transportation of battery waste, including black mass from lithium ion batteries.

# 5. Hazards associated with Lithium-ion Battery Recycling

## 5.1. Types of Hazards

A typical lithium-ion battery recycling process may have the following hazards associated with it:

- ▶ Gaseous and vapour hazards such as the generation of toxic or flammable gases and vapours during shredding or drying.
- ▶ Dust hazards from the various powders within lithium ion batteries
- ▶ Fire hazards from the various flammable components within lithium ion batteries or side reactions that can lead to fire hazards if not controlled
- ▶ Explosion hazards in certain scenarios if the chemicals are not safely contained and handled
- ▶ Toxic chemical hazards produced from some of the side reactions that can occur during the processing
- ▶ Corrosive chemical hazards from some of the side reactions that can occur during the processing

Table 2 summarises some of the components that may be present within shredded battery material. Excluded are some of the chemicals that may be generated by the side reactions should the battery experience heating as these are too numerous to name and their formation depends heavily upon the extent of heating experienced by the batteries. Chemicals included are; cathode and anode active powders, electrolyte components including organic solvents such as diethyl carbonate ( $C_5H_{10}O_3$ ) and ethyl methyl carbonate ( $C_4H_8O_3$ ), lithium hexafluorophosphate ( $LiPF_6$ ) and its decomposition products such as hydrofluoric acid (HF) and various phosphor-fluorides. Copper and aluminium foils as well as plastics and rubber make up the balance. There are a variety of hazards related to each of these compounds, some are flammable, others are toxic and some are carcinogenic. Recyclers must consider these risks and develop processes allowing for the safe handling and conveyance and storage of such material.

Table 2 Summary of hazards for different components in Lithium-ion batteries

Component	Chemical Formula	CAS Number	Hazard Statements	Hazard Labelling
Lithium cobalt oxide (LCO)	$LiCoO_2$	12190-79-3	H351: suspected of causing cancer H360Fcd: May damage fertility. Suspected of damaging the unborn child H400: very toxic to aquatic life H410: very toxic to aquatic life with long-lasting effects	
Lithium nickel manganese cobalt oxide (NMC)	Various; $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$	346417-97-8	H317: May cause an allergic skin reaction. H351: is Suspected of causing cancer.	
Lithium iron phosphate (LFP)	$FeLiO_4P$	15365-14-7	Not a hazardous substance	
Lithium Manganese Oxide (LMO)	$LiMn_2O_4$	12057-17-9	H302: Harmful if swallowed H332: Harmful if inhaled H413: May cause long-lasting harmful effects on aquatic life	

Table 2 Summary of hazards for different components in Lithium-ion batteries (continued)

Component	Chemical Formula	CAS Number	Hazard Statements	Hazard Labelling
Lithium Nickel Titanate (LTO)	$Li_2TiO_3$	12031-82-2	H302: Harmful if swallowed H315: Causes skin irritation H319: Causes serious eye irritation	
Lithium Nickel Cobalt Aluminium Oxide (NCA)	$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ $LiNi_{0.84}Co_{0.12}Al_{0.04}O_2$	193214-24-3	H317: May cause an allergic skin reaction. H351: is Suspected of causing cancer.	
Carbon Black	C	133-86-4	H251: Self-heating; may catch fire H351: Suspected of causing cancer H372: Causes damage to organs through prolonged or repeated exposure (lung)	
Graphite	C	7782-42-5	H319: Causes serious eye irritation. H335: May cause respiratory irritation.	
Lithium hexafluorophosphate	$LiPF_6$	21324-40-3	H302: Harmful if swallowed. H314: Causes severe skin burns and eye damage. H318: Causes serious eye damage. H335: May cause respiratory irritation. H372: Causes damage to organs (Bone, Teeth) through prolonged or repeated exposure if inhaled.	
Ethyl Methyl Carbonate*	$C_4H_8O_3$	623-53-0	H225: Highly flammable liquid and vapour	
Ethylene Carbonate*	$C_3H_4O_3$	96-49-1	H302: Harmful if swallowed H319: Causes serious eye irritation H373: May cause damage to organs (Kidney) through prolonged or repeated exposure if swallowed	
Lithium difluorophosphate	$LiPF_2O_2$	24389-25-1	H301: Toxic if swallowed H312: Harmful in contact with skin H314: Causes severe skin burns and eye damage H372: Causes damage to organs through prolonged or repeated exposure H411: Toxic to aquatic life with long lasting effects	
Vinylene Carbonate	$C_3H_2O_3$	872-36-6	H301: Toxic if swallowed H311: Toxic in contact with skin H317: May cause allergic skin reaction H373: May cause damage to organs (Liver, Stomach) through prolonged or repeated exposure if swallowed H411: Toxic to aquatic life with long lasting effects	
Fluoroethylene carbonate	$C_3H_3FO_3$	114435-02-8	H302: Harmful if swallowed H315: Causes skin irritation H317: May cause allergic skin reaction H319: Causes serious eye irritation	
Copper foil	Cu	7440-50-8	Not a hazardous substance	
Aluminium foil	Al	7429-90-5	H228: Flammable solid H261: In contact with water releases flammable gas	

\* Ethyl methyl carbonate and Diethyl carbonate are just two examples. Many other organic carbonates are used, see Table 5

Table 3 Other chemicals that may be present in the black mass

Component	Chemical Formula	CAS Number	Hazard Statements	Hazard Labelling
Lithium	Li	7439-93-2	H260: In contact with water releases flammable gases which may ignite spontaneously H314: Causes severe skin burns and eye damage	 
Lithium oxide	Li <sub>2</sub> O	2057-24-8	H314: Causes severe skin burns and eye damage	
Lithium Hydroxide	LiOH	1310-65-2	H301: Toxic if swallowed H314: Causes severe skin burns and eye damage	 
Hydrofluoric Acid	HF	7664-39-3	H300 + H310 + H330: Fatal if swallowed, in contact with skin or if inhaled H314: Causes severe skin burns and eye damage	 

## 5.2. Workplace Exposure Limits (WEL)

The first category to be aware of is the Workplace Exposure Limits (WEL). In the UK, WELs are occupational exposure limits set to ensure the health and safety of workers who may be exposed to hazardous material whilst at work. WEL limits are given as a maximum concentration of a hazardous substance in the air, averaged over a specified time average, known as time weighted averages (TWA). These limits are set over two time periods; long-term exposure (8 hours) and short-term exposure (15 minutes). It is illegal to exceed the limits assigned by a WEL and operators are encouraged to carry out risk assessments and install engineering controls to reduce the risk to health. Several risk assessments may need to be carried out as the risks can vary depending upon what activity is taking place in which area. Most cathode materials do not yet have a specific WEL, this does not mean that they are exempt or do not require controlling but rather a WEL has not yet been established.

In such cases, the WEL for the primary substance or most hazardous substance within the compound needs to be considered. For example, lithium cobalt oxide does not have an established WEL, but, as it is 93% cobalt oxide by mass, cobalt oxide should be taken as the chemical to which the WEL is applied. Operators need to be aware that the wording used within the HSE documentation do cover cathode materials. For example, in the case of cobalt, the wording used is 'cobalt and cobalt compounds' which also covers lithium cobalt oxide. Operators are encouraged to act in a proactive manner since WELs will eventually be established for the cathode materials and those that fail to install the necessary controls may find they have to redesign their plants to comply with the WELs in the near future. Table 4 below provides the WELs for substances that will and some that may be present on a lithium ion battery recycling plant.

Table 4 WELs for common substances encountered when shredding LIBs. Information taken from variety of sources such as EH40/2005 Workplace Exposure Limits<sup>1</sup>, relevant MSDS from Fisher Scientific<sup>2</sup> and Sigma Aldrich<sup>3</sup>

Substance	CAS number	Workplace exposure limit			
		Long-term exposure limit (8 hour TWA)		Short-term exposure limit (15 minute TWA)	
		ppm	mg/m <sup>3</sup>	ppm	mg/m <sup>3</sup>
Lithium cobalt oxide (LCO) *	12190-79-3	-	0.1	-	-
Lithium nickel manganese cobalt oxide (NMC) *	346417-97-8	-	0.1	-	-
Lithium iron phosphate (LFP) *	15365-14-7	-	5	-	-
Lithium Manganese Oxide (LMO) *	12057-17-9	-	0.5	-	-
Lithium Nickel Titanate (LTO) *	12031-82-2	-	0.1	-	-
Lithium Nickel Cobalt Aluminium Oxide (NCA) *	193214-24-3	-	0.1	-	-
Carbon Black	133-86-4	-	3.5	-	7
Graphite Inhalable dust	7782-42-5	-	10	-	-
Respirable dust		-	4	-	-
Copper dust	7440-50-8	-	1	-	2
Aluminium foil Inhalable dust	7429-90-5	-	10	-	-
Respirable dust		-	4	-	-
Lithium Hydroxide	1310-65-2	-	-	-	1
Hydrofluoric Acid	7664-39-3	1.8	1.5	3	2.5
Lithium hexafluorophosphate	21324-40-3	None established			
Vinylene carbonate	872-36-6	None established			
Lithium difluorosulphate	24389-25-1	None established			
Fluoroethylene carbonate	114435-02-8	None established			

\* No specific WELs have been established for most of the cathode powders used in lithium ion batteries but the WELs given relate to the primary substances found in the material.

<sup>1</sup> Health and Safety Executive. EH40/2005 Workplace Exposure Limits. Containing the list of workplace exposure limits for use with the control of substances hazardous to health regulations 2002; <https://www.hse.gov.uk/pubns/priced/eh40.pdf>

<sup>2</sup> <https://www.fishersci.co.uk/gb/en/customer-help-support/customer-support-search/browse/finding-safety-data-sheets.html>

<sup>3</sup> [https://www.sigmaaldrich.com/GB/en?gclid=Cj0KCCQiAyracBhDoARlsACGFcS4zIGHJJA9IDA4KgHc4RlbCdEWs98-HhBTehf4fOGDKYUBqO7Er1YaApYbEALw\\_wcB&gclid=aw.ds](https://www.sigmaaldrich.com/GB/en?gclid=Cj0KCCQiAyracBhDoARlsACGFcS4zIGHJJA9IDA4KgHc4RlbCdEWs98-HhBTehf4fOGDKYUBqO7Er1YaApYbEALw_wcB&gclid=aw.ds)

## 5.3 Employer Responsibilities Regarding Hazardous Substances

For many of the common cathode materials that contain nickel or cobalt, it is the responsibility of the employer to carry out the following<sup>4</sup>;

- ▶ Assess the risks to employees health and identify the precautions needed for their protection
- ▶ Prevent the exposure to hazardous substances or where this cannot reasonably be done, adequately control the exposure
- ▶ Reduce the exposure to hazardous substances so far as is reasonably practicable, and in any case below the assigned WEL
- ▶ Provide fit testing of any tight-fitting respirators
- ▶ Maintain all fume and dust controls in efficient working order
- ▶ Find out how much hazardous substances employees are exposed to, normally through a monitoring programme, and share results with the employee
- ▶ Arrange any health checks that are needed
- ▶ Inform, instruct and train all employees who may be exposed to the hazardous substances

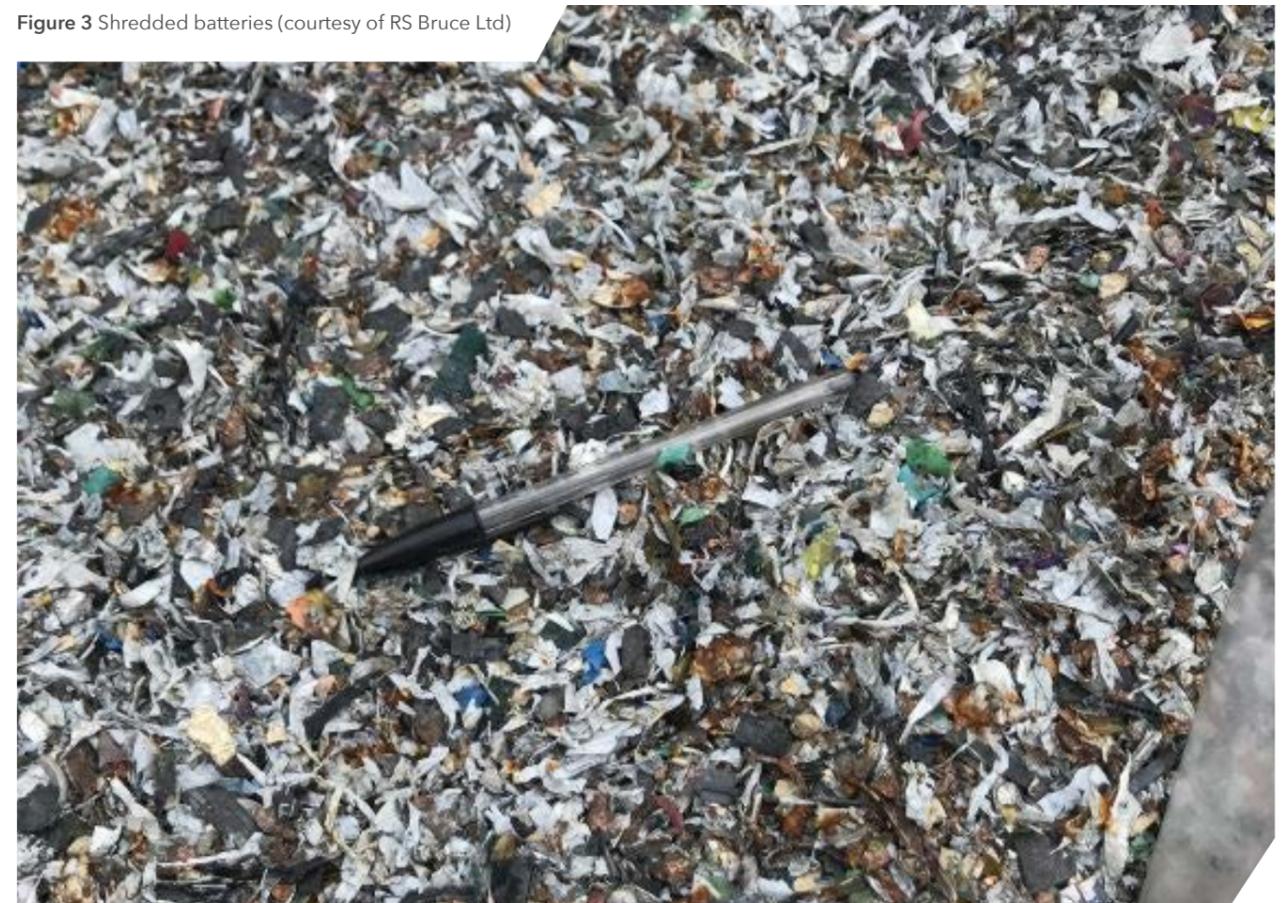
<sup>4</sup>Health and Safety Executive. Cobalt and You. Working with cobalt, are you at risk? <https://www.hse.gov.uk/pubns/indg442.pdf>

## 6. Acute Hazards to Human Health

To avoid physical exposure to the battery shred, the process should be designed such that the shredded components are processed internally, keeping the material within the process machinery and not exposed to the environment.

The plant should have sufficient engineering controls in place to keep the concentration of hazardous material within the work environment to less than the limits set by the WELs. The Workers should have suitable personal protective equipment (PPE) such as chemical and cut-resistant gloves, safety specs, hard hat, overalls that protect their skin from exposure as well the use of correct types of masks for the hazard, if required. Monitoring systems may be implemented to record and monitor the chemicals in the atmosphere and work environment. Alarm systems may be set up to warn workers in cases of elevated risk and other equipment such as self-contained breathing apparatus (SCBA) may be required to carry out certain tasks – such as entering an enclosed space where there is a risk of contacting electrolyte vapours.

Figure 3 Shredded batteries (courtesy of RS Bruce Ltd)



## 6.1 Cuts

Post shredding, the battery material can have very sharp edges created when the shredder blades cut through the various metal parts of the cells or modules. These sharp edges can easily damage and penetrate the skin. The shred may also be contaminated with electrolyte components which can enter the body through the cut.

## 6.2 Sensitising Powders

Many of the cathode active powders contain metal oxide powders such as nickel and cobalt oxides. These are known skin sensitisers and can cause allergic reactions if body parts are exposed to them.

## 6.3 Inhalation of Electrolyte Vapours

Shredded lithium-ion batteries generate large quantities of electrolyte vapours, consisting mainly of the organic solvents that are used in the electrolyte. These vapours produce a strong ethereal odour and can be irritating to the eyes and respiratory tract with prolonged exposure causing severe injury to vital organs such as the kidneys. The vapour from the electrolyte is at its most concentrated straight after the shredding so it is recommended that the shredded material is contained and conveyed within the process and not exposed to the open environment. The vapours coming off the shred may be routed through a wet scrubber, preferably using an alkaline solution before being combusted in a thermal oxidiser (or vice versa).

## 6.4 Potential Carcinogens

Cathode materials containing nickel or cobalt oxides are considered potentially carcinogenic. This means that there is sufficient evidence to suggest they do cause cancer but further testing is required. Such substances should be treated as if they do cause cancer. The recycling process will produce dust if the material is too dry. From Table 4, it can be seen that the exposure limits for some of the cathode dust is as low as 0.1mg/m<sup>3</sup>. Common material packaging methods found on recycling plants, such as the use of bulk bags, or even spouted bulk bags, may not be suitable for safely handling black mass. Operators are encouraged to look at other industries where potentially hazardous material is handled and conveyed. For example, the pharmaceutical industry has developed excellent methods for conveying and packaging active pharmaceutical ingredients (APIs) and such methods could be transferred to handling and packaging of black mass.



**Figure 4** Spouted bulk bags are unlikely to be suitable for the capture of the black mass. Picture; 123bigbags.com

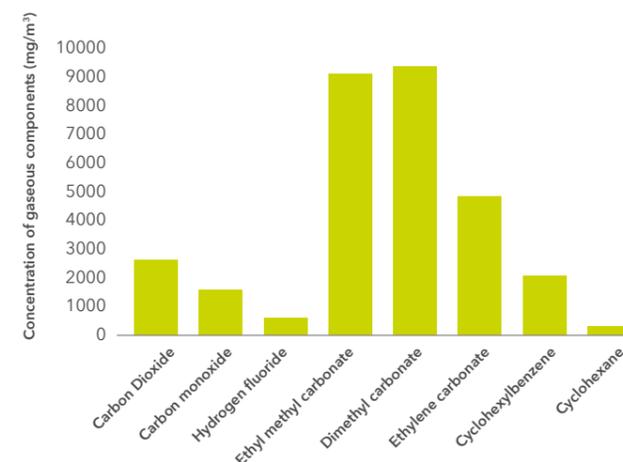
## 6.5 LiPF<sub>6</sub> Hazards

LiPF<sub>6</sub> is the most toxic chemical present in lithium-ion batteries. Not only is it toxic itself, but it can also generate further toxic and poisonous by-products if it is allowed to decompose. The LiPF<sub>6</sub> can be present in two forms; dissolved form or dry form. The dissolved form is how it is found inside the battery where it is dissolved into the organic solvents. This is the form most likely to be encountered prior to organic solvent treatment/evaporation. The dry form of LiPF<sub>6</sub> is most likely to be encountered post electrolyte solvent evaporation providing that the temperature inside the dryer is low enough to avoid thermal decomposition of the LiPF<sub>6</sub>.

## 6.6 Wet Shred LiPF<sub>6</sub> Hazards

One tonne of cells contains around 22kg of LiPF<sub>6</sub>. Hydrogen Fluoride gas as well as a variety of other flammable and toxic chemicals can be generated during the shredding process, particularly if the shredding is carried out when the cells still contain charge as shown in Figure 5. Gases and vapours produced during the shredding process requires treatment or capture. Operators are encouraged to look into the oil and gas industry to determine the types of treatments that could be used to remove the harmful and polluting substances from the outstream.

**Figure 5** Gas emissions from the electrolyte during and after the shredding of lithium-ion batteries at an 80% state of charge. Adapted from Diekmann et al<sup>5</sup>



Another danger of LiPF<sub>6</sub> is its tendency to hydrolyse upon coming into contact with water. If this occurs, each molecule of LiPF<sub>6</sub> generates at least two molecules of HF and one molecule of phosphoryl fluoride (POF<sub>3</sub>). The POF<sub>3</sub> is a highly corrosive and toxic gas that rapidly hydrolyses in water. If sufficient water is not present, it has the potential to become airborne and escape.

The dissolved LiPF<sub>6</sub> is likely to deposit on the parts of the machinery it comes into contact with - this could include shredder blades, shredder screen, outlet hopper, conveyors, inner linings of machinery and conveyance equipment, screens and other plant equipment. Over time, the corrosive nature of the fluoride products can cause corrosion and localised pitting, potentially allowing gas escape and weakening the overall structural integrity of the plant. A worker can easily come into contact with LiPF<sub>6</sub> or its associated by-products if they are exposed to any part of the process where the LiPF<sub>6</sub> has been conveyed through. This scenario is most likely to play out during routine maintenance or servicing of the equipment. Operators are encouraged to undertake necessary risk assessment to develop safe processes and procedures, allowing for maintenance to be carried out. They may want to neutralise the LiPF<sub>6</sub> prior to workers or contractors coming into contact with contaminated areas. The easiest way to achieve this would be to spray any area where work is to be carried out with a strong hydroxide solution such as sodium hydroxide. This will ensure the LiPF<sub>6</sub> is neutralised and work can be carried out. Operators could even design their processes with spray nozzles strategically placed around various parts of the plant to spray a neutralising solution at the end of each shift. The solution should be highly soluble so that it can easily be washed out of the products, avoiding contamination.

The presence of elemental lithium in the battery shred can prevent the formation of hydrofluoric acid by first reacting with the water to form LiOH which then reacts with the HF to form lithium fluoride, LiF. This only happens if both of the chemicals come into contact with the same batch of water. This is what happens during the wet treatment of the electrolyte. Operators who choose wet treatment must add further neutralising agents as the inherent elemental lithium may not be sufficient to neutralise all the LiPF<sub>6</sub>. The downside of wet processing is that it reduces the recycling efficiency as the electrolyte components which account for around 15% of the cell mass are destroyed or transformed into an unrecyclable state.

<sup>5</sup> J. Diekmann, S. Sander, G. Sellin, M. Petermann, A Kwade. Chapter 7: crushing of battery modules and Cells in Recycling Lithium ion Batteries, the Lithorec Way, 2018.

## 6.7 Dry Shred LiPF<sub>6</sub> Hazards

After the organic solvent evaporation, if the LiPF<sub>6</sub> is not thermally decomposed, it will precipitate out and be present in the solid form. This exposes it to moisture in the air. Some of the organic solvents are immiscible in water and offer some protection to the LiPF<sub>6</sub> when it is in a dissolved form, but, when it is in a solid form, that protection is no longer there. LiPF<sub>6</sub> is a known hygroscopic material and will react with the moisture in the air to hydrolyse into hydrofluoric acid and POF<sub>3</sub>. The hydrofluoric acid will be present in low concentrations all over the shredded material and must be washed out before the products are sold as the transportation companies and customers might require fluoride free or low fluoride concentration to be present in the products.

## 6.8 Hydrogen Fluoride Gas

Hydrogen fluoride gas is generated when HF molecules evaporate from a bulk hydrofluoric acid solution and enter the gas phase. This process can occur readily as hydrofluoric acid has a relatively high vapour pressure, allowing it to evaporate easily. The process is accelerated if the ambient temperature is high or if the shredding is carried out whilst there is sufficient charge in the cells. However, more concentrated gas streams are expected to be generated in the dryer as a result of the thermal decomposition of the LiPF<sub>6</sub> during the boiling off of the organic solvents.

Once most of the organic solvents have been boiled off, the LiPF<sub>6</sub> is left exposed and it can decompose if the temperature is high enough or hydrolyse if moisture is present in the environment. Normally, LiPF<sub>6</sub> is thermally stable up to 107°C, but in the presence of moisture, this temperature is lowered significantly.

A worker on a battery recycling plant may be exposed to hydrofluoric acid or HF gas in the following scenarios

- ▶ Exposure to concentrated gas. This is most acute in areas where the gas has had some time to build up - for example, upon the opening of a storage vessel where a relatively large volume of electrolyte vapour and HF gas mixture can be released into the environment
- ▶ Gas escape - during the boiling off of the organic solvents - if the dryer and ducting are not correctly sealed, or have been corroded over time, HF gas can escape into the environment
- ▶ Maintenance - particularly machinery that is upstream of the dryer as the 'wet' shred will deposit electrolyte solution on the inner linings of the plant machinery. Over time, this can hydrolyse or decompose and generate HF gas
- ▶ Blockage - if a blockage occurs in the process, an operator's instinct may be to quickly gain access to the blockage and remove it. They can be exposed to the electrolyte vapours (which may contain HF) as well as liquid electrolytes from the sides/linings of the process machinery

## 7. Inhalation of Carbon Black, Graphite and Metal Oxide Dust

### 7.1 Carbon Black

Carbon black is used as an additive in the electrodes to improve electrical conductivity. Carbon black is much lighter than both graphite and cathode powders and hence it is much more likely to become airborne and come into contact with workers. Long-term exposure can cause serious harm such as damage to organs or cancer as seen in Tables 2 and 3.

### 7.2 Graphite

Graphite is more dense than carbon black but it is still able to be entrained in air and generate dust. Though less hazardous than carbon black, the quantity available is much greater and therefore presents a bigger risk. Graphite dust can irritate the eyes and respiratory lining. Graphite dust containing elemental lithium is more hazardous for human health as the lithium will react with any moisture in the body to form lithium hydroxide solution (in a highly exothermic reaction) which is a highly corrosive caustic solution that can damage the eyes, nose and respiratory lining.

The extraction system should be carefully designed to not only protect workers but also enable recovery of the graphite and metal oxide dust. This can be achieved through the use of cyclones or a wet scrubber. Some operators may use filters as the primary means of dust collection but they should be aware that the build up of cake can contain elemental lithium alongside organic carbonates, generating a fire hazard.

### 7.3 Metal Oxide Dust

Dust from cathode materials such as LCO or NMC etc, can be very dangerous to human health since not only are they sensitising but they are also potentially carcinogenic. Cathode powders tend to have high densities so do not travel very far but the nature of the separation processes mean highly energetic movements could propel the material farther than would be the case naturally, generating cathode dust, particularly when the material has been dried of the organic carbonates.

## 8. Flammable and Explosive Hazards

### 8.1 Flammable solvent vapours

The biggest fire hazard associated with lithium-ion batteries comes from the organic solvent that make up the electrolyte. Some of these carbonates readily vaporise to form a flammable and potentially explosive atmosphere. Lithium-ion battery electrolytes consist of two organic solvents and lithium hexafluorophosphate (LiPF<sub>6</sub>) with small quantities of additives to help improve performance. Common additives include vinylene carbonate, fluoroethylene carbonate and lithium difluoro phosphate but the quantities in which they are added remains unknown, hence the recyclers should design their processes as if these chemicals are present in sufficient quantities to cause harm.

Table 5 below shows some of the organic solvents used in lithium-ion batteries as well as their properties. Of these, dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), diethyl carbonate (DEC) and ethylene carbonate (EC) are by far the most common. As can be seen, some of these solvents have low temperature boiling points and flash points, making them very dangerous if not stored and handled correctly. Many of the common electrolytes have flash points below 40°C which is easily exceeded during the shredding and drying processes.

Table 5 Properties of solvents used in Lithium-ion battery electrolytes. Adapted from Steffen Hess et al<sup>[6]</sup>

Organic Carbonate	Acronym	Boiling point (°C)	Vapour Pressure at 25°C (kPa)	Self Extinguishing Time, SET, (s/g)	Flash Point, FP, (°C) at 1 atm
Methyl tert butyl ether	MTBE	55		121	-28
Dimethoxy ethane	DME	84.5		122	-2
Ethyl Acetate	EA	77.1	14.3	98	0.5
Dimethyl carbonate	DMC	90.5	8.0	122	16
Ethyl methyl carbonate	EMC	107	3.9	143	23.5
Diethyl Carbonate	DEC	126	2.4	158	33
Cyclohexanol	cHexOH	160		190	68
Propylene carbonate	PC	242		-	135.5
Ethylene carbonate	EC	248		-	145.5

Whilst the organic solvents are still on the battery shred, the whole of the shred is highly flammable and can readily catch fire if oxygen is present and an ignition source is found. The risk of fire is greatest immediately after the shredding since the shredding process is a high friction activity, raising the temperature of the material. A further, more potent source of heat and ignition comes from the internal short circuits that occur when the cells and modules are being shredded. This risk level increases with increasing state of charge. For example, even a 10% state of charge can lead to temperatures in excess of 70°C<sup>[7]</sup>, well above the flash points of some of the electrolyte components. The rise in temperature occurs around 10 - 40 seconds after the shredding meaning that the risk of fire is still elevated in the collection vessel. Therefore, it is vital that the cells or modules are completely discharged before shredding and the shredding itself is carried out in an anoxic atmosphere and the downstream process units are all in a protective atmosphere until the organic solvent have been removed/treated. It is recommended that the shredder has the following safety features;

- ▶ Able to shred batteries in an inert atmosphere - whether this is using an inert gas, in a vacuum or in a spray of or submerged in an aqueous solution. Recyclers must be mindful that a vacuum has an inherent safety flaw in that, should a defect in the equipment arise (such as a hole in wall due to corrosion), oxygen will flow into the system, creating a flammable/explosive atmosphere whereas in cases of inert gas usage, the positive pressure will stop this from occurring. The use of an aqueous solution can lead to the mobilisation of fluoride ions which can increase corrosion. Some reagents can react with chemicals within the shredder and lead to failure - for example, a recycler may use caustic solutions to capture the fluoride ions but the hydroxide ions can react with the grease in the shredder and saponify it, leading to failure

- ▶ Fire/temperature detection capability to detect increases in temperature
- ▶ Fire suppression capability using a fit-for-purpose fire extinguishing media such as condensed aerosol fire suppression
- ▶ Explosion relief valve to safely direct and vent a high pressure event
- ▶ The shredder components (and other parts of the process where a flammable atmosphere is likely to be generated) should be rated to ATEX (equipment for explosive atmosphere) standards

The drying process is normally carried out in batch and drying times can be in the order of hours. This can create a mismatch in throughput between the shredder which is operating continuously or semi-continuously and the dryer which is operating in batch mode. In such cases, more than one dryer is required but some recyclers may store the shredded material in a pile in a bay whilst it is waiting for space to become available in the dryer. This is a very high risk activity that should be avoided. Whilst in a pile, the shredded material will emit toxic and flammable gases which will be difficult to deal with whilst the risk of fire is severely elevated as the heat build-up at the centre of the pile has no means of escape.

<sup>[6]</sup> Steffen Hess et al 2015 J. Electrochem. Soc. 162 A3084

<sup>[7]</sup> L Wuschke, H-G Jackel, T Leibner, U A Peuker. Crushing of Large Lithium ion Battery Cells. Waste Management 85, (2019), 317-326

Boiling off of the organic solvents in a dryer is a common method of stabilising the shred, allowing further processing to occur without the risk of fire. Some operators do this through the use of a vacuum to reduce the boiling point and create an oxygen-deficient atmosphere. Operators may also be inclined to increase the dryer temperature to reduce the processing time but this can generate other hazards such as;

- ▶ Self-sustaining fire - the cathode material contains 33% oxygen by mass, this oxygen becomes available for the propagation of fire once the temperature is high enough. There is enough flammable material within the dryer (such as graphite, organic solvents, and plastics) to create such a fire
- ▶ Elevated temperatures (above 200°C) can lead to the evolution of oxygen from the cathode material
- ▶ Smouldering fire - in some cases the fire may not be visible but may be a smouldering fire inside the pile of shredded batteries. In such cases, highly flammable and toxic gases will be generated. It would be a good practice to have various gas detectors (such as CO, CH<sub>4</sub>, HF) and temperature monitoring within the dryer so that it can be monitored

Some processes condense the boiled off vapours to form liquids that they could potentially sell to a customer. The condensed liquids can and do readily vaporise, generating a flammable vapour and potentially an explosive environment if stored in a confined space. One can easily envisage a scenario where an explosive atmosphere is generated in the headspace of a storage vessel, waiting for a spark to set it off. A good practice is to purge the storage tanks with nitrogen before filling them with flammable material. Operators should ensure storage vessels are certified for such chemicals and it is a good idea to store them under pressure, preferably under a nitrogen blanket to inhibit vaporisation of the material.

Not all the organic solvents can be boiled off the battery shred unless high temperatures are used (>250°C). Such temperatures can create hot spots which far exceed the temperature of the bulk material and initiate pyrolysis reactions which produce flammable and toxic gases such as H<sub>2</sub>, CH<sub>4</sub>, CO and a variety of fluoro-hydrocarbons. Most recyclers will use lower temperatures to obtain a recoverable organic solvent product which they may be able to sell to a customer. Unfortunately, this means not all of the organic solvents will be evaporated off and some will remain on the battery shred. These remaining organic solvents increase the flammability of the shred, requiring extra measures to be taken when processing and storing the material.

Some operators may wash the black mass to remove unwanted impurities. Washing of the black mass achieves the following;

- ▶ Enables the elemental lithium present in the black mass to react with water, generating lithium hydroxide (LiOH)
- ▶ Wets or dampens the black mass, inhibiting the formation of dust
- ▶ Hydrolyses the LiPF<sub>6</sub> into hydrofluoric acid (HF) and other fluoro-phosphate compounds which can be washed out (contained and neutralised)
- ▶ The LiOH can react with the HF to generate LiF which is not nearly as hazardous as HF

Recycler should ensure sufficient volumes of water is used to completely wash away the LiOH, LiF and fluoro-phosphates. The water can then be treated to remove the impurities.

## 8.2 Hydrogen evolution from wet processing

Some operators process their material using wet separation technology. Wet separation has the potential to reduce the fire hazards associated with dry processing. It also allows for the neutralisation of the LiPF<sub>6</sub> provided that a suitable reagent is used alongside the water. Wetting the battery shred can confer many advantages such as inhibiting dust formation, quick neutralisation of the LiPF<sub>6</sub>, reduction of the fire hazards associated with the organic electrolyte solvents and easier containment in cases of emergency. However, several disadvantages must also be considered;

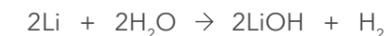
- ▶ Lower recycling efficiencies - wet processing destroys and contaminates the electrolyte, making it unsuitable for recovery
- ▶ More expensive plant
- ▶ Need for a suitable reagent alongside the water - failure to use the correct reagent can lead to severe corrosion (from the production of fluoride ions) and potential health and safety implications
- ▶ Some reagents can react with the metallic foils, generating hydrogen gas which is flammable and explosive

Wet processors must be aware of fire risks from other sources. Perhaps the biggest fire hazards come from the aluminium and lithium which are present in the shred or black mass. Aluminium is known to react with water and especially alkali hydroxides, producing heat and hydrogen. Below are some scenarios where a fire could easily start;

- ▶ Aluminium foil impurities within the black mass pile (which can be up to 2% by mass) react with the water, generating heat and hydrogen. Normally the reaction would be relatively slow as the aluminium foil will be protected by an oxide layer. In recycling plants, the aluminium foil will have been damaged by the process machinery, breaking the oxide layer and exposing the aluminium metal to the water.
- ▶ The reaction between the water and aluminium takes moisture away from the black mass, causing it to dry. 1kg of aluminium can react with up to 2kg of water and generating hydrogen.



- ▶ The hydrogen gas produced from the reaction is highly flammable and is self-igniting
- ▶ The aluminium-water reaction generates heat, causing even more drying. It is likely that localised drying occurs i.e. parts of the black mass pile where there is a high concentration of aluminium will be dried out first whereas areas of low aluminium concentration will remain wet
- ▶ Once the black mass reaches a moisture content where the graphite can ignite, the aluminium-water reaction or the evolution of hydrogen can cause a fire
- ▶ Fires have been reported in metal recycling plants where wet aluminium separation processes are used with the aluminium-water reaction being the main culprit
- ▶ Recyclers who dampen the black mass to avoid dust formation will experience elevated fire risk as the elemental lithium within the black mass reacts with water in a highly exothermic reaction, generating heat and hydrogen via the following reaction;



- ▶ The heat from the above reaction is sufficient to ignite the hydrogen
- ▶ The heat from the reaction may also be sufficient to destabilise the cathode material leading to the evolution of oxygen gas, which when combined with the hydrogen creates a very high risk of fire
- ▶ The LiOH generated from the lithium-water reaction can also react with the aluminium in another highly exothermic reaction, generating heat and hydrogen via the following reaction;



- ▶ The heat from the above reaction is sufficient to ignite the hydrogen and perhaps even the graphite or the organic solvents found within the black mass
- ▶ Recyclers who use reagents to neutralise the LiPF<sub>6</sub> must also be aware that any remaining reagents can and will react with the metallic foils (both copper and aluminium depending upon the reagent), generating heat and hydrogen (for example, NaOH with aluminium or NaCl which converts to HCl when it comes into contact with HF and can react with both copper and aluminium, generating heat and hydrogen gas)

Figure 6 Picture of black mass. Courtesy of RS Bruce



## 8.3 Dust Explosions

Black mass can readily become airborne and suspended in the air forming a dust cloud. In recycling plants, this can be a particularly acute problem since many of the machinery used for separation and material conveyance involves highly energetic movements such as granulation and vibration which tends to eject the material into the air. In unconfined areas, the black mass dust can be hazardous if workers are exposed to it as described in Section 6. In confined areas, the black mass dust can generate an explosive atmosphere if there is sufficient mass in the air and a source of ignition is found. On a battery recycling plant, there can be many sources of ignition, including the batteries themselves. In rare cases, the black mass may even cause a cell or a module to short circuit if it drops out of suspension, settles in between the battery terminals, and creates a pathway for the charge to flow. Needless to say, it is always a good idea to compartmentalise the different parts of the process (i.e. separate the discharging area from the shredding area, etc)

Black mass presents an elevated hazard level for dust explosions due to the presence of elemental lithium and organic carbonates. The black mass that is attained will contain some organic carbonates (even if most are boiled off) which are volatile and more flammable than the other components. The elemental lithium can easily react with oxygen or moisture in the air, generating heat and hydrogen (if reacting with moisture) which can set off the organic electrolyte and finally ignite the graphite, leading to a fire or an explosion if in a confined space.

## 8.4 Flammable and Toxic Gases from Pyrolysis

Pyrolysis is a common method used to deactivate cells prior to shredding. However, it is more suitable for smaller cells from portable applications rather than EV batteries which contain modules that may be too big for the pyrolysis reactor. Therefore, some recyclers may choose to pyrolyse the material post shredding to destroy the electrolyte. Pyrolysis of the battery shred offers some advantages such as making the shred safe for further processing, destroying the PVDF binder, making it easier to screen the black mass out, convert the elemental lithium into lithium carbonate, thereby making it safer than it would otherwise be. However, it also has some disadvantages which need to be considered – for example, it produces flammable and toxic gases which must be scrubbed and combusted. It also generates a very dry product that can easily become airborne. Control of temperature within the pyrolysis reactor is critical as the aluminium has a relatively low melting point of 660°C, which can easily be exceeded, especially in localised hotspots where combustion can occur from the inherent oxygen content of the cathode material. If the aluminium melts, it can clog up the pyrolysis reactor. High temperatures also increase corrosion, particularly since a significant amount of fluorides and phosphates are present within the feed material. Escape of toxic gases is difficult to control and recyclers must have significant safety features in place to ensure safe operation.

## 9. Summary

**Lithium ion battery recycling is a dangerous activity, which if not carried out in a highly controlled manner, can lead to serious injury or long term health issues.**

This document presented some of the hazards and risks associated with battery recycling. They can range from minor injuries such as cuts to more serious ones such as the inhalation and exposure to cancerous and or toxic chemicals. There are also a number of fire and explosion hazards that can arise on a battery recycling plant but these can be mitigated through intelligent design and safe working practices.

The onus is on the operator to design and install a recycling system capable of safely recycling lithium ion batteries and providing a safe work environment for its employees. Recyclers are encouraged to undertake a HAZOP, a HAZAN and a DSEAR analysis, carried out by skilled professionals within the battery field prior to the installation of a battery recycling plant. Battery chemistry and cell formats are continuously evolving and therefore any safety analysis must keep pace with the potential change in feedstock going into the plant. It is the duty of the operator to keep abreast of technical developments and prepare beforehand, particularly with respect to manufacturing scrap which can change rapidly. Operators are encouraged to actively monitor what is happening in the world and take necessary precautions or respond accordingly should something arise.

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