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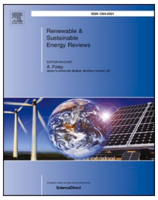

Risk management over the life cycle of lithium-ion batteries in electric vehicles

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ABSTRACT

Lithium-ion Batteries (LIB) are an essential facilitator of the decarbonisation of the transport and energy system, and their high energy densities represent a major technological achievement and resource for humankind. In this research, it has been argued that LIBs have penetrated everyday life faster than our understanding of the risks and challenges associated with them. The current safety standards in the car industry have benefited from over 130 years of evolution and refinement, and Electric Vehicle (EV) and LIB are comparably in their infancy. This paper considers some of the issues of safety over the life cycle of batteries, including: the End of Life disposal of batteries, their potential reuse in a second-life application (e.g. in Battery Energy Storage Systems), recycling and unscheduled End of Life (i.e. accidents). The failure mechanism and reports from a range of global case studies, scenarios and incidents are described to infer potential safety issues and highlight lessons that can be learned. Therefore, the safety risks of LIBs were categorised, and the regularity requirements to create and inform a wider debate on the general safety of LIBs were discussed. From the analysis, a range of gaps in current approaches have been identified and the risk management systems was discussed. Ultimately, it is concluded that robust educational and legal processes are needed to understand and manage the risks for first responders and the public at large to ensure a safe and beneficial transition to low carbon transportation and energy system.

1. Introduction

Lithium-ion batteries (LIBs) have penetrated deeply into society, finding a wide range of applications in personal electronic devices since their discovery and development in the 1980s and 90s, and more recently in larger energy systems for traction and energy storage. This is mainly owing to the unique characteristics of LIB technology, i.e. high energy densities, high voltage, good stability, low self-discharge rate, long-life cycle and availability of a wide range of chemistries with diverse electrode designs [1,2]. LIBs are incorporated into ever widening application areas and are to be found at scales as diverse as their usages. This is evidenced by the growth in the uptake of LIBs having increased eight fold between 2010 and 2018 to 160 GWh [3] and the steady increase in annual sales of LIBs which are predicted to be upwards of 4 TWh by 2040 [4]. In the UK, it is forecast that the number of LIBs reaching the end of their life from automotive applications would have reached approximately 75,000 units, or 28,000 t by 2025 [5]. The advent of lithium-ion technology and the paradigm shift in the energy and power density capabilities that it represents, are perceived as the enabling technology for an extremely broad range of energy storage applications. Accordingly, LIBs are increasingly recognised as essential and integral to enable the large-scale temporary storage of electrical energy from renewable energy sources.

The switch from fossil fuel to battery-powered vehicles is also generally perceived as an essential part of the global decarbonisation strategy [6–9]. Although there is no comprehensive study that quantifies the total carbon emissions by the entire LIB industry, it has been reported that the electric vehicle (EV) production phase (as opposed to its whole life cycle) is more carbon intensive than its fossil counterpart

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Nomenclature

Aging	The loss of capacity due to, e.g. loss of lithium ions or spallation of the anodes. This can be due to use (charging and discharging) and/or sitting at open circuit (calendar aging)
Anode	The positive electrode. In lithium-ion batteries this is most typically small particles of graphite.
Battery (pack)	The complete energy storage unit consisting of a number of modules
Capacity	The amount of charge stored in a battery or cell, usually specified in Amp hours (A h). 1 A h = 3600 Coulombs (C)
Cathode	The negative electrode. These typically comprise lithium transition metal oxides: *e.g.* lithium nickel manganese cobalt oxide ($LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$)
Cell	The smallest unit of a battery
Electrolyte	In electrochemistry, this term can refer either to the inorganic salt (*e.g.* $LiPF_6$) or to the salt + organic solvent
End of Life (EoL)	The point at which a battery ceases to be suitable for its current application. For automotive batteries this is typically 75–80% State-of-Health
Energy	The energy stored in a battery is specified in Watt hours (W h) or kiloWatt hours (kW h): 1 W h = 1 Amp Volt x 3600 s = 3600 AVs = 3600 Joules
Energy density	The energy per unit volume (litre) of battery
Galvanic cell	Usually just referred to as a cell. A device which when charged with electricity is in a higher energy state than when discharged. On discharge the chemical energy stored is released as an electrical current
LCO cathode	Lithium Cobalt Oxide, $LiCoO_2$
LFP cathode	Lithium iron (Ferrous) Phosphate, $LiFePO_4$
LMO cathode	Lithium Manganese Oxide e.g. $LiMn_2O_4$
Module	Manufacturer-specific term, e.g. collection of cells arranged in series and/or parallel
NCA cathode	(lithium) Nickel Cobalt Aluminium oxide, *e.g.* $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$
NMC cathode	(lithium) Nickel Manganese Cobalt oxide, *e.g.* $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ (NMC 111), $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (NMC 622)
Open circuit	The state when a battery or cell is disconnected from an external circuit
Open Circuit Voltage (OCV)	The potential difference (voltage) across the terminals of a cell or battery when no current is allowed to flow. This can be correlated with the State of Charge (SoC)
Salt	The inorganic compound employed to produce ions in the cell. This is typically lithium hexafluorophosphate ($LiPF_6$) which dissociates in the organic solvent to produce lithium cations (positively charged ions, Li^+) and hexafluorophosphate anions (negatively charged ions, PF_6^-)
Separator	A plastic film permeable to lithium and hexafluorophosphate ions that prevents the anode and cathode from touching and causing a short-circuit
Solid Electrolyte Interface (SEI)	The protective layer that forms on the anode during the first charge from reduction of the $LiPF_6$ and solvent which prevents further, explosive degradation of the electrolyte and thermal runaway
Solvent	Mixture of organic carbonates, containing ethylene carbonate, as this is essential for the formation of the SEI. Ethylene carbonate is a solid at room temperature and other carbonates are essential to reduce viscosity
Specific energy	The energy per kg of battery
State of Charge (SoC)	The amount of charge stored compared to that equivalent to full charge, expressed as %
State of Health (SoH)	The amount of charge stored currently when fully charged compared to that stored (when fully charged) at the beginning of the cell or battery life, expressed as %

[10]. More specifically, the impact of battery production significantly depends on where the battery materials are sourced, the place of battery manufacturing [11] (and the carbon intensity of the regional energy network used in manufacturing), the chemistry and capacity of the battery pack as well as structural materials used in modules and packs [12]. In the future, enhanced data on the carbon intensity of battery production should become available, as the EU are mandating publication of Life Cycle Assessment (LCA) data on new products [13]. The high level .in carbon intensity of EV battery manufacturing could be substantially reduced through the wider transition to low-carbon electricity. Moreover, the electricity used for charging batteries of electric vehicles has a significant role in reducing the GHG emissions of EVs and could significantly reduce such emissions during the life cycle of EVs if renewable sources are used for electricity generation [10].

The development of the battery systems required to achieve a lower carbon future within an acceptable techno-economic framework will almost certainly entail a major diversification in the cell chemistry, form factors and scale, the like of which has been hitherto unknown in the battery industry. Other battery challenges that face the industry are issues surrounding thermal management, aging and degradation, risk to asset and personal safety through unintentional accidents, ethical material, and supply chain management, and ultimately the control of and methods for battery recycling and disposal. Standardisation and regulation [14] can provide incentives and potential solutions to some of these issues, and there are efforts in this direction proceeding to the benefit of the industry [15,16], but there is little doubt that in the near term attempts at standardisation will be neither universal nor wholly able to achieve consensus. Whilst this remains true at present, the high costs of R&D associated with EV development, is driving the formation of many auto industry partnerships, even between traditional direct competitors, out of necessity. Although there is no consensus that diversity will not remain a common theme, in time, this trend may lead to a decrease in the technical variety in the marketplace.

With this increased use of LIBs, comes a delayed problem that can be anticipated: the growth in the number of LIBs that require End of Life (EoL) treatment and handling [17]. The different purposes that LIBs are used for are not exclusive; having been used in one application, there is potential for LIBs to be put to service in a second use, other than that which they were originally intended for. There have been many examples of second-use LIBs being used in stationary Battery Energy Storage Systems (BESS), for example in the Johan Cruijff Arena in Amsterdam [18].

2. Why focusing on LIB risk management and safety issues?

The potential benefits of broad uptake of battery systems across a wide range of applications is very well documented in both the academic and general literature, and as such there is an understandable, and quite correct, general enthusiasm for the technology as a sector. Indeed, maintaining a positive, public narrative around the benefits of a technology migration has been a proven necessity for garnering support for positive change in numerous sectors. As is demonstrated in this paper, whilst the vast majority of LIBs' life cycles are incident free, there is potential at a number of stages of a battery's life for reputationally damaging incidents to occur. It is therefore essential that participants in the whole lifecycle of the battery industry are well informed on battery risk management and safety issues so that all the positive gains that battery technology presents can be utilised. There is a perceived knowledge gap on LIB incidents as well as safety aspects and a significant and urgent need to educate all stakeholders, including the general public, first responders e.g. fire services and governmental organisations. In this study, and based on the cases presented, the safety risks for LIBs are categorised, regulatory requirements are discussed and information to create and feed into a wider debate on the End of Life risk management of EV LIB is provided. The authors believe that such a discussion is needed for this transformative technology to continue to enjoy public and governmental support and to feed into deliberations of the much-needed decarbonisation of the transport and energy sector. In this paper, the safety implications of the use of LIBs in EVs are collated and described. More specifically, among the different life cycle stages of LIBs (used in EVs), the focus of this review is on the EoL of LIBs, including repurposing (i.e. second life application in Battery Energy Storage Systems (BESS)) and recycling of LIBs (Fig. 1) among the process stages.

Several incidents are reported highlighting safety lessons that can be learned from them. In many cases, these incidents were caused by new LIBs and given the sometimes-unknown provenance of second-use batteries, there are additional risks and safety concerns. Whether first or second life, eventually LIBs must be disposed of correctly [19]. At the moment, the numbers of batteries making their way to final disposal is relatively low, but much higher volumes as the market for electric vehicles grows is expected [5,9]. As the volume of LIBs requiring EoL treatment increases, inevitably the probability of unsafe events occurring will increase [20]. Therefore, several incidents (attributed to LIBs) that have occurred in waste management facilities are discussed. The majority of these involve small LIBs [21], however, from them, there are lessons that can be inferred about the hazards and risks associated with larger LIBs at the end of their life. Chapter two of this paper contextualises the battery safety question and describes the scope of applications from which the points raised are drawn; in Chapter three the theoretical mechanisms of failures are considered from which the hazards and potential harm are outlined in Chapter four. Chapter five provides examples of where these failures have led to incidents and in Chapter six, a set of suggestions and guidelines are proposed. It is hoped that these insights will serve as a valuable tool for the battery industry to continue to maintain and improve its hitherto excellent safety record.

2. Contextualising the relative levels of risk of electric vehicle LIBs

For a balanced consideration of any safety concerns around LIBs, it is imperative that these hazards be situated against a broader landscape of the dangers that arise from pursuing our present fossil fuel trajectory. A temperature rise an average of 2 °C higher than pre-industrial levels will

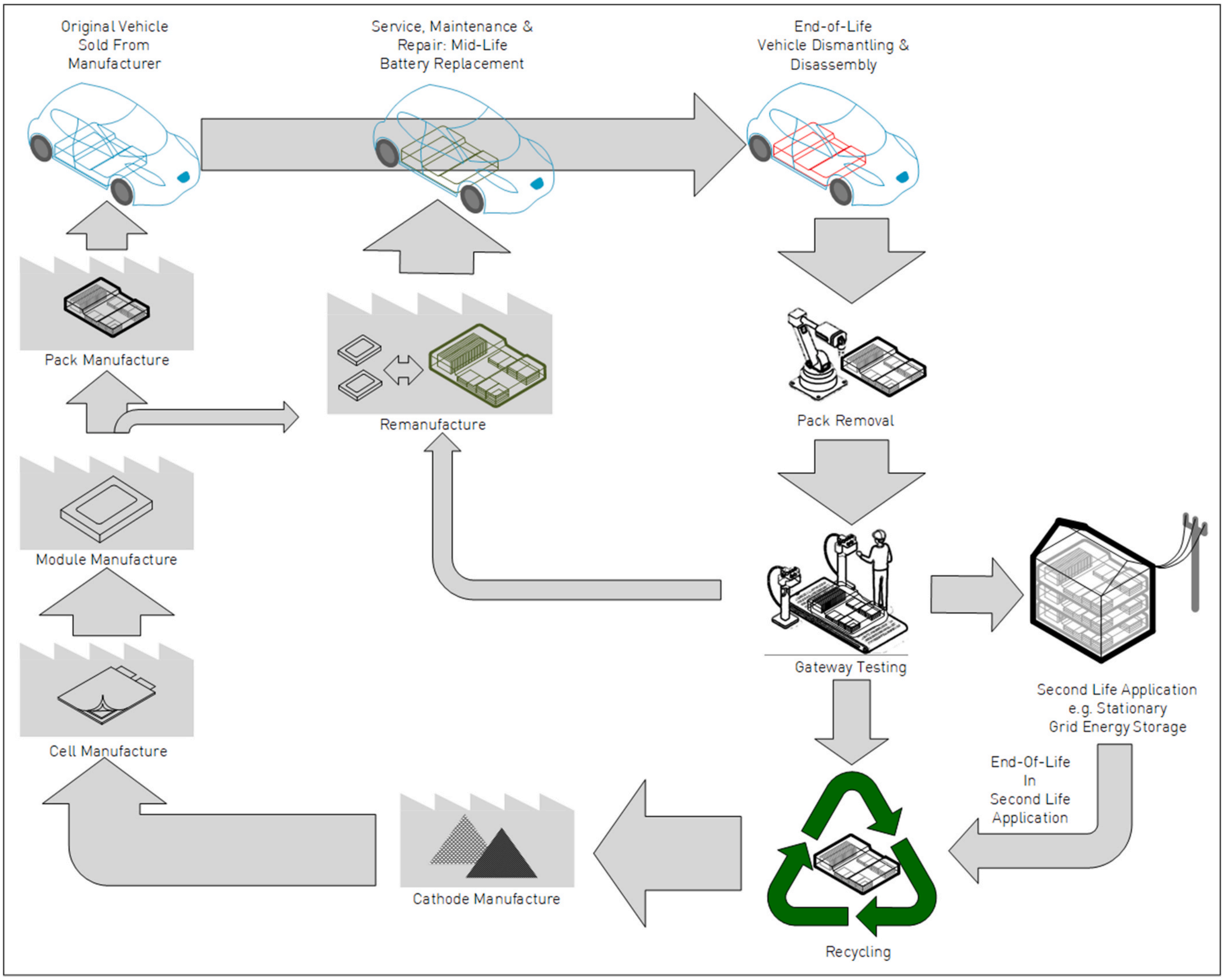


Fig. 1. Life cycle process stages of LIBs used in EVs.

result in the death of an additional 132,000 Europeans a year by the century's end as a direct result of heat-related mortality [22]. Additionally, the average temperature rise will result in a range of knock on effects, including [22]: the rise of pathogens and in turn, antibiotic resistance; growth in certain parasites; water- and food-borne diseases as well as decreased agricultural output and worker productivity through factors such as impaired sleep. Reduction of CO_2 levels therefore, has the potential to save millions of lives in Europe alone [22]. Local air pollution, mostly resulting from the burning of fossil fuels, also results in around half-a-million deaths annually just in Europe [22,23]. The development of ultra-low carbon automobility, and the use of energy storage devices in the electrification and decarbonisation of energy systems is imperative to avoid both local air pollution impacts and the global impacts arising from anthropogenic climate change. A large group of measures, including removing the most polluting diesel vehicles from the road could reduce our global warming trajectory by 0.5 °C, saving 2.5 million lives a year by 2050 [24]. Whilst the authors evaluate the risks associated with LIBs in this article, a balanced consideration of relative risks needs to contextualise these risks against a counterfactual future where LIB technology was not available.

2.1. Risks, safety and the car industry

The very high levels of safety that society enjoys using internal combustion engine vehicles is the result of learning and refinement over many decades. Today, few people would countenance driving a car without such basic amenities as seatbelts, anti-lock brakes and airbags. Yet it is not so long ago that these were either not available or considered luxury or optional items. A turning point for safety in the automotive industry, was the publication of the book "Unsafe at any speed" by Ralph Nader in 1965 [25]. In the USA, this landmark publication led to the development of the National Highway Traffic Safety Administration, greatly increased consumer awareness around the dangers of vehicles, and a clamour for improved safety. It catalysed a widespread change in the way that risk, danger, and safety was managed and marked a turning point for automakers. Traditional internal combustion engine (ICE) vehicles have enjoyed over a century of refinement to their safety systems, however, as a challenger technology, EVs have not been through this same learning curve. Given appropriate focus, resources and investment, this learning curve can be accelerated through proactive research rather than reacting to situations that arise and learning through experience. The perception by the public of EVs is shaped by experience, emotion, the media and other non-technical sources, with both the conventional media and social media providing a gateway for information [26]. Ultimately media stories on incidences or potential risks around EVs may prove more salacious than those extolling the environmental virtues of the technology. It is for this reason that the management of LIB safety is a critical area of focus to retain public confidence in one of the key technologies for a decarbonised future.

2.2. Battery energy storage systems (BESS) – A destination for second life LIBs

Energy is one of the key components of strategies for future urban design [27–29], which encompass electricity, gas and thermal grids in combination [30,31]. As an example, the benefit of such smart and flexible energy systems to the UK could amount to up to £40bn by 2050 [32]. Lithium-ion battery energy storage systems (LIB-ESS) are perceived as an essential component of smart energy systems and provide a range of grid services. Typical EV battery packs have a useful life equivalent to 200,000 to 250,000 km [33] although there is some concern that rapid charging (e.g. at $>$ 50 kW) can reduce this [34]. When an EV pack reaches 75–80% State of Health (SOH) and hence the end of (first) life, it remains a valuable commodity due to its remaining storage potential. Stationary applications such as grid support and support for renewable electricity generation demand lower power and energy densities than EVs and hence the repurposing of such packs is, in principle, economically and environmentally viable [18]. Supplies to buildings can be constrained because of weak local distribution grids.

Modelling of battery systems integrated with solar photovoltaics in domestic settings has shown that peak power demand can be reduced by anything from 8-32% [35], moreover, as well as reducing demand from the grid at peak times, such systems can also help ameliorate the equally challenging problem for grids of excess "power injection" at peak times. Depending on the mode of operation, Fares & Webber [35] have also shown that 'peak injection' can also be reduced by 5–42%. One application where grid reinforcement may be particularly important, is in the roll out of EVs. These have a significant requirement for power, particularly in the case of 'fast charging'. A building may already be close to the capacity of its connection thus the addition of high-rate vehicle chargers is not possible. One way to manage this challenge is through diversity (i.e. through demand management of the load), however, in other instances, a connection upgrade might be considered the most sensible option. This conventional approach can be expensive and disruptive and in a privatised market, it is the consumer who must finance the upgrade. The additional cost and disruption is particularly an issue in rural areas or locations with "weak" distribution grids.

An alternative approach would involve using domestic energy storage systems to provide additional capacity. A battery can provide "peak shaving"- storing electricity from the grid at times of low demand, and then providing additional output to supplement the grid supply at times of high demand. Since stationary BESS are potentially less demanding than transportation applications in terms of energy and power density requirements, used or 'second life' LIBs have been proposed for stationary energy storage applications.

Whilst the functionality of the domestic stationary storage system and the larger commercial installations described in Chapter one is, barring scale, essentially identical the context of these when viewed from safety perspective is very different. An LIB located in an isolated industrial unit far away from high population density with skilled operatives, presents a different risk profile to an LIB located in a domestic house, or perhaps block of flats with surrounded by unskilled ordinary users. As such understanding of not only functionality but also of the diversity of usage cases is necessary for all battery industry stakeholders.

Repurposed LIBs are already finding their way into second-life applications. One specific example is their use in the E-STOR chargers for EVs which employ repurposed Renault automotive batteries. E-Volt has installed a number of these systems in Dundee, UK and other companies have installed these systems in Belgium and Germany [36]. The Sacramento Metropolitan Utilities District in Sacramento (SMUD), USA, has recently installed two charging points utilizing used battery packs from Nissan Leafs integrated with 30 kV PV [37]. The Johan Cruijff Arena in Amsterdam is a showcase for the application of repurposed EV batteries [18]. The stadium houses a stationary LIB-ESS consisting of 340 new and 250 repurposed 24 kWh battery packs connected to 4200 rooftop photovoltaic modules and the electricity grid.

2.3. Performance considerations of second-life batteries

There is some scepticism over the use of repurposed batteries [38] on the basis that the degradation of such batteries due to calendar (time) and operational aging is not linear, with degradation generally accelerating towards the end of second life [39]. It was shown that the rate at which cells age can accelerate, presumably due to a change in ageing mechanism or initiation of an additional mechanism: the point at which this occurs is referred to as the "knee" [40]. This acceleration can occur in first life, depending upon usage, or in second life and hence the assumption that cells reaching 75–80% SOH are suitable for 2nd life applications is not necessarily valid, i.e. if the knee was passed during first life. Further, it was reported that mixing cells with different SOH can lead to significantly increased ageing [40]. Clearly a full understanding of SOH and the operational history of the cells to be employed in 2nd life applications is essential. Subsequently, there are concerns over the reliability and predictability demanded by grid support applications. These are exacerbated by the fact that few standards focus on the BMS or disclosure of the SOH and, more worryingly, there is still an absence of required installation or performance standards specific to repurposed LIBs or guarantees of lifetime. Repurposing of LIBs will be more economic at the module and pack level, rather than complete disassembly to cells. Modules will need to be sorted, as a minimum, based on similar state-of-health (SOH) and lifetime, then re-assembled into repurposed packs [18]. However, the operational history (aging) of the pack may have a significant impact on future life of lithium-ion cells, modules, and packs yet units with very different histories could, at end of first life, show the same SOH. Uneven temperature distribution in battery packs can lead to varying capacity loss and hence SOH across cells and modules of a pack [41]. Batteries may thus contain cells with a variety of SOH, details of which may or may not be available to re-manufacturers. Performance of cells may also be unpredictable owing to two main issues: firstly, the loss of active material through spallation and/or incorporation of lithium ions into the solid-electrolyte-interface (SEI) [42]. Secondly, the potential for gas evolution and lithium metal plating during routine operation [43–45]. Ultimately, the market is too new to have enough data in significant and useful quantities to understand properly to what degree second life batteries will become part of the makeup of the global battery system population. However, as this Chapter demonstrates, there are enough examples of the rollout and enthusiasm for second life as a concept to make it a model that battery safety stakeholders must take note of.

2.4. The effect of an unregulated market for used EV batteries

Whilst there is no consensus yet on the ultimate trajectory of second life applications, the market in second batteries certainly exists and is buoyant. The general population has a growing and largely uncontrolled ability to access ever more energetic LIB systems. For example, at the time of writing, 20 - 30Ah LIB pouch cells were available for sale from a few online stores for £20 - £28 per pouch cell. There are several automotive battery packs also on sale (variously described as 75–95 kWh, for up to £17,000), some without a BMS – a critical part of the pack safety system. Clearly, older EVs can be (and likely are being) worked on in unaffiliated garages or by non-expert owners leading to the potential for an entirely new type of hazard on the highway. The availability of individual modules and cells creates the potential for the proliferation of wholly unregulated domestic battery storage systems (so called “DIY battery packs”) which, without proper appreciation of the complexity of the required protections systems or the hazards of abused batteries equally poses a novel threat to personal and municipal safety. There is, therefore, a pressing need to include regulation (and enforcement thereof) for batteries at EoL to ensure that they are constrained within a proper reuse and recycling waste stream, and the proposed new EU Batteries Regulation could lead the world in this respect [46].

3. Potential failure mechanisms of LIBs

LIBs have by far the highest energy densities of all battery types, not least because of the high cell voltages (currently exceeding 4 V [47]) and lightweight construction. LIBs have mass energy densities up to *ca.* 1 MJ kg^{-1} [48], contain flammable plastics and solvents, and have frequently been the cause of fires [49,50]. Destructive failure of LIBs could happen during manufacturing, use or at EoL (including reuse and recycling). If the energy stored in a LIB is released rapidly, resistive, and chemical heating can result in thermal runaway to fire and explosion. The temperature of a LIB is determined by the rate at which heat can be dissipated compared to the rate at which it is generated. Such heat is generated under normal circumstances by the electrochemical operation of the battery and by resistive (or Joule) heating [41,51]:

$$q = I(U_{OCP} - V) + IT\mathrm{d}U_{OCP}/\mathrm{d}T = I^2R + IT\mathrm{d}U_{OCP}/\mathrm{d}T \qquad (1)$$

where q is the heat generation rate (W), T is the temperature (K), I is the current (A), U_{OCP} is the open-circuit voltage before current is drawn (V), V is the terminal voltage during discharge (V) and R is the resistance of the cell (Ω) due to all components between and including the terminals. I^2R is the resistive or Joule heat generated by all sources of irreversible heat and is exothermic (*i.e.* heat is generated) for both charging and discharging the cell. $IT\mathrm{d}U_{OCP}/\mathrm{d}T$ is the entropic or reversible heat generated due to the normal electrochemical operation of the cell. On charging, lithium ions move out of confinement in the cathode, where they are highly ordered, into the electrolyte in a state of (high disorder as Lithium ions are free to move in any direction) and then into the anode returning to a highly ordered state. It is, therefore, not clear whether this term is exothermic or endothermic on charge and discharge and q is thus generally dominated by the Joule term. Clearly, the Joule term increases rapidly with increasing charge and discharge current, as will the generation of heat. LIBs are stable under normal operation and are only forced into thermal runaway following some form of abuse. Possible forms of abuse are generally accepted to be [49,50,52,53]:

- Thermal: poor ventilation, poor design, high ambient temperatures, heat from cells in thermal runaway.
- Mechanical: mechanical deformation (impact from dropping or dropped objects, high G-loading, EV road traffic accidents, crushing in materials recovery facilities), penetration by metal objects (penetration of highway debris into the battery pack).
- Electronic: BMS failure and hence overcharge and over discharge, rapid charging.

In addition, there have been a number of incidents where EVs have apparently spontaneously ignited, the causes of which remain unclear: however, BMS failure, defects in design and/or manufacture (e.g. battery pack seals failing in wet weather [49] or the introduction of contaminant during manufacture [49,52]) are commonly postulated. Over-discharge can also result in catastrophic internal short circuit, as well as SEI failure and the generation of gas [54]. The most reported failures concern the forms of abuse listed above, and the events arising from these and resulting in thermal runaway are summarised below.

Both mechanical deformation and metal penetration cause essentially the same event that triggers thermal runaway: in that one or more anode and cathode pairs are forced into direct electronic contact or indirect contact via a metal object, resulting in significant internal short circuit and hence Joule heating [52,55]. Even very isolated local heating to temperatures > ca. 70 °C, results in SEI layer decomposition [52,55] which ultimately leads to the reaction running away. The reduction of the organic carbonates by the lithiated anode produces hydrogen [56], CO and various small-chain alkenes and alkanes in an exothermic process [57]. The SEI is able to self-heal up to ca. 120 °C [52,58] but it does so forming a less compact, and hence less protective, layer. As gases build-up, heat is produced [59,60] eventually leading to the failure of the separator. The temperature at which this occurs depends upon the composition of the separator and hence its melting point. Although these vary– polyethylene melts at 130 °C, polypropylene at 170 °C and ceramic-coated polymer/mixed polymer materials at ca. 200 °C [52,56]– it is highly likely that at least locally these temperatures will be attained and separators will fail. Once the separator fails, internal short circuits can occur leading to further heating. When the heat produced is sufficient, total failure of the SEI occurs with the attendant heat and gas production as previously described. Ultimately, the cathode structure collapses generating yet further heat and oxygen from the oxidation of the solvent. The temperature at which this occurs depends strongly upon the chemical composition of the cathode: the stability decreases as LFP > LMO > NCM(111) > NCA > LCO [52], which is why LFP cells are generally regarded as the safest. By this time, the various chemical and physical safety systems within the cells designed to break the internal ionic or external electronic circuits are redundant: chemical processes now dominate the production of heat and gases. When the exponential rate of heat production exceeds the linear rate of heat dissipation, the cell crosses the threshold into thermal runaway.

Overcharging results in the formation of lithium metal at the anode [53,61] and the complete delithiation of the cathode [52,56,62] resulting in structural collapse and the formation of highly reactive species that oxidise the solvent to produce oxygen [52]. In addition, the cell resistance increases, causing increased Joule heating. High charging rates and operation at $\leq 5\ ^{\circ}\mathrm{C}$ also causes lithium metal plating on the anode [53]. The metallic lithium reduces the solvent, with the associated evolution of gases and production of heat, and can be deposited and grow as dendrites which may grow sufficiently to penetrate the separator and cause an internal short circuit [53,63,64]. When the temperature exceeds 180 °C, the melting point of lithium [65], internal short circuits will occur, the consequences of which are discussed above. It has been reported [66] that lithium metal plating takes place at high temperatures, hence cells adjacent to those in thermal runaway may be heated to such an extent that they became unstable due to lithium metal plating.

Whilst the above summarises the current consensus on the model for thermal runaway there is currently no widely-accepted quantitative definition of thermal runaway [67,68]. Thus, He et al. [69] have suggested that thermal runaway should more specifically be defined as the self-sustaining heating process entered once the cell passes the point at which the thermally dissipative modes can no longer support the increase in heating. In addition, recent work has challenged other aspects of the general model showing that the oxygen produced during the collapse of the cathode structure can cross to the anode and react directly in a highly exothermic reaction ("chemical crosstalk"), producing ca. seven times more heat than the initial cathode collapse [70]. Moreover, the temperature at which this process takes place can be significantly lower than the melting point of the more stable separators: hence separator failure and subsequent internal short circuit are not necessary to initiate thermal runaway. Finally, the highly specific hazard represented by the vented gases, which form a white vapour cloud, has not been generally recognised, despite having been responsible for at least one vapour cloud explosion as is discussed in Chapter 5.

4. Origins and categorisation of risks associated with LIBs

There are three significant categories of local risk associated with the EoL processing of LIBs: electrocution, exposure to cell contents and fire [71]. The lowest unit of an EV battery packs is the galvanic cell: several cells are connected to form a string or module, and a pack consists of a collection of modules or strings. Taken as a whole, when a pack is first removed (or damaged), there are high voltages present that present a risk to life. It is only when the interconnects between modules and cells are removed, that the voltages of each module approach a level where they do not present a risk to human life. An inherent danger when removing busbars and interconnects, that a misplaced metallic component could cause a short circuit. This is in itself potentially very dangerous and also presents a fire risk.

There also broader risks such as those to business interests from reputational to financial losses (Fig. 2). For example, the fire in Shoreway cost the owners between six and eight million USD in restoration cost and lost business [72]. The South Korea and Surprise BESS fires have had an impact on customer confidence; not only has LG Chem suffered in terms of the growth of the company, but other BESS suppliers have suffered collateral damage [73]. These incidents have raised governmental concerns which may reduce the rate of uptake of BESS systems in the USA [74]. The fire at the Redux LIB site in Offenbach (Germany) caused major disruption to its business. In the Sections below some specific risks to health, environment and fire hazards are described in some more detail.

Fig. 2. General risk categories.

4.1. *Risks to health - exposure to cell contents*

LIBs' chemical composition includes reactive salts, volatile organic electrolytes and other additives; thus during the degradation process in LIBs, there are various hazardous and corrosive compounds formed that may increase air pollution or be carried by dust should the battery be mechanically breached [75–81]. In LIBs, the typical combination is $\mathrm{LiPF_6}$ in ethylene carbonate that can easily decompose to $\mathrm{PF_5}$ at temperatures below 200 °C and thereafter to $\mathrm{POF_3}$ [82]. While exposed to humid air (i.e. most natural atmospheres), $\mathrm{POF_3}$ hydrolyses to produce hydrofluoric acid (HF), which may result in harmful levels of the gas [83].

Accidental damage of LIBs could lead to toxic and flammable gas exposure. It is generally accepted that gas evolution or so-called 'gassing', takes place during routine operation of LIBs producing solids, liquids and gases [84]. There is insufficient analytical data in the public domain to make definitive statements of gassing products, but alkanes, alkenes, $\mathrm{CO_2}$, CO and HF have all been detected [56,85–88]. Gassing also takes place during initial charging of a battery, before and during the SEI formation, as the solvent and $\mathrm{LiPF_6}$ are in direct contact with the graphite anode [47,89,90].

An additional factor is the formation of hazardous and corrosive species during LIBs' operation [76,80,81,84,91–94] that are harmful to both humans and the environment. Alkylfluorophosphates have also been detected in "black mass" [95] (a derivative product of shredded LIBs). These included dimethyl fluorophosphate (DMFP) and diethylfluorophosphate (DEFP) which are known chemical warfare agents (CWAs), as well as other alkylfluorophosphates which have similar chemical structures to CWAs [96]. The presence of these species is of significant concern, although the concentrations reported were very low, *ca* $1\ \mathrm{mg\ m^{-3}}$. The leachate from LIBs buried in landfills, which is, in many jurisdictions illegal, could contain a variety of hazardous pollutants: these species could be transported via aquifers to locations away from the site of initial contamination [97–100]. This process poses the potential for toxic pollutants to present themselves at some significant geographic distance from the initial site of contamination.

4.2. Fire risks

As stated above, when LIBs are abused for example by heating, mechanical damage or overcharge, the SEI and polymer separators fail leading to chemical processes and internal short circuit, respectively, that produce heat, hydrogen and a wide variety of other gases [63,86,87,101,102]. If heat is produced faster than it can dissipate, thermal runaway can take place and the gases can vent through rupture or safety devices. The vapour so produced, which also contains vaporised solvent from the electrolyte [88], can ignite given suitable conditions and source of ignition. The vented vapour represents a clear hazard in terms of its toxicity and the possibility of explosion, and the fumes from burning LIBs also represent a toxic hazard. Of particular concern is the presence of HF in the fumes as it is increasingly accepted that HF is produced by burning LIBs [63]. Interestingly, Lecocq et al. [103] report HF is also produced by burning internal combustion engine vehicles, albeit in half the quantity observed from burning EVs. Further, whilst Sturk et al. [85] detected significant quantities of HF from burning pouch cells utilizing both 14 A h nickel manganese cobalt oxide (NMC) and 7 A h lithium iron phosphate (LFP) cathodes, and also found that assemblies of larger cells generated more HF per cell than single cells, they were unable to detect HF from a burning automotive battery pack. More recently, Larsson et al. [60] analysed the fumes from a range of LIB cells and observed significant amounts of HF. As a result, the authors estimated that between 20 and 200 mg of HF could be released per W h of an EV battery pack. For a burning 100 kW h automotive battery in a room with 1000 m^3 space, this equates to a level some 80–800 times the US National Institute for Occupational Safety and Health Immediate Danger to Life or Health (IDLH) level [104]. Based on Larsson et al.'s results, a 32 A h pouch cell burning in a 100 m^3 room would potentially exceed the IDLH level by a factor of 10. The toxicity of the fumes from burning LIBs has also been addressed by other authors including Ribière et al. [105] and Sun et al., [87]. Interestingly LFP cells, often perceived to be the safest, produced the highest levels of HF [60,85]. In general, there is a lack of essential, analytical information in the public domain on toxicity and flammability of LIB components and their combustion products which is exacerbated by the wide variation in the solvents, additives and cathode chemistries employed in commercial LIBs. Adding additional uncertainties to specific incidents, Larsson et al. found that the ratio of the energy produced during burning to the stored electrical energy depended strongly on the battery type [88]. Since both the battery type and current SOC of any battery undergoing thermal failure would be unknown to first responders the worst-case scenario should be assumed.

There are many examples in both media and literature of EV batteries re-igniting hours, days or even weeks after the initial incident [106]. As well as the danger of re-ignition, batteries that appear to have been extinguished may contain trapped toxic gases. In addition, there is the hazard of stranded electrical energy, either retained in the battery or present in cells ejected during explosion, or as a result of *e.g.* damage to an EV through collision, with the attendant risk of electric shock and arc flash [106]. Such stranded electrical energy is a potential hazard in incidents involving large-capacity battery storage LIBs [107].

4.3. Risks to the natural environment

LIBs may have a significant impact on the environment, with the magnitude of harm depending upon the stage of their life, *i.e.* mining of materials, manufacturing, first life, second life and EoL [108]. Mining clearly has a high potential for adverse environmental and human impact [34,109], particularly in developing countries due to, for example, lower regulatory standards [110]. Manufacturing can release harmful volatile organic electrolytes [83] and requires high energy consumption resulting in elevated GHG emissions [111–114]. During first life, the impact is relatively low both for humans and the natural environment: toxic chemicals are contained and hence any contamination could only arise from accidental release or fire. Scale and regulatory frameworks mean that it is very unlikely that industrial batteries such as EV LIBs will be landfilled on a large scale, at least in developed economies [115]. In Europe, the European Commission is committed to a LIB recycling industry that recovers materials of at least 50% of battery weight [116]. However, this industry is still in the development phase and there are only a few full-scale recycling facilities in operation [117–119]. Therefore, it is likely that in the immediate future, LIBs will be temporarily stored in dedicated facilities and/or in some jurisdictions where the regulatory regime permits, may be sent for landfill [120]. There is also the significant risk that LIBs will be disposed of illegally, either before or after the recovery of any materials of value such as copper, aluminium *etc.* [121]. This could happen for EV batteries in jurisdictions where a gate-fee is for authorised disposal, and is a persistent danger with smaller consumer cells, whose tracking and collection are more difficult to regulate. Spent LIBs contain toxic metals, flammable hazardous electrolytes, organic additives, and plastics [122,123]. The metals that may leach from LIBs in landfill are lithium, cobalt, nickel, chromium and copper [122]. There are also the chemical species present as additives [124], the most common of which are polymers, Lewis acids, sulphur-containing and phosphorus-containing additives, polyfluoroalkyl substituted ethylene carbonates and ionic liquids. Ionic liquids in particular have a very broad spectrum of environmental impact, including high persistence in soils [125–127] and low biodegradation properties [128]. There is, therefore, the distinct possibility of the contamination of soil, water and air, and of the harmful effects on human health [129]. In addition, there is the potential for fire in landfill sites for example when and if battery packs, modules or cells degrade or corrode, or during the abuse expected during the routine operation of such sites. Such fires could burn for significant periods, generating toxic fumes and polluting soil, groundwater and surface waters [83,130,131], and the effects could be exacerbated by the presence of other flammable materials and methane generated by biological processes. The extent and nature of such pollution is likely to depend upon the form factors and compositions of the LIBs, the type and location of the landfill and geo-climactic conditions [120,132,133].

Finally, materials recovery from LIBs may also impact the environment and human health [110]. Various studies [134–136] have shown that each of the currently employed recovery processes, *e.g.* hydrometallurgy, pyrometallurgy or direct recycling have an environmental impact. A recent comprehensive and comparative life cycle assessment (LCA) study on recycling of LIBs using pyrometallurgical and hydrometallurgical recycling showed that pyrometallurgical recycling can impose higher environmental risks in various mid-point impact categories such as global warming, carcinogenic and non-carcinogenic effect, ozone layer depletion and photochemical ozone creation, eutrophication etc., while hydrometallurgical recycling can only impose more risk on freshwater and terrestrial acidification [137,138]. The lower benefits of pyrometallurgical recycling are mainly associated with the higher amount of energy input required for the high temperature processing of waste as well as lack of lithium recovery (lithium ends up in the slag and will be landfilled or alternatively used in construction industry [137]). In general, the largest contributors to environmental impacts of pyrometallurgical and hydrometallurgical processes are the electricity consumption (and hence enhanced GHG emissions depending on which energy source is used for the electricity generation), the incineration of plastics (with the attendant formation of toxic gases and further CO_2 production), landfilling of residue (slag) and the use of organic solvents and acids (with the need for post-processing and clean up). All of these issues should be addressed in order to mitigate their impact: *e.g.* toxic gas emissions may be captured or remediated [19]. As mentioned earlier, potential illegal recycling of LIBs could create a serious burden on the environment, especially in developing economies [129,138–140]. Lax or poorly enforced regulations and the use of inadequate technology could have a very negative impact on the health and life quality of vulnerable communities [141–144].

5. End of Life LIB incidents

Given that the electric vehicle industry and second life vehicle industry is in its infancy, the corpus of real-world LIB incidents does not extend to every conceivable failure mechanism or possibility. Therefore, in taking a precautionary approach, the authors have attempted to draw together a body of knowledge relating to LIB incidents in a range of adjacent fields and infer potential challenges over the whole lifecycle of the LIB lifecycle. Summarised incidents are considered in three broad categories of BESS, waste facilities and unscheduled EoL i.e. accidents.

5.1. LIB incidents in BESS

Second life in BESS applications is regarded by many as a key enabler in maximizing the economic and environmental benefits of automotive LIBs. Whilst specific attention to second life applications is discussed in Ref. [145], in this Section, data is considered relating to all BESS, whether first or second life, as the safety issues raised are nearly identical for both, apart from the added complication that definitive data on the initial condition of second life batteries is difficult to obtain. There have been several significant fires and/or explosions involving LIB–ESS, e.g., Arizona Public Service Company, Flagstaff Arizona (USA) tested a new 1.5 MW BESS linked to a solar energy system when it was destroyed by fire. Subsequent investigation concluded that lack of ventilation and inadequate monitoring were the major causes of the incident and recommended improved ventilation, 24/7 monitoring and the ability to send remote alarms [146]. In Drogenbos (Belgium) in November 2017 a fire badly damaged the container of a 1 MW BESS after the fire detection and control system failed to control the blaze [147].

Following the fire in Flagstaff, a report was commissioned from DNV GL [148] by the New York State Energy Research and Development Authority and Consolidated Edison to address any likely issues surrounding the installation of BESS in and on buildings in New York City. The report concluded that the risks of installing BESS can be managed using existing codes and firefighting methods and that the fumes from burning LIBs are no more toxic than those form burning plastics. The report also suggested that the heat release rate from LIBs was lower than that expected from common domestic furniture items and that LIBs explode due to trapped flammable gases being released from cells and igniting. The likelihood of stranded energy was also highlighted. Following a second incident at a Pinnacle Facility, the McMicken LIB-BESS in Surprise, Arizona, four of the firefighters and a police officer were placed under observation due to detectable levels of hydrogen cyanide (HCN) in their protective clothing and the officer's uniform. Two of the firefighters required numerous surgeries to repair broken bones as they were thrown variously between 55 and 73 feet by the force of the explosion and suffered chemical burns. The results of the inspections also showed that HCN, as well as explosive gases, were detected in the container, and high levels of hydrogen are thought to have been present prior to the explosion. No attempt was made at the time to analyse for hydrogen fluoride (HF). The preliminary report on the Surprise incident was released on 6 August 2019 but did not provide any information on the possible causes [149,150], however, three detailed analyses have since been issued. The owners of the McMicken facility commissioned DNV GL to produce a report analysing the causes of the explosion [151]. This generated a counter-report produced by Exponent, commissioned by the suppliers of the lithium-ion cells, LG Chem [152]. A third report was produced by UL Firefighter Safety Research Institute [153].

5.1.1. The incident

The McMicken LIB-ESS consisted of 36 racks, of which 27 contained a vertical stack of 14 modules numbered bottom to top. Each module comprised 14 pairs of 64Ah NMC lithium-ion pouch cells arranged in a 2P14S configuration. The total rated capacity of the installation was 2.0 MWh. The racks were held in two rows in a container-style building dimensionally similar to a standard shipping container with two single access doors on one each of the long and short walls. Of the remaining racks one rack housed the communication system and 8 were being used to store spare components, paper and documents – evidence of poor housekeeping.

At 16:54:30 local time, cell pair 7 in module 2 failed. The specific cell (s) responsible could not be identified from the telemetry data recorded by the Battery Management System (BMS) as individual cell voltages were not recorded. The "minimum cell voltage" showed a drop from 4.061V to 3.818, and subsequent investigation of the rack carcass suggested module 2 and cell pair 7. The temperature of the electronic systems atop racks 15 and 17 started to increase at 16:54:44 from 40 °C to a peak of 49.8 °C over the next 54 s. At 16:55:20 the laser smoke detection system (which would respond to smoke, vapour or fine droplets of solvent) triggered and opened the main facility circuit breakers, 30 s after which, as designed, the system deployed the fire suppression agent, Novac 1230. Detailed timelines may be found in Refs. [151–153].

Of note is:

- The loss of all telemetry from the LIB-ESS at 17:44:08.
- The Hazardous Materials (HAZMAT) team that arrived on the scene (at ca. 18:28) after the first fire department teams noted low-lying white clouds of a gas/vapour mixture issuing from the structure and nearby components and drifting through the desert.
- The door on the side (as opposed to the end) of the container was opened at 20:00:54 and "a visible white gas/vapour mixture immediately poured out of the open door".
- The Emergency Response Plan (ERP) provided to the owners, Arizona Public Services (APS), did not have instructions on how to respond to a potential explosion or how to enter the container after discharge of the fire suppressant.
- The door was opened without an ERP being formulated.
- The Surprise Fire Department were unaware of the existence of the McMicken LIB-ESS. No first responders had been trained in the hazards associated with LIB-ESS.

From [153]: "At the moment of the deflagration event, the firefighters outside the hot zone described hearing a loud noise and seeing a jet of flame that extended at least 75 ft outward and an estimated 20 ft vertically from the southeast-facing door. In the event, E193 Capt and E193 FE were ballistically propelled against and under the chain-link fence that surrounded the ESS. E193 Capt came to rest approximately 73 ft from the opened door beneath a bush that had ignited in the event. E193 FE came to rest approximately 30 ft from the opened door. HM193 FF1 was projected toward the transformer and distribution box to the east of the ESS and remained within the fenced area. The entire HAZMAT team lost consciousness in the deflagration event. The event also dislodged or removed the SCBA face pieces and helmets from all of the HAZMAT team members."

5.1.2. Hazards of explosion

None of the reports dispute the timeline of events and all agree that the modules went into thermal runaway without ignition until the door was opened, and that the thermal runaway produced copious amounts of gas. The smoke alarm employed a laser and was triggered by the decrease in light penetration due to the gas production – which must have been opaque to some extent for that to occur. In fact, the UL report, quoting a fire officer who was first on the scene, draws attention to the production of a heavier-than-air white cloud. The DNV GL report quotes its expert as stating that "the composition of gases is constant across all form factors, chemistries and manufacturers" – an extremely important statement if correct. The evidence from controlled experimentation (Fig. 3), as well as reports in literature, seem to correlate with the above suggesting that under certain conditions dense grey-white smoke is formed upon cell failure.

The contention of the DNV GL report is that the release of the Novac

Fig. 3. The white vapour produced following nail penetration of a single automotive module (Envision-AESC module containing 8 x 53Ah NMC pouch cells) [154].

1230 suppressant prevented ignition of the gases produced by the cells in thermal runaway by displacing air from the container, and so allowed the gases to build up to dangerous levels. The cells were initially all at > 90% SOC but the vapour did not ignite due to the displacement of the air from the container by the suppressant. Hence the very significant implication of the findings of this incident is that if LIBs of any cathode chemistry, form factor or manufacturer are abused at a low SOC and/or the concentration of oxygen is reduced below that necessary for ignition in some way, the toxic white vapour so produced can build up and hence create a condition whereby there is a potential for flash fire, or in extreme cases vapour cloud explosions. This explosion hazard, along with the toxicity of the white vapour, could be faced by first responders wherever large LIBs are present, and one or more cells are in thermal runaway. Thus, as well as EV Road Traffic Collisions (RTCs) and LIB-ESS, the implications apply more generally to fires or incidents in storage warehouses, battery manufacturing plants, electric vehicle assembly plants, road, rail and sea transportation of EVs/battery packs - wherever large volumes of LIB's are present.

5.1.3. *Thermal runaway and the cause of the explosion*

The DNV GL and Exponent reports differ in terms of identifying the cause of the thermal runaway. The DNV GL report identifies the formation of lithium metal dendrites and the penetration of the separator between anode and cathode of cell pair 7 causing a catastrophic internal short circuit. The primary evidence for this model was the presence of lithium-rich deposits on the anodes of randomly selected undamaged cells in the McMicken LIB-ESS and on the anodes of undamaged cells from a sister site, Festival Ranch. The Exponent report disputes this model on the basis that the separators employed were coated with a ceramic layer that would resist penetration by the dendrites. The deposits were also not electronically conducting (and hence could not cause a short circuit) and even if they were, the thickness of the dendrites was insufficient to sustain the expected large current flows for any length of time before burning out. The Exponent report did not dispute the fact that the deposits contained lithium metal in some form as it acknowledged that they were pyrophoric on contact with air, as would be expected of metallic lithium. The alternative model proposed in the Exponent report is that electrical arcing sent cell pair 7 into thermal runaway, citing the facts as evidence that: (1) the position of cell pair 7 was next to arc damage on the rack framework; (2) the cells in rack 15 were being charged at 27A, but this suddenly switched direction to discharging at 4A; (3) there was evidence of water penetration into the container and (4) problems with the electrical insulation of the racks.

Lithium metal plating is associated with operation of LIBs at temperatures ≤ 5 °C, charging at high C-rates or with overcharging [53]. In other words, plating is associated with abuse in some form and is regarded as highly undesirable, yet neither report questions why plating occurred in an installation only ca. 2 years old. At 1 a.m. on 15 September 2020, there was an explosion and fire at the 20 MW LIB-ESS in Carnegie Road on Merseyside, UK. At the time of writing, the Merseyside Fire and Rescue Service are still investigating the cause. As with the McMicken LIB-ESS, the Carnegie Road installation was only ca. 2 years old. Recently, a LIB-ESS exploded at the Nathan campus of Griffith University in Brisbane, Australia [155] which is currently believed to have been due to an "unspecified" short circuit forcing one cell into thermal runaway. This incident is noteworthy as the lithium-ion cells involved employed lithium iron phosphate (LFP) cathodes, which are generally considered to be the to be safer and more stable than counterparts [56].

Between 2017 and 2018, 23 LIB-ESS installations caught fire in South Korea [156]. The details of the fires and their causes remain unclear [157] and the report by DNV GL on the incidents has not been made public. However, the South Korea Ministry of Trade and Industry and the country's Standards Committee stated at a local press briefing that the causes were down to poor battery management through failure of the BMS and/or faulty installation [158]. Recently, an expert panel found that malfunctions in batteries were mainly to blame for the fires [156]. As large BESS are planned and run by non-specialists such as developers and councils, a better understanding of the risks is needed. In the UK, the Department of Business, Energy and Industrial Strategy (BEIS) closed a consultation in December 2019 to give local councils the authority to grant planning permission to BESS irrespective of size [159].

5.2. LIB incidents in waste treatment facilities

The waste management industry is challenged by the growth in LIBs requiring EoL handling. Whilst the automotive LIB waste management industry is in its infancy, it is understandable that there are fewer incidents that have occurred that lessons could be drawn from – although, given the hazards involved, there will be more incidents anticipated as this industry scales. That said, very recently, a major incident occurred at Guangdong Brunp Recycling Technology, in Ningxiang city, China [160]. This resulted in one death, the injury of 20 people and a mushroom cloud that "could be seen from several kilometres away" [160]. To bring the fire under control, a "total of 288 firefighters and soldiers from 36 fire lorries were sent to the scene" [160]. In an early statement, the fire was attributed to "waste aluminium foil". Given that the Aluminium Foil is the Cathode of the LIB cell, it is also possible cathode materials were involved [161]. There have been more examples of accidents involving consumer goods batteries in mixed and household waste streams. Explosions and fires in Materials Recovery Facilities (MRFs) are increasing [162,163]. In Dunbar (Scotland) some 300 tonnes of refuse ignited in January 2019 in a storage building. 40 firefighters were needed to extinguish the fire [164]. Waste container of a recycling collection caught fire due to a small LIB being incorrectly included with Mixed Dry Recycling (MDR) materials [165]. Fires become more common place, for example of the 50 fires at the Shoreway in San Carlos (USA) Materials Recovery Facility (MRF) between 13 April 2013 and 29 September 2017, 50% due to lithium-ion batteries. The catastrophic fire on 9 September 2016 required over 100 firefighters to extinguish it, and the fire shut the facility for 3 months and cost over $8.5 M in restoration costs [166,167]. These incidents can be a result from the illicit or accidental concealing of LIBs in with, for example, lead-acid batteries. The routine handling of various waste materials in MRFs is likely to damage LIBs [163] causing batteries to ignite, or enter a pre-ignition incubation period. It should be noted that given the small size of these LIBs, they are more likely to be mixed with household waste and EV batteries are larger and harder to conceal, be accidently misplaced or mixed with other wastes. It has been estimated that there is a fire every week in German MRFs, 90% of which are caused by LIBs [168]. The presence of LIBs in Mixed Dry Recycling (MDR) is an increasing problem for recycling facilities, however, it is often difficult to ascertain for certain the cause of a fire in a waste or recycling facility as the material inevitably has to be pulled apart to gain access to the fire, concealing any small sources of ignition such as domestic LIBs. Nevertheless, it has been claimed that an MRF is lost every month in the USA as a result of battery fires [169,170]. A recent joint investigation by Eunomia Research & Consulting and Environmental Services Association (ESA) showed that LIBs are responsible for around 48% of all waste fires occurring in the UK per year, which costs some £158 million for the UK economy each year [171]. Accordingly, the report concludes that every year some 200 waste fires caused by LIBs occur in UK scrapyards. In Japan some 128 incidences in the year 2018 were recorded due to LIB fires or releasing smoke [172]. During the year to the end of December 2019, this figure had risen to 230 [173]. In the UK, from 510 fires in UK MRFs in 2017–18, it is estimated that up to 25% were caused by LIBs [174] and the Environmental Services Association estimates that there were ca. 250 fires, i.e. 38% of all fires, caused by small LIBs between April 2019 and March 2020 [175].

In the USA and Canada fires at waste facilities have increased by 26% from 2016 to 2019, from 272 reported fires to 343, respectively. Fires are largely underreported, however, and it is estimated that there were actually around 1800 fires at waste facilities in 2019 [176].

5.3. Unscheduled End of Life (road accidents)

In the context of EV LIBs, a set of hazards arise from damage to the batteries caused by road traffic accidents including electrocution, fire (shared with conventional ICE vehicles) and consequently exposure to cell contents and risk to the natural environment. This paper categorises these situations as "unscheduled EoL", where a vehicle reaches the EoL prematurely which also results in a non-standard vehicle for EoL processing, presenting extra hazards and challenges from a waste management perspective. In 2011, a Chevrolet Volt was subjected to a standard side-impact test and the car survived without apparently catching fire, only to ignite some three weeks later [177]. Some care should be exercised in using the term 're-ignition', as it is likely that ignition hours, days or weeks after an incident is due to some event triggering fire *e.g.* if the vehicle is moved, an arc from stranded electrical energy could cause ignition or, as was the case with the Chevrolet Volt, the fire was due to the damaged battery coolant system leaking and eventually causing electrical short circuit which ignited flammable gas from the cells [178]. Nevertheless, the phenomenon appears to be an unfortunate characteristic of EV fires.

In tests carried out by the Fire Protection Research Foundation (which supports the US National Fire Protection Association, NFPA) it was found that suppression of automotive battery fires required very large quantities of water due to re-ignition, with one battery re-igniting after 22 h [179]. In another case a spontaneous fire in San Francisco in December 2018 was apparently extinguished by the fire service using some 2000 gallons (∼9092 litres) of water, only to re-ignite hours later in a recovery yard. The first recorded incident of an EV spontaneously igniting in the UK occurred in Chester in November 2019 [180]. Another characteristic of EV fires is the possibility of violent explosions. In Shanghai in April 2019, and in San Francisco and Hong Kong in May 2019, Tesla EVs spontaneously ignited in domestic or public parking garages and exploded [181].

At present, globally, there are no clear or coherent procedures for fighting EV fires. Perhaps the most experienced firefighters in this respect are those from Mountain View in California who have worked extensively with Tesla, as the company is based in their area. The sum of all the challenges faced by firefighters is, perhaps, exemplified by the crash of a Tesla X SUV on Freeway 101 in Mountain View at 9.27 a.m. on 23 March 2018 [106]. The car crashed at 70 m.p.h., resulting in the front of the vehicle becoming detached, spraying some of the component cylindrical cells across the road, and the battery bursting into flames. The loose cells were charged and represented an immediate 'stranded energy' danger. The battery was exposed, allowing direct access to the firefighters' hoses and the fire was extinguished after *ca.* 8 min with significant amounts of water, although the damaged battery still showed signs of worrying activity. After *ca.* 2 h, Tesla specialists arrived and started collecting the loose cells from the lanes of the highway, removing cells from the damaged battery, and placing them in water. The six-lane freeway remained closed for 6 h, causing severe disruption. Eventually, after about 25% of the cells had been removed, the damaged vehicle was deemed safe to transport to a scrapyard, where the battery re-ignited twice within 24 h, and then again after 6 days. The NFPA recommend that EVs with damaged battery packs are stored at least 50 feet from any other vehicles and buildings.

Immersing damaged EVs in water is increasingly seen as a straightforward solution to fire, re-ignition and release of toxic gases. Thus when a Tesla ignited in Antwerp on 1 June 2019 the fire service dealt with the incident by placing the car into a large tank of water and leaving it overnight [106]. As a fire service without access to the necessary small mobile cranes, the Mountain View service has adopted the simple strategy of building dams around damaged batteries or EVs once in a scrapyard and flooding with water [106]. In China, a national platform was established in 2017 to monitor the mileage, location, performance, charging time and charging heat maps of EVs [182]. This facilitates the Chinese Ministry of Industry and Information Technology's requirement that representative samples of EVs are tested for safety purposes, with the fraction tested depending upon mileage and type of vehicle. Thus, for taxis, buses and haulage and logistic vehicles, manufacturers have to check at least 5% of vehicles that have travelled less than 62,000 miles, at least 10% that have travelled between 62,000 and 128,000 miles, and at least 20% of EVs that have travelled more than 128,000 miles. However, in China, in 2018, 40 fires were recorded involving a variety of manufacturers and models of EVs [183] suggesting that the testing and monitoring system is yet to be optimised. Further EV safety standards are planned for 2021 in China [184].

6. Safety measures, regulatory gaps and discussions

6.1. Risk management systems to ensure LIB safety

There are a variety of systems involved in LIB safety, both physical and chemical [185,186]. Some of these systems involve active management of the LIB cell whilst others are passive or intrinsic safety features built into the battery design. As the technology around EoL LIB management develops, there is room for development of further safety systems in the treatment of automotive cells in a second life and in the LIB recycling industry. Risk management systems for LIBs can be grouped into four Categories (Fig. 4).

Battery management systems' (BMS) functionality can be grouped into four main areas: monitoring, protection, computation, and communication. To ensure safe operation the BMS monitors the present (and in some cases historical) operating state of the battery measuring to what extent the battery is operating within its safe operating area (SOA). Protection systems vary but are essentially either hardware components/systems or changes to functional control of the battery system which are triggered by incursions of (or approaches to) the SOA envelope. The protection systems use information from the monitoring system to prevent the battery operating in a sustained manner outside the SOA – which could cause it to fail. Examples include overcurrent protection, voltage equalisation and instructions to the vehicle control system to operate in so-called "limp-home mode". The functionality of the computational system is heavily dependent on the complexity of the system, the application, and the required ongoing system knowledge requirements. At a basic level, the sub-system performs the processing of the monitoring data leading to actuation of the protection systems. Many BMS compute SOC to some degree; SOH and changes to SOA over life as well as many other parameters can be calculated through embedded modelling and ultimately the only real limit of capability of the sub-system to understand the behaviour of the battery in real-time is the available computational power. This is by far the greatest area of innovation and development in BMS technology. Finally, even the most capable BMS systems would be ineffectual without the ability to communicate the status of the battery system (a combination of the monitored and computed quantities and the status of the protection systems) to a user or system overseer. This subsystem may also include the facility to log data, which is of principal importance to asset operators as well as incident investigation – as is demonstrated above.

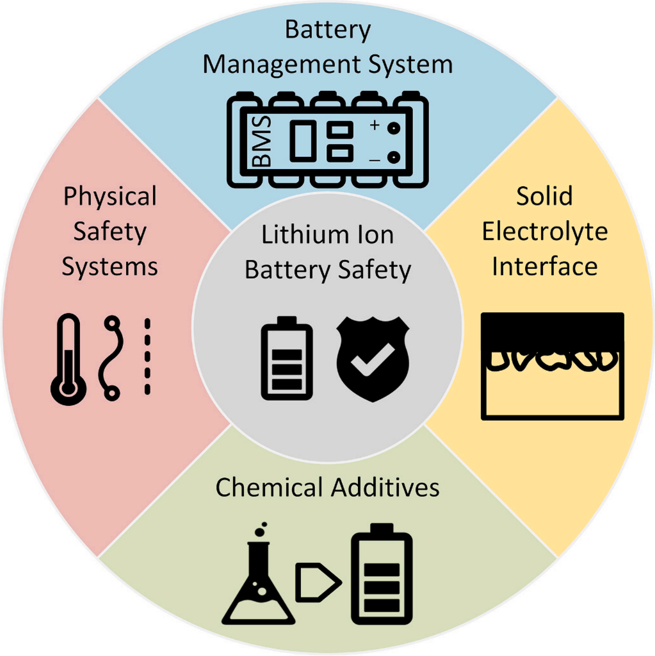


Fig. 4. Risk management systems for LIBs.

Clearly failure in any of the BMS subsystems has the potential to cause a battery system failure. Arguably, there is little left to innovate in monitoring and protection systems beyond, perhaps, novel energy management in balancing systems. However, the reliability and accuracy of these systems is of utmost importance as they form the first line of defence in system safety. Where complex models are incorporated into BMS systems, the integrity and fidelity of the models must be understood so the system (or a user) is able to make informed decisions on the ongoing operation of the system. Finally, robust and rapid communication, perhaps involving backup systems will allow early indication to users or system overseers to potential problems allowing mitigation actions to be put in place. Logging of operational data at highly granular level also greatly aids failure tracing.

The Solid Electrolyte Interface (SEI) is the other primary safety system. LIBs are unique in battery technology in that the fully-lithiated graphite anodes typically employed have around the same redox potential as that of metallic lithium [59] and hence should immediately reduce the organic carbonates employed in the electrolyte to hydrogen, various flammable gaseous hydrocarbons and heat [187]. The reason that this does not occur is the formation of a protective barrier, the SEI, which is permeable to lithium ions, between the anode and solvent during the first charge. The SEI continuously varies in thickness during the life of the battery, but overall trending to an increase in thickness and incorporating lithium ions as it does so [42].

The chemical additives employed as safety systems in LIBs are in the form of supplements which can form up to 5% of the electrolyte [185] and are generally commercial secrets, rendering any detailed knowledge of, for example, the potential toxicity of the electrolyte or its behaviour in a fire, impossible. The additives serve a number of purposes including: generating a gas if the cell is at risk of overcharging to trigger a current interrupt, improving SEI formation, enhancing the thermal stability of $LiPF_6$, forming chars that build up an isolating layer between the condensed and gas phases to stop combustion, producing scavenging radicals which terminate the radical chain reactions responsible for the combustion reactions in the gas phase, and preventing overcharging by absorbing the excess charge from the cathode and safely discharging it at the anode.

Physical safety systems generally seek to break the external electronic circuit, such as the current interrupt devices referred to above, and shutdown separators which break the internal ionic circuit. The latter are porous polyethylene films which melt at 132 °C [52,56] resulting in the closure of the ion-conducting pores, so breaking the internal ionic circuit and shutting down the battery. Systems that are intended to break the ionic or electronic circuits are essentially useless once thermal runaway happens and exothermic chemical reactions have escalated [52].

6.2. Regulatory regimes and information gaps

The UK currently has no codes, regulations or standards specific to the installation of industrial BESS or the selection of LIBs for repurposing in, for example, Battery Energy Storage Systems (BESS). The Microgeneration Certification Scheme (MCS), which publishes standards for the installation of small scale renewables in homes, has introduced standard guidance for the installation of BESS in domestic settings [188]. The lack of standards, regulations and guidance has potentially adverse implications for *e.g.* employees in the vehicle repair industry and members of the public who informally repurpose battery modules for domestic purposes (*e.g.* solar energy storage, *etc.*) [189]. However, it is not alone in this; globally, there is no clear understanding of the division of responsibility and liability between suppliers (manufacturers and remanufacturers) and consumers. This lack of clarity leads to uncertainty and unreasonable costs.

Outside of a few places such as Mountain View in California, there is a lack of publicly available information on the behaviour of LIBs in fires, rendering firefighting [106] largely down to guesswork in many cases (see the response of Antwerp firefighters above). The same is true of post-fire response: experience from previous EV fire incidents suggests that re-ignition is likely, but there is also the unique hazard of stranded energy. There are also growing concerns over the possible environmental impact owing to contamination of the water employed to fight the fires.

There are around 65 conventional vehicle fires in the UK per day, and the fire and rescue services aim to extinguish these and remove the remains within 1 h, allowing roads to re-open [190]. The time required for an electric vehicle to be accepted as fully extinguished is much longer and could be 6 or 8 h potentially causing major disruption to the transport network. Recently, concerns have been raised over the safety of the UK "Smart Motorways" initiative - as a key aspect of these proposed motorways is the absence of a hard shoulder [191]; the possibility of EV fires on such roads will add considerably to these concerns. There is also an increasing concern amongst first responders that vehicle recovery firms will cease to bid for recovery contracts and include exemption clauses, because of the additional risks associated with EVs [190].

A third risk that perhaps should be at least considered is that of cyber-attack, for example overriding the BMS. This is increasingly becoming recognised with respect to BESS employed in domestic solar energy systems [192] and there have already been incidents of hackers attacking national grid systems. Moreover, EV grid infrastructure, vehicle to grid concepts (V2G) or Energy – Internet technologies may also be prone to such attacks [193]. It is important to note that the introduction of a tighter regulatory regime, is not about hampering the development of the LIB industry; conversely, in establishing clear guidance and frameworks, it may enable growth in areas where there is uncertainty. At a time where LIBs remain a 'challenger' technology, ensuring the safety of the industry is key to managing the reputation and perception of LIB technology.

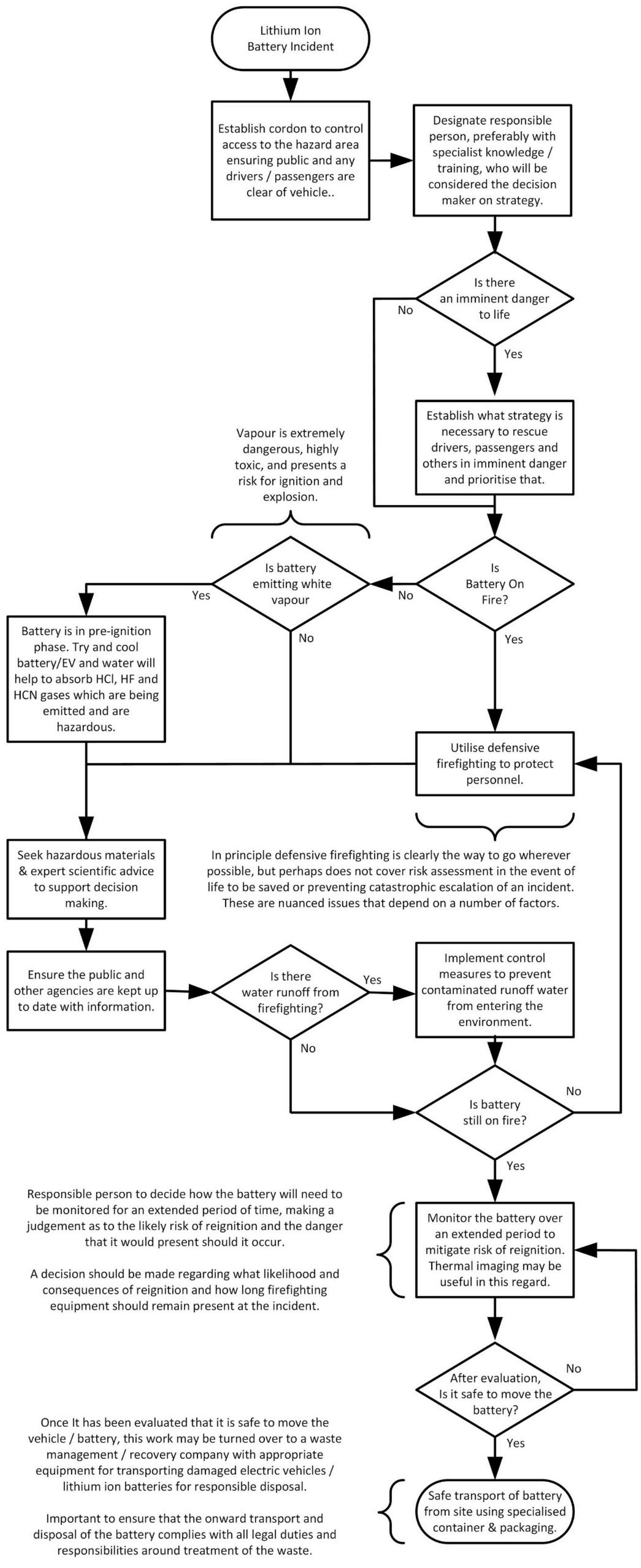
6.3. Discussions and suggestion for best practices

The US has also realised the potential safety implications of large LIBs and appears to be ahead of Europe and the UK in addressing them, possibly due to the flexibility of the standardisation systems from e.g. Underwriter Laboratories (UL). Thus the US National Fire Protection Association has produced a regularly updated training manual for fighting EV fires [194] and offers training on tackling such fires [195] as well as producing the NFPA 855 code for the installation of energy storage systems. Whilst this paper was under review, the NTSB released a safety report [196], highlighting how emergency responders should deal with LIB incidents. They identify that manufacturers guidance on how to deal with LIB fires is lacking, and identify knowledge gaps associated with dealing with high severity LIB fires [196]. At policy level, a US working group has been set up consisting of representatives from all entities in the LIB supply chain through to MRFs [163]. In North America, UL1973 is a well-established end-product standard aimed at the safe operation of stationary batteries in a variety of applications. The standard is employed by manufacturers in the US and Canada and is approximately equivalent to the UK BS EN 62619 (International Electrotechnical Commission standard IEC 62619). In the USA, compliance with standards such as those of UL are not driven by the law as in the UK, which is perhaps a disadvantage in terms of uniformity, but does allow rapid response to emerging challenges, *e.g.* LIBs. Thus, UL9540A is the test method on large scale fire testing for implementing an effective fire propagation as well as gas study on BESS. Most recently, recognising the increasing application of repurposed LIBs in BESS, UL1974 is the US and Canadian national standard for assessing the repurposing of batteries, modules *etc.* for new applications and is a process, rather than product safety standard. To be UL1974 compliant, sellers must have processes in place to determine the SOH of a battery or component thereof (*e.g.* a module), and for sorting and grading such batteries, modules, *etc.* UL1974 identifies the key items to be considered, provides recommended testing and evaluation procedures and makes reference to the appropriate end product standards that the repurposed batteries must comply with. 4R, a joint venture between Nissan and Sumitomo was recently the first company to be certified as UL1974 compliant [197]. In fact, the repurposing of automotive batteries in any real sense is being hindered by the conflict the manufacturers are experiencing when making new battery packs compliant with first life automotive requirements and second life stationary standards and statutory requirements [157]. In the UK current MSC guidance does stipulate that BESS can be located indoors, albeit with the caveat "5.7.1 All components shall be located so that escape routes from the premises are not impeded." and "5.7.2 Storage batteries shall be located so that a fire in the battery does not compromise protected escape routes." [198]. Although this does not necessarily mean second use batteries it does give some good advice on the location of batteries in general.

Industry, regulators and supporting organisations are aware of the safety risk management and hazards that can be caused by wrong handling of LIBs. In the USA the National Transportation Safety Board provided a risk emergency procedure for first responders [196] in November 2020 and the International Organization (ISO) [199] provide information for first and second responders for incidences with rechargeable electrical energy storage systems. The British Standards Institution (BSI) is working towards guidelines and code of practices that will provide auditable risk management standards [200–202] to deal with batteries for vehicle propulsion electrification. Indeed, it is advised to consider third-party certification/inspection/testing of product conformity as outlined by the Draft of PAS 7062 "Electric vehicle battery cells – Health and safety, environmental and quality management considerations in cell manufacturing and finished cell – Code of Practice" and PAS 7061 working on a Code of Practice for the safe and environmentally-conscious handling of battery packs and modules.

Fig. 5, sets out a simplified version of the present state of best practice on handling LIB incidences. This is based on discussions and current training offered by the UK National Fire Chiefs Council (NFCC) and it online digital learning course on dealing with LIBs incidents [203].

For example, if there is a battery incident the area requires cordoning off and a responsible person e.g. Fire Brigade, Police must be contacted. In case there is a risk of an imminent danger, people (e.g. driver, passenger, etc.) need to be rescued. In case the battery is on fire or emitting white smoke, different strategies to cool off the battery or protect personnel need to be employed. Hazardous materials guidance must be followed and the public, stakeholders and other related agencies must be kept updated on the incident. Here, existing water run-off from batteries should be considered and if the battery is still on fire, the battery needs to be monitored over an extended period to mitigate the risk of reignition. Finally, once the battery is safe to move, it should be transferred from the site using specialised container and packaging. It is clear that every LIB incident is very different and will require a nuanced evaluation of the situation and environment. As such, there remain significant challenges in reducing the complexity of incident management down to a simple flowchart structure, and this should not be taken as a comprehensive guide. However, this presents a simplified schema of present understanding on best practice. Of course, the knowledge on handling LIB incidents is evolving rapidly. Therefore, greater research and development of detailed knowledge and handling practices is needed, which in time will superseded this quite basic flowchart with a more comprehensive guide.



Vapour is extremely dangerous, highly toxic, and presents a risk for ignition and explosion.

In principle defensive firefighting is clearly the way to go wherever possible, but perhaps does not cover risk assessment in the event of life to be saved or preventing catastrophic escalation of an incident. These are nuanced issues that depend on a number of factors.

Responsible person to decide how the battery will need to be monitored for an extended period of time, making a judgement as to the likely risk of reignition and the danger that it would present should it occur.

A decision should be made regarding what likelihood and consequences of reignition and how long firefighting equipment should remain present at the incident.

Once It has been evaluated that it is safe to move the vehicle / battery, this work may be turned over to a waste management / recovery company with appropriate equipment for transporting damaged electric vehicles / lithium ion batteries for responsible disposal.

Important to ensure that the onward transport and disposal of the battery complies with all legal duties and responsibilities around treatment of the waste.

Fig. 5. Handling LIB incidents.

7. Conclusions

The depth of penetration of Lithium-ion Batteries (LIBs) into everyday life and the relative number of reported incidents demonstrate that, whilst potentially significant, the risks and hazards associated with LIBs can be and are, to a greater extent, generally managed in everyday use. In line with that the associated risks with LIBs are constantly and continually addressed and minimised through engineering and operational management. In addition, the successful mitigation of the significant risks and hazards in major industries such as chemicals and petrochemicals show that those associated with LIBs should also be manageable. However, this is not achieved through good fortune, rather through significant foresight and planning which the industry is justly able to promote. Nevertheless, of the known cases where LIB systems have failed, a number have, either in themselves or though propagation of further failures, resulted in significant damage to property, personal injury or even loss of life. This underlines that LIB technology shares, along with other highly societally integrated systems such as for example petroleum or domestic chemicals, the potential to be the cause of significant harm both physically and reputationally.

To these LIB-related systems, should be added the urgent need for the education of all stakeholders on the novelty of LIBs in energy storage due to their hitherto unencountered high energy densities and flammable constituents, and hence the safe location, use and disposal of these batteries and their components. The global need is to adopt a strategy for the entire lifecycle of LIBs urgently which should include serious consideration of the extent of public access, and uninformed access generally, to the most energetic LIBs, including automotive battery packs and their component cells and modules. Regulations, codes, and standards are required as part of this strategy, which should include the registration of new and existing BESS, domestic and industrial, with suitable authorities such as the local fire service and local council. The information supplied as part of this registration should include a statement specifying whether the components of the BESS are new or repurposed. This requires efficient record keeping, storage and retrieval, and that the information effectively be made available to first responders.

In terms of operational management of BESS, all electronic systems, and especially the BMS, should be fail- and cyber-safe. As well as any remote monitoring and control systems, BESS should have external panels, accessible to first responders both physically and in terms of the user interface. Such panels should show the status of the equipment and environment within the container, through (ideally) HF, hydrogen and temperature sensors, and have alarms to signal the presence of these gases and over-temperature. There is also a strong need for proper legislation and regulations concerning temporary storage prior to e.g. second use or recycling with a set of best practice to execute them. Without these, there is a high risk that LIBs are illegally disposed, recycled or landfilled. That could create serious threats (*i.e.* soil and air pollution, landfill fires) to the natural environment and to the public. Finally, "Sustainable energy sources are rapidly proliferating and very much needed, and energy storage is a critical component of it. This is a global fire protection problem, and we all have work to do in support of the safe evolution of this technology" [204].

Credit author statement

PAC: Conceptualization, Data collection and curation, Investigation, Writing – original draft, Writing – review & editing. PAA: Conceptualization, Writing – review & editing and funding acquisition. GDJH Writing – review & editing and Visualization. SML: Writing – review & editing and funding acquisition. WM: Writing – original draft, Writing – review & editing. MAR: Investigation, Writing – original draft, Writing – review & editing; MSW: Investigation, Writing – original draft, Writing – review & editing. OH: Conceptualization, Supervision, Writing – review & editing, and Project Administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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